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Dust in planetary nebulae

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Abstract. Infrared spectra from the *Spitzer Space Telescope* trace the evolution of carbon-rich dust from the asymptotic giant branch (AGB) to young planetary nebulae (PNe). On the AGB, amorphous carbon dominates the dust, but SiC and MgS also appear. In more evolved systems with warmer central stars, the spectra reveal the unidentified 21 μm feature, features from aliphatic hydrocarbons, and spectra from polycyclic aromatic hydrocarbons (PAHs), often with shifted feature positions indicative of the presence of aliphatics. More evolved systems with hot central stars show more typical PAH spectra, along with fullerenes and/or an emission feature known as the big-11 feature at $\sim$11 μm. This features arises from a combination of SiC and PAHs, and it is usually accompanied by a shoulder at 18 μm, which while unidentified might be from cool silicate grains. The strong emission from MgS and SiC in young PNe probably arises from coatings on carbonaceous grains.

Keywords. stars: AGB and post-AGB, planetary nebulae: general, dust

1. Introduction

In an effort to better understand the role of metallicity in the death of intermediate-mass stars, several projects used the Infrared Spectrograph (IRS; Houck *et al.* 2004) on the *Spitzer Space Telescope* (Werner *et al.* 2004) to obtain infrared spectra of post-main-sequence objects in the Large and Small Magellanic Clouds (LMC and SMC). The observed sample included dozens of post-AGB objects and planetary nebulae (PNe). Carbon-rich dust dominated the sample, and the nature of that dust will be the focus of this contribution.

The story of carbon-rich dust in PNe begins with the discovery of the unidentified infrared (UIR) emission features in the spectra of two young Galactic PNe by Gillett *et al.* (1973). The carrier of these spectral features is best described as polycyclic aromatic hydrocarbons (PAHs; Leger & Puget 1984; Allamandola, Tielens, & Barker 1985), because it must consist of hydrocarbons, those hydrocarbons need to be aromatic to withstand the harsh radiation fields where they are found, and they must contain enough carbon atoms to be at the boundary between large molecules and very small dust grains. Aromaticity requires that the hydrocarbons are built of many benzene rings, and the size constraint means that they must be polycyclic. Thus, they must be polycyclic, predominantly aromatic, and hydrocarbon, or, to put it simply, PAHs. (See Allamandola, Tielens, & Barker 1989 for a more thorough argument.)

PNe excite PAH emission in a thin photo-dissociation region at the boundary between an ionized bubble and the surrounding dust shell produced when the central star was still on the asymptotic giant branch (AGB). As the ionized region expands into the circumstellar dust shell, the PNe slowly but steadily destroys the dust grains. The PAHs are just the final stage for that dust as the ionization front reaches it.

The IRS sample of evolved stellar objects in the Magellanic Clouds gives us insights into the nature of carbon-rich dust and how it changes as the central star from a carbon star on the AGB to a hot white dwarf at the center of a mature PN. Sloan *et al.* (2014; hereafter S14) examined the full IRS sample of 27 carbon-rich post-AGB objects in the LMC and 15 in the SMC.

2. The asymptotic giant branch

The AGB is the starting point for the dust. To investigate the large samples of carbon-rich AGB stars observed by the IRS, Sloan *et al.* (2006) and Zijlstra et al. (2006) introduced the Manchester Method. Amorphous carbon dominates the dust they produce, but it does not generate any identifiable emission features in the infrared. The Manchester Method uses the [6.4]−[9.3] color, which samples the "continuum" from star plus dust in spectral regions unaffected by absorption bands or emission features, as a proxy for the dust-production rate. The [6.4]−[9.3] color reddens as the spectral contribution from amorphous carbon dust grows and buries the contribution from the central star. At the same time, the emission feature from SiC dust at ∼11.3 μm increases in strength, but the strongest SiC emitters have largely vanished at redder [6.4]−[9.3] colors where MgS dust emission at ∼30 μm grows strong.

This behavior suggests that MgS, which has a relatively low condensation temperature, condenses onto pre-existing grains in more optically thick dust shells (Lagadec *et al.* 2007; Leisenring *et al.* 2008), generating a MgS feature as it masks the emission from SiC. Zhukovska & Gail (2008) reached a similar conclusion independently from a theoretical perspective.

