INFRARED EMISSION SPECTRA FROM HYDROGENATED AMORPHOUS CARBON

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ABSTRACT

Thermal emission spectra from hydrogenated amorphous carbon (HAC) over the 2.5–15 μ m range have been obtained at temperatures between 573 and 773 K. These spectra are similar, but not identical, to absorption spectra of HAC samples subjected to the same thermal cycle. A distinct 3.29 μ m aromatic CH emission is found in samples heated to temperatures in excess of 723 K. This emission is also observed at lower temperatures in samples that have been thermally cycled to higher temperature. Laboratory emission spectra from HAC are shown to provide a good simulation of 3.2–3.6 μ m emission from dust in the extended atmospheres of post–asymptotic giant branch objects. The ratio of 3.4 and 3.3 μ m emission in such objects may be a useful indicator of evolutionary status.

Subject headings: infrared: ISM: lines and bands -- ISM: molecules -- stars: AGB and post-AGB

1. INTRODUCTION

An increasing number of narrow infrared emission features associated with polycyclic aromatic hydrocarbons (PAHs) have been detected in a variety of astronomical sources, including reflection nebulae, planetary nebulae, H II regions, galactic nuclei, and the diffuse interstellar medium (Allamandola, Tielens, & Barker 1989; Tielens 1993; Tokunaga 1996). Similar features have also been detected from emission post-asymptotic giant branch objects exhibiting mass loss such as WC and R CrB stars (Cohen, Tielens, & Bregman 1989; Buss et al. 1990; Geballe & van der Veen 1990), novae (Hyland & McGregor 1989), and a range of proto-planetary nebulae (Geballe et al. 1992). The ubiquitous nature of this emission together with its high brightness temperature in extended sources (Sellgren 1984) suggests that the carriers are abundant and contain 20-100 carbon atoms (Schutte, Tielens & Allamandola 1993; Allain, Leach, & Sedlmayr 1996). A population of particles with a much larger $(10^3 - 10^5)$ number of atoms is also indicated (Schutte et al. 1993). Identification of the carriers responsible for these emission features is a spectroscopic problem that is complicated by the fact that the emitters are in a size range that is intermediate between molecules and small particles. In addition, astrophysical spectra appear in emission while most laboratory data on PAH molecules are obtained in absorption (Flickinger & Wdowiak 1990; Kurtz 1992; Bernstein, Sandford, & Allamandola 1996; Beegle, Wdowiak, & Arnoult 1997), although there have been a few studies of PAHs in thermal emission (Kurtz 1992; Mennella, Collangeli, & Bussoletti 1992) and as UV-excited gaseous molecules (Shan, Suto, & Lee 1991; Brenner & Barker 1992; Schlemmer et al. 1994). Large PAH molecules will share many physical and chemical characteristics with small particles of carbonaceous materials such as hydrogenated amorphous carbon (HAC), quasi-carbonaceous condensate (QCC), or coal (Duley 1993 and references therein). Recently we have shown that molecular groups with IR spectral properties similar to PAH molecules are present in HAC (Scott & Duley 1996). However, these experiments were carried out in absorption. In this Letter we report the first IR spectra of HAC obtained in thermal emission at temperatures of up to ~800 K. The emission properties of this material offer additional insight into the IR emission spectra of post-AGB objects in which warm dust may be a contributor to PAH emission spectra.

2. EXPERIMENTAL

HAC films with a thickness of ~1 μ m were prepared by excimer laser ablation of graphite in a hydrogen atmosphere as reported previously (Scott & Duley 1996). Films were deposited on a stainless steel substrate and placed in a vacuum chamber. These samples were then heated by conduction to temperatures of up to ~800 K. IR emission spectra were recorded using a Bomem MB-100 FTIR spectrometer at a resolution of 4 cm⁻¹. The spectral range was 500–6000 cm⁻¹. The resulting emission spectra were processed by ratioing the emission from HAC to that of an uncoated stainless steel substrate at the same temperature, followed by a cubic polynomial baseline correction.

3. RESULTS AND DISCUSSION

Thermal emission spectra recorded from HAC at various temperatures between 425 and 775 K are shown in Figures 1 and 2. Spectra in Figure 1 cover the 3.2–3.8 μ m region and show a structured emission band near 3.4 μ m that is characteristic of aliphatic hydrocarbons. As the temperature of the sample is increased, the structure and intensity of this feature decreases, and a new emission band appears near 3.29 μ m. This new emission can be attributed to the CH stretching vibration in aromatic hydrocarbons (Duley & Williams 1981). Its appearance at high temperature accompanies the transformation of HAC from a polymeric to a protographitic solid (Scott & Duley 1996). Emission spectra in the 5–15 μ m region (Fig. 2) show an enhancement in the relative amplitude of the aromatic C—C ring vibration at 6.2 μ m and the 11.3 μ m aromatic CH bending vibration at high temperature. Emission peaks due to CH bending modes in molecular groups with two and three adjacent H atoms on aromatic rings are also apparent at ~12.3 and 13.2 μ m at 773 K. Emission spectra at lower temperature are characterized by sharper spectral features at ~5.8, 6.9, 7.3, and 10.4 μ m and weaker emission at 6.2 and 11.3 μ m. The feature at 5.8 μ m is likely due to an aldehyde group. The group of emission bands at 6.9, 7.3, and 10.4 μ m



