

# Organic matter in space: from star dust to the Solar System

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**Abstract** Organic compounds of high degree of complexity are now known to be widespread in the Universe, ranging from objects in our Solar System to distant galaxies. Through the techniques of millimeter-wave spectroscopy, over 140 molecules have been identified through their rotational transitions. Space infrared spectroscopy has detected the stretching and bending modes of compounds with aromatic and aliphatic structures. Analyses of samples of meteorites, comets, asteroids, and interplanetary dust also revealed a rich content of organic substances, some of which could be of extra-solar origin. We review the current state of understanding of the origin, evolution, nature, and distribution of organic matter in space. Also discussed are a number of unexplained astronomical phenomena whose origins could be traced to organic carriers.

**Keywords** Solar System · Stellar evolution · Infrared spectroscopy · Organic matter

## 1 Introduction

Although carbon is the 4th most abundant element in the Universe, the possibility of the widespread presence of organic matter in space was not seriously contemplated because the general perception was that the space density is too low for the synthesis of complex molecules. It was only since the 1970s after millimeter-wave spectroscopy has detected an increasing number of gas-phase carbon-based molecules in the interstellar medium (ISM) that astrochemistry has become a respectable discipline. The detection of

molecules in the outflow of evolved stars also led to the realization that molecules can form in the low density environment of stellar winds, soon after the element carbon was synthesized by nuclear reactions in the stellar core, dredged up to the surface, and released from the atmosphere.

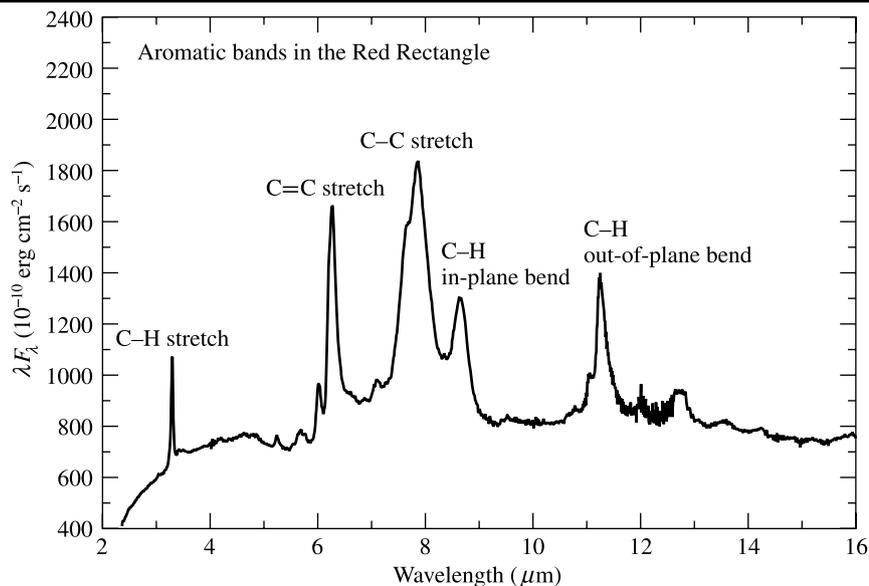
While the millimeter-wave technique is capable of detecting molecules consisting of over a dozen atoms, the high degree of complexity of interstellar organics was not appreciated until the development of astronomical infrared spectroscopy. A family of strong infrared emission bands at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7  $\mu\text{m}$  were first detected by the *Kuiper Airborne Observatory (KAO)* in the young carbon-rich planetary nebula NGC 7027 (Russell et al. 1977) and reflection nebula HD 44179 (Russell et al. 1978), and are now widely observed in H II regions, reflection nebulae, planetary nebulae, proto-planetary nebulae, and the diffuse ISM of our own and other galaxies (see Fig. 1). The widths of the features are much broader than molecular linewidths broadened by Doppler effects or turbulence and therefore they are designated as emission bands. Solar System objects, such as carbonaceous meteorites, interplanetary dust particles, and Martian rocks are also known to display these features. The energy emitted in these bands can be a significant fraction of the total dust continuum energy output of galaxies, and the identification of the carriers of these features is therefore important for the understanding of the chemical makeup of the ISM and galaxies.

The fact that the strengths of these infrared emission features correlate with the C/O ratio of planetary nebulae suggests a carbon-based carrier. Comparison with laboratory infrared spectroscopy of organic compounds has led to the identification that these features arise from stretching and bending modes of various CH and CC bonds in aromatic hydrocarbons (Duley and Williams 1981). For this reason, these strong infrared emission features are now known as

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**Fig. 1** The aromatic infrared bands (AIB) are prominent in HD 44179 (the Red Rectangle), a reflection nebula surrounding a B8-A0 central star in the late stages of stellar evolution. The vibrational modes of the aromatic units are identified in this *Infrared Space Observatory* (ISO) SWS01 and SWS06 spectrum



the aromatic infrared bands (AIB). The detection of aromatic compounds has led to the appreciation that all forms of carbon, including graphite, diamond, fullerene, carbyne) also exist in space (Henning and Salama 1998). A review of organic molecules in space was previously given by Ehrenfreund and Charnley (2000).

In this review, we summarize our present understanding of the presence of organic matter in the diffuse ISM, in the circumstellar environment, and in the Solar System. The possibility of a number of unexplained astronomical phenomena that may be due to organic compounds is also discussed. The chemical structures and possible laboratory analogs of extraterrestrial organics are presented. Near the end of the article, some speculations on the origin of these compounds and the possible links between stars and the Solar System are offered.

## 2 Organic molecules in the gas phase

As of 2008, more than 140 gas-phase molecules have been detected in the interstellar medium, including over 60 in the circumstellar envelopes of late-type stars. Most of these molecules were detected through their rotational transitions in the mm or sub-mm regions. The detected species cover all kinds of organic molecules, including hydrocarbons (e.g., methane  $\text{CH}_4$ , acetylene  $\text{C}_2\text{H}_2$ , ethylene  $\text{C}_2\text{H}_4$ ), alcohols (e.g., methanol  $\text{CH}_3\text{OH}$ , ethanol  $\text{C}_2\text{H}_5\text{OH}$ , vinyl alcohol  $\text{H}_2\text{C}=\text{CHOH}$ ), acids (e.g., formic acid  $\text{HCOOH}$ , acetic acid  $\text{CH}_3\text{COOH}$ ), aldehydes (e.g., formaldehyde  $\text{H}_2\text{CO}$ , acetaldehyde  $\text{CH}_3\text{CHO}$ , propenal  $\text{CH}_2=\text{CHCHO}$ , propanal  $\text{CH}_3\text{CH}_2\text{CHO}$ ), ketones (e.g., ethenone  $\text{H}_2\text{C}=\text{CO}$ , acetone,  $\text{CH}_3\text{COCH}_3$ ), amines (e.g., methylamine  $\text{CH}_3\text{NH}_2$ , cyanamide  $\text{NH}_2\text{CN}$ , formamide  $\text{NH}_2\text{CHO}$ ), ethers (e.g.,

dimethyl ether  $\text{CH}_3\text{OCH}_3$ , ethyl methyl ether  $\text{CH}_3\text{OC}_2\text{H}_5$ ), etc. Of particular interest are prebiotic molecules leading to the formation of proteins, carbohydrates, nucleic acids, and lipids. The simplest sugar, glycolaldehyde ( $\text{CH}_2\text{OHCHO}$ ), has been detected (Hollis et al. 2000). Active searches are now underway for the simplest amino acid glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) (Kuan et al. 2003a; Snyder et al. 2005) and for the parents of the bases that constitute the structural units of DNA and RNA, such as purine ( $c\text{-C}_5\text{H}_4\text{N}_4$ ) and pyrimidine ( $c\text{-C}_4\text{H}_4\text{N}_2$ ) (Kuan et al. 2003b). Pyrimidine is the base contained in cytosine (DNA and RNA), thymine (DNA), and uracil (RNA), whereas purine is the base for adenine (DNA and RNA) and guanine (DNA and RNA). Although extraterrestrial nucleobases have been found in meteorites (Sect. 5.1), they are yet to be detected in the ISM.

Other large molecules detected in recent years include ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) (Hollis et al. 2002), propenal ( $\text{CH}_2\text{CHCHO}$ ) and propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ ) (Hollis et al. 2004), acetone ( $\text{CH}_3\text{COCH}_3$ ) (Friedel et al. 2005), cyanoallene ( $\text{CH}_2\text{CCHCN}$ ) (Lovas et al. 2006), acetamide ( $\text{CH}_3\text{CONH}_2$ ) (Hollis et al. 2006a), cyanofomaldehyde ( $\text{CNCHO}$ ) (Remijan et al. 2008), and cyclopropenone ( $c\text{-H}_2\text{C}_3\text{O}$ ) (Hollis et al. 2006b). These detections were made possible by the construction of large single-dish telescopes (e.g., the 100-m Green Bank Telescope) and improving receiver sensitivities.

The detections of ring species such as cyclopropynylidyne ( $c\text{-C}_3\text{H}$ ), cyclopropenylidene ( $c\text{-C}_3\text{H}_2$ ), ethylene oxide ( $c\text{-C}_2\text{H}_4\text{O}$ ), etc., raise the possibility of the existence of other biochemically important ring molecules. Planar rings containing other heavy elements (N, O, S) in addition to C play a fundamental role in biochemistry. Examples of these ring structures include furan ( $\text{C}_4\text{H}_4\text{O}$ ), pyrrole ( $\text{C}_4\text{H}_5\text{N}$ ), and imidazole ( $\text{C}_3\text{H}_4\text{N}_2$ ). They are 5-membered rings with

one O atom (furan), one N atom (pyrrole) and two N atoms (imidazole). Furan forms the basis of simple sugars such as ribose and deoxyribose, the backbone molecules of RNA and DNA. Pyrrole forms part of the amino acid proline and is a constituent of heme (in hemoglobin) and chlorophyll (in chloroplast). Imidazole forms a side chain of the amino acid histidine and the biomolecules histamine and biotin. These molecules are yet to be detected.

For simple molecules, their identification by radio spectroscopic means can be extremely robust. Due to the low-temperature conditions in the ISM, the observed lines are very sharp and can match laboratory measurements to the accuracy of a few parts in  $10^7$  (Thaddeus 2006). However, the identification process becomes increasingly difficult for larger molecules. As the complexity of a molecule increases (both in terms of the number of atoms and the geometry), the number of excitable energy levels also increases. This spreads the molecular population thinly, resulting in weaker lines. Although the weakness of the lines can be overcome by improving receiver sensitivity, astronomical spectroscopy runs into the problem of line confusion as every frequency interval is filled with molecular lines, often from smaller species such as methanol. The identification of a complex molecule therefore requires the measurements of many transitions to be certain. Eventually we may run into a natural limit for the detection of large molecules through their rotational transitions by single-dish telescopes. We may therefore conclude that the failure to detect complex organic molecules through their rotational transitions does not necessarily imply the absence or low abundance of the molecule.

### 3 Synthesis of organic compounds in the circumstellar envelopes of evolved stars

The circumstellar envelopes of stars in the late stages of stellar evolution represent an ideal laboratory to study the formation of organic compounds. The process begins with the synthesis of the element carbon by the triple  $\alpha$  nuclear reaction in the core of asymptotic giant branch (AGB) stars. The dredge up of this element to the surface allows the formation of simple carbon molecules such as  $C_2$ ,  $C_3$ , CN, etc., in the photosphere. The initiation of a stellar wind during the late AGB stage results in the formation of gas-phase molecules in the outflow. Over 60 molecular species have been detected, and they include inorganics (e.g., CO, SiO, SiS,  $NH_3$ , AlCl, etc.), organics ( $C_2H_2$ ,  $CH_4$ ,  $H_2CO$ ,  $CH_3CN$ , etc.), radicals (CN,  $C_2H$ ,  $C_3$ ,  $HCO^+$ , etc.), chains (e.g., HCN,  $HC_3N$ ,  $HC_5N$ , etc.), and rings ( $C_3H_2$ ). Since the dynamical lifetime of the envelope is  $\sim 10^4$  yr, the chemical reactions that lead to the formation of these species must be shorter than this time scale. Interferometric observations also allow

the mapping of the molecular emission regions and therefore put further constraints on the reaction zone.

