

# A new model for the interpretation of the unidentified infrared bands (UIBs) of the diffuse interstellar medium and of the protoplanetary nebulae

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**Abstract:** In this work we started from the basic idea that the pure polycyclic aromatic hydrocarbons (PAHs) cannot be the real carriers of the unidentified infrared bands (UIBs), the emission spectra coming from a large variety of astronomical objects. Instead we propose a new model taken from petroleum chemistry which, we can show, is able to match both the UIBs and even the protoplanetary nebulae (PPNe) spectra. PAHs such as phenanthrene, benzoperylene, coronene and pentacene, are too pure and too specific to really exist in the interstellar medium. Instead our model proposes that the carrier of UIBs and PPNe are complex molecular mixtures like those obtained as fractions during the petroleum refining processes. These molecular mixtures are so complex that practically the investigators did not try to identify each individual component but characterized the mixture with an average molecular structure that takes into account both the average molecular weight and the average content of aromatic, naphthenic (cycloaliphatic) and aliphatic (paraffinic) fraction. We show by infrared spectroscopy that petroleum fractions obtained at certain steps of the refining process are able to match the UIBs and the PPNe infrared bands with the advantage of not being so specific as PAHs are. Namely we have used as samples a distillate aromatic extract (DAE) a treated residual aromatic extract (T-RAE) and finally a naphthenic oil. Among the three samples examined, the DAE sample was the best in matching the UIBs and PPNe spectra.

*Received 19 March 2002, accepted 13 May 2002*

**Key words:** UIBs, Infrared Spectra, protoplanetary nebulae, PAH, average molecular structure and petroleum fractions.

## Introduction

It is currently accepted that the diffuse interstellar medium and the circumstellar environment is populated by several different organic molecules and carbonaceous matter. This organic matter is also considered to be the source of both the ultraviolet (UV) bump at 217.5 nm, the diffuse interstellar bands (DIBs) and the unidentified infrared bands (UIBs) (Hoyle & Wickramasinge 1977, 1989, 1999a, b; Wickramasinge *et al.* 1989; Henning & Salama 1998; Ehrenfreund & Charnley 2000). Recently, we have reviewed (Cataldo & Pontier-Johnson 2002) the nature of the carbon dust, which is thought to be the source of the average interstellar extinction peak at 217.5 nm and have shown, in agreement with earlier calculations (Wickramasinge *et al.* 1999), that it cannot be described as pure graphite particles but rather by carbon black

particles, which are a form of highly disordered carbon. Furthermore, we have shown (Cataldo 2002) that the absorption spectra of several different types of carbonaceous matter, including carbon black, are not able to reproduce the peak at 217.5 nm on a laboratory scale; instead, the spectrum of carbon black is able to match the ultraviolet (UV) spectrum of the carbon dust present in some circumstellar shells of late-type stars. Only partial hydrogenation of carbon black may reproduce the interstellar extinction peak. Another interesting aspect discussed (Cataldo 2002) is the effect of absorbed polycyclic aromatic hydrocarbons (PAHs) on the spectra of a suspension of carbon black particles into an opportune matrix.

All of these enormous efforts dedicated to the identification of the carriers of both the DIBs and the UIBs are a result of the fact that we need to increase our knowledge concerning the

molecules and the chemical structure of the solids existing in the diffuse interstellar medium as well as in other interesting astronomical objects such as, for instance, the protoplanetary nebulae where new stars and possibly new planets are forming. We need this knowledge as a basis to understanding whether certain very complex chemical processes may occur in the interstellar medium especially on grain surfaces, and eventually to clarify whether life, also in its simplest form, is a ubiquitous phenomenon in the Universe.

The UIBs are observed in emission spectra from a large variety of astronomical objects and for this reason are considered essentially ubiquitous. The main bands appear at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7  $\mu\text{m}$  (Henning & Salama 1998; Ehrenfreund & Charnley 2000; Reynaud *et al.* 2001). These bands are attributed to polycyclic aromatic compounds both because they match the general band pattern of PAHs but also because they are emitted from regions where the radiative field is very low. Therefore only molecular entities such as the polycyclic aromatic hydrocarbons are small enough to be heated by a single-photon absorption (Allamandola *et al.* 1984; Leger & Puget 1984; Sellgren 1984). Theoretical calculations of the relative emission strengths of neutral and ionized PAH and laboratory studies have allowed the infrared (IR) emission bands to be successfully modelled by combining laboratory spectra of neutral and positively charged PAHs (Allamandola *et al.* 1999). The PAH hypothesis is now generally accepted and most favoured, although some criticism has been reported against it (see Guillois *et al.* 1999; Reynaud *et al.* 2001) on the grounds that:

- no pure PAH or PAH gas mixture has been found to reproduce convincingly the UIB spectrum found so far;
- the Infrared Space Observatory (ISO) has shown the UIBs are almost identical even for very different emission sources, irrespective of the intensity and dominant wavelength of the radiative field;
- although the PAH spectra are strongly altered in an ultraviolet radiation field by the changes caused in the ionization state, no spectral variations have been experimentally recorded in the UIBs excited by UV radiation.

