

## Prebiotic Astrochemistry and the Formation of Molecules of Astrobiological Interest in Interstellar Clouds and Protostellar Disks

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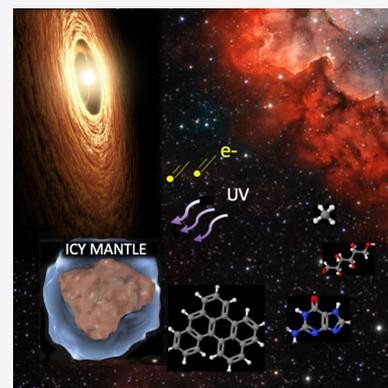
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**ABSTRACT:** Despite the generally hostile nature of the environments involved, chemistry does occur in space. Molecules are seen in environments that span a wide range of physical and chemical conditions and that clearly were created by a multitude of chemical processes, many of which differ substantially from those associated with traditional equilibrium chemistry. The wide range of environmental conditions and processes involved with chemistry in space yields complex populations of materials, and because the elements H, C, O, and N are among the most abundant in the universe, many of these are organic in nature, including some of direct astrobiological interest. Much of this chemistry occurs in “dense” interstellar clouds and protostellar disks surrounding forming stars because these environments have higher relative densities and more benign radiation fields than in stellar ejectae or the diffuse interstellar medium. Because these are the environments in which new planetary systems form, some of the chemical species made in these environments are expected to be delivered to the surfaces of planets where they can potentially play key roles in the origin of life. Because these chemical processes are universal and should occur in these environments wherever they are found, this implies that some of the starting materials for life are likely to be widely distributed throughout the universe.



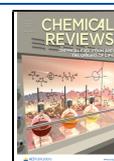
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## 1. INTRODUCTION

### 1.1. Historical Perspective

Prior to the middle of the last century, it was generally thought that the environments found in space were hostile to the formation and survival of molecules and that chemical reactions could not proceed efficiently. It was thus commonly assumed that most of the matter in space would exist as either atoms or amorphous dust grains rather than as individual molecules. Furthermore, densities in most astrophysical environments are low, and even when densities are higher, the primary elements available for chemistry are largely restricted to H and He (Figure 1), which would appear to significantly limit the complexity of possible chemistry. However, the development of new astronomical techniques, particularly the advent of telescopes, detectors, and spectrometers that operate in the radio, infrared (IR), and ultraviolet (UV)/visible portions of the electromagnetic spectrum, ultimately demonstrated that this was not true. A nice review of the early discoveries of interstellar molecules can be found in ref 1. Certainly, chemistry in space is often limited because of low densities and extreme temperatures (both high and low), but this is compensated for, in part, by the vast amounts of material and time available, and we now know that much of the material in circumstellar and interstellar environments is in molecular form.<sup>2–5</sup>

### 1.2. Environments

Matter in space can be thought of as being part of an immense cycle that includes the formation of stars in interstellar dense molecular clouds, the ejection of material from these same stars as they age, and the mixing of these materials back into new clouds (Figure 2). During this cycling process, a small fraction of the material ends up in planetary systems and can be incorporated into habitable planets. These environments span an enormous range of conditions (density, molecular concentration, temperature, radiation field, etc.), and it is therefore not surprising that the observed populations of materials vary considerably from one environment to another.

Many stars, late in their life cycles, undergo phases in which they lose portions of their mass to space through either gradual (stellar winds) or explosive (nova and supernova) processes. Where the outflow conditions allow, these materials can form molecules and dust grains. Depending on the local C/O ratios in the ejecta, the main products can be minerals (O-rich ejecta) or carbonaceous molecules and grains (C-rich ejecta).<sup>6,7</sup> Much of these materials are subsequently destroyed or modified in the diffuse interstellar medium (ISM), an environment that subjects them to sputtering, photodestruction, destructive shock waves from supernova, etc. Most individual molecules are unable to survive in the gas phase in the diffuse ISM, with the notable exception of polycyclic aromatic hydrocarbons (PAHs) and related species. These molecules are seen in the outflows of dying stars and are sufficiently robust to resist complete photolytic destruction in the diffuse ISM. As a result, they are a dominant form of molecular carbon found in many astrophysical environments.<sup>2,8–10</sup> With the exception of PAHs, most of the material in the diffuse ISM that is not atomic exists in the form of silicate grains and solid organic materials that contain aromatic and aliphatic components.<sup>6,11–13</sup>

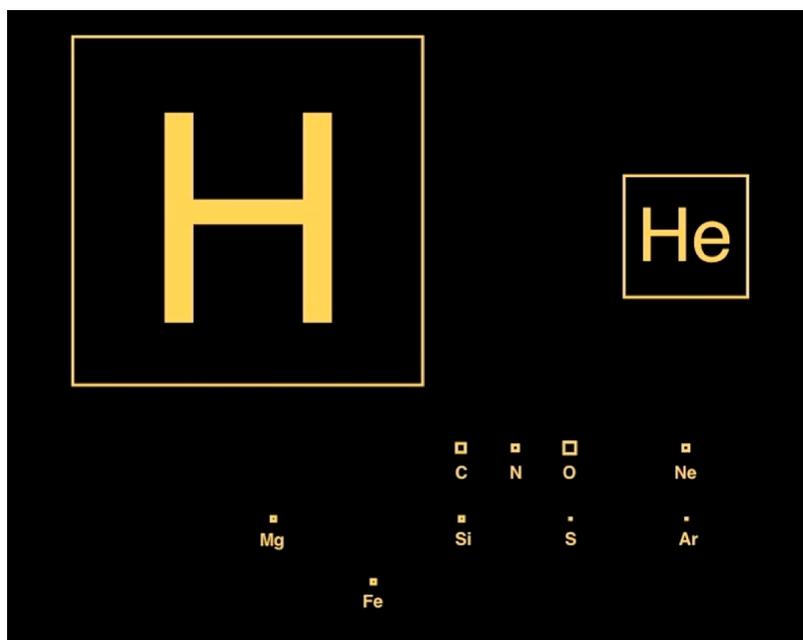
Perhaps the most compelling proof that at least some material survives the trip from stellar synthesis through the diffuse ISM is the existence of presolar grains found in meteorites. Indeed, presolar grains of different compositions (aluminum oxides, silicates, silicon carbide, graphite, etc.) have been found in meteorites, and their circumstellar origins have been demonstrated by the presence of nonsolar isotopic ratios that indicate formation processes in a variety of nucleosynthetic environments.<sup>14,15</sup>

However, from the perspective of prebiotic chemistry and astrobiology, one of the most interesting types of extraterrestrial environments is that of dense interstellar molecular clouds. These clouds contain enough material to be optically thick so that their interiors are protected from much of the stellar radiation that destroys most molecules in the diffuse ISM. The large opacities of these clouds also allow their interiors to cool to temperatures as low as 10–15 K. At these temperatures, most gas-phase species (the exceptions being H, H<sub>2</sub>, He, and Ne) will condense out onto dust grains in the form of ice mantles (Figure 3). Under these conditions, little “normal” chemistry of the sorts we are familiar with on Earth can take place, but chemical reactions occur nonetheless. For example, many atom–neutral and neutral–neutral reactions (e.g., between radical species or in species with unsaturated bonds) can also occur efficiently at low temperatures.<sup>16,17</sup> Chemistry can also occur via gas–grain reactions in which individual gas-phase atoms like H, C, N, and O collide with grains, react with resident surface species on the grains, and form new compounds.<sup>18</sup> More complex species can be formed when ionizing radiation is present. While the large optical depths of clouds screen out most stellar radiation, cosmic rays and the secondary energetic photons and electrons they create when colliding with interstellar matter produce some ionization, even in the densest clouds.<sup>19</sup> In addition, newly forming stars within dense interstellar clouds can also irradiate nearby materials. This ionizing radiation produces ions and radicals that are able to react even at low temperatures. Ions produced in the gas phase can react in an extensive chain of ion–molecule reactions that can lead to the formation of numerous gas-phase species.<sup>20,21</sup> However, the majority of the material (other than H and He) in dense clouds is frozen out in dust grain mantles, and it is ionizing radiation hitting these ices that likely produces the most complex molecular species.<sup>18,22–25</sup>

Similar chemical environments can also be found in the protostellar disks that surround newly forming stars and planetary systems.<sup>27</sup> These objects contain, by astronomical standards, high densities of material and are sufficiently optically thick to generate very low temperatures at their midplanes.<sup>28</sup> As a result, the materials in protostellar disks are expected to undergo many of the same processes considered for interstellar dense molecular clouds, albeit on shorter time scales.<sup>27,29</sup>

### 1.3. Focus of this Paper

While we will briefly discuss chemistry that occurs everywhere in the cycle described and shown in Figure 2, in this paper we will focus primarily on the chemistry that occurs in dense interstellar molecular clouds and protostellar disks, i.e., the environments in which new stars and planets form. These environments are of particular interest because: (1) they contain higher densities of materials and radiation conditions that drive richer chemistry, and (2) it is materials found in



**Figure 1.** The so-called Astronomer's Periodic Table. In this figure, the elements are shown associated with boxes whose areas are proportional to their cosmic abundances. Figure adapted with permission from ref 614. Copyright 2006 International Astronomical Union.

these environments that are ultimately incorporated into new planetary systems and delivered to the surface of planets via meteorites and dust particles (see section 2.4.5), where they may play a role in the emergence of life.

## 2. CHEMISTRY AT DIFFERENT STAGES OF THE LIFE CYCLE OF MATTER

The astrophysical environments discussed in this paper include conditions that contain temperatures ranging from 10 to  $10^6$  K and number densities ranging from 0.004 to  $10^6 n_{\text{H}} \text{ cm}^{-3}$ .<sup>30</sup> These environments are generally not physically directly accessible for study, either because they are separated from us by great distance (for example, the ejectae surrounding distant stars, the diffuse ISM, dense molecular clouds, etc.) or are separated from us in time (for example, the protosolar disk from which our Solar System formed over 4.5 billion years ago). Thus, most of what we know about the compositions of material in space, and the processes that form and modify them, are obtained by remote observations using telescopes and, in the case of objects in the Solar System, in situ spacecraft.

Our studies of distant objects are restricted to what we can learn from photons that arrive at ground-based, airborne, and spaceborne telescopes from these locations. As a result, the primary technique used for detecting and identifying chemical compounds in space is spectroscopy. Molecules in the gas phase can be identified by detecting their rotational transitions at microwave and radio wavelengths<sup>31</sup> or the rotational envelopes of their fundamental vibrational modes in the infrared.<sup>32</sup> Molecules in the solid state are generally not amenable to identification at longer wavelengths. The fundamental vibrational modes of molecules in the solid state can often still be detected in the infrared,<sup>33</sup> although spectral confusion can be a problem due to the overlapping of the modes of similar functional groups in different molecules. Finally, electronic and nuclear transitions of individual

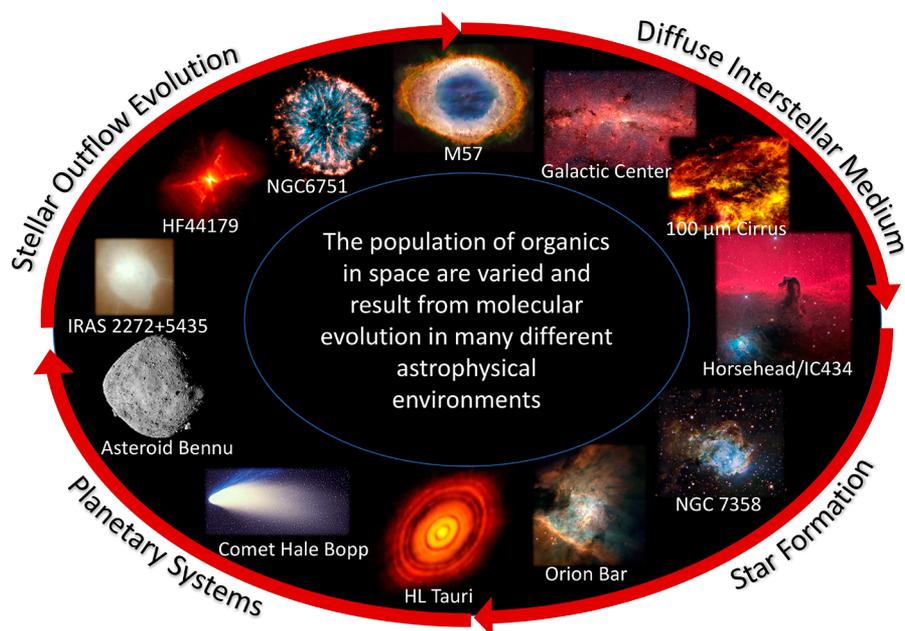
elements can also be detected at ultraviolet and higher energies.<sup>34</sup>

Depending on the nature of the astronomical environment in question, spectral features may be seen in either emission or absorption. Emission features occur when molecules “cool” after being excited by the absorption of energy from, for example, a photon or a particle collision. A good example of this is the nearly ubiquitous IR emission produced by polycyclic aromatic hydrocarbons in space after they absorb a UV photon.<sup>2</sup> Spectral features in absorption are measured when photons from a background source are absorbed by material between the source and the observer. In this case, the measured spectrum can contain features from both the source and the intervening material. Obtaining the spectrum of the intervening material then requires the observation of a suitable “standard” source that is spectrally similar to the object being observed, but that does not have intervening material along its line of sight. This is the approach, for example, for measuring the absorption features due to dust in the diffuse ISM that lies between Earth and the center of our Galaxy.<sup>11</sup>

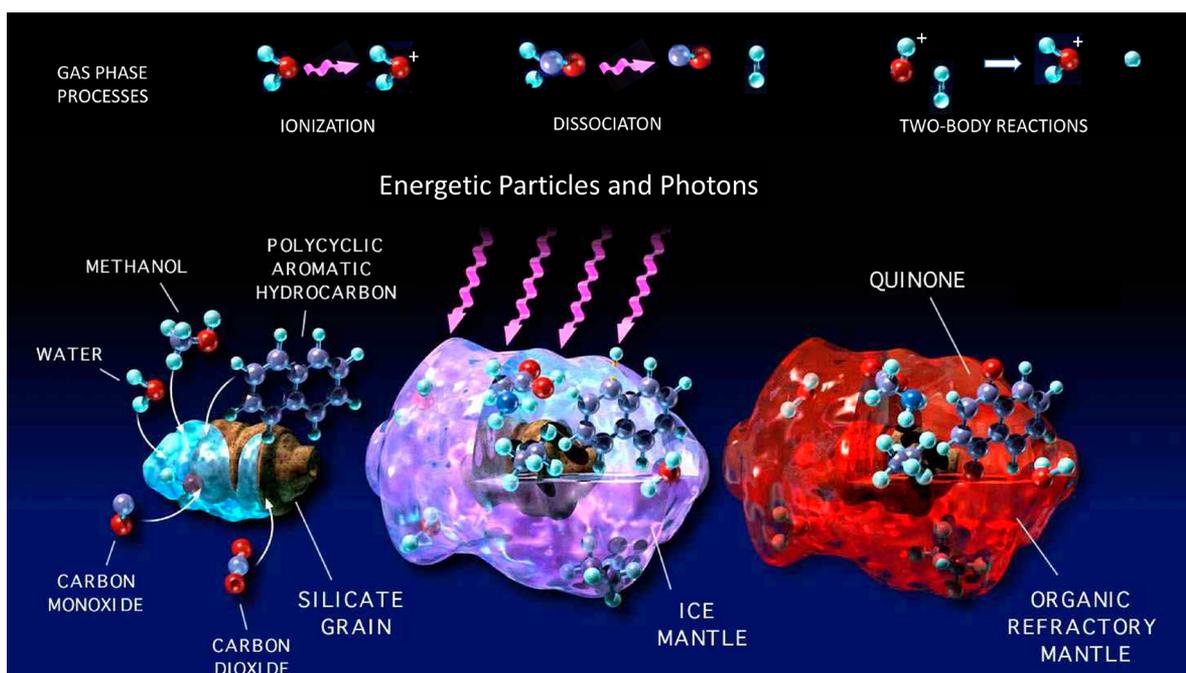
Whether spectral features are being observed in emission or absorption, it is worth keeping in mind that telescopic measurements are “line-of-sight” measurements. This means that any spectral features being observed could be associated with materials in the object being studied and all the materials along the same line of sight in front of, or behind, the object. As a result, it is often difficult to establish what the “local” concentrations of detected molecules are.

### 2.1. Stellar Ejectae

Stars play a key role in the injection of new materials into the interstellar medium that are then available to participate in chemistry. The nature of the ejected materials depends significantly on the nature of the original star. At the end of their normal main sequence lifetimes, stars having intermediate masses like our Sun usually eject material into space in a relatively gentle process that forms a planetary nebula. In contrast, more massive stars follow evolutionary processes that



**Figure 2.** Materials in space are cycled through a wide range of physical environments. As a consequence, the chemical processes that occur and their products vary significantly from environment to environment.

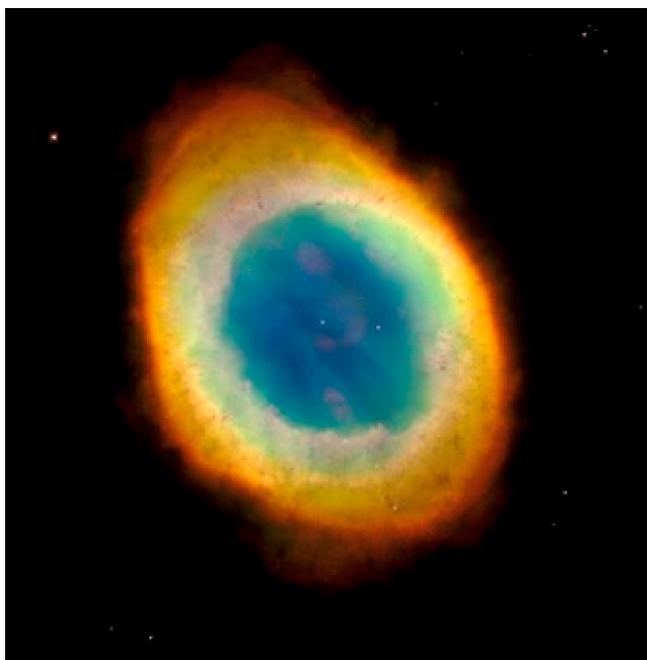


**Figure 3.** Chemical reactions in space can occur in the gas phase (top), as part of gas–grain interactions (lower left), through exposure to ionizing radiation (energetic photons and/or particles, lower middle), and via thermal cycling (lower right). These different processes occur in different space environments and yield different populations of products. Figure adapted with permission from ref 26. Copyright 1999 Springer Nature.

lead to novae and supernovae, which eject material into space in a far more explosive manner. These different types of ejecta differ in both composition and potential for chemistry within the outflow.

**2.1.1. Planetary Nebula.** Stars like the Sun spend many billions of years stably residing on the main sequence where the principle nucleosynthesis that is occurring is the fusion of H into He in the star's core. However, as the core of the star becomes depleted in hydrogen, the star enters a red giant phase in which the core contracts and begins to fuse He while

the outer envelope of the star expands and is gradually ejected into space (Figure 4). This phase in an intermediate star's evolution is short, typically lasting only a few tens of thousands of years. Once all of the red giant's atmosphere has been ejected, the outflowing material is exposed to harsh UV radiation from the hot luminous core that is exposed. This radiation ionizes much of the ejected material and produces the planetary nebula (note that this name is a misnomer as the nebula has nothing to do with planets).



