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infrared light on the composition of the dust
surrounding carbon-rich stars

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Infrared light on the composition of the dust surrounding carbon-rich stars

Infrarood studies naar de stofsamenstelling rond
koolstofrijke sterren
(met een samenvatting in het Nederlands)

Academisch Proefschrift

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Universiteit van Amsterdam

“l’essentiel est invisible pour les yeux”

Antoine de Saint-Exupéry, *Le Petit Prince*

Preface

My first contact with astrophysics was during the introductory astronomy lectures taught by Ed van den Heuvel. From this very first moment I have been captured by a certain charm present throughout astrophysics. Of course the beauty of simplicity, to reduce any given system to its essentials, can be found in astrophysics and physics alike.

However, the charm of astrophysics lies also in a totally different beauty. The beauty to do things in a clumsy, impractical way. For astronomy is a science with a history. In every corner of astronomy you find tantalising relics: habits, methods and units inherited from the past. They range from ‘O Be A Fine Girl, Kiss Me’ to plotting-axes that run the “wrong” way. Of course such silly details sometimes make me want to bang my head on the table, especially when converting $\text{ergs/cm}^2/\text{s}/\text{\AA}/\text{sr}$ to Jansky *again* and taking *again* more than three tries to get it right. But still, the fact that we have to use the observations from 1987 to study supernova 1987a, gives another dimension to the field.

On top of these charms, the study of the stars never fails to trigger a slight surprise in me. The same surprise that you will hear in the voice of non-astronomers: *“How can we learn so much about the stars, when they are so far away and all you get is a little bit of light?”*.

After finishing undergraduate astronomy it was very clear to me that I was trained for doing research. I am happy that Rens Waters and Xander Tielens asked me to do a research project under their supervision. That research has resulted in this thesis. I have certainly received a lot of support while doing my research and this is the place where I would like to express my gratitude.

First of all, I want to thank Xander and Rens for allowing me the independence I need to work well. Rens; your enthusiasm has often kept me going when I; after weeks of staring; could not find anything interesting anymore in the things that I was doing. Xander, I have enjoyed your practical approach and your encyclopedic knowledge of solid-state physics and literature. I will never forget that time when you took a paper with a only few references scribbled on it from your notebook and handed it to me. You didn’t remember what references these were but you said: “Maybe they are of some use.” and they were.

Words of thanks to Caroline and Els for the very fruitful collaborations that we have had. We started our PhD projects around the same time and I have learned much from observing the way you both handled things. I have always appreciated the support and the gentle way in which you could criticise me: “Maybe have another look at this?”. Ciska, you also started your PhD project together with me and we shared offices for more than three years. It was always very good to be able to directly ask and discuss all kind of hick-ups that came along with somebody as knowledgeable as you, even if (at times) these discussions could become quite heated.

In the course of the last four years I have met many great colleagues some of which have become good friends. It feels inappropriate to thank you here, because these friendships go much beyond my work. Simply know that you are in my heart.

This thesis is based largely on data obtained with Infrared Space Observatory (ISO) of the European Space Agency, in particular with data of the Short Wavelength Spectrometer (SWS). The support of the Dutch ISO Data Analysis Centre and the data reduction software

provided by the SWS consortium have contributed to our understanding of the data. The generous financial support of the Leids Kerkhoven-Bosscha Fonds has made it possible for me to attend several important conferences during my PhD project. This research has been financially supported by a *Pionier* grant (grant number 616-78-333) of NWO, the Netherlands Organization for Scientific Research.

Without the people and organisations mentioned above this thesis would not have been be what it is now. I hope that you will find some of the charm, surprise and beauty of the study of the stars captured in this thesis.

Sacha

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Introduction

In this thesis we study the dust around carbon-rich evolved stars. The main questions that we address are: “What is the composition of the dust that is formed around carbon-stars?”, “When are the various dust components formed during the AGB evolution?” and “What is the composition of the dust that is fed into the interstellar medium?”.

In this introduction I first give a brief outline of the properties and evolution of old stars and the very prominent rôle the dust plays in this evolution. Next, I describe the method(s) that we use to answer these questions. In Sect. 1.3 I give a short outline of this thesis with, for each of the following chapters, the main questions and the main conclusions.

1.1 The last stages of low-mass stellar evolution

This thesis deals with the last stages in the life of low- and intermediate-mass stars ($1 M_{\odot} \lesssim M_{*} \lesssim 8 M_{\odot}$). These stars, like the sun, spend by far the longest part of their life on the main sequence (MS). While on the main sequence hydrogen is transformed to helium in the core of the star by fusion.

After the hydrogen and helium in the core have been exhausted such stars will eventually go through a phase called the Asymptotic Giant Branch (AGB). In Fig. 1.1 we show the evolution of a low-mass star like the sun. As can be seen this evolution eventually leads to the AGB, post-AGB and planetary nebula phases. These phases are typified by a high luminosity ($\sim 10^4 L_{\odot}$) and mass loss.

Since by far the majority of all stars falls in this mass range, nearly all stars will go through an AGB phase. During the AGB phase they shed a major part of their envelope by means of a hefty, dust-driven wind. Through this outflow heavy elements produced in the stars interior are fed into the interstellar medium (ISM). In this thesis we present several studies of the composition of the dust in the stellar outflows and the fate of the solid matter that has been lost.

1.1.1 Asymptotic Giant Branch stars

AGB stars are located in the upper-right hand corner of the Hertzsprung-Russel diagram, i.e. they are very cool and bright which implies a very large stellar radius. Typical values are $T_{\text{eff}} \leq 3000 \text{ K}$, $L = 1000\text{--}10\,000 L_{\odot}$ and $R = 200\text{--}400 R_{\odot}$. At this point the star has a small C/O core with a radius of $\sim 3000 \text{ km}$. The core is surrounded by He and a very extended H-rich envelope with a radius of $\sim 10^8 \text{ km}$. At the base of the H-rich envelope, He can be formed

Figure 1.1: A sketch of the evolution of a low-mass star in the Hertzsprung-Russell diagram. The most important phases of low-mass star evolution are indicated. Stars on the main sequence exhibit steady hydrogen fusion in the core. After nuclear burning of H in the central part of the star has ceased, the star as a whole contracts a little and fusion of hydrogen in a shell around the core starts. As a result, the star ascends the Red Giant Branch (RGB). Subsequently helium fusion ignites in the core and the star reaches the Horizontal Branch (HB). After core helium fusion has stopped the star ascends the Asymptotic Giant Branch (AGB). During the AGB phase the star exhibits alternately H- and He-fusion in shells around the core. AGB stars suffer a strong mass loss by which the envelope of the star is removed. When the envelope has been lost almost completely the fusion layers of the star are exposed, the strong stellar wind ceases and the star enters the post-AGB phase. Due to the removal of the last remainder of the envelope, the very hot inner layers of the star become increasingly more visible and the stellar temperature rises. If this heating goes rapidly enough, the previously ejected material will be ionised by the hot central core and light up as a planetary nebula (PN).

through H-fusion. This increases the amount of He in the He shell. When the mass of this shell reaches a critical value, He-fusion ignites. For an excellent review of the physical and observational properties of AGB stars see Habing (1996).

Chemical evolution

During the period of He shell fusion – which is called a thermal pulse (TP) – heavy elements from the stellar interior are mixed into the H-rich envelope of the star. These heavy elements, predominantly carbon, oxygen and nitrogen, are transported to the surface through convection that reaches down to the region between the H and He-fusion shell (intershell) during a TP. Because C is produced in larger numbers than O in the intershell region the number ratio of C to O is increased with every thermal pulse. If C/O becomes larger than unity in the atmosphere the star is called carbon-rich (C-rich), otherwise the star is called oxygen-rich (O-rich). This enrichment in carbon manifests itself clearly in spectroscopic terms. The temperature in the atmosphere of AGB stars is low enough for several molecules to be stable. Due to the rapid formation and extreme stability of the carbon-monoxide (CO) molecule both C and O atoms are effectively locked up. If $C/O < 1$, i.e. O-rich, then O is left to form other molecules and one finds for example TiO, SiO and H₂O molecules in the atmosphere. In contrast, in the case of $C/O > 1$, i.e. C-rich, some C remains to form other molecules, like HCN and C₂H₂. Thus, the value of C/O determines the chemistry in the atmospheres of AGB stars and, likewise, determines the composition of the circumstellar (CS) dust.

Mass loss

Pulsations of the AGB atmosphere lift the atoms and molecules out to a distance where the temperature is sufficiently low (< 1500 K) for molecules to react to form solid particles (dust). These solids drive the mass loss of AGB stars, the most important property of AGB stars. The dust particles absorb the stellar light very efficiently; much more efficiently than do the atoms or molecules from which they are built. The AGB star is very luminous and each dust particle experiences a sizable radiation pressure which accelerates it against the gravitational pull of the star. Collisions between the accelerated solid particles and the gas couples the gas to the dust. Due to this gas-dust coupling AGB stars have a strong mass loss with a relatively low outflow velocity ($\lesssim 15$ km/s). Thus, the pulsations, the low temperature, the large stellar radius and the high luminosity work together to create dust, which is subsequently pushed away and makes the outer envelope gravitationally unbound. *It is the radiation pressure on the dust that drives the wind.*

While the star ascends the AGB towards higher luminosity, the mass-loss rate generally increases and may reach up to $\sim 10^{-4} - 10^{-3}$ solar masses per year. The dust absorbs the stellar light and, at high mass-loss rates, the star is completely obscured at optical and near infrared (IR) wavelengths by the circumstellar envelope (CSE). The energy absorbed by the dust is re-emitted in the infrared.

Prior to the AGB phase the evolution of the star is entirely dominated by fusion processes and the timescale of evolution is set by the rate at which the nuclear fuel (H or He) is consumed. However, in the AGB phase the mass loss determines the evolution. The envelope

mass which is lost at the top of the atmosphere through the outflow greatly exceeds the envelope mass lost at the bottom through fusion. Therefore, it comes as no surprise that the AGB phase is also terminated by the effects of mass loss. This occurs when almost the entire envelope has been shed.

1.1.2 Post-AGB stars

When the H-rich envelope of the AGB star is almost exhausted the star enters the post-AGB phase. Of the entire envelope only a few thousandth of a solar mass are left. The last remains are removed by hydrogen shell fusion. In this process the hot fusion layers will be closer and closer to the surface, the surface temperature rises, and the star rapidly moves to the left across the HRD. The dust formation ceases and the previously lost material disperses. The time it takes to move through the post-AGB phase into the subsequent planetary nebula phase depends strongly on the rate at which the last bit of H-rich envelope is burned and therefore depends on the luminosity of the star. Typically the post-AGB phase spans only 1000-10 000 years. As a consequence these stars are relatively rare.

The start of the post-AGB phase is marked observationally by two effects. First, the previously ejected matter keeps moving away from the star. This causes the column of obscuring dust along our line of sight to decrease and makes the star directly visible again. Secondly, as the ejected material expands it cools and the warmest dust disappears. When observed over a large wavelength range from the ultraviolet (UV) to the IR we can clearly see two separate contributions to the light. In the UV and visible range we see the central star directly while in the IR we receive the emission of the cool, expanding CS shell. A more complete overview of the properties of post-AGB stars and their evolution can be found in Szczerba & Górny (2001).

1.1.3 Planetary Nebulae

While the CSE is flowing away, the central star is heating up. At some point the temperature of the central star becomes so high ($T_{\text{eff}} \gtrsim 30\,000\text{ K}$) that its radiation ionises the CSE. This produces an optically visible planetary nebula (PN). In Fig. 1.2 we show photographs of the PN NGC 6369. A clearly extended nebula is observed with the star in the centre as the ionising source. The shell is predominantly visible in the optical and IR through very strong emission lines. The line emission is due the recombination of the ionised material. NGC 6369 is studied in detail in Chapter 5.

PN properties

The observed properties of PNe overlap somewhat with those of post-AGB stars. At UV and visible wavelengths we see the central star and in the IR the emission of dust dominates. The central stars of PNe (CSPNe) can reach very high temperatures, up to 400 000 K. A good and detailed description of the physics of both the CSPNe and the nebulae can be found in Habing & Lamers (1997). When the mass of the remaining H-rich envelope becomes too low

Figure 1.2: NGC 6369. A picture of ‘The Little Ghost’ nebula. The ring shaped emission is the old envelope of the star that now lights up due to the ionising light of the very hot star in the centre. On the right we show a detailed view of nebula obtained with the Hubble Space Telescope. Source: <http://pages.sbcglobal.net/loydo/> and Space Telescope Science Institute <http://www.stsci.edu>.

to sustain hydrogen burning, the surface temperature and luminosity drop and the core will slowly cool down to become a white dwarf.

An important subclass of PNe is the group of PNe with hydrogen-poor central stars, called [WC] stars. The atmospheres of these central stars have no or very little remaining hydrogen, leaving their atmospheres He and C-rich. Stellar models predict that all the hydrogen in the envelope of the star can be removed if the star goes through a TP after the mass of the envelope has dropped below $0.01 M_{\odot}$. However, the timescale for the occurrence of thermal pulses is much larger (10 000-100 000 yr) than the lifetime of a PN (~ 1000 -10 000 yr) and the theory has problems to explain the large fraction of [WC] stars (20 per cent) among PN. For a review of the [WC] star properties, the theory of their formation and its problems see Waters et al. (2001).

Processing of the ejected material

The very hard radiation field of the CSPN causes significant changes in the dust and gas in the nebula. As a direct consequence of the preponderance of UV photons the neutral gas becomes ionised and molecules dissociate. Very small dust grains can be directly photo-dissociated upon absorption of an energetic photon. Indirectly, the produced ions, especially He^{2+} and to a lesser extent H^{+} , will react with the surface of grains. These reactions cause the grains to be modified or eroded. Moreover, as the ionisation progresses into the ejected envelope shocks occur. Due to these shocks the composition of the gas and dust is altered as

well. Thus, while the ejected matter expands to get incorporated into the interstellar medium (ISM), its composition is substantially modified.

1.2 Dust

As already discussed above dust plays a central rôle in the evolution of AGB stars. Dust is the driver of the mass loss. Mass loss determines the evolution on the AGB and causes the termination of the AGB. Therefore, knowledge of the dust properties is crucial for understanding stellar evolution. An important step in acquiring this knowledge is of course a detailed understanding of the composition of the dust that is formed. However, the relevance of these tiny solid particles reaches far beyond the realm of stellar evolution.

1.2.1 Enrichment of the interstellar medium

There is a broader scope of interest in studying the properties of the outflows of evolved intermediate mass stars. These stars are important contributors of heavy elements and dust grains to the ISM. Stars are the production sites of all elements heavier than lithium. Stellar outflows are the means through which the produced elements are fed into the ISM. These elements can be incorporated in new stellar systems as the next generations of stars form. These heavy elements are the building blocks of *all* solid matter in our solar system, like the planets and the building blocks of biology.

Besides the importance of dust in this very general framework of ISM enrichment, the origin of the heavy elements and, intimately intertwined, the origins of life, there are specific astrophysical subjects in which it is very important to understand the dust physics in the outflows of evolved stars. For instance, polycyclic aromatic hydrocarbons (PAHs) are a family of complex molecules that are believed to be produced in the outflows of C-rich AGB stars. Emission due to PAHs is found in a wide variety of sources and is now used as a tool in extragalactic studies, where the relative strength of the PAH emission can distinguish starburst galaxies from active galactic nuclei (Lutz et al. 1997). Of course the physical interpretation of these distinctions can only be carried as far as our understanding of the PAH family goes.

1.2.2 Infrared spectroscopy

We choose to study the dust around evolved stars using mid infrared spectroscopy in the wavelength range from 2 to 200 μm . All these sources are very bright in the IR. The dust absorbs a large fraction of the stellar light and will radiate the absorbed energy in the infrared. As a result, a sizeable fraction of the luminosity is emitted in the IR. This fraction can reach ~ 100 per cent in the case of AGB stars with a high mass-loss rate, as the large column of dust causes the CSE to be completely opaque for UV and optical light.

A more important reason to study these stars in the IR, than the fact that these sources are bright at IR wavelengths, is the fact that in this wavelength range we directly observe the dust. The grains are heated to temperatures up to ~ 1500 K and as a result they will emit thermal radiation in the IR. However, the most important reason to use the mid-IR wavelength

range is that this region of the electro-magnetic spectrum holds the spectroscopic fingerprints of the dust components. In the mid-IR the emission is due to vibrationally excited molecules and solids. Different materials have different vibrational resonances and will therefore emit at different wavelengths. This allows to identify the dust components around a star.

In Fig. 1.3 and 1.4 we show examples of the IR spectra of O-rich and C-rich evolved stars, respectively, at various stages of the evolution described above. The AGB stars show self-absorbed dust features, due to the high optical depth through the CSE. The post-AGB stars and PNe have cooler dust that emits at longer wavelengths. They lack emission at the shortest wavelengths. It is also immediately apparent from comparing Fig. 1.3 and 1.4 that the chemical differences between O-rich and C-rich stars as discussed above are clearly expressed in the properties of the circumstellar dust. The circumstellar dust of O-rich evolved stars has been studied in detail by Molster (2000), Cami (2002) and Kemper (2002). In the following we concentrate on the C-rich evolved stars.

1.2.3 Key questions

The main questions we address in this thesis are:

- What types of dust condense in the outflows of C-rich AGB stars?
- Which solids condense when?
- How are these materials processed?
- In what form does the dust enter the ISM?

We answer these questions by studying the *composition* of the dust in relation to the *source type*. By comparing stars in different evolutionary stages and relating the changes in the dust to the varying physical conditions we try to unravel the history of the solids.

However, answering these questions is hampered by some aspects inherent to the analysis. We make extensive use of IR spectra obtained with the spectrographs on board the Infrared Space Observatory (ISO). Only space-borne instruments have an unobscured view in the complete 2-200 μm wavelength range. On earth most of the light is blocked by the atmosphere. A drawback of the ISO spectrographs is their limited spatial resolution. In our analysis this implies that we see the integrated light from the entire envelope and we are unable to resolve possible spatial variations in the dust composition. Such variations may come about if the dust production varies with time or if the dust is being modified.

A second limitation which we encounter frequently concerns the availability of laboratory measurements of astronomically relevant materials. Our analysis is heavily based on the comparison between astronomical spectra and laboratory spectroscopy of well characterised materials. These comparisons make it possible to determine whether these materials are present around the star. However, for several candidate materials laboratory spectra are lacking. For example, there is spectroscopic evidence that the PAH molecules present in PNe contain well over 100 C-atoms (see Chapter 2) while currently the largest molecule measured in the laboratory under astrophysically relevant conditions contains 59 C-atoms.

Figure 1.3: Examples of the IR spectra of oxygen-rich evolved stars. We show an AGB star with a high mass-loss rate (top panel). Due to the long column of silicate dust along the line of sight the 10 and 18 μm features are seen in deep absorption. The structure seen in emission longwards of 25 μm is due to crystalline silicates. The middle panel shows the post-AGB star HD 161796. The silicate features at 10 and 18 μm are seen in weak emission against a very strong cool dust continuum. The prominent emission features around 43 and 60 μm are due to crystalline water ice. The emission of the star is seen below 5 μm . In the bottom panel we show the spectrum of the planetary nebula NGC 6302. Perched on top of the emission due to crystalline silicates are very strong emission lines from the ionised plasma. There is a contribution from carbonates at 60 and 90 μm .

Figure 1.4: Examples of the infrared spectra of carbon-rich evolved stars. We show an AGB star with a high mass-loss rate (top panel). The narrow absorption at $\sim 14 \mu\text{m}$ is due to gas-phase C_2H_2 and HCN. We detect absorption due to solid SiC at $11 \mu\text{m}$. The emission near $30 \mu\text{m}$ is caused by solid MgS. In the second panel we show the post-AGB star SAO 34504. Due to the expansion of the CSE all features are found in emission. At $6-9$ and $11-17 \mu\text{m}$ we find hydrocarbon features. The origin of the emission near $20 \mu\text{m}$ is debated. This feature has only been found in emission in carbon-rich evolved stars and is primarily found in C-rich post-AGB stars. Below $5 \mu\text{m}$ the emission of the stellar photosphere is seen. In the lower panel we show the spectrum of the planetary nebula NGC 7027. The features at $3.3, 6.2, 7-9$ and $10-14 \mu\text{m}$ are due to polycyclic aromatic hydrocarbons. Perched on top of the dust emission are very strong emission lines from the ionised plasma.

A more fundamental limitation is due to the vibrational resonances that are the spectroscopic indicators of the composition. These resonances are specific for the type of materials that are present. However the frequency of the resonance is much more sensitive to directly neighbouring atoms in the molecules and solids than to the complete structure. For example, any H-atom bound to a C-atom will give rise to (amongst others) a resonance near $3.3\text{--}3.4\text{ }\mu\text{m}$, independent of the rest of the structure where the C-atom is bound to. In this sense the vibrational spectroscopic fingerprints are less unique than for example atomic line-transitions. This means that IR spectroscopy *alone* may not be able to answer the question of composition to the level of detail that we would like. Below, we discuss several supplementary approaches to help constrain the dust properties in circumstellar environments.

Condensation sequences

One important way to constrain the interpretation of the spectra is to use chemical models to predict which materials will form given the chemical and physical parameters of the dust condensation. Figure 1.5 gives an example of a chemical equilibrium calculation with $\text{C/O}=1.1$ (Lodders & Fegley 1999). It shows for a given pressure the temperature below which each of the indicated dust species condenses. The stellar interior lies to the top-left in the diagram (high pressure and temperature). When matter moves outwards, its temperature and pressure drop and it shifts down and to the right in the diagram. As one can see, at very high temperatures zirconium carbide (ZrC) and titanium carbide (TiC) are the only stable species. When the temperature drops below $\sim 1600\text{ K}$ graphite forms. As the temperature decreases further other species are formed as well.

Not shown in Fig. 1.5 is the effect of the abundances of the elements involved. ZrC is the most stable condensate. However, the amount of condensed ZrC will be very limited compared to SiC because there is only one Zr-atom for every 100 000 Si-atoms. Note, that although these models are important as a guide to determine which solids could be present, their use in our studies is rather limited. This is because in our studies we want to *derive* the poorly known physical parameters of the dust condensation process from its composition rather than the other way around. Of course, once the composition is known we can go back to these models to constrain the conditions under which the solid state material has condensed.

Moreover, these model predictions are based on *equilibrium* chemistry calculations. The atmosphere of an AGB star is *not* in equilibrium. Instead, the conditions change strongly due to pulsations and drift of grains and molecules through the envelope. As an example of the deviations between the predicted condensates and the observations, let us consider iron silicide (FeSi) and magnesium sulfide (MgS). From Fig. 1.5 FeSi is expected to form prior to MgS. However, MgS is abundantly detected around carbon stars (see Chapter 6) and FeSi has not been found. Each of the composing elements (Mg, Si, S and Fe) is present in similar amounts. Therefore, from the equilibrium calculation one expects to find FeSi too.

Presolar material

Another source of information on the dust formation around various types of stars comes from presolar dust. These dust grains formed prior to the formation of the sun, entered the

Figure 1.5: Equilibrium dust condensation diagram for a carbon rich AGB envelope (adapted from Lodders & Fegley 1999). The diagram shows which species will condense as a function of envelope pressure and temperature. The lines in the diagram mark the border below which the indicated species can condense. Marked with black letters are species that are known to form around carbon-rich stars, either from IR spectroscopy of these stars or from presolar grains (see also Sect. 1.2.3). The materials that have not been detected are marked with grey letters. Note that corundum (Al_2O_3) and spinel (MgAl_2O_4) are found in presolar materials but they are usually associated with oxygen-rich environments.

Figure 1.6: A transmission electron micrograph image of a thin section of presolar graphite grain from the Murchison meteorite (<http://presolar.wustl.edu/>). The 70 nm long crystal in the centre of the spherule is TiC, a refractory mineral that formed prior to the graphite, and served as a nucleation centre for its growth (Bernatowicz et al. 1996). The scale of the grain is 1 μm .

solar nebula when it formed and are virtually unaltered since. They are retrieved from meteorites and from cometary dust, collected high in the earth's atmosphere. The latter, called interplanetary dust particles (IDPs), form an important source of information on presolar dust because comets are believed to contain a large fraction of pristine materials. In Fig. 1.6 we show an image of a presolar graphite grain retrieved from the Murchison meteorite. Large differences are found between the isotopic ratios in these grains and the isotopic ratios of the sun. This shows that they are formed prior to the sun and remained intact during the formation of the solar system. In the case of this graphite grain the isotopic ratios point to formation in a carbon-star atmosphere. In these graphite grains inclusions of ZrC, MoC and TiC are found. The grain in Fig. 1.6 has a TiC inclusion at the centre that served as the nucleation centre for the graphite layer to grow on. This shows that TiC condensed prior to graphite, which is an indication of high pressure condensation (see Fig. 1.5).

Comparisons with other environments

A third way to help the interpretation of our IR spectra is to compare with observations of other environments, where chemical and physical conditions are different. As an example, consider MgS, a material that is only stable in the reducing environment around C-rich stars. We do not expect to find MgS in regions where $C/O < 1$. This is reflected in the IR spectra

of C-rich and O-rich environments: we do not find the “30” μm feature carried by MgS in O-rich environments.

Radiative transfer modelling

Finally, we use radiative transfer models to determine the CS dust composition. Model calculations can yield information on the composition, temperature, spatial distribution, abundance and the size of the dust grains. In Chapter 7, we consider the effect of hydrogenated amorphous carbon (HAC) on the IR spectra. In the literature HAC grains with very low IR absorption are proposed as the carrier for the hydrocarbon feature detected in C-rich post-AGB stars (see Fig. 1.4). From radiative transfer modelling we find that HAC grains are too cold to cause these features unless they are very small.

1.3 Outline of this thesis

The research presented in this thesis addresses the key questions mentioned above. We study the circumstellar dust composition in a variety of environments, focusing on the components that originate from C-rich evolved stars. In various places throughout this thesis we employ the techniques described in Sect. 1.2.3 to further constrain the dust composition.

Many astronomical sources show a set of emission features at 3.3, 6.2, 7.7, 8.6 and 11.2 μm . They are generally attributed to an ensemble of polycyclic aromatic hydrocarbon molecules (PAHs). However the exact nature of the carrier molecules has not been determined. Open questions remain of the typical size of these molecules, their charge state and the variations of the molecular ensemble with environment. PAH molecules originate from C-rich envelopes. In the presence of UV photons they are transiently heated to very high temperatures and emit strongly between 3 to 15 μm . In Chapter 2, we present IR spectra of PNe and low- and high-mass star forming regions. We detect PAH emission bands that vary considerably and systematically with source type. We compare the strength of these bands with laboratory measurements, which allows us to conclude that C-rich stars inject compact PAHs with 100–200 C-atoms into the ISM where they are subsequently processed.

In the following three Chapters (3,4,5) we present the discovery of new solid-state components. In Chapter 3, we present the first detection of the iron sulfide mineral in two planetary nebulae. This discovery may imply non-equilibrium dust formation as discussed above. In Chapter 4, we expand on this detection and compare the signature of iron sulfide in evolved stars with a similar signature found in the disks around young stars. We find that they exhibit the same signature and conclude that iron sulfide minerals are abundantly present in the disks around young stars while planet formation is taking place. This discovery is even more tantalising given the crucial rôle of iron sulfides in the catalysis of life on earth.

The “21” μm feature is an enigmatic feature that was discovered in the IRAS spectra of a handful carbon-rich post-AGB stars in the 1980’s. So far the carrier of the feature has not been firmly identified. Due to the fact that this feature was only detected in cool post-AGB stars it has been suggested that its carrier is an unstable material that is rapidly destroyed by UV light when the star enters the PN phase. We present the first detection of the “21” μm

feature in two C-rich PNe in Chapter 5. This shows that the carrier of the feature is not as unstable as previously believed.

Another dust constituent which had remained somewhat enigmatic is magnesium sulfide. The signature of MgS was recognised in C-rich circumstellar dust already in 1985. However, when studied in detailed the detection of MgS was not unambiguous. The identification of MgS is much debated. We construct a MgS model with very basic assumptions and compare it to the observations. In Chapter 6, we present this model and succesfully apply it to *all* available C-rich evolved stars for which sufficient data are available. We conclude that MgS is abundantly present in C-rich environments.

In Chapter 7, we present a radiative transfer model for the post-AGB star HD 56126. This star is member of a group of post-AGB stars that exhibit very strong emission from several dust species that are much debated. It shows emission due to amorphous carbon, PAHs features, the “21” and “30” μm features and broad plateau features between 6–9 and 11–17 μm . The latter have been associated with hydrogenated amorphous carbon. From the model we derived the abundance of the various dust components and the mass loss history of the star. We find that the star has had a very brief period (~ 1500 year) of very strong mass-loss ($\sim 3 \cdot 10^{-4} M_{\odot}/\text{yr}$) during which the entire envelope was shed.

Finally, the results from the work presented in this thesis are summarized in Chapter 8. We discuss the general outcome of the research presented here and the new and old questions that require further study. In the last chapter we also present some opportunities and directions for future research.

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The CH out-of-plane bending modes of PAH molecules in astrophysical environments

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Abstract

We present 10–15 μm spectra of a sample of H II regions, YSOs and evolved stars that show strong unidentified infrared emission features, obtained with the ISO/SWS spectrograph on-board ISO. These spectra reveal a plethora of emission features with bands at 11.0, 11.2, 12.0, 12.7, 13.5 and 14.2 μm . These features are observed to vary considerably in relative strength to each-other from source to source. In particular, the 10–15 μm spectra of the evolved stars are dominated by the 11.2 μm band while for H II regions the 12.7 is typically as strong as the 11.2 μm band. Analysing the ISO data we find a good correlation between the 11.2 μm band and the 3.3 μm band, and between the 12.7 μm and the 6.2 μm band. There is also a correlation between the ratio of the UIR bands to the total dust emission and the 12.7 over 11.2 μm ratio. Bands in the 10–15 μm spectra region are due to CH out-of-plane (OOP) bending modes of polycyclic aromatic hydrocarbons (PAHs). We summarise existing laboratory data and theoretical quantum chemical calculations of these modes for neutral and cationic PAHs. Due to mode coupling, the exact peak position of these bands depends on the number of adjacent CH groups and hence the observed interstellar 10–15 μm spectra can be used to determine the molecular structure of the interstellar PAHs emitting in the different regions. We conclude that evolved stars predominantly inject compact 100–200 C-atom PAHs into the ISM where they are subsequently processed, resulting in more open and uneven PAH structures.

2.1 Introduction

Many sources show a rich set of emission features at 3.3, 6.2, 7.7, 8.6 and 11.2 μm commonly called the unidentified infrared (UIR) emission features. These bands dominate the IR spectra of a wide variety of objects, including H II regions, PNe, post-AGB objects, YSOs, the diffuse ISM, galaxies and galactic nuclei (Cox & Kessler 1999). Understanding these features and the

origin and evolution of their carriers has become an important problem in astrophysics. These UIR bands are generally attributed to IR fluorescence of small (~ 50 C-atom) polycyclic aromatic hydrocarbons (PAHs) molecules.

Laboratory spectroscopy of PAHs shows that, besides the well known UIR bands, PAHs exhibit many weaker emission bands. In particular, the region from 10 to 15 μm has a rich spectrum due to the out-of-plane bending vibrations (OOP) of aromatic H-atoms. The peak wavelength of these modes depends on the structure of the molecule; in particular on the number of neighbouring H-atoms per ring (e.g. Bellamy 1958; Hudgins & Allamandola 1999). Here we present data in this region obtained with the Short Wavelength Spectrometer (SWS) (de Graauw et al. 1996) on-board the Infrared Space Observatory (ISO) (Kessler et al. 1996). The sensitivity and medium resolving power of the instrument allows us to detect and resolve several weak features predicted by the PAH hypothesis and to determine the molecular structure of the emitting PAHs and their evolution in space.

In Sect. 2.2, we present the observations of our sample of H II regions, YSOs, reflection nebulae (RNe) and evolved objects. The 10–15 μm regions of these sources are analysed in Sect. 2.3. The spectral characteristics of PAHs in this wavelength range as measured in the laboratory and calculated by quantum chemical theories are summarised in Sect. 2.4.1. In Sect. 2.4.2 the laboratory spectra are compared to the observed spectra. The molecular structures implied by the observed spectra are discussed in Sect. 2.5 while in Sect. 2.6 the origin and evolution of these molecular structures are examined. Finally in Sect. 2.7 our main results are summarised.

2.2 Observations

We include 29 high S/N spectra of 16 sources taken from the samples of H II regions, YSOs, and post-AGB objects. For the trend analysis presented in Sect. 2.3.4 we have added another 15 sources in which the S/N is such that we cannot reliably measure the weakest features but we determine the intensities of the stronger UIR bands with reasonable accuracy. All spectra presented here have been obtained with the SWS instrument in the AOT01/AOT06 scanning mode at various speeds, with resolving power ($\lambda/\Delta\lambda$) ranging from 500–1500 (see de Graauw et al. 1996), see Table 2.1 for details of the observations.

The data were processed using SWS interactive analysis product; IA³ (see de Graauw et al. 1996) using calibration files and procedures equivalent to pipeline version 7.0. If a source has been observed multiple times and these observations are of similar quality and of comparable flux-level these data are co-added after the pipeline reduction. Since the features we discuss here are fully resolved in all observing modes, we combine the data obtained in all different modes to maximise the S/N. Further data processing consisted of bad data removal, rebinning on a fixed resolution wavelength grid, removing fringes and splicing of the sub-bands to form a continuous spectrum.

For all spectra the amount of shifting between sub-bands required falls well within the calibration uncertainties in the region of interest: 7 to 16 μm . Any jumps between bands are due to either flux calibration and dark current uncertainties. The effect of dark current is most important in low flux cases while the flux calibration uncertainties will dominate

in bright sources. Below 20 Jy we apply offsets to correct for dark current uncertainties. In these low signal cases the typical noise level in the dark current measurements of 1–2 Jy introduces offset uncertainties >5 –10 per cent dominating the flux calibration uncertainties. Above 20 Jy we apply scaling factors to correct for flux calibration uncertainties. The splicing introduces little uncertainty in the measured strengths since most features fall completely within one ISO/SWS sub-band. An exception to this is the band strength of the $12.7\ \mu\text{m}$ feature. This feature is sensitive to the way band 2C (7 to $12.5\ \mu\text{m}$) and 3A (12 to $16.5\ \mu\text{m}$) are combined. This introduces an extra uncertainty of the band strength of typically 20–30 per cent for the weakest features.

Some SWS data, especially in band 3A, are affected by fringes. We have corrected for fringes in those sources where they occur, using the *aarfringe* tool of *IA³* on the rebinned spectrum. In the method we apply fringes are fitted with sine functions with periods in the range where fringes are known to occur and divided out. Note that the features we study here are much broader than any of fringe periods, therefore the intensities we measure are not directly affected by the fringes. However in some cases after fringe removal the continuum is more easily determined.

SWS spectra of many sources, including stars enshrouded in both carbon-rich and oxygen-rich dust and sources without any circumstellar material show very weak structure around 13.5 and $14.2\ \mu\text{m}$ at the 3 to 4 per cent level relative to the continuum possibly due to residual instrumental response. The emission features discussed here are all stronger than this with a maximum of 85 per cent of the continuum in the reflection nebula NGC 7023. Near $11.03\ \mu\text{m}$ there is a residual instrumental feature which coincides with the weak $11.0\ \mu\text{m}$ feature that we observe in our spectra. We have included the effect of this feature in the uncertainty on the intensities in Table 2.2.

Many sources in this sample have strong narrow emission lines in their spectrum, in particular the strong [Ne II] line at $12.81\ \mu\text{m}$ is perched on top of the $12.7\ \mu\text{m}$ UIR band. This line and the UIR band are easily separated at the resolution of the SWS instrument. We remove the contribution from this line by fitting a Gaussian profile to the line and subtracting that profile prior to rebinning. The spectrum of NGC 7027 has a very strong [Ne V] emission line at $14.32\ \mu\text{m}$. We have removed the part of the spectrum which contains this line.

We also include in Table 2.1 the spectral type of the illuminating source and an estimate of the flux density at the location where the PAH emission originates from in units of the average interstellar UV field (Habing 1968). We have derived these estimates from the observed IR flux (I_{IR}) and the angular size of the PAH emission region (Wolfire et al. 1989). This estimate is based on the assumption that all the UV light is absorbed in a spherical shell with the angular size of the object and re-emitted in the IR. The flux density at the shell is given by:

$$G_0 = \frac{4}{1.6 \cdot 10^{-6}} \left(\frac{1\ \text{pc}}{1\ \text{AU}} \right)^2 \frac{I_{\text{IR}}}{\theta^2} = 1.1 \cdot 10^{17} I_{\text{IR}} \theta^{-2}, \quad (2.1)$$

where G_0 is the UV flux density in $1.6 \cdot 10^{-6}\ \text{W/m}^2$ and θ is the angular diameter of the object in arcseconds. We have used for the size of the H II regions the measured radio sizes. This is reasonable since the PAHs are expected to be destroyed inside the H II region. For the other objects we estimate the size of the PAH emission region from ISOCAM data (Cesarsky et al. 1996) when available.

