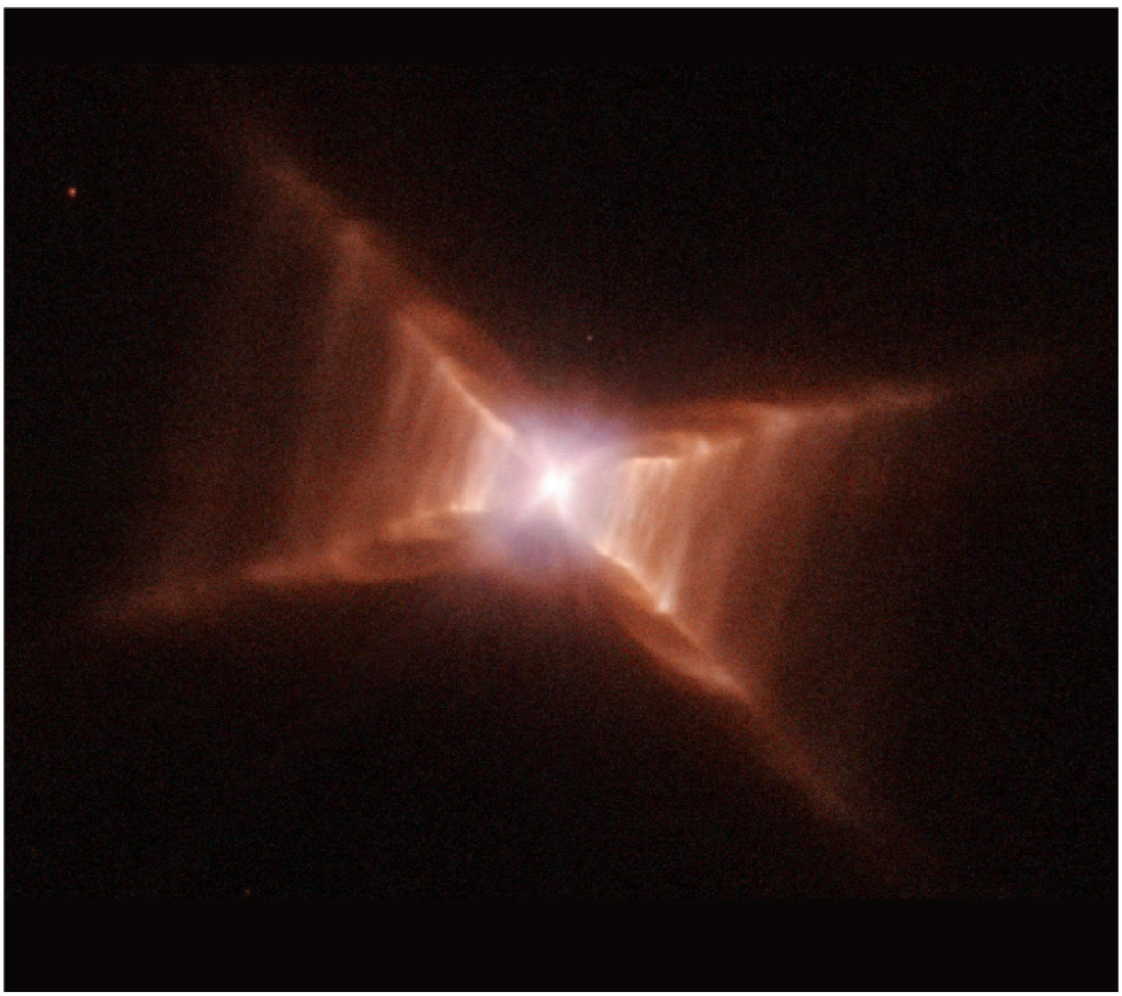
Issue 11 | September 2014

AstroPAH

A Newsletter on Astronomical PAHs



The Red Rectangle

Editorial

Dear Colleagues,

Welcome to the 11th release of AstroPAH. This month, our cover features the Red Rectangle nebula, a galactic evolved star which is the brightest known source of PAH IR bands. The NASA AMES Cosmic Simulation Chamber (COSmiC) experiment is the subject of our In Focus section.

We would like to thank our readers for the many contributions that arrived this month. Our Abstracts Section includes observational studies of PAHs in dwarf galaxies, active galactic nuclei (AGNs) and H II regions, theoretical and experimental works on superhydrogenated PAHs irradiated by X-rays, photodissociation of pyrene cations, anisotropy and size effects on PAH optical spectra, infrared high-resolution gas-phase spectroscopy of the cyclopropenyl cation, and a laboratory investigation of the role of PAHs in Titan's atmospheric chemistry.

In the 7th release of AstroPAH, the 168th Faraday Discussion on Astrochemistry of Dust, Ice and Gas was presented in the In Focus section. The papers and discussion associated with them are now available online. In particular, we would like to direct your attention to the discussion held on the paper of Maté et al. (Faraday Discuss., 2014, 168, 571-615). This paper on "Stability of carbonaceous dust analogues and glycine under UV irradiation and electron bombardment" presented conclusions (as described in AstroPAH #7) that were discussed at the FD168 and subsequently adjusted (not described in AstroPAH #7).

The next issue of AstroPAH will mark our **first anniversary** and will be out on 21 October 2014. To celebrate the event, we are preparing a special edition. You can contribute by sending us your answer to the following question:

What is the PAH-related question you would like to see solved in the next decades?

