

Synthesis of Organic Matter by Stars and its Effect on the Origin of Life on Earth

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Abstract. The last 10^5 years of stellar evolution represents the most active period of synthesis of organic compounds in a star's life. Over 60 gas-phase molecules, including rings, radicals, and molecular ions have been identified by millimeter-wave and infrared spectroscopic observations through their rotational and vibrational transitions. Space infrared spectroscopic observations of emissions from the stretching and bending modes of aliphatic and aromatic compounds have revealed a continuous synthesis of organic material over a period of only a few thousand years. These organic gases and solids are ejected into the interstellar medium through stellar winds and spread all over the Galaxy. Isotopic analysis of meteorites and interplanetary dust collected in the upper atmospheres have revealed the presence of pre-solar grains similar to those formed in evolved stars. This provides a direct link between star dust and the solar system and raises the possibility that the early solar system was chemically enriched by stellar ejecta. In this paper, we summarize the chemical structure of stellar organic matter and compare them to the organics found in meteorites, comets, asteroids, planetary satellites, and interplanetary particles. The possibility that external delivery of stellar organic matter had contributed to the origin of life of Earth is discussed.

1. Introduction

The development of millimeter-wave and infrared spectroscopy in the last 30 years has led to the discovery of over 160 molecular species in space through their rotational and vibrational transitions, a large majority of them organic molecules. The detected species cover all kinds of organic molecules, including hydrocarbons (e.g., methane CH_4 , acetylene C_2H_2 , ethylene C_2H_4), alcohols (e.g., methanol CH_3OH , ethanol $\text{C}_2\text{H}_5\text{OH}$, vinyl alcohol CH_2CHOH), acids (formic acid HCOOH , acetic acid CH_3COOH), aldehydes (e.g., formaldehyde H_2CO , acetaldehyde CH_3CHO , propenal CH_2CHCHO , propenal $\text{CH}_3\text{CH}_2\text{CHO}$), ketones (e.g., ketene H_2CCO , acetone, CH_3COCH_3), amines (e.g., methylamine CH_3NH_2 , cyanamide NH_2CN , formamide NH_2CHO), ethers (e.g., dimethyl ether CH_3OCH_3 , ethyl methyl ether $\text{CH}_3\text{OC}_2\text{H}_5$), etc. Molecules are found in star formation regions, dark clouds, diffuse clouds, circumstellar envelopes of stars, and in external galaxies. The fact that molecules are detected as far as $z = 6$ suggests that molecules were synthesized as early as 10 billion years ago.

Although the existence of organic grains in space has been speculated for some time (Hoyle & Wickramasinghe 1977; Duley & Williams 1979), the first serious identification of organic solid-state particles in the interstellar medium came after the discovery of the unidentified infrared emission (UIE) features in the planetary nebula NGC 7027 (Russell et al. 1977). The UIE feature at 3.3 μm was first identified as the C-H

stretching mode of aromatic compounds by R.F. Knacke (1977). This organic affiliation was extensively discussed by Duley & Williams (1981) who assign the 3.3 and 11.3 μm features to graphitic (aromatic) materials. In 1984, Léger & Puget (1984) suggested the UIE features as arising from PAH molecules excited by single-photon heating. In addition to the 3.3 and 11.3 μm features, they identified the 6.2 μm feature as due to aromatic C-C stretch, the 8.6 μm feature as the C-H in-plane bend, and the 11.3, 12.4 and 13.3 μm features as due to solo, duo and trio C-H out-of-plane bending modes. The PAH hypothesis was extended by Allamandola et al. (1985) who calculated the vibrational spectrum of gas-phase chrysene. These works have cumulated in two reviews in 1989 by Allamandola et al. (1989) and Puget & Léger (1989).

Recent spectroscopic observations by the ISO and Spitzer satellite have found UIE bands to be commonly present in starburst galaxies (Sturm et al. 2000; Smith et al. 2007). These results show that organic matter is not only present in our Galaxy, but is widespread all over the Universe (Kwok 2011).

