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Review

Synthesis of Organic and Inorganic Compounds in Asymptotic Giant Branch Stars

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Abstract: After the synthesis of carbon in the core of asymptotic giant branch (AGB) stars, carbon is dredged up to the surface by convection. Many carbon-based molecules are formed in the subsequently developed stellar wind. These include acetylene, which can link together to form benzene in post-AGB evolution. The emergence of the spectral signatures of aromatic and aliphatic compounds in the transition phase between AGB stars and planetary nebulae suggests that complex organic compounds can be formed in the circumstellar environment over very short (10^3 yr) timescales. We suggest that the carrier of the family of unidentified infrared emission bands is an amorphous carbonaceous compound—mixed aromatic/aliphatic nanoparticles (MAONs). The implications of the synthesis of complex organics in evolved stars are discussed.

Keywords: asymptotic giant branch stars; planetary nebulae; molecules; infrared bands; infrared spectroscopy

1. Introduction

The idea that organic matter was associated with life originated from the isolation of organic molecules from living organisms. The evidence included the extraction of the amino acid asparagine from asparagus by Louis Nicolas Vauquelin and Pierre Jean Robiquet in 1806; cysteine from urinary calculi (bladder stones) by William Hyde Wollastonthe in 1810; leucine from cheese by Joseph Louis Proust in 1819; and glycine from gelatin by Henri Braconnot in 1820. Different classes of organic molecules in living organisms were recognized as the building blocks of life—lipids (fatty acids) by Michel Eugène Chevreul in 1823, proteins by Gerardus Johannes Mulder in 1838, and carbohydrates (sugars) by Emil Fischer in 1877. The DNA molecule was isolated from the nuclei of yeast by Friedrich Miescher in 1869. It was therefore natural for scientists to believe that organic molecules could only be produced by living organisms, which possess a "vital force" separating them from inorganic compounds such as minerals.

This perception changed with the laboratory synthesis of biomolecules. It began with the synthesis of urea ($CO(NH_2)_2$) from ammonium cyanate (NH_4CNO) by Friedrich Wöhler in 1828; the synthesis of amino acid alanine from acetaldehyde, ammonia, and hydrogen cyanide by Adolph Strecker in 1850; and the synthesis of sugars from formaldehyde by Aleksandr Butlerov in 1861. The nucleobase adenine ($C_5H_5N_5$) was synthesized from hydrogen cyanide (HCN) and ammonia (NH_3) by Joan Oró in 1960 [1]. This was followed by the synthesis of guanine [2] and cytosine [3].

This laboratory work convincingly demonstrated that a vital force is not necessary for the existence of organic molecules. Today, organic molecules are defined as a group of molecules and compounds based on the element carbon (C), together with the elements hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and phosphorus (P).

The natural terrestrial environment contains a large reservoir of organics. In addition to biomass in the biosphere, the Earth's lithosphere contains coal, oil, and natural gas. The largest amount of organic matter on Earth is in the form of kerogen, which is a solid,

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insoluble, organic matter found in sedimentary rocks. This organic matter is a remnant of past life and is biological in origin [4]. The amount of abiological organics on Earth is very small in comparison [5]. Consequently, it was commonly believed that Earth was the sole domain of organic compounds. It was only recently that we learned from Solar System explorations and astronomical spectroscopic observations that organic matter is common in the Universe [6]. Where do these organic compounds come from and how are they synthesized? In this paper, we explore the possible origin of complex organic compounds in evolved stars.

2. Molecular Synthesis in the Stellar Winds of AGB Stars

Stellar molecular synthesis begins during the asymptotic giant branch (AGB) phase of stellar evolution. After the nucleosynthesis of the element carbon in the core through the triple-α reaction, C atoms are dredged up to the stellar surface through a convection process. In the low-temperature atmosphere of AGB stars, simple molecules such as C_2, C_3, and CN can form. As the surface layer is gradually being removed by a stellar wind, a variety of simple molecules are synthesized in the circumstellar envelope formed by the stellar wind. Through the technique of millimeter-wave spectroscopy, the rotational transitions of over 80 molecules have been detected in the circumstellar envelopes of AGB stars [7,8].

