Chapter 3

CARBONACEOUS ONION-LIKE PARTICLES: A POSSIBLE COMPONENT OF THE INTERSTELLAR MEDIUM

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Abstract: A carbonaceous material formed from a hydrocarbon plasma called quenched carbonaceous composite (QCC) is shown to have functional groups that approximate the positions of the interstellar 217.5 nm absorption and the infrared emission features at 3.3–11.3 μm. A form of this material, called “dark-QCC” has abundant carbonaceous onion-like particles. We present the results of various experiments involving QCC and conjecture that the carbonaceous onion-like particles in QCC may be a good laboratory analog to the carrier of the interstellar absorption and emission features. A scenario for dust formation from carbonaceous onion-like particles is presented.

Key words: Carbonaceous onion-like particle; circumstellar dust; infrared spectroscopy; infrared emission bands; dust analogs; high-resolution transmission electron microscope (HRTEM) imaging; interstellar dust; interstellar extinction bump; hydrocarbon plasma generation; quenched carbonaceous composite (QCC); UV spectroscopy

1. INTRODUCTION

Two of the outstanding questions regarding the composition of the interstellar medium (ISM) concern the origin of a strong ultraviolet
(UV) absorption at 217.5 nm and infrared emission features observed at 3.3, 6.2, 7.7, 8.6, and 11.3 μm that are observed in many sources in and outside of our Galaxy (Fitzpatrick, 2004; Peeters et al., 2004). We will discuss the production of a laboratory analog with spectral properties that suggest that these features could arise from a type of carbonaceous condensate produced from a hydrocarbon plasma. The work described here was originally motivated by the possibility that the 217.5 nm ISM absorption arises from carbonaceous material. A laboratory apparatus was fabricated to produce carbonaceous material that had an absorption band near 220 nm (Sakata et al., 1983, 1994). When the infrared absorption was measured, it was found that this material had absorption bands with assignments similar to that deduced for the ISM infrared emission features.

The 217.5-nm interstellar absorption band dominates the interstellar extinction curve. This absorption band is observed in lines of sight to hot stars and is very common in our galaxy (Fig. 1). There are strong

![Figure 1](image.png)

*Figure 1.* The UV to infrared spectrum of star HD 147701 (adapted from Fitzpatrick, 2004) with a noticeable very strong UV absorption band at 217 nm. The relative flux density $F_\lambda$ has units of ergs cm$^{-2}$ μm$^{-1}$
indications that this band involves a type of carbonaceous material (Mennella et al., 1996; Rouleau et al., 1997; Henning et al., 2004).

With regard to the infrared emission features, it is now generally accepted that the 3.3, 6.2, 7.7, 8.6, and 11.3 μm emission bands arise from a material that contains aromatic functional groups (Sellgren, 2001; Peeters et al., 2004) (Fig. 2). These emission features are observed around planetary nebulae, in star formation regions, and in the diffuse ISM. These bands are seen in emission because they arise from very small grains and are easily heated by UV radiation (Sellgren, 2001). Much work has gone into explaining the non-thermal emission mechanism, and a robust conclusion is that the particles giving rise to the emission bands must be less than 5 nm (Draine, 2003; Blakes et al., 2004).

![Figure 2. Spectrum of the infrared emission features (IEF) in the planetary nebula NGC 7027. Data is adapted from Peeters et al. (2004). The emission lines in the object have been removed so that the infrared emission features may be seen more clearly. Strong emission from the C–H stretch and the C–H out of plane bending in aromatic structures are evident at 3.3 and 11.3 μm. There is also emission at 3.4–3.5 μm that appears to come from side groups on aromatic structures as well. The relative flux density $F_\lambda$ has units of $W \text{ m}^{-2} \mu\text{m}^{-1}$](image-url)
Precise identification of the emitting material has not been possible to date. Many terms are used to refer to these bands, such as polycyclic aromatic hydrocarbon (PAH) bands, unidentified infrared (UIR) emission features, infrared emission features (IEF), and others (Peeters et al., 2004). We will refer to these features as “IEF” here. Note, however, that these emission bands are commonly referred to in the astronomical literature as “PAHs”, which is used as a generic term (Hudgins and Allamandola, 2004), even though there has been no spectroscopic detection of any specific PAH molecule in the interstellar medium to date (Clayton et al., 2003).

2. SYNTHESIS OF THE LABORATORY ANALOG AND ITS PROPERTIES

During 1970–1980 many molecules were detected in the ISM and circumstellar environment of stars. To study the formation of molecules, Sakata (1980) built an apparatus for the synthesis of interstellar molecules from simple radicals of plasmic gas. He hypothesized that materials formed from plasmic gases should have some similarities to the materials formed around evolved stars because the materials should be formed from chemically active and simple species.

The plasma was generated using a microwave generator in a small chamber made of quartz glass with a volume of 25 cm³, which was inserted in a microwave waveguide. Radio frequency generators and microwave generators are often used for formation of plasmic gas. In a plasmic gas formed by a radio frequency generator, the neutral source gas often remains in high abundance. But in Sakata’s apparatus, the source gas was decomposed completely into highly excited plasmic gas. The plasmic gas streamed into a vacuum chamber through a nozzle 7 mm in length and 1 mm in diameter. The nozzle collimated the plasmic gas beam. A schematic of the apparatus is shown in Fig. 3. In addition to molecules, solid materials formed in the ejecta from the collimated gas beam. These solids were also expected to be present in the circumstellar environment. This was the start of our study of dust formation in the laboratory.

Methane was initially used as a source of carbon and hydrogen. To make radicals, source gases (CH₄, H₂, etc.) were decomposed in the plasma chamber. By analysis of a quadrupole mass spectrometer, polyynes [H(C≡C)ₙH; n = 1–5], and aromatic molecules, benzene,
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naphthalene, and five-member rings compounds, were detected in the gas beam ejected into vacuum chamber (Sakata, 1980).

A solid material was condensed from the collimated gas beam. A circular spot of a brown-black solid appeared on the quartz-glass substrate placed perpendicular to the beam. A lighter colored brown-black material was deposited around the central spot (substrate B in Fig. 3) (Sakata et al., 1983). This material was named “quenched carbonaceous composite” (QCC) because it was made from carbon and hydrogen (carbonaceous), was formed through rapidly cooling (quenching) of the plasmic gas, and was a mixture of chemical compounds, i.e. it is a composite solid.

