# POLYYNES AND INTERSTELLAR CARBON NANOPARTICLES

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#### ABSTRACT

Laboratory experiments show that long-chain polyyne molecules are often components of the type of carbon nanoparticle (CNP) that can be associated with the infrared (IR) emission bands attributed to polycyclic aromatic hydrocarbons (PAHs). These molecules are attached to peripheral sites on PAH molecules and have in excess of six carbon atoms. IR spectra of CNPs containing a variety of sp-bonded carbon chains in conjunction with PAH groups are reported in this paper. We find that polyyne sidechains produce several notable spectral features in the 4.3 and  $5.7 \,\mu m$  (2300–1750 cm<sup>-1</sup>) range, some of which may be present in interstellar emission. A deeper search for these features in absorption or emission in interstellar sources would indicate if polyyne chains are commonly attached to PAH emitters.

Key words: astrochemistry - infrared: ISM - ISM: lines and bands - ISM: molecules - methods: laboratory

Online-only material: color figures

## 1. INTRODUCTION

Infrared (IR) observations have indicated for some time that a wide variety of carbonaceous materials are present in the interstellar medium (ISM; van Dishoeck 2008; Kwok 2009, and references therein). These take the form of hydrocarbon molecules and dust consisting of aromatic and aliphatic compounds. The dimensions of these particles extend from that of single molecules (sizes  $\leq 1$  nm) to carbon nanoparticles (CNPs; sizes of 1-10 nm) to small grains (sizes > 10 nm). Within this size range, larger particles such as CNPs and small grains likely contain the same types of molecular components as are observed as free molecules in certain emission sources. The overall structure corresponds to ring compounds exhibiting primarily sp<sup>2</sup>-hybridized carbon bonding connected by a network of aliphatic chains (Jones et al. 1990; Kwok et al. 2001; Dartois et al. 2005). These chains will have mixed sp,  $sp^2$ , and sp<sup>3</sup> hybridized bonded carbon composition.

Identifying the nature of the interstellar aliphatic hydrocarbon component has been a challenge to laboratory astrophysicists, but experiments now suggest that the composition of this material is reasonably well replicated in hydrocarbon condensates such as a-C:H (Dartois et al. 2005), hydrogenated amorphous carbon (HAC; Scott et al. 1997), quenched carbonaceous condensate (QCC; Wada et al. 2009), and CNP samples (Hu & Duley 2007). –CH<sub>2</sub> and –CH<sub>3</sub> groups dominate in these materials and are primarily present in sp<sup>3</sup> bonded aliphatic chains attached to ring molecules. The presence of –CH<sub>2</sub> and –CH<sub>3</sub> groups is confirmed through observation of characteristic IR absorption bands near 3.4, 6.85, and 7.25  $\mu$ m (2940, 1460, and 1380 cm<sup>-1</sup>) associated with vibrations of these species (Chiar et al. 2000; Pendleton & Allamandola 2002).

Further information on the composition of aliphatic chains in interstellar carbonaceous material will be obtained through observation of vibrational bands associated with the carbon atoms in these chains. For example, sp-bonded polyyne chains ( $-C \equiv C_n$  will give rise to one or more well defined  $C \equiv C$  stretching bands in the 4.5–5  $\mu$ m range (2200–2000 cm<sup>-1</sup>) (Tabata et al. 2006), while sp-bonded cumulenic chains ( $C=C=C)_n$  produce bands at somewhat longer wavelength associated with C=C vibrational modes (Lucotti et al. 2006). The vibrations of sp<sup>3</sup> C–C

and sp<sup>2</sup> C=C bonds are less well constrained as they can occur over a much wider wavelength range (Colthup et al. 1990). The detection of IR spectral features associated with  $C \equiv C$  and C=C bonds in then of fundamental interest in defining the composition and structure of aliphatic hydrocarbons in interstellar sources (Allamandola et al. 1999). The properties of polyynes and cumulenes, collectively referred to as "carbynes" are discussed in Hermann et al. (2006).

In recent work, we have shown that IR spectra of CNPs produced by femtosecond (fs) laser ablation of graphite simulate many of the bands observed in carbon-rich emission sources (Hu et al. 2006; Hu & Duley 2007, 2008a). The structure of these condensates indicates that they can also contain sp-bonded carbon chains in association with ring molecules (Hu et al. 2007; Hu & Duley 2008c) and so we have examined our spectra for evidence of spectral features corresponding to these compounds. These spectra are reported here to enable a search for sp-bonded carbon chains in interstellar absorption and emission sources.