If you want your contributions to appear in the next issue, the deadline is 3 October 2014. For more information on AstroPAH, visit our website:

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

Best regards

The Editorial Team

AstroPAH Newsletter

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PAH Picture of the Month

The Red Rectangle is an intriguing carbon-rich bipolar nebula produced by the mass-loss of the evolved central star (HD 44179), which is surrounded by an oxygen-rich disk. A complex chemistry is acting, as testified by the number of spectroscopical features observed at different wavelengths, such as blue luminescence, extended red emission, as well as silicate and PAH bands.

Credits: Hubble-NASA/ESA, Hans Van Winckel (Catholic University of Leuven, Belgium) and Martin Cohen (University of California).

In Focus:
The NASA Ames Cosmic Simulation Chamber (COSmIC)

by The COSmIC science team

Polycyclic aromatic hydrocarbons (PAHs) play an important role in astrophysics and have been the target of extensive laboratory studies. PAHs are found in meteorites and interplanetary dust particles and have been suggested to carry the ubiquitous unidentified infrared bands (UIBs) seen in emission in a wide variety of interstellar and extragalactic environments as well as some of the over 400 diffuse interstellar bands (DIBs) seen in absorption in the spectra of diffuse interstellar clouds.

Until the late 90s, laboratory measurements relied solely on matrix isolation spectroscopy (MIS) where PAH ions were isolated in a solid rare gas matrix at very low temperature and submitted to vacuum ultraviolet radiation to mimic the interstellar medium conditions. However, even in the least perturbing (low polarizability) neon matrices the interaction of the trapped PAHs with the rare gas atoms of the solid lattice induced a frequency shift and a broadening of the band profile that precluded a direct comparison with astronomical data. Measuring the spectra of PAH ions in the gas phase represented an experimental challenge because PAHs are large, nonvolatile molecules that need to be vaporized and ionized. Several groups started developing gas phase experiments in the late 90s; one of them led by Farid Salama at NASA Ames Research Center was the Cosmic Simulation Chamber (COSmIC).

The COSmIC simulation facility was developed to measure the absorption spectra of neutral and ionized PAH in the gas phase under experimental conditions that were representative of astrophysical environments (interstellar medium, circumstellar medium and planetary atmospheres). The idea of setting up this laboratory facility to simulate space environments began as a Director's Discretionary Fund (DDF) project initiated by Farid Salama in 1996, and its realization represented a true success story for Ames' DDF program that provided seed funds for new (and risky) innovative research projects. The implementation of the COSmIC facility resulted from a collaboration between Ames' space research scientists (Farid Salama, Ludovic Biennier and Lou Allamandola), and Los Gatos Research (LGR) scientists (Anthony O'Keefe, Jim Scherer and Manish Gupta) through a Small Business Innovative Research (SBIR) contract awarded by NASA to LGR.

This pioneering facility was originally composed of a pulsed supersonic expansion plasma source, the Pulsed Discharge Nozzle (PDN), coupled to a pulsed cavity ringdown spectrometer (CRDS). With this setup, large carbon-containing molecules and ions could be generated and maintained under interstellar-like conditions, while simultaneously measuring their absorption spectra in the near-UV to visible range. In the early 2010s, a reflectron time-of-flight mass spectrometer (TOF-MS) was added to the experimental setup as a complementary diagnostic tool (see description below) to monitor the molecular growth in the plasma, in real time. **Figure 1** shows a global view of the COSmIC facility, and close-up views of the chamber with the CRDS apparatus, and the TOF-MS rotating to face the PDN vacuum chamber.

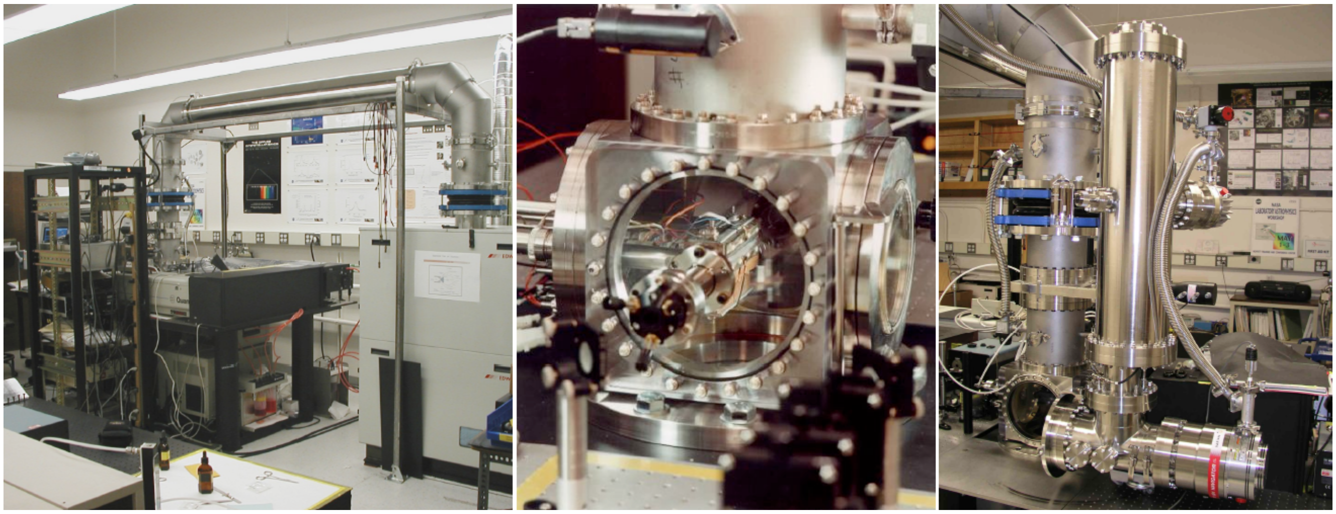


Figure 1 - Left: The COSmIC laboratory Facility. Center: close-up view of the initial COSmIC system consisting of a Pulsed Discharge Nozzle coupled to a Cavity Ringdown Spectrometer. Right: the last addition to COSmIC, the TOF-MS can be rotated to face the PDN vacuum chamber or set aside for solid phase experiments (adapted from Salama 2008).