MgS has an interesting story. Forrest *et al.* (1981) first discovered the 30 μm emission feature in spectra of carbon-rich PNe and dust-enshrouded objects like IRC +10216 from the *Kuiper Airborne Observatory*. Goebel & Moseley (1985) identified the carrier as MgS. In some PNe, the 30 μm feature is so strong, MgS cannot be the carrier without violating abundance constraints, at least if the grains are solid MgS (Zhang *et al.* 2009). However, Lombaert et al. (2012) showed that a layer of MgS can reproduce the observed 30 μm feature and avoid the abundance problem, and as pointed out the IRS observations suggest exactly this geometry. S14 considers other objections to MgS and concludes that it is still a strong candidate for the 30 μm carrier.

3. Aliphatic hydrocarbons

If PAHs are the form that carbonaceous grains take when they are heavily photo-processed in a UV field, what do the grains look like in milder conditions? Peeters *et al.* (2002) provided some important clues by classifying all of the PAH spectra observed with the Short-Wavelength Spectrometer (SWS) on the *Infrared Space Observatory* into three groups. Figure 1 illustrates these, plus some newer classifications. The Class A spectrum is typical for H II regions around young stars, and Class B is typical for PNe. The spectra differ most notably in the 7–9 μm region, with Class A PAHs showing a feature at 7.65 μm, while in Class B PAH spectra, the feature at 7.85 μm is stronger. In two spectra, both post-AGB objects, an emission feature at ∼8.2 μm dominates the emission at 7.65 and 7.85 μm.

The IRS observed several more Class C PAH spectra, all of which are excited by central objects with temperatures $\lesssim$ 6500 K (Sloan *et al.* 2007). The PAH features in the 3 μm regime provide more clues. Usually, the 3.29 μm C–H stretching mode from PAHs dominates the 3.40 μm feature attributed to an aliphatic C–H stretching mode, but some post-AGB objects show much stronger 3.40 μm features (e.g. Geballe & van

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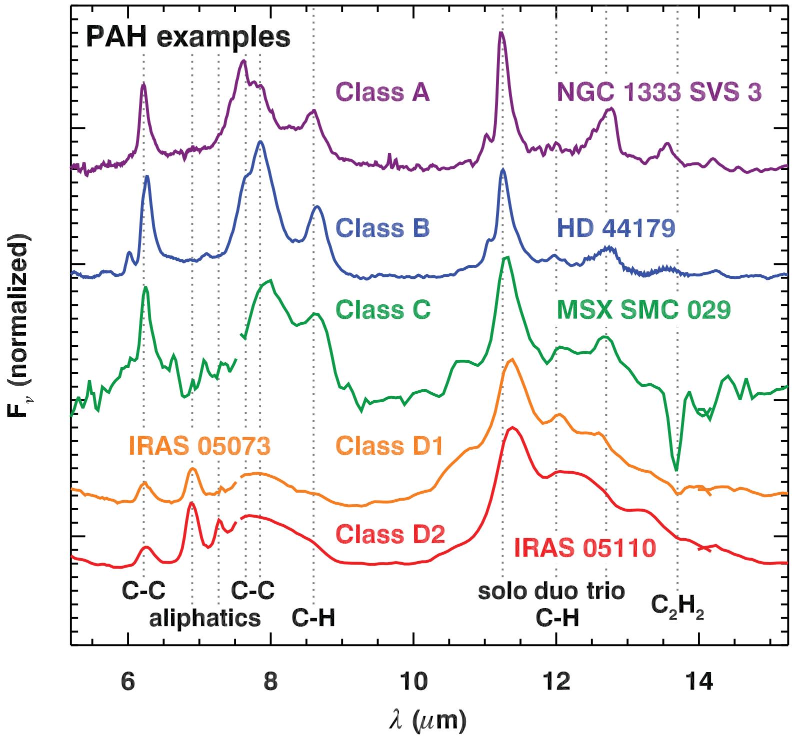

Figure 1. Sample spectra for each PAH class. An in-plane C–H bending mode produces the 8.6 μm feature, while out-of-plane C–H bending modes produce the 11.2, 11.9, and 12.7 μm features, with the number of adjacent H atoms in an aromatic ring determining the wavelength. Aliphatic hydrocarbons produce the features at 6.85 and 7.25 μm, and acetylene absorption appears at 13.7 μm in many post-AGB objects.

der Veen 1990; Geballe *et al.* 1992), in one case even in absorption (Chiar *et al.* 1998). Together, the evidence suggests that aliphatic hydrocarbons can survive alongside PAHs if the radiation field is cool enough. In the hotter radiation fields associated with Class A and Class B PAHs, the relatively fragile aliphatics are destroyed. Laboratory analysis by Pino *et al.* (2008) confirmed that the presence of aliphatics shifts the PAH features to longer wavelengths. When aliphatics can survive, we observe the PAHs as a Class C spectrum.