**Figure 4.** The famous Ring Nebula is a planetary nebula produced by the ejection of material from the envelope of a dying star that is reaching the end of its normal nucleosynthetic lifetime on the main sequence. Image PRC99-01, Space Telescope Science Institute, Hubble Heritage Team, AURA/STScI/NASA.

Despite the radiation from the central core of the star, materials in the outflow can undergo chemical reactions to form new molecules. The nature of the materials formed depend critically on the O/C ratio of the expelled material.<sup>6,7</sup> Initially, one of the main reactions is the combination of C and O to form the very stable carbon monoxide molecule. The subsequent chemistry depends critically on which element, C or O, is depleted first. If  $C/O < 1$ , then there is excess O available to react with Si to form silicates. If  $C/O > 1$ , then there is excess C to form organic materials as well as carbides such as SiC and TiC.

It is known that PAH molecules form in C-rich stellar winds surrounding aging stars,<sup>2</sup> but the exact mechanisms for their formation are not known, and this has been a hot area of research in recent years. There are many facets to this problem including whether their formation is dominated by ion–molecule reactions, neutral radical–radical reactions, or something in between such as neutral radical–molecule reactions. All these processes have been studied both experimentally and computationally.<sup>17,35</sup> There is also the question as to whether PAHs form strictly from the continued addition of  $C_2$ ,  $C_3$ , or  $C_4$  groups (i.e., small organic molecules containing either 2, 3, or 4 carbon atoms) with concomitant ring closures,<sup>36–39</sup> or whether the larger PAHs end up forming by the addition of two smaller PAH molecules wherein their last ring has not yet closed. A variation on this latter process can occur when two smaller PAH molecules form a cluster and are then chemically activated by one or more UV photons creating radical cations, neutral radicals, or some combination of these, thus enabling the two smaller PAH molecules to react with one another.<sup>40–42</sup> One aspect that needs to be considered, however, is that in association mechanisms via either ion–molecule or neutral radical–radical reactions, there generally will not be a third body to eliminate excess energy, hence for

small molecules, the new molecule will need to either be stabilized by emission of a photon or more likely ejection of a small fragment such as H or CH.<sup>43</sup> As the PAH or complex organic molecule becomes larger, the excess energy can be rapidly converted into vibrational energy via intramolecular vibrational relaxation (IVR), giving the molecule sufficient time to emit an IR photon before it falls apart. In all likelihood, all of the mechanisms discussed here are probably in operation with the dominant mechanism(s) determined by the specific conditions present in a particular astrophysical environment.

Emission features seen in the IR spectra of carbon-rich planetary nebulae were for many years referred to as the unidentified infrared bands (UIBs). However, in the late 1980s, the PAH hypothesis stated that the UIBs were due to cascade IR emission spectra originating from PAH molecules and their derivatives, including cations and neutral radicals.<sup>2,44,45</sup> The PAH hypothesis is now generally accepted by astronomers to be the source of the UIBs, and thus these bands are now generally referred to as the aromatic infrared bands (AIBs). Further, the definition of PAH-related molecules has expanded to include partially hydrogenated PAH molecules ( $H_n$ -PAHs), PAH molecules with one or more aliphatic chains attached, and nitrogenated PAH molecules, usually called polycyclic aromatic nitrogen heterocycles (PANHs), among other possible derivatives.<sup>46,47</sup>

The AIBs observed in different astrophysical objects exhibit small changes relative to one another, including variations in their relative intensities, band profiles, and slight shifts in band positions, which are clues about the chemical and physical conditions present.<sup>46–48</sup> For example, the presence of a small shift in the peak position of the  $6.2 \mu\text{m}$  band has been suggested as an indicator of the presence of some PANH molecules in the emitting PAH population.<sup>46,49,50</sup> To allow astronomers to determine the most likely composition of the various PAH and PAH-related molecules, the NASA Ames PAH database (hereafter referred to as “PAHdb”) has been developed and successfully employed.<sup>51–53</sup> PAHdb consists of experimental (matrix isolation) IR spectra as well as computed IR spectra using density functional theory (DFT) methods, and relatively small one-particle basis sets, under the double harmonic approximation. The overwhelming majority of the data derives from DFT calculations. The PAHdb incorporates the aforementioned data into a cascade emission model in order to model the type of spectra that astronomers actually observe. However, the lack of anharmonic information about the vibrational frequencies significantly limits the usefulness of this approach.

Recently, Mackie et al.<sup>54</sup> have developed an approach to compute a fully anharmonic cascade IR emission spectrum of PAH molecules which should allow for a much more accurate representation of the spectra that astronomers actually observe and should allow for a much better interpretation of the observations that are expected to come from the James Webb Space Telescope (JWST). This approach is novel and has been shown to be reasonably accurate when compared to high-resolution absorption spectra,<sup>54,55</sup> although improvements can be made, for example, by using better electronic structure methods and basis sets, and including 3:1 resonances in the polyads. However, even for the levels of theory being used, the calculations are somewhat expensive, and at least for now they cannot be performed on PAH molecules with more than about 25–30 C atoms. Because it is generally believed that the PAH molecules present in the diffuse ISM consists of around 50–

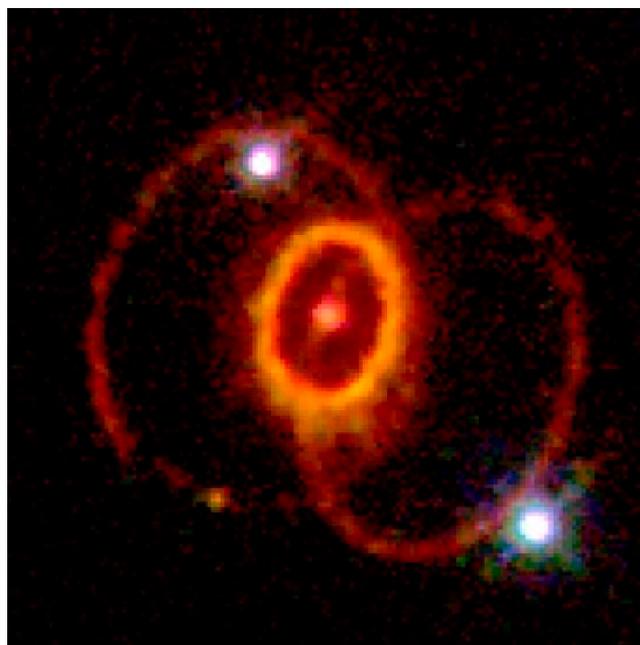
100 C atoms,<sup>56</sup> the approach developed by Mackie et al.<sup>54</sup> will need further development so that it can be applied to larger PAH molecules and their derivatives.

An important component of PAH-related molecules is those whose IR spectra contain aliphatic C–H stretching modes near 3.4  $\mu\text{m}$  in addition to the typical aromatic C–H stretching modes near 3.3  $\mu\text{m}$ .<sup>57,58</sup> These aliphatic features can result from two possible types of modification to the parent PAH molecule, either a partial hydrogenation of an aromatic ring<sup>2,48,59</sup> or by the attachment of a small aliphatic chain to an aromatic ring.<sup>57,58,60</sup> Both of these can result from the photoprocessing of a parent PAH molecule in C-rich planetary nebulae, and because the UV radiation fields may be intense, any attached aliphatic chain would likely be small because it would otherwise be ultimately destroyed.

One approach astronomers have used to determine the degree of hydrogenation of PAH molecules (or the degree to which aliphatic chains have been incorporated) is to compare the ratio of the integrated intensities of the 3.4 and 3.3  $\mu\text{m}$  bands.<sup>2,48,58,61</sup> By plotting the ratio of the integrated (3.4/3.3  $\mu\text{m}$ ) band intensities vs the ratio of the number of aliphatic to aromatic C–H bonds for a set of partially hydrogenated PAHs and/or PAHs with an aliphatic chain, one can fit a line to the data and determine the slope of the line. This slope, referred to as  $\alpha$ , can be thought of as the ratio of aliphatic versus aromatic C–H bond oscillator strength per bond. For gas-phase experimental data, both high-resolution and low-resolution,  $\alpha$  was recently found to be 1.57 for PAH molecules spanning a large range of hydrogenation,<sup>58</sup> which is in reasonable agreement with the value determined from theoretical calculations, i.e., 1.69,<sup>61</sup> although the sets of molecules used in these two studies are somewhat different. Note that the correlation between the aliphatic/aromatic intensity ratios and the ratio of the number of aliphatic/aromatic C–H bonds, or, in other words, the fit to a line, is very good (see Figure 7 in ref 58). These values are somewhat lower than that determined from matrix isolation experiments, i.e., 2.76,<sup>48</sup> which indicates that the IR modes of aromatic C–H stretching vibrations are suppressed more due to the matrix than the IR intensity of aliphatic C–H stretches.<sup>62</sup>

Thus, measuring the ratio of the 3.4–3.3  $\mu\text{m}$  band intensity in astronomical observations yields significant information about the nature of the organic material in an astrophysical objects, including C-rich planetary nebulae, and a very good early example of this is given by Sandford et al.,<sup>11</sup> where they examined not only the ratio of aliphatic to aromatic C–H bonds but also the ratio of  $-\text{CH}_2-$  to  $-\text{CH}_3$  groups in the aliphatic material for various astrophysical targets. There is much more chemical and physical information to be gleaned from details of the AIBs. For example, recent work at longer wavelengths has placed additional constraints on the nature of partially hydrogenated PAHs ( $\text{H}_n$ -PAHs) in stars just entering their protoplanetary nebular phases.<sup>47</sup> Thus, why the AIBs differ in different sources still has much to tell us and this will be vitally important once the *JWST* era begins. Hence, this is why studies aimed at improving the spectroscopic data in the PAHdb remains an active area of research and will remain so for the foreseeable future.

**2.1.2. Novae and Supernovae.** Novae and supernovae represent a small fraction of the universe's stars that eject materials into space via powerful and highly luminous explosive events. These explosive events are triggered by a variety of conditions depending on the star(s) involved.



**Figure 5.** Supernova SN 1987A was a type-II supernova that was observed in 1987. It is located in the Large Magellanic Cloud (LMC), a dwarf satellite of the Milky Way, and is the closest observed supernova since the observation of Kepler's Supernova in 1604. Image from the Hubble Telescope, Space Telescope Science Institute.

Because of the high energies involved in these explosions, they are generally not ideal environments for the formation of new chemical compounds in the ejected material. For example, the ejecta from the supernova SN 1987A in the Large Magellanic Cloud (Figure 5) has been monitored since the supernova exploded in 1987, and relatively little has been seen in terms of molecular formation in the outflow materials, and what has been observed is largely restricted to simple molecules like CO.<sup>63</sup> Indeed, the ejection of materials from these objects may well be responsible for the net destruction of molecular materials as the powerful shock waves they produce sweep up and process material in the surrounding ISM.<sup>64</sup> For this reason, we will not devote much consideration to chemical processes in these objects.

However, it should be noted that while these objects do not themselves seem to play a major role in the production of organic molecular complexity, they still play a major role in overall astrochemistry because they are key sites for nucleosynthesis and produce many of the heavier elements of the periodic table beyond C, N, and O that are important for organic chemistry (for example, S and P).<sup>65</sup> Thus, while these objects are not the sites of complex chemistry, they provide the elemental constituents that can participate in such chemistry in other environments.

## 2.2. The Diffuse ISM

**2.2.1. Conditions in the Diffuse ISM.** It has been known since the 1930s that the “empty space” between the stars is not truly empty but contains small amounts of diffuse material.<sup>66,67</sup> The initial evidence came from the observation of interstellar “reddening” produced as visible light from distant objects travels long distances through the interstellar medium.<sup>68,69</sup> The subsequent use of multiwavelength spectroscopy has demonstrated that the diffuse ISM contains atomic and molecular gas, as well as dust grains containing amorphous silicates, and

aromatic and aliphatic hydrocarbons. In the sections below, we concentrate on the organic fraction of these materials.

The diffuse ISM is characterized by low column densities, typically  $\sim 10^{20}$  H-nuclei  $\text{cm}^{-2}$  or less, with regions that are subject to high UV fluxes and others that experience shocks from supernova explosions.<sup>56,70,71</sup> The diffuse ISM is mainly composed of  $\text{H}_2/\text{H}$  with less abundant heavier elements, largely in atomic form. Diffuse clouds are sometimes further broken down into diffuse atomic clouds, diffuse molecular clouds, or translucent clouds, depending on their column densities or  $\text{H}_2/\text{H}$  and CO abundance ratios. We will mainly focus on diffuse molecular clouds where the abundance ratio of electrons to H atoms is  $\sim 10^{-4}$ , and similarly the abundance of cations is elevated relative to dense molecular clouds (see Figure 1 of ref 71). The chemistry of the diffuse ISM is mainly driven by the intense UV photon fields and thus is largely associated with the destruction and/or ionization of small molecules. Hence the main molecular components of diffuse molecular clouds are large molecules and grains which can withstand the high radiation fields, although smaller organic molecules have been identified in the diffuse medium.<sup>72</sup> It is well established that polycyclic aromatic hydrocarbons (PAHs) and their derivatives, and aliphatic components, are the main molecular species present in diffuse molecular clouds because they are able to survive the harsh UV radiation fields,<sup>56</sup> as discussed in the following section.

**2.2.2. PAHs.** Infrared images taken of the diffuse ISM show the presence of diffuse clouds (Figure 6) that are referred to as



**Figure 6.** A composite image of the South Celestial Pole made using data taken by NASA's Infrared Astronomical Satellite (IRAS)<sup>76</sup> at wavelengths of 12, 60, and 100  $\mu\text{m}$ . The emission in this field is dominated by an "infrared cirrus" resulting from the heating of dust and molecules in the diffuse ISM by surrounding stellar radiation. Image from the Infrared Processing and Analysis Center (IPAC).

the Infrared Cirrus. Infrared spectra taken from these clouds show many of the same family of spectral features (AIBs) associated with the presence of PAHs and related molecular species as described in section 2.1.1, including the aromatic C–H stretching band near 3.3  $\mu\text{m}$ .<sup>73–75</sup> This is not entirely surprising because PAHs are one of the few classes of organics that are robust enough to survive the high radiation fields

found in these environments, and one would expect the PAHs being injected into the diffuse ISM from aging stars with strong UV radiation fields to survive.

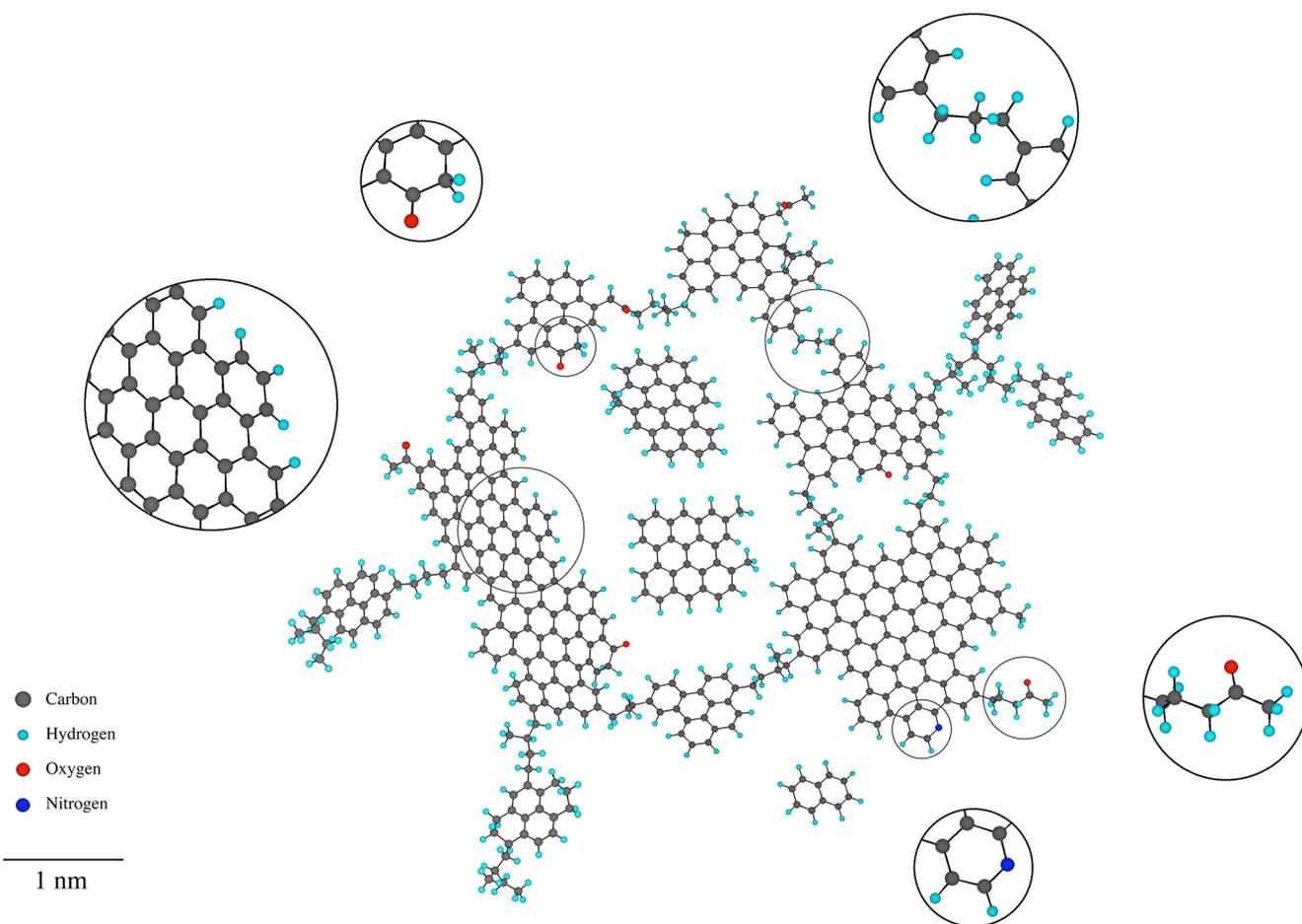
**2.2.3. Aliphatics.** Unlike PAHs, which were identified in the diffuse ISM through the IR emission features produced when these molecules are excited by interstellar UV photons, the presence of aliphatic hydrocarbons in the diffuse ISM was established by the detection of the aliphatic C–H stretching bands seen in absorption in the spectra of distant stars.<sup>11,13,77</sup>

The features are seen near 2955, 2925, and 2870  $\text{cm}^{-1}$  (3.38, 3.42, and 3.48  $\mu\text{m}$ ). The first two bands are interpreted as being due to the asymmetric C–H stretching vibrations of  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups, respectively, while the third feature is thought to be a blend of the symmetric C–H stretching mode of the same groups.<sup>11</sup> The observation that the two symmetric features do not show up as separate, distinct features suggests that the aliphatics in question are associated with some form of electronegative group. The relative intensities of the bands suggest that the material has an overall  $-\text{CH}_3/-\text{CH}_2-$  ratio of  $\sim 2.5$ . Indeed, a reasonable fit to the features is provided by the IR spectrum of *n*-butanol. However, the materials responsible for these features are extremely unlikely to be individual, simple aliphatic molecules, as these would be quickly destroyed by UV radiation. Instead, it is thought that the aliphatic groups in question are probably incorporated into dust grains, where they exist as part of some form of macromolecular material that consists of aromatic units interlinked by aliphatic and other chains<sup>11,13,78</sup> (Figure 7).

