On the carbonaceous carriers of infrared plateau and continuum emission

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ABSTRACT

This study explores the molecular origins of plateaus and continua underlying the infrared and far-infrared (far-IR) bands emitted by compact nebulae, especially protoplanetary nebulae. Computational organic chemistry codes are used to deliver the vibrational integrated band intensities of various large, typical carbonaceous structures. These spectra are composed of a rather continuous distribution of weak modes from which emerge the fingerprints. The 6–18 μm region is interspersed with a great many weak lines, to which the plateaus are assigned. Similarly, the far-IR spectrum is ascribed to the phonon (skeletal) spectrum which is readily identified beyond 18 μm.

The absorptivities and absorption cross-sections per interstellar H atom deduced from these spectra are comparable with those of laboratory dust analogues and astronomical measurements, respectively. Moreover, the 5–35 μm spectra of two typical protoplanetary nebulae were reasonably well simulated with combinations of molecules containing functional groups which carry the 21- and 30-μm bands, and molecules devoid of these but carrying strong phonon spectra.

These results may help understand the emergence of plateaus, the origin of continua underlying far-IR bands, as well as the composition of circumstellar dust.

Key words: astrochemistry – dust, extinction – ISM: lines and bands – planetary nebulae: general.

1 INTRODUCTION

In a recent publication, Kwok & Zhang (2011) analysed the infrared (IR) spectra of three typical nebulae: a protoplanetary nebula (PPN), a PN and an H II region. They found that a general and meaningful decomposition of these spectra can be made into (atomic) lines, (molecular) bands, plateaus (underlying bands in spectral regions where their density is high) and one or more continua underlying all. Following Kahanpää et al. (2003), they suggested, on the basis of their analysis of spectral archives, that plateaus and continua might somehow be linked to bands through a physical relationship. They went on to surmise that amorphous organic solids with mixed aromatic–aliphatic structure are good candidate carriers.

Many unidentified IR band (UIB) sources are also known to emit an underlying continuum starting around 6 μm and rising beyond (see, for instance, Smith et al. 2007), which cannot be assigned to the central star, nor to thermal silicate dust.

The purpose of the present work is to determine the nature of the relationship, if any, between bands, plateaus and continua. More precisely we seek to determine if the underlying plateaus and continua, or part of them, can be due to the same structure that carries the bands. Kwok, Volk & Bernath (2001) addressed the plateau problem long ago, and attributed this phenomenon to a complex collection of alkane and alkene side chains. It is argued below that aliphatic carriers are not the sole origin of plateaus, which also occur in more ‘aromatic environments’, like PNe and photodissociation regions (see Kwok & Zhang 2011).

There is a natural tendency to associate preferentially lines and bands with atoms and molecules, on one hand, and continua with solid grains, on the other hand. However, where is the limit between grains and large molecules? Li & Draine (2012) aptly suggested that large molecules, ultrasmall grains and very small grains be considered as synonymous terms. They also set an upper size limit at 0.025 μm for ‘very small grains’ (including polycyclic aromatic hydrocarbons) for which they computed stochastic heating, larger sizes being the domain of ‘grains’ (including ‘classical grains’). In space, however, dust granules evolve into atoms and molecules and vice versa, depending on the environment. Besides, the carriers of the UIBs are known to be relatively large structures essentially made of carbon and hydrogen, while the underlying continuum, too, is most often attributed to some form of hydrogenated carbon (see, for instance, Rouleau & Martin 1991). It is therefore likely that a more or less smooth transition occurs between these types of spectra, being driven by continuous grain size variation.

