

Organic Compounds in Circumstellar and Interstellar Environments

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Abstract Recent research has discovered that complex organic matter is prevalent throughout the Universe. In the Solar System, it is found in meteorites, comets, interplanetary dust particles, and planetary satellites. Spectroscopic signatures of organics with aromatic/aliphatic structures are also found in stellar ejecta, diffuse interstellar medium, and external galaxies.

From space infrared spectroscopic observations, we have found that complex organics can be synthesized in the late stages of stellar evolution. Shortly after the nuclear synthesis of the element carbon, organic gas-phase molecules are formed in the stellar winds, which later condense into solid organic particles. This organic synthesis occurs over very short time scales of about a thousand years.

In order to determine the chemical structures of these stellar organics, comparisons are made with particles produced in the laboratory. Using the technique of chemical vapor deposition, artificial organic particles have been created by injecting energy into gas-phase hydrocarbon molecules. These comparisons led us to believe that the stellar organics are best described as amorphous carbonaceous nanoparticles with mixed aromatic and aliphatic components.

The chemical structures of the stellar organics show strong similarity to the insoluble organic matter found in meteorites. 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 old stars. This provides a direct link between star dust and the Solar System and raises the possibility

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that the early Solar System was chemically enriched by stellar ejecta with the potential of influencing the origin of life on Earth.

Keywords organic matter · stellar evolution · origin of life

1 Introduction

Baryonic matter in the Universe can be in several forms. The ionized (plasma) component was the first state of matter to be studied. It manifests itself in the form of self-luminous gaseous bodies such as stars, gaseous nebulae, and collections of stars (star clusters, galaxies). The molecular state of matter was discovered in the 20th century and over 170 interstellar molecules have been detected through their rotational and vibration transitions using the techniques of millimeter-wave and infrared spectroscopy, respectively. The solid state of matter in the form of interstellar grains was first studied through selective extinction in the optical and later through self-emission in the infrared.

Early models based on the shape of the extinction curve generally assumed graphite, iron, or ice as the chemical ingredients of interstellar solid grains. With advances of infrared spectroscopy, it is now possible to identify the chemical contents of interstellar grains through comparisons with laboratory spectroscopy. Crystalline solids have highly ordered lattice structures and have optically active lattice vibrational modes and a number of minerals have been identified in the interstellar medium in this way. In comparison, organic amorphous solids have many electronic states resulting in broad absorption bands. If macromolecular organic solids exist in space, they can be identified by their visible colors, albedo, absorption bands in the visible/UV, and infrared vibrational bands in either emission or absorption. In this paper, we discuss the nature of organic solids in stellar and interstellar environments and their possible relationship with organic matter found in the Solar System.

2 Stellar synthesis of organics

The element carbon (C) is synthesized during the late stages of stellar evolution in the asymptotic giant branch (AGB) phase. The element is dredged up from the core to the surface through convective processes in the stellar envelope. Near the end of the AGB, a strong stellar wind develops which in less than one million years can completely deplete the stellar envelope. Molecules begin to form under low temperature and density conditions in the outflow. As the result of such mass loss, circumstellar envelopes are built up around AGB stars and over 70 circumstellar molecules have been detected through their rotational transitions. The kinds of molecules detected include inorganics (CO, SiO, SiS), organics (C_2H_2 , CH_4 , C_2H , C_4H , C_5 , H_2CO), nitrogen species (HCN, NH_3 , C_3N , CH_3CN), phosphorus compounds (CP, PH_3 , PN), radicals (CN, C_2H , C_3 , HCO^+), metals (AlCl, MgNC, ALF, NaCN, KCl),

rings (C_3H_2), and chains (HC_3N , HC_5N , HC_7N) (Cernicharo et al. 2011; Ziurys 2014). AGB stars are prolific molecular factories.

As soon as the outflow reaches certain distances from the star such that the temperature drops below the condensation temperature, solids condense from the gas phase in the stellar winds. The most common kinds of solids detected are amorphous silicates and silicon carbide (SiC) (Kwok et al. 1997). These solids manifest themselves through infrared emissions due to lattice vibrational stretching and bending modes. In fact, the amount of solids produced is so large that some stars can be completely obscured by circumstellar materials and the optical output of star light is totally converted to infrared continuum emission by circumstellar grains. A strong excess of infrared radiation is therefore an observational characteristic of evolved stars.