The Pulsed Discharge Nozzle (PDN)

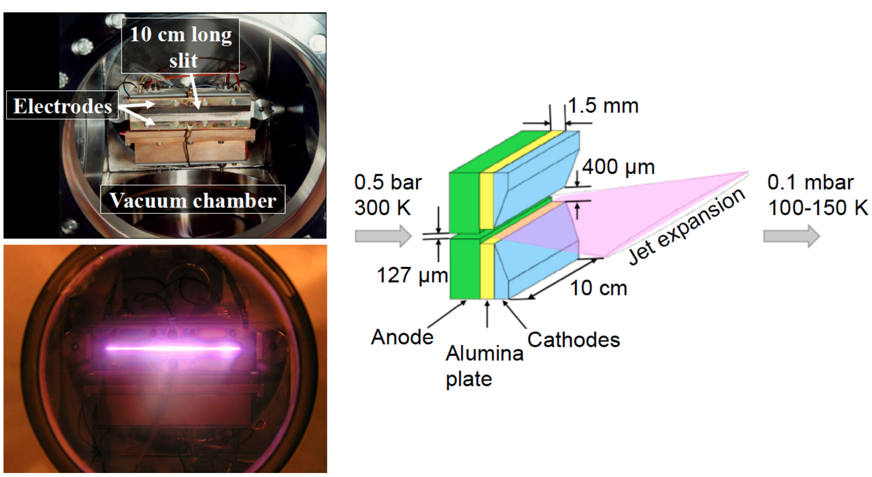


Figure 2 - Top left: Front view of the PDN showing the copper reservoir and electrodes along the slit. Bottom left: view of the PDN planar plasma jet expansion. Right: Schematics of the PDN (adapted from Broks et al., 2005). The gas enters the slit on the left side (green) and subsequently expands through the region between anode and cathodes (yellow) where the discharge is generated, before further expanding in the COSmIC chamber (pink).

The PDN consists of a copper reservoir in which high-pressure gas accumulates and then escapes in pulses through a very thin slit, generating a planar supersonic jet expansion, i.e. adiabatically cooling the gas and reducing the pressure. PAH molecules can be placed inside the heated reservoir to be vaporized and seeded in a beam of argon gas, or gas mixtures can directly be injected in the PDN using various gases and a set of mass flow controllers. In the stream of the expansion, high voltage is applied to electrodes placed along the slit, generating a pulsed plasma discharge and ionizing the molecules present in the expansion. These molecules and ions are then at a low temperature of about 100 Kelvin (-170 C), which corresponds to the average interstellar temperature; and are isolated, as in low-density interstellar regions. Pictures of the PDN before and after turning the plasma on as well as a schematic of the design are shown in **Figure 2**.

Cavity RingDown Spectroscopy (CRDS)

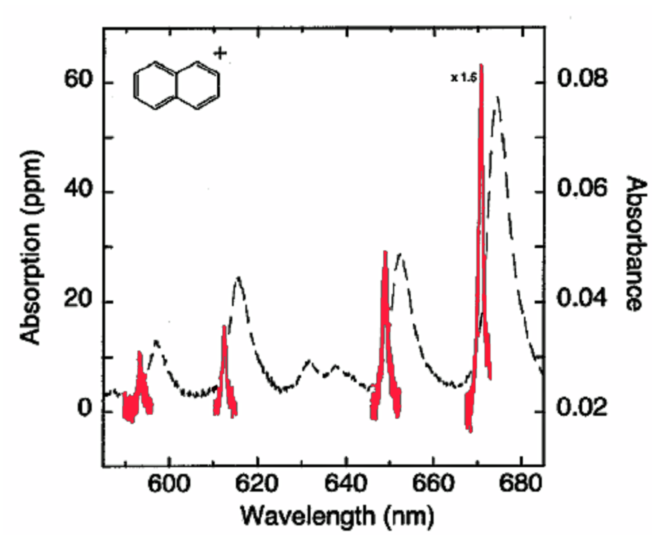


Figure 3 - Comparison of cavity ringdown spectroscopy (CRDS) (red solid line) and the Ne matrix isolation spectroscopy (black dashed line) measurements of the vibronic progression of the $D_2 \leftarrow D_0$ electronic transition band system of the naphthalene cation (adapted from Biennier et al. 2003).

The spectrum of the molecules and ions formed in the PDN can then be measured with CRDS, an ultrasensitive, non-intrusive direct absorption technique for absorption measurements of materials present at extremely low concentrations (sub-ppm levels). **Figure 3** shows the absorption spectrum of the naphthalene cation obtained in the gas phase with COSmIC compared to the one obtained in the solid phase with MIS technique, highlighting the visible broadening and shifting of the bands induced by the MIS technique.

