

## Neutral and ionized PAHs: contribution to the interstellar extinction

F. Salama, C. Joblin and L. J. Allamandola

NASA-Ames Research Center, Moffett Field, CA 94035, U.S.A.

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**Abstract.** A detailed study of the UV-to-near-IR absorption spectra of neutral and ionized polycyclic aromatic hydrocarbons (PAHs) is reported. The experimental results obtained using Matrix isolation spectroscopy combined with the general spectroscopic properties of PAHs derived from theoretical modeling are compared with astronomical observations. From this study, it is concluded that: (i) small neutral PAHs (less than 25 carbon atoms) absorb only in the UV and cannot contribute to the known diffuse interstellar bands, although they may contribute to the extinction curve. A search for their spectral signatures should provide a test to the PAH model and should allow us to set significant limits for the abundances of specific PAHs; (ii) small ionized PAHs (less than 25 carbon atoms) absorb in the visible and near-IR close to the position of well-known diffuse interstellar bands. Based on these promising results it is argued that PAH ions constitute good candidates to explain the diffuse interstellar bands. An assessment of the PAH/diffuse interstellar band proposal is made and predictions for new diffuse interstellar bands to be searched for are presented.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been postulated as an important, ubiquitous component of the interstellar medium based on their high stability against UV radiation and the close resemblance of their IR spectral signature with the interstellar IR emission bands observed between 3.2 and 14.0  $\mu\text{m}$ . For a detailed description of the PAH model, the reader is referred to the abundant literature which has been devoted to this topic [see, e.g. Allamandola *et al.* (1989), Puget and Léger (1989)]. According to the model, PAHs are expected to be present as a mixture of free, neutral and ionized gas phase mol-

ecules following a large size distribution which ranges from small molecules (<25 carbon atoms) to large graphitic platelets. Thus, PAHs can be viewed as a component of the missing link between the gas phase and the solid phase of interstellar dust.

Although the PAH model has proven to have substantial predictive power and is gaining wide acceptance by the astrophysical community, some important questions remain to be addressed. For example, the UV-visible to IR energy transfer of PAHs (neutral and ions) needs to be quantitatively measured to test if they can account for the intensities observed in interstellar spectra. Also, the potential contribution of PAHs to the interstellar extinction curve (in its far-UV, UV and visible parts) needs to be assessed using (relevant) quantitative laboratory data. A recent laboratory study (Joblin *et al.*, 1992) has shown that a mixture of PAHs could contribute significantly to the UV part of the interstellar extinction. A search for structures on the UV interstellar extinction, associated with specific PAHs, would provide, however, the ultimate test for the PAH model. Neutral and ionized PAHs have also been proposed as possible carriers for the diffuse interstellar bands (DIBs) (Van der Zwet and Allamandola, 1985; Léger and d'Hendecourt, 1985; Crawford *et al.*, 1985). DIBs are weak absorption bands superimposed on the interstellar extinction curve. They number more than 100 and extend from the near-UV to the near-IR (Herbig and Leka, 1991; Jenniskens and Désert, 1994; Joblin *et al.*, 1990). The DIB identification represents the longest standing unresolved problem in astrophysical spectroscopy despite its importance to a better understanding of the physical and chemical properties of interstellar clouds. These few examples illustrate the strong need for quantitative data on PAHs (neutral and ions)—at a basic molecular level—to better understand dust properties. Tailored laboratory experiments—which come as close as possible to the conditions known (or expected) in the interstellar medium—combined with high resolution observations can provide such answers.

We describe here the laboratory program initiated to determine the UV, visible and near-IR spectroscopic

characteristics of neutral and ionized PAHs. This experimental work is supported by the modeling of the charge state and spectral properties of PAHs expected in the diffuse interstellar medium (Salama *et al.*, 1995). In the first part of the program, small PAHs (<25 carbon atoms) and their derivatives have been studied (Salama and Allamandola, 1991, 1992a, b, 1993; Salama *et al.*, 1994). This report describes the results obtained with a selected set of PAH candidates and the conclusions derived for this subclass of the PAH family. An assessment of the PAH model predictions is made in the context of the DIB issue and predictions are made for new interstellar absorption bands to be searched for.

## Experimental

Few experimental data are available on the spectroscopy of charged PAHs and most of the data available are not appropriate for astrophysical applications because they are taken in perturbing media [i.e. glassy or organic matrices; for a review see Shida and Iwata (1973)]. The interaction between the trapped PAH ion and its environment induces strong perturbations of the energy levels which result in large shifts of the electronic transitions compared to the ideal case of a free, isolated PAH ion.

Matrix isolation spectroscopy represents a particularly well suited technique for the measurement of the spectroscopic properties of minimally perturbed PAH cations by allowing one to maintain PAHs truly isolated at low temperature (4–15 K) in an inert medium. Among the rare gases commonly used as matrix-cage material (Ne, Ar, Kr and Xe), solid neon provides the best (i.e. less polarizable) medium for the study of quasi-unperturbed electronic spectra of ions. Until molecular jet spectroscopy techniques are developed and adapted to study cold, isolated PAH ions in the gas phase (a difficult task considering the low vapor pressure and the high reactivity of PAH ions), neon-matrix isolation spectroscopy (MIS) remains the best (and only) tool available to laboratory astrophysicists to simulate the conditions of the diffuse interstellar medium.

