

## POLYCYCLIC AROMATIC HYDROCARBON IONS AND THE DIFFUSE INTERSTELLAR BANDS

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### ABSTRACT:

Neutral naphthalene ( $C_{10}H_8$ ), phenanthrene ( $C_{14}H_{10}$ ), and pyrene ( $C_{16}H_{10}$ ) absorb strongly in the ultraviolet and may contribute to the extinction curve. High abundances are required to produce detectable structures. The cations of these PAHs absorb in the visible.  $C_{10}H_8^+$  has 12 discrete absorption bands which fall between 6800 and 5000 Å. The strongest band at 6741 Å falls close to the weak 6742 Å diffuse interstellar band (DIB). Five other weaker bands also match DIBs. The possibility that  $C_{10}H_8^+$  is responsible for some of the DIBs can be tested by searching for new DIBs at 6520, 6151, and 5965 Å, other moderately strong naphthalene cation band positions. If  $C_{10}H_8^+$  is indeed responsible for the 6742 Å feature, it accounts for 0.3% of the cosmic carbon. The spectrum of  $C_{16}H_{10}^+$  is dominated by a strong band at 4435 Å in an Ar matrix and 4395 Å in a Ne matrix, a position which falls very close to the strongest DIB, that at 4430 Å. If  $C_{16}H_{10}^+$ , or a closely related pyrene-like ion is indeed responsible for the 4430 Å feature, it accounts for 0.2% of the cosmic carbon. We also report an intense, very broad UV-to-visible continuum which is associated with both ions and could explain how PAHs convert interstellar UV and visible radiation into IR.

### INTRODUCTION:

Polycyclic aromatic hydrocarbons (PAHs) have recently been recognized as an important component of the carbon containing material in the interstellar medium (ISM). Molecular PAHs are thought to be ubiquitous and abundant throughout the ISM implying that an important fraction of elemental carbon is locked up in these species. These molecules in their ionized /1a/ and/or neutral/1b/ forms have been proposed as the carriers of the family of interstellar infrared emission bands between about 3.2 and 14.0  $\mu\text{m}$ . To account for the observed intensities in the infrared (IR) energy range requires that the carriers of the bands must be small ( $< 10$  Å) /2/ and must absorb over a wide energy range: from the ultraviolet (UV), to the visible and, in some cases, the near infrared (NIR) /3/. PAH molecules are extremely stable in their neutral and ionized forms /4/ and present the means by which interstellar UV radiation is converted into discrete infrared emission bands in a collision-free medium (through infrared fluorescence). However, small neutral PAHs absorb only in the UV /5/ and thus can be responsible only for a small fraction of the UV/Visible to IR energy transfer needed to account for the intensities observed. In the objects which emit the characteristic IR spectrum, most of the PAHs are expected to be ionized /1a/ and thus to absorb in the visible and NIR/6/. The ubiquitous presence of ionized PAHs in the interstellar medium make them very attractive candidates for the diffuse interstellar absorption bands (DIBs) /7/. Although the DIBs have been known since 1920 /8/ and recognized as interstellar over a decade later /9/, the identification of the carrier(s) responsible for these features has remained elusive to this day. Thus *understanding the DIBs is the longest standing unsolved problem in interstellar spectroscopy*. Numbering now more than a hundred, and extending from about 4400 Å to the near infrared /10/, the

DIBs differ widely in depth, width and shape. These facts make a compelling case to abandon the concept of a single carrier. The nature of the carriers (grains versus free gas-phase molecules) is also not settled. The DIB intrinsic profiles derived from recent high-resolution, low-noise observations /11/, combined with the invariability of their central wavelengths over different lines-of-sight which sample distinct environments, strongly suggest that the DIB carriers are independent of the dust grains that produce the visual extinction.

While PAHs have been postulated as an important interstellar constituent on the basis of the IR emission spectra, the UV-visible-NIR absorption properties of the *free, unperturbed species*, which are required to understand the radiation and energy balance in space, are not known. The spectroscopic data available are from absorption spectra of neutral and ionized PAHs isolated in strongly perturbing media /6, 12 - 14/ or from photoelectron spectra which do not provide information on all the possible optical transitions /15/. Matrix isolation spectroscopy provides a perfect tool to study these properties of PAHs /16/. Not only does the matrix technique simulate the low temperature (4 - 15 K) and isolation in space, but it is also particularly well-suited to the study of such large, reactive species. Among the rare gases commonly used as matrix-cage material ( Ne, Ar, Kr, and Xe), solid neon and, to a lesser extent, solid argon provide the best (i.e less polarizable) inert medium for the study of quasi-unperturbed electronic spectra of ions /16/. Argon is more convenient to use than neon because of its higher sublimation temperature, and is often chosen to explore the experimental parameters important to optimize ion yield. Neon, however, is the least perturbing solid medium, generally producing shifts in vibronic band positions of only several tenths of a percent with respect to the gas phase values /16/. Thus, while the argon matrix spectra are important, the neon matrix results are considered more relevant for direct astrophysical applications.