FIG. 1.—Thermal emission from HAC at various temperatures. Note the change in relative amplitude between 3.29 and 3.4–3.5 μ m features due to annealing at high temperatures. The bottom spectrum is for HAC annealed at 773 K and then returned to 723 K.

are observed only at low temperature and are attributable to vibrational modes in nonaromatic hydrocarbons. The appearance of these bands is then indicative of HAC material that has not been heated to temperatures above \sim 700 K. In general, emission spectra of HAC at a given temperature are similar to



FIG. 2.-Thermal emission from HAC at various temperatures



FIG. 3.—Comparison between thermal emission of IRAS 05341+0852 (*circles*) and that from a two-component HAC dust mixture (*solid line*). Component (a) is the 650 K emission from HAC that was deposited at 77 K. Component (b) is the 800 K emission from HAC that was deposited at 300 K and subsequently annealed to ~850 K.

those observed in absorption. Some differences are found, however, particularly with respect to the relative amplitude of individual components. This may be attributed, in part, to difficulty in assigning the baseline in emission spectra together with the broadness of some of the spectral features. Table 1 summarizes the differences between absorption and emission spectra of HAC. The major difference is the appearance of a broad feature in thermal emission spectra between 5.7 and 9.0 μ m. The peak of this emission is near 8.0 μ m, but a secondary maximum occurs near 8.6 μ m in emission spectra at 773 K. A variety of aromatic C-C, CH, and aliphatic CH modes appear in this spectral range (Bellamy 1958). Spectra in Figures 1 and 2 suggest that small particles of HAC will emit IR spectral features very similar to those observed in astronomical sources when their temperature is raised to 700-800 K. Such temperatures will exist for larger particles in the extended atmospheres of post-AGB objects and may also be created by stochastic heating of very small particles (Duley 1973; Sellgren 1984) in nebulae and in the diffuse interstellar medium. A recent study of IR emission by stochastically heated HAC dust shows that strong emission can occur at $3.3-3.4 \mu m$ under certain conditions (Bartlett & Duley 1996). Comparison between laboratory and astronomical spectra is complicated, however, by the fact that the composition and structure of HAC is temperature dependent (see Figs. 1 and 2) while dust particles in astronomical sources can be at a range of temperatures. "Old" and "new" dust with a range of thermal exposures may also be present. Thermal processing of HAC involves activated reactions (Duley 1996) that can progress rapidly at equilibrium temperatures in excess of ~200 K but that may be inhibited

TABLE 1 Comparison between Spectral Features Seen in Emission from HAC and Those in Absorption Spectra

Absorption ^a	Emission ^b
(µm)	(µm)
3.21	Not seen
3.29	No change
3.38	No change
3.42	No change
3.46	Broadens
3.50	Shift to 3.51
	5.9 (likely aldehyde impurity)
6.25	No change
6.91	No change
7.27	No change
7.88	Broad peak 5.7-9.0
8.63	
9.5	Not seen
	10.3
11.4	No change
12.3	No change
13.2	No change

^a At 300 K, after heating to 700–800 K in vacuum (Scott & Duley 1996). ^b At 700–800 K.

under stochastic heating conditions. Our laboratory spectra of HAC indicate that the 3.29 μ m emission peak is produced only by material that has been thermally processed through heating to temperatures in the 700–800 K range. With stochastic heating and an average photon energy of 6 eV, these temperatures will be reached in HAC particles with 30–40 atoms. It may be significant that the 3.3 μ m brightness temperature in astronomical sources showing the discrete IR emission feature is typi-

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cally in the ~1000 K range (Sellgren 1984), as this is indicated as the annealing temperature required to produce a 3.29 μ m aromatic resonance in HAC. Using a mixture of thermally processed HAC materials, we find that a good spectroscopic fit can be obtained between laboratory emission spectra of HAC and those of various evolved, post-AGB objects. An example of such a fit to the 3–4 μ m spectrum of IRAS 05341+0852 (Joblin et al. 1996) is shown in Figure 3. In this fit, emission in the 3.4–3.6 μ m range is produced primarily by HAC that has not been heated to temperatures in excess of 650 K. The 3.29 μ m emission is from the warmer HAC dust that has been heated to temperatures between 773 and 873 K. Similar fits have been obtained to 3–4 μ m spectra of IRAS 04296+3429 and CRL 2686. Our experiments suggest that the 3.4/3.3 μ m ratio may be a useful diagnostic parameter in describing the evolution of AGB and post-AGB stars such as the type B objects identified by Geballe (1996) and Tokunaga (1996). In objects such as IRAS 05341+0852 in which this ratio is large, the dust temperatures must be low, and any new dust has not been exposed to the interstellar UV radiation field for a long enough time to result in the appearance of the 3.29 μ m feature. Objects such as IRAS 22272+5435 (Geballe et al. 1992) that exhibit a smaller 3.4/3.3 μ m ratio are more evolved and may contain a component of older HAC dust that has been subjected to thermal processing at higher temperatures or to an extended period of stochastic heating in the ambient UV radiation field. The spectrum of NGC 7027, with a strong 3.3 μ m feature and weak 3.4 μ m emission, suggests that dust in this object is at an evolutionary endpoint with a large content of aromatic hydrocarbon species.

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