

Search for coronene and ovalene cations in the diffuse interstellar medium

P. Ehrenfreund¹, B.H. Foing², L. d'Hendecourt³, P. Jenniskens⁴, and F.X. Désert³

¹ Leiden Observatory, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands

² Solar System Division, ESA/SSD, ESTEC/SO, NL-2200 Noordwijk AG, The Netherlands

³ Institut d'Astrophysique Spatiale, Bat. 121, F-91405 Orsay, France

⁴ NASA-Ames Research Center, MS: 245-6, Moffett Field, CA 94035, USA

Received 10 October 1994 / Accepted 13 December 1994

Abstract. Recent studies suggest carbon-containing molecules as the best candidates for the carriers of the unidentified diffuse interstellar bands (DIBs), considering their abundance and ability to form stable bonds in interstellar space. The spectra of the naphthalene and pyrene cations in a neon matrix were recently reported, indicating a link between these small polycyclic aromatic hydrocarbon (PAH) ions and some diffuse bands. We have searched for new DIBs in the near-infrared and around 4592 Å in order to identify the coronene ($C_{24}H_{12}$) and ovalene ($C_{32}H_{14}$) cations in the diffuse medium. Due to their pericondensed structure these molecules should be among the most stable PAHs in the interstellar medium. The absorption spectra of both molecules were recently measured in solid neon. We report on the search for the bands at 9465/4592 Å and 9780 Å, and derive corresponding limits on the presence of the coronene and ovalene cations in the diffuse interstellar medium. From these results, we discuss a possible selective destruction mechanism of PAHs through dication formation, and the role of PAH compounds as possible DIB carriers.

Key words: interstellar medium: molecules – dust – molecular data

1. Introduction

Diffuse interstellar features have been extensively studied by Herbig between 4430 and 6800 Å (Herbig 1975). In recent astronomical observations many additional DIBs were detected (Herbig & Leka 1991; Jenniskens & Désert 1994) and measurements at high resolution and higher signal to noise ratio will probably reveal many more weak diffuse bands. Most of the DIBs are found in the range between 5000–8000 Å. Astronomical measurements below 4400 Å and in the near IR are scarce and only a few diffuse bands have been detected (Joblin

et al. 1990; Foing & Ehrenfreund 1994a,b; Hibbins et al. 1994). A wide variety of possible carriers have been reviewed by Smith et al. (1977) and van der Zwet (1987).

Recent observational evidence however indicates that carbon-containing molecules are the best candidates and favour large gas phase molecules over small dust grains. In particular polycyclic aromatic hydrocarbons (PAHs), fullerenes and their ions were suggested to be interesting carrier molecules (Léger & d'Hendecourt 1985; Van der Zwet & Allamandola 1985; Kroto 1987; Léger et al. 1988; Kroto & Jura 1992). PAHs, probably present as a mixture of neutral and ionized species, are likely responsible for the set of infrared emission bands in the 2 - 15 μm range, which are observed in many different objects like reflection and planetary nebulae, H II regions and even external galaxies (Léger & Puget 1984; Szczepanski & Vala 1993). The presence of PAHs in the diffuse medium is also suggested by the 12 μm IRAS Cirrus and by the 3.3 μm diffuse emission (Giard et al. 1988) as well as by the recent detection of the 6.2 μm emission (Ristorcelli et al. 1994). PAHs are thus suggested to be the most abundant free organic molecules, ubiquitous in space and remarkably stable. They also show strong transitions in the UV/Visible (Bennema 1959). A significant fraction of PAH molecules can be singly ionized in strongly irradiated regions, like reflection nebulae or planetary nebulae (van der Zwet & Allamandola 1985). The fraction of ionized PAHs in the diffuse interstellar medium may be only 10 % (Verstraete et al. 1991), although some discrepancies exist in this number (d'Hendecourt & Léger 1987). Whether neutral or ionized molecules can be DIB carriers as well as the size of these molecules has been a debated subject. Small neutral PAH molecules show strong transitions in the blue and UV. Transitions for larger molecules will shift towards longer wavelengths (Platt 1956; Birks 1970; Leach 1987). PAH ions will absorb in the visible and the first transition may fall in the IR or near IR (Leach 1987). The first transition (i.e. the lowest energy transition) of ionized PAHs have usually low oscillator strengths (of the order of 10^{-3} at the most). A condensed configuration of the DIB carrier should

Send offprint requests to: P. Ehrenfreund

be of advantage. For instance, the absence of a strong band in the 6.5 - 7.2 μm range indicates that compact rather than non-compact PAHs are responsible for the infrared emission bands (Léger et al. 1989). However, PAHs which are responsible for the IR emission may not necessarily also be the carriers of the DIBs.

Comparison of astronomical observations of DIBs to available laboratory data of specific molecules is crucial to solve the problem of the diffuse bands. Laboratory measurements, using rare gas matrix isolation techniques and UV photolysis have provided recently a set of spectra of PAHs, PAH ions and similar species, which allow a good comparison with interstellar data. The spectra of the naphthalene cation and the pyrene cation measured in a neon matrix showed promising coincidences (Salama & Allamandola 1991, 1992a,b). The naphthalene cation shows several bands, which coincide with the position of diffuse bands, and a substituted pyrene molecule might be the carrier of the strong DIB at 4430 Å (Salama & Allamandola 1992a,b; Léger et al. 1995). The detection of two diffuse bands in the near infrared at 9577 and 9632 Å that are consistent with laboratory measurements of C_{60}^+ in a neon matrix has recently been reported (Foing & Ehrenfreund 1994a).

This paper presents a search for the absorption signature of coronene and ovalene cations in the DIB spectrum. These molecules are well studied in the laboratory and are thought to be stable against photodissociation due to their pericondensed structure.

