LABORATORY SYNTHESIS OF HYDROGENATED AMORPHOUS CARBON FILMS

M. OGMEN AND W. W. DULEY

Physics Department, York University, Toronto, Ontario, Canada Received 1988 July 11; accepted 1988 August 16

ABSTRACT

Hydrogenated amorphous carbon (HAC) films have been prepared by direct condensation of cool carbon vapor at low temperatures. Quantitative absorption coefficients for these films have been obtained between 0.16 and 20 μ m. The ratio $\tau(3.4 \ \mu\text{m})/A_v$ for this material is shown to lie in the range 1.5×10^{-3} to 2.2×10^{-2} . Spectra of HAC at 3.4 μ m are quite similar to those seen in comet Halley and in the Galactic source IRS 7. Similarities with Orgueil extract are also observed. HAC formed via condensation in the ISM may be an early stage in the evolutionary cycle for interstellar dust.

Subject headings: infrared: spectra — interstellar: grains — laboratory spectra — meteors and meteorites

I. INTRODUCTION

All models for interstellar grains require the presence of significant quantities of condensed carbon (cf. Whittet 1984 for a review). The form and composition of this carbon condensate is less certain. This uncertainty is aggravated by the wide range of possible carbon solids-extending from soot through amorphous carbon to graphite and diamond. At one time or another all of these forms of carbon as well as other allotypes have been suggested as major components of interstellar dust. One problem in reaching any clear understanding of the nature of interstellar dust is the lack of laboratory data on the spectral properties of relevant carbon condensates over a wavelength range extending from the IR to the vacuum ultraviolet (VUV). Complete data exist for graphite (Huffman 1977; Draine 1984), but only partial data covering either the IR or VIS-UV are available for other carbon-based materials (Williams and Arakawa 1972; Sakata et al. 1983; Duley 1984; Colangeli et al. 1986; Wdowiak, Flickinger, and Cronin 1988). In addition, the formation of these laboratory condensates often involves conditions that are quite dissimilar to those existing in the interstellar medium.

In this *Letter*, we report on the spectral absorption of hydrogenated amorphous carbon films formed by condensation from a low-temperature hydrogen-rich gas. Our observations extend from the middle-infrared to the VUV and provide, for the first time, a possible connection between IR absorption and extinction in the visible and UV.

III. EXPERIMENT

The object of these experiments was to prepare thin (<100 nm thick) films on a transparent substrate by condensation from a hydrogen-rich gas under low kinetic temperature conditions. Carbon vapor, mainly in atomic form, but with traces of C_2 and C_3 , was obtained from graphite using excimer laser (308 nm) evaporation. This evaporation technique was similar to that reported previously (Duley 1984). Carbon vapor, produced in this way, is translationally and vibrationally hot. To reduce this excitation, the vapor was entrained in a flow of room temperature He/H₂ gas. Time of flight mass spectrometer scans of the ejecta showed that translational temperature has been lowered to ~300 K at the position where samples were collected. Quartz (suprasil) and sodium chloride windows were located 3 cm from the focus to condense this cooled

carbon vapor. The resulting films of hydrogenated amorphous carbon formed at a rate of ~0.1–0.5 nm s⁻¹. These films, that were clear to the eye, appeared rough to a scale size of ≤ 40 nm when examined under the electron microscope. The thickness of these films was measured directly in the electron microscope and verified by the method of Fizeau fringes. Infrared spectra of films on NaCl substrates were recorded in transmission in a Nicolet 20 SX FTIR spectrometer. Measurements of film transmission in the visible were obtained using a SPEX 1500SP spectrometer with a tungsten light source and EMI 9558QB photomultiplier tube. UV-VUV spectra were measured in transmission in vacuum using a deuterium lamp source. The short-wavelength limit to these measurements was 160 nm.

III. RESULTS

The infrared absorption spectrum of a hydrogenated amorphous carbon (HAC) film produced by condensation of cool carbon vapor on a NaCl window is shown in Figure 1. The major absorption peaks seen in this and other HAC films are listed in Table 1, together with a tentative identification of the origin of these features in terms of functional groups. The relatively sharp group of absorption lines near 3000 cm⁻¹ arise from methylene (CH₂) and methyl groups (CH₃). A broad shallow absorption at 3420 cm⁻¹ likely arises from phenolic OH groups. Absorption at 1707 cm⁻¹ is relatively intense in these samples and could derive from the CO stretch in an aromatic aldehyde (-HCO) group. Absorption at 1150 cm⁻¹ could arise from terminal ether or alcohol groups (Bellamy 1954). These groups, containing oxygen, arise from a low level $(\leq 0.1\%)$ of O₂ in the He/H₂ carrier gas. The fact that absorption features attributable to O-bearing groups are observed with comparable amplitude to the CH_n groups shows the high reactivity of HAC with respect to oxygen. This point has been discussed elsewhere (Duley and Williams 1986). Varying the H_2/He ratio in the carrier gas produced films with different hydrogen contents. The hydrogen content can be estimated from the CH_n absorption coefficient, α , at 2930–2945 cm⁻¹ since $\alpha(CH) = \sigma(CH)n(CH)$, where σ is the cross section for absorption and n(CH) is the density of CH groups in the material. With $\sigma(CH) = 1.7 \times 10^{-20} \text{ cm}^{-2}$ (Dischler, Bubenzer, and Koidl 1983) n(CH) ranges from 9×10^{21} cm⁻³ when $\alpha = 153 \text{ cm}^{-1}$ to $2.8 \times 10^{22} \text{ cm}^{-3}$ for $\alpha = 480 \text{ cm}^{-1}$. These

