Infrared emission from hydrogenated amorphous carbon and amorphous carbon grains in the interstellar medium

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ABSTRACT
The correlations deduced by Boulanger et al. from IRAS maps of the Chamaeleon, Taurus and Ursa Major molecular cloud complexes are interpreted in terms of the evolutionary HAC model of interstellar dust. In particular, regions of relatively strong 12-μm emission may be regions where recently accreted carbon is being converted by ambient UV to small PAHs in situ. Regions of weak 12-μm emission are probably quiescent regions where carbon has been annealed to amorphous carbon. Observational consequences of these inferences are briefly described.

Key words: molecular processes – dust, extinction – ISM: molecules – infrared: interstellar: continuum.

1 INTRODUCTION
Boulanger et al. (1990) have analysed IRAS images of the Chamaeleon, Taurus and Ursa Major molecular cloud complexes, and have demonstrated in particular that the emission in the 12-μm band is distributed very differently from that in the 100-μm band. The detailed results of their analysis are listed in Section 2. Boulanger et al. conclude that the variations detected represent real local relative changes in the abundances of the 12-μm and 100-μm carriers. These results represent an important development in the study of the interstellar medium, and place constraints on models of interstellar grains.

Boulanger et al. propose a mechanism to account for the relative-abundance changes. They assume that rapid cycling of large amounts of carbon on to and off grains occurs on a timescale of ~10^5 yr, during which surface carbon, in the form of a volatile molecular anhydrous ice, is photoprocessed to produce organic material. Small organic particles are then assumed to be released to the gas by photodesorption, localized heating, or turbulence, and there they undergo spike heating on the absorption of a UV or visible photon, cooling by the emission of mid-IR photons.

Our understanding of the nature of interstellar dust continues to develop as new observations reveal further details. In Section 3, we discuss recent data on the IR emission features and we show that there exist – as assumed by Boulanger et al. – that the chemical nature of dust varies from place to place reflecting the local conditions. In Section 4 we discuss IR HAC emission, and in Section 5 we indicate how carbonaceous grains, containing both hydrogenated amorphous carbon (HAC) and amorphous carbon (αC), may account for the observations of Boulanger et al., and we discuss briefly the implications of this interpretation.

2 OBSERVATIONAL RESULTS
The principal results of Boulanger et al. (1990) are concerned with IRAS intensities I at 12 and 100 μm:

(i) the colour R(12,100) = I(12)/I(100) varies by more than an order of magnitude in each cloud complex, with values ranging from 5 to 0.25 × the average value in the solar neighbourhood;
(ii) colour variations are seen on all scales, from several parsecs to ~0.1 pc;
(iii) no significant variations are seen in I(100)/A_V between clouds of widely differing IR colour;
(iv) there is a marginal dependence of R(12,100) on gas velocity (cf. Heiles, Reach & Koo 1988);
(v) the average colours R(12,100), R(25,100) for the three complexes coincide with the average colours for the solar neighbourhood, despite the variations described in (i);
(vi) there is a possible systematic decrease of R(12,100) with I(100), with a scatter of a factor ~3±1 in R about this trend;
(vii) the largest R(12,100) values are found at low I(100);
(viii) there are examples of positions without detectable 12-μm emission at all values of I(100);
(ix) I(12) and I(25) are constrained so that the scatter in R(12,25) is about a factor of 2, one order of magnitude smaller than the scatter in R(12,100);
(x) R(60,100) colours show considerable scatter, comparable to that for R(12,100).
3 INTERSTELLAR DUST