Considering the need for reliable, quantitative, spectroscopic data on neutral and ionized PAHs under conditions relevant to astrophysical environments (i.e *isolated species* in the least perturbing solid media possible: inert gas matrices) to test the existing theories and their implications, we have initiated a systematic program to investigate their UV-Visible-NIR spectroscopic properties. In the first part of this program, the small PAHs, naphthalene (C<sub>10</sub>H<sub>8</sub>) /17/, phenanthrene (C<sub>14</sub>H<sub>10</sub>) and pyrene (C<sub>16</sub>H<sub>10</sub>) /18/, in their neutral and positive ion forms, have been considered. Here, the spectroscopic characteristics of these molecules are briefly reviewed and the aspects of this study which are relevant to astrophysical applications are discussed. This work has been described in detail in reference 19.

## RESULTS AND DISCUSSION:

The experimental apparatus, described in detail in reference 17 (a), consists of a computer-controlled UV-Visible-NIR spectrometer system, coupled to a liquid helium flow-cooled cryogenic cell, and operating in the 1800 - 9000 Å range with 5 Å resolution. The matrix-isolated samples were prepared by either condensing a gas mixture of naphthalene, pre-diluted in the inert gas (Ar or Ne), or by co-condensing the pure inert gas with the PAH vapor from the vacuum deposition furnace (as in the case of phenanthrene and pyrene) onto the 4.2 K substrate. The solid matrix was then spectroscopically analyzed. The matrix to reactant ratios (M:R) were kept in the range 600 - 1000 in all the experiments described here. The PAH cations were formed *in-situ*, by direct, one-photon ionization of the neutral precursor isolated in the rare-gas matrix.

### A. Spectroscopy of Neutral PAHs

Naphthalene (C<sub>10</sub>H<sub>8</sub>). The characteristics of the UV-to-NIR absorption spectrum of naphthalene isolated in a Ne matrix have been discussed in detail in references 17 (a - c) and only a brief summary is given here. Over the wavelength range covered in these experiments (1800 - 9000 Å), neutral naphthalene exhibits three distinct vibronic band systems with different intensities peaking at 2116, 2685, and 3076 Å.. The strongest system, that at 2116 Å (2162 Å in Ar), has an oscillator strength, *f*, on the order of 1.0 (Figure 2) and dominates the neutral spectrum /20/. No absorption is observed in the visible range (Figure 3).

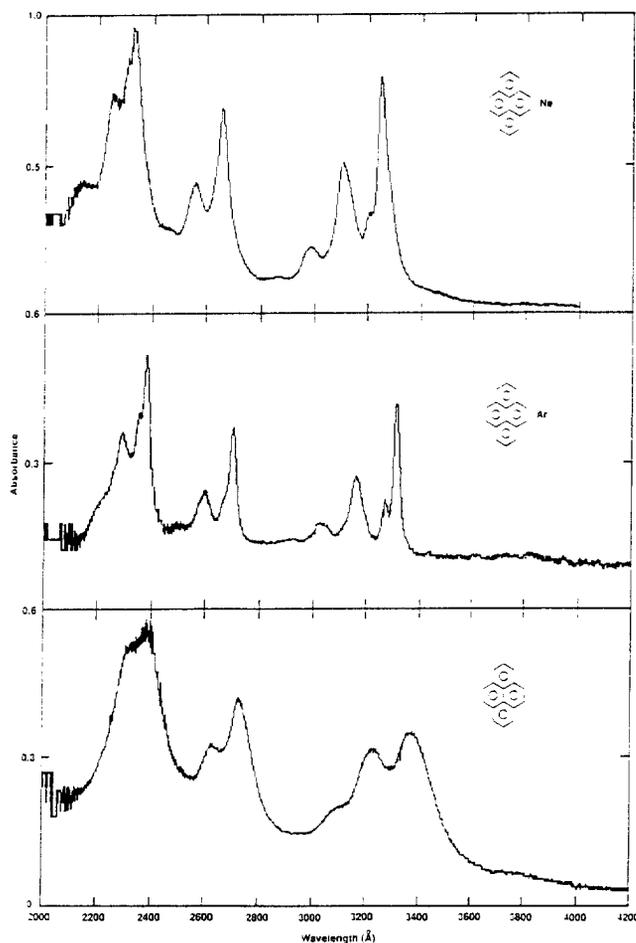


Figure 1: The absorption spectrum of pyrene ( $C_{16}H_{10}$ ) at 4.2 K. **Top:** Isolated in a neon matrix. **Center:** Isolated in an argon matrix. **Bottom:** Pure solid. Note the influence of isolation on the spectrum. From reference 19.

