Astrochemistry VII – Through the Cosmos from Galaxies to Planets
Proceedings IAU Symposium No. 332, 2017
M. Cunningham, T. Millar & Y. Aikawa, eds.

doi:10.1017/S1743921317011619

Recent Progress in Laboratory Astrophysics Achieved with NASA Ames' COSmIC Facility

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Abstract. We describe the characteristics and the capabilities of the laboratory facility, COSmIC, that was developed at NASA Ames to generate, process and analyze interstellar, circumstellar and planetary analogs in the laboratory. COSmIC stands for 'Cosmic Simulation Chamber' and is dedicated to the study of neutral and ionized molecules and nanoparticles under the low temperature and high vacuum conditions that are required to simulate various space environments such as diffuse interstellar clouds, circumstellar outflows and planetary atmospheres. Recent results obtained using COSmIC will be highlighted. In particular, the progress that has been achieved in the domain of the diffuse interstellar bands (DIBs) and in monitoring, in the laboratory, the formation of circumstellar dust grains and planetary atmosphere aerosols from their gas-phase molecular precursors. Plans for future laboratory experiments on interstellar and planetary molecules and grains will also be addressed, as well as the implications of the studies underway for astronomical observations and past and future space mission data analysis.

Introduction

The Cosmic Simulation Chamber (COSmIC) was developed to generate, process, and analyze interstellar, circumstellar and planetary analogs in the laboratory (Salama (2008)). COSmIC is dedicated to the study of neutral and ionized molecules and nanoparticles under the low temperature and high vacuum conditions that are required to simulate space environments. The COSmIC experimental setup (Figures 1 and 2) is composed of a Pulsed Discharge Nozzle (PDN) expansion, that generates a plasma in the stream of a free supersonic jet expansion, coupled to high-sensitivity, complementary in situ diagnostics: cavity ring down spectroscopy (CRDS) and laser induced fluorescence (LIF) systems for photonic detection, and Reflectron Time-Of-Flight Mass Spectrometer (ReTOF-MS) for mass detection in real time (Rickets, *et al.* (2011)). *read more at:* `https://www.nasa.gov/feature/ames/cosmic`

1. INTERSTELLAR APPLICATIONS: Astronomical Surveys: Searching for the Signature of Neutral and Ionized PAHs in Absorption and in Emission

1.1. *Absorption Spectroscopy*

Cavity ring-down spectra of neutral and ionized PAH molecules isolated in a free cold jet expansion with Ar buffer gas have been measured in COSmIC, and then compared

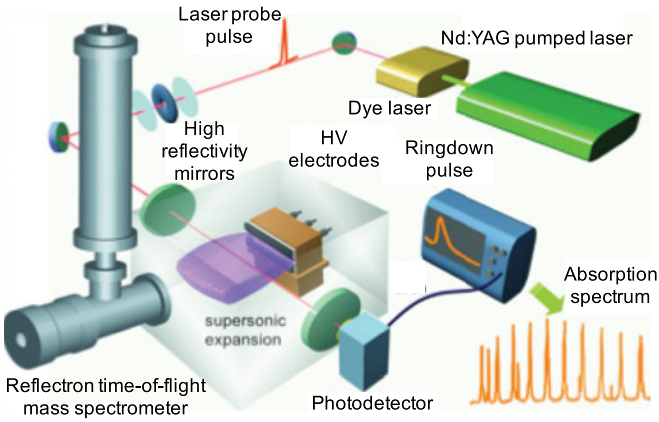

Figure 1. Schematic of the COSmIC experimental setup.

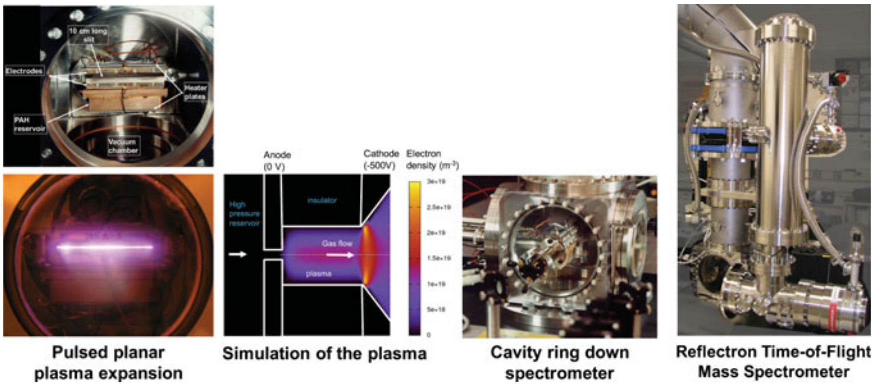

Figure 2. (Left) Picture of the pulsed discharge nozzle with and without plasma discharge. (Middle left) Simulation of the plasma discharge (Broks *et al.* (2015)). (Middle right) Picture of the cavity ringdown spectrometer (CRDS). (Right) Picture of the reflectron time-of-flight mass spectrometer.

