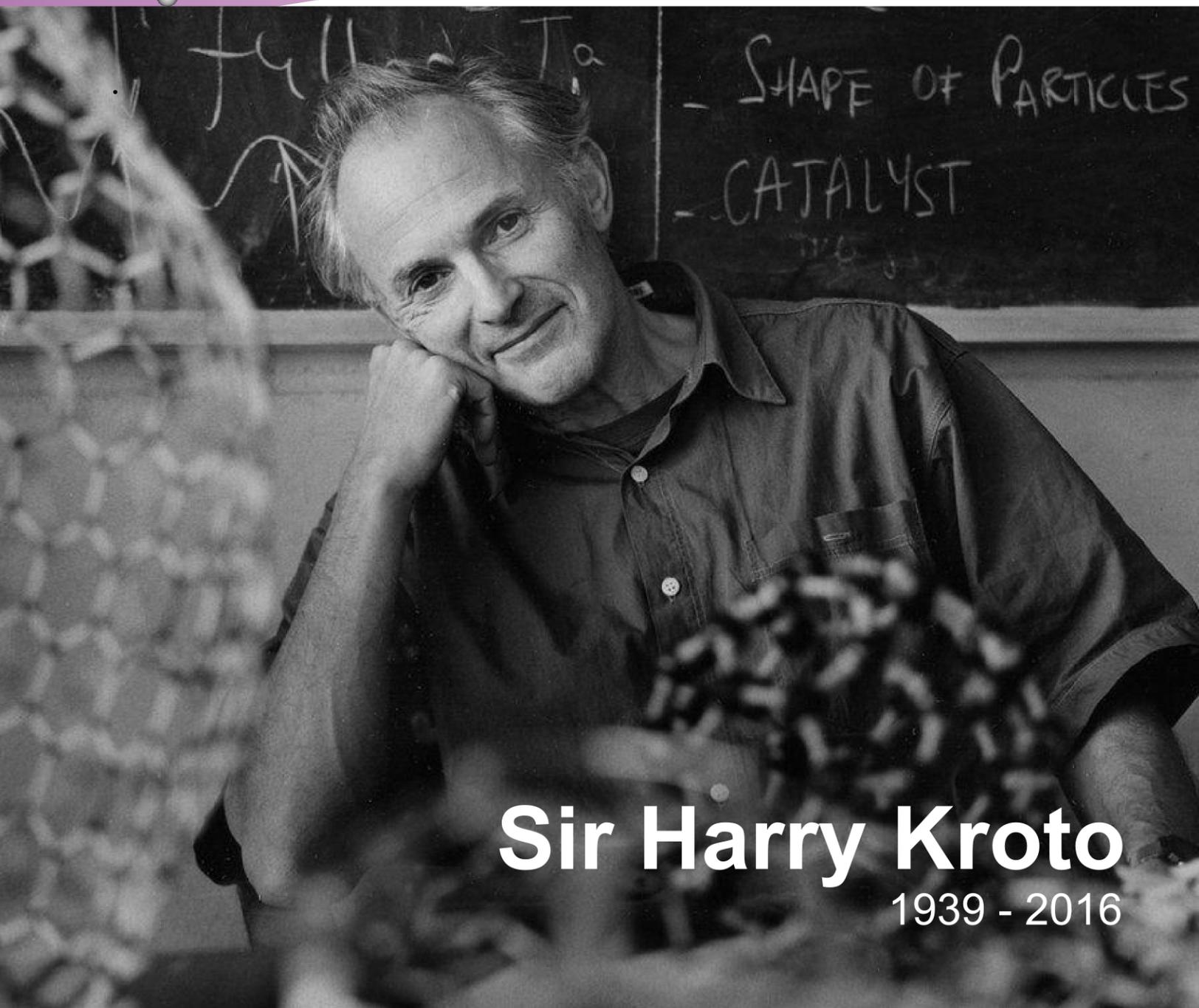


AstropAH

A Newsletter on Astronomical PAHs

Issue 28 | May 2016



Sir Harry Kroto

1939 - 2016

Editorial

Dear Colleagues,

Welcome to the May issue of AstroPAH.