The most interesting alternative to the PAH hypothesis is that the UIBs derive from the excitation of a carbonaceous amorphous solid like coal. In particular, anthracite (a type of natural coal with a high aromatic content) shows an infrared spectrum which is in agreement with the UIB spectrum (Papoular *et al.* 1993; Guillois *et al.* 1996, 1999).

A topic related to UIBs covers the spectrum of protoplanetary nebulae (PPNe). In fact, the PPNe infrared spectrum is similar to that of UIBs with an additional feature at 13.3  $\mu\text{m}$ ; other features in PPNe not present in UIBs are the bands at 3.4, 6.9, 7.2 and 12.2  $\mu\text{m}$  (Hrivnak *et al.* 2000). This spectrum resembles that of a carbonaceous disordered solid, also incorporating an aliphatic component (semi-anthracite coal; see Reynaud *et al.* 2001). However, the coal hypothesis has drawbacks of its own. In fact, coal is a semiconductor with small bandgap and hence can exhibit a strong electronic continuum in the near infrared, which is not observable in the interstellar spectrum.

Recently, Reynaud, Guillois and colleagues (2001) have proposed new carbonaceous materials that seem to match the UIBs and the PPNe spectra, avoiding the apparent contradiction that solid coal-like carbon is needed to reproduce the interstellar spectrum, while PAH molecules are needed to satisfy the one-photon transient heating model. These new carbonaceous materials have been produced by IR laser pyrolysis of small hydrocarbons to synthesize a family of hydrogenated aromatic nanoparticles that have been further processed by heavy-ion bombardment to match the spectrum of PPNe IRAS 07134+1005. Additionally, ion-bombarded polystyrene film has been used to match the spectrum of PPNe IRAS 22272+5435.

The basic guidelines lying behind these experimental developments and their success is the idea that PAHs are too small and too specific to be able to reproduce the universal UIB spectrum. However, coal is not a good model either because the problem presented in the near-infrared (NIR) part of the spectrum and its large particle size. Hence, only nanoparticles should be small enough to undergo the one-photon heating process in a low radiative field and should be large enough to match the UIB spectrum. Basically all authors (Ehrenfreund & Charnley 2000; Reynaud *et al.* 2001) have adopted the idea that the carriers of the UIBs are large PAH ranging from a few hundred carbon atoms down to 50 carbon atoms.

In their excellent review Ehrenfreund & Charnley (2000) conclude the section pertaining to UIBs with the following words: 'although the nature of molecules responsible for the infrared emission bands is no doubt aromatic, the individual components will have to be identified in future laboratory experiments'.

In the present paper, we discuss the new concept that these molecules, which are responsible for the UIB emission or the PPNe spectra, cannot be found among single individual components but must be described by a general chemical model that we will take from petroleum and coal chemistry.

## Experimental

### Materials

In the present investigation we have taken into consideration some products derived from petroleum refinement processes (Prince 1997). In particular, we have studied samples of highly viscous oil derived from the distillation of crude petroleum according to the following processing steps: crude petroleum is distilled at atmospheric pressure as a first step of its refinement. This first step is called topping. During this process the volatile fraction is separated from a non-volatile residue (Prince 1997). This residue in its turn is then subjected to distillation under reduced pressure to give both a vacuum distillate and a vacuum residue.

The vacuum residue is deasphalted with pentane extraction (Prince 1997) to give a fraction free from asphaltenes and resins but which needs a further furfural extraction to remove the extractable undesired aromatic fraction and leaving as

Table 1. General chemical composition of the oils used based on carbon atom type

	DAE	T-RAE	Naphtenic
% Aromatic fraction	45	27	15
% Naphtenic fraction	25	38	34
% Paraffinic fraction	30	35	51
% PAHs on total oil	20	4	< 3
Glass transition temperature	−36	−45	−58

unextractable matter a base oil for lubrication known as brightstock. We have used the highly aromatic furfural extractable matter, which is known as the residual aromatic extract (RAE). More precisely, the sample we have studied was a treated RAE (T-RAE), because the RAE fraction has been subjected to a further extraction treatment to lower its PAH content below 3%.

Another sample that was the subject of our study was derived from the vacuum distillate. One of the heaviest fractions of the vacuum distillate is the base for the preparation of the so-called lube basestock. The lube basestock is the insoluble fraction remaining after a furfural extraction of the distillate, which removes the heavy aromatic fraction from it. The heavy aromatic extractable fraction derived from the distillate is called the distillate aromatic extract (DAE) and has been prepared according to the process described and used in the present work.

