A 3.4 μm absorption band in amorphous carbon: implications for interstellar dust

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Summary. The infrared absorption spectrum of hydrogenated amorphous carbon solids shows features at 3.38, 3.41 and 3.48 μm corresponding to discrete bands in the spectrum of IRS-7. Interstellar amorphous carbon dust with chemisorbed CH_2 and CH_3 groups may be a significant component of interstellar dust in diffuse clouds.

Evidence has been accumulating that suggests that graphite dust may not be an important interstellar solid (Czyzak & Santiago 1973; MacLean 1983; Massa, Savage & Fitzpatrick 1983). Physically and chemically, it is more plausible that the condensation of carbon in late-type stars or supernovae should produce amorphous or sooty carbon dust. We have shown (Duley & Williams 1981, henceforth Paper I) that this dust may be detectable via the observation of discrete absorption and emission features near 3.3 μm and elsewhere in the infrared.

In Paper I, several of the observed infrared features in emission objects such as NGC 7027 (Merrill, Soifer & Russell 1975) and the Orion ridge (Aitken *et al.* 1979; Jones *et al.* 1980) were tentatively related to specific surface functional groups on amorphous carbon. Absorption features seen in the spectrum of the galactic centre (Willner *et al.* 1979; Wickramasinghe & Allen 1980) were similarly assigned. Firm identifications were, however, precluded at that time because of a lack of laboratory data on the infrared spectrum of hydrogenated amorphous carbon (HAC) solids. Such data is now available and will be compared here with new observational data.

The HAC infrared spectrum is characterized by features at $2975 \, \text{cm}^{-1}$ ($3.48 \, \mu\text{m}$), $2930 \, \text{cm}^{-1}$ ($3.41 \, \mu\text{m}$) and $2955 \, \text{cm}^{-1}$ ($3.38 \, \mu\text{m}$), e.g. Fig. 1 (Watanabe, Hasegawa & Kirata 1982). Similar spectra have also been reported by Wieder, Carbona & Guarnieri (1979), Catherine & Turban (1979), Sussman & Ogden (1981) and McKenzie & Briggs (1981) for carbon solids prepared under a wide variety of conditions. All three peaks in this spectrum arise from the CH stretching vibration in CH_2 and CH_3 groups bonded to C atoms on the periphery of hexagonal C rings.

Laboratory spectra of HAC solids exhibit little evidence of absorption by aromatic CH groups. These groups are formed by the direct bonding of H atoms to peripheral C atoms (Paper I) and should absorb near 3.3 μm. Since atomic hydrogen is abundant in the inter-
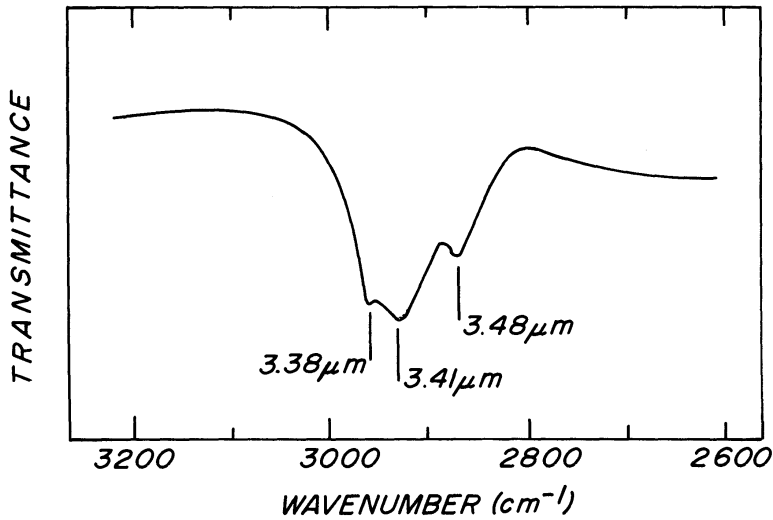
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Figure 1. Absorption spectrum of HAC dust between 2600 and 3200 cm^{-1} (Watanabe *et al.* 1982).

stellar gas but is not necessarily a major component over laboratory carbon film during condensation, the absence of a 3.3 μm feature in Fig. 1 is understandable.

The absorption strength of the 3.4 μm CH band associated with HAC surface groups is somewhat smaller than that observed in the spectra of condensed organic solids (Duley & Williams 1979). The absorption cross-section per CH bond, σ(CH), can be obtained from laboratory spectra when the hydrogen content of the samples is known. Typically, σ(CH) lies in the range between 1×10^{-20} and 6×10^{-20} cm^2. We will use an average value, σ(CH) = 3×10^{-20} cm^2 (*cf.* 10^{-19} cm^2 in Paper I).

Since $\tau(3.4\,\mu\text{m}) = \sigma(\text{CH})N(\text{CH})$ where $N(\text{CH})$ = column density of CH bonds in CH$_3$ and $N(\text{CH}) = \beta N(\text{C}) = \beta \times 3.7 \times 10^{-4} N(\text{H})$ where $N(\text{H})$ = H column density, β = fraction of C in CH bonds and 3.7×10^{-4} = fractional abundance of C relative to H, one obtains $\tau(3.4\,\mu\text{m}) = 3.7 \times 10^{-4}\,\beta\sigma(\text{CH})N(\text{H})$. Then, since $N(\text{H}) = 1.9 \times 10^{21}\,A_v$ cm^{-2},

$$\tau(3.4\,\mu\text{m})/A_v = 7.03 \times 10^{17}\,\beta\sigma\,(\text{CH})$$

$$= 0.02\beta.$$

As the measured value of this ratio in diffuse clouds is $\tau(3.4\,\mu\text{m})/A_v \sim 4.5 \times 10^{-3}$ one obtains $\beta = 0.225$, similar to that observed in laboratory samples (Wieder *et al.* 1979; Watanabe *et al.* 1982).

