

Heavy petroleum fractions as possible analogues of carriers of the unidentified infrared bands

Franco Cataldo¹ and Yeghis Keheyan²

¹*Soc. Lupi Chemical Research Institute, Via Casilina 1626/A, 00133 Rome, Italy*
e-mail: cdcata@fashnet.it

²*Istituto per lo Studio Dei Materiali Nanostrutturati, Universita' Roma 1, P. Le A. Moro 5, Rome, Italy*

Abstract: The Fourier-transform infrared spectra and the electronic spectra of a series of petroleum fractions of different composition and origins have been studied. Furthermore, these fractions have been modified through the Scholl reaction, a reaction that causes an increase in the aromatic content of the fractions by causing the formation of polycyclic aromatic hydrocarbons (PAHs) or larger PAHs if they were already present in the pristine samples. It is shown that some heavily aromatic petroleum fractions are able to match the emission spectra of the protoplanetary nebula IRAS 22272 + 5435. Additionally, it is shown that the modified petroleum fractions are able to match the infrared spectrum of anthracite, a high-rank type of coal that has been proposed as the material responsible for the emission of the unidentified infrared bands (UIBs), but which can also be thought of as a model of the kerogen found in meteorites or assumed to be present in cometary nuclei. It is shown that the petroleum fractions considered in this work can be considered even better candidates than coal as a model for the matter present in protoplanetary nebulae and the carrier of the UIBs.

Received 15 January 2003, accepted 5 February 2003

Key words: petroleum fractions, aromatic content, infrared spectra, unidentified infrared bands.

Introduction

Recently we have reported that certain heavy petroleum fractions are able to match certain spectra of protoplanetary nebulae (PPNe) such as those of the object IRAS 22272 + 5435 but also, more generally, can explain certain features of the unidentified infrared (IR) bands (UIBs) (Cataldo *et al.* 2002a, b). Furthermore, we have proposed the concept of 'average molecular structure' to describe the carriers of UIBs and PPNe. This concept is taken from petroleum chemistry and has been discussed elsewhere (Cataldo *et al.* 2002a). The concept of average molecular structure is used when fractions of complex mixtures of molecules are isolated during the petroleum refining processes. Usually it is virtually impossible in these cases to identify the chemical structure of each component of the fractions and therefore the simplest approach is to have an average composition of the fraction itself together with an average molecular structure and an average molecular weight, which can be considered as an idealized model of the fraction under study. Elsewhere we have enumerated the reasons of this approach (Cataldo *et al.* 2002a). Therefore, instead of searching for simple molecules or simple synthetic mixtures of molecules with two or three components, we should look directly at complex mixtures and use these mixtures as a model to see if these fractions are able to match the UIBs or the PPNe emission

spectra. This approach of selecting and using naturally occurring complex mixtures has already been indirectly used by Reynaud *et al.* (2001) and Guillois *et al.* (1999), when they proposed anthracite coal as a possible carrier of the UIBs.

The carriers of the UIBs or of the emission spectra of the PPNe appear to be in the form of cosmic dust (Guillois *et al.* 1999; Reynaud *et al.* 2001). The structural composition of the cosmic dust has not yet been clarified but the main features of the UIBs or PPNe spectra appear to be caused by a complex mixture of organic molecules condensed into solid grains. These grains are referred to as interstellar carbon dust or 'refractory organics'. The chemical structure of these grains should vary according to a number of conditions: the grains may contain (in their organic part) aggregates of 'raw' molecules formed in the dark nebulae according to:

- the gaseous ion–molecule reaction mechanism,
- the Fischer–Tropsch reaction (Kress & Thielens 2001; Hayatsu & Anders 1981),
- Miller–Urey synthesis,
- the Berthelot reaction (hydrocarbon pyrolysis with formation of PAH and carbon soot),
- carbon grains may also derive from crosslinking reactions of polyne chains (Cataldo & Capitani 1999).

Once formed these grains may also undergo other reactions under the action of any kind of radiation and thermal cycles, and could have a different degree of hydrogen content. The hydrogen content of the carbon dust affects its optical properties (Cataldo 2002). Special attention has been paid to this specific aspect in recent works (Cataldo & Pontier-Johnson 2002).

The connection between the UIBs and the PPNe spectra is that both the molecular clouds and the protoplanetary nebulae should have similar basic carriers, but the presence of a more reprocessed and diversified organic matter can be deduced from the PPNe spectra in comparison with the UIBs. In other words, it appears that the organic and carbonaceous matter present in the protoplanetary nebulae should be closer in composition to that found in carbonaceous chondrites. The organic matter present in carbonaceous chondrite is in large part kerogenic in nature. This means that it is a highly complex, crosslinked organic matter that is insoluble and unextractable with common solvents. Usually only 10% of the organic matter of a carbonaceous chondrite is extractable while the remaining 90% is completely unextractable, ill-defined macromolecular material called kerogen (Hayatsu & Anders 1981; Lipschutz & Schultz 1999). In the extractable 10% a plethora of organic compounds have been identified: approximately 400 different organic compounds as reported by Lipschutz & Schultz (1999), including aminoacids, hydrocarbons, carboxylic acids, PAH and purine and pyrimidine bases. The presence of kerogen in the meteorites and also in the cometary nuclei (see the discussion of Moroz *et al.* 1998) permits the inference to be drawn that the meteoritic and cometary kerogen is derived directly from interstellar grains, in which case interstellar grains must be largely kerogenic in character.

A study on the meteoritic kerogen has been made by Hayatsu & Anders (1981) using gentle oxidative degradation. Under these conditions a mixture of carboxylated aromatic compounds have been produced ranging from benzene substituted with two to six carboxylic groups to crysene having two to three carboxylic groups. Also polycarboxylic derivatives (various other polycyclic aromatic compounds having up to four condensed rings) have been identified. Polycarboxylic acids of phenol, fluorenone, benzophenone, anthraquinone, benzothiophene and benzofuran have been produced together with derivatives of pyridine quinoline and carbazole. It is interesting to note that all the products found in meteoritic kerogen have been produced in the oxidative degradation of bituminous coal of terrestrial origin (Van Krevelen 1993), although in this case also other derivatives including acridone, dibenzodioxine, xanthone, benzoanthraquinone and others were found while the derivatives of crysene, biphenyl, phenol were not found. Furthermore, the degradation of terrestrial kerogen from sedimentary rock also gives mixtures of aromatic carboxylic acids provided that it has the correct degree of aromaticity (Durand 1980).