Our cover this month honours Professor Sir Harold Kroto who recently passed away. Kroto's contribution to chemistry has been enormous. We all know him for his Nobel-prize winning discovery of Buckminsterfullerene, which has been revolutionary and led to many new research lines in molecular chemistry, material science, nanotechnology and more. In astrochemistry, we now know that these fullerenes exist in space and that they play an important role in carbon chemistry and are linked to PAH processing. We are saddened by his passing and our thoughts are with Sir Harold Kroto's family.

In this issue of AstroPAH, our In Focus, written by Salma Bejaoui, describes the study of PAH and soot formation in combustion, and in particular, the Laser Induced Fluorescence technique for the detection of PAHs. The abstract section presents papers on the mysterious 21 μm band, the reassessment of the importance of fullerene compounds, and interpretation of subtle variations in PAH emission bands.

We would like to encourage you to also send us contributions for the Picture of the Month, the In Focus, and upcoming event to distribute amongst our community. You can send us your contributions anytime. For publication in June, see the deadlines below. Visit our webpage or contact us for more information.

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

The Editorial Team

**Next issue: 21 June 2016.
Submission deadline: 10 June 2016.**

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PAH Picture of the Month

Professor Sir Harold Walter Kroto (1939-2016), british scientist known for the discovery of fullerenes (Kroto et al. 1985, *Nature* 318, 162).

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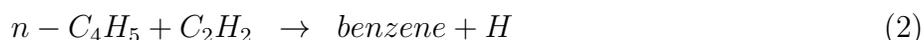
Studying PAH and Soot Formation in Combustion *The Case of Laser Induced Fluorescence (LIF)*

by Salma Bejaoui

The formation of polycyclic aromatic hydrocarbons (PAHs) and soot particles is one of the central focus of the community of combustion. The interest in the subject arises from the urgent need to reduce the total emissions from chemical reactions into the atmosphere through improving the efficiency of the combustion process. The research activities involve experimental, theoretical, and computational efforts and cover a diverse spectrum of the physics and chemistry fields. Both the combustion and astrophysical communities are interested in understanding the formation processes and growth of PAHs and subsequent solid particles, but in two completely different environments. The goal of this *In Focus* is to provide a basic understanding of the different steps that lead to soot particle formation in “flame” conditions that are generally close to atmospheric pressure and high temperature; and to give an overview of the laser induced fluorescence technique, one of the diagnostic tools used to probe PAHs in flames.

From PAHs to Soot Particles

PAHs are formed in a fuel-rich combustion at high temperature (1100K-1800K). The formation of the first aromatic ring is a key step in such processes. The two most cited reactions leading to cyclization are the pathways proposed by Frenklash & Wang [1991]:



The first reaction is a higher temperature route (approximately above 1500 K) while the second is activated at lower temperature (above 1500 K) [Frenklash & Wang 1991, Richter & Howard 2000]. Once formed, aromatic rings grow by a sequential two-step process: H-abstraction, which activates the aromatic molecules, and acetylene addition, which propagates molecular growth and cyclization (HACA mechanism). The transition of gas-phase species to solid particles is probably the least understood part of the soot formation process despite the large number of studies on this subject [Bockhorn et al. 2007, D’Anna 2009, Wang 2011]. In this nucleation (or inception) process, it is assumed that heavy PAH molecules are converted to nascent soot particles when their molecular mass reaches approximately 2000 amu and their

effective diameter is about 1.5 nm [Richter & Howard 2000]. In the absence of a basic understanding of the inception process, many kinetic models [Appel et al. 2000, Wen et al. 2005, Singh et al. 2006] assume that the first particles are formed from the coalescence of two gaseous PAHs, in particular, two pyrene dimers (404 amu) are often chosen as precursors of soot nuclei. It has recently been demonstrated, however, that this dimer cannot survive at flame temperature (the binding energy is too low) [Wang et al. 2011].

Nuclei then grow according to a well-known surface growth reaction involving C_2H_2 (notably through the HACA mechanism) [Frenklach & Wang 1991] and, by extension, involving heterogeneous reactions between gas-phase PAHs and active sites available on soot surfaces. The collisions between particles during the mass growth process significantly increase the particles' size and decrease their number without changing the total mass of soot present in the flame. The aggregation process occurs when soot particles stop coagulating after a collision, and start sticking together without merging. Aggregates of soot are formed from primary particles whose diameter ranges from 10 to 50 nm.