The fingerprint spectral region of hydrocarbon molecules extends from 3 to about 13 μm. When O, N and S atoms are included in the structure as in kerogens and CHONS [representing the most abundant elements in the interstellar medium (ISM), i.e. H, C, O, N and S], other specific bands emerge below and above that range.
especially strengthened, around 30 μm, by the presence of oxygen
(see Papoular 2000; Grishko & Duley 2002). On the other hand,
the theory of solids teaches that their continuum is associated with
phonons (also called skeletal modes in molecular parlance) which
extend all over the structure, by contrast with the fingerprint features,
whose vibrations are spatially limited to chemical functional
groups. According to Debye (see Rosenberg 1988), the upper limit
of the phonon frequency in crystals is
$$\omega_{\text{ph}} = (6\pi^{2}N^{1/3})^{1/3}v,$$
(1)
where \(N\) is the atomic density of the solid and \(v\) the sound velocity.
Typically, on the Earth, \(N = 10^{23} \text{atoms cm}^{-3}\) and \(v = 2000 \text{m s}^{-1}\),
leading to a Debye wavelength of \(\sim 20 \mu m\), roughly defining a lower
limit to the phonon spectrum. A little or no phonon continuum is
therefore to be expected below this limit. For a finite sample, the
higher wavelength limit is set by the size and shape of the sample
and increases with its size, reaching into the millimetre range.

Moreover, Debye’s elementary theory also shows that the spectral
density of phonons increases as the square of their frequency, i.e.
the maximum density occurs at Debye’s wavelength. The phonon
continuum should therefore overlap prominent PPN bands (21 and
30–35 μm) and perhaps even the redder UIBs.

As shown in the present work, these general results are confirmed
by the modelling of large and complex molecules and so evoke
the possibility that the feature carriers themselves might also be
responsible for at least part of the underlying continuum. This, in
turn, prompts the more general question of the composition of the
continuum carriers.

In the case of oxygen-rich stellar envelopes, no attempt was ever
made to distinguish the 10- and 18-μm peaks from their ‘underlying
continuum’: they are all fitted together with measurements on model
carriers.

In C-rich environments, on the other hand, it is usually agreed
that the continuum is carried by some form of hydrogenated amor-
phous carbon (HAC), while the 11.3-μm feature, if any, is due to
some form of silicon carbide (SiC) both in solid grain form.
The question then arises whether the HAC assignment is not too restric-
tive, as it excludes the likely presence of heteroatoms. In the same
vein, one may wonder if nanosized structures may contribute to the
continuum, as do solid (microsized) grains, and if so, then what
their temperature should be to fit observed spectra.

The problem of the plateau is different, as these are localized in the
fingerprint regions, and are therefore more likely to be linked to
each fingerprint.

On top of these issues, one may question the rationale behind the
modelling of the underlying ‘continuum’ with blackbodies having
a monotonous emissivity (\(\lambda^{-2}\)); indeed, even some HAC materi-
als exhibit far-infrared (far-IR) features on top of their extended
continuum (Grishko et al. 2001).

These issues are best illustrated in compact, luminous nebulae.
PNe are particularly interesting in this respect, as several were
measured up to very long wavelengths (see, for instance, Zhang &
Kwok 1991), thus providing an opportunity to revisit models of the
continuum per se and far beyond the fingerprints.

To tackle these problems, we consider below several carbona-
ceous structures of different sizes and compositions which will be
processed by means of standard molecular modelling algorithms to
deliver absorption and emission spectra, as described in Section 2.
No attempt is made here to model specific astronomical features in
detail. The aim is rather to try and illustrate as best we can the emer-
gence of plateaus and continua which is shown below to be largely
independent, qualitatively speaking, of particular structures. While
these examples of structures that were chosen here are strongly inspi-
red by the kerogen model of UIB carriers developed by Papoular
(2001a, 2010, 2012), many more aromatic carriers, like those pro-
based by Li & Draine (2012), or mixtures of aliphatic and aromatic
organic nanoparticles (proposed by Kwok & Zhang 2011), would
fit as well.

Obviously, electronic absorption is not taken into account in this
study, which is only concerned with atomic and molecular vibra-
tions.

This paper is organized as follows. Absorption spectra of simple
and pure hydrocarbon chains shown in Section 3 illustrate the for-
mation of a phonon spectrum, clearly separated from the usual CH
bands, as the size increases. An HAC model is built in Section 4
by interlinking branched (ramified) chains, increasing the number
of sp² bonds, and adding a small amount of oxygen; this blurs the
boundary between fingerprints and phonons, and gives rise to
features within the phonon range. Finally, Section 5 discusses struc-
tures that were invoked to model UIBs and PN features by analogy
with the constitutive components of kerogens, as suggested by Pa-
poular (2001a, 2011) and Kwok & Zhang (2011): short, branched
or oxygen-bridged alkane chains (–CH₂–), naphthenic chains (linear
chains of benzenic rings) and small, compact, benzenic ring clusters
interconnected with the former. The phonon spectrum is evidenced
in all cases and may extend to several thousands of micrometres in
wavelength. In all cases, bands are found to coexist with plateaus or
continua.

