

The PAH hypothesis: a computational experiment on the combined effects of ionization and dehydrogenation on the IR signatures^{*}

F. Pauzat, D. Talbi, and Y. Ellinger

Equipe d'Astrochimie Quantique, Laboratoire de Radioastronomie Millimétrique, Ecole Normale Supérieure et Observatoire de Paris, 24 rue Lhomond, F-75231 Paris Cedex 05, France

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Abstract. IR spectra of anthracene and pyrene derivatives, serving as models for isolated, linear and isolated, compact PAHs, respectively, have been calculated using ab-initio quantum mechanical methods. The separate and combined effects of ionization and multiple dehydrogenation have been studied. This study confirms and refines the trends of our preliminary paper on the smallest possible PAH, naphthalene. If small PAHs are responsible for any UIR bands, they should be ionized and partially dehydrogenated, with a few triple bonds at the periphery of the carbon skeleton.

Key words: molecular data – molecular processes – ISM: molecules – infrared: ISM: lines and bands

1. Introduction

The emission lines observed in various celestial objects, at 3050, 1610, 1300, 1150 and 885 cm^{-1} (3.3, 6.2, 7.7, 8.6, and 11.3 μm) (Aitken 1981; Willner 1984) and referred to as the UIR bands (Unidentified Infra Red emission bands) have been the object of many theoretical and experimental studies. The hypothesis that these emissions are produced by free, molecular Polycyclic Aromatic Hydrocarbons (PAHs) has been suggested by Leger and Puget (1984) and Allamandola, Tielens, and Baker (1985). The original assignments were based on comparison of laboratory infrared spectra with space data. However, when considered in more detail, this comparison was not really satisfying. If the agreement was reasonably good for the band positions, it was not for the band intensities. Some tentative explanations implying the dehydrogenation of the emitters or temperature effects have been proposed but no clear cut conclusion could be reached.

Moreover, because of the physical conditions in the regions where the UIR bands are observed, PAHs, if they exist as individual species, are most likely ionized, i.e. positively charged,

and partially dehydrogenated (Leger and Puget 1984; Allamandola et al. 1985; Van der Zwet and Allamandola 1985, Omont 1986; Puget and Leger 1989). If such a statement is accepted, then comparison to laboratory data of neutral species can only rationalize the part of the interstellar emission which comes from what remains as neutral species. However, considering the wide range of conditions under which the IR emission features are observed, and the wide variation in the appearance of the observed spectrum (both in the position and in the relative intensity of the bands) it would not be realistic to dismiss any contribution from neutral PAHs; even if ionized PAHs are likely to be the dominant source of the interstellar IR emission, 100% ionization cannot be achieved. Thus, in addition to a clear view of the properties of neutrals, understanding and interpreting the observed interstellar IR features within the PAHs hypothesis requires equal knowledge of the spectra of ionized and/or dehydrogenated species.

Previous theoretical studies (DeFrees et al. 1989; Pauzat et al. 1992; DeFrees et al. 1993) of the IR spectra of naphthalene, anthracene and pyrene, have shown that vibrational frequencies and intensities can be evaluated for small neutral PAHs from ab initio quantum mechanical calculations with good agreement with the experimental data available, encouraging the application of the same treatment to the corresponding ionized species. The results were very exciting, outlining the strong effect of the ionization on the IR spectra, an effect which was confirmed, a posteriori, by experiments (Szczepanski et al. 1992, Szczepanski et al. 1993, Vala et al. 1994, Hudgins et al. 1994, Leger et al. 1995; Hudgins and Allamandola 1995). At that point of the study, the main result is that ionized derivatives are better candidates to explain the interstellar IR emission (DeFrees et al. 1993), the intensity ratios for the CH stretching band at [3.3 μm ; 3030 cm^{-1}] to the blend of CC stretching and CH in-plane bending vibrations at [(6.2+7.7) μm ; (1610+1300) cm^{-1}] being close to the ratio observed in IR sources. Very recently, this important result has been confirmed by an extensive study of a series of PAHs using density functional theory (Langhoff 1996). The significant consequence of such a result is that it is no longer necessary to remove most of the hydrogens from

^{*} Appendix A is only available in electronic form at CDS via <http://cdsweb.u-strasbg.fr/abstract.html>

the PAHs (Jourdain de Muizon et al. 1990; Joblin et al. 1994) in order to reconcile observations and laboratory work; such a removal was highly questionable from a chemical point of view.

Nevertheless, dehydrogenation - within reasonable limits - is still an important point to be investigated. Following the observational arguments for the existence of non-adjacent (solo) peripheral hydrogen atoms and eventually doubly adjacent (duo) hydrogens arguing for dehydrogenated PAHs, we have carried out an extensive ab-initio study (Pauzat et al. 1995) on naphthalene derivatives, looking for the effect of separate and combined ionization and multiple dehydrogenations. This study pointed out that if small PAHs are at the origin of the UIR bands, then these carriers should be mostly ionized but only partly dehydrogenated. However, taking into account the limitations and possible distortions due to the size of the model, we seek confirmation of what we considered as trends only. Taking into account the nice agreement of our calculations with the experiments of Weimer et al. (1995) on 2,3-Naphthyne, we felt confident to extend our study to larger models.

In the present paper, we are presenting an ab-initio study of these effects on two other compounds featuring different families, i.e., anthracene as a model for linear PAHs (polyacenes), and pyrene as a model for compact PAHs. Effects of double and quadruple dehydrogenations are considered, combined or not with ionization, and discussed in relation to the main characteristics of the IR interstellar emission.

This paper is organized as follows. First, a review of our theoretical model is given in Sect. 2. Then we discuss the effects on the IR spectra of anthracene and pyrene, of a double and a quadruple dehydrogenation (Sect. 3), a single ionization (Sect. 4) and a combined dehydrogenation and ionization (Sect. 5). In each section, a comparison with our previous results on naphthalene is given. General conclusions in connection with spectra observed in space are presented in the last section.

2. Theoretical background

All electronic calculations have been done at the Hartree-Fock level using Gaussian 92 (Frisch et al. 1992) computer code. A restricted formalism (RHF) has been used for closed shell systems, $C_{14}H_{10}$, $C_{14}H_8$, $C_{14}H_6$, $C_{16}H_{10}$, $C_{16}H_8$, $C_{16}H_6$, and a restricted open shell formalism (ROHF) for open shell systems $C_{14}H_{10}^+$, $C_{14}H_8^+$, $C_{14}H_6^+$, $C_{16}H_{10}^+$, $C_{16}H_8^+$, $C_{16}H_6^+$. The atom numbering used as reference for the dehydrogenated species is presented in Fig. 1.

The calculated structures are given in Figs. 2 and 3 for anthracene and pyrene derivatives respectively. A classic 3-21G basis set has been used as in our previous study of the effect of ionization and/or dehydrogenation on naphthalene.

Because self-consistent wavefunctions do not account for electronic correlation, calculated vibrational frequencies have to be scaled before comparison can be made. Instead of using the straightforward method where all frequencies are scaled with a unique factor, we have scaled each type of vibration by an adapted factor, according the following procedure. The normal mode analysis allows us to link each frequency to a local

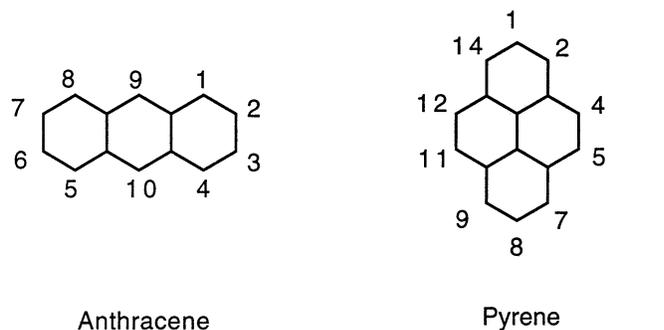


Fig. 1. Atom numbering

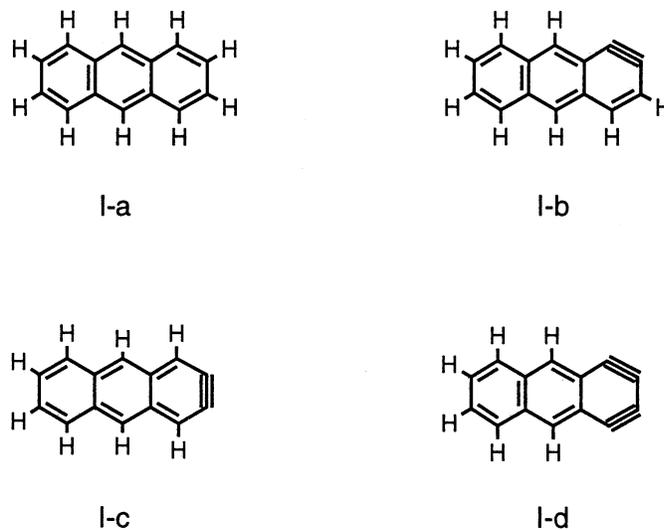


Fig. 2. Anthracene and its dehydrogenated derivatives

motion (CH stretching, CC stretching, CCC in-plane bending, CH in-plane bending, CH out-of-plane bending, CCC out-of-plane bending or ring torsion which are respectively referred as $r(CH)$, $R(CC)$, $a(CCC)$, $b(CH)$, $e(CH)$, $t(CCC)$). For each type of motion, a scaling factor is deduced after comparison (minimizing the mean root square deviation) between the calculated and the experimental IR spectra values for the neutral fully hydrogenated molecules (in the present case anthracene and pyrene). So doing we correct the frequencies for the missing correlation effects but also for anharmonic effects which are generally specific to the type of vibrations and cannot be addressed by a uniform scaling. Variations of the scaling factors between anthracene and pyrene or between the neutral parent and the corresponding cation, when experimental numbers were available for the latter were small and quite similar, i.e. less than 0.01. So we decided to use common scale factors for anthracene and pyrene, which are the following: 0.905 for the CH stretching, 0.90 for the CC stretching, as well as for the CCC and CH in-plane bendings, 0.86 for the CH and CCC out-of-plane bendings. The complete IR spectra thus obtained for all the derivatives studied are given in the appendix tables.