Combustion Processes: Diffusion Flame Versus Premixed Flame

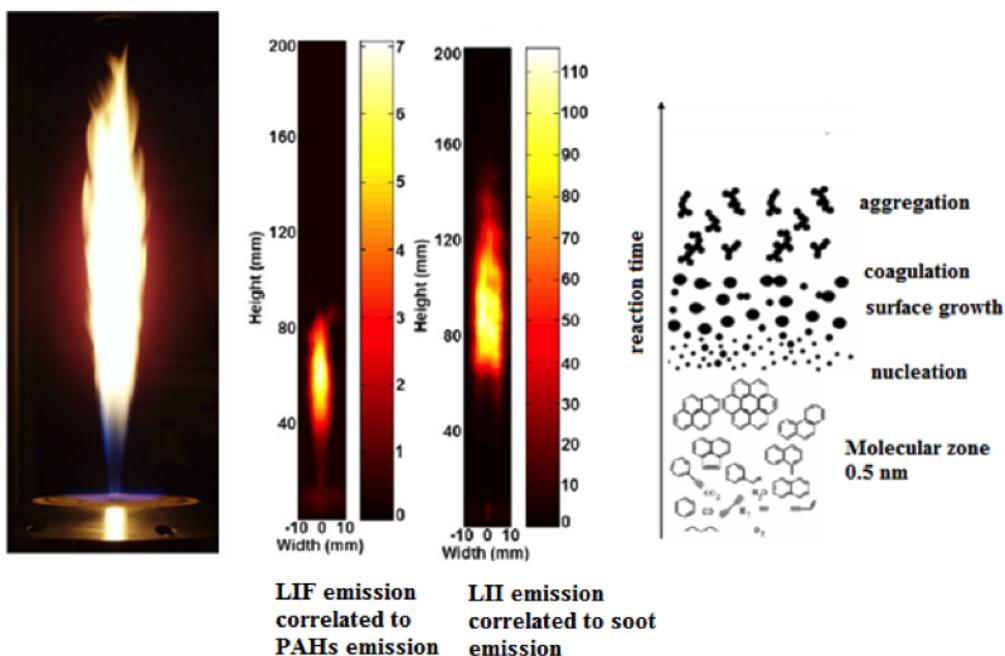


Figure 1 - (Left) 2D map of a diffusion flame of gasoline [Lemaire 2010]. 532 nm excitation is used for laser induced fluorescence (LIF) measurements to excite PAHs while laser induced incandescence (LII) at 1064 nm excitation is used to excite soot particles [Lemaire 2010]. (Right) Process of formation and growth of soot particles in a flame [Bockhorn 1994].

Diffusion flame – A diffusion flame is a flame in which the oxidizer combines with the fuel by diffusion. As a result, the flame speed is limited by the rate of diffusion. This type of flame is the best prototype of the soot formation mechanism described by the Bockhorn diagram [Bockhorn 1994]. Indeed, as shown in **Figure 1**, a diffusion flame is stratified and exhibits three principal regions, according to the Height Above the Burner, or HAB (where the combustion is ignited).

The first region illustrates the formation of the first aromatic ring and the growth of PAHs (blue color). In the second region, nuclei are formed and nascent particles coexist with high molecular mass compounds (light yellow color). The third region, where only soot exists, highlights the surface growth of the solid particles, their agglomeration and aggregation.

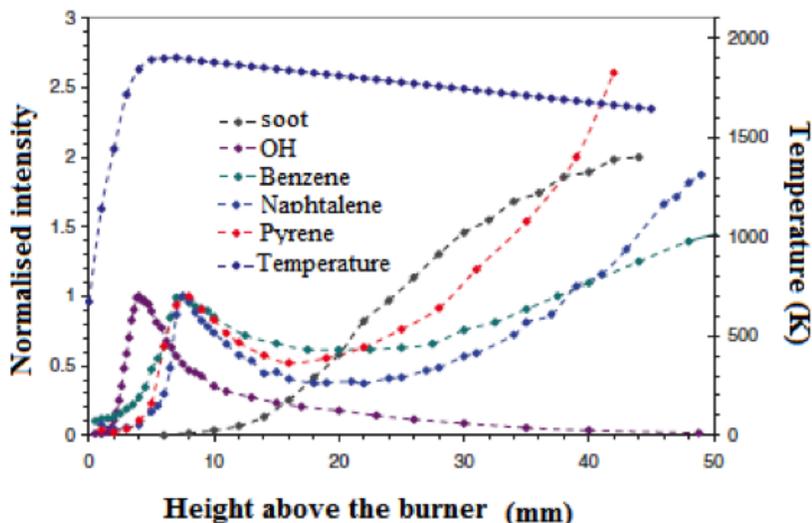


Figure 2 - Chemical structure of a rich-premixed flame of methane [Wartel et al. 2011].