2. Laboratory spectroscopy

2.1. The coronene cation

The spectrum of the coronene cation was measured in solid neon (Ehrenfreund et al. 1992). The measurements indicated a strong absorption at 4592 Å (full width half maximum FWHM = 28 Å) with an oscillator strength of $1.2 \cdot 10^{-2}$ and a sharp transition at 9465 Å (FWHM = 16 Å) with an oscillator strength of $1.8 \cdot 10^{-3}$, suitable candidates to be searched for by astronomical observations. Based on the photoelectron spectra of coronene the band at 9465 Å corresponds to the first transition of the coronene ion from orbital E_{2u} to E_{1g} , is symmetry allowed and shows a strong vibronic progression towards shorter wavelengths. The characteristic bands of the coronene ion are listed in Table 1.

There is strong evidence that DIBs are due to gas phase molecules. To ensure a correct identification an important criteria is to know how much neon or argon matrices are shifting the position of the absorption peak compared to the gas phase. Possible shifts between neon matrix and gas phase values, expressed in terms of energy (cm^{-1}) depend on the specific molecule, on the specific state of the molecule and on the wavelength of the expected transition. Whereas in the blue this shift will likely not exceed 40-100 cm^{-1} (8-20 Å), reflecting the slightly stronger guest-host interaction in higher excited states, smaller shifts are expected for infrared transitions involving lower excited states. A 40 cm^{-1} shift will correspond to ± 35 Å at 9500 Å. Based on Bondybey & Miller (1983) and previous studies or reported

Table 1. Spectroscopic parameters of the characteristic coronene ion bands (Ehrenfreund et al. 1992). The value in parenthesis represents the f-value for the whole vibronic progression from 7932-9465 Å

λ (Å)	Coronene cation			f
	ν (cm^{-1})	FWHM (Å)		
4592	21786	28		$1.2 \cdot 10^{-2}$
5020	19920	36		$2.3 \cdot 10^{-3}$
6160	16234	170		$1.7 \cdot 10^{-3}$
6800	14706	300		$7.1 \cdot 10^{-3}$
9465	10565	16		$1.8 \cdot 10^{-3}$ (5.10^{-3})

identifications in the red and infrared, we expect a probable shift for a PAH cation in neon matrix of $\pm 10 \text{ cm}^{-1}$ or (± 9 Å) at 9500 Å, with a higher limit of 40 cm^{-1} .

2.2. The ovalene cation

The spectrum of the second transition of the ovalene cation (the first one being forbidden) in the near-infrared in a neon matrix is shown in Fig. 1 (for a detailed technical description, see Ehrenfreund et al. 1992). The strong band at 9780 Å corresponds to the transition from orbital B_{2g} to A_u and is symmetry allowed. Unfortunately the oscillator strength has not been estimated in this experiment, which was performed in similar but less complete manner than the coronene results. For the coronene ion the second ionic transition visible at 4592 Å has the highest oscillator strength. In analogy with the coronene ion the second ionic transition of ovalene appearing at 9780 Å should be the strongest band. Experiments are under-way to derive precisely the f values and FWHM of this transition.

The spectrum of the ovalene cation between 4000-7000 Å displays two bands at 4632 and 4720 Å (Ehrenfreund et al. 1992). The irradiation of ovalene in this experiment was performed after the deposition only for a limited time, due to technical limitations. It can therefore not be excluded that additional weak bands may appear after further UV photolysis between 4000-7000 Å. The band at 4720 Å is close to the diffuse band at 4726 Å in band position (Ehrenfreund et al. 1992). The band width however is broader in the laboratory (12 Å), than in interstellar space (5 Å).

3. Observations

Spectra of reddened stars in the appropriate wavelengths ranges were obtained with the 1.52 m Coude telescope and spectrograph Aurelie at the Observatoire de Haute Provence (OHP) in France on September 14, 1992 and February 16, 1993. The spectral resolving power was set to $R=36.000$ or $\Delta\lambda = 0.27$ Å using a 1200 grooves/mm grating, a dispersion of 7.2 Å/mm, and covering the range of 200 Å on the 2048-diode array. The spectral domain at 9450 Å is significantly absorbed by Earth atmospheric water and required a detailed telluric correction. A part of the near-infrared spectrum is saturated by water lines and

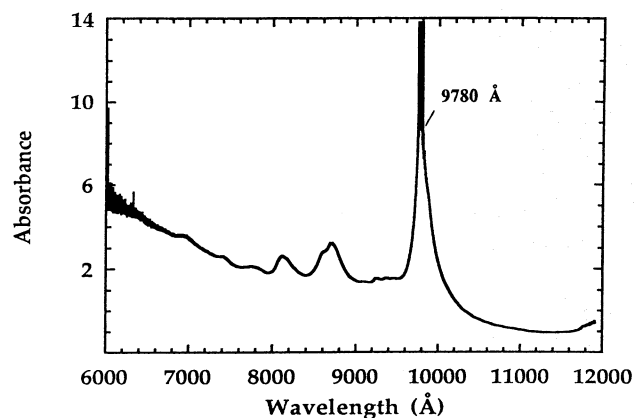


Fig. 1. The near infrared absorption spectrum of ionized ovalene isolated in a 4 K neon matrix

Table 2. Programme stars listed in Figs. 2-5

Star	Spectral Type	$E_{(B-V)}$
HD205021	B1IV	0
HD25642	A0IV	0
HD197345	A2I	0.09
HR6714	B5Ib	0.12
HR7977	B3Ia	0.53
HD21389	A0Iae	0.54
HD187982	A1Iab	0.68
HD20041	A0Ia	0.72
HD15497	B6Ia	0.85
HD186745	B8Ia	0.94
HD217086	O7	0.95
HD183143	B7Ia	1.28
BD 404220	O7	2.00

therefore difficult to observe from OHP. Photon and instrumental noise correspond to S/N of 50-200 per resolution element. However the strong telluric absorption in the NIR cause the photon statistics to be worse, especially in the saturated cores. A careful correction of stellar lines in the blue range was attempted, which improved the possibility of detecting DIBs over previous studies (Jenniskens & Désert 1994). The program stars were selected to cover a range of interstellar reddening $E_{(B-V)}$ from 0 to 2, and spectral types from O7 to A0, see Table 2. The spectra were reduced and analysed at OHP and ESA/SSD using IHAP and IDL software analysis packages.

