

THE DECOMPOSITION OF HYDROGENATED AMORPHOUS CARBON: A CONNECTION WITH POLYCYCLIC AROMATIC HYDROCARBON MOLECULES

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ABSTRACT

We have produced thin solid films of hydrogenated amorphous carbon (HAC) by vapor deposition in vacuum and have investigated the structure and infrared spectra of these materials under conditions in which they are at the point of decomposition. We find that the IR absorption spectrum of HAC under these conditions contains all the major spectral components seen in emission in nebulae. In addition, high-resolution scanning tunneling microscopy of HAC prior to decomposition reveals protographitic islands with dimensions $\sim 1\text{--}5$ nm showing that polycyclic aromatic hydrocarbon (PAH)-like molecular groups evolve from HAC. These experimental results suggest for the first time how PAHs and HAC may be related and how PAH molecules could evolve from HAC in regions of high excitation. The material produced as HAC decomposes is a very low density carbonaceous “aerogel” consisting primarily of these aromatic protographitic clusters in a weakly connected friable network. These protographitic clusters may be the source of interstellar graphite grains.

Subject headings: dust, extinction — infrared: ISM: lines and bands — ISM: abundances — ISM: molecules

1. INTRODUCTION

Infrared absorption spectra of dust in interstellar clouds show that a carbonaceous component similar to hydrogenated amorphous carbon (HAC) is present, and that the composition of this material is variable (Sandford et al. 1991; Allamandola et al. 1992; Sellgren, Smith, & Brooke 1994; Pendleton et al. 1994; Brooke, Sellgren, & Smith 1996). This variability can be seen through changes in the relative amplitude of the narrow IR absorption features near $3.4\ \mu\text{m}$, through the appearance of different CH_n absorption features in dark clouds (Smith, Sellgren, & Tokunaga 1989; Brooke et al. 1996), and through a variation in the profile and central wavelength of the extended red emission (ERE) (Witt & Boronson 1990), which may reflect compositional changes in the emitting HAC dust (Furton & Witt 1993). Such variability can arise from UV irradiation, through interaction with cosmic rays, via heating, and as a result of chemical interactions with the ambient interstellar gas (Jones, Duley, & Williams 1990; Sorrell 1990, 1991). Infrared spectra of HAC deposited at low temperatures by plasma deposition show that the hydrogen content and bonding can be influenced by thermal and radiative interactions (Ogmen & Duley 1988; Duley 1994). In the laboratory, HAC is found to graphitize on heating (Wada, Gaczi, & Solin 1980; Smith 1984; Fink et al. 1984; Grill, Patel, & Meyerson 1990). This occurs in a series of stages on heating to temperatures $T \gtrsim 600$ K and is characterized by a loss of hydrogen and by closing of the band gap (Robertson & O'Reilly 1987) as the proportion of sp^2 hybridized bonded carbon atoms increases relative to sp^3 bonded atoms. IR absorption spectra show that this is accompanied by suppression of the $3.4\ \mu\text{m}$ absorption due to aliphatic groups and the growth of a $3.3\ \mu\text{m}$ absorption attributable to aromatic CH groups (Dischler, Bubbenzer, & Koidl 1983).

Spectral features due to aromatic molecular groups are also observed in IR emission from a wide variety of astronomical sources (Allamandola, Tielens, & Barker 1989) and suggest that there may be a link between a condensate such as HAC and the aromatic compounds observed in emission in these sources (Jones et al. 1990; Duley 1993). This correlation is weakened, however, by the lack of overlap between IR spectral features seen in absorption in HAC solids (Ogmen & Duley 1988) and those appearing in emission (Allamandola et al. 1989); specifically, the observation that the principal IR emission peaks (3.3 , 6.2 , $11.3\ \mu\text{m}$) can be assigned to polycyclic aromatic hydrocarbons (PAHs), while absorption features in low-temperature HAC deposits (3.4 , $6.9\ \mu\text{m}$) are dominated by bands arising from aliphatic hydrocarbons.

A hierarchical relationship between the PAH compounds observed in emission sources and HAC has been implied for some time (Duley 1986; Borghesi, Bussoletti, & Colangeli 1987; Blanco, Bussoletti, & Colangeli 1988; Duley 1989; Duley & Jones 1990). In this model, PAH molecules would be formed from HAC in emission sources and released from dust. If such a connection was justified, one would expect that in the transitional state, the aromatic spectral features observed in emission from PAHs would be observed in the absorption spectrum of HAC. In particular, one would expect to see absorption features at 3.3 , 6.2 , and $11.3\ \mu\text{m}$, with the latter wavelength being diagnostic of the level of hydrogenation of the PAH groups involved (Duley & Williams 1981; Allamandola et al. 1989). One would also expect to see a change in the mechanical structure of HAC that would make it possible for PAH molecules to be released.

