

## 1

## History and Introduction

The term organic matter was originally created to refer to compounds derived from natural living things which are fundamentally different from those derived from nonliving substances (inorganic matter). It was believed that living things possess a “vital force” which is absent in nonliving things. By the early nineteenth century, advances in chemical techniques had led to the isolation and discovery of an increasing number of organic molecules from living biological organisms. These included amino acids such as asparagine (isolated from asparagus in 1806), cysteine (extracted in 1810 from urinary calculi), leucine (1819, from fermenting cheese), and glycine (1820, from gelatin), fatty acids (1823), proteins (1838), DNA (1869, from yeast nuclei), and the nucleic acid bases guanine (1882), thymine (1883), adenine (1886), cytosine (1894), and uracil (1900) as well as deoxyribose (1909). These and other organic molecules represent the building blocks of life.

At the same time, it was commonly and firmly believed by many chemists that these molecules could only be produced by living organisms. While inorganic matter could be produced in the laboratory by chemical means, scientists thought organic matter could not be synthesized from inorganic matter because it lacked the “vital force”. Although the form of this “vital force” was never precisely described or defined, it was believed to be electrical in nature and involved in the rearrangement of molecular structures. In 1823, Friedrich Wöhler (1800–1882) heated an inorganic salt ammonium cyanate ( $\text{NH}_4\text{NCO}$ ) and turned it into urea ( $[(\text{NH}_2)_2\text{CO}]$ ), an organic compound isolated from urine. Although ammonium cyanate and urea are made up of the same atoms, their molecular structures are different. This experiment suggested that it was possible to convert an inorganic molecule into an organic one by artificial means, without the magic of “vitalism”. This was the beginning of the disappearance of the concept of “vital force” from the scientific arena.

This pioneering work on abiotic synthesis was followed by the laboratory synthesis of the amino acid alanine (from a mixture of acetaldehyde, ammonia, and hydrogen cyanide) by Adolph Strecker (1822–1871) in 1850 and the synthesis of sugars (from formaldehyde) by Aleksandr Mikhailovich Butlerov (1828–1886) in 1861. However, it was not until the 1960s that the first nucleobase adenine ( $\text{C}_5\text{H}_5\text{N}_5$ ) was synthesized abiotically (from HCN and  $\text{NH}_3$ ) [1]. This was followed by the synthesis of guanine [2] and cytosine [3].

Biochemistry developed as the systematic study of biological forms and functions in terms of chemical structures and reactions. In the mid-nineteenth century, it was thought that “vitalism” from living yeast cells was the key to the fermentation of sugar into alcohol. In 1897, Eduard Büchner (1860–1917) discovered that yeast extracts could ferment sugar into alcohol and living cells were not necessary. This marked the beginning of the realization that biomolecules (which we now call enzymes), not the “vital force”, are responsible for fermentation. Enzymes have since been shown to be the catalysts that accelerate chemical reactions in biological systems.

In 1926, James Sumner found that urease, an enzyme that catalyzes the hydrolysis of urea into  $\text{CO}_2$  and  $\text{NH}_3$ , is a protein. Shortly after, it was found that several other crystallized digestive enzymes are also proteins. The basis of one of the key elements of life – enhancing the rates of chemical reactions efficiently and selectively – was reduced to the study of the structures and functions of protein molecules.

Now, our definition of organic matter has evolved from something that possesses a special nonphysical element such as the “vital force” to a group of molecules and compounds based on the chemical element carbon (C). The element carbon is unique in its versatility for forming different chemical bonds. Not only is carbon able to connect with other C atoms to form different structures (see Chapter 2), it can also combine with other elements such as hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and phosphorus (P) to form a great variety of molecular forms. This group of molecules forms the basis of living organisms.

We note that four elements – hydrogen, oxygen, carbon, and nitrogen – make up more than 99% of the mass of most cells. These four elements are also the first, third, fourth, and fifth most abundant elements in the Universe. The existence of biomolecules is therefore built upon chemical elements that are abundantly available. The first step in molecular synthesis depends on the creation and distribution of chemical elements in the Universe.