# 2. LABORATORY SPECTRA

Sample preparation and diagnostic techniques used in these experiments are described in detail elsewhere (Hu et al. 2007; 2008). Generally samples produced by fs laser ablation of graphite are assembled from a range of well defined CNPs. The building blocks of each CNP appear to be relatively constant and consist of assemblies of aromatic ring structures (including polycyclic aromatic hydrocarbons (PAHs)), connected by a variety of interlaced carbon chains. The relative concentration of chains in individual samples is variable and depends on such parameters as the incident laser intensity during irradiation and the presence or absence of ambient gas during ablation. IR and Raman spectra clearly show features that can be associated with the characteristic vibrations of  $CH_2$  and  $CH_3$  groups (Hu et al. 2007). These groups can bond directly to surface sites on PAH groups within each CNP, or they may be components of a variety of aliphatic chains. In many samples, CH<sub>2</sub> groups are found to be much more abundant than CH<sub>3</sub> groups, indicating that chains are quite long or are heavily branched.

Our analysis indicates that sp-bonded chains are present in many, but not all, samples. The key diagnostic is the observation



**Figure 1.** Laboratory spectra of CNP samples in the region of the C  $\equiv$  C stretching band in polyynes and the C=C band in cumulenes. (a) Sample prepared by ablation of graphite in acetylene, C<sub>2</sub>H<sub>2</sub>; (b) sample prepared in ethylene, C<sub>2</sub>H<sub>4</sub>; (c) sample prepared in H<sub>2</sub>: (d) as in (c) but in a different part of the deposit. The peaks near 2100 cm<sup>-1</sup> (4.76  $\mu$ m) are likely from polyyne chains, while those at 1900–1970 cm<sup>-1</sup> (5.26–5.08  $\mu$ m) may arise from cumulenic chains. The normalized profile of the 3.3  $\mu$ m band as measured in our CNP samples (Hu & Duley 2008b) is compared, after scaling to lower energy, to the peak at 1900 cm<sup>-1</sup> (5.26  $\mu$ m) in the lower trace.

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of two or more spectral features between 4.3 and 5.6  $\mu$ m (2300–1800 cm<sup>-1</sup>) attributable to the stretching vibrations of C=C and C = C groups. Several additional modes are also present at longer wavelengths, but spectral features from these vibrations overlap with other features from rings in this range. In addition, we do not observe the stretching vibration of acetylenic CH groups near 3350 cm<sup>-1</sup> (2.985  $\mu$ m) in our spectra, indicating that sp chains in these CNP samples act as bridging groups between rings. As a result, we have focused our studies on the spectral region near 5  $\mu$ m. One characteristic of spectra in this region is that the energy of the C=C and C = C stretching vibrations depends on the length of the chain, together with the nature of its terminating groups (Lucotti et al. 2006). This can be an advantage in identification when the chain length is well defined (Tabata et al. 2006), but most of our samples contain chains

of various lengths likely terminating on a number of different structures. For this reason, spectra are frequently broadened and contain multiple components. To avoid this problem as much as possible, and to provide spectra for comparison with observation, we have selected spectra from samples where the chain length appears to be more constrained (Figure 1). These spectra are for samples prepared in  $H_2$ ,  $C_2H_2$ , and  $C_2H_4$ .

The sharpest lines in these spectra have a FWHM of 9- $12 \text{ cm}^{-1}$  (0.023–0.03  $\mu$ m). This width arises from a combination of lifetime and site broadening and is typical of linewidths seen in other spectral regions in our samples (Duley 2008). Although these four spectra all show two separate lines, each spectrum contains a number of weaker features in this wavelength range (Table 1). The two strongest lines that are observed in each spectrum are highly characteristic of chains containing 6-12 carbon atoms (Tabata et al. 2006; Lucotti et al. 2006; Wakabayashi et al. 2007), although it is impossible to determine the nature of the terminating groups at the end of these chains from these spectra. The chain length can, nevertheless, be approximately estimated from the data provided by Tabata et al. (2006) as they measured the energy of the  $C \equiv C$  stretching vibration for size-selected H-terminated polyynes as well as for polyynes terminated with Ag atoms (Figure 2). A point to note here is that, although these are Raman spectra, the reduction in symmetry that occurs when these chains are bonded to other chemical groups means that these frequencies can also be IR active. Density functional theory (DFT) calculations confirm this effect and show that the strongest band in this region shifts by  $\sim -25 \mbox{ cm}^{-1}$  when a  $C_6$  or  $C_8$  polyyne is bonded to PAHs such as pyrene, C<sub>16</sub>H<sub>10</sub>, or coronene, C<sub>24</sub>H<sub>12</sub>. Since a variety of small PAH groups are present in our samples (Hu et al. 2007) it is expected that the energies of the measured  $C \equiv C$  bond stretching vibrations will occur between the  $C_nH_2$  and  $AgC_nH$ energies reported by Tabata et al. (2006). With this assumption, the energies of the bands at 2092 cm<sup>-1</sup> (4.870  $\mu$ m) and (2131, 2139 cm<sup>-1</sup>) (4.693, 4.675  $\mu$ m; Figure 1) would correspond to the C  $\equiv$  C band in C\_8 and C\_{10} chains. Features observed at lower energies may correspond to even longer polyynes, but are more likely due to cumulene chains (Lucotti et al. 2006). The appearance of numerous features in laboratory spectra (Figure 1) indicates that our samples contain a mixture of chains having different lengths and terminations.