Premixed flame – A premixed flame is a flame in which the oxidizer has been mixed with the fuel before it reaches the flame front. This type of flame is commonly used to model the chemistry of soot formation since its physical, chemical and thermodynamic boundary conditions are well monitored, especially for laminar and 1D flames. As in the diffusion flame, a first region can be defined, at lower Heights Above the Burner (HAB), where the formation and the growth of PAHs occur. However, once

soot particles are formed in the flame, any HAB position above this nucleation site contains a large pool of species, from gaseous molecules with a large scale of aromatic sizes to solid particles containing mono grains and/or aggregates. **Figure 2** shows an example of the chemical structure found in the second region of a premixed flame.

Detection of PAHs in Flame Using Laser Induced Fluorescence

PAH are good candidates for detection by laser-based techniques because they have high absorption coefficients and quantum yields [Berlman 1971]. Most PAHs have strong absorption bands in the UV range (200-300 nm) and their fluorescence emission spectra shift to higher wavelengths with an increase in PAH size [Zizak et al. 1996, Bejaoui et al. 2014], as shown in **Figure 3**.

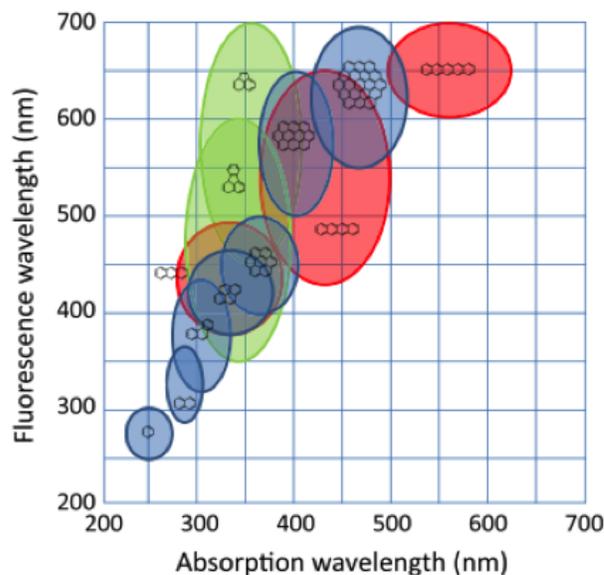


Figure 3 - Lowest energetic absorption spectral range and fluorescence emission of several PAHs potentially formed in flames at ambient temperature [Bejaoui et al. 2014].

In situ LIF measurements – The use of UV wavelengths to excite a flame is not an easy task however. It can make the qualitative interpretation of the emission spectra more difficult, especially in the premixed flame where different classes of PAHs coexist and can fluoresce simultaneously. As a consequence, the UV excitation leads to broad-band emission spectra that cannot be assigned to particular PAH classes. The situation is noticeably different in the case of a diffusion flame, which offers a stratification of the PAH size classes. In the diffusion flame, the spectral shift, observed as a function of HAB, can be connected to the PAH size classes and the growth of PAHs. **Figure 4** illustrates the differences in LIF detection between a diffusion flame and a premixed flame.

