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SPECTROSCOPY OF PAH MOLECULES AND IONS : FROM THE LABORATORY TO ASTRONOMICAL OBSERVATIONS

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Abstract. An extensive program has been developed to characterize the physical and chemical properties of carbon molecules and ions in space and to describe how they influence the radiation and energy balance. We review recent progress in the experimental and observational studies of an important class of carbon materials (PAHs) in the diffuse interstellar medium and discuss global astrophysical implications and future directions.

1 Introduction

Carbon molecules and ions play an important role in space. Polycyclic Aromatic Hydrocarbons (PAHs) are an important and ubiquitous component of carbon-bearing materials. PAHs are the best-known candidates to account for the infrared emission bands (UIR, Allamandola et al. 1999) and PAH spectral features are now being used as probes of the interstellar medium (ISM) in extra-galactic environments (Smith et al. 2007). In the model dealing with the interstellar spectral features, PAHs are present as a mixture of radicals, ions and neutral species. PAH ionization states reflect the ionization balance of the medium while PAH size, composition, and structure reflect the energetic and chemical history of the medium. PAHs constitute the building blocks of interstellar dust grains and play an important role in mediating the energetic and chemical processes in the ISM. PAHs are also thought to be among the carriers of the diffuse interstellar absorption bands (DIBs). Their specific contribution to the interstellar extinction and to the DIBs in particular remains, however, unclear. The DIBs are ubiquitous spectral absorption features observed in the line of sight of stars that 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). DIBs are also detected in extragalactic environments (Cox et al. 2007)). 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 (Salama et al. 1996).

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Laboratory Astrophysics provides the tool for the analysis and the optimization of astronomical data. The quality and, hence, the relevance of the analysis is directly correlated to the degree of relevance of the laboratory measurements to the physical phenomenon under investigation. Thus, a major challenge for laboratory astrophysics is to mimic (in a realistic way) the harsh physical conditions that exist in the emission and absorption interstellar zones. To properly address the issue of the identification of the DIBs, for example, astronomical observations must be compared to laboratory spectra that are measured in an environment where *gas phase* molecules and ions are isolated, cold and exposed to strong ultraviolet radiation fields. PAHs are refractory materials and represent a particularly difficult challenge for gas-phase laboratory studies. We present here the absorption spectra of neutral and ionized laboratory analogs of interstellar 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 analysis of astronomical data.

2 Results and discussion

Due to the low vapor pressure of the PAHs and the ultra-fast non-radiative processes of internal electronic conversion that take place in these large molecular ion systems prohibiting the detection by laser-induced fluorescence or by multiphoton excitation, and in the absence of direct absorption spectroscopy techniques with high enough sensitivity, PAH ion absorption was traditionally measured with the help of Matrix Isolation Spectroscopy (MIS). In MIS experiments, neutral and ionized PAHs are trapped and isolated at low temperature (< 5 K) in solid neon matrices where the perturbations induced in the spectrum of the trapped molecules and ions are minimum (Salama 1996). A large database of the spectra of neutral and ionized PAHs was developed using this technique. The MIS data was used to derive a general assessment of the PAH-DIB proposal (Salama et al. 1999). The advantage of MIS is to allow trapping and stabilizing a large column density of cold and isolated PAH ions formed in-situ, by one-photon ionization of the neutral precursor. The major drawback of this technique is the perturbation that is induced in the spectra in terms of band profiles and band peak positions as illustrated in Figure 2.

It was only recently that the long-awaited *direct* measurements of the absorption spectra of cold PAH ions in the gas-phase were finally achieved (Romanini et al. 1999, Biennier et al. 2003, Biennier et al. 2004, Sukhorukov et al. 2004, Tan & Salama 2005a, Tan & Salama 2005b, & Salama 2006) together with laser depletion mass spectroscopy measurements (Bréchignac & Pino 1999, Pino et al. 1999).