![Diagram of experimental setup](image)

**Figure 3.** The experimental setup for producing QCC samples. The hydrocarbon plasma is produced in a microwave discharge tube. The plasmic gas is injected through a small orifice into a vacuum chamber. Filmy-QCC was collected on a quartz substrate A, located on the wall of the vacuum chamber. Dark-QCC was collected on substrate B, located in the plasmic beam. A combination of dark and yellow material was collected on substrate C. (for more details, see Sakata et al., 1983, 1994)
A yellow-brown, filmy material was simultaneously deposited on a wall of the apparatus. The material was soluble in organic solvents, acetone, methanol, benzene; it was named “filmy-QCC”. The color of the material deposited very close to the plasmic chamber was brown, and the color of the material deposited far from the plasmic chamber was yellow. These colors indicate different chemical compositions of the materials.

The solid formed on the substrate in the plasmic beam was named dark-QCC (Sakata et al., 1987). The filmy-QCC is relatively rich in hydrogen compared with dark-QCC. Infrared and mass spectroscopy analyses showed that filmy-QCC is a mixture of various PAHs and other hydrocarbons. When filmy-QCC was heated in a vacuum, it became carbonized, and this material was called “thermally altered filmy-QCC” (TAF-QCC) (Sakata et al., 1990).

During synthesis of QCC, intensive radiation was emitted from the plasmic gas and Hα, Hβ, C2, and CH lines were observed. The emission intensities depended on many factors such as the power of the magnetron generator, duration of the plasma, and gas pressure. Approximate temperatures can be estimated from the emission-line intensities. The temperature of electronic excitation of atomic hydrogen was approximately 6000 K. The vibrational temperature of C2 was about 3000 K (Sakata et al., 1983). The plasma was a non-equilibrated plasma with the electronic excitation temperature >vibrational temperature >rotational temperature.

3. **UV SPECTRA AND STRUCTURE OF QCC MATERIALS**

3.1 **UV Spectra of QCC**

A dark-QCC that formed from a plasmic gas with a starting pressure 4 torr of methane and a microwave input power of ca. 300-350 W showed a broad absorption peak around 220 nm. Dark-QCC samples were prepared by washing them with acetone to remove soluble organic molecules. Using different mixtures of hydrogen and methane yielded QCC samples with different peak wavelengths (Wada et al., 1998). We obtained QCC samples with a maximum absorbance from 200 to 260 nm (Fig. 4). Organic molecular condensates (filmy-QCC) formed abundantly together with dark-QCCs peaking around 220 nm; filmy-QCC was relatively poor in the dark-
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QCC peaking around 230 nm and absent in the dark-QCC peaking at 250 nm. However, any proposed material for the carrier of the 217.5-nm feature must account for the nearly constant wavelength of the peak absorption in the ISM (Rouleau et al., 1997; Henning et al., 2004).

![Absorbance vs Wavelength](image)

Figure 4. UV spectra of QCC as a function of the wavelength of maximum absorbance and gas mixture (a) ca. 200 nm; 100% CH₄, (b) ca. 220 nm; 100% CH₄, (c) ca. 230 nm; 50% H₂, 50% CH₄, (d) ca. 250 nm; 70% H₂, 30% CH₄, (e) ca. 260 nm; 100% CH₄.

Samples (b), (c), and (d) were obtained outside of the plasma chamber (substrate B in Fig. 3) and are described by Wada et al. (1998). In addition, we collected solid samples in the plasmic chamber (substrate C in Fig. 3). A yellow solid with maximum absorbance at ca. 200 and a black solid with maximum absorbance at 260 nm were collected and are shown here as curves (a) and (e), respectively.
There are some rare classes of stars where the absorption peak is near 250 nm, as in R CrB stars (Hecht et al., 1984; Drilling and Schoenberner, 1989), and thus the ca. 250-nm QCC could be a laboratory analog for the absorbing material. The types of carbonaceous material formed in circumstellar environments depend on the chemical abundances and physical conditions, such as density, temperature, and cooling rate of the gas.

3.2 Structure of QCC Materials

We were able to produce various dark-QCCs with an absorption peak from ca. 200 nm to 260 nm. An interesting question is whether there is a correlation between the peak wavelength and the structure of the dark-QCCs. Various kinds of carbon solids have been studied with high-resolution transmission electron microscopy (HRTEM) (Oberlin and Bonmamy, 2001; Inagaki et al., 2004). We studied several samples of deposited QCC by HRTEM using a Hitachi H-9000 EM (Sakata et al., 1994; Wada et al., 1998, 1999; Goto et al., 2000). The QCC samples were mounted on a carbon thin-film supported by a standard copper, electron microscope, mesh grid. The dark deposit was generally too thick to obtain HRTEM images but good images were obtained in thin areas at the periphery of QCC samples (Fig. 5).

3.2.1 Dark-QCC

We found a variety of carbon structures in QCC. Except for the ca. 200-nm QCC sample, all QCC deposits have a complex microstructure. In the HRTEM images of the (002) lattice fringes we can see the aromatic graphene sheets stacked in a parallel sequence (Fig. 5d). Lattice fringes have the 0.336-nm spacing for (002) lattice fringes of graphite, but larger lattice-fringe spacings are common for graphitic carbons, even in nicely uniform, parallel ribbons. In many images of QCC, the carbon layers are curved and stacked concentrically.

We summarize below the characteristic features seen in the QCC images shown in Fig. 5, listed according to increasing wavelength of absorption peak position. For each item we give the color of the material, the composition of the starting gas, the microwave power, and the substrate location (cf. Fig. 3):
Figure 5. High-Resolution Transmission Electron Micrographs of QCC samples corresponding to the UV spectra shown in Fig. 4. The scale bar in each image is 10 nm.
1. ~200-nm QCC (yellow, 100% CH₄, 270 W, substrate C): Two solids of different color, i.e. yellow and black, were produced in the plasma chamber. The yellow solid appears amorphous in HRTEM image and has an absorption band at about 200 nm. It was not soluble in acetone and is therefore more polymerized than filmy-QCC (Fig. 5a).