When the stellar wind completely depletes the stellar envelope and the core is exposed, ultraviolet radiation from the hot core can photoionize the circumstellar gas, resulting in the illumination of the circumstellar nebula through the emission of the recombination lines of hydrogen and helium and collisionally excited lines of heavy elements. These bright visible objects are called planetary nebulae (Kwok 2000). One of the most unexpected discoveries in 20th century astronomy was the detection of the unidentified infrared emission (UIE) features in the spectrum of planetary nebulae. A family of broad infrared bands at 3.3, 6.2, 7.7, 8.6 and 11.3 μm was found in the spectrum of the planetary nebulae NGC 7027 (Russell et al. 1977). These UIE bands are later found to be common in C-rich planetary nebulae, interstellar emission and reflection nebulae, diffuse clouds in the galactic halo, and external galaxies. The strengths of the UIE bands are so strong that up to 20% of the total energy output from some galaxies is emitted in these bands (Smith et al. 2007).

In order to determine the origin of these UIE bands, it would be useful to first find out when their carrier is first synthesized. While the UIE bands are strong in planetary nebulae, they are not seen in their progenitor AGB stars. The carrier of the UIE bands must therefore be synthesized during the evolutionary stage between the AGB and planetary nebulae stages. Objects in this transition stage are called pre- or proto-planetary nebulae. These transition objects are difficult to identify in the optical because their circumstellar materials are neutral and do not have emission lines. The first identification of pre-planetary nebulae was therefore achieved through their infrared properties (Kwok 1993). Follow-up infrared spectroscopic studies of these objects show that they already possess UIE bands. This suggests that the carriers of the UIE bands are formed during the pre-planetary nebulae stage (Kwok et al. 1999). Since the transition from AGB to planetary nebulae only takes a few thousand years, we can conclude that the carrier of UIE bands are synthesized over similar time scales.

3 Carrier of the unidentified infrared emission bands

Soon after the discovery, the UIE bands were identified as stretching and bending modes of aromatic compounds (Knacke 1977; Duley et al. 1979, 1981; Puetter et al. 1979). The resemblance of the UIE bands to the spectrum of automobile exhaust led to the suggestion that the carrier of the UIE bands are polycyclic aromatic hydrocarbon (PAH) molecules (Allamandola et al. 1985). Since PAH molecules are simple, the PAH hypothesis has become the most popular explanation to the UIE phenomenon in the astronomical community. Although there have been a number of alternative models proposed: including hydrogenated amorphous carbon (Jones et al. 1990), quenched carbonaceous composites (Sakata et al. 1987), coal and kerogen (Papoular et al. 1989; Papoular 2001), or petroleum fractions (Cataldo et al. 2004), they were never able to challenge the dominant position of the PAH hypothesis.

The detection of aliphatic features at 3.4 and 6.9 μm in pre-planetary nebulae and planetary nebulae raised doubts about the carrier of the UIE bands being a pure aromatic species like PAH. The presence of strong and broad plateau emission features around 8 and 12 μm also suggests the existence of aliphatic side groups (Kwok et al. 2001). The wide presence of the 3.4 μm feature in absorption in the Galaxy (Wickramasinghe and Allen 1980; Pendleton et al. 1994) and external galaxies (Spoon et al. 2004; Dartois et al. 2007; Yamagishi et al. 2012) has raised our consciousness about the importance of the aliphatic component. In fact, the strengths of the aliphatic features are such that at least 15% of the carbon reservoir in our Galaxy must be in the form of sp^3 bonded (Dartois 2011).

These developments led to the proposal that the carriers of UIE are mixed aromatic/aliphatic organic nanoparticles (MAON, Kwok and Zhang 2011, 2013). MAONs are 3-dimensional structures consisting of aromatic rings of different sizes and aliphatic chains of different lengths and random orientations. They also contain impurities such as O, S, and N. The exact aromatic to aliphatic ratio depends on the radiation environment, the original gas-phase components, and the H content.