4. Results

4.1. Coronene cation

Figure 2 shows a series of the telluric corrected spectra for the measured stars, centred at 9465 Å. From a composite spectrum combining with equal weight the 4 more reddened stars and scaled to $E_{(B-V)} = 4$, one can recognize the weak absorptions

Table 3. Lines appearing after division of the stars by a reference spectrum. These bands may be DIBs, or remnants due to correction of stellar or telluric lines. Stellar lines distant from the measured bands by more than 1 Å (or 30 km/s) can not contaminate the band measurement and are indicated by "too far". Transitions of rare elements are marked as "not plausible". Transitions of neutral and low ionization potential atoms should correspond to features decreasing with hotter stellar effective temperature, which is not observed, and thus will appear only as "minor blends", if present

Possible DIBs observed in the 9400-9500 Å range			
λ in Å	Stellar lines	λ in Å	Stellar identification
9404	Ne I	9405.75	too far
9407	Xe II	9407.57	not plausible
9409	Ar I	9408.66	minor blend
9413	Ne I	9412.32	minor blend
	Si II	9412.72	minor blend
	Kr II	9413.32	not plausible
	Si I	9413.506	minor blend
	Fe I	9414.14	too far
9422	Si I	9421.78	minor blend
9431	N II	9431.2	minor blend
	Ti I	9431.77	minor blend
	Mg I	9432.76	too far
9450	Kr I	9450.88	not plausible
	Cu II	9451.6	too far
9465	Na I	9465.9	minor blend
	N I	9464.23	too far
	Cu II	9463.71	too far
	He I	9463.61	resolved
9498	O I	9498.04	probable
	O I	9499.39	too far

present in the spectrum, which then can be tested in individual spectra for DIB criteria, i.e. gradual increase with $E_{(B-V)}$ and no relation to stellar or atmospheric features. Several lines are observed in the range ± 50 Å from the expected transition at 9465 Å (outside the telluric band cores). These have equivalent width above 200 mÅ for $E_{(B-V)} = 4$ and show a progression with increasing $E_{(B-V)}$. In Table 3 these lines are compared to stellar lines listed in the Moore catalogue (Moore 1972) at the same or near-by position. All programme stars are supergiants except BD 404220 and HD 217086. Therefore spectra could contain the same stellar lines, but the presence of these bands in the spectrum of the O7 star BD 404220 is a good indicator of a true DIB. DIBs can be hidden by the abundant telluric remnants and it can not be excluded that a corresponding stronger DIB may still be detected from a dry observational site. In the telluric corrected spectra in Fig. 2, a band at 9466 Å is found, located 1 Å shifted from the laboratory transition. However the band is weak and narrow (full width at half maximum = FWHM of 2 Å) and could be partly masked by a stellar transition such as Na I (9465.9 Å). Other lines of N I (9464.23 Å), Cu II (9463.71 Å) and He I (9463.61 Å) are far enough not to affect the 9466 Å range. The stellar line subtraction may not have been perfect.

From this band we can derive an upper limit of the DIB strength per unit reddening of 75 mÅ.

Figure 3 shows in the 4590 Å range a series of spectra of stars divided by standards of same or very similar spectral type. This division allows us to search for weak DIBs normally hidden under stellar lines. The well known DIB at 4502 Å can be seen in all stars, growing with increasing $E_{(B-V)}$. Near 4583 Å (FWHM = 2.1 Å) and 4550 Å (FWHM = 1.8 Å) features appear in the star HD15497 and in the highly reddened star HD183143 with equivalent widths of 76 and 70 mÅ per unit reddening, respectively. The narrow feature at 4583 Å coincide with a number of stellar lines (4582.98 Å for Ne I, 4583.44 Å for Ti II, 4583.84 Å for Fe II) and may thus be a remnant of imperfect stellar line subtraction rather than a DIB. Note that near 4550 Å a similar feature is found and here too are a number of stellar lines that normally obliterate weak DIBs (4549.19 Å and 4549.47 Å for Fe II, 4549.62 Å for Ti II, 4550.64 Å for Ne I). However the absence of these two bands in HD 217086 suggests that these bands are stellar lines (most probably Fe II). Therefore no new narrow DIBs are present in this range above 70 mÅ/ $E_{(B-V)}$. A broad band at 4600 Å (FWHM = 28 Å), measured in HD183143 is listed in Jenniskens & Desert (1994) as a doubtful DIB with an equivalent width of 450 mÅ normalized to $E_{(B-V)} = 1$. A very shallow feature around 4600 Å is observed in our three more reddened star spectra with FWHM > 30 Å. Corresponding equivalent width are 1.5, 0.9 and 0.6 Å for programme stars of reddening 0.73, 0.95 and 1.16, respectively. The curvature is smallest for HD183143, which implies that the feature is not proportional to reddening. We do not believe that the curvature is related to the flat field correction or other instrumental effects, as the stars were all observed the same night and as we obtain a perfectly straight ratio spectrum for HD20041/HD21389. Thus this shallow feature seems real, but is difficult to associate with a unique classical interstellar DIB, because its position and shape varies in the 3 more reddened stars, and its strength does not increase with reddening. A variation in position is highly unusual for a DIB.

Based on these observational limits, and the known oscillator strength for the coronene cation band at 4592 Å of $f = 1.2 \cdot 10^{-2}$ (Ehrenfreund et al. 1992), we estimate an upper limit for the abundance after Spitzer (1961) $\Delta W_\lambda = \lambda_o^2 \cdot N \cdot f \cdot \pi \cdot e^2 / mc^2$. Using an upper limit of the total equivalent width of 70 mÅ for the 4592 Å band per unit reddening $E_{(B-V)}$ derived from our observations, and assuming a ratio $C/H = 3.7 \cdot 10^{-4}$ and hydrogen column density per unit interstellar absorption of $N_H/A_V = 2.10^{21} \text{ cm}^{-2}$ with $A_V = 3 E_{(B-V)}$, we calculate that less than 0.03 % of the cosmic carbon could be in the form of the coronene cation. For the band at 9466 Å (using the oscillator strength of $f = 1.8 \cdot 10^{-3}$, Ehrenfreund et al. 1992), the corresponding upper limit for the abundance of the coronene cation would be 0.05 % using the measured equivalent width of 75 mÅ per unit reddening. The discrepancy in the abundance limits for this two lines, although small, argues against the coronene cation as the common origin of these bands.