Micron-size solid-state particles can be directly detected by their thermal radiation in the infrared spectrum. Direct condensation from gas to solid results in a disordered structure. The first circumstellar solids discovered were amorphous silicates, which were identified by their Si–O stretching and Si–O–Si bending modes at 9.7 and 18 µm, respectively. These features are detected in over 4000 O-rich AGB stars by the Low-Resolution Spectrometer (LRS) on board the *Infrared Astronomical Satellite* (*IRAS*) all-sky survey [9]. These features can be in emission or in self-absorption, depending on the amount of mass in the circumstellar envelope. Other mineral species detected include different forms of refractory oxides [10]. The solid particle silicon carbide (SiC) is detected in over 700 C-rich AGB stars [9].

3. Synthesis of Complex Organics in Post-AGB Evolution

A family of broad infrared emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 µm (commonly referred to as unidentified infrared emission—UIE—bands) was first detected in the spectrum of the planetary nebula NGC 7027 [11]. Since then, UIE bands have been detected in planetary nebulae, reflection nebulae, HII regions, novae, in the diffuse interstellar medium in the Milky Way Galaxy, and in external galaxies [12,13].

Planetary nebulae are descendants of AGB stars after their H envelope has been completely depleted by the stellar wind and photoionized by the exposed stellar hot core [14]. Since the carriers of the UIE bands are synthesized in situ, planetary nebulae are ideal objects to study their origins. To witness the first emergence of the UIE bands, we need to identify objects in transition between the AGB and planetary nebulae stages (often referred to as proto-planetary nebulae). Approximately 30 proto-planetary nebulae were discovered from their infrared properties as a result of the follow-up of the *IRAS* all-sky survey [15]. The observation of these proto-planetary nebulae led to the detection of the 3.4 µm aliphatic C–H stretch [16], and the broad 8 and 12 µm emission plateau features [17]. The plateau features are identified as the superposition of the in-plane and out-of-plane bending modes of various aliphatic side groups [17].

3.1. Origin of the UIE Bands

Shortly after their discovery, UIE bands were suggested to be vibrational modes of organic compounds. The 3.3 and 11.3 µm bands were identified as the C–H stretching and bending modes of aromatic compounds [18,19]. The astronomical UIE bands have also been suggested to be related to the laboratory-synthesized complex organic polymer tholins [20]. However, these ideas were not initially accepted by the astronomical community.

Further observations with the *Infrared Space Observatory* and the *Spitzer Space Telescope* found that the UIE family consists of the following features: (i) aromatic bands at 3.3 and 11.3 µm; (ii) aliphatic bands at 3.4 and 6.9 µm; (iii) major unidentified bands at 6.2, 7.7, and 8.6 µm; (iv) minor bands at 15.8, 16.4, 17.4, 17.8, and 18.9 µm (in proto-planetary nebulae [21], in reflection nebulae [22], and in galaxies [23]); and (v) broad plateau features at 8, 12, and 17 µm (Figure 1).