4. The 21 μm sources

Carbon-rich objects which have evolved past the AGB show a rich variety of spectra, as Figure 2 illustrates. Post-AGB objects can show the 21 μm feature, which was discovered by Kwok *et al.* (1989) in the Galaxy. Volk *et al.* (2011) found several more sources with the still-unidentified 21 μm feature in the Magellanic Clouds. Figure 3 plots two typical spectra. The 21 μm feature always appears with several other features, although any given feature may be absent from a given spectrum. Generally, most of the 21 μm spectra show emission features at 6.85 and 7.25 μm attributed to aliphatic hydrocarbons. They also show features at 15.4 and 17.1 μm which S14 attributes to aliphatic hydrocarbons with triple C–C bonds. Chains which end with this bond produce the 15.4 μm feature. Displacing the triple bond one atom inward shifts the feature to 17.1 μm. A triple bond suggests some dehydrogenation, which could indicate increasing photoprocessing as the central source reveals itself.

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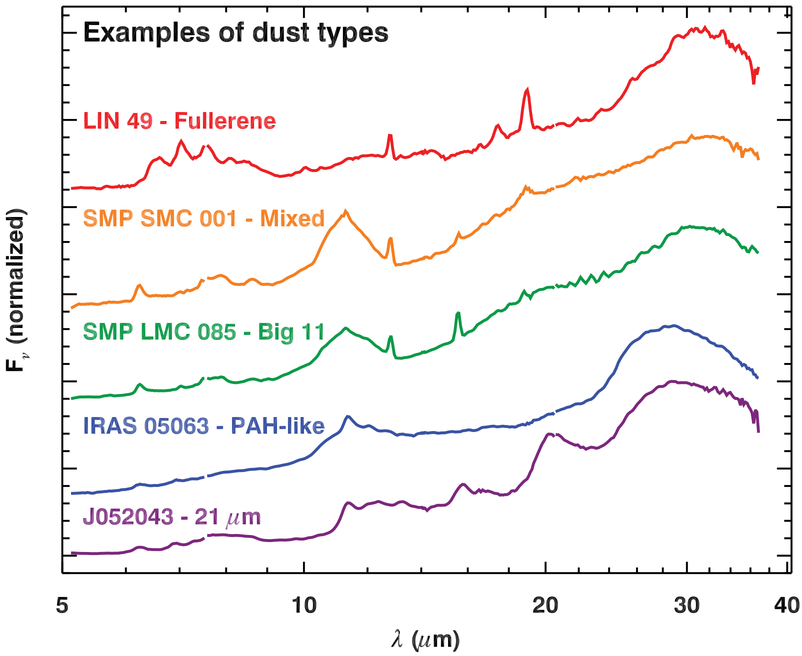

Figure 2. Examples of the well-populated classes of dust spectra identified by S14 in the sample of carbon-rich post-AGB spectra in the Magellanic Clouds.

Cerrigone *et al.* (2011) noted an association between the 21 μm feature and PAHs, but the additional evidence points more to aliphatics. An association does not necessarily imply an identification; it could be that the carrier of the 21 μm feature appears in conditions which are also favorable for aliphatic hydrocarbons.

Matsuura *et al.* (2014) introduced a new class of PAH spectra, Class D (Figure 1). In Class D PAHs, emission fills what is usually a valley between the C–C modes at 6–8 μm and the 8.6 μm in-plane C–H bending mode. In addition, the shape of the 11–13 μm PAH complex changes, with a much stronger contribution between 11.2 and 12.7 μm. S14 broke the Class D PAHs into two groups, with D2 distinguished from D1 by a shift of the 11.9 and 12.7 μm features to ~12.4 and 13.2 μm. Most of the 21 μm sources are associated with some form of Class D PAH emission. As Figure 3 shows, the classification at 6–9 μm does not always agree with that at 11–13 μm. What produces Class D PAH spectra is not known, but aliphatic hydrocarbons seem to be a likely suspect.

