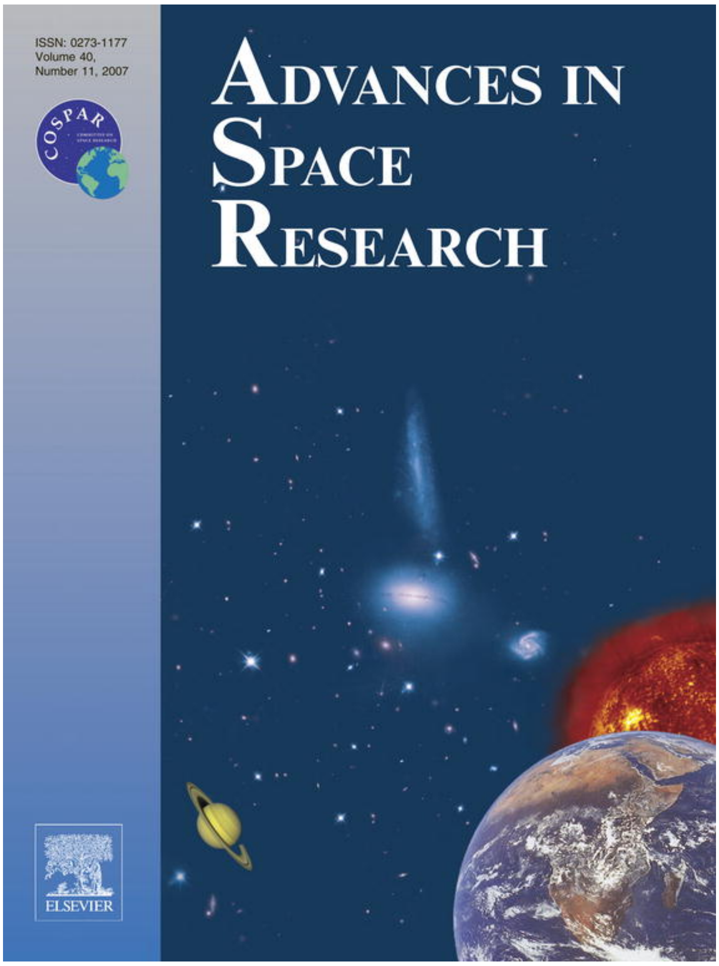
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Enrichment of the solar system by organic compounds delivered from evolved stars

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Abstract

Recent infrared spectroscopic observations have detected emission features due to the stretching and bending modes of aliphatic and aromatic compounds in the circumstellar envelope of evolved stars. These observations show that complex organic compounds can be synthesized in the low-density circumstellar environment over time scales of thousands of years. The identification of similar compounds in the solar system suggests that these stellar materials can survive the long trip through the Galaxy and be deposited in the early solar system. The possible role of such chemical enrichment of the solar system by stellar materials on the development of pre-biotic substances and the origin of life needs to be further explored.

Keywords: Interstellar molecules; Infrared spectroscopy; Aromatic compounds; Stellar evolution; Planetary nebulae; Origin of life

1. Introduction

Since the Miller–Urey experiment in 1953 (Miller, 1953; Miller and Urey, 1959), the endogenous origin of organic matter has remained popular for 50 years. The discovery of extensive presence of organic compounds in primitive meteorites, specifically carbonaceous chondrites (Cronin and Chang, 1993), has raised the possibility that some of the organic matter on Earth may have been delivered from extraterrestrial sources. Recent advances in millimeter and submillimeter-wave spectroscopy have made possible the detection of 146 gas-phase molecules in the interstellar medium (as of June 2006, http://aramis.obspm.fr/mol/list-mol.html), a majority of which are organic molecules. These detections clearly show that organic molecules of moderate complexity can be synthesized beyond the terrestrial environment, even under extreme low densities.

Since most of the astronomical detection of interstellar molecules relies on the rotational transitions, there is a limit to the degree of complexity for molecules to be detected by this technique. As the number of energy levels increase with the complexity of the molecule, the relative population in each of the rotational states decreases, therefore producing a weaker line. Even with increasing instrument sensitivity, there is a limit at which the millimeter and submillimeter-wave spectrum is filled with weak lines, making definite identification impossible.