It is generally accepted that diffuse cloud dust consists mainly of amorphous silicate and carbonaceous materials. Aromatic (sp² bonding) carbonaceous matter is certainly responsible for the emission features at 3.3, 6.2, 7.7, 8.6 and 11.3 μm, though whether the material is in free-flying polycyclic aromatic hydrocarbons (PAHs) or present as a solid is currently uncertain. The free-flying PAH hypothesis has been critically assessed by several authors (cf. Salisbury et al. 1988; Donn, Allen & Khanna 1989). No PAH spectrum has yet been found which fits the observed emission features (Sakata et al. 1990), whereas Duley & Jones (1990) have shown that the small PAHs naphthalene and anthracene, dispersed in a matrix, provide a satisfactory match. PAHs dispersed in an aliphatic polymeric matrix is a good description of HAC. Flickinger, Wdowiak & Gómez (1991) conclude from a comparison of laboratory and astronomical line profiles that the PAHs responsible for the 3.3-μm emission feature may be condensed rather than free-flying. Condensed PAHs would be a description of HAC/αC with high sp²:sp³ ratio. Tokunaga et al. (1991) made high-resolution studies of the 3.3-μm feature in a number of astronomical sources. They found two types of profile: Type 1 is found in planetary nebulae and H II regions, peaks at a wavelength of $\lambda = 3.289$ μm and is relatively broad; Type 2 is rarer, occurs towards stellar sources, peaks at a wavelength of $\lambda = 3.296$ μm and is relatively narrow. Amorphous aromatic materials and heated PAHs appear to provide the best fits. The result of Tokunaga et al. may be interpreted (following Flickinger et al. 1991) by assuming that broad profiles arise from a wide range of condensed PAHs, whereas narrow profiles are seen where the range of PAHs is also narrow. Evidently, smaller PAHs can be driven out of condensed material so that the grains contain predominantly a narrow range of larger PAHs. This interpretation is supported by observations of HD 44179 which possesses a 3.3-μm feature the width of which increases with distance from the star. The underlying IR continuum in HD 44179 is also very wide compared to that observed in the planetary nebula NGC 7027 (Russell, Soifer & Willner 1977, 1978), suggesting that the dust in the former object contains PAHs of a wide size range.

The HAC model of interstellar dust (Duley 1985; Jones, Duley & Williams 1990; the acronym HAC was first coined by Duley & Williams 1983) is in harmony with these observations. In this model, carbon is deposited on dust initially in polymeric form (sp³). Irradiation by UV can lead to H-loss and some conversion to aromatic form (sp²). Prolonged exposure to UV leads to a low-H-content graphitic amorphous carbon. The trend can be reversed by energetic H-atoms in insertion reactions (Jones et al. 1990). Therefore, the carbonaceous material responds to changes in its environment. This model accounts for interstellar visual and UV extinction (Duley 1987; Duley, Jones & Williams 1989) for the variations it exhibits (Jones, Duley & Williams 1987), for IR extinction (Duley & Whittet 1992), for the Extended Red Emission (ERE) (Duley 1985; Duley & Williams 1988a) and for the Very Broad Structure (Duley & Whittet 1990). PAHs dispersed in a polymer matrix have poor coupling between neighbours so that bulk thermal conductivity is low and local hotspots can be caused by absorption of a single photon in one PAH (Duley & Williams 1988b). In this paper, we interpret the 12-μm emission in terms of local hot spots in carbonaceous material consisting of PAHs distributed in a medium of polymers and voids. We infer that the observational information constrains the αC:HAC ratio in the dust.

It is perhaps worth noting that the 'molecular organic ice, lacking H₂O', referred to by Boulanger et al. as giving rise to the aliphatic C–H absorption along the path to IRS7 in the Galactic Centre (Allen & Wickramasinghe 1981; Butchart et al. 1986) is, in fact, the aliphatic HAC of the carbonaceous grains first identified by Duley & Williams (1981, 1983). Conversion of this aliphatic material to aromatic HAC (photodarkening) does not lead to free-flying PAH, at least in the laboratory. Deposition and evaporation cycles on timescales of ~10⁵ yr are unlikely in the interstellar medium.