2. ~220-nm QCC (dark brown/black, 100% CH₄, 350 W, substrate B): This dark material is formed in the gas beam ejected from the plasma and contains abundant multi-layer, carbonaceous onion-like particles (Fig. 5b). This material is referred to as dark-QCC.

3. ~230-nm QCC (dark brown/black, 50% CH₄ + 50% H₂, 270 W, substrate B): The shape of the concentric multi-layer carbon structures is typically polyhedral rather than spherical (Fig. 5c).

4. ~250-nm QCC (black, 30% CH₄ + 70% H₂, 270W, substrate B): The linear and bent structures may be polyhedrons (Fig. 5d). The HRTEM appearance is very similar to glassy carbon (Oberlin, 1989).

5. ~260-nm QCC (black, 100% CH₄, 300 W, substrate C): The structure is straighter and longer than in the 250-nm QCC sample. We also find curled semispherical components attached to peripheral graphitic layers (Fig. 5e).

This series of QCC materials shows the growth of the carbon network that occurred between wavelengths 220 nm and 260 nm. The ca. 250-nm and ca. 260-nm QCCs have a well-developed carbon network of larger and flat layers that are stacked together. The carbon network in the ca. 250-nm QCC has a bent, ribbon-like structure. The number of graphitic layers is nearly the same as the number of layers in the carbonaceous onion-like particles. This suggests that onion-like particles might be a precursor of the ribbon-like structure.

In Fig. 6 we show low-magnification images of another sample of dark-QCC along with high-magnification images (insets). The QCC sample shows a bump around 220 nm. It is composed of many fine particles. The fine particles are about 5 to 15 nm in diameter and seem to be very similar to the onion-like particles. However, the particles are not perfectly onion-like: their shells are not always closed. Some shells are connected to the next shell. The central core of some spherules seems to be vacant (Fig. 6a). This is larger than the size of C₆₀, which is 0.7 nm in diameter. In addition, many shell fragments are attached to their surface.
A typical onion-like particle is shown in Fig. 7. The onion-like particle is composed of about 10,000 carbon atoms. The central shell of an onion-like particle is about the same size of C\textsubscript{450} fullerene. Fullerenes have a closed cage structure because they incorporate five-member rings in their networks. A model of a fragmented shell observed in the QCC onion-like particle is presented in Fig. 7.

The concentric spherule on the left side of the HRTEM image of Fig. 7 is composed of more fractured shells than that of the one in the center of this image. It is composed of very small fragments. A structure 0.6 nm in length corresponds to a carbon network with 2–3 carbon rings aligned linearly. PAH molecules with this size are fluorene, coronene, and anthracene, among many others. A structure 1.3 nm in length corresponds to a carbon network with 5–6 carbon rings aligned linearly. Circumanthracene fits this size. However, in the plasma-produced QCC, not all of these PAHs may be perfect molecules. It is likely that they lost some peripheral hydrogen atoms. The onion-like particles are an intermediate material between PAHs and carbon onions. They are composed of broken shells, shell fragments, PAH-like components, and possibly fullerene. We view the particles in the HRTEM images as roughly concentric layers with imperfections. The particles contain hydrogen, so they are
carbonaceous and not pure carbon onions. We conclude that the onion-like particles with many fragmented shells are the major components of the QCC.

![Diagram of onion-like particles and PAHs](image)

*Figure 7.* High-resolution transmission electron microscope image of onion-like QCC spheres (center) and a C₉₀₀ fullerene model (top right) having the approximate diameter of the second, inner shell of the carbon onion. “PAH” indicates fragments of the carbon onion that are planar or curved structures. A curved fragment of the carbon onion is shown in the sphere on the left. It is only partially hydrogenated, and there are dangling bonds (radicals) as indicated by the “+” symbol.

3.2.2 Thermally Altered Filmy-QCC (TAF-QCC)

PAHs are the main component of the filmy-QCC. When the filmy-QCC was heated at 350 °C for 20 min inside a small quartz glass vessel, spherules with no discernable structure and a diameter of about
5 to 20 nm appeared in the initially amorphous filmy-QCC (Sakata et al., 1994). The sizes of the newly formed spheres are similar to those of the carbonaceous onion-like particles observed in the original dark-QCC samples (Fig. 6). The filmy-QCC began to carbonize at temperatures of 500–600 °C. Abundant onion-like particles were found in the carbonized TAF-QCC. This TAF-QCC shows a 220 nm absorption peak and a 3.3 μm C–H peak (Sakata et al., 1990, 1994). It is unclear whether the onion-like particles were formed in the initially amorphous filmy-QCC or formed from the gas that evaporated from the filmy-QCC and was trapped in the quartz container.

3.3 Comparison to Other Carbonaceous Materials and the Origin of the 220-nm Absorption Band

In addition to QCC, many other types of carbonaceous materials have been proposed as possible carriers of the 217.5-nm absorption. These include processed hydrogenated amorphous carbon (HAC) (Duley and Lazarev, 2004; Mennella, 2004), nano-sized carbon grains formed in Ar-H2 gas mixtures containing carbon vapor (Schnaiter et al., 1998), and coal material (Papoular et al., 1996). Papoular et al. (1996) provide a summary of the properties of these materials. In the case of HAC, the 217.5-nm absorption is produced by thermal processing of HAC or by UV irradiation (Duley and Lazarev 2004; Mennella, 2004). The 217.5-nm band is also produced by ion bombardment of carbon grains formed in Ar or in H2 (Mennella et al., 1997).

As already noted, our 220-nm QCC samples contain onion-like particles (Figs. 5 and 6) and they are thus not completely amorphous carbon. In this respect, QCC is not similar to HAC. Another type of carbonaceous laboratory analog that shows onion-like particles is the evaporation of graphite electrodes in the presence of H2 (see Fig. 4 in Henning et al., 2004).