 Table 1

 Spectral Components Arising from Stretching Vibrations of C=C and C  $\equiv$  C Chains Shown in Figure 1

Energy	Wavelength	FWHM	Primary Spectrum
$(cm^{-1})$	(µm)	$(cm^{-1})$	(Figure 1)
2254	4.437	9	d
2139	4.675	25	с
2131	4.693	40	d
2092	4.780	14	a, b
2009	4.978	12	с
1971	5.0735	13.5	с
1950	5.128	23	а
1945	5.141	13	b
1900	5.263	12	с
1896	5.274	18	d
1880	5.319	8.5	b
1867	5.356	16	b
1805	5.540	37	а
1769	5.652	23	d



**Figure 2.** Energies of the principle  $C \equiv C$  stretching band in Raman spectra of size-selected polyynes. (a) Circles, molecules having H termination at both ends (H ( $-C \equiv C$ )<sub>n</sub> – H); (b) squares, molecules having Ag termination (Tabata et al. 2006) at one end and H at the other. Corresponding bands for HC<sub>n</sub> molecules terminated with PAH at one end as present in our samples are shown as triangles.

#### 3. DISCUSSION

The presence of sp-bonded polyyne chains in certain interstellar and circumstellar objects has been known for some time (Bell et al. 1997; Chernicharo et al. 2001), but the more general question of the overall abundance of sp-bonded species in the general ISM has yet to be answered. The largest sp-chain molecules that have been detected in interstellar sources are all cyano-polyynes, but these occur with such low abundance  $(10^{-10} \text{ to } 10^{-11} \text{ rel-}$ ative to hydrogen) that there is little hope of detecting these species in IR absorption or emission (Kroto et al. 1987). In fact, these molecules are detectable in radio spectra only because they have high electric dipole moments. Large sp-bonded chains without—CN terminal groups would be virtually invisible in radio spectra, but could be detectable via absorption and emission in the C = C and C=C stretching region near 5  $\mu$ m.

Mid-IR absorption spectra of dark clouds and embedded protostars are characterized by a complex of bands in the 2136–2141 cm<sup>-1</sup> (4.68–4.67  $\mu$ m) region attributable to ices containing CO molecules (Whittet 2002). Another broad feature assigned to OCN<sup>-</sup> is also observed at 2165 cm<sup>-1</sup> (4.619  $\mu$ m) (Pendleton et al. 1999). These bands are also seen in Sgr A\* toward the Galactic center (Chiar et al. 2000) and all occur in the same wavelength range as that of the polyyne,  $(C - C \equiv C)$ , and cumulenic, (C=C=C), stretching bands. DFT simulations indicate that the polyyne and cumulene bands near 5  $\mu$ m are approximately twice as intense as the 3.3  $\mu$ m CH stretching vibration in coronene or pyrene molecules with attached sp chains. As a result, with calculated intensities of 100–150 km mol<sup>-1</sup>, these bands would be difficult to detect in dark cloud material when strong CO and OCN<sup>-</sup> bands are observed.