In this Letter we show that such aromatic absorption bands are present in the spectrum of HAC prior to dissolution, confirming that PAH molecules may evolve from HAC solids in regions of high excitation. We also observe morphological changes in HAC that suggest how PAH fragments may break away from the HAC network.

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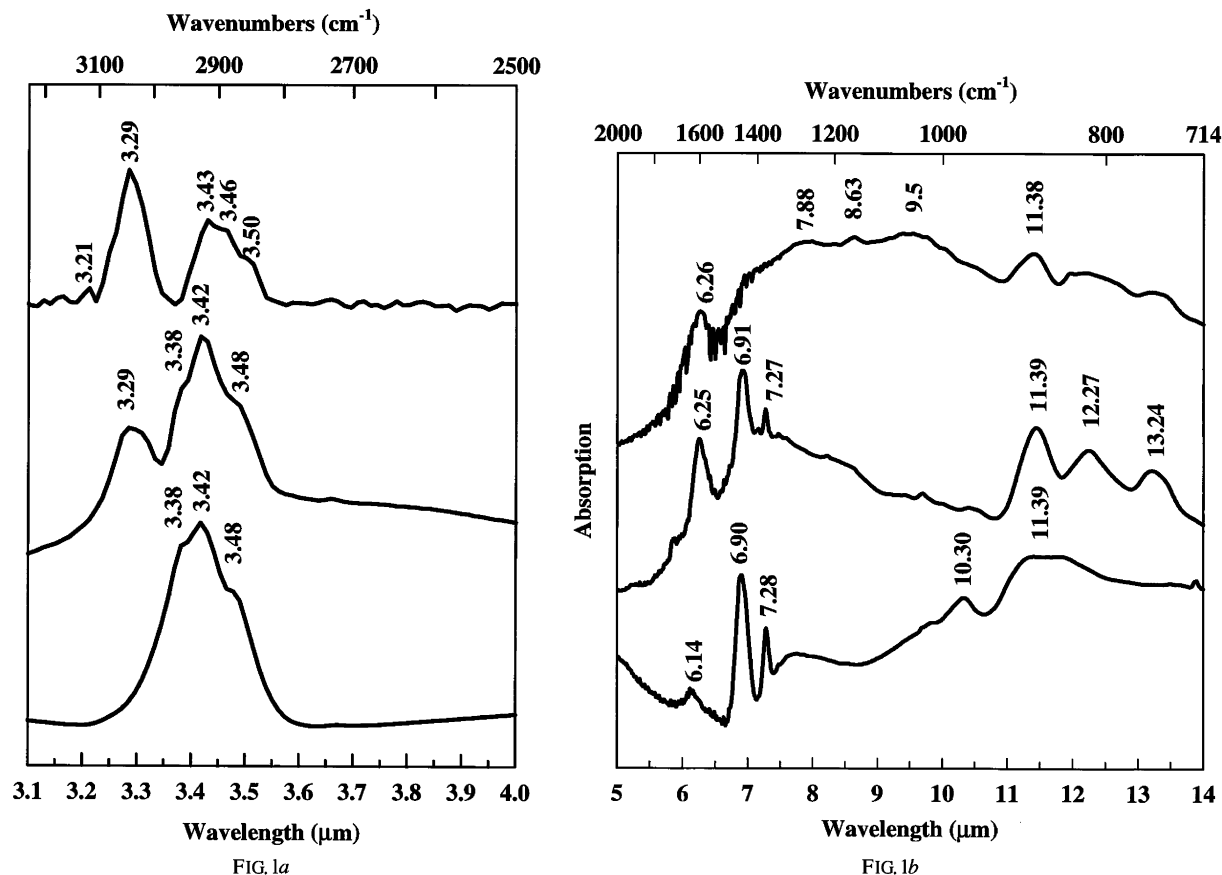


FIG. 1.—(a) Absorption spectrum of HAC, as deposited (*bottom*); heated to 700 K (*middle*); and heated to 800 K (*top*). Spectral range 3.1–4.0 μm . (b) Same as (a), but for spectral range 5.0–14 μm .

2. EXPERIMENT AND RESULTS

HAC films were prepared using 308 nm XeCl laser ablation of graphite in the presence of ≈ 1 torr of H_2 . Films were deposited on a KCl substrate held at room temperature in the configuration used previously for deposition of amorphous silicates (Scott & Duley 1996). IR absorption spectra were obtained with a Bomem FTIR spectrometer over the 2.5–15 μm wavelength range. Samples deposited at 300 K were heated for 2–3 hr in vacuum ($\approx 10^{-5}$ torr) at temperatures up to 825 K to promote decomposition and graphitization. After this treatment, which resulted in the evolution of hydrogen and other hydrocarbon gases, a loosely bonded fragile residue remained on the KCl window.