All of these results suggest that meteoritic kerogen should have a chemical structure recalling that of coal and certain terrestrial types of kerogen. Furthermore, the formation of

polycarboxylic acids is proof of the presence of condensed aromatic rings forming aromatic 'clusters' linked together by aliphatic or ether bridges, which is also the chemical structure of coal and certain kerogens. Based on the definition of kerogen, coal is also a kerogen (Durand 1980).

In a recent paper, Moroz *et al.* (1998) have presented a collection of infrared spectra of natural bitumens. The purpose of that work was to create a reference library with an organic sequence of different natural bitumens having an increasing degree of aromatic fraction and a decreasing H/C ratio. Then this reference library can be used in the identification of the chemical composition of certain bodies (or part of them) of the solar system in the case of a match between the bitumen spectra and the spectra of the surface of the bodies.

Similarly, with the present work we would like to present the spectral evolution of certain petroleum fractions by increasing their aromatic content with the aid of some chemical reactions. The IR spectra obtained will be compared with the spectra of natural bitumens, coal, natural kerogen and the spectra of reference protoplanetary nebulae such as IRAS 22272 + 5435 and with the UIB spectra.

Experimental

Materials

In this study we have used the following materials.

- A sample of standard anthracite coal (reference material no. 65) supplied by the Commission of the European Communities 'Community Bureau of Reference BCR' with an individual identification analysis no. 417.
- A sample of distillate aromatic extract (DAE), which we have already described in detail and used in our previous works (Cataldo *et al.* 2002a, b).
- One sample of petroleum pitch denominated BREA having 12% insolubles in toluene, a ring and ball softening point of 97 °C and a coke yield in close cup of 48%. This sample was supplied by Repsol YPF (Spain).
- Two liquid petroleum fractions identified as 'fraction 1' and 'fraction 2', respectively, the distillation curves of which are presented and discussed in the 'Results and discussion' section, supplied by Repsol YPF (Spain); fraction 1 contains 38% PAH, mainly naphthalene, methylnaphthalenes, biphenyl and acenaphthylene/acenaphthene. Fraction 2 contains 15.6% phenanthrene, but also fluorene, anthracene, fluoranthene and pyrene. The elemental analysis shows that fractions 1 and 2 have more or less the same composition: C = 92% and H = 8%.
- One heavy petroleum fraction identified as BQ-1 with a very high C/H ratio, also supplied by Repsol YPF (Spain).

Chemical modification of the petroleum fractions

In order to cause a polycondensation reaction of the petroleum fractions mentioned above and to induce the formation of highly condensed polynuclear aromatics, use was made of Friedel-Crafts catalysts and high temperature. This kind of reaction is known as a Scholl reaction (Fieser & Fieser 1967; Hassner & Stumer 1994).

Scholl's reaction over the distillate aromatic extract DAE (a heavy petroleum fraction)

DAE oil (7.3 g) was treated with 2.5 g of anhydrous $ZrCl_4$ and 3.4 g of anhydrous $AlCl_3$. The mixture was heated in a closed flask at 200 °C for 5 h. After cooling the chlorides were hydrolysed with an excess of aqueous HCl 20% and the organic matter was completely recovered by extraction with CH_2Cl_2 . The dichloromethane solution was washed with water, dried over Na_2SO_4 and filtered before recording the spectra after solvent evaporation.

In another run, DAE oil (8.4 g) was stirred in a melt of $AlCl_3/NaCl$ (20.0 and 4.0 g, respectively) at 200 °C for 8 h. The work-up was exactly the same as described for the first run.

Scholl's reaction over the petroleum pitch

The petroleum pitch denominated 'Brea' (2.0 g) was heated at 200–230 °C with a melt of 15.0 g of anhydrous $AlCl_3$ and 3.0 g of NaCl for 4 h. The reaction mixture was poured into an excess of aqueous solution of HCl 20% and hydrolysed under stirring. Then the mixture was filtered under reduced pressure. The black insoluble matter recovered on the filter was washed thoroughly with water and dried in air. The yield was 1.4 g.

Scholl's reaction over petroleum fractions 1 and 2

Each of petroleum fractions 1 or 2 were treated separately (10.5 g each) with 5.6 g of anhydrous $AlCl_3$ and heated 3 h at 200 °C. After hydrolysis of $AlCl_3$ with an excess of aqueous HCl 20%, the organic part of the reaction mixture was extracted using CH_2Cl_2 . The solubility in this solvent was complete in both cases. The extracts were washed several times with water, separated from the water phase with a separatory funnel and dried over anhydrous Na_2SO_4 before distilling off the solvent and recording the spectra.

Scholl's reaction over the petroleum fraction BQ-1

The highly viscous oil BQ-1 (30.0 g) was treated with 17.3 g of anhydrous $AlCl_3$ at 180 °C for 6 h. Then the $AlCl_3$ was hydrolysed with an excess of aqueous HCl 20% and the organic fraction was recovered by extraction using CH_2Cl_2 . The organic matter produced after the Scholl reaction was slowly soluble in dichloromethane and part of it did not dissolve at all. The FT-IR spectra and the electronic spectra have only been recorded for the soluble part of the product after evaporation of the solvent.

Spectroscopic investigations

The FT-IR spectra were recorded on a ThermoNicolet FT-IR spectrometer (IR300 model) or on a Perkin-Elmer 1710 spectrometer on thin films of samples between two KBr discs or embedded into KBr pellets. The electronic spectra were recorded in ethanol or again as a thin film over quartz plates on a Shimadzu UV160A spectrophotometer.

Results and discussion

Based on our earlier results where we have shown the interesting spectral analogy between certain heavy petroleum

fractions and the spectra of certain protoplanetary nebulae (Cataldo *et al.* 2002a, b) we have selected a series of petroleum fractions and studied their electronic and infrared spectra. Furthermore, we have systematically chemically modified the petroleum fractions used by treating them with Friedel Crafts catalysts. The treatment implies a polycondensation reaction known as Scholl's reaction (Fieser & Fieser 1967; Hassner & Stumer 1994). With the aid of this reaction we were able to induce the increment of the degree of aromatic content and the degree of polycondensation of the aromatic fraction composing the samples studied.

A typical example of Scholl's reaction is the transformation of 1-phenyl-benz(a)anthracene (having four fused aromatic rings and one phenyl substituent) into dibenzo-(a,1)-pyrene (having six condensed aromatic rings) (Hassner & Stumer 1994).