Object	Obs. ^a Mode	α [J2000]	δ [J2000]	TDT ^b	Sp.Type [KK]	C_0 [$1.6 \cdot 10^{-6} \text{W/m}^2$]	Obj.Type
AFGL 437	01(2)	03 07 23.68	+58 30 50.62	86300810	O8.5	1E5	Star forming region
IRAS 03260+3111	01(3)	03 29 10.37	+31 21 58.28	65902719	B9	2E4	Herbig AeBe
NGC 2023	01(3)	05 41 38.30	-02 16 32.59	65602309	B1.5V	3E2	Refl. Nebula
HD 44179	01(4)	06 19 58.20	-10 38 15.22	70201801	B8V	5E6	post-AGB
IRAS 07027-7934	01(2)	06 59 26.30	-79 38 48.01	73501035	WC10	2E7	PN
HD 97048	01(4)	11 08 04.61	-77 39 16.88	61801318	A0	2E4	Herbig AeBe
IRAS 12405-6238	01(3)	12 43 31.93	-62 55 11.39	29400410	O9.5	3E5	H II
HEN 2-113 [†]					WC10	6E4	PN
—	01(1)	14 59 53.49	-54 18 07.70	07903307			
—	01(2)	14 59 53.49	-54 18 07.70	43400768			
IRAS 15384-5348	01(2)	15 42 17.16	-53 58 31.51	29900661		1E4	H II
CD-42 11721(off)	01(2)	16 59 05.82	-42 42 14.80	28900461	B0	—	Herbig AeBe (off pointing)
CD-42 11721 [†]					B0	—	Herbig AeBe
—	01(2)	16 59 06.82	-42 42 07.60	08402527			
—	01(2)	16 59 06.80	-42 42 07.99	64701904			
IRAS 17047-5650 [†]					WC10	5E6	PN
—	01(3)	17 09 00.91	-56 54 47.20	13602083			
—	01(1)	17 09 00.91	-56 54 48.10	27301339			
HB 5	01(3)	17 47 56.11	-29 59 39.70	49400104	120 ^c	—	PN
NGC 6537	01(3)	18 05 13.14	-19 50 34.51	70300475	A0	—	PN
GGD 27-ILL [†]					B1	3E6	Star forming region
—	01(2)	18 19 12.04	-20 47 30.98	14802136			
—	01(2)	18 19 12.03	-20 47 30.59	14900323			
IRAS 18240-0244	01(1)	18 26 40.00	-02 42 56.99	14900804	WC8	—	PN
IRAS 18317-0757	01(2)	18 34 24.94	-07 54 47.92	47801040	O8	—	H II
IRAS 18416-0420	01(2)	18 44 15.19	-04 17 56.40	13402168	O5.5	—	H II
IRAS 18502+0051	01(2)	18 52 50.21	+00 55 27.59	15201645	O7	—	H II
TY CRA [†]					B9	6E3	Herbig AeBe
—	01(3)	19 01 40.71	-36 52 32.48	33400603			
—	01(1)	19 01 40.70	-36 52 32.59	34801419			

—	01(3)	19 01 40.71	−36 52 32.48	71 50 2003	WC9	1E5	PN
BD +30 3639	01(3)	19 34 45.20	+30 30 58.79	86 50 0540	O7	6E6	H II
IRAS 19442+2427	01(2)	19 46 20.09	+24 35 29.40	15 00 0444	B2	1E4	Herbig AeBe
BD+40 4124	01(3)	20 20 28.31	+41 21 51.41	35 50 0693	08	1E5	H II
S106 IRS4	01(2)	20 27 26.68	+37 22 47.89	33 50 4295	B3	5E2	Ref. Nebula
NGC 7023 [†]	01(4)	21 01 31.90	+68 10 22.12	20 70 0801			
—	01(2)	21 01 30.40	+68 10 22.12	48 10 1804			
NGC 7027 [†]					200 ^d	2E5	PN
—	01(4)	21 07 01.71	+42 14 09.10	02 40 1183			
—	01(1)	21 07 01.70	+42 14 09.10	23 00 1356			
—	01(2)	21 07 01.70	+42 14 09.10	23 00 1357			
—	01(3)	21 07 01.70	+42 14 09.10	23 00 1358			
—	06	21 07 01.50	+42 14 10.00	33 80 0505			
—	01(4)	21 07 01.63	+42 14 10.28	55 80 0537			
IRAS 21190+5140	01(2)	21 20 44.85	+51 53 26.59	15 90 1853	—	2E5	H II
IRAS 21282+5050 [†]					O9	1E5	PN
—	01(2)	21 29 58.42	+51 03 59.80	05 60 2477			
—	01(3)	21 29 58.42	+51 03 59.80	15 90 1777			
—	01(2)	21 29 58.42	+51 03 59.80	36 80 1940			
IRAS 22308+5812	01(2)	22 32 45.95	+58 28 21.00	17 70 1258	O7.5	3E3	H II
IRAS 23030+5958	01(2)	23 05 10.57	+60 14 40.60	22 00 0961	O6.5	7E3	H II
IRAS 23133+6050	01(2)	23 15 31.44	+61 07 08.51	22 00 1506	O9.5	7E5	H II

Table 2.1: Source list. Observational details of the sources used in this study.^aSWS observing mode used (see de Graauw et al. 1996). Numbers in brackets correspond to the scanning speed.^bTDT number which uniquely identifies each ISO observation.[†]These spectra have been obtained by co-adding the separate SWS spectra also listed in the table, see text.^cEffective temperature from Gesicki & Zijlstra (2000). ^dEffective temperature from Latter et al. (2000).

2.3 Results

2.3.1 Overview

In Fig. 2.1 we present spectra of three typical sources to illustrate the spectral detail present and the variety of underlying continua. Even more so than previous IRAS/LRS and ground-based studies suggested (Cohen et al. 1985; Roche et al. 1989; Witteborn et al. 1989), the complete 11–15 μm spectra reveal an extremely rich collection of emission features with bands at 10.6, 11.0, 11.23, 12.0, 12.7, 13.5, and 14.2 μm . These features are perched on top of an emission plateau of variable strength, which extends across the entire region.

2.3.2 Continuum

In order to compare the intrinsic strength of the UIR bands in the different sources, we subtract a continuum, splined through points from 9–10.5 and 14.5–15.5 μm and through points near 11.8 and 13.1 μm . Since GGD 27 and IRAS 18416 have broad solid CO_2 absorption features beyond 15 μm , we take 14.7 μm to be the continuum rather than extending to 15.5 μm . Typical examples of the continua are included in Fig. 2.1. Besides the chosen points, the continuum also runs through the local minimum at 10.9, 12.2 and 14.0 μm with the exception of the Red Rectangle. This object has excess emission around these wavelengths, which could be related to the presence of crystalline silicates in the vicinity of HD 44179 (Waters et al. 1998). For any reasonable choice of continuum points, the underlying plateau ranges from about 10 to 14 μm , peaking at about 12 μm . At first sight, the plateau of GGD 27 seems to differ with an onset at about 11 μm and peaking around 13 μm . However, this likely reflects the effects of foreground silicate absorption. The PN IRAS 21282+5050 does show a plateau that differs, peaking at 12 μm but extending all the way to 17 μm .

2.3.3 Emission bands

We show the continuum subtracted spectra of the 16 objects with the highest S/N in Fig. 2.2. Perusal of the spectra reveals a plethora of weaker features. NGC 7027, HD 44179 and IRAS 21282 have a very weak, broad feature near 10.6 μm . Almost all these sources show a feature at 11.0 μm , except for GGD 27, where the feature is possibly present but only at the 1σ level. The weak 12.0 μm band is detected in 10 out of 16 sources. The 13–15 μm range contains the newly discovered weak 13.5 and 14.2 μm features (Fig. 2.3). Structure near 13.5 μm is present in all sources except HEN 2-113, however for IRAS 21282 and IRAS 18317 the band is replaced by a feature that peaks at a shorter wavelength. A feature near 14.2 μm is found in all sources although the actual peak position varies considerably (c.f., IRAS 03260 and IRAS 15384). This variation in peak position of these two weak bands is quite in contrast with that of the 11.2 and 12.7 μm bands which almost invariably peak at about the same wavelength (see below). *A priori*, it is not given that the spectral structure near 14 μm is actually related in the different sources. Possibly, rather than one molecular vibration with a varying peak position, at this weak level of emission, we are probing different bands whose relative strengths reflect the conditions in the different sources.

Figure 2.1: Spectra of 3 sources that show features in the region of interest. The dashed lines are the continua mentioned in the text.

In Fig. 2.2 we show the continuum subtracted spectra after normalising to the integrated strength of the $12.7 \mu\text{m}$ feature. The sources are ordered according to the strength of the $11.2 \mu\text{m}$ feature relative to the $12.7 \mu\text{m}$ band. Relative to the $12.7 \mu\text{m}$ band, the sources with the weakest $11.2 \mu\text{m}$ feature are the H II regions (at the bottom of Fig. 2.2), while the evolved stars show the strongest $11.2 \mu\text{m}$ band.

The spectral characteristics of the features are summarised in Table 2.2. Note that the uncertainties quoted in the Table reflect the noise level and the freedom in drawing the continuum *within* the methodology used to measure these bands. Other ways of decomposing the broad, blended bands and the underlying continuum will give other results (e.g. Boulanger et al. 1998; Uchida et al. 2000; Verstraete et al. 2001). However these differences are *systematic* differences and do not affect the source-to-source variations we observe. The intensities of the 11.2 and $12.7 \mu\text{m}$ features are obtained by direct integration above the chosen con-

Figure 2.2: An overview of the observed features. All spectra have been continuum subtracted and are scaled to have the same integrated intensity in the $12.7 \mu\text{m}$ feature. The sources are ordered according to their $11.2/12.7 \mu\text{m}$ band strength ratio (bottom to top). The ratio of the $11.2 \mu\text{m}$ to the $12.7 \mu\text{m}$ feature spans a full decade.

[▽]Sources with broad solid CO_2 absorption beyond $15 \mu\text{m}$.

Figure 2.3: An overview of the observed features near 13.5 and 14.2 μm . [▽]HD 44179 and NGC 7027 have been scaled by a factor of 0.3.

tinuum. We measure the peak position of the 11.2 and 12.7 μm bands by fitting them with template spectra of these features. The template spectrum for the 11.2(12.7) μm feature is constructed by adding the continuum subtracted spectra with each 11.2(12.7) μm feature normalised to have the same integrated intensity. This way each source has equal contribution to the template spectrum. We use a χ^2 -minimisation routine to fit the template to the sources, allowing for both a wavelength shift and scaling in strength. The shifts that we determine for the 11.2 μm band are very small except for HD 44179 and IRAS17047 where this band is much broader than the template spectrum (c.f., Table 2.2, see also Peeters et al. (2002). Although there are differences between the detailed profiles of the 12.7 μm band we detect no significant shift of the band as a whole. For the weak features near 13.5 and 14.2 μm , the parameters have been determined through fitting of Gaussian profiles. We adopted a local linear continuum for the very weak 11.0 μm feature because of the severe blending of this band with the 11.2 μm band. The weak 12.0 μm band is close to both the 11.2 and the 12.7 μm band. For only a few sources we measure the intensity of this band, for the other sources we refrained from detailed analysis. However Table 2.2 does note whether we detect this band.

The profile of the 11.2 μm feature is asymmetric with a sharp blue rise and a more gradual decline to longer wavelengths (Roche et al. 1989; Witteborn et al. 1989). This will be discussed in more detail for this sample by Peeters et al. (2002). The 12.7 μm band is also asymmetric but in the opposite way with a slow blue rise and a sharp red decline between 12.8 and 12.9 μm . Because of their intrinsic weakness, the profiles of the 10.6, 11.0, 12.0, 13.5, and 14.2 μm features in the individual sources are not well determined however in the averaged spectrum, these features appear symmetric (cf., Fig. 2.7).

2.3.4 Trends

Given the large range of band strength ratios in the region of interest and the smooth variations in this ratio, it is of interest to investigate the correlation of the strength of all UIR emission bands with these variations. As a class all the planetary nebulae with a Wolf-Rayet central star (HEN 2-113, BD+30, IRAS17047, IRAS 07027 and IRAS 18240) as well as the post-AGB star HD 44179 show a distinctly different UIR spectrum characterised by a shift in of the 6.2 and 7.7 μm bands towards 6.3 and 8 μm respectively (Peeters et al. 2002). Because of these spectral differences we have not included them in the following trend analysis in which they also separate out as a peculiar subgroup. These objects will be discussed in detail in a forthcoming paper.

Because here we want to study variations in the *relative* strength of the UIR bands to each other, not differences in absolute intensities differences due to intrinsic luminosity and distance of the source, we use 3-feature intensity ratio correlations. Although we observe variations in all ratios, we find only three that correlate and these are shown in Figures 2.4–2.6. First, we find that the CH stretch mode at 3.3 μm correlates with the 11.2 μm band (cf. Fig. 2.4). Note that the slope of the trend is roughly 1, which means that the $I_{11.2}/I_{3.3}$ is on the average constant at a value of 3–4.

Second, the 12.7 μm band correlates with the CC stretch mode at 6.2 μm , albeit with more scatter (cf. Fig. 2.5) than the 11.2/3.3 ratio. The 7–9 μm complex is well correlated with the 6.2 μm band and similar plots can be made with these interchanged. Inspection of Fig. 2.2

Figure 2.4: Bands strength ratios as derived from the SWS spectra. Hexagons are H II regions, stars intermediate mass star forming regions, squares RNe and triangles are PNe.

and Table 2.2 shows that there is some indication for both the $I_{13.5}/I_{11.2}$ and the $I_{14.2}/I_{11.2}$ μm band to be higher in H II regions, however only about half the sources have such high S/N that these intensities can be reliably measured and this trend is not statistically significant.

Lastly, we show in Fig. 2.6 the correlation between the ratio of the flux emitted in the PAH bands relative to the total flux emitted in the IR (I_{IR}) and the changing $I_{12.7}/I_{11.2}$ ratio. We measure the I_{IR} by integrating the SWS data and Long Wavelength Spectrometer (LWS) data if available. For those sources without LWS data we use a blackbody fitted to IRAS measurements in the wavelength region from 45–200 μm . We do not apply corrections for aperture differences between the instruments. We estimate an uncertainty of 15 per cent on the I_{IR} . Again different classes of objects occupy different parts in this diagram.

We also checked for correlations between band strength ratios and the flux density; G_0 , however we do not detect any correlations.

We emphasise that, while all UIR bands show a loose correlation in the absolute intensity (see also Cohen et al. 1986, 1989), these three are the only tight correlations present in this sample.

Figure 2.5: Bands strength ratios as derived from the SWS spectra. Plotting symbols are the same as in Fig. 2.4.

2.3.5 Comparison with other studies

It is interesting to compare the result we obtained from the SWS spectra with results by other authors. Studying many locations in the diffuse interstellar medium Chan et al. (2000) find that the relative bands strengths of the 6.2, 7.7 and the 11.2 μm features do not vary systematically over a wide range of intensities of the incident radiation field. Their observed ratios of $I_{11.2}/I_{6.2}$ cluster around 0.8, the value we observe in the RNe and the YSOs. Studying a few RNe at various locations Uchida et al. (2000) with ISO/CAM (Cesarsky et al. 1996) find only small variations in band strength ratios. The $I_{11.2}/I_{6.2}$ ratios they derive with the method which is most similar to ours (method 2) are like those we find for the RNe. Their $I_{12.7}/I_{11.2}$ ratios are however systematically lower than ours. This is due to the lower spectral resolution of the CAM spectra which results in blending and smearing of the weakish band at 12.7 μm . The SWS spectra are not affected by smearing since the features are fully resolved. The results of these authors, like the results we present here, demonstrate that similar types of sources show similar PAH band strength ratios. Our results also demonstrate how *different classes of objects show systematic differences in their PAH spectra*.

Observations of the starforming region M17 have suggested that the 13.5 μm band is cor-

Figure 2.6: The ratio between the flux emitted in the PAH bands over the total amount of IR radiation against the $I_{12.7}/I_{11.2}$ ratio. Plotting symbols are the same as in Fig. 2.4.

related with the mid-IR continuum Verstraete et al. (1996). Such a correlation is important to establish since it might yield information on the size of the carriers of the $13.5\ \mu\text{m}$ band. We have examined whether a correlation is also present in the sample of sources we study here. We have therefore compared the $15\text{--}16\ \mu\text{m}$ continuum with the strength of the $13.5\ \mu\text{m}$ band. We find strong variations, by a factor of $\simeq 100$ in the strength of the mid-IR continuum relative to the $13.5\ \mu\text{m}$ band. These strong variations are not surprising considering the fact that we look at very diverse regions with large differences in dust composition and temperature distributions. For example the evolved object HD44179 has contributions from crystalline silicates around $15\ \mu\text{m}$ (Waters et al. 1998). Many H II regions have a strongly rising continuum due to warm dust. However we would also like to point to the two observations of CD-42 11721 where the $13.5\ \mu\text{m}$ band is equally strong but the dusty continuum is missing in the off-pointed observation. These two observations show the $15\ \mu\text{m}$ continuum and the $13.5\ \mu\text{m}$ feature to be decoupled even within the same object.

(1) Source	(2) $\Delta\lambda_{11.2}^a$ [$10^{-3}\mu\text{m}$]	(3) $I_{11.2}$ [10^{-14}W/m^2]	(4) $I_{12.7}^b$ [10^{-14}W/m^2]	(5) $\lambda_{c,13.5}^c$ [μm]	(6) $I_{13.5}$ [10^{-14}W/m^2]	(7) $\lambda_{c,14.2}^c$ [μm]	(8) $I_{14.2}$ [10^{-14}W/m^2]	(9) $I_{11.0}$ [10^{-14}W/m^2]	(10) $I_{12.0}^d$ [10^{-14}W/m^2]	(11) I_{plateau}^e [10^{-14}W/m^2]
IRAS 03260	0.9(0.1)	15.8(0.4)	6.4(0.4)	13.57(2)	1.7(0.1)	14.19(2)	0.9(0.1)	0.8(0.1)	n	22
HD 44179	12.6(0.5)	118.1(6.4)	26.3(1.4)	13.61(2)	13.4(0.5)	14.21(2)	8.6(1.3)	4.8(2.3)	5	112
HEN 2-113	2.7(0.3)	17.0(1.0)	5.6(1.0)	—	—	14.26(5)	4.7(1.8)	0.5(0.5)	d	30
IRAS 15384	0.0(0.6)	14.5(0.8)	13.5(0.6)	13.52(2)	1.5(0.3)	14.30(2)	2.7(0.1)	0.6(0.1)	2	66
CD -42(off)	-6.5(0.2)	22.2(0.6)	11.3(0.5)	13.55(2)	1.7(0.5)	14.22(2)	0.8(0.2)	1.0(0.1)	2	25
CD -42	-8.2(0.8)	31.7(1.5)	16.7(1.0)	13.53(2)	1.6(0.6)	14.22(2)	1.6(0.3)	1.9(0.3)	1	58
IRAS 17047	11.8(0.4)	25.1(1.0)	11.6(1.0)	13.50(3)	1.8(1.3)	14.23(3)	2.2(1.0)	1.3(0.8)	n	145
GGD 27	2.6(0.6)	8.9(0.6)	5.4(0.5)	13.57(2)	2.1(0.2)	14.27(4)	1.5(0.9)	1.4(0.1)	d	3
IRAS 18317	6.5(0.1)	10.5(0.2)	15.6(0.3)	13.44(2)	2.0(0.3)	14.22(2)	2.2(0.2)	0.2(0.1)	1	83
IRAS 18416	-2.3(0.3)	12.8(0.9)	9.8(0.5)	13.55(2)	2.4(0.4)	14.18(3)	3.1(1.2)	1.2(0.3)	n	52
TY CRA	-5.0(0.3)	15.5(0.1)	4.7(0.2)	13.54(2)	1.3(0.3)	14.21(2)	0.5(0.1)	0.8(0.1)	n	13
S 106	-4.1(0.1)	19.7(0.9)	15.6(1.0)	13.56(2)	2.7(1.2)	14.19(2)	3.6(0.2)	1.1(0.3)	2	61
NGC 7023	-3.9(0.2)	9.6(0.8)	4.3(0.3)	13.50(2)	1.1(0.2)	14.21(2)	0.7(0.3)	0.5(0.1)	n	11
NGC 7027	2.8(0.2)	142.7(5.4)	35.9(2.5)	13.52(2)	9.7(1.5)	14.26(2)	11.1(1.5)	4.0(1.7)	6	451
IRAS 21282	4.2(1.4)	20.4(0.7)	6.2(0.2)	13.40(2)	1.5(0.4)	14.22(2)	1.7(0.6)	0.6(0.3)	y	104
IRAS 22308	-3.2(0.5)	8.9(0.4)	5.8(0.6)	13.55(4)	1.3(0.6)	14.23(2)	2.1(0.1)	0.7(0.1)	n	9

Table 2.2: Peak position and strength of the features observed in the 10–15 μm for the sources shown in Fig. 2.2. The intensities $I_{11.2}$, $I_{12.7}$, $I_{11.0}$, $I_{12.0}$ and I_{plateau} are the integrated fluxes of the features after continuum subtraction (columns 3, 4, 9, 10 and 11). The position of the 11.2 and 12.7 μm features are determined by fitting the template profile to the spectra in which we allow for a wavelength shift and a scaling of the template (column 2). The properties of the features around 13.5 and 14.2 are determined by fitting Gaussian profiles to the data (columns 5–8). Numbers in parentheses are uncertainties.

^aShift of the 11.2 μm feature relative to the template 11.2 μm profile. The template profile peaks at 11.229(0.001) μm .

^bNo significant shifts of the 12.7 μm profile are observed with respect to the mean 12.7 μm profile. The mean profile ranges from 12.2–12.95 μm with the peak position at 12.804(0.005) μm . Typical uncertainty in the position determination 0.006 μm .

^cCentral wavelength of the fitted Gaussian profile, uncertainties are given in parentheses in units of $10^{-2}\mu\text{m}$.

^dTypical error on $I_{12.0}$ is $0.5 \cdot 10^{-14}\text{W/m}^2$; d means detected but not measured; n means not detected.

^eTypical error on I_{plateau} is $10 \cdot 10^{-14}\text{W/m}^2$.

	λ_{low}^a [μm]	λ_{up}^a [μm]	$A^{b\dagger}$ [km/mol]	A_{neutral}^b [km/mol]	A_{cation}^b [km/mol]
Solo	10.6	11.4	24.8(13.5)	25.7(14.2)	24.1(12.9)
Duo	11.35	12.8	4(2.5)	4.4(2.4)	3.7(2.5)
Trio	12.5	13.3	9.6(5.9)	10.1(5.3)	9.0(6.5)
Quartet	13.0	13.9	12.0(4.8)	11.5(5.5)	12.6(3.9)

Table 2.3: Wavelength region limits and the integrated absorption cross-sections for the CH out-of-plane bending modes. Summary of the laboratory results on CH out-of-plane bending modes for solo, duo, trio and quartet hydrogens on matrix isolated neutral polycyclic aromatic hydrocarbons and their cations. (Adapted from Hudgins et al. (in prep.)).

^a λ_{low} is the lower limit of the region in μm . λ_{up} is the upper limit of the region in μm .

^bThe cross-section values for the solo, trio, and quartet modes per hydrogen are the averages over the spectra in the database. However, the A values for the duo mode per hydrogen decreases rapidly with size and settles to slightly less than 4 km/mol for PAHs with more than 24 carbon atoms. This value is more appropriate to use in determining the edge structures of PAHs that dominate emission in this wavelength region.

[†]Total average cross-sections over both neutrals and cations in the database.

2.4 The CH out-of-plane bending modes

2.4.1 Laboratory spectroscopy of the OOP modes

Chemists have long recognised the diagnostic value of the aromatic CH out-of-plane bending features in the 11 to 15 μm spectral region for the classification of the aromatic ring edge structures present in a particular sample (e.g. Bellamy 1958). Specifically, the positions of the bands in this spectral region reflect the number of adjacent CH groups on the peripheral rings of the PAH structure (Bellamy 1958; Allamandola et al. 1985; Cohen et al. 1985; Leger et al. 1989; Roche et al. 1989; Witteborn et al. 1989; Allamandola et al. 1999; Hudgins & Allamandola 1999). Traditionally, aromatic rings carrying CH groups which have no neighbouring CH groups (termed "non-adjacent" or "solo" CH groups) show IR activity between 11.1 and 11.6 μm . Likewise, activity between 11.6 and 12.5 μm is indicative of two adjacent CH groups ("doubly-adjacent" or "duet" CH's) on the periphery of the PAH. Three adjacent CH groups ("triply-adjacent" or "trio" CH's) are indicated by activity in the 12.4 to 13.3 μm region, and four adjacent CH groups ("quadruply-adjacent" or "quartet" CH's) by activity between 13 and 13.6 μm . Five adjacent CH groups ("quintuply-adjacent" or quintet CH's) are indicated by features falling in the 13 to 13.7 μm range. Trios and quintets also show a weak CCC bending mode in the 14–14.5 range. Other CCC bending modes occur in the 15–20 μm range and have been discussed in the astrophysical context by Van Kerckhoven et al. (2000) and Moutou et al. (2000). Over the years the reliability of this region to yield insight into the molecular structure and ring sidegroup placement on aromatic samples has been verified again and again (see Hudgins & Allamandola (1999) and references therein). However, most of these chemist's guidelines were based on studies of small PAHs where varying patterns of sidegroup substitution were employed to achieve different degrees of CH

Figure 2.7: A comparison of the average interstellar spectrum (top) with the ranges for the out-of-plane bending modes (bottom). The average spectrum was obtained by co-adding the continuum subtracted spectra after normalisation to the 12.7 μm band strength. The boxes indicate the wavelength regions associated with the out-of-plane bending vibrations for different types of adjacent hydrogen atoms determined from matrix isolated spectroscopy of neutral and cationic PAHs (see Hudgins et al. (in prep.) for details). In this comparison it should be kept in mind that the emission process leads to a small ($\simeq 0.1 \mu\text{m}$) wavelength redshift in the peak position.

adjacency. Furthermore, these chemist's 'rules-of-thumb' are based on spectroscopic studies of aromatic molecules in solution or solid mixtures, environments quite different from that of the emitting aromatic species giving rise to the interstellar features presented here. To obtain infrared data more relevant to the interstellar situation on larger molecules with the spectral details in this region determined by PAH structure rather than side-group substitution pattern, several groups have undertaken new spectroscopic studies of PAHs carried out under more appropriate conditions (e.g. see Szczepanski et al. (1995) and references therein; Hudgins et al. (in prep.) and references therein). Thanks to this effort, the mid-IR spectra of a few gas phase and many matrix isolated neutral and ionised PAHs are now available. In the Astrochemistry Laboratory at NASA Ames this work has been expanded considerably, including an extensive set of theoretical calculations, aimed to specifically address the questions raised by these new ISO spectra. Since a detailed presentation and analysis of the 11 to 15 μm region of the expanded dataset of matrix isolated PAH spectra will be published separately (Hudgins et al., in prep.), only the salient points are summarised here and used in the analysis presented

below. The IR spectra of matrix isolated PAHs compare favourably with the available spectra of gas phase PAHs, for both neutral PAHs and cationic PAHs (see also Piest et al. 1999) and validates the use of the matrix isolation method to obtain astronomically relevant data.

There are two points that emerge from an analysis of the laboratory database that are of particular importance to the observational data presented here. The first involves the effect of ionisation on the characteristic wavelength regions of the various CH adjacency classes. The second is the intrinsic integrated absorption strengths (A values) which are derived for the various adjacency classes. Together these results provide the tools to not only *qualitatively* infer the sorts of PAH edge structures present, but also *quantitatively* determine their relative amounts. As shown below, this allows one to place stringent constraints on the emitting interstellar PAH family.

2.4.2 OOP modes in the interstellar spectrum

Fig. 2.7 and Table 2.3 summarise the key points presented in Hudgins et al. (in prep.) that are applicable to this work. Fig. 2.7 schematically compares the average UIR spectrum with the wavelength regions associated with different hydrogen type for neutral and ionised isolated PAHs, while Table 2.3 lists the specific wavelength limits and the integrated band strengths per CH group as a function of hydrogen adjacency for all PAHs in the NASA Ames database. The regions indicated for the neutral PAHs differ slightly from those indicated by Bellamy (1958). We deem our results more astrophysically representative because of the larger set of molecules studied and because no substitution with strongly electro-negative groups were involved. Moreover our data were measured on isolated PAHs in inert matrices, rather than in solid mixtures.

Perusal of Fig. 2.7 and the wavelength limits listed in Table 2.3 shows that, while the ranges for neutral PAHs are not modified substantially compared to Bellamy (1958), ionisation causes some important changes in region boundaries. These data expand on the initial report that the PAH cation solo hydrogen position is substantially blue shifted with respect to the wavelength for its neutral counterpart while the domains indicative of the other types of hydrogen are less affected by ionisation (Hudgins & Allamandola 1999). Considering these modified domains and taking into account the roughly $0.1 \mu\text{m}$ redshift in the peak position for PAHs emitting at temperatures of $\sim 500\text{--}1000 \text{ K}$ (Flickinger et al. 1991; Brenner & Barker 1992; Colangeli et al. 1992; Joblin et al. 1995; Cook & Saykally 1998) allows us to draw the following conclusions.

- The broad, weak interstellar emission feature between 10.6 and $10.7 \mu\text{m}$ and the stronger distinct interstellar band peaking near $11.0 \mu\text{m}$ fall in the region unambiguously attributable to PAH cations.
- Adjusting for the $0.1 \mu\text{m}$ redshift, the bulk of the $11.2 \mu\text{m}$ interstellar band falls squarely within the solo region for the neutral PAHs and also, at the long wavelength end of the range for solo, cationic aromatic CH bonds.
- The domains indicated in Fig. 2.7 show that regardless of the region definitions used, there can be little doubt that the weak interstellar $12 \mu\text{m}$ band arises from duo modes.

- Interestingly, the blueward skewed profile of the moderately strong band at $12.7 \mu\text{m}$ seems to fall better within the envelope for trio hydrogens in ionised PAHs and does not agree well with the envelope for trio modes in neutral PAHs. An origin in duo modes of neutral PAHs is also consistent (Fig. 2.7).
- The weak $13.5 \mu\text{m}$ feature falls in the quartet domain. However, this also overlaps the lower of the two domains characteristic of the quintet region, and so, although we consider this highly unlikely, it is possible that quintet types of PAH structure could contribute to this band as well.

The large laboratory database and the high quality of the ISO interstellar spectra allows us to compare the *distribution* of peak positions of the individual modes with the bands observed in the interstellar spectrum. From the measured peak positions and cross-sections from the Hudgins database we construct a synthetic spectrum of a mixture of PAHs for comparison with the observed interstellar UIR bands. We construct such a spectrum on a mode-per-mode basis. Per mode, we take for each molecule which shows this mode the measured peak position and cross-section per CH bond and convolve this with a Gaussian profile. These contributions we add. The resulting envelopes per mode are normalised to the number of molecules exhibiting this mode and corrected for the number of CH bonds in one functional group. The measured cross-sections for the duo modes show a systematic decrease with increasing PAH size settling to a value of $\simeq 4 \text{ km/mol}$. To be consistent with the cross-section for the largest measured PAHs the contribution of the duo modes have been scaled down by a factor $1/4$. This way each envelope shows the distribution over wavelengths, while each area corresponds to the average absorption cross-section per *group* in the database, see Table 2.3. Thus the synthetic spectrum for each mode is given by:

$$S_m(\lambda) = \left(\sum_i G(\lambda, A_{m,i}, \lambda_{\text{peak},m,i}) \right) \frac{N_{\text{CH},m} W_m}{N_{\text{mol},m}}, \quad (2.2)$$

where S_m is the synthetic spectrum for mode m , λ the wavelength, $A_{m,i}$ the cross-section of the mode m in molecule i and $\lambda_{\text{peak},m,i}$ the corresponding peak position. $G(\lambda, X, Y)$ is a Gauss function with $\text{FWHM} = 10 \text{ cm}^{-1}$, $\text{surface} = X$, $\text{peak position} = Y$. $N_{\text{CH},m}$ designates the number of CH bonds in one functional group, $N_{\text{mol},m}$ the total number of molecules with mode m . W_m is a weighing factor which equals 1, $1/4$, 1 and 1 for solo, duo, trio and quartet modes respectively to account for the decrease in strength of the duo modes in larger PAHs. The summation is done over all molecules in the database. The resulting envelopes are shown in Fig. 2.8 for both the neutral and cationic PAHs.

One should bear in mind, that the measured species are probably smaller than those that dominate the interstellar population and that, for stability reasons, the interstellar PAH family might be skewed to a few of these molecules or the edges structures they represent (cf. Sect. 2.5). Comparing the interstellar spectrum (Fig. 2.8b) with these averaged laboratory spectra (Fig. 2.8a,c) allows us to further refine the discussion of Sect. 2.4.1:

- The position of the strongest band at $11.23 \mu\text{m}$ agrees well with the measured position of solo transitions in neutral PAHs but does not agree with the position of the cationic solos

Figure 2.8: Comparison between the mean interstellar spectrum (panel (b)) and synthetic PAH spectra showing the distribution over peak positions of the OOP modes in the Hudgins database Hudgins et al. (in prep.). The shaded surfaces in panel (a) and (c) represent the contributions per mode for neutral and positively charged PAHs respectively. Each area represents the average absorption cross-section per functional group.

	s/d	s/t	s/q
NGC 7207	7.7	4.6	28.5
IRAS 18317	3.4	0.8	10.2

Table 2.4: Relative number of solo, duo, trio and quartet groups in NGC 7207 and IRAS 18317. The ratio of the number of solo to duo (s/d), solo to trio (s/t) and solo to quartet (s/q) groups for NGC 7207 and IRAS 18317 as deduced from their 10 to 15 μm spectra.

even after including a 0.1 μm shift due to the high temperature of interstellar PAHs. It is however important to note that the solo mode of the largest cation in the database peaks at 11.2 μm , the longest wavelength of all measured cationic solo modes.

- The peak of the 12.7 μm emission feature falls at slightly shorter wavelength than the centre of weight for both the neutral and cationic trio modes. Also, the blue wing of the 12.7 μm band in the interstellar spectra does not coincide with any strong emission bands of the PAH species in the database.
- The centre of weight of the neutral quartet vibrations is 13.4 μm which matches better with the position of the 13.5 μm UIR band in the interstellar spectrum than does the centre of weight for cationic quartets (13.25 μm).

Summarising the above we find that the overall match between the UIR spectra and the neutral species is best. There are significant differences between the combined laboratory measurements and the interstellar spectra. In particular the precise assignment of the 12.7 μm feature is uncertain. Given the above observations, we feel that while the assignment with trio modes is attractive, the case is not completely compelling. These issues might be resolved when larger species are measured in the laboratory. However it is clear that the 11.0 and 11.2 μm feature are due to *solo* CH bonds in ionised and neutral PAHs respectively, and the bands at longer wavelength are due to *multiplets*.

It is also immediately clear from Fig. 2.8 that the interstellar spectrum does not reflect an equal distribution over the different functional groups but is dominated by the contribution of solo modes. This reflects the molecular structure of the emitting PAHs.

2.5 The molecular structures of interstellar PAHs

It is now possible to quantify the relative amounts of the various types of CH groups on the periphery of the interstellar PAHs which dominate the emission in this wavelength range and derive the types and sizes of interstellar PAH structures implied. This is achieved by analysing the peak positions and integrated band strengths listed in Table 2.2 with the laboratory data summarised in Table 2.3. In the following we assume that the 11.2 μm emission band arises from the solo vibrations, the 12.0 μm band from duo modes, the 12.7 μm from trios and the 13.5 μm from quartets. From the laboratory data we get the intrinsic strength of solos relative to the duos, trios and quartets as 6.2, 2.6 and 2.1 respectively (see Table 2.3). From the intensities of the individual features listed in Table 2.2 for NGC 7207 we see that the observed

Structure 1. $C_{134}H_{36}$; $s/d=8.0$; $s/t=4.0$; $s/q=16.0$ Structure 2. $C_{129}H_{37}$; $s/d=7.0$; $s/t=2.8$; $s/q=14.0$ Structure 3. $C_{121}H_{35}$; $s/d=6.0$; $s/t=2.4$; $s/q=12.0$ Structure 4. $C_{115}H_{37}$; $s/d=4.0$; $s/t=1.1$; $s/q=8.0$

Figure 2.9: Examples of molecular structures simultaneously satisfying the structural constraints set by the observed band strength ratios of the number of solo, duo and trio modes for different interstellar regions. The number of solo, duo, trio and quartet functional groups are noted s , d , t and q respectively. Solo modes are associated with long straight molecular edges. Duos and trios, on the other hand, correspond to corners. Quartets are due to pendant rings attached to the structure. The numbers in the molecular structures indicate the number of adjacent CH groups per aromatic ring.

solo to duo, solo to trio and solo to quartet intensity ratios are 23.8, 4.0, 14.7 respectively. We conclude that in NGC 7027 the ratio of the number of solo CH bonds to CH bonds in duo, trio and quartet groups are 3.8, 1.5 and 7.1. Taking into account the number of CH's per functional group there are 7.7, 4.6 and 28.5 solo (groups) relative to the duo, trio and quartet groups. For IRAS 18317 these values are (see also Table 2.4) 3.4, 0.8 and 10.2 respectively. These two sources represent the extremes in the observed intensity ratio in our sample.

Examples of the types of PAHs which simultaneously satisfy these different structural constraints are shown in Fig. 2.9. In constructing these structures one should keep in mind that solo H's represent long straight edges, while the corners in the structures give rise to duos or trios. To match the dominance of the $11.2\ \mu\text{m}$ feature in NGC 7027 one is naturally driven towards rather large molecules with at least $\simeq 100$ –200 carbon atoms and long straight edges. This is entirely in keeping with previous theoretical calculations of the molecular sizes of the PAH species which account for most of the emission in these features (Schutte et al. 1993). As illustrated in Fig. 2.9 structure 1 approximates the ratios listed in Table 2.4 for NGC 7027, these ratios requires a preponderance of solo hydrogens over duos and trios. The extreme quartet to solo group ratio observed for NGC 7027 is not well reproduced even by figure 2.9 structure 1. In order to reproduce that ratio in one single molecule one requires to go to even larger molecules. Rather, we surmise the extreme ratio reflects the presence of molecules without *any* quartet groups. Quartet groups represent pendant rings on the molecule, which can be taken off without altering the other ratios strongly. Of course many other PAH structures that match the observed ratios are possible. However these structures are all very similar to this and the conclusion is the same: in NGC 7027 the PAH family is dominated by large compact PAHs.

In contrast, for IRAS 18317 the situation is very different. The observed ratios force one to include more corners or uneven edges. Structure 4 in Fig. 2.9 illustrates one way of achieving this. Of course this effect can also be achieved by going to smaller compact structures of the type shown in structure 1 or by breaking up structure 4 in two or more fragments. Structures 2 and 3 shown in Fig. 2.9 are intermediate between these two extremes and have solo/duo, solo/trio, and solo/quartet ratios consistent with the relative interstellar band intensities shown in Fig. 2.2 for the objects which lie between the extremes, NGC 7027 and the IRAS 18317. Thus we observe a structural evolution where closed, compact species dominate the emission in some regions, while open, uneven structures are more important in others. We surmise that this structural evolution as revealed by the smooth spectral evolution shown in Fig. 2.2 reflects the variations in chemical history and excitation environment in these regions.

2.6 Discussion

In this section we will discuss the assignment of 11.2 and 12.7 interstellar bands and observed variations in 11.2/12.7 μm ratio and their correlation with other UIR bands in view of their underlying physical causes (Sect. 2.6.1). In the past these variations have been attributed to dehydrogenation. We reconsider this suggestion in Sect. 2.6.2.

2.6.1 The 11.2, 12.7 μm emission features.

Since quantum calculations show that the CH stretch (3.3 μm band) is inherently very weak in ionised PAHs (Langhoff 1996), the 3.3 μm emission band is likely a measure of the neutral PAH contribution. Based on both the peak position of the 11.2 μm band (Sect. 2.4.2) and its correlation with the 3.3 μm band (Sect. 2.3.4) we assign this band to solo CH out-of-plane bending vibrations of neutral PAHs. This result means that in evolved stars the OOP spectrum is dominated by contributions from the *neutral* PAHs. We already assigned the weak bands at 10.6 and 11.0 μm to cations (Sect. 2.4.2). Even though the absorption cross-sections for the OOP modes do not change upon ionisation, we cannot directly derive the ionisation fraction from the measured band strength ratios. This is due to the fact that ionisation does strongly affect the strength of other modes, which in turn influences the fraction of absorbed energy emitted at any wavelength (Bakes et al. 2001).

The spectral identification of the 12.7 band is much less clear and it is not possible at this time to assign this band unambiguously to either neutral or cationic PAHs. In the existing database there is only one species with a strong band that matches well in position, which ‘happens’ to be a cation. Furthermore the strength of the interstellar 12.7 μm band correlates with the strength of the 6.2 μm feature (see Sect. 2.3.4). The strength of the modes between 6 and 9 μm are greatly enhanced upon ionisation, and thus, one way to understand this correlation is to assume that the 12.7 is also predominantly carried by cations.