A computer-controlled UV visible–near-IR spectrograph, coupled to a helium-cooled cryogenic cell, is used to measure the absorption spectra of neutral and ionic PAHs in the 180–1060 nm range under conditions relevant to astrophysical environments. A detailed description of the experimental apparatus and technique is reported elsewhere (Salama *et al.*, 1994) and only a synopsis will be given here.

Briefly, the experimental apparatus consists of a cryogenic sample chamber which is part of an ultra-high vacuum system and consists of four ports at 90° and two gas injection ports at 45°. The cryogenic sample holder suspended at the center of the chamber is cooled down to 4.2 K by a variable temperature, liquid helium transfer cryostat. The substrate (sapphire window) can be positioned to face alternatively the spectroscopy ports, the gas injection ports, an irradiation lamp or vacuum deposition furnace. The spectral light sources consist of a 160–360 nm output deuterium lamp for UV spectroscopy and a

320–2500 nm output tungsten filament lamp for visible–near-IR spectroscopy. The computer-driven monochromator is equipped with three interchangeable gratings of variable linear dispersion blazed at 300 and 650 nm for UV and visible–near-IR spectroscopy, respectively. A UV fiber optic cable guides the focused light collected at the spectroscopy port of the cryogenic sample chamber to an optical fiber adaptor (OFA) mounted on the entrance slit of the monochromator. The photon detector consists of a thermoelectrically cooled charge-coupled device (CCD) area array detector sensitive in the spectral range 180–1060 nm. The CCD is mounted directly on the exit port of the monochromator and interfaced to the computer system. The ionization source is a microwave-powered, flow discharge hydrogen lamp generating photons of 10.2 eV energy (Lyman  $\alpha$  line). The PAH sample is simultaneously condensed with the neon gas onto the cold (4.2 K) substrate. The frozen matrix is then analyzed spectroscopically. Ions are generated *in situ* from the stable precursor, via vacuum UV photoionization.

## Results

### Neutral PAHs

The absorption spectra of all small (<25 carbon atoms), neutral PAHs show transitions in the UV–near-UV range (180–400 nm). These absorption band systems are associated with vibronic transitions between the electronic states of the molecule and can be classified, in a first approximation, into very strong (oscillator strength,  $f$ , of the order of 1), moderately strong ( $f$  of the order of 0.1) and weak ( $f$  of the order of 0.001). Some representative spectra are shown in Figs 1–4 for the PAHs naphthalene ( $C_{10}H_8$ ), phenanthrene ( $C_{14}H_{10}$ ), pyrene ( $C_{16}H_{10}$ ) and benzo(ghi)perylene ( $C_{22}H_{12}$ ) isolated in neon matrices. Note that this class of PAHs does not absorb in the visible–near-IR range. (It is also interesting to note that in the case of naphthalene, for example, the largest shift observed for the band positions, compared to the gas phase, is 0.5 nm for the strongest band at 221.6 nm. This corresponds to a 0.25% gas phase-to-neon matrix relative shift in energy and can be compared to the 2.5% shift observed in the more polarizable argon matrix.)

### PAH cations

Vacuum UV irradiation of the neutral PAHs isolated in neon matrices produces new spectral features in the UV–near-IR range (180–1060 nm). All the new features are found to be associated with the PAH cation ( $PAH^+$ ) formed by direct one-photon ionization of the neutral precursor. Some representative spectra are shown in Figs 5–8 for the PAH cations naphthalene ( $C_{10}H_8^+$ ), phenanthrene ( $C_{14}H_{10}^+$ ), pyrene ( $C_{16}H_{10}^+$ ) and benzo(ghi)perylene ( $C_{22}H_{12}^+$ ).

These spectra show many interesting features:

- (i) In all cases, a single band dominates the entire

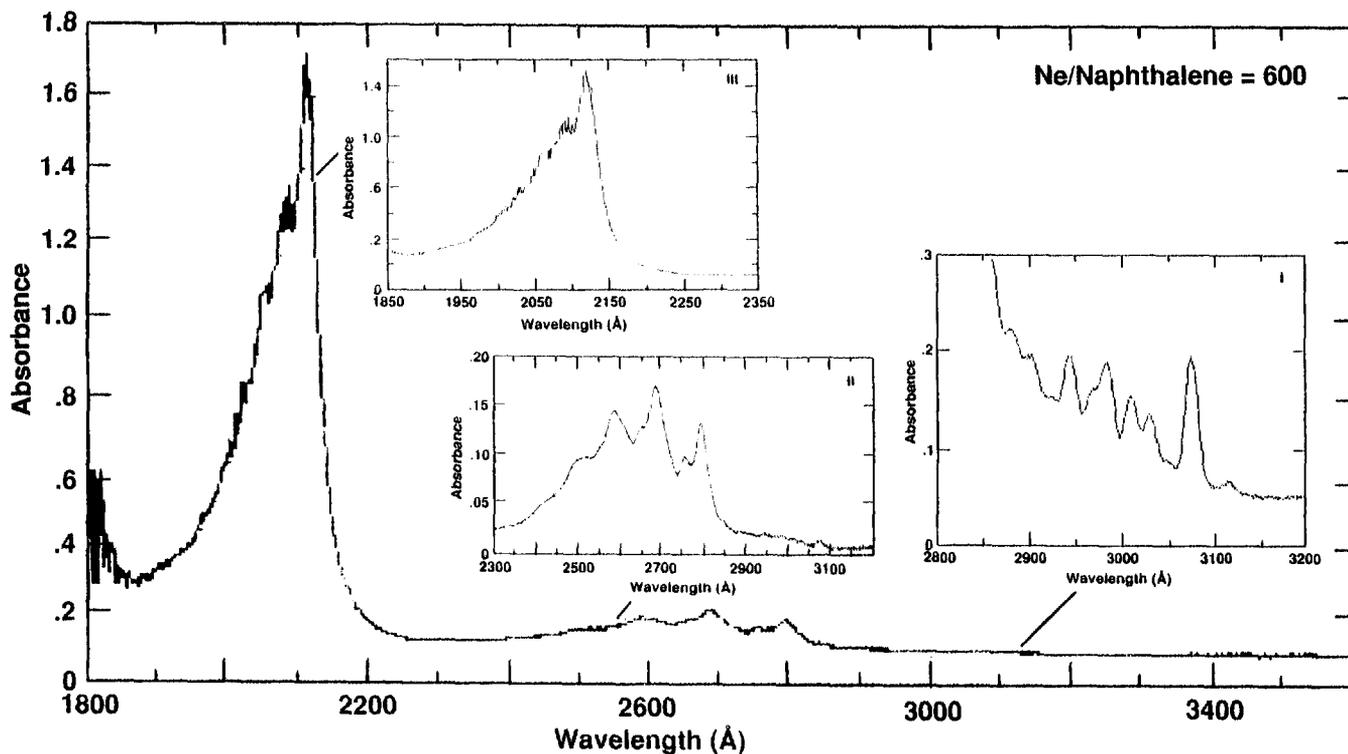


Fig. 1. Absorption spectrum of naphthalene ( $C_{10}H_8$ ) isolated in a neon matrix at 4.2 K. From Salama and Allamandola (1991)

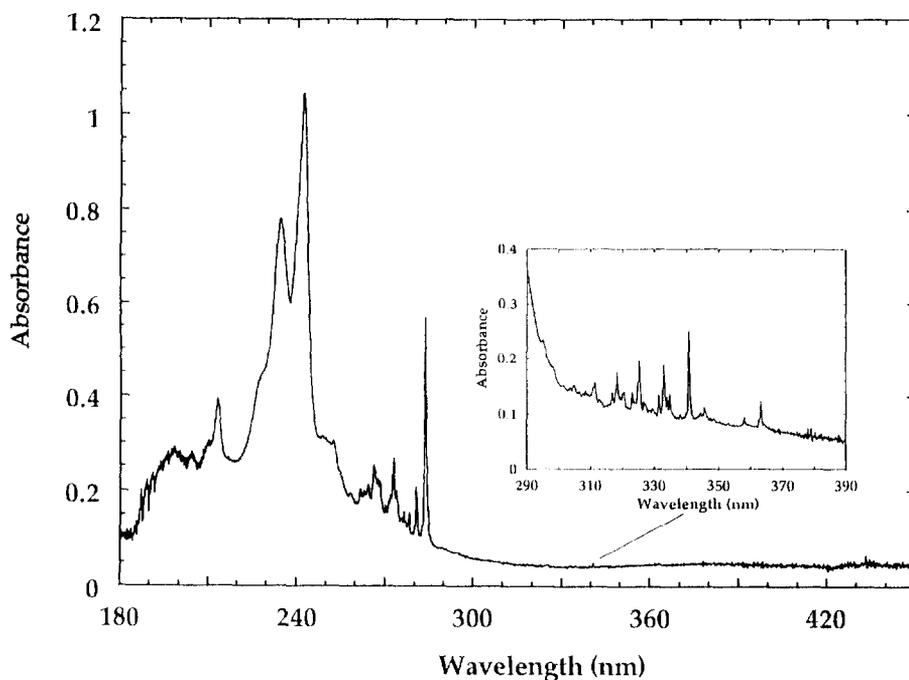


Fig. 2. Absorption spectrum of phenanthrene ( $C_{14}H_{10}$ ) isolated in a neon matrix at 4.2 K. From Salama *et al.* (1994)

- absorption spectrum in the near-UV–near-IR range (the spectral range of interest for the DIB issue).
- (ii) In the case of non-compact PAHs (such as naphthalene and phenanthrene), the strongest ion absorp-