With the initial PDN-CRDS configuration, COSmIC was successfully used to synthesize, process and characterize neutral and ionized interstellar PAH analogs. Among others, naphthalene ($C_{10}H_8^+$), acenaphthene ($C_{12}H_{10}^+$), pyrene ($C_{16}H_{10}^+$), 1-pyrenecarboxyaldehyde ($C_{17}H_{10}O^+$) and 1-methylpyrene ($C_{17}H_{12}^+$) cations (Biennier et al. 2003, 2004; Tan & Salama, 2006), and perylene ($C_{20}H_{12}$) and benzo(ghi)perylene ($C_{22}H_{12}$) neutrals (Tan & Salama, 2005a, 2005b) were characterized.

Time-of-Flight Mass Spectrometer (TOF-MS)

These initial gas phase experiments also showed that, in addition to forming cold isolated molecules and ions, the plasma in the PDN produced complex chemistry. The production of soot in the plasma discharge was evidenced by the accumulation of solid deposits on the electrodes of the PDN (Biennier et al., 2004). In collaboration with Richard Zare, Jamie Elsila and Hassan Sabbah at Stanford University, Microprobe laser-desorption laser-ionization mass spectrometry (μL2MS) was performed on soot collected on the electrodes, and showed the presence of molecules of heavier mass than the seeded PAHs. These observations led to the award of a second Director's Discretionary Fund to Farid Salama in 2003 to explore this promising research avenue.

As a result, a reflectron TOF-MS was added to the experimental setup (Ricketts et al., 2011) to monitor, in situ, the chemical processes occurring in the plasma, and to attempt to better understand the formation of solid dust grains from the growth of molecular precursors in the gas phase in circumstellar outflows. The principle of mass spectrometry is to measure the mass to charge ratio of ionized species. On COSmIC, the plasma discharge in the PDN is used as an external ionization source (as opposed to the usual internal ionization sources that fragment the molecules). The plasma-generated ions present in the free-jet expansion are then skimmed and attracted into the TOF-MS before being directly detected without undergoing fragmentation.

The addition of this complementary analytical tool to the COSmIC system has allowed for the analysis of plasma-generated chemical products, and has opened the door to another dimension of science enabled by COSmIC, including two recent studies presented below: a thorough laboratory investigation of PAH formation and destruction in the circumstellar outflows of carbon stars (Contreras & Salama, 2013), and simulations of Titan's atmospheric chemistry at low temperature (Sciamma-O'Brien et al, 2014).

Laboratory investigation of PAH formation and destruction in the circumstellar outflows of carbon stars

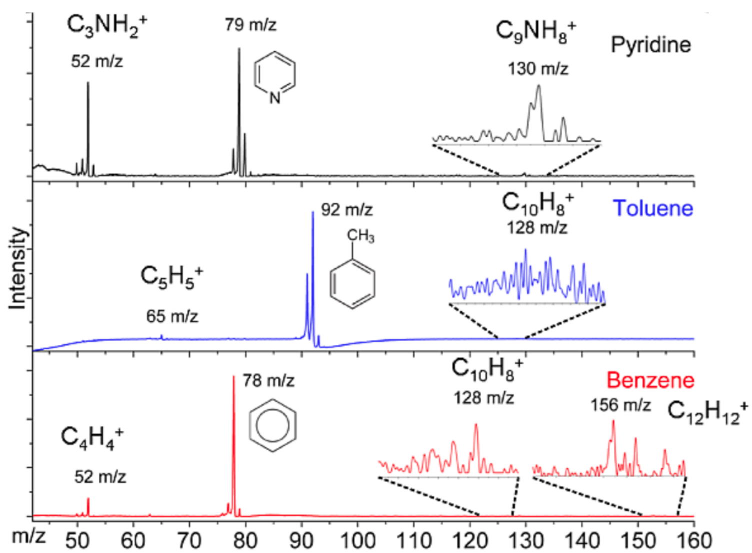


Figure 4 - Mass spectra of plasmas generated in argon gas seeded with benzene (C_6H_6), toluene (C_7H_8) and pyridine (C_5H_5N) (extracted from Contreras & Salama, 2013).

Using COSmIC's unique design, it is possible to investigate the formation and destruction processes of carbon-bearing molecules and ions that are potential precursors of carbonaceous grains and represent interstellar dust analogs. In a recent study by Contreras & Salama (2013), a variety of PAH and hydrocarbon molecular precursors as well as species that include the cosmically abundant atoms O, N, and S, were seeded in argon in the PDN, and studied by mass spectrometry using the TOF-MS. As an example of the many results of this extensive study, **Figure 4** shows the mass spectra of plasmas generated in argon gas seeded with benzene (C_6H_6), toluene (C_7H_8) and pyridine (C_5H_5N). Fragmentation of the precursors and production of heavier products are observed, including the detection of a molecule at 128 m/z that could be naphthalene in the C_6H_6 and C_7H_8 experiments, and its analogous N-containing ion at 130 m/z for the C_5H_5N experiment.

The results of this laboratory study seem to indicate that the most promising routes for molecular growth and for the formation of large molecular species in the outflows of carbon stars are the routes that begin with small unsaturated carbon chains leading to the formation of benzene rings and the subsequent formation of small polycyclic aromatic hydrocarbon structures that act as seed units for the formation of larger grains (for more details, see Contreras & Salama, 2013).