**Phenanthrene ( $C_{14}H_{10}$ ).** The UV-to-NIR absorption spectrum of phenanthrene isolated in an Ar matrix consists of several distinct band systems with very different intensities. Over the wavelength range covered in these experiments (2400 - 9000 Å), neutral phenanthrene exhibits 3 band systems peaking at 2894, 3436, and 3875 Å. No absorption is observed in the visible range.

**Pyrene ( $C_{16}H_{10}$ ).** Neutral pyrene isolated in Ne and Ar matrices shows only three distinct band systems (Figure 1) over the wavelength range covered in our experiments (1800 - 9000 Å). The strongest absorptions peak at 2320 (2374), 2655 (2694), and 3258 (3306) Å in a Ne (Ar) matrix. All of these bands have similar intensities. Neutral pyrene does not absorb in the visible (Figure 4 a). Also indicated in figure 1 is the absorption spectrum of a solid film of pure pyrene. Here the strongest absorptions peak at 2385, 2720, and 3372 Å. Figure 1 shows the influence of intermolecular interactions on band positions and profiles and illustrates the importance of isolating the molecule under study in an inert gas matrix cage to properly simulate the "free" molecules in interstellar environments.

**Astrophysical Implications of the Neutral PAH Spectra.** From the astrophysical perspective, these results indicate that: (i) Small, neutral PAHs (less than 20 carbon atoms) do not absorb in the visible and therefore cannot contribute to the known DIBs (DIBs have not yet been found in the UV). (ii) The three PAH molecules studied have strong UV absorption bands with oscillator strengths in the range 0.2 - 1.0. If present, they could contribute substructure to the UV portion of the interstellar extinction curve. The cross sections of the strongest bands are  $4.0 \times 10^{-16}$ ,  $1.1 \times 10^{-16}$  and  $1.5 \times 10^{-16} \text{ cm}^2 \text{ molecule}^{-1}$  in the case of naphthalene /20/, phenanthrene and pyrene /14/ respectively. In order for these species to produce substructure on the extinction curve at the 10% level would require neutral PAH

abundances of respectively  $1.3 \times 10^{-7}$ ,  $2.0 \times 10^{-7}$ , and  $1.5 \times 10^{-7}$  with respect to hydrogen. This is high compared to the overall PAH abundance deduced from IR observations which ranges from  $2.0 \times 10^{-7}$  -  $5.4 \times 10^{-7}$  /1, 2/.

Furthermore, as mentioned above, the fraction of PAHs in the neutral form depends on the ionization balance along the specific line-of-sight and should be small in the general ISM.

### B. Spectroscopy of Ionized PAHs.

**The Naphthalene Cation ( $C_{10}H_8^+$ ).** The new spectral features associated with the naphthalene cation that arise upon VUV irradiation (Figs 2 and 3) fall into seven band systems (not all shown here) peaking at 6741 (6750), 4560, 3769 (3798), 3050 (3010), 2760 (2745), 2443, and 2227 (2191) Å respectively in a Ne (Ar) matrix. A continuum is also produced which is apparently associated with the cation. The growth of the cation continuum with VUV irradiation is