## 1.1

### Origin of Chemical Elements

Studies on stellar nucleosynthesis in the 1950s have led to the current realization that most of the chemical elements are synthesized in stars [4]. Helium is made by fusing hydrogen into helium in the core during the main sequence and in a shell above the core in the red giant phase. The element carbon is created by helium-burning<sup>1)</sup> (the triple- $\alpha$  process), first through core burning and later through shell burning above an electron-degenerate carbon-oxygen core. For massive ( $> 10 M_\odot$ ) stars, direct nuclear burning continues with the production of oxygen, neon, magnesium, silicon, and so on, culminating in the synthesis of iron, the heaviest el-

1) Although the term “burning” has the connotation of a chemical reaction, it is used in astronomical literature to mean nuclear fusion.

element that can be formed through direct nuclear burning. The other heavy elements, from yttrium and zirconium to uranium and beyond, are produced by neutron capture followed by  $\beta$  decay [5].

For the majority of stars ( $\sim 95\%$ , corresponding to stars with initial masses less than  $\sim 8 M_{\odot}$ ), direct nuclear burning does not proceed beyond helium, and carbon is never ignited. Most of the nucleosynthesis occurs through slow neutron capture (the *s* process) during the asymptotic giant branch (AGB), a brief phase ( $\sim 10^6$  yr) of stellar evolution where hydrogen and helium burn alternately in a shell. These newly synthesized elements are raised to the surface through periodic “dredge-up” episodes, and the observation of short-lived isotopes in stellar atmospheres provides direct evidence that nucleosynthesis is occurring in AGB stars [6].

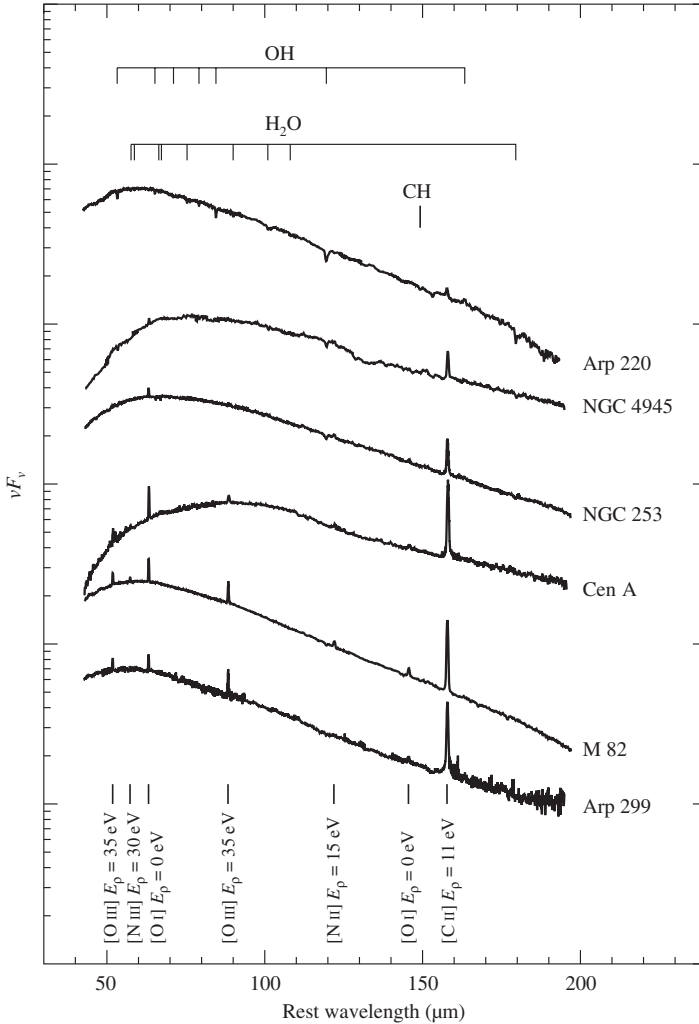
Other than the light elements H, He, D, and Li, which were produced in significant quantities during the Big Bang, all the other natural chemical elements are made in stellar furnaces. They are made in or near the core of stars, brought to the surface by convection, and ejected into interstellar space by stellar winds and supernovae explosions. With spectroscopic observations of distant galaxies (which means also looking back in time), we can detect the same elements through their atomic transitions. The element hydrogen (H) can be detected through its recombination lines (e.g., Lyman  $\alpha$ ,  $n = 2-1$ ) to a distance of redshift ( $z$ ) of 7 [7], corresponding to more than 10 billion years back in time.<sup>2)</sup> The fine-structure lines of oxygen have been detected in galaxies with  $z = 3.9$  [8]. In the far infrared, fine-structure lines of C, N, and O and rotational lines of simple molecules such as CH, OH, and H<sub>2</sub>O can be seen in emission and absorption respectively in the spectra of galaxies (Figure 1.1). With modern radio telescopes equipped with sensitive receivers, the molecule carbon monoxide (CO) has been detected in very distant quasars and galaxies [9, 10]. The most distant detection of molecular gas is in the quasar J1148+5251 at the redshift of 6.42 [11] (Figure 1.2). Photometric observations at the infrared and submillimeter wavelengths have detected excess infrared emission from galaxies and quasars at even similar distances [12]. This infrared excess cannot be due to starlight and is generally interpreted to be due to reemission by interstellar solid-state particles heated by starlight. Since these solids must be made of heavy elements,<sup>3)</sup> we know that the synthesis of chemical elements occurred soon ( $< 10^9$  yr) after the Big Bang.