4.2. Ovalene

Figure 4 shows a series of the telluric corrected spectra centred at 9780 Å in order to identify the second transition of the ovalene cation. A composite spectrum combining the 4 reddened stars with $E_{(B-V)}$ between 0.54 and 1.28 and scaled to $E_{(B-V)} = 4$ is also shown in Fig. 4. This region is relatively free from telluric remnants, which appear as isolated spikes in the spectra, and surprisingly displays no strong DIBs. We find a weak possible DIB in the astronomical spectrum at 9783 Å with a measured equivalent width of 30 mÅ per unit reddening. There are no further bands stronger than 30 mÅ/ $E_{(B-V)}$ seen within ± 100 Å. The second transition of the ovalene cation appears strong in a neon matrix and therefore an oscillator strength f of 0.01, in analogy with the second transition of the coronene ion at 4592 Å ($f = 1.2 \cdot 10^{-2}$) is possible. If the band at 9783 Å is attributed to the ovalene cation, the abundance of ovalene is very low as observed for the coronene cation. Assuming $f = 0.001 < f < 0.01$ and a DIB with 30 mÅ/ $E_{(B-V)}$, the percent of cosmic carbon in ovalene ion would range from 0.05 to 0.005 %. The measurement of the oscillator strength of the ovalene cation will allow to derive an accurate abundance limit of this molecule in the future and experiments are now underway to estimate this value.

From these results we can derive upper limits for the abundance of the pericondensed PAH cations coronene and ovalene, (0.05 % of the cosmic carbon) which are definitely lower than similar estimates for the naphthalene and pyrene cations (0.2 - 0.3 % of the cosmic carbon)(Salama & Allamandola 1993).

5. Discussion

Measurements of DIBs in Orion have shown that the relative DIB strength $W/E_{(B-V)}$ reflects an interplay between ionization and recombination and between destruction and creation of the DIB carrier. At high reddening all DIBs in Orion decrease with increasing $E_{(B-V)}$ (Jenniskens et al. 1994). This is also observed for the Taurus and Ophiuchus dark clouds (Adamson et al. 1991). Using the different states of hydrogen as an indicator of the UV field, a typical behaviour of specific DIBs is apparent. The decline in band strength of many DIBs observed in dense clouds, where the UV field is attenuated, suggests that neutral precursors of DIB carriers and low ionization energy molecules dominate in this environment. These data support strongly a large molecular carrier in ionized state, e.g. a PAH cation (Jenniskens et al. 1994). Inside dense clouds a spectroscopic search for the neutral precursors of these ions is strongly recommended.

If a mixture of PAHs molecules is responsible for the DIBs, then neutral species, monocations, double ionized PAHs, radicals, dehydrogenated PAHs, substituted PAHs (e.g. with an attached side-groups) and their photofragments may be also present. Whereas neutral and monocations are probably predominant, the other mentioned PAH products may exist only as transient species in the interstellar medium. Their transitions