Soot prepared in Ar-H2 atmospheres also showed the 220-nm absorption with variations in the wavelength of maximum absorption. Rotundi et al. (1998) studied the correlation between the wavelength of maximum absorption and the structure of particles in the condensed soot samples. They found various forms of carbon particles, incl. chain-like aggregates of 7–15 nm spheres, bucky-onions, bucky-tubes, and graphitic carbon ribbons in their samples. They could not find any obvious differences in the abundance of these particles among the soot samples and concluded that the internal structures of chain-like
aggregates caused the variations in the wavelength of maximum absorption.

dé Heer and Ugarte (1993) investigated the relationship between the peak of the UV absorption and the shape of the carbon onion particles. They made soot samples by arc discharge in a heated tube. By annealing samples at various temperatures, they formed carbon onion particles with different shapes. Their result indicated that the width of the UV absorption band changed with annealing temperature, however, the absorption maximum appeared about 260 nm in all samples, which were dispersed in water.

dé Heer and Ugarte (1993) showed that the onion particles annealed at 2250 °C have a more polyhedral shape than the particles of the 220-nm QCC. The 220-nm QCC, on the other hand, is not stable when heated to such high temperatures. Heating the 220-nm QCC at 700 °C for 20 minutes leads to loss of volatile materials (Wada et al., 1999). The peak absorbance of the residual material was reduced by 75% compared to unheated QCC, and the peak was shifted to 234 nm. It suggests that onion-like particles in the 220-nm QCC are composed of organic or carbonaceous materials that evaporated or are modified at high temperature.

In our experiments, clear differences in the structure were detected in the QCCs as the wavelength of the maximum absorption changes. The shift to longer wavelengths of the maximum absorption corresponds to changes in the size and flatness of the carbon network.

From the molecular approach, the absorption band of organic materials at ca. 200 nm results from electronic excitation of π bond electrons (π-π*). It is well known that π electrons are delocalized by the conjugation of π bonds and that the conjugation stabilizes the bonds. As conjugation increases, the absorption peak caused by π electrons is shifted to longer wavelengths. For example, 1,3-butadiene and 1,3,5-hexatriene show a peak at 217 nm and 258 nm, respectively.

The wavelength of maximum absorption is at 200 to 260 nm in QCC. The 220-nm absorption band can be explained by a

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structure. A wavelength of 260 nm was the maximum found in a well-developed carbon network of QCC. Rotundi et al. (1998) also found that by processing soot, the absorption band was shifted up to 260 nm.

Graphite has well-delocalized π electrons but the UV absorption of graphite will shift to shorter wavelengths if the π electrons are
localized within a small number of carbon atoms because of the formation of defects. Using amorphous carbon as a starting material, Mennella et al. (1997) performed an experiment to break the C-network by bombardment with helium ions. They found that an absorption peak around 220 nm was produced as a result.

Does a curved structure result in localization of the \( \pi \) electrons? Tomita et al. (2001) made spherical carbon onions by heating particles of nanodiamond to 1700 °C and polyhedral carbon onions by further heating to 1900 °C. By electron energy-loss spectroscopy, they found localized \( \pi \) electrons in the spherical carbon onions. On the other hand, in the polyhedral carbon onions, the \( \pi \) electrons were delocalized. Tomita et al. (2004) calculated the extinction bump of spherical carbon onions with defective structures and found a reasonable fit to the 220-nm interstellar extinction band. However, experiments are needed to confirm these calculations.

From the above discussion, we concluded that the size of conjugation of the \( \pi \) bond is a main factor for the wavelength of maximum absorption. By perturbation of the development of the carbon network, such as the inhibition of the chemical bond formation with hydrogen, defect formation by ion bombardment, or the formation of defective curved structure, the wavelength of maximum absorption is shifted to shorter wavelengths. Although the size of the chemical bonds responsible for the peak wavelength is very small, with the enlargement of the conjugation of the \( \pi \) electrons, the structure of the QCC particles is changed as seen in HRTEM images.

Although carbonaceous material with conjugated carbon bonds does have absorption near 220 nm due to \( \pi-\pi^* \) electronic transitions, there is no clear mechanism for achieving the near constancy of the 217.5-nm band observed in the interstellar medium. This is presently an unsolved problem. A major difficulty in producing a good laboratory analog is that we are unable to reproduce isolated particles as in the ISM. There are also other possibilities. From an analysis of interplanetary dust particles, Bradley et al. (2005) presented another idea for the carrier of the interstellar 217.5-nm absorption. They suggested both organic carbon and OH-bearing amorphous silicates could contribute to the absorption.
4. IR SPECTRA

4.1 IR Spectra of QCC Materials

The infrared spectra of QCC samples are presented in Fig. 8. The spectra of the dark-QCC were measured after washing with acetone to remove organic molecules. Samples were directly collected on a KBr or BaF₂ substrate; therefore their thickness is not uniform.

Figure 8. IR spectra of (a) filmy-QCC, (b) dark-QCC, and (c) TAF-QCC. Spectra (a) and (b) are discussed in detail by Wada et al. (2003). The aromatic C–H stretching mode can be seen at 3.3 μm; the C–H out-of-plane bending mode at 11.4-13.2 μm; the skeletal in plane vibration mode of C=C at 6.25 μm; the deformation of CH₂ and the asymmetric deformation of CH₃ at 6.9 μm; and the symmetric deformation of CH₃ at 7.27 μm. We are not sure about the identification of the 7.7 and 8.6 μm bands reported by Sakata et al. (1987)
The filmy-QCC shows strong IR bands with weak continuous background absorption (Fig. 8a), while the 220-nm and 250-nm dark-QCC material shows strong background absorption (Figs. 8b and 8c). The TAF-QCC also shows strong background absorption.

Bands caused by C–H stretching vibration modes appear at 3–4 μm. A band at 3.3 μm (stretching mode) and a band at 11.4 μm (out-of-plane bending mode) are caused by the aromatic C–H bond. They are observed in all samples except the 250-nm dark-QCC sample, which is consistent with the HRTEM data showing no major structural difference between dark-QCCs and TAF-QCCs. Carbonized TAF-QCC shows a 3.3 μm band (aromatic C–H). Dark-QCC shows weak a 3.3 μm band and strong ca. 3.4 μm and ca. 3.5 μm bands due to the stretching vibration of methylene (CH₂) and methyl (CH₃). TAF-QCC is the only material that does not show the ca. 3.4 μm and ca. 3.5 μm bands, since heating had caused the loss of the aliphatic component.