This tells us that the laws of physics and chemistry are spatially universal over the Universe and also through time. Chemical elements were made in the first generation of stars, and the heavy elements created by these stars are used as raw materials to form the next generation of stars.

2) Redshift ( $z$ ) is a measure of how much the observed wavelength of a spectral line has changed as a result of Doppler effect due to the expansion of the Universe. Given a cosmological model, the value of redshift can be used to infer the distance of the galaxy from which the line is emitted and

the time it took for the light to reach us (see Appendix C).

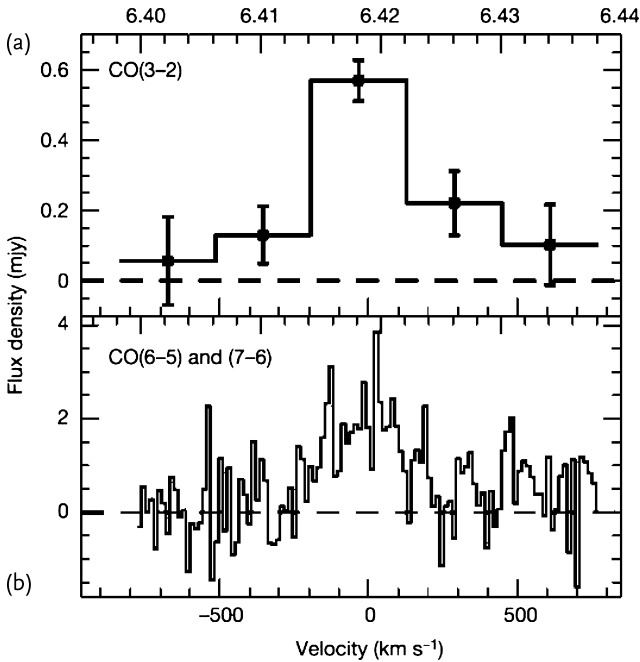
3) Astronomers refer to all elements heavier than H and He as heavy elements. They are also referred to as “metals”. This usage is different from definitions used in physics or chemistry.



**Figure 1.1** ISO LWS spectra of six infrared bright galaxies showing that external galaxies have the same atomic and molecular spectra as in the terrestrial laboratory. Emission lines due to ions of C, O, and N can be seen in the

spectrum. Absorption features due to simple molecules such as OH, CH, and H<sub>2</sub>O can also be seen. All spectra have been shifted in wavelength to rest wavelengths. Figure adapted from [13].

We can derive the relative abundances of chemical elements from the strengths of atomic lines in the photospheric spectra of stars by making use of atomic parameters from laboratory measurements and models of stellar atmospheres [14]. Assuming hydrostatic and thermodynamic equilibrium and using the equations of radiation transfer, the observed fluxes of atomic lines can be translated into column densities, from which the relative abundances are obtained. The most abundant element is H (71% by mass), followed by He (27%), O (1%), C (0.3%), and N (0.1%).



**Figure 1.2** The redshifted CO rotational transitions  $J = 4-3$  and  $J = 5-4$  from the quasar J1148+5251 at the redshift of 6.42, showing that molecular synthesis was already happening over 10 billion years ago. (a) The

spectrum for CO  $J = 3-2$  line was obtained at the Very Large Array (VLA) and (b) is an average of the CO  $J = 6-5$  and  $J = 7-6$  line obtained at Plateau de Bure Interferometer (PdBI). Figure adapted from [11].