4 Chemical structure of interstellar organics

Astronomical observations have shown that the interstellar medium of our Galaxy and external galaxies are filled with complex organics. These organics have both aromatic and aliphatic components and may not have a fixed structure. It is well known that carbonaceous solids with mixed hybridization states are natural products of combustion. Soot is the result of combustion of hydrocarbon molecules in a flame and has a chemical structure that consists of islands of aromatic rings connected by aliphatic chains (Chung and Violi 2011). The side groups can be made of C and H ($-\text{CH}_3$, $-\text{CH}_2$), or include heavy elements such as O and N ($-\text{HCO}$), $-\text{OH}$, $-\text{NH}_2$). These heavy

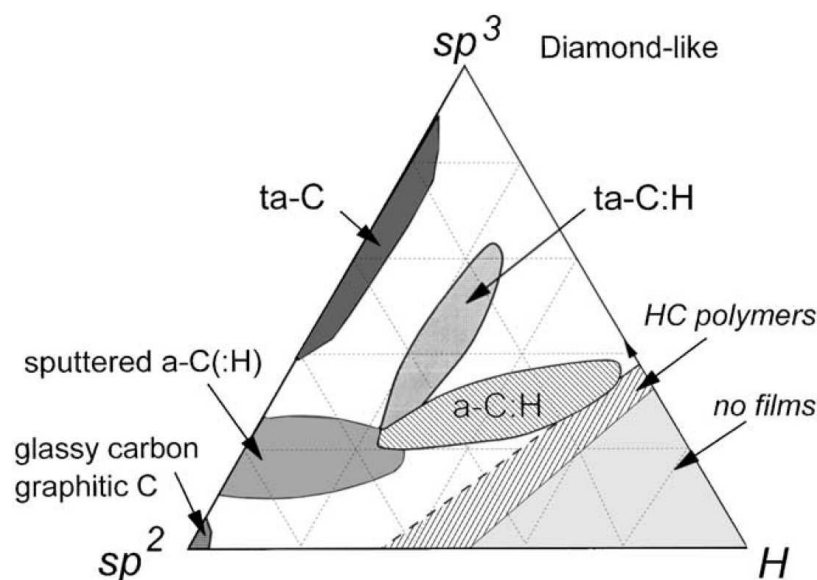


Fig. 1 Phase diagram of amorphous carbon based on pure C and H compounds (from Robertson 2002).

elements can also be incorporated in the ring system as well as in the side groups.

By introducing H into graphite (sp^2) and diamond (sp^3), a variety of amorphous C-H alloys can be created. Geometric structures of different long- and short-range can be created by varying the sp^2/sp^3 hybridization ratios. A schematic of possible structures of amorphous carbonaceous solids is shown in Figure 1. The lower left corner of the triangle represents graphite, the top corner represents diamonds, PAHs are on the bottom edge, and various forms of amorphous hydrogenated carbon can exist in the middle. The infrared spectra of these amorphous carbonaceous materials (Dischler et al. 1983) resemble the astronomical UIE bands seen in planetary nebulae and pre-planetary nebulae (Figure 2). Since these amorphous carbonaceous solids have absorption bands in the visible, they can be easily excited by visible light from stars.

Carbonaceous solids with the structures described in Figure 1 have also been artificially synthesized in the laboratory. The techniques that have been used include microwave irradiation of plasma of 4-torr methane (Sakata et al. 1987; Godard et al. 2011), hydrocarbon flame or arc-discharge in a neutral of hydrogenated atmosphere (Colangeli et al. 1997; Mennella et al. 2003), laser ablation of graphite in a hydrogen atmosphere (Scott and Duley 1996; Mennella et al. 1999; Jäger et al. 2008), infrared laser pyrolysis of gas phase molecules (C_2H_4 , C_4H_6) into C-based nanoparticles (Herlin et al. 1998), photolysis of methane at low temperatures (Dartois et al. 2004), and flame combustion of C_2H_2 , C_2H_4 , C_3H_6 mixed with O_2 into soot (Pino et al. 2008;

