



AstropAH

A Newsletter on Astronomical PAHs

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A Space Butterfly



Editorial

Dear Colleagues,

We are very happy to be back this month of April with the latest in the PAH field. Some of us are at the International Astronomical Union S350 Symposium for laboratory astrophysics in Cambridge, UK, typing notes away with so many interesting astrochemical lectures. This is a growing field and the attendance and diversity in topics has shown the plurality of studies by combining laboratory, theoretical and observational approaches.

For this issue, we are delighted to have our interview of the month with Professor Hai Wang from Stanford University. Professor Wang tells us about his about driver for the study of mechanisms of PAH and soot formation in synergy with the development of chemical kinetic models.

Our Abstracts section contains new publications on polyacenes and diffuse interstellar bands, phosphorous PAHs and coronene cations, among others!

We thank you for your growing dedication and interest in AstroPAH. If you wish to contact us, feel free to use our email: astropah@strw.leidenuniv.nl. We certainly hope you enjoy reading our April newsletter, and look forward to seeing you again next month.

Thank you to everyone!

The Editorial Team

**Next issue: 23 May 2019.
Submission deadline: 10 May 2019.**

AstroPAH Newsletter

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PAH Picture of the Month

A Spitzer view of Westerhout 40 (or W 40) a giant cloud of gas and dust where new stars may form. The composite image shows the 8.0 μm band, dominated by PAH emission, giving the nebula its reddish features. Stars are brighter in the shorter wavelengths, the 3.6 μm Spitzer band, which is represented in blue. Some of the youngest stars are surrounded by dusty disks of material, which glow in yellow (5.8 μm band).

Credits: NASA/JPL-Caltech



An Interview with Prof. Hai Wang

Hai Wang is Professor of Mechanical Engineering at Stanford University. Prior to his appointment at Stanford, he was the Northrop Chair in Engineering and Professor of Aerospace and Mechanical Engineering at USC. He received his Ph.D. in Fuel Science from Penn State in 1992. He was a Professional Research Staff at Princeton University from 1994 to 1996 before starting his faculty career at the University of Delaware. He is best known for his work on the mechanisms of PAH and soot formation in combustion and development of chemical kinetic models for fuel combustion. He has made contributions in the application of ab-initio quantum chemistry and reaction rate theory in chemical kinetics. He contributed to the understanding of transport theory of nanoparticles and large molecules, atmospheric heterogeneous chemistry, nanocatalysis, and nanomaterials synthesis, characterization and applications. He was the recipient of the NSF CAREER award in 1999, the Senior Research Award from the Viterbi School of Engineering at USC in 2011, the AIAA Propellant and Combustion Award in 2018, and the Humboldt Research Award in 2019. He is a fellow of ASME and the Combustion Institute. He currently serves as the Editor-in-Chief of *Progress in Energy and Combustion Science*.



Thank you for accepting to do this interview. First, can you tell us when and why you started studying PAHs in sooting flames?

Thank you very much for offering me the chance to be interviewed.

It was the late 80's when I started my Ph.D. study with Michael Frenklach at Penn State. At the time, soot formation was one of the most challenging and unresolved fundamental problems of combustion (and it still is today to an extent). As a young graduate student, I did not know what I got myself into. Very little was known at a mechanistic level about the process to soot in flames. We did know that PAHs form in flames where oxygen is deficient, and we also knew that soot is primarily composed of PAHs. However, we did not understand exactly how PAHs grow in size and how they transform from a two dimensional molecular structure to clusters and finally to primary soot particles. We thought that having a detailed reaction mechanism of PAH formation in flame environments would be beneficial for us to probe the mechanism and kinetic processes. For that purpose, I studied the thermochemistry of PAH

species using semi-empirical quantum chemistry methods, that were just becoming feasible then for small to moderate-sized PAHs, to calculate the electronic and molecular structures of PAHs. With the help of quantum chemistry calculation and reaction rate theories, we put the Hydrogen-Abstraction-Carbon-Addition (HACA) mechanism together to describe the mechanism and kinetic rates of PAH formation in flames (Wang et al. 1997 and Frenklach et al. 1991). That was a piece of work that took us more than 10 years to complete and publish, but I consider myself lucky to have had the opportunity to tackle such a difficult problem.

How do you think the combustion research you do can help better understand astrophysical PAHs? And how has Astrophysical PAH research helped you in your research?