It is important to state here that Scholl's reaction, which is a reaction using strong Friedel–Crafts catalysts, cannot be considered as a reaction occurring in the organic substrate of the nebulae or in meteorites exactly as we have conducted it in our laboratory. We have used Scholl's reaction to show a principle: the principle that certain organic fractions can increase their aromatic content under certain precise circumstances. Since we cannot use geological timescales in our work, we have used the Scholl's reaction to demonstrate a principle. However, it is known to any clever organic geochemist (and this is also very clearly explained and written in the books by Durand 1980 and Van Krevelen 1993) that the simple thermal processing of organic matter for instance at only 200 °C or lower temperatures but over geological times produces a gradual polycondensation reaction of the organic substrate which in the end yields kerogen, coal and petroleum. The gradual polycondensation reaction is usually represented by an increase of the aromatic content of the sedimentary organic matter as measured by infrared, C-NMR or ESR spectroscopy, or as indicated by the elemental H/C and O/C ratios plotted in a Van Krevelen diagram. Usually, the higher the burial depth and the permanence in these conditions are, which favour the metamorphism of the organic substrate, the higher the aromatic fraction of the matter (Durand 1980; Van Krevelen 1993). Furthermore, the rocks in touch with the organic matter may act as catalysts for the polycondensation reactions and hence may accelerate the process of the increase in aromatic content of the organic matter. This aspect has already been discussed by Hayatsu & Anders (1981).

IR spectral evolution after DAE structure modification through Scholl's reaction. A comparison with the emission spectrum of the protoplanetary nebula IRAS 22272 + 5435

DAE oil has been studied in detail in our previous works and we have shown the good match between its infrared spectrum and the emission spectra of certain protoplanetary nebulae (Cataldo *et al.* 2002a, b). Here we show that its further aromatization through Scholl's reaction leads to a better match with the PPNe spectrum considered.

The spectrum of DAE is shown in Fig. 1(a) and it is characterized by the four bands due to the out-of-plane aromatic

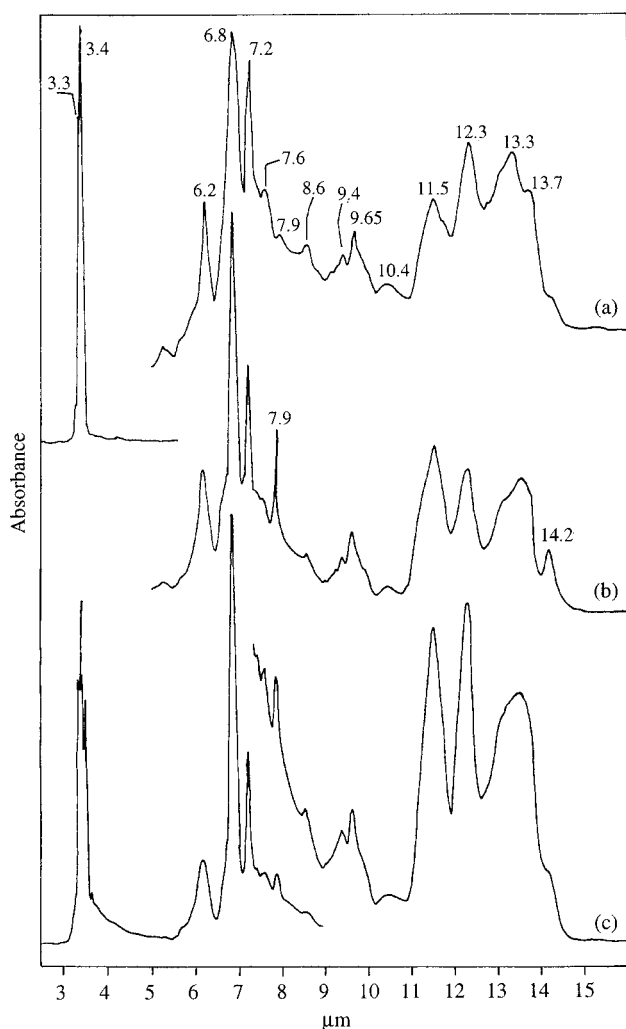


Fig. 1. FT-IR spectra. (a) Petroleum fraction known as DAE (see the text for further details). The spectrum is from a pristine sample. (b) DAE modified after the treatment with NaCl-AlCl_3 . The higher degree of aromatic content and the higher degree of benzene ring polycondensation in comparison with pristine DAE can be deduced by the increased intensity of the bands at 11.5 and 12.3 μm and reduced intensity of the band at about 13.5 μm . (c) DAE modified after the treatment with $\text{ZrCl}_4\text{-AlCl}_3$. The same comments as for spectrum (b) follow.

C—H wagging bands at 11.5, 12.3, 13.3 and 13.7 μm . The band at 11.5 μm suggests a high degree of substitution of the aryl ring so that only a lone H atom remains attached to the ring. The band at 12.3 μm suggests the presence of two to three adjacent H atoms attached to the ring. The bands at 13.3 and 13.7 μm both suggest four adjacent hydrogen atoms attached to the ring. The aromatic character of DAE is further suggested by the 3.3 μm band (an aromatic C—H stretching band), by the aromatic ring ‘quadrant’ stretching at 6.2 μm and ring ‘semicircle’ stretching at 6.8 μm (Reynaud *et al.* 2001).

The aliphatic or cycloaliphatic character of DAE is underlined by the presence of the 3.4 μm band as well as the aliphatic bending at 7.2 μm and the olefinic wagging at 10.4 μm (Reynaud *et al.* 2001).

Fig. 1(b) shows the changes of the DAE spectrum induced by a treatment with $\text{AlCl}_3/\text{NaCl}$ catalyst. The band at 11.5 μm (a lone H atom on a benzene ring) shows a significant increase in intensity, while bands at about 13.3 μm (four adjacent H atoms in a ring) and the aliphatic band at 7.2 μm appear much weaker. Therefore, there was an increase in the degree of polycondensation as suggested by new band at 14.2 μm , which can be assigned to three-substituted benzene rings.

The treatment of DAE with a $\text{ZrCl}_4\text{-AlCl}_3$ catalyst (see Fig. 1c) causes the growth of the bands at 11.5 and 12.3 μm with the simultaneous reduction of the band due to the four adjacent H atoms, suggesting again an increase in the degree of polycondensation of the benzene rings. The band at 7.2 μm appears significantly smaller than the aromatic band at 6.8 μm , in agreement with this interpretation.

The spectrum of Fig. 1(c) should be compared with the spectrum recorded from the protoplanetary nebula IRAS 22272 + 5435 (taken from Reynaud *et al.* 2001) and shown in Fig. 2. The spectrum of the nebula is dominated by the intense bands at 6.2 and 6.8 μm due to the aromatic ring stretching and by the very intense bands at 11.3 and 12.2 μm caused by the C—H wagging of aromatic compounds having numerous condensed benzene rings. The bands at 13.3 and 14.3 μm due to highly hydrogenated rings appear weak. The general analogy of Fig. 2 with the spectrum of DAE oil after Scholl’s reaction shown in Fig. 1(c) is impressive, suggesting both the aromatic nature of the material present in the protoplanetary nebula and even a general complex chemical structure similar to that of the modified DAE oil.