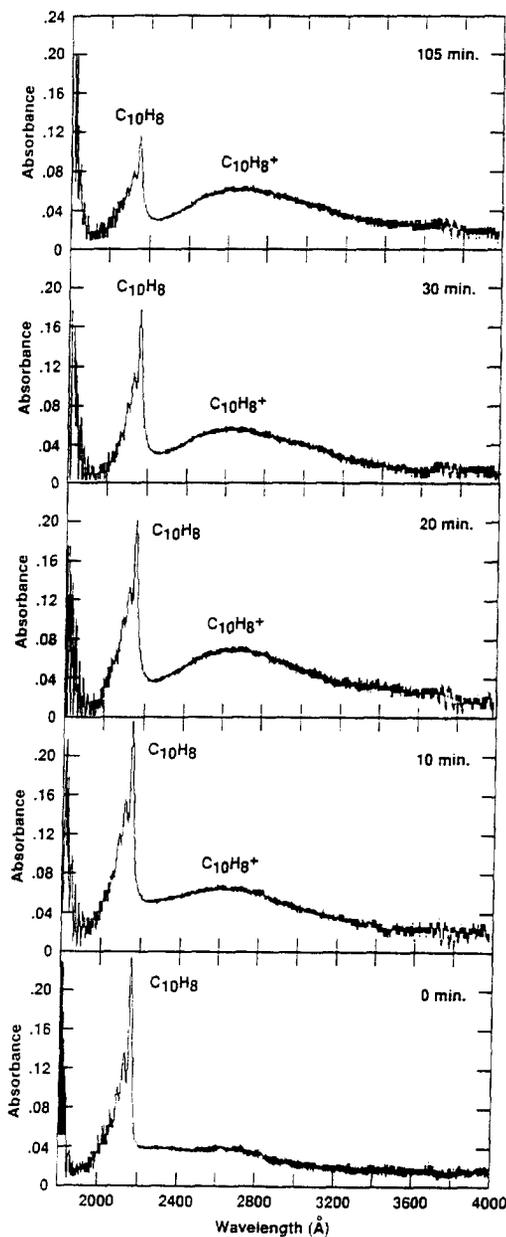


Figure 2: The growth of the naphthalene cation ( $C_{10}H_8^+$ ) continuum and simultaneous depletion of the neutral precursor ( $C_{10}H_8$ ) absorptions as a function of irradiation time in an argon matrix at 4.2 K. From reference 17 c.

correlated with the growth of the discrete cation absorption features and the depletion of the neutral precursor absorptions. A detailed discussion of these results has been given in references 17 and only a synopsis is given here. Two features of the cation absorption spectrum are particularly relevant to astrophysical questions: (i) the visible-NIR vibronic system with the strongest peak at 6741 Å in Ne and 6750 Å in Ar, and (ii) the broad and strong continuum extending from the UV to the visible (2000 - 3800 Å, with a weak tail extending to ~ 5100 Å). The vibronic system consists of several discrete bands as shown in figure 3. Band positions are listed in Table 1 where they are also compared to known DIBs. The continuum is shown in figure 2. A variety of experiments were carried out to test if the continuum arose from other carriers including solvated electrons and PAH anions /17 a, b/. These possibilities were eliminated, indicating that the positive naphthalene ion produces the continuum.

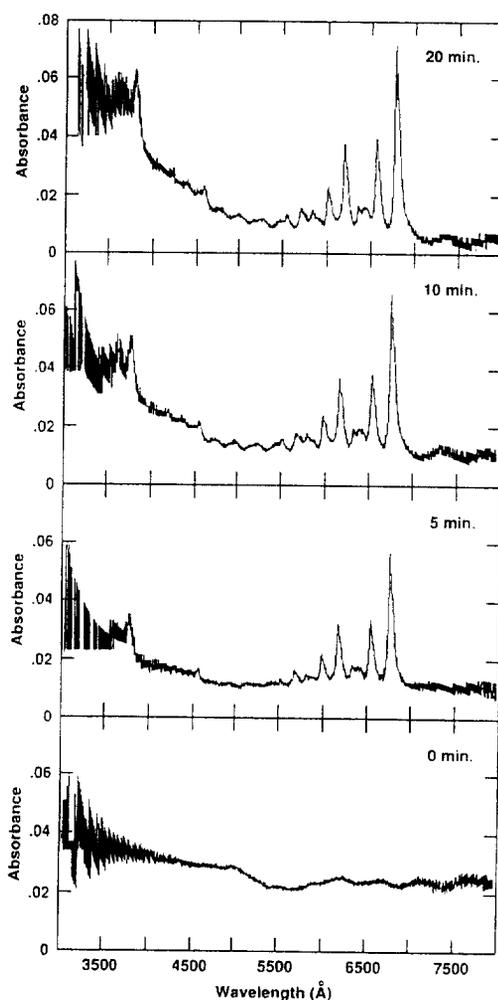


Figure 3: The growth of the naphthalene cation ( $C_{10}H_8^+$ ) absorption spectrum as a function of irradiation time in a neon matrix at 4.2 K. Note that neutral naphthalene does not absorb in the visible. From reference 17 c.