Table 1. Computed IR spectra: frequencies and integrated intensities for neutral anthracene and pyrene

Vibration	Stretch CH	Vibrations CC				in-plane CH	out-of-plane CH			
		Solo	Duo	Trio	Quatro					
Observed	3.3 μm 3030 cm^{-1}	5.2 μm 1920 cm^{-1}	6.2 μm 1610 cm^{-1}	7.7 μm 1300 cm^{-1}	8.6 μm 1160 cm^{-1}	11.3 μm 885 cm^{-1}	11.9 μm 840 cm^{-1}	12.7 μm 790 cm^{-1}	14.0 μm 710 cm^{-1}	
C₁₄H₁₀ (Fig. 1-a)										
λ (μm)	3.3		6.1-6.5	6.8-7.6	7.8-8.6	11.2			14.0	
ν (cm^{-1})	3030		1640-1540	1470-1320	1280-1160	885			710	
I (km/mol)	129		23	9	22	87			127	
C₁₄H₈ (Fig. 1-b)										
λ (μm)	3.2-3.3	4.8	6.1-6.5	6.7-7.8	8.0-8.6	11.1	12.9		13.7	
ν (cm^{-1})	3120-3030	2080	1640-1540	1490-1280	1250-1160	900	775		730	
I (km/mol)	77	1	31	47	12	79	11		71	
C₁₄H₈ (Fig. 1-c)										
λ (μm)	3.2-3.3	5.2	6.1-6.5	6.7-7.9	8.0-8.6	11.1			13.8	
ν (cm^{-1})	3120-3030	1920	1640-1540	1490-1270	1250-1160	900			725	
I (km/mol)	76	4	11	25	23	96			73	
C₁₄H₆ (Fig. 1-d)										
λ (μm)	3.3	5.2-5.5	6.1-6.5	6.8-7.9	8.1-9.6	11.1			13.7	
ν (cm^{-1})	3030	1920-1820	1640-1540	1470-1270	1230-1040	900			730	
I (km/mol)	46	103	23	40	9	61			64	
C₁₆H₁₀ (Fig. 2-a)										
λ (μm)	3.2-3.3		6.2-6.3	6.7-7.0	8.0-9.2		11.9	13.7		
ν (cm^{-1})	3120-3030		1610-1590	1490-1430	1250-1090		840	730		
I (km/mol)	136		30	27	24		162	16		
C₁₆H₈ (Fig. 2-b)										
λ (μm)	3.2-3.3	5.0	6.3-6.7	7.0-7.9	8.0-9.4	11.6	12.4	13.4		
ν (cm^{-1})	3120-3030	2000	1590-1490	1430-1270	1250-1060	860	805	745		
I (km/mol)	83	9	31	27	45	74	49	7		
C₁₆H₈ (Fig. 2-c)										
λ (μm)	3.3		6.3-6.4	6.7-7.9	8.2-9.2		12.1	13.3		
ν (cm^{-1})	3030		1590-1560	1490-1270	1220-1090		825	750		
I (km/mol)	85		64	44	21		128	13		
C₁₆H₆ (Fig. 2-d)										
λ (μm)	3.2-3.3	5.0	6.2-6.6	6.7-7.9	8.0-9.4	11.6	12.6	13.3		
ν (cm^{-1})	3120-3030	2000	1610-1520	1490-1270	1250-1060	860	795	750		
I (km/mol)	51	19	41	78	61	59	22	3		
C₁₆H₆ (Fig. 2-e)										
λ (μm)	3.2-3.3	4.7	6.4-6.7	7.6-7.7	8.0-9.3	11.5	12.4	13.0		
ν (cm^{-1})	3120-3030	2130	1560-1490	1320-1300	1250-1080	870	805	770		
I (km/mol)	37	15	22	6	105	85	50	1		
C₁₆H₆ (Fig. 2-f)										
λ (μm)	3.2-3.3	5.0	6.4-6.7	7.2-7.7	8.0-8.6	11.6	12.7			
ν (cm^{-1})	3120-3030	2000	1560-1490	1390-1300	1250-1160	860	790			
I (km/mol)	48	19	22	30	39	104	27			
C₁₆H₆ (Fig. 2-g)										
λ (μm)	3.2-3.3	5.0	6.3-6.6	6.8-7.8	7.9-9.3	11.7	12.1	13.2		
ν (cm^{-1})	3120-3030	2000	1590-1520	1470-1280	1270-1080	855	825	755		
I (km/mol)	38	12	52	50	33	32	58	10		
C₁₆H₆ (Fig. 2-h)										
λ (μm)	3.3		6.3-6.6	7.1-7.3	8.3-9.4		12.5			
ν (cm^{-1})	3030		1590-1520	1410-1370	1200-1060		800			
I (km/mol)	26		119	33	36		112			

3. IR spectra of neutral anthracene and pyrene derivatives

3.1. The fully hydrogenated species

The IR spectra (Fig. 4) of neutral anthracene and pyrene (Tables A-I-a and A-II-a), have been studied in detail in a previous work (DeFrees et al. 1993); consequently we will only recall their

main characteristics. The integrated intensities for each type of vibration (Table 1) show the following trends:

for anthracene:

1. strong CH stretching vibrations around [$3.3 \mu\text{m}$; 3030 cm^{-1}].