- tion lies at the low energy end of the spectrum, while it is the opposite which is observed for compact PAHs [such as pyrene and benzo(ghi)perylene].
- (iii) The oscillator strength associated with the strongest

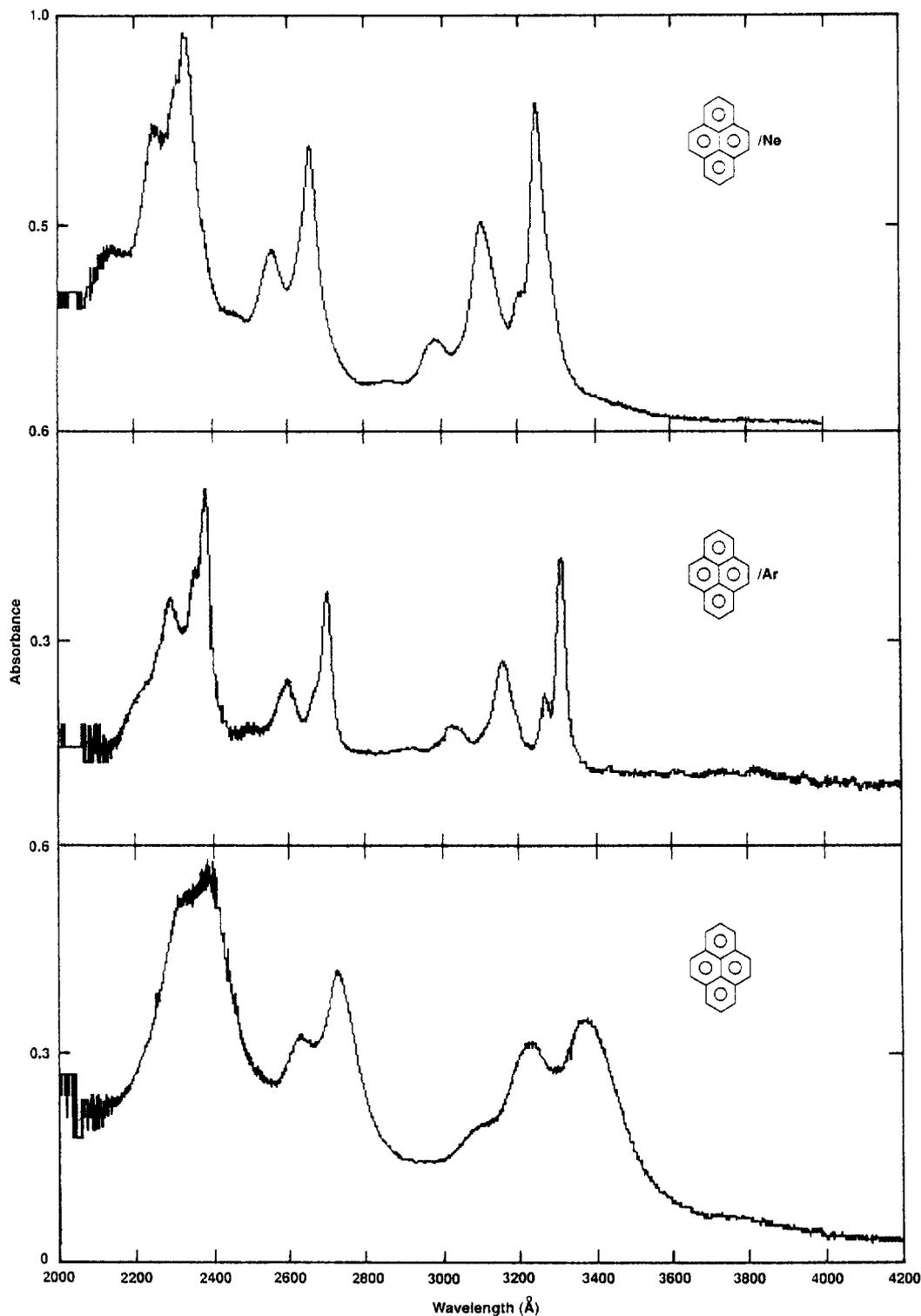


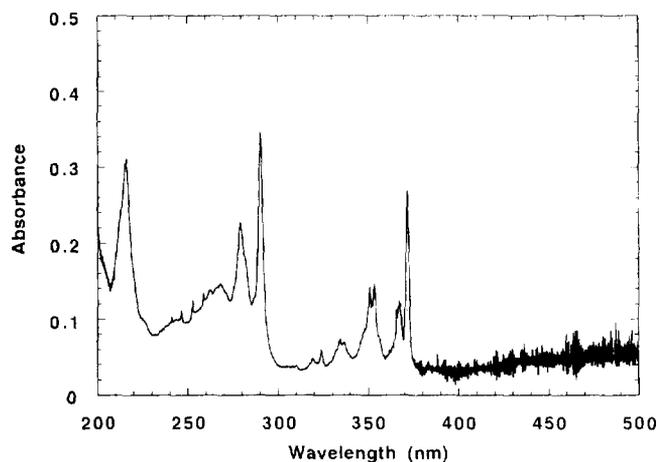
Fig. 3. Absorption spectrum of pyrene ( $C_{16}H_{10}$ ) at 4.2 K. Top: isolated in a neon matrix ; middle: isolated in an argon matrix ; bottom : pure solid. From Salama and Allamandola (1993)

ion transition is of the order of 0.001 for non-compact PAHs and of the order of 0.1 for compact PAHs.