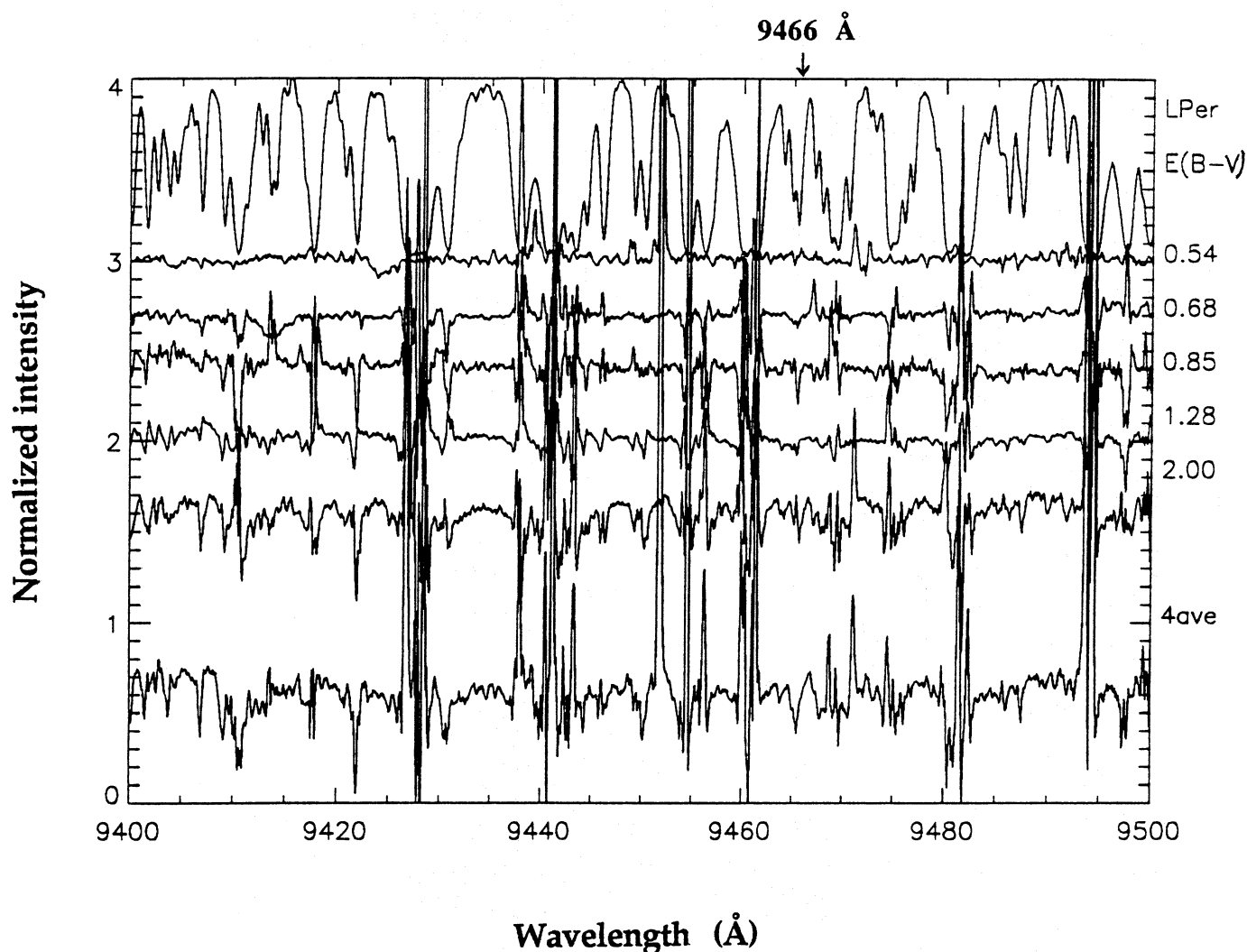


Fig. 2. Sequence of reduced spectra, centred at 9450 Å (normalised to unity and offset for display) of program stars with increasing reddening $E_{(B-V)}$. Each observed star spectrum has been divided after instrumental corrections by a spectrum of a reference star of similar spectral type. (A spectrum of λ Per at the top shows the saturated telluric water absorption lines.) This allowed to divide the stellar lines and limit flat field variations. Residuals from telluric water lines are partly seen as narrow features in this range. New DIBs are possibly detected at 9404 Å and 9466 Å, increasing with $E_{(B-V)}$. An average composite spectrum corresponding to $E_{(B-V)} = 4$ is shown at the bottom

should however give rise to many additional bands in the visible, different from the spectra of the monocations.

The DIBs show a distinction in families and variations according to the environment (Krelowski & Westerlund 1987; Josafatsson & Snow 1987; Jenniskens et al. 1994). Their central wavelength however is very constant and their behaviour in dense and diffuse environments and their observed dependence on the UV field follows rather simple rules (Jenniskens et al. 1994). The complexity of visible absorption created by the different transient forms of PAHs during their evolution in the cycle of diffuse and dense clouds is not manifested in current observations of the DIBs. One possibility could be that all these additional features are very weak, near the confusion limit, and may be detected only by ultra high S/N measurements. The assumption that numerous additional DIBs can be detected by such measurements will limit also a direct identification of the

DIB carriers with laboratory results. If the number of detected DIBs increases strongly, then nearly every laboratory band will have a counterpart within 5 Å and coincidences could then be just a random process. However the determination of accurate wavelength separations and relative oscillator strength together with DIB intercorrelations may allow a more precise identification within a 'forest' of DIBs.

Considering PAH ions as possible DIB carriers, we can compare how their ionization properties and destruction pathways relate to current observations. According to recent data the naphthalene cation shows coincidence in band position with several known DIBs (Salama & Allamandola 1993). A few bands have no counterpart in astronomical spectra and some intensity mismatches compared to laboratory data do occur. The pyrene molecule shows a strong band at 4395 Å in neon matrix and at 4435 Å in argon (Salama & Allamandola 1992b). It is sug-