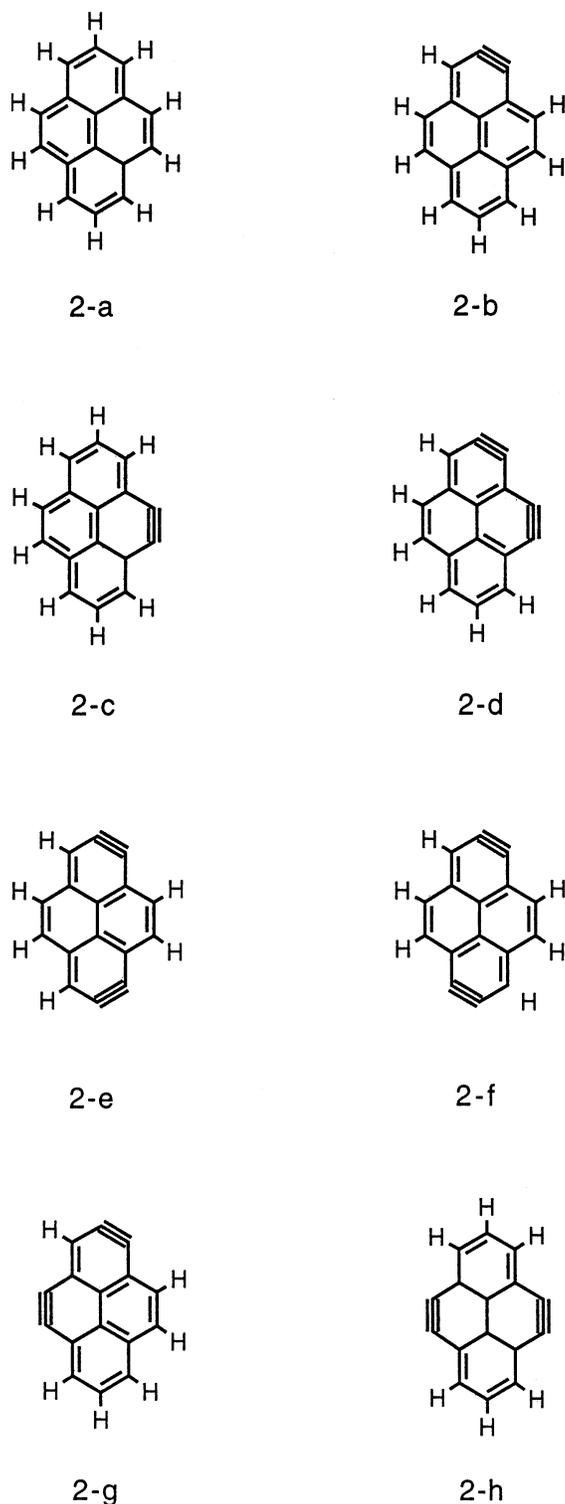


Fig. 3. Pyrene and its dehydrogenated derivatives

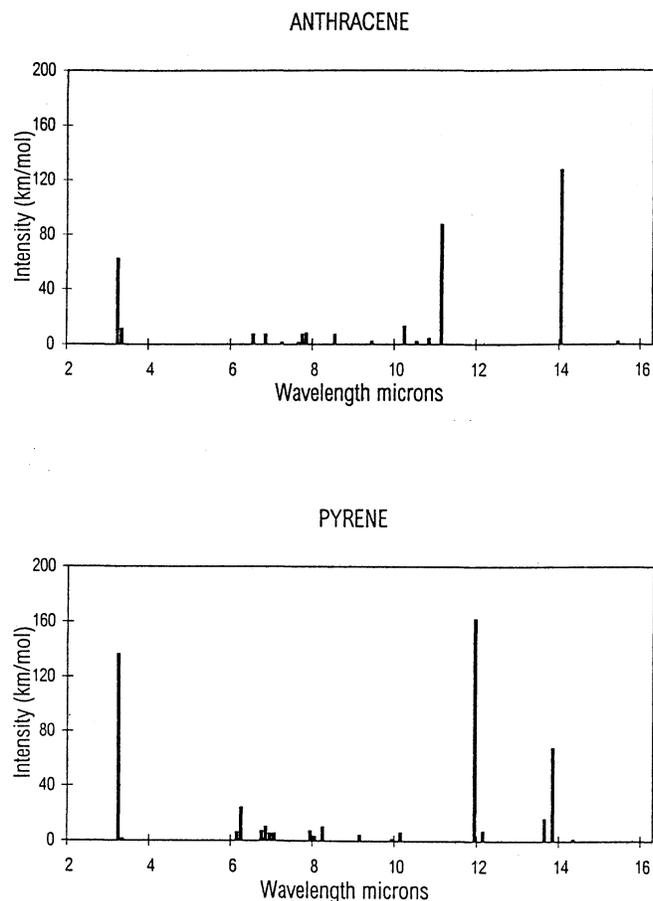


Fig. 4. Histogram representation of the IR absorption band intensities of neutral anthracene and pyrene.

2. medium to weak bands between [6.1-7.6 μm ; 1640-1320 cm^{-1}] corresponding to a blending of CC stretching vibrations.
3. medium absorptions between [7.8-8.6 μm ; 1280-1160 cm^{-1}] featuring hydrogen in-plane bending vibrations.
4. strong signatures at [11.2; 890 cm^{-1}] and [14.0 μm ; 710 cm^{-1}] corresponding to the CH out-of-plane bending motion of hydrogens in solo and quarto positions, respectively.

for pyrene:

1. strong CH stretching vibrations around [3.3 μm ; 3030 cm^{-1}].
2. medium bands between [6.2-7.0 μm ; 1630-1430 cm^{-1}] corresponding to a blending of CC stretching vibrations.
3. medium signatures between [8.0-9.2 μm ; 1250-1090 cm^{-1}] featuring hydrogen in-plane bending vibrations.
4. strong and medium absorptions at respectively 11.9 and 13.7 μm corresponding to the CH out-of-plane bending vibrations of hydrogens in duo and trio positions, respectively.

As was concluded in our previous study (DeFrees et al.1993), bands for the neutral anthracene and pyrene are close

Table 2. Computed IR spectra: frequencies and integrated intensities for anthracene and pyrene cations

Vibration	Stretch CH	Vibrations CC			in-plane CH	out-of-plane CH			
		Solo	Duo	Trio		Quatro			
Observed	3.3 μm 3030 cm^{-1}	5.2 μm 1920 cm^{-1}	6.2 μm 1610 cm^{-1}	7.7 μm 1300 cm^{-1}	8.6 μm 1160 cm^{-1}	11.3 μm 885 cm^{-1}	11.9 μm 840 cm^{-1}	12.7 μm 790 cm^{-1}	14.0 μm 710 cm^{-1}
C₁₄H₁₀⁺ (Fig. 1-a)									
λ (μm)	3.3		6.5-6.6	6.8-7.7	8.0-8.5	11.0			13.5
ν (cm^{-1})	3030		1540-1520	1470-1300	1250-1180	910			745
I (km/mol)	14		92	137	2041	41			147
C₁₄H₈⁺ (Fig. 1-b)									
λ (μm)	3.2-3.3	5.0	6.5-6.7	6.8-7.8	8.0-9.3	10.9	12.6		13.4
ν (cm^{-1})	3120-3030	2000	1540-1490	1470-1280	1250-1080	915	795		745
I (km/mol)	22	182	76	247	1816	37	27		81
C₁₄H₈⁺ (Fig. 1-c)									
λ (μm)	3.2-3.3	5.1	6.5-6.7	6.9-8.0	8.3-8.8	10.8			13.4
ν (cm^{-1})	3120-3030	1960	1540-1490	1450-1250	1200-1140	925			745
I (km/mol)	21	11	77	538	1220	49			80
C₁₄H₆⁺ (Fig. 1-d)									
λ (μm)	3.2-3.3	5.2-5.8	6.6	6.8-8.0	8.0-9.5	10.9			13.4
ν (cm^{-1})	3120-3030	1920-1720	1520	1470-1250	1250-1050	915			745
I (km/mol)	20	636	161	223	1156	26			74
C₁₆H₁₀⁺ (Fig. 2-a)									
λ (μm)	3.2-3.3		6.5	6.7-7.4	8.3-9.2		11.7	13.2	
ν (cm^{-1})	3120-3030		1540	1490-1350	1200-1090		855	755	
I (km/mol)	6		364	181	1510		149	3	
C₁₆H₈⁺ (Fig. 2-b)									
λ (μm)	3.2-3.3	5.2	6.3-6.6	6.7-8.0	8.3-9.5	11.3	11.8-12.4	13.3	
ν (cm^{-1})	3120-3030	1920	1590-1520	1490-1250	1200-1050	885	845-805	750	
I (km/mol)	13	101	44	447	1140	42	80	4	
C₁₆H₈⁺ (Fig. 2-c)									
λ (μm)	3.3	4.9	6.4-6.6	6.8-8.0	8.2-9.5		11.9	12.9	
ν (cm^{-1})	3030	2040	1560-1520	1470-1250	1220-1050		840	775	
I (km/mol)	2	292	295	479	1198		102	14	
C₁₆H₆⁺ (Fig. 2-d)									
λ (μm)	3.2-3.3	4.9-5.2	6.5	6.7-7.7	8.0-9.4	11.3	12.1	13.3	
ν (cm^{-1})	3120-3030	2040-1920	1540	1490-1300	1250-1060	885	825	750	
I (km/mol)	9	287	27	434	776	35	14	12	
C₁₆H₆⁺ (Fig. 2-e)									
λ (μm)	3.2	5.4-5.8	6.6	6.9-7.7	8.0-9.5	11.1	12.0-12.5		
ν (cm^{-1})	3120	1850-1720	1520	1450-1300	1250-1050	900	830-800		
I (km/mol)	7	254	599	318	817	41	52		
C₁₆H₆⁺ (Fig. 2-f)									
λ (μm)	3.2	5.6	6.7	6.9-7.8	8.4-9.0	11.2	12.3		
ν (cm^{-1})	3120	1790	1490	1450-1280	1190-1110	885	810		
I (km/mol)	1	373	534	425	653	52	42		
C₁₆H₆⁺ (Fig. 2-g)									
λ (μm)	3.2-3.3	4.9-5.2	6.5	6.7-7.9	8.1-9.5	11.3	11.9		
ν (cm^{-1})	3120-3030	2040-1920	1540	1490-1270	1230-1050	885	840		
I (km/mol)	16	380	32	391	779	10	68		
C₁₆H₆⁺ (Fig. 2-h)									
λ (μm)	3.2	5.2		6.8-7.8	8.2-9.4		12.4		
ν (cm^{-1})	3120	1920		1470-1280	1220-1060		805		
I (km/mol)	4	610		310	2290		87		

in position to the interstellar ones, but their relative intensities are far from reproducing the interstellar emissions.

3.2. Effect of a double dehydrogenation

Two doubly-dehydrogenated anthracene structures have been considered, depending on whether hydrogen removal takes

place at position 1-2 (Fig. 2, scheme 1b) or 2-3 (Fig. 2, scheme 1c) on the skeleton. Other possible isomers where removal of two non-adjacent hydrogens leads to the formation of a biradical (as dehydrogenation in positions 1 and 3), have not been considered because of the high instability of these biradical structures. Any other possibility is equivalent to one of the two first ones. The same considerations for pyrene lead us to consider dehydro-

