

## ORGANIC DUST IN THE INTERSTELLAR MEDIUM

SUN KWOK

Space Astronomy Laboratory, Faculty of Science, The University of Hong Kong, Hong Kong, China

*E-mail: sunwok@hku.hk*

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### ABSTRACT

The traditional view of dust in the interstellar medium is that it is made of graphite and silicates. In this paper, we discuss the evidence for complex organics being a major component of interstellar dust. Comparison between astronomical infrared spectra and laboratory spectra of amorphous carbonaceous materials suggests that organics of mixed aromatic-aliphatic structures are widely present in circumstellar, interstellar, and galactic environments. Scenarios for the synthesis of these compounds in the late stages of stellar evolution are presented.

*Key words:* interstellar dust: infrared spectroscopy: fullerene: PAH : unidentified infrared emission bands

### 1. INTRODUCTION

Since interstellar dust was discovered about a century ago by the technique of selective extinction, the chemical composition of dust has been generally assumed to be either minerals or ice. Although the possibility of organic dust had been proposed as early as the 1970s (Hoyle & Wickramasinghe, 1977), these suggestions were not taken seriously because it was generally thought that interstellar conditions are too hostile for the formation of organic dust.

The discovery of a family of unidentified infrared emission (UIE) bands at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$  in the planetary nebula NGC 7027 (Russell et al., 1977) opened up the possibility of an organic solid component in the Universe. The UIE bands are widely present in planetary nebulae, in emission and reflection nebulae, in diffuse clouds in the galactic halo, and in external galaxies. Soon after their discovery, the UIE bands were identified as due to stretching and bending modes of aromatic compounds (Knacke, 1977; Duley & Williams, 1979; Duley et al., 1981). The strengths of the UIE bands are so strong that a significant fraction of the interstellar carbon pool must be locked up in organic dust. The energy emitted in the UIE bands can account for up to 20% of the total energy output of some galaxies. The UIE bands have also been observed to  $z \sim 2$ , suggesting that organic synthesis occurred as early as 10 billion years ago.

### 2. THE PAH HYPOTHESIS

The resemblance of the UIE bands to the spectrum of automobile exhaust led to the suggestion that the carrier of the UIE bands are polycyclic aromatic hydrocarbon (PAH) molecules (Allamandola et al., 1985).

The PAH model was preferred over the organic dust model because by the 1980s, a large number of gas-phase molecules had been identified in space through their rotational transitions and it was easier to accept gas-phase molecules as the carrier of the UIE bands than organic solids. In the past 25 years, the PAH hypothesis has become the dominant theory for the origin of the UIE features. This theory assumes that the UIE features are the result of infrared fluorescence from small ( $\sim 50$  C atoms) gas-phase PAH molecules being pumped by far-ultraviolet photons (Tielens, 2008). The strongest support for the PAH hypothesis is that single-photon excitation of PAH molecules can account for the 12  $\mu\text{m}$  excess emission in cirrus clouds in the diffuse interstellar medium observed by the IRAS satellite (Sellgren, 1984, 2001). Although there have been a number of alternative models proposed as the carrier of the UIE bands, including hydrogenated amorphous carbon (HAC, Jones et al., 1990), quenched carbonaceous composites (Sakata et al., 1987), coal and kerogen (Papoular et al., 1989; Papoular, 2001), and petroleum fractions (citepcataldo2004), the PAH hypothesis has remained firmly entrenched in the astronomical literature for the last 25 years. However, when examined closely, the PAH hypothesis faces several problems as an explanation of the UIE phenomenon:

- PAH molecules have well-defined sharp features but the UIE features are broad;
- PAHs are primarily excited by UV, with little absorption in the visible, but UIE features are seen in PPN and reflection nebulae with no UV radiation;
- The strong and narrow predicted gas-phase features in the UV are not seen in interstellar extinction curves to very low upper limits ( $10^{-10} - 10^{-8}$  PAH

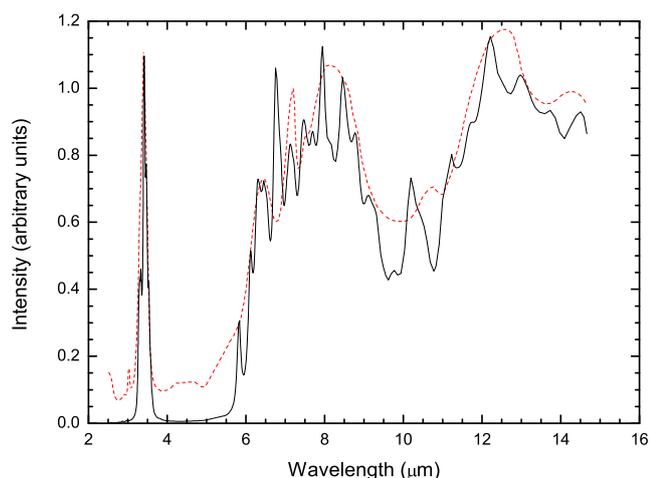


Figure 1. Fitting of the laboratory infrared spectrum (solid line) of HAC obtained by Dischler et al. (1983) using the PAHdb model (dashed line). The fact that the PAH model can fit the HAC spectrum suggests that such fittings do not represent robust tests of the PAH hypothesis.