Absorption spectra of HAC deposited at 300 K and after heating in vacuum are shown in Figure 1. Wavelengths and energies of individual spectral features are listed in Table 1. Some of these spectral features are also observed in the thermal degradation of other organic materials such as cellulose (Blanco et al. 1988) or in the thermal decomposition of hydrocarbons (Kiefer et al. 1981). It is evident that at the point of decomposition, HAC has evolved from a hydrogen-rich solid in which aliphatic hydrocarbon compounds dominate to a material consisting primarily of aromatic rings. Spectral features in the 11.3–13.2 μm region characteristic of solo, duo, and trio aromatic hydrogen, respectively, appear prior to decomposition. At the threshold for decomposition (upper spectrum), only the band due to solo H remains, indicating

that the aromatic molecules retained in HAC under these conditions are dehydrogenated.

Scanning tunneling microscope (STM) images of the surface of HAC, recorded before and after heat treatment in vacuum, are shown in Figure 2 (Plate L12). An image of the surface of crystalline graphite is also included for comparison. These images are similar to those reported by Cho et al. (1992) for amorphous carbon (aC) films deposited at high temperature. Figure 2b shows the growth of graphitic islands (seen edge on) as the volatile hydrocarbon component is removed from HAC. A higher magnification STM image reveals the hexagonal structures associated with graphitic material in the upper right quadrant of Figure 2d. Such graphitic islands are separating from the HAC framework as decomposition proceeds and demonstrate a physical connection between HAC and PAH clusters.

3. DISCUSSION

The IR absorption spectrum of HAC prepared at 300 K shows the 3.4 and 6.9 μm features attributable to CH_n vibrations in aliphatic and olefinic hydrocarbons. That at 7.28 μm can be attributed to CH_3C groups, while that at 10.3 μm likely arises from cyclo-compounds such as cyclohexane. The presence of aromatic CH is indicated by the broad absorption band at $\sim 11.4 \mu\text{m}$ and the weak peak near 6.14 μm . These structures are all known to be components of HAC (Robertson & O'Reilly 1986).