Accompanying this molecular outflow is the condensation of solid-state species, the most common of which are amorphous silicates and silicon carbide, both have strong spectroscopic features in the mid-infrared. Near the end of the AGB, the mass loss rate of the star is so high that the star itself is totally obscured by its circumstellar dust envelope. During this stage, acetylene ( $C_2H_2$ ) molecules begin to appear, and can be detected through the  $\nu_5$  vibrational band at  $13.7 \mu m$  (Volk et al. 2000).

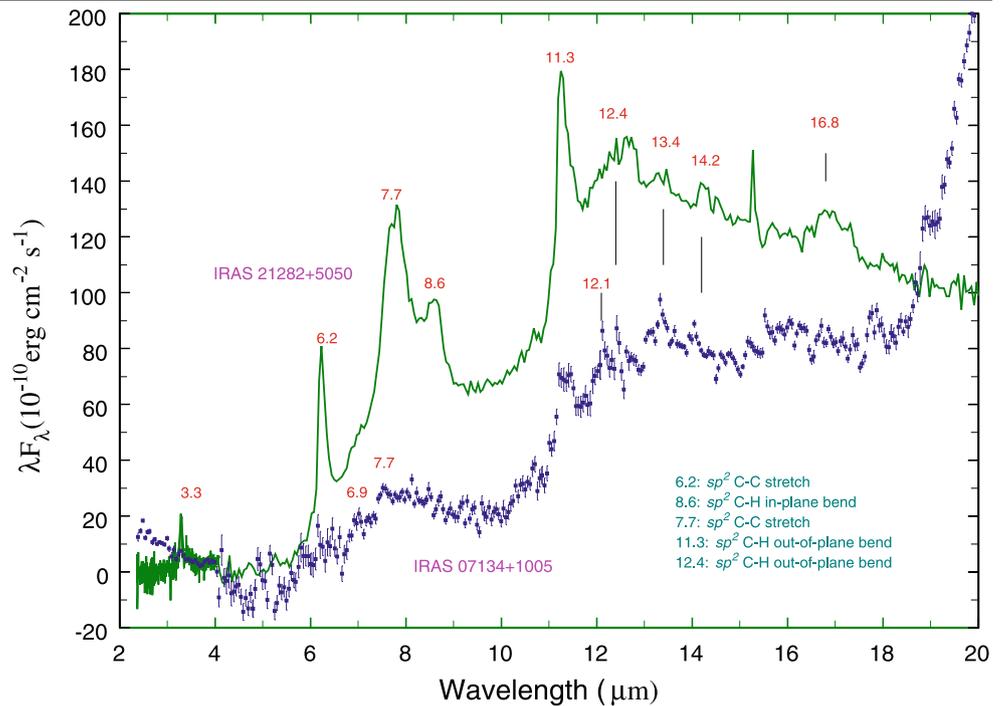
After the stellar wind completely depletes the hydrogen envelope of the AGB star, the star begins to evolve to higher temperatures to the post-AGB (or proto-planetary nebulae, PPN) phase of evolution. During this stage, polymerization of acetylene leads to the formation of diacetylene ( $C_4H_2$ ) and triacetylene ( $C_6H_2$ ), culminating in the formation of benzene (Cerricharo et al. 2001). It is also during the PPN phase that we witness the first emergence of the AIB features, suggesting the formation of aromatic structures. Signatures of small aromatic units with 2, 3, or 4 exposed H corners can be found in PPN in the form of the 12.1, 12.4, 13.3  $\mu m$  out-of-plane bending mode features (Fig. 2) (see Sect. 6.1). Also present are the 3.4 (Fig. 3) and 6.9  $\mu m$  features due to aliphatic C–H stretch and bending modes (Kwok et al. 1999). Broad emission plateau features at 8 and 12  $\mu m$  are identified as the summation of in-plane and out-of-plane bending modes of a mixture of aliphatic side groups attached to the aromatic rings (Kwok et al. 2001).

The PPN phase lasts about  $10^3$  yr, followed by the planetary nebulae (PN) stage when the circumstellar envelope is photo-ionized by the hot exposed core of the AGB progenitor. During the PN stage, the aliphatic features weaken and the aromatic features become stronger. These transformations can be understood as the result of photochemistry, where the side groups are cut off by exposure to ultraviolet light and ring closure and cycloaddition lead to larger aromatic rings (Kwok et al. 2001). The spectral evolution during the AGB-PPN-PN transition demonstrates that active chemical synthesis can occur in the low-density circumstellar envelope, and the changing radiation environment can lead to changes in the structure of the organic compounds over time scales as short as several hundred years (Kwok 2004).

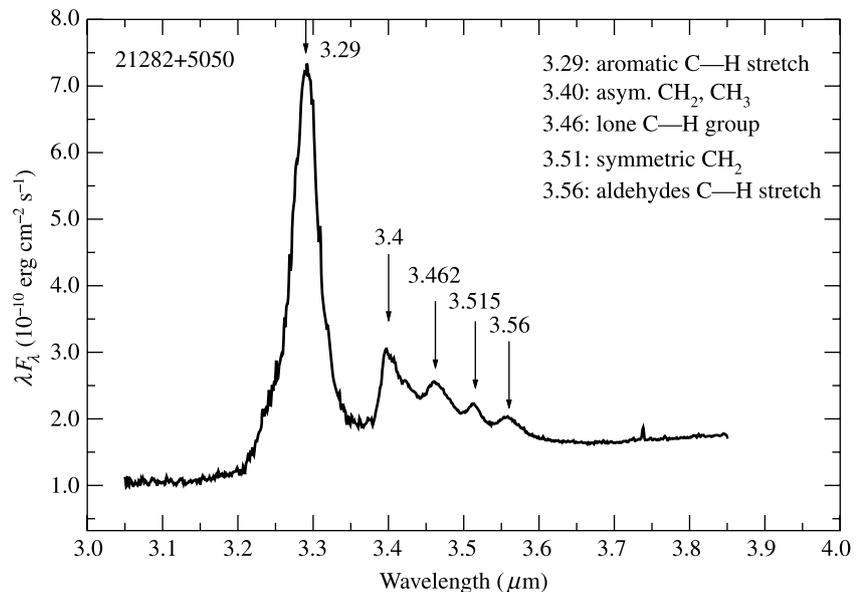
### 4 Organic compounds in the diffuse interstellar medium and external galaxies

The chemical nature of solid-state particles in the diffuse interstellar medium can be inferred from their spectral features in absorption against background stars or infrared continuum sources, the strongest of which are the 217 nm feature

**Fig. 2** *ISO SWS01* spectra of the young PN IRAS 21282+5050 and the PPN IRAS 07134+1005, showing various aromatic C–H and C–C stretching and bending modes at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$ . The PPN spectra are characterized by the 12.1, 12.4, 13.3  $\mu\text{m}$  out-of-plane bending mode features from small aromatic units



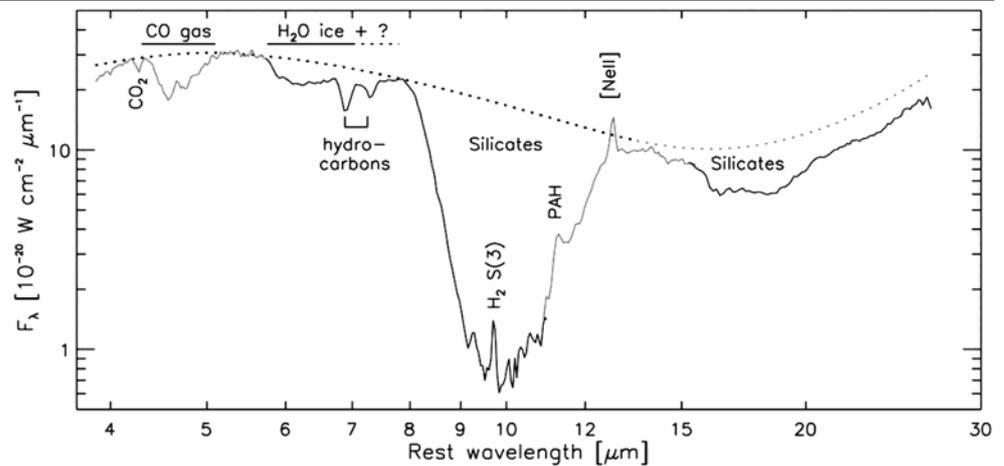
**Fig. 3** A spectrum of the young planetary nebula IRAS 21282+5050 showing the 3.56  $\mu\text{m}$  feature possibly attributed to the aldehyde group, in addition to the 3.4  $\mu\text{m}$  aliphatic features (Hrivnak et al. 2007)



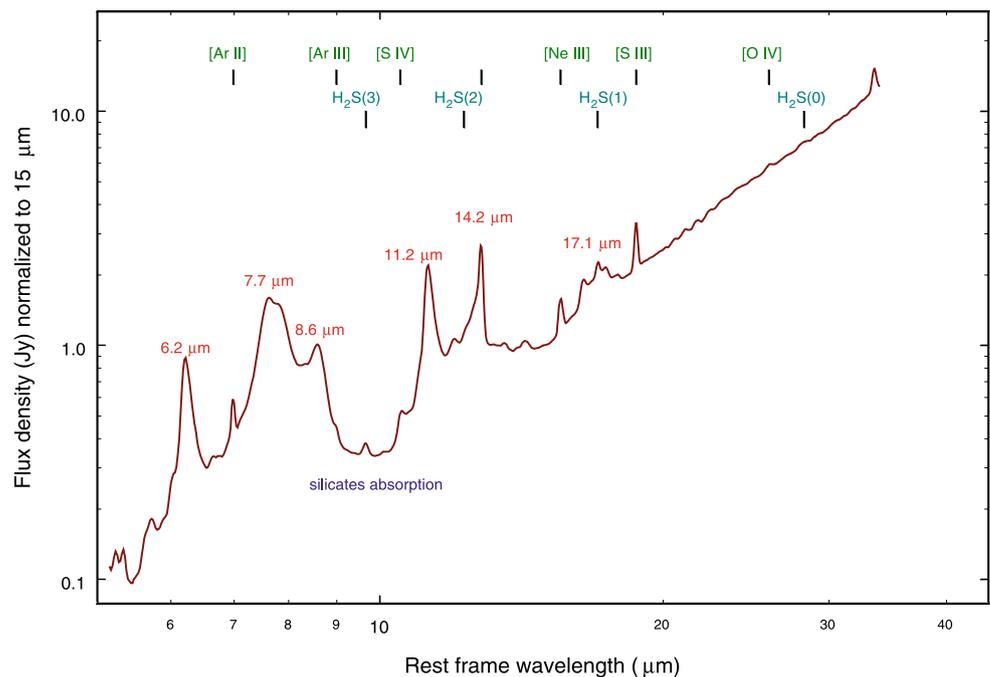
(Sect. 6.3), and the 10 and 18  $\mu\text{m}$  silicate features. In addition, features at 3.4, 6.8, and 7.2  $\mu\text{m}$  have been observed and they are generally interpreted as due to the stretching and bending modes of methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) groups of aliphatic materials (Chiar et al. 2000). The strengths of the aliphatic features compared to those of the aromatic features suggest that aliphatic materials are dominant in the diffuse interstellar medium. These features can also be seen in absorption along the line of sight to external galaxies (Fig. 4).