In order to ascertain the relevance of these model outcomes to the
present astronomical issues, in Section 6, the computed spectral
intensities are quantitatively compared, on one hand, with the ab-
sorptivities measured on various laboratory model candidates and,
on the other hand, with the astronomical absorption cross-sections
per H atom measured towards various solar environments.

Finally, in Section 7, the emission spectra of our model carriers
are computed for the case of radiative equilibrium in a strong radi-
ation field, as in compact nebulae. Fits to a couple of astronomical
spectra are displayed and the best-fitting carrier number densities
and temperatures are discussed.

Consequences of these findings are discussed in the Conclusion
section.

2 COMPUTATIONAL METHODS

When studying emission from dust (or big molecules), at least two
opposite generic circumstances must be considered, namely strong
and weak excitation by ambient radiation (or any other process).
In the latter case, which applies mainly to the ISM, the interval
between two successive excitation events is so long that the dust
particle returns to its ground state in between; this case is outside
the scope of the present study, as we are interested here in compact
nebulae. On the other hand, in the first case, energy accumulates in
the particle until it reaches radiative equilibrium, say, at temperature
\(T_{\text{dust}}\); then, the spectral radiance at wavelength \(\lambda\) is that of a grey
body,
$$I_{\lambda} = \alpha(\lambda) d \, \text{BB}(T_{\text{dust}}, \lambda),$$
(2)
where \(\alpha\) is the absorptivity of the material, in cm⁻¹, \(d\) its depth
in cm along the line of sight and BB the blackbody law; the optical
thickness is assumed much smaller than 1. For a solid, \(\alpha\) is a
continuous function of the solid’s dielectric functions or extinction
coefficient, which are also continuous. Molecular spectra, on
the other hand, are discrete line spectra, and \(\alpha\) for a single line

is deduced from the corresponding integrated band absorption, $A$, by

$$
\alpha(\lambda) = 10^2 A(\lambda) \frac{C}{\Delta \nu},
$$

where $\alpha(\lambda)$ is in $\text{cm}^{-1}$, $\Delta \nu$ is the bandwidth ($\text{cm}^{-1}$) and $C$ is the molecular density (molecules $\text{l}^{-1}$) along the line of sight. For one type of structure, equation (2) then translates into

$$
I_\nu = 10^2 A(\lambda) \frac{LC}{\Delta \nu} \text{BB}(T_d, \lambda),
$$

where $L$ is the thickness of the emitting cloud.

To approach a continuous spectrum, it is necessary to consider either very large structures or a large number of smaller, non-identical structures. The latter are computationally more tractable and will be adopted here.

The implementation of the above considerations is based on the use of various algorithms of computational organic chemistry, as embodied in the HyperChem software provided by Hypercube, Inc., and described in detail in their publication HC50-00-03-00 and cursorily, for astrophysical purposes, in Papoular (2001b). Here I use the improved version HyperChem 7.5. While almost all the computations used standard algorithms, some required writing special-purpose subroutines, a capability also provided by the software.

Semi-empirical methods provided by the software (PM3 and AM1, acronyms for Parameterized Model No 3 and Austin Model No 1) were used for molecules up to about 500 atoms in size; their accuracy for spectral frequencies is a few per cent. Anharmonicity is built in the algorithms, in terms of parameters which are tailored by comparison with laboratory experiments on hydrocarbon molecules.

Details of the computation procedure can be found in Papoular (2001b). Briefly, a structure is first sketched on the computer screen. Its geometry is then automatically optimized by minimizing the total potential energy. With semi-empirical simulation methods, it is then possible to launch a normal-mode analysis which delivers the spectrum of integrated absorption bands, $A(\nu)$, at frequency $\nu$. A very useful subroutine allows one to study the characters of each mode individually by displaying on the screen the velocity vector of each atom of the molecule. This velocity field is a powerful tool for distinguishing fingerprints from plateaus or continua.