Thus, seemingly, the 11.2 μm and 12.7 μm bands represent a dichotomy of interstellar PAHs with the former carried mainly by neutral and the latter by positively charged PAHs. The origin of this interrelation between charge and spectral characteristics is unclear. There is no indication in the laboratory experiments for a causal relation between, for example, charge state and the relative strength of the solo to trio modes. Considering also the discussion on the molecular structures implied by the relative fraction of the solos to duos and trios (Sect. 2.5; Fig. 2.9) we are forced to conclude that the good correlation between the 11.2 and 3.3 μm bands and between the 12.7 and the 6.2 μm bands reflects *a correlation of molecular structure and charge state with environment*. Indeed when using PAHs containing some 50 C-atoms (Leger & Puget 1984) the correlation between the $I_{11.2}/I_{6.2}$ and $I_{3.3}/I_{6.2}$ is well reproduced by model calculations of Bakes et al. (2001) by only varying the degree of ionisation. Thus, those environments which favour large PAHs and the 11.2 μm band (structure 1 in Fig. 2.9) also favour neutral PAHs. While in regions where open uneven molecular structures and the 12.7 μm band (structure 4 in Fig. 2.9) dominate, PAHs are predominantly charged.

This is probably also the origin of the correlation between the $I_{\text{PAH}}/I_{\text{IR}}$ ratio and the $I_{12.7}/I_{11.2}$ (cf. Fig. 2.6). The $I_{\text{PAH}}/I_{\text{IR}}$ measures the PAH/dust abundance ratio. The loose correlation suggests that for the ISM sources the PAH abundance is lower. We recognise that PNe inject freshly synthesised PAHs into the ISM where they are mixed and processed by FUV photons and shocks. This processing will lead to a slow destruction of the PAHs.

The dominant molecular structure reflects the integrated history of the PAH family and we note that all sources with a strong 11.2 μm band are PNe, which have formed their PAHs within the last some 1000 years. Because open uneven molecular structures are kinetically more reactive to the addition of carbon atoms than compact structures, the predominance of the latter in chemically reactive regions where PAHs have recently formed can be rationalised.

(Frenklach & Feigelson 1989; Cherchneff et al. 1992). In contrast regions with relatively strong 12.7 μm bands are all H II regions where luminous stars illuminate material which has been processed in the ISM for some 10^9 years. This processing irreversibly leads to a breaking down of the molecular structure because reformation is prohibited by the low temperature of the ISM.

This does not directly explain why the 11.2 μm band correlates with the neutral PAH indicator while the 12.7 μm emission feature correlates with bands attributed to ions. The charge state is rapidly set by the charge balance, which is dominated by local physical conditions, or more specifically the ionisation parameter, $(G_0 \sqrt{T_{\text{gas}}})/n_e$, where G_0 is the FUV radiation field, T_{gas} is the gas-temperature and n_e the electron density. Thus rather than history, ionisation reflects the present. Possibly most of the destruction is occurring presently and is also driven by local physical conditions.

2.6.2 Dehydrogenation

We have argued that the smooth changes in the band strength ratios in the region of interest are caused by variations in the edge-structure of the dominant emitting species. However other effects can also be of influence on the emitted spectra. Most notably dehydrogenation. There has been a long debate in the literature on the effect of dehydrogenation on the spectral characteristics of the 10–15 μm region. Originally when only the 11.2 UIR band was known, its dominance had been attributed to extreme ($\sim 90\%$) dehydrogenation of the emitting aromatic species leaving only solo hydrogens (Duley & Williams 1981). However, this question was revisited when IRAS revealed the presence of duos and trios in the interstellar PAH family (Cohen et al. 1985). Theoretical studies of the dehydrogenation of interstellar PAHs have shown that for PAHs larger than about 25 C-atoms hydrogenation through reactions with abundant atomic H is more important than H loss through unimolecular dissociation (Tielens et al. 1987; Allamandola et al. 1989; Jochims et al. 1994; Allain et al. 1996; Jochims et al. 1999). Hence, with a typical PAH size of 50 C-atoms dehydrogenation should have no effect on the UIR spectrum.

Observationally, our analysis also argues against dehydrogenation. First, we observe a constant ratio of the 3.3 μm band (all CH oscillation) to the 11.2 μm band (only solo CH oscillation). However, we would expect a non-linear behaviour since, when dehydrogenation commences the number of solo H increases as duos and trios are converted to solo's and only at high dehydrogenation does the relation between the 3.3 and the 11.2 μm bands become linear (Schutte et al. 1993). Secondly, if the variation in $I_{12.7}/I_{11.2}$ reflects dehydrogenation than we would expect that decreasing H coverage (i.e. decreasing $I_{12.7}/I_{11.2}$) would correlate with increasing CC/CH mode emission (i.e. $I_{6.2}/I_{11.2}$). The opposite is actually observed (cf. Fig. 2.5). We conclude therefore that dehydrogenation has little influence on the observed interstellar UIR spectrum.

2.7 Summary

We have presented new 10–15 μm spectra of evolved stars, H II regions, RNe and YSOs. We observe very rich UIR spectra with strong bands at 11.2 and 12.7 μm and weaker bands at 10.6, 11.0, 12.0, 13.5 and 14.2 μm . These spectra show large variations in the band strength ratios between sources, especially in the 11.2 and 12.7 μm feature ratio. Evolved stars have a dominant 11.2 μm feature while in H II regions the 12.7 and 11.2 are typically equally strong. We find that the 11.2 μm band correlates with the CH stretch band at 3.3 μm and that the 12.7 μm band correlates with the CC stretch band at 6.2 μm .

We have summarised new laboratory spectroscopy results for the CH out-of-plane bending vibrations on isolated neutral and cationic PAHs. Different number of adjacent CH bonds give rise to vibrations in distinctly different wavelength regions. The modes are therefore good diagnostics of the molecular structure of the emitting species. Upon ionisation the solo CH vibrations are shifted to shorter wavelength compared to the solo modes in neutral. The cross-sections per mode are not strongly modified upon ionisation. We attribute the weak bands at 10.6 and 11.0 μm to solo modes in positively charged PAHs, the strong 11.2 μm band the solo modes in neutral. The weak 12.0 μm band we assign to the duo modes, the 12.7 μm to trio modes and the 13.5 μm feature to quartet vibrations.

From the average cross-sections per mode we have constrained the relative numbers of solo, duo, trio and quartet CH groups in different sources for the PAH species that effectively emit in this wavelength region. The spectra of PNe with a dominant 11.2 μm feature arises from large (~ 100 –150 C-atom) compact PAHs with long straight edges. In contrast the H II region spectra are due to smaller or more irregular PAHs.

We propose a scenario in which large compact PAHs are formed in the winds around evolved stars. These PAHs are consequently degraded in the ISM. From the correlations between charge indicators, which are set by the local physical conditions, and the 11.2/12.7 μm band strength ratio, which is determined by the molecular structure, we conclude that much of this degradation happens on a short timescale in the emission objects itself.

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The detection of iron sulfides in Planetary Nebulae

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Abstract

We present and discuss the detection, through mid IR spectroscopy, of iron sulfides in the carbon rich ejecta of evolved stars. We find the spectroscopic signature of iron sulfides at $23\ \mu\text{m}$. We also find weak features at ~ 34 , 38 and $44\ \mu\text{m}$. The positions of these features correspond well with the resonances of the iron sulfide troilite. However, the relative strength of the $23\ \mu\text{m}$ versus the other bands does not match the laboratory measurements, which suggests the presence of other iron sulfides besides troilite. The same broad feature around $23\ \mu\text{m}$ has been found in young stellar objects. This detection may imply a carbon star origin for part of the iron sulfides found in meteorites and interplanetary dust particles.

3.1 Introduction

Infrared (IR) spectroscopy is an important tool to study the composition of the circumstellar envelopes (CSEs) around stars at various stages of evolution. Evolved stars shed their envelopes. The composition of their CSE reflects the physical and chemical conditions in the extended atmosphere of these stars. The CSE of young stellar objects (YSOs) holds information on the molecular cloud composition, the material which formed the stars and possibly their planetary systems. The building blocks of our solar system can also be studied through different methods. Most notably by studying meteorites, comets and interplanetary dust particles (IDPs). These solar system objects contain materials which are believed to be unaltered during the formation of our solar system. Iron sulfides are an important constituent of all these solar-system building blocks (e.g. Kerridge 1976; Lawler et al. 1989; Dai & Bradley 2001).

We are studying the IR spectra of planetary nebulae (PNe) to measure which materials are produced in the outflows around evolved stars and fed into the interstellar medium (ISM). In this chapter we present and discuss the detection of a broad feature at $23\ \mu\text{m}$ and weaker features at 34 , 38 and 44 in two C-rich PNe. A similar broad feature is found in the spectra of YSOs (See also Chapter 4). Based on the correspondence with the laboratory spectrum of the

iron sulfide troilite we claim iron sulfides to be a constituent of these PNe. The spectroscopic match is not perfect and we present possible explanations for the observed discrepancies.

3.2 The observations

We present the mid IR spectra of two PNe. M2-43 and K3-17 were observed with the Short Wavelength Spectrometer (SWS) (de Graauw et al. 1996) on-board the Infrared Space Observatory (ISO) (Kessler et al. 1996) in observing mode AOT01 (TDT 14900804 and 49900640). The data were processed using SWS interactive analysis product; IA (see de Graauw et al. 1996) using calibration files and procedures equivalent to pipeline version 10.1. Further data processing consisted of bad data removal and rebinning on a fixed resolution wavelength grid. The match between the individual sub-bands is excellent for K3-17. For M2-43 the data of sub-band 3A (12.5–16.5 μm) are systematically too low compared to the neighbouring sub-bands. We have shifted sub-band 3A by +7 Jy. The detection of the feature we discuss here is not influenced by this shifting.

3.3 Description of the spectrum

We show the SWS spectrum of the prototypical C-rich PN NGC 7027 in Fig. 3.1a. We show the spectra of M2-43 and K3-17 from 10 to 45 μm in Fig. 3.1b. The mid IR spectra of these nebulae are typified by two broad emission features: one centred on $\sim 23 \mu\text{m}$, and the other at 34 μm . The spectrum of M2-43 shows some weak structures on top of both these features with local maxima at 15.5, 20, 22.3, 38 and 44 μm . The structure near 28–29 μm is unreliable. We construct a simple model continuum by fitting a modified blackbody ($F_{\nu}(\lambda) = B_{\nu}(\lambda, T) \times \lambda^{-p}$, where $B_{\nu}(\lambda, T)$ is the Planck function) to continuum points around 9–10, 16 and 45 μm . We keep the power (p) fixed at 1.0, a value which in general fits the mid IR spectra of C-rich PNe well. These continua are shown in Fig. 3.1a,b and the excess emission above the continuum is shown in Fig. 3.1c.

A very broad emission feature extending from 25–45 μm is abundantly detected in IR spectra of a variety of C-rich evolved objects ranging from intermediate mass loss AGB stars to PNe (Forrest et al. 1981). The feature is attributed to MgS (e.g. Nuth et al. 1985; Goebel & Moseley 1985, see also Chapter 6). In the PNe this feature usually peaks near 34 μm , see Fig. 3.1a for a clear example of the feature. The broad feature in M2-43 and K3-17 strongly resembles the feature found in other PNe except for the weak substructures in the 30–45 μm range detected in M2-43.

The feature peaking near 23 μm is not found in other PNe. A broad feature like this is however found in the CSE of YSOs where it had previously been ascribed to FeO (Bouwman et al. 2000). However, we identified this feature with iron sulfides (Chapter 4). We show for comparison the feature of the YSO; AB Aur in Fig. 3.1b. The feature is obtained after subtracting a radiative transfer model from the SWS spectrum. The feature found in the YSO is very close to the feature found in the PNe, which shows that M2-43 and K3-17 contain the same solid state component as is found around the YSOs and which causes the 23 μm feature in both environments.

Figure 3.1: The SWS spectra of the nebulae exhibiting the 23 μm feature are shown in panel b. Panel a shows a typical C-rich PN without the 23 μm feature. The model continua are indicated in the panels a and b by dotted lines. The spectrum of M2-43 is offset for clarity. We show the feature found in AB Aur for comparison (solid grey line). Panel c shows the ratio of the excess flux to the continuum flux. The excess of K3-17 is offset for clarity and the zero level is indicated by the dashed line. Panel d shows the normalised κ_{abs} of FeS (black line) and FeO (grey line) particles with a CDE shape distribution.

3.4 Comparison with laboratory data

Begemann et al. (1994) measured the IR reflectance of troilite (FeS). These authors find four strong resonances in the wavelength range we discuss here, a broad feature peaking at $23\ \mu\text{m}$ and narrower features at 33 , 38 and $43\ \mu\text{m}$. We show the emission from FeS in a continuous distribution of ellipsoids (CDE) shape distribution in Fig. 3.1c. The feature at $23\ \mu\text{m}$ matches well with the emission excess found in M2-43 and K3-17, also the signatures of the sharper features at 38 and $43\ \mu\text{m}$ match well to the weak features found in M2-43. The presence of the $33\ \mu\text{m}$ feature is not obvious from the SWS spectrum. We show in Fig. 3.2a our attempt to remove the contribution of MgS. We have modelled the emission due to MgS in a optically thin CDE calculation using the optical constants from Begemann et al. (1994). We vary the strength and temperature of the MgS feature in order to match most of the $34\ \mu\text{m}$ component. We find a temperature of $150\ \text{K}$. This temperature appears very reasonable given the fitted continuum temperature of $165\ \text{K}$. Fig. 3.2b shows the residue after removing both the continuum contribution and the emission due to the MgS component. In the residue a feature near $34\ \mu\text{m}$ is also present.

Based on the correspondence in feature positions between the laboratory spectrum and the astrophysical spectra we identify FeS as the carrier of the $23\ \mu\text{m}$ feature. However it is clear from a comparison between Fig. 3.1 panels b and c that the band strength ratio (BSR) for FeS and the nebular spectra do not correspond well. In the laboratory spectrum the narrow long wavelength features are much stronger than observed in these nebulae. Below we discuss possible effects, that influence the BSRs.

Firstly, the temperature of the emitting grains influences the observed BSRs. Warmer grains emit stronger towards shorter wavelengths, thereby increasing the strength of the $23\ \mu\text{m}$ band relative to the other bands. However, increasing the temperature to $720\ \text{K}$ makes the $23\ \mu\text{m}$ band only equally strong in peak strength to the $38\ \mu\text{m}$ band. The evaporation temperature of FeS is $720\ \text{K}$. Increasing the temperature much beyond the typical continuum temperature of $200\ \text{K}$, enhances the blue side of the broad $23\ \mu\text{m}$ band contrarily to what is observed in the nebular spectra. We conclude that a simple temperature effect cannot explain the differences in the BSRs.

Secondly, the BSRs may be influenced by the particle shape. We compare in Fig. 3.3a the mass absorption coefficient (κ_{abs}) of spherical particles and from a CDE-shape distribution. As can be seen the resonances are slightly shifted but the BSRs are hardly affected.

Thirdly, the particle might not be homogeneous. We simulated the absorption by a FeS grain embedded in a layer of MgS in the electrostatic approximation following Bohren & Huffman (1983, chapter 5). The simulated κ_{abs} from FeS grain with a MgS coating of 10 and 50 per cent by volume are shown in Fig. 3.3a. The shortest wavelength resonance is strongly enhanced compared to the longer wavelength bands also the $23\ \mu\text{m}$ band shifts towards longer wavelength. This behaviour is due to the strong resonance of MgS at $26\ \mu\text{m}$. The grain with a 50 per cent by volume MgS coating shows only a single broad resonance at $25\ \mu\text{m}$.

Lastly, the BSRs can be affected if the material measured in the laboratory does not have the exact same lattice structure or composition as the material emitting in these nebulae. The material measured by Begemann et al. (1994) is troilite (FeS), however the iron sulfides most commonly found in cometary material and interplanetary dust particles is pyrrhotite

Figure 3.2: The mid IR spectrum M2-43. We show in panel a the modelled continuum (dashed), the modelled emission of MgS at a temperature of 150 K (black) and the composite modelled spectrum (grey drawn). In panel b we show the residue after subtracting the composite model from the observed spectrum. In a comparison with FeS (CDE) at $T=150$ (grey line) we recognise the major resonances of FeS at 23, ~34 and 38 μm .

(Fe_{1-x}S) (Tomeoka & Buseck 1984). Unfortunately there are no published optical constants for pyrrhotite that cover the whole wavelength range of interest. We show the absorbance of pyrrhotite and iron sulfide inclusion from an IDP to 26 μm in Fig. 3.3b. Both spectra show a broad resonance at 23 μm . In order to further examine the effects of differences due to composition and lattice structure we have used the published optical constants for pyrite (FeS_2) (Verble & Wallis 1969). The emission from pyrite grains is shown by the grey line in Fig. 3.3b. The dominant band is at 24 μm . There are some weaker but sharp resonances at 28.5 and 34 μm . As can be seen by comparing the FeS and the FeS_2 spectra the resonance around 23 μm due to the Fe-S stretch is observed in all these iron sulfides. The longer wavelength bands vary more. One might speculate that the 23 μm band is generic to all Fe-S bearing materials while the longer wavelength bands are more sensitive to the lattice structure and may be suppressed in case the lattice is disordered.

Figure 3.3: The effect of particle shape, coating and composition on the optical properties of iron sulfide grains. We show in panel a the normalized κ_{abs} of spherical FeS grains (black line), FeS in a CDE shape distribution (grey line), spherical FeS grains with a coating of MgS of 10 per cent by volume (dashed line) and 50 per cent by volume (dotted line). In panel b we show κ_{abs} , normalized at 23 μm for different types of iron sulfides: FeS (black line), FeS₂ (grey line), Fe_(1-x)S (dashed line) and the IDP iron sulfide (dotted line). All calculations are done in the Rayleigh limit when the particle radius is much smaller than the wavelength. The temperature of the grains is 200 K.

3.5 Discussion

The fact that we find the 23 μm feature in the spectra of PNe and YSOs may have implications for the origin of the iron sulfide in our solar system and it puts constraints on the carrier: it must be a plausible component in these chemically very different environments.

Previously it has been suggested that the 23 μm feature in YSOs is carried by FeO (Bouwman et al. 2000). FeO exhibits a single sharp resonance at 20 μm . This resonance broadens and shifts to 23 μm in a CDE shape distribution (Begemann et al. 1995) (e.g. Fig. 3.1). This identification relieves the problem with the long wavelength resonances of FeS. Against this identification argues the thermo-dynamical unstability of FeO. Moreover, FeO is not expected to form in a C-rich environment. The SWS spectra of M2-43 and K3-17 shown no evidence for O-rich dust like silicates. Instead they show all the typical C-rich dust components: the “30” μm feature and the emission due to polycyclic aromatic hydrocarbons (Allamandola

et al. 1989) at 3.3, 6.2, 7.7 and 11.3 μm . Iron sulfides are predicted to form in a reducing environment like the outflows of C-rich evolved stars (Lodders & Fegley 1999).

Similarly, our simulations of the coated FeS cores with MgS mantles demonstrate a possible way to circumvent the problems with the weak or absent long wavelength resonances, however MgS is not stable in an O-rich circumstellar disk of a YSO. Therefore, these calculations are more a proof of concept rather than a direct candidate for carrier identification. A mantle material which has a strong resonance near 23 μm enhances the 23 μm feature of the iron sulfide core compared to the longer wavelength resonances and brings the BSRs closer to the observed ones. Of course, this material may well be an iron sulfide like pyrrhotite. Such a coated grain is a special case of the mixture of iron sulfide phases discussed above.

An important question concerns the production of FeS in the outflow around carbon stars. Model calculations show that in carbon star atmospheres Fe condenses into metallic iron at high temperatures (Lattimer et al. 1978). At lower temperatures S condenses into MgS. At even lower temperatures iron sulfides may form through a gas-solid interaction between H_2S and the metallic iron. Because the number ratio of S to Mg is close to unity, S is effectively locked up. Based on these calculations iron sulfides are not expected to form abundantly. However these predictions are based on thermochemical equilibrium calculations without taking the dynamics of the outflow into account. One could envision that if the gas cools rapidly during the outflow the condensation of MgS might not be complete and S in the form of H_2S could still be available to react with the metallic iron. Within this scenario we would conclude that the outflows in M2-43 and K3-17 have cooled more rapidly than those nebulae which do not exhibit the 23 μm feature. The fact that we detect the “30” μm feature, which is due to MgS at a strength which is not less than in other C-rich PNe indicates that the MgS condensation cannot have been very suppressed.

Secondly, the presence of iron sulfide in these nebulae may be due to an unusually high S/Mg ratio. However, this is unlikely since neither S nor Mg are produced during the evolution of these objects requiring these peculiar abundance patterns to be present throughout the material from which these stars formed.

Thirdly, the difference between ‘normal’ C-rich PNe and those exhibiting the 23 μm feature could be the particle size. 1 μm sized iron sulfide particles are opaque in the mid IR leaving them undetectable.

Iron sulfides are abundantly found in meteoritic material, in which they are actually the most important S bearing component. Previously iron sulfides have not been detected around evolved stars. This had led to the understanding that *all* the iron sulfides in our solar system have been produced during the formation of our solar system. The amount of iron sulfides found in meteorites excludes the carbon star atmospheres as their sole production place, but these new findings imply that *there may be a presolar source of iron sulfides in our solar system*.

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Identification of iron sulfide grains in protoplanetary disks

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Sulfur is depleted in cold dense molecular clouds with embedded young stellar objects (Joseph et al. 1986), indicating that most of it probably resides in solid grains. Iron sulfide grains are the main sulfur species in cometary dust particles (Schulze et al. 1997; Dai & Bradley 2001), but there has been no direct evidence for FeS in astronomical sources (Palumbo et al. 1997), which poses a considerable problem, because sulfur is a cosmically abundant element. Here we report laboratory infrared spectra of FeS grains from primitive meteorites, as well as from pyrrhotite ($[\text{Fe}, \text{Ni}]_{1-x}\text{S}$) grains in interplanetary dust, which show a broad FeS feature centred at ~ 23.5 micrometres. A similar broad feature is seen in the infrared spectra of young stellar objects, implying that FeS grains are an important but previously unrecognized component of circumstellar dust. The feature had previously been attributed to FeO (Meeus et al. 2001; Waters et al. 1999; Henning et al. 1995). The observed astronomical line strengths are generally consistent with the depletion of sulfur from the gas phase (Joseph et al. 1986), and with the average Galactic sulfur/silicon abundance ratio (Anders & Grevesse 1989). We conclude that the missing sulfur has been found.

Spectroscopic analyses of primitive meteorites, cometary dust particles and synthetic analogue materials in the laboratory provide constraints and serve as ‘ground truth’ for evaluating various hypotheses on the nature of interstellar grains. Comets are primitive bodies that are widely believed to be a large reservoir of preserved interstellar and circumstellar grains along with presolar organic matter. The comparison of laboratory infrared data on cometary dust with astronomical spectra has been facilitated by the high-quality spectra obtained from the Infrared Space Observatory (ISO) (Kessler et al. 1996). An emission feature is observed (Meeus et al. 2001; Bouwman et al. 2000) in ISO spectra at $\sim 23.5 \mu\text{m}$ and is compared here with iron sulfide minerals from meteorites, interplanetary dust particles (IDPs) and terrestrial sources which show infrared features in the same spectral range (Fig. 4.1). Figure 4.2 shows infrared spectra from iron oxide and iron sulfide mineral standards. Wüstite (FeO) and magnetite (Fe_3O_4) show only one strong, narrow feature at $\sim 17.5 \mu\text{m}$. FeO has been used to

Figure 4.1: Infrared spectra of young stars showing a pronounced $23.5 \mu\text{m}$ feature from iron sulfide grains. (a) The mid-infrared spectra of the young stars AB Aurigae, HD163296 and the evolved star M2-43. The grey lines in the AB Aur and HD163296 spectrum represent model fits to the full ISO spectra using amorphous silicates, metallic Fe and carbonaceous material (Bouwman et al. 2000). The grey line in the M2-43 spectrum is a fit to the continuum using amorphous carbon and MgS. (b) Residuals after subtracting ISO spectra from the observed ISO spectra. (c) Infrared spectra of troilite (FeS) and of pyrite (FeS_2) calculated from optical constants, and of pyrrhotite (Fe_{1-x}S) from laboratory measurements. We note the major resonances of FeS at 23, 33 and 38 μm in the residual spectrum of M2-43. PAHs, polyaromatic hydrocarbons; λF_{λ} , flux in units of Wm^{-2} .

model the 23 μm feature in ISO spectra because the position of the FeO feature can be shifted to 23 μm in calculated spectra using experimentally derived optical constants combined with theoretical grain shapes and sizes (Henning et al. 1995). Pyrrhotite exhibits a strong, broad, asymmetric absorption maximum centred at $\sim 23.5 \mu\text{m}$, whereas the feature in troilite is closer to 22 μm . The pyrrhotite spectrum also shows a weak shoulder at $\sim 17.5 \mu\text{m}$ that is consistent with iron oxide. Pyrrhotite is well known to quickly form a thin surface oxide layer when exposed to ambient atmospheric conditions. Figure 4.3 shows infrared spectra from two pyrrhotite-rich IDPs (L2011*B6 and U2012A-2J) together with 23.5 μm features from two Herbig stars (HD163296 and AB Aurigae) (van den Ancker et al. 2000). The sulfide mineral standards, as well as the sulfides in the IDPs, provide an excellent match to the 23.5 μm feature in young stellar objects in terms of peak positions, shapes and widths (Fig. 4.1 and 4.3), although minor differences do exist.

The 23.5 μm band observed in circumstellar disks surrounding young stars matches that of troilite (FeS) in the evolved star M2-43 (Fig. 4.1). The identification of FeS in M2-43 is based on the good match in peak positions between laboratory and astronomical spectra of not only the 23.5 μm band, but also the longer-wavelength bands at 34, 38 and 44 μm , and because iron sulfides are a predicted dust component in carbon-rich evolved stars (Lodders & Fegley 1999). We observe that the 23.5 μm band is consistently much stronger in the astronomical data than in the laboratory spectrum of FeS derived from optical constants (Begemann et al. 1994). The 34, 38 and 44 μm bands of troilite, although weakly present in the evolved star, are not detected in the young stars; however, we point out that there is spectral structure present in the AB Aurigae spectrum (at low spectral contrast) at approximately the correct wavelength positions for the long-wavelength peaks of FeS (Fig. 4.1). The lack of a clear signature of FeS in the 30 μm region of the young star can be attributed largely to temperature differences between the FeS in the evolved star and young star. All published spectra of iron sulfides show a characteristic 23.5 μm feature and additional features at longer wavelengths ($>30 \mu\text{m}$) (Begemann et al. 1994; Nuth et al. 1985; Lennie & Vaughan 1992). The position and strength of these long-wavelength features vary with mineralogical speciation (Fig. 4.1) and crystallinity (Nuth et al. 1985). In addition, grain size and grain shape have significant effects on the sharpness and position of the infrared features. The astronomical spectra almost certainly reflect a mixture of iron sulfide phases (as do most cometary IDPs (Dai & Bradley 2001)), which also serves to enhance the 23.5 μm band strength with respect to the longer-wavelength bands.

If the ISO feature is indeed due to iron sulfides, then the grains must be small because we were only able to collect useful absorption spectra from specimens $<200 \text{ nm}$ thick. When the sample thickness exceeds $\sim 200 \text{ nm}$, the sulfide standards became infrared opaque, which is consistent with our calculated mass absorption coefficient. There is an extensive literature on similar effects observed for SiC and other dense, strongly infrared-absorbing materials (Lennie & Vaughan 1992; Hofmeister et al. 2000). ISO spectra from comet Hale-Bopp show a significantly sharper feature at $\sim 23.5 \mu\text{m}$ attributed to forsterite (Mg_2SiO_4) (Malfait et al. 1998; Crovisier et al. 1997). The overlap with forsterite makes it difficult to determine if a broader underlying feature, consistent with iron sulfide, is present in the Hale-Bopp spectrum. As noted above, however, the grain size of the sulfides strongly influences whether or not the feature will be detected.

Figure 4.2: Infrared transmission spectra from iron oxides are compared with iron sulfide standards. The iron oxides display a narrow diagnostic feature between 17 and 18 μm whereas the iron sulfides have a broad feature showing its intensity maximum between 22 and 24 μm . Also shown for comparison is the spectrum from meteoritic forsterite (Mg_2SiO_4) which displays several Si-O bending modes between 15 and 25 μm . Spectra were obtained using a SpectraTech IruS Fourier transform infrared microspectrometer on the intense infrared beamline (U10B) at the National Synchrotron Light Source at Brookhaven National Laboratory. The infrared instrument is sensitive over the 2.5–28.5 μm (4 000–350 cm^{-1}) wavelength range, although the spectra become very noisy above $\sim 26 \mu\text{m}$ owing to absorption of the signal in the KBr beamsplitter. Infrared spectra were collected from ultramicrotome thin sections of terrestrial pyrrhotite, troilite, synthetic wüstite and magnetite that were sectioned in epoxy and supported on carbon-film transmission electron microscope (TEM) grids. We used an aperture of $32 \times 32 \mu\text{m}$ for the measurements because smaller apertures resulted in spectral artefacts from diffraction effects at long wavelengths. Final baseline corrected (and smoothed) spectra were obtained by subtracting the background spectrum from the thin carbon film substrates from the sample spectrum. Between 256 and 1 000 scans (interferograms) were collected from each specimen with 4 cm^{-1} resolution.

One fundamental question regarding these results is whether the amount of iron sulfide required to produce the infrared feature is consistent with abundance constraints imposed by gas-phase depletions in dense molecular clouds. For this analysis, we compared the intrinsic strength of the 18 μm silicate feature to the 23.5 μm sulfide feature, because it minimizes the effects of temperature gradients on the band-strength analysis (the 10 μm silicate band is very sensitive to the presence of hot silicate grains). The relative band strength can be related quantitatively to composition provided we know μ^{sil} and μ^{FeS} (the molecular weights of astronomical silicate and FeS), $\kappa_{\text{sil}}^{18\mu\text{m}}$ and $\kappa_{\text{FeS}}^{23.5\mu\text{m}}$ (the mass absorption coefficients for the silicate and FeS respectively), and $I_{18\mu\text{m}}$ and $I_{23.5\mu\text{m}}$ (the intensities of the 18 and 23.5 μm features observed in the ISO spectra). There are however, several assumptions that enter into this calculation. We assume that the grain temperature differences are negligible, and we know that the full-widths at half-maximum for both features are approximately the same, so these terms drop out of the calculation. The mass absorption coefficient of the 18 μm silicate feature depends on the composition of the silicate (Mutschke et al. 1998). We adopt a $\kappa_{\text{sil}}^{18\mu\text{m}}$ of $\sim 1\,000\text{ cm}^2\text{g}^{-1}$, which is somewhat lower than the widely used value (Draine & Lee 1984) of $1\,200\text{ cm}^2\text{g}^{-1}$, because we do not factor in the underlying continuum. We have calculated a $\kappa_{\text{FeS}}^{23.5\mu\text{m}}$ of $\sim 1\,340\text{ cm}^2\text{g}^{-1}$ from our laboratory spectra of pyrrhotite, which is similar to other reported values (Nuth et al. 1985), but is significantly larger than that obtained using reflectance methods (Begemann et al. 1994). This large difference in cross-sections requires further investigation. Using the band strengths extracted from the ISO spectra of HD163296, we obtain a $[\text{S}/\text{Si}]_{\text{calc}} \simeq 0.63$. This ratio is consistent with the cosmochemical (solar) abundance (Anders & Grevesse 1989) of Si and S (atom ratio 0.52). We conclude from this analysis that the sulfur abundance constraints are broadly consistent with the infrared spectra, although the error bars are large. The implication of this analysis is that most if not all of the sulfur resides in solid grains of FeS.

In the diffuse interstellar medium, sulfur is usually not strongly depleted from the gas phase (Savage & Sembach 1996), indicating that little sulfur is incorporated into solid grains in this environment. Either iron sulfides are not produced in significant quantities in stellar outflows, or their lifetime in the interstellar medium is very short owing to rapid destruction. One probable mechanism for their destruction is the reduction of iron sulfide through irradiation, a process that produces Fe metal as a by-product and returns sulfur to the gas phase. A similar mechanism is known to occur in lunar Fe-oxides exposed to the solar wind (Christoffersen et al. 1996) as well as in GEMS (proposed presolar silicate grains) in cometary IDPs (Bradley 1994). The situation is very different in cold, dense molecular clouds, where sulfur is highly depleted from the gas phase (Joseph et al. 1986). In these environments, only trace amounts of sulfur in molecular form or in ice mantles are detected (Palumbo et al. 1997). Therefore, we believe the bulk of the depletion must be accommodated through incorporation of sulfur into solid grains of iron sulfide. The bulk of the iron sulfide is formed either in the collapse phase of the molecular cloud, or in the disk surrounding the young star. Support for this hypothesis comes from observations of iron sulfide grains in IDPs which are intimately associated with carbonaceous material showing H and N isotopic signatures of molecular cloud environments (Keller et al. 2000, 1997).

Figure 4.3: Infrared spectra of sulfide standards and sulfide-rich IDPs compared to '23.5 μm ' features in two Herbig stars showing similar peak positions, shapes, and bandwidths. The '23.5 μm ' features of AB Aur and HD 163296 were obtained by subtracting our best-fit radiative transfer model (Bouwman et al. 2000) without the contribution of 'FeO' (see van den Ancker et al. 2000). The dust components used in our best-fit model include glassy silicates, forsterite, carbonaceous material, metallic iron and water ice. The IDP infrared spectra were collected from ultramicrotome thin sections (~ 70 nm thick) of IDPs that had been sectioned in sulfur and supported on carbon-film TEM grids under the same conditions as given in Fig. 2. L2011*B6 is a fragment of a deuterium-rich cluster IDP, indicating that it contains some presolar molecular cloud material. The mineralogy of L2011*B6 is dominated by pyrrhotite grains, as well as minor GEMS (glass with embedded metal and sulfides), enstatite and carbonaceous material. U2012A-2J is also dominated by low-Ni Fe-sulfides.

From ISO data, crystalline magnesium-rich silicates (forsterite and enstatite) have been recently discovered in a number of sources. It is probable that iron sulfides are manifest in many ISO spectra as well. Iron sulfides, magnesium-rich crystalline silicates and amorphous silicates are the main components of primitive cometary IDPs. These results thus provide new links between primitive IDPs, comets and presolar materials, and resolves a long-standing dilemma. Iron sulfides have long been recognized as a major component of primitive meteoritic materials, but until now they had escaped detection in astronomical observations of objects similar to the early solar nebula. Isotopic measurements for both iron and sulfur in primitive IDPs may uniquely identify presolar iron sulfide grains. A major implication of this work is that early Earth and other Solar System bodies accreted most of their sulfur in the form of crystalline iron sulfide grains.

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The discovery of the “21” μm and “30” μm emission features in Planetary Nebulae with Wolf-Rayet central stars

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Abstract

We report the discovery of the “21” μm and “30” μm features in the planetary nebulae around the hydrogen-deficient stars HD 826 and HD 158269. The carriers of these features are known to be produced in outflows around carbon-rich stars. This discovery demonstrates that the bulk of the dust in these nebulae has been produced during a carbon-rich phase before the atmospheres of these stars became hydrogen poor. This is the first time that the “21” μm feature has been detected in any planetary nebula. It shows that once formed its carrier can survive the formation of the nebula and the exposure to the UV radiation of the hot central star. This means that the carrier of “21” μm feature is not transient: the absence of the feature sets limits on the production of its carrier.

5.1 Introduction

The precise evolutionary channel leading to the formation of Planetary Nebulae (PNe) with Wolf-Rayet ([WC]) central stars ([WC]-PNe) is not well established. While abundance studies of central stars of [WC]-PNe indicate that they are very H-poor, the nebulae show ample evidence for H-rich gas (e.g. Górny & Stasinska 1995) and dust. Model calculations of AGB evolution show that the transition from H-rich to H-poor may be the result of a thermal pulse (TP) when the envelope mass has dropped below some threshold value, which may be as high as $\sim 0.01 M_{\odot}$ (Herwig et al. 1999). It is not well understood whether this TP occurs when the star is still on the AGB or during the post-AGB evolution. For some stars, like V605 Aql, this transition has clearly occurred during the post-AGB phase. These systems harbour a small H-poor nebula within a large H-rich old nebula (e.g. Pollacco et al. 1992). The stellar C IV emission line in V605 Aql implies a [WC] spectral type (Guerrero & Manchado 1996). On the other hand, statistical analysis of the [WC]-PNe show that they are as a group not older

α [J2000]	δ [J2000]	TDT ^a	obs.mode ^b	obs.id
NGC 40; HD 826; IRAS 00102+7214				
00 13 01.10	+72 31 19.09	30003803	SWS01(3)	SWS_CAL
00 13 00.91	+72 31 19.99	44401917	SWS01(2)	MBARLOW
00 13 01.10	+72 31 19.09	81101203	SWS06	SWS_CAL
00 13 00.91	+72 31 19.99	47300616	LWS01	MBARLOW
NGC 6369; HD 158269; IRAS 17262–2343				
17 29 20.80	–23 45 32.00	45601901	SWS01(1)	SGORNY
17 29 20.80	–23 45 32.00	31100910	LWS01	CZHANG

Table 5.1: Source list. Observational details of the sources used in this study.

^aTDT number which uniquely identifies each ISO observation.

^bSWS/LWS observing mode used (see de Graauw et al. 1996; Clegg et al. 1996). Numbers in brackets correspond to the scanning speed.

than other PNe (Górny 2001) and thus most of their central stars must have lost their H-rich envelope during or very soon after the AGB.

We are studying the infrared spectra of [WC]-PNe in order to reconstruct the mass loss history and chemical evolution of these objects. The dust content not only traces the conditions during the preceding phases; links them to precursor objects but also shows the type of materials fed into the ISM. The IR spectral appearance of C-rich evolved stars differs strongly from AGB, post-AGB to PNe objects. This is often interpreted as evidence for transient dust components.

In this chapter we report on the discovery of the “21” μm and “30” μm dust features in two [WC]-PNe (NGC 40 ([WC 8]) and NGC 6369 ([WC 4])). These are ascribed to C-rich dust. The detection of the “21” μm feature is the first in a PN. We show that these detections imply that the TP which converted these stars to C-rich objects did not remove all H from the atmosphere of the star and was not responsible for the termination of the AGB. Furthermore, these observations may establish an evolutionary link between the [WC]-PNe and the “21” μm emitting post-AGB objects with cool central stars.

5.2 The observations

The data were obtained using the Short Wavelength Spectrometer (SWS) (de Graauw et al. 1996) on-board the Infrared Space Observatory (ISO) (Kessler et al. 1996). Details on the observations are given in Table 5.1.