The common presence of aromatic compounds in external galaxies was first recognized by *ISO* observations. Strong AIB features are seen in starburst galaxies such as M82 and NGC 1068 (Genzel and Cesarsky 2000; Sturm et al. 2000). The increased sensitivity of the *Spitzer* IRS instrument over the *ISO* SWS has resulted in a much larger sample of galaxies detected with AIB emissions (Brandl et al. 2006) (Fig. 5). The large equivalent widths of the AIB features show that a significant fraction of the total energy output of these galaxies are emitted in these features (Fig. 6). This

**Fig. 4** *Spitzer Space Telescope* Infrared Spectrograph (IRS) spectrum of the ultraluminous infrared galaxy IRAS F00183–7111 showing the aliphatic features at 6.8 and 7.2  $\mu\text{m}$  in absorption. Figure adapted from Spoon et al. (2004)



**Fig. 5** Averaged *Spitzer* IRS spectrum of 13 starburst galaxies. The AIB features, as well as some atomic and  $\text{H}_2$  molecular lines are marked. The strong broad absorption feature at 10  $\mu\text{m}$  is due to amorphous silicates. Figure adapted from Brandl et al. (2006)



clearly shows that complex organic compounds are highly abundant in these galaxies.

## 5 Organic compounds in the Solar System

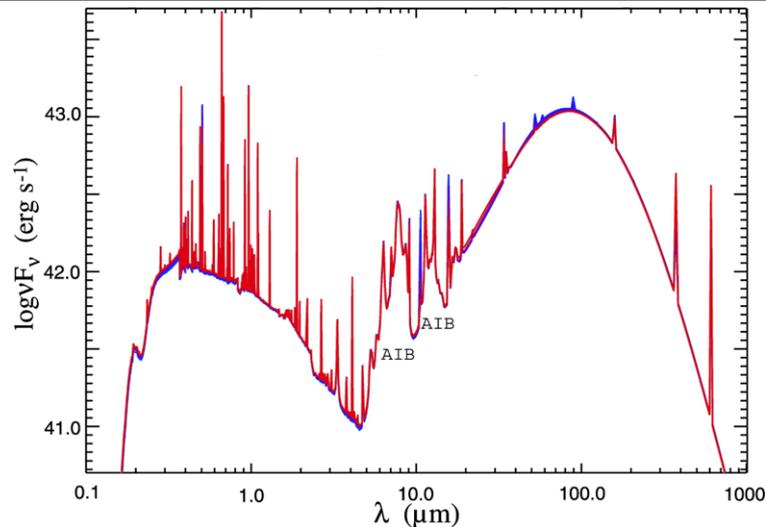
Besides the Sun, the Solar System consists of the planets and their satellites, asteroids, comets, and minor bodies in the outer Solar System. The general perception for the chemical composition of these bodies is that they are made up of metals, minerals, and ices. However, in recent years, organics are increasingly recognized as another major component. Among these bodies, Earth is the most well studied, but organics on Earth are dominated by results of life, a unique element in the Solar System. For the asteroids and

comets, they can be studied through meteorites and micrometeorites that fall on Earth. The ability to send spacecrafts to the planets, satellites, and comets has opened a new avenue of close spectroscopic observation and direct sample collection. Consequently, our appreciation and understanding of the organic components of the Solar System have increased dramatically.

### 5.1 Meteorites

Pre-biotic organic matter have been known to be present in primitive carbonaceous chondrite meteorites since the 1980s (Cronin et al. 1987). Through the use of different solvents, various components of the soluble fraction can be extracted and analyzed. Among the extractable organic matter are carboxylic acids (Shimoyama et al. 1989), amino acids (Cronin

**Fig. 6** Model spectral energy distributions (SED) of starburst galaxies showing the importance of AIB emissions in the energy output of these galaxies. The SED has two major components: an optical component (peaking at  $\sim 0.4 \mu\text{m}$ ) due to photoionized gas and an infrared component (peaking at  $\sim 100 \mu\text{m}$ ) due to dust. The narrow features are atomic lines and the broad features between 5 and 20  $\mu\text{m}$  marked as AIB are due to aromatic compounds. Figure adapted from Groves et al. (2008)

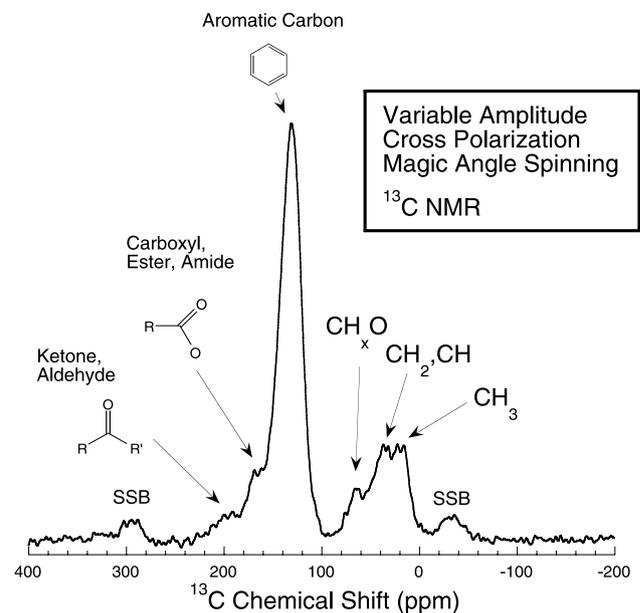


et al. 1995), aromatic hydrocarbons (Gilmour and Pillinger 1994), heterocyclic compounds (adenine, guanine, hypoxanthine, xanthine, uracil, thymine, cytosine, etc.) (Stoks and Schwartz 1981), aliphatic hydrocarbons (Cronin and Pizzarello 1990), amines, amides (Pizzarello et al. 1994), alcohols, aldehydes, ketones and other sugars. It is fair to say that almost all biologically relevant organic compounds are present in carbonaceous meteorites, although our assumption is that these are all of non-biological origin. In terms of abundance, aromatic hydrocarbons make up the largest fraction of the soluble organic compounds in meteorites, followed by carboxylic acids (Botta and Bada 2002).

The remaining and the majority (>70%) of the organic matter is in the form of insoluble macromolecular solids, which are now commonly referred to as Insoluble Organic Matter (IOM) (Cronin et al. 1987). Modern pyrolysis gas chromatography characterizes IOM as predominantly aromatic, with solid-state nuclear magnetic resonance spectroscopy finding various functional groups (Fig. 7). Release of oxygen-containing molecules such as phenols, propanone, and nitrogen heterocyclics as a result of pyrolysis suggests that the IOM contains impurities. The structure of IOM can therefore be summarized as a complex organic solid composed of aromatic and aliphatic functional groups, as well as oxygen-containing functional groups.

Comparison of the IOM in the Murchison, Tagish Lake, Orgueil, and EET92042 meteorites shows remarkable similarity (Cody and Alexander 2005). Roughly speaking, the chemical structure of IOM resembles that of kerogen on Earth (Kerridge 1999) (see Sect. 7.4). Cody and Alexander (2005) note that while the aromatic fraction increases from EET 92042, to Orgueil, to Murchison, to Tagish Lake, there is a corresponding decrease in aliphatic content.

The similarity between the 3.4  $\mu\text{m}$  aliphatic feature observed in meteorites and the absorption feature seen in



**Fig. 7** Functional groups identified in the Murchison IOM. The two features marked as SSB are spinning side bands of the main peak in this  $^{13}\text{C}$  NMR spectrum. Figure adapted from Cody et al. (2008)

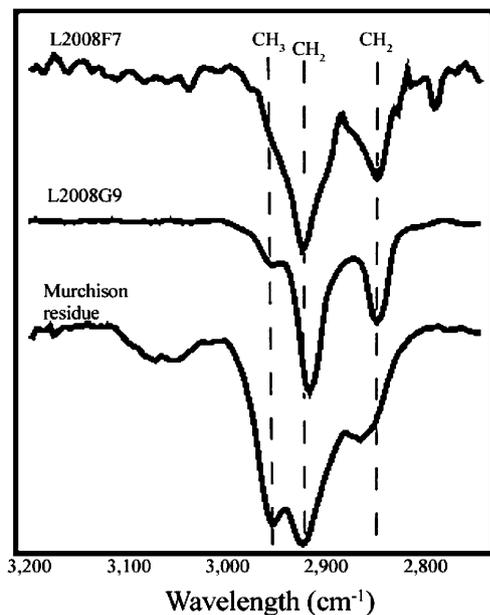
the Galactic Center has led to the suggestion that the diffuse ISM contains similar organic material as the IOM (Ehrenfreund et al. 1991; Pendleton and Allamandola 2002). The anomalous isotopic ratios of noble gases trapped in fullerenes ( $\text{C}_{60}$  to  $\text{C}_{400}$ ) in the Allende and Murchison meteorites point to their extraterrestrial origin (Becker et al. 2000). The carbon isotope ratios of nucleobases in the Murchison meteorite also show signs that they are interstellar (Martins et al. 2008). The elevated ratios of  $^{15}\text{N}/^{14}\text{N}$  and D/H in organic globules in the Tagish Lake meteorite provides additional evidence that interstellar organics are present in the present Solar System (Nakamura-Messenger

et al. 2006). Although early theories on the origin of meteoritic organics concentrated on synthesis in the solar nebula, the latest evidence suggests that the solar nebula only plays a role of secondary processing of pre-existing interstellar materials.

## 5.2 Interplanetary dust particles

Interplanetary dust particles (IDPs) are micron-size particles from asteroids or comets that enter the Earth's atmosphere. Laboratory analysis of IDPs collected from the stratosphere by high-flying aircraft with aerogel collectors has shown that they are rich in organic content. X-ray absorption near-edge structure spectroscopy and infrared spectroscopy have found aliphatic  $\text{CH}_2$  and  $\text{CH}_3$ , carbonyl ( $\text{C}=\text{O}$ ), and carbon ring structures in IDPs (Flynn et al. 2003). Figure 8 shows a comparison of the infrared spectra of IDPs with the Murchison meteorite. While both show the  $3.4 \mu\text{m}$  aliphatic features, the Murchison has a much stronger  $3.28 \mu\text{m}$  aromatic feature, suggesting that the Murchison is more aromatic than IDPs.

Isotopic measurements of IDPs have shown evidence for deuterium enrichment, with D/H values as high as 50 times the Solar System values being found (Messenger 2000). These results suggest that these IDPs contain remnants of interstellar materials which survived the formation of the Solar System.



**Fig. 8** The infrared absorption spectra of IDP L2008F7 and L2008G9 and the Murchison meteorite showing the aliphatic stretching modes of  $\text{CH}_2$  and  $\text{CH}_3$ . Note the similarity with the planetary nebula spectrum in Fig. 3. Figure adapted from Flynn et al. (2003)

## 5.3 Comets

Spectroscopic observations in the UV, optical, IR, and millimeter wave regions have discovered many molecular species in comets, showing that their chemical make-up is much more complex than “dirty snow balls”. Ices of water, hydrocarbons, alcohols, acids, etc., have been identified. The presence of volatile ices such as  $\text{CO}$  and  $\text{CH}_4$  shows that these ices are pristine and may have been preserved for the entire history of the Solar System (Mumma et al. 2001, 2003). Time-of-flight mass spectrometers onboard of spacecrafts sent to intercept Comet Halley in 1986 have measured 5000 particles and found evidence for inorganic minerals as well as organic refractory materials consisting of H, C, N, O (Kissel et al. 1986a, 1986b).

Particles ejected from the Comet 81P/Wild 2 were collected by the Stardust spacecraft and the samples were returned to Earth. The samples were analyzed using a variety of techniques, including mass spectrometry, chromatography, X-ray, IR, and Raman spectroscopy, etc. A wide range of aromatic and other organics are present, similar to the IOM found in meteorites except for higher O and N contents. The detection of D and  $^{15}\text{N}$  enrichments suggests that some particles may be of presolar origin (Sandford et al. 2006).