The Titan Haze Simulation experiment: probing Titan's atmospheric chemistry at low temperature

COSmIC is also utilized to study the complex chemistry that occurs at low temperature (>200 K) in Titan's atmosphere, and leads to the production of heavy organic molecules and subsequently solid aerosols that form the orange haze surrounding Titan. COSmIC's unique design allows cooling down gas mixtures to Titan-like temperature (∼150 K) before inducing the chemistry by plasma. In addition, because of the pulsed nature of the plasma, the residence time of the gas in the discharge is only a few microseconds, which leads to a truncated chemistry and allows for the out-of-the-beaten-path study of the first and intermediate steps of Titan's chemistry.

In the study presented in Sciamma-O'Brien et al. (2014), a systematic mass spectrometry analysis was performed using five gas mixtures to study the gas phase chemistry of Titan. Pure N_2, N_2-CH_4 (90:10), N_2-CH_4-C_2H_2 (85:10:5), N_2-CH_4-C_6H_6 (85:10:5), and N_2-CH_4-C_2H_2-C_6H_6 (80:10:5:5), were selected to probe specific pathways associated with the presence of acetylene and benzene. **Figure 5** gives a comparison of the experimental mass spectra obtained for the different mixtures, showing the evolution of the chemical growth observed when adding heavier precursors to the initial gas mixture. The results of this gas phase study have been compared to observational data from the Cassini Plasma Spectrometer-Ion Beam Spectrometer (CAPS-IBS) and have provided very promising results that illustrate the unique power of the COSmIC/THS laboratory approach to help analyze and better understand return data from Cassini's instruments.

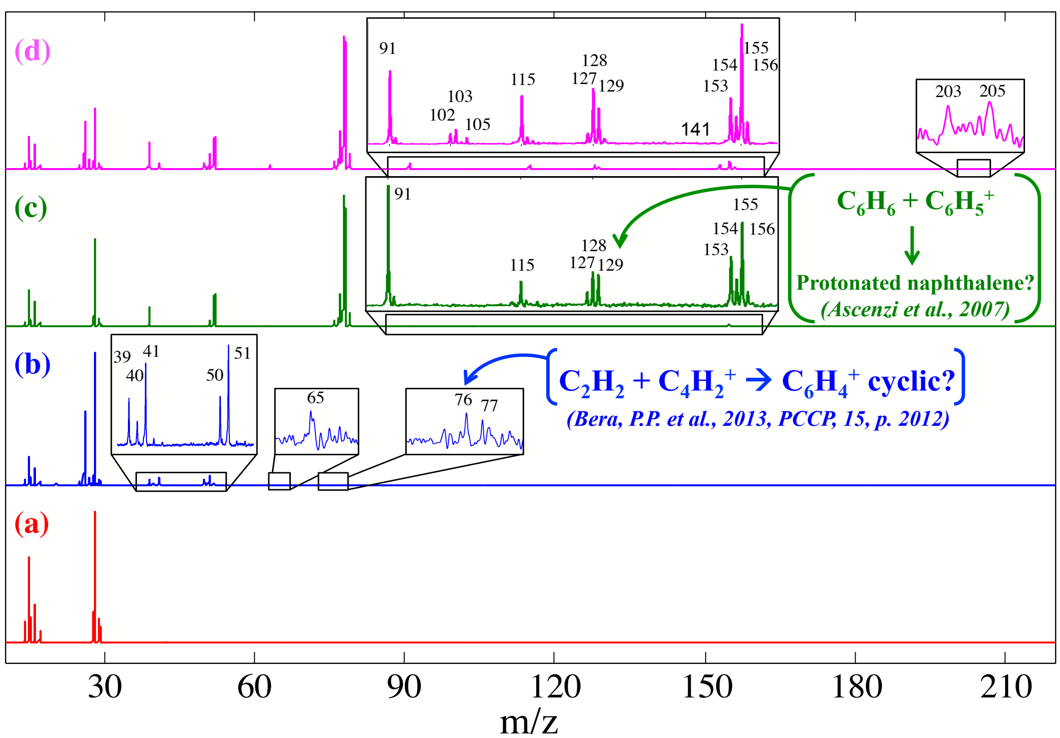


Figure 5 - TOF-MS spectra of N_2-CH_4 (a), N_2-CH_4-C_2H_2(b), N_2-CH_4-C_6H_6 (c), and N_2-CH_4-C_2H_2-C_6H_6 (d) showing the growth evolution of the chemistry in the THS experiment (adapted from Sciamma-O'Brien et al., 2014).