The spectrum of a petroleum pitch and its chemical modification through Scholl’s reaction. A comparison with the UIBs

The distillation of the bituminous residues produced from the petroleum refinement processes leaves a residue, which is known as petroleum pitch. The petroleum pitch used in this work had a softening point of 97 °C and was able to give a good yield in petroleum coke when heated in a close cup. The FT-IR spectrum of the pitch used in this work is shown in Fig. 3(a). The petroleum pitch usually has a fraction that is insoluble in toluene and a higher fraction that is insoluble in petroleum ether. In order to study the spectrum of the precipitated fraction in comparison with the pristine pitch, we have dissolved 10 g of pitch in 80 ml of toluene. After the separation of the insoluble fraction we precipitated the solubilized pitch by adding an excess of acetone. The precipitated pitch was recovered by filtration. The spectrum of the pitch recovered after the precipitation is shown in Fig. 3(b) in comparison with the FT-IR spectrum of the raw pitch (Fig. 3a). We can observe that the differences are minor and involve an higher intensity for the bands at 6.2 and 11.4 μm , suggesting a slight enrichment in the aromatic content.

The treatment of the petroleum pitch with a Friedel–Crafts catalyst leads to profound changes in the chemical structure. The FT-IR spectrum of the treated pitch is shown in Fig. 3(c). The small band at 14.2 μm of Fig. 3(a) disappeared completely and simultaneously the band at 13.5 μm due to four

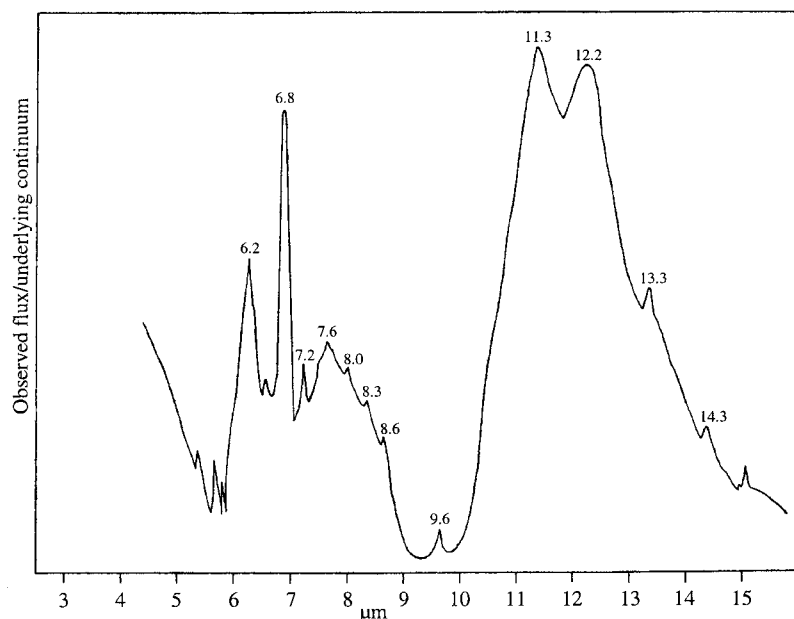


Fig. 2. Infrared emission spectrum. Protoplanetary nebula IRAS 22272 + 5435 (taken from Reynaud *et al.* 2001).

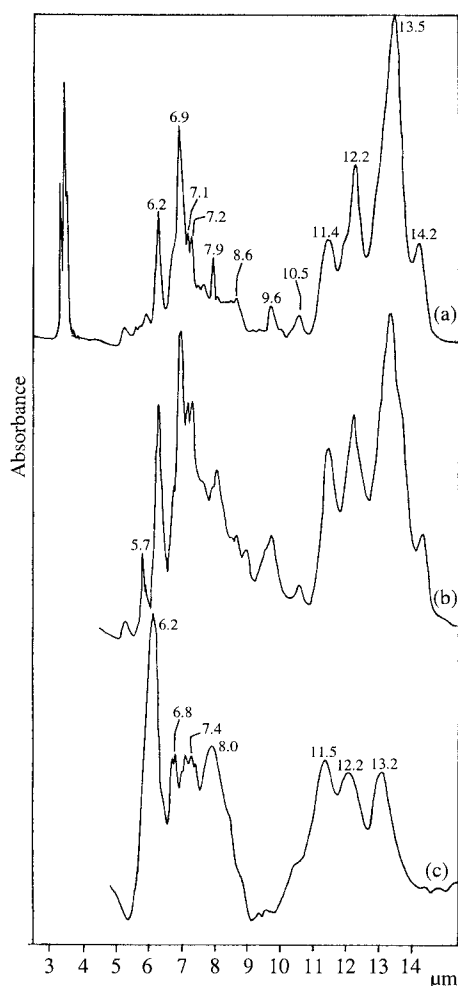


Fig. 3. FT-IR spectra. (a) Neat petroleum pitch. (b) Petroleum pitch after precipitation in acetone. (c) Petroleum pitch after a polycondensation reaction with $\text{AlCl}_3\text{-NaCl}$.

adjacent H atoms in the benzene ring has also undergone a drastic reduction, now being as intense as the band at 12.2 μm . The band at 11.5 μm appears the most intense. In contrast to the modified DAE spectrum of Fig. 1(c), the spectrum of the modified petroleum pitch of Fig. 3(c) is characterized by an intense peak at 6.2 μm rather than at 6.8–6.9 μm . Both peaks are due to aromatic stretching and the difference in intensity is due to a different geometric condensation of the benzene rings caused by Scholl's reaction. By comparing the spectrum of Fig. 3(c) with that of the protoplanetary nebula (Fig. 2), we can affirm that the best match is provided by the spectrum of modified DAE rather than by the modified pitch. On the other hand, the modified pitch shows a series of bands that are more in line with the typical UIB bands: 3.3, 6.2, 7.7, 8.6, 11.3, 12.7 μm . All the mentioned bands are present in the spectrum of Fig. 3(c) with the exclusion of the band at 8.6 μm , which appears as a shoulder only.

Concerning the gradual modification of different petroleum fractions through Scholl's reaction

As reported in the experimental section, we have selected two petroleum fractions that are liquid at room temperature and rich in PAH content: fractions 1 and 2. As described in the experimental section fraction 1 was richer in smaller PAHs than fraction 2.