These characteristics are verified for all small PAH cations studied to date and are most probably verified for

larger PAH cations (see below for a general discussion of neutral and ionized PAH spectral properties).

The effect of the environment on the electronic spectra of charged PAHs is even more drastic here as compared to the case of the neutral molecules. For example, the



**Fig. 4.** Absorption spectrum of benzo(ghi)perylene ( $C_{22}H_{12}$ ) isolated in a neon matrix at 4.2 K

strongest pyrene cation absorption falls at 439.5 nm in a neon matrix (Salama and Allamandola, 1992b), while the same band is shifted to 443.5 and 450.0 nm in argon (Salama and Allamandola, 1992b) and organic (Shida and Iwata, 1973) matrices, respectively. No gas phase data are available for comparison although the shift expected from a neon environment should be small [a fraction of a percent; in the case of the fully substituted fluorobenzene cation (a mono ring molecule), where data are available, the relative shift in energy between the gas phase and neon matrix is of the order of 0.3% (Bondybey and Miller, 1983)]. Thus, it is demonstrated again that neon matrix measurements provide the only experimental data appropriate for astrophysical applications until we reach the state where we will be able to measure the spectroscopy of cold, isolated PAH ions in the gas phase.

## Discussion and astrophysical implications

### *General properties of neutral and single-ionized PAHs*

The experimental technique used here (i.e. MIS) to study isolated PAHs is a difficult and lengthy procedure when dealing with such a large family of low vapor pressure, reactive species. To be fully effective, the experimental work needs then to be supported and guided by theoretical considerations which help reduce the large original family of molecules into a series of subclasses having similar spectral properties. This can help build a useful database by allowing one to focus the experimental studies on the representative elements of each subset.

The classification of the spectral properties of neutral PAHs has been established many years ago [for representative reviews on the subject see, e.g. the pioneering work of Platt (1949), Streitwieser (1961) and Clar (1964)]. No equivalent classification has been established, however, for single-ionized PAHs except for the preliminary studies of Shida and Iwata (1973) and Khan *et al.* (1993). In an attempt to fill this gap, we have recently completed a detailed study of the UV-visible-near-IR properties of neutral and ionized PAHs [see Salama *et al.* (1995) and references therein]. The purpose of the study

was to extrapolate the general spectral properties of these species towards large size molecules up to the graphitic limit and to derive significant constraints regarding astrophysical implications.

The main conclusions, relevant to the present discussion, are:

- (i) The absorption band energies of neutral and ionized PAHs can be described as a function of the size of the molecular species. This is illustrated in Fig. 9, where the absorption onset of neutral PAHs and the strongest absorption band energy of single-charged PAHs are expressed in terms of the number of benzenoid rings (size) included in the molecular structure.
- (ii) The absorption band energies of neutral PAHs shift towards lower energies (longer wavelengths) when the molecular size increases.
- (iii) The strongest absorption band energy of compact PAH ions shifts towards lower energies (longer wavelengths) when the molecular size increases.

### *Neutral PAHs*

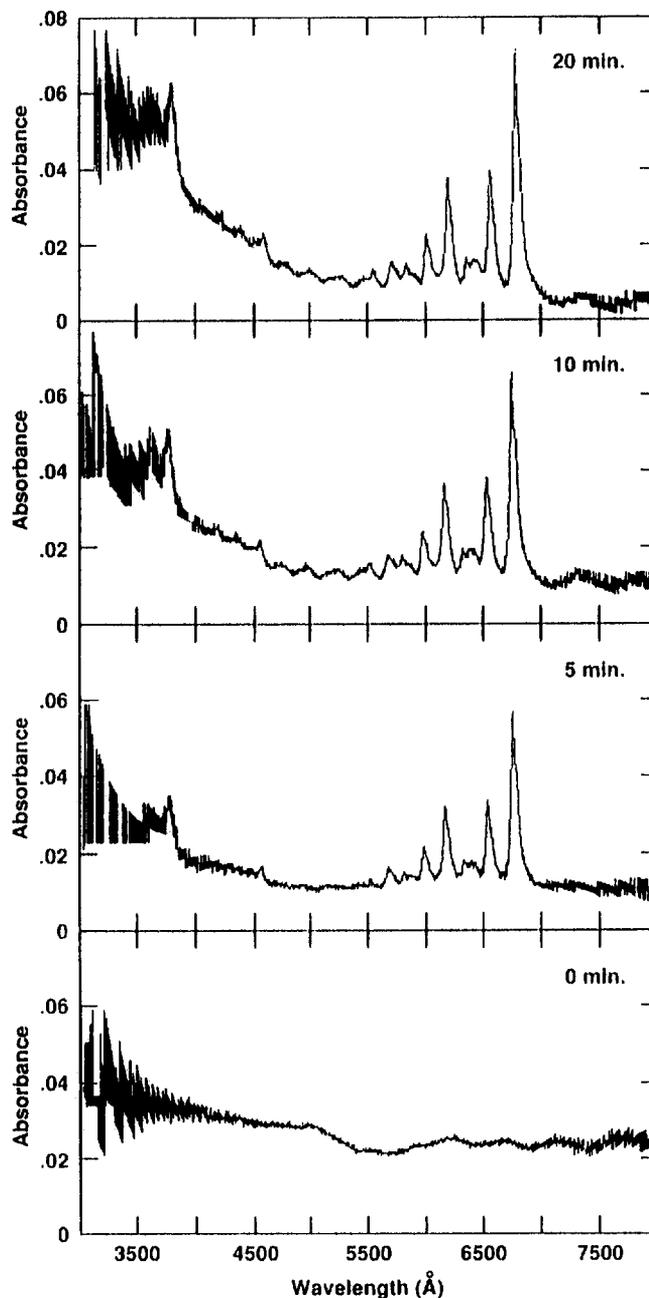
In the case of small neutral PAHs (less than 10 rings, i.e. less than 20–30 carbon atoms), the astrophysical implications derived from the combined experimental and theoretical study are the following:

- (i) These PAHs absorb only in the UV ( $\lambda < 390$  nm) and, hence, cannot contribute to the known DIBs. This is illustrated by the absorption spectra shown in Figs 1–4 and by the energy-to-molecular size relation described in Fig. 9.
- (ii) All these molecules have strong UV absorption bands (oscillator strengths in the range 0.2–1.0) and could produce, if present, substructure on the UV interstellar extinction curve. For these species to produce substructure on the extinction curve at the 10% level would require a neutral PAH abundance in the range  $1.0 \times 10^{-7}$  to  $2.2 \times 10^{-7}$  with respect to hydrogen. A search for the stronger UV features on the interstellar extinction curve would provide a test to the PAH model and would allow one to establish significant limits on the abundances of specific PAHs. Such a search, to be effective, requires an instrument with enough resolution (about 0.5 nm). The FOS onboard the HST is, presently, the only instrument capable of obtaining these data.

### *Single-ionized PAHs*

In the case of small PAH ions (less than 10 rings, i.e. less than 20–30 carbon atoms), the astrophysical implications derived from the combined experimental and theoretical studies are the following:

- (i) Contrary to their neutral precursors, ionized PAHs absorb in the visible and near-IR (see Figs 5–8) and thus could contribute to the DIBs. Moreover, the



**Fig. 5.** Growth of the naphthalene cation ( $C_{10}H_8^+$ ) absorption spectrum as a function of irradiation time in a neon matrix at 4.2 K. From Salama and Allamandola (1992a)

relation between the absorption energy and the size of the molecular ion (Fig. 9) shows that large PAH ions (larger than about 100 rings, i.e. 250-300 carbon atoms) are not expected, if present, to significantly contribute to the DIBs.

- (ii) A comparison of the stronger PAH ion transitions measured in neon matrices with the known DIBs is shown in Table 1. This comparison indicates a surprisingly good agreement in wavelength positions between the two sets [i.e. a relative shift in energy of 0.3% (at the most), which corresponds to the relative shift expected between neon matrix measurements and gas phase data; see Experimental section].

- (iii) It is striking, when looking at Table 1, to note that all compact PAH ion absorptions come close to strong and broad DIBs, while all non-compact PAH absorptions come close to weak and narrow DIBs. This effect, which has been observed recently (Salama, 1994), could offer a plausible explanation for the recent attempts to group DIBs into “families” according to the degree of correlation of their strengths and widths (Krelowski and Walker, 1987; Jenniskens, 1994).

There are two ways in which one can examine the possible contribution of any given PAH ion to the DIBs. One

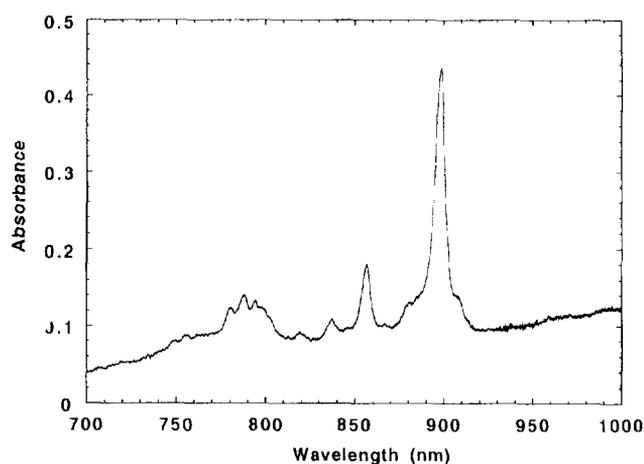


Fig. 6. The visible-near-IR absorption spectrum of the phenanthrene cation ( $C_{14}H_{10}^+$ ) isolated in a neon matrix at 4.2 K. From Salama *et al.* (1994)

