

*Letter to the Editor***Chemical evolution of carbonaceous materials in the last stages of stellar evolution\***Sun Kwok<sup>1</sup>, Kevin Volk<sup>1</sup>, and Bruce J. Hrivnak<sup>2</sup><sup>1</sup> Department of Physics and Astronomy, University of Calgary, Calgary, T2N 1N4 Canada<sup>2</sup> Department of Physics and Astronomy, Valparaiso University, Valparaiso, IN 46383, USA

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**Abstract.** The out-of-plane bending modes of aromatic C-H bond at 11.3, 12.1, 12.4, and 13.3  $\mu\text{m}$  were detected in the ISO SWS spectra of the proto-planetary nebulae IRAS 07134+1005 and IRAS 22574+6609. In addition, unidentified emission features at 17.8, 18.9, and 19.1  $\mu\text{m}$  were detected in the SWS01 and SWS06 spectra of IRAS 07134+1005. The similar strengths of the 12.1, 12.4, and 13.3  $\mu\text{m}$  features relative to the 11.3  $\mu\text{m}$  feature, together with the presence of strong aliphatic CH bands at 3.4 and 6.9  $\mu\text{m}$ , demonstrate a lower aromaticity of the emitting material, compared to those at the later planetary nebulae stage. This suggests a chemical and physical evolution of the carbonaceous dust during the transition between these two phases.

**Key words:** stars: circumstellar matter – stars: AGB and post-AGB – ISM: planetary nebulae: general – infrared: ISM: lines and bands – infrared: stars

**1. Introduction**

The element carbon (C) is produced by triple- $\alpha$  reactions and dredged up from the helium-burning shell to the surface during the asymptotic giant branch (AGB) phase of stellar evolution. When the abundance of C exceeds that of oxygen (O), carbon-based molecules (C<sub>2</sub>, CN, etc) begin to form in the photosphere after nearly all the O is used up in forming CO. This marks the formation of a carbon star. The low temperature environment of the AGB star allows many C-based molecular species to be formed. These molecules are ejected as part of the stellar wind, until almost the entire hydrogen (H) envelope is depleted by mass loss. The loss of the H envelope causes the star to evolve to higher temperatures. When the star is hot enough to emit a significant amount of UV photons, the circumstellar envelope will be ionized, creating a planetary nebula (PN).

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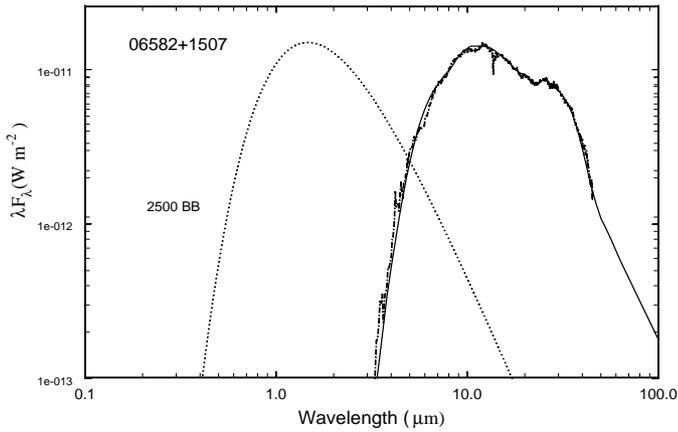
In the past two decades, infrared spectroscopic observations have revealed many molecular/solid-state emission features, including some of unknown origin, from objects in the AGB to PN phases of evolution. The family of unidentified infrared bands (UIB) at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$ , identified as due to various vibrational modes of aromatic hydrocarbon bonds, is commonly found in C-rich PN. These features, have been suggested to be due to gas-phase molecules such as polycyclic aromatic hydrocarbons (Puget & Léger 1989; Allamandola et al. 1989), quenched carbonaceous composite (Sakata et al. 1987), or carbonaceous solids such as coal (Papoular et al. 1989). Since the evolution from AGB to PN takes place over only several thousand years, the best way to identify the carriers of the UIB is to observe objects in transition between the AGB and PN phases. In this *Letter*, we report the detection of several new emission features from observations with the *Infrared Space Observatory (ISO)*, and discuss the implications of the changing infrared spectra on the evolution of the circumstellar chemistry from the AGB to PN phases.