The distillation curves of these two fractions are shown in Fig. 4. Fraction 1 consists of more volatile components than fraction 2, distilling in the large part between 175 and 220 $^\circ\text{C}$. Conversely, fraction 2 contains less volatile components, 80 % of them distilling at temperatures above 200 $^\circ\text{C}$. About 10 % of them distill above 300 $^\circ\text{C}$. Thus, fraction 2 contains higher molecular weight components than fraction 1, with PAH having a greater number of condensed rings (on average) in comparison with fraction 1.

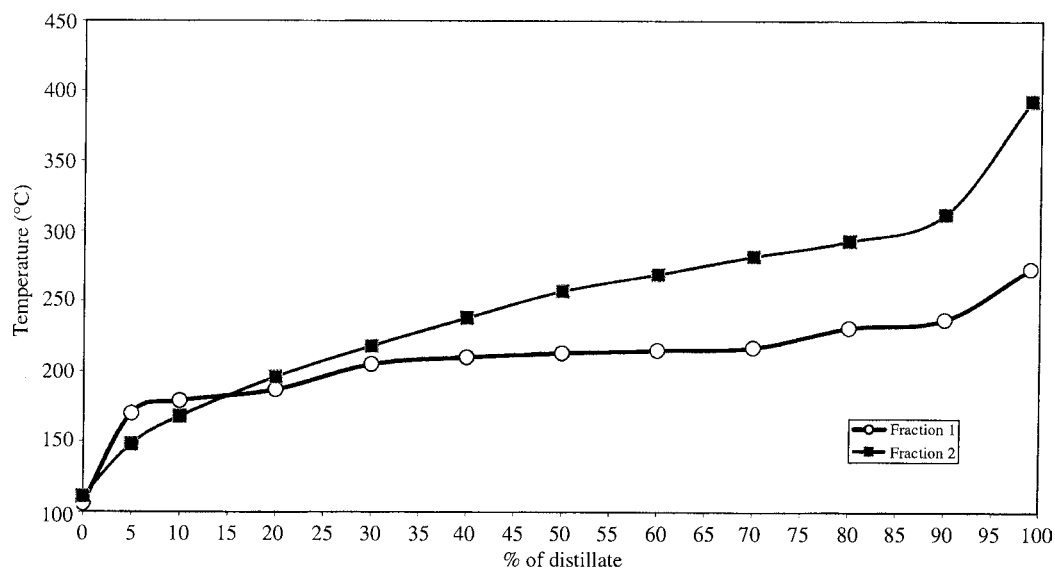


Fig. 4. Distillation curves Petroleum fraction no. 1; petroleum fraction no. 2.

This is illustrated in Fig. 5 where the electronic spectra of the two fractions in ethanol are compared with raw DAE oil. The series of shoulders at longer wavelengths in Fig. 4 are due to a mixture of PAHs. The longer the wavelength of the peaks is the larger the PAH contained. Based on these spectra we can easily make the deduction that the largest PAH (in terms of the number of condensed rings) are contained in DAE oil (see our discussion in a previous work: Cataldo *et al.* 2002a), followed by fraction 2 and then by fraction 1. We also used another heavy petroleum fraction called BQ-1, having a high C/H ratio, the electronic spectrum of which is not shown in Fig. 5.

Fig. 6(a) shows the FT-IR spectrum of fraction 1; in the aromatic bending region we can already distinguish at least six bands at 12.3, 12.7, 13.0, 13.4, 13.9 and 14.3 μm , respectively, in agreement with its nature as a complex mixture of different aromatic compounds. The treatment of fraction 1 by Scholl's reaction causes several changes in the aromatic bending region of the spectrum. The band at 12.7 μm is reduced in intensity; the absorption bands at 13.2 and 13.9 μm are no longer detectable, while a new broad band appears at 11.4 μm (see Fig. 6b). All of this is consistent with the success of the condensation reaction. If we compare Figs 6(b) and (c), we can see that the two spectra are very similar with the exclusion of the band at 13.0 μm , which in Fig. 6(b) appears buried. This means that Scholl's reaction has transformed fraction 1 into fraction 2 or, which is the same, has increased the degree of condensation of the benzene rings. If we now treat fraction 2 with the Friedel-Crafts catalyst, the spectrum of Fig. 6(d) is obtained, showing that fraction 2 has been transformed into the same product derived from the polycondensation of DAE. To observe this, compare Fig. 6(d) with Fig. 1(b), which refers to the modified DAE. The similarity of the spectra is striking. In both spectra we observe the bands at 6.2, 6.9, 7.2, 11.5, 12.3, 13.4 and 14.3 μm with the same intensity ratios. Only the band at 7.9 is more pronounced in Fig. 1(b) compared with Fig. 6(d).

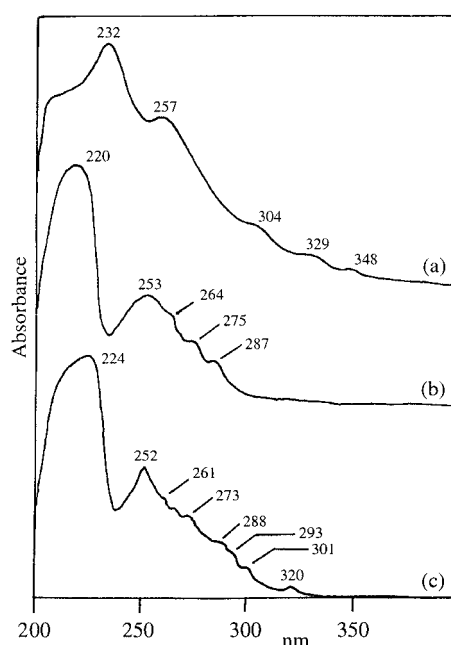


Fig. 5. Electronic spectra in ethanol. (a) DAE petroleum fraction. (b) Petroleum fraction named 'fraction 1'. (c) Petroleum fraction named 'fraction 2'.

The spectrum of the pristine BQ-1 fraction (Fig. 6e) appears somewhat peculiar but in certain instances resembles more the spectrum of fraction 1 after Scholl's treatment (compare spectrum 6e with 6b). In any case, Scholl's treatment of BQ-1 also transforms this fraction into a highly aromatic product, for which the FT-IR spectrum (Fig. 6f) is completely analogous to the spectrum of modified Fraction 2 (Fig. 6d) and modified DAE (Fig. 1b).