Some constraints can be placed on the distribution of this material within the diffuse ISM by comparing the observed strengths of the bands along lines of sight to different stars throughout the Galaxy. The strengths of the aliphatic features correlate well with the strength of the silicate Si–O stretching bands seen near 10  $\mu\text{m}$  along the same lines of sight but do not correlate precisely with the extinction of visible light. This suggests that the aliphatics and silicates could reside on the same grains (although this is not required), and that grains responsible for these IR features are not identical to the population of materials responsible for much of the observed visual extinction. It also suggests that the distribution of this carbonaceous component of the diffuse ISM is not uniform throughout the Galaxy but instead may increase in density toward the center of the Galaxy. Possible models of the distribution of such aliphatic materials suggest that the inner portion of the Milky Way has a carrier density that is 5–35 times higher than in the local ISM. Depending on the model used, the density of aliphatic material in the local ISM is about 1–2  $-\text{CH}_3$  groups  $\text{m}^{-3}$  and about 2–5  $-\text{CH}_2-$  groups  $\text{m}^{-3}$ .<sup>79</sup>

## 2.3. Dense Interstellar Molecular Clouds

**2.3.1. Conditions in Dense Interstellar Molecular Clouds.** Interstellar dense molecular clouds are complex structures, and conditions within them vary considerably with location (Figure 8). While molecular clouds account for only a few percent of the volume of the Galaxy, interstellar matter accounts for about 10–15% of the mass of the Milky Way's galactic disk, where it is largely concentrated near the galactic plane and along its spiral arms.<sup>80</sup> The vast majority of the mass of these clouds consists of gas-phase H and  $\text{H}_2$  (see Figure 1). The mean densities of "dense" clouds are typically  $\sim 100$ – $300$   $\text{H}_2$   $\text{cm}^{-3}$ , but these clouds are very inhomogeneous and contain regions of higher density called clumps or cores with



**Figure 7.** Because simple, gas-phase aliphatic hydrocarbons would be quickly destroyed by radiation in the diffuse ISM, it is thought that the observed aliphatic IR features seen in absorption toward distant stars are due to aliphatic moieties associated with more complex materials in dust grains. Figure adapted with permission from ref 13. Copyright 2002 International Astronomical Society.



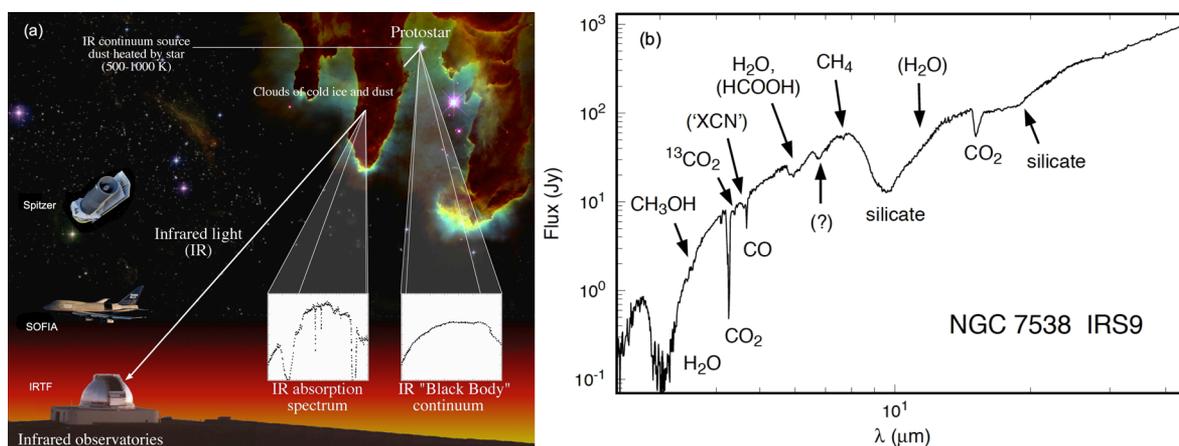
**Figure 8.** The Keyhole Nebula. This is a small dark cloud of cold gas molecules, ice, and dust within the much larger Eta Carinae Nebula complex in the constellation Carina. Dense cloud environments support a rich mix of gas-phase, gas-grain, and irradiation chemistry and are the sites of star and planet formation. (Image PRC00-06, Space Telescope Science Institute, Hubble Heritage Team, AURA/STScI/NASA.)

densities up to  $\sim 10^4$   $\text{H}_2$   $\text{cm}^{-3}$  (which is still a better vacuum than that found in most terrestrial vacuum systems).<sup>81</sup> These cores typically have temperatures of 10–20 K.<sup>82,83</sup> The surfaces of these clouds are exposed to significant radiation

from the surrounding diffuse ISM, but as one moves deeper into quiescent parts of these clouds, this external radiation is effectively screened out. However, materials in the interior of dense clouds are still exposed to some ionizing radiation from cosmic rays as well as UV photons and secondary electrons created by cosmic ray interactions.<sup>84–86</sup>

Because of the low temperatures in these clouds, most volatile materials are condensed into icy grain mantles that surround dust particles within the clouds. These materials can be probed by measuring the IR spectra of background or embedded stars or protostars. Foreground materials in the cloud produce absorption features superimposed on the largely blackbody IR radiation produced by the background sources (Figure 9a). These spectra typically show absorption features characteristic of ices made up of relatively simple molecules (Figure 9b). The most abundant ice-phase molecule is  $\text{H}_2\text{O}$ , but a host of other simple species are seen, including  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$ .<sup>3,4,12,33,87–89</sup>

The densest part of these clouds can become unstable and collapse to form new stars and planetary systems.<sup>90</sup> These newly formed stars warm the surrounding cloud and can ultimately lead to the breakup of the cloud.<sup>91</sup> The wide range of temperatures and pressures allows chemistry to occur via a number of processes, including gas-phase reactions involving ions and neutrals, gas-grain surface reactions involving atoms and small molecules, and solid-state grain mantle reactions



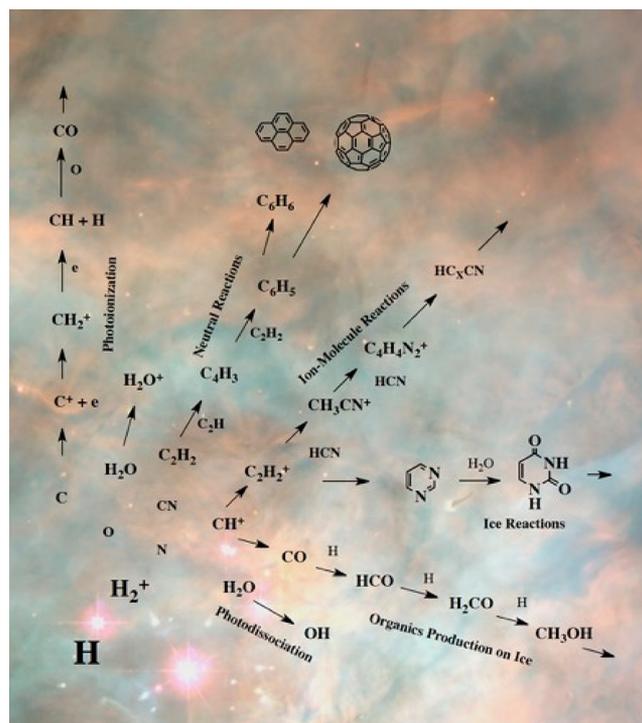
**Figure 9.** (a) The materials in dense clouds can be probed by measuring the IR absorption features superimposed on the spectra of embedded and background IR sources. (b) The absorption bands seen in dense cloud spectra are dominated by silicate dust and ice mantles made of a mixture of simple, volatile molecules. (b) Reproduced with permission from ref 87. Copyright 1996 EDP Sciences.

driven by ionizing radiation. These various processes are described in more detail in the following sections.

**2.3.2. Gas-Phase Chemistry.** In dense molecular clouds, the molecular number density, mostly  $\text{H}_2$ , is typically  $10^4$ – $10^6$   $\text{cm}^{-3}$  at their cores. The temperature is typically low, between 10 and 100 K, but can be higher in hot cores. An increased density compared to interstellar diffuse molecular clouds means that stellar radiation from outside stars does not penetrate deep inside the dense cloud. Despite the low temperature and lack of external stellar radiation, these clouds are considered to be great laboratories of molecular synthesis in the ISM and many molecules have been identified in them.<sup>5</sup> To date, more than 175 molecules have been identified from the gas clouds via their spectra,<sup>89</sup> although most of these molecules are relatively small and consist of 12 or less atoms. An example of a dense cloud is the Taurus Molecular Cloud-1 (TMC-1), in which over 60 molecular species have been identified.

Molecular formation in dense molecular clouds is dictated by molecular collisions, which are, although greatly increased compared to diffuse clouds, still very low, and most collisions do not result in a chemical reaction (Figure 10). Molecular collisions that do result in a reaction can be of two types: (1) neutral–neutral molecular reactions that generally require significant activation energies and are thus less likely to take place given the low temperatures of these clouds, and (2) ion–molecule reactions that do not require activation energy and are thus more likely to be successful. Despite the lack of external stellar radiation dense molecular clouds are not completely devoid of ionizing radiation. Indeed, materials in dense clouds are exposed to cosmic rays, cosmic-ray-generated electrons, and UV photons produced by the de-excitation of  $\text{H}_2$  molecules excited by the impact of cosmic-ray-generated electrons, the Prasad–Tarafdar mechanism.<sup>86</sup> These energetic and ionic species power molecular excitation and ion formation. In particular, energetic ions can lead to physical and chemical changes, e.g., by photoionizing and/or photodissociating species, or via ion–molecule reactions, which play a significant role in the formation of small-sized molecules in the gas phase.

**2.3.2.1. Photoionization and Photodissociation.** Photoionization of small species such as diatomic hydrides of carbon, oxygen, nitrogen, and some other small molecules such as



**Figure 10.** Representative chemical processes in the dense molecular clouds, photodissociation, photoionization, neutral–neutral, reactions, ion–molecule reactions, and reactions in ices leading to ever growing molecular complexity, set on a background of OMC-1 in the Orion Molecular Cloud.

$\text{H}_2\text{O}$ ,  $\text{HCO}$ , and  $\text{H}_2\text{CO}$  is known to occur in the dense molecular clouds by the action of ionizing radiation.<sup>92,93</sup> Photodissociation follows the excitation of molecules by UV to excited states that are either directly dissociative or predissociative, with reaction rates of  $\sim 10^{-11}$  or lower in the dark clouds. These excited molecules then dissociate into their atomic components, either as radicals or ions. Such reactions include the dissociation of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{HCO}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{CO}$ , and  $\text{H}_2\text{O}$ .<sup>94</sup> Photodissociation rates typically range between  $10^{-14}$  and  $10^{-10}$   $\text{s}^{-1}$  and depend on the depth and UV flux of the dark molecular cloud. Photodissociation and photoionization produce ions and radicals from small species, but these

processes are also involved in ion–molecule reactions for further growth of the material into larger molecules.

**2.3.2.2. Ion–Molecule Reactions.** Molecular ions can form via direct ionization of neutral molecules exposed to UV radiation and/or cosmic rays (energetic particles, mostly protons) via ion–molecule type reactions due to direct electrostatic attraction of ions and neutrals, via attachment of protons with neutral molecules, or via collisional transfer or exchange of charge from ionized  $\text{H}_2$  or  $\text{H}_3^+$ .<sup>95–100</sup> Ions have larger cross sections for chemical reactions so that ion–molecule reactions are effective, barrierless in the entrance channel, and usually fast (they take place at the collision rate), with rate constants as high as  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .<sup>101</sup> This implies that they do not require an activation energy or high temperature to cross the reaction barriers. Instead of following the Arrhenius equation, their reaction kinetics are better described by the Langevin equation.<sup>102,103</sup> These reactions sometimes show a negative temperature dependence, i.e., they become faster at lower temperature. For these reasons, ion–molecule reactions play an important role in starting molecular growth in low-temperature dark dense molecular clouds.<sup>104,105</sup> Chemistry involving carbon, nitrogen, and oxygen starts off with ion–molecule type reactions<sup>89,106</sup> toward forming molecules of 2–6 atoms. Although this mechanism only leads to the formation of molecules that are rather small, these gas-phase molecular syntheses result in the formation of molecules such as formaldehyde and methyl alcohol,<sup>107</sup> which are the seeds of complex interstellar organic chemistry.

Of the approximately 175 molecules that are observed in dense molecular clouds, some 60 of them are observed in TMC-1. These molecules include cationic species ( $\text{CH}^+$ ,  $\text{OH}^+$ ,  $\text{SH}^+$ ,  $\text{HCO}_2^+$ ,  $\text{C}_3\text{H}^+$ ,  $\text{H}_2\text{COH}^+$ ,  $\text{C}_{60}^+$ , etc.), anions ( $\text{C}_8\text{H}^-$ ,  $\text{C}_6\text{H}^-$ ,  $\text{CN}^-$ ), and many neutral molecules that include amines, nitriles, aldehydes, carboxylic acids, and alcohols,<sup>89</sup> i.e., molecules of great astrobiological interest. Chemical models to explain the formation of molecules in the gas phase were first proposed in the early 1980s and now include over 450 species, thousands of chemical reactions, and rate constants.<sup>108</sup> Nevertheless, chemical models for dark clouds still lack a lot of key reactions, their products, and their formation rate constants. Laboratory and theoretical investigations of the formation of new reaction pathways, leading to the formation of complex organic molecules via ion–molecule reactions have allowed a better understanding of the formation of specific molecules.<sup>37,43,109–115</sup> Some theoretical investigations were carried out to investigate the possibility of formation of nitrogenated heterocyclic molecules by the reaction of HCN with acetylene and other hydrocarbons.<sup>109</sup> Pyrimidine cation was proposed, based on laboratory and theoretical data, to be synthesized via such a mechanism in cold molecular clouds.<sup>116</sup> However, no nitrogenated heterocyclic molecules have been identified in the interstellar molecular clouds thus far,<sup>117–120</sup> although they are found in abundance in meteorites,<sup>121–127</sup> indicating that nitrogen heterocycles are formed abiotically in space. Laboratory experimental work also focused on the ion–molecular formation of bicyclic aromatic molecules such as anthracene and other PAHs.<sup>36,128–130</sup> Larger molecules tend to be frozen on cold grains and mixed in CO and  $\text{H}_2\text{O}$  ices in cold dense media, which makes it difficult for them to be observed in the gas phase. Nevertheless, identification of large molecular species, including neutral, cationic, and anionic species in the cold, dense ISM indicate that these species can

be formed under such conditions, probably via two-body collisions.

**2.3.2.3. Radical–Molecule Reactions.** Some neutral–neutral reactions, especially when they include radicals, have been shown to be sometimes barrierless, and occurring substantially fast, even at low temperatures relevant to dark cloud environments.<sup>17,131–134</sup> For example, a combination of experimental studies and quantum chemical calculations showed that the reaction between a pyridyl radical and butadiene proceeds via a barrierless pathway in the entrance channel to form *N*-heterocycles.<sup>135,136</sup> Therefore, nitrogenated heterocyclic molecules may be synthesized in the cold ambient temperatures of dark clouds, as the barriers for their formation are submerged.

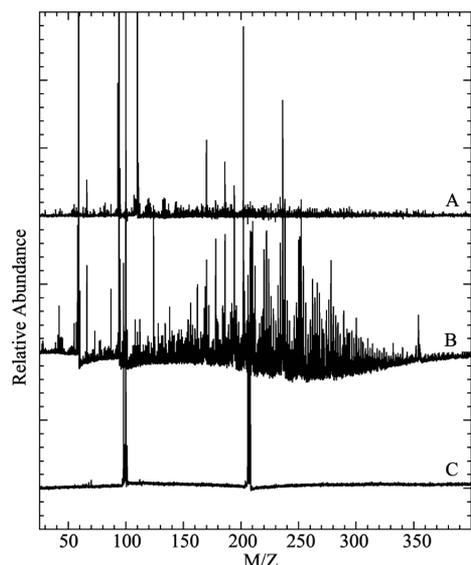
**2.3.3. Gas–Grain Chemistry.** Although most of species in the ISM have been detected in the gas phase, a non-negligible fraction of them is believed to have formed in the solid phase on the surface of small, cold grains and then released to the gas phase via photoinduced or thermal desorption. These grains are usually made of silicates or carbonaceous matter (graphite or soot-like material). They are believed to be formed in the outflows of red giant stars.<sup>137–140</sup> These grains are cold ( $\sim 100 \text{ K}$  in diffuse clouds and  $\sim 10 \text{ K}$  in dense clouds), so that most gas-phase species present can condense on their surface,<sup>141,142</sup> with the exception of  $\text{H}_2$  and He in all ISM media, and species such as CO,  $\text{N}_2$ , and  $\text{O}_2$  in warmer environments. This does not mean, however, that CO,  $\text{N}_2$ , and  $\text{O}_2$  cannot be present in colder ices, where they can be trapped inside ice matrices made of mixtures of other frozen species.

Dust grains increase the probability for reactions between species to take place, as species are closer to each other and thus have a higher probability to meet. Reactions between species are then only limited by their diffusion properties on the surface of the grains. Grain surfaces can play the role of catalyst, as it is the case for the formation of  $\text{H}_2$ . Indeed,  $\text{H}_2$  cannot be formed in the gas phase because of the excess energy resulting from its formation leads to the redissociation of the  $\text{H}_2$ , and grain surfaces play the role of a third body to absorb this excess energy and allow for the formation of  $\text{H}_2$ .<sup>143–148</sup> Depending on the local  $\text{H}/\text{H}_2$  ratio in a given environment, chemical models show that other simple molecules such as  $\text{O}_2$ ,  $\text{N}_2$ , or hydrides ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ) can also form.<sup>18,149–151</sup> In dense cloud environments where  $\text{H} > \text{H}_2$ , these reactions create  $\text{H}_2$  and hydrides like  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  from the hydrogenation of C, N, and O. On the other hand, when  $\text{H} < \text{H}_2$ , reactions involving heteroatoms become important and species like  $\text{N}_2$  and  $\text{O}_2$  predominate. Consequently, grain surface reactions will depend on the type of ice mantles in which they take place, either polar, H-bonded ices, or less polar ices containing unsaturated molecules, as supported by astronomical observations.<sup>152–154</sup>

The icy mantles that form on the surface of grains is also very important for the chemical evolution of interstellar environments. Indeed, ice matrices create a medium in which species can diffuse, interact, and be stabilized by the matrix via intermolecular interactions. Because such icy mantles only form in environments where temperatures are very low ( $10\text{--}100 \text{ K}$ ), reactions are mostly limited by the mobility of the species in the ice. Ice matrices can also stabilize reactive species created from the irradiation of the condensed species, such as radicals and ions. Because reactions involving radicals are typically barrierless, even at very low temperatures, this

mechanism provides an efficient way to form larger, more complex molecules within the ices.<sup>109</sup>

**2.3.4. Radiation-Driven Chemistry and the Photolysis of Ices.** **2.3.4.1. Overview of the Chemistry.** Chemical processing within low-temperature (<20 K) astrophysical ices is largely driven by ionizing radiation in the form of high-energy photons and cosmic rays that break bonds in the molecules in the ice and produce ions and radicals that can react even at such low temperatures. When reactants are next to each other, some products can be formed immediately, while others only form when the ices are warmed and species become more mobile (Figure 3).