Recent advances in infrared spectroscopy, in particular from space-based observatories, have opened the possibility of detecting the stretching and bending modes of complex molecules. These observations reveal the presence of organic compounds consisting of hundreds of atoms, with definite aromatic and aliphatic structures. Most interestingly, we now have evidence that these compounds are formed over a very short time ($\sim 10^4$ yr) during the late stages of stellar evolution. In this paper, we will summarize the evidence for the synthesis and chemical evolution of organic compounds, and discuss their possible relationship to similar compounds found in meteorites.

2. From the asymptotic giant branch to planetary nebulae

Our appreciation of the importance of molecular synthesis in the circumstellar environment began with the

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detection of amorphous silicate grains and gas-phase molecules (such as CO) in the outflow of asymptotic giant branch (AGB) stars. The AGB represents a brief ($\sim 10^6$ yr) phase of stellar evolution where hydrogen (H) and helium (He) shells above an electron-degenerate carbon–oxygen (C–O) core burn alternatively into He and C. During the He-burning phase, newly synthesized nuclei (including heavy elements created by neutron capturer processes) are brought up to the surface by dredge-up episodes. As an increasing amount of C is dredged up and the surface abundance of C finally exceeds that of O, surplus C atoms not in the form of CO are available to form other C-based molecules. The emergence of molecules C_2, C_3, and CN in the photospheric spectrum defines the class of AGB stars called carbon stars. The high rate of mass loss on the AGB will eventually deplete the envelope of the star and gradually expose the hot core. As the envelope thins to below $10^{-3} M_{\odot}$, the star will begin to increase in temperature. Through a combination of H shell burning and mass loss, the envelope becomes thinner, leading to an increase of stellar temperature. When the stellar temperature reaches 20,000 K, the ultraviolet photon output from the star will begin to photoionize the circumstellar envelope, creating a planetary nebula (PN, Kwok, 2000). The intervening phase between the end of AGB and the onset of photoionization, is called the proto-planetary nebula (PPN) phase (Kwok, 1993).The evolutionary track of a $3M_{\odot}$ star from the main sequence to the red giant branch (RGB) to the AGB and PN is shown in Fig. 1.

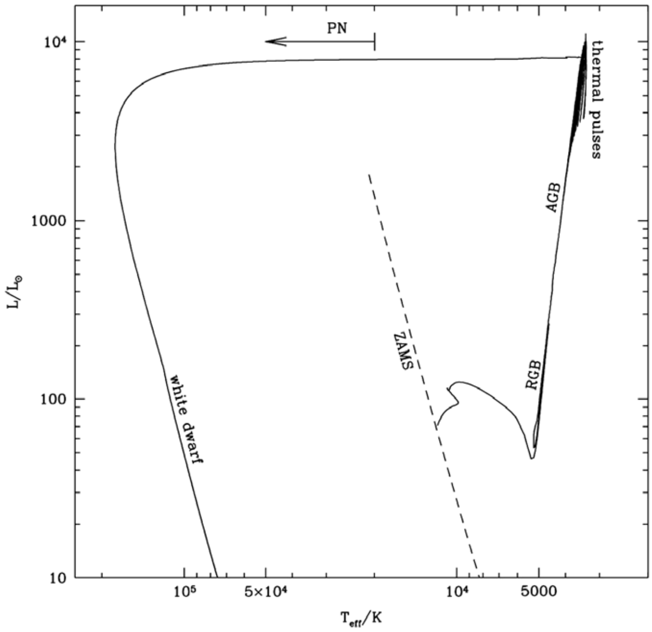

Fig. 1. The evolutionary track of a $3M_{\odot}$ star on the Hertzsprung–Russell diagram beginning from the zero-age-main sequence (ZAMS), through the RGB and AGB to PN. The transition between the AGB and the PN phases is called the post-AGB phase and objects in this phase is called PPN (figure courtesy of Thomas Blöcker).