Finally, we have used a naphtenic oil prepared from a naphtenic rich crude petroleum (Venezuelan crude). Also in this case the vacuum residue is treated with pentane to remove asphaltenes and resins, but is then sent for hydrotreatment which implies hydrogenation at 250 °C and 20–60 bar of hydrogen over Ni–Mo catalysts supported on high surface area alumina (Prince 1997). With this treatment the level of PAH is also brought below 3%. The basic characteristic properties of the naphtenic oils used in the present study are illustrated in Table 1. Thus the materials used in the present work were all commercially available. The DAE oil was Esar-90 from Agip, Italy, the T-RAE oil was Processoil-1000 from ESSO–EXXON Italy and finally the naphtenic oil was Nytex 840 from Nynas, Sweden.

The samples of DAE, T-RAE and naphtenic oil were studied as received. Additionally they have been further processed as described below.

#### Chemical modification of DAE

DAE oil (2 ml) was treated with 0.3 g of montmorillonite KP10 (an acidic catalyst) and heated in a closed flask to the direct flame of an alcohol stove for 5 min. The colour of the oil turned from dark brown to black. Then the mixture was cooled to room temperature, extracted with 20 ml of CH<sub>2</sub>Cl<sub>2</sub> and the solution was filtered through a paper filter for quantitative analysis. All the catalyst remained in the filter paper while the CH<sub>2</sub>Cl<sub>2</sub> solution was used to record the FT-IR spectrum by growing a film over a KBr plate.

#### Chemical modification of naphtenic oil

Naphtenic oil (3 ml) was added to a pre-melted mixture of AlCl<sub>3</sub>/NaCl (respectively 1.8 and 0.5 g). The mixture was shaken and heated in a closed flask over the direct flame of an alcohol stove. The oil became dark. The mixture was cooled and treated with an excess of 12% HCl to hydrolyze the catalyst and then it was extracted with 25 ml of CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was separated from the aqueous acidic phase with the aid of a separatory funnel. The CH<sub>2</sub>Cl<sub>2</sub> solution was filtered through a paper filter and then used to prepare a film of the reacted oil over a KBr plate to record the FT-IR spectrum.

#### Chemical modification of T-RAE oil

T-RAE oil (9.5 g) was diluted with 18 g of CH<sub>2</sub>Cl<sub>2</sub> and stirred with 3.0 g of ZrCl<sub>4</sub> and 2.8 g of AlCl<sub>3</sub>. After 1 h the CH<sub>2</sub>Cl<sub>2</sub> was distilled off and the mixture was heated at about 150 °C for 1.5 h. After cooling the work-up was the same as described in the case of the naphtenic oil.

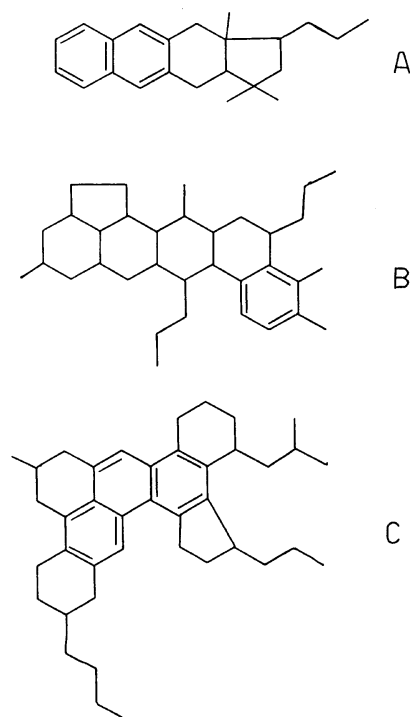
#### Spectroscopic investigations

The FT-IR spectra were recorded on a Perkin–Elmer 1710 spectrometer on thin films of samples between two KBr discs. The electronic spectra were recorded in ethanol or again as a thin film over KBr plates (at 0 °C in this latest case) on a Shimadzu UV160A spectrophotometer.