3 PURE HYDROCARBON CHAINS

A very large number of typical structures were previously analysed (Papoular 2011a), from which some can be selected for the present purposes. If the continuum properties are to be properly highlighted, it is better to start with the simplest possible structure so as to avoid unwanted fingerprints. An example of this is the alkane chain ($-\text{CH}_2-$), a pure hydrocarbon, which is known to be a major constituent of kerogens (see Behar and Vandenbroucke 1986). The only fingerprints are the CH stretching (~3.4 $\mu$m) and CH in plane and out-of-plane (7–13 $\mu$m) vibrations, distinctly separate from the phonon modes. This is illustrated in Fig. 1 which plots the normal-mode spectra of Chain 1, with 53 atoms (17 C, 36 H), Chain 2, obtained by concatenating two identical copies of Chain 1, and Chain 5, obtained by concatenating two identical copies of Chain 2, with 263 atoms (87 C, 176 H). Two other structures were also analysed (but are not represented in Fig. 1): Chain 3, with 206 atoms (68 C, 138 H) and Chain 4, with 257 atoms (85 C, 172 H).

As predicted, the phonon spectrum begins near 18 $\mu$m; it is clearly separated from the fingerprints below; its upper limit increases almost linearly with the chain length. Also, the spectral density of phonons decreases steeply as $\lambda$ increases. For all three structures, the relative number of phonon vibrations is about 21 per cent. In general, these differ from fingerprint modes in that their intensity is weaker, and that each mode extends over the whole structure.

Fig. 2 elaborates on these spectral properties in the typical case of Chain 5. Both the density and the intensity of the modes are represented in three generic spectral windows. The straight line encompassing all three windows is a power law in $\lambda^{-2}$ which illustrates Debye’s law. Remarkably, within the near- and mid-IR bands, the mode densities are well above this line. The shape of a particular band (for instance, the 3.3-$\mu$m band) is determined both by the
mode densities, which peak roughly in the middle, and the mode intensities, which are more dispersed near the middle of the band.

Note the strong dispersion of band intensities, even within a small range of wavelengths. Both within the CH stretchings and the mid-IR fingerprint regions, very weak and very strong bands coexist. However, none is observed between 3.6 and 6 μm, and 13.5 and 17 μm, where there are no phonons. What happens is made clear by visualizing the atomic velocity vectors on the screen: two very close modes of vibration, both involving the same type of functional group, can have so different topologies that in one the vibrational dipole moments add up constructively as they do for a single well-defined chemical group, while in the other they compensate each other more or less. The observed closeness of very strong and very weak lines is characteristic of finite and disorder systems (but forbidden by symmetry in atomic crystals).

This phenomenon holds a clue to the formation of spectral plateaus. Fig. 3 displays histograms of the integrated intensities within each of four characteristic spectral windows around 3.3, 3.4, 8.6 and 20 μm. The abscissa represents successive 0.02 km molecule⁻¹ bins of mode intensity, while the ordinate plots the number of mode counts in each bin. In the three fingerprint windows, the number of counts decreases steeply with increasing intensity; most of the counts correspond to weak intensities. The latter form an almost continuous pedestal from which only a few distinct features protrude, giving the impression of fingerprints sitting upon a ‘plateau’. This phenomenon is easily modelled mathematically by adding up a few strong and many weak Lorentzian profiles, all with a finite width, within a finite interval of frequencies. The inverse process, disentangling the plateau from the protruding fingerprints, is much more difficult to carry out without preconceptions. A mathematical construction of a spectral plateau is only an approximate representation of the distribution of weak vibrational modes.