At the same time, the increasing size and luminosity of the star lead to a pulsating atmosphere. As the gas expands and cools, atoms combine to form molecules and gas condenses directly into solid phase to form micron-size grains. Radiation pressure on grains causes the upper layers of the star to be ejected in the form of a stellar wind (Kwok, 1975). This wind creates a molecular circumstellar envelope around the star, extending over several thousand astronomical units (AU). The most common solid particles are amorphous silicates in O-rich stars and silicon carbide (SiC) in carbon stars. These particles are identified by their lattice vibrational modes in the infrared. Since the dynamical time of the circumstellar envelopes created by these winds is of the order of 10^4 yr, these detection represents the first evidence that molecular synthesis can occur rapidly in a low-density environment.

3. Inorganic compounds

The kinds of molecules and solid particles form in the circumstellar envelopes of AGB stars are dependent on the chemical composition of the stars. Because CO molecules take up most of the lesser element of oxygen and carbon, oxides are generally found in oxygen-rich AGB stars, whereas organic compounds are generally limited to carbon-rich AGB stars.

Silicates is the most abundant group of minerals in the Earth's crust. Although most of the terrestrial silicates are in crystalline form, most of the silicates found in AGB stars are amorphous. This is consistent with the expectation that amorphous structure results from rapid condensation from the gas phase in AGB winds. The 9.7 and 18 μm features of amorphous silicates are detected in over 4000 O-rich AGB stars (Kwok et al., 1997; Fig. 2). During the *ISO* mission, a rich family of narrow emission bands due to crystalline silicates was found in the spectra of AGB stars and PNe (Jäger et al., 1998). Crystalline silicates can be in the form of olivine ($Mg_{2-2x}Fe_{2x}SiO_4$, where $0 \leqslant x \leqslant 1$) or pyroxene ($Mg_{1-x}Fe_xSiO_3$). Analyses of the observations suggest that the crystalline silicates in AGB

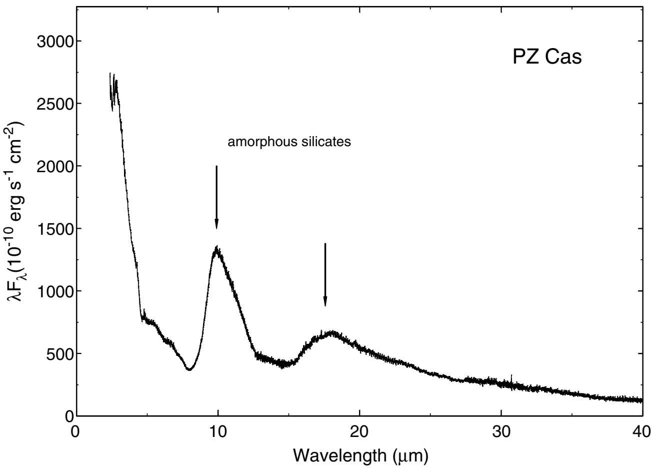

Fig. 2. *ISO SWS* spectrum of the O-rich AGB star PZ Cas showing the 9.8 and 18 μm amorphous silicate emission features.

stars are magnesium rich ($x \approx 0$). From the strengths of the crystalline silicate features one can estimate that the abundance of crystalline silicates is small in comparison to amorphous silicates. An example of the crystalline silicate features observed in the PN Cn1-1 is shown in Fig. 3.

In addition to silicates, a variety of refractory oxides may also be present in circumstellar envelopes of AGB stars. A broad feature centered around 13 μm, first discovered by the IRAS LRS (Sloan et al., 1996), could be due to corundum (α-Al_2O_3, which has a feature at 12.7 μm), glass (amorphous SiO_2, 12.3 μm), spinel (12.95 μm), or rutile (13.4 μm) (Posch et al., 1999). An emission feature at 19.5 μm observed by ISO has been attributed to mixture of Mg–Fe-oxides (e.g., $Mg_{0.1}Fe_{0.9}O$) (Posch et al., 2002).