to the average spectrum (S/N) of the program reddened stars along lines of sight probing translucent interstellar clouds (Salama, *et al.* (2011)). Upper limits for the column densities of the PAH molecular carriers were calculated at the wavelengths associated with specific vibronic transitions of the PAH molecules according to the formula (Frisch (1972)):

$N(cm^{-2}) = 1.13 \cdot 10^{20} EW(\AA)/\lambda(\AA)^2 \cdot f$ where EW is the equivalent width and f is the oscillator strength or the 'f value' of the vibronic transition that is being considered.

The comparison of these unique laboratory data with high-resolution, high signal-to-noise ratio spectra (Figure 3) led to the following findings:

• The abundance of the specific neutral and ionized PAHs examined in this study must be very low in the individual translucent interstellar clouds probed in the survey (PAH features remain below the level of detection).

• The derived column densities for neutral PAHs in these lines-of-sight range from 10^{11} to $10^{13} cm^{-2}$.

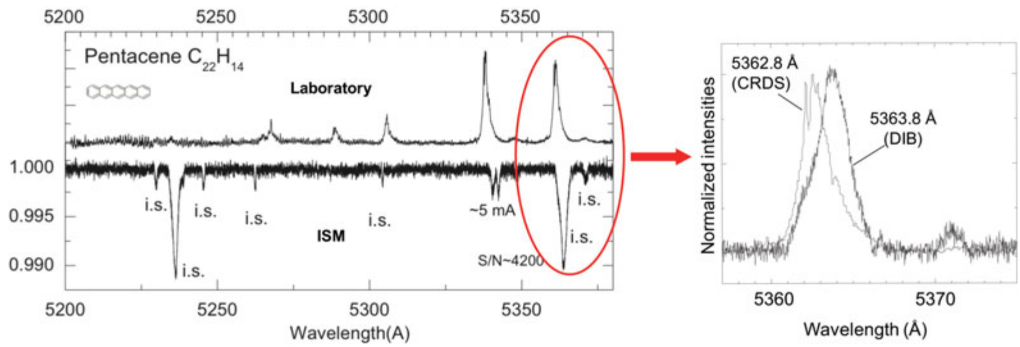

Figure 3. (Left) Cavity ring-down spectrum of pentacene ($C_{22}H_{14}$) prepared in a cold jet expansion with Ar buffer gas is compared to the average spectrum of the program stars (S/N 4200) (Salama, *et al.* (2011)). (Right) Comparison of the 5362.8 Å absorption band of jet-cooled pentacene ($C_{22}H_{14}$) measured in the laboratory with cavity ring-down spectroscopy with a FWHM of 1.9Å and the 5363.8 Å DIB, FWHM = 2.1Å extracted from the average spectrum of the program stars (S/N 2100).

• Neutral PAHs exhibit intrinsic band profiles that are similar to the profile of the narrow DIBs indicating that the carriers of the narrow DIBs must have close molecular structure and characteristics.

• The absorption bands of PAH ions are intrinsically broad (very fast relaxation time). The bands exhibit a close similarity with the strong 4430 Å DIB.

This study was the first quantitative survey of neutral and ionized PAHs in the optical range and it opened the way for unambiguous quantitative searches of PAHs in a variety of interstellar and circumstellar environments.*(read more at:* `nasa.gov/centers/ames/news/releases/2011/11-35AR.html`*)*

1.2. *Emission Spectroscopy*

In preparation for the development of a Laser Induced Fluorescence (LIF) diagnostic on COSmIC, a preliminary study was conducted on a matrix isolation experiment. LIF spectra of neutral PAHs measured in 10 K inert-gas matrices were investigated and compared with the luminescence spectra measured in the Red Rectangle Nebula, a protoplanetary nebula that is one of the brightest known sources of extended red emission as well as of ubiquitous infrared (UIR) band emissions (Bejaoui *et al.* (2005)). These measurements indicate that small neutral PAHs can contribute to the blue fluorescence observed in the Red Rectangle.