A great question! I think that the underlying thermodynamic driving forces for the formation of astrophysical and flame PAHs are identical. That is, PAHs form because of entropy increase due to dehydrogenation or the release of H₂ that accompanies the formation and growth of PAH molecules. The entropy effect is amplified under high-temperature and/or low-pressure conditions. In that context, the kinetic processes leading to PAH formation in flames and in interstellar media may have mechanistic aspects that are similar to each other. The other aspect is that diagnosing PAH and soot by a range of laser techniques we use in combustion research requires the knowledge of the optical properties of PAHs and PAH clusters, one of the areas that may be central to the understanding of astrophysical PAHs. So, I would say that the understanding of astrophysical PAHs is curiosity driven to a large extent, and flame PAHs are relevant to our ability to design more efficient and less polluting engines. Over the years, I learned a lot from reading papers from the astrophysical PAH research community. I have been stealing ideas from this community and take them to our research community. I would say that this is a classic example about the unintended consequence of scientific research. Thirty years ago, Lou Allamandola showed the similarity between the Orion Bar emission spectrum and the Raman spectrum of soot from auto exhaust (Allamandola et al. 1985). Then, it was our applied research that helped to initiate a curiosity driven research into astrophysical PAHs. Thirty years later, we are taking knowledge from the astrophysical PAH community to understand how soot forms in flames and ultimately use this knowledge to build better engines.

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

For flame studies, I would say that the problem of soot nucleation has been bothering us for many years. As I indicated in a review paper published in 2011 (Wang 2011), there is still no viable mechanism thus far to explain why PAHs cluster with each other under the flame temperatures (> 1600 K). Most of the PAHs we detect from young soot particles, whether by aerosol mass spectrometry or by other methods, tell us that young soot is comprised of moderately-sized PAHs such as coronene. Some of the PAH species contain five-membered ring structures and can have stable free radicals due to resonant stabilization, but the binding energies we know about these PAHs, whether it is through van der Waals force or pi-bonding, are all too weak to overcome the entropy effect that tears the clusters apart at flame temperatures. A simple argument is, the boiling point of coronene is about 800 K, and it should vaporize at flame temperatures. Why then would it condense? Clearly, an unknown binding force must be playing a role there. Borrowing from the findings from the Astrophysical PAH community, we have looked into the role of metal cations in facilitating PAH bindings, but the experimental work proves to be difficult because a trace amount of metal is sufficient

to provide the number of soot nuclei we see in flames. Other ideas have emerged in recent years, and this is becoming an active research area in flame PAH and soot studies. Naively, I would venture to guess that this problem may be relevant also to PAH clustering in interstellar media.

Can you tell us about your latest research project?

My latest research project in the area of PAH and soot formation is the measurement of optical band gap of nascent or young soot particles. We found that in the particle size range of 2-10 nm, flame-formed carbon nanoparticles or nano carbon grains have well defined optical band gap, and the band gap varies with the particle size in a manner that can be described by existing quantum confinement theory. Loosely speaking, these particles behave like quantum dots, despite the fact that they become a broadband absorber as they grow larger into mature soot- the material we find in diesel exhaust. We have a qualitative explanation for such an effect by examining the $\pi-\pi^*$ interactions and the energy band structures in PAH clusters. The next step is to try and understand how the PAH structure and particle composition impact the band gap when the size effect is fully defined and quantified. A secondary question that is related to the band gap is the fluorescence of PAHs versus the lack of fluorescence in as-formed carbon nanoparticles. We are trying to understand why PAH clustering would diminish the fluorescence as the answer to this question may give us hints about the soot nucleation question I talked about earlier.

You just started a sabbatical in Germany, what research will you conduct there?

Thank you for asking this question. I will be spending three months here at University of Duisburg-Essen working with Professor Christof Schulz, who is a brilliant laser diagnostics expert. His group uses flame and plasma to synthesize nanomaterials and nanoparticles, including graphene, the glamorous, big sister of PAHs. I hope to learn from him about in situ optical property diagnostics, to help us understand the optical behaviors of PAHs and PAH clusters better. I hope I can be of some help in their studies of soot formation in high-pressure flames and shock tubes. A very neat idea they are pursuing is the synthesis of large graphene flakes in plasma. We are exploring the question about what processes and conditions, and hence the underlying chemistry, encourage PAHs to grow from vapor precursors only into two-dimensional molecular structures.