**Figure 11.** The microprobe laser-desorption laser-ionization mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) spectra of an ice photolysis residue and two controls. Trace A is the mass spectrum of a control, i.e., a UV-irradiated  $\text{H}_2\text{O}$  ice in which no organic synthesis is expected. Trace B is the mass spectrum of a UV-irradiated  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 100:50:1:1$  ice mixture at 15 K, which shows hundreds of peaks, each corresponding to the mass of one or more organic compounds produced from the UV irradiation of the starting ices. Trace C is the mass spectrum of an unphotolyzed ice mixture like that used for B. The peak at  $m/z = 100$  is toluene- $d_{10}$  added during analysis as a standard, and the peaks at 204, 206, 207, and 208 correspond to lead desorbed from the brass sample substrate. Reproduced with permission from ref 24. Copyright 2004 Elsevier.

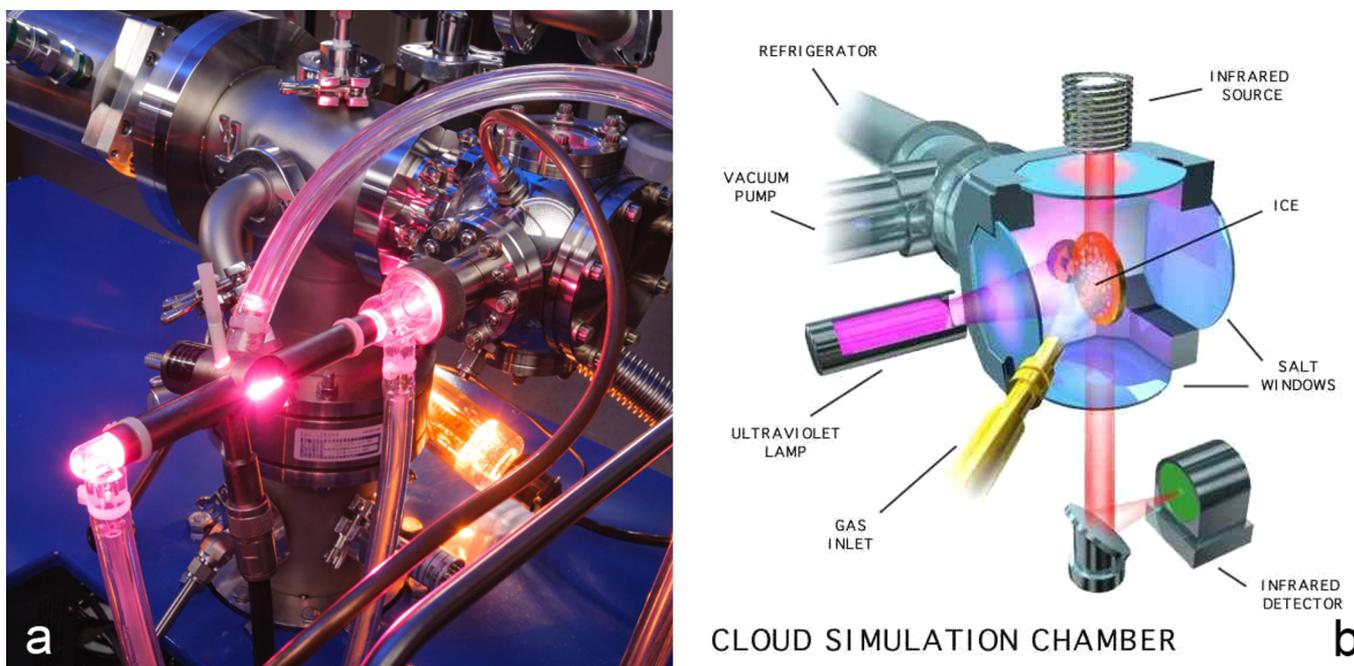
Exposure of ices with even the simplest compositions to ionizing radiation results in the production of an extremely complex mixture of products. Figure 11 shows the mass spectrum of the refractory material (residue) consisting of the products resulting from the UV irradiation of an  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 100:50:1:1$  ice at 15 K and recovered at room temperature, demonstrating the production of hundreds to thousands of new, more complex, refractory molecular species.<sup>24</sup> If polycyclic aromatic hydrocarbons (PAHs) or heterocyclic molecules are present in the starting ice mixtures, an even more diverse set of products is produced.

This chemistry is very “robust” in the sense that the types of materials produced are relatively insensitive to many of the environmental parameters of the irradiation, although their relative and total abundances may vary. For example, the temperature of the ice during irradiation is relatively unimportant; all that is required is that the ice be cold enough

that the starting materials of interest remain condensed during the irradiation.<sup>155,156</sup>  $\text{H}_2\text{O}$  is the dominant species in many astrophysical ices, and in  $\text{H}_2\text{O}$ -rich ices irradiation processes yield similar products over the entire 10–150 K temperature range.<sup>23</sup> In many ices, this processing is similarly insensitive to the source of the ionization; identical ices yield similar products independent of whether they are irradiated by energetic protons or UV photons.<sup>157–160</sup> The basic suite of products is even relatively insensitive to the composition of the ices themselves, provided they contain fragmentable molecular sources of C, H, O, and N. For example, amino acids are produced by the irradiation of ices independent of whether the initial carrier of C in the ices is  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ , or a combinations of those,<sup>155,161–163</sup> and whether the initial carrier of N is  $\text{NH}_3$  or  $\text{HCN}$ .<sup>164</sup>

**2.3.4.2. Description of Laboratory Studies.** Processing of ices with energetic photons and/or particles have been studied in the laboratory for more than three decades. These studies include: (i) measurements of spectra of pure ices and ice mixtures, mostly in the infrared<sup>165–181</sup> and ultraviolet;<sup>182–187</sup> (ii) measurements of IR band strengths of individual ices in their pure matrix and when embedded in other ice matrices;<sup>165,166,188–190</sup> (iii) measurements of photoabsorption cross sections of individual ices in their pure matrix and when embedded in other ice matrices when subjected to ionizing radiation such as UV photons, electrons, protons, and heavier ions;<sup>185,186,191–194</sup> (iv) measurements of optical constants of pure ices and ices in mixtures;<sup>178–180,182,189,190,195–198</sup> (v) measurements of binding energies of pure ices and when embedded in other ice matrices;<sup>165,199–205</sup> (vi) studies of the formation of, and reactions between, radicals and ions from pure ices, ice mixtures, and PAHs in ice matrices;<sup>128,130,206–215</sup> (vii) formation of complex organic molecules in ice matrices at low temperature<sup>216–218</sup> and during the warm-up of ices;<sup>219–222</sup> and (viii) formation of refractory molecules from ices processed by UV photons or energetic particles that are recovered in the resulting residues at room temperature,<sup>23,223–229</sup> including a wide range of molecules of astrobiological interest that are described in detail in section 2.3.4.4.

Laboratory experiments are typically conducted in vacuum chambers pumped to high or ultrahigh vacuum pressures ( $<10^{-7}$  mbar). A picture and schematic of one of the vacuum systems used at NASA Ames Research Center are shown in Figure 12. Ice samples, either pure ices or ice mixtures, are typically deposited from the gas phase onto a substrate (IR-transparent windows such as KBr, CsI,  $\text{MgF}_2$ , or ZnSe for IR studies, and metals such as aluminum, copper, gold, or quartz microbalances). Deposition is usually done via an inlet tube, although some studies have used microcapillary arrays for gas deposition.<sup>230–234</sup> The deposition is usually controlled with a needle valve and can be adjusted for each experiment. The substrate onto which ice samples are deposited is cooled down to cryogenic temperatures, typically 5–20 K when using a liquid helium cryostat or  $\sim 80$  K when using a liquid nitrogen cryostat. Gas-phase samples are usually obtained from the vapors of pure liquids (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , benzene, pyrimidine) or from gas lecture bottles for other species (e.g.,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ). Vapors and gas are usually mixed prior to deposition onto the substrate, using a gas mixture manifold. In some cases, more refractory species, mostly solids such as powders and crystals, can also be added to the mixtures. However, because these species have a very low



**Figure 12.** (a) Photograph of one of the vacuum systems at NASA Ames Research Center used to irradiate ice mixtures and produce organic residues, with the UV lamp on. (b) Schematic of the vacuum chamber showing the substrate, how the gases are deposited to the substrate, how they are irradiated, and how they can be analyzed using IR spectroscopy.

vapor pressure or no vapor pressure at all, they are codeposited with the other gas samples through a separate tube that is itself heated with a resistive heat tape in order to sublime the refractory species. The temperature at which the tube needs to be heated is determined prior to the experiments in order to control the sublimation and deposition rate. This is the method used to embed most PAHs and some *N*-heterocycles in ice mixtures.<sup>159,209,210,212,214,235–247</sup>

Ices can be irradiated with a wide range of photon and energetic particle sources.

***H<sub>2</sub> UV Lamps.*** The most common light source used to process ices in the laboratory is the microwave-powered  $H_2$  discharge lamp. This lamp mostly emits Lyman- $\alpha$  photons (121.6 nm, 10.2 eV) and a continuum of  $H_2$  bands in the 155–165 nm range (7.5–8.0 eV), with a photon flux of  $\sim 10^{15}$  photons  $cm^{-2} s^{-1}$ .<sup>248</sup> Such a UV source is a good analogue to the UV radiation field in the cold astrophysical environments.<sup>164,185,186,235</sup>  $H_2$  lamps can be used in different configurations by modifying the pressure of the flowing  $H_2$  gas, adding He, and/or adding filters, in order to increase/decrease the intensity of a given band or spectral range, or to cut off a whole portion of the emission spectrum.<sup>249</sup>

***Synchrotron Radiation.*** Another type of light source routinely employed to irradiate ice samples is synchrotron radiation. Most synchrotron experiments use photon energies in the UV/extreme UV (EUV)<sup>250–257</sup> and X-ray ranges.<sup>258–264</sup> Synchrotron facilities are available in different countries (e.g., ALS in the USA, SOLEIL in France, Spring-8 in Japan, NSRRC in Taiwan, LNSL in Brazil) and provide photon beams that are tunable. Each beamline has its specific properties in terms of energy range (typically, from vacuum UV to hard X-rays), spectral resolution, spatial resolution, and fluxes. Photons emitted by such beamlines can be monochromatic or span a wide range of energies. Although monochromatic light sources are not directly relevant to astrophysical conditions, the flexibility of synchrotron beams allows for studies of specific

processes and reactions, because the energy can be optimized to be absorbed by a given compound, e.g., for the study of photoinduced processes such as photodissociation, photo-desorption, or chemical reactions as a function of the energy of the light irradiating a sample. Synchrotron beams have also been used to irradiate ice samples with circularly polarized UV light (UV-CPL) in order to induce an asymmetry in the photoprocessing of chiral compounds. For instance, amino acids such as alanine and 2,3-diaminopropanoic acids in residues produced from the UV-CPL irradiation of  $H_2O:CH_3OH:NH_3$  ice mixtures at low temperature showed enantiomeric excesses that were correlated to the polarization of the incident photons.<sup>265–267</sup>

***Energetic Protons and Ions.*** In dense molecular clouds that are too optically thick for UV photons to penetrate, cosmic rays may be the dominant source of irradiation for chemistry to happen. Cosmic rays consist of a variety of high-energy charged particles, mostly atomic nuclei, that are dominated by protons. The effects of high-energy proton bombardment (0.8 MeV, typically generated by a Van de Graaff accelerator) on ices of astrophysical interest have been extensively studied for ices relevant to the ISM or cold Solar System objects (icy satellites, comets).<sup>159,268–275</sup> Several of these studies compared the effects of energetic protons to UV photons.<sup>158,160,206,276</sup> Energetic protons can break chemical bonds that cannot be broken with UV photons (e.g., the  $N\equiv N$  bond in  $N_2$ ), but comparison studies have shown for example that the UV irradiation or the 0.8 MeV proton bombardment of astrophysical ice analogues resulted in the production of organic residues whose IR spectra are very similar,<sup>158</sup> indicating that the formation of complex organic molecules from ices often does not significantly depend on the energy source itself, although some products can only be formed via proton bombardment,<sup>206</sup> allowing us to distinguish UV-induced chemistry from proton-induced chemistry. It must be noted that the interaction between protons and interstellar

molecules can create secondary UV photons and electrons, which are believed to play an important role in the ensuing chemistry when ices are bombarded by energetic protons. Finally, some experiments have used more energetic, heavy, highly charged atomic ions to irradiate ices, such as 15.7 MeV  $^{16}\text{O}^{5+}$  or 46 MeV  $^{56}\text{Ni}^{13+}$  ions provided by the GANIL accelerator in France.<sup>277–279</sup>

**Electron Bombardment.** Electrons can also be a source of irradiation in the ISM and the Solar System. These electrons can be generated as byproducts of interaction between cosmic rays and molecules in the ISM or from the strong magnetic fields of giant planets (mainly, Jupiter and Saturn). Experiments using electrons can be divided in two categories, as both the effects of high-energy<sup>280–287</sup> and low-energy (<20 eV) electrons<sup>288–290</sup> on ices have been studied, and both shown to induce chemistry in ices. Energetic electrons can break bonds that UV photons cannot, so that electron-induced chemistry is expected to be different from that induced by UV photons. For example, although Lyman- $\alpha$  photons (10.2 eV) are energetic enough to break the  $\text{N}\equiv\text{N}$  bond (9.8 eV) in  $\text{N}_2$ , the absorption cross section of this bond at this wavelength is too small<sup>291</sup> so that  $\text{N}_2$  can only be dissociated via a photoinduced process involving another atom or molecule. One study of UV irradiation and electron bombardment of  $\text{N}_2:\text{CH}_4:\text{CO}$  (100:1:1) ice mixtures, i.e., ices simulating the surface of Pluto and other trans-Neptunian objects (TNOs) showed that the residues produced from electron bombardment were twice as rich in nitrogen as the equivalent residues produced from UV irradiation.<sup>284,292</sup> Finally, a comparison study between the effects of low-energy (<20 eV) and high-energy (1 keV) electrons on methanol ice at 85 K showed that similar products are formed in both experiments, suggesting that the chemistry induced by high-energy electrons may be attributable to low-energy secondary electron interactions with the methanol ice.<sup>290</sup>

A wide range of spectroscopic and analytical techniques have been used to study the chemical and physical composition and evolution of ices from low to higher temperatures, their photoirradiation or bombardment with energetic particles, and the resulting residues produced during these experiments and recovered at room temperature.

**IR Spectroscopy and Microscopy.** Infrared spectroscopy is one of the main techniques used to determine the chemical composition of ices at low temperature in situ and to monitor its evolution with time and when subjected to ionizing radiation. Spectroscopy in the mid-IR range gives information about the chemical bonds present in the ices and allows for the quantification of some of the carriers responsible for these modes. With a few exceptions, IR spectroscopy of the ices in dense clouds does not allow for the identification of individual species but rather for the presence of the main chemical moieties (i.e., hydroxyls, carbonyls, aliphatic vs aromatic chains). There are a few important exceptions though, as IR modes associated with  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and sometimes  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{CO}$ ,  $\text{HNCO}$ ,  $\text{NH}_4^+$ , and the  $\text{HCO}^\bullet$  radical can be seen in cold interstellar ices.<sup>23,222,270,293–295</sup> Identifications of these bands depend strongly on the ice mixtures and on the astrophysical environments, as the presence of a large number of different species and their molecular interactions result in spectral confusion. It must, however, be noted that when observing ices in astrophysical environments, several IR bands associated with organic material may be masked by the presence of broad IR bands associated with Si–O modes from

silicates around  $10\ \mu\text{m}$  ( $\sim 1000\ \text{cm}^{-1}$ ).<sup>296–306</sup> Nevertheless, IR spectroscopy remains one of the most used techniques to study ices in the laboratory and to compare laboratory data with astronomical observations from IR space observatories such as *IRAS*, *ISO*, and *Spitzer*.<sup>3,4,12,87,307–315</sup>

In addition, IR spectroscopy (in particular IR microscopy) is an important tool to study the composition of the refractory organic residues produced from the irradiation of ices, even though only chemical groups and bonds can be identified in such IR spectra. Two notable exceptions are the identification in room-temperature residues of the ammonium ion ( $\text{NH}_4^+$ )<sup>4,228,265,295,308,316</sup> and hexamethylenetetramine (HMT) thanks to the presence of several of its IR bands.<sup>23,228,317,318</sup> HMT is believed to be very abundant in residues,<sup>319</sup> and therefore in any material resulting from the photoprocessing of astrophysical ices, and may be one of the sources of amino acids as well as other compounds of astrobiological interest found in meteorites (see section 2.3.4.4 for more details).

IR spectroscopy in the near- and far-IR ranges can also provide information about the composition of organic materials both in laboratory studies and astronomical observations. For instance, near-IR observations are common for the study of cold Solar System objects such as TNOs, including Pluto, Charon, and 2014 MU<sub>69</sub> (Arrokoth), which were recently visited by the *New Horizons* mission.<sup>320–326</sup> Such observations resulted in the detection of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  on Pluto,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  on Charon, and  $\text{H}_2\text{O}$  and possibly  $\text{CH}_3\text{OH}$  on Arrokoth. On the other hand, far-IR spectroscopy is used to study lattice modes of larger organic compounds such as PAHs.<sup>327–329</sup> These modes, which can be observed in astronomical spectra, support the presence of these large PAH compounds in different astrophysical environments.<sup>70</sup>

**Raman Spectroscopy and Microscopy.** Raman spectroscopy has been used as a complementary technique to IR spectroscopy to study spectral properties of ices of astrophysical interest.<sup>330,331</sup> Raman spectroscopy is a useful tool to study ice species that are not IR active and thus cannot be studied using IR spectroscopy, such as  $\text{N}_2$  and  $\text{O}_2$ . However, to date, only a few Raman spectroscopy studies applied to astrophysical ices have been reported for specific pure compounds ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ) or ice mixtures ( $\text{H}_2\text{O} + \text{CH}_4$ ,  $\text{H}_2\text{O} + \text{CH}_4 + \text{N}_2$ ,  $\text{H}_2\text{O} + \text{C}_6\text{H}_6$ ).<sup>332–334</sup> Other reported laboratory Raman spectroscopy studies of ices are for terrestrial samples,<sup>335–337</sup> but they support the use of this technique to study ices of astrophysical interest containing  $\text{N}_2$  and  $\text{O}_2$  and to detect them in astrophysical objects. Raman spectroscopy is also often used to obtain additional information on structural properties of carbonaceous and hydrocarbon samples.<sup>338–345</sup> However, there are not many laboratory Raman data for irradiated ice mixtures of astrophysical interest, with a few exceptions,<sup>330</sup> and no Raman data for organic residues produced from the photoprocessing of such ices.