The harsh physical conditions of the interstellar medium are now simulated in the laboratory by associating a molecular beam with an ionizing discharge to generate a cold plasma expansion. Isolated PAH ions are formed from the neutral precursors at low temperature ($\sim 100K$) and their spectra are measured using cavity ring down spectroscopy (CRDS). These experiments provide unique information on the spectra of free, cold PAH molecules and ions in the gas phase that can now be *directly* compared to observational spectra. Our approach, relies on the association of a cold plasma source (pulsed discharge nozzle, PDN) with high sensitivity CRDS and time-of-flight mass spectrometry and is independent of inter- and

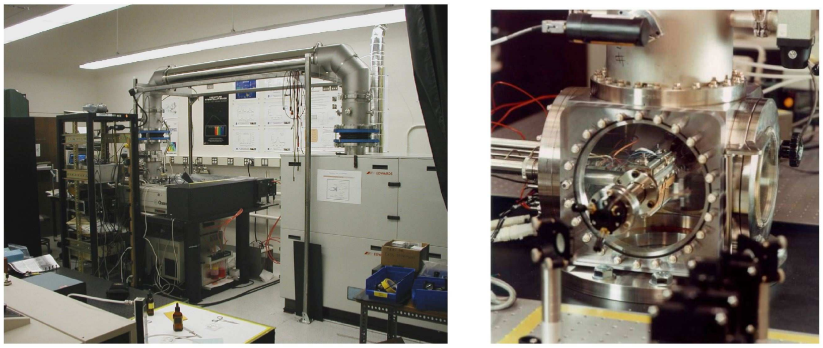

Fig. 1. Configuration of the Laboratory Facility. *Right:* close-up view of the Chamber consisting of a Pulsed Discharge Nozzle coupled to a Cavity Ringdown Spectrometer apparatus and Reflectron time-of-flight mass spectrometer.

intra- molecular processes. The experimental approach has been described previously (Biennier et al. 2003, Biennier et al. 2004, Tan & Salama 2005a). Briefly, the PDN combines a supersonic slit jet that cools down the carrier gas seeded with aromatics ($< 1\%$), with two electrodes that produce a discharge in the stream of the planar expansion to ionize the mixture when required. 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 mass spectrometer (RETOF-MS) is coupled to the chamber to detect the radicals and particles that are formed in the discharge (Figure 1). Detailed investigations of the flow dynamics in the PDN (Biennier et al. 2006) were fed into a plasma modeling program (Broks et al. 2005a, Broks et al. 2005b) that describes the electron density and energy, as well as the argon ion and metastable atom number density allowing a full characterization of the plasma. This analysis show that a glow discharge is formed in the PDN source (Remy et al. 2005) and that soft penning ionization of the neutral PAH precursors is the dominant mechanism that leads to the formation of cold PAH ions. We report the absorption spectra measured with this new approach.

PAH ions: The electronic spectra of a few selected PAH ions (see Table 1) 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. We have 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). Detailed analysis of band profiles indicates that the vibronic bands are typically broad (FWHMs of the order of a few tens of cm^{-1}), lack substructure and exhibit ultra fast relaxation times (a few tens to a few hundred fs), 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. The characteristics of the PAH ion bands measured to date are recapitulated in Table 1 where they are compared to the strong

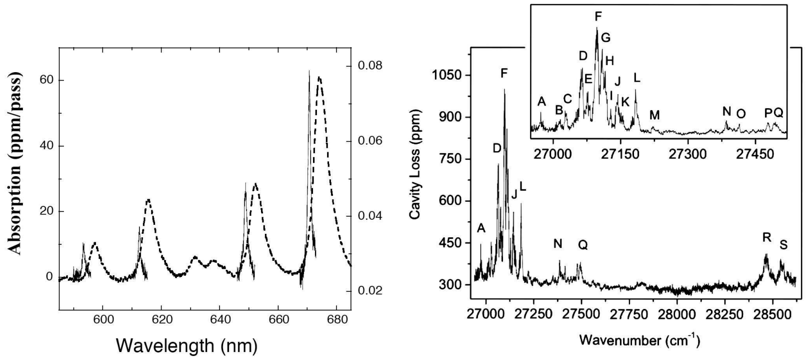

Fig. 2. *Left:* Comparison of CRDS (Biennier et al. 2003) and MIS (Salama & Allamandola 1991) spectra. The interactions of the trapped $C_{10}H_8^+$ with the atoms of the solid neon matrix induce a frequency shift and a spectral broadening of the electronic spectrum. *Right:* Cavity ringdown spectrum of neutral benzoperylene ($C_{22}H_{12}$), the largest PAH molecule measured to date in the gas phase (Tan & Salama 2005b).