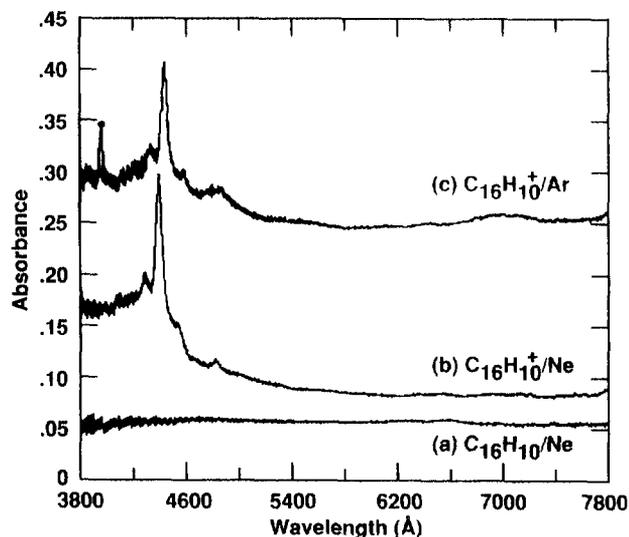


Fig. 7. The visible absorption spectra of: (a) pyrene ( $C_{16}H_{10}$ ) isolated in a neon matrix at 4.2 K; (b) the pyrene cation ( $C_{16}H_{10}^+$ ) in a neon matrix at 4.2 K; (c) the pyrene cation ( $C_{16}H_{10}^+$ ) in an argon matrix at 4.2 K. The dot (·) indicates a band arising from an impurity in the sample. From Salama and Allamandola (1992b)

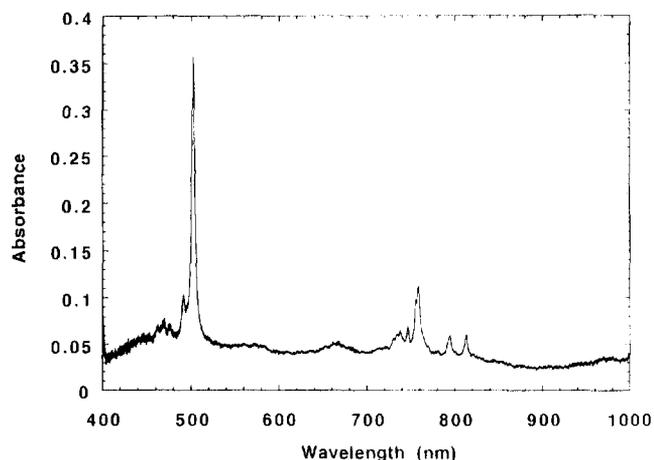


Fig. 8. Absorption spectrum of the benzo(ghi)perylene cation ( $C_{22}H_{12}^+$ ) isolated in a neon matrix at 4.2 K

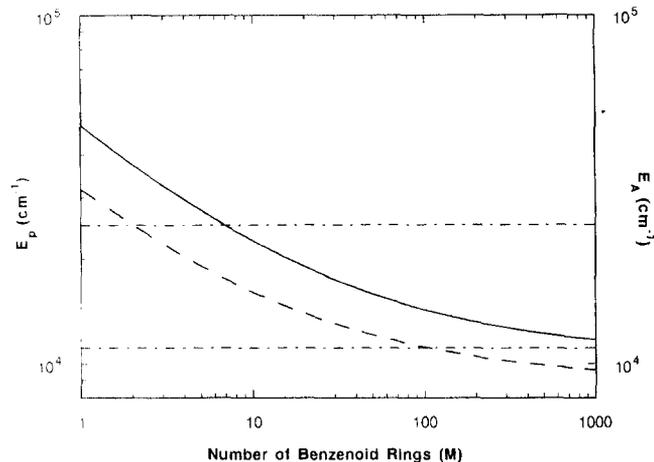


Fig. 9. Neutral ( $E_p$ , top curve) and ionized ( $E_A$ , bottom curve) PAH band energy (in  $cm^{-1}$ ) as a function of the number of benzenoid rings ( $M$ ) in the molecular structure. The two horizontal dotted lines define the energy range in which the DIBs are observed. From Salama *et al.* (1995)