5. Young carbon-rich PNe

Young PNe show spectra that S14 described as "Fullerene," "Mixed," and "Big-11". Cami (2017) will address the fullerene sources in a separate contribution to these proceedings. The fullerene class blends smoothly into the mixed class, which show features from both fullerenes and PAHs (typically Class B). These spectra blend smoothly into the Big-11 class, which shows a strong feature at ~11 μm (hence the name) and a shoulder at ~18 μm.

Figure 4 illustrates two Big-11 spectra. S14 showed that the big-11 feature is mostly SiC emission, with some PAH emission superimposed. Bernard-Salas *et al.* (2009) noted that if the big-11 feature were SiC, it would be puzzling why it is so much stronger in Magellanic PNe than in Galactic PNe, given the lower metallicities in the LMC and SMC.

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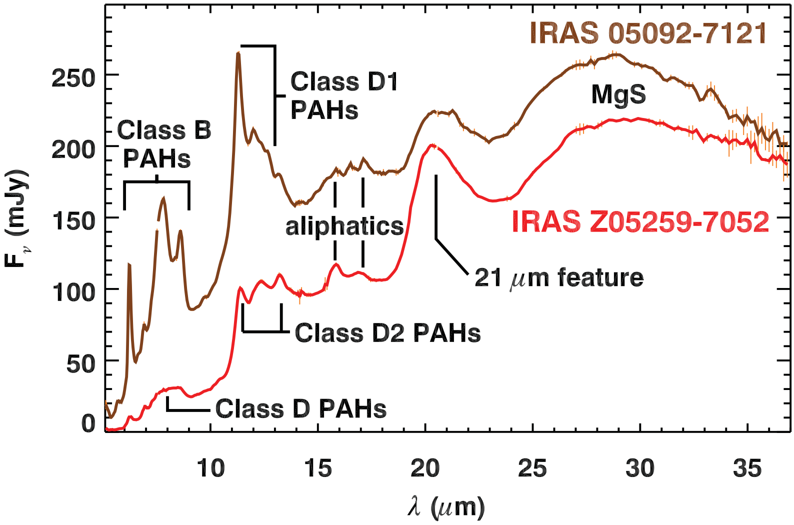

Figure 3. The IRS spectra of two spectra with 21 μm feautures. Both spectra also show strong MgS emission at ∼30 μm, and they show features at 15.4 and 17.1 μm which S14 have identified with aliphatics. They also show unusual PAHs, with IRAS Z05259 showing Class D2 PAHs and IRAS 05092 showing a mixture of Class D1 and Class B PAHs. These combinations of different PAHs at different wavelengths are not uncommon in the 21 μm sources.

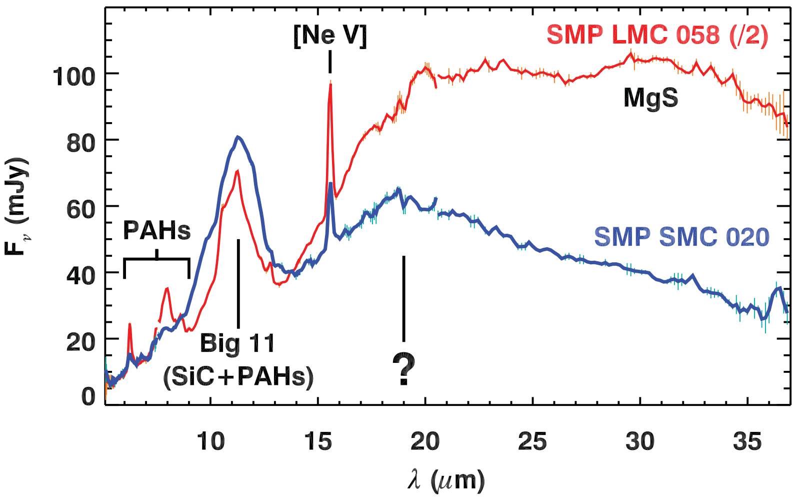

Figure 4. The IRS spectra of two Big-11 sources. The spectrum of SMP LMC 058 (divided by two here) is typical, with clear PAH emission in the 6–9 μm region, a big-11 feature from a combination of SiC and PAHs, a shoulder in the spectrum ∼18 μm, and an MgS feaure at ∼30 μm. The spectrum of SMP SMC 020 is a more extreme case, with a much more pronounced big-11 feature due to a lack of cool dust. The carrier of the 18 μm shoulder is not known, but if it were really cool silicates, as originally suggested by Bernard-Salas *et al.* (2009), that raises some interesting possibilities.