4 IR EMISSION FROM HAC

In the 'hot spot' model (Duley & Williams 1988b), the coupling between one PAH and its environment is assumed to be controlled by a bond which we shall here take to be chemical, so that the energy quantum is about $\Delta = 0.4$ eV. This would have the effect of localizing a portion of the input energy at the absorption site over a time-scale that permits non-equilibrium IR emission ($10^{-3}–1$ s). Superheating of localized sites in condensed matter has been observed in several systems (Malinovsky 1987) and is responsible for photostuctural changes at illumination or irradiation levels that lead to no bulk heating of the medium (e.g. Compagnini et al. 1990). Such photostuctural modifications have been observed in HAC (Iida, Ohtaki & Seki 1984; Duley & Pinho, unpublished work). It would seem that the time-scale for energy retention by a molecule in a loosely bonded isolated configuration is intermediate between that of a free molecule (seconds) and a molecule in a dense solid (picoseconds). This point is being investigated experimentally in the laboratory (Papoular, Reynaud & Nenner 1990; Pinho & Duley, unpublished work). We can calculate the temperature rise $\Delta T$ for the absorption of a UV photon in a PAH, and the associated wavelength $\lambda_m$ of radiation, for the small hot spot created. This is shown in Table 1. A smaller value of $\Delta$ would represent weaker coupling and, for a given size, hot spot temperatures would be higher and wavelengths shorter. These calculations suggest the assignments given in Table 2.

Table 1. Temperature rise ($\Delta T$) and associated wavelength ($\lambda_m$) of radiation for absorption of a UV photon in a PAH.

<table>
<thead>
<tr>
<th>Number of rings $N_R$</th>
<th>$\Delta T$ (K)</th>
<th>$\lambda_m$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>830</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>390</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>255</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>157</td>
<td>23</td>
</tr>
<tr>
<td>30</td>
<td>106</td>
<td>34</td>
</tr>
<tr>
<td>40</td>
<td>80</td>
<td>46</td>
</tr>
</tbody>
</table>
Table 2. Assignments for infrared emission from HAC.

<table>
<thead>
<tr>
<th>Emission</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>UIR</td>
<td>$N_R &lt; 3$, transient</td>
</tr>
<tr>
<td>IRAS 12 μm</td>
<td>UIR with $\lambda \gtrsim 7 \mu m$</td>
</tr>
<tr>
<td>IRAS 25 μm</td>
<td>$N_R \sim 5-8$, transient</td>
</tr>
<tr>
<td>IRAS 60 μm</td>
<td>$N_R \sim 10-30$, transient</td>
</tr>
<tr>
<td>IRAS 100 μm</td>
<td>Larger molecules and equilibrium</td>
</tr>
<tr>
<td></td>
<td>Thermal emission from dust</td>
</tr>
<tr>
<td></td>
<td>Equilibrium thermal emission from grains in steady state.</td>
</tr>
<tr>
<td></td>
<td>Transient heating of entire small $(a \sim 10 \text{ nm})$ well annealed grains</td>
</tr>
</tbody>
</table>

If the evolution is not terminated by a shock, then the evolution is as illustrated in Fig. 2.

The assignments in Table 2 suggest that $J(100)$ traces the grains which are mainly HAC-coated silicate. Emission at 100 μm should arise from thermal emission by all dust, and in fact represents whatever energy remains when all other (non-equilibrium) emission has occurred. It will contain a component from both small and large grains. The variability found by Boulanger et al. then reduces to a mechanism for varying the proportion of carbon with $N_R \lesssim 8$. This proportion could be reduced either by passage of a moderate-velocity shock, or by UV annealing of aromatic HAC to aC. It could be increased in an atomic medium subject to regular low-velocity shocks in which deposition of polymeric carbon and its conversion to aromatic carbon occur, but where insufficient time prevents the conversion to aC.

5 COMPARISON WITH OBSERVATIONS AND DISCUSSION

We have developed a simple description of the evolutionary HAC model of interstellar dust, as described in the previous section. The description accounts for the deposition of gaseous carbon (C) in polymeric form (P) on the silicate substrate, the conversion of this carbon to small poly cyclic units (S), and the annealing to large poly cyclic units (L) or amorphous carbon (aC). This development is represented by

$$C \rightarrow aP \rightarrow S \rightarrow L.$$  

Here the rate $\alpha$ is given by $\alpha^{-1} = 10^9 \text{ cm}^3 \text{ yr}^{-1}$ (cf. Charnley, Whittet & Williams 1990), where $n$ is the total

Figure 1. Diagram indicating the chemical structure of the carbonaceous mantle.