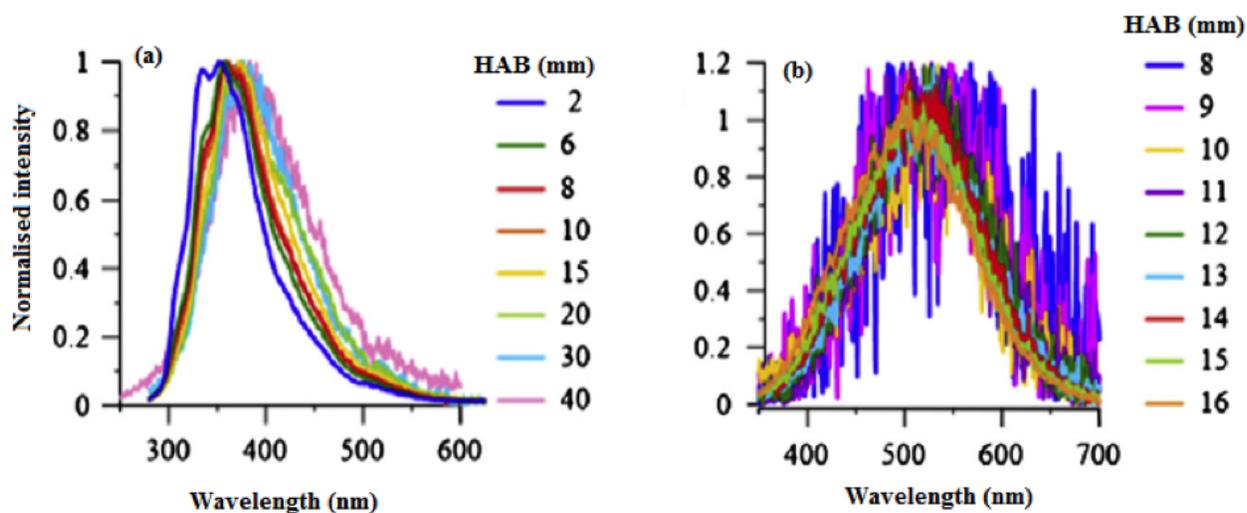


Figure 4 - Normalized LIF spectra detected with excitation at 266 nm at different Height Above Burner (HAB) in the diffusion (a) and premixed flame (b) [Bejaoui et al. 2014].

To promote the use of LIF for the detection of large PAHs, excitation can be moved from the UV to the visible range. Some attempts to characterize PAH classes according to the excitation spectral range, from 250 to 514 nm, have been proposed by Petarca & Marconi [1989] and Beretta et al. [1985]. They demonstrated that under flame conditions, PAHs could absorb and fluoresce in both the UV and visible spectral ranges. Notably, fluoranthene ($C_{16}H_{10}$) or acenaphthylene ($C_{12}H_8$), which are known to only absorb in the UV at room temperature, absorb and fluoresce strongly in the visible region around 500 nm at flame temperatures [Beretta et al. 1985]. The explanation for this anomalous fluorescence points to the existence of a “hidden transition” towards high temperatures which favors the fluorescent transition from S_1 to some hot vibrational levels of S_0 because of particularly favorable Franck-Condon factors [Beretta et al. 1985, Coe et al. 1981]. The reverse argument is that these high levels of S_0 are sufficiently populated at flame temperature and so they can absorb energy under visible laser excitation leading to some new red-shifted features in the excitation spectrum. Coe et al. [1981] generalized these arguments by stating that a species is likely to absorb in the visible at high temperatures if it fluoresces in that region at room temperature. **Figure 5** illustrates this principle.