**TABLE 1** Naphthalene and Pyrene Cation Bands Compared with Some of the DIBs.

DIBs <sup>a</sup>	Equivalent Width (Å) <sup>a</sup>	PAH <sup>+</sup> (in Ne) <sup>b</sup>	DIBs <sup>a</sup>	Equivalent Width (Å) <sup>a</sup>	PAH <sup>+</sup> (in Ne) <sup>b</sup>	DIBs <sup>a</sup>	Equivalent Width (Å) <sup>a</sup>	PAH <sup>+</sup> (in Ne) <sup>b</sup>
4428	3.40; ---; ---; 3.60	4395 <sup>c</sup> (vs); 4435 <sup>d</sup> (vs)	5780	0.88; 0.24; 0.16; 0.80	5784 <sup>e</sup> (m)	6376	0.09; 0.04; 0.07; 0.11	6376 <sup>e</sup> (w)
---	---	5114 <sup>e</sup> (w)	5850	0.10; 0.07; 0.02; 0.13	5848 <sup>e</sup> (m)	---	---	6520 <sup>e</sup> (s)
---	---	5341 <sup>e</sup> (w)	---	---	5965 <sup>e</sup> (s)	6742	0.06	6741 <sup>e</sup> (vs)
5508	0.03	5503 <sup>e</sup> (w)	---	---	6151 <sup>e</sup> (s)	---	---	---
---	---	5658 <sup>e</sup> (m)	6314	0.80	6314 <sup>e</sup> (w)	---	---	---

<sup>a</sup> From ref. 10 (a); data correspond to observations toward HD 183143, HD 167264, HD 26571, and HD 168625 respectively; <sup>b</sup> Refs .17 (a) & 18; wavelength uncertainty is  $\pm 5$  Å; <sup>c</sup> Pyrene; <sup>d</sup> Pyrene in argon; <sup>e</sup> Naphthalene. [vs, s, m, and w indicate very strong, strong, moderate, and weak respectively].

2. **The Phenanthrene Cation ( $C_{14}H_{10}^{\pm}$ ).** Some preliminary results on the phenanthrene cation in an Ar matrix are presented here. The absorption spectrum of  $C_{14}H_{10}^+$  shows 5 bands peaking at 3239, 3306, 3391, 3460, and 4311 Å. We did not detect the strong NIR absorption band previously reported at 8980 Å /12 b/ in these initial experiments due to the rapid drop in the response of our monochromator in the 9000 - 10,000 Å range. No strong visible absorption bands were detected. These initial experiments do not show definitive evidence for a strong UV continuum growing in under the strong neutral phenanthrene bands which span the 2000-3000 Å range. However, there is evidence for an unstructured continuum in the near UV. Further work is in progress to optimize the cation yield and to measure its full spectrum in Ne and Ar matrices.

3. **The Pyrene Cation ( $C_{16}H_{10}^{\pm}$ ).** The new spectral features associated with  $C_{16}H_{10}^+$  are shown in Fig. 4. The discrete features (all are not shown here) peak at 3606 (3965), 4293 (4333), 4395 (4435), 4546 (4575), and 4840 (4878) Å in a Ne (Ar) matrix. Figure 4 shows that the entire UV-Vis-NIR spectrum of  $C_{16}H_{10}^+$  is dominated by the strong absorption band which falls at  $4395 \pm 5$  Å in Ne and  $4435 \pm 5$  Å in Ar matrices, remarkably close to the peak position of the well-known 4430 Å DIB. The characteristics of this strong absorption band have been discussed in reference 18. The effect of matrix material on band positions is dramatically illustrated here where a red shift of 40 Å is measured when going from Ne to Ar (Fig. 5). A continuum is also produced which extends from 2000 to 3600 Å having a weak tail out to  $\sim 5100$  Å (not all shown). The growth of the continuum and discrete absorption features produced by VUV irradiation is correlated with the depletion of the neutral precursor absorption. A film of solid pyrene which is similarly irradiated does not show any new discrete features.

In view of the proximity of the matrix isolated pyrene cation band to the well-known 4430 Å DIB, it is of interest to study the influence of side-groups on the pyrene moiety to determine if pyrene-like species might indeed be responsible for this DIB. In order to investigate the influence of side groups on the pyrene cation spectrum, we have measured the 1-pyrenecarboxaldehyde cation ( $C_{17}H_{10}O^+$ ) spectrum. The aldehyde side group (HC=O) perhaps represents an extreme (and unlikely ?) case for an interstellar molecular side-group. Its interest, however, lies in the fact that it should provide an upper limit to the magnitude of the pyrene cation absorption shift that one might expect when pyrene is substituted with other, perhaps more likely, side groups such as  $CH_2$ ,  $CH_3$ . Indeed, alkylated pyrene derivatives have been recently detected in Murchison meteorite samples /21/. Smaller shifts would be expected from these other groups because they cannot participate in the aromatic network. As illustrated by figure 4d, apart from a 122 Å blue-shift, the overall spectral appearance is remarkably unchanged from that of the pyrene cation itself.

