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Laboratory Spectroscopy of Large Carbon Molecules and Ions in Support of Space Missions

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ABSTRACT

One of the major objectives of Laboratory Astrophysics is the optimization of data return from space missions by measuring spectra of atomic and molecular species in laboratory environments that mimic interstellar conditions (WhitePaper (2002, 2006)). Among interstellar species, PAHs are an important and ubiquitous component of carbon-bearing materials that represents a particularly difficult challenge for gas-phase laboratory studies. We present the absorption spectra of jet-cooled neutral and ionized PAHs and discuss the implications for astrophysics. The harsh physical conditions of the interstellar medium have been simulated in the laboratory. We are now, for *the first time*, in the position to *directly* compare laboratory spectra of PAHs and carbon nanoparticles with astronomical observations. This new phase offers tremendous opportunities for the data analysis of current and upcoming space missions geared toward the detection of large aromatic systems (HST/COS, FUSE, JWST, Spitzer).

1. Introduction, Laboratory Approach & Results

Polycyclic aromatic hydrocarbons (PAHs) constitute the building blocks of interstellar dust grains and play an important role in mediating the energetic and chemical processes in the interstellar medium (ISM). Their specific contribution to the interstellar extinction, and in particular to the diffuse interstellar bands (DIBs) remains, however, unclear. The DIBs are ubiquitous spectral absorption features observed in the line of sight of stars that

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are obscured by diffuse interstellar clouds. More than 300 bands have been reported to date spanning from the near UV to the near IR with bandwidths ranging from 0.4 to 40 Å (Tielens & Snow (1995)). The present consensus is that the DIBs arise from gas-phase organic molecules and ions that are abundant under the typical conditions reigning in the diffuse ISM. The PAH hypothesis is consistent with the cosmic abundance of Carbon and Hydrogen and with the required photostability of the DIB carriers against the strong VUV radiation field in the diffuse interstellar clouds.

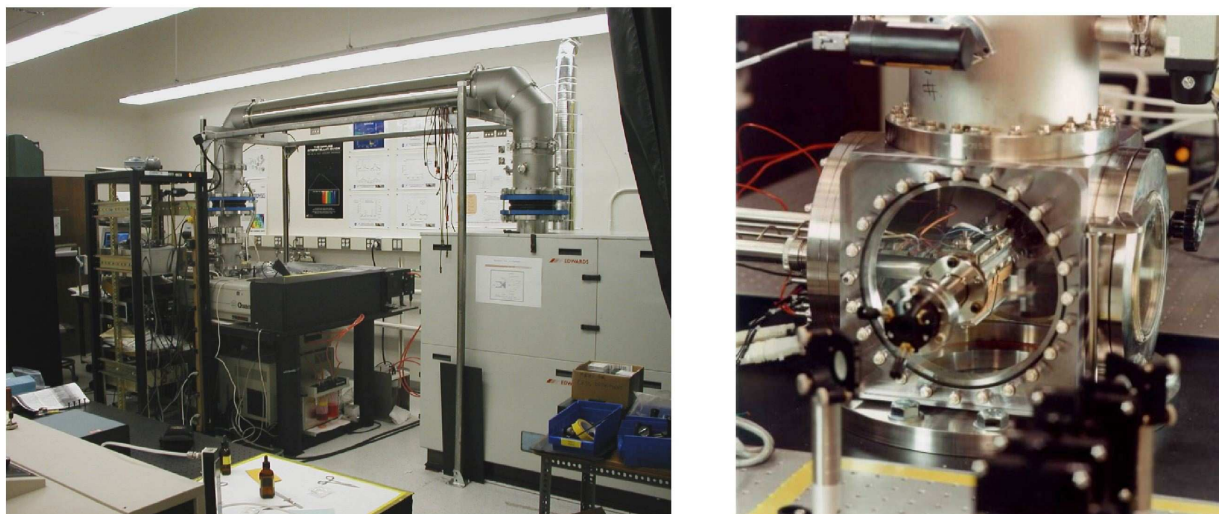


Fig. 1.— *Left side:* Current configuration of the Laboratory Facility. *Right side:* close-up view of the Chamber consisting of a Pulsed Discharge Nozzle coupled to a Cavity Ringdown Spectrometer apparatus and Reflectron time-of-flight mass spectrometer.