In the phonon window, the histogram is almost flat and limited to weak intensities. These are responsible for the far-IR continuum, as well as for the plateaus. Here, however, fingerprints are much less frequent. To illustrate the emergence of far-IR fingerprints, a Chain 1b was built from a Chain 1 by replacing one of its CH₂ groups, in the middle, by an O atom (O bridge), a substitution that is likely to occur in space in view of the abundance of the species involved.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{histogram.png}
\caption{(Colour online) Histograms of the integrated intensities within each of four characteristic spectral windows around 3.3 (red squares), 3.4 (green dots), 8.6 (blue triangles) and 20 μm (purple stars), in the spectrum of Fig. 2. The abscissa represents successive 0.02 km molecule⁻¹ bins of mode intensity, while the ordinate plots the number of mode counts in each bin. In the three fingerprint windows, the number of counts decreases steeply with increasing intensity; most of the counts correspond to weak intensities. In the phonon window, the histogram is almost flat and limited to weak intensities.
\end{figure}

It is also known to occur frequently in kerogens, and to enhance the intensity of many other vibrations of the same structure. Its spectrum is shown in Fig. 1(d). The fingerprints now extend below 3 μm and above 13 μm, and far above the phonon edge, especially around 40 μm. Also, note the band intensities, higher by an order of magnitude than those of the previous structures.

The comments made above on the coexistence and meaning of strong and much weaker vibrations within a small frequency range also apply to this structure, around 40 μm and, by extension, to the PPN features.

Even a minute alteration of a given structure (such as subtraction or addition of a –CH₂– group, or a slight bending of the chain) suffices to change all mode frequencies, albeit to a very small extent. None of the computed mode frequencies coincides with any other. A myriad of such structures along a line of sight may indeed mimic a continuum of frequencies, be it a band, a plateau or a phonon continuum. In real particles, this transition to a continuous spectrum is expedited by the anharmonicity of bonds, which couples neighbouring modes and imparts a finite width to each. In the frame of the present treatment, approaching continuity will only become possible after enough similar, but not identical, spectra have been obtained.

In any event, the emergence of embryonic ‘plateaus’ and continua in such simple structures makes one wonder if (all) the continuum underlying a band should be assigned to an altogether different material from the carrier of the band itself, and gives it a temperature of its own. The two may be, at least partially, inseparable.

4 HAC-LIKE STRUCTURES

HAC is a prime carrier candidate for the continuum. Several models of HAC have been proposed (see, for instance, Dischler et al. 1983a; Robertson 1986; Duley 1995; Walters & Newport 1995). By contrast with the previous structures, these are ramified (cross-linked). Most of these models are designed for material science and do not include oxygen. In space, however, the inclusion of oxygen atoms in such structures is highly probable. One of such objects studied in this work, including four oxygen bridges, was built along these lines; it is represented in Fig. 4. Another HAC-like structure was derived from the previous one by replacing all four O atoms with C atoms. These structures are not intended as new materials but, rather, as yet other models of laboratory HAC, used here on the same footing as other types of models to understand the origin of plateaus and continua.

The spectra of both structures are shown in Fig. 5. The gap observed between 14 and 17 μm in the previous spectra is now partially filled. This is due to the higher connectivity of C atoms in this structure, which couples mid- and far-IR modes and gives rise to mixed modes in the gap. Most importantly, the intensities
are increased, on average, by a factor of about 10. As was the case for Chain 1b (Fig. 1), the insertion of oxygen gives rise to several additional high intensity modes from 30 to 100 μm.

5 CHONS OR KEROGEN-LIKE STRUCTURES

More complicated and richer structures, containing some of the most abundant elements in the ISM (H, C, O, N and S), and called CHONS for this reason, have often been proposed as interstellar dust. On the Earth, kerogens are also known to carry these elements, arranged in aromatic structures as well as pentagons, as illustrated in Fig. 6, inspired by the work of Speight (1994). The integrated intensity spectrum of this structure is shown in Fig. 7(a) (ker1). Another, very similar structure was obtained by replacing just one SH group by an H atom (ker2). Its spectrum is plotted in Fig. 7(b).

A larger kerogen-like structure, ker3 (493 atoms), was built by interlinking five identical structures of the type drawn in Fig. 6 (101 atoms). This is the largest structure that could be analysed with semi-empirical methods to give its normal-mode vibrations (1 month computation time). Its spectrum is shown in Fig. 7(c).