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FIG. 1.—Infrared absorption spectrum of a HAC film with a hydrogen content of 2.8×10^{22} cm⁻³

densities should be compared to the carbon atom density $n(C) \sim 8 \times 10^{22}$ cm⁻³ in these films. Since each C atom can in principle combine with several H atoms, this result indicates that the level of hydrogenation in these films is relatively small. Watanabe, Hasegawa, and Kurata (1982) report —CH group densities some 2–3 times higher than these values in HAC films produced by plasma deposition from hydrocarbons.

A plot of the absorption coefficient α (cm⁻¹) for HAC films between 1.8 and 7 eV is given in Figure 2. The value of α is seen to increase almost linearly with photon energy *E*, between 2 and 4 eV. The values of α then becomes relatively independent of energy for $E \leq 7$ eV. The optical gap, E_g , for these materials can be estimated from a plot of $(\alpha E)^{1/2}$ versus *E* (Davis and Mott 1970). Values of E_g derived using this method range from 0.75 to 1.3 eV with the lowest value being obtained for films with $n(CH) < 10^{22}$ cm⁻³. These values are smaller than those obtained by Watanabe, Hasegawa, and Kurata (1982) but are compatible with the relatively low hydrogen content of our films. We note that there is no indication of enhanced 220 nm absorption in these films. Our samples are therefore different from the QCC films prepared by Sakata *et al.* (1987).

TABLE 1 IR Absorption Features Observed in HAC Condensate

| Wavelength (µm) | Energy (cm ⁻¹) | Identification | Comments | |
|--------------------|-------------------------------|---------------------------|---|--|
| 2.92 | 3420 | Phenolic OH | | |
| 3.396 | 2945 | $-CH_3$ | Variable CH ₂ /CH ₃ ratio | |
| 3.413 | 2930 | -CH, | 2/ 3 | |
| 3.464 | 2887 | -CH ₃ | | |
| 3.489 | 2866 | $-CH_{2}$ | | |
| 4.74 | 2109 | Aromatic CEN | | |
| 5.86 | 1707 | Aromatic HCO | | |
| 6.21 | 1610 | Aromatic C=C | Enhanced by VUV | |
| 6.9 | 1450 | -CH. | 2 | |
| 7.27 | 1374 | -CH. | | |
| 8.05 | 1156 | Ether, alcohol | | |
| 11.55 | 865 | Aromatic -CH ₂ | Wavelength varies | |
| 12.35 | 810 | 3 | with hydrogenation | |

To simulate aging of this material in the interstellar medium, samples were exposed to the full light from the deuterium lamp in vacuum for several hours. The resulting spectrum of an irradiated film is shown in Figure 3. The most noticeable effect of this irradiation involves the appearance of the aromatic ring C=C stretch at 1610 cm⁻¹. This shows that HAC can be graphitized by exposure to UV radiation in vacuum, an effect that may be important in the interstellar medium (Jones, Duley, and Williams 1987). Photodarkening of HAC films by UV radiation has also been reported by Iida, Ohtaki, and Seki (1984).

TABLE 2

COMPARISON BETWEEN HAC ABSORPTION (cm⁻¹) (PRESENT DATA) WITH ASTRONOMICAL ABSORPTION

| HAC | IRS 7ª | Comet Halley ^b | Orgueil ^e | Emission |
|---------|--------|---------------------------|----------------------|-----------------------|
| 3420 | 3390 | | | |
| | | 3010 | | 3049 (3.28 µm) |
| 2945 | 2964 | 2976 | " 2940 " | $2940 (3.40 \ \mu m)$ |
| 2930 | 2929 | 2946 | | |
| 2887 | 2875 | 2857 | | |
| 2866 | | | | |
| 2109 | | | | |
| 1707 | | | 1710 | |
| 1610 | | | 1620 | 1620 (6.2 μm) |
| 1450 | | | 1458 | ···· |
| | | | | 1300 (7.7 µm) |
| 1374 | | | 1380 | |
| | | | 1235 | |
| 1156 | | | | $1160 (8.6 \mu m)$ |
| | | | 1042 | (oro piii) |
| 810-865 | | | 885 | 885 (11.3 µm) |
| | | | 830 | 000 (1110 pini) |
| | | | 760 | |
| | | ••• | 620 | |

^a Butchart et al. 1986.