Hence, in this section, we have shown that by a careful selection of the petroleum fractions and by the use of Scholl's reaction it is possible to gradually increase the aromatic content of the petroleum fractions, i.e. the degree of condensation

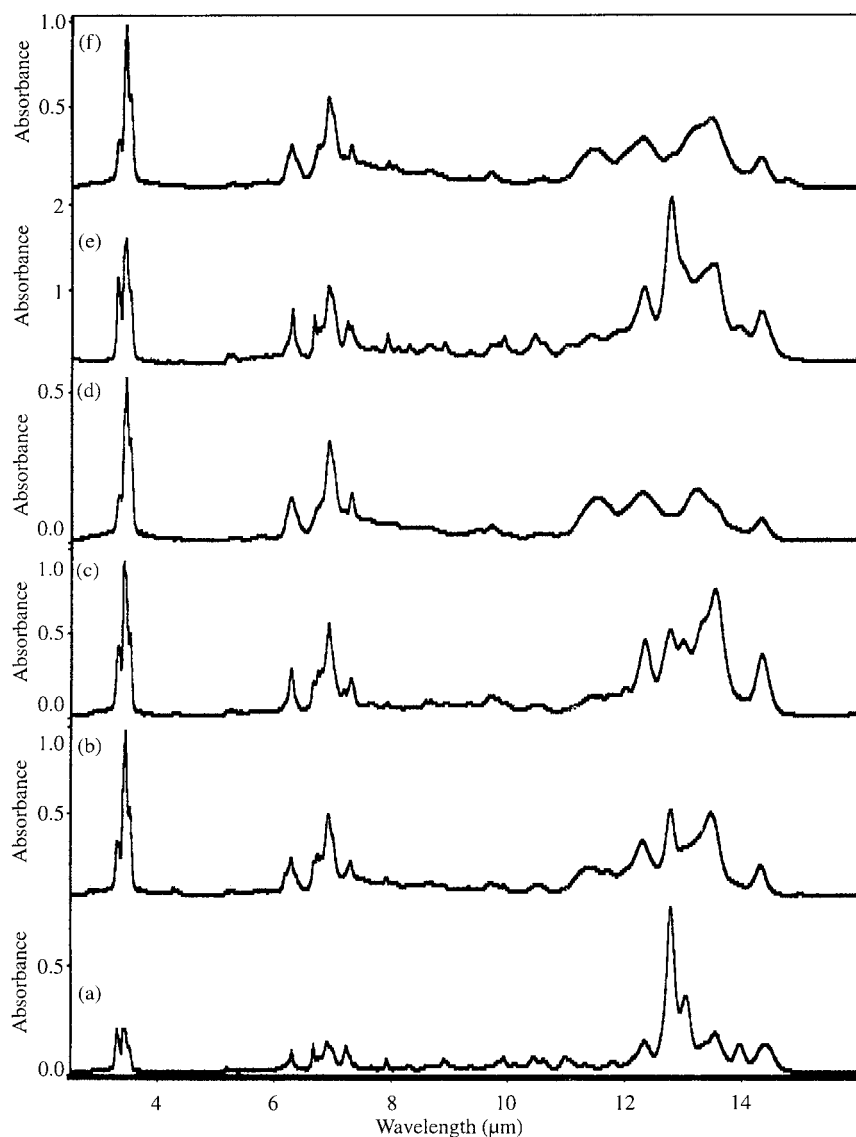


Fig. 6. FT-IR spectra. (a) Petroleum fraction no. 1, pristine. (b) Petroleum fraction no. 1 after Scholl's reaction (increased aromatic content versus a). (c) Petroleum fraction no. 2, pristine. (d) Petroleum fraction no. 2 after Scholl's reaction (increased aromatic content versus c). (e) Petroleum fraction BQ-1, pristine. (f) Petroleum fraction BQ-1 after Scholl's reaction (increased aromatic content versus e).

of the benzene rings. The consequent spectral evolution has been recorded accordingly. Schematically we can summarize the following (each arrow implies a Scholl's reaction):

DAE \rightarrow modified DAE

fraction 1 \rightarrow fraction 2 (=modified fraction 1)
 \rightarrow modified fraction 2 (=DAE)

fraction 1 \rightarrow BQ-1 (=modified fraction 1)
 \rightarrow modified BQ-1 (=DAE).

Thus,

DAE=modified fraction 2=modified BQ-1.

DAE oil fraction is simply the natural end product of a series of polycondensation reactions occurring in 'lighter'

petroleum fractions ('lighter' in the sense of having lower aromaticity).

*Infrared spectral evolution towards coalification:
 a comparison of coal and kerogen spectra*

In the preceding sections we have shown that different petroleum fractions having a different origin and a different degree of aromatic content can converge to a more or less unique final product characterized by having three or four IR absorption bands in the spectral window where the aromatic C—H wagging mode appears. This final product resembles DAE in composition. In the case of DAE, we have shown that its modification through Scholl's reaction increases the absorption bands at 11.6 and 12.3 μm and reduces the bands at 13.4 and 14.3 μm . The resulting spectrum is able to match the emission spectrum of a protoplanetary nebula.

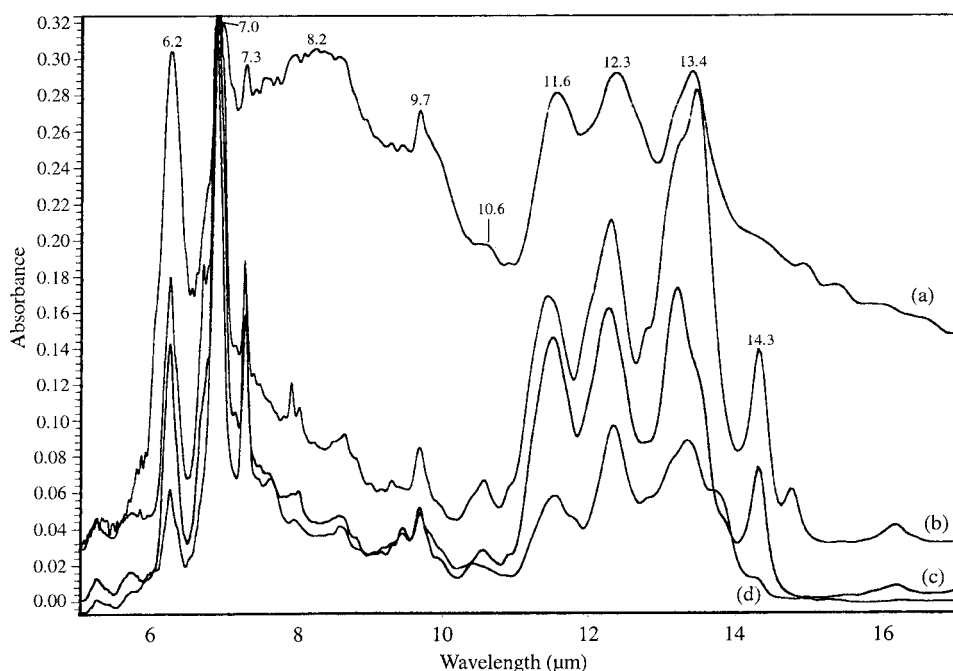


Fig. 7. FT-IR spectra. (a) Coal (anthracite); (b) petroleum fraction BQ-1 after Scholl's reaction; (c) petroleum fraction no. 2 after Scholl's reaction; (d) DAE petroleum fraction.