2. CIRCUMSTELLAR APPLICATIONS: Formation of carbon dust grains in circumstellar outflows of late carbon stars - From PAHs to carbon nanoparticles

Condensation experiments (Kimura & Saito (2010)) have concluded that 'Evolved stars supply organic materials into space. The organic materials evolve and alter to form more complex organic molecules before incorporation into the star formation stage (Figure 4). PAHs are the most plausible molecules abundantly produced within the gas ejected from evolved stars. During the growth of PAH molecules, and as they move away from the central star, larger PAHs coagulate to form carbon grains.'

In COSmIC, simple hydrocarbons (CH_4, C_2H_2,...) and PAHs seeded in Ar gas can be used as precursors to study grain formation in the gas phase. These Ar-based

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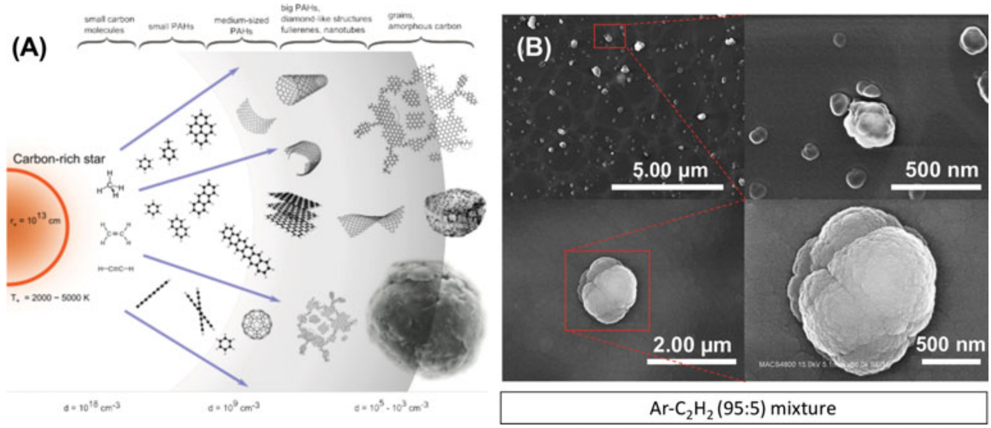

Figure 4. ((Left - A) Cartoon of carbon grain formation in the atmosphere of late-type carbon-rich stars (Contreras & Salama (2013)). (Right - B) SEM images of cosmic dust analogs formed in an Ar-based mixture in COSmIC.

mixtures are injected in the Pulsed Discharge Nozzle, generating a supersonically-cooled expansion in which a plasma discharge dissociates and ionizes the precursors and induces chemistry, producing hydrocarbon ions that can then be extracted and directly detected by Reflectron Time-of-Flight Mass Spectrometry, without fragmentation (Contreras & Salama (2013)).

The chemistry induced by plasma in these hydrocarbon-seeded argon jet expansions results in the formation of soot nanoparticles (nm-sized grains and μm-sized aggregates) that can be deposited onto different substrates for further ex situ analysis like Scanning Electron Microscopy (SEM) as shown in Figure 4. *read more at:* `nasa.gov/press/2014/may/nasa-simulator-successfully-recreates-space-dust`

These Ar-hydrocarbon plasma experiments have shown that:

• The use of cold plasma sources as tools for exploring the formation (and destruction) processes of carbon-bearing molecules is relevant to astrophysical environments.

• The combined techniques of PDN-CRDS-ReTOFMS are useful to study the dynamic behavior of soot particles formed in the plasma.

• Deposition of soot material and further characterization with scanning electron microscopy can provide insight into how the grains form in the gas phase.

• Three distinct types of materials are observed in the deposition of plasma formed carbon grains: bedding (10-50 nm nanoparticles covering the substrate), grains (100-300 nm) and aggregates (500-1000 nm).

• All the material exhibits a cauliflower-like morphology, similar to that of amorphous carbon solid particles.

3. PLANETARY APPLICATIONS: Simulating Titan's atmospheric chemistry at low temperature

Titan, Saturn's largest moon, has a dense atmosphere, mainly composed of nitrogen (N_2 at 95-98%) and methane (CH_4 at 2-5%). In Titan's atmosphere, a complex organic chemistry is induced by solar UV radiation and electron bombardment from Saturn's magnetosphere and leads to the production of heavy neutral, positively and negatively charged molecules and subsequently solid aerosols that form the orange haze surrounding Titan. We use the Titan Haze Simulation (THS) experiment on COSmIC to study Titan's