The data were processed using SWS interactive analysis product; IA³ (see de Graauw et al. 1996) using calibration files and procedures equivalent to pipeline version 9.5. NGC 40 has been observed multiple times and the data have been co-added after the pipeline reduction and bad data removal. Since the features we discuss here are fully resolved in all observing modes, we can safely combine the data obtained in all different modes maximising the S/N. Further data processing consisted of rebinning on a fixed resolution wavelength grid. The

Figure 5.1: Overview of the spectra of NGC 40 and NGC 6369. For comparison we also show the spectra of HD 56126, HD 187885 and NGC 7027. The dashed lines represent the continua we draw.

match between the individual sub-bands is excellent for both sources and there is no need to splice the sub-bands.

We compare the SWS spectra with the available IRAS photometry and the IRAS/LRS spectra. We find that the IRAS photometry lies well above the SWS observations. This indicates that the sources are more extended than the SWS apertures. Indeed the optical nebulae associated with NGC 40 and NGC 6369 are $60''$ and $30''$ while the largest SWS aperture measures $20 \times 33''$. Surprisingly the shape and slope of the SWS and IRAS/LRS spectra correspond very well. This indicates that the SWS spectrum is representative of the *bulk* of the dust in those nebula even if we do not see *all* dust emission.

Extended sources give rise to aperture jumps between the SWS sub-bands most notably around $29 \mu\text{m}$ because at this wavelength the effective aperture changes from $14 \times 27''$ to $20 \times 33''$. We do not observe a flux jump in NGC 6369 and at most a jump of 20 percent in NGC 40. This means that there is not more dust located in the larger aperture. NGC 6369 has a ring-like structure in the optical. The SWS spectrum was taken from the east part of this ring and the largest aperture sees more of its relatively empty inner part.

The LWS spectra are observed through a circular aperture of $1'$. We do see a flux jump between the SWS and LWS spectra. The factors needed to bring the SWS and LWS spectra together at $45 \mu\text{m}$ are the same needed to bring the SWS and the IRAS/LRS spectra together, demonstrating that the LWS instrument does see the entire nebula.

5.3 Description of the spectra

We show the observed spectra of NGC 40 and NGC 6369 from 10 to 45 micron in Fig. 5.1c,d. Both mid-IR spectra are dominated by broad emission excesses from 20–25 and 26–45 μm . We also detect emission from polycyclic aromatic hydrocarbons (PAHs) (Allamandola et al. 1989) between 3.3–12.7 μm . NGC 40 also has a strong unidentified emission plateau from 10–19 μm . We concentrate on the two broad features around 20 and 30 μm . For comparison we also show the SWS spectra of the 21 μm objects HD 187885 and HD 56126 and the C-rich PN NGC 7027 (Fig. 5.1a,b,e, respectively).

A broad feature peaking near 21 μm is found to be an important component of the IR spectra of some C-rich proto-planetary nebulae (PPNe) (e.g. Kwok et al. 1989). This feature has up to now only been detected in a very uniform group of post-AGB sources; C-rich, within a narrow temperature range (Kwok et al. 1999), metal poor and s-process enhanced (Van Winckel & Reyniers 2000). These sources are generally termed the “21 μm objects”.

A very broad emission feature extending from 25–45 μm is abundantly detected in IR spectra of a variety of C-rich evolved objects ranging from intermediate mass loss AGB stars to PNe (Forrest et al. 1981). The feature is tentatively ascribed to MgS (e.g. Nuth et al. 1985; Goebel & Moseley 1985; Begemann et al. 1994). Hrivnak et al. (2000) show that the “30” μm feature in the 21 μm objects consists of a 26 and a 30 μm component. An extensive survey of the “30” μm feature in a wide range of C-rich evolved objects shows that its peak position can vary from 26 μm to 34 μm (Chapter 6), see Fig. 5.1b,e for an example of this shift. The two [WC]-PNe show a peak near 34 μm as do most regular C-rich PNe. In contrast in the 21 μm objects the “30” μm feature usually peaks at 26 μm as it does in most AGB stars.

Figure 5.2: A comparison of the observed emission features compared with the “21” μm (solid line) and the “30” μm (dashed line) features as derived from HD 56126 and NGC 7027 respectively.

To compare the features we observe in NGC 40 and NGC 6369 with other sources we extract the profiles of the excess emission. We construct a simple model continuum by fitting a modified blackbody ($F_{\nu}(\lambda) = B_{\nu}(\lambda, T) \times \lambda^{-p}$, where $B_{\nu}(\lambda, T)$ is the Planck function.) to continuum points around 9–10, 16 and 45 μm . We keep the power (p) fixed at 0.5, a value which fits those sources well and also matches the slope of the LWS spectra when available. These continua are shown as dashed lines in Fig. 5.1. The excess emission in both sources is shown in Fig. 5.2.

For comparison we show the “30” μm feature of the C-rich PN NGC 7027 in Fig. 5.2. The “30” μm feature in the two [WC]-PNe compares well, both in peak position and in width, with the other PNe. The discrepancies at the longest wavelength may reflect the difficulties to draw a continuum for the spectrum of NGC 7027. The SWS and LWS spectra of NGC 7027 show a depression around 42 μm . This might be due to a residual instrumental effect.

For the comparison of the “21” μm feature in the [WC]-PNe with that in 21 μm objects, we have decomposed the emission from the latter objects in a 21 μm and a 26 μm component (see also Fig. 5.1). The thus derived “21” μm component rises steeply from 18.4 to 20.1 μm and slowly tapers off until 24.6 μm . See also (Volk et al. 1999) who show the profile to be identical in all known 21 μm sources. We compare this profile to the excesses found in NGC 40 and NGC 6369 in Fig. 5.2. The profile compares well with the new observations,

specifically the sharp rise and the long tail towards longer wavelengths. We also find an extra contribution near $21.5 \mu\text{m}$ not found in the $21 \mu\text{m}$ objects. This is the first time the “21” μm feature has been detected in an object other than a PPN with a low mass progenitor.

5.4 Discussion

The “21” μm feature is absent during the AGB phase, therefore its carrier is generally thought to have formed during a short period of enhanced mass loss which terminated the AGB phase. However this scenario does not explain why it is not detected in their successors, the PNe. This has led to the suggestion that the carrier is a transient, unstable constituent of the dust. These new detections demonstrate that the “21” μm carrier can survive into the PN phase, where it is exposed to UV radiation field of the hot central star; *it is a non-transient, stable dust component*. von Helden et al. (2000) identified TiC as the carrier of the “21” μm feature. The non-transient nature of the feature further strengthens its identification with the refractory TiC. This identification however implies extreme conditions during formation with high densities and consequently very high mass-loss rates: typically $>10^{-4} \text{ M}_{\odot}/\text{yr}$.

The detection of these features in the spectra of [WC]-PNe has ramifications for our understanding of their evolution. The “30” μm feature is characteristic for the C-rich ejecta of AGB and post-AGB objects. The dominance of this band in the spectra of these [WC]-PNe implies that the bulk of the dust in these nebula was formed during a preceding C-rich phase. Clearly, the transition from O-rich to C-rich and the transition from H-rich to H-poor are decoupled for these objects. Thus, these nebulae have undergone normal AGB evolution from O-rich to C-rich well before the loss of the last $0.01 \text{ M}_{\odot}$ turned the central star into a [WC] star.

This seems to be a very general characteristic for [WC]-PNe. The mid-IR spectra of all of these objects are dominated by the well known emission features due to PAHs (Cohen et al. 1989, 1999). The strong 3.3, 8.6, and $11.3 \mu\text{m}$ bands in these spectra attests to the presence (and importance) of H during the formation of the PAHs. In contrast, population I WC stars show mid IR spectra characterised by strong continua with very weak absorption features at 6.2 and $7.7 \mu\text{m}$ without any sign of the 3.3 and $11.2 \mu\text{m}$ feature (Chiar & Tielens 2001). We conclude that the [WC]-PNe went through a H-rich, C-rich phase during which the PAHs condensed.

The “21” μm feature has been detected in C-rich post-AGB objects, however not in their precursors, the carbon stars. Hence, the “21” μm carrier have must formed at the end of the AGB, during a burst of mass loss, which lasted short compared to the post-AGB phase, i.e. $\lesssim 1000$ years. If we assume that the “21” μm carrier in the [WC]-PNe nebulae condensed similarly to all other known $21 \mu\text{m}$ emitting sources, this means this mass loss burst occurred *prior* to the TP which turned the star H-poor. Between leaving the AGB and this TP these objects may have appeared similar to the $21 \mu\text{m}$ objects. Likewise if a cool $21 \mu\text{m}$ object were to suffer a TP – turning it H-poor – it would become a PN similar to these PNe. We conclude that NGC 40 and NGC 6369 could represent successors to some of the cool $21 \mu\text{m}$ objects and that the *last* TP followed the mass loss burst. The low dynamical ages of the nebulae of NGC 40 and NGC 6369 (~ 5000 and ~ 1500 yr) and the much longer timescale for TPs

($\gtrsim 10^4$ yr) shows that the production of the “21” μm carrier is not triggered by a TP.

It is tempting to further explore the evolutionary link between the “21” μm emitting PPNe and the [WC]-PNe, given the fact that these PPNe are the only objects known to exhibit the feature apart from the two PNe we present here. Van Winckel & Reyniers (2000) show that the 21 μm objects as a group are metal poor albeit with large intrinsic range ($[\text{Fe}/\text{H}] = -0.3$ to -1.0). Abundance determinations of NGC 40 and NGC 6369 (Perinotto 1991) show that $[\text{Ne}/\text{H}]$ is -0.8 and -0.5 . Assuming that the Ne abundance in those PNe is representative for the total metallicity (e.g. Pottasch 1984, chapter III.E), this means they fall in the range also observed for the 21 μm objects.

It is important to note that there cannot be a one-to-one correspondence between the 21 μm objects and the [WC]-PNe. Many [WC]-PNe show *no* signature of a long lasting C-rich mass-loss phase. Rather these nebulae are typified by a mixed chemistry with warm ejecta from both an O-rich and a C-rich phase (Waters et al. 1998). This is interpreted as evidence for a short (~ 1000 yr) transition phase during which the star first became C-rich and shortly after H-poor (Waters et al. 1998; Cohen et al. 1999), because the O-rich ejecta predate the C-rich material while still being close to the star. The “21” μm feature is not present in the mid-IR spectra of these mixed chemistry sources, excluding them as successors to the 21 μm objects. Likewise not every 21 μm object may evolve to become H-poor. Whether a star becomes H-poor is determined by the remaining envelope mass at the time of the last TP. Thus, the question arises where the PNe with the H-rich central stars and the “21” μm feature are. Due to observer bias few such PNe have been observed with SWS, however those which have been studied show no “21” μm feature. We now know that the feature is not transient. *Thus the absence of the feature implies non-production of its carrier.* Hence, those objects have not gone through a phase in which they produced the “21” μm carrier. We conclude that the chemical evolution, as determined by the H content of the atmosphere of the central star, and the mass-loss history; specifically the mass loss burst as traced by the “21” μm feature, are decoupled.

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The carrier of the “30” μm emission feature in evolved stars

A SIMPLE MODEL USING MAGNESIUM SULFIDE

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Abstract

We present 2–45 μm spectra of a large sample of carbon-rich evolved stars in order to study the “30” μm feature. We find the “30” μm feature in a wide range of sources: low mass loss carbon stars, extreme carbon-stars, post-AGB objects and planetary nebulae. We extract the profiles from the sources by using a simple systematic approach to model the continuum. We find large variations in the wavelength and width of the extracted profiles of the “30” μm feature. We modelled the whole range of profiles in a simple way by using magnesium sulfide (MgS) dust grains with a MgS grain temperature different from the continuum temperature. The systematic change in peak positions can be explained by cooling of MgS grains as the star evolves off the AGB. In several sources we find that a residual emission excess at $\sim 26 \mu\text{m}$ can also be fitted using MgS grains but with a different grains shape distribution. The profiles of the “30” μm feature in planetary nebulae are narrower than our simple MgS model predicts. We discuss the possible reasons for this difference. We find a sample of warm carbon-stars with very cold MgS grains. We discuss possible causes for this phenomenon. We find no evidence for rapid destruction of MgS during the planetary nebula phase and conclude that the MgS may survive to be incorporated in the ISM.

6.1 Introduction

The far infrared (IR) spectra of carbon-rich evolved objects; i.e. carbon-rich AGB stars (C-stars), post asymptotic giant branch objects (post-AGBs) and planetary nebulae (PNe) are typified by a broad emission feature around 30 μm . This “30” μm feature was first discovered in the far-IR spectra of CW Leo, IC 418 and NGC 6572 by Forrest et al. (1981). Since then this feature has been detected in a wide range of carbon-rich evolved objects from intermediate mass loss C-stars (Yamamura et al. 1998) to post-AGBs and PNe (Omont 1993; Cox 1993; Omont et al. 1995; Jiang et al. 1999; Szczerba et al. 1999, see also Chapter 5). The feature

is commonly found in C-rich post-AGBs and PNe however with varying band shapes and varying feature to continuum ratios (Goebel & Moseley 1985; Waters et al. 2000; Hrivnak et al. 2000; Volk et al. 2002)

Goebel & Moseley (1985) proposed solid magnesium sulfide (MgS) as the possible carrier of the “30” μm feature. Their suggestion is based on the coincidence of the emission feature with the sole IR-resonance of MgS (Nuth et al. 1985; Begemann et al. 1994) and the fact that MgS is one of the expected condensates around these objects (Lattimer et al. 1978; Lodders & Fegley 1999). Several authors have taken up on this suggestion and compared observations with laboratory measurements of MgS. These comparisons were further facilitated by the publication of the optical constants of MgS in the IR range by Begemann et al. (1994). These authors found that the far IR excess of CW Leo can be successfully modelled using MgS grains with a broad shape distribution.

More recently, Jiang et al. (1999) and Szczerba et al. (1999) have modelled the spectra taken with the Short Wavelength Spectrometer (SWS) (de Graauw et al. 1996) on-board the Infrared Space Observatory (ISO) (Kessler et al. 1996) of the C-star IRAS 03313+6058 and the post-AGB object IRAS 04296+3429 respectively. They find that for these sources which show a strong “30” μm feature, the elemental abundances of Mg and S are consistent with MgS as the carrier of the feature.

Hrivnak et al. (2000) and Volk et al. (2002) have analysed ISO spectra of a sample of post-AGBs. They find that the profile of the “30” μm feature varies between sources. Although these authors state that this decomposition is not unique, they find that their “30” μm feature is composed of two sub features: one feature peaking near 26 μm and an other near 30 μm . Using these two components in varying relative amounts they are able to explain the range of features found in their sample. Based on the discovery of these sub features they consider the carrier(s) of the “30” μm feature to be unidentified.

Other materials have also been proposed as carriers of the “30” μm feature. Duley (2000) suggests that the “30” μm feature may be indicative of carbon-based linear molecules with specific side groups. Such molecules have strong absorption bands throughout the 15–30 μm range. Papoular (2000) discusses the possible contribution of carbonaceous dust grains with oxygen in the structure. Some of these materials may show IR emission in the 20–30 μm range. Since the optical properties of such grains are sensitive to the exact composition they might be able to explain the range of features found in the C-rich evolved stars. Recently, Grishko et al. (2001) have proposed hydrogenated amorphous carbon (HAC) as a possible carrier of the “30” μm feature.

The ISO mission has provided an excellent database of observations to study the properties of the “30” μm feature in detail and test the suggested identifications *systematically*. The wavelength coverage of the SWS instrument (2–45 μm) is sufficient to determine a reliable continuum. The sensitivity of the ISO spectrograph allows detection of relatively weak features. The resolving power of the instrument ($\lambda/\Delta\lambda = 500\text{--}1500$) makes it feasible to study possible substructure in the “30” μm feature. Thus these observations allow a study of the “30” μm feature in unprecedented detail in a large sample of sources.

In this chapter, we investigate the shape and strength of the “30 μm ” in a wide range of objects from visual visible C-stars, extreme C-stars, post-AGBs to PNe in order to further test the MgS or other identifications and map systematic differences between the feature in

different classes of sources.

This chapter is organised as follows. In Sect. 6.2, we describe the sample and the data reduction. In Sect. 6.3, we present the way in which we modelled the continuum in order to extract the feature properties. In Sect. 6.4, we present the full range of extracted profile shapes and peak positions of the “30” μm feature and we discuss the possible ways of interpreting the observed profiles. In Sect. 6.5, we develop a simple model using MgS for the “30” μm feature. In Sect. 6.6, we present the model results and compare them to the astronomical spectra. In Sect. 6.7, we present a correlation study between several feature properties and stellar parameters. Finally, in Sect. 6.8, we discuss the implications of our model results and the consequences for the MgS identification. In particular, we discuss possible causes for the deviating profiles and the possibility that MgS produced in carbon-rich evolved stars will be incorporated in the interstellar medium (ISM).

6.2 Observations

We present observations obtained with ISO of a sample of bright IR sources at different stages along the evolutionary track from C-star via post-AGB object to PN. The observations presented here consist of data obtained with the ISO/SWS using astronomical observing template 06 and 01 at various speeds. These observing modes produces observations from 2.3 to 45 μm with a resolving power($\lambda/\Delta\lambda$) ranging from 500 to 1500. The sample consists of all carbon-rich evolved objects in the ISO archive which exhibit a “30” μm feature stronger than 8 Jy peak intensity and have been observed over the full 2.3–45.2 μm wavelength range of the ISO/SWS. This peak intensity and the typical noise level of SWS band 4 (29–45.2 μm) allows to extract a reasonably reliable feature strength and profile. The complete wavelength coverage is needed in order to provide a sufficient baseline to estimate the continuum. We have further completed the sample with all observed C-stars with an IRAS 25 μm flux over 13 Jy. These sources serve as a control group since we would expect to detect the “30” μm feature based on this brightness, the typical noise levels and the typical feature over continuum level. These sources without the “30” μm feature detected are listed separately in Table 6.1. It should be emphasised that the ISO archive does not contain a statistically representative sample of objects. The database of observations for the carbon stars provides a reasonable sampling over stellar properties (e.g. mass-loss rates or colour temperatures). However the post-AGB sample is heavily biased towards the “21” μm objects; a peculiar type of C-rich post-AGB object. The sample of PNe contains a collection of either bright, well-known or well-studied objects without a proper statistical selection. It also contains a relatively large proportion of PNe with hydrogen-poor central stars. The total sample of 75 sources contains 48 C-stars, 14 post-AGB objects and 13 PNe. We have detected the “30” μm feature in 36 out of 48 C-stars.

We present in Fig. 6.1 the IRAS two-colour diagram for the sources in our sample following van der Veen & Habing (1988). There are four sources in our sample without an entry in the IRAS point source catalogue. For these sources we have used ISO/SWS and LWS observations at 12, 25, 60 and 100 μm to calculate the IRAS colours. For IRAS Z02229, no measurements at 60 and 100 μm are available. In Fig. 6.1, the warmest sources are located

Figure 6.1: The IRAS two-colour diagram for the sources studied in this sample. The triangles represent the C-stars, the squares are the post-AGB objects, the stars are the PNe and the diamonds are the C-stars without a “ $30\ \mu\text{m}$ ” feature detected. The dashed line represents the position of blackbodies of different temperatures. The dotted line sketches the evolution of a C-star with a detached, expanding and cooling circumstellar shell.

in the lower left corner. These are the optically visible carbon stars with a low present-day mass-loss rate ($\dot{M} \simeq 10^{-8} - 10^{-7} M_{\odot}$). With increasing mass loss the stars become redder and move up and to the right. After the AGB, when the mass loss has terminated, the dust moves away from the star and cools; i.e. these sources move further to the top-right corner of the diagram. The C-stars located above the main group of C-stars have a clear $60\ \mu\text{m}$ excess. This is evidence for an additional cool dust component. Some of these sources are known to have an extended or detached dust shell around them (Young et al. 1993). The empty region between the C-stars and the post-AGBs is physical. When the mass loss stops the star quickly loses its warmest dust and within a short time span ($< 1000\ \text{yr}$) the star moves to the right in the two-colour diagram. Notice how the sources without a detected “ $30\ \mu\text{m}$ ” feature cluster on the left of the diagram, i.e. among the warmest C-stars.

6.2.1 Data reduction

The SWS data were processed using SWS interactive analysis product; IA³ (see de Graauw et al. 1996) using calibration files and procedures equivalent with pipeline version 10.1. Further data processing consisted of extensive bad data removal primarily to remove the effects

of cosmic ray hits and rebinning on a fixed resolution wavelength grid. If a source has been observed multiple times and these observations are of similar quality and of comparable flux-level these data are co-added after the pipeline reduction. These sources are indicated in Table 6.1 with a dagger (†). Since the features we discuss here are fully resolved in all observing modes, we combine the data obtained in all different modes to maximise the S/N. Although the wavelength coverage of the SWS instrument is well suited to study the profile of the “30” μm feature, there are some important instrumental effects which hamper the unbiased extraction of the emission profiles. We discuss these below.

Splicing

One complete SWS AOT01 spectrum is obtained in 12 different subbands. These subbands are observed through 3 different rectangular apertures which range in size from $14'' \times 20''$ at the shortest wavelengths to $20'' \times 33''$ at the longest wavelengths. All these data are independently flux calibrated and need to be combined to form one continuous spectrum for one source. We apply scaling factors to combine the different subbands to obtain the continuous spectra. The C-stars and post-AGB objects we present in this study all have a small angular extent even compared to the smallest aperture used. Therefore we don’t expect large jumps to be present due to the differences between the apertures used. The angular extent of some PNe can be large compared to the sizes of the apertures. If there is a clear indication of flux jumps due to aperture changes we have not included the source in our sample.

Leakage

At wavelengths longer than between 26 and 27.5 μm the data of SWS subband 3D are affected by leakage adding flux from the 13 μm region. The sources used to derive the instrumental response function are all stellar sources without circumstellar material. These calibration sources are all very blue and emit much more flux at 13 μm relative to 26 μm than the cool, red sources we present in this study. Therefore these calibrators are more affected by the leakage than our sources. The instrumental response function derived in this way has been implicitly corrected for leakage for the blue sources. This resulted in fluxes in red sources to be systematically underestimated. More recent calibrations ($\geq$ OLP 10.0), have been corrected for this effect. With the improved calibrations, the resulting slopes of the spectra beyond 26 μm have been checked and are in general agreement with the slope of subband 4.

The 27.0-27.5 and 27.5-29.0 μm region

At wavelengths longer than 27.0 μm the data of subband 3D show a sharp increase which is found throughout the complete database of ISO/SWS observations independent of source type. The data of subband 3E (27.5-29.0 μm) are generally unreliable both in shape and absolute flux level. These combined instrumental effects make it inherently difficult to interpret the 27-29 μm spectra. Any substructure detected solely in this region alone should be distrusted.

Figure 6.2: Examples of the splicing of the SWS band 3D (19.5–27.5 μm) and 4 (28.9–45.2 μm) data. We show the data before (grey line) and after splicing (black line). All data have been scaled to form a continuous spectrum. As can be seen; after splicing, the slope of band 3D and band 4 match. We do not show the band 3E data. The sharp rise at 27 μm in R Scl and IRC+40 450 is an instrumental artifact (see text for details).

The instrumental effects between 27 and 29 μm and the fact that each of the subbands is independently flux calibrated make it necessary to devise a strategy for splicing the band 3D, 3E and 4 data. There is unfortunately no objective way to choose this strategy. We choose to assume minimal spectral structure between the end of subband 3D and the beginning of band 4, i.e. to splice the subband 3D–4 data in such a way that the matching slopes of 3D and 4

also match in flux level. Some examples are shown in Fig. 6.2. The observed discontinuities between subbands are relatively small (< 20 per cent) and can be understood as the result of absolute flux calibration uncertainties alone.

6.2.2 Full spectra

The resultant spectra for the sources that exhibit a “30” μm feature are shown in Fig. 6.3, 6.4. The SWS spectra of this large group of objects show a spectacular range in colour temperature, molecular absorption bands and solid state features. The C-stars have molecular absorption bands of C_2H_2 at 3.05, 7–8 and 14 μm , of HCN at 7 and 14 μm , CO at 4.7 μm and C_3 at 4.8–6 μm . The sharp absorption band at 14 μm is due to C_2H_2 and HCN. There is an emission feature due to solid SiC at 11.4 μm . In the reddest C-stars, we find the SiC in absorption. We also find evidence for a weak depression in the 14–22 μm range in the reddest objects. This depression could be due to aliphatic chain molecules like those found in RAFGL 618 (Cernicharo et al. 2001).

The post-AGBs and PNe exhibit many, sometimes broad solid state emission features. In many sources we find emission due to polycyclic aromatic hydrocarbons in the 3–15 μm range. There is a broad plateau feature from 10–15 μm which may be due to hydrogenated amorphous carbon (Guillois et al. 1996; Kwok et al. 2001). Many post-AGBs and two PNe in the sample have a feature peaking at 20.1 μm , called the “21” μm feature in the literature. Recently the carrier of this feature has been identified with TiC (von Helden et al. 2000). The feature at 23 μm found in IRAS 18240 and PN K3-17 is likely due to FeS (Chapter 3). These absorption and emission features have to be taken into account when determining the profile of the “30” μm feature or the shape of the underlying continuum.

Focusing on the “30” μm feature we can see variations in the strength and shape of the band. The most marked difference is however a shift in the peak position going from 26 μm in some of the AGB stars to 38 μm in the PNe. The dashed line in Fig. 6.3 and 6.4 indicates $\lambda=26$ μm . There are systematic changes in the appearance of the “30” μm feature from the C-stars to the PNe. The feature in the C-stars almost exclusively peaks at 26 μm . There are some exceptions like R Scl. In the post-AGB sample, the feature is broader and in some sources the feature peaks long ward of 26 μm . In the PNe sample, there are *no* sources that peak at 26 μm . However, the appearance of a broad feature like the “30” μm feature is sensitive to the shape of the underlying dust continuum, especially since we have a sample with such a wide range of continuum colour temperatures.

Figure 6.3: Overview of the spectra of carbon stars exhibiting the “30” μm feature. The spectra are ordered according to continuum temperature from high to low temperature, bottom to top, left to right. The dashed line marks $\lambda=26 \mu\text{m}$.

Figure 6.4: Overview of the spectra of post-AGB objects (left panel) and PNe (right panel) exhibiting the “30” μm feature. The spectra are ordered according to continuum temperature from high to low temperature, bottom to top. The dashed line marks $\lambda=26 \mu\text{m}$. The spectrum of RAFGL 618 although warmer than NGC 3918 is shown at the top of the PNe for clarity.

Object	IRAS name	Obs. ^a Mode	α (J2000)	δ (J2000)	TDT ^b	Sp./T kK	Obj. Type
NGC 40	00102+7214	01(3)	00 13 01.10	+72 31 19.09	30003803	WC	PN
IRAS 00210+6221	00210+6213	01(1)	00 23 51.20	+62 38 07.01	40401901		C-star
IRAS 01005+7910	01005+7910	01(2)	01 04 45.70	+79 26 47.00	68600302	OBe	post-AGB
HV Cas	01080+5327	01(1)	01 11 03.50	+53 43 40.30	62902503		C-star
RAFGL 190	01144+6658	01(2)	01 17 51.60	+67 13 53.90	68800128		C-star
R Scl [†]	01246—3248						C-star
—		01(2)	01 26 58.10	—32 32 34.91	37801213		
—		01(2)	01 26 58.05	—32 32 34.19	37801443		
IRAS Z02229+6208	Z02229+6208	01(1)	02 26 41.80	+62 21 22.00	44804704	G0	post-AGB
RAFGL 341	02293+5748	01(1)	02 33 00.16	+58 02 04.99	80002450		C-star
IRC+50 096	03229+4721	01(2)	03 26 29.80	+47 31 47.10	81002351		C-star
IRAS 03313+6058	03313+6058	01(1)	03 35 31.50	+61 08 51.00	62301907		C-star
U Cam	03374+6229	01(2)	03 41 48.16	+62 38 55.21	64001445		C-star
RAFGL 618	04395+3601	01(3)	04 42 53.30	+36 06 52.99	68800561	B0	PN
W Ori	05028+0106	01(3)	05 05 23.70	+01 10 39.22	85801604		C-star
IC 418	05251—1244	01(2)	05 27 28.31	—12 41 48.19	82901301	36 ¹	PN
V636 Mon	06226—0905	01(1)	06 25 01.60	—09 07 16.00	86706617		C-star
RAFGL 940	06238+0904	01(2)	06 26 37.30	+09 02 16.01	87102602		C-star
IRAS 06582+1507	06582+1507	01(2)	07 01 08.40	+15 03 40.00	71002102	F5	post-AGB
HD 56126 [†]	07134+1005						
—		06	07 16 10.20	+09 59 48.01	71802201		
—		06	07 16 10.30	+09 59 48.01	72201702		
—		01(3)	07 16 10.20	+09 59 48.01	72201901		
CW Leo	09451+1330	06	09 47 57.27	+13 16 42.82	19900101		C-star
NGC 3918	11478—5654	01(1)	11 50 18.91	—57 10 51.10	29900201		PN
RU Vir	12447+0425	01(2)	12 47 18.43	+04 08 41.89	24601053		C-star
IRAS 13416-6243	13416—6243	01(3)	13 45 07.61	—62 58 18.98	62803904		post-AGB
II Lup	15194—5115	06	15 23 04.91	—51 25 59.02	29700401		C-star
V Crb	15477+3943	06	15 49 31.21	+39 34 17.80	25502252		C-star
PN K 2-16 [†]	16416—2758					WC	PN

—	01(1)	16 44 49.10	−28 04 05.02	29 30 20.10	
—	01(2)	16 44 49.10	−28 04 05.02	67 50 12.41	
IRAS 16594+4656	16594−4656	17 03 09.67	−47 00 27.90	45 80 04.41	post-AGB
NGC 6369	17262−2343	17 29 20.80	−23 45 32.00	45 60 19.01	PN
IRC+20 326	17297+1747	17 31 54.90	+17 45 20.02	81 60 12.10	C-star
CD-49 11554	17311−4924	17 35 02.41	−49 26 22.31	103 00 63.6	post-AGB
PN HB 5	17447−2958	17 47 56.11	−29 59 39.70	49 40 10.4	PN
RAFGL 5416	17534−3030	17 56 36.90	−30 30 47.02	121 02 00.4	C-star
T Dra	17556+5813	17 56 23.30	+58 13 06.38	34 60 17.02	C-star
RAFGL 2155	18240+2326	18 26 05.69	+23 28 46.31	47 10 02.61	C-star
IRAS 18240-0244	18240−0244	18 26 40.00	−02 42 56.99	149 00 80.4	PN
IRC+00 365	18398−0220	18 42 24.68	−02 17 25.19	49 90 13.42	C-star
RAFGL 2256	18464−0656	18 49 10.35	−06 53 03.41	48 30 05.63	C-star
PN K 3-17	18538+0703	18 56 18.05	+07 07 25.61	49 90 06.40	PN
IRC+10 401	19008+0726	19 03 18.10	+07 30 43.99	87 20 12.21	C-star
IRAS 19068+0544	19068+0544	19 09 15.40	+05 49 05.99	47 90 13.74	C-star
NGC 6790	19204+0124	19 22 57.00	+01 30 46.51	13 40 11.07	70 ³ PN
RAFGL 2392	19248+0658	19 27 14.40	+07 04 09.98	85 80 12.0	C-star
NGC 6826	19434+5024	19 44 48.20	+50 31 30.00	27 20 07.86	50 ⁴ PN
IRAS 19454+2920	19454+2920	19 47 24.25	+29 28 11.78	52 60 13.47	post-AGB
HD 187885	19500−1709	19 52 52.59	−17 01 49.58	14 40 34.6	post-AGB
RAFGL 2477	19548+3035	19 56 48.26	+30 43 59.20	56 10 08.49	C-star
IRAS 19584+2652	19584+2652	20 00 31.00	+27 00 37.01	52 60 08.68	C-star
IRAS 20000+3239	20000+3239	20 01 59.50	+32 47 33.00	185 00 53.1	G8 post-AGB
V Cyg [†]	20396+4757				C-star
—	01(2)	20 41 18.20	+48 08 29.00	42 10 01.11	
—	01(2)	20 41 18.20	+48 08 29.00	42 30 03.07	
NGC 7027 [†]					200 ⁵ PN
—	01(4)	21 07 01.71	+42 14 09.10	02 40 11.83	
—	01(1)	21 07 01.70	+42 14 09.10	23 00 13.56	
—	01(2)	21 07 01.70	+42 14 09.10	23 00 13.57	
—	01(3)	21 07 01.70	+42 14 09.10	23 00 13.58	
—	01(4)	21 07 01.63	+42 14 10.28	55 80 05.37	

S Cep	21358+7823	01(1)	21 35 12.80	+78 37 28.20	56200926	C-star
RAFGL 2688		01(3)	21 02 18.80	+36 41 37.79	35102563	post-AGB
RAFGL 2699	21027+5309	01(1)	21 04 14.70	+53 21 02.99	77800722	C-star
IC 5117	21306+4422	01(1)	21 32 30.83	+44 35 47.29	36701824	PN
RAFGL 5625	21318+5631	01(1)	21 33 22.30	+56 44 39.80	11101103	C-star
IRAS 21489+5301	21489+5301	01(1)	21 50 45.00	+53 15 28.01	15901205	C-star
SAO 34504	22272+5435	01(2)	22 29 10.31	+54 51 07.20	26302115	post-AGB
IRAS 22303+5950	22303+5950	01(1)	22 32 12.80	+60 06 04.00	77900836	C-star
IRAS 22574+6609	22574+6609	01(2)	22 59 18.30	+66 25 49.01	39601910	post-AGB
RAFGL 3068	23166+1655	01(2)	23 19 12.48	+17 11 33.40	37900867	C-star
RAFGL 3099	23257+1038	01(1)	23 28 16.90	+10 54 40.00	78200523	C-star
IRAS 23304+6147	23304+6147	01(3)	23 32 44.94	+62 03 49.61	39601867	post-AGB
IRAS 23321+6545	23321+6545	01(1)	23 34 22.53	+66 01 50.41	25500248	post-AGB
IRC+40 540	23320+4316	01(2)	23 34 27.86	+43 33 00.40	38201557	C-star

non detections						
R For	02270-2619	01(1)	02 29 15.30	-26 05 56.18	82001817	C-star
SS Vir	12226+0102	01(1)	12 25 14.40	+00 46 10.20	21100138	C-star
Y CVn	12427+4542	01(2)	12 45 07.80	+45 26 24.90	16000926	C-star
RY Dra	12544+6615	01(3)	12 56 25.70	+65 59 39.01	54300203	C-star
C* 2178	14371-6233	01(1)	14 41 02.50	-62 45 54.00	43600471	C-star
V1079 Sco	17172-4020	01(1)	17 20 46.20	-40 23 18.10	46200776	C-star
T Lyr	18306+3657	06	18 32 19.99	+36 59 55.50	36100832	C-star
S Set	18476-0758	01(2)	18 50 19.93	-07 54 26.39	16401849	C-star
V Aql	19017-0545	01(2)	19 04 24.07	-05 41 05.71	16402151	C-star
V460 Cyg	21399+3516	01(1)	21 42 01.10	+35 30 36.00	74500512	C-star
PQ Cep	21440+7324	01(1)	21 44 28.80	+73 38 03.01	42602373	C-star
TX Psc	23438+0312	06	23 46 23.57	+03 29 13.70	37501937	C-star

Table 6.1: Source list. Observational details of the sources in this study.

^a SWS observing mode used (see de Graauw et al. 1996). Numbers in brackets correspond to the scanning speed.

^b TDT number which uniquely identifies each ISO observation.

[†] These spectra have been obtained by co-adding the separate SWS spectra also listed in the table, see text.

T_{eff} from ¹Mendez et al. (1992), ²Perinotto (1991), ³Kaler & Jacoby (1991), ⁴Quigley & Bruhweiler (1995) and ⁵Latter et al. (2000).

6.3 Continuum

In order to extract the profiles of the “30” μm features and compare them from source to source, we model the underlying continuum due to the emission of other circumstellar (CS) dust components. First, we present the way we construct these continua and in Sect. 6.4, we discuss the resulting profiles.

To model the underlying continuum we use a simplified approach. We represent the continuum with a single temperature modified blackbody,

$$F(\lambda) = A \times B(\lambda, T) \times \lambda^{-p}, \quad (6.1)$$

where λ is the wavelength, $F(\lambda)$ is the flux density of the continuum, $B(\lambda, T)$ is the Planck function of temperature T , p is the dust emissivity index and A is a scaling factor.

We have chosen this approach to estimate the continuum over doing a radiative transfer calculation for reasons of simplicity. The bulk of the CS dust around these sources consists of some form of amorphous carbon grains that do not exhibit sharp emission features in the wavelength range of interest. Therefore, a radiative transfer calculation will not yield extra insight into the shape or strength of the continuum while introducing many more modelling parameters. This method has the advantage that we can compare the feature in such a diverse group of sources in a consistent way. Of course Eq. (6.1) does not directly allow us to incorporate important effects such as optical depth or temperature gradients. However varying the p -parameter can mimic these effects to some extent.

The p -parameter reflects the efficiency with which the dust grains can emit at wavelengths larger than the grain size. Reasonable values of p in the region of interest are between 1 and 2. Crystalline materials have this value close to 2 and amorphous materials have a p -value between 1 and 2, while layered materials have an emissivity index close to 1. A temperature gradient in the dust shell will result in a broader spectral energy distribution (SED). This is mimicked by a lower value of p . Likewise an optically thick dust shell will result in a broader SED, which again can be reproduced by reducing the value of p .

We use a χ^2 fitting procedure to determine the values of T and p fitted to selected continuum points in the ranges 2–22 μm . If available we also use the LWS spectra to verify the continuum at the long wavelength end of the “30” μm feature. The 50–100 μm continuum gives an even stronger constraint on the value of p . For most cases the resultant continuum runs through the 45 μm region of the SWS spectrum. A remarkable exception to this is the spectrum of RAFGL 3068. The 2–24 μm spectrum is well fitted with a single 290 K Planck function. However we find a large excess of this continuum at 45 μm and the available LWS spectrum is not well represented in level or slope. Possibly this is due to the optically thick dust shell or a biaxial dust/temperature distribution.