broad DIB at 4428 Å that exhibits very similar characteristics. The 4428 DIB is an averaged Lorentzian profile resulting from measurements in the lines-of-sight of 35 highly-reddened O and early B stars with reddening, E(B-V), ranging from 1.0 to 2.5 mag and located in the Cyg OB2 association (Snow et al. 2002). The preliminary conclusion that can be derived from this comparison is that if PAH ions contribute to the DIBs they contribute to a class of *broad* DIBs. The search for weaker broad DIBs has been inconclusive so far. This would tend to indicate the absence of these specific ions in the line of sights that were probed. The non-observation might also be due, however, to the difficulty of extracting weak broad features in the astronomical spectra. The case will only be settled when dedicated surveys of broad DIBs with low error bars will be available for comparison with the laboratory data.

Neutral PAHs: The electronic spectra of the cold (50 K rotational temperature) neutral methylnaphthalene ($C_{11}H_{10}$), acenaphthene ($C_{12}H_{10}$), phenanthrene ($C_{14}H_{10}$), pyrene ($C_{16}H_{10}$), perylene ($C_{20}H_{12}$), pentacene ($C_{22}H_{14}$) and benzoperylene ($C_{22}H_{12}$) were also measured in the gas-phase in order to compare with astronomical spectra (Tan & Salama 2005a, Tan & Salama 2005b, Rouillé et al. 2004, Rouillé et al. 2007). Typical spectra are shown in Figures 2 & 3. Neutral PAHs exhibit narrower bands than the ions (FWHMs are of the order of only a few cm^{-1}) with a profile that is *closely* similar to the profile of the narrower DIBs. The case is strikingly illustrated in the comparison of the 5363 Å band of neutral pentacene, ($C_{22}H_{14}$), with the narrow ($< 2Å$ FWHM) 5364 Å DIB detected with the echelle spectrograph of the OHP 2m-telescope (Figure 3). Note that $C_{22}H_{14}$ exhibits another band of similar strength at 5340 Å where only a weaker feature is found in the astronomical spectra. Additional comparisons are being performed between laboratory spectra and the astronomical spectra of a limited set of 7 reddened O and B observed with the ELODIE/OHP and the UVES/VLT telescopes in the 3130 Å to 5400 Å range. The stars have reddening E(B-V) ranging from 0.95 to 1.35 mag. Features can be detected at the 0.2% level when co-adding all spectra. From these comparisons, we were able

Table 1. Electronic state peak positions and band widths of cold gas-phase PAH ions measured in the laboratory are compared to the characteristics of the strong broad 4428 ÅDIB

Molecular ion	Electronic State	λ (Å)	$\Delta\ \lambda$ (Å)
Naphthalene$^+$ $[C_{10}H_8^+]^{a,1}$	D_2	6707.7	10
Naphthalene$^+$ $[C_{10}H_8^+]^{b,2}$	D_3	4548.5	19
Acenaphtene$^+$ $[C_{12}H_{14}^+]^{a,1}$	D_2	6462.7	22
Fluorene$^+$ $[C_{13}H_{10}^+]^{c,2}$	D_3	6201.7	53
Phenanthrene$^+$ $[C_{14}H_{10}^+]^{d,2}$	D_2	8919.0	12
Anthracene$^+$ $[C_{14}H_{10}^+]^{e,1}$	D_2	7087.6	47
Pyrene$^+$ $[C_{16}H_{10}^+]^{f,1}$	D_5	4362.0	28
Pyrene$^+$ $[C_{16}H_{10}^+]^{g,2}$	D_4	4803.3	30
Pyrene$^+$ $[C_{16}H_{10}^+]^{g,2}$	D_2	7786.6	97
Methylpyrene$^+$ $[C_{17}H_{12}^+]^{h,1}$	D_5	4411.3	10
		(4413.3; 4409.3)	
Pyrene(COH)$^+$ $[C_{17}H_{10}O^+]^{h,1}$	D_8	4457.8	20
Pyrene(COH)$^+$ $[C_{17}H_{10}O^+]^{h,1}$		4442.7	
Pyrene(COH)$^+$ $[C_{17}H_{10}O^+]^{h,1}$		4431.4	
4428Å DIB[i]		*4428.4 ± 1.4*	*17.3 ± 1.64*