The 11.3 μm feature, due to the stretch mode of the Si–C bond of silicon carbide, is detected in emission in 700 carbon stars (Kwok et al., 1997), making it the most common solid-state feature in C-rich circumstellar envelopes (Fig. 4). In more evolved carbon stars, the dust continuum is featureless, possibly due to amorphous carbon.

The formation of carbonates is often cited as an important step in the evolution of the early Earth, as carbonates on Earth are the result of carbon dioxide dissolving in liquid water. Consequently, the suggestion that calcite ($CaCO_3$, with a feature at 92.6 μm) and dolomite ($CaMg(CO_3)_2$, 62 μm) may have been detected in the hot ionized environment of PNe is therefore interesting and unexpected (Kemper et al., 2002).

The unidentified 21 μm feature was first discovered in four PPNe from observations by the IRAS LRS (Kwok et al., 1989). High resolution ($\Delta\lambda/\lambda \simeq 2000$) ISO observations have found that all features have the same intrinsic profile and peak wavelength (20.1 μm) (Volk et al., 1999). There is no evidence for any discrete sub-structure due to molecular bands in the observed spectra, suggesting that the 21 μm feature is either due to a solid substance or a mixture of many similarly structured large molecules.

As of 2006, there are 12 known 21-μm sources, all are carbon-rich stars in the post-AGB phase of evolution (Fig. 5). The fact that all of the 21-μm sources are carbon-rich strongly suggests that the carrier of this feature is carbon-based. Possible candidates that have been proposed include large polycyclic aromatic hydrocarbon (PAH) clusters, hydrogenated amorphous carbon (HAC) grains, hydrogenated fullerenes (Webster, 1995), nanodiamonds (Hill et al., 1998), and TiC nanoclusters (von Helden et al., 2000).

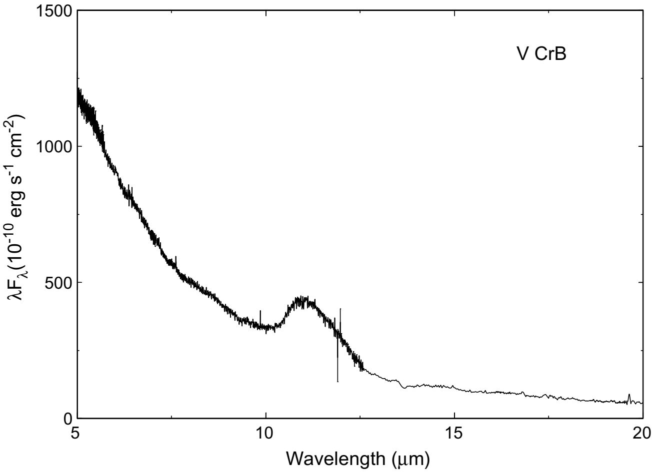

Fig. 4. *ISO SWS* spectrum of the carbon star V CrB showing the 11.3-μm SiC emission feature.

The unidentified emission feature around 30 μm was discovered in the spectra of carbon stars and PNe from *Kuiper Airborne Observatory* (KAO) observations (Forrest et al., 1981). More recently, the 30 μm feature is found to be common in carbon-rich PPNe, especially those showing the 21 μm emission feature. The fact that a significant fraction (~20%) of the total luminosity of the object is emitted in this feature suggests that the carrier must be composed of abundant elements (Hrivnak et al., 2000). The first suggested identification was solid MgS based on a comparison with laboratory measurements (Goebel and Moseley,

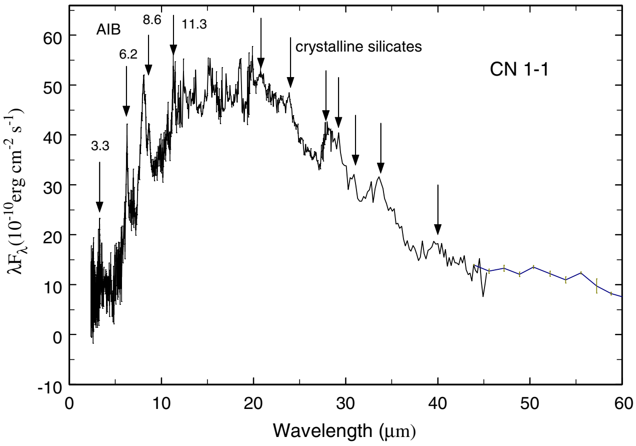

Fig. 3. *ISO SWS* spectrum of the PN Cn1-1 showing the presence of both aromatic infrared bands (AIB) and crystalline silicate emission features.