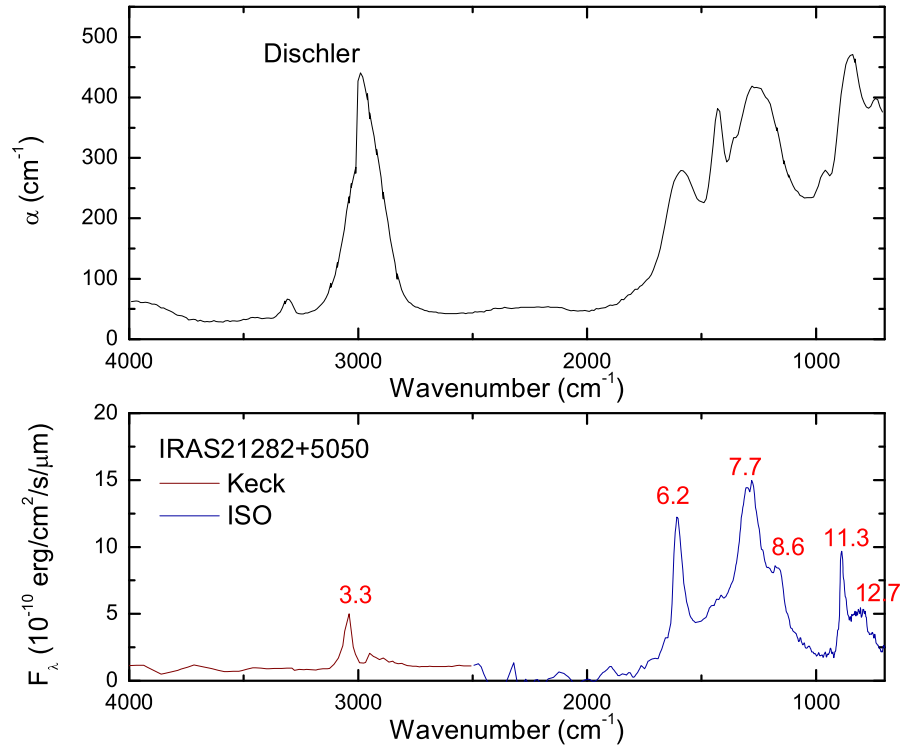


Fig. 2 Laboratory infrared spectra of hydrogenated amorphous carbon (top, from reference (Dischler et al. 1983)) compared to the astronomical spectrum of the planetary nebula IRAS 21282+5050 (bottom panel). The UIE bands are labeled by their wavelengths in μm .

Carpentier et al. 2012). The ease that these compounds can be created suggests that complex amorphous organic solids may be widely present in space.

5 Fullerenes and MAONs

The fullerene (C_{60}) molecule was first synthesized in the laboratory and later found in carbonaceous rocks (Buseck 1992). Geological fullerenes are believed to be either brought to Earth from extraterrestrial impactors, or formed in high temperature conditions during impacts. The first astronomical detection of fullerene was in the H-poor planetary nebula Tc-1 (Cami et al. 2010). It was later also detected in reflection nebulae (Sellgren et al. 2010), in H-rich planetary nebulae (García-Hernández et al. 2010), and in pre-planetary nebulae (Zhang and Kwok 2011). Although Tc-1 does not show UIE bands, the aliphatic 8 and 12 μm plateau features are strongly present (Figure 3). In the pre-planetary nebula IRAS 01005+7910, all three plateau features at 8, 12, and 17 μm seen in planetary nebulae with UIE bands are found (Zhang and Kwok 2013). As a matter of fact, plateau features are present in all