Figure 2. (a) Carbon fractional abundances in gas phase and mantle. Curves show gas phase (C), polymeric in mantle (P), small PAH in mantle (S), and large PAH in mantle (L). (b) Ratios of polymeric carbon and aC in the mantle. $P/(S+P+L)$ is the fraction of the mantle that is polymeric, and $L/(S+P+L)$ is the fraction of the mantle that is aC.
hydrogen nuclei number density in the interstellar cloud; \( \beta_i \) is the so-called photodarkening rate (Iida, Ohtaki & Seki 1984; Duley & Williams 1988a) and we use here \( \beta_i = L_\nu \nu^{-s}/(10^6 \text{ yr}) \) where \( L_\nu \) measures the strength of the radiation field in terms of the average interstellar value (cf. Draine 1978), and \( \tau_\nu \) is the optical depth in the ultraviolet. We take \( \beta_s = \beta_i/2 \) to account for the fact that conversion to \( \alpha \)C requires more H-atom removal than the conversion \( P \to S \).

Fig. 2(a) shows curves calculated with \( n = 200 \text{ cm}^{-3}, L_\nu = 1 \) and \( \tau_\nu = 1 \), appropriate for many diffuse clouds. Gaseous carbon (C) falls with time as carbon accretes on to grains; polymeric carbon (P) rises initially, and is converted to small aromatics (S), which - if time permits - are converted to large PAHs (L), i.e. \( \alpha \)C. Thus, initially, the sp\(^3\) fraction is high, while at late times the \( \alpha \)C fraction is high (Fig. 2b).

In reality, the evolution of the carbon material is interrupted intermittently by shocks which return carbonaceous material to the gas. If one assumes that the shocks sweep all the carbonaceous material into the gas, then the evolution would be given precisely by Figs 2(a) and (b), up to each shock event. Some carbon may be retained, and the subsequent mantle composition would then be different. In this paper, however, we shall assume that all mantle carbon is returned to the gas during the shock.

We now consider the conclusions of Boulanger et al., as listed in Section 2, in the light of the evolutionary HAC model (Figs 2a and b). This model indicates how the carriers of the various emissions may vary in time.

(i) The scatter in \( R(12,100) \) is attributed to variations in the HAC: \( \alpha \)C ratio. Where \( R \) is 0.25 times its average value, the carbonaceous dust is mostly annealed to \( \alpha \)C. Such regions should be quiescent. Where \( R \) is 5 times average, the carbon must be recently accreted, following a shock. Regions of large \( R \) should not be large, i.e. should not exceed 1 pc.

(ii) The variations in \( R \) involve regions of shocks and boundary layers (where carbon is removed), and larger quiescent regions where accreted carbon has been processed.

(iii) The observed uniformity of \( I(100)/A_V \) confirms that \( I(100) \) is a good measure of total dust density, and implies that variations in \( I(12) \) are caused by a separate component.

(iv) As discussed previously (Duley & Williams 1984, 1986; Jones et al. 1990), carbonaceous grains are eroded in shocks. Weak shocks will first remove the outer polymeric layer so that the role of PAHs is enhanced. Stronger shocks will strip more of the carbonaceous material, including the sp\(^3\) material. Thus the dependence of \( R(12,100) \) on shock velocity is to be expected.

(v) The uniformity of the average colours \( R(12,100) \) and \( R(25,100) \) implies that the average conditions in the three complexes - in spite of local variations - are similar to those in the solar neighbourhood.

(vi) The systematic decrease (albeit with considerable scatter) of \( R(12,100) = I(12)/I(100) \) with increasing \( I(100) \), close to a \( 1/I(100) \) behaviour, noted by Boulanger et al., implies that \( I(12) \) is constrained within a certain range. This is consistent with the expected behaviour of HAC. To maintain \( I(12) \) at a certain level, the carbonaceous material must be rich in HAC which is subject to a normal UV field. The grains cannot be fully converted to \( \alpha \)C, so the frequency of shocks must be high enough to arrest the annealing process.