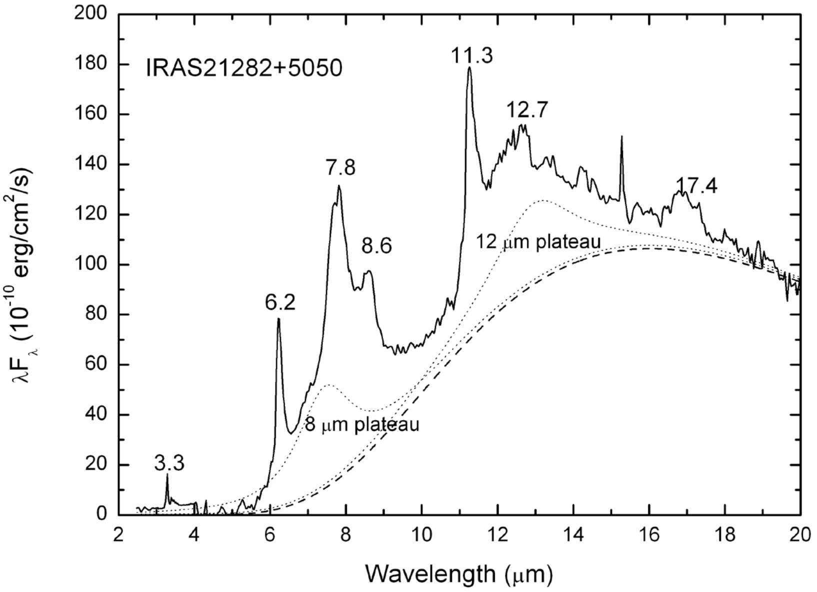

Figure 1. *Infrared Space Observatory* spectrum of the planetary nebula IRAS 21282+5050. The strong UIE bands are marked in units of microns. The two dotted lines are fit to the 8 and 12 µm plateau features, and the dashed line is an approximation to the thermal emission continuum by solid-state particles.

While we now recognize that the carrier of the UIE bands is almost certainly an organic compound, the exact chemical structure of the carrier remains unknown. After the wide detection of molecules in the interstellar medium, polycyclic aromatic hydrocarbon (PAH) molecules as carriers of the UIE bands became popular [24,25]. In the PAH hypothesis, the UIE bands are the result of infrared fluorescence from small (~50 C atoms) gas-phase PAH molecules being pumped by far-ultraviolet photons [26].

Although PAH molecules are known to have C–H stretching modes around 3.3 µm, the actual wavelengths of C–H stretching are shortward of the 3.3 µm UIE band [27,28]. PAH molecules generally have out-of-plane bending modes around 10–14 µm, but fitting to the observed UIE 11.3 µm band requires a mix of PAH molecules [29]. The assignments of the 6.2, 7.7, and 8.6 µm UIE bands to PAH molecules are more difficult. It was suggested that the 6.2 µm band is due to C–C stretching and the 8.6 µm band is due to the C–H in-plane bending modes of PAH molecules [30]. The 7.7 µm UIE band has no obvious counterpart in PAH spectra and has been suggested to be due to the blending of several C–C stretching modes [24]. Since C–C stretching modes in PAH molecules are generally very weak, it was later proposed that the 6.2 and 7.7 µm bands are due to ionized PAH molecules, which tend to show stronger C–C stretching modes [31,32]. However, experimental results show that the C–C vibrational modes of PAH ions generally occur at wavelengths longer than 6.2 µm [33,34]. By increasing the size of the molecules, the peak of the band can shift to shorter wavelengths, but never as short as 6.2 µm [34]. In order to account for this discrepancy, it was suggested that some of the C atoms in specific positions in the ring should be replaced by nitrogen [34].

In addition, the PAH hypothesis faces the following problems: (i) PAH molecules have well-defined sharp features, but the UIE bands are broad; (ii) PAH molecules are primarily excited by UV and absorb poorly in the visible spectrum, but UIE bands are seen in proto-planetary nebulae and reflection nebulae, objects with very little UV background radiation. The shapes and peak wavelengths of UIE bands in reflection nebulae are found to be independent of the temperature of the exciting stars [35]; (iii) the strong and narrow gas-phase PAH molecular electronic bands are not detected in interstellar extinction curves to very low upper limits [36–38]; (iv) no specific PAH molecule has been detected in space (the closest molecules are two double-ring molecules with nitrile functional groups [39] and two pure hydrocarbon cyclic molecules with 5-member rings [40]); (v) there are great difficulties in reconciling the band positions and relative intensities of laboratory PAH spectra with astronomical UIE spectra [41]; and (vi) the large number of free parameters in the PAH model fitting suggests that such fittings are not very meaningful [42].

In response to these criticisms, the PAH model has been revised to incorporate ionization states and large sizes to increase the absorption cross sections in the visible spectrum; introduce dehydrogenation, superhydrogenation, and minor aliphatic side groups to explain the aliphatic features; and appeal to a large mixture of different PAH molecules to explain the lack of detection of individual PAH molecules. Since known PAH molecules have problems reproducing the wavelengths of the UIE bands, a large mixture of diverse PAH molecules is needed to fit the observed astronomical spectra. Hetro-atoms such as N and O are also introduced to explain the 6.2 and 11.3 µm features. In a recent version of the hypothesis, it is stated that "Within the astrophysical context, the PAH family includes PAH related species such as, for example, PAHs with side groups, hetero-substituted PAHs, fully or partially (de)hydrogenated PAHs, and PAH clusters" [43]. Therefore, the PAH hypothesis has moved away from the chemical definition of PAH molecules to a hybrid model.