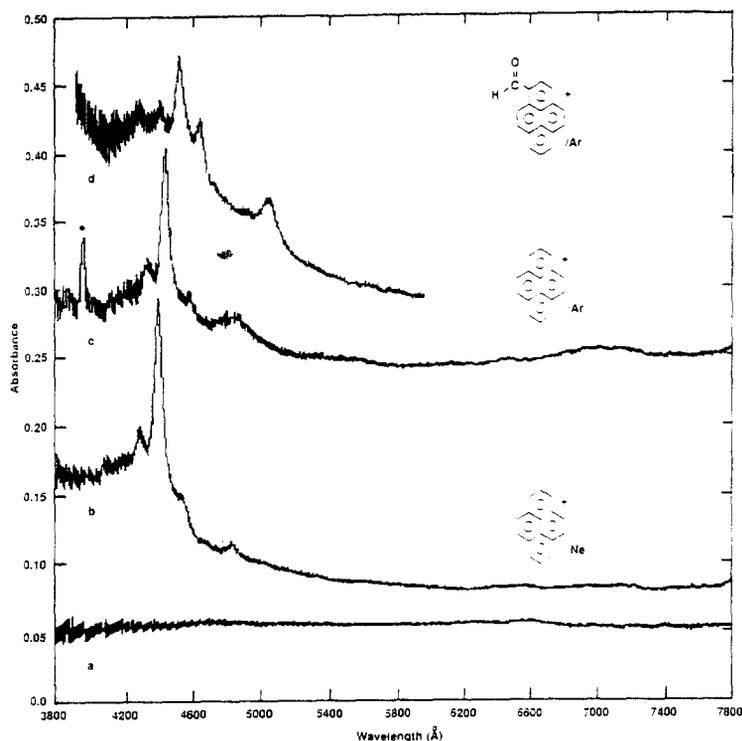


Figure 4: The visible absorption spectra of (a) pyrene ( $C_{16}H_{10}$ ) isolated in a neon matrix at 4.2 K; (b) the pyrene cation ( $C_{16}H_{10}^+$ ) in a neon matrix at 4.2 K, (c) the pyrene cation ( $C_{16}H_{10}^+$ ) in an argon matrix at 4.2 K, and (d) the 1-pyrenecarboxaldehyde cation ( $C_{17}H_{10}O^+$ ) in an argon matrix at 4.2 K. The dot (\*) indicates a band arising from an impurity in the sample. From reference 19.

4. **Astrophysical Implications of the PAH Cation Spectra.** The astrophysical implications of the discrete absorption features of the PAH cations are considered. The implications for the broad continua are discussed further in ref. 17 c. Contrary to their neutral precursors, *ionized PAHs absorb at discrete frequencies in the visible and thus could contribute to the DIBs.* The comparison of the PAH cation discrete features with the DIBs, shown in Table 1, indicates that the  $C_{10}H_8^+$  and  $C_{16}H_{10}^+$  bands show a remarkable agreement with some of the DIBs.

In the case of the naphthalene cation ( $C_{10}H_8^+$ ), 6 out of 12 of its discrete features match DIBs. There are two ways in which one can consider the possible contribution of the naphthalene cation to the DIBs. One extreme is to require that *all* of the  $C_{10}H_8^+$  bands, regardless of their intensity, have known DIB counterparts. Another approach is to only require that the strongest  $C_{10}H_8^+$  band(s) be present. The former approach *requires* a high fractional naphthalene abundance among the PAHs, the latter, a substantially lower abundance.