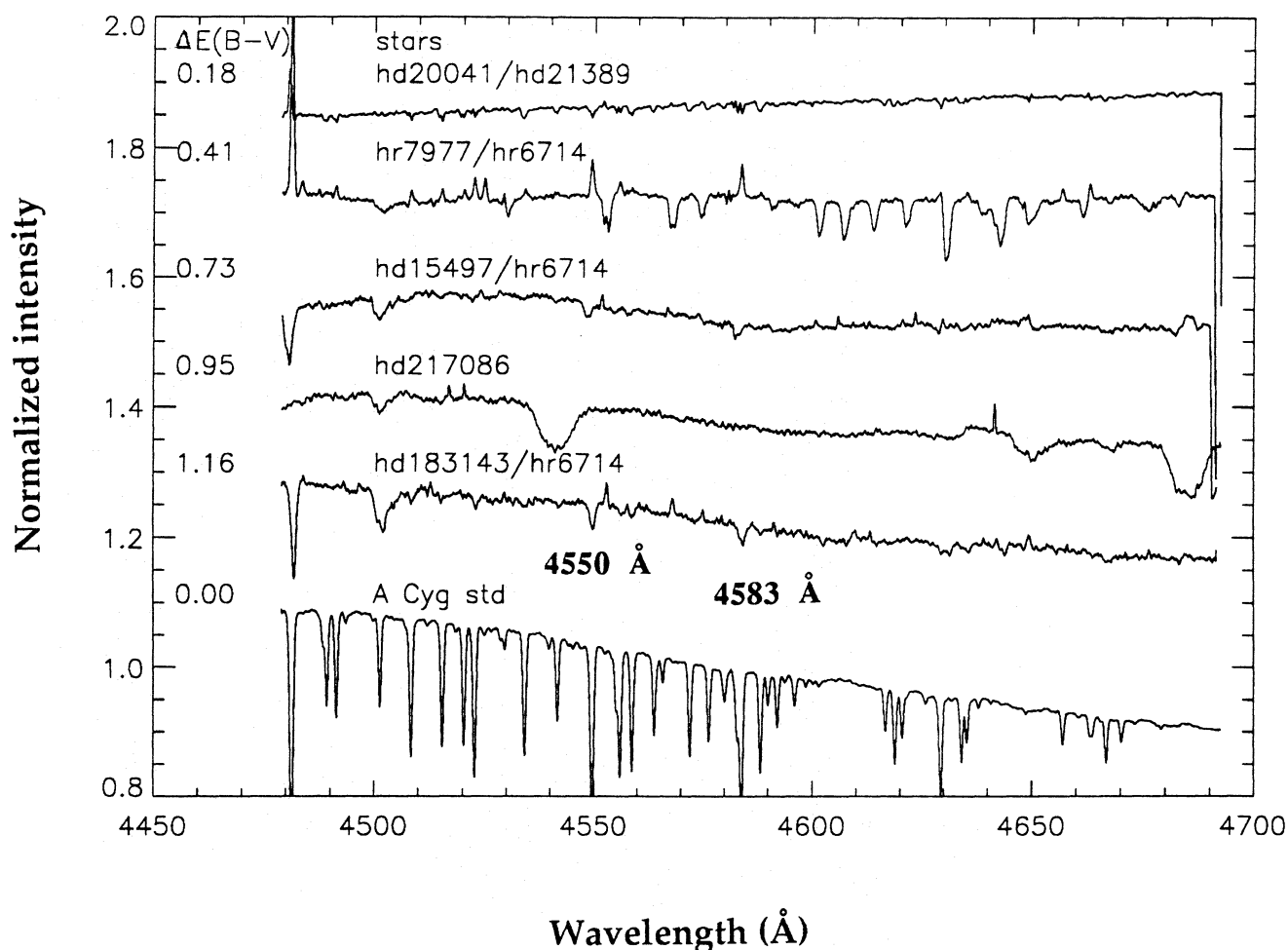


Fig. 3. Sequence of reduced spectra (normalised to unity) of program stars with increasing reddening. Each observed star spectrum has been divided after instrumental corrections by a spectrum of a reference star of similar spectral type and the difference of reddening $\Delta E_{(B-V)}$ is also indicated. The known DIB at 4502 Å is confirmed. Narrow features ascribed to residuals from stellar lines correction were found at 4550 Å and 4583 Å in the extinguished stars HD15497 and HD183143. A shallow feature at 4600 Å (FWHM = 40 Å and optical depth of 0.04) appears in the most reddened stars but with a varying shape, position and strength, which is not consistent with a classical DIB

gested that a substituted pyrene molecule or methylene-pyrene is the origin of the strongest of all DIBs at 4430 Å. (Salama & Allamandola 1992b; Léger et al. 1995). Assuming that the latter identifications with DIBs are correct, then our result that coronene and ovalene are less abundant in space forces to reconsider the stability criteria of interstellar PAHs.

Destruction of PAHs probably involves doubly charged PAHs (Leach 1987). If the difference between the first and second ionization potential is larger than 13.6 eV, the molecules should survive in all environments where neutral hydrogen is found. If less than 13.6 eV, then the DIB carriers are destroyed in photodissociation regions. Jenniskens et al. (1994) found that indeed some DIB carriers (notably 6284 and 5780 Å), which likely have a difference between the first and second ionisation potential larger than 13.6 eV, survive in environments where neutral hydrogen is found. If photons stronger than 13.6 eV are present (as judged from the presence of ionised hydrogen) then the DIB carrier is absent. The values of first and second ion-

ization potential vary from molecule to molecule but the ratio of double to single ionization potential remains relatively constant. From new measurements of more than 20 PAHs a value of $I^{++}/I^+ = 2.65 \pm 0.06$ has been derived (Tobita et al. 1994). These data show also that $\Delta I = I^{++} - I^+$ lies below 13.6 eV for many PAHs. Jochims et al. (1994) argues that nascent PAH ions of any size formed by photoionization in HI regions will preferentially relax by infrared emission. Those that have $N_C < 30-40$ will tend to relax by photofragmentation, after absorption of a second UV photon of sufficient energy, rather than by infrared radiative relaxation (Jochims et al., 1994). Dehydrogenation of doubly ionized PAHs could be also an important process. Collisions between He^+ and neutral PAH can produce doubly charged cations in dense regions. The recombination of these PAH^{++} with electrons could be dissociative rather than radiative and would provide a steady loss of these large molecules (Millar 1992).