Figure 7 illustrates the concept that the final product of the aromatization process of all the petroleum fractions treated with a Friedel–Crafts catalyst is a DAE oil. In fact, in Fig. 7 we can observe the strict spectral analogy between the DAE spectrum (Fig. 7d) and the spectra of the aromatized fraction 2 (Fig. 7c) and BQ-1 (Fig. 7b) fractions. The spectral similitude appears to be striking for all the key absorption bands but especially for three absorption bands in the aromatic wagging region at 12.3 and at 13.4 μm . The unique difference is the peak at 14.3 μm , which is more intense for the modified fraction 2 and BQ-1 in comparison with DAE.

Another interesting aspect shown in Fig. 7 is the fact that the band pattern of a high-rank coal (Fig. 7a) is practically the same as the band pattern of the modified petroleum fractions just discussed (cf. Figs 7a and b–d). The best match is offered by the DAE oil (cf. Figs 7d and a). This spectral similarity of course does not imply that coal has exactly the same chemical structure as DAE for instance. In fact, we know that coal is a high molecular weight polymeric material with a structure of aromatic ‘clusters’ connected with aliphatic, heteroatomic and cycloaliphatic bridges (Van Krevelen 1993). The high molecular weight of coal derives from its highly crosslinked nature, which makes it insoluble in all common solvents. From this specific behaviour, coal can be defined as a kerogen. On the other hand, DAE oil is made by a mixture of different molecules but its average molecular weight is low, around 1000 dalton and its average chemical structure is that of a polycyclic aromatic compound with naphtenic and aliphatic attachments. In a previous work we have given detailed accounts concerning the chemical structure of the DAE petroleum fraction, using the concept of ‘average molecular structure’ (Cataldo *et al.* 2002a, b).

Despite these neat differences, the IR spectra of DAE and of coal are very similar. A further interesting observation concerns the IR spectrum of a kerogen. Certain natural kerogen types having a high aromatic content show the same spectrum as coal and hence as DAE (Durand 1980). Similarly, some natural bitumens with an adequate degree of aromatic level again show the same spectra as Fig. 7. If we look into the work of Moroz *et al.* (1998), we can see that gilsonite (asphaltite), kerite and certain anthraxolite show infrared spectra which, at least in the aromatic wagging spectral window, resemble the spectra of coal or the modified petroleum fractions. Again, natural kerogen and bitumens do not have the same chemical structure as coal, but they have some similarities and in practice these classes of materials represent an earlier stage towards the complete coalification process. This specific aspect of coalification is treated very well in the books by Van Krevelen (1993) and Durand (1980).

Coal, and more precisely anthracite coal, has been proposed as a component of interstellar carbon dust (Guillois *et al.* 1999), and as the carrier of the UIBs but in the light of the present spectroscopic results, highly aromatic petroleum fractions and to a lesser extent certain kerogen/bitumens can also be considered as other possible candidates in place of coal.

The UIBs are observed in emission spectra from a large variety of astronomical objects and for this reason are considered to be essentially ubiquitous. The main bands appear at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm . These bands are attributed to polycyclic aromatic compounds both because they match the general band pattern of PAHs and 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 single-photon absorption. The PAH hypothesis is now generally accepted and the most favoured one, although some criticism has been reported against it (see Reynaud *et al.* 2001) on the grounds that:

- no pure PAH or PAH gas mixture has been found to reproduce convincingly the UIBs spectrum found so far;
- the Infrared Space Observatory (ISO) has shown that the UIBs are almost identical even in very different emission sources irrespective of the intensity and the preponderant 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 ultraviolet radiation.

The most interesting alternative to the PAH hypothesis is that the UIBs derive from the excitation of a carbonaceous amorphous solid such as coal. In particular, anthracite, a type of natural coal with a high aromatic content.

However, the coal hypothesis has drawbacks of its own. In fact, coal is a semiconductor with a small band gap and hence can exhibit a strong electronic continuum in the near infrared, which is not observable in the interstellar spectrum.

Conversely, as already stated in our previous work (Cataldo *et al.* 2002a, b), icy high aromatic petroleum fractions may be the real carriers thanks also to their low molecular weight. In fact, the molecular weight of these fractions is small enough to allow the single-photon heating process, which is somewhat problematic with coal and furthermore the petroleum fractions will not exhibit the problems linked to a continuum spectrum in the near-infrared (see the next paragraph). In other words, by using the high aromatic petroleum fractions as a model we are just extending the PAH hypothesis and we are moving to new model compounds where we have a mixture of PAHs, with a large part of them being also alkylated or containing naphthenic rings. The processes that lead to the formation of the petroleum fractions in the dense molecular clouds and in the protoplanetary nebulae are the same as those already postulated for the formation of PAHs or other abiotic processes which we have discussed briefly in previous works (Cataldo *et al.* 2002a, b). The mixing of different chemical species leads to the formation of compounds analogous to the aromatic petroleum fractions. Once the organic fractions analogous to the petroleum fractions studied in this work are incorporated in comets and meteorites in the solar nebula, they are gradually transformed into the meteoritic kerogen under the continuous action of the solar and cosmic radiation and under the possible effects of heating and cooling cycles.

Some notes on the electronic spectra

In the previous section we have also mentioned the importance of the spectrum in the ultraviolet, visible and near-infrared of the matter that could be a possible candidate as the carrier of the UIBs. The solid-state electronic spectrum of pristine DAE on a quartz support is shown in Fig. 8(a). It is characterized by a maximum at 238 nm, a value which

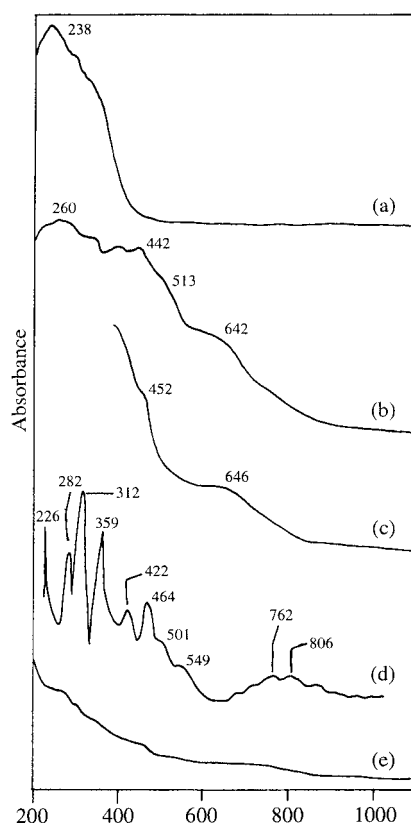


Fig. 8. Electronic spectra (thin films on a quartz substrate). (a) DAE petroleum fraction; (b) petroleum fraction no. 1 after Scholl's reaction; (c) petroleum fraction no. 2 after Scholl's reaction; (d) petroleum fraction BQ-1 after Scholl's reaction (first derivative of spectrum e); (e) petroleum fraction BQ-1 after Scholl's reaction.