Note that these spectra carry the strongest integrated intensities of all the structures studied here. This is an effect of the inclusion of aromatic rings and OH functional groups. The near- and mid-IR fingerprints are prominent in these spectra (see Figs 8 and 9).

6 COMPARISON WITH LABORATORY AND ASTRONOMICAL MEASUREMENTS

For purposes of comparison with laboratory measurements and astronomical observations, the absorption intensity spectra have to be averaged, as they are with any spectrometer having a finite spectral resolution. This is a delicate operation because of their large dispersion mentioned above. It was effected here by first concatenating as many spectra of the same category as are available. Each concatenated spectrum was then broken into three intervals: 3–4, 5–17 and beyond 17 μm, and each was smoothed by adjacent averaging over N points. In each interval, N was chosen so as to smooth the spectrum without erasing the features. As noted earlier, the larger the structure and the larger the number of concatenated spectra of similar structures, the lesser the smoothing necessary.
These averages were then converted into absorptivity curves using equation (3), with a uniform C-atom density of $8.3 \times 10^{22}$ cm$^{-3}$, typical of a solid. As the radiative lifetime of IR vibrations is very long, the bandwidth is more likely determined by the non-radiative lifetime, which, for present purposes, is the relaxation time constant for the vibrational dynamic equilibrium to settle after perturbation of the molecule, and is of the order of 1 ns (Papoular 2006), corresponding to $\Delta \nu = 0.0333$ cm$^{-1}$. The resulting conversion formula is

$$\alpha = 4.2 \times 10^5 \frac{A}{N_C},$$

where $N_C$ is the number of carbon atoms in the selected structure.

The results are shown in Fig. 8 for the three alkane chains of Figs 1(a)–(c) (concatenated spectra), for the HAC-like structures of Fig. 5 (concatenated) and for the kerogen-like structures of Fig. 7 (concatenated).

Also plotted in Fig. 8 are representative results of measurements on black polyethylene (charged with carbon-black pigments at 3 per cent by weight) by Blea et al. (1970), on amorphous hydrocarbon (a-C:H) by Dischler, Bubenzer & Koidl (1983) and on various carbonaceous grains by Mennella, Colangeli & Bussoletti (1995). The values obtained by the latter authors are given in cm$^{-2}$ g$^{-1}$, so they had to be converted into cm$^{-1}$ by multiplying them with the corresponding densities in cm$^{-3}$: 1.8 for benzene burning (BE) HAC BE; 1.5 for Mercier coal; and 2.1 for graphite.

Observe again that the presence of benzenic rings and OH groups in the model structures of Fig. 7 enhances absorbance by a factor of about 10 over that of the pure hydrocarbons of Fig. 5.

We seek now to compare our simulation results with the dust c-ss per H atom deduced from observations by Mezger, Mathis & Panagia (1982). For this purpose, we note that the absorption c-ss of a molecule is linked to its integrated band absorption by

$$\sigma \text{(cm}^2\text{per H atom)} = \frac{A \text{(km mole}^{-1})}{6 \times 10^{18} \Delta \nu \text{(cm}^{-1})},$$

where $n$ is the density of molecules in cm$^{-3}$. Assume also that the mass ratio of dust to hydrogen gas is 1/300, half of which is in carbonaceous dust, the latter entirely consisting of alkane chains.

The cross-section per H atom is then given by

$$\sigma \text{(cm}^2\text{per H atom)} = \frac{A \text{(km mole}^{-1})}{N_C \times 6 \times 10^{18} \times 300 \times 2 \times 12 \times 0.0333}.$$

This is plotted in Fig. 9 for the three alkane chains of Figs 1(a)–(c) (concatenated spectra), for the HAC-like structures of Fig. 5 (concatenated) and for the kerogen-like structures of Fig. 7 (concatenated). For comparison, cross-sections measured by Mezger et al. (1982) towards compact and extended H II regions are plotted on the same graph. Also included are cross-sections deduced by various authors from absorption measurements towards solar neighbourhoods, as compiled by Mezger et al. in their table A1. These results are confirmed, beyond 100 µm, by data from the Planck satellite (see e.g. Abergel et al. 2011).