For the situation illustrated in Fig. 2, the interval between shocks of velocity adequate to remove most of the carbon (\( \lesssim 20 \text{ km s}^{-1} \)) must be \( \sim 5 \) Myr. Then, the colour \( R(12,100) \) will show a \( 1/I(100) \) behaviour. \( I(100) \) measures the whole extent of the cloud. \( I(12) \) originates in the regions exposed to the UV radiation field, and is therefore stronger at cloud edges.

(vii) The discussion in (vi) also indicates why the largest \( R(12,100) \) values should be found at low \( I(100) \).

(viii) If there is no detectable 12-\( \mu \)m emission at certain positions, then either the carbonaceous dust is so recently deposited that no UV-induced conversion to small PAHs has occurred, or UV-induced annealing has continued for sufficient time that all the material has been graphitised (see Fig. 2). In the first case, the regions must have recently been shocked, perhaps within about the last 1 Myr. In the second case, the regions must be quiescent and have continued to be so for about 10 Myr. It should be possible to discriminate observationally between these possibilities. In the former case, UV extinction should be anomalously strong while visual extinction should be weak, and the reverse is true in the latter case. Additionally, in the former case strong ERE, peaking at \( \lambda \approx 550 \text{ nm} \), must be present.

(ix) According to Table 2 and our proposed model, the carriers of \( \text{IRAS} 25-\mu \text{m} \) band emissions are PAHs with \( N_r \approx 10-30 \), while the 12-\( \mu \)m carriers are smaller. In a uniform annealing process, the amount of carbon passing through each PAH size range in the direction of graphitic carbon is also steady. Therefore, a uniform ratio of \( I(12) / I(25) \) is to be expected. The implications of the observation that the scatter in \( R(12,25) \) is more constrained than the scatter in \( R(12,100) \) is that the normal ratio of the abundances of small to medium-sized PAHs in the mantle is reasonably uniform. One can see from Fig. 2(a) that (for the choice of parameters used there) this is true for the period of about 3 to about 7 Myr. We therefore infer that the interval over which shocks recur should lie in this range. We note from Fig. 2(b) that this interskoch interval maintains an sp\(^3\):sp\(^2\) ratio of the order of unity, as required by the interstellar extinction observations (Jones, Duley & Williams 1987). Duley (1992) has recently proposed that luminescence due to electron–hole recombination in UV radiatively processed HAC, analogous to the Extended Red Emission (ERE), but occurring at longer wavelengths, may also contribute to non-equilibrium radiation fluxes at 12 and 25 \( \mu \)m. This emission is distinct from that due to vibrational transitions and would appear as a broad band at wavelengths \( \lambda \gtrsim h\nu / E_g \), where \( E_g \) is the band gap energy. It can be excited by all photons with \( h\nu > E_g \) and thus could be enhanced in regions where visible and near-IR photons are abundant. The determination of the relative importance of this luminescent and non-equilibrium thermal radiation from PAHs should be possible from spectral observations within the 12- and 25-\( \mu \)m bands.

(x) The origin of the \( \text{IRAS} 60-\mu \text{m} \) emission is unclear. There is probably a contribution from both PAHs with \( N_r \gtrsim 30 \) and from equilibrium emission from grains. Since the PAH population is necessarily varying as a consequence of shocks, some variation in \( R(60,100) \) is to be expected. The observation that the scatter in \( R(60,100) \) is comparable to that in \( R(12,100) \) implies that the bulk of the 60-\( \mu \)m emission is from large PAHs which are intermittently removed by shocks.
Some other consequences follow from these identifications. For example, in regions where $I(12)$ is higher than average, we should expect emission at 3.3 μm in suitable circumstances. High $I(12)$ implies a recent deposition of carbon in a UV-rich environment, so this material probably contains a range of sp$^3$ and sp$^2$ bonding and the extinction curve is probably normal. Visual ERE would be expected under these conditions for suitable geometries. In regions where $I(12)$ is low and $I(100)$ is high, most of the carbonaceous material must have been annealed to αC. In such situations, the far-UV extinction should be anomalously low, and there should be no visual ERE. Where both $I(12)$ and $I(100)$ are low, the region must be of narrow extent (so that few large grains are present) and have been so recently shocked that new deposition of carbon is not extensive, implying post-shock times ≤1 Myr.

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