The derived chemical abundances (primarily from solar observations) are called cosmic abundances.<sup>4</sup> These values are different from terrestrial chemical abundances as the Earth's atmosphere has been unable to keep lighter elements within the grasp of the Earth's gravity. The observed cosmic abundances of chemical elements are generally consistent with present models of primordial (Big Bang) and stellar nucleosynthesis.

In the interstellar medium (ISM), atomic nuclei are not only in atomic or ionic forms, but can also be part of molecules and solids. The molecular abundances relative to molecular hydrogen ( $H_2$ ) can be derived from spectroscopic observations of the rotational or vibrational lines (Chapter 3). The observed fluxes of the lines are analyzed with excitation models based on our knowledge of the temperature and density of the region, together with solutions to the equation of transfer. The abundances of solids can also be derived from the strengths of vibrational bands, but the results are less accurate than those of molecular abundances.

Given the availability of the elements, it is therefore no surprise that the four most common elements in the Universe (H, O, C, N) comprise 99% of the mass

4) Strictly speaking, these are solar abundances, which can be different from the elemental abundances determined from meteorites or from values derived in the interstellar medium.

of living matter. Because of its chemical inertness, He is not an essential element in the chemistry of life. Among molecules, water ( $\text{H}_2\text{O}$ ) is the most abundant in living organisms, often accounting for the majority of the mass. Living organisms also contain highly complex molecules, in particular, polymers such as proteins, carbohydrates, and nucleic acids. These polymers are built from monomers of about three dozen or so of amino acids, sugars, purines, and pyrimidines. These biomolecules in turn are probably synthesized from simpler molecules such as  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{NH}_3$ .

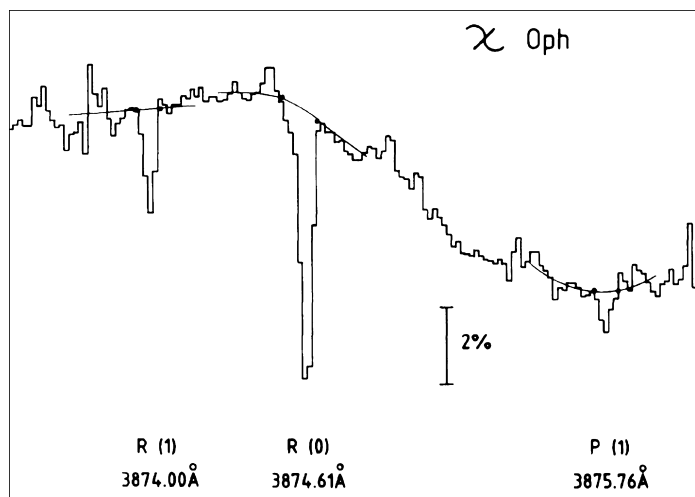
The Universe consists of not just atoms and ions, but also complex molecules and solids. At this time, we do not know of the upper limits for the complexity of these compounds in the Universe. We do know that more than 160 molecules and a variety of complex solids are made naturally by stars and interstellar clouds, and they are spread over the entire Galaxy.

## 1.2

### Extraterrestrial Organics

While it has been demonstrated that biomolecules can be artificially produced in the laboratory from inorganic matter, the question remains as to whether this process can occur naturally. Although carbon is the fourth most abundant element in the Universe, the possibility of the widespread presence of organic matter in space was not seriously contemplated at first because space density was thought to be too low for the synthesis of complex molecules. The first evidence for the existence of molecules in space can be traced to 1937, when Theodore Dunham and Walter Sydney Adams found that the spectra of early-type stars obtained at Mount Wilson Observatory contained a number of unidentified absorption lines in addition to known atomic lines [15]. One of the lines at 430.03 nm was identified by Pol Swings and Leon Rosenfeld [16] as due to the  $A^2\Delta - X^2\Pi$  band of CH molecule by simply comparing the astronomical spectra to the spectra of CH in a flame of an ordinary Bunsen burner. In 1940, lines from the other excited electronic states of  $B^2\Sigma^-$  and  $C^2\Sigma^+$  to the ground  $X^2\Pi$  at 388.9 and 314.5 nm were measured in the laboratory [17]. These lines of CH as well as the  $B^2\Sigma^+ - X^2\Sigma^+$  transition of CN all have interstellar counterparts in the spectra of Dunham and Adams. Figure 1.3 is a modern spectrum showing the  $R(1)$ ,  $R(0)$ , and  $P(1)$  lines of CN in absorption against the stellar continuum background. Another unidentified interstellar line at 423.26 nm was identified as the  $A^1\Pi - X^1\Sigma^+$  transition of  $\text{CH}^+$  [18].