It appears from Figs 8 and 9 that the absorptivities of kerogen-like model materials, used elsewhere to mimic the UIBs as well as the PPN far-IR features, are strong enough that they may also carry a non-negligible fraction of the observed astronomical far-IR continuum. Recall that $\sigma$ in equation (6) scales like the mass ratio of dust to hydrogen gas. According to recent estimates, the value assumed here for this ratio, 1/300, is only a lower bound. The resulting values of $\sigma$ are therefore conservative estimates.

In both figures, the shape of the curves between 10 and 100 µm is roughly a power law with exponent about 1.5. The levelling off beyond 100 µm is disputable as the density of modes is too weak in that range. Computations of the emission of these structures by monitoring the variations of their dipole moments under perturbation (as elaborated by Papoular 2012) point, rather, to a nearly-constant slope down to 1000 µm and beyond.

Note that while graphite is a very efficient continuum carrier, it can hardly be invoked in the present instance, for it has never been identified, nor is it likely to form, in circumstellar environments.

7 EMISSION SPECTRA

We have still to confront the model emission spectra with astronomical ones. For this purpose, we select two spectra of PPNs (IRAS 22330+6147 and 22574+6609), exhibiting prominent 21- and 30-µm features, which were obtained by Zhang, Kwok & Hrivnak (2010) with the IR spectrometer embarked on the Spitzer satellite. A tentative fit to the conspicuous 21-µm bands in these spectra was previously obtained by Papoular (2011) with a carrier model featuring the thiourea functional group (SC(NH$_2$)$_2$) associated with various carbonaceous structures (mainly compact and linear aromatic clusters). In the same study, it was also found that the equally conspicuous 30-µm band could be modelled by a combination of aliphatic chains made of CH$_2$ groups, oxygen bridges and OH functional groups. The concatenation of the spectra of all these structures gave the band spectrum reproduced in Fig. 10 from fig. 11 of the cited paper.

In order to fit the spectrum of a PPN, it was necessary to associate the band emissions with the emissions of two grey bodies having different temperatures, and absorptivities scaling like $\lambda^{-2}$. The only difference between the procedure followed in the paper just cited and the one used here is that, here, the grey bodies are replaced by tailored combinations of the three groups of structures described in Sections 3–5 above, and designated hereafter by ‘dust’ or ‘continuum model carriers’: (a) the three alkane chains of Figs 1(a)–(c) (concatenated spectra); (b) the HAC-like structures of Fig. 5

\[ \sigma (\text{cm}^2\text{per H atom}) = \frac{A \text{(km mole}^{-1})}{N_C \times 6 \times 10^{18} \times 300 \times 2 \times 12 \times 0.0333} = \frac{A \text{(km mole}^{-1})}{1.44 \times 10^{21} N_C}. \]
Figure 10. The smoothed integrated intensity spectrum resulting from the concatenation of the spectral lines of thiourea and thiourea derivatives with compact aromatics, thiourea derivatives with linear aromatics and aliphatic chains with attached OH chemical groups. The 21-µm feature peaks at 20.7 µm; FWHM = 2.3 µm. Note the shoulder at 26 µm, reminiscent of the 26-µm spectral component conjectured by Kwok and collaborators. Adapted from fig. 11 in Papoular (2011).

Table 1. Temperatures and relative compositions of band and continuum model carriers for (1) IRAS 223304+6147 and (2) IRAS 22574+6609. Temperatures are in units of K.

| Name     | (1)  | (2)  |
|----------|------|------|
| T (band) | 170  | 160  |
| T (warm) | 170  | 160  |
| T (cool) | 80   | 110  |
| T (cold) | –    | 60   |
| Band     | 0.018| 0.003|
| Warm dust| 0.008| 0.002|
| Cool dust| 0.974| 0.019|
| Cold dust| –    | 0.976|

(concatenated); and (c) the kerogen-like structures of Fig. 7 (concatenated). In fact, it appeared, ultimately, that the alkane chains did not help because of a strong peak near 13 µm. Neither did the kerogens, because of strong spectral massifs from 25 to 50 µm; these are due to out-of-plane vibrations of the clusters of benzenic rings. Only the HAC-like structures were therefore retained. It was also found that at least two or three different dust temperatures were necessary: warm, cool and cold. The model carriers of the 21- and 30-µm bands were taken from Papoular (2011) and their concatenated spectrum is that of Fig. 10. For the two selected PPNe, Table 1 details the temperatures and relative number densities of band and continuum model carriers. The relative compositions of the latter are the same for all two (or three) temperatures. The standard deviations between the spectrum and fit are, respectively, 0.18 and 0.1 (in the same arbitrary emission units as the ordinates), i.e. less than 10 per cent of the peak emission.