S14 found that the big-11 feature is dominated by SiC, with a smaller contribution from PAHs, and to solve the abundance problem, they suggested that the feature could arise from a layer of SiC on the grains, much like MgS. If grains composed of both amorphous carbon and SiC are exposed to a hot radiative environment, as happens in young PNe, one might expect the aliphatic hydrocarbons to be removed preferentially on the surface

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of the grain, leaving a SiC-rich coating which would enhance the 11.3 μm SiC feature. In other words, weathering of carbonaceous grains in harsh radiation fields would lead to enhanced SiC emission. In the Galaxy, it is expected that the carbonaceous grains contain an SiC core and an amorphous carbon mantle (Leisenring *et al.* 2008), making a coating of SiC less likely.

Most of the spectra with a big-11 feature also show a shoulder at 18 μm, which has proven to be a conundrum. Bernard-Salas *et al.* (2009) suggested that the feature could arise from the O–Si–O stretching mode in silicates, but silicate grains would be surprising in a carbon-rich environment. The lack of a 10 μm silicate feature would require that the silicates were cold. S14 discounted the likelihood, as it would require dual chemistry.

PNe with dual chemistry are plentiful in the Galactic Bulge (e.g., Gutenkunst *et al.* 2008), but Guzman-Ramirez *et al.* (2014) found that these sources show silicate emission inside the PAH emission and suggested that the PAHs formed after the dissociation of CO in these nebulae. The young carbon-rich Galactic PN BD+30 3639 also shows PAHs and silicates in its spectrum, but in this case the silicates appear to be *outside* the PAHs (Guzman-Ramirez *et al.* 2015). In this case, the silicates could be dust which formed before dredge ups made the AGB star carbon-rich.

It is interesting to speculate that the carbon-rich Magellanic PNe with the 18 μm shoulder in their spectra might be similar to BD+30. Cold silicates would be far from the central star, which would be consistent with their having formed before dredge-ups made the stars carbon-rich. However, this is only one possibility. For the moment, the 18 μm shoulder remains unidentified.

6. Summary

Spectra from the IRS on *Spitzer* of evolved carbon-rich objects in the Magellanic Clouds trace the chemical evolution of dust as the central star evolves from the AGB to a hot white dwarf and the circumstellar dust shell evolves into a PN. The spectral properties of the carbon stars on the AGB suggest that the grains might be layered with MgS, which can dominate the emission from more evolved objects. As the central star heats up, photoprocessing of the carbonaceous grains increases, leading to spectra with 21 μm features, aliphatic hydrocarbons, and Class D PAHs. The photoprocessing can also produce objects with Class C PAHs, and as the object evolves into a young PNe, more typical emission from Class B PAHs appears, along with the big-11 feature and/or fullerenes. The big-11 feature is primarily from SiC, and its strength suggests the SiC fraction might be higher on the surface of the grains, perhaps due to photoprocessing. The big-11 feature is usually accompanied by a shoulder at 18 μm, for which the carrier is not known. If the 18 μm feature arose from cool silicate grains, it could point to dual chemistry in Magellanic PNe.

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Discussion

Pagomenos: Could you comment on the 21μm feature only being observed in the presence of the 30μm feature, which you are convinced can be attributed to MgS?

Sloan: I should have mentioned that in these samples, there always seems to be one source that violates whatever trend we see. The geometries are complex, and we can expect inclination, evolutionary, and chemical effects. Nevertheless, we usually see MgS with the 21μm feature, and usually with a specific shape and wavelength position.

Van Winckel: If you explain the changing chemistry of BD +30.3639 due to the thermal pulses (cold O-rich dust in the outside, C-rich in the inner part which was expelled when the star turned C-star), you need heavy mass loss both when the star was an M star and when it was a C star. Does this matches with the ages of the different circumstellar components? A star needs probably more than 1 thermal pulse to go from M to C. Could the O-rich dust not be stored in a stable disc? (e.g. the Red Rectangle mix?) This could also explain the processing and high crystallinity.

Sloan: It would only take 1 thermal pulse to cross the C/O = 1 boundary and cross from O-rich to C-rich dust. But I agree that we should not rule out disks, especially when the crystalline silicates are present.

Q: 1) What is the carrier of the 18-μm feature in C-rich objects? 2) Can we include/consider silicate grains in SED modeling for the 18-μm feature showing C-rich objects?

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