Solid phase studies

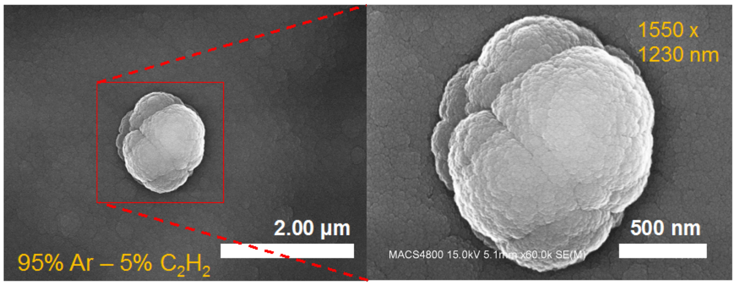
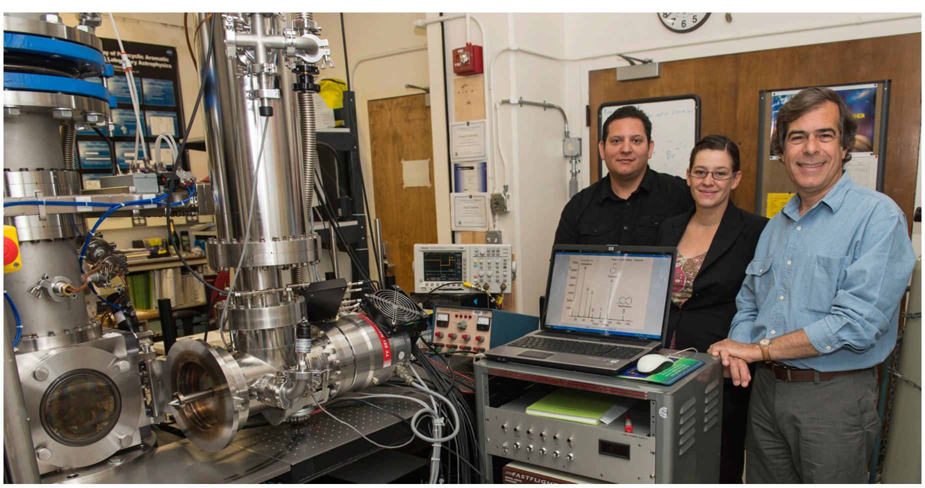


Figure 6 - SEM images of interstellar dust analogs produced in Ar-C_2H_2 mixture in COSmIC (extracted from NASA press release 14-129).

In addition to the gas phase, the solid phase of the COSmIC experiments is now being studied, both in the context of interstellar grains and Titan aerosols. Solid aerosols are formed through molecular growth in the plasma expansion and are deposited on a variety of substrates for further ex situ analyses. The first results of the interstellar grain studies (produced in argon-acetylene mixtures) were the subject of a recent NASA press release (#14-129) earlier this year. Scanning electron microscopy (SEM) imaging showed the presence of nanoparticles on the order of 10 nm size, grains ranging from 100-500 nm and aggregates of grains up to 1.5 μm in diameter, as shown in **Figure 6** (extracted from the press release). Preliminary results of the THS solid phase analyses are consistent with the gas phase results in showing an evolution of the chemical growth when adding heavier precursors to the initial gas mixture: SEM images have shown that aggregates produced in N_2-CH_4-C_2H_2-C_6H_6 mixtures are much larger (up to 5 μm in diameter) than those produced in N_2-CH_4 mixtures (0.1-0.5 μm).

Since its creation in the late 1990s COSmIC has been in continuous evolution and has proven to be a very valuable asset for the simulation of astrophysical and planetary environments. The latest addition of a new dimension in the solid phase analyses complements the on-going gas-phase research and offers another very promising avenue.



The COSmIC team at NASA Ames Research Center: (from right to left) **Dr. Farid Salama** is a member of the Astrophysics Branch at NASA Ames Research Center and a senior member and co-founder of the Astrophysics & Astrochemistry Laboratory where he is the head of the COSmIC group. **Dr. Ella Sciamma-O'Brien** and **Dr. Cesar S. Contreras** are research associates at Bay Area Environmental Research Institute (BAERI) and members of the Astrophysics Branch at NASA Ames Research Center.

Recent Papers

Dust evolution in the dwarf galaxy Holmberg II

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A detailed photometric study of star-forming regions (SFRs) in the galaxy Holmberg II has been carried out using the archival observational data from the far infrared to the ultraviolet obtained with the GALEX, Spitzer, and Herschel telescopes. Spectroscopic observations with the 6-m BTA telescope (Special Astrophysical Observatory of the Russian Academy of Sciences) are used to estimate the ages and metallicities of SFRs. The ages of SFRs have been correlated for the first time with their emission parameters in a wide spectral range and with the physical parameters determined by fitting the observed spectra. It is shown that the fluxes at 8 and 24 μm characterizing the emission from polycyclic aromatic hydrocarbons (PAHs) and hot dust grains decrease with age, but their ratio increases. This implies that the relative contribution from PAHs to the total infrared flux increases with age. It is hypothesized that the detected increase in the ratio of the fluxes at 8 and 24 μm is related to the increase in the relative PAH fraction due to the destruction of larger grains.

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Astronomy Letters 40, 278 (2014)

http://adsabs.harvard.edu/abs/2014AstL...40..278W

Deexcitation Dynamics of Superhydrogenated Polycyclic Aromatic Hydrocarbon Cations after Soft-x-Ray Absorption

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We have investigated the response of superhydrogenated gas-phase coronene cations upon soft X-ray absorption. Carbon (1s) $\longrightarrow \pi^\star$ transitions were resonantly excited at $h\nu$ = 285 eV. The resulting core hole is then filled in an Auger decay process, with the excess energy being released in the form of an Auger-electron. Predominantly highly excited dications are thus

formed, which cool down by hydrogen emission. In superhydrogenated systems, the additional H atoms act as a buffer, quenching loss of native H atoms and molecular fragmentation. Dissociation and transition state energies for several H loss channels were computed by means of density functional theory. Using these energies as input into an Arrhenius-type cascade model very good agreement with the experimental data is found. The results have important implications for the survival of polyaromatic hydrocarbons in the interstellar medium and reflect key aspects of graphene hydrogenation.