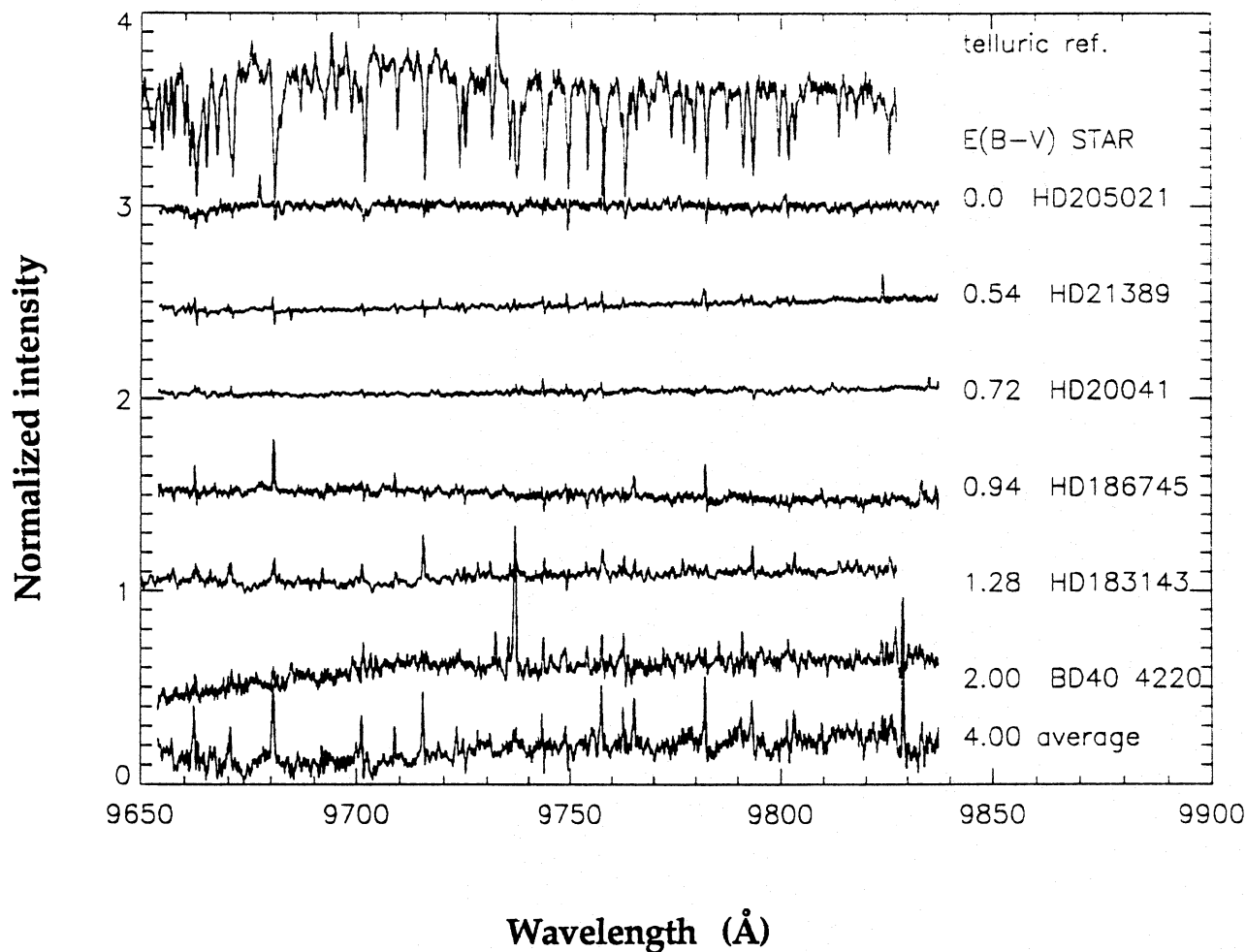


Fig. 4. Sequence of reduced spectra (normalised to unity) of program stars with increasing reddening $E(B-V)$. Each observed star spectrum has been divided after instrumental corrections by a spectrum of a reference star of similar spectral type. An average composite spectrum corresponding to $E(B-V) = 4$ is shown at the bottom, which displays small features at 9672, 9783 and 9798 Å (Foing & Ehrenfreund 1994b) with equivalent width 30 mÅ per unit reddening. A telluric reference spectrum is shown at the top. No stronger DIBs are observed in this range

The double ionization potential have recently been measured for various PAHs by Tobita et al. (1994). Whereas molecules with a somewhat higher ionization energy from PAH^+ to PAH^{++} (ΔI) like naphthalene (13.35 eV) and pyrene (12.35 eV) show coincidences with observed features in the interstellar medium, molecules with a lower ΔI like coronene (11.5 eV) and ovalene (11.3 eV) do not have obvious counterparts in astronomical spectra. Therefore naphthalene and pyrene are expected to be destroyed by higher energy photons than the pericondensed coronene and ovalene. Having ΔI closer to the ionization potential of hydrogen of 13.6 eV might help molecules like naphthalene to survive better, because less photons are available in this range due to the efficient absorption by the H Lyman continuum above 13.6 eV and by molecules like CO and H_2 just below, as well as increased dust extinction at shorter wavelengths. Due to its low ΔI of 11.5 eV coronene could lead more efficiently to the dication, which can eventually be dehydrogenated or fragmented. The ionization rate

$$\eta = \int_{\Delta I} \sigma_{\nu} \phi_{\nu} dE$$

where σ_{ν} is the cross section and ϕ_{ν} is the UV field, varies drastically with the ionization potential ΔI . Taking for ϕ_{ν} a Draine (1978) field: $\phi_{\nu} = 1.658 \times 10^6 E - 2.152 \times 10^5 E^2 + 6.919 \times 10^3 E^3$ in photon $\text{cm}^{-2} \text{s}^{-1} \text{sr}^{-1} \text{eV}^{-1}$ with E in eV and taking a cross section $\sigma_{\nu} = \sigma_0 = 10^{-16} \text{cm}^2$ (Leach 1987), we find a photoionization rate of $1.7 \times 10^{-9} \text{s}^{-1}$ for coronene ion ($\Delta I = 11.5 \text{eV}$) which is faster compared to $1.2 \times 10^{-10} \text{s}^{-1}$ for the naphthalene ion ($\Delta I = 13.35 \text{eV}$). The corresponding rates can be compared for PAHs with different second ionization energy in Fig. 5 giving the UV field (Draine 1978) and the integrated UV field between the ionisation energy and the 13.6 eV cut-off. Due to the strong gradient in the short wavelength dust extinction, the UV field slope will be dramatically modified in extinguished regions which will shield furthermore molecules like naphthalene and pyrene cations from being doubly ionized.

From the data of Tobita et al. (1994), which contain 28 PAHs of different structures and sizes, the following trends can be

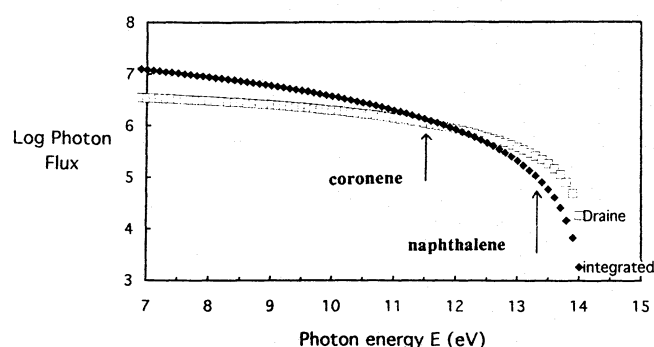


Fig. 5. Dependence on ionization rates of various PAHs according to the UV interstellar field. The UV field (Draine 1978) ϕ_ν in photon $\text{cm}^{-2} \text{s}^{-1} \text{sr}^{-1} \text{eV}^{-1}$ and the integrated UV field I_{UV} beyond the cation ionization potential IP (in photons $\text{cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$) are given. The ionization potential IP of some typical PAH cations are indicated. The ionization rates can be estimated by multiplying I_{UV} by $4 \pi \sigma$ where σ is the PAH ionization cross section

noted: small PAHs (up to 14 C atoms) have in general a ΔI above 12 eV, and the majority above 13 eV. The clear cut off with a ΔI smaller than 12 eV is seen for molecules containing more than 18 C atoms. Certainly the structure also does play a role, e.g. the chain-like PAHs like tetracene and pentacene have a lower ΔI than PAHs with the same number of C-atoms but more compact structure. From this very valuable but limited data sets (28 PAHs) only trends can be derived, to narrow down the choice of stable DIB candidates. For the diffuse interstellar medium with normal UV conditions this implies that PAHs with more than 18 C atoms form relatively fast dications, which can later be dehydrogenated, fragmented or form radicals. This would limit the possibility for detection of DIBs associated with PAH monocations above 18 C atoms. Whether dications, dehydrogenated or radical cations of PAHs do contribute to the DIB spectrum can only be tested when laboratory data of such species are available. PAH cations which are possible DIB carriers are however just a part of the interstellar medium inventory of molecules and PAHs responsible for the infrared emission might be of much larger size.