The values for T and p are listed in Table 6.2. One remarkable fact is that the C-stars are well fitted by a single temperature Planck function over the complete wavelength range of SWS. The IR SEDs of the post-AGBs and PNe are in general less broad and many sources are better fitted with a p -value of 1. We stress however that the derived p values cannot be used to constrain the crystal structure or the average size of the dust grains in view of the aforementioned effects of temperature gradients and optical depth.

cont.								“30” μm feature								cont.								“30” μm feature							
Object	T_{cont} [K]	p		$\lambda_{\text{c},30}$ [μm]	fwhm flux [W/m ²]	P/C	T_{MGS} [K]	Object	T_{cont} [K]	p		$\lambda_{\text{c},30}$ [μm]	fwhm flux [W/m ²]	P/C	T_{MGS} [K]																
NGC 40	150	0		33.6	10.1	5.9e-13	0.7	110	T Dra	1210	0		30.2	10.1	4.8e-13	0.4	200														
IRAS 00210	285	0.5		28.4	10.7	6.4e-13	0.8	300	RAFGL 2155	460	0		28.8	8.2	5.7e-12	0.6	400														
IRAS 01005	130	1		30.0	11.1	6.6e-13	1.5	220	IRAS 18240	160	1		32.8	13.1	1.0e-12	1.0	130														
HV Cas	1040	0.2		33.5	10.6	1.5e-13	0.3	100:	IRC+00 365	910	-0.3		28.6	11.7	1.9e-12	0.4	500														
RAFGL 190	275	0		30.9	13.0	1.6e-12	0.3	180	RAFGL 2256	390	0		29.5	12.0	1.9e-12	1.0	350														
R Scl	2605	-0.2		33.2	13.9	1.1e-12	1.1	90	K3-17	100	1		34.1	11.5	1.0e-12	0.9	90														
IRAS Z02229	235	0		29.1	10.1	8.3e-12	1.7	300	IRC+10 401	765	0		30.0	10.0	2.0e-12	0.3	300														
RAFGL 341	380	0		29.8	9.4	9.4e-13	0.4	250	IRAS 19068	1165	-0.7		28.5	10.1	2.0e-13	0.4	500:														
IRC+50 096	855	-0.2		28.8	9.2	1.9e-12	0.3	500	NGC 6790	290	0		29.8	15.6	9.8e-13	1.4	300														
IRAS 03313	325	0		28.6	7.8	5.4e-13	0.4	300	RAFGL 2392	890	0		27.7	8.6	3.4e-13	0.5	500														
U Cam	1775	0		31.9	11.8	3.9e-13	0.6	150	NGC 6826	150	0		32.7	10.5	1.1e-12	2.0	120														
RAFGL 618	235	-1		38.0	10.9	5.4e-12	0.2	40 ^a	IRAS 19454	140	1		36.3	13.1	6.4e-13	0.3	50														
W Ori	2450	0		31.3	8.4	3.1e-13	0.4	150	HD 187885	175	0		29.6	10.8	5.2e-12	1.0	200														
IC 418	120	1		30.8	11.3	5.5e-12	0.9	180	RAFGL 2477	290	0		30.7	12.5	2.3e-12	0.6	170														
V636 Mon	1215	0		29.8	10.1	1.7e-13	0.2	250:	IRAS 19584	580	0		28.1	7.5	8.5e-13	1.5	400														
RAFGL 940	810	0		28.2	10.2	3.5e-13	0.5	500	IRAS 20000	210	0		29.4	12.1	2.5e-12	1.5	300														
IRAS 06582	315	0		29.5	10.3	1.1e-12	0.4	300	V Cyg	1110	0		30.5	11.5	1.3e-12	0.3	200														
HD 56126	170	0		30.0	12.0	2.9e-12	0.8	150	NGC 7027	125	1		32.8	11.0	1.7e-11	0.4	110														
CW Leo	535	0		28.6	8.8	2.7e-10	0.6	400	S Cep	1340	0.1		31.2	9.4	4.4e-13	0.2	130														
NGC 3918	90	1		33.3	8.5	7.1e-13	1.0	120	RAFGL 2688	200	-1		31.1	10.4	5.9e-11	0.3	70 ^a														
RU Vir	1045	0		30.4	10.1	5.3e-13	0.6	180	RAFGL 2699	540	0		29.0	11.4	5.9e-13	0.7	300														
IRAS 13416	115	1		31.6	15.8	2.8e-12	0.4	200 ^a	IC 5117	130	1		31.2	9.7	7.3e-13	0.6	150														
II Lup	625	0		29.5	10.1	3.9e-12	0.3	400	RAFGL 5625	300	0		30.3	11.8	4.4e-12	0.4	200														
V Crb	1430	0		30.4	10.1	1.8e-13	0.3	150:	IRAS 21489	415	0		29.3	9.7	1.1e-12	0.6	350														
K2-16	155	0.5		34.4	12.0	3.4e-13	0.3	80	SAO 34504	210	0		29.1	10.3	1.3e-11	2.0	250														
IRAS 16594	140	1		29.8	12.1	9.9e-12	0.9	250	IRAS 22303	345	0		30.3	10.5	1.0e-12	0.7	300														
NGC 6369	100	1		34.6	10.1	9.5e-13	1.1	90	IRAS 22574	160	0		31.2	13.6	5.9e-13	0.4	150														

IRC+20 326	770	-0.7	29.1	10.2	7.4e-12	0.5	300	RAFGL 3068	290	0	32.4	14.7	8.4e-12	0.4	120
CD-49 11554	140	1	30.2	14.0	4.7e-12	0.7	200 ^a	RAFGL 3099	470	0	29.5	10.9	2.6e-12	0.7	400
HB 5	120	0	35.5	11.5	1.0e-12	0.4	70	IRAS 23304	115	1	30.1	13.4	2.3e-12	1.1	250
RAFGL 5416	290	0	30.4	12.5	2.2e-12	0.5	220	IRAS 23321	175	0	34.5	13.3	6.6e-13	0.3	70
IRC+40 540	485	0	28.6	9.1	8.9e-12	0.6	400	non detections							
R For	1215	0	-	-	<1e-14	<0.1	-	T Lyr	3305	0	-	-	<1e-14	<0.1	-
SS Vir	2040	0	-	-	<1e-14	<0.1	-	S Sct	2105	0	-	-	<4e-14	<0.3	-
Y CVn	2200	0	-	-	<2e-13	<0.2	-	V Aql	3665	-0.3	-	-	<1e-14	<0.1	-
RY Dra	2525	0	-	-	<1e-13	<0.2	-	V460 Cyg	2875	0	-	-	<5e-14	<0.5	-
C* 2178	1110	0	-	-	<1e-13	<0.5	-	PQ Cep	1625	0	-	-	<1e-14	<0.1	-
V1079 Sco	3085	-0.5	-	-	<5e-14	<0.2	-	TX Psc	3105	0	-	-	<3e-14	<0.1	-

Table 6.2: Measured properties. T_{cont} , p are the parameters of the modified blackbody function fitted to the continuum. $\lambda_{c,30}$ and P/C are the feature centroid position and peak over continuum ratio. T_{MgS} is the derived temperature of the MgS grains.
^aTemperature determination uncertain due to optically thick MgS emission.

6.4 Profiles

Using the continua defined in this way, we measure the following properties of the “30” μm feature: the centroid wavelength ($\lambda_{c,30}$), i.e. the wavelength where the integrated flux in the feature at either side is equal; the full width at half maximum (fwhm); the flux in the “30” μm feature and the height of the peak of the “30” μm feature *after* continuum subtraction over the continuum ratio, i.e. the peak to continuum ratio (P/C). The measured values are listed in Table 6.2. We list upper limits for P/C and the flux for the sources without detection. In Fig. 6.6, we show the relation between the [25]-[60] colour and $\lambda_{c,30}$. There is a clear reasonably smooth trend for the feature to move to longer wavelengths with redder IRAS colours. This indicates that the temperature of the dust is an important parameter in determining the profile of the “30” μm feature since [25]-[60] is a direct measure of the dust temperature provided that the dust composition in the different sources is similar.

We first try to remove the effect of temperature by dividing by the continuum; a method that is commonly applied. Using the modelled continua as described in Sect. 6.3, we convert the observed features to relative excess emission by dividing by the continuum and subtracting 1.

If the feature emission is optically thin and the temperature of the carriers of the feature is equal to the continuum temperature the derived excess emissions are proportional to the absorptivity (κ_{abs}) of the carrier and if the carrier is the same in these sources then the derived band shape should be the same for all sources. However, we find large variations in the derived profiles. In Fig. 6.7, we show some examples of the derived profiles. Most notable are variations in peak position and the appearance around 26 μm . Such changes, albeit within a smaller range of feature peak positions have led other authors (Volk et al. 2000, 2002) to conclude that the “30” μm feature is composed of two features and the observed variations are due to varying relative contributions of these two components. One key question is: “What possible causes could there be for the observed large variations in band shape?”. We discuss three possibilities below. First, optical depth effects. Second, temperature effects. Finally, we discuss multiple band carriers.

The optically thin assumption most likely holds because the optical depth in the circumstellar shell strongly decreases towards longer wavelengths. Note, in this respect that the “30” μm feature is never found in absorption (however, see also Sect. 6.6.2). Hence, optical depth effects are not responsible for the observed profile variations.

Whether the temperature of the amorphous carbon grains (defining the shape of the continuum) and the temperature of the “30” μm carrier are equal is very uncertain. The temperature of a dust grain in a circumstellar envelope is determined by the distance to the star, the absorption properties in the wavelength range where the star or the dust shell emits light and the grain size. In case the temperature of the grains species responsible for the continuum and the “30” μm emission feature are not the same, the resulting excess profiles will also not be the same from source to source *even if the carrier of the band is the same*. The differences will be very pronounced when the emission feature is broad. In this case systematic difference between sources are bound to occur in league with the strongly changing continuum temperature. Thus, the temperature of the carrier of the “30” μm feature is an important parameter that determines the profile of the emission.

Figure 6.5: Examples of the fitted continuum. We show the spectra (black line), the selected continuum points (diamonds) and the fitted modified blackbody (grey line).

Figure 6.6: Centroid of the “30” μm feature with respect to the [25]-[60] colour. The symbols are like in Fig. 6.1. There is a clear trend for the centroid position of the “30” μm feature to move to longer wavelengths the redder the object is.

There may be multiple carriers involved as discussed before. In this case the feature near $26 \mu\text{m}$ dominates in the warmest objects while the cooler objects are more and more dominated by emission towards $35 \mu\text{m}$. However, this scenario has its difficulties since it would require changes in the composition of the dust in the relatively dispersed and cold nebular surroundings of a post-AGB object or even during the PN phase. Such chemical changes can only occur extremely slowly, if at all.

Lastly, variations in grain shape or variations in shape distribution can influence the emission profiles. The optical properties of materials with a high value of the refractive index are sensitive to the grain shape. Variations in the shape distribution will lead to variations in the profiles.

In our analysis, we will focus on explaining the profile variations with temperature variations and the effects of variations in the shape distribution of the emitting dust grains.

Figure 6.7: Emissivities for different sources as deduced from the ISO spectra. There are large differences in the profile of the excess emission. Notice the shift in peak position and change in width of the circumstellar “30” μm feature going from the C-stars to post-AGBs to PNe (top to bottom).

6.5 MgS

Since, it has been demonstrated for a few sources that MgS is a viable candidate (Begemann et al. 1994; Jiang et al. 1999; Szczerba et al. 1999), we first test MgS as a possible candidate for the carrier of the feature. With the large sample of good quality spectra in this study we are able to test this possible identification systematically in a large population of evolved objects.

As explained above we cannot derive *a priori* information on the temperature of the “30” μm carrier from the observations. Our knowledge is further limited by the fact that even for some of the candidate materials like MgS or FeS the optical properties are measured only in a limited wavelength range. We lack measurements in the UV, optical and near-IR range, which may well dominate the dust heating. We have decided to test the MgS identification, leaving the grain temperature as a free parameter. We adopt the method we describe below.

6.5.1 Material

We use the optical constants as published by Begemann et al. (1994). Of the materials they measured, $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{S}$ is closest to pure MgS. The real and imaginary part of the refractive index (n and k values) are given from 10-500 μm .

Figure 6.8: The effect of grain shape. We show the absorptivity of MgS as a function of grain shape. The numbers between brackets refer to the axis ratios of the elliptical grains. For comparison we show the derived emissivities of RAFGL 190 and NGC 7027.

6.5.2 Shapes

From the n and k values we can calculate the absorption cross-sections for various grain shapes and shape distributions in the Rayleigh limit following Bohren & Huffman (1983, chap. 5, 9 and 12). The absorption cross-section of MgS around $30\ \mu\text{m}$ is very sensitive to the grain shape. In Fig. 6.8, we show the results of using different grain shapes on the absorption properties of MgS. We use a continuous distribution of ellipsoids (CDE) for the grain shapes. This shape distribution was used by Begemann et al. (1994) and gave a good fit to the “30” μm feature observed in CW Leo. The same shape distribution was further used by Jiang et al. (1999) and Szczerba et al. (1999). They found reasonable fits for the two sources they study. As can be clearly seen in Fig. 6.8 when comparing the spheres with the CDE calculations, the feature broadens and the peak position shifts to longer wavelengths using the CDE shape distribution. The width of the feature calculated using CDE matches that of

Figure 6.9: The effect of grain temperature on the MgS emission feature. We fold the κ_{abs} of MgS in a continuous distribution of ellipsoids (CDE) shape distribution with a Planck function of different temperatures. The shape and position of the feature are modified substantially.

the observed “30” μm feature well (e.g. RAFGL 190 in Fig. 6.8, see also Fig. 6.18).

6.5.3 Temperature

To estimate the MgS temperature (T_{MgS}) we use the continuum *subtracted* spectra with the continuum as derived in Sect. 6.3. The emission from MgS grains is calculated using the κ_{abs} folded with a Planck function with the temperature of the grain. Due to the smooth and broad shape of the resonance the profile of the emission is very sensitive to T_{MgS} . In particular the peak position changes strongly with T_{MgS} . This allows us to estimate T_{MgS} from the continuum subtracted profiles. This method is most sensitive for $T_{\text{MgS}} < 300$ K. Above 300 K, further changes in the profile are more subtle since the major part of the feature falls in the Rayleigh-Jeans domain of the Planck function.

We use this temperature estimate and the observed band strength in the continuum subtracted spectra to synthesise a MgS feature in order to compare with the astronomical spectra. In conclusion, we adopt MgS with a CDE shape distribution and allow both the strength and the temperature of the MgS grains to vary with respect to the underlying continuum.

6.6 Model results

In Fig. 6.10 we show a few typical examples of how our model results compare to the observed spectra. In Fig. 6.18 in Sect. 6.10 we show the observed spectra, the composite of the continuum and the synthetic MgS feature and the residuals after subtracting the MgS feature for the complete sample. The fits are very satisfactory in 50 out of 63 cases. In ~ 25 sources the synthetic spectra obtained with this very simple model are able to explain the detailed profile of the “30” μm feature very well. The onset and range of the feature and even the slight depression between 26–30 μm are reproduced by the model. We show a zoomed view of the 30 μm region of a few sources that are very well fitted by this simple model in Fig. 6.11. Notice the different apparent shapes of the feature that the model is able to explain. Volk et al. (2002) discuss the “30” μm feature in IRAS 23304 and find that they need 2 separate unidentified components in order to understand the shape of the feature. Fig. 6.11 illustrates that this is not necessarily required.

Examining the complete sample of observed “30” μm features and the synthetic spectra, we find there are some systematic deviations. In the sample of C-stars and post-AGB objects there are numerous examples where the major part of the “30” μm feature is explained well by our model, but the observed spectra show excess emission in the 26 μm region. The excess is not accounted for using our CDE fits. The most extreme case is IRAS 19584 but several sources exhibit the same behaviour. In Sect. 6.6.1, we discuss the origin of this discrepancy.

In some cases the synthetic spectra over-predict the flux at the longest wavelengths. This can be due to the very simplistic method we have used to estimate the continuum level. As the dust optical depth decreases with increasing wavelengths, the continuum level estimated from shorter wavelengths might over-predict the true continuum level. Note, however, that the discrepancies between the modelled and the observed spectra in the 26 μm region and the 40 μm region cannot be considered completely independently. If we were to weaken the strength of the MgS feature this would yield a better fit around 45 μm but would increase the discrepancy around 26 μm . We also note that MgS produces a weak continuum contribution at 45 μm (see for example Fig. 6.9). This continuum contribution is already taken into account when fitting the overall continuum, but it is still present in the calculated MgS contribution. Therefore, our model may slightly over-predict the fluxes near 45 μm .

As a class, the spectra of most PNe show another systematic difference. The peak position of the “30” μm feature lies in general at longer wavelengths than in the post-AGB sources. This is in accordance with the picture of a slowly expanding and cooling dusty envelope. We can simulate the same shift in peak position using MgS grains. However the fits we obtain fail to reproduce the relatively narrow width of the observed profile. We discuss this deviation of the profiles in Sect. 6.6.3.

There are 4 sources in the sample that have a broader “30” μm feature than can be fit by our simple model. Of these sources, IRAS 13416 and CD-49 11554 show a slightly flattened and broadened feature while in the cases of RAFGL 618 and RAFGL 2688 the feature is very broad with a depression around 30 μm . The latter sources are known to have a very large dust column along the line of sight. Most likely the feature shape is due to optical depth effects. We discuss these sources further in Sect. 6.6.2.

Despite these systematic deviations it is clear that our simple model is able to explain the

Figure 6.10: Examples of the modelling results using measured MgS optical constants in a CDE shape distribution. We show the observed spectra (black), the modelled continua (dashed), the spectra with the MgS contribution subtracted (gray) and the composite of the continuum and the MgS contributions (thin black line).

Figure 6.11: Examples of spectra that are very well fitted with MgS in a single temperature, CDE shape distribution. The black lines represent the data and the grey line the model. The different sources have been offset for clarity. The excess around $23\ \mu\text{m}$ in IRAS 18240 is due to FeS (Chapter 4 and 3). Notice how the model is able to explain the profile of the “30” μm feature found in the full range of objects in our sample.

profile of the “30” μm feature in good detail in a very wide range of objects. We conclude that the carrier of the “30” μm feature in the C-stars and post-AGB objects is solidly identified with MgS and that *the variations in peak position reflect differences in grain temperature*.

6.6.1 26 μm excess

As discussed above we find about 25 sources that are very well fitted by our simple model. Using similar parameters we also find about 25 sources which show an excess near $26\ \mu\text{m}$. Evidently, there is a contribution from an additional dust component in the latter sources. In considering this additional dust component we find that MgS itself is the best candidate. The wavelength region where this excess occurs ($26\ \mu\text{m}$) is also the wavelength where the generic main resonance of MgS occurs. Spherical MgS grains exhibit a resonance at $26\ \mu\text{m}$. In our model, the MgS profile is broader and peaks at a longer wavelength because we use the calculated absorption cross-sections in a CDE shape distribution. There is no a priori

Figure 6.12: Some examples of sources with a 26 μm excess compared to the model spectra. We show the data (full black line) the model using the CDE calculation (full grey line) and the composite model using both spherical MgS grains and the CDE calculation (dashed line). We show below the emission of spherical MgS grains at a temperature of 250 K. The continuum in RAFGL 2155 runs above the observed spectrum at the shortest wavelengths, this may be due to molecular absorptions (see Sect. 6.2.2)

reason why the shape distribution should be close to this distribution. In this respect, it is rather surprising that our simple model works so well for so many sources. We can simulate a different shape distribution by adding the contributions of spherical grains to the CDE profile. This approach is permitted since we assume optically thin emission and thus the contribution of different components add linearly. In Fig. 6.12, we show the result of such a composite model for one C-star and for one post-AGB object. The relative amounts of spherical grains added to the model is ~ 35 per cent. We keep the temperature of the spherical and the CDE grains the same as in the initial model. As can be seen the spherical grains contribute at the position where our initial model fails. We conclude that variations in the distribution over grain shapes can explain the variations we observe in the profile of the “30” μm feature.

Figure 6.13: The effects of optical depth of the profile of the MgS emission. We show the absorbed MgS emission following Eq. (6.2) and (6.3) (grey dashed and solid lines), the profile of the “30” μm feature of RAFGL 2688 (solid black line) and the optically thin MgS emission (dashed black line).

6.6.2 Optically thick shells

The feature found in CD-49 11554, IRAS 13416, RAFGL 618 and RAFGL 2688 is different from the others in the sense that it is broader and flatter. This is especially true for RAFGL 618 and RAFGL 2688 where the profile even shows a central depression. We investigate the effect of optical depth on the emission profile. We model the effect of optical depth with two simple limiting cases.

$$I_1(\lambda) = B(\lambda, T_{\text{MgS}}) \times (1 - e^{-\rho \kappa_\lambda l}) \quad \text{and} \quad (6.2)$$

$$I_2(\lambda) = I_0(\lambda, T_{\text{MgS}}) \times e^{-\rho \kappa_\lambda l}, \quad (6.3)$$

where T_{MgS} is the temperature of the MgS, $B(\lambda, T)$ is the Planck function of temperature T , ρ is the mass density of MgS, l is the column length and $I_0(\lambda, T)$ is MgS emission of temperature T . $I_1(\lambda)$ is the limiting case of a column of MgS with a single temperature of T_{MgS} . $I_2(\lambda)$ represents the case of foreground absorption only; i.e. MgS emission of temperature T_{MgS} obscured by a column of MgS with negligible emission. In both cases the resulting profile will be broader than the optically thin case. For a long column $I_1(\lambda)$ approaches $B(\lambda, T_{\text{MgS}})$ while $I_2(\lambda)$ becomes double peaked with a depression where κ_λ peaks. The resulting $I_1(\lambda)$ profile will never show a central depression. We show the effects of incorporating the optical depth in Fig. 6.13. Indeed, these methods yield a broadened profile closer to what is observed.

Figure 6.14: The absorptivity of MgS grains coated with various types of materials. The modelled grains are composed of 80 per cent MgS and 20 per cent coating by volume. The models have been obtained by adding 5 ellipsoidal core-mantle grain of axes ratios (10:1:1), (3:1:1), (1:1:1), (3:3:1) and (10:10:1) of equal volume. For comparison we show the absorptivity of MgS in a CDE distribution (7) and the excess in NGC 7027 (8). We show the absorptivity of FeS (1) and amorphous carbon (5) grains with a MgS coating, both with core volume of 20 per cent of the grain. None of the modelled composite grains is able to explain the profile of the emission found in many PNe.

The second method reproduces the central depression found in RAFGL 2688. It is important to stress that the curves shown in Fig. 6.13 are not the result of a proper radiative transfer modelling of the CS shell or an attempt to fit the observed spectrum of the source. Nevertheless, they are able to explain the general characteristics of the “30” μm profile in the deviant sources well.

6.6.3 PNe profiles

For 9 out of 13 PNe the observed “30” μm feature is much narrower than in our model. Of the other four cases we discussed the profile of RAFGL 618 in Sect. 6.6.2. It is important to note that the remaining three cases (NGC 6790, IRAS 18240 and K 2-16) are the PNe with the highest continuum temperature among the PNe in our sample.

In Fig. 6.8, we compare the shape of the “30” μm profile of NGC 7027 with the profiles due to differently shaped MgS grains. As can be seen an oblate MgS grain with an axes ratio of 10:10:1 exhibits a “30” μm feature which peaks at the right position. At present we don’t know of a physical reason for a preferred oblate grain shape in PNe, and a broader CDE shape distribution in the C-stars and post-AGB objects (see also Sect. 6.8.4).

The shape of a resonance is also influenced by the presence of a coating. MgS is very hygroscopic. Under conditions where oxygen is available in the gas phase MgS can be oxidised and transformed into MgO (Nuth et al. 1985; Begemann et al. 1994). It is possible that the MgS is transformed as the central star of the PN heats up and the UV radiation pro-

gressively dissociates the CO molecules yielding gas phase oxygen. This could lead to MgS grains which are coated by a thin layer of MgO. We have modelled such grains using the electrostatic approximation following Bohren & Huffman (1983, chap. 5). The result is shown in Fig. 6.14, curve 6. As can be seen the “30” μm resonance is split into two features due to the MgO coating. The feature at the red wavelength is shifted to longer wavelengths compared to the pure MgS resonance. However the main feature is on the blue side of 25 μm towards the strong resonance at 18 μm in the pure MgO material, in clear contrast with the observations.

We explore other possible coatings on MgS grains to test their ability to explain the narrow feature observed in the PNe and the lack of emission at 26 μm . We find that of the composite grains we tested none give a satisfactory explanation. Mixtures of MgS and FeS have been discussed in the literature to investigate the nature of the “30” μm feature (Beegmann et al. 1994; Men’shchikov et al. 2001; Henning 2000). Curves 1 and 2 in Fig. 6.14 show the result of embedding an FeS core in a mantle of MgS and embedding a MgS core in a mantle of FeS, respectively. The latter compares most favourably with the position of the feature in the PNe. However, the substructure found in the spectrum of the composite grain around 33–37 μm is not found in the PNe spectra.

Szczerba et al. (1999) examine grains of amorphous carbon with a mantle of MgS to compare with the 30 μm feature in two post-AGB objects. We show simulated spectra of such grains and MgS grains coated with amorphous carbon in Fig. 6.14, curves 3 and 4 respectively. Curve 3 clearly does not match the observed feature in the PNe. As can be seen in curve 4 the MgS grains coated with amorphous carbon absorb less at 26 μm than pure MgS and are therefore a better spectral match to the “30” μm feature of the PNe. However, the feature to continuum ratio in these grains is about a factor 2.5 lower than in the pure MgS grains requiring a factor 2.5 more mass in the MgS component in order to explain the observed band strength. Note also that such grains will still produce a weak feature at 26 μm while in some PNe spectra we find no excess at that wavelength at all.

Lastly, in curve 5 (Fig. 6.14) we show the effect of water ice on the MgS grains. The effects on the optical properties of a water ice coating are marginal and the profile cannot explain the PNe observations. We conclude that of the composite materials we have experimented with MgS grains coated with amorphous carbon give the best spectral match. However we find no composite grains that match satisfactorily.

We stress that although our model does not reproduce the “30” μm profile in the PNe in its width it is safe to assume that *its carrier is MgS based*. These PNe are believed to be the evolutionary descendants of the sources which exhibit the MgS feature. The shift in peak position compared to the post-AGB objects follows naturally from an expanding and cooling shell. Also, the feature strength for the PNe is similar to these found in the post-AGBs further strengthening the physical link between the MgS in the C-stars and the post-AGBs on one hand and the “30” μm feature in the PNe on the other (see also Sect. 6.7).

6.7 Correlations

Using the large database of sources available we can study some of the properties of the “30” μm feature statistically. We have found it most convenient to characterise the sources

Figure 6.15: “30” μm feature properties versus the peak wavelength of the continuum. The symbols are the same as in Fig. 6.1. We show in panel (a) the ratio of the integrated flux in the “30” μm feature to the integrated flux in the SWS spectrum. In panel (b), we show the peak over continuum values. We also show the average values for the C-stars, the post-AGBs and the PNe. The non-detections are not taken into account in determining the mean values. The centroid wavelength of the “30” μm feature is shown in panel (c).

Figure 6.16: The centroid position of the “30” μm feature versus the MgS temperature in the model. The symbols are the same as in Fig. 6.1. We show a power-law function fitted to the data with the dashed line.

by the temperature of the fitted continuum. We use the wavelength where the derived continuum peaks ($\lambda_{\text{max,cont}}$) as an indicator of the continuum temperature. The derived continuum temperature itself is less well suited because of the systematic difference in the power law index we find between classes of sources. The sources are rather uniformly distributed over $\lambda_{\text{max,cont}}$ as well.

First, we show in Fig. 6.15(a) the relation between the $\lambda_{\text{max,cont}}$ and the ratio of the integrated flux in the “30” μm feature to the total flux in the SWS spectrum (I_{30}/I_{SWS}). The C-stars demonstrate a clear increase of I_{30}/I_{SWS} with decreasing continuum temperature. The post-AGB objects emit systematically a larger fraction, of up to 25 per cent, in their “30” μm feature. The PNe emit a similar fraction in the “30” μm feature as the post-AGB objects although with a larger scatter. Notice that the sample contains a number of PNe with warm dust indicative of young PNe. There are a few sources which do not follow the general trend. The C-stars, R Scl, IRAS 19584 and RAFGL 2256, exhibit an atypically strong “30” μm feature. These latter two sources are further typified by very weak molecular absorptions near 14 μm (see also Fig. 6.3). These observed anomalies are indicative of deviating conditions in the outflows of these sources, possibly a recently halted period of efficient dust formation. The post-AGB object IRAS 19454 has a very weak and cold “30” μm feature. RAFGL 618 has a

weak feature due to self-absorption (see Sect. 6.6.2).

The increasing strength of the “30” μm feature in the AGB stars is not surprising. Since the emission is optically thin I_{30} is proportional to the amount of MgS. The low values of I_{30}/I_{SWs} for the warmest C-stars reflects the fact that there is little dust around these sources and most of the IR radiation comes from the stellar photosphere. Cooler C-stars have more dust and thus more MgS. The difference between the coolest C-stars and the post-AGBs is more surprising. The fact that post-AGBs emit a larger fraction in the “30” μm feature is due to two effects. First since the dust shell becomes optically thin in the visible some fraction of the light is emitted at shorter wavelengths. Second, the temperature of the MgS decreases less rapidly than the temperature of the other dust components (see below).

It is clear that any dust component which produces 30 per cent of the IR light has to be abundant. In order to quantify the (relative) amounts of MgS present in the CS shells of these objects will require radiative transfer modelling which is beyond the scope of this chapter. We can however in first approximation study the relative amounts of MgS compared to the other cold dust components by studying the peak to continuum ratio (P/C). In Fig. 6.15(b), we show the P/C versus the $\lambda_{\text{max,cont}}$. The majority of the sources lies within the 0.3–1.0 range in P/C. We indicate a few clear outliers. R Scl, IRAS 19584 and RAFGL 2256 have a very strong “30” μm feature indicating again that these sources have ‘too much’ MgS for a normal C-star. The PNe NGC 6790 and NGC 6826 have an exceptionally strong MgS feature. Note that NGC 6790 also has a very warm continuum, much like a post-AGB source or a very young PN. The strong SiC band at 11 μm is consistent with this. We also show the averages for each of the classes of sources. The average P/C for C-stars is 0.5, for post-AGB objects 1.0 and for the PNe it is 0.9. The similar ratios for the post-AGB objects and the PNe suggests that the carrier of the “30” μm feature in the PNe is indeed directly related to the MgS feature in the post-AGBs. Furthermore, the similar ranges found for the post-AGB objects and the PNe argues against any process which results in a destruction of the MgS grains during the PN phase.

In Fig. 6.16, we show the derived MgS temperature versus the centroid position of the “30” μm feature. The two are well correlated. For convenience, we have fitted a power-law function (without physical meaning) to the relation.

$$T_{\text{MgS}} = 5.1 \cdot 10^{14} (\lambda_{\text{c},30})^{-8.34} \quad (6.4)$$

It is not surprising that T_{MgS} and $\lambda_{\text{c},30}$ are correlated since we have used the feature profile to estimate the T_{MgS} . However, using Fig. 6.16 or Eq. (6.4) one can easily derive the MgS temperature from a given observation. Also indicated in the figure are IRAS 13416 and RAFGL 2688; as can be seen they fall outside the correlation. This is due to the optical depth effects discussed above.

Lastly, we show in Fig. 6.17 the relation we find between the temperature of the continuum (T_{cont}) and the temperature of the MgS (T_{MgS}). We find, tracing the evolution from hot dust sources (C-stars) to the PNe, that the MgS temperature decreases correspondingly. Surprisingly, we find for warmest sources in the sample, with $T_{\text{cont}} > 1000$ K, very cold MgS. We propose two explanations for this phenomenon. First, it may be due to the absorption properties of MgS. If MgS cannot efficiently absorb the stellar light in the optical or near-IR part of the spectrum the grains remain cold. Alternatively, the MgS grains may be located

Figure 6.17: The derived MgS temperature versus the continuum temperature. The symbols are the same as in Fig. 6.1. We show in the box in the lower right the continuum temperature of the sources without a “30” μm feature detected. The inset shows a blow up on a logarithmic scale up of the sources with a continuum temperature below 1000 K.

further away from the star (see below). In the inset, we show a blow-up of the left side of the figure. There is a clear correlation between T_{cont} and T_{MgS} . The MgS in the post-AGB sources is systematically warmer than expected on the basis of the C-stars. Apparently, in the process of becoming a post-AGB object, when the dust shell becomes detached and moves away from the star, the general dust cools down more rapidly than does the MgS. Note that the difference in dust temperature between the coldest C-stars and the warmest post-AGBs is seen most clearly in the [12]-[25] colour or $\lambda_{\text{max,cont}}$ but is also found in the [25]-[60] colour (e.g. Fig. 6.1). The different behaviour of the continuum and the MgS is nicely illustrated in Fig. 6.15(c) where we show that while the continuum becomes redder the position of the “30” μm feature does not change. This effect is the cause for the discontinuity between the C-stars and the post-AGB object seen in Fig. 6.15(a) and (b). The physical cause for this must be due to the fact that MgS is actually (partially) heated by mid-IR radiation. The mid-IR radiation is much slower to respond to the termination of the AGB. Conversely, this implies that mid-IR radiation is a less important heating agent for the other dust components present.

6.8 Discussion

6.8.1 Carrier

The models using MgS we present do very well in explaining the profile of the feature found in the C-stars and post-AGB objects. The model does not do as well in explaining the profile of the feature found in the PNe. However, the smooth relation found between the [25]-[60] colour and the $\lambda_{c,30}$ shows a gradually changing profile with dust temperature. This suggests one carrier or closely related carriers. Also the similar P/C values for the different classes of objects is indicative of one carrier.

Recently Grishko et al. (2001) proposed HAC as the carrier of the mid-IR emission features in C-stars, post-AGBs and PNe. HAC is a very plausible dust component in those environments (e.g. Duley & Williams 1981; Goebel 1987; Borghesi et al. 1987; Henning & Schnaiter 1999). However, the mid and far-IR optical properties of HAC are dominated by a λ^{-1} continuum (Bussoletti et al. 1987). Grishko et al. (2001) identified some 13 weak spectral features in the range from 19–120 μm . The strongest of which occur at 21, 27 and 57 μm . We consider HAC a unlikely candidate for the circumstellar “30” μm emission feature because the laboratory features are weak in contrast to the astronomical data and because the far-IR features of HAC are not observed in the astronomical spectra.

6.8.2 The effect of model simplifications

It is remarkable that our simple model works so well. We have applied various simplifications in order to be able to study the whole sample in a unified way. These simplifications necessarily lead to differences between the models and the observations. Instead of assuming a single temperature modified blackbody for the shape of the continuum one can certainly obtain a more detailed fit by taking into account the structure of the CS envelope and the opacities of the different molecular and dust constituents. Our method works well because the contributions of the other known other dust components around 30 μm are well behaved, smooth and thus indeed form a continuum. Moreover, the shape of our modelled continuum between 20–50 μm is not a strong function of the emissivity index (p) and varying the p -parameter or the temperature doesn’t yield qualitatively different continuum shapes or levels. We already pointed out that in some cases our model fails at the longest wavelengths of the SWS observations, which may be related to our method to estimate the continuum.

We use a single temperature for the MgS to model its contribution. In the very extended envelope of a C-star or in the nebulous environments in the post-AGBs and PNe, the temperature of any dust component will not be constant but decreases as a function of the distance to the star. The fact that we still get good results using a single temperature is a clear indication that the emission is optically thin and that the density of the MgS falls off sharply with distance. In an optically thin environment we know that $T_{\text{dust}} \propto \sqrt{R}$, where R is the distance to the star. If the density distribution drops with distance as R^{-2} or steeper, the contributions are weighted to the highest temperature part of the envelope where T_{dust} and thus the source function is highest. If the density distribution is flatter there is relatively more dust far away than close by. In this case we will observe MgS with a range of temperatures. Also sources

that are not optically thin will emit a feature broader than our single temperature MgS model (see also Sect. 6.6.2). We conclude that in the majority of the sources the “30” μm emission is due to optically thin emission which is dominated by the highest temperature MgS closest to the star.

6.8.3 Shape

We find that a CDE shape distribution fits many observations well. A CDE shape distribution is used to model a collection of irregularly shaped grains. Irregularly shaped grains can for example result from grain growth by agglomeration (Blum et al. 2000).

We find evidence for differences in the shape distributions between sources. We have tested for correlations between the strength of the 26 μm excess (due to spherical MgS grain) and the CDE component and other parameters like the mass-loss rate, the P/C, the continuum temperature or the feature temperature. We find no clear correlations. We do however note that we find little evidence for the 26 μm excess in the hottest C-stars. Stars in our sample with a continuum temperature above 1000 K do not exhibit the excess. Below 1000 K we find both sources with and without the 26 μm excess. Note also that the occurrence rate of the 26 μm excess in the sample of post-AGB objects is high. Because the emission in the post-AGB phase may be dominated by the dust closest to the star and hence lost at the tip of the AGB during a phase of heavy mass loss (at a rate much higher than during the general AGB phase), this might suggest that the shape distribution of the grains changes to become more spherical towards the end of the AGB, possibly as a function of mass-loss rate.

6.8.4 Planetary nebulae

The profile of the “30” μm feature we find in most PNe is narrower than in our model. The largest discrepancy occurs around 26 μm . Our model fits are able to explain the shift in centroid position observed in the PNe; however, the models that explain the band-shift best, over-predict the flux at 26 and 40 μm .

There are several observational properties that are important when considering explanations for the observed discrepancies. First, there is the similar values of P/C in the sample of post-AGBs and PNe (Fig. 6.15b). This indicates that the carriers are related and similar in abundance. Second, the smooth trend we find in the centroid position of the “30” μm feature with the [25]-[60] colour (Fig. 6.6). The PNe profiles follow the general trend. This indicates that the main effect for the peak shift *also in the PNe* is due to temperature. We also note that there are three non-PNe sources in our sample with cold MgS (R Scl, IRAS 19454 and IRAS 23321). These sources are well fitted by our model. This indicates that the narrow profiles are particular to the PN environment.

We have explored possible MgS based heterogeneous grains and variations in MgS grain shape. The heterogeneous grains we have explored do not compare satisfactorily with the observed profile in the PNe. MgS grains coated with a layer of amorphous carbon provide a somewhat better match in terms of the band shape however the contrast of the feature with respect to the continuum is strongly reduced. The reduced band strength is in contradiction with the observed peak over continuum ratios.

We find that the emission from plate-like MgS grains appears similar to the feature found in the PNe. In Sect. 6.6.1 we consider an extra contribution of spherical MgS grain to the “30” μm feature at 26 μm . The varying strength of this contribution demonstrates that there are variations in the grains shape distribution between sources. The question is: “Is it possible that the narrow “30” μm feature in the PNe is carried by flattened MgS grains?” This would either imply that the MgS grain shape distribution in the PNe is heavily skewed to the plate-like grains or that the oblate grains emit more efficiently.

The origin of these variations in the shape distribution are unclear. They may reflect variations in the formation and destruction of grains. We do not know of a mechanism that drives towards oblate grains shapes during the PN-phase or a mechanism that selectively destroys spherical and prolate grains. Note, that the peak over continuum value in the PNe is similar to those found in the post-AGB objects arguing against a destruction of a part of the MgS grains. It is important to remark that in the CDE distribution only ~ 20 per cent of the grains is oblate with an axis ratio of $1:\frac{1}{5}$ or more extreme, i.e. with axes ratios of $1:X:Y$, where Y is smaller than $\frac{1}{5}$ and X can vary between $\sqrt{X}$ and 1. Such axes ratios are required in order to shift the peak position to the wavelength where the “30” μm feature in the PNe peaks and to suppress the emission at 26 μm .