Other bands that arose from duo, trio, and quartet aromatic C–H bonds appear at 11.9–12.0 μm and 13.2–13.3 μm. These bands are strong in the filmy-QCC (Fig. 8a), but weak in TAF-QCC and dark-QCC. A very small hump can be seen at 12.5–12.7 μm in both QCC samples (Figs. 8b and 8c).

It is well known that thermal heating destroys aliphatic bonds. We reported a variation of infrared features of the 3–4 μm region during carbonization of filmy-QCC at temperatures of 500–600 °C (Sakata et al., 1990; Goto et al., 2000). A band caused by C=C vibration exists at 6.2–6.3 μm in the QCC samples. Usually, a single C=C bond shows a band at 5.9–6.1 μm. The peak moves to longer wavelengths when the double bond is weakened by conjugation. Small absorption bands at 7.7 μm and 8.6 μm that correspond to interstellar IEF (infrared emission features; Fig. 2) are often seen in the broad 8-μm band of TAF-QCC and dark-QCC (see, Sakata et al., 1987); they are the very weak features seen in Fig. 8. However, QCC does not have the strong bands at 7.6/7.9 μm and 8.6 μm in the IEF. In addition, there is a difference in the wavelength of the peaks for the out-of-plane bending mode of aromatic C–H, which are at 11.4 μm in QCC and 11.25 μm in the IEF.

As a whole, the spectra of TAF-QCC samples have similarities to the observed interstellar IEF, although the relative QCC band strengths are different from IEF. Similar spectra for heated HAC material were obtained (Scott and Duley, 1996), and it indicates that the infrared active functional groups reported by Sakata et al. (1987) have no unique origins in terms of the nature of the carbon phase, the mode of formation, or thermal processing.
4.2 Comparison to Other Carbonaceous Materials

Similar IR absorption bands are observed in dark-QCC (Fig. 8), HAC heated to 427 °C (Scott and Duley, 1996) and nano-sized carbon grains formed in an H$_2$ atmosphere (Schnaiter et al., 1998). Thus, these three materials have similar functional groups. In addition, carbonized TAF-QCC and HAC heated to 527 °C (Scott and Duley, 1996) also show very similar spectra, namely a strong aromatic band at 3.3 μm and a weak aliphatic band at 3.4 μm.

At the level of our current understanding, there appear to be structural differences between these materials even though the infrared active functional groups appear to be similar. Compare, for example, the carbon nanostructures shown in our Figs. 6 and 7 with those shown in Fig. 2 of Scott and Duley (1996) and in Fig. 2 in Schnaiter et al. (1998). In carbonaceous material, atomic groups attached to the peripheral site cause major IR bands. Therefore, similar IR bands appear even if carbonaceous materials would have a different bulk structure. Both the dark-QCC and TAF-QCC samples are reasonable interstellar dust analogs because they contain nanometer-sized particles (Fig. 7) that have the approximately correct functional groups of the particles that are thought to reside in the ISM.

5. A POSSIBLE SCENARIO FOR THE FORMATION OF THE IEF CARRIER

We conjecture that dust processing around evolved stars progresses as follows: Spectral-type M giant and supergiant stars and OH/IR stars are the largest carbon and silicate dust-producing sources in our Galaxy (Gehrz, 1989; Kwok, 2004). Such stars in the last stages of stellar evolution are known as asymptotic giant branch (AGB) stars. Mass loss in this stage of evolution leads to copious production of dust. During the period of maximum mass-loss and dust production, these stars are totally obscured at visible wavelengths, but they are very bright IR sources. Carbonaceous dust, like dark-QCC, is formed at the location of high temperature and high gas density in the mass-loss process of AGB stars. On the other hand, organic condensations such as filmy-QCC are formed in cooler regions of the circumstellar environment of AGB stars.

The AGB phase ends when mass loss stops and the star collapses into a white dwarf star. The white dwarf star has an extremely high surface temperature and is a source of intense UV radiation. Thus, UV
and visible photons irradiate the surrounding dust, and the resulting nebular emission is known as a planetary nebula (PN). As the temperature rises in the PN phase of the central star, organic dusts are heated and thermally altered by UV photons. They are polymerized through dehydrogenation and finally carbonized in a process similar to the production of TAF-QCC. Thermal processing is very effective for making isolated aromatic C-H bonds.

Both filmy-QCC and dark-QCC become mostly carbonaceous onion-like particles containing a small amount of hydrogen through thermal alteration. Both materials exhibit the 220-nm absorption bump. In the photo-dissociation zone of PNs, the carbonaceous onion-like particles are partially destroyed. Shell fragments are gradually broken off from the onion-like particles. The shell fragments absorb UV photons, and are heated stochastically. Some of the fragments are ionized by UV photons. The very small particles (<5 nm) produce the IEF but the larger dust, e.g. the carbonaceous onion-like particles (Fig. 7; central object), is not observed because it is not heated stochastically to high temperatures. Finally, the shell fragments and onion-like particles that survived in the shell of a PN are ejected into the ISM.

The IEF carrier phases are also widespread in the diffuse ISM of the Galaxy, where they are well mixed with large dust particles (Onaka et al., 1996). According to our hypothesis, the onion-like dust particles are gradually eroded by shock waves, UV irradiation, and bombardment by atoms and ions. These erosion processes create small PAH-like shell fragments in the ISM that become the IEF carriers.

When the shell fragments are ionized, strong C=C and –C–C– skeletal emission will be observed because of dipole formation. When onion-like particles absorb UV energy, they show the 217.5-nm extinction bump. Allain et al. (1996) and Vuong and Foing (2000) made estimates of the stability of PAHs in the ISM and concluded that small PAHs are unstable and are easily dehydrogenated, whereas large PAHs are hydrogenated and stable in the ISM.

We note that Jones (1997) and van Winckel (2003) reviewed dust production and processing by UV radiation, and dust ejection into the ISM, and that Tokunaga (1997) and Waters (2004) summarized the rich variety of infrared spectra observed in AGB stars and planetary nebulae. The PAH model was discussed by Hudgins and Allamandola (2004), Scott and Duley (1996) discussed thermally altered HAC, and irradiated HAC was discussed by Mennella et al. (1997, 2002). Papoular et al. (1996) reviewed the coal model. We recommend these papers for other points of view than expressed in our scenario.
6. SUMMARY AND CONCLUSIONS

We synthesized quenched carbonaceous materials from a hydrocarbon plasma. Dark-QCC composed of defective onion-like particles showed an absorption feature similar to the interstellar 217.5-nm bump. The absorption maximum shifted to the longer wavelengths as the carbon structure changed into a polyhedral form. The IEF in evolved stars is well simulated by thermally-altered filmy-QCC. However, the shape and position of the IEF in space was not reproduced precisely by the QCC spectra. Nevertheless, QCC shows functional groups that have many similarities to the observed spectra. We believe QCC is a good analog for the carbonaceous dust in space.