What was the most important advice somebody gave you?

The most important advice was probably given by my father that it is better to be useful sometimes than be right always. It stuck with me for a long time.

How do you balance your professional and personal life?

Balance life to me is always about the lack of such a balance in reality, I guess, and that is the reason we keep reminding ourselves about the need to have a balance. So, life to me is like a sinusoidal curve oscillating between some equilibrium. My kids once asked me what I would be if I was not a scientist. I told them that I would be a chef or a plumber. So, a big part of my personal life evolves around cooking (I like to eat) and fixing things in the house. I like travel and theatre, and am hoping to do more of it in the coming years.

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Abstracts

Polyacenes and diffuse interstellar bands

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The identification of the carriers of the diffuse interstellar bands (DIBs) remains to be established, with the exception of five bands attributed to C_{60}^+ , although it is generally agreed that DIB carriers should be large carbon-based molecules (with ~ 10 -100 atoms) in the gas phase, such as polycyclic aromatic hydrocarbons (PAHs), long carbon chains or fullerenes. The aim of this paper is to investigate more specific possible carriers among PAHs, namely elongated molecules, which could explain a correlation between the DIB wavelength and the apparent UV resilience of their carriers. More specifically, we address the case of polyacenes, $C_{4N+2}H_{2N+4}$, with $N \sim 10$ -18 fused rectilinear aligned hexagons. Polyacenes are attractive DIB carrier candidates because their high symmetry and large linear size allow them to form regular series of bands in the visible range with strengths larger than most other PAHs, as confirmed by recent laboratory results up to undecacene ($C_{46}H_{26}$). Those with very strong bands in the DIB spectral domain are just at the limit of stability against UV photodissociation. They are part of the prominent PAH family of interstellar carbon compounds, meaning that only $\sim 10^{-5}$ of the total PAH abundance is enough to account for a medium-strength DIB. After summarizing the limited current knowledge about the complex properties of polyacenes and recent laboratory results, the likelihood that they might meet the criteria for being carriers of some DIBs is addressed by reviewing the following properties: wavelength and strength of their series of visible bands; interstellar stability and abundances, charge state and hydrogenation; and DIB rotation profiles. No definite inconsistency has been identified that precludes polyacenes from being the carriers of some DIBs with medium or weak strength, including the so-called C_2 DIBs. But, despite their many interesting properties, additional experimental data about long acenes and their visible bands are needed to make robust conclusions.

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On the formation of phosphorous polycyclic aromatics hydrocarbons (PAPHs) in astrophysical environments

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The formation of Phosphorous-containing Polycyclic Aromatic Hydrocarbons (PAPHs) in astrophysical contexts is proposed and analyzed by means of computational methods [B3LYP-D3BJ/ma-def2-TZVPP, MP2-F12, CCSD-F12b and CCSD(T)-F12b levels of theory]. A bottom-up approach based on a radical-neutral reaction scheme between acetylene (C_2H_2) and the CP radical was used investigating: **a)** the synthesis of the first PAPH (C_5H_5P) “phosphinine”; **b)** PAPH growth by addition of C_2H_2 to the C_5H_4P radical; **c)** PAPH synthesis by addition reactions of one CP radical and nC_2H_2 to a neutral PAH. Results show: **I)** the formation of the phosphinine radical has a strong thermodynamic tendency (-133.3 kcal/mol) and kinetic barriers ≤ 5.4 kcal/mol; **II)** PAPH growth by nC_2H_2 addition on the radical phosphinine easily and exothermically produces radical (1a- or 1-phospha-naphtalenes with kinetic barriers ≤ 7.1 kcal/mol and reaction free energies ≤ -102.5 kcal/mol; **III)** the addition of a single $CP+nC_2H_2$ to a neutral benzene generates a complex chemistry where the main product is 2-phospha-naphtalene; **IV)** because of the CP radical character, its barrierless addition to a PAH produces a resonant stabilized PAPH, becoming excellent candidates for addition reactions with neutral or radical hydrocarbons and PAHs; **V)** the same energy trend between all four levels of theory continues a well-calibrated computational protocol to analyze complex organic reactions with astrochemical interest using electronic structure theory.