Table 3. Computed IR spectra for anthracene and pyrene derivatives

Vibration	Stretch CH		Vibrations CC		in-plane CH		out-of-plane CH			Quarto
	3.3 μm 3030 cm^{-1}	5.2 μm 1920 cm^{-1}	6.2 μm 1610 cm^{-1}	7.7 μm 1300 cm^{-1}	8.6 μm 1160 cm^{-1}	Solo 11.3 μm 885 cm^{-1}	Duo 11.9 μm 840 cm^{-1}	Trio 12.7 μm 790 cm^{-1}	14.0 μm 710 cm^{-1}	
C₁₄H₁₀										
λ (μm)	3.3		6.1-6.5	6.8-7.6	7.8-8.6	11.2				14
ν (cm^{-1})	3030		1640-1540	1470-1320	1160	885				710
I (km/mol)	129		23	9	22	87				127
C₁₄H₈										
λ (μm)	3.2-3.3	4.8-5.2	6.1-6.5	6.7-7.9	8.0-8.6	11.1	12.9			13.7-13.8
ν (cm^{-1})	3120-3030	2080-1920	1640-1540	1490-1270	1250-1160	900	775			730-725
I (km/mol)	77	2	24	40	17	85	7			72
C₁₄H₆										
λ (μm)	3.3	5.2-5.5	6.1-6.5	6.8-7.9	8.1-8.6	11.1				13.7
ν (cm^{-1})	3030	1920-1820	1640-1540	1470-1270	1230-1160	900				730
I (km/mol)	46	103	23	40	9	61				64
C₁₆H₁₀										
λ (μm)	3.2-3.3		6.2-6.3	6.7-7.0	8.0-9.2		11.9	13.7		
ν (cm^{-1})	3120-3030		1610-1590	1490-1430	1250-1090		840	730		
I (km/mol)	136		30	27	24		162	16		
C₁₆H₈										
λ (μm)	3.2-3.3	5.0	6.3-6.7	6.7-7.9	8.0-9.4	11.6	12.1-12.4	13.3-13.4		
ν (cm^{-1})	3120-3030	2000	1590-1490	1490-1270	1250-1060	860	825-805	750-745		
I (km/mol)	84	6	42	33	37	49	76	9		
C₁₆H₆										
λ (μm)	3.2-3.3	4.7-5.0	6.2-6.6	6.7-7.9	8.0-9.4	11.5-11.6	12.1-12.7	13.0-13.2		
ν (cm^{-1})	3120-3030	2130-2000	1610-1520	1490-1270	1250-1060	870-860	825-790	770-755		
I (km/mol)	42	15	44	47	54	57	45	4		
C₁₄H₁₀⁺										
λ (μm)	3.3		6.5-6.6	6.8-7.7	8.0-8.5	11.0				13.5
ν (cm^{-1})	3030		1540-1520	1470-1300	1250-1180	910				740
I (km/mol)	14		92	137	2041	41				147
C₁₄H₈⁺										
λ (μm)	3.2-3.3	5.0-5.1	6.5-6.7	6.8-8.0	8.0-9.0	10.8-10.9	12.6			13.4
ν (cm^{-1})	3120-3030	2000-1960	1540-1490	1470-1250	1250-1110	925-915	795			745
I (km/mol)	22	125	76	344	1617	41	18			81
C₁₄H₆⁺										
λ (μm)	3.2-3.3	5.8	6.6	6.8-8.0	8.0-9.0	10.9				13.4
ν (cm^{-1})	3120-3030	1720	1520	1470-1250	1250-1110	915				745
I (km/mol)	20	633	161	223	1156	26				74
C₁₆H₁₀⁺										
λ (μm)	3.2-3.3		6.5	6.7-7.4	8.3-9.2		11.7	13.2		
ν (cm^{-1})	3120-3030		1540	1490-1350	1200-1090		855	755		
I (km/mol)	6		364	181	1510		149	3		
C₁₆H₈⁺										
λ (μm)	3.2-3.3	4.9-5.2	6.3-6.6	6.7-8.0	8.2-9.5	11.3	11.8-11.9	12.9-13.3		
ν (cm^{-1})	3120-3030	2040-1920	1590-1520	1490-1250	1220-1050	885	845-840	775-750		
I (km/mol)	9	165	128	458	1159	28	87	7		
C₁₆H₆⁺										
λ (μm)	3.2-3.3	4.9-5.8	6.5-6.7	6.8-7.9	8.0-9.5	11.1-11.3	11.9-12.5	13.3		
ν (cm^{-1})	3120-3030	2040-1720	1540-1490	1470-1270	1250-1050	900-885	840-800	750		
I (km/mol)	9	344	192	392	881	28	55	4		

A weighted average for the different possible isomers has been done for each molecule

generation only in positions 1-2 (Fig. 3, scheme 2b) and 4-5 (Fig. 3, scheme 2c). The corresponding IR spectra are reported in the appendix in Tables A-I-b, A-I-c, A-II-b, A-II-c. The intensities, summed per type of vibrations can be found in Table 1. Taking into account that in space each of the possible dehydrogenated structures will make a contribution to the total emission, we have reported the averaged summed intensities obtained by at-

tributing its statistical weight to each dehydrogenated species (Table 3).

If we first consider Table 1 where integrated intensities can be found for each of the doubly-dehydrogenated species, we see that the two anthracene isomers present roughly similar spectra, in band positions and intensities, except for some differences which originate in obvious structural differences, such as the

presence or absence of duo hydrogens. Thus, it appears that the total energy released in the (11.3-12.7 μm ; 885-790 cm^{-1}) feature corresponding to CH out-of-plane bending vibrations of solos and/or solo+duos hydrogens is practically independent of the individual positions of the bands which contains the structural information. The same conclusion can be drawn for the two doubly-dehydrogenated pyrenes.

Let us now consider the numbers in Table 3 and compare the spectra of the doubly-dehydrogenated species to their corresponding fully hydrogenated parents. It appears that the statistically averaged IR spectra of the C_{14}H_8 and C_{16}H_8 species are rather similar, in band positions, to the IR spectra of $\text{C}_{14}\text{H}_{10}$ and $\text{C}_{16}\text{H}_{10}$ respectively, apart from the expected emergence of new bands due to dehydrogenation. More precisely:

for doubly-dehydrogenated anthracene:

1. the CH stretching vibrations are still located around [3.3 μm ; 3030 cm^{-1}].
2. the CC stretching is found between [6.1-7.9 μm ; 1640-1270 cm^{-1}], which indicates some tendency to widen the overall feature towards longer wavelengths.
3. the CH in-plane bends fall in the range [8.0-8.6 μm ; 1250-1160 cm^{-1}].
4. the CH out-of-plane bends appear at [11.1 μm ; 900 cm^{-1}] and [13.7-13.8 μm ; 730-720 cm^{-1}], for the hydrogens in solo and quarto positions, respectively, which shows a small shift towards shorter wavelengths for this last vibration.

Due to the removal of the two hydrogens, new bands appear:

1. around [5.0 μm ; 2000 cm^{-1}], featuring the stretching vibration for the CC benzyne bond.
2. around [12.9 μm ; 770 cm^{-1}] showing the characteristic of the out-of-plane motion of the duo hydrogens, created by the 1-2 dehydrogenation of anthracene (see Table 1).

An overall comparison of the doubly-dehydrogenated species to their corresponding fully hydrogenated parent shows that the averaged intensities, integrated over each type of vibrations (Table 3) present only little fluctuations, staying roughly of the same order of magnitude. The CH vibrations seem logically to decrease, due to the loss of hydrogen atoms, and the CC vibrations to increase, due to the loosening of the bonds. However, if we want to analyze these intensities more precisely, we can proceed with a statistical point of view: a value is called statistical if it is equal to the corresponding fully hydrogenated value reduced proportionally to the dehydrogenation of the molecule. Then, taking into account the percentage of the anthracene hydrogenation (80%), the values reported in Table 4 show the following trends:

1. the CH stretching vibration intensity is only 3/4 of the statistical value.
2. the CH in-plane and out-of-plane bending vibrations intensities are almost equal to the statistical value.

Table 4. Evolution of the IR intensities of the CH vibrations with dehydrogenation for anthracene and pyrene

Molecule	% H	CH stretching		CH in-plane		CH out-of-plane	
		neutral	cation	neutral	cation	neutral	cation
$\text{C}_{14}\text{H}_{10}$	100	100	100	100	100	100	100
C_{14}H_8	80	60	157	77	79	77	74
C_{14}H_6	60	36	143	41	57	58	53
$\text{C}_{16}\text{H}_{10}$	100	100	100	100	100	100	100
C_{16}H_8	80	62	150	154	77	75	80
C_{16}H_6	60	31	150	225	58	60	57

Intensities are referred to 100% for the molecule with all 10 hydrogens .
Weighted averages over the different possible isomers have been calculated for each molecule

for doubly-dehydrogenated pyrene:

1. as for the fully hydrogenated pyrene, the CH stretching vibrations are located around [3.3 μm ; 3030 cm^{-1}].
2. the CC stretching are found between [6.3-7.9 μm ; 1590-1270 cm^{-1}], with the same trend towards longer wavelengths as in anthracene.
3. the CH in-plane bends are in the range [8.0-9.4 μm ; 1250-1060 cm^{-1}].
4. the CH out-of-plane bends appears at [12.1-12.4 μm ; 830-810 cm^{-1}] for the duo hydrogens, and at [13.3-13.4 μm ; 750-740 cm^{-1}] for the trio hydrogens. These values point to small but noticeable shifts towards longer wavelengths for the duos and towards shorter wavelengths for the trios.

Here too, due to the removal of the two hydrogens, new bands appear at:

1. [5.0 μm ; 2000 cm^{-1}], featuring the stretching vibration for the CC benzyne bond.
2. [11.6 μm ; 860 cm^{-1}] arising from the out-of-plane motion of a solo hydrogen (created by the 1-2 dehydrogenation of pyrene (see Table 1)).