Fig. 2 shows a comparison of the laboratory spectrum of HAC (Fig. 1) with that of the source IRS-7 near the galactic centre (Allen & Wickramasinghe 1981). Features in IRS-7 at 3.40 and 3.48 μm appear in the spectrum of the laboratory sample. A further shoulder at 3.48 μm is likely also present in both spectra. The laboratory spectrum provides an excellent match to the interstellar curve near 3.4 μm. This suggests that HAC may be a major component of dust in diffuse clouds. Using $A_v \sim 40$ for IRS-7, then $\tau(3.4\,\mu\text{m}) = 0.8\,\beta = 0.31$ (from Fig. 2). Hence, β(IRS-7) = 0.38, implying that carbon dust in this object may contain slightly more hydrogen than dust in other sources.

As noted in Paper I, absorption at $\sim 3.3\,\mu$m is characteristic of aromatic CH bonds (Bellamy 1954). IRS-7 shows such a feature at 3.295 μm consistent with aromatic CH bonds in interstellar carbon dust. The ratio of 3.3 and 3.4 μm absorption/emission strengths is expected to be quite variable and will depend on the thermal and chemical history of the carbon solid. We have shown qualitatively (Paper I) that emission sources should exhibit
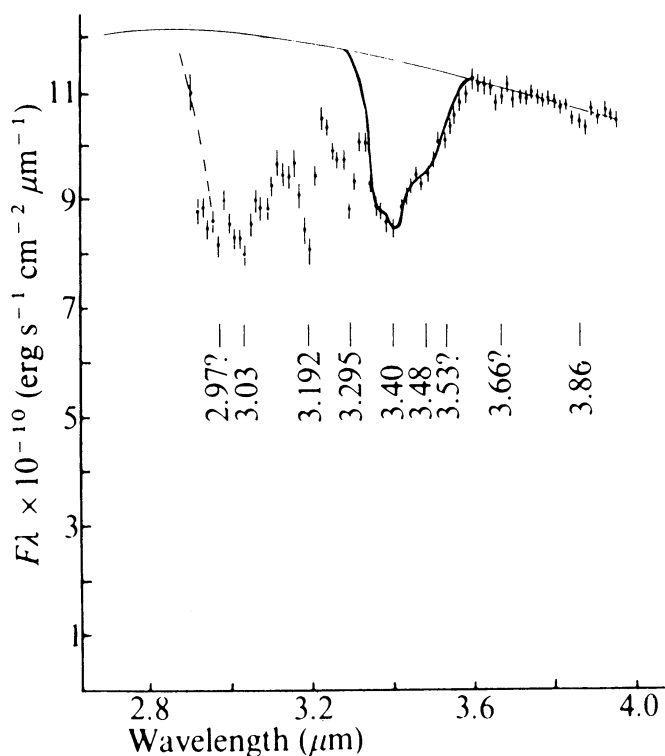
Figure 2. Spectrum of IRS-7 (Allen & Wickramasinghe 1981) showing absorption by amorphous carbon dust near $3.4\,\mu$m (solid line). The absorption feature at $3.295\,\mu$m may be due to CH groups bound to HAC surfaces.

enhanced $3.3\,\mu$m features and that the $3.4\,\mu$m line should be weak in these sources. However, both 3.3 and $3.4\,\mu$m lines should be observed in absorption in diffuse cloud material.

The spatial distribution of emission in the 3.3, 3.4 and $11.3\,\mu$m features has been the subject of several recent observational studies (Jones *et al.* 1980; Sellgren 1981; Aitken & Roche 1983). Generally, emission in the 3.3, 3.4 and $11.3\,\mu$m features in objects such as NGC 7027 or the Orion ridge occurs from dust in a shell around a central ionized region, suggesting that the concentration of CH bearing surface groups on HAC dust is temperature dependent.

Using laboratory (Lemmon 1973; Bar-Nun, Litman & Rappaport 1980) and theoretical (Rye 1977) data the surface condition of carbon grains can be related to temperature. In diffuse clouds C insertion reactions ensure that only CH_2 and CH_3 groups are present on HAC dust, absorbing near $3.4\,\mu$m and at other infrared wavelengths (Paper I). Heating dust to $\sim 500\,$K eliminates most CH_2 and CH_3 groups, while reactions with H atoms form aromatic CH groups, with spectral features seen in emission at 3.3 and $11.3\,\mu$m. If the dust temperature rises further, reactions with energetic H atoms sweep molecular groups from the surface. These carbon grains radiate a continuum, and the 3.3, $11.3\,\mu$m and other discrete emission features are absent.

The observation of discrete infrared emission features from objects such as NGC 7027 and the Orion ridge occurs, therefore, only from an interface region where the dust temperature is high enough to yield significant thermal emission at $3-12\,\mu$m, but also where the temperature is still low enough that CH, CH_2 and CH_3 groups are present on the surface. Laboratory studies of thermal desorption of chemisorbed hydrogen from HAC have shown that significant hydrogen evolves at temperatures in the range $750-900\,$K (Nyaiesh &

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Nowak 1983). Thus, an upper limit to the temperature of the dust observed to emit at 3.3 μm in these astronomical sources would be $\lesssim 750\,\mathrm{K}$.

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