## Results and discussion

#### A model from petroleum chemistry to interstellar chemistry

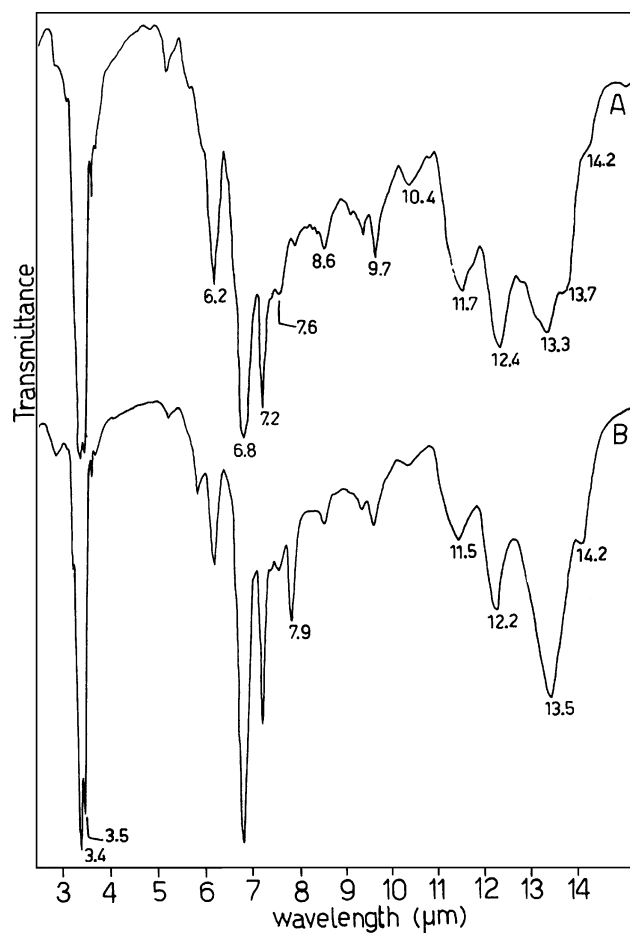
One of the main aims of research in the field of UIBs is to identify the individual molecules that are responsible for the infrared emission bands. Our proposal is instead to consider a general molecular model that may be used to understand the average molecular structure of the carriers of the UIBs. In other words, we agree with Papoular *et al.* (1993), Guillois *et al.* (1996, 1999) and Reynaud *et al.* (2001), and the basic idea that PAHs are too small and too specific to be able to reproduce the universal UIB spectrum. A similar problem was faced in petroleum chemistry and also by coal chemistry (see Van Krevelen 1993) when one attempts to identify the individual components of raw petroleum and coal, or better, the individual components of certain petroleum fractions obtained after distillation and extraction (Purdy 1960; Smith *et al.* 1961; Proskouriakov & Drabkine 1983). The great difficulty is in isolating all the individual molecular components within a certain petrochemical fraction or in assigning an unequivocal molecular structure to coal; however, a method has been found to determine their average composition. This method is still in use today and involves the so-called carbon-type analysis. This method assumes that each fraction under analysis is relatively homogeneous as a result of a certain number of refining operations. Hence, the amount of aromatic, naphtenic (cycloaliphatic) and paraffinic carbon atoms can be established by infrared spectroscopy (Brandes method), by proton-NMR and C<sup>13</sup>-NMR spectroscopy, and even by a standard method known as ASTM D2140 working on the basis of the refractive



**Scheme 1.** Average molecules representing the petroleum fractions used in the present study. A, DAE; B, T-RAE; C, naphthenic oil.

index of the fraction under analysis and of its specific gravity. For instance, in Scheme 1 we have represented three average molecules which reasonably represent the petroleum fractions used in the present study (DAE, T-RAE and naphthenic oil) (Purdy 1960; Smith *et al.* 1961; Proskouriakov & Drabkine 1983). Structure A represents a molecule of 23 carbon atoms (average molecular weight of 306 Da), 10 atoms of which are aromatic, seven of which are naphthenic and six of which are paraffinic. Thus the carbon atom analysis implies that a certain petroleum fraction can on average be described by structure A and have a 43.5% aromatic fraction ( $C_A$ ), 30.4% naphthenic fraction ( $C_N$ ) and 26.1% paraffinic fraction ( $C_P$ ). Similarly, structure B tells us that the fraction in question is represented by an average structure like that having an average molecular weight of 458 Da with  $C_A = 17.6\%$ ,  $C_N = 47.0\%$  and  $C_P = 64.6\%$ . Finally, structure C tells us analogously that the average molecule we are considering is on average composed by 40 carbon atoms and has an average molecular weight of 533 Da. Its composition is  $C_A = 35\%$ ,  $C_N = 35\%$  and  $C_P = 30\%$ .

Therefore if it is already difficult to identify each type of individual molecule in complex terrestrial mixtures of petroleum fractions for which we have the physical sample available, it should be even more difficult to know the individual molecules in complex interstellar mixtures for which we have available only optical spectra. The practical approach has been to determine an average structure with an average molecular weight defining this structure on the basis of its aromatic/naphthenic and paraffinic content. In our opinion the same approach must be applied in the case of the UIBs and the supposed PAH carriers. The flaws in the PAH model, which



**Fig. 1.** FT-IR spectra. A, DAE oil; B, DAE oil chemically modified. Spectrum A is the best match of UIB bands and PPNE bands (see also Table 2).

we have already reviewed in the introduction, are the continuous search for larger PAH (or mixture thereof) and other chemical substrates for a better match to the UIB bands and the clear fact that we cannot stick to the idea that a simple PAH can really be present in the diffuse interstellar bands because they are too specific. This leads us to propose the adoption of the petrochemical approach just described to the case of interstellar molecules. Thus, average molecules such as A, B and C of Scheme 1 may be present in space in a frozen condition in minute grains. These average molecules represent a possible average structure of the oil samples used in the present study.