An overall comparison of the averaged intensities of Table 3, leads to the same conclusion as for anthracene. If these intensities are analyzed from a statistical point a view taking into account the percentage of the pyrene hydrogenation (80%), the statistical values reported in Table 4 show that:

1. the CH stretching vibration intensity is 3/4 of the statistical value as in anthracene
2. the CH out-of-plane bending vibration intensity is almost equal to the statistical value as in anthracene.
3. the CH in-plane bending vibration, in contrast, has an intensity twice the statistical value. This surprising increase may be rationalized by strong mixing with the CC stretching vibrations; part of this increase should in fact be attributed to the close neighbour CC vibration which has shifted its own band down to the CH in-plane vibration area.

The conclusion to be drawn here, is that the effect of a double dehydrogenation, previously observed for naphthalene, is reproduced for anthracene and pyrene. Apart from the CH out-of-plane bending vibrations, intensities for the CH motions, in

particular the CH stretching, are not proportional to the number of hydrogens left on the cycles.

3.3. Effect of a quadruple dehydrogenation

For naphthalene, a quadruple dehydrogenation where half of the hydrogens are removed, affects its IR spectrum drastically. For anthracene and pyrene, a quadruple dehydrogenation corresponds to still 60% hydrogenation, and might be more reasonable to consider.

For anthracene, only one quadruple dehydrogenation has been studied (Fig. 2, scheme 1d), because the other isomers would be, either non stable bi-radicals, or a model for two double dehydrogenations and not a real quadruple dehydrogenation. For pyrene, with the same criteria of selection, five different isomers have to be considered (Fig. 3, schema 2d to 2h); the corresponding IR spectra can be found in the appendix (Tables A-I-d and A-II-d to A-II-h).

When comparing the individual IR spectra of the five possible quadri-dehydrogenated pyrene derivatives, it can be observed that the width of the spectral region in which the bands fall varies from one isomer to another, leading either to localized or to broad features without obvious reason. From the normal coordinate analysis, it becomes clear that it is no longer possible to label a band as pure CC or pure CH in-plane bend. Some motions that used to be dominant CH bending vibrations in the fully hydrogenated species acquire a CC component that shifts the bands to higher energies; the reverse is true of dominant CC vibrations which are shifted to lower energies by CH bend contamination. In fact, both spectral regions [6.7-7.9 μm ; 1490-1260 cm^{-1}] and [8.0-9.4 μm ; 1250-1060 cm^{-1}] are now a mixture of CC and CH in-plane motions and any assignment to a specific type of displacement is illusory.

Let us now compare IR spectra of the quadri-dehydrogenated species with their corresponding fully hydrogenated parents. Considering the averaged spectra of Table 3, we notice that the IR spectra of the quadri-dehydrogenated anthracene and pyrene still resemble those of the corresponding fully hydrogenated species in position, with intensities logically decreasing for the CH vibrations and increasing for the benzyne bond vibration. The trends are the same as for double dehydrogenation, only more obvious. More precisely, if we analyze these intensities by taking into account the percentage of hydrogenation (60%), the statistical values reported in Table 4 show that:

for quadri-dehydrogenated anthracene:

1. the CH stretching vibration intensity is hardly more than half of the statistical value.
2. the CH in-plane bending vibration intensity is 2/3 of the statistical value.
3. the CH out-of-plane bending vibration intensity is equal to the statistical value.

for quadri-dehydrogenated pyrene:

1. the CH stretching vibration intensity is about half of the statistical value;
2. the CH in-plane bending vibration intensity is almost 4 times the statistical value (this increase is once more attributed to the strong mixing with the CC stretching vibrations).
3. the CH out-of-plane bending vibration intensity is equal to the statistical value.

The tendency observed for doubly-dehydrogenated anthracene and pyrene, is confirmed with quadruple dehydrogenation:

1. the CH stretching vibrations at [3.3 μm ; 3030 cm^{-1}] decrease in intensity as was suspected but not proportionally to the number of hydrogens removed (more rapidly in fact);
2. the CH in-plane vibrations also have a tendency to decrease more rapidly, except if the effect is countered by coupling with the CC vibrations.
3. the CH out-of-plane vibrations are proportional to the hydrogen content.

These conclusions are in total agreement with those drawn from the previous study of the effect of dehydrogenation on naphthalene.

Let us now consider the astrophysical implications of the results presented above. To make it easier for the discussion we will follow a now well-accepted approach that relies on the comparison of the intensities to the "6.2+7.7" μm [(1610+1300) cm^{-1}] band. The ratios of the averaged summed intensities over the so-called "3.3" μm [3030 cm^{-1}], "5.2" μm [1920 cm^{-1}], "6.2" μm [1610 cm^{-1}], "11.3" μm [880 cm^{-1}] features to the "6.2+7.7" μm reference are reported in Table 5 for anthracene and pyrene, at different stages of dehydrogenation. It is clear that these ratios are affected by dehydrogenation but not enough or not in a way that we could have expected. If we compare these numbers to the corresponding values deduced from the interstellar emissions (Table 5), it is obvious that these ratios are definitively too large by one order of magnitude for the CH stretching and CH out-of-plane vibrations. Even if we extend our trends to somewhat larger PAHs with the possibility of more dehydrogenation, there is no way to reconcile the different ratios which respond to dehydrogenation differently. In particular we have to take into consideration some kind of saturation of the effects with extensive dehydrogenation.

The conclusion at this point of the study is that small neutral PAHs, even dehydrogenated, are not the dominant carriers of the UIR bands. Moreover the discrepancies observed will not be removed by more extensive dehydrogenation.

4. The IR spectra of ionized anthracene and pyrene

The IR spectra of ionized anthracene and pyrene have already been presented in detail in our previous paper (DeFrees et al. 1993); they can be found in the appendix (Tables A-I-a and A-II-a). Summed intensities are in Table 2. The shifts in the positions of the bands resulting from ionization stay rather small,

Table 5. Integrated intensities normalized to the $6.2 + 7.7 \mu\text{m}$ feature

Molecule	3.3 (μm) 3030 (cm^{-1})	5.2 (μm) 1920 (cm^{-1})	6.2 μm 1610 (cm^{-1})	11.3 μm 885 (cm^{-1})
$\text{C}_{14}\text{H}_{10}$	4.03		0.72	6.69
C_{14}H_8	1.20	0.03	0.37	2.56
C_{14}H_6	0.73	1.6	0.37	1.98
$\text{C}_{16}\text{H}_{10}$	2.40		0.53	3.12
C_{16}H_8	1.12	0.08	0.56	1.79
C_{16}H_6	0.46	0.16	0.48	1.16
$\text{C}_{14}\text{H}_{10}^+$	0.06		0.40	0.82
$\text{C}_{14}\text{H}_8^+$	0.05	0.30	0.18	0.33
$\text{C}_{14}\text{H}_6^+$	0.05	1.65	0.42	0.26
$\text{C}_{16}\text{H}_{10}^+$	0.01		0.67	0.28
$\text{C}_{16}\text{H}_8^+$	0.02	0.28	0.22	0.21
$\text{C}_{16}\text{H}_6^+$	0.02	0.60	0.33	0.15
observed*	0.04-0.06	0.03-0.05	0.31-0.39	0.15-0.23

Summed intensities used for the ratios correspond to the weighted averaged of Table III. The "11.3" intensities are relative to all the CH out-of-plane bending vibrations (solo-duo-trio-quarto)
* deduced from the observations of Cohen et al. 1989

mainly non significant for most of them. We can conclude that the CC and CH in-plane vibrations tend to show a small shift towards longer wavelengths while the CH out-of-plane vibrations move in the opposite direction. But the main changes that characterise the IR spectra of the cationic species, relative to the neutral species, shows up in the intensities:

1. the CH stretching vibrations around [$3.3 \mu\text{m}$; 3030 cm^{-1}], which are strong in the neutral molecule, decrease in intensity by at least one order of magnitude in both anthracene and pyrene.
2. the bands between [$6.8\text{-}7.7 \mu\text{m}$; $1470\text{-}1300 \text{ cm}^{-1}$] for anthracene and [$6.7\text{-}7.4 \mu\text{m}$; $1490\text{-}1350 \text{ cm}^{-1}$] for pyrene, featuring CC vibrations of medium intensity in the neutral molecule, increase by one order of magnitude.
3. the bands between [$8.0\text{-}8.5 \mu\text{m}$; $1250\text{-}1180 \text{ cm}^{-1}$] in anthracene, and [$8.3\text{-}9.2 \mu\text{m}$; $1200\text{-}1090 \text{ cm}^{-1}$] in pyrene, corresponding to CH in-plane bending vibrations increase surprisingly by two to three orders of magnitude.
4. the CH out-of-plane bending vibrations in both anthracene and pyrene are little affected by ionization with a very small tendency to decrease.

The features around [$10.0\text{-}10.5 \mu\text{m}$; $1000\text{-}950 \text{ cm}^{-1}$] corresponding to the skeleton deformations have not been mentioned in the neutral molecules because of their weakness. In the anthracene cation these bands are still weak; they increase in the pyrene cation, as in naphthalene (Pauzat et al. 1995). Since, in larger compact PAHs - even not so large if one consider the structures approaching coronene (Langhoff 1996) - these peculiar vibrations are not significant, even in the cation, we do not expect to see them among the bands observed. Consequently, we will not elaborate any further.