Acknowledgements. We thank Alessandra Rotundi for helpful comments on our manuscript. Akira Sakata conceived the method of producing QCC, and he was the driving force behind the development of QCC as a laboratory analog for the carbonaceous materials in the ISM. He passed away in 1995, and we dedicate this paper to him. The authors would like to thank S. Kimura and C. Kaito for their HRTEM analyses at Ritsumeikan University, F. Drabik for assistance with the figures, and L. Good for assistance with the manuscript.

7. REFERENCES


3. Carbonaceous Onion-Like Particles


A typical onion-like particle is shown in Fig. 7. The onion-like particle is composed of about 10,000 carbon atoms. The central shell of an onion-like particle is about the same size of \( \text{C}_{450} \) fullerene. Fullerenes have a closed cage structure because they incorporate five-member rings in their networks. A model of a fragmented shell observed in the QCC onion-like particle is presented in Fig. 7.

The concentric spherule on the left side of the HRTEM image of Fig. 7 is composed of more fractured shells than that of the one in the center of this image. It is composed of very small fragments. A structure 0.6 nm in length corresponds to a carbon network with 2–3 carbon rings aligned linearly. PAH molecules with this size are fluorene, coronene, and anthracene, among many others. A structure 1.3 nm in length corresponds to a carbon network with 5–6 carbon rings aligned linearly. Circumanthracene fits this size. However, in the plasma-produced QCC, not all of these PAHs may be perfect molecules. It is likely that they lost some peripheral hydrogen atoms. The onion-like particles are an intermediate material between PAHs and carbon onions. They are composed of broken shells, shell fragments, PAH-like components, and possibly fullerene. We view the particles in the HRTEM images as roughly concentric layers with imperfections. The particles contain hydrogen, so they are
carbonaceous and not pure carbon onions. We conclude that the onion-like particles with many fragmented shells are the major components of the QCC.

![Diagram of onion-like carbonaceous particles and PAH](image)

*Figure 7. High-resolution transmission electron microscope image of onion-like QCC spheres (center) and a C_{960} fullerene model (top right) having the approximate diameter of the second, inner shell of the carbon onion. “PAH” indicates fragments of the carbon onion that are planar or curved structures. A curved fragment of the carbon onion is shown in the sphere on the left. It is only partially hydrogenated, and there are dangling bonds (radicals) as indicated by the “*” symbol.*

### 3.2.2 Thermally Altered Filmy-QCC (TAF-QCC)

PAHs are the main component of the filmy-QCC. When the filmy-QCC was heated at 350 °C for 20 min inside a small quartz glass vessel, spherules with no discernable structure and a diameter of about
5 to 20 nm appeared in the initially amorphous filmy-QCC (Sakata et al., 1994). The sizes of the newly formed spheres are similar to those of the carbonaceous onion-like particles observed in the original dark-QCC samples (Fig. 6).

The filmy-QCC began to carbonize at temperatures of 500–600 °C. Abundant onion-like particles were found in the carbonized TAF-QCC. This TAF-QCC shows a 220 nm absorption peak and a 3.3 μm C–H peak (Sakata et al., 1990, 1994). It is unclear whether the onion-like particles were formed in the initially amorphous filmy-QCC or formed from the gas that evaporated from the filmy-QCC and was trapped in the quartz container.

3.3 Comparison to Other Carbonaceous Materials and the Origin of the 220-nm Absorption Band

In addition to QCC, many other types of carbonaceous materials have been proposed as possible carriers of the 217.5-nm absorption. These include processed hydrogenated amorphous carbon (HAC) (Duley and Lazarev, 2004; Mennella, 2004), nano-sized carbon grains formed in Ar–H₂ gas mixtures containing carbon vapor (Schneider et al., 1998), and coal material (Papoular et al., 1996). Papoular et al. (1996) provide a summary of the properties of these materials. In the case of HAC, the 217.5-nm absorption is produced by thermal processing of HAC or by UV irradiation (Duley and Lazarev 2004; Mennella, 2004). The 217.5-nm band is also produced by ion bombardment of carbon grains formed in Ar or in H₂ (Mennella et al., 1997).

As already noted, our 220-nm QCC samples contain onion-like particles (Figs. 5 and 6) and they are thus not completely amorphous carbon. In this respect, QCC is not similar to HAC. Another type of carbonaceous laboratory analog that shows onion-like particles is the evaporation of graphite electrodes in the presence of H₂ (see Fig. 4 in Henning et al., 2004).

Soot prepared in Ar–H₂ atmospheres also showed the 220-nm absorption with variations in the wavelength of maximum absorption. Rotundi et al. (1998) studied the correlation between the wavelength of maximum absorption and the structure of particles in the condensed soot samples. They found various forms of carbon particles, incl. chain-like aggregates of 7–15 nm spheres, bucky-onions, bucky-tubes, and graphitic carbon ribbons in their samples. They could not find any obvious differences in the abundance of these particles among the soot samples and concluded that the internal structures of chain-like
aggregates caused the variations in the wavelength of maximum absorption.

de Heer and Ugarte (1993) investigated the relationship between the peak of the UV absorption and the shape of the carbon onion particles. They made soot samples by arc discharge in a heated tube. By annealing samples at various temperatures, they formed carbon onion particles with different shapes. Their result indicated that the width of the UV absorption band changed with annealing temperature, however, the absorption maximum appeared about 260 nm in all samples, which were dispersed in water.

de Heer and Ugarte (1993) showed that the onion particles annealed at 2250 °C have a more polyhedral shape than the particles of the 220-nm QCC. The 220-nm QCC, on the other hand, is not stable when heated to such high temperatures. Heating the 220-nm QCC at 700 °C for 20 minutes leads to loss of volatile materials (Wada et al., 1999). The peak absorbance of the residual material was reduced by 75% compared to unheated QCC, and the peak was shifted to 234 nm. It suggests that onion-like particles in the 220-nm QCC are composed of organic or carbonaceous materials that evaporated or are modified at high temperature.