per H, compared to the level of  $10^{-7}$  expected from the strengths of the infrared bands) (Clayton et al., 2003; Salama et al., 2011; Gredel et al., 2011);

- No specific PAH molecules have been detected in space in spite of the fact that PAH molecules are simple and their vibrational and rotational frequencies are well known;
- No PAH emission spectrum has been able to reproduce the UIE spectrum w.r.t. either band positions or relative intensities (Schlemmer et al., 1994; Cook et al., 1996; Cook & Saykally, 1998; Wagner et al., 2000);
- The shapes and peak wavelengths of UIE features are independent of the temperature of the exciting star (Uchida et al., 2000).

In order to avoid these problems the PAH model has to appeal to a mixture of PAHs of different sizes, structures (compact, linear, branched) and ionization states, as well as artificially broadening the intrinsic molecular line profiles. Actual fits to the astronomical observations are accomplished by having a population of mixed PAH molecules and ions with variable relative abundances and adding up and broadening their vibrational lines (Allamandola et al., 1999; Cami, 2011). In order to test the validity of such fits, we have used the fitting code and data in the NASA Ames PAH IR Spectroscopic Database (Boersma et al., 2014) to fit a variety of non-PAH spectra, including silicates, HAC (Figure 1), coal, and even artificial spectra. We found that all these non-PAH spectra can be well fitted by PAH mixtures, suggesting that the ability to fit the UIE spectra does not necessarily mean that they are due to PAH molecules (Zhang & Kwok, 2014).

### 3. THE MAON HYPOTHESIS

The discoveries of the  $3.4 \mu\text{m}$  feature (due to C–H aliphatic stretch) in absorption in the Galaxy (Wickra-

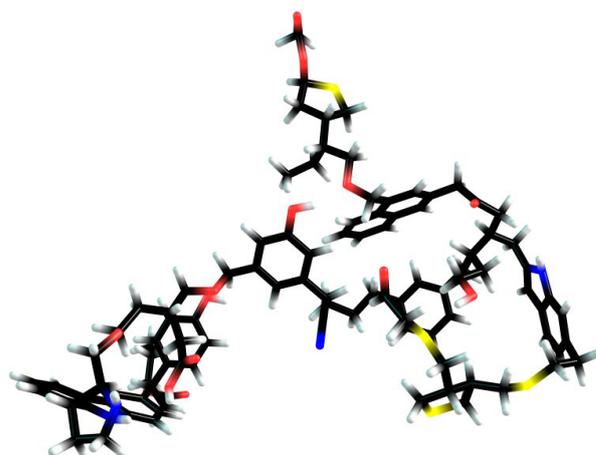


Figure 2. A 3-D illustration of a possible partial structure of a MAON particle. Carbon atoms are represented in black, hydrogen in light grey, sulphur in yellow, oxygen in red, and nitrogen in blue. There are 101 C, 120 H, 14 O, 4 N, and 4 S atoms in this example. The number of heavy elements has been intentionally exaggerated for the purpose of illustration.

masinghe & Allen, 1980) and external galaxies (Spoon et al., 2004) have led to an increased attention to aliphatic structures as a component of organic dust. The detection of the  $3.4$  and  $6.9 \mu\text{m}$  aliphatic features and strong emission plateau features around  $8$  and  $12 \mu\text{m}$  in pre-planetary nebulae has also demonstrated that the aliphatic and aromatic components are produced together in the late stages of stellar evolution (Kwok et al., 1999, 2001). These observations have motivated us to propose mixed aromatic/aliphatic organic nanoparticles (MAON) as an alternative explanation to the UIE phenomenon (Kwok & Zhang, 2011, 2013). The MAON hypothesis is different from the PAH model in several ways. MAONs are amorphous (with no fixed structure); contain rings of different sizes and chains of different lengths and random orientations; are not pure C/H compounds but contain impurities such as O, N, and S; and are 3-D (not 2-D as in PAH) in geometric structure. The exact aromatic to aliphatic ratio in a MAON particle depends on radiation environment (photochemistry), original gas-phase components, and H content. A MAON particle will consist of multiple units similar to the one shown in Figure 2.