3.2. Laboratory Synthesis of Carbonaceous Solids

In order to identify possible carriers of the UIE bands, it would be useful to see what carbonaceous products can naturally exist in the interstellar medium. By introducing H into graphite (hybridization sp^2) and diamond (hybridization sp^3), a variety of amorphous C–H alloys can be created [44]. When external energy is injected into a collection of hydrocarbon gasses and the released compounds are collected on a cool substrate, different forms of amorphous hydrogenated carbon materials can be identified. Examples of laboratory techniques to synthesize artificial amorphous hydrocarbons include the microwave irradiation of methane [45,46], arc-discharge in a hydrogenated atmosphere [47,48], the laser ablation of graphite in a hydrogen atmosphere [49–51], the infrared laser pyrolysis of gas-phase hydrocarbons [52], the photolysis of methane at low temperatures [53], amd the flame combustion of acetylene (C_2H_2), ethylene (C_2H_4), and propylene (C_3H_6) mixed with oxygen (O_2)-forming soot [54,55]. The infrared spectra of these carbonaceous materials show broad features that qualitatively resemble the astronomical UIE bands.

The results of these laboratory experiments suggest that the natural product of combustion is a complex, amorphous, hydrogenated carbonaceous material. A recent experiment designed to simulate molecular and solid synthesis in circumstellar low-temperature and low-density conditions has produced simple molecules such as acetylene and ethylene, as well as carbonaceous solids such as amorphous carbon nanograins and aliphatic carbon clusters [56]. These results suggest that amorphous organics with mixed hybridization states can form under circumstellar conditions.

4. Mixed Aromatic/Aliphatic Organic Nanoparticles (MAONs) as Carrier of UIE Bands

As an alternative to the PAH hypothesis, we proposed that the UIE bands are due to mixed aromatic/aliphatic organic nanoparticles (MAONs) [28,57]. MAONs are complex organic solids with amorphous structures characterized by a highly disorganized arrangement of small units of aromatic rings linked by aliphatic chains. They contain impurities in the forms of O, N, and S, and are composed of rings of different sizes and chains of different lengths and random orientations (Figure 2). In order to understand the vibrational spectra of complex organics, we performed quantum chemistry calculations beginning with PAH molecules with aliphatic side groups [58], followed by an analysis of the nature of the 3.3/3.4, 6.2, and 11.3 μm UIE bands [29,59,60], and analyzed the spectral properties of molecules with MAON-like structures [61]. We found that many spectral features of complex organics are due to coupled vibrational modes and further work is needed to fully understand the spectral properties of complex organics.