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Phys. Rev. Lett. 113, 053002 (2014)

http://journals.aps.org/prl/abstract/10.1103/PhysRevLett.113.053002

Nuclear 11.3μm PAH emission in local active galactic nuclei

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We present Gran Telescopio CANARIAS CanariCam 8.7 μm imaging and 7.5 – 13 μm spectroscopy of six local systems known to host an active galactic nucleus (AGN) and have nuclear star formation. Our main goal is to investigate whether the molecules responsible for the 11.3 μm polycyclic aromatic hydrocarbon (PAH) feature are destroyed in the close vicinity of an AGN. We detect 11.3 μm PAH feature emission in the nuclear regions of the galaxies as well as extended PAH emission over a few hundred parsecs. The equivalent width (EW) of the feature shows a minimum at the nucleus but increases with increasing radial distances, reaching typical star-forming values a few hundred parsecs away from the nucleus. The reduced nuclear EWs are interpreted as due to increased dilution from the AGN continuum rather than destruction of the PAH molecules. We conclude that at least those molecules responsible for the 11.3 μm PAH feature survive in the nuclear environments as close as 10 pc from the AGN and for Seyfert-like AGN luminosities. We propose that material in the dusty tori, nuclear gas discs, and/or host galaxies of AGN is likely to provide the column densities necessary to protect the PAH molecules from the AGN radiation field.

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MNRAS, 443, 2766 (2014)

http://mnras.oxfordjournals.org/content/443/3/2766

Photodissociation of Pyrene Cations: Structure and Energetics from $C_{16}H_{10}{}^{+}$ to $C_{14}{}^{+}$ and almost everything in between

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The unimolecular dissociation of the pyrene radical cation, $C_{16}H_{10}{}^{+\bullet}$, has been explored using a combination of computational techniques and experimental approaches, such as multiple photon absorption in the cold ion trap PIRENEA and imaging Photoelectron Photoion Coincidence Spectrometry (iPEPICO). In total twenty-two reactions, involving the fragmentation cascade (H, C_2H_2 and C_4H_2 loss) from the pyrene radical cation down to the $C_{14}{}^{+\bullet}$ fragment ion, have been studied using PIRENEA. Branching ratios have been measured for reactions from $C_{16}H_{10}{}^{+\bullet}$, $C_{16}H_8{}^{+\bullet}$ and $C_{16}H_5{}^{+}$. DFT calculations of the fragmentation pathways observed experimentally and postulated theoretically, lead to seventeen unique structures. One important prediction is the opening of the pyrene ring system starting from $C_{16}H_4{}^{+\bullet}$ radical. In the iPEPICO experiments, only two reactions could be studied, namely R1 $C_{16}H_{10}{}^{+\bullet} \rightarrow C_{16}H_9{}^{+}$ + H (m/z = 201) and R2 $C_{16}H_9{}^{+} \rightarrow C_{16}H_8{}^{+\bullet}$ + H (m/z = 200). The activation energies for these reactions were determined as 5.4 $\pm$ 1.2 and 3.3 $\pm$ 1.1 eV respectively.

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The Titan Haze Simulation experiment on COSmIC: probing Titan's atmospheric chemistry at low temperature

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The aim of the Titan Haze Simulation (THS) experiment is to contribute to a better understanding of aerosol formation in Titan's atmosphere through the study of the chemical formation pathways that link the simpler gas phase molecules resulting from the first steps of the N_2-CH_4 chemistry, to the more complex gas phase precursors of aerosols; and more specifically, to investigate the role of polycyclic aromatic hydrocarbons (PAHs) and nitrogenated polycyclic aromatic hydrocarbons (PANHs), among other hydrocarbons, in this process. In the THS experiment developed at the NASA Ames Cosmic simulation facility (COSmIC), Titan's atmospheric chemistry is simulated by a pulsed plasma jet expansion at temperature conditions ($\sim$150 K) close to those found in Titan's atmosphere in regions where aerosols are formed. In addition, because of the very short residence time of the gas in the plasma discharge, only the initial steps of the chemistry occur, making the COSmIC/THS a unique tool to study the first and intermediate (when adding heavier precursors to the initial N_2-CH_4 mixture) steps of Titan's atmospheric chemistry at low temperature as shown in the study presented here. We further illustrate the potential of COSmIC/THS for the simulation of Titan's atmospheric chemistry by presenting very promising results from a preliminary comparison of the laboratory data to data from the Cassini Plasma Spectrometer Ion Beam Spectrometer (CAPS-IBS) instrument.

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Optical and infrared emission of H II complexes as a clue to the PAH life cycle

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We present an analysis of optical spectroscopy and infrared aperture photometry of more than 100 H II complexes in nine galaxies. Spectra obtained with the 6-m telescope of SAO RAS are used along with archival data from *Spitzer* and several ground-based telescopes to infer a strength of polycyclic aromatic hydrocarbon (PAH) emission, age, properties of the UV radiation field, and metallicity of studied H II complexes. Physical properties (age, radiation field parameters, metallicity) are related to the F_8/F_{24} ratio used as a proxy for the PAH abundance in order to reveal factors that may influence the PAH evolution in H II complexes. The well-known

correlation between the F_8/F_{24} ratio and metallicity is confirmed in the studied complexes. The infrared flux ratio also correlates with the [O III]$\lambda 5007/\mathrm{H}\beta$ ratio which is often considered as an indicator of the radiation field hardness, but this correlation seems to be a mere reflection of a correlation between [O III]$\lambda 5007/\mathrm{H}\beta$ and metallicity. In separate metallicity bins, the F_8/F_{24} ratio is found to correlate with an age of an H II complex, which is estimated from the equivalent width of $\mathrm{H}\beta$ line. The correlation is positive for low metallicity complexes and negative for high metallicity complexes. Analysing various mechanisms of PAH formation and destruction in the context of found correlations, we suggest that PAH abundance is likely altered by the UV radiation within H II complexes, but this is not necessarily due to their destruction. If PAHs can also form in H II complexes due to some processes like aromatisation, photodestruction, shattering and sputtering of very small grains, the net F_8/F_{24} ratio is determined by a balance between all these processes that can be different at different metallicities.