2. Evolved stars as a source of organic matter in the Galaxy

While organic molecules and the UIE features are seen in a variety of galactic environments, the only place that we have direct evidence of organic matter actually being synthesized is in the circumstellar envelopes of evolved stars. Molecules and solids can be seen to be forming in the expanding envelopes ejected by asymptotic giant branch (AGB) and planetary nebulae. Due to the dynamical times of the envelopes, we know that the chemical time scale of formation must be less than 10^4 yr (Kwok 2004). Over 60 molecular species have been detected in the circumstellar envelopes of AGB stars and planetary nebulae, and they include inorganics (e.g., CO, SiO, SiS, NH₃, AlCl, etc.), organics (C₂H₂, CH₄, H₂CO, CH₃CN, etc), radicals (CN, C₂H, C₃, HCO⁺, etc.), chains (e.g., HCN, HC₃N, HC₅N, etc.), and rings (C₃H₂). In the spectra of planetary nebulae, the UIE features are very strong, showing that complex organic matter are being synthesized in the late stages of evolution.

The fact that the UIE features are not seen in AGB stars and only emerge during the post-AGB phase has led to the strong interest in proto-planetary nebulae as the site of organic synthesis. In addition to the 3.3, 6.2, 7.7, and 11.3 μm aromatic features, aliphatic features at 3.4 and 6.9 μm arising respectively from symmetric and asymmetric C-H stretching and bending modes of methyl and methylene groups attached to aromatic rings have been detected (Jourdain de Muizon et al. 1990; Kwok et al. 1999). Features at 15.8, 16.4, 17.4, 17.8, and 18.9 μm have also been found (Zhang et al. 2010). In addition to the discrete features, broad emission features up to several microns wide are also seen. These broad plateau features include features at 8 and 12 μm and a broad feature covering the 15-20 μm region. The 8 and 12 μm emission plateaus can be identified as collective in-plane and out-of-plane bending modes of a mixture of aliphatic side groups attached to aromatic rings (Kwok et al. 2001). The 15-20 μm plateau feature is particularly strong in some proto-planetary nebulae and has been suggested to arise from C-C-C in-plane bending of aromatic rings (Van Kerckhoven et al. 2000).

While it is difficult to understand how complex organics can form under such low density conditions (the densities in the circumstellar envelopes are lower than the best vacuum that can be achieved in a terrestrial laboratory), observations provide concrete evidence for their formation on time scales as short as a few hundred years, based on

the evolutionary time scales of proto-planetary nebulae. The case is even more dramatic in novae, where the UIE features can be seen appearing on week-long time scales when the spectra evolution of novae are monitored after their outburst (Evans et al. 2005).

3. Carrier of the unidentified infrared emission features

In the last 20 years, the term PAH is commonly used in the astronomical literature to refer to the UIE features. The wide acceptance of the PAH hypothesis is best summarized by Tielens who stated in his Annual Reviews of Astronomy & Astrophysics article: “these features are (almost) universally attributed to the IR fluorescence of far-ultraviolet (FUV)-pumped polycyclic aromatic hydrocarbon (PAH) molecules, containing 50 C atoms” (Tielens 2008).

In spite of the PAH bandwagon, a small minority holds different opinions on the origin of the UIE bands. Other suggestions for the carrier of the UIE bands include hydrogenated amorphous carbon (HAC) (Jones et al. 1990), quenched carbonaceous composite (QCC) (Sakata et al. 1984, 1987), soot (Pino et al. 2008), coal and kerogen (Papoular et al. 1989; Papoular 2001), and petroleum fractions (Cataldo et al. 2004). One property common to all these proposals is that these candidates are all amorphous carbonaceous matter with disorganized structures, in contrast to the pure and highly structured PAH molecules.

It is interesting to note that in laboratory simulations experiments, when graphite or other gaseous mixtures of hydrocarbon molecules are bombarded with energy sources, the end products are often carbonaceous particles containing islands of sp^2 rings connected by a network of aliphatic chains (Colangeli et al. 1995; Herlin et al. 1998; Menzella et al. 2002; Hu & Duley 2007; Duley & Hu 2009), and sometimes include fragments of fullerenes (Jäger et al. 2009).

The most commonly used argument against a coal or other grain models is that solids are too cold to radiate in the near infrared (Puget et al. 1995). However, single photon heating may not be the only way that the organic grains can be heated. Other recently proposed mechanisms include chemical (Duley & Williams 2011) and collisional heating (Papoular 2012).

The discovery of aliphatic discrete and broad emission features in proto-planetary nebulae suggest that the carrier of the UIE bands cannot be a pure aromatic compound, and is much more likely to have a mixed aromatic/aliphatic structure (Kwok et al. 1999, 2001). Spectral decomposition analysis of the infrared spectra of planetary nebulae, proto-planetary nebulae, H II regions, and novae all show strong aliphatic components, leading to the suggestion that the UIE bands are best explained by emissions from nanoparticles with mixed aromatic/aliphatic structures (Kwok & Zhang 2011).