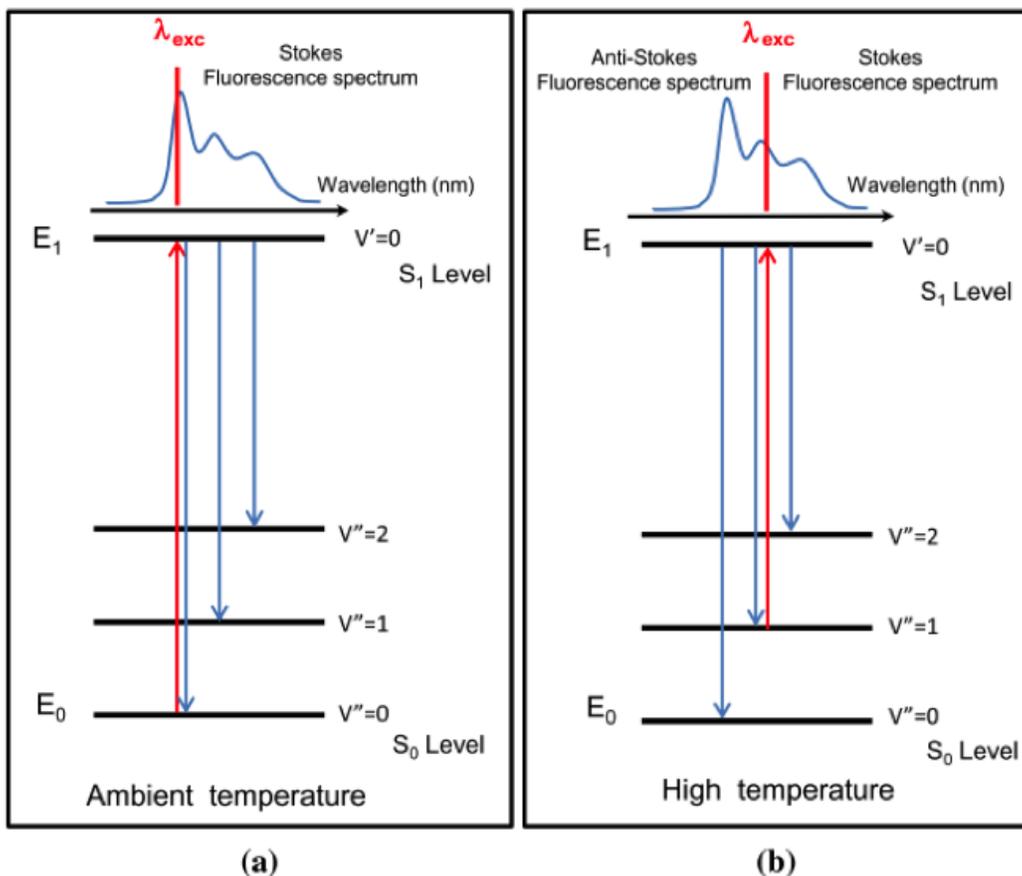


Figure 5 - Fluorescence spectrum as a function of the excitation wavelength under ambient temperature (a) and flame temperature (b) [Bejaoui et al. 2014].

In a recently published study, laser induced fluorescence measurements using visible excitation wavelengths were performed in a premixed flame of methane and a diffusion flame of Diesel [Bejaoui et al. 2014]. Results highlighted that PAHs can absorb and fluoresce up to 680 nm. Fluorescence emission spectra showed Stokes and anti-Stokes components. A discussion on these non-conventional absorption and fluorescence features is provided in Bejaoui et al. [2014] on the basis of the knowledge of PAH spectroscopy and flame kinetics. Through the study of different families of PAHs, it was shown that only a limited number of PAHs fluoresce at the observed wavelengths. Large pericondensed PAHs are unlikely to give rise to such signals. However, other species based on three dimensional arrangements of fragments of relatively small gaseous PAHs, possibly including aromatic rings with five carbons, could be responsible for the absorption features observed for wavelengths above 550 nm. The rubicene ($C_{26}H_{14}$) and its derivatives also exhibit some absorption features up to 650 nm at room temperature and could also be a good candidate. Because of their late formation in the flame, all these gaseous species could be at the origin of the formation of the first nuclei leading to soot particles.

Ex situ LIF measurements: Jet cooled

LIF (JC-LIF) – As discussed above, laser induced fluorescence of PAHs in flame conditions are broad and exhibit an unstructured emission due to the high temperature and the diverse pool of fluorescent species. The only way to make selective measurements of PAHs is to reduce the rovibrational temperature of the sampled species inside a supersonic jet expansion. This technique is called Jet cooled LIF and was applied to detect benzene, naphthalene, pyrene and fluoranthene in sooting flames [Mercier et al. 2008, Wartel et al. 2010, Wartel et al. 2011, Mouton et al. 2016]. The main drawback of the method is that the range of species detectable is limited to the stable ones. After flame extraction, the sampled flow is cooled down to 90 K by free jet expansion at 0.1 Pa. A laser beam is directly sent into the free jet in order to probe the cooled PAHs sampled from the flame. **Figure 6** shows

a comparison between two naphthalene spectra: one recorded at room temperature and low pressure [Behlen et al. 1981], and one recorded under jet cooled conditions after flame sampling [Wartel et al. 2010]. It illustrates how the rovibrational cooling in the jet expansion allows for the fine tuning of the excitation wavelength on the absorption bands of the PAH spectra, ultimately allowing the selective detection of PAHs by LIF. Under jet-cooled conditions, the LIF signal becomes independent of quenching variations and can therefore be directly calibrated into absolute concentrations by internal calibration. Sensitivity in the ppb range has been attained during pyrene [Wartel et al. 2011] and fluoranthene [Mouton et al. 2016] measurements in sooting flames with an estimated uncertainty of $\pm 10\%$.