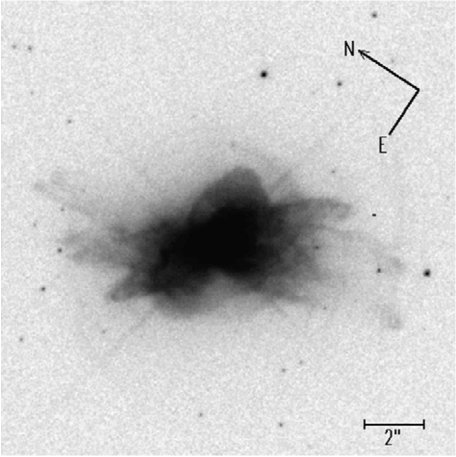

Fig. 5. *HST* WFPC2 V-band image of the 21-μm source IRAS 16594–4656.

1985). The alternative suggestion that the carrier is a carbonaceous material continues to be popular because the feature is only seen in carbon-rich objects.

As carbon stars evolve with increasing luminosity to the peak of the AGB, the mass loss rate is so high that the circumstellar material completely obscures the central star and this phase is referred to as extreme carbon stars (Volk et al., 2000). The 11.3 μm SiC feature also gradually weaken and the dust continuum is dominated by a featureless component, most likely due to some form of amorphous carbon. Fig. 6 show the 5–45 μm spectrum of the extreme carbon star IRAS 21318 + 5631. In this spectral range, the entire continuum is due to dust emission, most of which is amorphous carbon. The 21 and 30 μm features, which will become much stronger in the PPN phase, can also be seen. The strong absorption feature at 13.7 μm is due to v_5 vibrational band of acetylene. The exact chemical structure of this amorphous carbon is unclear, although it is suspected to resemble carbon black or soot observed in the terrestrial environment (Cataldo, 2004). Soot particles are 10–30 nm spherical units with each sphere containing 10^5 C atoms and varying amount of H atoms. Carbon black is similar to soot but with a higher C/H ratio (Harris and Weiner, 1985). It is speculated that the formation of such amorphous carbon begins with acetylene forming polyyne chains to fullerenes and then to amorphous carbon dust.

4. Organic compounds

A family of strong infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm were first detected by the *KAO* in the young carbon-rich PN NGC 7027 (Russell et al., 1977), and have since been widely observed in PNe, H II regions, reflection nebulae, and galaxies (Fig. 7). These features are identified with the aromatic C–H stretch (3.3 μm), aromatic C–C stretch (6.2 and 7.7 μm), aromatic C–H in-plane bend (8.6 μm), and aromatic C–H out-of-plane bending (11.3 μm) modes (Duley and Williams, 1981). These features are collectively referred to as aromatic infrared bands (AIB). The discovery of the AIB in both circumstellar and interstellar sources has led to the suggestion that extraterrestrial aromatic compounds may play a role in terrestrial biological evolution (Ehrenfreund et al., 2006).

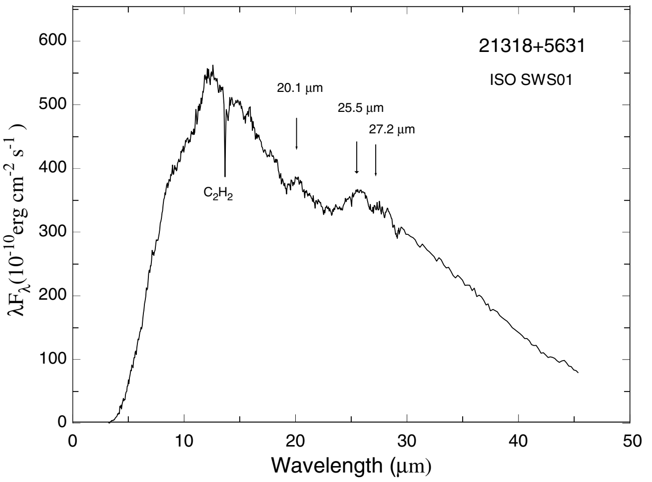

Fig. 6. *ISO SWS* spectrum of the extreme carbon star IRAS 21318 + 5631 showing a continuum due to amorphous carbon and unidentified emission features at 21 and 30 μm.