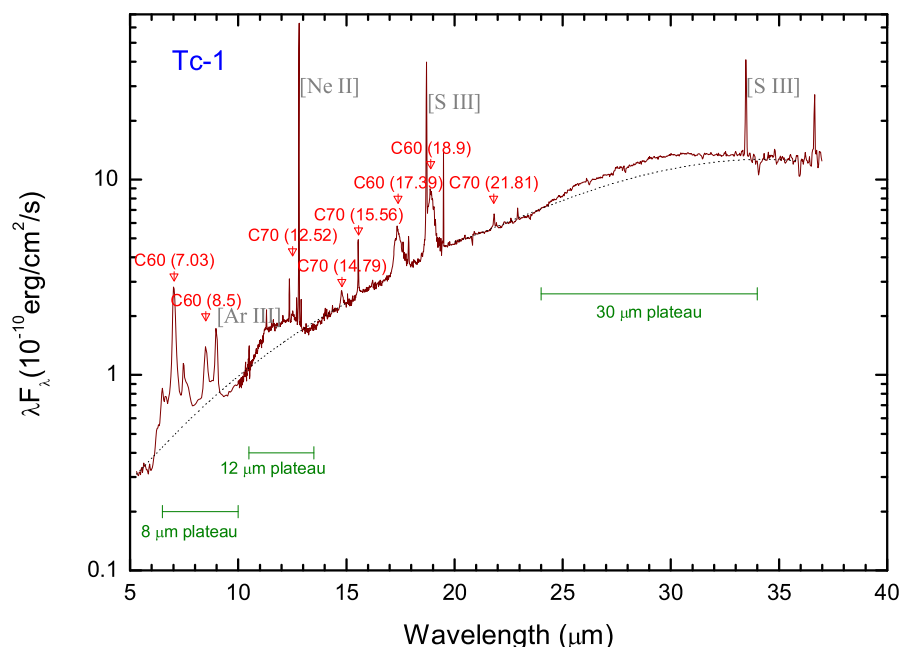


Fig. 3 The *Spitzer* IRS spectrum of planetary nebula Tc-1 shows C_{60} and C_{70} emission bands (in red) as well as broad emission plateau features at 8, 12, and 30 μm (in green). The narrow lines are atomic lines (in grey). No UIE bands are seen in this object.

planetary nebulae with C_{60} (Otsuka et al. 2013). Several C_{60} -PN (Tc-1, SMP SMC 16, SMP LMC 56) have plateau features but no UIE bands, implying the carriers of the plateau features are not aromatic in origin. The possibility that MAONs are precursors of fullerenes has been speculated (García-Hernández et al. 2012; Bernard-Salas et al. 2012).

6 Organics in the Solar System

It is well known that carbonaceous meteorites contain insoluble organic matter (IOM) that is similar in chemical structure to kerogen (Kerridge 1999). IOM is composed of highly substituted single ring aromatics, substituted furan/pyran moieties, highly branched oxygenated aliphatics, and carbonyl groups (Cody et al. 2011) and contains other hetero-elements such as S and N (Derenne and Robert 2010). Average elemental abundance of IOM can be represented by the formula $C_{100}H_{46}N_{10}O_{15}S_{4.5}$ (Pizzarello and Shock 2010). At the very least, this is evidence that IOM is a product of abiotic organic chemistry and Nature can make complex organics without life.

In planetary satellites, we have learned from the *Cassini* results that organic haze is a major component in the atmosphere of Titan and these nanoparticles are blown into dunes by Titan's surface winds. The surface of Titan is

covered by lakes of liquid methane and ethane and the total amount of hydrocarbons on Titan is larger than the oil and gas reserves on Earth (Lorenz et al. 2008). There has been some debate as to whether these complex organics are tholins (Sagan and Khare 1979) or HCN polymers (Matthews and Minard 2008). Comparisons between the $3.4 \mu\text{m}$ feature observed in Titan haze is similar to that seen in comets and pre-planetary nebulae (Kim et al. 2011). It has been suggested that the carrier of the $3.4 \mu\text{m}$ feature in comets originates from interstellar organic matter embedded in comets during the early stages of the Solar System (Mennella 2010).

In the past, it was commonly believed that planets and other Solar System objects formed from a well-mixed primordial nebula of chemically and isotopically uniform composition. All solid bodies were assumed to be made afresh and no solid primordial material was thought to have survived the formation process (Suess 1965). Isotopic studies of meteorites have identified solid grains of presolar origin, including diamonds, SiC, corundum, and spinel. These presolar grains are consistent with their being of AGB origin (Davis 2011). The amount of IOM brought in during early heavy bombardment is estimated to account for 1-3% in weight contribution to the terrestrial organic pool (Mautner et al. 1995). It is therefore quite possible that the early Earth was enriched by extraterrestrial organics.

7 Implications on the Origin of Life

Through the technique of infrared spectroscopy, we now know that old stars are able to synthesize complex organic solids with aromatic/aliphatic structures over very short ($\sim 10^3$ yr) time scales under low-density conditions. Since almost all stars go through the AGB–pre-planetary nebulae–planetary nebulae stage, large amount of organics are produced and distributed all over the Galaxy (Kwok 2004). The detection of pre-solar grains in meteorites suggests that grains from AGB stars can survive the journey through the interstellar medium and reach the Solar System. It is probable that stellar organics was part of the primordial materials that formed the Solar System. Macromolecular organics in meteorites, interplanetary dust particles, comets, and planetary satellites show similarities with organics produced by planetary nebulae. Is this a coincidence or do they share a common origin? It would be worthwhile for us to further explore to what extent the Solar System was enriched by stellar organics and to what extent the early Earth was chemically enriched by extraterrestrial organics. Since planetary systems are now known to be common among stars, the wide production of organic materials by stars in the Galaxy implies that the Earth may not be unique in having been enriched by stellar organics. This may have significant implications on the existence and distribution of life in our Galaxy.

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