To properly address the issue of the identification of the DIBs, astronomical observations must be compared to laboratory spectra that are measured in an astrophysically relevant environment i.e. with the molecules/ions isolated, cold and in the *gas phase*. This task represents a serious experimental challenge because PAHs are large, non-volatile molecules. Furthermore, due to the ultra-fast non-radiative processes of internal electronic conversion that take place in these large molecular systems, detection by laser-induced fluorescence or by multiphoton excitation cannot be employed. Because of all these technical limitations, it was only recently that direct measurements of the absorption spectra of cold neutral and ionized PAHs in the gas-phase were achieved (Romanini et al. (1999); Biennier et al. (2003, 2004); Tan & Salama (2005a,b, 2006); Huisken (2006)). Our approach, relies on the association of a cold plasma source (pulsed discharge nozzle) with high sensitivity direct absorption techniques (cavity ring down spectroscopy, CRDS, multiplex integrated cavity output spectroscopy (MICOS) and time-of-flight mass spectrometry and is independent of inter- and intra- molecular processes (Salama et al. (2006)). The experimental approach has been described previously (Biennier et al. (2003, 2004); Tan & Salama (2005a)). Briefly, the pulsed discharge nozzle combines a supersonic slit jet that cools down the carrier gas

seeded with aromatics ($\sim 1\%$), with two electrodes that produce a discharge in the stream of the planar expansion to ionize the mixture when needed. The PAH vapor pressure is increased by heating a pick-up cell that contains the sample upstream the Argon flow. A cavity ringdown spectrometer probes the expansion several mm downstream with a sub-ppm absorption sensitivity. A reflectron time-of-flight (RETOF) mass spectrometer is coupled to the chamber to detect the radicals and particles that are formed in the discharge (Figure 1). We report the experimental results regarding the electronic spectroscopy of several cold neutral and ionized PAH in the gas phase that have been obtained with this new approach (Biennier et al. (2003, 2004); Tan & Salama (2005a,b, 2006)).