6. Conclusion

On the basis of laboratory measurements of the coronene cation and by comparison with astronomical spectra at 4590 Å and in the near IR in different environments, weak spectral features could be detected above the noise level leading to an abundance limit of 0.05 % or less of the cosmic carbon for this molecule. The laboratory spectrum of the ovalene cation may have a weak counterpart at 9783 Å in astronomical spectra. However no strong DIBs are detected in the range 9780 Å \pm 100 Å, implying again a very low abundance (< 0.05 % at present) for this molecule. These abundances are typically smaller than those of naphthalene and pyrene (or their substituted homologues) that have been suggested to account for the 6741 and 4430 Å DIBs, respectively. The implication that pericondensed PAHs are less

abundant than these small PAHs is unexpected. However, from this result we can derive conclusions about the role of PAH ions as possible DIB carriers. We find that the ionization properties of the cation determining their resistance against UV radiation could produce pathways for selective destruction. Certain PAH cations (e.g. naphthalene) are only destroyed by more energetic photons, which are scarce in the diffuse medium. Thus the photostability of the cation against high energy UV photons may determine the survival in the diffuse medium. These results may help in the search for the true carriers of the diffuse bands.

Acknowledgements. We thank Tom Millar and Werner Schmidt for extended and fruitful discussions. We also thank A. Collier-Cameron and the staff of OHP for their efficient support during the observations. PE is a recipient of a fellowship of the European Community ERBCH-BICT940939.

References

- Adamson A.J., Whittet D.G.B., Duley W.W 1991, MNRAS 252, 234
 Bennema P. et al. 1959, Mol. Phys. 2, 431
 Birks J. B. 1970, Photophysics of aromatic molecules (Wiley, New York)
 Bondybey V.E., Miller T. 1983, Molecular ion Spectroscopy, Structure, and Chemistry, eds. Miller T., Bondybey V.E. North Holland Publishing Company, 125
 Draine B.T. 1978 ApJS 36, 595
 Ehrenfreund P., d'Hendecourt L., Verstraete L. et al., 1992, A&A 295, 257
 Foing B.H, Ehrenfreund P. 1994a, Nat. 369, 296
 Foing B.H., Ehrenfreund P. 1994b, in Proceedings 'Diffuse Interstellar Bands', in press
 Giard M. et al. 1988, A&A 201, L 1
 d'Hendecourt L., Léger A. 1987, A&A 180, L 9
 Herbig G.H. 1975, ApJ 196, 129
 Herbig G.H., Leka K.D. 1991, ApJ 382, 193
 Hibbins et al. 1994, in Proceedings 'Diffuse Interstellar Bands: Contributed Papers', 31
 Jenniskens P., Ehrenfreund P., Foing B.H. 1994, A&A 281, 517
 Jenniskens P., Désert X. 1994, A&AS. 106, 39
 Joblin C., Maillard J.P., d'Hendecourt L., Léger A. 1990, Nat. 346, 729
 Jochims H.W., Rühl E., Baumgaertel, H., Tobita S., Leach S. 1994, ApJ 420, 307
 Josafatsson K., Snow T.P. (1987) ApJ 319, 436
 Kroto H.W. 1987, Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Léger A. and d'Hendecourt L., Reidel Publishing Company, 197
 Kroto H.W., Jura M. 1992, A&A 263, 275
 Krelowski J., Walker G.A.H. 1987, ApJ 312, 860
 Leach S. 1987, in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Léger A. and d'Hendecourt L., Reidel Publishing Company, 99
 Léger A., Puget J.L. 1984, A&A 137, L5
 Léger A., d'Hendecourt L. 1985, A&A 146, 81
 Léger A., d'Hendecourt L., Verstraete L., Schmidt W. 1988, A&A 203, 415
 Léger A., d'Hendecourt L., Defourneau D. 1989, A&A 216, 148
 Léger A., d'Hendecourt L., Defourneau D. 1995, A&A 293, L53
 Millar T. 1992, MNRAS 259, 35

- Moore C.E. 1972, A multiplet Table of Astrophysical Interest, revised edition, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand (U.S)
- Platt J.R. 1956, ApJ 123, 486
- Ristorcelli I. et al. 1994, A&A 286, L 23
- Salama F., Allamandola L. 1991, J. Chem. Phys. 94, 6964
- Salama F., Allamandola L. 1992a, ApJ 395, 301
- Salama F., Allamandola L. 1992b, Nat. 358, 42
- Salama F., Allamandola L. 1993, J. Chem. Soc. Faraday 89 (13), 2277
- Smith W.H., Snow T.P., York D.G. 1977, ApJ 218, 124
- Spitzer L. 1978, in Physical Processes in the Interstellar Medium, Wiley
- Szczepanski J., Vala. M. 1993, ApJ 414, 646
- Tobita S., Leach S., Jochims H. et al., 1994, Canadian Journal of Physics, in press
- Van der Zwet G.P., Allamandola L.J. 1985, A&A 146, 76
- Van der Zwet G. P. 1987, Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger A. and d'Hendecourt L., Reidel Publishing Company, 351
- Verstraete L., Léger A., d'Hendecourt L., Dutuit O., Defourneau D. 1991, A&A 237, 436