## 5.4 Asteroids

The first hint of presence of organic matter in asteroids came from their red colors. The extreme red colors and low (0.01–0.15) albedos of some asteroids are difficult to explain by minerals or ices, but can be accounted for by polymer-type organic compounds which are structurally similar to kerogen (Gradie and Veverka 1980). Cruikshank et al. (1998) were able to fit the optical properties of the extremely red Centaur object 5145 Pholus by diffusely scattered sunlight from tholins (Sect. 7.5).

## 5.5 Planetary satellites

Organic molecules are commonly found in the atmospheres of planets Jupiter, Saturn, Uranus, Neptune, Pluto, as well as satellites such as Titan and Triton. In addition to water ice, frozen hydrocarbons are also believed to be present in the icy surfaces of many planetary satellites, including Triton, Ganymede, Callisto, etc.

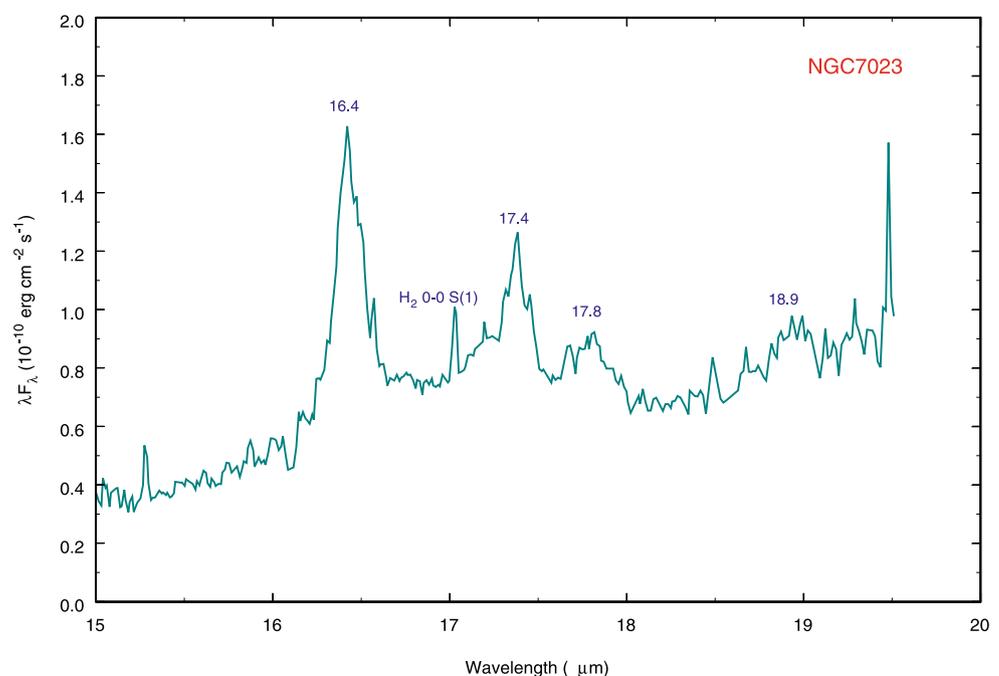
Spectroscopic observations with the Visible-Infrared Mapping Spectrometer (VIMS) on board the Cassini spacecraft of Saturnian satellites Iapetus, Phoebe, and Hyperion have also found evidence for aromatic and aliphatic hydrocarbons (Cruikshank 2008). Cassini-Huygens observations of Titan have also confirmed the scenario that methane is being converted to complex hydrocarbon-nitrile compounds in

the atmosphere of Titan. The condensation of these nanoparticles (or macromolecules) on the surface resulted in dunes and lakes found by Cassini RADAR observations. The total amount of hydrocarbons on Titan is estimated to be larger than the oil and gas reserves on Earth (Lorenz et al. 2008).

## 6 Organic compounds as carriers of unsolved astronomical phenomena

Our ability to spectroscopically observe and identify ions, atoms, molecules, and solids from the Solar System to distant galaxies demonstrates clearly the universality of the laws of physics and chemistry throughout the Universe. The identification of forbidden lines of atomic ions (e.g., 500.7 nm line of  $O^{++}$ ) and rotational transitions of molecular radicals (e.g.,  $HCO^+$ ) not seen in the terrestrial environment further highlights the success of modern astrophysics and astrochemistry (Kwok 2006). However, to this date, there are still a number of outstanding unsolved mysteries relating to spectroscopic features commonly seen around stars, in the interstellar medium, and in external galaxies. There are strong suspicions that some of these phenomena involve organic carriers whose spectroscopic properties are not known, or organic materials that do not exist or have not yet been artificially synthesized on Earth. Below are some astronomical phenomena that require further advances in chemistry for explanation.

**Fig. 9** *Spitzer* IRS spectrum of the reflection NGC 7023. The UIE features are marked. Figure adapted from Sellgren et al. (2007)



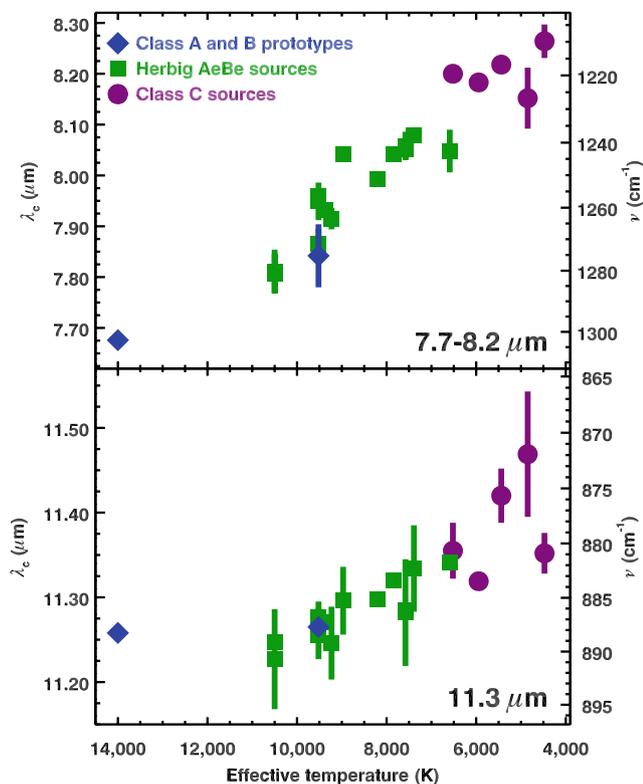
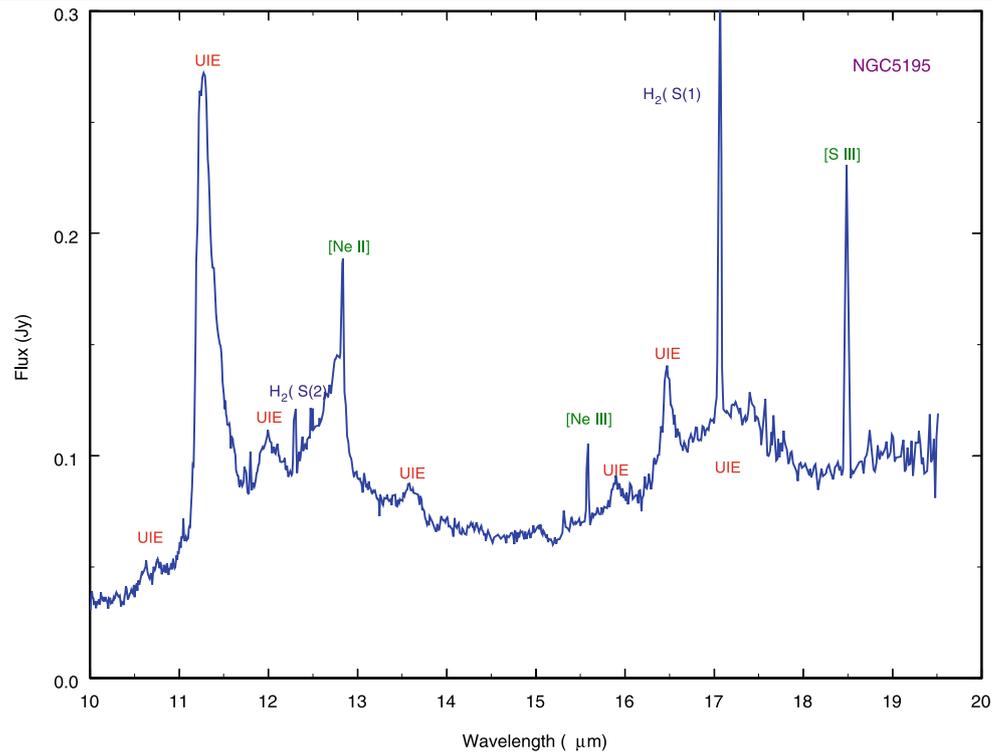
### 6.1 Unidentified infrared emission features

The term unidentified infrared emission (UIE) features refers to a family of emission features including the AIB at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$ , aliphatic features at 3.4 and 6.9  $\mu\text{m}$ , broad emission plateaus at 8, 12, and 17  $\mu\text{m}$ , as well as a host of weaker features that are too broad to be atomic or molecular lines. The assignment of the vibrational modes of the AIB can be seen in Fig. 1. In the 11–15  $\mu\text{m}$  region, the C–H out-of-plane bending modes of aromatic units with different number of exposed corners can give rise to features of different wavelengths. For example, the 11.3, 12.1, 12.4, and 13.3  $\mu\text{m}$  features can be assigned to a lone C–H group, two, three, or four adjacent C–H groups, respectively (Hudgins and Allamandola 1999). A feature at 16.4  $\mu\text{m}$  has also been suggested to arise from C–C–C in-plane bending (Van Kerckhoven et al. 2000). Other features at 17.4, 17.8, and 18.9  $\mu\text{m}$  are also seen in PPN (Kwok et al. 1999) and reflection nebulae (Sellgren et al. 2007) (Fig. 9).

By fitting the observed *Spitzer* IRS spectra of galaxies (Fig. 10), Smith et al. (2007) have identified a list of UIE features from 5.27 to 33.10  $\mu\text{m}$  (Smith et al. 2007, Table 3). The UIE features are classified into class A, B or C by Peeters et al. (2002) according to their profiles and peak wavelengths. Sloan et al. (2007) have found the peak wavelengths of the 7.7 and 11.3  $\mu\text{m}$  to be correlated with the temperature of the central stars (Fig. 11), which they interpreted to be the result of change in the aliphatic to aromatic content ratio.

In addition to hydrogen, methyl ( $-\text{CH}_3$ ) or methylene ( $-\text{CH}_2$ ) side groups, it is also possible that other side

**Fig. 10** The UIE features are commonly observed in star-forming galaxies as can be seen in this *Spitzer* IRS spectrum of NGC 5195. The amount of energy emitted in the bands can be as high as 20% of total infrared fluxes observed, suggesting that significant amount of organic matter is produced in these galaxies. Figure adapted from Smith et al. (2007)



**Fig. 11** The correlation between the peak wavelengths of the 7.7 and 11.3  $\mu\text{m}$  features with central star temperatures. Figure adapted from Sloan et al. (2007)

groups such as carbonyl ( $\text{C}=\text{O}$ ), aldehydic ( $-\text{HCO}$ ), phenolic ( $\text{OH}$ ), and amine ( $\text{NH}_2$ ) be attached to the aromatic units. These could give rise to the other UIE features and the broad plateau features (Kwok et al. 2001).