The fact that up to three different dust temperatures had to be invoked while only one temperature was used for the band carriers clearly shows that the dust carriers extend farther from the central star than the band carriers, and that their temperature is therefore distributed continuously over the radial distance.

Obviously, the fits can be improved by tailoring separately the components of dust and band carriers. In particular, the model carriers of the 21- and 30-µm bands are quite distinct (Papoular 2011); other astronomical spectra may therefore require different relative contributions from these components.

8 CONCLUSION

The main outcomes of this work are as follows:

(1) Several generic, aliphatic and aromatic hydrocarbon structures were built by means of molecular modelling codes. Their
vibrational spectra were obtained by normal-mode analysis. The molecules are large enough that their spectra extend up to several thousand micrometres.

(2) The skeletal or phonon modes are clearly identified by the distribution of the atomic velocity vectors in each mode. In all samples, their minimum wavelength is about 18 μm, as predicted by Debye’s law. In spectra of pure hydrocarbons, the phonon region is clearly separated from the mid-IR fingerprints.

(3) In every elementary frequency interval over the spectra, the dispersion of integrated absorption line intensities is considerable: about a factor of 10. This is characteristic of disordered and ‘impure’ structures by contrast with pure, infinite crystals. As the particle size increases and/or as the number of slightly different structures increases along the same line of sight, the ‘weak’ modes in the mid-IR fingerprint regions form plateaus beneath the bands, and a continuum in the phonon region. No continuum is found below 6 μm.

The fact that the same structure carries the fingerprints as well as their underlying plateaus validates the suggestion of Kahanpää et al. (2003) and Kwok & Zhang (2011) referred to in the Introduction. The same structure also carries part of the underlying continuum.

(4) The structures considered here to illustrate and explain the formation of plateaus and continua are inspired from the wide variety of constituents of kerogens taken as a whole. In space they may perhaps be invoked as precursors or the debris of the proposed kerogen-like UIB carriers (Papoular 2011). Nevertheless, the underlying interpretation of plateaus and continua is largely independent of this particular choice.

(5) Intensities all over the spectrum are considerably enhanced by the inclusion of only a few per cent heteroatoms, especially oxygen. The absorptivities of our structures then become comparable to those of candidate model dust materials measured in the laboratory.

(6) Computed absorption cross-sections per H atom in space are compatible with those deduced from extinction measurements in the solar neighbourhood.

(7) Increasing the size of a molecule at constant structure and composition does not change the general characters of its spectrum; only the spectral density of lines increases and the spectrum extends farther into the far-IR. There is a smooth transition between spectra of molecules and grains.

(8) This information was applied to the synthesis of spectra that fit observed PPN spectra. This exercise confirmed that simple carbonaceous structures may well provide at least part of the continuum underlying far-IR features. It also suggested that the temperature of the continuum carriers is continuously distributed rather than limited to one or two specific values.

These results may help understand the emergence of plateaus, the origin of continua underlying far-IR bands, as well as the composition of circumstellar dust.

(9) The same interpretation should be applicable to plateaus and continua underlying the UIBs (3–20 μm). For instance, the slowly rising continuum of the cool dust component, at 80 K, in Fig. 11 is reminiscent of the slowly rising spectrum of NGC 1482 (Smith et al. 2007) or the Orion Bar (Kwok and Zhang 2011). Indeed, UIBs are generally observed in colder, interstellar media, and so both the composition and temperature of the accompanying ‘dust’ should be different from those for the case of PPN. The treatment of this case is outside the scope of the present paper.

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