**Mass Spectrometry.** Mass spectrometry is also often used to identify compounds that are desorbed from an ice surface during photoprocessing and/or warm-up to room temperature. This allows for the identification of some of the photoproducts produced in the ices but difficult to identify using IR spectroscopy due to their weak bands and/or the presence of other species whose IR bands dominate or mask those of less abundant species. Mass spectrometry is also used in temperature program desorption (TPD) experiments, in which the volatile compounds subliming from the warming ice can be

identified thanks to their mass.<sup>202,204,219,346–353</sup> Identifying these volatile compounds is important because a lot of them do not remain in the final organic residues recovered at room temperature, and their identification may provide important information about the formation mechanisms of organic compounds taking place in the ice at low temperature or during warm-up, by identifying the missing links between the ices and the more complex, refractory molecules constituting the residues.<sup>219–222,346,347</sup> In addition, mass spectrometry, most of the time in combination with TPD, is used to study processes of radiation-induced desorption of pure ices and ice mixtures.<sup>249,347–357</sup> Finally, more recent studies have used Orbitrap high-resolution mass spectrometry to analyze the composition of laboratory residues as well as meteoritic samples.<sup>358–363</sup> The high-resolution of this mass spectrometry technique allows for the identification of compounds which have very similar molecular masses but have very different chemical formulas (e.g., CO vs N<sub>2</sub>).

*ReTOF-MS and L<sup>2</sup>MS.* Reflectron time-of-flight mass spectrometry (ReTOF-MS) is a recent technique used together with soft VUV ionization to target specific molecules and discard others. Ionization energies are tuned from a Nd:YAG laser. In particular, this technique has been used to identify and distinguish compounds that have the same chemical formula (isomers) and therefore cannot be distinguished using standard mass spectrometry, for example, during their sublimation from ices that have been exposed to energetic electrons.<sup>364–367</sup> This technique has also been proposed to be used for the detection of microorganisms by elemental composition analyses of regolith samples, permafrost samples, and extraterrestrial icy bodies.<sup>368</sup> Two-step laser desorption/ionization mass spectrometry (L<sup>2</sup>MS) is another powerful analytical technique used to analyze a broad variety of samples. L<sup>2</sup>MS decouples the desorption process from the ionization process by using a different laser for each step. By decoupling desorption from ionization, it provides the added flexibility of allowing both laser power and wavelength to be optimized independently for each step. For the desorption process, it has been shown that an IR laser (typically, a CO<sub>2</sub> laser) can efficiently desorb a wide range of molecules, while the ionization step is performed subsequently with a UV laser.<sup>369</sup> It has proven very useful for studying ices,<sup>370,371</sup> laboratory residues produced from ice photolysis<sup>24,159</sup> (Figure 11), Titan tholin laboratory analogues,<sup>372–376</sup> PAHs,<sup>377,378</sup> and carbonaceous meteorites.<sup>379–384</sup>

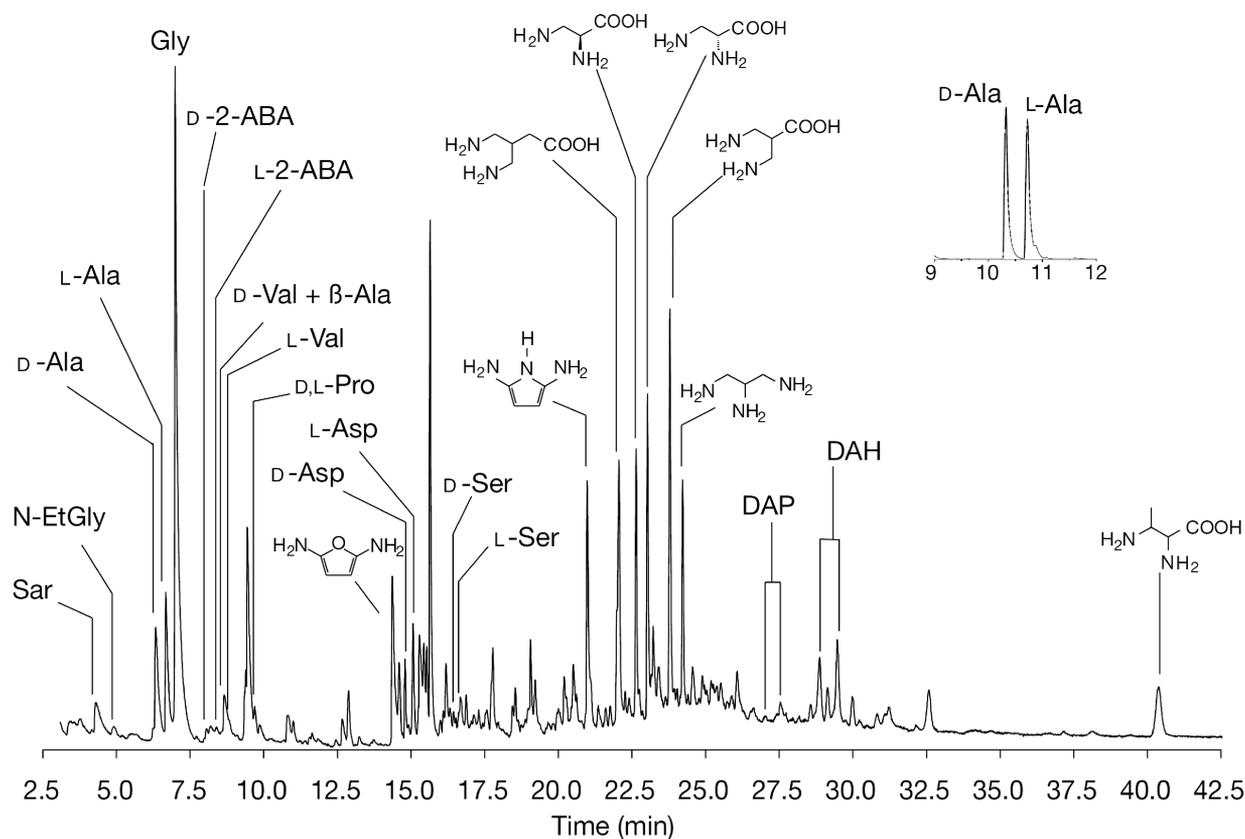
*XANES Spectroscopy.* Other laboratory analytical techniques are mainly used to study the composition of the organic residues resulting from the photoprocessing of ices. These residues are very complex materials consisting of hundreds or thousands of organic compounds (Figure 11).<sup>24</sup> Therefore, it is impossible to list the full inventory of molecules that constitute such residues. Complementary to IR spectroscopy, X-ray absorption near-edge structure (XANES) spectroscopy is a powerful technique to obtain information about the functional groups present in residues as a whole.<sup>229</sup> In addition, XANES spectroscopy allows for the determination of relative elemental composition, e.g., N/C and O/C ratios, which is not possible using IR spectroscopy. Such elemental composition measurements showed that laboratory organic residues tend to be richer in nitrogen and oxygen compared with samples returned from Comet Wild 2 by the *Stardust* mission,<sup>229,385–387</sup> interplanetary dust particles,<sup>388–390</sup> and meteorites.<sup>391</sup>

*HPLC and GC-MS.* Because organic residues are made of hundreds or thousands of compounds<sup>24</sup> (see Figure 11), a lot of laboratory studies searched for the presence of specific compounds in these residues, regardless of their abundance. The first families of compounds searched for were molecules of astrobiological interest such as amino acids, sugar derivatives, and nucleobases (see section 2.3.4.4). The main techniques used to search for and identify such compounds are high-performance liquid chromatography (HPLC), which can also be coupled to mass spectrometry (LC-MS), and gas chromatography coupled to mass spectrometry (GC-MS). Chromatography techniques allow for the separation of constituents of mixtures via either their diffusion properties in solvents (HPLC, LC-MS) or their diffusion through capillary columns, which are coated with various surfaces that are specifically chosen to interact with given functional groups and heated with a given temperature ramp (GC-MS). In the case of GC-MS, an additional step of derivatization is common before injection of the samples into the column. Derivatization results in the addition of a chemical group (or “tag”) to the molecules of interest in order to make them more volatile and obtain a better separation. When separation of chiral compounds is required, derivatization with chiral tags results in the formation of diastereomers that can be more easily separated, even when using a nonchiral column.<sup>392</sup> Another way to separate chiral compounds is to use a capillary column coated with a chiral material.<sup>162,265–267,393,394</sup> Finally, chromatography techniques can be used together with high-resolution mass spectroscopy for the identification of organics in both laboratory and meteoritic samples.<sup>359,362,363,395–397</sup> Such a GC-MS/high-resolution time-of-flight mass spectrometer was onboard the lander of the Rosetta mission that landed on Comet 67P/Churyumov–Gerasimenko.<sup>398</sup>

The use of HPLC and GC-MS resulted in the identification of a wide variety of organic compounds in laboratory residues produced from the UV irradiation of astrophysical ice analogues, including amino acids,<sup>155,161–164,265,394,399</sup> sugar derivatives,<sup>392,400–402</sup> as well as other organics of astrobiological interest such as urea, hydantoin, and several aldehydes.<sup>161,403,404</sup> When small *N*-heterocycles and PAHs are mixed with ices, pyrimidine-, and purine-based nucleobases<sup>245,246,405–408</sup> as well as *N*- and *O*-heterocycles<sup>244</sup> are also formed.

*Fluorescence Microscopy.* Fluorescence microscopy has been used to study the physical properties of vesicles that spontaneously form when residues are taken with a solvent.<sup>409</sup> Using fluorescent molecules, such a study demonstrated that vesicles could encapsulate and release these fluorescent molecules when changing the conditions of the solvent. This result has important astrobiological implications, as meteorites have also shown to contain such vesicle-forming materials, which could have served to make the first protocells and facilitate the first chemical reactions that resulted in the emergence of life on the primitive Earth<sup>410,411</sup> (see sections 2.3.4.4 and 3.2).

*NanoSIMS.* Nanoscale secondary-ion spectrometry (nanoSIMS) is often used to determine the isotopic composition and distribution of samples. Although this technique has been extensively used to analyze meteoritic samples,<sup>412–417</sup> interplanetary dust particles (IDPs),<sup>418–421</sup> and cometary samples from the *Stardust* mission,<sup>422,423</sup> it is only very recently that this technique was applied to the analysis of laboratory organic residues in order to verify whether isotopic fractionation of H,



**Figure 13.** GC-MS chromatogram of an organic residue produced from the UV irradiation of an  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO}:\text{CO}_2$  (2:1:1:1:1) ice mixture at 12 K that was acid hydrolyzed and derivatized before analysis. It shows the identification of 16 amino acids and several other organic compounds in one same residue. Reproduced with permission from ref 162. Copyright 2002 Nature Research.

N, O, and C could be induced by photochemistry. Indeed, meteoritic samples show distinctive isotopic enrichments in heavier isotopes (mostly D and  $^{15}\text{N}$ ), which are believed to have a circumstellar or interstellar heritage<sup>424–429</sup> (see section 2.5). Preliminary experiments studying the effect of irradiation on astrophysical sample analogues showed measurable deuterium enrichment in residues that were produced from the UV irradiation of astrophysical ice mixture analogues, followed by the irradiation of the residues themselves with UV and X-ray photons.<sup>430,431</sup> However, these results must be repeated and confirmed to establish to what extent photochemistry can play a role in the isotopic fractionations observed in meteorites.

**2.3.4.3. Theoretical Methods.** The main challenge for the theoretical calculations of reactions between gas-phase and condensed-phase species and formation mechanisms of the resulting products is to find the correct balance between accuracy and affordability of the calculations. Ab initio quantum chemical methods are suitable for computing structures, energies, chemical reaction pathways, UV–visible, IR, and microwave spectroscopic parameters, as well as reaction rate constants among others. For small- to medium-size molecules, these parameters have been shown to be comparable in accuracy to experimental data. For molecules that are up to about 15 atoms, coupled cluster theory with singles and doubles, and perturbative triples CCSD(T) excitation is considered to be reliably accurate. For systems larger than these, CCSD(T) becomes prohibitively expensive, and other more approximate methods such as density functional theory (DFT), for which a suite of functionals

tuned for specific problems are available, and Møller–Plesset perturbation theory methods are usually required. Typically, B3LYP, a widely used hybrid density functional with Becke’s three-parameter exchange<sup>432</sup> along with Lee, Yang, and Parr’s correlation functional<sup>433</sup> provides a good balance between expense of the calculation and accuracy for large systems but is not as good to simulate non-covalent interactions and calculate energy barriers for transition states. More modern functionals such as the  $\omega\text{B97X-D}$ ,  $\omega\text{B97M-V}$ , and M06-2X functionals provide overall better performance and are used for these calculations. Moreover, as range-separated functionals, they reduce the self-interaction error<sup>434,435</sup> and are thus suitable to describe radical cations. To model the effect of an extended ice matrix environment, a conductor-like solvent model C-PCM<sup>436</sup> from the class of polarizable continuum models (PCM)<sup>437</sup> is used. Specifically, an implementation that ensures continuous potential energy surfaces as a function of changes in molecular geometry is most suitable.<sup>438,439</sup> In this model, the bulk is represented as a polarizable medium characterized by its dielectric constant,  $\epsilon$ . The solvent dielectric represents the condensed phase and enables the study of the effect of the solvent.

**2.3.4.4. Examples of Ice Irradiation Products.** In the sections below, we discuss some of the classes of compounds of astrobiological interest that can be produced when astrophysical ice analogues are exposed to radiation. Residues formed from the irradiation of astrophysically relevant ice mixtures at low temperature are made of hundreds if not thousands of organic molecules.<sup>24</sup> Because of the extreme difficulty to identify all these compounds, a different approach

was used. Instead of trying to identify all compounds present in the residues, analytical methods were set up to search for the presence of specific compounds, no matter how abundant or representative of the whole residues these compounds were.

**Amino Acids.** The first family of compounds that was extensively searched for in such residues is the amino acids because (i) as the building blocks of proteins in all terrestrial life they are biologically and astrobiologically relevant, (ii) they are found in primitive meteorites, both proteinic and nonproteinic,<sup>440–450</sup> and (iii) analytical techniques optimized to search for them were already existing.

Residues produced from the UV irradiation of ice mixtures containing H<sub>2</sub>O, carbon sources such as CH<sub>3</sub>OH, CO, CO<sub>2</sub>, and/or CH<sub>4</sub>, and nitrogen sources such as NH<sub>3</sub> or HCN were shown to contain a wide variety of amino acids, including both proteinic and nonproteinic amino acids in measurable abundances.<sup>155,161–164,265–267,394</sup> These amino acids were shown to be produced from photoprocesses in the ices rather than resulting from biological contamination in several distinct ways. First, the residues were found to contain nonproteinic amino acids with abundances comparable to proteinic amino acids of similar molecular masses; terrestrial biological contamination would not have contained comparable concentrations of nonproteinic amino acids. Second, the distribution of these amino acids by molecular mass/size does not follow a biological pattern; instead, laboratory residues display an amino acid distribution in which glycine, the smallest amino acid, is by far the most abundant, and the abundance of larger amino acids decreases exponentially with their molecular mass, as expected for a nonbiological distribution in which larger molecules are built up from smaller precursors. Third, these experimental studies include a number of control experiments that demonstrated that no amino acids were made when either the ice or the radiation source were omitted, while all other experimental protocols were strictly adhered to. Finally, in many cases, experiments were carried out in which the starting ices were isotopically labeled with <sup>13</sup>C, <sup>15</sup>N, and/or <sup>18</sup>O, and it was shown that the resulting amino acids were isotopically marked appropriately.

Up to 16 amino acids, both proteinic and nonproteinic, were found in one single residue<sup>162</sup> (Figure 13). Although starting with simple organic compounds such as CH<sub>3</sub>OH and CH<sub>4</sub> as carbon sources in the starting ice mixtures along with H<sub>2</sub>O and NH<sub>3</sub> typically led to larger amounts of amino acids in the final residues,<sup>155</sup> using only CO<sub>2</sub> as a carbon source also resulted in the formation of a wide variety of amino acids.<sup>163</sup> Interestingly, the irradiation of a mixture of naphthalene (C<sub>10</sub>H<sub>8</sub>), the simplest polycyclic aromatic hydrocarbon (PAH), and H<sub>2</sub>O:NH<sub>3</sub> ices with 4–45 eV photons (UV/EUV range) also resulted in the formation of several amino acids although their distribution was different from other residues, as they showed high abundances of amino acids containing aromatic rings.<sup>399</sup> Therefore, the formation of amino acids from the UV irradiation of ice mixtures is chemically robust in the sense that it only requires that the starting mixtures consist of C, H, O, and N atoms.<sup>155,164</sup> Finally, a few studies reported the detection of simple dipeptides in laboratory ice photolysis residues.<sup>363,451</sup> These dipeptides include glycylglycine (Gly-Gly), glycylalanine (Gly-Ala), glycylserine (Gly-Ser), and leucylalanine (Leu-Ala).

The distribution of amino acids in laboratory residues is comparable to the distribution of amino acids identified in meteorites; although the variety of meteoritic amino acids is

significantly wider, with more than 70 different amino acids identified to date.<sup>443,448</sup> Interestingly, some meteoritic amino acids have been shown to display small *L*-enantiomeric excesses.<sup>444,446,447,452</sup> Several hypotheses have been proposed to explain the origin of such excesses via parent body processes,<sup>453,454</sup> but no clear link has been established with the fact that all proteinic amino acids in biological are *L*-enantiomers. However, the distribution and absolute concentration of amino acids can vary widely from one meteorite to another due to processes taking place in the meteorites' parent bodies (mostly asteroids)<sup>455,456</sup> such as aqueous alteration and thermal metamorphism. Indeed, the distribution of  $\alpha$ ,  $\beta$ , and  $\gamma$ -amino acids seems to be correlated to the meteoritic group of the carbonaceous chondrites in which they were identified (CM, CI, CV, CO, CR), which is itself correlated to the level of aqueous alteration and thermal metamorphism experienced by the parent body.<sup>450,454,457</sup> In any case, the similarities between the distribution of amino acids in laboratory residues produced from the UV irradiation of astrophysical ice analogues and the distribution of meteoritic amino acids support a scenario in which photoprocessing of ices in cold astrophysical environments is a plausible source for meteoritic organics.