^b Wickramasinghe and Allen 1986.

° Wdowiak et al. 1988.

^d Gillett et al. 1973.



FIG. 2.—Absorption coefficient α (cm⁻¹) vs. energy for HAC films with hydrogen densities (a) 2.8×10^{22} cm⁻³, (b) 1.46×10^{22} cm⁻³, and (c) 9×10^{21} cm⁻³.

IV. DISCUSSION

The present experiments show that a range of hydrogenated amorphous carbon solids can be prepared by direct condensation of cool carbon vapor on silica substrates at translational temperatures that do not exceed 300 K. In this regard, the solids produced are probably most closely related to those existing in cool interstellar clouds. Some similarity to cometary and meteoritic dust might also be expected. A comparison between IR features observed in these HAC films and IR spectra of astrophysical materials is given in Table 2. It is apparent from both Table 2 and inspection of the spectrum of IRS 7 published by Butchart *et al.* (1986) that a close correspondence exists between HAC spectra and that of IRS 7 in the 2.8–3.6 μ m (3570–2778 cm⁻¹) region. In addition to absorption by CH_n groups, the broad feature near 2.95 μ m in IRS 7 suggests the presence of -OH groups, perhaps bound to an organic substrate.

Similar CH_n features to those appearing in HAC have also been observed in the spectrum of comet Halley (Wickramasinghe and Allen 1986; Knacke, Brook, and Joyce 1986) as well as in the Orgueil extract studied by Wdowiak, Flickinger, and Cronin 1988). Such material would appear to be fairly widespread in interstellar dust. It likely evolves into the emitter of the UIR features when exposed to a more energetic radiative environment.



FIG. 3.—Infrared absorption spectrum of HAC film irradiated for 3 hr in vacuum. The appearance of an extra peak at 1610 cm⁻¹ indicates increasing graphitization.

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The 1707, 1610, 1450, and 1374 cm^{-1} features in HAC are also observed in the insoluble Orgueil residue (Wdowiak, Flickinger, and Cronin 1988). The strong 1707 cm⁻¹ (5.86 μ m) feature is indicative of oxidized carbons (Painter et al. 1981). Its absence from emission spectra suggests that the HCO group may leave the surface of interstellar dust grains in a more energetic environment. UV radiation may enhance this reaction (Duley and Williams 1986).

Absorption features at 1450 cm⁻¹ (6.9 μ m) and 1374 cm⁻¹ (7.27 μ m) arise in CH_n groups and should be present whenever strong absorption is seen at 2940 cm⁻¹ (3.4 μ m). They should be present in the spectrum of IRS 7. Spectral features between 750 and 890 cm⁻¹ are very indicative of aromatic CH₃ groups with the number and wavelength of these features depending on degree of substitution and hence on the amount of hydrogenation. Their occurrence in the Orgueil and "emission" spectra signals the presence of xylene-like structures in dust. HAC is characterized in the visible and near-UV by an absorption coefficient that increases linearly with λ^{-1} . As expected, increasing hydrogen content results in a reduction in absorption. This effect has been observed in HAC films prepared in other ways (McKenzie and Briggs 1981; Watanabe, Hasegawa, and Kurata 1982; Smith 1984) and reflects the diminution of sp^2 (graphitic) bonding, when C atoms bond to hydrogen. Thin

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films of HAC on small interstellar grains will show a λ^{-1} extinction dependence in the visible (Duley 1987; Jones, Duley, and Williams 1987) because of the linear dependence of α . The difference in α between the B and V bands, $\alpha_b - \alpha_v$ together with α_v can be used to obtain an effective value of R = $\alpha_{\nu}/(\alpha_B - \alpha_{\nu})$. The value of R ranges from 1 in films with large hydrogen content to 1.65 when $n(H) = 9 \times 10^{21}$ cm⁻³. For amorphous carbon (aC) in nonhydrogenated form (Duley 1984), R = 3.4. This material prepared by the direct condensation of carbon in vacuum is much more strongly absorbing in the visible and has $E_q \sim 0.25$ eV. A bandgap this small is characteristic of a photographitic material (Robertson and O'Reilly 1987).

Since α has been measured at both the 3.4 μ m and V bands, the present data can be used to estimate the ratio $\tau(3.4 \,\mu\text{m})/A_{\mu}$ for HAC dust. We find that $1.5 \times 10^{-3} \le \tau (3.4 \ \mu m/A_v) \le$ 2.2×10^{-2} . Whittet (1988) estimates $\tau(3.4/A_v) \sim 10^{-2}$ for the dust toward Sgr A IRS 7 which lies in the above range. However, A_{v} in interstellar clouds will, of course, contain a contribution from silicate dust. This will have the effect of diluting absorption due to the carbon dust in these objects, thus reducing $\tau(3.4/A_{\rm e})$.

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W. W. DULEY and M. OGMEN: Physics Department, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3

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