The possibility that carbon chains containing  $C \equiv C$  and C=Cstructures could be detected in diffuse galactic IR emission has been discussed by Allamandola et al. 1999. They concluded, from the absence of strong emission in the 5  $\mu$ m range in this spectrum, that separate carbon chains as a class were not significant components of interstellar material in the diffuse ISM. It is more likely, however, that any carbon chains that exist in interstellar or circumstellar sources are attached to the hydrocarbon molecules responsible for the IR emission features attributed to PAH, rather than being separate molecules. Attachment of a carbon chain to another molecule will increase the radiation stability of the combined species as the ability of a



**Figure 3.** Profile of the 5.25  $\mu$ m emission feature in HD 44,179 (Sloan et al. 2003; blue line) compared to the spectral feature at 5.274  $\mu$ m (1896 cm<sup>-1</sup>) in a CNP sample prepared in hydrogen (Figure 1(d)). The laboratory spectrum has been shifted by +10 cm<sup>-1</sup> (-0.028  $\mu$ m) to facilitate comparison with the profile of the interstellar feature.

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molecule to redistribute photon energy without decomposition scales rapidly with the number of atoms in the molecule (Allain et al. 1996a, 1996b). Spectra shown in Figure 1 are produced from molecules of this kind, and so are more representative of the type of ring-chain species that should be present in interstellar sources, particularly in cool circumstellar environments and regions where hydrocarbon material has not been heavily processed by UV radiation (Sloan et al. 2007; Keller et al. 2008). Spectra of molecules containing chains are characterized by one or more narrow lines associated with  $C \equiv C$  and C=C groups and so should be directly comparable to interstellar observations.

Observations of IR emission lines in many sources including HD 44179 and NGC 7027 (Boersma et al. 2009) show emission features at 5.25 and 5.7  $\mu$ m accompanying the other aromatic emission bands at 3.3, 6.2, and 11.3  $\mu$ m. A viable interpretation of the 5.25 and 5.7  $\mu$ m features is that they correspond to combination, difference, and overtone bands of the PAH species responsible for the other aromatic emission peaks. Nevertheless, given the proximity of these features to some of the bands shown in Figure 1, there is the possibility that emission by sp-bonded chains may contribute to one or both of these lines. The interstellar feature at 5.25  $\mu$ m in particular is very similar to that at 5.274  $\mu$ m (1896 cm<sup>-1</sup>) in Figure 1(d). This similarity extends to the profiles of the two features (Figure 3), as both the interstellar and laboratory bands exhibit a sharp rise at short wavelengths followed by a slow decline to 5.43  $\mu$ m. Figure 1(d) also shows another band peaking at 5.652  $\mu$ m (1769 cm<sup>-1</sup>) overlapping the interstellar feature at 5.65–5.75  $\mu$ m (1770–  $1739 \text{ cm}^{-1}$ ) (Boersma et al. 2009; Figure 3). The small energy differences ( $\sim 5 \,\mathrm{cm}^{-1}$ ) between the laboratory features and those observed in astrophysical spectra can be attributed to slightly different chemical bonding environments in the CNP samples compared to those in interstellar particles.

These are interesting coincidences that suggest that there is at least some possibility that sp-bonded chains are indeed attached to the aromatic ring compounds in IR emission sources. The agreement between the shapes of the laboratory band profiles and those of the interstellar features is also relevant as similar agreement is found in our simulation of the 3.28  $\mu$ m aromatic CH emission (Hu & Duley 2008b). A comparison between the profile of the 5.263  $\mu$ m feature reported here and that of the 3.3  $\mu$ m CH band in our CNP samples (Hu & Duley 2008b) is shown in Figure 1(d). It is evident that the two profiles are essentially identical, suggesting that the 5.263 and 3.3  $\mu$ m features arise in the same molecular complex in our samples.

## 4. CONCLUSIONS

We have obtained laboratory spectra of CNP samples containing sp-bonded chains (polyynes and cumulenes) for comparison with astrophysical spectra. These spectra show a number of well defined, narrow, features in the 4.5–5.7  $\mu$ m range that can be associated with the stretching vibrations of  $C \equiv C$  and C=Cbonds in long carbon chains attached to ring compounds. These features may be detectable in absorption in interstellar clouds, although they overlap with spectral lines arising from CO and XCN<sup>-</sup> ices. Since two of these bands occur within 0.013  $\mu$ m  $(5 \text{ cm}^{-1})$  of the IR emission bands at 5.65 and 5.7  $\mu$ m in interstellar spectra, we suggest that sp chains may contribute to these bands in interstellar emission sources. A striking similarity in profile between the 5.263 and 3.3  $\mu$ m features in our CNP samples appears to be replicated in the interstellar spectra. On this basis, we suggest that a component of PAHs in interstellar sources have attached sp-bonded chains.

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