The first approach shows that, while several  $C_{10}H_8^+$  bands have peak positions which fall within 5 Å (the resolution element of our spectrometer) of DIB positions, there is a relative intensity mismatch between the  $C_{10}H_8^+$  band intensities and the DIB equivalent widths reported by Herbig /10 a/ in the specific case of HD 183143. Moreover, as shown in Table 1, with the remarkable exception of the very strong 6741 Å  $C_{10}H_8^+$  band, none of the other strong  $C_{10}H_8^+$  bands have known DIB counterparts while most of the weaker members do show a good match with DIBs. When going through such comparisons, however, one should keep in mind that the intensity ratios of most DIBs are highly variable from one object to another due to the difficulties inherent in making observations of such very weak features, and the fact that the measurements often constitute an ill-defined average over all clouds situated along the line-of-sight /10, 11/. It is also not clear in published tabulations which spectral regions have been thoroughly searched for DIBs and which have not been because of obscuration by atmospheric, stellar, or interstellar lines. Hence, one can imagine that the weaker naphthalene cation bands might be responsible for some of the DIBs while the

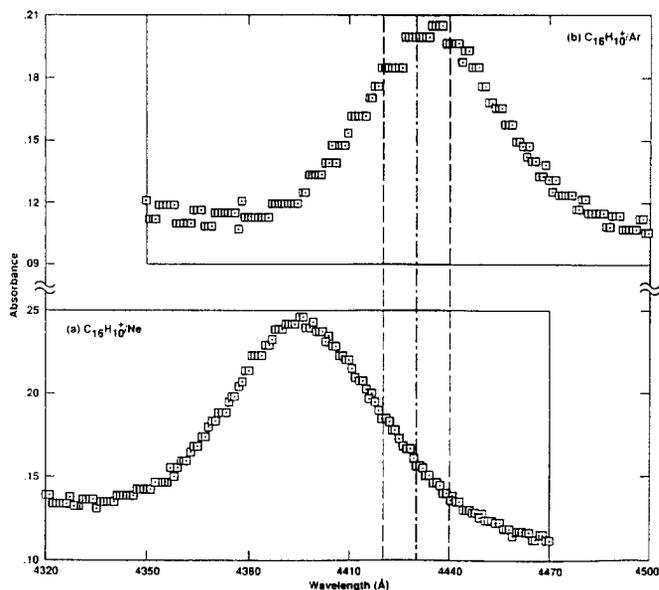


Figure 5: Comparison between the position and halfwidth of the well-known 4430 Å DIB (shaded band) with the strongest visible absorption band of the pyrene cation ( $C_{16}H_{10}^+$ ) isolated in (a) neon and (b) argon matrices at 4.2 K.

interstellar counterparts of the stronger naphthalene cation bands have not yet been recognized as DIBs. However, if this is the case, it should be established why the stronger  $C_{10}H_8^+$  bands are not observed (i.e. if these features are hindered by stellar, atmospheric or instrumental features or if they simply escaped detection). Consequently, to test for  $C_{10}H_8^+$  in the ISM, observations should be carried out to search for the stronger bands of  $C_{10}H_8^+$  - which are predicted at 6520 Å, 6151 Å, and 5965 Å /17/- along the same lines-of-sight with the 6741 Å DIB. It should also be kept in mind that a specific ion may be present in abundance along one line-of-sight and considerably weaker along another. The small number of DIBs (~ 15%) which could be accounted for by  $C_{10}H_8^+$  demonstrates that *one PAH ion ( $C_{10}H_8^+$  in this case) cannot explain all of the DIBs in this wavelength range*. This comparison suggests, however, that a family of different PAH ions may well explain some (or most?) of the DIBs.

The second approach would be to soften the requirements for a molecular species to contribute to the DIBs by requiring that only the strongest PAH ion bands be evident and that subsequent searches be made for the less intense bands. If this criterion is adopted, the match between the strongest naphthalene cation band at 6741 Å and the 6742 Å DIB is intriguing. Using the  $C_{10}H_8^+$  oscillator strengths measured in our experiments ( $f = 4.0 \times 10^{-4}$ ) /17 a/, we calculate that 0.3 % of the available carbon would be required to be in the form of  $C_{10}H_8^+$  if the naphthalene cation is responsible for the 6742 Å DIB along the line-of-sight to HD183143.