Such changes in the intensities must obviously affect considerably the comparison with the observed spectra. This can be visualized in Table 5 where are reported ratios to the "6.2+7.7" μm [$1610+1300 \text{ cm}^{-1}$] reference band intensity. The much

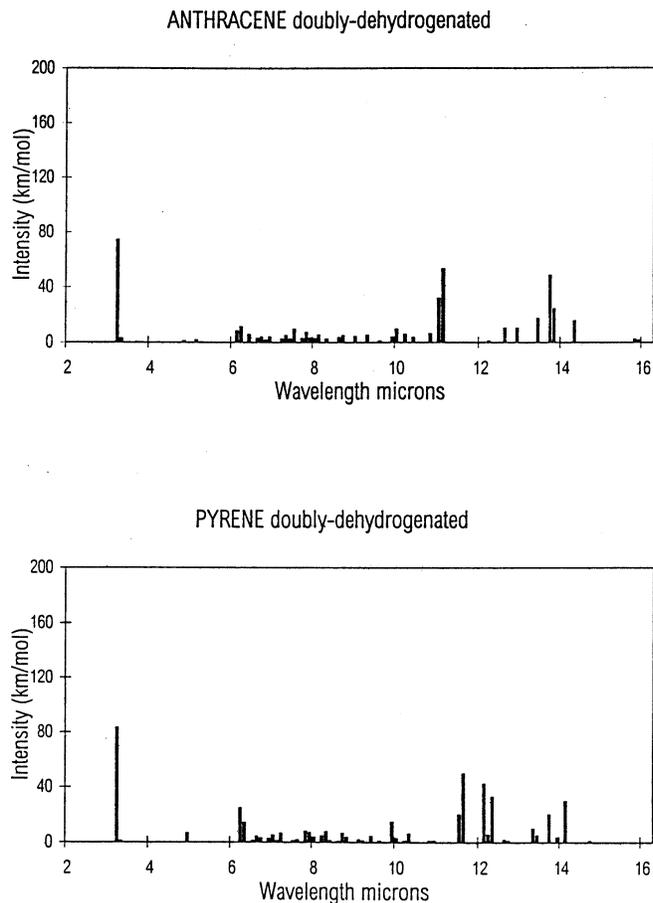


Fig. 5. Histogram representation of a statistically weighted sum of the IR absorption band intensities of doubly-dehydrogenated neutral anthracene and pyrene.

better match between calculated relative intensities for the ions and observed values, confirms the idea that a large proportion of the PAHs, if they exist, should be ionized, since a partial dehydrogenation does not explain the CH/CC ratio, when ionization does. These conclusions are in complete agreement with our previous results on naphthalene.

The main conclusion drawn from this ab-initio study of ionized species, already discussed in DeFrees et al (1993), and confirmed by a recent density functional approach (Langhoff 1996) is that ionization has a large effect on the intensities of the IR spectra and that the corresponding relative intensities are in better agreement with the observations than are those of their neutral and dehydrogenated neutral parents.

5. Effect of combined ionization and dehydrogenation

5.1. Effect of double dehydrogenation

The positive ions corresponding to the doubly-dehydrogenated structures studied in Section 3 have been considered. The IR spectra can be found in the appendix (Tables A-I-b, A-I-c, A-II-b and A-II-c); the intensities summed for each type of vibration are reported in Table 2 and the averaged summed intensities in

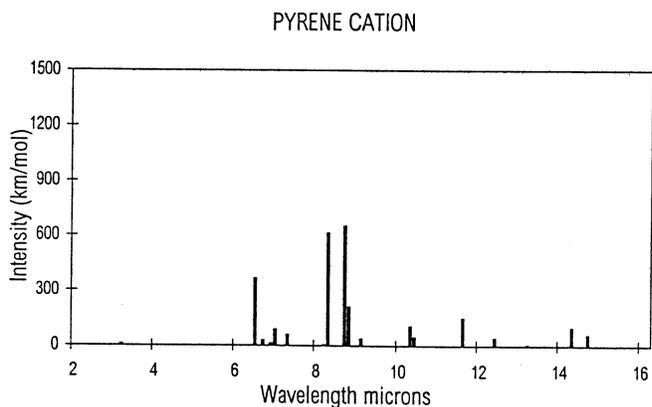
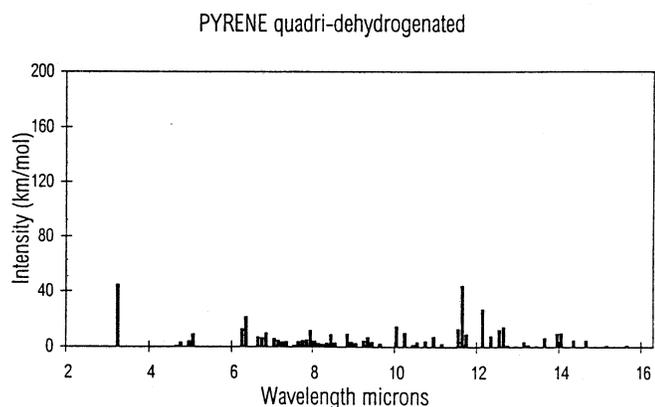
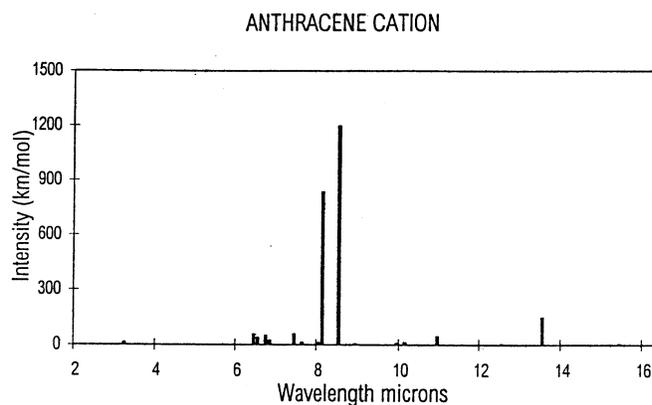
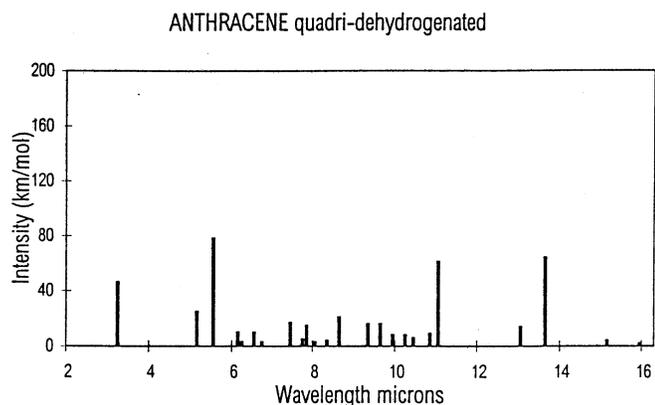


Fig. 6. Histogram representation of a statistically weighted sum of the IR absorption band intensities of quadri-dehydrogenated neutral anthracene and pyrene.

Fig. 7. Histogram representation of the IR absorption band intensities of anthracene and pyrene cations.

Table 3. The averaged spectra corresponding to the statistical weight of each structure are reported in Fig. 8.

The similarities between the IR spectra of the two neutral doubly-dehydrogenated isomers of each compound were found to be strong. This behaviour is reproduced for the corresponding cations, with the same restrictions, as can be seen from the numbers in Table 2, for the couple of isomers of the two $C_{14}H_8^+$ and $C_{16}H_8^+$ systems.

Let us now focus on the averaged summed intensities (Table 3), and compare the numbers obtained for each doubly-dehydrogenated cation to its fully hydrogenated parent. We notice that the IR spectra resemble the parent's: the centers of the overall features are about the same but the spectral range over which the individual bands fall is wider, a tendency observed for the neutral molecules when subject to dehydrogenation, and amplified here with the combined effect of ionization. Again we find the emergence of the same new bands due to dehydrogenation.

for doubly-dehydrogenated anthracene:

1. medium CH vibrations around $[3.3 \mu\text{m}; 3030 \text{ cm}^{-1}]$.

2. strong CC vibration around $[5.0 \mu\text{m}; 2000 \text{ cm}^{-1}]$ featuring a CC stretching for a benzyne triple bond.
3. a strong pattern of aromatic CC stretching vibrations between $[6.5\text{-}8.0 \mu\text{m}; 1540\text{-}1250 \text{ cm}^{-1}]$. At that point, let us mention that looking to the individual spectra (Tables A-I-b and A-I-c) of the appendix, shows that some bands featuring CH bending vibrations have been shifted in that region, contributing to the intensity increase of this feature.
4. strong CH in-plane bending vibrations in the range $[8.0\text{-}9.0 \mu\text{m}; 1250\text{-}1110 \text{ cm}^{-1}]$. Here too, the individual spectra show shifted CC stretching vibrations in this region of the spectra.
5. strong CH out-of-plane bending vibration at $[10.8\text{-}10.9 \mu\text{m}; 930\text{-}920 \text{ cm}^{-1}]$ corresponding to the non-adjacent solo hydrogen atoms.
6. medium CH out-of-plane bending vibration at $[12.6 \mu\text{m}; 790 \text{ cm}^{-1}]$ corresponding to duo hydrogens, emerging in the 1-2 doubly-dehydrogenated species (see Table 2 and Fig. 2b).
7. strong CH out-of-plane bending vibration at $[13.4 \mu\text{m}; 750 \text{ cm}^{-1}]$ corresponding to the quatro hydrogen atoms.