The possibility that the molecular structures shown in Scheme 1 could be representative of the PAHs causing the UIBs is based on the fact that the molecules present in the interstellar clouds or in the protoplanetary nebulae are thought to have a relatively high molecular weight of at least 50 carbon atoms. Hence, for instance, structure C may already match this basic concept. Additionally, the PAHs are thought to be partially hydrogenated. The partial hydrogenation implies necessarily the presence of naphthenic or cycloaliphatic structures accompanying the aromatic structures and these structures are also present in Scheme 1. Finally, the PAHs causing

Table 2. *Infrared bands synopsis*

UIBs	PPNe	IRAS 07134+1005	IRAS 22272+5435	DAE oil	Modified DAE oil	T-RAE oil or naphthenic	Modified T-RAE oil	Modified naphthenic			
3.3	3.3			3.3	3.3		3.3	3.3			
				3.4	3.4	3.4	3.4	3.4			
				3.4			3.4	3.4			
						3.6		3.5	3.5		
								3.5			
								3.7			
						5.2	5.25				
						5.4	5.4				
						5.7	5.7		5.7		
						5.8			5.8		
6.2	6.2			6.25	6.25	6.25	6.2	6.25			
								6.35			
								6.55			
							6.9	6.9	6.9	6.9	6.85
							7.2	7.2	7.25	7.25	7.25
7.7	7.7	7.5		7.6	7.6	7.5	7.65	7.65			
								7.7	8.15	7.9	
							8.0	7.9			
8.6	8.6			8.0							
				8.3				8.3			
				8.6	8.6	8.65	8.55	8.65			
					9.45	9.3					
					9.6	9.7	9.7	9.7			
11.3		10.6		10.4	10.4	10.3	10.3	10.35			
			11.3	11.7	11.5	11.5	11.5	11.5			
			12.2	12.4	12.3	12.3	12.4	12.3			
			13.3	13.3	13.5	13.5	13.6	13.5			
				13.7	13.8	13.8	13.85	13.8			
			14.2	14.3	14.2	14.2		14.2			
			15.5	15.5							

the UIBs are nowadays thought to be alkylated. Again, this principle is also matched by the structures of Scheme 1.

All of these premises suggest that the molecules of Scheme 1 may really represent the structures of molecules giving rise to the UIBs, and we have some good terrestrial compounds that may be representative of the parent molecules present in space: some petroleum fraction, the preparation of which we have described in some detail in the experimental section. Now it is time to test spectroscopically the structural analogy linking our model with the PAHs of the UIBs.

#### *Infrared spectroscopy of DAE: a comparison with UIBs and PPNe bands*

In Table 1 we have reported the typical chemical composition (by carbon atom type) of three petroleum fractions derived from the fractionation of petroleum. The details have already been reported in the experimental section. From Table 1 we can deduce that DAE is the most aromatic material studied followed by T-RAE and naphthenic oil. Both of the latter two compounds have a significantly high naphthenic fraction but the oil called naphthenic also has a preponderant paraffinic fraction. It is also interesting to note that the free PAH content of DAE is about 20% of the oil, while it is very small in the case of the other oils. Another feature of the materials studied here is the fact that they are highly viscous oils at room temperature but they have a glass transition temperature ( $T_g$ ) similar to that of other common polymers, below that temperature they are almost glassy solids. In this glassy state they may occur in space since their  $T_g$  lies in the range of  $-36$  to

$-58$  °C, even though we have studied them at room temperature in this present study.

In Fig. 1(A) we present the FT-IR spectrum of DAE oil (see Table 1 for its carbon type analysis), which is characterized by a spectrum that matches all the UIB bands but also the PPNe bands as shown in Table 2. The aromatic fraction of DAE is clearly suggested by the  $3.3$   $\mu\text{m}$  band (aromatic C—H stretching band), by the aromatic ring ‘quadrant’ stretching at  $6.2$   $\mu\text{m}$  and the ring ‘semicircle’ stretching at  $6.8$   $\mu\text{m}$  (Colthup *et al.* 1990; Reynaud *et al.* 2001). Other interesting features that are in line with the aromatic character of DAE are the in-plane C—H bending at  $11.63$  and  $10.31$   $\mu\text{m}$  and a series of aromatic C—H wagging bands at  $11.7$ ,  $12.4$ ,  $13.3$  and  $13.7$   $\mu\text{m}$ . The band at  $11.7$   $\mu\text{m}$  suggests a high degree of substitution of the aryl ring so that only a lone H atom remains attached to the ring: this is consistent with structure C of Scheme 1, for example (also in structure A we have a phenyl ring with isolated H atoms). The band at  $12.4$   $\mu\text{m}$  suggests the presence of two to three adjacent H attached to the ring, more or less in line with structure B of Scheme 1. The bands at  $13.3$  and  $13.7$   $\mu\text{m}$  suggest both four adjacent hydrogen atoms attached to the ring, somewhat in line with structure A of Scheme 1. The weak band at  $14.2$   $\mu\text{m}$  may be assigned to the out-of plane bending of a three-substituted phenyl ring or five adjacent H (Colthup *et al.* 1990; Reynaud *et al.* 2001). The aliphatic or cycloaliphatic character of DAE is underlined by the presence of the  $3.4$   $\mu\text{m}$  band as well as the aliphatic bending at  $7.2$   $\mu\text{m}$  and the olefinic wagging at  $10.4$   $\mu\text{m}$  (Reynaud *et al.* 2001). The treatment of DAE with an acidic catalyst, a montmorillonite (a bentonite clay) does not cause major changes in the IR