## 6.2 Diffuse interstellar bands

The *diffuse interstellar bands (DIB)* are absorption bands formed in interstellar clouds seen against the spectra of stars. Since their initial discovery in 1922 (Heger 1922) and the identification of their interstellar origin in the 1930s (Merrill 1934), approximately 300 bands from near UV to near IR have been detected. DIBs have now been seen in external galaxies and in the spectra of quasars behind galaxies with redshifts up to 0.5 (Sarre 2006). It is interesting to note that in spite of the widespread presence, none of the bands is identified. Although the bands show a variety of widths, strengths, and profiles, they share the common property that they are all too broad ( $\text{FWHM} \sim 0.06\text{--}4 \text{ nm}$ ) to be attributed to atomic lines. Consequently, molecular and solid-state origins have been extensively studied. The invariance of the wavelengths and the narrowness of some bands suggest that the carriers are gas-phase molecules, and the bands arise from electronic transitions of these molecules.

No matter what the carrier of the DIBs may be, they must be made up of abundant elements because the total amount of interstellar absorption due to all known DIBs is very large. Organic compounds are favored because only carbon atoms have the rich chemistry necessary to create the large

variety of molecules to account for the DIBs (Snow and McCall 2006). Candidates that have been suggested include carbon chains, PAHs, fullerenes or nanotubes, including their variations in ionization and hydrogenation states. The reason that the carriers have not yet been identified is because the carrier molecules are probably unstable under laboratory conditions. Although no solution exists at this time, the ubiquitous nature of DIBs seems to imply that complex organic compounds are widespread in the ISM.

### 6.3 The 217 nm feature

The prominent feature in the interstellar extinction curve was extensively observed by the *International Ultraviolet Explorer (IUE)* satellite (Stecher 1965, 1969) and is found to have a remarkable constancy in its peak wavelength ( $217.5 \text{ nm} \pm \leq 25\%$ , corresponding to  $5.7 \text{ eV}$  or  $4.6 \mu\text{m}^{-1}$ ). The strength of the feature requires that the carrier be made of abundant elements such as C, Mg, Si, Fe, etc. It has been attributed to absorption by small interstellar graphite grains, arising from the  $\pi-\pi^*$  transition of  $sp^2$  carbon. Another resonance due to  $\sigma-\sigma^*$  transition occurs at 80 nm which could be responsible for the rise of the extinction curve toward the UV. However, a good model fit of observed data with graphite can only be achieved with fine-tuning of the optical constants and particle sizes and shapes. It has been suggested that a complete surface reconstruction to the  $sp^2$  carbon in diamond can delocalize the  $\pi$  electrons and create a surface mode analogous to that of graphite. The strong absorption coefficient of diamond in the UV can also make diamond a contributor of extinction in the UV. Absorption spectroscopy of carbon onions shows a feature at  $4.55 \pm 0.1 \mu\text{m}^{-1}$  with a width of  $1.2\text{--}1.6 \mu\text{m}^{-1}$ . This coincidence, together with the stability of carbon onions, suggests that they could be the carrier of the 217 nm feature. Since photoreflexive measurements of anthracite produces a close fit to the 217 nm feature, the possibility that this feature arises from a complex carbonaceous compound cannot be ruled out.

### 6.4 Extended red emission

*Extended red emission (ERE)* is a broad ( $\Delta\lambda \sim 80 \text{ nm}$ ) emission band with a peak wavelength between 650 and 800 nm. ERE was first detected in the spectrum of HD 44179 (the Red Rectangle) (Cohen et al. 1975; Schmidt et al. 1980) and is commonly seen in reflection nebulae (Witt and Schild 1988; Witt and Boroson 1990). ERE has also been detected in dark nebulae, cirrus clouds, planetary nebulae, H II regions, diffuse interstellar medium, and in haloes of galaxies. The central wavelength of the emission seems to shift from object to object, or even in different locations within the same object.

Since many solids emit visible luminescence when exposed to UV light, it is assumed that ERE is a photoluminescence process powered by far UV photons. In the diffuse ISM, approximately 4% of the energy absorbed by dust at wavelengths below  $0.55 \mu\text{m}$  is emitted in the form of ERE, suggesting that the carrier of ERE must be a major component of the interstellar grains. It has been estimated that the intrinsic quantum yield of ERE is as high as 50%, and the ERE carrier intercepts  $\sim 20\%$  of the photons absorbed by interstellar dust in the 90–550 nm range. This limits the chemical composition of the ERE carrier to a few abundant and highly depleted elements, such as C, Fe, Si, and Mg (Smith and Witt 2002). Since metals do not undergo photoluminescence, the most likely candidates are C and Si.

Proposed carriers of the ERE include hydrogenated amorphous carbon (HAC), Quenched carbonaceous composites (QCC),  $C_{60}$ , and silicon nanoparticles. In a material with mixed aromatic and aliphatic composition such as HAC, the tunneling of excitation energy from one aromatic ring to another is inhibited by the presence of  $sp^3$  material, resulting in wider bandgaps (Duley 2001). Orange-red fluorescent emissions peaking from 670 to 725 nm are found in the spectra of QCC. Since this fluorescence rapidly decays upon exposure to air, it suggests that the fluorescence is caused by radicals and highly unsaturated molecules in QCC (Sakata et al. 1992). Crystalline silicon nanoparticles with 1.5–5 nm diameters have been suggested to possess the optical properties to satisfy the spectral and quantum efficiency requirements (Ledoux et al. 1998; Witt et al. 1998). Experimental studies have shown the silicon nanoparticles can have quantum efficiencies near 100% and absorption coefficients ten times higher than average interstellar dust. Because the number of surface atoms relative to the number of volume atoms is high for nanoparticles, in order to avoid non-radiative recombination all the dangling Si bonds at the surface of the nanocrystal are passivated by H or O atoms.

### 6.5 The 21 and 30 micron emission features

The strong emission feature at  $21 \mu\text{m}$  was first discovered in four PPN from observations by the *Infrared Astronomical Satellite (IRAS)* Low Resolution Spectrometer (LRS) (Kwok et al. 1989). High resolution ( $\lambda/\Delta\lambda = 2000$ ) *ISO* observations have found that all features have the same intrinsic profile and peak wavelength ( $20.1 \mu\text{m}$ ) (Volk et al. 1999). There is no evidence for any discrete sub-structure due to molecular bands in the observed spectra, suggesting that the  $21 \mu\text{m}$  feature is either due to a solid substance or a mixture of many similarly structured large molecules.

A list of the currently discovered  $21\text{-}\mu\text{m}$  sources is listed in Table 1. The fact that all of the  $21 \mu\text{m}$  sources are carbon rich strongly suggests that the carrier of this feature

**Table 1** Summary of the spectral features of carbon-rich PPNe and 21  $\mu\text{m}$  sources<sup>a</sup>

Object	SpT	C/O	C <sub>2</sub> ,C <sub>3</sub>	3.3	3.4	6.2	6.9	7.7	8.6	8br	11.3	12.3	Class <sup>b</sup>	C <sub>2</sub> H <sub>2</sub>	15.8	21	30 $\mu\text{m}$
02229+6208	G8 Ia	...	Y,Y	Y	Y:*	Y:	Y	N	N	Y	Y	Y	A	...		Y	Y
20000+3239	G8 Ia	...	Y,...	Y	Y*	Y	Y	N	N	Y	Y	Y	A	...		Y	Y
05113+1347	G8 Ia	2.4	Y,Y	Y:	Y:	...	...	...	...	...	Y	Y	...	N:*	Y:*	Y	Y
22272+5435	G5 Ia	1.6	Y,Y	Y	Y	Y	Y	Y	N	Y	Y	Y	B		Y:	Y	Y
07430+1115	G5 Ia	...	Y,Y	Y	Y	...	...	...	...	Y:	Y:	...	A	...	...	Y*	Y
23304+6147	G2 Ia	2.8	Y,Y	Y*	Y:*	Y	Y	Y	Y	Y	Y	Y	A	Y:*	Y*	Y	Y
05341+0852	G2 Ia	1.6	Y,Y	Y	Y	Y	Y	N	N	Y	Y	Y*	B	Y*	Y*	Y	Y
22223+4327	G0 Ia	1.2	Y,Y	Y	N						Y		A			Y	Y
04296+3429	G0 Ia	...	Y,Y	Y	Y			Y			Y	Y	B			Y	Y
AFGL 2688	F5 Iae	1.0	Y,Y	Y	Y	Y	Y:	N	N	Y	Y	N:	A	Y		Y:	Y
06530–0230	F5 I	2.8	Y,Y	Y*	N	...	...	...	...	...	Y*	Y*	A	Y*	Y*	Y*	Y*
07134+1005	F5 I	1.0	Y,N	Y	Y:	...	Y	Y	N	Y	Y	Y	A		Y:	Y	Y
19500–1709	F3 I	1.0	N,N	N	N					Y:	Y	Y:	...		Y:	Y	Y
16594–4656	B7	...	N,N	Y	N	Y	N	Y	Y	Y:	Y	Y:	A			Y	Y
01005+7910	B0 I	1.2	N,N	Y	Y*	Y	N	Y	Y	N	Y	N	A	...	...	N:	Y
22574+6609	...	...	...,...	...	...	Y	Y	Y	N	Y	Y	Y*	...	Y*	N*	Y	Y
19477+2401	...	...	...,...	...	...	...	...	...	...	...	...	...	...	...	...	Y*	Y

<sup>a</sup>Note 1: Colon indicates a marginal or uncertain detection, blank indicates lack of information, “...” indicates that the object has not been observed in this spectral region. Table adapted from (Hrivnak et al. 2008)

<sup>b</sup>Classification scheme of Geballe (1997) at 3.3, 3.4  $\mu\text{m}$

is carbon-based. Since the AIB emission features are also seen in the 21  $\mu\text{m}$  sources (see Table 1), it is likely that the carrier of the 21  $\mu\text{m}$  feature is related to aromatic ring carbon compounds, or even larger molecules that might form from such compounds. Possible candidates that have been proposed include large PAH clusters, HAC grains, hydrogenated fullerenes, nanodiamonds, TiC nanoclusters, nano-SiC grains with carbon impurities, and cold SiC grains with amorphous SiO<sub>2</sub> mantles (see Posch et al. 2004; Speck and Holmeister 2004 and references therein).

The unidentified emission feature around 30  $\mu\text{m}$  was discovered from *KAO* observations (Forrest et al. 1981). It was first seen in carbon-rich AGB stars (e.g. IRC+10216 and AFGL 2688) and PN (e.g. IC 418 and NGC 6572). More recently, the 30  $\mu\text{m}$  feature was found to be common in carbon-rich PPN, especially those showing the 21  $\mu\text{m}$  emission feature.

The origin of the 30  $\mu\text{m}$  feature is not known. The fact that a significant fraction ( $\sim 20\%$ ) 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. The alternative suggestion that the carrier is a carbonaceous material continues to be popular because the feature is only seen in carbon-rich objects.

## 7 Chemical structure of organic matter in space

Although we now appreciate the ubiquitous nature of organic compounds in the Universe, the exact chemical compositions or structures of these compounds are not known. In spite of some very strong proponents for the polycyclic aromatic hydrocarbons (PAH) hypothesis, claiming that the AIB features are due to infrared fluorescence of far-ultraviolet-pumped PAH gas-phase molecules (Tielens 2008), the real situation is much more complex. We now know that the AIB features are seen in PPN (Kwok et al. 1999) and reflection nebulae with low-temperature central stars (Uchida et al. 2000) where the UV radiation background is negligible. The observed AIB features are not sharp, as it would be the case if they are due to molecular emission. Furthermore, the features often lie on top of strong plateau features or broad continuum, which have to originate from a solid or nano-particles. Most importantly, no specific PAH molecule has been identified by astronomical spectroscopy. It is therefore quite likely that the observed AIB emissions do not arise from pure PAH molecules, but from a more complex compound with aromatic structures. Below, we discuss a number of candidates that have been proposed in the literature as possible carriers of the AIB features, as well as possible constituents of organic matter in the Solar System.