In our experiments, clear differences in the structure were detected in the QCCs as the wavelength of the maximum absorption changes. The shift to longer wavelengths of the maximum absorption corresponds to changes in the size and flatness of the carbon network.

From the molecular approach, the absorption band of organic materials at ca. 200 nm results from electronic excitation of \( \pi \) bond electrons (\( \pi-\pi^* \)). It is well known that \( \pi \) electrons are delocalized by the conjugation of \( \pi \) bonds and that the conjugation stabilizes the bonds. As conjugation increases, the absorption peak caused by \( \pi \) electrons is shifted to longer wavelengths. For example, 1,3-butadiene and 1,3,5-hexatriene show a peak at 217 nm and 258 nm, respectively.

The wavelength of maximum absorption is at 200 to 260 nm in QCC. The 220-nm absorption band can be explained by a

\[
-C=\overline{C}-=\overline{C}-
\]

structure. A wavelength of 260 nm was the maximum found in a well-developed carbon network of QCC. Rotundi et al. (1998) also found that by processing soot, the absorption band was shifted up to 260 nm.

Graphite has well-delocalized \( \pi \) electrons but the UV absorption of graphite will shift to shorter wavelengths if the \( \pi \) electrons are
localized within a small number of carbon atoms because of the formation of defects. Using amorphous carbon as a starting material, Mennella et al. (1997) performed an experiment to break the C-network by bombardment with helium ions. They found that an absorption peak around 220 nm was produced as a result.

Does a curved structure result in localization of the \( \pi \) electrons? Tomita et al. (2001) made spherical carbon onions by heating particles of nanodiamond to 1700 °C and polyhedral carbon onions by further heating to 1900 °C. By electron energy-loss spectroscopy, they found localized \( \pi \) electrons in the spherical carbon onions. On the other hand, in the polyhedral carbon onions, the \( \pi \) electrons were delocalized. Tomita et al. (2004) calculated the extinction bump of spherical carbon onions with defective structures and found a reasonable fit to the 220-nm interstellar extinction band. However, experiments are needed to confirm these calculations.

From the above discussion, we concluded that the size of conjugation of the \( \pi \) bond is a main factor for the wavelength of maximum absorption. By perturbation of the development of the carbon network, such as the inhibition of the chemical bond formation with hydrogen, defect formation by ion bombardment, or the formation of defective curved structure, the wavelength of maximum absorption is shifted to shorter wavelengths. Although the size of the chemical bonds responsible for the peak wavelength is very small, with the enlargement of the conjugation of the \( \pi \) electrons, the structure of the QCC particles is changed as seen in HRTEM images.

Although carbonaceous material with conjugated carbon bonds does have absorption near 220 nm due to \( \pi-\pi^* \) electronic transitions, there is no clear mechanism for achieving the near constancy of the 217.5-nm band observed in the interstellar medium. This is presently an unsolved problem. A major difficulty in producing a good laboratory analog is that we are unable to reproduce isolated particles as in the ISM. There are also other possibilities. From an analysis of interplanetary dust particles, Bradley et al. (2005) presented another idea for the carrier of the interstellar 217.5-nm absorption. They suggested both organic carbon and OH-bearing amorphous silicates could contribute to the absorption.
4. IR SPECTRA

4.1 IR Spectra of QCC Materials

The infrared spectra of QCC samples are presented in Fig. 8. The spectra of the dark-QCC were measured after washing with acetone to remove organic molecules. Samples were directly collected on a KBr or BaF₂ substrate; therefore their thickness is not uniform.

![Graph showing IR spectra of QCC materials](image)

*Figure 8. IR spectra of (a) filmy-QCC, (b) dark-QCC, and (c) TAF-QCC. Spectra (a) and (b) are discussed in detail by Wada et al. (2003). The aromatic C–H stretching mode can be seen at 3.3 μm; the C–H out-of-plane bending mode at 11.4–13.2 μm; the skeletal in plane vibration mode of C=C at 6.25 μm; the deformation of CH₂ and the asymmetric deformation of CH₃ at 6.9 μm; and the symmetric deformation of CH₃ at 7.27 μm. We are not sure about the identification of the 7.7 and 8.6 μm bands reported by Sakata et al. (1987)*
The filmy-QCC shows strong IR bands with weak continuous background absorption (Fig. 8a), while the 220-nm and 250-nm dark-QCC material shows strong background absorption (Figs. 8b and 8c). The TAF-QCC also shows strong background absorption.

Bands caused by C–H stretching vibration modes appear at 3–4 \( \mu \text{m} \). A band at 3.3 \( \mu \text{m} \) (stretching mode) and a band at 11.4 \( \mu \text{m} \) (out-of-plane bending mode) are caused by the aromatic C–H bond. They are observed in all samples except the 250-nm dark-QCC sample, which is consistent with the HRTEM data showing no major structural difference between dark-QCCs and TAF-QCCs. Carbonized TAF-QCC shows a 3.3 \( \mu \text{m} \) band (aromatic C–H). Dark-QCC shows weak a 3.3 \( \mu \text{m} \) band and strong ca. 3.4 \( \mu \text{m} \) and ca. 3.5 \( \mu \text{m} \) bands due to the stretching vibration of methylene (CH\(_2\)) and methyl (CH\(_3\)). TAF-QCC is the only material that does not show the ca. 3.4 \( \mu \text{m} \) and ca. 3.5 \( \mu \text{m} \) bands, since heating had caused the loss of the aliphatic component.

Other bands that arose from duo, trio, and quartet aromatic C–H bonds appear at 11.9–12.0 \( \mu \text{m} \) and 13.2–13.3 \( \mu \text{m} \). These bands are strong in the filmy-QCC (Fig. 8a), but weak in TAF-QCC and dark-QCC. A very small hump can be seen at 12.5–12.7 \( \mu \text{m} \) in both QCC samples (Figs. 8b and 8c).