spectrum other than small band shifts as illustrated in Fig. 1(B) (compare with Fig. 1A) – the disappearance of the band at 13.7  $\mu\text{m}$  and the growth of the band at 13.5  $\mu\text{m}$ . Another effect of the treatment is the growth of the 7.9  $\mu\text{m}$  band, which may be attributed to isomerization reactions occurring in the aliphatic and cycloaliphatic part of the molecules. In conclusion, the treatment with montmorillonite had only minor effects on the chemical structure of DAE.

Now, looking at Table 2, we can observe that all the bands of DAE are completely coincident with the ISO spectrum of the PPNe IRAS 22272+5435 published by Hrvina *et al.* (2000) with the exclusion of two weak bands at 3.6 and 9.45  $\mu\text{m}$ . Despite this exciting success of a perfect match between the band pattern of DAE oil and the ISO spectrum of PPNe IRAS 22272+5435, the band intensity of DAE oil however does not match the intensity of the bands of the mentioned PPNe object above 10  $\mu\text{m}$ . In fact, in Fig. 1(A) the most intense bands are at 12.4 and 13.3  $\mu\text{m}$  and after the catalytic treatment the most intense band appears at 13.5  $\mu\text{m}$  followed by the band at 12.2 and that at 11.5  $\mu\text{m}$  (Fig. 1B), while in the IRAS spectrum the most intense band appears at 11.3  $\mu\text{m}$  followed by a 12.2  $\mu\text{m}$  band of approximately the same intensity and finally followed by weak bands at 13.3, 14.3 and 15.5  $\mu\text{m}$ . This suggests that the carriers of the bands in the PPNe object are more aromatic in character with a larger degree of polycondensation of the phenyl rings and a lower degree of hydrogenation in comparison with DAE. Although not perfect, the band intensity of DAE is closer to those of the other PPNe object IRAS 07134+1005 (Hrvina *et al.* 2000). In any case all the ubiquitous UIB and the PPNe bands are present in our DAE compound and are always the most intense or among the most intense bands of the IR spectrum. Thus it is demonstrated that the carriers of the UIBs and of the PPNe can be reasonably thought to have average structures somewhat similar to those shown in Scheme 1 rather than to pure and simple PAHs or to coal (see, for instance, the spectra of Papoular *et al.* (1993) on coal in comparison with UIB bands).

#### *Infrared spectroscopy of T-RAE and naphthenic oil: a comparison with UIBs and PPNe bands*

Notwithstanding that in Table 1 we have shown that T-RAE oil and naphthenic oil are chemically different in terms of their carbon atoms analysis, the FT-IR spectra of these two oils are almost identical. This may be a result of the fact that the difference is too small to be easily discernible by a not extremely sensitive technique like FT-IR spectroscopy. Thus, in Fig. 2(A) we show the spectrum of the T-RAE, but the spectrum of the naphthenic oil is the same. The T-RAE has a strong band at 13.8  $\mu\text{m}$ , which suggests a high degree of hydrogenation of the aromatic ring (four adjacent H atoms per ring), while the bands at 12.3 and 11.5  $\mu\text{m}$  are quite weak. At this stage of course T-RAE and naphthenic oil are not able to match the spectral intensity of the IRAS objects reported in Table 2 as well as DAE oil, although once again these two oils are able to match the band pattern of the PPNe spectral carriers. In order to increase the aromatic content of the T-RAE oil, a treatment

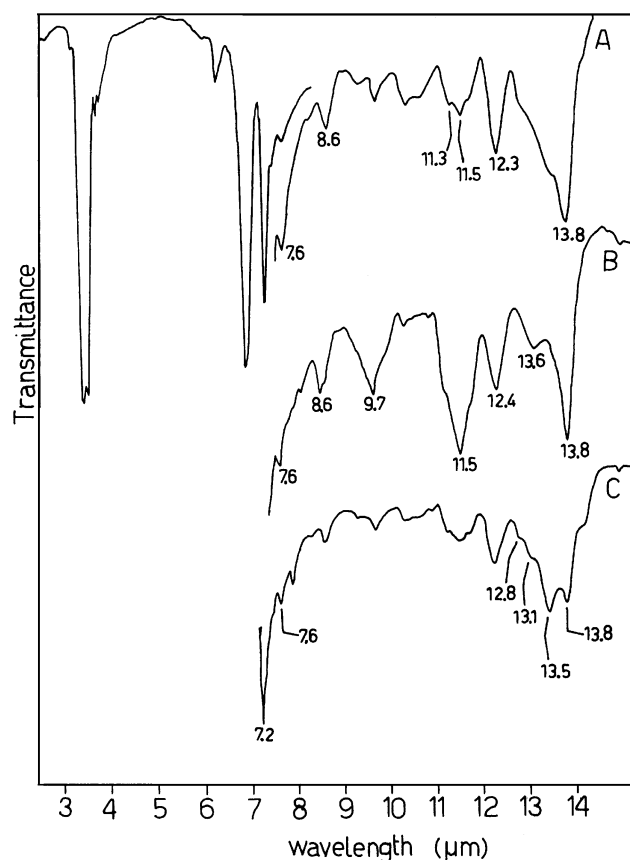


Fig. 2. FT-IR spectra. A, T-RAE oil; B, T-RAE chemically modified; C, naphthenic oil chemically modified.