Alternatively, these inferred shape variations may result from a shape dependent heating of grains. In the C-stars, likely, heating and cooling occurs at IR wavelengths. Because the grains are small compared to these wavelengths the temperature will be shape independent. However, in the PNe heating occurs through absorption of visible and UV radiation, which scales with the cross-section. Hence in that case dust temperatures will be shape dependent. Indeed flattened grains have on average a larger geometric cross-section compared to their volume than spherical or prolate grains.

As noted before, the PNe in the sample with the warmest dust continuum are well fitted by our model. The model fails in the PNe sample at MgS temperatures below ~ 90 K. Perhaps, the observed discrepancies are due to changes in the optical properties of pure MgS at low temperatures. No laboratory measurements of MgS at these temperatures are published. FeO has the same lattice structure as MgS and measurements of FeO at different temperatures (10 K, 100 K, 200 K and 300 K) are available (Henning & Mutschke 1997). We have used FeO as an analogue to examine the effect of temperature. The trend with lower temperature is for the FeO resonance at 20 μm to become narrower and stronger with respect to the continuum. There is a small shift in the peak position. Comparing the 300 K measurement to 10 K the latter resonance peaks ~ 0.1 μm more to the blue for spherical grains. Like MgS, FeO is also very sensitive to the shape of the grains. Using a CDE shape distribution the resonance of the 10 K sample lies ~ 1 μm on the blue side of the 300 K resonance. If we translate this behaviour to the MgS data and the “30” μm feature in the PNe it worsens the situation since we would expect a stronger contribution at shorter wavelengths exactly where our model already over-predicts. As an alternative, one might speculate that a change in lattice structure at low temperatures may occur resulting in different optical properties. It is interesting to note that Berthold (1964) reports that MgS can condense in two lattice structures: cubic and hexagonal. This author finds that hexagonal MgS exhibits a narrower mid-IR resonance than cubic and amorphous MgS.

We conclude that, although it is possible to find MgS based candidate materials that provide a better spectral match to the observed “30” μm feature in the PNe no explanation for the “30” μm profiles in the PNe is completely satisfactory at this time.

6.8.5 MgS Temperature

We have found that the “30” μm feature is very well explained with MgS provided that the continuum temperature and the MgS can be substantially different from each other (see also Fig. 6.17). Moreover, the temperature difference changes between classes of sources. In the C-stars we find that MgS is colder than the continuum while in the post-AGB sample the MgS grains are warmer. The temperature difference and the fact that the continuum temperature varies relative to the MgS temperature implies that the MgS grain are not in thermal contact with the amorphous carbons grains that carry the continuum. Thus, MgS is condensed in these environments into separate grains.

The relatively warm hot MgS that we observe in the post-AGB sample is certainly a phenomenon that deserves further study. As pointed out above, this must be due to a difference in the heating properties of MgS relative to the other dust constituents. We suggest that due to the strong resonance in the mid-IR MgS is (partially) heated by IR radiation. This may cause a temperature difference as observed. It requires measured optical constants for MgS over a much wider wavelength range than now available and radiative transfer modelling to understand the detailed temperature behaviour of the MgS grains.

We have shown in Fig. 6.17 that the warmest C-stars that exhibit the “30” μm feature have cold MgS. We consider two possible explanations for this behaviour. First, MgS can be cold because it is unable to absorb the radiation from the central source efficiently. This would require that the MgS grains are very transparent in the visible and near-IR where these warm C-stars emit most of their radiation. In this case a *cooler* star will emit more radiation at wavelengths where MgS can absorb and as a result the MgS grains will be *warmer*. This explanation is consistent with our notion that MgS is (partially) heated by IR radiation.

A second intriguing possibility is that the MgS around these sources is located far away from the star. R Scl, U Cam and W Ori are known to have a detached dust shell (Zuckerman 1993). These shells are formed during an earlier phase when the mass-loss rate was higher than the current mass-loss rate (Willems & de Jong 1988). If during this phase the AGB star was already a C-star, MgS could have condensed in the outflow and be present in the detached shell. We have sketched in Fig. 6.1 the evolution of a star which suffers a brief period of enhanced mass loss. First, the star becomes redder during the phase of high mass loss. When the shell becomes detached the 12 μm flux quickly drops while the inner edge of the dust shell moves away from the star and the warmest dust is rapidly lost. The star moves back to the locus of the warmest C-stars but with an excess of cold dust. The excess of cold dust is observable as a 60 μm excess. The sources mentioned above indeed show the 60 μm excess. We note that some stars with 60 μm excess do not show the “30” μm feature.

To distinguish between these two possibilities requires radiative transfer modelling and a more detailed investigation of these particular sources which is beyond the scope of this chapter. The location and temperature of the MgS in the warmest C-stars will be further discussed in a forthcoming paper (Hony et al., in prep.).

6.8.6 MgS in the ISM

The behaviour of the MgS we find in this study has implications for our understanding of the fate of MgS that is produced during the C-star phase. Previously, the existence of MgS in the ISM has been excluded because of the lack of spectral signature at $26\ \mu\text{m}$. We have shown that at low dust temperatures no emission signature is expected at $26\ \mu\text{m}$. For the dust temperatures in the ISM we would expect a smooth feature at wavelengths longer than $35\ \mu\text{m}$. In this respect it is interesting to note that the peak to continuum (P/C) values in the post-AGB and PNe sample are similar. We find no evidence for a rapid destruction by the UV radiation field in the PN. This shows that the MgS will indeed be injected into the ISM. Of course, in the ISM the contrast will be much less because the injected material will be diluted with other star-dust and general ISM material. Nevertheless a search for the “30” μm feature in the ISM may be very worthwhile. In this respect it is important to note that Chan et al. (1997) have discussed a broad emission feature they observed along several lines of sight towards the galactic centre. The feature they observed is similar to the “30” μm feature observed in the C-rich post-AGB objects.

6.9 Summary and concluding remarks

We present a large sample of 63 ISO/SWS spectra of carbon-rich evolved objects that exhibit a “30” μm feature. The feature is detected along the complete evolutionary track from low mass loss C-stars and extreme C-stars via post AGB objects to PNe.

We present a simple approach to determine the continuum. We study the profile of the “30” μm feature after continuum subtraction. We find large systematic variations in the appearance of the “30” μm feature. We firmly identify the carrier of the feature with MgS in a CDE shape distribution. The profile of the observed feature is consistent with MgS provided that the temperature of the MgS can be different from the bulk of the dust. This approach allows us to model, in a unified way, the profiles of the “30” μm feature in a wide range of objects even when the feature can appear extremely different.

We find an additional component at $26\ \mu\text{m}$ in ~ 25 sources. We argue that this component is due to differences in the distribution over shapes of the MgS grains; specifically, it requires a distribution more weighted to spherical MgS grains. We find no clear correlations of this excess with other properties of the sources. The self-absorbed “30” μm features of RAFGL 618 and RAFGL 2688 reflect the high optical depth in the “30” μm feature in these sources.

We find that the typical profile of the “30” μm feature in the PNe is narrower than predicted by our model. We consider several possible explanations. We find that flattened MgS grains provide a better spectral match to the “30” μm feature in the PNe. However it is presently unclear why in the PNe environment the “30” μm feature is dominated by flattened grains.

We find that the temperature of the MgS grains is different from the bulk of the dust. Therefore, they cannot be in thermal contact with the other dust species but must exist as separate grains. In the C-stars MgS is colder than the other dust while in the post-AGB objects MgS is warmer. Likely, this is because the MgS is efficiently heated by mid-IR radiation

which is less important in the C-stars.

The behaviour of the temperature of the MgS for the hottest C-stars is enigmatic. The hottest sources have very cold MgS grains. We propose two explanations for this phenomenon. First, the “30” μm feature in these sources may be due to a previous mass-loss phase and the MgS is thus located far from the source and cold. Second, the MgS grains absorb very inefficiently in the optical and near-IR and therefore the hottest C-stars do not heat the MgS grains well.

We examine the feature over continuum ratio to study the relative proportion of MgS to the other dust components. We find no evidence for rapid destruction of MgS grains during the PNe phase and possibly MgS grains may survive to be incorporated into the ISM.

We would like to emphasise the need for further measurements of the optical properties of astrophysically relevant materials at *all relevant* wavelengths. This study has put forwards some very interesting questions in relation to the absorption properties of MgS in the optical and near-IR and also concerning low temperature effects. Unfortunately, no published laboratory measurements are available to test some of our scenarios and conclusions.

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6.10 Appendix: model fits

Figure 6.18: “30” μm feature modelled using MgS optical properties. We show the observed spectra (black), the modelled continua (dashed), the spectra with the MgS contribution subtracted (gray) and the composite of the continuum and the MgS contributions (thin black line).

Figure 6.18: (continued).

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Figure 6.18: (continued).

Figure 6.18: (continued).

Figure 6.18: (continued).

Figure 6.18: (continued).

Figure 6.18: (continued).

Figure 6.19: C-stars with a weak or without a “30” μm feature. We also show the fitted continuum (dashed line). The sources are sorted according to decreasing continuum temperature. We refrain from showing a MgS model. In those cases where the strength of the “30” μm feature allowed to extract a temperature of the MgS the value is listed in Table 6.2.

Figure 6.19: (continued).

The circumstellar envelope of HD 56126

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Abstract

We present a detailed study of the circumstellar envelope of the post-AGB “21 μm object” HD 56126. We build a detailed dust radiative transfer model of the circumstellar envelope in order to derive the dust composition and mass, and the mass-loss history of the star. To model the emission of the dust we use amorphous carbon, hydrogenated amorphous carbon, magnesium sulfide and titanium carbide. We present a detailed parametrisation of the optical properties of hydrogenated amorphous carbon as a function of H/C content. The mid-IR imaging and spectroscopy is best reproduced by a single dust shell from 1.1 to 2.6'' radius around the central star. This shell originates from a short period during which the mass-loss rate exceeded $10^{-4} \text{ M}_{\odot}/\text{yr}$. We find that the strength of the “21” μm feature poses a problem for the TiC identification. The low abundance of Ti requires very high absorption cross-sections in the UV and visible wavelength range to explain the strength of the feature. Other nano-crystalline metal carbides should be considered as well. We find that hydrogenated amorphous carbon in radiative equilibrium with the local radiation field does not reach a high enough temperature to explain the strength of the 3.3–3.4 and 6–9 μm hydrocarbon features relative to the 11–17 μm hydrocarbon features. We propose that the carriers of these hydrocarbon features are not in radiative equilibrium but are transiently heated to high temperature. We find that 4 per cent of the dust mass is required to explain the strength of the “30” μm feature, which fits well within the measured atmospheric abundance of Mg and S. This further strengthens the MgS identification of the “30” μm feature.

7.1 Introduction

Post-asymptotic giant branch stars (post-AGBs) are objects in which the high AGB mass-loss has ceased while the remaining star is not (yet) hot enough to ionise the surrounding material. These objects are characterised by a double-peaked spectral energy distribution (SED). In the UV and visible range the central star is visible. In the mid-infrared (IR) range the light is dominated by emission from the dusty circumstellar envelope (CSE). Post-AGB stars are the prime objects to study stellar evolution near the very end of the AGB because they are the most recent evolutionary descendants of the AGB stars. Mass loss near the tip of the AGB is

not well understood. There are indications that the mass-loss rates near the end of the AGB exceed the values predicted by the existing dust driven wind models (e.g. CRL 2688). There is also increasing evidence that non-spherical mass loss is common near the end of the AGB phase. Since AGB evolution timescales are determined by mass loss, these poorly understood phenomena limit our knowledge of the evolution of these objects and the subsequent stages.

Mass loss determinations are directly coupled to the composition of the newly condensed dust. The dust composition of the CSE reflects the physical conditions in the outer atmospheres of the AGB star during the phase when the dust was formed and the processing that took place afterwards. We study the composition of the dust surrounding the post-AGB star HD 56126. This star is member of a class of rare objects that exhibit an emission feature at $21\ \mu\text{m}$ (Kwok et al. 1989). The 12 (see Kwok et al. 1999, and references therein) post-AGB stars that show this feature are commonly referred to as the “ $21\ \mu\text{m}$ objects”. The “ $21\ \mu\text{m}$ objects” form a group with rather homogeneous properties: carbon-rich and s-process enhanced (Van Winckel & Reyniers 2000) with large IR excesses (Kwok et al. 1989), spectral types G or F (Hrivnak 1995). Volk et al. (1999) have shown that the shape of the “ $21\ \mu\text{m}$ ” feature between different sources shows hardly any variation. Recently we have reported the detection of the same feature in two PNe (Chapter 5) and Volk et al. (2002) have reported on its detection in the PN IC 418.

Besides the “ $21\ \mu\text{m}$ ” feature the “ $21\ \mu\text{m}$ objects” exhibit other infrared emission features that are unique to these environments. The carriers of many of these features have not been firmly identified and there is considerable debate in the literature on the composition of the dust around the “ $21\ \mu\text{m}$ objects”. In the next paragraphs we shortly review these features and the proposed carriers.

The carrier of the “ $21\ \mu\text{m}$ ” feature has remained unidentified for more than a decade, although several candidates have been considered: urea $\text{OC}(\text{NH}_2)_2$ (Sourisseau et al. 1992), SiS_2 (Goebel 1993; Begemann et al. 1996), fullerenes (Webster 1995), nano-diamond (Hill et al. 1998), hydrogenated amorphous carbon (HAC) (Grishko et al. 2001) and oxygen bearing side groups in coal (Papoular 2000). However, none of the spectroscopic comparisons between the laboratory spectra of the suggested materials and the emission from the post-AGB stars is satisfactory. Recently we have suggested titanium carbide nano-crystals (nano-TiC) as the carrier of the “ $21\ \mu\text{m}$ ” feature (von Helden et al. 2000). This identification is based on *i*) the excellent spectroscopic match of nano-TiC with the $21\ \mu\text{m}$ feature, *ii*) the fact that the nano-TiC resonance does not depend on the crystal size for the size-range for which measurements are available – in good agreement with its observed constant profile, *iii*) the fact that TiC is found in presolar grains (Bernatowicz et al. 1996) for which the isotopic ratios imply an origin in the CSE of carbon-rich evolved stars (Anders & Zinner 1993).

We note that nano-TiC identification is not commonly accepted either. The main counter argument is that the conditions (high density and pressure during dust formation) required to form TiC in the ejecta of carbon-rich evolved stars may not be met (Kwok et al. 2002). Another argument against nano-TiC is the strength of the “ $21\ \mu\text{m}$ ” feature. Since Ti is a rare element it may be difficult for TiC to produce a feature that stands out as much as it does.

As explained above the “ $21\ \mu\text{m}$ objects” exhibit other emission features for which the carriers are still under debate. Besides the well-known unidentified infrared (UIR) bands at 3.3, 6.2, “7.7” and 11.2, generally attributed to polycyclic aromatic hydrocarbon (PAH) molecules

(Allamandola et al. 1989), these sources exhibit a $3.4\ \mu\text{m}$ feature and broad emission features (so-called plateau features) between $6\text{--}9$ and $11\text{--}17\ \mu\text{m}$ (Buss et al. 1990; Justtanont et al. 1996). As a class, the emission bands observed from the “ $21\ \mu\text{m}$ objects” are distinctly different from the UIR features from most sources (see Sect. 7.3.1). Kwok et al. (2001) have discussed these features in terms of alkane and alkene side groups on very large aromatic molecules and small carbonaceous particles. Guillois et al. (1996) have compared them to those measured in coal (a natural terrestrial carbonaceous compound). The spectroscopic match with coal is very encouraging. However, a fundamental questions concerning the identification is whether carbonaceous grains can reach the temperatures required to emit strongly in the $6\text{--}9\ \mu\text{m}$ range.

Lastly, these sources exhibit a strong, broad feature between $23\text{--}45\ \mu\text{m}$ (Omont et al. 1995; Szczerba et al. 1997; Hrivnak et al. 2000), called the “ $30\ \mu\text{m}$ feature”. The carrier of the “ $30\ \mu\text{m}$ feature is identified with magnesium sulfide (MgS) (see Chapter 6 and references therein). The identification of the “ $30\ \mu\text{m}$ feature with MgS seems solid but open questions remain on the heating of the MgS grains and the amount of MgS required to explain the prominence of the feature.

A meaningful approach towards the identification of the various dust components in the CSE of these post-AGBs is that of radiative transfer modelling of the SED of these objects. This may also help to improve our understanding of the mass loss at the very end of the AGB phase. Such modelling allows a comparison of the emission characteristics of candidate materials and CSE emission and yields insight into the relative contributions of the different materials present in the CSE.

We have elected to model HD 56126 (IRAS 07134+1005, SAO 96709, BD+10 1470) in detail. HD 56126 has the strongest “ $21\ \mu\text{m}$ feature relative to the other dust features of all known “ $21\ \mu\text{m}$ objects”. Therefore, HD 56126 provides the strongest constraint on the abundances needed to explain the “ $21\ \mu\text{m}$ feature. This is even more so because the photosphere of the star is metal poor (Van Winckel & Reyniers 2000). Both the central star and the dust shell of this source have been well studied in the literature. Especially important in this respect are images at various wavelengths in the mid-IR in which the source is well resolved (Meixner et al. 1997; Dayal et al. 1998; Jura et al. 2000; Kwok et al. 2002, and this work). These images are essential to constrain the model parameters.

This chapter is organised as follows: In Sect. 7.2 we give the stellar parameters of HD 56126. In Sect. 7.3 we present the infrared measurements that we use. In Sect. 7.4 we consider the energy balance in the nebula and constrain the stellar effective temperature. In Sect. 7.5 we list the parameters that we use to model the absorption and emission in the CSE of HD 56126. The optical properties of the dust constituents are discussed in Sect. 7.6. In Sect. 7.7 we present the model results. In Sect. 7.8 we discuss our findings and finally in Sect. 7.9 we give a summary and conclusions.

7.2 Stellar parameters

HD 56126 is a bright star with a visual magnitude of 8.3. The star has been classified as a F5 supergiant by Nassau et al. (1965). More recently Hrivnak et al. (1989) published a

Walraven					
V	V-B	B-U	U-W	B-L	
-0.548	0.365	0.75	0.556	0.312	(Pel 1976)
-0.555	0.400	0.766	0.588	0.322	(van Genderen et al. 1986)
Johnson (van Genderen et al. 1986)					
B	V				
9.13	8.23				
Near-IR (Hrivnak et al. 1989)					
J	H	K	L	M	
6.92	6.66	6.65	6.43	6.10	
Strömgren					
<i>b-y</i>	(<i>v-b</i>)-(<i>b-y</i>)	(u- <i>v</i>)-(v- <i>b</i>)			
0.639	0.182	1.477		(Olsen 1993)	
<i>u</i>	<i>y</i>	[ergs s ⁻¹ cm ⁻² Å ⁻¹]			
1.03e-12	1.71e-12			(Ueta et al. 2000)	
Geneva (van Winckel, priv.comm.)					
U	B	B1	B ₂	V ₁	G
11.010	8.337	9.452	9.616	8.970	9.213

Table 7.1: UV to IR photometric data of HD 56126. Units are magnitudes unless given explicitly.

medium resolution optical spectrum and determined the spectral type to be F0-5I, consistent with the previous spectral classification. There are several photospheric abundance determinations published for HD 56126 (Parthasarathy et al. 1992; Klochkova 1995; Van Winckel & Reyniers 2000). These studies all demonstrate the low photospheric metallicity of the star, with a value of $[\text{Fe}/\text{H}] = -1.0$ and enrichment of C, N, O and the s-process elements. There is less agreement on the exact amount of enrichment of the CNO-elements. While Parthasarathy et al. (1992) and Van Winckel & Reyniers (2000) find a C/O value close to unity, Klochkova (1995) determine a lower abundance of O and derive a C/O value of ~ 1.5 .

The conversion from spectral type to effective temperature (T_{eff}) is not clear-cut. Due to the peculiar abundance one should be critical of applying standard spectral type calibrations based on solar type abundances. For example, the tables of de Jager & Nieuwenhuijzen (1987) quote 6370 for a F5I star with solar abundances. Values of T_{eff} for HD 56126 within a large range (5900–7250 K) are derived by various methods. We give most weight to the temperatures determined in detailed abundance analysis using high resolution spectroscopy (Parthasarathy et al. 1992; Van Winckel & Reyniers 2000). These studies yield a high value of the effective temperature (7000–7250 K). This temperature corresponds to a F1-2I spectral classification, still within the range derived by Hrivnak et al. (1989). Such a high value for T_{eff} also fits better with the observed spectral energy distribution (SED) (see below).

Jura et al. (2000) have made the case that the low iron abundance of the star, the high galactic latitude ($b=+10^\circ$) and its high radial velocity make it probable that HD 56126 is a population II star with a zero age main-sequence mass of $\sim 1.1 M_\odot$.

The distance (d) to HD 56126 is poorly known. Values between 2 and 3 kpc are used

Instrument	HD 56126 ISO observations			
	Obs. ^a	α	δ	TDT ^b
	Mode	(J2000)	(J2000)	
SWS	06	07 16 10.20	+09 59 48.01	71802201
SWS	06	07 16 10.30	+09 59 48.01	72201702
SWS	01(3)	07 16 10.20	+09 59 48.01	72201901
LWS	01	07 16 10.20	+09 59 47.80	72201802

Table 7.2: Details of the ISO observations used in this study.

^aObserving mode used see de Graauw et al. (1996) and Clegg et al. (1996). Number in brackets correspond to the scanning speed.

^bTDT number which uniquely identifies each ISO observation.

in the literature. Yuasa et al. (1999) derive a statistical distance of 2.12 kpc from a principle component analysis based on IRAS photometry and molecular expansion velocity. Knapp et al. (2000) derive 2.4 kpc from the radial velocity assuming that the radial velocity is due to the galactic rotation while Jura et al. (2000) derive 2.3 kpc from the theoretical luminosity of $6600 L_{\odot}$ and the observed flux. In the following we elected to use $d=2.4$ kpc. Note that this distance yields a luminosity of $6000 L_{\odot}$ which is higher than expected ($\sim 3000-4000 L_{\odot}$) (e.g. Boothroyd & Sackmann 1988) for a star with a $\sim 1.1 M_{\odot}$ ZAMS mass on the basis of the initial mass-final mass relation and core-mass-luminosity relation. In view of the uncertain distance, we explicitly give the distance dependence of the values that we derive.

7.3 Observations and data reduction

7.3.1 Infrared spectroscopy

For the spectral energy distribution (SED) of HD 56126 we use IR data obtained with the Short Wavelength Spectrometer (SWS) (de Graauw et al. 1996) and Long Wavelength Spectrometer (LWS) (Clegg et al. 1996) on-board the Infrared Space Observatory (ISO) (Kessler et al. 1996). These data consist of one SWS/AOT01 spectrum from 2.3–45 μm , two SWS/AOT06 spectra covering the ranges 16.5–24 and 23–43 μm and a LWS spectrum from 45 to 200 μm . Details of the ISO observations are given in Table 7.3.1.

The SWS data reduction steps involved the removal of cosmic ray hits. Next, we combine all available data from the SWS observations in order to optimise the signal-to-noise ratio. We correct each separate observation, subband and detector combination in such a way that its average equals the average of all available data at the corresponding wavelength. Below 12 μm we apply an offset and above 12 μm a scaling to the data. We apply an additional scaling factor of 1.1 to the data of sub-band 3C (16–19.5 μm) to form a continuous spectrum. Finally, the data are rebinned to a fixed resolution grid of $\lambda/\Delta\lambda=200$.

Data reduction of the LWS observation consisted of extensive bad data removal, rebinning on a fixed resolution grid of $\lambda/\Delta\lambda=50$ and splicing of the data to form a continuous spectrum.

Figure 7.1: The spectral energy distribution of HD 56126. We show the IUE data (crosses), optical and near-IR photometry (triangles) (see Table 7.1 for details), IRAS photometry (diamonds) and the ISO/SWS spectra (solid line). In grey we show near-IR spectroscopy from Kwok et al. (1990) and Oudmaijer et al. (1995). For reference we also show a Kurucz model (dotted line) of the central star with $T_{\text{eff}}=7250$ K, $\log g=1.0$ and $[M/H] = -1.0$ (Kurucz 1993) reddened with $E(B-V)=0.33$ using a standard extinction law (Savage & Mathis 1979). The standard extinction law is clearly not applicable. In grey we indicate the contribution of the “21” μm feature and the dashed area indicates the “30” μm feature due to magnesium sulfide. Note that on this scale surface corresponds to energy. Therefore one may readily see that an appreciable amount of energy is emitted in the “21” and “30” μm features. The inset shows the Kurucz model before reddening (solid line) and the reddened model atmosphere (dotted line).

Figure 7.2: The 3 to 17 μm spectrum of HD 56126 after removing the contribution of the star and the dust continuum. Several emission features due to vibrationally excited C-H and C-C bonds in hydrogen-carbon compounds are identified. We have indicated the features due to aromatic (grey lines) and aliphatic (black lines) structure. The inset shows a blow-up of the 3 μm region, where the dominant aromatic 3.3 μm and the weaker 3.42 μm signature are observed. For reference we show the spectrum of the PN NGC 7027 as a prototypical PAH spectrum (grey). The emission features of HD 56126 are markedly different from the PAH spectrum of NGC 7027.

We apply scaling factors to the data from 45–70 μm and offsets at longer wavelengths. The data of detector 7 (130–140 μm) are very bad and we have replaced those by a constant level of 10 Jy, the average of the much better data on either side of detector 7. The combined SWS/LWS spectrum together with data from the literature is presented in Fig. 7.1.

The SED of HD 56126 is double peaked. At wavelengths shorter than 4 μm we see the stellar photosphere directly. At longer wavelengths the dust emission dominates. We see continuum emission which peaks at ~ 25 μm with strong broad emission features perched on top. In Fig. 7.1 we indicated the broad continuum due to amorphous carbon (a-Carbon) and the “21” μm , “30” μm and the plateau feature, (tentatively) identified with titanium carbide, magnesium sulfide, and HAC or PAHs, respectively.

In Fig. 7.2 we show a detailed view of the plateau features. We indicate the emission that can be attributed to aromatic and aliphatic bonds separately. Notice the differences with the

Figure 7.3: TIMMI2 image of HD 56126 in the $11.9\ \mu\text{m}$ narrow band filter. The scale on the top left indicates $1''$. There are three emission maxima on a ring-like structure (indicated by a dotted line) at $\sim 1.1''$ from the centre (indicated by the '+'-sign). The grey-scale shows the square of the measured intensity to enhance the contrast of the emission maxima. The contours indicate the 5–95 per cent intensity levels in steps of 10 per cent. The outer contour (5 per cent) lies at $\sim 2.4''$ from the centre.

emission spectrum of the planetary nebula NGC 7027 in feature shape and relative strength of the bands. The aliphatic component is much stronger in HD 56126 than in NGC 7027.

7.3.2 N-band imaging

We also obtained an $11.9\ \mu\text{m}$ image with the TIMMI2 (Reimann et al. 2000; Käufel et al. 2000) mid-IR camera attached to the ESO 3.6m telescope at La Silla, Chile on 25 December 2001. The camera is equipped with a 320×240 pixel array; we applied a pixel scale of $0.3''/\text{pixel}$. We used a chop throw of $15''$ north-south and a nod of $15''$ east-west. This allowed for both the chopped as well as the noded positions to fall onto the detector. We combined the positive and negative images resulting from the chopping and nodding positions. The images were reduced using a shift-and-add technique, where the shift between individual frames was determined from a least-squares comparison between the individual frames. The resulting image was then deconvolved using an empirically determined point spread function obtained by observing HD 32887 with the same set-up as HD 56126. We show the final image in Fig. 7.3.

The TIMMI2 $11.9\ \mu\text{m}$ image shows a clearly resolved envelope of $\sim 5''$ diameter. The emission peaks at $1.1''$ to the east from the centre of the nebulae. There are two other local intensity maxima: in the west and in the north, although the latter is not clearly resolved. Our $11.9\ \mu\text{m}$ image is consistent with other mid-IR imaging studies (Meixner et al. 1997; Dayal et al. 1998; Jura et al. 2000; Kwok et al. 2002) that show the same morphology throughout the $8\text{--}21\ \mu\text{m}$ wavelength range. The emission maximum in the north is resolved in the images of Kwok et al. (2002). We derive the azimuthal averaged intensity profile from Fig. 7.3 to compare with the model output.

Component	Flux [10^{-12} W/m ²]	Frac _{total} %	Frac _{dust} %
Total	33.6	100	-
Star	14.8	44	-
Dust	18.8	56	100
Dust components			
a-Carbon	11.6	35	62
HAC/PAHs	3.0	9	16
MgS	2.7	8	14
TiC	1.5	4	8

Table 7.3: The integrated contributions of the different components of the spectral energy distribution (see Fig. 7.1). We list the integrated flux (column 2), the fraction of the total luminosity (column 3) and the fraction of the IR luminosity (column 4).

7.4 Basic considerations

Before we describe the details of our model we consider a few basic properties and the simple constraints that we can derive from them.

7.4.1 Energy balance

In Fig. 7.1 equal areas under the curve correspond to equal energy and it is clear that most of the energy is emitted in the IR. In Table 7.3 we specify the fractions of the energy emitted by each of the components in Fig. 7.1. Only 44 per cent of the light comes from the star directly while 56 per cent has been absorbed in the CSE and re-emitted in the IR. This implies that the extinction averaged over all angles around the star must be appreciable. Using a standard extinction law and a 7250 K Kurucz model atmosphere (Kurucz 1993) we estimate that the average A_V equals 1.1, which corresponds to $\tau_V=1.2$. However, such a value for the visual extinction corresponds to hardly any extinction in the near and mid-IR. Thus the near-IR (2–4 μm) observations give the true continuum level of the star since no obvious dust contribution is detected in this wavelength range. Therefore, for a given effective temperature of the stellar photosphere there is no freedom in choosing the absolute scale. With this we can directly compare the integrated flux in the observed SED to the integrated flux from the model atmosphere. In Fig. 7.4 we show the integrated flux in the *complete* observed SED (F_{obs}) divided by the integrated flux in a Kurucz model atmosphere (F_{atm}) as a function of T_{eff} . As parameters of the Kurucz models we choose $\log g=1.0$ and a metallicity of $[\text{Fe}/\text{H}]=-1.0$ as determined for this star. For T_{eff} in the range 7000–7500 K $F_{\text{obs}}/F_{\text{atm}}$ is approximately one. This ratio should be close to unity if the following assumptions hold. *i*) The extinction in the near-IR is negligible. *ii*) The extinction along our line of sight is similar to the average value of the extinction.

The first assumption holds unless there is a large amount of grey extinction. Extinction caused by particles smaller than the wavelength at which they absorb falls off steeply when

Figure 7.4: The ratio of the observed integrated flux over the integrated flux from the Kurucz model atmosphere scaled to the near-IR observations versus the effective temperature of the model atmosphere. The hatched area indicates the range in which this ratio equals unity within the uncertainties. We indicate the position of the corresponding spectral types taken from de Jager & Nieuwenhuijzen (1987) for supergiants along the top abscissa.

going to longer wavelengths. This is illustrated by the inset in Fig. 7.1 where we show a Kurucz model atmosphere with $T_{\text{eff}}=7250$ K before and after reddening with standard interstellar extinction. The extinction in the UV and visible is substantial but the flux level at wavelengths beyond $2 \mu\text{m}$ is hardly affected. Grey extinction is due to dust grains much larger than the wavelength at which they absorb. Typically these grains should have a diameter of at least several μm in order to cause wavelength independent extinction up to $4 \mu\text{m}$. It is unlikely that a large amount of such big grains grow in stellar outflows. Moreover, the presence of these large dust grains would have strong implications for the understanding of the complete nebula, most notably the nebular mass budget. These implications are discussed in Sect. 7.8.3.

The second condition, concerning the extinction along the line of sight compared to the average extinction, is more debatable. The mid-IR images as published by Meixner et al. (1997); Dayal et al. (1998) and Jura et al. (2000) show clear deviations from spherical sym-

metry. These asymmetries are due to a non-spherical distribution of the dust around the star. We can write a simple expression for the flux observed from the system.

$$F_{\text{obs}} = \underbrace{(1 - \eta_{\text{los}}) F_{\text{atm}}}_{\text{UV+visible}} + \underbrace{\eta_{\text{aver}} F_{\text{atm}}}_{\text{IR}} \Leftrightarrow \frac{F_{\text{obs}}}{F_{\text{atm}}} = 1 - \eta_{\text{los}} + \eta_{\text{aver}}, \quad (7.1)$$

where η_{los} is the fraction of the stellar flux absorbed in the line of sight towards the earth and η_{aver} is the fraction of the stellar flux absorbed, averaged over all lines of sight from the star. In this we assume that the energy absorbed in the CSE is re-emitted isotropically in the IR. The energy budget equation is further constrained by the observational fact that $\eta_{\text{aver}} = 1.25(1 - \eta_{\text{los}})$. This yields with Eq. (7.1) $F_{\text{obs}}/F_{\text{atm}} = 2.25 - 2.25 \eta_{\text{los}}$.

In case $\eta_{\text{los}} < \eta_{\text{aver}}$ (i.e. when we are viewing the system relatively unobscured) $F_{\text{obs}}/F_{\text{atm}}$ is larger than unity. This is due to light that the star emits in directions away from the direction of the earth. When this light is absorbed in the CSE and partly re-emitted towards earth we measure extra flux. This would allow for a lower T_{eff} than the 7000 K we derive from Fig. 7.4. However the observations put strong constraints on the importance of this effect. Mathematically η_{los} and η_{aver} can of course be in the range 0–1, but in practise the UV and visible photometric data reveal a reddened star and η_{los} must be larger than τ_V (~ 0.33). This is further corroborated by the fact that 56 per cent of the flux is emitted in the IR part of the spectrum. In Eq. (7.1) a value of η_{los} lower than 0.33 requires η_{aver} to be over 0.85. This corresponds to the unlikely situation in which the star is completely surrounded by an opaque CSE with a small hole through which we happen to view the star unobscured. Reasonable values of η_{los} are within 0.44–0.6 which corresponds to $F_{\text{obs}}/F_{\text{atm}} = 1.26$ –0.9 and $T_{\text{eff}} = 6800$ –7500 K.

It is important to note that both Meixner et al. (1997) and Dayal et al. (1998) have constructed models for HD 56126 in which $\eta_{\text{los}} > \eta_{\text{aver}}$ in order to reproduce the observed mid-IR morphology. This yields a T_{eff} in the high end tail of the range mentioned above. Likewise, interstellar extinction can be considered as an added contribution to η_{los} also yielding a higher effective temperature for the central star. Bogaert (1994, chapter 3) has observed stars in the vicinity of HD 56126 and estimates the interstellar contribution to the reddening to be $E(B-V)_{\text{IS}} = 0.04$. We conclude that a high effective temperature in the range 7000–7500 K fits best with all observed properties of HD 56126. In the following we use $T_{\text{eff}} = 7250$ K as derived by Van Winckel & Reyniers (2000).

7.4.2 Feature strength

What is also directly apparent from Fig. 7.1 is the large fraction of the light emitted in the IR features. We have indicated the HAC/PAH features and the “21” and “30” μm features. Together these features carry 40 per cent of the total IR flux (see also Table 7.3). Any self-consistent radiative transfer modelling of the nebula must take absorption and emission by the feature carriers into account. The reason for this is twofold. First, the feature carriers cause an important part of the reddening of the star. Thus, when comparing model results to the observed photometry these are essential to assess the validity of the model. Second, in the CSE these components absorb a sizeable part of the stellar light and thus determine, in part,

the temperature structure of the CSE as a whole. The temperature structure of the CSE is a very important parameter that translates directly into observables like the mid-IR spectrum and mid-IR surface brightness.

The strength of the IR features as seen in Fig. 7.1 also exposes the enigma of this nebula. Several of the observed features are supposedly carried by materials composed of elements with low abundances. The key question is: “Is it possible that trace species can cause such strong features?”. Note that this question applies not only to TiC concerning the “21” μm feature but similarly to the “30” μm feature which is produced by MgS. While Mg and S are both more abundant than Ti they are relatively unimportant in comparison to C (Van Winckel & Reyniers 2000) that causes the continuum.

7.5 Model

The purpose of this study is to construct a detailed model of the CSE of HD 56126. In our modelling we focus on two key questions:

- The composition of the CSE, i.e. the amount of the various dust components present. As we have already outlined in Sect. 7.1 we observe emission from several components for which various carriers have been proposed. However, which of these components are present has not been firmly determined or the amounts of these carriers in the nebula have not been quantified.
- The location of the dust. The latter is important since there is considerable disagreement in the literature regarding the evidence for a superwind phase (with mass loss rates possibly exceeding $10^{-4} M_{\odot}/\text{yr}$). Meixner et al. (1997) and Dayal et al. (1998) describe the mass-loss history with a low mass-loss phase followed by a superwind phase. Recently, Kwok et al. (2002) have obtained high angular resolution mid-IR images and find no evidence for a large-scale sudden ejection of material. On the other hand, von Helden et al. (2000) have proposed that the “21” μm feature is carried by TiC clusters and that the formation of these clusters requires an short phase of extreme mass loss.

Note that the observed mid-IR emission is not spherically symmetric but shows three intensity maxima along the limb-brightened inner edge of the dust shell (Meixner et al. 1997; Dayal et al. 1998; Jura et al. 2000; Kwok et al. 2002) (see also Fig. 7.3). We ignore this non-sphericity in our model because doing so greatly reduces the number of free parameters without compromising our analysis of the dust composition and density as a function of distance from the star. Because the nebula is largely optically thin, the deviations from spherical symmetry do not influence our conclusions. To confine the radial extent of the dust we compare the model results with the azimuthal averaged intensity profiles derived from the mid-IR images.

To model the absorption and emission of the circumstellar dust we use the dust radiative transfer program MODUST. This code solves the radiative transfer equation in spherical geometry subject to the constraint of radiative equilibrium. This yields the temperature of the dust. The code allows to have several different dust components of various grain sizes

and shapes. The density of the grains as a function distance can be prescribed in various ways. MODUST yields both the model SED and intensity maps. We refer to Bouwman et al. (2000) and Bouwman (2001) for a description of techniques used in MODUST. The following parameters for modelling the HD 56126 system are used:

- The input spectrum of the central star is given by a line blanketed Kurucz model atmosphere (Kurucz 1991). We use $T_{\text{eff}}=7250$ K and $\log(g)=1.0$. With these parameters and the observed total integrated light of $33.6 \cdot 10^{-12} \text{ W/m}^2$ the radius and luminosity of the star are related to the distance by:

$$R_{\star} = 20.5 d \text{ and } L_{\star} = 1051 d^2, \quad (7.2)$$

where $R_{\star}$ is the stellar radius in units of solar radii, $L_{\star}$ is the stellar luminosity in units of solar luminosities and d is the distance to the earth in kiloparsecs.

- The location of the dust is constrained by mid-IR imaging. The intensity maximum which is observed at $\sim 1.1''$ from the star corresponds to the inner edges of the dust shell in the case of optically thin emission, which is certainly satisfied at IR wavelengths. Because dust emission is clearly observed in all mid-IR images out to a $\sim 2.6''$ radius this constitutes a lower limit for the extent of the dust shell. However, the upper limit of the extent is not well constrained by current imaging and in the following we will treat the outer radius as a free parameter.
- The dust density (ρ) as a function of distance from the star (r) is specified in the form:

$$\rho = \rho_0 \left(\frac{r}{r_0} \right)^{-p}, \quad (7.3)$$

where ρ_0 is the dust density at the location of the inner edge of the shell (r_0) and the power p determines the steepness of the density profile. For a time-independent mass loss $p=2$. If the mass-loss rate has increased over time $p > 2$.