**2. Observations**

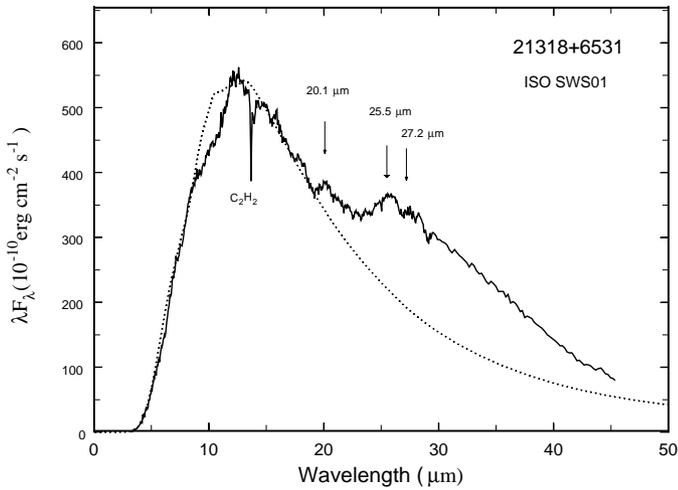
From the *IRAS* sky survey, we have identified a number of extreme carbon stars with circumstellar envelopes so thick that their stellar photospheres are entirely obscured (Volk et al. 1992), as well as transition objects (called proto-planetary nebulae, or PPN) in evolution between the AGB and PN phases (cf. Kwok 1993). A number of extreme carbon stars and C-rich PPN were observed with *ISO* Short Wavelength Spectrometer (SWS) in the SWS01 ( $\lambda/\Delta\lambda \sim 500$ ) and SWS06 ( $\lambda/\Delta\lambda \sim 2000$ ) modes under the *ISO* guest observer programs `skwok.21micron`, `skwok.ext_cstar`, `kvolk.21micpro`, and `bhrivnak.swsppn02`.

**3. Results**

Fig. 1 shows the spectral energy distribution of the extreme carbon star IRAS 06582+1507. The SWS01 spectrum is very well fitted by a radiation transfer model. We can see that the photospheric output of the star (assumed to be a 2500 K blackbody)



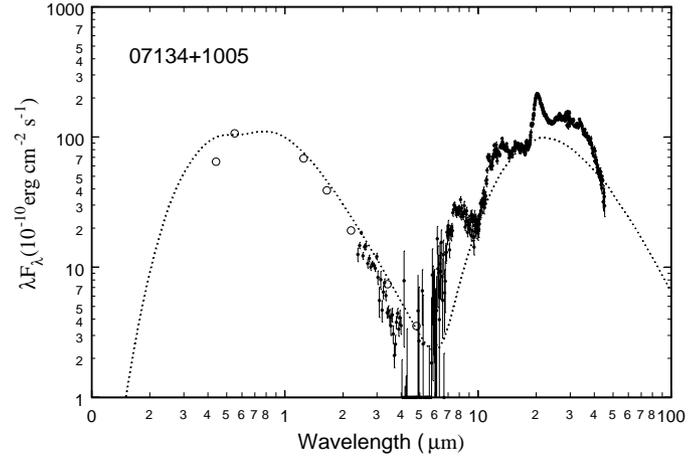
**Fig. 1.** The spectral energy distribution of the extreme carbon star IRAS 06582+1507. The solid line is a model fit to the *ISO SWS01* spectrum (shown as a dashed line, for details see Volk et al. 1999b). The underlying stellar spectrum (assumed to be a 2500 K blackbody) is shown in a dotted line.



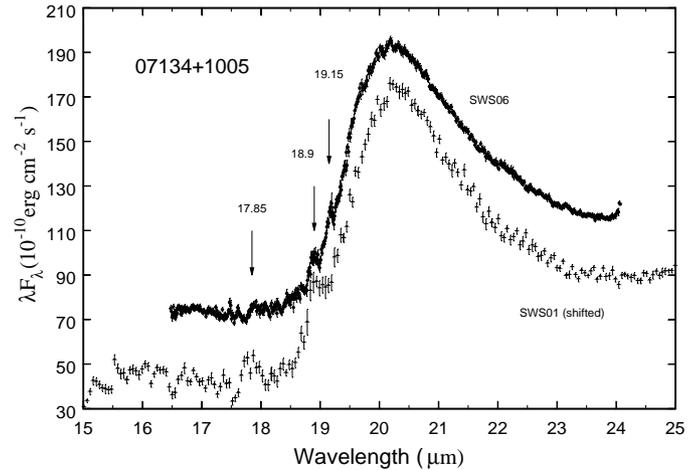
**Fig. 2.** The *ISO SWS01* spectrum of the extreme carbon star IRAS 21318+6531. The model continuum is shown as a dotted line.