extreme is to search for all of the ion bands, regardless of their intensity, among the DIBs. Another approach is to only require that the strongest ion band(s) be present. The former requires a higher fractional abundance among the PAHs than the latter. In all PAH ion spectra measured to date it is clear, however, that one single band dominates the entire absorption spectrum in the visible-near-IR range (see the Results section and Figs 5–8). Thus, we approach the problem from the point of view of “one PAH, one DIB” (i.e. by requiring that, in a first step, only the strongest absorption band of each potential PAH ion candidate be present, or searched for, in the DIB spectrum). This approach is further supported by the following reasoning. (i) PAHs form an extremely rich chemical family [particularly when including derivatives such as methyl and ethyl PAHs which have been recently proposed (Salama and Allamandola, 1992b, 1993) and shown (Léger *et al.*, 1995; this work) to be very good candidates]. (ii) A distribution of PAHs is expected in the interstellar medium. Although some arguments may be used to reduce the original large number of potential candidates [e.g. by a study of their spectral properties as a function of the molecular size (see discussion above), by examining their stability as a function of the molecular structure: compact PAHs being more stable than linear or non-compact PAHs, they would be expected to survive longer in the interstellar medium] one is still faced with very large subsets of molecules to consider. (iii) It is difficult to conceive why and how only very few specific PAHs would dominate any given size distribution. If we require that most of the vibronic bands of any given PAH ion must be found in the DIB spectrum (i.e. each PAH responsible for at least 10 DIBs), this implies that a total population of 15–20 different PAH ions would be sufficient to explain all the known DIBs. It appears more realistic to expect to find one (the strongest) or two bands belonging to any given PAH candidate in the DIB spectrum. This argument is particularly valid here, because in all PAH ion spectra measured, it is clear that one single band dominates the entire absorption spectrum in the visible-near-IR range.

**Table 1.** Comparison of PAH<sup>+</sup> strong absorption bands with known DIBs

PAH <sup>+</sup>	$\lambda_{\text{peak}}$ (Å) str. bands (neon matrix)	DIBs (Å)†
Pyrene (C <sub>16</sub> H <sub>10</sub> <sup>+</sup> )	4395* (4430 in Ar)	4429
1-Methylpyrene (CH <sub>3</sub> -C <sub>16</sub> H <sub>9</sub> <sup>+</sup> )‡	4442*	4429
4-Methylpyrene (CH <sub>3</sub> -C <sub>16</sub> H <sub>9</sub> <sup>+</sup> )	(4577)	4595 (?)
	4828	4824
	7576	7581
Naphthalene (C <sub>10</sub> H <sub>8</sub> <sup>+</sup> )	6742*	6741
	6520	6520
Phenanthrene (C <sub>14</sub> H <sub>10</sub> <sup>+</sup> )	8983*	
	8568	8572
Tetracene (C <sub>18</sub> H <sub>12</sub> <sup>+</sup> )	8648*	8648
Benzo[ghi]perylene (C <sub>22</sub> H <sub>12</sub> <sup>+</sup> )	5022*	5039 (?)
	7584	7581; 7586
	7552	7558 (?); 7562
	7943	7935 (prob.)
Coronene (C <sub>24</sub> H <sub>12</sub> <sup>+</sup> )§	4590*	4595
	9465	9466

\* Strongest transition.

† Herbig (1975); Sanner *et al.* (1978); Herbig and Leka (1991); Jenniskens and Désert (1994), and Ehrenfreund and Foing (1995).

‡ See also Léger *et al.* (1995).

§ See also Ehrenfreund *et al.* (1992).

In the case of compact PAH ions, the strongest absorption band has a large oscillator strength (of the order of 0.1) and tends to be broad (because it falls in the high energy range of the spectrum). In the case of non-compact PAH ions, the strongest absorption band has a small oscillator strength (of the order of 0.001) and tends to be narrower (falling in the low energy end of the spectrum). Finally, using the oscillator strengths measured in the laboratory, abundances of the order of 0.2–0.3% of the cosmic carbon are calculated for PAH ions such as naphthalene and pyrene (see Table 1) if these ions are indeed responsible for DIB features.

## Conclusion

A detailed study of the UV–near-IR spectroscopy of neutral and ionized PAHs has been performed. Combining the experimental results obtained for these species trapped and isolated in a cold (4 K), inert environment (neon) with the results of a study of their general spectral properties, the following conclusions have been reached. (i) MIS is an appropriate tool to simulate the interstellar medium environment provided the low polarizability, inert gas neon is chosen as the matrix material. This technique stands as the only alternative available to measure the absorption spectra of cold, isolated PAH ions until reliable, adequate, gas phase experiments (such as jet spectroscopy) are developed. (ii) Neutral and ionized PAHs absorb strongly in the UV. A search for their spectral signatures would provide a test to the PAH model and would allow one to set significant limits for the abundances of specific PAHs. (iii) Small ionized PAHs (less than 25 carbon atoms) appear to be very good candidates (if not the best candidates) to explain (some of) the DIBs. This comes from the combination of many factors: the

recognition that DIBs are most probably due to a family of closely related, gas phase molecular species, the high abundance of PAHs derived from interstellar IR emission spectra, the high stability of PAHs against UV photons, the fact that their absorption spectra are always dominated by one single band which falls close to a known DIB, and the ability of the PAH model to explain the distribution of DIBs between strong and weaker features as a direct consequence of the spectral properties related to the compact and non-compact PAH subclasses.

In conclusion, we stress the fact that enormous progress has been made in just the last few (2–3) years in terms of the quality of the laboratory and observational data available to address issues as complex as the identity of the DIB carriers and that we may be close to a better understanding of the material present in the diffuse interstellar medium. Such progress has been made possible only because of all the research work preceding it and it is hoped that this study will simulate, in turn, new experimental and observational research.

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