While the evidence for the existence of organic compound with an aromatic component in the Universe is overwhelming, the evidence for the presence of PAH molecules is far less strong. PAH molecules have pure C and H chemical compositions and have well-defined and sharp vibrational features. However, the observed UIE features are broad. In order to fit the observed spectra, one has to use a complex mixture of PAH molecules of different sizes and charged states (Allamandola et al. 1999; Peeters et al. 2002; Draine & Li 2007; Cami 2011). Since the electronic, vibrational, and rotational transitions of PAH molecules are well known, one would expect that PAH molecules would be easily detectable in emission or absorption if they are indeed widespread in

the interstellar medium. On the contrary, not a single PAH molecule has been positively identified in the interstellar medium.

Some may argue that whether the UIE features are due to PAHs or organic solids is only a question of semantics. However, PAH is a precisely defined term in chemistry and is specific in its meaning of chemical composition and structure. It is of pure C and H composition and has a sp^2 , graphite-like structure. Even when one extends the definition of PAH to large clusters of rings, it still has a regular structure and is fundamentally different from a mixed element (C, H, O, S, N, ..), amorphous, disorganized, mixed sp^2/sp^3 structure. It is clear that PAH molecules are totally inadequate as a model of circumstellar and interstellar organics.

4. Relations with the Solar System

The presence of complex organics in the Solar System was known since the work of Cronin et al. (1987). The soluble component of carbonaceous meteorites include carboxylic acids, sulfonic and phosphonic acids, amino acids, aromatic hydrocarbons, heterocyclic compounds, aliphatic hydrocarbons, amines and amides, alcohols, aldehydes, ketones, and sugar related compounds, and almost all biologically relevant organic compounds are present. In addition, there is a Insoluble Organic Matter (IOM) component which is a macromolecular material similar to kerogen (Kerridge 1999). Although the origin of these organics is not clear, it is commonly believed that they were synthesized during the condensation of the solar nebula. The traditional view has been that planets and other Solar System objects were formed from a well-mixed primordial nebula of chemically and isotopically uniform composition (Suess 1965), and the Solar System was completely isolated and detected from other stellar systems.

The discovery of presolar grains in meteorites showed that solids made by stars can travel across the Galaxy and be embedded in the early solar system (Bernatowicz et al.; Zinner 1998). The kinds of presolar grains that have been found include diamonds, silicon carbide, corundum, spinel, etc. These detections demonstrate a direct link between evolved stars and the Solar System. The excesses in D, ^{13}C , ^{15}N , in meteoritic organics also suggest possible interstellar origins of these materials (Martins et al. 2008; Nakamura-Messenger et al. 2006).

Laboratory analysis of interplanetary dust particles (Flynn et al. 2003) and spectral analysis of Titan haze (Kim et al. 2011) have found signatures of $3.4\ \mu\text{m}$ C-H aliphatic stretching modes, similar to those found in proto-planetary nebulae. Analysis of the IOM shows a chemical structure made up of aromatic rings and aliphatic chains, as well as containing O, N, and S impurities (Derenne & Robert 2010; Cody et al. 2011). These properties bear a remarkable resemblance to the structure of organics found in planetary nebulae and proto-planetary nebulae. These coincidences suggest the possibility that the Solar System organic may represent remnants of organic dust ejected by evolved stars (Kwok 2009).

Since the Miller-Urey experiment, it has been commonly believed in the scientific community that life on Earth originated from simple molecules and developed into increasing complexity through chemical reactions. The discovery of stellar organics opened the possibility that the Earth may have inherited organics of sufficient complexity to make life on Earth to have an earlier and easier start (Ehrenfreund et al. 2006). The key question is whether comets, asteroids, and interplanetary dust particles can deliver sufficient quantities of stellar organics to Earth to make a difference. Another

possibility is that the primordial Earth may have had accreted large quantities of organics at the time of its formation. If either of these scenarios is true, then life must be much more common and widespread than previously believed, as planets in other stellar systems must also have been benefited by the spread of organic grains by evolved stars in the Galaxy.

5. Conclusion

Infrared spectroscopic observations have identified the synthesis of complex organics during the late stages of stellar evolution. These organics have a mixed aromatic and aliphatic components and their chemical structures are similar to the organics found in meteorites and interplanetary dust particles. We suggest that the early Solar System may have been enriched by organic grains ejected by evolved stars and the development of life in the early Earth may have been assisted by the presence of these extraterrestrial stellar organic materials.

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