is shifted entirely to the infrared as the result of circumstellar extinction. The very high optical depth of the dust envelope implies a very high mass loss rate, and the star is likely to be near the end of its AGB evolution.

Fig. 2 shows the *ISO SWS01* spectrum of another extreme carbon star, IRAS 21318+6531. The absorption line at  $13.7 \mu\text{m}$  is due to the  $\nu_5$  fundamental vibrational transition of  $\text{C}_2\text{H}_2$ . This feature is also detected in 3 other extreme carbon stars (IRAS 00210+6221, 06582+1507, 21489+5301, Volk et al. 1999b). Three broad emission features can be seen at  $20.1$ ,  $25.5$ , and  $27.2 \mu\text{m}$ . The  $20.1 \mu\text{m}$  feature, known as the  $21 \mu\text{m}$  feature in the literature, is a strong, unidentified feature which has previously been seen only in C-rich PPN (Kwok et al. 1989), and is detected here for the first time in an AGB star. The  $30 \mu\text{m}$  feature, which has previously been detected in AGB stars, PPN, and PN, is resolved into two components: one with a central wavelength of  $27.2 \mu\text{m}$  (FWHM



**Fig. 3.** The spectral energy distribution of the PPN IRAS 07134+1005. The *ISO SWS01* spectrum is fitted by a radiation transfer model (the continuum part of the model is shown as a dotted line). The circles are ground-based photometry. The component on the left is from the reddened stellar photosphere and the component on the right is from the dust shell.



**Fig. 4.** The *ISO SWS06* and *SWS01* (shifted) spectra of IRAS 07134+1005 in the  $20 \mu\text{m}$  region.

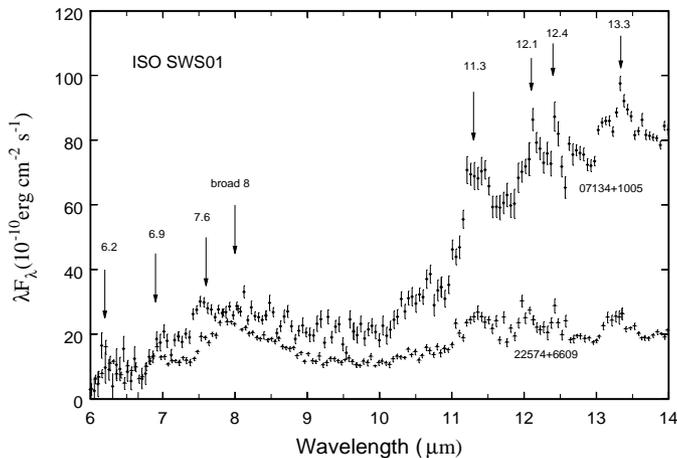
$\sim 20 \mu\text{m}$ ) and another narrower feature at  $25.5 \mu\text{m}$ , with a width of  $\sim 3 \mu\text{m}$  (Fig. 2). These two features can also be seen in the *ISO SWS01* spectra of PPN (Hrivnak et al. 1999).

Fig. 3 shows the spectral energy distribution of a C-rich PPN. The  $21 \mu\text{m}$  feature is now very prominent, and broad emission plateaus around  $8$ ,  $12$ , and  $30 \mu\text{m}$  can be seen above the continuum. The observed  $8 \mu\text{m}$  feature is similar to the broad feature seen in the laboratory spectrum of coal and hydrogenated amorphous carbon (HAC, Scott et al. 1997). The broadness and smoothness of these features are suggestive of a solid-state carrier, and probably in an amorphous state.