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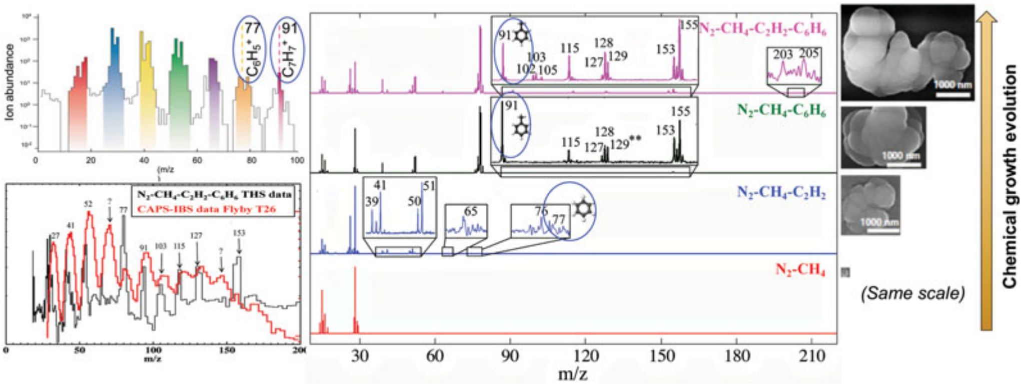

Figure 5. (Top left) INMS positive ion spectrum showing the peaks at 77 and 91 also observed in the THS mass spectra. (Top bottom) Comparison between the Cassini CAPS-IBS spectrum from Flyby T26 (red) (adapted from Crary *et al.* (2009)) and the THS experimental spectrum obtained in the N_2-CH_4-C_2H_2-C_6H_6 plasma (black) degraded to CAPS-IBS' resolution. (Courtesy of J. Westlake.) (Middle) THS mass spectra of the positive ions produced in N_2-CH_4, N_2-CH_4-C_2H_2, N_2-CH_4-C_6H_6, and N_2-CH_4- C_2H_2 -C_6H_6 gas mixtures, showing the chemical growth evolution in the THS experiment when gradually injecting heavier hydrocarbons in the initial gas mixture. (Right) SEM images of aggregates formed in the same four gas mixtures.

atmospheric chemistry and aerosol evolution at low temperature. In the THS, the gas is cooled to Titan-like temperature (~150 K) in the supersonic expansion of the PDN before inducing the chemistry by pulsed plasma, and remains at low temperature in the plasma discharge (~200 K). The pulsed nature of the plasma results in a truncated chemistry. Different N_2-CH_4-based gas mixtures can be injected in the plasma, with or without the addition of heavier precursors present as trace elements on Titan, in order to monitor the evolution of the chemical growth from molecular reactions to the formation of aerosols (Figure 5). Both the gas- and solid phase products resulting from the plasma-induced chemistry can be analyzed (Sciamma-O'Brien, *et al.* (2014), (2017)).

A recent mass spectrometry study (Sciamma-O'Brien, *et al.* (2014)) has shown the unique capability of the THS to monitor the first and intermediate steps as well as specific chemical pathways in Titan's N_2-CH_4 atmospheric chemistry. The mass spectra obtained in various N_2-CH_4-based gas mixtures in the THS experiment show that the N_2-CH_4 chemistry induced in the THS results in the production of species that match certain regions of the observational spectra returned by the Cassini Ion Neutral Mass Spectrometer (INMS) and Cassini Plasma Spectrometer (CAPS) instruments, as shown in Figure 5. The Titan aerosol analogs produced in the THS can be deposited on substrates and characterized ex situ. A scanning electron microscopy analysis of the THS solid aerosols has shown that heavier precursors lead to more complex chemistry and hence to larger aggregates, in agreement with the results of the mass spectometry gas phase analysis, as shown in Figure 5.

The gas and solid phase analyses conducted on the THS experiment have demonstrated that:

• COSmIC can be used to study for the first time, the first an intermediate steps of Titan's chemistry and the early stages of aerosol formation, at Titan like temperature (150 K) with the THS experiments.

• The solid phase analysis is consistent with the gas phase analysis and has shown that when larger molecules are present in the initial mixture, a more complex chemistry has time to occur in the pulsed discharge and produce heavier products and larger aerosols

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(Sciamma-O'Brien, *et al.* (2014), (2017)). The THS can therefore be used to study the early stages of aerosol growth on Titan

• The gas phase analysis can be compared to CAPS-IBS data but some regions are missing. By changing the composition of the initial mixture, we will be able to determine what specific chemical pathways lead to the production of the species still missing in our spectra.

Acknowledgments

This work is supported by the NASA Astronomy and Physics Research and Analysis (APRA) and the Solar System Workings Program Elements of the Science Mission Directorate. The authors acknowledge the technical support of R. Walker and E. Quigley. E.S.O. and C.S.C are Research Associates with BAER Institute. S.B. is a NASA Post-doctoral Fellow (NPP) at NASA-Ames Research Center.

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