Theoretical calculations of formation of amino acids starting from astrophysically relevant precursors mainly focused on the gas-phase synthesis of small amino acids such as glycine, alanine, and serine and involved the Strecker reaction as well as Becherer–Berg reactions.<sup>458–462</sup> Some studies have also used DFT calculations to examine the formation of amino acids starting from methyleneimine in both gas- and condensed-phase ices.<sup>463,464</sup> Finally, one theoretical study investigated the formation of glycine in dense clouds that are intermittently heated and pressurized due to shocks.<sup>465</sup>

**Sugars and Related Compounds.** Another family of organics that are important for biology and astrobiology and have been searched for in laboratory residues are sugars and sugar derivatives. Sugars are carbohydrates that are omnipresent in modern biology, as they are used as building blocks for RNA (ribose) and DNA (2-deoxyribose), cellulose, cell walls, but also food for microorganisms, as well as energy storage in the form of glycogen and starch.<sup>466,467</sup> Sugar derivatives such as sugar alcohols and sugar acids, collectively referred to as “polyols”, are also widely present in modern biological structures and processes. For example, glycerol is the structural backbone of triglycerides, an important class of lipids and main constituents of body fat in humans, other vertebrates, and vegetable fat.<sup>467,468</sup> Other variants of polyols include deoxysugar derivatives such as 2-deoxyribose, the sugar used in DNA.

Like amino acids, sugar derivatives have been found in carbonaceous meteorites such as Murchison, Murray, NWA 801, and NWA 7020 and include sugar alcohols, sugar acids, sugars, sugar diacids, and deoxysugar acids.<sup>469–471</sup> Abundances of meteoritic sugar derivatives range from 15 ppm for glycerol (3-carbon sugar alcohol) and 9 ppm for glyceric acid (3-carbon sugar acid),<sup>469</sup> down to 25–180 ppb for ribose and its isomers (5-carbon sugars),<sup>471</sup> indicating that the total abundance of sugar derivatives in meteorites is typically higher than the total abundance of amino acids. In addition, like in the case of meteoritic amino acids, several meteoritic sugar acids have shown to display enantiomeric excesses.<sup>470</sup> Although the mechanisms leading to these enantiomeric excesses in meteoritic organics have not been determined, scenarios

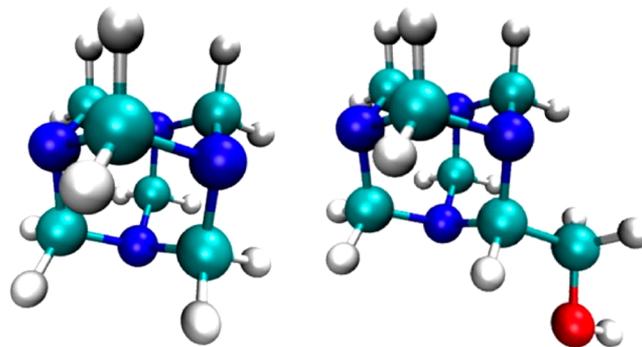
have been proposed.<sup>472</sup> Several of these scenarios involve a molecular symmetry breaking induced by circularly polarized light (CPL),<sup>265–267,473–479</sup> while other proposed scenarios involve magnetic fields.<sup>480</sup> However, it is not clear at which stage (molecular cloud, protosolar nebula, Solar System) such a symmetry breaking took place and whether meteorites' parent body processes such as aqueous alteration were involved in the creation and/or amplification of the enantiomeric excesses measured in meteoritic amino acids and sugar derivatives.<sup>481</sup>

In addition, like amino acids, sugar derivatives are expected to be abundantly formed from the UV irradiation of astrophysically relevant ice mixtures. However, the search for polyols in laboratory residues is very recent because, unlike amino acids, the sugar derivatives include a large variety and number of compounds, which include all aldose sugars, ketose sugars, their sugar alcohols and sugar acids variants, all their diacids variants, and all their deoxy variants.<sup>469,481</sup> In addition, most of polyols with four carbon atoms or more can exist in linear forms but also in five-member ring (furanose) and six-member ring (pyranose) cyclic forms, each with two possible anomers ( $\alpha$  or  $\beta$ ) depending on the orientation of one  $-OH$  group. Finally, a large majority of polyols are chiral compounds, i.e., they exist in two enantiomeric forms that are mirror images of each other, doubling again the number of possible structures for most sugar derivatives.<sup>470</sup> These analytical challenges could be overcome only recently thanks to specific protocols and better instrumentation, leading to protocols allowing for a more systematic search for sugar derivatives in laboratory ice photolysis residues.<sup>400,401</sup>

The analysis of residues produced from the UV irradiation of simple ice mixtures containing  $H_2O$  and  $CH_3OH$ , in the presence or absence of  $NH_3$ , showed the presence a wide variety of sugars, sugars alcohols, sugar acids, and deoxy variants of these containing 3–5 carbon atoms in detectable amounts.<sup>392,400–402</sup> Among these sugar derivatives, the RNA sugar ribose<sup>392,402</sup> and the DNA deoxysugar 2-deoxyribose<sup>392</sup> were unambiguously identified by using  $^{13}C$ -labeled  $CH_3OH$  in the starting ices to confirm that ribose, 2-deoxyribose, and all other sugar derivatives were indeed formed from ice photoprocesses rather than due to biological contamination. The distribution of polyols in residues produced from ices containing  $H_2O$  and  $CH_3OH$  show that sugar alcohols are formed with the highest abundances, followed by sugars and sugar acids. The dominance of sugar alcohols suggests a formation pathway involving the polymerization of  $CH_3OH$ , via  $\cdot CH_2OH$  radicals and/or ions,<sup>400,401</sup> followed by their oxidation into sugars and sugar acids. A formose-type reaction mechanism, i.e., polymerization of formaldehyde  $H_2CO$ ,<sup>482,483</sup> was also suggested to explain the formation of sugar derivatives.<sup>402</sup> However, no experimental or theoretical evidence were provided to support this mechanism.

The distribution of meteoritic sugar derivatives is somewhat different from the distribution observed in laboratory residues, as meteorites contain mostly sugar alcohols, sugar acids, sugar diacids, deoxysugar acids, and smaller quantities of sugars.<sup>469,471</sup> This discrepancy may result from several factors. First, the laboratory residues in which sugar derivatives were identified were all produced from the UV irradiation of ice mixtures containing  $H_2O$  and  $CH_3OH$  as the only carbon source,<sup>392,400–402</sup> while astrophysical ices are known to contain other carbon sources such as  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $H_2CO$ , and  $HCN$ .<sup>3,4,33,87,308,310</sup> The contribution of these compounds on

ice photochemistry may affect the distribution of the resulting sugar derivatives. Another factor that may have played a role is the effect of aqueous alteration and thermal metamorphism in asteroids, i.e., meteorites' parent bodies.<sup>455,456</sup> Such parent body processes are known to significantly affect the distribution of amino acids in meteorites,<sup>450,453,454,457</sup> and it is reasonable to assume that they also significantly affect the distribution and relative abundances of other organic compounds including sugar derivatives.

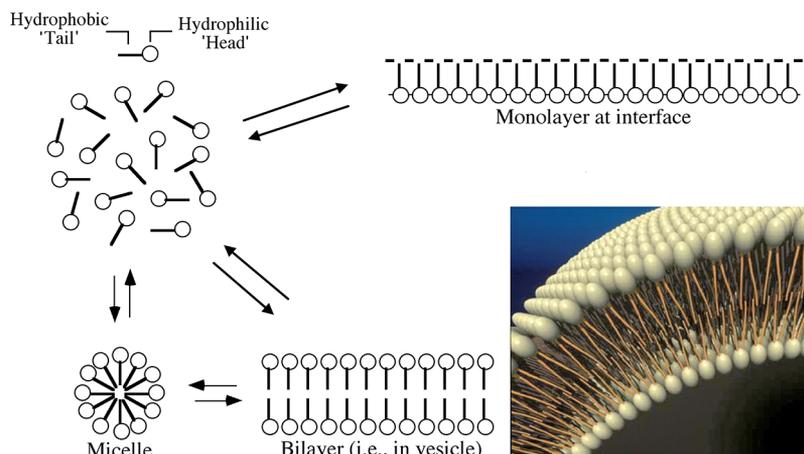


**Figure 14.** The structures of hexamethylenetetramine (HMT) (left) and HMT-methanol (right). HMT and variants that consist of HMT with a hydrogen replaced by a different functional group are believed to be major products of the irradiation of many astrophysical ice analogues.

**HMT and Related Compounds.** One of the first molecules to be uniquely identified in the population of products from ice irradiation studies was hexamethylenetetramine (Figure 14,  $C_6H_{12}N_4$ ; hereafter referred to as HMT).<sup>23</sup> HMT is highly soluble in water and polar organic solvents and has an adamantane cage-like structure with “corners” consisting of nitrogen atoms and “edges” consisting of methylene ( $-CH_2-$ ) bridges.

HMT is one of the most abundant products formed when ices containing C, H, O, and N are irradiated at low temperature and warmed.<sup>23,228,317,318</sup> In laboratory residues produced from the UV irradiation of interstellar ice analogues containing  $H_2O$ ,  $CH_3OH$ ,  $NH_3$ , and  $CO$ , the column densities of HMT produced were typically slightly more than 1% of the original ice's total column density.<sup>23</sup> Because only about 5% of the original ice's column density usually ends up in the refractory residues recovered at room temperature, this suggests an HMT abundance on the order of tens of percent in the residues. Subsequent studies have demonstrated that numerous HMT variants, in which one of the peripheral H atoms on the HMT skeleton is replaced with another functional group, are also made during these experiments, for example, HMT- $CH_2OH$  (Figure 14).<sup>319,484</sup>

This family of molecules is of interest for several reasons. First, HMT is known to produce a multitude of new organics under photodegradation,<sup>23,485,486</sup> thermodegradation,<sup>487</sup> hydrothermal degradation,<sup>488</sup> and acidic hydrolysis.<sup>489</sup> Many of these products (e.g., amino acids, nitriles, and a variety of *N*-heterocycles) are of astrobiological interest. The degradation products of other HMT variants are not currently known, but it is likely that the degradation of other HMT variants produce similar products to those from HMT, i.e., methylamines, methane, ammonia, oxides of carbon and nitrogen, *N*-heterocycles, and a wider range of amino acids, plus additional



**Figure 15.** Because long-chain amphiphiles have both a hydrophilic “head” and a hydrophobic “tail”, they can self-assemble into structures that maximize contact of the heads with surrounding water and minimize contact of the tails with surrounding water. This can lead to the formation of bilayers or more complex structures that wrap on themselves to form vesicular structures.

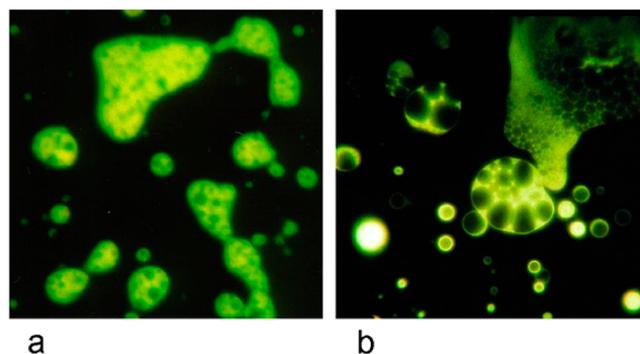
products unique to the composition of their side groups. Also, HMT has been proposed as a source for the CN and HCN observed in comets.<sup>486</sup>

Finally, HMT and its variants may be detectable in space, both because they are expected to be abundant products and because all the members of this family share the common HMT cage as a major part of their structure. Therefore, they produce a number of IR bands that fall at similar positions and have similar strengths. Theoretical calculations of HMT and HMT variants with different functional groups have been performed using  $\omega$ B97X-D functional together with a correlation-consistent polarized triple- $\zeta$  (cc-pVTZ) basis set. These substituted HMT molecules include HMT-OH, HMT-NH<sub>2</sub>, HMT-CH<sub>3</sub>, HMT-CN, HMT-OCN, HMT-OCH<sub>3</sub>, HMT-CH(OH)CHO, and HMT-NHCHO, for which structures and vibrational spectra were computed.<sup>490</sup> HMT itself is symmetric and does not possess a permanent dipole moment and thus does not have a pure rotational spectrum. In contrast, HMT-CH<sub>2</sub>OH and other variants may be detectable in space because they are abundant products, because they are not as symmetric as HMT thanks to the presence of the side groups, and therefore possess a nonzero dipole moment, and because all the members of this family share the common HMT cage which produces a number of IR bands that fall at similar positions and have similar strengths, making them easier to be detected in space as a family.<sup>490</sup>

**POM and Related Compounds.** One of the most abundant intermediary products that is formed by the irradiation of interstellar ice analogues is formaldehyde (H<sub>2</sub>CO)<sup>23,215,228,491–494</sup> and is seen in actual interstellar ices.<sup>493,495,496</sup> It is formed by both H addition to abundant CO<sup>497–502</sup> and through photodegradation of abundant CH<sub>3</sub>OH.<sup>227,494,503,504</sup> H<sub>2</sub>CO is highly reactive, and warming of ices that contain H<sub>2</sub>CO usually results in its polymerization, of which polyoxymethylene (POM; chemical formula: [CH<sub>2</sub>O]<sub>n</sub>) and related compounds are the most common detected products.<sup>215,317,492,505,506</sup> Polymerization is greatly aided by the presence of NH<sub>3</sub>, and even small traces of NH<sub>3</sub> (NH<sub>3</sub>/H<sub>2</sub>CO > 0.005) are sufficient to convert >40% of the H<sub>2</sub>CO into organic residues. Although POM is made via polymerization of pure H<sub>2</sub>CO, the reaction of H<sub>2</sub>CO with other compounds such as H<sub>2</sub>O, CH<sub>3</sub>OH, and NH<sub>3</sub> will result in the production of POM chains in which some of the end

groups and peripheral H atoms of POM are replaced by –OH, –COOH, –CH<sub>3</sub>, and –NH<sub>2</sub> groups.<sup>23,228</sup> POM has been proposed as the parent molecule of the H<sub>2</sub>CO observed in comets.<sup>507,508</sup>

**Amphiphiles.** The presence of amphiphiles in ice irradiation residues is of considerable interest for astrobiology because this class of compounds can self-assemble when placed in liquid water into vesicular structures (Figure 15). Such structures could play key roles in the early stages of the origin of life.<sup>509</sup>



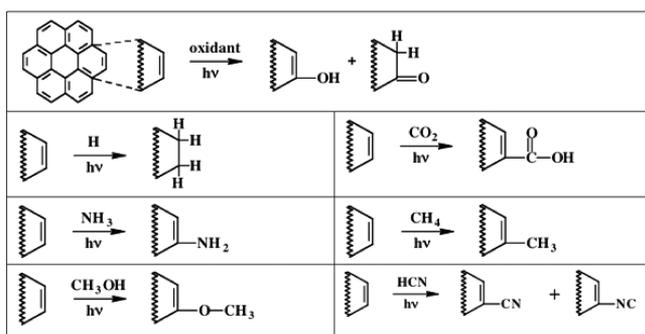
**Figure 16.** Images of vesicular structures formed when (a) residues created by the irradiation of astrophysical ice analogues, and (b) soluble organics extracted from the primitive meteorite Murchison, are put in liquid water. Adapted with permission from Figures 4 and 6 of ref 409. Copyright 2001 National Academy of Sciences.

If the organic residues produced from the irradiation of ices containing molecules like H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, and CO are placed in water, portions of the material spontaneously self-assemble into vesicular structures (Figure 16).<sup>409,510</sup> The spontaneous formation of vesicles indicates the presence of amphiphilic compounds in the residues. Separation of the residues into aliquots using HPLC yields multiple fractions which form vesicles, indicating that there the vesicles are not being made by a single amphiphilic compound but by a family of such compounds. These vesicles are also shown to fluoresce under UV light, but it is not clear whether the fluorescence is caused by the amphiphiles themselves or by fluorescent molecules incorporated into the vesicle walls.<sup>409</sup> The vesicular structures made from the residues are capable of trapping dyes

in their interiors via successive cycles of wetting and drying, i.e., these structures are not simply droplets of immiscible materials but have interior volumes.<sup>409</sup> Wetting/drying cycles of this sort have been proposed as a probable mechanism by which relatively impermeant molecules could be captured by membranes in prebiotic environments.<sup>511</sup>

Similar vesicular structures are made when the soluble fractions of some primitive meteorites, such as the carbonaceous chondrite Murchison, are placed in water (Figure 16).<sup>410,411</sup> However, it is not known what, if any, structural similarities there may be between the amphiphiles found in primitive meteorites and those observed in laboratory irradiation residues.<sup>409</sup> Indeed, the molecular compositions of the amphiphiles both observed in meteorites and made via ice irradiation and warm-up are currently unknown, but it is extremely unlikely they resemble the lipids used in modern biological membranes. Nonetheless, their presence in abundance in meteorites and laboratory ice photolysis residues suggests they could play a key role in the early development of life on planets.<sup>509</sup>

**Quinones and Other Functionalized PAHs.** As noted earlier, polycyclic aromatic hydrocarbons (PAHs) are among the most abundant molecules seen in space and are found in a wide variety of astrophysical environments.<sup>2,8–10</sup> At the low temperatures found in interstellar dense molecular clouds, PAHs are expected to be efficiently frozen out of the gas phase into icy grain mantles on more refractory dust grains.<sup>239</sup> Once incorporated into astrophysical ices, PAHs can participate in the same irradiation-driven chemistry processes as the other simpler molecules present, namely H<sub>2</sub>O, CO, CH<sub>3</sub>OH, NH<sub>3</sub>, etc. Because of the relatively high stability of the aromatic skeletal structure of PAHs, much of the chemistry associated with the radiation processing of PAHs in mixed molecular ices involves the replacement of peripheral H atoms with other functional groups<sup>159,235–237,241</sup> (Figure 17). The exact reaction path(s) for the formation of functionalized PAHs are not known, although it is likely that many of the paths involve PAH cations as intermediaries, as PAH cations are efficiently made when PAHs are irradiated in H<sub>2</sub>O-rich ices.<sup>128,130,207–214</sup>



**Figure 17.** The irradiation of PAHs in mixed-molecular ices can result in the substitution of peripheral H atoms with a multitude of different chemical functional groups.