It is well known that thermal heating destroys aliphatic bonds. We reported a variation of infrared features of the 3–4 \( \mu \text{m} \) region during carbonization of filmy-QCC at temperatures of 500–600 °C (Sakata et al., 1990; Goto et al., 2000). A band caused by C=C vibration exists at 6.2–6.3 \( \mu \text{m} \) in the QCC samples. Usually, a single C=C bond shows a band at 5.9–6.1 \( \mu \text{m} \). The peak moves to longer wavelengths when the double bond is weakened by conjugation. Small absorption bands at 7.7 \( \mu \text{m} \) and 8.6 \( \mu \text{m} \) that correspond to interstellar IEF (infrared emission features; Fig. 2) are often seen in the broad 8-\( \mu \text{m} \) band of TAF-QCC and dark-QCC (see, Sakata et al., 1987); they are the very weak features seen in Fig. 8. However, QCC does not have the strong bands at 7.6/7.9 \( \mu \text{m} \) and 8.6 \( \mu \text{m} \) in the IEF. In addition, there is a difference in the wavelength of the peaks for the out-of-plane bending mode of aromatic C–H, which are at 11.4 \( \mu \text{m} \) in QCC and 11.25 \( \mu \text{m} \) in the IEF.

As a whole, the spectra of TAF-QCC samples have similarities to the observed interstellar IEF, although the relative QCC band strengths are different from IEF. Similar spectra for heated HAC material were obtained (Scott and Duley, 1996), and it indicates that the infrared active functional groups reported by Sakata et al. (1987) have no unique origins in terms of the nature of the carbon phase, the mode of formation, or thermal processing.
4.2 Comparison to Other Carbonaceous Materials

Similar IR absorption bands are observed in dark-QCC (Fig. 8), HAC heated to 427 °C (Scott and Duley, 1996) and nano-sized carbon grains formed in an H$_2$ atmosphere (Schnaiter et al., 1998). Thus, these three materials have similar functional groups. In addition, carbonized TAF-QCC and HAC heated to 527 °C (Scott and Duley, 1996) also show very similar spectra, namely a strong aromatic band at 3.3 μm and a weak aliphatic band at 3.4 μm.

At the level of our current understanding, there appear to be structural differences between these materials even though the infrared active functional groups appear to be similar. Compare, for example, the carbon nanostructures shown in our Figs. 6 and 7 with those shown in Fig. 2 of Scott and Duley (1996) and in Fig. 2 in Schnaiter et al. (1998). In carbonaceous material, atomic groups attached to the peripheral site cause major IR bands. Therefore, similar IR bands appear even if carbonaceous materials would have a different bulk structure. Both the dark-QCC and TAF-QCC samples are reasonable interstellar dust analogs because they contain nanometer-sized particles (Fig. 7) that have the approximately correct functional groups of the particles that are thought to reside in the ISM.

5. A POSSIBLE SCENARIO FOR THE FORMATION OF THE IEF CARRIER

We conjecture that dust processing around evolved stars progresses as follows: Spectral-type M giant and supergiant stars and OH/IR stars are the largest carbon and silicate dust-producing sources in our Galaxy (Gehrz, 1989; Kwok, 2004). Such stars in the last stages of stellar evolution are known as asymptotic giant branch (AGB) stars. Mass loss in this stage of evolution leads to copious production of dust. During the period of maximum mass-loss and dust production, these stars are totally obscured at visible wavelengths, but they are very bright IR sources. Carbonaceous dust, like dark-QCC, is formed at the location of high temperature and high gas density in the mass-loss process of AGB stars. On the other hand, organic condensations such as filmy-QCC are formed in cooler regions of the circumstellar environment of AGB stars.

The AGB phase ends when mass loss stops and the star collapses into a white dwarf star. The white dwarf star has an extremely high surface temperature and is a source of intense UV radiation. Thus, UV
and visible photons irradiate the surrounding dust, and the resulting nebular emission is known as a planetary nebula (PN). As the temperature rises in the PN phase of the central star, organic dusts are heated and thermally altered by UV photons. They are polymerized through dehydrogenation and finally carbonized in a process similar to the production of TAF-QCC. Thermal processing is very effective for making isolated aromatic C-H bonds.

Both filmy-QCC and dark-QCC become mostly carbonaceous onion-like particles containing a small amount of hydrogen through thermal alteration. Both materials exhibit the 220-nm absorption bump. In the photo-dissociation zone of PNs, the carbonaceous onion-like particles are partially destroyed. Shell fragments are gradually broken off from the onion-like particles. The shell fragments absorb UV photons, and are heated stochastically. Some of the fragments are ionized by UV photons. The very small particles (<5 nm) produce the IEF but the larger dust, e.g. the carbonaceous onion-like particles (Fig. 7; central object), is not observed because it is not heated stochastically to high temperatures. Finally, the shell fragments and onion-like particles that survived in the shell of a PN are ejected into the ISM.

The IEF carrier phases are also widespread in the diffuse ISM of the Galaxy, where they are well mixed with large dust particles (Onaka et al., 1996). According to our hypothesis, the onion-like dust particles are gradually eroded by shock waves, UV irradiation, and bombardment by atoms and ions. These erosion processes create small PAH-like shell fragments in the ISM that become the IEF carriers.

When the shell fragments are ionized, strong C=C and –C—C—skeletal emission will be observed because of dipole formation. When onion-like particles absorb UV energy, they show the 217.5-nm extinction bump. Allain et al. (1996) and Vuong and Foing (2000) made estimates of the stability of PAHs in the ISM and concluded that small PAHs are unstable and are easily dehydrogenated, whereas large PAHs are hydrogenated and stable in the ISM.

We note that Jones (1997) and van Winckel (2003) reviewed dust production and processing by UV radiation, and dust ejection into the ISM, and that Tokunaga (1997) and Waters (2004) summarized the rich variety of infrared spectra observed in AGB stars and planetary nebulae. The PAH model was discussed by Hudgins and Allamandola (2004), Scott and Duley (1996) discussed thermally altered HAC, and irradiated HAC was discussed by Mennella et al. (1997, 2002). Papoular et al. (1996) reviewed the coal model. We recommend these papers for other points of view than expressed in our scenario.
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7. REFERENCES


3. Carbonaceous Onion-Like Particles