In addition to the AIBs seen in PNe, emission features at 3.4 and 6.9 μm due to aliphatic C–H stretch and bending modes are found in the spectra of PPNe and young PNe (Jourdain de Muizon et al., 1990; Kwok et al., 1999). Fig. 8 shows the simultaneous presence of the 3.3 μm aromatic feature and the 3.4 μm aliphatic feature in the spectrum of the young PN NGC 7027. Furthermore, emission features at 11.3, 12.1, 12.4, and 13.3 μm, which can be identified as arising from out-of-plane vibrational modes of aromatic C–H bonds with, respectively, 1, 2, 3, or 4 C–H bonds per edge of an aromatic ring, have also been detected (Kwok et al., 1999).

Aromatic and aliphatic bands are not the only emission features seen in the infrared spectrum of PPN. Also present are broad emission features at 8 and 12 μm (Fig. 9). Since the 6.9 μm band is known to originate from a mixture of $-CH_2-$ and $-CH_3$ bending modes, associated bending modes of other side groups are quite likely to be present. Similarly, the 11.3 μm aromatic C–H out-of-plane bending mode can be accompanied by a complex set of features due to out-of-plane vibrations of alkenes (Kwok et al., 2001). The existence of the 8 and 12 μm broad emission features therefore suggests that the chemical structures of these carbonaceous compounds are complex, and probably include a variety of alkane and alkene side groups attached to aromatic rings.

Interstellar diamonds are first positively identified through the C–H stretching modes of hydrides attached to the crystalline surface (Guillois et al., 1999). It has also been suggested that the widely observed extended red emission (ERE) phenomenon is due to photoluminescence of nanodiamonds (Chang et al., 2006).

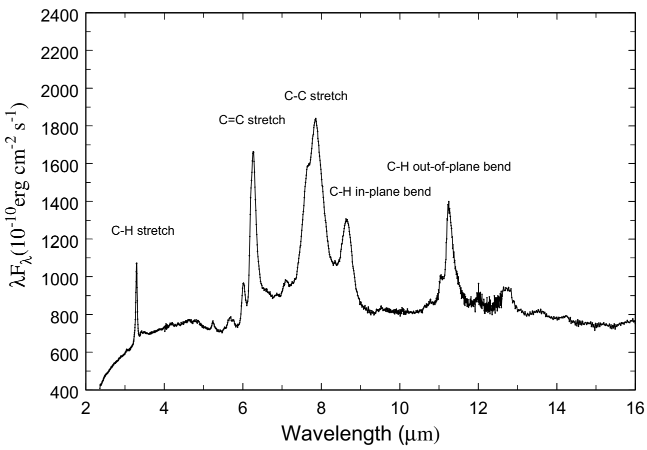

Fig. 7. *ISO SWS* spectrum of the Red Rectangle (HD44179) showing the AIB emission bands.

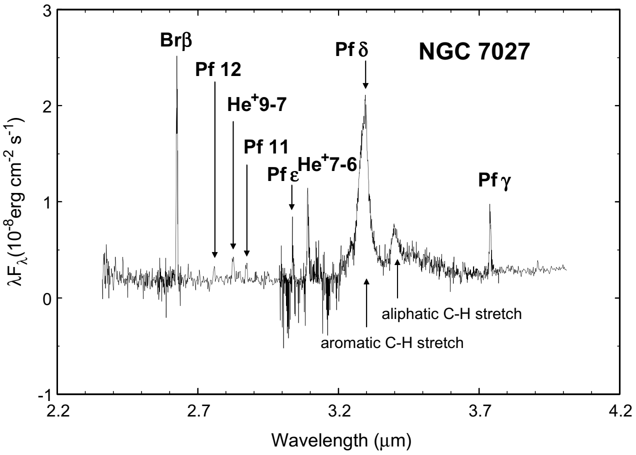

Fig. 8. *ISO SWS* spectrum of the PN NGC 7027 showing both the 3.3 aromatic and 3.4 aliphatic C–H stretch emission features.