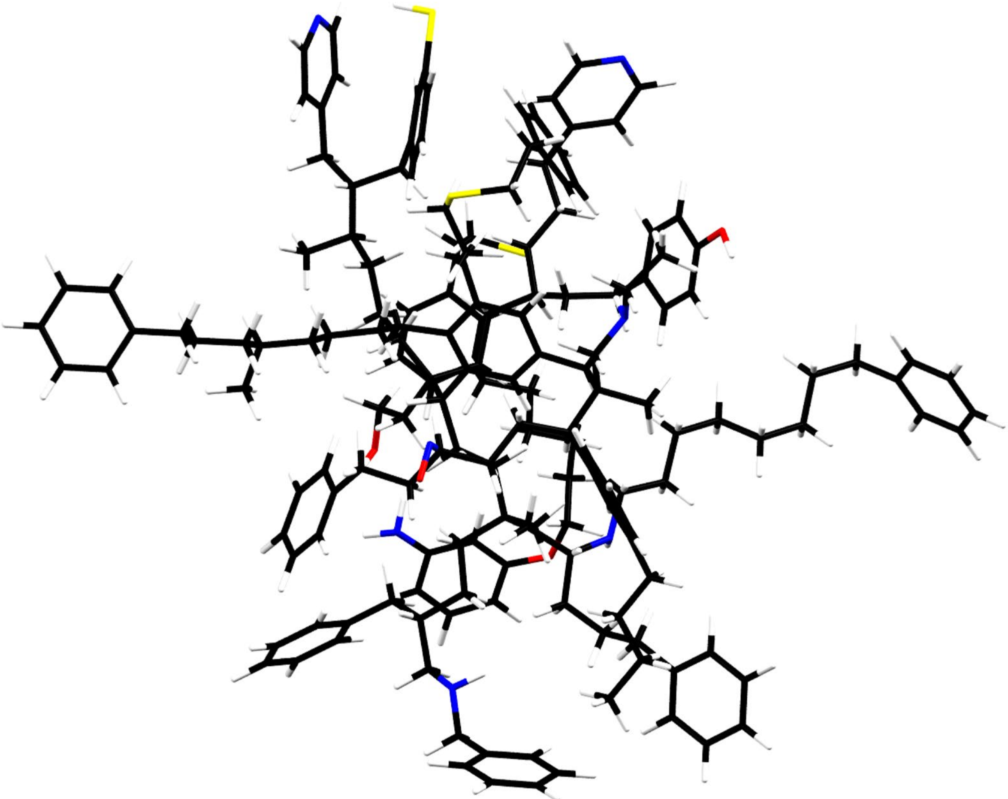

Figure 2. An example of an MAON molecule with 169 C atoms (in black) and 225 H atoms (in white), 4 O atoms (in red), 7 N atoms (in blue), and 3 S atoms (in yellow). It is characterized by a highly disorganized arrangement of small units of aromatic rings linked by aliphatic chains. A typical MAON particle may consist of multiple structures like this one. Figure courtesy of Seyed Abdolreza Sadjadi.

The difference between the PAH and MAON models is not just a question of semantics as there are fundamental differences between the two models, namely (i) is the carrier of UIE composed of free-flying gas molecules or solids? (ii) Is it purely aromatic or mixed sp^2/sp^3? (iii) Is its geometry planar or three dimensional? (iv) Are the carriers small (<50 C) or large (~10^3 C)? (v) Are they composed of only C and H or do they have impurities? (vi) Are their structures pure rings or do they contain rich functional groups? (vii) Is the chemical structure regular with repeatable patterns or amorphous, containing different sizes of aromatic islands and variable aliphatic chain lengths and orientations?

The correct identification of the carrier of the UIE bands is important as the UIE bands have been used as tracers of star formation in galaxies [62,63], as tracers of elemental and chemical evolution of galaxies [64], and to estimate the properties of the background radiation fields [65].

5. Circumstellar Chemical Synthesis

Planetary nebulae and novae are the only astronomical objects where we can directly witness organic synthesis in action. The chemical timescale of synthesis is constrained by dynamical and evolutionary timescales of planetary nebulae, which are of the order of 10^4 years. Complex organics are observed to form under very low density ($<10^6$ cm^{-3}) conditions over very short (10^3 yr) timescales. How complex organics could form under these conditions is difficult to understand theoretically, but observationally, there is no doubt that it is happening. A way to understand the sequence of chemical synthesis is to observe the chemical contents of objects in consequential evolutionary stages from AGB to proto-planetary nebulae [66]. A possible scenario for the synthesis of aromatic and aliphatic materials begins with the synthesis of acetylene (C_2H_2), which is detected in highly evolved carbon stars [67]. These linear molecules can bend together to form benzene [68]. Multiple aliphatic side groups can attach to these islands of aromatic rings (see Figure 4 of ref. [17]).

6. Summary

Organic compounds are now found to be not just confined to the terrestrial environment, but are present throughout the Universe, even during early epochs [69]. Although AGB stars have been known since the 1950s to be sources of heavy elements in the Universe [70,71], recent research has demonstrated that molecules, including complex organics, can be efficiently synthesized abiologically during the AGB and post-AGB phases of stellar evolution. Therefore, evolved stars can play a role in the formation and distribution of complex organics in the Universe.

Planetary explorations have discovered that complex organics are commonly present in asteroids, comets, planetary satellites, and interplanetary dust particles [72]. The conventional wisdom is that these organics were formed during the early stages of Solar System formation. With the discovery of the stellar synthesis of organics, it is possible that the primordial Solar System could have been enriched by stellar ejecta, and these stellar organics were embedded in the primordial Solar System [73]. The role that these stellar organics may play in the origin of life on Earth is yet to be explored [74].

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