- The grain size distribution for each separate dust component can be specified with a powerlaw in the form:

$$n(a) \propto a^{-q}; \quad (a_{\min} \leq a \leq a_{\max}), \quad (7.4)$$

where a is the grain radius, $n(a)$ it the number density of grains with radius a and $a_{\min}$ and $a_{\max}$ are the minimum and maximum grain radius, respectively.

- We choose to keep the dust composition constant as a function of distance from the star. This means that the *relative* fraction of each grain material component, specified by chemical composition and size is fixed throughout the nebula. The dust shell consists of separate grain populations, i.e. each dust grain contains one material, implying that separate species can have different temperatures at the same location.

7.6 Optical properties

In this section we discuss the optical properties of the various solid state components that we use to model the HD 56126 system. Some of these materials have been well characterised in the laboratory over the broad wavelength range required for radiative transfer modelling. For other materials these data are not available and we describe how we treated the optical properties of these materials.

7.6.1 Carbonaceous compounds

There is general consensus that the mid-IR continuum in these sources is due to (hydro)carbon dust grains, possibly with inclusion of hydrogen. The UIR bands at ~ 3.3 , $6-9$ and $10-17 \mu\text{m}$, indicated in Fig. 7.1 and 7.2 correspond to the vibrational resonances of aromatic and aliphatic C-H and C-C bonds. Despite this general consensus, the exact nature of the carrier is under much debate. This is partly due to the many different structures in which carbon can appear. There are three possible bonding types between the carbon-atoms: sp^1 , the aromatic sp^2 bond, as in graphite, and the aliphatic sp^3 bond, as in diamond. It is due to this diversity of bonding types of carbon and the resulting diversity in material properties of the various carbonaceous compounds that carbonaceous dust in space has evaded firm identification. In the following we consider amorphous carbon and hydrogenated amorphous carbon.

Amorphous carbon

The most prominent dust component that we observe is the mid-IR continuum. It carries ~ 60 per cent of the IR flux. This emission is generally attributed to amorphous carbon (a-C). We use the values of the complex refractive index of amorphous carbon as published by Preibisch et al. (1993). These data range in wavelength from 0.1 to $800 \mu\text{m}$, which is sufficient to properly model the absorption and emission properties.

Hydrogenated amorphous carbon

The emission between $3-4$ and $11-17 \mu\text{m}$ is indicative of vibrationally excited C-H bonds. This indicates that the CSE contains a compound of carbon and hydrogen. When looked at in detail both emission from H-atoms bound to sp^2 and sp^3 sites is observed (Buss et al. 1990; Kwok et al. 2001). Such a mixture of hydrogen bonds is generally found in hydrogenated amorphous carbon (HAC). HAC is a likely condensate in H-rich and C-rich circumstellar ejecta. Therefore we include HAC in our model.

There is extensive literature on the properties of HAC in the material and surface science literature, where it is commonly referred to as *a-C:H* or *diamond-like amorphous carbon*. HAC films have received much attention as optical coatings because they can be manufactured to be relatively transparent in the $2-6 \mu\text{m}$ range; see Robertson (2002). As a result of this interest such films have been studied in great detail, we refer to Robertson (2002) for an excellent review of HAC properties. Here we only discuss the optical properties relevant

for the current study. Note that because of its application as optical coating the material research has been focused on those materials with low IR absorption. The more graphite-like materials, with high IR absorption levels (see below), have received much less attention.

HAC is a semiconductor. Its structure can be represented as sp^2 bonded clusters surrounded by sp^3 regions. The optical properties from the near-UV to the near-IR are determined by the π -electrons of the graphitic sp^2 bonds. This is due to the fact that the π -electrons are weaker bound than the σ -electrons of the sp^3 hybridisation. By varying the formation conditions, the sp^2/sp^3 ratio can be varied, which in turn allows to tune the absorptivity of HAC (Dischler et al. 1983). It is shown that the near-UV to visual absorption is determined by the size of the aromatic domains in the material (e.g. Angus et al. 1986; Robertson 1986, 2002). HAC contains a range of sizes of the aromatic domains and the level of absorption depends on the size of the largest aromatic clusters present in the structure at the concentration of few per cent.

In the visual range, HAC absorptivity has an empirically determined square-root dependence on photon energy and is usually expressed in the form of the so-called Tauc law (Tauc 1973):

$$\alpha(E)E = A_T (E - E_T)^2, \quad (7.5)$$

where E is the photon energy of the incoming light, $\alpha(E)$ is the absorptivity as a function of energy, A_T is a constant that determines the slope and E_T is the Tauc gap. E_T and the optical band-gap (i.e. the energy level above which photons couple efficiently to the valence electrons) are directly linked to the average size of the sp^2 domains.

At sub-band-gap energies the electronic absorptivity declines exponentially and is commonly expressed in an Urbach law:

$$\alpha = \alpha_U \exp \frac{E}{E_U}, \quad (7.6)$$

where E_U is the Urbach energy that determines the width of the tail, while α_U is a constant that determines the level. The width of the tail, i.e. E_U , is determined by the disorder in the material. Hydrogenated amorphous carbon is a heterogeneous material with a range of bond types and sizes of sp^2 bonded domains. As a consequence, the tail is broad. Typical values of the important parameters in the above equations are: $A_T \simeq 300 \text{ cm}^{-1}/\text{eV}$, $E_T \simeq 0\text{--}2 \text{ eV}$ and $E_U \simeq 200 \text{ meV}$.

In the IR range, the contribution of the electrons to the absorptivity is in general small, unless one goes to materials with very large aromatic domains, the limiting case of which is the conductor graphite that exhibits a very strong electronic continuum in the IR. The IR absorption of HAC is dominated by vibrational resonances.

We combine the observed optical properties of different HAC materials from various authors in order to determine the dependence on structural parameters from the UV to the IR. We use the H/C ratio as the parameter that determines the material properties. Note, that similar variations in the sp^2/sp^3 ratio as described below are observed in pure amorphous carbon films (e.g. Robertson 2002). However, here we study the effect of H/C because the astronomical spectra clearly show (through the features between 10 and 17 μm) that there are H-atoms bound to the C-atoms.

Figure 7.5: The optical parameters of HAC as a function of H content. The panels show, from top to bottom: 1) the fraction of carbon bonded by sp^2 bonds. 2,3,4) The integrated strength of the 11–17, 6–9 and the 3.3+3.4 μm bands, respectively. 5) The Urbach energy (see Eq. (7.6)). 6) The Tauc energy (see Eq. (7.5)).

Compagnini et al. (1995) have studied the optical and IR absorptivity of HAC films as a function of hydrogen content. These authors list the parameters for both the Tauc law in the visible and the Urbach tail dominating the electronic continuum in the IR. For the HAC materials concerned here, hydrogen incorporation determines the structural parameters because hydrogen inclusion favours sp^3 bonding. Hydrogen incorporation therefore limits the size of the graphitic domains. Thus, with increasing hydrogen content the electronic absorption decreases and the optical gap increases. This can be seen in Fig. 7.5, where we give the optical parameters of HAC as a function of hydrogen content.

A clear correlation is found between the optical gap and the strength of the integrated aromatic plus aliphatic CH stretching feature around $3.3\ \mu\text{m}$ (Dischler 1987). We use this relation to link the strength of the CH stretching mode to the electronic continuum level (cf., Fig. 7.5).

Bounouh et al. (1995) discuss the influence of annealing on the IR vibrational spectrum of HAC. Annealing removes H and as a result produces more and more graphite-like HAC. We use the strengths of the vibrational bands at 3.3 , 3.4 , $6-9$ and $10-17\ \mu\text{m}$ for their series I material to empirically determine the strength of the bands as a function of H/C ratio.

HAC material also exhibits a far-IR continuum due to vibrations. Unfortunately, these contributions have not been studied well because they contain little diagnostic value for the material properties. Following Schutte et al. (1993), we estimate the level of the far-IR vibrational continuum from the vibrational resonances observed in aromatic molecules. Moutou et al. (1996) have measured the far-IR spectra of a variety of different PAHs. We use the resonances these authors find to define an average far-IR continuum. We apply the following procedure to construct this average. We take the wavelength and absorption cross-section per C-atom for each of the 125 resonances listed in Tab. 3 of Moutou et al. (1996) and convolve these with a Gauss function with a full-width-at-half-maximum of $80\ \text{cm}^{-1}$. After adding the contributions we renormalise by dividing by the total number of molecules (40) in the database and converting to absorptivity values in cm^{-1} using a typical value for the density of $2\ \text{g/cm}^3$. The far-IR contribution that we obtain in this way is not completely smooth but shows some structure (see the $20-50\ \mu\text{m}$ range in Fig. 7.6). This structure is most likely due to the fact that we included 'only' 40 molecules in a limited size range to construct the average absorption. A larger number of molecules will probably fill in the gaps and yield a smoother far-IR continuum. Since this spectral structure is weak compared to the near- and mid-IR features and is lost in the emission from other dust components in the circumstellar spectrum, we have refrained from (arbitrarily) smoothing it out. The optical gap and the sp^2 fraction are correlated as explained above. The measured relation for a large number of HAC and a-C materials is given in Robertson (2002, Fig. 58) from which we derive the sp^2 fraction (cf., Fig. 7.5). The final estimate for the far-IR vibrational continuum is the product of the sp^2 fraction and the average far-IR "continuum" as measured from PAHs. The estimate that we obtain is a lower limit to the real vibrational contribution to the far-IR absorptivity because we only consider the contributions due to the graphitic (sp^2) fraction in HAC, while in reality the sp^3 skeleton will also contribute.

We show the dependence of the various parameters on the hydrogen incorporation in Fig. 7.5. The strong increase in the Tauc and Urbach energy with $H/(H+C)$ is apparent. Likewise, the 3.3 and $3.4\ \mu\text{m}$ CH stretch modes increase with $H/(H+C)$ fraction. Notice how the

Figure 7.6: Absorption coefficient (α) of HAC as a function of wavelength for changing values of hydrogen content. For details concerning the method used to derive the absorptivity, see text.

strength of the C-H out-of-plane bending modes between 11 and 17 μm (in Fig. 7.5 represented by I_{12}) increases with decreasing H content. This seemingly contradictory behaviour is caused by the fact that in absolute terms the H bonded to sp^2 sites increases during annealing. In this process some of the H bonded to the sp^3 sites is converted into H bonded to sp^2 sites. The absorptivity per sp^2 C-H bond is much larger than per sp^3 C-H and the result is an increase of I_{12} . In contrast the aliphatic CH stretching modes around 3.4 μm are stronger than the aromatic modes (3.3 μm)

The wavelength dependent absorption cross-sections are shown in Fig. 7.6. The main effect is that the *complete* continuum level from the UV to the IR decreases with increasing hydrogen content. Because the UV/visible part of the spectrum decreases less than the IR, HAC with a higher H concentration will be warmer. While the continuum increases and the CH stretching modes at 3.3 strengthen with increasing H content, the mid-IR resonances between 6–9 and 10–17 μm diminish in relative strength. In the following we refer to HAC with $\text{H}/(\text{H}+\text{C}) = x$ as HAC_x .

7.6.2 Coal

Guillois et al. (1996) have carried out a spectroscopic comparison between the emission fea-

Figure 7.7: A comparison between the optical properties of HAC as derived from our model and “standard coal” as taken from Guillois et al. (1994). The continuum of coal lies between the $H/(H+C)=0.10$ and the $H/(H+C)=0.25$ curves.

tures of carbon-rich post-AGBs and terrestrial coals. This comparison looks very promising. Of course the CSE of post-AGB objects do not contain coals as such since coals are the product of the biological cycle in the earth-ecosystem. However, it may be worthwhile to consider materials with a very different formation mechanism as analogues to circumstellar materials.

In stark contrast to HAC, the optical properties of coal have been studied much less and no spectra that cover the full wavelength range from the UV to the IR for one single sample are available. Moreover there is a large spread in the derived complex refractive index of coals; see for example the comparisons made in Manickavasagam (1993) and Bhattacharya et al. (1996). This large spread is probably due to the wide variety of coal structural properties, even for materials that are labelled the same. When studying more controlled and limited samples of coal similar trends as described in Sect. 7.6.1 are recovered. For example, Ibarra et al. (1996) find a very similar dependence of the aromatic fraction on the hydrogen content as found in HAC. Likewise, similar behaviour for the strength of the 3.3 versus the 3.4 μm band as a function of aromaticity (towards anthracite) is found (Černý 1996). Brewster & Kunitomo (1984) find a significant increase in the free electron absorptivity upon graphitisation, again the same as is found in HAC. Unfortunately, there are no coal data available that cover the UV to the IR obtained using one single sample. However, from the similar behaviour found

in coals and in HAC we conclude that our HAC model applies to coals as well.

One important difference between coals and HAC is the inclusion of atom impurities, primarily O and mineral phases in coals. Of course our HAC model will not be able to reproduce the effects of these impurities. The effects of impurities in the CSE of carbon stars must however be limited because impurities have clear spectroscopic signatures like strong emission from O-H ($\sim 3 \mu\text{m}$) and C=O groups ($5.8 \mu\text{m}$) (Puente et al. 1998). Such signatures are not detected in the astronomical spectrum. We conclude that in so far coal can be used as an analogue for astronomical carbonaceous grains, its spectral properties can be well represented by those of HAC.

In Fig. 7.7 we show a comparison between the optical properties as derived from our model and the optical properties of “standard coal” taken from Guillois et al. (1994). Their coal optical properties are not derived from one single sample and the data from 0.7 to $3 \mu\text{m}$ are not measured but interpolated. The interpolated optical properties in coal are higher than the Urbach tail in HAC_{0.25}. At the same time, the IR absorption properties adopted by Guillois et al. (1994) are much weaker than the HAC_{0.25} features. This difference will give rise to a higher temperature for the “coal” than for HAC.

7.6.3 Magnesium sulfide

Begemann et al. (1994) have published the measured values of the complex refractive index (n and k values) in the $10\text{--}500 \mu\text{m}$ range of $\text{Mg}_x\text{Fe}_{(1-x)}\text{S}$ with $x=0.0, 0.1, 0.5, 0.75, 0.9$. They find little difference between the samples with $x=0.75$ and $x=0.9$ and these authors suggest that the $x=0.9$ sample is a good substitute for MgS. In order to reliably model the MgS contribution we need the optical properties in the UV to near-IR range as well. These data are unfortunately not available. We have opted to assume a grain size (a_{model}) and calculate the mid-IR absorption cross section from the n and k values in a continuous distribution of ellipsoids (CDE) shape distribution following Bohren & Huffman (1983, Chapter 12). We use the CDE distribution because this yields an emission profile closest to the observed profile in many carbon rich evolved stars (e.g. Begemann et al. 1994; Szczerba et al. 1999, see also Chapter 6). By dividing the obtained cross section by the geometrical cross section we obtain the dimensionless absorption efficiency $Q(\lambda)$. In the wavelength range 0 to $1 \mu\text{m}$ we assume $Q=1$, from 1 to $2 \mu\text{m}$ we decrease Q linearly to 0 and from 2 to $10 \mu\text{m}$ we take $Q=0$.

The assumptions above are of course unrealistic and will (most likely) overestimate the visual absorption for a given grain size. However, this does not influence the derived mass as we can easily derive the MgS grain temperature from the emission profile (see Chapter 6). In thermal balance the MgS temperature is determined by the ratio of visual over the IR absorption efficiency. In general the IR efficiency decreases more rapidly with decreasing grain size than the UV and visible efficiency. Therefore, using the MgS temperature derived from the peak of the feature, there exists a grain radius (a_{CSE}) for which the absorption equals the observed emission in the MgS band. This value of a_{CSE} will be smaller or equal to the initial assumed grain size a_{model} . The mass that we derive does not depend on the grain size since the individual grains are optically thin at $30 \mu\text{m}$ and therefore the emission scales with the mass (see also Sect. 7.7.4).

7.6.4 Titanium carbide nano-crystals

The identification of TiC as the carrier of the “21” μm feature is based on the wavelength coincidence of a strong resonance found in TiC nano-crystals with the “21” μm feature (von Helden et al. 2000). The optical properties of such nano-crystals have so far not been determined in the laboratory. The optical properties of TiC in the bulk have been studied extensively (Lye & Logothetis 1966; Alward et al. 1975; Ihara et al. 1975; Lynch et al. 1980; Pflüger et al. 1984; Koide et al. 1990, 1993; Delin et al. 1996; Espinosa-Magaña et al. 2002). Although these studies are focused on the high energy range (the longest wavelength presented is 12 μm), they consistently find a large free electron contribution to the optical properties in the infrared. Henning & Mutschke (2001) present the first mid-IR spectroscopy of bulk TiC. Their spectrum indeed shows a strong mid-IR continuum due to free electrons. They find no resonance at 20.1 μm and only a very weak resonance near 19 μm , much weaker than the resonance found in nano-TiC.

In principle one can predict how some changes in spectral behaviour occur when comparing bulk optical properties with those of small (<200 atoms) clusters (Kreibig & Vollmer 1995). One of the effects is the limitation on the electron mean free-path (Kreibig & Frangstein 1969). This effect is caused by “free” electrons that are scattered off the surface of the nano-crystal with a frequency that exceeds the frequency of collisions in the bulk material. In order to quantitatively calculate changes in the optical constants with respect to the bulk optical properties requires separating the contribution of non-conducting electrons to the optical absorption from the free-electron contribution. For example, a detailed description of how to apply this correction for silver is given in Alvarez et al. (1997). This separation is based on fitting the optical properties over a wavelength range where the free-electron contribution to the absorption provides the dominant source of opacity. However, in TiC there is no wavelength range where this is clearly the case. For example Koide et al. (1993) find (besides free-electron opacity) inter-band transitions, due to non-conducting electrons, up to 12 μm ; the longest wavelength they measured. As a consequence, the estimated contribution due to free electrons derived in one wavelength range yields results that clearly over- or underestimate the free-electron contribution in other wavelength ranges.

Another observed effect is the strengthening of the 20 μm resonance. If we translate the strength of the 20 μm feature in nano-crystalline TiC to bulk samples this resonance would stand out clearly in the spectrum. Instead, a feature is barely detected (Henning & Mutschke 2001). This immediately shows that bulk TiC cannot explain the observed “21” μm feature. *Therefore, if TiC is the carrier of the “21” μm feature the TiC must be in grains or polycrystalline domains smaller than a few hundred atoms.*

Other quantum effects may also be important in nano-crystalline materials. The localisation of the electrons may result in a material that behaves like a semi-conductor or insulator in the nano-crystalline phase even if the bulk material is a good conductor. Such behaviour has been observed for example in mercury (Busani et al. 1998).

The issues outlined above leave it impossible to derive reliable optical constants for TiC nano-crystals in a simple semi-empirical way. It is clear that these issues can only be satisfactorily resolved by laboratory measurements of the optical properties of nano-TiC. Still, for our radiative transfer calculations some assumptions about the optical properties of TiC must

be made. For the emission of the TiC grains we have adopted an approach similar to the one outlined above for MgS. We use the absorption profile and strength for TiC nano-crystals as presented by von Helden et al. (2000) and assume a constant level for the UV/visible absorption efficiency. This yields a TiC mass as a function of the UV/visible absorption level.

7.7 Radiative transfer modelling

7.7.1 Initial model

We first model only the dust continuum due to amorphous carbon. We use the parameters as described above. As a starting point for the fitting procedure we use a constant mass loss and outflow velocity profile ($\rho \propto r^{-2}$) during a period of 10 000 years. This corresponds to an envelope with radius of $\sim 10''$. We use a single grain size of $0.1 \mu\text{m}$. Amorphous carbon grains of this size reach the highest temperature in radiative equilibrium, given the radiation field of the central star. We vary the density at the inner edge of the envelope (ρ_0) to fit the emission at the shortest wavelengths of the SWS spectrum. The emission at the shortest wavelengths is sensitive only to the warmest dust which allows us to derive the mass of the warmest amorphous carbon grains. We choose 9–10 and $18 \mu\text{m}$ as reference points. Below $9 \mu\text{m}$ the data are noisy and/or the contributions from the star and the features are more difficult to estimate while at longer wavelengths the emission is partly due to cooler grains.

7.7.2 Cold component/extent of the nebula

The model that we construct in this way over predicts the flux levels beyond $40 \mu\text{m}$ by ~ 10 – 20 per cent, i.e. the model contains too much cold material. At the same time the modelled $11.9 \mu\text{m}$ spatial intensity profile drops more steeply than observed within the closest $2.6''$. The same has been noted by Meixner et al. (1997) and Jura et al. (2000). Meixner et al. (1997) use $\rho \propto r^{-1}$ ($p=1$) in order to fit their mid-IR images. However, this introduces even more cold dust located far from the star.

Because the ‘ $p=2$ ’-model over predicts the flux levels at the longest wavelengths together with the fact that the observed intensity profile from the inner envelope (1 – $2.6''$) requires $p=1$, prompts us to limit the extent of the nebula.

From an observational point of view there is no evidence that the envelope extends beyond $\sim 2.6''$. All available images show only emission from this inner region. Note, that this is not conclusive evidence because the available mid-IR images are all at wavelength shorter than $25 \mu\text{m}$, i.e. at the Wien side of the dust emission (see Fig. 7.1). This emission is extremely sensitive to the dust temperature and the cool dust far away from the star does not contribute much. Deep optical images that show scattered light from the nebula (Ueta et al. 2000) show no evidence for emission outside the $\sim 3''$ radius. Noteworthy in this respect is that the very high quality continuum images at 10 and $18 \mu\text{m}$, as presented by Kwok et al. (2002), are very similar in morphology and *size* while a dust envelope that continues beyond $3''$ would cause the $18 \mu\text{m}$ images to be ~ 25 per cent larger than the $10 \mu\text{m}$ image, where the size is measured at 10 per cent of the peak intensity. This ‘growing’ with increasing wavelength is

	H/C	$T_{\max}$ [K]	$F_{6-17,\text{HAC}}/F_{6-17,\text{obs}}$
a-C	0	170	-
HAC _{0.10}	0.11	188	1.4
HAC _{0.20}	0.25	190	1.7
HAC _{0.30}	0.43	195	1.4
HAC _{0.35}	0.54	205	0.8
HAC _{0.40}	0.67	205	0.5
HAC _{0.45}	0.82	205	0.2

Table 7.4: HAC temperature and band strength as a function of H/(H+C). H/C is the relative number of H-atoms to C-atoms. $T_{\max}$ is the maximum temperature of the grains. $F_{6-17,\text{HAC}}/F_{6-17,\text{obs}}$ is ratio of the integrated flux emitted in the plateau features in the model over the observed integrated flux in the plateau features, assuming equal mass of HAC_{*X*} and amorphous carbon.

not observed. We construct a model with the same parameters as above but with $p=1$. This model fits the observed $11.9\ \mu\text{m}$ intensity profile much better than a r^{-2} law. From this we derive an upper limit on the outer radius of the envelope of $4''$. A larger envelope produces too much far-IR flux.

Up to now we only considered $0.1\ \mu\text{m}$ amorphous carbon grains. In reality grains of different sizes are expected to form (Dominik et al. 1989). We use a standard MRN size distribution (Mathis et al. 1977): $n(a) \propto a^{-3.5}$. We use $0.01\ \mu\text{m}$ and $1.0\ \mu\text{m}$ as the smallest and largest grain radius, respectively.

As described above the outer radius of the envelope is determined spectroscopically from the far-IR flux levels, i.e. the relative amounts of warm and cool a-C. A grain-size distribution affects these relative amounts because grains of different size reach different temperatures. Therefore, by using a grain-size distribution the outer radius can be further constrained. With the grain-size distribution as described we find that with a size of $4''$ the predicted far-IR fluxes are 50 per cent too high. We find that the best fitting outer radius of the envelope is $2.6''$. We use this outer radius in the following analysis.

7.7.3 HAC temperature

We include HAC as an additional component to a-C. We vary H/C and the amount of HAC to best fit the observations. We do not aim to fit the features in detail but aim to determine if HAC reaches the temperature needed to explain the relative band strength of the broad emission features. With increasing H/C both the UV/visible and the IR absorptivity decrease. Because the IR absorptivity decreases more steeply, grains with a high H/C will be warmest. On the other hand, the amount of HAC required to explain the energy emitted in the features increases with H/C content because HAC with high H/C absorbs the stellar light less efficiently. In Table 7.4 we give the temperature that HAC grains reach at the inside of the envelope and the strength of the features as a function of hydrogen content. All HAC grains are warmer than a-C grains. In the H/(H+C)=0.35–0.45 range HAC grain reach a maximum

temperature of ~ 205 K. $F_{6-17, \text{HAC}}/F_{6-17, \text{obs}}$ gives the integrated strength of the plateau features relative to the observed strength assuming that the total HAC mass is equal to the a-C mass. Note, that we list the *total* flux emitted in the two plateau features. In all cases the flux emitted in the 10–17 μm band dominates and the 6–9 μm band is too weak compared to the observations, i.e. the temperature is too low.

As can be seen from Table 7.4, HAC_{0.35} is optimal in the sense that it reaches a high temperature while requiring ‘only’ equal mass as contained in a-C. To get the band strength of the 6–9 and 10–17 μm features right we would have to decrease the inner radius of the envelope. The band strengths are correct only when we would decrease the inner radius to $\sim 0.5''$. At $0.5''$ the HAC grains reach a temperature of ~ 290 K. However, such a small inner radius of the dust envelope is inconsistent with the available mid-IR images.

The comparison with the observations becomes worse in the 3 μm region. In our model HAC_{0.35} produces no discernible aromatic 3.28 μm or aliphatic 3.42 μm feature while both are observed (Kwok et al. 1990). We conclude that HAC grains in radiative equilibrium do not reach the temperature required to explain the observed strength of the 3 and 6–9 μm features relative to the 10–17 μm plateau features.

7.7.4 Magnesium sulfide

Before we include MgS in our model we derive the mass of the MgS component in a simple, relatively model independent, way. In the limit of grains much smaller than the wavelength (Rayleigh limit), the absorptivity of a grain scales linearly with the mass of the grain. In the optically thin case the observed flux can thus be expressed in terms of distance from the earth (d), grain temperature (T) and total mass (M) alone. This can easily be derived in the following way. Consider the flux density emitted by a single grain (f_1) of radius a and temperature T :

$$f_1(\lambda, a, T(a)) = 4\pi a^2 Q(\lambda, a) \pi B(\lambda, T(a)) = 3V(a) \frac{Q(\lambda, a)}{a} \pi B(\lambda, T(a)), \quad (7.7)$$

where λ is the wavelength, $Q(\lambda, a)$ is the absorption efficiency; thus $4\pi a^2 Q(\lambda, a)$ is the effective radiating surface of the grain, $\pi B(\lambda, T(a))$ is the black body flux density emitted per unit area and $V(a)$ is the volume of the grain. In the Rayleigh limit $\frac{Q(\lambda, a)}{a}$ is independent of a and therefore T is independent of a and we can write:

$$\begin{aligned} f_1(\lambda, a, T) &= 3 \frac{M(a)}{\rho} C(\lambda) \pi B(\lambda, T) \Rightarrow \\ f_{\text{tot}} &= \sum_i 3 \frac{M(a_i)}{\rho} C(\lambda) \pi B(\lambda, T) = 3 \frac{M_{\text{tot}}}{\rho} C(\lambda) \pi B(\lambda, T), \end{aligned} \quad (7.8)$$

where $M(a)$ is the mass of the grain, ρ is the density of the material $C(\lambda) = \frac{Q(\lambda, a)}{a}$ and f_{tot} is the total flux density emitted by all grains, the summation is done over all grains (i) and M_{tot} is the total mass of the grains. Integrating over wavelength and correcting for the distance we

finally obtain:

$$\begin{aligned}
 F_{\lambda_{0,1}} &= \frac{1}{4\pi d^2} \int_{\lambda_0}^{\lambda_1} 3 \frac{M_{\text{tot}}}{\rho} C(\lambda) \pi B(\lambda, T) d\lambda \quad \text{and} \\
 M_{\text{tot}} &= \frac{4}{3} F_{\lambda_{0,1}} d^2 \rho \left(\int_{\lambda_0}^{\lambda_1} C(\lambda) B(\lambda, T) d\lambda \right)^{-1}, \tag{7.9}
 \end{aligned}$$

where $F_{\lambda_{0,1}}$ is the observed flux integrated between $\lambda=\lambda_0$ and $\lambda=\lambda_1$. The last term in Eq. (7.9) depends only on T for a given material. The peak position of the “30” μm feature is a good indicator of T for MgS (Chapter 6) and we derive $T_{\text{MgS}} \simeq 150$ K from the observed peak position in the spectrum of HD 56126. Using the measured values $\rho = 3 \text{ g/cm}^3$, $F_{10,50} = 2.7 \cdot 10^{-12} \text{ W/m}^2$ and $d=2400 \text{ pc}$ we find $M_{\text{MgS}} = 9 \cdot 10^{-6} M_{\odot}$.

If we assume that all S is condensed in the form of MgS we can calculate the total corresponding envelope mass (M_{env}). Van Winckel & Reyniers (2000) have measured the atmospheric abundance by number of both Mg/H and S/H to be $\sim 4 \cdot 10^{-6}$, which yields a M_{env} of $0.06 M_{\odot}$. The mass of the envelope is variously estimated by fitting the SED and mid-IR imaging at $0.54 M_{\odot}$ (Meixner et al. 1997), $0.26 M_{\odot}$ (Dayal et al. 1998) and $0.4 M_{\odot}$ that we derive below. We conclude that the abundances of Mg and S are consistent with the strength of the “30” μm feature.

Of course these values of M_{MgS} and M_{env} are lower limits. First, because we have assumed that *all* the MgS is at 150 K. In reality there will be a range of temperatures. The colder grains are more “hidden” and this increases M_{MgS} , see Eq. (7.9). However, decreasing T_{MgS} to 100 K increases M_{MgS} by a factor 5 which still yields a reasonable value for M_{env} . However such a temperature is too low to be compatible with the observed peak position of the “30” μm feature. Second, because we assume that all Mg- and S-atoms are condensed into MgS to derive M_{env} from M_{MgS} . We point out that there are no other Mg or S bearing components identified in the nebula. We conclude that from a simple analysis the strength of the MgS feature as observed in HD 56126 is compatible with the available Mg- and S-atoms.

We include MgS in the radiative transfer model using the optical properties as described in Sect. 7.6.3. The only free parameters are the MgS grain size and the relative mass fraction. We find that a grain size of $a_{\text{MgS}} \simeq 0.01\text{--}0.02 \mu\text{m}$ fits best with the observed profile of the “30” μm feature. Larger grains are too cold and cause the “30” μm feature to peak at longer wavelength than observed. The mass of the MgS component is 4 per cent of the a-C, or $1.5 \cdot 10^{-5} M_{\odot}$ at $d=2.4 \text{ kpc}$; this is in excellent agreement with the $0.9 \cdot 10^{-5} M_{\odot}$ we derive from the simple considerations above, assuming $T_{\text{MgS}}=150 \text{ K}$.

7.7.5 Titanium carbide

As discussed above (Sect. 7.6.4) only TiC nano-crystals are expected to show a strong “21” μm feature. Such nano-crystals will undergo a temperature spike upon absorption of a single UV/visible photon. Cooling then occurs through emission in the “21” μm feature. The mass of TiC is directly determined from the energy balance: the IR flux is equal to the absorbed UV/visible flux, which is given by our radiative transfer calculation. In Fig. 7.8

Figure 7.8: The mass of the TiC component as a function of the UV/visible absorption coefficient (α). We show the TiC mass derived from the strength of the “21” μm feature for different values of the UV/visible absorption coefficient (black line). A higher absorption coefficient requires less TiC. The grey diamond indicates the measured absorption coefficient of bulk TiC. The right abscissa shows the corresponding total envelope mass. The hatched area indicates reasonable values for the total envelope mass. The absorption coefficient of nano-TiC needs to be ~ 20 times higher than bulk to be compatible with the observed strength of the “21” μm feature.

we show the mass of TiC in the envelope that we derive as a function of the UV/visible absorption coefficient using the Ti/H abundance of $1.3 \cdot 10^{-8}$ (Van Winckel & Reyniers 2000). We also show the measured absorption coefficient of bulk TiC. It is clear from Fig. 7.8 that bulk TiC can not explain the strength of the feature even if all the energy absorbed would be emitted solely in the “21” μm resonance. In order to be compatible with the observed band strength nano-TiC needs to absorb 20 times more efficiently per Ti-atom in the $0.2\text{--}0.7 \mu\text{m}$ wavelength range than bulk TiC. This corresponds to a visual absorption efficiency (Q_{vis}) of ~ 8 for a $10 \times 10 \times 10$ -atom nano-crystal. Such a high value for the visual absorption coefficient is only possible if, due to the nanometer size scale, a strong electronic resonance is present in nano-TiC. This problem is already evident in the complete spectrum as presented in Fig. 7.1. Either the carrier of the “21” μm feature is as abundant as MgS or it has a much higher UV/visible absorptivity.

7.8 Results and discussion

7.8.1 Best fit model

In Fig. 7.9 we compare the predicted and observed SED. Our best model fits the observations in many details. Note that the ordinate scale is linear while previously published SED fits are compared on a logarithmic basis. The peak of the SED, the shape and strength of the “30” μm feature and the shape of the “21” μm feature are very well explained by the model. There are two places where the model fails to reproduce the details of the observations: *i*) The UV flux levels are over predicted. It is clear that an important UV absorption component is missing in our model. Laboratory studies of the UV absorption properties of MgS and TiC are therefore needed. *ii*) The strength of the 6–9 μm band is too small in the model. The discrepancy in at 6–9 μm is discussed in Sect. 7.8.4.

In Table 7.5 we summarise the main parameters of the best fit model. We find that the observations are best explained with a compact dust shell that extends from 1.1–2.6″. The mass of the *dust* contained in the shell is $\sim 7 \cdot 10^{-4} M_{\odot}$. Assuming a constant outflow velocity of 10.7 km/s (Knapp et al. 1998) we calculate that the mass-loss commenced 2800 yr ago and halted 1200 yr ago. Using a value of 220, as is often used for carbon-rich circumstellar matter, for the $M_{\text{gas}}/M_{\text{dust}}$ we find that the time averaged mass-loss rate is $\sim 10^{-4} M_{\odot}/\text{yr}$. We find that 2 per cent of the dust (by mass) is contained in MgS, consistent with the observed photospheric abundance of Mg and S.

7.8.2 Previous dust models

The circumstellar environment of HD 56126 has been studied before using both mid-IR spectroscopic and imaging observations (Meixner et al. 1997; Dayal et al. 1998; Hrivnak et al. 2000; Jura et al. 2000). It is useful to compare the parameters we derive to those found before. The main difference between our model and previous work is the fact that we treat the dust composition in considerable detail. However, there are other significant differences as well. We find that the CSE of HD 56126 is well represented by a compact shell of 2.6″ radius. We have argued above that a larger outer radius will cause an increase of the size of the nebula with increasing wavelength, contrary to the observations. Of course, a preceding phase with a much lower mass-loss rate would go undetected. The model of Skinner et al. (1995) contains a more extended component. The absence of this more extended component in our model is reflected in relatively low envelope mass of $0.15 M_{\odot}$ that we derive. This is because cold material far away does not contribute to the mid-IR fluxes but does contain mass. This “hidden” component is therefore important in determining the total envelope mass. Imaging at sub-mm wavelengths is needed to better constrain the cold envelope mass.

Skinner et al. (1995) find $M_{\text{env}} = 0.54 M_{\odot}$ at a distance of 3 kpc, with two-thirds of the mass in the extended component. The mass of the inner component that they derive corresponds well to the mass of the a-C grains that we derive after correcting for the distance. Dayal et al. (1998) derive an envelope mass of $0.26 M_{\odot}$ at 2.7 kpc, which corresponds to $0.2 M_{\odot}$ at 2.4 kpc. These authors use a compact model with all dust contained within 2.2″ but with two distinct fixed temperatures. In view of the difference in approach, the envelope mass they find

Figure 7.9: A comparison between the observed SED (triangles) and our best fitting model (thick grey line). The model reproduces the dust continuum and the “30” μm feature very well. The model does not reproduce the strength of the 6–9 μm feature and the extinction in the UV. Underneath the IR emission spectrum we give an indication of the contributions of the various dust components offset by $\sim 5 \cdot 10^{-12}$ W/m².

and our mass determination are compatible. Hrivnak et al. (2000) derive a mass-loss rate of $3.6 \cdot 10^{-5} M_{\odot}/\text{yr}$ at the distance of 2 kpc, which corresponds to $5 \cdot 10^{-5} M_{\odot}/\text{yr}$ at 2.5 kpc, about half of the value that we find. Jura et al. (2000) model the density in the envelope as the result of a “dying” wind, i.e. a decreasing mass-loss rate with time. This is qualitatively consistent with the $\rho_0 (R/R_{\text{in}})^{-1}$ density prescription that we use. These authors find a maximum mass-loss rate of $\sim 3 \cdot 10^{-5} M_{\odot}/\text{yr}$. However, they model the emission of the dust with a simplified amorphous carbon opacity function. This yields a mass estimate compatible with the warmest a-C grains ($a=0.1 \mu\text{m}$) in our model. Correcting for the mass of the other grains, the different distance and the $M_{\text{gas}}/M_{\text{dust}}$ ratio they use, they find $11 \cdot 10^{-5} M_{\odot}/\text{yr}$ compatible with the mass-loss rate that we derived.

7.8.3 Envelope mass; $M_{\text{gas}}/M_{\text{dust}}$

The total envelope mass that we and other authors derive scales with the gas-to-dust mass ratio. For carbon-rich AGB and post-AGB stars values between 200 and 250 are often used (e.g. Jura 1986; Meixner et al. 1997) and in the above derivations we have used 220. However this value is very uncertain. Because the bulk of the dust is carbon-based one can expect $M_{\text{gas}}/M_{\text{dust}}$ to strongly depend on the C/O ratio. The photospheric abundances determination of Van Winckel & Reyniers (2000) yield $[\text{C}/\text{H}]=8.53-8.77$ and $\text{C}/\text{O}=0.7-1.4$. Taking values in the high end of this range and assuming that all carbon is locked in either CO (70 per cent) or dust (30 per cent) we find $M_{\text{gas}}/M_{\text{dust,C}} \gtrsim 600$, in which $M_{\text{dust,C}}$ is the mass of the carbon-based dust component. This high value of $M_{\text{gas}}/M_{\text{dust}}$ follows directly from the elemental abundance measurements. We find $M_{\text{dust,C}}=6.8 \cdot 10^{-4} M_{\odot}$ (see Table 7.5) which corresponds to $M_{\text{gas}}=0.4 M_{\odot}$. When we consider that the star had a ZAMS-mass of $\sim 1.1 M_{\odot}$ and the core-mass is roughly $0.6 M_{\odot}$ we conclude that nearly the entire envelope was lost during a high mass loss phase of ~ 1500 yr. We also conclude that only a small amount of the dust can be “hidden” in cold grains, either far away from the star or in larger grains. This argues strongly against the importance of grey extinction due to large grains. Using the envelope mass of $0.4 M_{\odot}$ we find a high time-averaged mass-loss rate of a $\sim 3 \cdot 10^{-4} M_{\odot}$. We conclude that *HD 56126 has experienced a short period (1500 year) of very strong mass loss ($3 \cdot 10^{-4} M_{\odot}/\text{yr}$) during which the entire envelope was lost*. If we adopt lower C/H and C/O values this conclusion would only be strengthened.