Fig. 4 shows the *SWS06* spectrum of IRAS 07134+1005 in the  $20 \mu\text{m}$  region. Narrow features at  $17.85$ ,  $18.90$ , and  $19.15 \mu\text{m}$  can be seen on top of the broad  $21 \mu\text{m}$  feature. The  $17.85$  and  $18.90 \mu\text{m}$  features are also seen in our *SWS01* spectrum, so there is no doubt that they are real. Although we are uncertain of the

**Table 1.** Summary of the changes in relative strengths of the infrared emission features as stars evolve from AGB to PN

IR features ( $\mu\text{m}$ )	Origin	Extreme Carbon Stars	PPN	PN
primarily features: 3.3, 6.2, 7.7, 11.3	aromatic stretch and bending modes	no	yes	strong
secondary features 3.4, 6.9 12.1, 12.4, 13.3	C-H aliphatic stretch and bend C-H out-of-plane bend with 2, 3, and 4 adjacent H atoms	no	yes	weak
broad 8, 12	-	no	yes	weak
broad 21	-	weak	strong	no
broad 30	-	yes	yes	yes

**Fig. 5.** The ISO SWS01 spectrum of 2 C-rich PPN with emission features labeled.

origin of these features, we note that gas phase  $\text{C}_{60}$  molecules have strong vibrational bands at  $17.54$  ( $\nu_{27}$ ) and  $18.94$   $\mu\text{m}$  ( $\nu_{28}$ ) (at 960 K, Nemes et al. 1994). The other strong band of  $\text{C}_{60}$  at  $7.09$   $\mu\text{m}$  ( $\nu_{25}$ ) unfortunately overlaps with the aliphatic C-H bending mode at  $6.9$   $\mu\text{m}$  and the  $8.53$   $\mu\text{m}$  band ( $\nu_{26}$ ) is not detected.

The SWS01 spectra between 6–14  $\mu\text{m}$  of two C-rich PPN are shown in Fig. 5. In addition to the broad plateaus, features of narrower widths ( $\Delta\lambda < 0.5$   $\mu\text{m}$ ) at 6.2, 6.9, 7.6, 11.3, 12.1, 12.4, and 13.3  $\mu\text{m}$  can be seen. We note in particular the detection of features at 11.3, 12.1, 12.4 and 13.3  $\mu\text{m}$ , which can be identified as arising from out-of-plane vibrational modes of aromatic C-H bonds with respectively 1, 2, 3, or 4 C-H bonds per edge of an aromatic ring (Allamandola et al. 1989; Herlin et al. 1998). While a broad feature at 12.2  $\mu\text{m}$  has previously been detected in the ground-based spectra of three 21- $\mu\text{m}$  sources (Justtanont et al. 1996), the 12.1 and 12.4  $\mu\text{m}$  features are clearly resolved in our spectra. The existence of the 13.3  $\mu\text{m}$  feature was predicted by Guillois et al. (1996) and its detection here, together with its presence in IRAS 16594-4656 (García-Lario et al. 1999), confirms that this feature is indeed common in PPN. More importantly, we note that 12.1, 12.4, and 13.3  $\mu\text{m}$  features are comparable in strength to the 11.3  $\mu\text{m}$  feature, which is totally dominant in the spectra of PN.

The different relative strengths of the UIB features between PN and PPN have previously been noted in the case of the 3.3  $\mu\text{m}$  feature. This feature, due to aromatic C-H stretch, is usually much stronger than the 3.4  $\mu\text{m}$  feature (due to aliphatic C-H stretch) in PN (Joblin et al. 1996), but in PPN the 3.4  $\mu\text{m}$  feature can be as strong as the 3.3  $\mu\text{m}$  feature (Geballe et al. 1992). This suggests an increase of aromatic bonds ( $sp^2$ ) relative to aliphatic bonds ( $sp^3$ ) as a star evolves from a PPN to PN. The 6.9  $\mu\text{m}$  feature, due to C-H aliphatic bond, is seen only in C-rich PPN (specifically only in objects showing the 21  $\mu\text{m}$  feature, Buss et al. 1990; Hrivnak et al. 1999), and disappears totally in PN. These results, together with those presented here, suggest that the 3.4, 6.9, 12.1, 12.4, 13.3 and 21  $\mu\text{m}$  features develop only after the AGB and weaken or disappear when the star evolves to the PN phase. A summary of the feature strengths as a function of evolution is given in Table 1.