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Anisotropy and Size Effects on the Optical Spectra of Polycyclic Aromatic Hydrocarbons

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The electronic and optical properties of polycyclic aromatic hydrocarbons (PAHs) present a strong dependence on their size and geometry. We tackle this issue by analyzing the spectral features of two prototypical classes of PAHs, belonging to D_{6h} and D_{2h} symmetry point groups and related to coronene as multifunctional seed. While the size variation induces an overall red shift of the spectra and a redistribution of the oscillator strength between the main peaks, a lower molecular symmetry is responsible for the appearance of new optical features. Along with broken molecular orbital degeneracies, optical peaks split and dark states are activated in the low-energy part of the spectrum. Supported by a systematic analysis of the composition and the character of the optical transitions, our results contribute in shedding light to the mechanisms responsible for spectral modifications in the visible and near UV absorption bands of medium-size PAHs.

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AKARI Infrared Camera Observations of the 3.3μm PAH Feature in Swift/BAT AGNs

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We explore the relationships between the 3.3 μm polycyclic aromatic hydrocarbon (PAH) feature and active galactic nucleus (AGN) properties of a sample of 54 hard X-ray selected bright AGNs, including both Seyfert 1 and Seyfert 2 type objects, using the InfraRed Camera (IRC) on board the infrared astronomical satellite $AKARI$. The sample is selected from the 9-month $Swift$/BAT survey in the 14–195 keV band and all of them have measured X-ray spectra at $E \leq 10$ keV. These X-ray spectra provide measurements of the neutral hydrogen column density ($N_{\rm H}$) towards the AGNs. We use the 3.3 μm PAH luminosity ($L_{3.3\mu\rm m}$) as a proxy for star formation activity and hard X-ray luminosity ($L_{14-195\rm keV}$) as an indicator of the AGN activity. We search for possible difference of star-formation activity between type 1 (un-absorbed) and type 2 (absorbed) AGNs. We have made several statistical analyses taking the upper-limits of the PAH lines into account utilizing survival analysis methods. The results of our $\log(L_{14-195\rm keV})$ versus $\log(L_{3.3\mu\rm m})$ regression shows a positive correlation and the slope for the type 1/unobscured AGNs is steeper than that of type 2/obscured AGNs at a 3σ level. Also our analysis show that the circum-nuclear star-formation is more enhanced in type 2/absorbed AGNs than type 1/un-absorbed AGNs for low X-ray luminosity/low Eddington ratio AGNs, while there is no significant dependence of star-formation activities on the AGN type in the high X-ray luminosities/Eddington ratios.

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The mid-infrared appearance of the Galactic Mini-Starburst W49A

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The massive star forming region W49A represents one of the largest complexes of massive star formation present in the Milky Way and contains at least fifty young massive stars still enshrouded in their natal molecular cloud. We employ *Spitzer*/IRS spectral mapping observations of the northern part of W49A to investigate the mid-infrared (MIR) spatial appearance of the polycyclic aromatic hydrocarbon (PAH) bands, PAH plateau features, atomic lines and continuum emission. We examine the spatial variations of the MIR emission components in slices through two of the ultra compact-H II (UC-H II) regions. We find that the PAH bands reproduce known trends, with the caveat that the 6.2 μm PAH band seems to decouple from the other ionized PAH bands in some of the UC-H II regions – an effect previously observed only in one other object: the giant star forming region N66 in the LMC. Furthermore, we compare the nature of the emission surrounding W49A to that of 'diffuse' sightlines. It is found that the surrounding emission can be explained by line of sight emission, and does not represent true 'diffuse' material. Additionally, we examine the MIR appearance of star formation on various scales from UC-H II regions to starburst galaxies, including a discussion of the fraction of PAH emission in the 8 μm IRAC filter. We find that the MIR appearance of W49A is that of a starburst on large scales yet its individual components are consistent with other galactic H II regions.

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Laboratory Gas-phase Detection of the Cyclopropenyl Cation (c-$C_3H_3^+$)

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The cyclopropenyl cation (c-$C_3H_3^+$) is the smallest aromatic hydrocarbon molecule and considered to be a pivotal intermediate in ion-molecule reactions in space. An astronomical identification has been prohibited so far, because of a lack of gas-phase data. Here we report the first high resolution infrared laboratory gas-phase spectrum of the ν_4 (C-H asymmetric stretching) fundamental band of c-$C_3H_3^+$. The c-$C_3H_3^+$ cations are generated in supersonically expanding planar plasma by discharging a propyne-helium gas pulse, yielding a rotational temperature of $\sim$35 K. The absorption spectrum is recorded in the 3.19 μm region using sensitive continuous-wave cavity ring-down spectroscopy. The analysis of about 130 ro-vibrational transitions results in precise spectroscopic parameters. These constants allow for an accurate comparison with high-level theoretical predictions, and provide the relevant information needed to search for this astrochemically relevant carbo-cation in space.

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