## 7.1 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbon (PAH) molecules are benzene rings of  $sp^2$ -hybridized C atoms linked to each other in a plane, with H atoms or other groups saturating the outer bonds of peripheral C atoms. PAH molecules can be divided into two general classes: compact PAHs where some C atoms belong to three rings (e.g., pyrene  $C_{16}H_{10}$ ) and non-compact PAHs where no C atom belongs to more than two rings (e.g., naphthalene  $C_{10}H_8$ ) (Salama 1999). A list of common PAHs and their vibrational frequencies can be found in: <http://astrochemistry.ca.astro.it/database>.

The interest in PAH molecules as a possible constituent of the ISM began with the suggestion that they could be responsible for the AIBs (Allamandola et al. 1989; Puget and Léger 1989). Small, neutral PAHs are primarily excited by UV light, as laboratory measurements show a sharp cutoff in the UV with little absorption in the visible. In order to better match the observations, studies of PAHs have been extended to include PAH ions and clusters. Also relevant are nitrogen-substituted PAH molecules. Since the N atom can replace a CH group in an aromatic ring without significant change to the molecule's chemical structure, such heterocyclic aromatic compounds are of particular interest because of their biochemical implications.

If present, interstellar PAHs could contribute to the energy balance of the ISM through the absorption of diffuse starlight. Absorption of UV photons results in a rapid redistribution of the photon energy among the vibrational modes of the molecule. In a low density environment where collisional deexcitation is not possible, the molecules undergo spontaneous deexcitation via infrared fluorescence, leading to the emission of infrared features. The absorption of diffuse UV light can also lead to the ejection of electrons through the photoelectric effect, which can contribute to the heating of the interstellar gas.

## 7.2 Hydrogenated amorphous carbon and carbon nanoparticles

HAC is created by laser ablation of graphite in a hydrogen atmosphere. Chemically, HAC is similar to soot, which is formed by combustion of hydrocarbon molecules in a flame. The structure of HAC contains 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 has been proposed as being responsible for the AIBs as well as ERE, 21  $\mu\text{m}$  feature, etc.

A similar technique has yielded samples of carbon particles of nm size with mixed aromatic/aliphatic structures. Spectra of these particles have shown similarity with the astronomical AIB profiles (Hu and Duley 2008 and references therein). Other forms of carbon nanoparticles have

been made using hydrocarbon flame or arc discharge in an hydrogenated atmosphere (Colangeli et al. 1995) or using infrared laser pyrolysis of hydrocarbons (Herlin et al. 1998).

## 7.3 Quenched carbonaceous composites

QCC are produced by the technique of hydrocarbon plasma deposition where methane gas is heated to 3000 K with a microwave generator, allowed to expand into a vacuum chamber and condensed on a room-temperature substrate. The resultant dark, granular material is shown by electron microscopy to have an amorphous structure. Since QCC consists of only H and C and the conditions under which it is synthesized resemble the circumstellar environment of AGB stars, it could have astrophysical significance. Mass spectrometry of QCC suggests that its aromatic component typically consists of 1 to 4 rings, and most have only 1–2 rings (Sakata et al. 1983). Infrared spectroscopy of QCC reveals a mixture of  $sp$ ,  $sp^2$ , and  $sp^3$  sites. Upon heating, the strengths of the  $sp^2$  features increase relative to the  $sp^3$  features, suggesting that QCC can become graphitized at high temperatures.

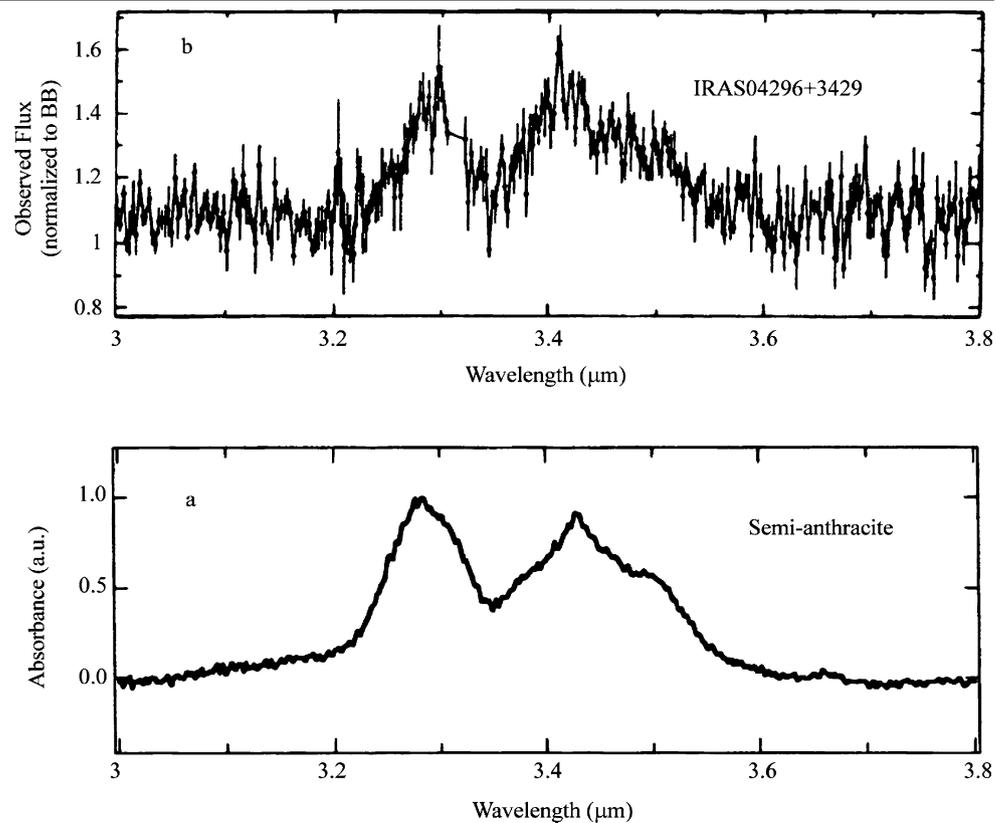
## 7.4 Kerogen and coal

*Coal*, formed from fossilized hydrocarbon materials, also contains a mixture of  $sp$ ,  $sp^2$ , and  $sp^3$  bonds. In addition to its aromatic character, coal also contains rich oxygen functional groups. Coal is believed to have evolved naturally with time through heat and pressure, changing from “low-rank” to “high-rank” through decreasing H and O contents. Structurally, it increases its long-range order by stacking aromatic planes to form randomly oriented basic structural units, eventually ending as graphite.

*Kerogen* is a solid sedimentary, insoluble, organic material found in the upper crust of the Earth (Durand 1980). In contrast to coal, which is found in bulk rocks, kerogen is usually found in sand-like dispersed form. Structurally, kerogen can be represented by random arrays of aromatic carbon sites, aliphatic chains ( $-\text{CH}_2-$ ) $_n$ , and linear chains of benzenic rings with functional groups made up of H, O, N, and S attached. The O atoms can be in ester ( $-\text{O}-\text{C}=\text{O}$ ), ether ( $\text{C}-\text{O}-\text{C}$ ), or hydroxyl ( $-\text{OH}$ ) groups (Papoular 2001).

The laboratory spectra of coal and kerogen show a lot of similarity with astronomical spectra of PPN (Papoular et al. 1996; Guillois et al. 1996; Papoular 2001). The 3.4  $\mu\text{m}$  feature and the broad emission plateaus at 8 and 12  $\mu\text{m}$  seen in PPN are difficult to explain by pure aromatic materials but correspond well with mixed aromatic/aliphatic compounds such as coal and kerogen (Ehrenfreund et al. 1991; Guillois et al. 1996) (Fig. 12).

**Fig. 12** Comparison between the 3.3 and 3.4  $\mu\text{m}$  emission features in PPN IRAS 04396+3429 (*top*) to the absorbance spectrum of semianthracite coal. Figure from Guillois et al. (1996)



### 7.5 Tholin and HCN polymers

Tholins are refractory organic materials formed by UV photolysis of reduced gas mixtures ( $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , etc.) under cold plasma conditions (Sagan and Khare 1979). X-ray diffraction studies of tholins show a disordered or quasi-amorphous structure. Various functional groups have been identified through infrared spectroscopy, including cyanides ( $-\text{CN}$ ), aliphatic  $\text{CH}_2$  and  $\text{CH}_3$ , amines ( $\text{NH}_2$ ) and  $\text{C}=\text{N}$  groups. The optical properties of tholins is dependent on the chemical composition and the  $sp^2/sp^3$  ratio.

Under suitable conditions, HCN molecules can polymerize spontaneously to HCN polymers (Matthews and Minard 2006). HCN polymer is an amorphous hydrogenated carbon nitride with some structural similarity to (but possibly simpler than) tholins. Reflectance spectra of tholins and HCN polymer have been obtained in the laboratory, showing a variety of overtone and combination bands (see, e.g., de Bergh et al. 2008) (Fig. 13).

The difference between this group and the previous groups of carbonaceous compounds is the incorporation of the N atom.

### 7.6 Biological materials

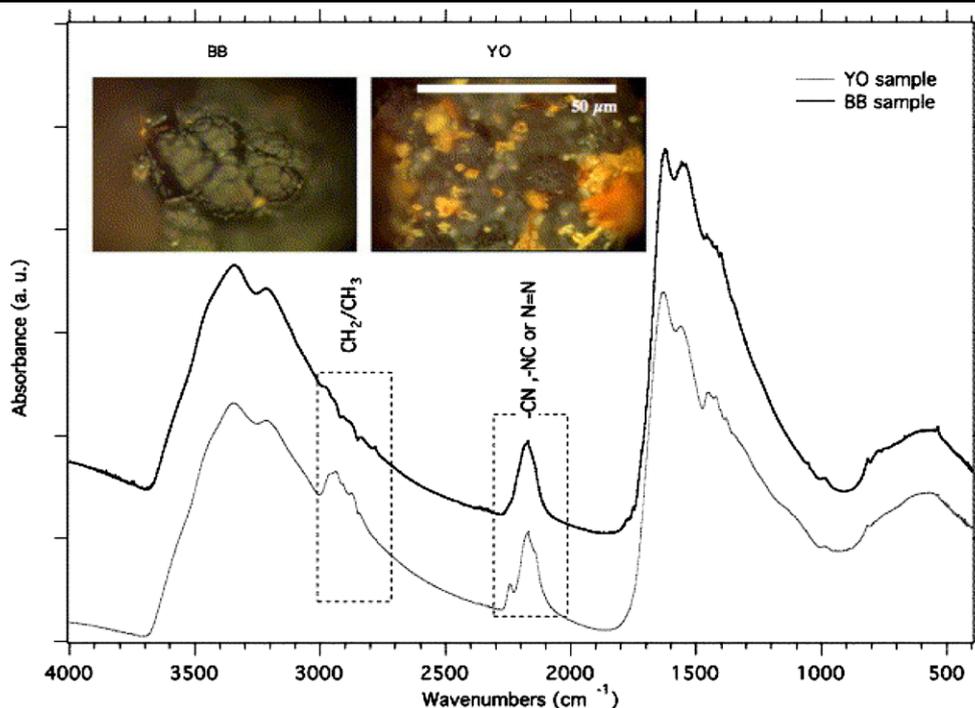
The possibility that the 3.4  $\mu\text{m}$  and other astronomical spectral features are due to biological materials (e.g., bacteria)

has been made by Hoyle et al. (1982). Comparison of the laboratory spectrum of *E. coli* bacteria with high resolution astronomical spectra shows that they do not match well (Pendleton and Allamandola 2002). At present, there is no convincing evidence for the existence of biological materials in space.