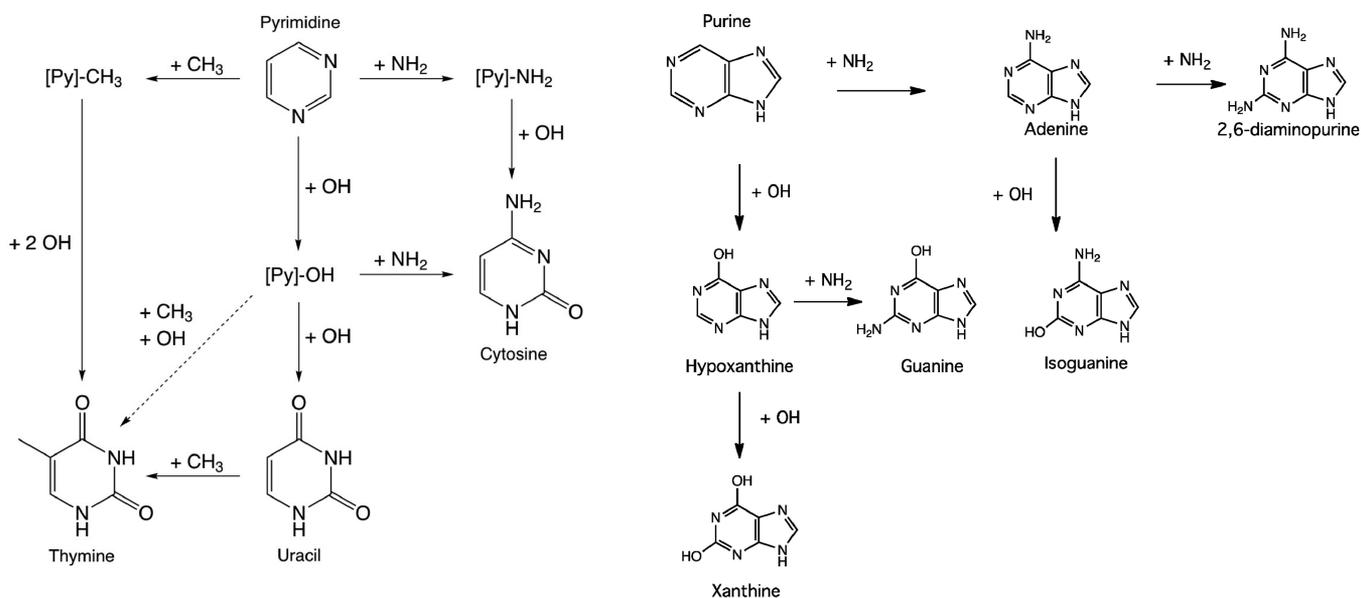
Because H<sub>2</sub>O and, to a lesser extent CH<sub>3</sub>OH, are abundant in interstellar ices, it is not surprising that the peripheral addition of O atoms to PAHs in the form of =O and -OH groups is common and that quinones and aromatic alcohols are major products.<sup>159,235–237,241</sup> In addition, when “bays” are present in the peripheral structure of the PAH, bridging O atoms result in the formation of aromatic ethers.<sup>159,237</sup> The

formation of quinones is of particular interest because this class of molecules play essential roles in biochemistry. For example, the UV photolysis of the two-ring PAH naphthalene in H<sub>2</sub>O ice produces 1,4-naphthoquinone as an abundant product.<sup>236</sup> Naphthoquinones perform key biochemical functions, such as electron transport and sulfur reduction, in organisms all across the tree of life.<sup>512,513</sup> In particular, 1,4-naphthoquinone is the structural backbone for several biomolecules, often referred to as menaquinones, including the vitamin K family, which consist of 2-methyl-1,4-naphthoquinone derivatives, and are known for their role in blood coagulation and in binding calcium to bones and other tissues.<sup>514</sup>

**Heterocycles and Nucleobases.** Another family of organic compounds that are of great astrobiological interest and that are found in both meteorites and laboratory residues is heterocycles and functionalized heterocycles, including nucleobases. Heterocycles are cyclic aromatic hydrocarbons in which one or several of the carbon atoms constituting the molecular backbone are substituted with heteroatoms, i.e., nitrogen and/or oxygen atoms. Nucleobases, the building blocks of the genetic material in RNA and DNA, are functionalized nitrogen heterocycles (hereafter, *N*-heterocycles) based on two molecular backbones: pyrimidine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>) and purine (C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>).

*N*-Heterocycles have been detected in abundance in meteorites,<sup>121–127</sup> indicating that they can be formed under totally abiotic conditions. However, despite the extensive search for such *N*-heterocycles in astrophysical environments in the gas phase, they have not been found to date,<sup>117–120</sup> and only an upper limit for the abundance of pyrimidine could be derived from these observations.<sup>119</sup> Nevertheless, because of their abundant presence in meteorites, several mechanisms for their formation in astrophysical environments have been proposed, both experimentally and theoretically. One proposed mechanism involves a pathway similar to that for the formation of PAHs, i.e., the condensation of three acetylene (C<sub>2</sub>H<sub>2</sub>) molecules in the gas phase,<sup>515,516</sup> in which one or several of these C<sub>2</sub>H<sub>2</sub> have been replaced with HCN or HNC.<sup>116,517,518</sup> Other proposed mechanisms include the pentamerization of HCN into the purine base adenine.<sup>519,520</sup> Recent experiments have also shown that both *N*- and *O*-heterocycles can form from the substitution of carbon atoms in the backbone of PAHs with nitrogen and oxygen atoms when small PAHs such as benzene and naphthalene are mixed with H<sub>2</sub>O + NH<sub>3</sub> ices at low temperature (<20 K) and subjected to UV radiation,<sup>244</sup> although the exact molecular mechanism has not been determined. These experiments resulted in the formation of pyridine (C<sub>5</sub>H<sub>5</sub>N) from the substitution of carbon atoms with N atoms in benzene (C<sub>6</sub>H<sub>6</sub>), as well as quinolines (C<sub>9</sub>H<sub>7</sub>N) and coumarin (C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>) isomers from the substitution of carbon atoms in naphthalene (C<sub>10</sub>H<sub>8</sub>) with N and O atoms, respectively. However, no pyrimidine or purine were detected in these experiments.<sup>244</sup>

When the *N*-heterocycles pyrimidine and purine are present in laboratory astrophysical ice analogues dominated by H<sub>2</sub>O and containing NH<sub>3</sub> and CH<sub>4</sub> and are subjected to UV radiation at low temperature, all the canonical nucleobases used in modern biology as genetic material for RNA and DNA, namely uracil (RNA), cytosine (RNA/DNA), thymine (DNA), adenine (RNA/DNA), and guanine (RNA/DNA), as well as a number of their isomers, can be formed.<sup>245,246,405–408</sup> Finally, a very recent study showed for the first time that several pyrimidine- and purine-based nucleobases can be



**Figure 18.** All of the five nucleobases and many of their isomers can be produced by side group addition reactions when pyrimidine (left) and purine (right) are exposed to ionizing radiation while frozen in ices containing simple molecules known to be in astrophysical ices.

formed from the UV irradiation of simple  $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{CH}_3\text{OH} = 5:2:2:2$  ice mixtures at 10 K,<sup>363</sup> demonstrating that all building blocks of modern biological compounds can form from the UV irradiation of simple ice mixtures under astrophysical conditions.

All of these experimental results on the formation of *N*-heterocycles and nucleobases, together with their presence in meteorites, highlight the complexity and the important role of ice photochemistry in the formation of complex organic compounds of significant astrobiological interest. In particular, it was found that the UV irradiation of pyrimidine in realistic astrophysical ice mixtures consisting of  $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{NH}_3$  and  $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CH}_4 + \text{NH}_3$  results in the formation of large amounts of uracil, some cytosine, and very little thymine.<sup>408</sup> These results, confirmed by quantum calculations,<sup>521</sup> in which thymine may be a minority compound among all the organics delivered to the early Earth via meteorites,<sup>522–525</sup> may explain why the first genetic material for all life on Earth was based on RNA, which has uracil and no thymine, and not DNA, which has thymine and no uracil. Such a scenario leading to the RNA-world hypothesis has been extensively discussed in the literature.<sup>526–528</sup>

Comprehensive quantum chemistry work has been performed to unravel the chemistry of formation of the pyrimidine- and purine-based nucleobases, e.g., uracil, cytosine, thymine, adenine, guanine, as well as their isomers and other variants, by simulating reactions in gas- and condensed-phase environments when pyrimidine and purine are mixed with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_3\text{OH}$  ices.<sup>521,529,530</sup> Challenges for the theoretical calculations of the formation mechanisms of the nucleobases is in optimizing the balance between accuracy and affordability of the calculations. The sizes of these systems are too large for more accurate coupled cluster methods, apart from a few specific cases. These systems are better studied using density functional theory (DFT) and Møller–Plesset perturbation theory methods. Theoretical calculations starting from acetylene and hydrogen cyanide and resulting in the formation of pyrimidine and purine bases were carried out under simulated gas-phase conditions that are more relevant to

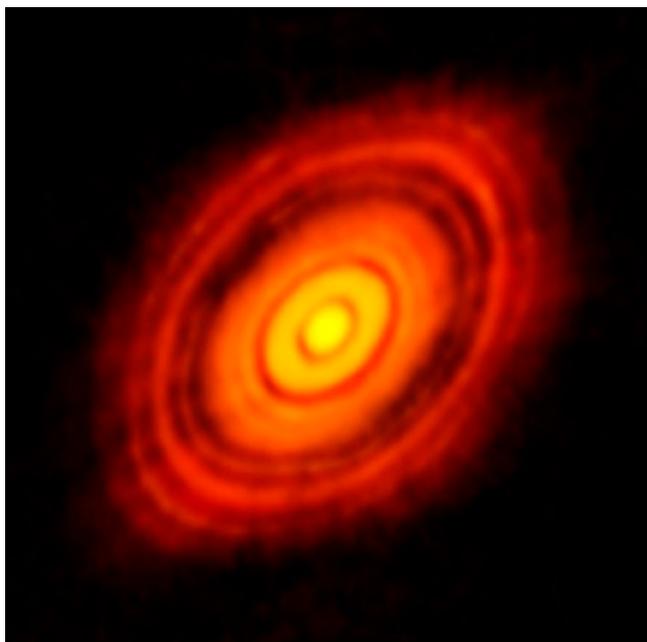
stellar winds from aging stars (section 2.1) and dense molecular clouds (section 2.3).<sup>116,518</sup> DFT and Møller–Plesset perturbation theory methods (see section 2.3.4.3) were used to study systems in which condensed-phase purine and pyrimidine were mixed in astrophysical ice analogues and subjected to ionizing radiation, resulting in the formation of nucleobases<sup>521,529,530</sup> (Figure 18).

The calculations reveal that (i) the formation of the nucleobases uracil, cytosine, thymine, adenine, and guanine is energetically and kinetically favorable, (ii) the gas-phase mechanism of their formation is ineffective, and the presence of several water molecules is necessary, so that such reactions must take place in condensed-phase  $\text{H}_2\text{O}$ , (iii) mechanisms involving a cationic route in which the purine or pyrimidine cation reacts with photoproducts from ice photolysis should dominate, and (iv) the cationic formation mechanism is facilitated by (and only by) an  $\text{H}_2\text{O}$  matrix. Therefore, in the reactions taking place in these experiments, the  $\text{H}_2\text{O}$  ice matrix plays two important roles: it is a supplier of reactants (H atoms and  $\bullet\text{OH}$  radicals), and it serves as a catalyst by solvating the products. However, the  $\bullet\text{OH}$  radicals generated in these systems inhibit reactions between pyrimidine/purine with other reactants such as methyl or amino groups from the photodecomposition of  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ , respectively. Quantum chemical calculations predict that the formation of uracil and cytosine from pyrimidine in ices are rather easy, while the formation of thymine is not because it requires one additional reaction step and because  $\bullet\text{OH}$  radicals compete with  $\bullet\text{CH}_3$  radicals to react with pyrimidine,<sup>521,529</sup> which is supported by experimental data.<sup>405–408</sup> Similarly, adenine, guanine, isoguanine, hypoxanthine, and a whole variety of other purine-related products have been predicted to be synthesized based on gas-phase as well as condensed-phase calculations of purine mixed in astrophysical ice analogues<sup>530</sup> and supported by experiments.<sup>245,246</sup>

## 2.4. Protostellar Disks and the Delivery of Organics to Planets

When the concentration of material in a dense molecular core reaches a critical value, it can collapse to form a new star.<sup>90,531</sup>

Angular momentum in the material in the core causes the cloud to flatten as it collapses, and this creates a protostellar disk of dust, gas, and ice surrounding the forming protostar (Figure 19).<sup>532,533</sup> Ultimately the radiation and stellar jets



**Figure 19.** An image of the disk surrounding the star HL Tau. HL Tau is a very young star surrounded by a disk of gas and dust. The ring gaps in the disk are thought to be associated with the formation of larger bodies in the disk. Credit: ALMA (NRAO/ESO/NAOJ); C. Brogan, B. Saxton (NRAO/AUI/NSF).

associated with the formation of new stars leads to the disruption of the original interstellar cloud.<sup>534</sup> The dust and gas densities in the protostellar disks that surround forming stars are significantly higher than in the general dense cloud medium, and, as a result, disks are expected to be good environments for additional chemistry.<sup>27</sup>

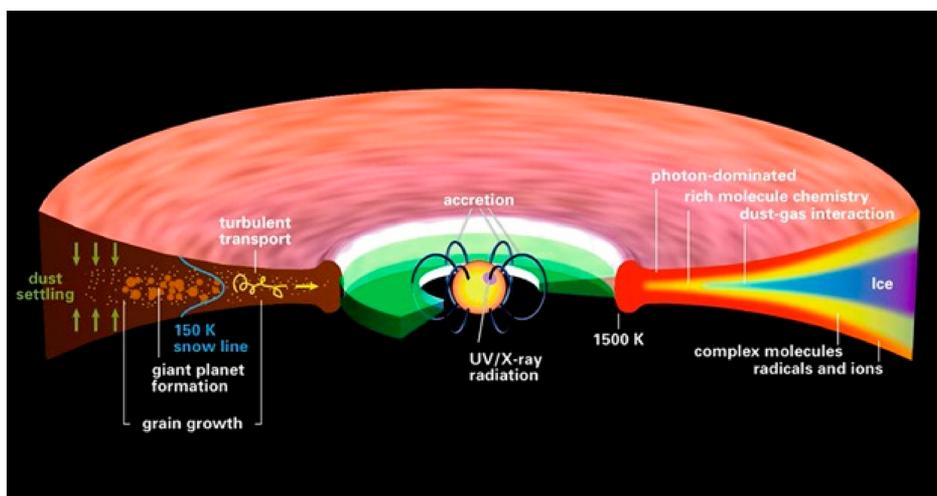
**2.4.1. Conditions in Protostellar Disks.** Physical and chemical conditions in protostellar disks vary over wide ranges, depending on location within the disk, i.e., the distance from the central forming star, the vertical scale height within the disk, and time. For example, conditions at the inner edge of the disk near the forming star can involve temperatures high enough to vaporize rocks, while the midplane of the middle and the outer parts of the disk can be at temperatures as low as 10 K.<sup>27</sup> Temperatures generally increase as you approach the central star, and at any given distance from the star they increase with increasing vertical scale height within the disk.

Given this wide range of environments, many of the chemical processes described for interstellar clouds can also happen in disks at some locations and times. For example, gas-phase and gas-grain reactions much like those that can occur in dense molecular clouds are expected to also occur in protostellar disks.<sup>27,535</sup> Because of the higher densities and, in some locations, temperatures, many of these processes occur at an accelerated rate compared with interstellar conditions.

The effects of radiation are somewhat different in protostellar disks, however. Because of the shorter time scales, relatively high densities, and optical depths of these disks during their early stages, radiation effects are largely confined to the inner edge and surface portions of the disk. Because disks flare in the vertical direction with increasing distance from the central star (Figure 20), most of their surfaces are exposed to radiation from the central star as well as from the general surrounding radiation field. Mixing of materials within the disks also results in materials cycling between zones having different temperatures and radiation fluxes, which can result in different materials experiencing very different thermal and radiation processes.

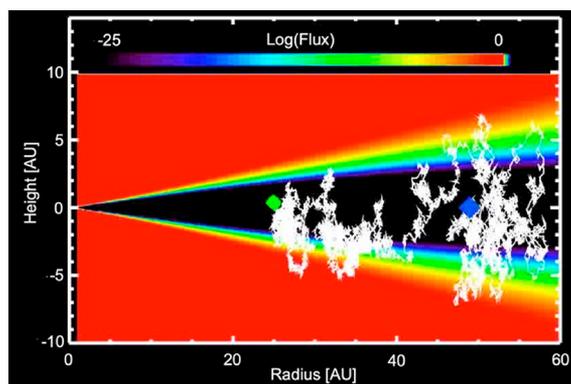
In the sections that follow, we concentrate on those chemical processes that differ in some significant way from similar processes taking place in dense molecular clouds.

**2.4.2. Ice Photochemistry.** As noted above, materials in protostellar disks are in constant dynamic motion. In addition to orbiting the central protostar, turbulence, and the exchange of angular momentum also cause them to move vertically in the disk and to move in toward or away from the central



**Figure 20.** Protostellar disks contain a wide variety of environmental conditions that change as the disk evolves. Temperatures can range from as low as  $\sim 10$  K in the midplane of the disk far from the star up to temperatures near the central forming star that are hot enough to vaporize rock-forming minerals. Similarly, the radiation field is very low in the disk midplane but grows more intense as the inner edge or surface of the disk are approached. Reproduced with permission from ref 27. Copyright 2013 American Chemical Society.

protostar.<sup>29</sup> As a result, small grains within the protostellar disk can follow semistochastic paths that span large portions of the disk. As particles move vertically in the disk, they can undergo multiple episodes in which they condense volatile ice mantles near the midplane of the disk cycling, carry these ices up to heights where the optical depth of the disk is small enough to allow photolysis of the ices to occur, and then descend again to accumulate more ice, and so on. Modeling of this process suggests that for typical small grains in the disk, ice mantles can be exposed to radiation doses that exceed those in typical dense molecular clouds by orders of magnitude<sup>29</sup> (Figure 21).



**Figure 21.** Individual dust grains in protostellar disks move through the disk as the disk evolves. Typical dust grains can make multiple excursions between the disk midplane where low temperatures allow ice mantles to form on the grain and the disk's surface where these ices can be irradiated and sublimated away. This figure shows an example path for one of a large suite of particle trajectories described in ref 29. The protostar is located at coordinates (0,0), and the blue and green diamonds correspond to the particle's starting and ending locations, respectively.

Thus, all of the same ice irradiation processes described for dense clouds are expected to occur in protostellar disks, although they may process a higher fraction of volatiles with higher total radiation doses over shorter time scales. With the exposure of more molecules to large numbers of photons, it is possible that ice irradiation in disks could lead to the formation of larger and more complex products than is typical in dense clouds.

**2.4.3. Post-Sublimation Irradiation Processes.** The movement of grains in protostellar nebulae is expected to result in many particles being lofted to sufficient heights above the disk midplane that they will warm to temperatures sufficient to result in the sublimation of any ice mantles they may have.<sup>29</sup> This will allow ions and radicals made within the ices to find each other, interact, and form more complex organic species. While some of these grains will subsequently descend toward the disk midplane and reaccumulate new ices, some particles will remain at disk heights with smaller optical depths, where the previously formed organics will continue to be exposed to ionizing radiation (Figure 21).

Laboratory experiments have been carried out to imitate these additional exposures by exposing previously made ice photolysis residues to additional UV or X-ray radiation. These experiments show that additional radiation exposure of the residues results in the elimination of hydrogen and the conversion of aliphatic bonds into aromatic bonds.<sup>229</sup> C,N,O-XANES spectra of these reirradiated residues look very similar to those of the insoluble organic material (IOM) that

dominates the carbonaceous fraction of primitive meteorites, suggesting that this process may be responsible for processing much of the C-containing components of meteorites. Furthermore, experiments of irradiation of laboratory ice photolysis residues with additional X-ray and UV/EUV photons showed measurable D fractionations,<sup>430,431</sup> indicating that protostellar disk processes may also be related to the isotopic anomalies seen in IDPs, meteorites, and comet samples (see section 2.5).