with Friedel–Crafts catalyst has been made (see the experimental section). In this case the treatment was completely successful since it caused a dramatic increase of the band at 11.5  $\mu\text{m}$  owing to lone H atoms attached to the ring, which means a lower degree of hydrogenation and a higher degree of polycondensation of the aromatic rings (see Fig. 2B and compare with Fig. 2A). The band at 11.5  $\mu\text{m}$  now shows the same intensity as the band at 13.8  $\mu\text{m}$ , which originally was the most intense one. The spectrum of Fig. 2(B) is closer both in band pattern and in intensity to the spectra of the PPNe IRAS objects discussed in the preceding paragraph.

In contrast, with the positive response of the T-RAE oil to the treatment with a Friedel–Crafts catalyst, the naphthenic oil treated with  $\text{AlCl}_3$  shows the unexpected growth of a 13.5  $\mu\text{m}$  band, which is not present in the PPNe or the UIBs spectra (see Fig. 2C).

#### *Electronic spectroscopy of DAE and naphthenic oil*

The carriers of UIBs may also be the same molecules and macromolecules that give rise to the interstellar UV bump at 217 nm as already discussed in the introductory section of this work. Graphitized or disordered carbon materials with a low hydrogen content may be present in some circumstellar shells of late-type stars, where the peaks at 240–250 nm have been recorded and attributed to more ordered and partially graphitized carbonaceous matter. More hydrogenated carbon

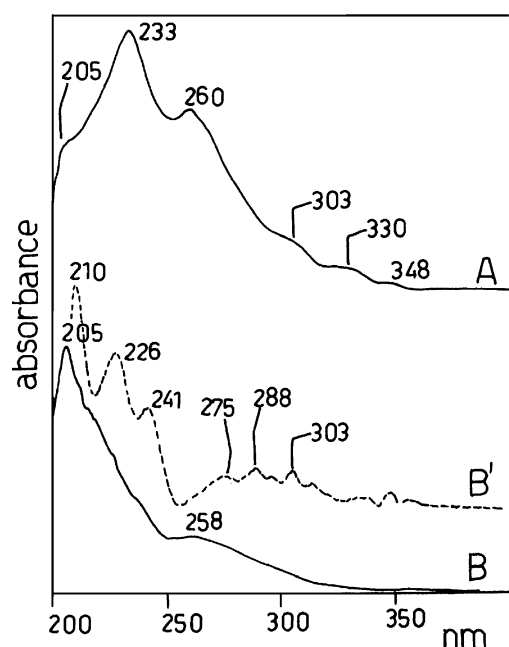


Fig. 3. Electronic spectra. A, DAE oil in ethanol; B, naphthenic oil in ethanol; B', first derivative of spectrum in B.

materials (i.e. carbon blacks having a high degree of hydrogen content) are more likely to be the source of the 217 nm interstellar feature. However, more complex materials with a kerogenic nature such as the organic fraction extractable from meteorites are also able to reproduce the mentioned interstellar feature (Sakata *et al.* 1999). Kerogen is defined, in a broad sense, as any organic macromolecule having a very complex nature that cannot be described by a single unequivocal structure but only by an average structure which is insoluble in common solvents. Certain petroleum fractions enter into this broad definition together with certain other complex materials such as shale, bitumen, pitch and even coal or coal derivatives. These complex macromolecules can be produced by specific chemical reactions or even by the degradation of more complex molecules having a biological nature or in the Earth during the formation of petroleum, coal and shale.

Electronic spectroscopy is a complementary tool for studying the degree of aromatic content of certain molecules. In Fig. 3(A) we report the electronic spectrum of DAE oil in ethanol. The spectrum is characterized by two maxima in the ultraviolet region at 233 and a 260 nm. Additional features are the shoulders at 205, 303, 330 and 348 nm. A simple search in a collection of UV spectra (Friedel & Orchin 1951) suggests to us that a DAE average molecule contains three condensed aromatic rings of anthracene or phenanthrene type. Thus, the structure of DAE could be assimilated into structure C of Scheme 1. However, to match the real composition of the DAE oil, structure C should have a lower naphthenic content. Conversely, the less aromatic naphthenic oil (see Table 1 for its average composition) shows an electronic spectrum (Fig. 3B) with a maximum at 205 nm and a shoulder at 258 nm. Although the first derivative of the spectrum (Fig. 3B') shows the presence of several other absorption bands, the spectrum of Fig. 3B suggests that only one isolated aromatic ring is present