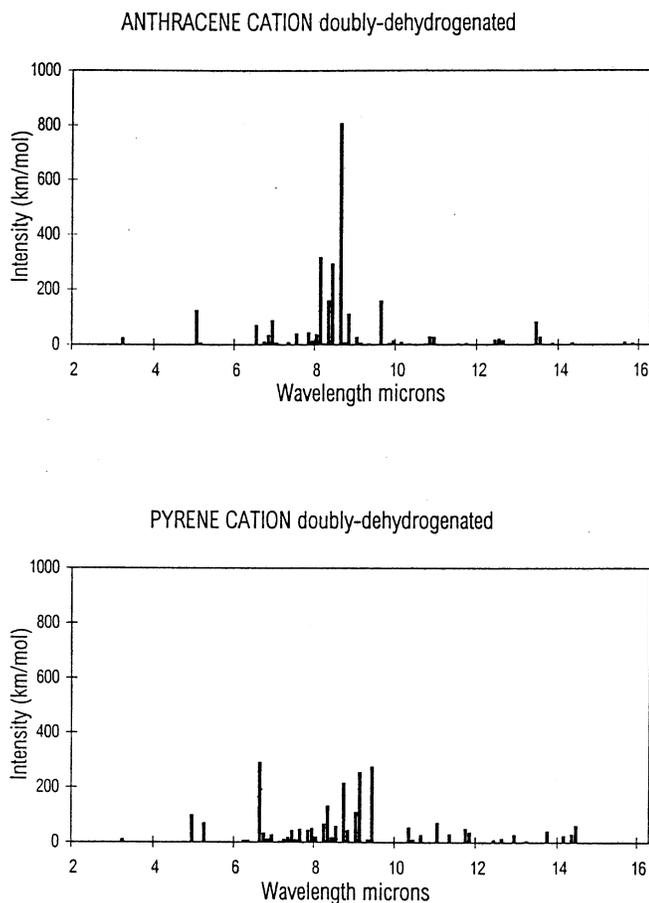


Fig. 8. Histogram representation of a statistically weighted sum of the IR absorption band intensities of doubly-dehydrogenated anthracene and pyrene cations.

for doubly-dehydrogenated pyrene:

1. weak CH stretching vibrations around [$3.3 \mu\text{m}$; 3030 cm^{-1}].
2. strong CC vibrations around [$4.9\text{--}5.2 \mu\text{m}$; $2040\text{--}1920 \text{ cm}^{-1}$] featuring a CC stretching for a benzyne triple bond
3. strong pattern of aromatic CC stretching vibrations, mixed with CH in-plane bending vibrations between [$6.3 \mu\text{m}$; 1590 cm^{-1}] and [$8.0 \mu\text{m}$; 1250 cm^{-1}] (Tables A-II-b and A-II-c)
4. strong CH in-plane bends mixed with CC stretching vibrations in the range $8.2\text{--}9.5 \mu\text{m}$; $1220\text{--}1050 \text{ cm}^{-1}$].
5. strong CH out-of-plane bending vibration at [$11.3 \mu\text{m}$; 880 cm^{-1}] emerging in the 1-2 dehydrogenated pyrene (see Table 2 and Fig. 3b).
6. weak CH out-of-plane bending vibration at [$12.9\text{--}13.3 \mu\text{m}$; $770\text{--}750 \text{ cm}^{-1}$] corresponding to hydrogens in trio position.
7. a strong CH out-of-plane bending vibration at [$11.8\text{--}11.9 \mu\text{m}$; $850\text{--}840 \text{ cm}^{-1}$] corresponding to hydrogens in duo position.

Considering intensities, it appears that the effects of ionization and dehydrogenation combine most of the time. The remarks made in the preceding sections for the two effects are additive, slightly moderated by the fact that ionization seems to enhance considerably the intensity of the new [$5.2 \mu\text{m}$; 1920

cm^{-1}] band and that, surprisingly, dehydrogenation seems to counterbalance a little or at least to moderate the very strong effect of ionization on the [$3.3 \mu\text{m}$; 3030 cm^{-1}]. If we now look at the statistical values reported in Table 4, we notice that:

for doubly-dehydrogenated anthracene:

1. the CH stretching vibration intensity is increased by dehydrogenation, reaching values twice the statistical value.
2. the CH in-plane bending and the CH out-of-plane bending vibration intensities are close to their respective statistical values.

for doubly-dehydrogenated pyrene:

1. the CH stretching vibration intensity is increased with dehydrogenation, being almost twice the statistical value, as in anthracene.
2. the CH in-plane bending vibration intensity is equal to the statistical value and the CH out-of-plane bending vibration is close to it, as in anthracene.

At that point, we can conclude that most of the important effect of ionization observed in the IR spectra of anthracene and pyrene is still present in the doubly-dehydrogenated species. More than that, a comparison between the calculated and observed relative intensity ratios reported in Table 5 shows that the agreement already remarkable for the ionized anthracene and pyrene is even better when considering the doubly-dehydrogenated species.

5.2. Effect of a quadruple dehydrogenation

The IR spectra for the positive ions of the quadri-dehydrogenated anthracene and pyrene considered in Section 3, can be found in the appendix (Tables A-I-d and A-II-d to II-h); summed intensities are reported in Table 2. The averaged spectra corresponding to the statistical weight of each structure are reported in Fig. 9.

When comparing the quadri-dehydrogenated cations to their corresponding doubly-dehydrogenated precursors (see Table 3), we see that:

1. the vibrations are quite unchanged in wavelength.
2. the vibration describing the CC benzyne motion increases, as suspected, because of the presence of one more bond of this type.
3. the intensities for the CH motions show no drastic changes, but keep the same tendency to level off for the CH stretching vibrations while logically decreasing for the CH in plane-bending vibrations. Even if these changes are small in absolute values, these trends have clear consequences when referenced to the statistical values of Table 4:

for quadri-dehydrogenated anthracene:

1. the CH stretching vibration intensity is 2.4 times the statistical value.

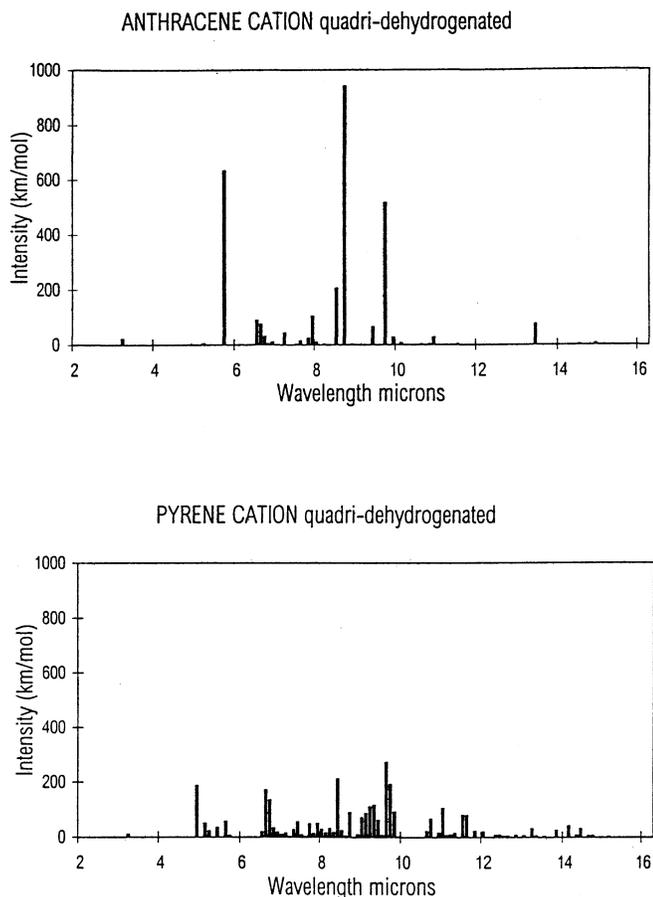


Fig. 9. Histogram representation of a statistically weighted sum of the IR absorption band intensities of quadri-dehydrogenated anthracene and pyrene cations.

2. the CH in-plane bending vibration intensity is equal to the statistical value while the CH out-of-plane bending is close to it (lower by 10%).

for quadri-dehydrogenated pyrene:

1. the CH stretching vibration intensity is 2.5 times the statistical value.
2. the CH in-plane and out-of-plane bending vibrations intensities are equal to the statistical values.

If we now consider (Table 5 the ratios of the summed intensities of the different features for the ionized quadri-dehydrogenated anthracene and pyrene, to the so-called "6.2+7.7" μm [(1610+1300) cm^{-1}] band, we see that they are close to the ratios of the corresponding ionized doubly-dehydrogenated parents.

However, if we compare these ratios to the numbers deduced from the interstellar emissions as given in Table 5 our last partial conclusion would be that the enhancement of the intensity of the benzyne bond vibration by ionization shows that dehydrogenation should be limited in order to keep this intensity in reasonable accordance with observations.

6. Discussion and conclusions

The analysis of the IR spectra of anthracene and pyrene allows more refined and reliable conclusions than those obtained only from a study of the naphthalene model. However, it is worth mentioning here that all the statements which follow are consistent with our previous conclusions (Pauzat et al. 1995). This is a proof that our calculations are consistent and that the tendencies obtained before with such a small model were not artefacts.