Jet cooled LIF could be applied to study the spectroscopic features of isolated and cold PAHs, i.e., in experimental conditions representative of astrophysical environments. Such information would be useful to interpret the blue luminescence observed in stars like HD 44179, in the Red Rectangle nebula, which is attributed to the emission of PAHs excited with UV light coming from the center of the star [Vijh et al. 2004].

Acknowledgments

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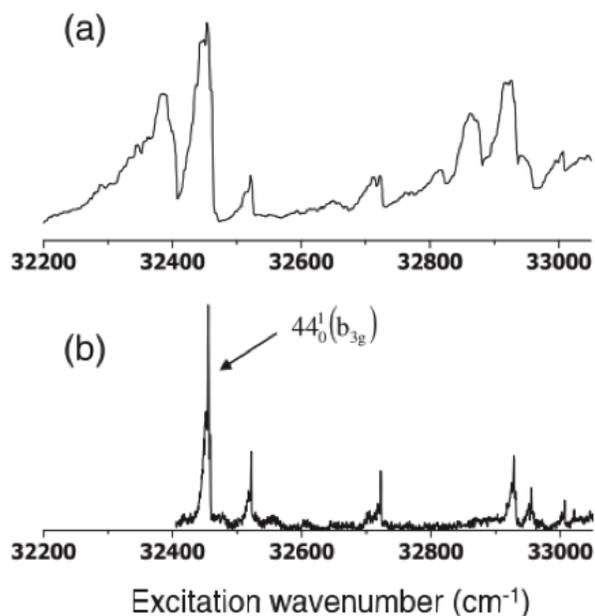


Figure 6 - Excitation spectra of naphthalene. (a) Room temperature (300 K) naphthalene vapor at 6.66×10^{-3} Pa [Behlen et al. 1981]. (b) Naphthalene extracted from the flame cooled down in a supersonic jet (90 K, 0.5 Pa) [Wartel et al. 2010].



Salma Bejaoui is a NASA postdoctoral fellow at NASA Ames Research Center. She joined the COSmiC team to study the spectroscopic features of PAHs and dust precursors under conditions relevant to astrophysics. Cavity ring down spectroscopy and laser induced fluorescence are the main diagnostics used in her research applied to detect the absorption and emission of cold and isolated PAHs. She received a PhD from PC2A laboratory where she applied laser-based diagnostics such as LII and LIF to study the formation process of PAHs and soot in flame conditions. Email: Salma.bejaoui@nasa.gov

Selected bibliography supporting this *In Focus*

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Abstracts

On the Relation between the Mysterious 21 μm Emission Feature of Post-Asymptotic Giant Branch Stars and Their Mass Loss Rates

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Over two decades ago, a prominent, mysterious emission band peaking at $\sim 20.1 \mu\text{m}$ was serendipitously detected in four preplanetary nebulae (PPNe; also known as “protoplanetary nebulae”). To date, this spectral feature, designated as the “21 μm ” feature, has been seen in 27 carbon-rich PPNe in the Milky Way and the Magellanic Clouds. The nature of the carriers of this feature remains unknown although many candidate materials have been proposed. The 21 μm sources also exhibit an equally mysterious, unidentified emission feature peaking at 30 μm . While the 21 μm feature is *exclusively* seen in PPNe, a short-lived evolutionary stage between the end of the asymptotic giant branch (AGB) and planetary nebula (PN) phases, the 30 μm feature is more commonly observed in all stages of stellar evolution from the AGB through PPN to PN phases. We derive the stellar mass loss rates (\dot{M}) of these sources from their infrared (IR) emission, using the “2-DUST” radiative transfer code for axisymmetric dusty systems which allows one to distinguish the mass loss rates of the AGB phase (\dot{M}_{AGB}) from that of the superwind (\dot{M}_{SW}) phase. We examine the correlation between \dot{M}_{AGB} or \dot{M}_{SW} and the fluxes emitted from the 21 and 30 μm features. We find that both features tend to correlate with \dot{M}_{AGB} , suggesting that their carriers are probably formed in the AGB phase. The nondetection of the 21 μm feature in AGB stars suggests that, unlike the 30 μm feature, the excitation of the carriers of the 21 μm feature may require ultraviolet photons which are available in PPNe but not in AGB stars.