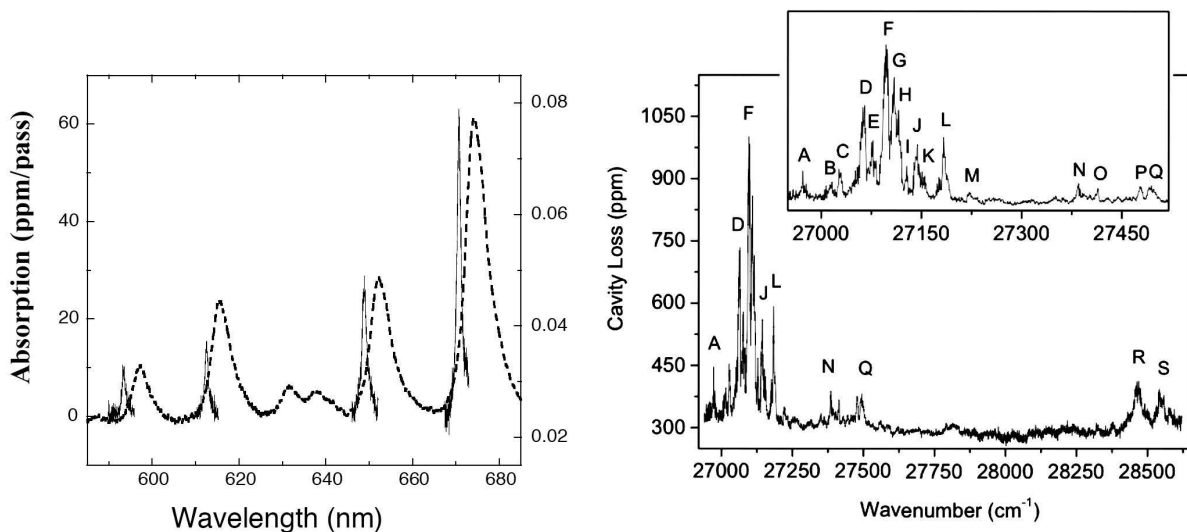


Fig. 2.— *Left*: Comparison of CRDS (Biennier et al. (2003)) and MIS/Ne (Salama & Allamandola (1991)) spectra. The interactions of the trapped Np^+ with the atoms of the solid neon matrix induce a frequency shift and a spectral broadening of the electronic spectrum. This figure illustrates dramatically the need for gas-phase experiments for a decisive, unambiguous, identification of the DIBs. MIS remains however critical for the pre-selection of potential candidates. *Right*: Cavity ringdown spectrum of the neutral PAH benzoperylene ($C_{22}H_{12}$), the largest PAH molecule measured to date in the gas phase (Tan & Salama (2005b)).

PAH ions: The electronic spectra of the cold naphthalene ($C_{10}H_8^+$), acenaphthene ($C_{12}H_{10}^+$), pyrene ions ($C_{16}H_{10}^+$) and some derivatives, methyl pyrene ($C_{17}H_{12}^+$) and carboxaldehyde pyrene ($C_{17}H_{10}O^+$) were measured in order to derive their *intrinsic* characteristics for comparison with interstellar spectra. A typical spectrum is shown in Figure 2 where the gas-phase CRD spectrum is compared to the solid matrix spectrum illustrating the strongly perturbing effect induced by the phonons of the solid lattice on band profiles and bandwidths. The vibronic bands are typically broad and without substructure, a characteristic of non-radiative intramolecular relaxation processes that explains the UV photon pumping mechanism that occurs in the ISM and the observations of the UIR emission by radiative

cascade. Detailed analysis of the band profile leads to the determination of FWHM of of the order of 25 cm^{-1} . This value corresponds to a 220 fs ultra fast relaxation time and is very close to the value derived for the strong 4428 ÅDIB (Snow et al. (2002)). We have also demonstrated that the discharge does not affect the vibrational temperature of the aromatic ions formed in the cold plasma expansion (Remy et al. (2005); Biennier et al. (2006)).

Neutral PAHs: The electronic spectra of the cold neutral Methyl Naphthalene ($\text{C}_{11}\text{H}_{10}$), Acenaphthene ($\text{C}_{12}\text{H}_{10}$), Phenanthrene ($\text{C}_{14}\text{H}_{10}$), Pyrene ($\text{C}_{16}\text{H}_{10}$), Perylene ($\text{C}_{20}\text{H}_{12}$), Pentacene ($\text{C}_{22}\text{H}_{14}$) and Benzoperylene ($\text{C}_{22}\text{H}_{12}$) were also measured in order to compare directly with astronomical spectra of DIBs. A typical spectrum is shown in Figure 2. By comparison with astronomical observations we were able to derive upper limits to the abundances of individual PAHs in the observed lines of sight. Values of the order of 10^{-4} to 10^{-6} are derived for the fraction of cosmic carbon locked up in these PAHs.

2. Perspectives and Conclusions

These preliminary results strongly validate our original experimental approach associating a cold plasma source with a cavity ringdown spectrometer and a time-of-flight mass spectrometer. These experiments provide first hand data on the spectroscopy and on the molecular dynamics of *free, cold* large carbon-containing molecules and ions in the gas phase. We are now, for the first time, in the position to directly search for *individual* PAH molecules and ions in astronomical observations in the UV-NIR range. This new phase offers tremendous opportunities for the data analysis of current and upcoming space missions.

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