# Gas Phase Spectroscopy of Cold PAH Ions: Contribution to the Interstellar Extinction and the Diffuse Interstellar Bands

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## 1. Introduction

Polycyclic Aromatic Hydrocarbon molecules (PAHs) are ubiquitous in the interstellar medium (ISM) and constitute the building blocks of interstellar dust grains. Despite their inferred important role in mediating the energetic and chemical processes in the ISM, their exact contribution to the interstellar extinction, and in particular to the diffuse interstellar bands (DIBs) remains unclear. The DIBs are spectral absorption features observed in the line of sight of stars that are obscured by diffuse interstellar clouds. More than 200 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 free flying, gas-phase, organic molecules and/or ions that are abundant under the typical conditions reigning in the diffuse ISM. PAHs have been proposed as possible carriers (Allamandola et al. 1985; Léger & D'Hendecourt 1985). 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. A significant fraction of PAHs is expected to be ionized in the diffuse ISM.

## 2. Laboratory Approach

Extensive laboratory efforts have been engaged in the last decade to evaluate the potential of neutral and ionized PAHs as DIB carriers using Matrix Isolation Spectroscopy (MIS) (Salama 1999). In MIS, PAHs are isolated in a solid rare gas matrix at very low temperature and submitted to VUV radiation to mimic the ISM conditions. However even in the least perturbing media (neon matrices) the interaction of the trapped PAHs with the rare gas atoms of the solid lattice induces a frequency shift and a broadening of the band profile precluding thus a decisive comparison with astronomical data. MIS surveys over a broad spectral range are critical however for the pre-selection of the most promising candidates. 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 that need to be vaporized and ionized. 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 very recently that two groups were able to measure the absorption spectra of cold PAH ions in the gas-phase (Romanini et al. 1999; Bréchignac & Pino 1999). The approach followed by Bréchignac et al. is an indirect method based on the messenger method that measures the photodissociation spectrum of the rare gas – aromatic ion complex formed by two photons two colors photoionization (Bréchignac & Pino 1999). Our approach is a direct method, that relies on the association of a cold plasma source (pulsed discharge nozzle) with a high sensitivity direct absorption technique (cavity ring down spectroscopy or CRDS) and led to the first detection of the naphthalene ion in the gas phase (Romanini et al. 1999). This versatile method possesses the advantage of being independent of inter- and intra- molecular processes. Following the pioneering scheme of Nesbitt et al. (Davis et al. 1997), the pulsed discharge nozzle combines a supersonic slit jet (Liu et al. 1996) that cools down the Ar 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. The PAH vapor pressure is increased by heating a pick-up cell that contains the sample upstream the Ar flow. A cavity ringdown spectrometer probes the expansion several mm downstream with sub-ppm absorption sensitivity (Biennier et al. 2002).