PLATE L12

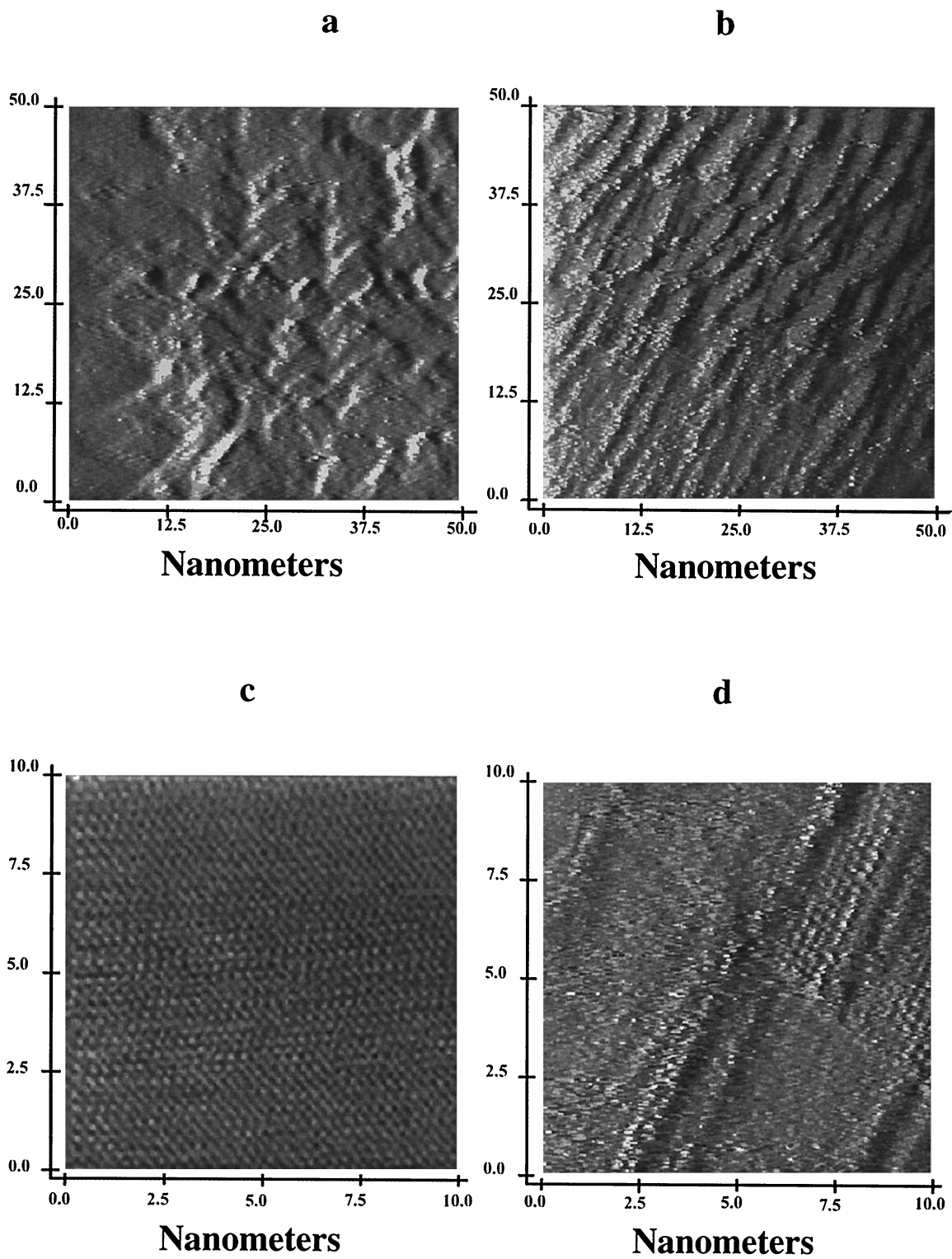


FIG. 2.—STM scans of HAC. (*a*) As prepared; (*b*, *d*) heated to 800 K in vacuum; (*c*) surface of crystalline graphite.

SCOTT & DULEY (see 472, L124)

TABLE 1

ABSORPTION FEATURES IN HAC: WAVELENGTH (μm), (energy cm^{-1})

As Deposited (300 K) Emission ^a	Heated to 700 K	Heated to 800 K	Unidentified Infrared
		3.21 (3115)	
	3.29	3.29 (3040)	3.29
3.38 (2960)	3.38 (2960)		3.34
3.42 (2920)	3.42 (2920)	3.43 (2915)	3.4
3.48 (2875)	3.48 (2875)	3.46 (2890)	3.46
		3.50 (2860)	3.51
			3.56
6.14 (1630)			
	6.25 (1600)	6.26 (1595)	6.2
6.90 (1450)	6.91 (1445)		
7.28 (1375)	7.27 (1375)		
		7.88 (1270)	7.6–8.0
		8.63 (1160)	8.7
		9.5 (1050)	
10.3 (970)			
11.39 (878)	11.39 (878)	11.38 (879)	11.2
	12.27 (815)		
	13.24 (755)		

^a Major UIR components from Allamandola, Tielens, & Barker 1989.

On heating, HAC evolves toward a protographitic material through loss of hydrogen, desorption of hydrocarbon molecules, and the growth of sp^2 hybridized bonded aromatic rings (Schenk et al. 1992). This can be followed in the absorption spectrum through the weakening of the 3.4 and 6.9 μm bands and the enhancement of spectral features such as those at 3.29, 6.26, and 11.4–13.24 attributable to aromatic rings. When this is occurring, HAC also loses its mechanical integrity as voids appear in the film. The resulting solid is a loosely connected highly friable structure analogous to an aerogel of aromatic

clusters. A discussion of the properties of such a structure is given elsewhere (Duley 1993).

Prior to the decomposition of HAC in vacuum, absorption bands attributable to two and three adjacent H atoms on aromatic rings disappear, leaving the 11.39 μm feature of solo CH. This suggests that dehydrogenation is almost complete by the time HAC decomposes and shows that a connection exists between molecular groups seen in IR emission in photodissociation fronts and other sources and those present in HAC as it decomposes. Indeed, our experimental data support a model in which PAH molecules are produced from HAC through sputtering and shock heating (Duley 1994; Allain, Leach, & Sedlmayer 1996). As this process is likely to result in the liberation of PAH radicals, rather than fully hydrogenated molecules such as coronene, etc., this would account for the difficulty to date in obtaining a spectroscopic simulation of the “aromatic” PAH IR emission features in laboratory experiments.

4. CONCLUSIONS

We have demonstrated a possible connection between HAC deposited at low temperature and PAH molecules. In experiments in which HAC is heated to a temperature that produces decomposition, the resulting solid (*a*) is a low-density highly friable network of loosely connected protographitic islands and (*b*) contains PAH molecular groups whose IR absorption spectrum mimics that of the unidentified infrared (UIR) emission features. This loosely connected network may have novel physical and optical properties.

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