7.8.4 The temperature of the HAC

One of the main discussion points concerning the relation between HAC (or any other solid carrier) and the 3 to $17 \mu\text{m}$ features found in C-rich environments is whether a solid particle *in radiative equilibrium* is able to explain the observed spectra. In particular the large feature to continuum ratios found in the astronomical spectra and the relatively short wavelengths ($3 \mu\text{m}$) at which emission is found appear difficult to obtain in radiative equilibrium. Indeed, one can immediately see from Fig. 7.1 precisely that difficulty; the peak of the SED lies beyond $20 \mu\text{m}$ while strong features on a weak continuum are present in the $5-17 \mu\text{m}$ range. The fundamental question is whether solid grains can reach the temperature required to emit efficiently at these wavelengths.

Central star			Comments	
d	[kpc]	2.4		
T_{eff}	[K]	7250		
$R_{\star} \propto d^2$	$[R_{\odot}]$	49		
$L_{\star} \propto d^2$	$[L_{\odot}]$	6000		
Dust shell				
$R_{\text{in}} \propto d$	[cm]	$4.0 \cdot 10^{16}$	1.1''	
$R_{\text{out}} \propto d$	[cm]	$9.3 \cdot 10^{16}$	2.6''	
v_{exp}	[km/s]	10.7		Knapp et al. (1998)
$\Delta t_{\text{in}} \propto d/v_{\text{exp}}$	[yr]	1200		
$\Delta t_{\text{out}} \propto d/v_{\text{exp}}$	[yr]	2800		
ρ_0	$[\text{g}/\text{cm}^3]$	$8 \cdot 10^{-22}$		
α		-1	$\rho(R)=\rho_0 \left(\frac{R}{R_{\text{in}}}\right)^{\alpha}$	
Dust species		Mass	%	
dust $\propto d^2$	$[M_{\odot}]$	$6.9 \cdot 10^{-4}$	100	
a-C $\propto d^2$	$[M_{\odot}]$	$3.4 \cdot 10^{-4}$	49	$a=0.01-1 \mu\text{m}$
HAC $\propto d^2$	$[M_{\odot}]$	$3.4 \cdot 10^{-4}$	49	$\text{H}/(\text{H}+\text{C})=0.35$
MgS $\propto d^2$	$[M_{\odot}]$	$1.4 \cdot 10^{-5}$	2	CDE
TiC $\propto d^2$	$[M_{\odot}]$	$8 \cdot 10^{-6}$	—	$Q_{\text{vis}}=Q_{\text{bulk}}$
TiC $\propto d^2$	$[M_{\odot}]$	$3 \cdot 10^{-7}$	—	$Q_{\text{vis}}=10$
Envelope				
$M_{\text{env}} \propto d^2$	$[M_{\odot}]$	0.15	$M_{\text{gas}}/M_{\text{dust}}=220$	
$\langle \dot{M} \rangle \propto dv_{\text{exp}}$	$[M_{\odot}/\text{yr}]$	$1 \cdot 10^{-4}$	$M_{\text{gas}}/M_{\text{dust}}=220$	
$M_{\text{gas}}/M_{\text{dust}}=600$, see Sect. 7.8.3				
$M_{\text{env}} \propto d^2$	$[M_{\odot}]$	0.40	$M_{\text{gas}}/M_{\text{dust}}=600$	
$\langle \dot{M} \rangle \propto dv_{\text{exp}}$	$[M_{\odot}/\text{yr}]$	$3 \cdot 10^{-4}$	$M_{\text{gas}}/M_{\text{dust}}=600$	

Table 7.5: The best fitting model: parameters and derived quantities.

We have tested this by building a detailed model of the optical properties of HAC. We find that in radiative equilibrium HAC does not reach a high enough temperature at the location of the dust. We have tested this too for “coal” with the opacities as published by Guillois et al. (1994), even though the main difference with HAC is due to the interpolation these authors applied. We find that their “coal” reaches a maximum temperature of ~ 350 K at the inner edge of the dust shell. Which is not high enough to explain the relative band-strength of the plateau features ($\sim 500-600$ K).

This implies that the carriers that give rise to the plateau features are not in radiative equilibrium with the stellar radiation field. Most likely these features are due to very small dust grains or large molecules that are transiently heated to high temperature. From the PAH features that are present in the spectrum (especially at $3.3 \mu\text{m}$) it is clear that a family of aromatic molecules is present. The plateau features may well be carried by an “extended PAH family” of aromatic molecules and clusters with attached aliphatic sides groups.

7.8.5 Magnesium sulfide

We find that the amount of MgS required to explain the strength of the “30” μm feature is consistent with the measured abundances of Mg and S. Taking into account the envelope mass that we derived above ($0.4 M_{\odot}$ for $M_{\text{gas}}/M_{\text{dust}}=600$) we conclude that only 25 per cent of the Mg- and S-atoms need to be condensed into MgS to explain the strength of the feature. Because HD 56126 is metal-poor this implies that in other sources that are generally more metal-rich the strength of the “30” μm feature is also consistent with the MgS identification.

7.8.6 Titanium carbide

We have put TiC in our model. The optical properties of nano-crystalline TiC are too poorly understood to accept or reject the TiC identification for the “21” μm feature. We do note clearly that the bulk optical properties of TiC are incompatible with the peak position, feature-over-continuum ratio and strength of the “21” μm feature. The opacities of nano-TiC need to be ~ 20 times higher in the visible than measured in the bulk in order to explain the strength of the feature. It is interesting to note that a very similar resonance has been found in other nano-crystalline metal carbides, like VC, NbC (von Helden et al. 2001; van Heijnsbergen et al. 2002). Of course these species will not contribute much to the “21” μm feature because of the much lower elemental abundance of Nb and V. Better understanding the physics that gives rise to this resonance in nano-carbides may give further insight into the identification of the “21” μm feature. We conclude that the question of the identification of the “21” μm feature is still open and that nano-crystalline metal carbides remain very interesting candidates. Given the abundance of Fe and Ni, cubic iron-, nickel carbides (Haxonite) may be good first candidates for future studies.

7.9 Summary and conclusions

- We have presented a detailed study of the circumstellar envelope of the post-AGB star HD 56126. We present a large body of data from the literature, ISO spectroscopy and IR imaging. From a simple energy balance consideration we find a high effective temperature 7250 ± 250 K for the central star consistent with the temperature derived from detailed abundance analyses.
- We have built a detailed dust radiative transfer model of the circumstellar envelope of HD 56126. To model the emission of the dust we use amorphous carbon (a-C), hydrogenated amorphous carbon (HAC), magnesium sulfide (MgS) and titanium carbide (TiC). We present a detailed parametrisation of the optical properties of HAC as a function of H/C content.
- The radiative transfer model explains the ISO spectroscopy from 2–200 μm in great detail. The dust mass we derive is consistent with the dust mass as previously derived by other authors. We find that the mid-IR imaging and spectroscopy is best reproduced by a single dust shell from 1.1 to 2.6'' radius around the central star. This compact shell

originates from a short period of very high mass-loss during which the mass-loss rate exceeded $10^{-4} \text{ M}_{\odot}/\text{yr}$.

- “Classical” HAC grains in radiative equilibrium with the local radiation field do not reach a high enough temperature to explain the strength of the 3.3–3.4 and 6–9 μm hydrocarbon features relative to the 11–17 μm hydrocarbon features. Hence we conclude that these features are carried by very small dust grains (or large molecules) which fluctuate in temperature upon absorption of a single UV/visible photon.
- The strength of the “30” μm feature is compatible with its identification with MgS. This further strengthens the MgS identification of the “30” μm feature. The MgS temperature, derived from the observed profile allows an accurate determination of the MgS mass. We conclude that about 25 per cent of the Mg and S are locked up in MgS grains.
- We find that the observed strength of the “21” μm feature poses a problem for the TiC identification. The low abundance of Ti requires very high absorption cross-sections in the UV and visible wavelength range to explain the strength of the feature. Laboratory studies of the UV absorption properties of TiC nano-crystals are therefore urgently needed. Other nano-crystalline metal carbides also exhibit similar resonances as found in nano-TiC and these metal carbides should also be investigated in the laboratory to clarify the nature of these resonances and the identification of the “21” μm feature.

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Conclusions and outlook

8.1 The questions that we asked

The research presented in this thesis is concentrated on the following questions:

- What types of dust condense in the envelopes around carbon-stars?
- Which solids condense when?
- How are these materials subsequently processed?
- In what form does the dust enter the interstellar medium?

8.2 The questions that we answered

We have presented several detailed infrared studies on carbon-rich evolved stars. From these studies we have gained a much more complete insight in the composition of the dust around these stars.

We have discovered the first two PNe that exhibit an emission feature very similar to the “21” μm emission feature found in some carbon-rich post-AGB stars. From this we deduce that the carrier of the “21” μm feature is not as transient as previously believed but is resistant to the UV photons from the hot central star. Furthermore, both these Planetary Nebulae contain a hydrogen-poor central star and we conclude from the carbon-rich dust signatures that the atmospheres of these two stars became carbon-rich long before they became hydrogen-poor. This is contrary to some other PNe with hydrogen-poor central stars in which the infrared spectra point to a time-coincidence of the transition to C-rich and to H-poor.

We present the first evidence for iron sulfide grains outside our solar system. We find iron sulfide in the disks of young stars and in two carbon-rich Planetary Nebulae. From chemical equilibrium calculations iron sulfide grains are not expected to condense and these observations therefore pose new questions for the condensation models.

By studying the 10–15 μm wavelength region of many sources that show strong PAH emission we show that C-stars inject predominantly large (~ 200 C-atoms), compact PAHs into the ISM. Such PAH molecules are required to explain the predominance of the 11.2 μm feature in carbon-rich PNe. These PAHs are processed during their lifetime in the ISM. However the PAH structure is closely correlated with environment and most of the processing may occur locally.

We have carefully tested the magnesium sulfide identification for the “30” μm feature. We find that both the profile and the strength of the feature are completely consistent with the MgS identification. We conclude that the circumstellar environment of carbon-rich AGB

stars, post-AGB stars and PNe contains MgS. We find only a few low mass-loss carbon-stars without evidence for MgS. We find no evidence for a rapid destruction of these MgS grains and therefore these grains may survive into the ISM phase.

We have constructed a radiative transfer model of the post-AGB star HD 56126 that explains the 2–200 μm spectroscopy and the mid-IR images well. We find that the circumstellar envelope contains amorphous carbon, MgS and PAHs. The broad 6–9 and 10–17 μm features cannot be due to hydrogenated amorphous carbon in radiative equilibrium. We deduce a short period (~ 1500 year) during which the entire envelope, equivalent to $\sim 0.4 M_{\odot}$, was lost. The identification of the carrier of the “21” μm feature remains an open question. However, because the “21” μm feature is only found in objects that have already departed from the AGB, it is likely that the conditions for the condensation of the carrier are only met at the very end of the AGB evolution.

8.3 The questions that remain

Naturally, there are also several important issues that have not been resolved by the studies presented here. The most obvious of those is the precise location of the dust components. Using spectroscopic information alone there is always a certain ambiguity. For example in particle size and distance from the illuminating star. Both these parameters influence the temperature of the dust and therefore the resulting spectra. Spatial information gives a direct handle on the mass-loss history because in general material lost at earlier times will be located further away from the star. A good example of this is the cool magnesium sulfide that we have discovered around warm carbon-stars. Without further information we are unable to determine whether this is due to the optical properties of MgS or because it is located in a shell far from the star. If this MgS is indeed located away from the star this would prove directly that these stars were already C-rich at the time they produced this shell.

We are able to draw much firmer conclusions on the circumstellar envelope of HD 56126 because we use both infrared spectroscopic and imaging observations. With these data combined the interpretations are much better constrained than using spectroscopic data alone.

We find an indication of a relation between the low metallicity and the occurrence of the “21” μm feature. Whether there is a relation between the two should be further explored.

Although we have a much more complete inventory of the composition of the dust surrounding various types of carbon-rich stars, important open questions remain on the relation between the different classes of objects. While the post-AGB objects and PNe show PAH and other complex molecular emissions features, we find no evidence for these molecules in the AGB stars. Possibly these molecules are the result of the shattering of the previously condensed dust due to UV photons or shocks. Spatial information may be able to differentiate between those mechanisms.

One intriguing mystery concerns the fate of iron in the carbon-rich surroundings. Iron is an abundant element that condenses rather easily and one would expect to be able to find the component that contains the iron atoms. The presence of iron sulfides in two PNe suggests that iron may usually be contained in metallic iron grains. These can be transformed into iron sulfide grains through a gas-solid reaction with sulfur-bearing molecules like H_2S . Per-

haps this reaction occurred efficiently in these particular PNe because of an unusually high abundance of such sulfur-bearing molecules.

8.4 Laboratory studies

The type of analyses that we have performed in this study relies heavily on the comparison with laboratory measurements of candidate materials. Throughout this thesis we have mentioned laboratory measurements that are missing and required to analyse evolved C-rich stars.

PAHs

With ISO the UIR bands have been observed in great detail in a large variety of sources. The variations within the astronomical spectra have been extensively and systematically described. From these data many interesting correlations with source type have surfaced. Some of these correlations are described in Chapter 2. These studies suggest that the interstellar PAH ensemble contains very large molecules and complexes of molecules. Laboratory measurements of these large molecules will aid in the interpretation of the astronomical spectra in physical terms.

Pyrrhotite

In Chapters 3 and 4 we describe the detection of iron sulfide through the $23\ \mu\text{m}$ feature and weak features at longer wavelength. The relative band strengths do not fit the available laboratory measurements of iron sulfides. We suggest that pyrrhotite might exhibit band strengths compatible with the astronomical spectra. To test this the $10\text{--}50\ \mu\text{m}$ optical constants of pyrrhotite are required.

Magnesium sulfide

Our studies suggest that magnesium sulfide grains are abundantly present around carbon-rich evolved stars (see Chapters 6 and 7). To determine the amount, grain size and location of the MgS, the optical constants of MgS from 0.1 to $10\ \mu\text{m}$ are required.

We also find a deviating profile of the feature due to the coldest MgS grains ($<100\ \text{K}$). We suggest that this may arise from MgS in a hexagonal lattice structure. This suggestion can be tested with laboratory measurements of such MgS grains.

Metal carbide nano-crystals

Several nano-crystalline metal carbides exhibit a strong resonance near $20\ \mu\text{m}$. We require knowledge of the absorption properties of these nano-crystals in the UV and visible range to be able to determine the relation of this resonance with the “21” μm feature found in the IR spectra of some carbon-rich evolved stars.

8.5 The future is bright!

A wealth of new observing facilities, that can provide follow up research to the work presented in this thesis, is or will soon be available. Here I sketch some of the possible questions in the framework of the dust surrounding evolved stars that one can address with those new facilities.

VLT

The study of several dust components is hampered by the small number of objects available to study. For example, only 14 sources that exhibit a “21” μm feature are known and only two evolved stars that show the presence of iron sulfides are known (Chapter 3). The VLT Imager and Spectrometer for mid Infra Red (VISIR) is an instrument planned for the Very Large Telescope (VLT) in Chili. VISIR will provide Q-band (16–24 μm) spectroscopy and imaging with unprecedented sensitivity. This sensitivity allows to search for more of these stars and studying them in a more systematic and statistical way.

The MID-infrared Interferometric instrument (MIDI) on the VLT can observe in the N-band (8–13 μm) with a very high spatial resolution. This allows to study the geometry of the inner dust shell, the possible onset on non-spherically symmetric mass loss and its relation to the dust composition.

SIRTF

A large uncertainty in the parameters that we derive, like dust mass and luminosity of the star, is due to the uncertain distances for evolved stars. An independent distance determination greatly reduces this uncertainty. The Infrared Spectrograph onboard the Space Infrared Telescope Facility (SIRTF) is sensitive enough to take high quality 10–40 μm spectra of evolved stars in the Magellanic Clouds to which the distances are much better known.

SOFIA

We have identified carbon stars with emission due to very cold MgS. This may be due to the fact that the MgS is located in a detached shell around the star. The Faint Object InfraRed CAmera for the SOFIA Telescope (FORCAST) onboard the Stratospheric Observatory For Infrared Astronomy (SOFIA) is capable of imaging at 30 μm with a spatial resolution of 2". With this instrument it will be possible to directly determine the location of the cold MgS.

ALMA and Herschel

From mid-IR observations alone it is difficult to derive the total dust budget. Especially the mass of the cold dust is not well constrained (see also Chapter 7). The Atacama Large Millimeter Array (ALMA) and the Herschel Space Observatory will provide imaging and spectroscopy in the (sub-)millimetre range. Complementary submillimeter imaging observations will help to get a more complete insight in the dust mass and location.

Nederlandse samenvatting

In dit proefschrift presenteer ik een zestal studies naar de eigenschappen van zogenaamde “oude sterren”. Het einde van het leven van verreweg de meeste sterren verloopt zoals beschreven in dit proefschrift. Over ongeveer 5 miljard jaar wordt onze zon ook een dergelijke ster. In deze samenvatting wil ik een beeld schetsen van deze oude sterren, de vragen die we hebben omtrent hun eigenschappen en de antwoorden die we hebben verkregen middels dit zestal studies.

Oude sterren

De sterren die ik heb onderzocht zijn ooit allemaal heel vergelijkbaar geweest met onze zon. Het allergrootste deel van hun leven zijn dergelijke sterren eigenlijk vrij saai: in het centrum van de ster is de temperatuur en druk heel hoog en daardoor botsten waterstof atomen vaak en hard op elkaar. Door deze botsingen vindt kernfusie plaats waarbij veel energie vrij komt. Deze energie sijpelt langzaam naar buiten. Aan de buitenkant verliest de ster deze energie in de vorm van licht: de ster straalt.

Dit proces van kernfusie verloopt heel gecontroleerd. Dit komt doordat de kern van de ster als een heel gevoelige thermostaat optreedt. Gaat de temperatuur te veel omhoog dan zet de kern van de ster uit, de energielevering neemt af en de temperatuur gaat vanzelf weer omlaag. Sterren kunnen dit proces miljarden jaren volhouden voordat de waterstof in hun centrum op is.

Uiteindelijk raakt de waterstof natuurlijk toch uitgeput. Dan verliest de ster ook zijn “thermostaat” en raakt in onbalans. De ster ondergaat nu een aantal veranderingen. Tenslotte wordt de ster een zogenaamde ‘Rode Reus’. Rode Reuzen zijn koele en enorm grote sterren. In figuur 1 is te zien hoe groot een Rode Reus is. De zon is op deze schaal niet meer dan een stip. De planeetbanen van de binnenste drie planeten liggen tegen die tijd ruim in de Rode Reus. De energie wordt nog steeds opgewekt middels kernfusie. Deze kernfusie vindt niet meer plaats in het centrum van de ster (de kern) maar in een dunne laag rond die kern. De structuur van deze sterren blijkt een stuk minder stabiel te zijn en Rode Reuzen worden gekarakteriseerd door sterke pulsaties waarbij de afmeting van de ster verandert. Tegelijkertijd zijn deze reuze sterren enorm helder. De hoeveelheid uitgestraalde energie per seconde kan wel 10 000 keer zoveel zijn als de zon nu per seconde uitstraalt.

Deze vier eigenschappen (de grote helderheid, de enorme afmeting, de lager temperatuur

Figuur 1: Schematisch overzicht van ons zonnestelsel met de afstanden van de binnenste vier planeten tot de zon. De kleine stip links is de zon nu op schaal. De planeten zijn duizend maal te groot afgebeeld omdat ze anders niet te zien zouden zijn. Het grijze gebied geeft aan hoe groot de zon zal zijn als Rode Reus. Mercurius, Venus en de aarde liggen allemaal binnen de toekomstig afmeting van de zon.

en de veranderlijkheid) zorgen ervoor dat de buitenste lagen van de ster niet langer vastgehouden kunnen worden. Normaal gesproken is de zwaartekracht van een ster zo groot dat het de ster gemakkelijk bijeenhoudt. Dit is echter niet het geval bij Rode Reuzen. De buitenkant van een Rode Reus beweegt dusdanig dat er materiaal ver weggeduwd wordt. Hier is het zo koud dat de atomen chemische verbindingen met elkaar aangaan. Er vormen zich dan kleine stofdeeltjes. Hierbij kun je bijvoorbeeld denken aan sigarettenrook of roet uit de uitlaat van een oude auto. Deze stofdeeltjes zijn heel belangrijk en mijn onderzoek heeft zich geconcentreerd op de eigenschappen van deze stofdeeltjes.

De gevormde stofdeeltjes kunnen heel goed licht tegenhouden. Dit is ook de oorzaak waardoor rook zwart is: al het licht wordt geabsorbeerd. Door het geabsorbeerde licht worden de stofdeeltjes weggeblazen van de ster. Hetzelfde effect van blazen met licht kun je zien in de staart van een komeet. In figuur 2 is duidelijk te zien dat een komeet twee staarten heeft. De richting van de bovenste staart wordt bepaald door de lichtdruk door de straling van de zon en diens zonnewind. Rode reuzen zijn veel helderder dan onze zon en bovendien is de zwaartekracht aan hun oppervlak veel minder sterk doordat de ster zo groot is. De stofdeeltjes voelen het effect van de lichtdruk veel meer dan de zwaartekracht en worden weggeblazen.

Figuur 2: Foto van de komeet Hale-Bopp, die in april 1997 goed zichtbaar was. De twee staarten zijn duidelijk te zien. De bovenste staart wijst altijd precies weg van de zon als gevolg van de stralingsdruk en de zonnewind. De andere staart volgt meer de beweging van de komeet.

Massaverlies

Met het wegblazen van deze vaste-stof deeltjes wordt een belangrijk proces (het massaverlies) in oude sterren in gang gezet. Op hun pad weg van de ster nemen de stofdeeltjes andere atomen en moleculen mee. De ster ontwikkelt een forse sterrewind en verliest veel materie. Dit massaverlies is belangrijker dan de kernfusie die binnenin de ster plaats vindt.

Ten eerste komen op deze manier belangrijke zware atomen die gevormd zijn door kernfusie binnenin de ster (zoals koolstof en zuurstof) in de ruimte tussen de sterren terecht. Later kunnen daar dan weer andere sterren en planeten stelsels uit ontstaan. Die zware atomen vormen de basis voor planeten en mogelijke leven op die planeten. Alle atomen behalve waterstof en helium zijn gevormd in het binnenste van sterren. Dat wil zeggen dat bijna alles wat we hier op aarde kennen het (bij)product is van kernfusie in sterren en hun sterrewinden.

Ten tweede verandert de ster meer door wat er aan de buitenkant plaats vindt dan door de kernfusie. Dit is precies omgekeerd van de situatie van de zon. De kernfusie bepaalt de hele structuur van de zon, terwijl in Rode Reuzen het levenspad gedicteerd wordt door massaverlies middels de sterrewind. Om deze sterren te kunnen begrijpen moeten sterrenkundigen dus juist het massaverlies doorgronden.

Sommige sterren verliezen wel een duizendste van de totale massa van de zon in één jaar. Dit kan geen enkele ster lang volhouden. De Rode Reuzen fase duurt dan ook kort en deze sterren zijn relatief bijzonder. Denk, om dit te begrijpen, bijvoorbeeld aan je dertigste verjaardag. Je dertigste verjaardag duurt slechts kort ten opzichte van je hele leven en dus zijn er slechts weinig mensen die juist vandaag dertig worden. De Rode Reuzen fase zou je ook

Figuur 3: Twee voorbeelden van Planetaire Nevels. Links de (bijna) ronde jonge Planetaire Nevel IC 418. Rechts is de schitterende “Mier Nevel” Menzel 3 te zien. De hete kern is zichtbaar als een heldere punt in het midden van de nevel. De rest is allemaal materiaal dat verloren is tijdens de Rode Reuzen fase en nu oplicht. Met dank aan: R. Sahai, B. Balick, A. Hajian, NASA, ESA en ‘The Hubble Heritage Team’.

kunnen beschouwen als één dag in het leven van een ster.

Het einde van de Rode Reuzen fase wordt ook bepaald door het massaverlies. Wanneer de totale ijle buitenkant van de ster is weggeblazen komt de kern steeds meer bloot te liggen. Deze kern is heel heet, de temperatuur loopt op en hierdoor kunnen zich geen stofdeeltjes meer vormen.

Planetaire Nevels

De kern wordt meer en meer zichtbaar en daardoor steeds heter. Wanneer de ster heter wordt dan ongeveer 30 000 graden Celsius dan wordt het materiaal dat uitgestoten is geïoniseerd. Het uitgestoten materiaal licht op en een schitterende nevel wordt zichtbaar. Een TL-buis straalt ook licht uit door dit proces. Deze nevels worden Planetaire Nevels genoemd omdat ze vroeger met kleine telescopen een beetje op planeten leken. In figuur 3 zijn twee recente opnamen van Planetaire Nevels te zien. Het hete overblijfsel van de ster is te zien als een heldere pit. De rest is allemaal materiaal dat tijdens de Rode Reuzen fase is weggeblazen.

In figuur 3 is ook duidelijk te zien hoe zeer Planetaire Nevels van elkaar kunnen verschil-

Figuur 4: Het infrarood spectrum van de Planetaire Nevel NGC 7027 verkregen met de ruimte telescoop ISO. De vingerafdrukken van enkele stofcomponenten zijn aangegeven: polycyclische aromatische koolwaterstoffen (PAK's) amorf koolstof (roet) en magnesium sulfide (MgS). De smalle lijnen komen van het geïoniseerde gas in de Planetaire Nevel.

len in vorm. Het is niet duidelijk wanneer deze verschillen zijn ontstaan. Het is mogelijk dat dit al gebeurt is tijdens de Rode Reuzen fase of dat dit plaats vindt tussen de Rode Reuzen fase en de Planetaire Nevel fase.

Stofdeeltjes

Hierboven heb ik al aangegeven dat de stofdeeltjes een cruciale rol spelen in het massaverlies van oude sterren. Toch weten we niet zoveel van dit stof. We weten niet precies hoe, waar en wanneer het zich vormt. We weten ook niet wat de stofsamenstelling is (welke atomen met elkaar zijn samengegaan) of welk stof uiteindelijk terecht komt in de ruimte tussen de sterren. Er zijn enkele belangrijke oorzaken aan te wijzen waarom we dit niet goed weten.

Allereerst zijn Rode Reuzen sterren schaars en er zijn dus niet veel goede kandidaten om te bestuderen. Daarnaast bemoeilijken de stofdeeltjes zelf het onderzoek aan deze sterren. Zoals gezegd absorberen de stofdeeltjes het licht. Daardoor worden de sterren aan het oog onttrokken. De sterren die veel materiaal uitstoten zijn volstrekt onzichtbaar. Het stof wordt wel warm als gevolg van het licht dat ze absorberen en ze zullen warmtestraling bij infrarode golflengtes uitstralen. Helaas komt deze infrarode straling erg slecht door de atmosfeer van de aarde. Het is dus zeer moeilijk om deze sterren te bestuderen vanaf de aarde. Daarom heb ik voor mijn onderzoek gebruik gemaakt van de gegevens van een satelliet. De ruimte telescoop ISO (Infrared Space Observatory) heeft gegevens verzameld in het infrarood licht in het golflengte bereik tussen 2 en 200 micrometer. Dit is precies het bereik waar Rode Reuzen helder zijn.

Naast het feit dat deze sterren heel helder zijn in het infrarode licht is het ook zeer belangrijk dat juist in dit golflengte gebied veel materialen een duidelijke vingerafdruk achterlaten. Wanneer we het licht opsplitsen naar golflengte krijgen we een spectrum (een regenboog is het opgesplitste licht (spectrum) van het zonlicht). In het infrarode licht kunnen we middels een spectrum onderscheid maken tussen verschillende materialen. Het ene materiaal straalt beter een bepaalde golflengte dan een ander materiaal. Ontvangen we veel licht bij juist die golflengte dan betekent dat dus dat er veel van dit materiaal aanwezig is.

In figuur 4 is het infrarood spectrum van de Planetaire Nevel NGC 7027 getoond. Er zijn enkele zeer karakteristieke pieken te zien. De allersmalste lijnen in de figuur worden veroorzaakt door het geïoniseerde gas in de Planetaire Nevel. Dit gas zorgt er voor dat we zulke mooie nevels zien oplichten. Daarnaast zijn er ook bredere pieken te zien. Die komen van de complexe moleculen als de polycyclische aromatische koolwaterstoffen en van stofdeeltjes zoals roet en magnesium sulfide.

Door de infrarood spectra van oude sterren te bestuderen kunnen we dus achter de samenstelling van het uitgestoten materiaal komen. Soms kunnen we tevens iets leren over de temperatuur. Dit komt doordat de sterkte en vorm van de pieken afhangt van de temperatuur. Met die temperatuur is het mogelijk om te bepalen hoe ver het materiaal zich van de ster bevindt want dicht bij de ster is het warmer dan verder weg. In ons zonnestelsel vinden we dat ook. Zo is het op Mars gemiddeld -63 graden Celsius terwijl het op Mercurius $+167$ graden Celsius is.

Open vragen

De belangrijkste vragen die we hebben over deze oude sterren zijn:

- Hoe verloopt de stofvorming en het massaverlies tijdens de Rode Reuzen fase?
- Hoe verandert het massaverlies vlak voor het einde van de Rode Reuzen fase?
- Welke stofdeeltjes vormen zich rond Rode Reuzen?
- Wanneer vormt het stof zich?
- Verandert de samenstelling van het stof als de ster meer massa verliest?
- Wat gebeurt er met de stofsamenstelling tijdens de Planetaire Nevel fase?
- Wat is de samenstelling van het materiaal dat uiteindelijk terecht komt tussen de sterren?

Dit zijn veel vragen en de antwoorden op deze vragen komen door het combineren van gegevens van vele verschillende studies. Zo is het nodig om in detail de scheikunde in het materiaal rond oude sterren in kaart te brengen. Verder is het bijvoorbeeld belangrijk om te beschikken over modellen voor de structuur van Rode Reuzen en modellen voor de interactie tussen de stofdeeltjes die worden weggeblazen en de rest van het materiaal. Natuurlijk moeten we ook weten welk stof zich vormt.

Dit proefschrift

Ik heb mij tijdens het onderzoek dat ik in dit proefschrift presenter geconcentreerd op het laatste gebied: de samenstelling van de stofdeeltjes. *Welke stofdeeltjes zijn er nou eigenlijk aanwezig? Zijn er verschillen in de samenstelling te zien bij verschillende soorten sterren? Wat gebeurt er met het stof naderhand?*

Polycyclische aromatische koolwaterstoffen

In het tweede hoofdstuk van dit proefschrift onderzoeken we de polycyclische aromatische koolwaterstoffen (PAK's) in verschillende soorten sterren. PAK's worden gevormd rond Rode Reuzen. Reeds vanaf het begin van de jaren tachtig is duidelijk dat heel veel sterren (jonge sterren, oude sterren en zelfs hele sterrenstelsels) allemaal een serie van emissie pieken laten zien op infrarode golflengte bij 3.3, 6.2, 7.7 en 11.3 micrometer. In het midden van de jaren tachtig werd duidelijk dat deze pieken afkomstig zijn van een familie van grote moleculen: de PAK's. Hier op aarde komen PAK's voor in teer, ruwe aardolie en uitlaatgassen van auto's. Er is echter nog steeds discussie over de precieze oorsprong van de emissie pieken uit de ruimte en er is nog nooit één specifiek PAK molecule met zekerheid aangetoond bij een andere ster.

Wij vergelijken de PAK's rond 30 verschillende sterren waarbij we ons hebben geconcentreerd op de rand van de moleculen. Een aantal emissie pieken zijn afkomstig van de rand van deze moleculen. Hierdoor kunnen we specifiek die rand bestuderen. We bestuderen de emissie voor jonge sterren, oude sterren en stervormingsgebieden. We vinden dat systematisch de PAK emissie banden veranderen. Jonge sterren lijken op elkaar, de oude sterren lijken op elkaar en de stervormingsgebieden lijken op elkaar maar onderling vinden we grote verschillen. We interpreteren deze verschillen als volgt: Rode Reuzen maken grote, gelijkmatige PAK moleculen. Hierna worden ze langzaam afgebroken en de randen worden steeds rafeliger.

De 21 micrometer emissie band

In hoofdstuk 3 presenter ik de ontdekking van een speciale emissie band in de spectra van twee Planetaire Nevels. Welk materiaal deze emissie veroorzaakt is onduidelijk. Een zelfde band was wel reeds bekend bij sterren die nog geen Planetaire Nevel waren maar nog nooit gezien bij Planetaire Nevels. Hierdoor dacht men dat het materiaal dat de emissie veroorzaakt misschien niet erg stabiel is en vernietigd wordt door het licht van de hete ster.

Deze ontdekking toont aan dat het materiaal stabiel is dan werd aangenomen. Bovendien behoren deze twee Planetaire Nevels tot een bijzondere groep van Planetaire Nevels. Op het oppervlak van de hete ster is namelijk helemaal geen waterstof meer aanwezig. Hoe en wanneer de waterstof is verwijderd is niet goed bekend. Met de ontdekking van deze en andere emissie banden kunnen we de geschiedenis van deze twee Planetaire Nevels beter in kaart brengen.

IJzer sulfide

In de volgende twee hoofdstukken (4 en 5) beschrijf ik de eerste ontdekkingen van ijzer sulfide buiten ons zonnestelsel. In ons zonnestelsel worden op talloze plaatsen ijzer sulfide

gevonden: Op aarde, in meteorieten en in kometen. Wij presenteren de eerste aanwijzingen voor de aanwezigheid van ijzer sulfide rond oude sterren. Het is niet duidelijk hoe het ijzer sulfide daar gevormd is. De huidige chemische modellen voor de stofvorming rond oude sterren voorspellen geen aanwezigheid van ijzer sulfide. Daarnaast vinden we ook ijzer sulfide in de schijven rond jonge sterren. Dit laatste wordt des te interessanter als je bedenkt welke rol ijzer sulfiden hier op aarde spelen. Biologen denken dat ijzer sulfiden een belangrijke rol hebben gespeeld bij het ontstaan van leven. Ook nu nog spelen ijzer-zwavel verbindingen een vitale rol in organische cellen. In het algemeen wordt aangenomen dat in de schijven rond jonge sterren planeten worden gevormd. De aanwezigheid van ijzer sulfide rond die sterren laat zien dat ook bij andere sterren de condities zeer gunstig lijken voor de vorming van leven.

Magnesium sulfide

De oude sterren die ik heb bestudeerd hebben allemaal een brede emissie band rond de 30 micrometer. Deze band wordt veroorzaakt door magnesium sulfide. In figuur 4 is deze band aangegeven. Wanneer je de vorm van de band in verschillende bronnen vergelijkt lijkt het er op dat het niet dezelfde band is. Wij hebben daarom in hoofdstuk 6 alle bronnen met deze band systematisch onderzocht. We vinden dat magnesium sulfide onomstotelijk deze band veroorzaakt. De vorm van de band verandert doordat de temperatuur van het magnesium sulfide anders is dan de temperatuur van de rest van het stof. Daarnaast vinden we een groep van sterren die nu (even) geen magnesium sulfide produceren maar vroeger wel. Dit magnesium sulfide bevindt zich ver van de ster en is dus koud. We vinden geen aanwijzing voor de vernietiging van magnesium sulfide in de Planetaire Nevel fase. Waarschijnlijk komen magnesium en zwavel dus als magnesium sulfide deeltjes terecht tussen de sterren.

HD 56126

De laatste studie betreft een gedetailleerd onderzoek aan de ster HD 56126. Deze ster laat vele emissie banden zien waarover discussie bestaat. Onder andere de PAK banden, de magnesium sulfide band en de 21 micrometer emissie band. Door middel van een gedetailleerd model hebben we de beste kandidaat-materialen voor de verschillende emissie pieken getest. Uit ons model vinden we de aanwezige hoeveelheid van de verschillende materialen en de plek waar deze zich bevinden. We tonen aan dat deze ster ongeveer 2000 jaar geleden begonnen is met heel veel massa te verliezen. Dit is ongeveer 1000 jaar gelden gestopt. In die tijd is er vijftig procent van de massa van de ster uitgestoten.

Conclusies

Door middel van gedetailleerde studies aan de infrarood gegevens van oude sterren hebben we het stof rond deze sterren onderzocht. We hebben de aanwezigheid van een aantal nieuwe materialen in de ruimte ontdekt. We hebben een completer beeld van de samenstelling, locatie en het lot van het stof rond koolstofrijke oude sterren verkregen. Daarmee verschaffen de hier gepresenteerde studies een rijker inzicht in het stof rond oude sterren en deze sterren zelf.

Glossary

Acronyms

a-C, a-Carbon	Amorphous carbon
AGB	Asymptotic Giant Branch
BSR	Band strength ratio
C-rich	Carbon-rich
C-stars	Carbon stars
CDE	Continuous distribution of ellipsoids
CS	Circumstellar
CSE	Circumstellar envelope
CSPN	Central star of a planetary nebula
ESA	European Space Agency
FWHM	Full-width-at-half-maximum
GEMS	Glass with embedded metal and sulfides
HAC	Hydrogenated amorphous carbon
HB	Horizontal Branch
HRD	Hertzsprung-Russel diagram
IDP	Interplanetary dust particle
IR	Infrared
ISM	Interstellar medium
ISO	Infrared Space Observatory
LWS	Long Wavelength Spectrometer
MS	Main sequence
nano-TiC	Titanium carbide nano-crystal
O-rich	Oxygen-rich
OOP mode	Out-of-plane bending mode
PAH	Polycyclic aromatic hydrocarbon
PN	Planetary Nebula
post-AGB	Post-Asymptotic Giant Branch
PPN	Proto-Planetary Nebula
RGB	Red Giant Branch
RN	Reflection Nebula
SED	Spectral energy distribution
SWS	Short Wavelength Spectrometer
TEM	Transmission electron microscope
TP	Thermal pulse
UIR bands	Unidentified infrared bands
UV	Ultraviolet
YSO	Young stellar object

Chemical composition

Corundum	Al_2O_3
Enstatite	MgSiO_3
Forsterite	Mg_2SiO_4
Haxonite	FeC
Iron silicide	FeSi
Magnetite	Fe_3O_4
Pyrite	FeS_2
Pyrrhotite	$\text{Fe}_{(1-x)}\text{S}$
Spinel	MgAl_2O_4
Troilite	FeS
Wüstite	FeO
Urea	$\text{OC}(\text{NH}_2)_2$