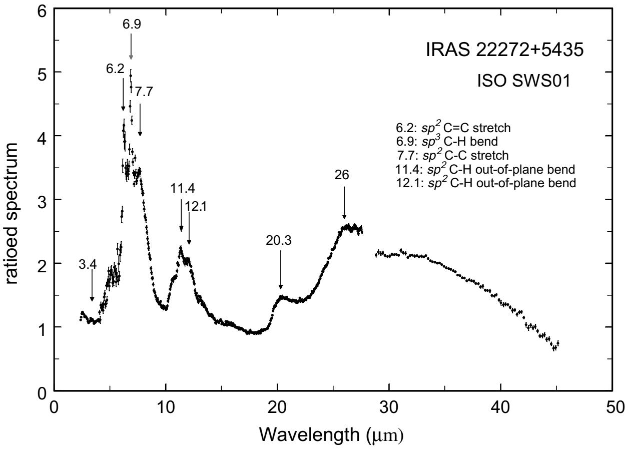

Fig. 9. *ISO SWS* spectrum of the PPN IRAS 22272 + 5435 showing broad emission features at 8 and 12 μm after the removal of a continuum. The detected narrow emission features and their peak wavelengths are marked on the spectrum. The identification of some of these features are listed in the legend.

5. Possible carriers of the aromatic and aliphatic features

The discovery of aromatic features has led to vigorous discussions in the literature on the nature of the carriers. Most of the suggestions center on aromatic hydrocarbons, both natural and artificially created substances. For example, carbonaceous nanoparticles have been produced by chemical vapor deposition (Sakata et al., 1987), combustion (Colangeli et al., 1995), laser ablation (Scott and Duely, 1996), and laser pyrolysis of hydrocarbons (Herlin et al., 1998). Below we summarize some of the most popular models, and discuss their relevance in the circumstellar environment.

- Polycyclic aromatic hydrocarbons: PAH molecules are benzene rings of sp^2-hybridized C atoms linked to each other in a plane, with H atoms or other radicals saturating the outer bonds of peripheral C atoms. PAH molecules were first proposed as the carrier of the AIBs in the diffuse interstellar medium because their small sizes (<1 nm) allow them to be heated to high temperatures (~1000 K) by stochastic heating (Puget and Léger, 1989; Allamandola et al., 1989; Sellgren, 2001). However, small gas-phase PAH molecules are unlikely to be the carrier of the AIB seen in PPNe and PNe. The AIBs in these objects always sit on top a strong continuum, which cannot be provided by small PAH molecules. The width of the AIB features and the consistency of the peak wavelengths also argue against the idea that they are produced by a mixture of different PAH molecules. The carrier is more likely to be a solid-state compound, consisting of at least hundreds of carbon atoms.
- Hydrogenated amorphous carbon: Hydrogenated amorphous carbon (HAC) consists of islands of aromatic (sp^2) bonded C atoms joined together with a variety of peripheral sp^2 and sp^3 bonded hydrocarbons (Jones et al., 1990). HAC can be formed in the laboratory by direct condensation of carbon vapor from a H-rich atmosphere, and have been observed to show similar spectral features as in PPNe (Scott et al., 1997).
- Quenched carbonaceous composites: Quenched carbonaceous composites (QCC) are produced by the technique of hydrocarbon plasma deposition. Methane gas is heated to 3000 K with a microwave generator and allowed to expand into a vacuum chamber and condensed on a room-temperature substrate (Sakata et al., 1984). The resultant dark, granular material is shown by electron micrography to have an amorphous structure. Mass spectroscopy of QCC suggests that its aromatic component typically consists of 1–4 rings, and most have only 1–2 rings. Infrared spectroscopy of QCC reveals a mixture of sp, sp^2, and sp^3 bonds (Wada and Tokunaga, 2006). Since the conditions under which QCC is synthesized resemble the circumstellar environment of AGB stars, its laboratory production may shed some light on the solid-state condensation process in the envelopes of AGB and post-AGB stars.
- Kerogen: Coal, formed from fossilized hydrocarbon materials, also contains a mixture of sp, sp^2, and sp^3 bonds like HAC and QCC. The possibility that coal-like material (e.g., kerogen) can be responsible for the AIB was first suggested by R. Papoular (Papoular et al., 1989). Structurally, kerogen can be represented by random arrays of aromatic carbon sites, aliphatic chains (–CH_2–$_n$), and linear chains of benzenic rings with functional groups made up of H, O, N, and S attached. Comparison of the infrared spectra of kerogen shows that they are very similar to those of PPNe (Guillois et al., 1996; Papoular et al., 1996; Papoular, 2001.)