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<https://pubs.rsc.org/en/content/articlelanding/2019/cp/c9cp00547a#!divAbstract>

The Sequence of Coronene Hydrogenation Revealed by Gas-phase IR Spectroscopy

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Gas-phase coronene cations ($C_{24}H_{12}^+$) can be sequentially hydrogenated with up to 24 additional H atoms, inducing a gradual transition from a planar, aromatic molecule toward a corrugated, aliphatic species. The mass spectra of hydrogenated coronene cations $[C_{24}H_{12+n_H}]^+$ show that molecules with odd numbers of additional hydrogen atoms (n_H) are dominant, with

particularly high relative intensity for “magic numbers” $n_H = 5, 11, \text{ and } 17$, for which hydrogen atoms have the highest binding energies. Reaction barriers and binding energies strongly affect the hydrogenation sequence and its site specificity. In this contribution, we monitor this sequence experimentally by the evolution of infrared multiple-photon dissociation (IRMPD) spectra of gaseous $[\text{C}_{24}\text{H}_{12+n_H}]^+$ with $n_H = 3-11$, obtained using an infrared free electron laser coupled to a Fourier transform ion cyclotron mass spectrometer. For weakly hydrogenated systems ($n_H = 3, 5$) multiple-photon absorption mainly leads to loss of H atoms (and/or H_2). With increasing n_H , C_2H_2 loss becomes more relevant. For $n_H = 9, 11$, the carbon skeleton is substantially weakened and fragmentation is distributed over a large number of channels. A comparison of our IRMPD spectra with density functional theory calculations clearly shows that only one or two hydrogenation isomers contribute to each n_H . This confirms the concept of hydrogenation occurring along very specific sequences. Moreover, the atomic sites participating in the first 11 steps of this hydrogenation sequence are clearly identified.

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The Polycyclic Aromatic Hydrocarbon Mass Fraction on a 10 pc scale in the Magellanic Clouds

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We present maps of the dust properties in the Small and Large Magellanic Clouds (SMC, LMC) from fitting Spitzer and Herschel observations with the Draine & Li (2007) dust model. We derive the abundance of the small carbonaceous grain (or polycyclic aromatic hydrocarbon; PAH) component. The global PAH fraction (q_{pah} , the fraction of the dust mass in the form of PAHs) is smaller in the SMC ($1.0^{+0.3}_{-0.3}\%$) than in the LMC ($3.3^{+1.4}_{-1.3}\%$). We measure the PAH fraction in different gas phases (H II regions, ionized gas outside of H II regions, molecular gas, and diffuse neutral gas). H II regions appear as distinctive holes in the spatial distribution of the PAH fraction. In both galaxies, the PAH fraction in the diffuse neutral

medium is higher than in the ionized gas, but similar to the molecular gas. Even at equal radiation field intensity, the PAH fraction is lower in the ionized gas than in the diffuse neutral gas. We investigate the PAH life-cycle as a function of metallicity between the two galaxies. The PAH fraction in the diffuse neutral medium of the LMC is similar to that of the Milky Way (4.6%), while it is significantly lower in the SMC. Plausible explanations for the higher PAH fraction in the diffuse neutral medium of the LMC compared to the SMC include: a more effective PAH production by fragmentation of large grains at higher metallicity, and/or the growth of PAHs in molecular gas.

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Gas phase synthesis of [4]-helicene

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A synthetic route to racemic helicenes via a vinylacetylene mediated gas phase chemistry involving elementary reactions with aryl radicals is presented. In contrast to traditional synthetic routes involving solution chemistry and ionic reaction intermediates, the gas phase synthesis involves a targeted ring annulation involving free radical intermediates. Exploiting the simplest helicene as a benchmark, we show that the gas phase reaction of the 4-phenanthrenyl radical ($[C_{14}H_9]^*$) with vinylacetylene (C_4H_4) yields [4]-helicene ($C_{18}H_{12}$) along with atomic hydrogen via a low-barrier mechanism through a resonance-stabilized free radical intermediate ($C_{18}H_{13}$). This pathway may represent a versatile mechanism to build up even more complex polycyclic aromatic hydrocarbons such as [5]- and [6]-helicene via step-wise ring annulation through bimolecular gas phase reactions in circumstellar envelopes of carbon-rich stars, whereas secondary reactions involving hydrogen atom assisted isomerization of thermodynamically less stable isomers of [4]-helicene might be important in combustion flames as well.

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