## 3. Experimental Results

We report the preliminary experimental results regarding the electronic spectroscopy of several cold PAH cations in the gas phase that have been obtained with this new instrument (Biennier et al. 2002). The electronic spectrum of the cold naphthalene ion ($C_{10}H_8^+$) was first measured in order to compare directly with the results obtained during the feasibility phase (Romanini et al. 1999) and because MIS (Salama & Allamandola 1991) and gas-phase molecular depletion experiments (Pino et al. 1999) were already available. We have measured the first four strongest absorption bands at 670.70, 648.89, 612.52 and 593.35 nm (Fig. 1) two of which are reported for the first time. The bands correspond to the vibrational progression of the $^2B_{3g}(D_2) \leftarrow X^2A_u(D_0)$ electronic system of Np$^+$ ($C_{10}H_8^+$). There is an excellent agreement with the band positions measured in the previous gas- phase experiments confirming the 0.5% redshift observed in the band positions when the species is trapped in a solid neon matrix. The four bands are broad and without any 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 a FWHM of 25 cm$^{-1}$. This value corresponds to an ultra fast relaxation time of 220 fs and is very close to the value found by molecular depletion experiments in which they measure the intrinsic band profile. We can therefore conclude that the discharge does not affect the vibrational temperature of the aromatic ions formed in the cold plasma expansion.
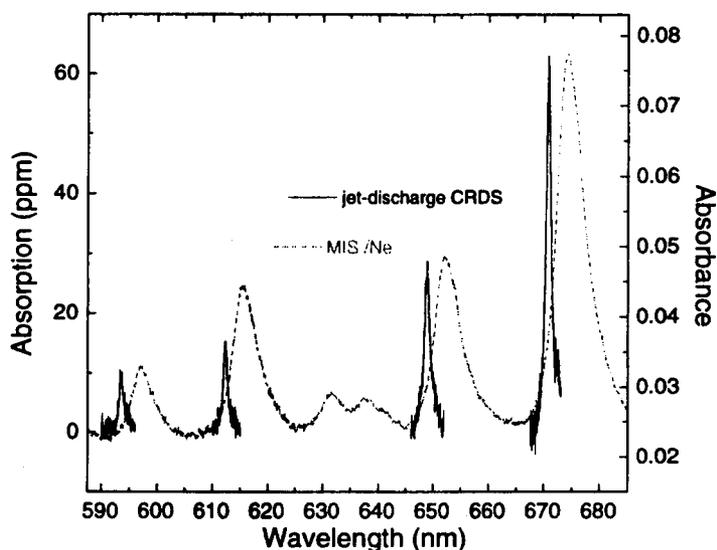
Fig. 1.— Comparison of CRDS (Biennier *et al.* 2002) and MIS/Ne (Salama & Allamandola 1991) spectra. The interactions of the trapped $Np^+$ with the atoms of the solid neon matrix induce a frequency shift and a spectral broadening of the electronic spectrum. This figure illustrates dramatically the need for gas-phase experiments for a decisive, unambiguous, identification of the DIBs. MIS remains however critical for the pre-selection of potential candidates.

The acenaphthene ion $(C_{12}H_{10}^+)$ was chosen for the next step. Acenaphthene belongs to the class of hydrogenated PAHs that are also thought to be present in the ISM. We have measured for the first time in the gas phase the absorption spectrum of the cold Acenaphthene ion $(Ac^+)$. In this preliminary work, we report the vibration-less (0-0) $B_1(D_2) \leftarrow XA_2(D_0)$ electronic absorption spectrum of $Ac^+$ that peaks at 646.31 nm. The fitting of the profile results in a bandwidth of 2.3 nm (54 $cm^{-1}$) that is twice broader than the corresponding value for the naphthalene ion and that corresponds to a 100 fs relaxation time. Based on unpublished results from the NASA-Ames group, the $Ac^+$ molecular ion electronic absorption band is redshifted by 0.3% (or -42 $cm^{-1}$) when it is trapped into a Neon matrix (648.1 nm) and its width is about 3.9 nm (92 $cm^{-1}$ or 1.7 times the gas phase value) (Halasinski & Salama 2002). This might be explained by the increased rigidity induced in Ac by the additional three C-C bonds, making less vulnerable to the matrix-induced cage effect as compared with Np.

The study has now been extended to the pyrene ion $(C_{16}H_{10}^+)$. Ionized pyrene derivatives are considered as good candidates for the carrier of the strong 4430 Å DIB (Salama & Allamandola 1992). We report the vibration-less (0-0) $^2A_u(D_5) \leftarrow {}^2B_{3g}(D_0)$ electronic transition. The band centered at 436.6 nm reveals an extremely large width (3.6 nm or about 190 $cm^{-1}$) slightly smaller than its solid-phase value (about 4 nm in a neon matrix). This value provides a value of 30 fs for the relaxation time from $D_5$ to $D_4$ through electronic internal conversion. The peak position of the electronic spectrum of the free flying pyrene cation is blue shifted by 0.6 % compared to its value when trapped in a neon matrix.

## 4. Perspectives and Conclusion

These preliminary results strongly validate our original experimental approach associating a cold plasma source with a cavity ringdown 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 compare laboratory spectral data on free PAH ions with astronomical observations in the UV-NIR range. Work is currently under progress in collaboration with J. Krelowski to assess the naphthalene ion as carrier for two newly detected large DIBs centered at 6704 and 6486 Å. This new phase offers tremendous opportunities for the data analysis of current and upcoming space missions (e.g., HST data and the COS instrument).

## Acknowledgments

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