#### 4. Discussion

Table 1 clearly suggests an evolutionary change of the chemical composition of the carbonaceous materials from AGB to PN phases. The relative strengths of the 12.1, 12.4 and 13.3  $\mu\text{m}$  features in comparison to the 11.3  $\mu\text{m}$  feature suggests a gradual decrease in the number of peripheral H per edge ring, implying a progressive formation of clusters of rings into more structured units. Laboratory studies of coal have found that the highly hydrogenated bands (such as the 13.3  $\mu\text{m}$  band) weaken as the H content of coal is reduced (Guillois et al. 1996). Perhaps a similar process is at work here. The loss of H is consistent with the conversion from  $sp^3$  to  $sp^2$  bonds, as evidenced by the weakening of the 3.4 and 6.9  $\mu\text{m}$  features.

Acetylene is widely believed to be the first building block of aromatic hydrocarbons (Cherchneff et al. 1992), and the detection of this molecule in extreme carbon stars confirms that such building blocks are indeed available. But what are the sizes of the products, small gas-phase molecules or solid particles? Dust created by laboratory simulations such as soots (Colangeli et al. 1995), HACs (Scott & Duley 1996), or nanopowders (Herlin et al. 1998) all show aliphatic characters with infrared spectra similar to those of PPN. Radiation transfer models show that up to 8% of the entire energy output of an extreme carbon star can be emitted in the 30  $\mu\text{m}$  feature (Volk et al. 1999b). In PPN, the 30  $\mu\text{m}$  feature can carry as much as 20% of the total emitted energy (Hrivnak et al. 1999). Such

efficiencies suggests that these features originate from a solid. Comparison of the 21  $\mu\text{m}$  profiles of eight sources has shown that they all have the same intrinsic shape and peak wavelengths, and thus are more consistent with the feature arising from a solid-state material (Volk et al. 1999a).

Since all stars that show the 21 and 30  $\mu\text{m}$  features are C-rich, and if the carrier is a solid, then what form of C is it? Nanodiamonds have been proposed as a possible carrier of the 21  $\mu\text{m}$  feature (Hill et al. 1998), but the weakness of the proposed transition cannot account for the strength of the observed 21  $\mu\text{m}$  feature. While the 3.4, 11.4, 12.2, and 13.3  $\mu\text{m}$  features are seen in the laboratory spectrum of coal (Guillois et al. 1996), there are no strong features around 20  $\mu\text{m}$  in demineralized coal (Sourisseau et al. 1992). HAC grains share many of the similar infrared signatures as coal but again no strong feature at 20  $\mu\text{m}$  has been reported. Webster (1995) has proposed that the 21  $\mu\text{m}$  feature is due to a mixture of fullerene molecules of different degrees of hydrogenation. However, the lack of substructure and the uniformity of the observed profiles of the 21  $\mu\text{m}$  feature do not support this hypothesis (Volk et al. 1999a). A successful theory should ideally explain the UIB, the plateaus, and the 21 and 30  $\mu\text{m}$  features as well as their changing relative strengths from the AGB to PN phases as reported here. Such changes can be the result of a combination of chemical, physical, and radiative excitation conditions. Not only do the central stars undergo a factor of ten change in temperature in several thousand years, but high-velocity collimated outflows are also believed to begin in the PPN phase to shape the morphology of the nebulae. Could these processes cause the a loss of H and a re-ordering of the chemical structure to create more C=C bonds? The AGB-PN transition therefore offers the best opportunity to study the formation and evolution of carbonaceous materials in space.

## 5. Conclusions

The detections of the 21 and 30  $\mu\text{m}$  features in extreme carbon stars confirm the direct chemical link between AGB stars, PPN, and PN. The detection of the 13.3  $\mu\text{m}$  feature, identified as the C-H out-of-plane vibration with 4 H on the side of an aromatic ring, signifies the formation of small aromatic units. The decreasing strengths of the 3.4, 6.9, 12.1, 12.4, and 13.3  $\mu\text{m}$  features relative to the 3.3, 6.2, and 11.3  $\mu\text{m}$  features as stars evolve from PPN to PN suggest a change from aliphatic to aromatic structures and groupings into larger aromatic units. These results

show that chemical evolution leading to the synthesis of highly structured organic compounds can take place in a circumstellar environment over only a few thousand years.

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