The strengths of the short wavelength ( $3.3$  and  $7.7 \mu\text{m}$ ) UIE features suggest that they cannot be due to thermal excitation of bulk materials. They can only be excited by stochastic heating of nanoparticles by single high energy photons, or by transient heating through the release of chemical energy (Duley & Williams, 2011).

The discovery of fullerene ( $\text{C}_{60}$ ) in planetary nebulae (Cami et al., 2010) has led to the association of plateau emission features with  $\text{C}_{60}$ . In fact, all planetary nebulae showing  $\text{C}_{60}$  also have plateau emission features. This has led to the suggestions that MAONs are precursors to fullerene (García-Hernández et al., 2012; Bernard-Salas et al., 2012).

Advances in computational technologies have made

possible to perform quantum chemical calculations of vibrational frequencies of complex organics with  $>100$  C atoms. We have begun calculations of large PAH and MAON molecules to identify their vibrational modes for comparison with astronomical observations (Sadjadi et al., 2014). For example, in addition to the 8 and 12  $\mu\text{m}$  plateau features, there is also a broad plateau feature around 17  $\mu\text{m}$  which has not been identified. We are exploring whether this feature can be the result of mixed C skeleton and C–H bending modes.

#### 4. PATHWAY OF ORGANIC SYNTHESIS

From millimeter-wave and infrared spectroscopic observations of asymptotic giant branch (AGB) stars, pre-planetary nebulae, and planetary nebulae, we can put together a scenario of organic synthesis. Starting with simple molecules such as  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_2\text{H}$ , and  $\text{CN}$ , acetylene ( $\text{C}_2\text{H}_2$ ) is formed near the end of the AGB. Acetylene can bend and join together to form the first aromatic molecule benzene ( $\text{C}_6\text{H}_6$ ) in the pre-planetary nebulae phase. Several rings can link together to form base aromatic units on which various aliphatic side chains can be attached as peripherals of the aromatic rings. These elementary structures can be further processed by photochemistry after the onset of ultraviolet radiation during the planetary nebulae stage. These organic particles are ejected into the interstellar medium, into molecular clouds, and maybe even to the early Solar System (Kwok, 2004). It is possible that the present Solar System contains remnants of stellar organic dust.

#### 5. TIME SCALE OF CIRCUMSTELLAR SYNTHESIS

The evolutionary lifetimes of planetary nebulae and pre-planetary nebulae are  $10^4$  and  $10^3$  yr, respectively, so we know that organic dust is formed on timescales shorter than these evolutionary time intervals. Even more dramatic is the formation of organic dust in novae. The 3.3 and 3.4  $\mu\text{m}$  UIE features and the 8 and 12  $\mu\text{m}$  plateau features have been observed to emerge in the spectra of novae over time intervals of weeks (Evans et al., 2005). This is direct evidence that organic dust can easily form in the circumstellar environment.

#### 6. RELATIONS WITH OTHER UNEXPLAINED SPECTRAL PHENOMENA

Besides the UIE bands, there are a number of longstanding unsolved spectroscopic problems in the interstellar medium. These include the diffuse interstellar bands (DIB), the 217.5 nm absorption feature, extended red emission (ERE), and the 21 and 30  $\mu\text{m}$  emission features. These are not isolated or localized phenomena as these spectral features have been widely detected in circumstellar and interstellar media, in the Galactic haloes, and in galaxies. Because of their ubiquitous nature, their carriers must be made of common and abundant elements. Over 400 DIBs have been observed to date and they are most likely due to electronic transitions of gas-phase unknown C-based molecules. Amorphous carbonaceous solids often have strong band gaps in the

UV and a member of this class of organic solids could be the carrier of the 217 nm band. Organic solids are also capable of self luminescence in the visible and therefore are good candidates as carriers of ERE. The 21 and 30  $\mu\text{m}$  features are closely related to the UIE phenomenon and may have similar origins. It is clear that amorphous organic solids have the potential to help solve many mysteries of the interstellar medium and should be further studied (Kwok, 2014).

#### 7. CONCLUSIONS

Contrary to popular belief that organics are too difficult to synthesize in space, we now have strong observational evidence that complex organics with aromatic/aliphatic structures are produced in circumstellar envelopes on a large scale, over short ( $\sim 10^3$  yr) time intervals, and under low-density conditions. The exact chemical processes leading to their synthesis is not understood theoretically. What is not in doubt is that Nature can produce organic grains efficiently and they are widely present all over the Universe, from the Solar System, to stars, to interstellar space, and in distant galaxies (Kwok, 2011). Such a prevalent presence of organic materials in the Universe has potential significant implications on the energy balance of galaxies, on radiative energy exchange between stars and the interstellar medium, chemical enrichment of the Solar System, and the origin of life (Kwok, 2013).

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