## 8 Laboratory simulations of molecular synthesis

Since the original Miller-Urey experiment (Miller 1953) where a mixture of methane, ammonia, hydrogen, and water under spark discharges were found to be able to produce amino acids, there have been many follow-up experiments to test the synthesis of organic matter under simulated primitive Earth atmospheres under different energy inputs such as ultraviolet light (Sagan and Khare 1971) or heat (Harada and Fox 1964). With the discovery of gas-phase molecules in the ISM, there have been a number of attempts to study the possibility of organic synthesis on the surface of dust grains under interstellar conditions. Starting with simple ices such as  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_2$ , etc., at low ( $\sim 10$  K) temperatures, an organic substance called “yellow stuff” can be produced by subjecting the sample to UV irradiation and subsequent warming. When this substance was carried into space and subjected to 4 months of solar radiation, its color changed from yellow to brown. The near-infrared spectrum

**Fig. 13** Laboratory spectra of two samples of tholins: black/brown (BB) and yellow/orange (YO). The 3.4  $\mu\text{m}$  aliphatic  $\text{CH}_2/\text{CH}_3$  and the 4.6  $\mu\text{m}$  nitrile ( $-\text{CN}$ ) and isocyanide ( $-\text{NC}$ ) groups are identified. Figure from Bernard et al. (2006)



of the final sample (termed organic refractory matter, Greenberg et al. 1995 shows the 3.4  $\mu\text{m}$  feature due to the methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) aliphatic groups (see Fig. 3), as well as features suggestive of alcohols and carboxylic acids.

Ultraviolet photolysis of ices containing  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ , and  $\text{NH}_3$  (in ratios consistent with ices in molecular clouds) can create a rich variety of moderately complex organic molecules such as ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), formamide ( $\text{HC}(=\text{O})\text{NH}_2$ ), acetamide ( $\text{CH}_3\text{C}(=\text{O})\text{NH}_2$ ), nitriles ( $\text{R}-\text{C}\equiv\text{N}$ ), and hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ), as well as more complex unidentified organic materials that include amides ( $\text{H}_2\text{NC}(=\text{O})-\text{R}$ ), ketones ( $\text{R}-\text{C}(=\text{O})=\text{R}'$ ), and polyoxymethylenes (POM,  $(-\text{CH}_2\text{O}-)_n$ ), where R represents a generalized alkyl group. HMT, which contains four N per molecule, is one of the major organic residues produced by photolysis. It has been known since the 1970s that HMT formed spontaneously at room temperature when pure ammonia and formaldehyde were mixed. Since hydrolysis of HMT by concentrated acid can yield amino acids, the formation of this molecule in the ISM has great significance (Bernstein et al. 1995).

Ultraviolet photolysis of amorphous water ice mixed with  $\text{CH}_3\text{OH}$ ,  $\text{HCN}$ , and  $\text{NH}_3$  followed by warming and ice sublimation leaves behind an organic residue which contains N-formyl glycine, cycloserine, and glycerol upon analysis with gas chromatography-mass spectrometry and liquid chromatography. After hydrolysis, glycine, alanine, serine, glycerol, ethanolamine and glyceric acid are observed. Similar experiments using different initial ingredients also yield

many amino acids. These results suggest that spontaneous generation of amino acids in the ISM is possible (Bernstein et al. 2002; Muñoz Caro et al. 2002).

Similar efforts have also been made to produce nucleic acid bases, which are believed to be essential for the generation of life. Proton irradiation of carbon monoxide, nitrogen and water under simulated interstellar conditions has been shown to be able to yield uracil, one of the four RNA bases (the others being cytosine, adenine, and guanine). Thymine, the base that substitutes for uracil in DNA, has been reported to be present under proton irradiation of a mixture of methane, carbon monoxide, and ammonia (Kobayashi et al. 1995, 2004).

## 9 Delivery of organic compounds to Earth and its implications on the origin of life

The current thinking of the history of the Solar System is that most of the mass of the original solar nebula was incorporated into the Sun, and the remaining planetesimals aggregated into planets or ejected from the Solar System. However, a small fraction of the pristine materials reside in comets and asteroids. These bodies were not subjected to the extensive processing as the rest of the Solar System and therefore may retain much of the original nebular materials, including organic compounds.

The possibility that the early Earth was enriched by organic compounds delivered by extraterrestrial sources have been under discussion for some time (Anders 1989). The

contributions from comets, asteroids, IDPs, can be substantial, particularly during the heavy bombardment period (Chyba and Sagan 1992). However, the most direct link between stars and the Earth is found in the presolar grains in meteorites, where diamonds (Lewis et al. 1987), silicon carbide (Bernatowicz et al. 1987), corundum (Nittler et al. 1997), and silicates (Nagashima et al. 2004) are found to have isotopic ratios identifiable with AGB stars (Zinner 1998). This demonstrates clearly that inorganic minerals manufactured in AGB stars can survive through journeys over the ISM and reached the Solar System and the Earth.

Although there is no corresponding strong evidence of organic compounds having arrived from outside the Solar System, there is evidence that the organic compound D/H ratios in some Solar System objects have non-solar values (Ehrenfreund et al. 2002). The excess of D,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , etc., found in some IOM also points to an interstellar origin (Keridge 1999; Alexander et al. 2008).

One may argue whether extraterrestrial abiological kerogen-like materials can be of any relevance to the origin of life on Earth. The experiment by Deamer (1997) shows that membrane structures can be developed from lipid-like organic components from the Murchison meteorite. This opens the possibility that cellular life can follow.

Whether such extraterrestrial delivery is responsible for or has accelerated the process of creation of life is a matter of conjecture. What we do know is that the ingredients for life are commonly produced by stars, and are widely spread over the Galaxy by stellar winds. If these stellar materials played a role in the origin of life on Earth, they could have easily done the same elsewhere in the Galaxy. The chemical link between AGB stars, the ISM, the early Solar System, and the Earth represents an area of study with great potentials and significance.

## 10 Conclusions

In the past 30 years we have witnessed major progress in the observation of gas-phase molecules by using radio astronomical techniques. The detections of organic molecules of every class left no doubt that stars and interstellar clouds are capable of synthesizing complex molecules from atoms under low-density conditions. However, the radio technique has its own limits and the search for large pre-biotic molecules through their rotational transitions will be difficult. Large organic compounds, including organic solids with thousands of atoms, manifest themselves through their vibrational modes and their chemical nature can be discerned by infrared spectroscopy. Astronomical detections of the stretching and bending modes of aromatic compounds have shown that complex organic matter is widely present in the Universe, from the circumstellar envelopes of stars, to diffuse interstellar medium, to distant galaxies. Although most

of the previous observational efforts have been concentrated in the near- and mid-infrared regions, extension of infrared spectroscopy to the far infrared for the detection of low-frequency bending modes will be the next frontier for the discovery and identification of organic compounds.

The fact that some astronomical phenomena such as the 217 nm feature, DIB, ERE, etc., have remained unexplained after several decades of observational investigation suggests further laboratory work is needed, both in the study of the spectroscopic properties of known materials and in the synthesis of new materials. Nano-particles are of particular interest because the spectral properties of nano-particles may be different from the bulk materials due to the limited mobility of electrons. The asymmetries introduced by boundary effects may also allow certain vibrational modes to become infrared active. These astronomical mysteries will not be solved without a strong input from the laboratory community.

The studies of Solar System objects have the advantage that samples can be collected and analyzed by a wide variety of techniques in the laboratory, thus giving a more precise determination of the nature of organic compounds in the Solar System. It is interesting to note that Solar System organics share many similar properties with astronomically observed organic matter. Although researchers in different communities use different terms to refer to this complex organic matter (e.g., CHON in the comet community, IOM in the meteorite community, PAH in the astronomy community, and tholins in the planetary community), it is quite possible that all these organic matter share some common chemical structures or even common origins. Our understanding of the origin of organic matter can much benefit from cross-discipline fertilization. With the upcoming space missions in astronomical spectroscopy and in experimental probes into comets, asteroids, and planetary satellites, we can expect much further progress in this field.

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## References

- Alexander, C.M.O'D., Cody, G.E., Fogel, M., Yabuta, H.: In: Kwok, S., Sandfor, S. (eds.) IAU Symposium 251: Organic Matter in Space, CUP (2008)
- Allamandola, L.J., Tielens, A.G.G.M., Barker, J.R.: *Astrophys. J. Suppl. Ser.* **71**, 733 (1989)
- Anders, E.: *Nature* **342**, 255 (1989)
- Becker, L., Poreda, R.J., Bunch, T.E.: *Proc. Natl. Acad. Sci.* **97**, 2979–2983 (2000)
- Bernard, J.-M., et al.: *Icarus* **185**, 301 (2006)