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Interstellar fullerene compounds and diffuse interstellar bands

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Recently, the presence of fullerenes in the interstellar medium (ISM) has been confirmed and new findings suggest that these fullerenes may possibly form from PAHs in the ISM. Moreover, the first confirmed identification of two strong diffuse interstellar bands (DIBs) with the fullerene, C_{60}^+ , connects the long standing suggestion that various fullerenes could be DIB carriers. These new discoveries justify reassessing the overall importance of interstellar fullerene compounds, including fullerenes of various sizes with endohedral or exohedral inclusions and heterofullerenes (EEHFs). The phenomenology of fullerene compounds is complex. In addition to fullerene formation in grain shattering, fullerene formation from fully dehydrogenated PAHs in diffuse interstellar clouds could perhaps transform a significant percentage of the tail of low-mass PAH distribution into fullerenes including EEHFs. But many uncertain processes make it extremely difficult to assess their expected abundance, composition and size distribution, except for the substantial abundance measured for C_{60}^+ . EEHFs share many properties with pure fullerenes, such as C_{60} , as regards stability, formation/destruction and chemical processes, as well as many basic spectral features. Because DIBs are ubiquitous in all lines of sight in the ISM, we address several questions about the interstellar importance of various EEHFs, especially as possible carriers of diffuse interstellar bands. Specifically, we discuss basic interstellar properties and the likely contributions of fullerenes of various sizes and their charged counterparts such as C_{60}^+ , and then in turn: 1) metallofullerenes, 2) heterofullerenes, 3) fullerenes, 4) fullerene-PAH compounds, 5) $H_2@C_{60}$. From this reassessment of the literature and from combining it with known DIB line identifications, we conclude that the general landscape of interstellar fullerene compounds is probably much richer than heretofore realized. EEHFs, together with pure fullerenes of various sizes, have many properties necessary to be suitably carriers of DIBs: carbonaceous nature; stability and resilience in the harsh conditions of the interstellar medium; existing with various heteroatoms and ionization states; relatively easy formation; few stable isomers; spectral lines in the right spectral range; various and complex energy internal conversion; rich Jahn-Teller fine structure. This is supported by the first identification of a DIB carrier as C_{60}^+ . Unfortunately, the lack of any precise information about the complex optical spectra of EEHFs and most pure fullerenes other than C_{60} and about their interstellar abundances still precludes definitive assessment of the importance of fullerene compounds as DIB carriers. Their compounds could significantly contribute to DIBs, but it still seems difficult that they are the only important DIB carriers. Regardless, DIBs appear as the most promising way of tracing the interstellar abundances of various fullerene compounds if the breakthrough in identifying C_{60}^+ as a DIB carrier can be extended to more spectral features through systematic studies of their laboratory gas-phase spectroscopy.

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Interpreting the subtle spectral variations of the 11.2 and 12.7 μm polycyclic aromatic hydrocarbon bands

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We report new properties of the 11 and 12.7 μm emission complexes of polycyclic aromatic hydrocarbons (PAHs) by applying a Gaussian-based decomposition technique. Using high-resolution *Spitzer* Space Telescope data, we study in detail the spectral and spatial characteristics of the 11 and 12.7 μm emission bands in maps of reflection nebulae NGC 7023 and NGC 2023 (North and South) and the star-forming region M17. Profile variations are observed in both the 11 and 12.7 μm emission bands. We identify a neutral contribution to the traditional 11.0 μm PAH band and a cationic contribution to the traditional 11.2 μm band, the latter of which affects the PAH class of the 11.2 μm emission in our sample. The peak variations of the 12.7 μm complex are explained by the competition between two underlying blended components. The spatial distributions of these components link them to cations and neutrals. We conclude that the 12.7 μm emission originates in both neutral and cationic PAHs, lending support to the use of the 12.7/11.2 intensity ratio as a charge proxy.

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