[1]CRDS, [2]Laser Depletion MS, [a]Biennier et al. 2003, [b]Pino et al. 1999, [c]Bréchignac et al. 2001, [d]Bréchignac & Pino 1999, [e]Sukhorukov et al. 2004, [f]Biennier et al. 2004, [g]Pino 1999, [h]Tan & Salama 2006, [i]Snow et al. 2002

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 (Cami et al. 2005). These preliminary results await comparison with higher-resolution astronomical data.

Discharge products and formation of carbon particles: We have identified the formation of CH as one of the high-energy plasma fragmentation products formed in the PDN through the measurement of its (A-X) (0-0) absorption band. We have simultaneously observed an increase in the extinction of the CRD signal caused by the formation of carbon nanoparticles in the plasma and the formation of soot on the electrodes of the PDN source. Analysis of the soot with μ L^{2}MS has shown the formation of larger PAH particles in the discharge (Biennier et al. 2005). These preliminary findings hold some potential for exploring the formation (and destruction) processes of carbon bearing molecules in space and is the subject of current investigations.

3 Conclusions and future perspectives

These preliminary results validate our original approach associating a cold plasma source with a CRD spectrometer and a TOF mass spectrometer for generating and characterizing laboratory analogs of large interstellar molecules. 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

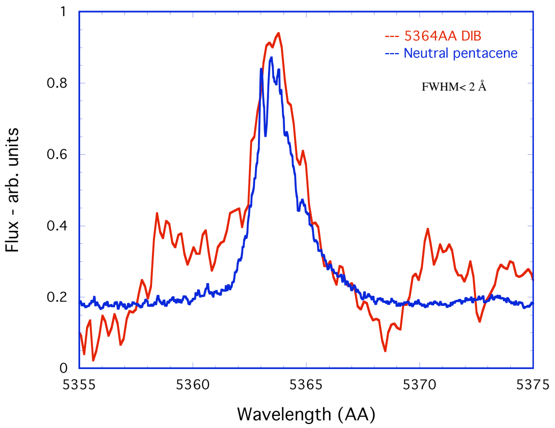

Fig. 3. Comparison of band profiles of jet-cooled pentacene ($C_{22}H_{14}$) with CRDS and the 5363.8$\mathring{A}$ DIB measured with the OHP echelle spectrograph (see text). The laboratory band was slightly shifted in wavelength for illustration purposes

first time, in the position to directly search for *individual* PAH molecules and ions in astronomical observations. We've been able to determine the intrinsic band profile of neutral and ionized cold PAHs in the gas phase leading to two main findings:
- PAH ions absorption bands are intrinsically broad (very fast relaxation time). The bands exhibit a close similarity with the strong 4430 Å DIB. Confirming or invalidating the presence of a class of weaker, broad (few tens of Å) DIBs is now called for and is a challenge for future astronomical observations.
- Neutral PAH bands are intrinsically narrow (1 -2 Å) are as many of the observed DIBs making the search for neutral PAHs more promising. The laboratory spectra of cold neutral PAHs are decongested making it possible *for the first time* to perform unambiguous searches for specific PAH molecules in astronomical spectra and derive meaningful upper limits for their abundances.

This new phase offers tremendous opportunities for the data analysis of space missions. The Cosmic Origins Spectrograph (COS) due to be installed on the Hubble Space Telescope in the next servicing mission will search for the signature of large aromatic molecules and ions in the UV extinction of highly reddened stars. This new generation of laboratory experiments coupling a RETOF-MS to a PDN-CRDS instrument also provides a powerful tool for a better understanding of the formation mechanisms of carbonaceous dust nanoparticles from molecular precursors in the circumstellar shells of carbon rich stars. This is the topic of future exciting research.

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