recalls that we have measured on industrial carbon black in an attempt to simulate the diffuse interstellar bands (DIBs) bump at 217.5 nm and to verify whether the carbon dust is the carrier of the mentioned 'bump' (Cataldo 2002). The maximum of absorption we have measured on various types of carbonaceous matter was found localized at 250–265 nm. There are many reasons why we have found that value rather than the expected value, ranging from a 'matrix effect' where the carbon particles were embedded, to the 'clumping' of carbon particles, the degree of hydrogenation of the particles and so on. In fact, today it is believed that the 'bump' of the interstellar extinction of light is due to hydrogenated carbon black dust rather than to raw carbon black dust. In any case, peaks at 240–250 nm have been recorded in some circumstellar shells of late-type stars where carbon dust or organic matter may exist in a less hydrogenated and more graphitized state. The value reported in Fig. 8(a) for DAE also suggests that kerogen grains instead of carbon black could explain the interstellar extinction of light.

Figs 8(b) and (c) refer to modified fractions 1 and 2, respectively. Both spectra have been recorded in the solid state over quartz support. The high aromatic content of these complex organic mixtures causes the shift of the peak at 260 nm and a series of new shoulders at longer wavelength can be observed, for instance at 442, 452, 513, 642 and

646 nm that are consistent with the polycyclic aromatic nature of the compounds studied.

Figs 7(d) and (e) are, respectively, the first derivative and the absorption spectrum of the quartz surface of a modified BQ-1 petroleum fraction. Fig. 7(e) shows that the maximum of absorption of the curve is at a wavelength below 200 nm. However, the first derivative of the absorption curve demonstrates a series of features, the shortest wavelength of which appears at 226 nm. Again, all the spectral features shown by the first derivative of the absorption curve are completely consistent with the polycyclic aromatic nature of the modified BQ-1 petroleum fraction.

It is also interesting to note that despite the IR spectral similarity discussed in Fig. 6 between the various modified petroleum fractions, the electronic spectra are able to demonstrate differences between the products.

Conclusions

We have shown that certain petroleum fractions, especially after a chemical modification made with the scope to increase their aromatic content or the degree of polycondensation of the PAHs, are able to match the spectra of protoplanetary nebulae and also the spectra of the unidentified infrared interstellar bands. Thus, these petroleum fractions can be used as model for the matter present in the interstellar medium or in the protoplanetary nebulae. It has also been discussed that these fractions can be considered to be an even better model than coal. It has also been discussed that the petroleum fractions may be incorporated in carbonaceous meteorites or in cometary nuclei during the evolution of protoplanetary nebulae.

The IR spectra of several pristine and chemically modified petroleum fractions have been presented at different levels of aromatic and PAH content. These spectra can also be used in the identification of the matter present in the chondritic meteorites, and also in the identification of the composition of asteroids and cometary nuclei.

From the astrobiological standpoint it is quite ironic that we are using terrestrial samples derived from sedimentary and

reprocessed organic matter, which in turn has been formed from living organisms to try to understand certain spectral features of interstellar space or the complex organic matter present in meteorites or in comet nuclei.

Acknowledgements

We are deeply indebted to ASI, the Italian Space Agency, Viale Liegi 26, 00198 Rome, Italy for financial support of the present work. Our thanks also go to Repsol, Spain and Dr Mario Esteban Martínez for the samples of petroleum fractions used in the present study.

References

- Cataldo, F. (2002). *Fullerenes Nanotubes Carbon Nanostructures* **10**, 155–170.
- Cataldo, F. & Capitani, D. (1999). *Mater. Chem. Phys.* **59**, 225.
- Cataldo, F. & Pontier-Johnson, M.A. (2002). *Fullerenes Nanotubes Carbon Nanostructures* **10**, 1–14.
- Cataldo, F., Keheyán, Y. & Heymann, D. (2002a). *Int. J. Astrobiol.* **1**, 79.
- Cataldo, F., Keheyán, Y. & Heymann, D. (2002b). *Proc. 2nd Eur. Workshop on Exo/Astrobiology*, Graz, Austria, September 16–19, ESA Publications Division. ESTEC, Noordwijk.
- Durand, B. (1980). *Kerogen. Insoluble Organic Matter from Sedimentary Rocks*. Editions Technip, Paris.
- Guillois, O., Ledoux, G., Nenner, I., Papoular, R. & Reynaud, C. (1999). *Solid Interstellar Matter: the ISO Revolution*, Les Houches Workshop, February 2–6, 1998, Lecture 7, eds D'Endecourt, L., Joblin, C. & Jones, A. Springer-Verlag, Berlin, Germany and EDP Science, Les Ulis.
- Fieser, L.F. & Fieser, M. (1967). *Reagents for Organic Synthesis*, pp. 1027–1029. Wiley, New York.
- Hayatsu, R. & Anders, E. (1981). *Topics Current Chem.* **99**, 1–37.
- Hassner, A. & Stumer, C. (1994). *Organic Syntheses Based on Name Reactions and Unnamed Reactions*, p. 336. Elsevier, Amsterdam.
- Kress, M.E. & Tielens, A.G.G.M. (2001). *Meteoritics Planet. Sci.* **36**, 75–91.
- Lipschutz, M.E. & Schultz, L. (1999). *Encyclopedia of the Solar System*, pp. 629–671. eds Weissmann, P.R., McFadden, L.A. & Johnson, T.V. Academic, San Diego, CA.
- Moroz, L.V., Arnold, G., Korochantsev, A.V. & Wasch, R. (1998). *Icarus* **134**, 253–268.
- Reynaud, C., Guillois, O., Herlin-Boime, N., Rouzard, J.N., Galvez, A., Clinard, C., Balanzat, E. & Ramillon, J.M. (2001). *Spectrochim. Acta* **A57**, 797–814.
- Van Krevelen, D.W. (1993). *Coal. Typology, Physics, Chemistry and Constitution*, 3rd edn, Chapter 20. Elsevier, Amsterdam.