In summary, the carbonaceous compounds seen in PPNe and PNe are likely to include both aromatic and aliphatic components as well as impurities such as O and N (Papoular, 2001).

6. Stardust in the solar system

Spectral signatures of grains produced in AGB stars, PPNe, and PNe are now found in solar system objects. The silicate features, both amorphous and crystalline, are seen in comets and interplanetary dust (Sandford and Walker, 1985). Infrared spectra of organic extract sublimate from the Murchison meteorite show the 3.4 μm aliphatic features that are similar to those observed in PPNe (Pendleton and Allamandola, 2002). This feature has also been observed in comets (Davies et al., 1993) and interplanetary dust (Clemett and Maechling, 1993). Isotopic studies of meteorites have also identified grains of solar origin, including diamonds (Lewis et al., 1987), SiC (Bernatowicz et al., 1987), corundum and spinel (Nittler et al., 1997). These grains therefore represent an important link between stars and the solar system (Zinner, 1998). The dominant organic matter in carbonaceous chondrites are similar to kerogen. The insoluble organic matter isolated from Orgueil, Murchison, and Tagish Lake meteorites are found to consist of a network of relatively small polyaromatic units cross linked by short, highly branched aliphatic chains (Derenne et al., 2006). Such structures are very similar to the carbonaceous compounds seen in PPNe (Kwok et al., 2001).

These results suggest that comets, interplanetary dust, and meteorites preserve pristine stellar material not processed by the early solar nebula, and our ability to perform laboratory analysis of these materials through mass spectroscopic and isotopic analysis has given us a direct link to inorganic and organic compounds produced by stars. Results from the STARDUST mission are expected to shed further light on this proposed stars-solar system connection.

7. Summary

We have learned that chemical synthesis of complex organic and inorganic compounds can take place in the low-density circumstellar environment over very short (10^3 yr) time scales during the late stages of stellar evolution. By tracing the change in the infrared spectra of carbon stars to PPNe to PNe, we found definite evidence for chemical evolution (Kwok, 2004). Infrared spectroscopic observations have clearly demonstrated that solid-state compounds of both organic and inorganic nature are produced in abundance in the circumstellar envelopes of evolved stars. The ejection of these grains into the interstellar medium suggests that circumstellar grains is a major source of interstellar grains, some of which may have survived the formation of the solar system. The detections of pre-solar grains in meteorites and the detection of high deuterium to hydrogen ratio in interplanetary dust particles have supported this stellar-solar system connection. These grains are apparently sturdy enough such that they survived the long journey through the interstellar medium to have arrived at the early solar system. Although the pre-solar grains in the inner solar system were likely to have been destroyed, those beyond the orbit of Neptune may have preserved their original chemical composition. A significant amount of these stellar organic materials could have been delivered to Earth during the heavy bombardment phase of the early Earth. Whether these extraterrestrial organic compounds play any role in the subsequent biological evolution needs to be explored by further studies.

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