After these early discoveries, it took another 26 years before the next molecule, OH, was discovered by radio spectroscopy. The  $\lambda$  18 cm  $A$ -doublet transition of OH was observed in absorption against a background radio source in 1963 [20]. This was followed by the detection of the  $\lambda$  1.3 cm inversion transition of ammonia ( $\text{NH}_3$ ) in 1968 [21], the  $\lambda$  1.4 cm  $5_{23}-6_{16}$  maser rotational transition of water ( $\text{H}_2\text{O}$ ) in 1969 [22], and the  $\lambda$  6.2 cm  $1_{10}-1_{11}$  of formaldehyde ( $\text{H}_2\text{CO}$ ) in 1969 [23]. The development of millimeter-wave receivers led to the detection of  $J = 1-0$  rotational transitions of CO, HCN, and  $\text{HC}_3\text{N}$  in 1970.



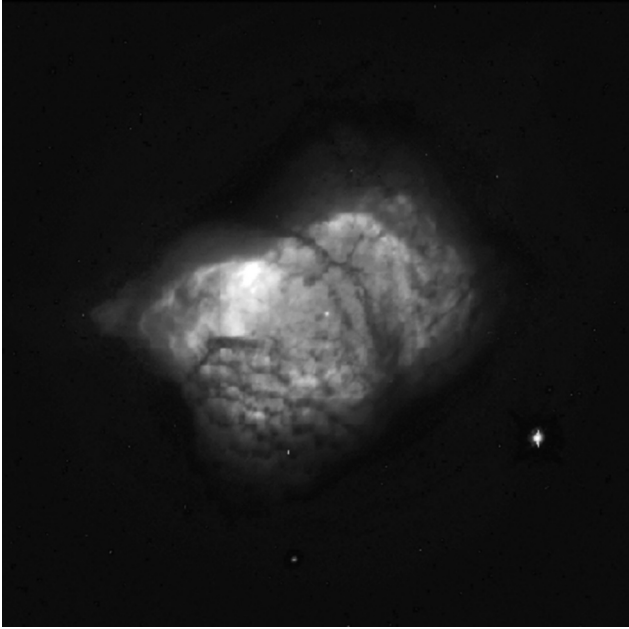
**Figure 1.3** Interstellar CN lines appearing in absorption against the stellar continuum of the star  $\chi$  Oph. These electronic transitions are the first indication of the existence of molecules in the diffuse interstellar medium. Figure adapted from [19].

The explosion in the number of detections of gas-phase molecules in the interstellar medium led to the recognition of astrochemistry as a new scientific 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 is synthesized by nuclear reactions in the stellar core, dredged up to the surface, and released from the atmosphere [24].

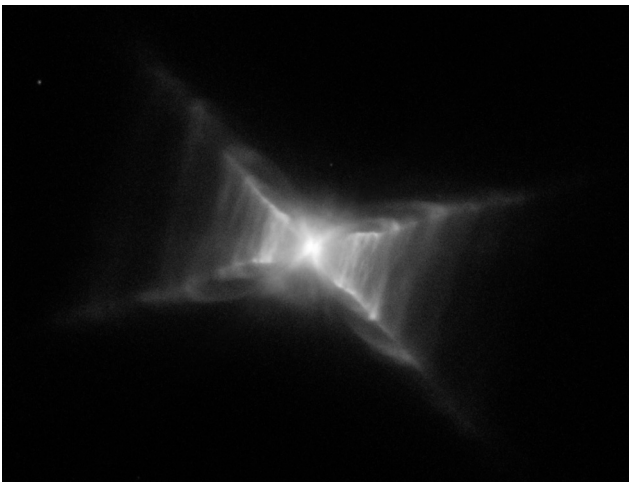
While the millimeter-wave technique is capable of detecting molecules consisting of more than a dozen atoms, the high degree of complexity of interstellar organics was not appreciated until the development of astronomical infrared spectroscopy. A family of strong infrared emission bands at 3.3, 6.2, 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 [25] (Figure 1.4) and reflection nebula HD 44179 [26] (Figure 1.5). Since the initial discovery, these features are now widely observed in HII regions, reflection nebulae, planetary nebulae, proto-planetary nebulae, and the diffuse ISM of our own and other galaxies.