- Bernatowicz, T., Fraundorf, G., Ming, T., Anders, E., Wopenka, B., Zinner, E., Fraundorf, P.: *Nature* **330**, 728 (1987)
- Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Chang, S., Scharberg, M.A.: *Astrophys. J.* **454**, 327 (1995)
- Bernstein, M.P., Dworkin, J.P., Sandford, S.A., Cooper, G.W., Allamandola, L.J.: *Nature* **416**, 401 (2002)
- Botta, O., Bada, J.L.: *Surv. Geophys.* **23**, 411 (2002)
- Brandl, B.R., et al.: *Astrophys. J.* **653**, 1129 (2006)
- Cerricharo, J., et al.: *Astrophys. J.* **546**, L123 (2001)
- Chiar, J.E., et al.: *Astrophys. J.* **537**, 749 (2000)
- Chyba, C.F., Sagan, C.: *Nature* **355**, 125 (1992)
- Cody, G.D., Alexander, C.M.O'D.: *Geochim. Cosmochim. Acta* **69**, 1085 (2005)
- Cody, G.D., Alexander, C.M.O'D., Kilcoyne, A.L.D., Yabuta, H.: In: Kwok, S., Sandford, S. (eds.) *IAU Symposium 251: Organic Matter in Space*, CUP (2008)
- Cohen, et al.: *Astrophys. J.* **196**, 179 (1975)
- Colangeli, L., Mennella, V., Palumbo, P., Rotundi, A., Bussoletti, E.: *Astron. Astrophys. Suppl. Ser.* **113**, 561 (1995)
- Cronin, J.R., Pizzarello, S.: *Geochim. Cosmochim. Acta* **54**, 2859 (1990)
- Cronin, J.R., Pizzarello, S., Frye, J.S.: *Geochim. Cosmochim. Acta* **51**, 299 (1987)
- Cronin, J.R., Cooper, G., Pizzarello, S.: *Adv. Space Res.* **3**, 91 (1995)
- Cruikshank, D.P.: *Icarus* **193**, 334 (2008)
- Cruikshank, D.P., et al.: *Icarus* **135**, 389 (1998)
- de Bergh, C., Schmitt, B., Moroz, L.V., Quirico, E., Cruikshank, D.P.: In: Barucci, M.A., Boehnhardt, H., Cruikshank, D.P., Moridelli, A. (eds.) *The Solar System Beyond Neptune*, p. 483. University of Arizona Press, Tucson (2008)
- Deamer, D.: *Microbiol. Mol. Biol. Rev.* **61**, 239 (1997)
- Duley, W.W.: *Astrophys. J.* **553**, 575 (2001)
- Duley, W.W., Williams, D.A.: *Mon. Not. R. Astron. Soc.* **196**, 269 (1981)
- Durand, B.: In: Durand, B. (ed.) *Kerogen-Insoluble Organic Matter from Sedimentary Rocks*, p. 13. Editions Technip, Paris (1980)
- Ehrenfreund, P., Charnley, S.B.: *Ann. Rev. Astron. Astrophys.* **38**, 427 (2000)
- Ehrenfreund, P., Robert, F., d'Hendecourt, L., Behar, F.: *Astron. Astrophys.* **252**, 712 (1991)
- Ehrenfreund, P., et al.: *Rep. Prog. Phys.* **65**, 1427 (2002)
- Flynn, G.J., Keller, L.P., Feser, M., Wirick, S., Jacobsen, C.: *Geochim. Cosmochim. Acta* **67**, 4791 (2003)
- Forrest, W.J., Houck, J.R., McCarthy, J.F.: *Astrophys. J.* **248**, 269 (1981)
- Friedel, D.N., Snyder, L.E., Remijan, A.J., Turner, B.E.: *Astrophys. J.* **632**, L95 (2005)
- Geballe, T.R.: In: Pendleton, Y.J., Tielens, A.G.G.M. (eds.) *From Stardust to Planetesimals*, p. 119. ASP, San Francisco (1997)
- Genzel, R., Cesarsky, C.J.: *Annu. Rev. Astron. Astrophys.* **38**, 761 (2000)
- Gilmour, I., Pillinger, C.T.: *Mon. Not. R. Astron. Soc.* **269**, 235 (1994)
- Gradie, J., Veverka, J.: *Nature* **283**, 840 (1980)
- Greenberg, et al.: *Astrophys. J.* **455**, L177 (1995)
- Groves, B., Dopita, M.A., Sutherland, R.S., Kewley, L.J., Fishera, J., Leitherer, C., Brandl, B., van Breugel, W.: *Astrophys. J. Suppl. Ser.* **176**, 438 (2008)
- Guillois, O., Nenner, I., Papoular, R., Reynaud, C.: *Astrophys. J.* **464**, 810 (1996)
- Harada, K., Fox, S.W.: *Nature* **201**, 335 (1964)
- Henning, Th., Salama, F.: *Science* **282**, 2204 (1998)
- Heger, M.L.: *Lick Obs. Bull.* **337**, 141 (1922)
- Herlin, N., Bohn, I., Reynaud, C., Cauchetier, M., Galvez, A., Rouzaud, J.-N.: *Astron. Astrophys.* **330**, 1127 (1998)
- Hollis, J.M., Lovas, F.J., Jewell, P.R.: *Astrophys. J.* **540**, L107 (2000)
- Hollis, J.M., Lovas, F.J., Jewell, P.R., Coudert, L.H.: *Astrophys. J.* **571**, L59 (2002)
- Hollis, J.M., Jewell, P.R., Lovas, F.J., Remijan, A., Møllendal, H.: *Astrophys. J.* **610**, L21 (2004)
- Hollis, J.M., Lovas, F.J., Remijan, A.J., Jewell, P.R., Ilyushin, V.V., Kleiner, I.: *Astrophys. J.* **643**, L25 (2006a)
- Hollis, J.M., Remijan, A.J., Jewell, P.R., Lovas, F.J.: *Astrophys. J.* **642**, 933 (2006b)
- Hoyle, F., Wickramasinghe, N.C., Al-Mufti, S., Olavesen, A.H.: *Astrophys. Space Sci.* **81**, 489 (1982)
- Hrivnak, B.J., Volk, K., Kwok, S.: *Astrophys. J.* **535**, 275 (2000)
- Hrivnak, B.J., Geballe, T.R., Kwok, S.: *Astrophys. J.* **662**, 1059 (2007)
- Hrivnak, B.J., Volk, K., Geballe, T.R., Kwok, S.: In: Kwok, S., Sandford, S. (eds.) *IAU Symposium 251: Organic Matter in Space*, CUP, p. 213 (2008)
- Hu, A., Duley, W.W.: *Astrophys. J.* **677**, L153 (2008)
- Hudgins, D.M., Allamandola, L.J.: *Astrophys. J.* **516**, L41 (1999)
- Jones, A.P., Duley, W.W., Williams, D.A.: *R. Astron. Soc. Q. J.* **31**, 567 (1990)
- Kerridge, J.F.: *Space Sci. Rev.* **90**, 275 (1999)
- Kissel, J., et al.: *Nature* **321**, 280 (1986a)
- Kissel, J., et al.: *Nature* **321**, 336 (1986b)
- Kobayashi, K., Kasamatsu, T., Kaneko, T., Koike, J., Oshima, T., Saito, T.: *Adv. Space Res.* **16**, 21 (1995)
- Kobayashi, K., Takano, Y., Masuda, H., Tonishi, H., Kaneko, T., Hashimoto, H., Saito, T.: *Adv. Space Res.* **33**, 1277 (2004)
- Kuan, Y.-J., Charnley, S.B., Huang, H.-C., Tseng, W.-L., Kisiel, Z.: *Astrophys. J.* **593**, 848 (2003a)
- Kuan, Y.-J., Yan, C.-H., Charnley, S.B., Kisiel, Z., Ehrenfreund, P., Huang, H.-C.: *Mon. Not. R. Astron. Soc.* **345**, 650 (2003b)
- Kwok, S.: *Nature* **430**, 985 (2004)
- Kwok, S.: *Physics and Chemistry of the Interstellar Medium*. University Science Books, Herndon (2006)
- Kwok, S., Volk, K.M., Hrivnak, B.J.: *Astrophys. J.* **345**, L51 (1989)
- Kwok, S., Volk, K.M., Hrivnak, B.J.: *Astron. Astrophys.* **350**, L35 (1999)
- Kwok, S., Volk, K., Bernath, P.: *Astrophys. J.* **554**, L87 (2001)
- Ledoux, G., et al.: *Astron. Astrophys.* **333**, L39 (1998)
- Lewis, R.S., Ming, T., Wacker, J.F., Anders, E., Steel, E.: *Nature* **326**, 160 (1987)
- Lorenz, R.D., et al.: *Geo. Res. Lett.* **35**, L02206 (2008)
- Lovas, F.J., Remijan, A.J., Hollis, J.M., Jewell, P.R., Snyder, L.E.: *Astrophys. J.* **637**, L37 (2006)
- Martins, Z., et al.: *Earth Planet Sci. Lett.* **270**, 130 (2008)
- Matthews, C.N., Minard, R.D.: *Faraday Discuss.* **133**, 393 (2006)
- Merrill, P.W.: *Publ. Astron. Soc. Pac.* **46**, 206 (1934)
- Messenger, S.: *Nature* **404**, 968 (2000)
- Miller, S.L.: *Science* **117**, 528 (1953)
- Mumma, M.J., et al.: *Astrophys. J.* **546**, 1183 (2001)
- Mumma, M.J., DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Gibb, E., Novak, R.: *Adv. Space Res.* **31**, 2563 (2003)
- Muñoz Caro, G.M., et al.: *Nature* **416**, 403 (2002)
- Nagashima, K., Krot, A.N., Yurimoto, H.: *Nature* **428**, 921 (2004)
- Nakamura-Messenger, K., Messenger, S., Keller, L.P., Clemett, S.J., Zolensky, M.E.: *Science* **314**, 1439 (2006)
- Nittler, L.R., Alexander, C.M.O'D., Gzo, X., Walker, R.M., Zinner, E.: *Astrophys. J.* **483**, 475 (1997)
- Papoular, R.: *Astron. Astrophys.* **378**, 597 (2001)
- Papoular, R., Conard, J., Guillois, O., Nenner, I., Reynaud, C., Rouzaud, J.-N.: *Astron. Astrophys.* **315**, 222 (1996)
- Peeters, E., et al.: *Astron. Astrophys.* **390**, 1089 (2002)
- Pendleton, Y.J., Allamandola, L.J.: *Astrophys. J. Suppl. Ser.* **138**, 75 (2002)
- Pizzarello, S., Feng, X., Epstein, S., Cronin, J.R.: *Geochim. Cosmochim. Acta* **58**, 5579 (1994)
- Posch, T., Mutschke, H., Andersen, A.: *Astrophys. J.* **616**, 1167 (2004)
- Puget, J.L., Léger, A.: *Annu. Rev. Astron. Astrophys.* **17**, 161 (1989)
- Remijan, A.J., Hollis, J.M., Lovas, F.J., Stork, W.D., Jewell, P.R., Meier, D.S.: *Astrophys. J.* **675**, L85 (2008)

- Russell, R.W., Soifer, B.T., Willner, S.P.: *Astrophys. J.* **217**, L149 (1977)
- Russell, R.W., Soifer, B.T., Willner, S.P.: *Astrophys. J.* **220**, 568 (1978)
- Sagan, C., Khare, B.N.: *Science* **173**, 417 (1971)
- Sagan, C., Khare, B.N.: *Nature* **277**, 102 (1979)
- Sakata, A., Wada, S., Okutsu, Y., Shintani, H., Nakada, Y.: *Nature* **301**, 493 (1983)
- Sakata, A., Wada, S., Onaka, T., Tokunaga, A.T.: *Astrophys. J.* **393**, L83 (1992)
- Salama, F.: In: D'Hendecourt, L., Joblin, C., Jones, A. (eds.) *Solid Interstellar Matter: the ISO Revolution*, p. 65. EDP Sciences, Springer, Berlin (1999)
- Sandford, S., et al.: *Science* **314**, 1720 (2006)
- Sarre, P.J.: *J. Mol. Spec.* **238**, 1 (2006)
- Schmidt, G.D., Cohen, M., Margon, B.: *Astrophys. J.* **239**, L133 (1980)
- Sellgren, K., Uchida, K.I., Werner, M.W.: *Astrophys. J.* **659**, 1338 (2007)
- Shimoyama, A., Naraoka, H., Komiya, M., Harada, K.: *Geochem. J.* **23**, 181 (1989)
- Sloan, G.C., et al.: *Astrophys. J.* **664**, 1144 (2007)
- Smith, T.L., Witt, A.N.: *Astrophys. J.* **565**, 304 (2002)
- Smith, J.D.T., et al.: *Astrophys. J.* **656**, 770 (2007)
- Snow, T.P., McCall, B.J.: *Annu. Rev. Astron. Astrophys.* **44**, 367 (2006)
- Snyder, L.E., Lovas, F.J., Hollis, J.M., et al.: *Astrophys. J.* **619**, 914 (2005)
- Speck, A.K., Holmeister, A.M.: *Astrophys. J.* **600**, 986 (2004)
- Spoon, H.W.W., et al.: *Astrophys. J. Suppl. Ser.* **154**, 184 (2004)
- Stecher, T.P.: *Astrophys. J.* **142**, 1683 (1965)
- Stecher, T.P.: *Astrophys. J.* **157**, L125 (1969)
- Stoks, P.G., Schwartz, A.W.: *Geochim. Cosmochim. Acta* **45**, 563 (1981)
- Sturm, E., Lutz, D., Tran, D., Feuchtgruber, H., Genzel, R., Kunze, D., Moorwood, A.F.M., Thornley, M.D.: *Astron. Astrophys.* **358**, 481 (2000)
- Thaddeus, P.: *Phil. Trans. R. Soc. B* **361**, 1681 (2006)
- Tielens, A.G.G.M.: *Annu. Rev. Astron. Astrophys.* **46**, 289 (2008)
- Uchida, K.I., Sellgren, K., Werner, M.W., Houdashelt, M.L.: *Astrophys. J.* **530**, 817 (2000)
- Van Kerckhoven, C., et al.: *Astron. Astrophys.* **357**, 1013 (2000)
- Volk, K., Kwok, S., Hrivnak, B.J.: *Astrophys. J.* **516**, L99 (1999)
- Volk, K., Xiong, G.-Z., Kwok, S.: *Astrophys. J.* **530**, 408 (2000)
- Witt, A.N., Boroson, T.A.: *Astrophys. J.* **355**, 182 (1990)
- Witt, A.N., Schild, R.E.: *Astrophys. J.* **325**, 837 (1988)
- Witt, A.N., Gordon, K.D., Furton, D.G.: *Astrophys. J.* **501**, L111 (1998)
- Zinner, E.: *Ann. Rev. Earth Planet. Sci.* **26**, 147 (1998)