Apart from confirming the striking effect of ionization on the intensities of the IR spectra, with the ratio CC vibrations/CH stretchings increasing by two orders of magnitude, it is time now to outline two points about the effect of dehydrogenation:

The first and fundamental one is that the strong effect observed with ionization is kept for dehydrogenated structures.

The second one is that dehydrogenation affects differently the intensity of the CH stretchings in the neutral molecules and in their corresponding cations: these CH vibrations, whose intensities logically decrease with the number of hydrogens in the neutral molecules (even if not proportionally), slightly increase or tend to a stable value with dehydrogenation in the cations. This behaviour cannot be related to geometry effects, the corresponding normal mode remaining a pure CH stretching; it is more likely connected to the sensitivity of the dipole function in these highly polarizable ions. The [8.6 μm ; 1150 cm^{-1}] region, generally assigned to CH in-plane vibrations, is difficult to rationalize. There are two reasons for this difficulty. First, the strong mixing of the CH and CC local coordinates within the same normal mode makes the attribution uneasy or confused; second, the displacement of the vibrations themselves within the bands whose specific regions are overlapping each other.

The region between [11 μm ; 900 cm^{-1}] and [14 μm ; 700 cm^{-1}] corresponding mainly to the CH out-of-plane presents the same behaviour for neutrals and cations, both following the statistical evolution in a most reasonable way. This can be explained by the fact that these vibrations, belonging to a different symmetry, are not coupled to the in-plane motions which are the most affected by dehydrogenation.

Another important point confirmed by this study is that dehydrogenation induces the emergence of several new bands, with significant intensities:

1. CH out-of-plane bending vibrations, respectively for solo, duo, and trio hydrogens, whose signatures are at about [11 μm ; 900 cm^{-1}], [12.0 μm ; 830 cm^{-1}] and [13.0 μm ; 770 cm^{-1}].
2. benzyne bonds vibrations whose signatures appear around [5.0 μm ; 2000 cm^{-1}].

If we consider these results from the point of view of the free molecular PAHs, the bands observed at [11.3 μm ; 880 cm^{-1}], [11.9 μm ; 840 cm^{-1}] and [12.7 μm ; 790 cm^{-1}] (Allamandola 1990) are certainly the signatures of the CH out-of-plane bending vibrations for hydrogens, in positions solo, duo and trio respectively; the observation of a feature at [13.5 μm ; 740 cm^{-1}] would certainly be the signature of quarto hydrogens. We have to emphasize here that ionization shifts these bands towards

shorter wavelengths. This blueshifting of the CH out-of-plane modes in cations, although predicted in our first reports on fully hydrogenated species, was not stressed in view of possible uncertainties in transferring the scaling procedure from the neutral to the ionic species. It appears to be a general trend for both genuine and dehydrogenated PAHs as confirmed by recent experiments (Hudgins et al; 1994; Hudgins and Allamandola 1995a,b) and calculations by Langhoff (1996) using the completely different approach of density functional theory. A blueshifting of the same order of magnitude is observed with dehydrogenation in both neutral and positive ions for quatros and trio hydrogens while the solo hydrogen positions appears little affected. By contrast, duo hydrogens are slightly redshifted. Considering all factors, and because most of the positions are somewhat too high for the initial parent neutral molecules, this is again a good point in favor of ionized dehydrogenated species.

The band observed in the range [5.1-5.3 μm ; 1960-1890 cm^{-1}] (Allamandola et al. 1989) and attributed to an overtone/combination of CH vibrations could also be a signature for a benzyne bond. These stretching frequencies which are too high for the neutrals are shifted by 50 cm^{-1} in the average towards longer wavelengths with ionization, which puts them in a better position for the cations. In that case the restriction about the amount of possible dehydrogenation quoted in the preceding paragraph has to be taken into account, not to get a too intense band in that region. The strong intensity of this type of vibration can certainly be used as an argument against extensive dehydrogenation which will increase the number of triple bonds.

Keeping in mind all the preceding conclusive points, if we now look at the raw numbers displayed in Table 5 the best agreement with the ratios deduced from the observations is that of the $\text{C}_{14}\text{H}_8^+$ and $\text{C}_{16}\text{H}_8^+$ species. It confirms the results of our preceding study on naphthalene when it was found that $\text{C}_{10}\text{H}_6^+$ species, i.e. doubly-dehydrogenated ionized molecules, provided the best match to the interstellar spectra. At that point of our theoretical investigations, we believe that moderately dehydrogenated cations are certainly as good a choice as fully hydrogenated PAH cations for explaining the UIR bands considering free-flyer carriers, which is still a debated option.

The relative intensities of the CC benzyne stretching, which are still too strong by a factor of 10 compared to the band observed at this wavelength is thus the last intensity discrepancy; it is reasonable to say that in more compact PAHs, where the numbers of aromatic bonds will be relatively more important, the intensity for this band will be weakened relatively to the others.

Finally, if one wants to push the speculation further, a closer discriminating look at the band positions displayed in Table 3, indicates that the best agreement is for ionized pyrene derivatives. Could that be an argument for compact PAHs versus linear ones? At all events, it is coherent with the photofragmentation of PAH positive ions that show the larger fragility of the linear structures (Granucci et al. 1995, 1996).

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References

- Aitken, D.K., 1981, In IAU Symposium 96, Infrared Astronomy, Wynn-Williams, C.G., Cruikshank, D.P., Eds., (Reidel: Dordrecht), p. 207.
- Allamandola L.J., Tielens A.G., Baker J.R., 1985, Ap. J. Letters, 290, L25. Allamandola L.J., Tielens A.G., Baker J.R., 1989, Ap. J. Suppl., 71, L733.
- Allamandola L.J., Bregman J.D., Sandford S.A., Tielens A.G., Witteborn F.C., Wooden D.H., Rank D., 1989, Ap. J. Lett., 345, L59.
- Allamandola L.J., 1990, In Topics in Current Chemistry, Cyvin, S., Gutman, J., Eds., (Springer: Berlin), vol. 153, p. 1.
- Cohen M., Tielens A.G., Bregman J., Witteborn F.C., Rank D.M., Allamandola L.J., Wooden D.H., Jourdain de Muizon M., 1989, Ap. J., 341, 246. DeFrees D.J., Miller M.D., Talbi D., Pauzat F., Ellinger Y., 1993, Ap. J., 408, 530.
- DeFrees D.J., Miller M.D., 1989, In Interstellar Dust, Allamandola, L.J., Tielens, A.G.G.M., Eds., NASA, CP 3036, p. 173
- Frisch M.J., Head-Gordon M., Trucks G.W., Foresman J.B., Schlegel H.B., Raghavachari K., Robb M.A., Binkley J.S., Gonzales C., DeFrees D.J., Fox D.J., Whiteside R.A., Seeger R., Melius C.F., Baker J., Martin R.L., Kahn L.R., Stewart J.J.P., Fluder E.M., Topiol S., Pople J.A., 1992, Gaussian 92, Gaussian, Inc., Pittsburg PA.
- Hudgins D.M., Sandford S.A., Allamandola L.J., 1994, J. Phys. Chem., 98, 4243.
- Hudgins D.M., Allamandola L.J., 1995, J. Phys. Chem., 99, 3033.
- Hudgins D.M., Allamandola L.J., 1995, J. Phys. Chem., 98, 4243.
- Joblin C., d'Hendecourt L., Leger A., Defourneau D., 1994, Astron. Astrophys., 281, 923.
- Jourdan de Muizon M., d'Hendecourt L.B., Geballe T.R., 1990 Astron. Astrophys., 227, 526.
- Granucci G., Ellinger Y., Boissel P., 1995, Chem. Physics, 191, 165, Granucci G., Ellinger Y., 1996, to be published
- Langhoff S.R., 1996, J. Phys. Chem., 100, 2819.
- Leger A. and Puget J.L., 1984, Astron. Astrophys., 137, L5.
- Leger A., d'Hendecourt L. and Defourneau D., 1996, Astron. Astrophys., in press.
- Omont A., 1986, Astron. Astrophys., 164, 159.
- Pauzat F., Talbi D., Ellinger Y., 1995 Astron. Astrophys., 293, 263.
- Puget J.L., Leger A., 1989, Ann. Rev. Astron. Astrophys. 27, 161.
- Salama F., Allamandola L.J., 1991, J. Chem. Phys., 94, 6964.
- Szczepanski J., Roser D., Personnette W., Eyring M., Pellow R., Vala M., 1992, J. Phys. Chem., 96, 7876.
- Szczepanski J., Vala M., Talbi D., Parisel O., Ellinger Y., 1993, J. Chem. Phys., 96, 4494.
- Vala M., Szczepanski J., Pauzat F., Parisel O., Talbi D., Ellinger Y., 1994, J. Phys. Chem., 98, 9187. Van der Zwet, G.P., Allamandola, L.J., 1985 Astron. Astrophys. 146, 76.
- Weimer H.A., McFarland B.J., Li S., Weltner Jr. W., 1995, J. Phys. Chem., 99, 1824.
- Willner, S.P., 1984, In Galactic and extragalactic Infrared Spectroscopy, Kessler, M.F., Phillips, J.P., Eds. (Reidel: Dordrecht), p. 37.