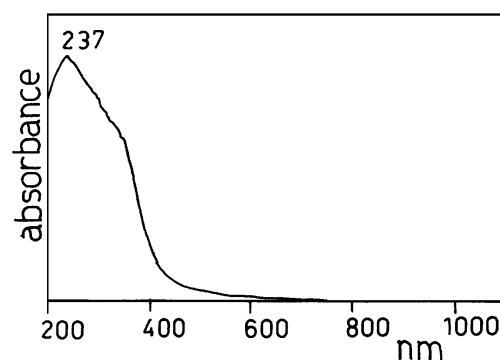


Fig. 4. Electronic spectrum of DAE oil in the solid state as film over a KBr plate at 0 °C.

in each average molecule of naphthenic oil. Therefore, on average the naphthenic oil may be reasonably assumed to be represented by structure B of Scheme 1. The other absorption bands suggested by the first derivative of spectrum 3B (Fig. 3B') suggest that many different molecules are present as impurities, with a higher degree of aromatic content.

In Fig. 4 we have recorded the solid-state spectrum of DAE as a film over a KBr plate (cooled at 0 °C). It is also interesting to note that DAE material, which has already been demonstrated here to have an interesting FT-IR spectrum in reasonable agreement with the emission spectra of UIBs and PPNe, as in the case of carbon black it shows a maximum in the UV at 237 nm. Thus the model of DAE molecule seems to be a good starting point for the interpretation of the chemical structure of the molecules giving rise to UIBs, PPNe and also for the dust of late-type stars.

## Conclusions

The present study has shown the merit of the new model we are proposing for the interpretation of the UIB and PPNe spectra.

First of all, since we are dealing with a mixture of molecules and we cannot easily identify each individual molecule, the most practical approach is to draw an average molecular structure that could be representative of the molecular mixture we are dealing with. We are just proposing to apply to the astrochemistry field an approach that has been used successfully in the field of petroleum chemistry (Melpolder *et al.* 1954a, b) and in coal science (Van Krevelen 1993) for a long time.

The PAH model proposed to explain UIBs is not completely satisfactory and at present researchers are looking to find larger PAHs than those already used as model compounds to reproduce the UIBs and some DIBs. It is thought that only PAHs having more than 50 carbon atoms may reproduce the UIBs.

With our model, we are already proposing to consider molecules having about 50 or more carbon atoms. The advantage of our model lies in the fact that we are describing a complex mixture of molecules with an average molecular structure. This average molecular structure already has a relatively high molecular weight and is composed of both an

aromatic, a naphthenic and a paraffinic fraction. Several times researchers in this field have claimed that the PAHs in the interstellar medium may be alkylated (i.e. should contain lateral paraffin chains attached to the polycyclic molecule), they have also talked about the hydrogenation degree of a PAH in order to explain some spectral feature. With our model we are already considering these aspects. Structure C of Scheme 1 may be much more hydrogenated, and in such a case the degree of aromatic content will be very low but the naphthenic fraction will grow. Conversely, the degree of hydrogenation can be very low and in this case the aromatic fraction will grow at the expense of the naphthenic fraction.

We already have access to terrestrial samples that can be described by the average structures reported in Scheme 1. These samples are complex molecules having an average molecular weight in the range of 300–550 Da and are obtained from petroleum refining processes. These molecules, in our opinion, must be closer to the molecules populating the interstellar medium and are composed simultaneously of an aromatic, a naphthenic and a paraffinic part. Thus they are not as specific as simple and pure PAHs such as coronene or phenanthrene. Furthermore, they present a certain versatility: their degree of hydrogenation and hence their aromatic and naphthenic content can change according to the environment where these molecules are present.

The infrared spectra of the petroleum fraction we have used in this study match completely both the band pattern of UIBs and of PPNe. The best material among those tested is DAE oil.

It is astonishing that petroleum fractions may exist in the PPNe. It is extremely difficult today to accept and admit their biological origin. An enormous amount of experimental and theoretical work is needed to draw such a conclusion firmly. Moreover, a sufficient number of chemical reactions are known that can generate these complex organic fractions without advocating more exotic conditions of formation (from the Fischer–Tropsch reaction (Kolbel & Engelhardt 1952) to the old reactions proposed by Berthelot (1866) and Mendeleev (1877) for the inorganic origin of petroleum and discussed by Oparin (1938) in his book on the origin of life).

Instead, these complex organic fractions formed from chemical reactions that may be the basis for the construction or maintenance of life, as originally proposed by Oparin (1938) for life on Earth.

### Acknowledgements

We are deeply indebted to ASI, the Italian Space Agency, Viale Liegi 26, 00198 Rome, Italy for financial support of the present work. We also wish to thank the editor of *Int. J.*

*Astrobiol.*, Dr S. Mitton, for his valuable and stimulating suggestions in improving the original manuscript.

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