Regarding the pyrene cation,  $C_{16}H_{10}^+$ , figure 5 shows that the strongest absorption feature of  $C_{16}H_{10}^+$  is intriguingly close to the strong 4430 Å DIB when isolated in a Ne matrix and matches it when isolated in an Ar matrix. The importance of matrix material is dramatically illustrated here where a red shift of 40 Å is measured when going from a Ne to an Ar matrix. Thus, the good agreement observed between the 4435 Å absorption of  $C_{16}H_{10}^+$  in Ar and the 4430 Å DIB, although suggestive, may only be coincidental (i.e. induced by the matrix effect). As discussed earlier, vibronic band positions in a Ne matrix are believed to better represent the free gas-phase values which are presumably the values one should use in comparisons with the DIBs. Nonetheless, these results raise the interesting possibility of a connection between  $C_{16}H_{10}^+$  and the 4430 Å DIB. i.e.: Is the proximity of the 4395 Å absorption of  $C_{16}H_{10}^+$  to the 4430 Å DIB only a coincidence? or is it an indication that the carrier of the 4430 Å DIB may be the pyrene cation ( $C_{16}H_{10}^+$ ) or a closely related, pyrene-like species?. Side-groups which do not participate in ring aromaticity (such as  $CH_2$ ,  $CH_3$ , ...) are known to induce a red shift of PAH cation vibronic transitions on the order of 30-50 Å /12 a/ while, as shown in the previous section, an aldehyde side group can induce a red shift of about 120 Å. Thus this result raises the serious possibility that a substituted pyrene cation is responsible for the 4430 Å DIB. The 40 Å cation band matrix shift also argues for gas phase DIB carriers. If any DIBs originate in a solid

material, significant compositional variations from one line-of-sight to another should produce detectable wavelength shifts. Although extensively searched for observationally, no such shifts have been reported. The 4430 Å interstellar absorption, when observed, is the strongest and the broadest (FWHM  $\sim$  20 Å) of the known DIBs /10 a/. It is also highly variable in depth and is weaker towards objects with strong FUV extinction /11/. The suggestion that a mixture of different PAH ions may well explain some (or most?) of the DIBs seems to be supported by the present results on the pyrene cation. Using the  $C_{16}H_{10}^+$  oscillator strength of 0.126 in Ar, implies that 0.2 % of the cosmic carbon must be in the form of  $C_{16}H_{10}^+$  if the pyrene cation is responsible for the 4430 Å DIB.

## CONCLUSION

This paper describes the spectroscopic properties of the neutral and ionized PAHs naphthalene ( $C_{10}H_8$ ), phenanthrene ( $C_{14}H_{10}$ ), and pyrene ( $C_{16}H_{10}$ ) isolated in inert gas matrices under conditions relevant to astrophysical environments. The main conclusions are as follows:

Neutral PAHs show strong absorptions in the ultraviolet and may produce weak structures on the extinction curve. However, to produce detectable features requires high abundances for each specific PAH compared to the total predicted abundance of PAHs.

PAH cations absorb in the visible and near infrared, making them good candidates for the carriers of the diffuse interstellar bands

- The strongest band of  $C_{10}H_8^+$  falls at 6741 Å, matching the weak 6742 Å DIB. Five other weaker bands (6376, 6314, 5848, 5784, and 5503) also fall very close to the positions of known DIBs. The possibility that  $C_{10}H_8^+$  is responsible for some of the diffuse interstellar bands can be tested by searching for new DIBS at 6520, 6151, and 5965 Å, other strong naphthalene cation band positions. If  $C_{10}H_8^+$  is indeed responsible for the 6742 Å feature, it accounts for 0.3% of the cosmic carbon.
- In the case of the pyrene cation ( $C_{16}H_{10}^+$ ), the spectrum is dominated by a single intense band which falls remarkably close to the well-known 4430 Å DIB. This suggests that a closely related, pyrene-like molecular ion could be responsible for this band. If  $C_{16}H_{10}^+$  carries the 4430 Å feature, it accounts for 0.2% of the cosmic carbon.
- Both cation spectra show a remarkably intense, very broad continuum extending from the UV to the visible. If a continuum is a general property of PAH cations, this characteristic will have a strong impact on our understanding of how PAHs convert interstellar UV and visible radiation into IR radiation.

The ultimate solution to the challenging problem of the diffuse interstellar bands can only be obtained through a detailed and systematic comparison of the DIBs with appropriate laboratory data. Before this can be achieved, much more laboratory work coupled with a detailed and systematic DIB observing program is needed.

We hope that we have demonstrated the importance of performing laboratory studies under conditions strictly relevant to those reigning in the diffuse interstellar medium. Although difficult to simulate, these conditions must be met, especially for the study of charged molecular species, since this *is the only way to definitely assess the relevance of specific molecular ions* to the DIBs. From the observational point of view, the recent availability of multichannel detectors now makes it possible to measure high-quality DIB spectra, including intrinsic profiles, and to detect new features. Considering these instrumental improvements, it is important that a new, high-resolution survey of the DIBs be carried out along as many lines of sight as possible.

The combination of these new, high-quality laboratory and observational data should go a long way to solving the long-standing "mystery" of the DIB carriers and better understand the physical and chemical properties of the diffuse interstellar medium.

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