The widths of the features are much broader than molecular linewidths broadened by Doppler effects or turbulence and are therefore designated as emission bands. The energy emitted in these bands can be a significant fraction of the total infrared continuum energy output of galaxies, and the identification of the carriers of these features is therefore important for understanding 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 the stretching and bending modes of various CH



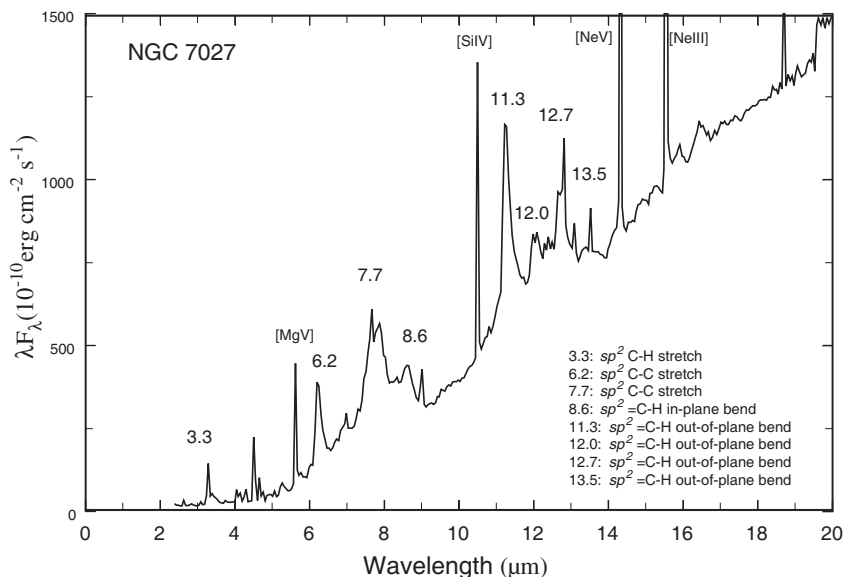
**Figure 1.4** Color composite image of HST WFPC 2 observations of the young planetary nebula NGC 7027, the first astronomical object to be found to have AIB emission. For a color version of this figure, please see the Color Plates at the beginning of the book.



**Figure 1.5** HST WFPC2 false color image of HD 44179, the Red Rectangle. The Red Rectangle is the stellar object with the strongest AIB emissions. Credit: ESA, NASA, H. Van

Winckel, and M. Cohen. For a color version of this figure, please see the Color Plates at the beginning of the book.





**Figure 1.6** The ISO SWS spectrum of the planetary nebula NGC 7027. The narrow features are atomic emission lines due to fine-structure transitions of heavy elements (e.g.,

the [N III] line at 15.6  $\mu\text{m}$ ). The broad features marked by wavelengths are due to stretching and bending modes of aromatic compounds. Their identifications are listed in the legend.

and CC bonds in aromatic hydrocarbons [27]. For this reason, these strong infrared emission features are now known as the aromatic infrared bands (AIB) (Figure 1.6).

In this book, we summarize the evidence for the presence of organic matter in the Universe. The organics include molecules in the gaseous form and large, bulk solids consisting of hundreds or thousands of atoms. Methods of detecting organic compounds range from remote spectroscopic observations with telescopes to laboratory analysis of samples collected from space or on Earth. With the technique of infrared and millimeter-wave spectroscopy, specific molecules can be identified through their vibrational and rotational transitions and examples of groups of organic molecules are discussed in Chapter 3. We discuss the diverse environments where organic compounds are found, including clouds in the diffuse ISM (Chapter 4), distant galaxies (Chapter 5), the ejecta of stars (Chapter 6), and various objects in the Solar System (Chapter 7). Unexplained astronomical phenomena that may be due to organic compounds are discussed in Chapter 8. The chemical structures and possible laboratory analogs of extraterrestrial organics are presented in Chapter 9. Near the end of the book, some speculations on the origin of these compounds and the possible links between stars and the Solar System are offered.