**2.4.4. Implications for Meteoritic Materials.** The many processes described previously (circumstellar, interstellar, and protostellar) all play a role in the formation and evolution of organic materials that can ultimately end up being incorporated into aggregating planetesimals in the forming planetary system. In the case of our own Solar System, these materials can now be found in comets and asteroids and can be collected on Earth in the form of interplanetary dust particles (IDPs) and meteorites. Thus, it is reasonable to compare the materials expected from the previously described processes with the organic materials in cosmic dust, meteorites, and samples returned by spacecraft from comets and asteroids. Items in which interstellar and protostellar processes may play key roles in establishing some of the more prominent characteristics of meteoritic organics, including the abundance of insoluble organic material,<sup>345,391,396,536–546</sup> the trapping of noble gases,<sup>547–557</sup> isotopic anomalies in D and <sup>15</sup>N,<sup>418,558–561</sup> and the presence of molecules of astrobiological relevance that could play key roles in the origin and evolution of life.<sup>121–127,410,411,440–450,469,522–525</sup> For additional discussion about the nature of organics in extraterrestrial samples, see ref 472.

**2.4.5. Delivery to Planetary Surfaces via Dust and Meteorites.** Once organic materials are incorporated into small bodies like comets and asteroids in a new planetary system, they can then be delivered to planets. The importance of the arrival of these materials to subsequent chemistry on planetary surfaces depends in large part on the circumstances of their arrival. The collisions of entire asteroids or comets with a planet are energetic events that will result in the destruction of much of the organic materials in the impactor as well as severely modify many of those on the planet, although some parent body organics are expected to survive and the energy of the impact can also create new compounds.<sup>562–565</sup> Under such circumstances, much of the molecular diversity of the original impactor may be lost, although their constituent components (H, C, N, O, etc.) will be added to the planet's inventory. In this case, the role of previous astrochemistry may largely only be to take biologically important elements like H, C, N, and O and convert them from simple molecules like H<sub>2</sub>, CO, etc., that would not originally have been accreted by the planet and lock them down in the form of more complex materials capable of being collected into a comet or asteroid and subsequently delivered to the planet. Under these circumstances, the main importance of these materials is in establishing the total reservoir of the biological elements of the planet.

However, much of the material accreted by a forming planet, particularly in its later stages of formation, comes from the accretion of smaller bodies in the form of dust and meteorites, and this process continues long after the primary planetary formation process is over. Even today, 4.5 billion years after its formation, the Earth continues to accrete material in the form of cosmic dust and meteorites, and the rate of accretion of these types of objects was much higher in the planet's early

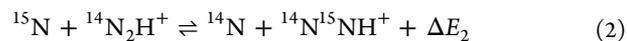
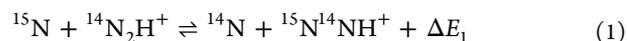
history.<sup>566</sup> In the case of planets with atmospheres, the accretion of dust particles and meteorites is a particularly effective way of delivering premedic organics to planetary surfaces without destroying them<sup>522–525</sup> (Figure 22). Indeed, it is apparent from the study of contemporary interplanetary dust particles and meteorites that complex organics can survive through the accretion process (see, e.g., ref 472). Thus, at least a portion of the molecular complexity produced by preplanetary chemistry should be delivered to the surfaces of young planets, which suggests that newly formed planets can be expected to be seeded with complex organics of the types described previously (section 2.3.4.4), including a multitude of chemical species of astrobiological importance (see section 3).

## 2.5. Isotopic Effects

Nonterrestrial isotopic ratios are seen in many chemical elements in extraterrestrial materials. Many of these are associated with presolar grains found in extraterrestrial samples that are due to nucleosynthetic processes associated with the formation of dust in the circumstellar environments of aging stars. These nucleosynthetic processes can yield distinctive, nonterrestrial isotopic ratios in many elements, including C, N, and O, that depend on the type of star and nucleosynthetic processes responsible.<sup>14,15</sup> However, in this paper, we will concern ourselves only with isotopic effects associated with chemistry, not nucleosynthesis, i.e., we will concentrate on interstellar and protostellar chemical fractionation processes, not stellar and circumstellar nucleosynthetic processes. In particular, we will concentrate on D/H and <sup>15</sup>N/<sup>14</sup>N fractionations because these are the most common isotopic anomalies seen in extraterrestrial materials like IDPs, meteorites, and comet samples.<sup>418,558–561</sup> Both the D and <sup>15</sup>N enrichments appear to be carried by organic materials and are often found concentrated in microscopic “hotspots” within meteorites, IDPs, as well as *Stardust* samples.<sup>391,418,559–561</sup>

There are a number of gas-phase, gas-grain, and solid-state processes occurring in space that can fractionate hydrogen and nitrogen, most of which favor the accumulation of the heavier isotope in the more complex products,<sup>567–569</sup> although gas-phase processes for <sup>15</sup>N fractionation in organic materials have recently been called into question, which will be discussed below. The majority, but not all, of these processes occur at very low temperatures, where the different zero-point energies of the isotopes can result in significant fractionation during reactions. In the sections below, we discuss the isotopic fractionations that can occur in space via gas-phase, gas-grain, and photolytic reactions.

**2.5.1. Gas-Phase Chemistry.** As indicated above, there are many solar system materials that have been found to contain very small “hotspots” of D and <sup>15</sup>N enhancement relative to the terrestrial abundance. The largest <sup>15</sup>N enhancement for meteoritic material has  $\delta^{15}\text{N} > 3000\%$ <sup>560</sup> where  $\delta^{15}\text{N} = 1000 \times [({}^{15}\text{N}/{}^{14}\text{N})_x / ({}^{15}\text{N}/{}^{14}\text{N})_{\oplus} - 1]$  and  $({}^{15}\text{N}/{}^{14}\text{N})_{\oplus}$  is the Earth’s atmospheric isotopic ratio of 0.003678,<sup>570</sup> while  $\delta^{15}\text{N} > 1000\%$  has been observed in IDPs and *Stardust* samples.<sup>418,559,561</sup> Astronomers, astrochemists, and astrochemical modelers have been trying to explain these excesses for decades. Rodgers and Charnley<sup>571</sup> obtained some promising results from their chemical reaction network models for dense molecular clouds at low temperatures based on <sup>15</sup>N exchange reactions that had been proposed earlier by Terziewa and Herbst.<sup>572</sup> These key exchange reactions are as follows:



where the exothermicities are  $\Delta E_1 = 0.23 \text{ kJ mol}^{-1}$  and  $\Delta E_2 = 0.30 \text{ kJ mol}^{-1}$ . The exothermicities are very small, being driven only by the difference in the zero-point energies of the  $\text{N}_2\text{H}^+$  entities in reactions 1 and 2. These very small exothermicities are also why the exchange reactions 1 and 2 only become important at very low temperatures. Rodgers and Charnley<sup>571</sup> obtained values of  $\delta^{15}\text{N} > 3000\%$  in the upper layer of ammonia ice, with some models exceeding  $\delta^{15}\text{N} > 10\,000\%$ , and they concluded that these results may help to explain the <sup>15</sup>N hotspots seen in collected extraterrestrial materials. However, Roueff et al.<sup>573</sup> later published a paper where, among other things, they examined the entrance channel for reactions 1 and 2 (and similar reactions) using high level ab initio calculations and, not surprisingly, found very large barriers, on the order of  $\sim 100 \text{ kJ mol}^{-1}$ , meaning that these reactions would not proceed at low temperatures. Roueff et al.<sup>573</sup> also made a significant attempt to improve the zero-point energies for the various isotopic exchange reactions including anharmonic effects and updated  $\Delta E_1$  and  $\Delta E_2$  to be 30.4 and 38.5 K, respectively. Since then, Wiström and Charnley,<sup>574</sup> and more recently Loison et al.,<sup>575</sup> have revisited <sup>15</sup>N enhancement using their chemical reaction networks using the corrections of the Roueff et al.<sup>573</sup> study and have found no significant <sup>15</sup>N enhancement in N-containing species. Thus, it now appears that neither ion–molecule nor atom–molecular ion gas-phase chemical reactions can explain the significant <sup>15</sup>N enrichment that is found in the primitive solar system materials.

It has been known for many years that D fractionation occurs through ion–molecule reactions in the gas phase at low temperatures.<sup>568,569</sup> An example of how this process works can be understood by considering the cyclopropenylidene (*c*-C<sub>3</sub>H<sub>2</sub>) molecule. When a D<sup>+</sup> is added to *c*-C<sub>3</sub>H<sub>2</sub> through an ion–molecule reaction, the *c*-C<sub>3</sub>H<sub>2</sub>D<sup>+</sup> cation forms, and when that cation is involved in another ion–molecule exchange reaction, the *c*-C<sub>3</sub>HD molecule is preferentially formed. Deuterium enhancement in more complex molecules occurs because the zero-point energy of the D-containing molecule is smaller relative to the H-containing species, and thus the D/H exchange reactions are exothermic, similar to reactions 1 and 2.<sup>567,576,577</sup> However, the D/H mass ratio is essentially two, so the C–D, N–D, and O–D vibrational frequencies are significantly lower than their C–H, N–H, and O–H analogues, and thus the effect on the zero-point energies is much larger. For example, Roueff et al.<sup>573</sup> show that the zero-point energy difference for CD/CH is 535.5 K, while that for ND/NH is 621.6 K. However, the larger exothermicity in D/H exchange reactions is not the reason these reactions proceed at low temperatures while the <sup>15</sup>N exchange reactions do not. Instead, these reactions occur because in the D/H ion–molecule exchange reactions it is really D<sup>+</sup> and H<sup>+</sup> that are being exchanged so there is not a pair of electrons being broken and formed simultaneously as must occur in the <sup>15</sup>N exchange reactions.

The other type of gas-phase reactions that can occur in D/H exchange are exoergic reactions involving radicals. These can still proceed at low temperatures provided there is no barrier, or that any barrier is “submerged” below the reactants which can occur when there is an initial association complex. As

indicated, the exothermicity of all of these D/H exchange reactions is still small, so they become more important and lead to more significant fractionation at low temperatures, generally as the gas temperature falls below  $\sim 70$  K.<sup>578</sup>

Finally, it is important to note that the astronomical detection of deuterated molecules in the gas phase shows that the abundance of multiply deuterated species relative to singly deuterated species is sufficiently large to be difficult to explain solely by gas-phase ion–molecule reactions. This suggests that D enrichments seen in gas-phase molecules may not be due solely to gas-phase chemical processes, and it is generally assumed that some of the observed fractionations are caused by separate grain-related processes (for example, gas–grain reactions; see following section) that subsequently liberate molecules into the gas phase.<sup>573,579</sup>

**2.5.2. Gas–Grain Chemistry.** Gas–grain chemistry is expected to produce isotopic enrichments, in particular in deuterium (D), in the icy mantles from the mass fractionation that becomes significant at low interstellar temperatures (10–100 K).<sup>567,580</sup> In these environments, enrichment in heavier isotopes is believed to result mainly from gas accretion processes. At very low temperatures, chemical reactions are mostly limited by the mobility of the accreting species, with smaller species expected to be more mobile than larger ones. Therefore, H atoms, that are adsorbed on the surface or released from photoinduced bond breaking of hydrogenated species, are expected to be the most mobile species. When two H atoms meet and react, the resulting H<sub>2</sub> molecule can desorb from the grain, leading to a decrease in the hydrogen concentration in the ice (indeed, this is believed to be the primary formation process of molecular hydrogen in the universe).<sup>143–148</sup> Because deuterium is twice as heavy as hydrogen, D atoms are less mobile, and thus less reactive, decreasing the probability of D atoms subliming from the grain, and therefore increasing the concentration of deuterium.

However, ice mantles may also contain atomic N, O, and C, and hydrogen addition to these species results in the production of simple hydrides like NH<sub>3</sub>, H<sub>2</sub>O, and CH<sub>4</sub>, and these species can end up concentrating D relative to H. Models of this process suggest that it can produce fractionations that result in D/H ratios in the icy mantles as high as 0.1 for small molecules such as H<sub>2</sub>O and CH<sub>3</sub>OH,<sup>567,580–585</sup> i.e., values that are much higher than enrichments resulting from ion–molecule reactions in the gas phase. Because the ices also contain a larger proportion of the total mass of complex molecules in dense clouds, this process may be one of the major ones for producing D/H fractionations in dense clouds (more details can be found in the citations provided).

A similar effect is likely to occur for other atoms, although this effect may be significantly limited due to the small relative differences between the mass of the isotopes for other elements of interest (<sup>13</sup>C/<sup>12</sup>C, <sup>15</sup>N/<sup>14</sup>N, <sup>17</sup>O/<sup>16</sup>O, <sup>18</sup>O/<sup>16</sup>O), their lower abundances, and the fact that their most likely initial reactions will be with hydrogen.

Finally, thermal and photoinduced desorption could also result in an isotopic fractionation. Indeed, because heavier isotopes have higher masses, their desorption efficiencies may be lower, resulting in an enrichment in heavier isotopes on the grains. Such an effect is likely to be more significant for D enrichment, as deuterium is twice as heavy as hydrogen.<sup>583,586,587</sup> Therefore, this process is expected to affect more significantly molecules with a higher number of hydrogen

atoms, but it could also take place for heavier elements to a smaller degree.<sup>588</sup>

**2.5.3. Photolytic Chemistry.** There are several photolytic processes that occur in space that are expected to yield D enrichments in more complex organic materials. Most, but not all, require chemistry at low temperatures.

One process that does not require low temperature involves unimolecular dissociation reactions in gas-phase PAHs that absorb energetic photons.<sup>2,567,568,589</sup> As noted earlier, the C=C multiple bonding and  $\pi$  electrons of PAHs makes them much more stable against photolytic disruption in space than most other molecules. This allows PAHs to survive in astrophysical environments where other species would quickly be destroyed, and explains why PAHs are one of the most ubiquitously distributed and abundant classes of molecules in the interstellar medium.<sup>2,8–10</sup> However, while PAHs are relatively immune to complete photodestruction by interstellar UV photons, individual PAHs, particularly smaller ones, may still absorb UV photons that contain more energy than they can vibrationally accommodate and one or several bonds will break. The most likely bonds to break are the peripheral C–H bonds. Because of the zero-point energy difference between C–D and C–H bonds, the rate of D loss from interstellar PAHs by this process should be lower than that of H. Because both H and D will return to this molecular site from the more massive ambient gas phase, repeated processing is expected to gradually enrich interstellar PAHs in D relative to the ambient gas. At steady-state equilibrium, the fraction of peripheral D relative to H is expected to be 3 times the local gas-phase ratio of D/H, which can range from  $10^{-5}$  to  $10^{-3}$ , in interstellar photodissociation regions and, at least for small PAHs, in dense clouds.<sup>2,567</sup>

This process differs from enrichment by ion–molecule and gas–grain reactions in several ways. First, low temperatures are not required to produce fractionations via this process. Second, the extent of the D enrichment depends critically on the PAH size and is expected to be most significant for PAHs in the range of sizes between C<sub>10</sub>H<sub>8</sub> (naphthalene) and C<sub>42</sub>H<sub>18</sub> (hexabenzocoronene). Deuterium enrichment is not expected in benzene because it is not stable in the interstellar radiation field and because enrichment in PAHs having more than  $\sim 40$  carbon atoms is not expected due to the fact that larger PAHs have large numbers of vibrational modes that can accommodate the maximum energy of typical interstellar UV photons and are therefore stable against photolytic bond cleavage.

Deuterium enrichment of complex organics can also occur during the irradiation of astrophysical ices in interstellar cloud and protosolar disk environments. As noted earlier, many of the molecular species that condense out into icy grain mantles in cold environments may be previously enriched in D and/or <sup>15</sup>N via processes such as gas-phase ion–molecule reactions (section 2.5.1) and gas–grain reactions (section 2.5.2). Once in the ice, these molecules can serve as a D- and <sup>15</sup>N-enriched reservoir from which other species can be themselves enriched. As discussed in section 2.3.4, irradiation and warming of these ices leads to the formation of new, more complex molecules. Laboratory studies of astrophysically relevant mixed-molecular ices in which some of the original species are D- or <sup>15</sup>N-enriched have shown that the D and <sup>15</sup>N end up in many of the reaction products.<sup>23,164,244,485,568,590,591</sup> Thus, ice photolysis can propagate previous fractionations into new, more complex molecular species. Finally, processes such as the aromatization of aliphatic compounds formed from photoprocessed ices at

low temperature may also lead to an enrichment in D. Indeed, aromatization of aliphatic carbon bonds drives H atoms away, and at low temperature, this may result in a loss rate of H atoms higher than the loss rate of D atoms, leading to an enrichment in D. However, such processes have not been observed experimentally to date.

At dense cloud temperatures and in the colder portions of protostellar disks, PAHs will condense onto refractory dust grains along with most other gas-phase species where they will be subjected to the same radiation processing as the other ice components (section 2.3.4.4). Laboratory irradiation simulations of PAH-bearing interstellar ice analogues containing D-enriched H<sub>2</sub>O show that UV photolysis results in rapid D enrichment of the PAHs through aromatic D → H exchange, D atom addition, and exchange through keto–enol tautomerism.<sup>235</sup> Each of these processes produce different compounds with characteristic deuteration patterns and D labilities.<sup>568</sup> Simple D → H exchange reactions result in D-enriched PAHs in which the D resides in relatively nonlabile locations, while D atom addition reactions result in D-enriched H<sub>n</sub>-PAHs in which the D resides in relatively nonlabile aliphatic rings attached to aromatic rings. In contrast, enrichment via keto–enol tautomeric exchange results in the D atoms being located on rings in sites that contain oxygen atoms and that are relatively labile. Deuterium enrichments produced in aromatic species in this manner are expected to occur largely independently from the PAH molecular size but should show specific regiochemical behaviors.

Similar processes can happen for the propagation of <sup>15</sup>N enrichments in simple ice-phase molecules into more complex organics. When PAHs are present in the ices, the <sup>15</sup>N can be passed along in the form of N-containing side groups substituting for peripheral H atoms or can be substituted for skeletal C atoms in the PAHs to form heterocycles.<sup>244</sup> If heterocycles are already present in the ice, photon-driven exchange reactions can also swap N atoms between the <sup>15</sup>N-enriched ice and skeletal N in the heterocycles.<sup>244</sup>

The photolysis-driven isotopic processes described above for ices involve the forward propagation of previous fractionations into new, more complex molecular species. However, there is some evidence that ice photolysis can also produce intrinsic fractionations, at least for D. The organic residues resulting from photoprocessing of interstellar/protostellar ice analogues having normal terrestrial isotopic compositions have been shown to contain bulk D enrichments, and, in several cases, specific molecular products have been shown to be enriched in D as well.<sup>592,593</sup> The exact mechanism(s) that result in this fractionation are not currently understood. It is known that the irradiation of interstellar ice analogues results in the production of H atoms that combine to form H<sub>2</sub> that subsequently escapes from the ice.<sup>594,595</sup> If this H<sub>2</sub> is isotopically light, then this would result in an overall increase in the D/H ratio in the remaining ice.

Finally, experiments have shown that when astrophysically relevant organic materials are processed by ionizing radiation, the resulting materials can show measurable D enrichments. For example, electron irradiation of organic precursors having an initial terrestrial isotopic composition have been shown to produce D fractionations comparable to those seen in primitive meteorites like Orgueil.<sup>596</sup> Similarly, experiments in which organic residues produced from the UV irradiation of realistic astrophysical ice analogues were themselves irradiated with extreme UV or X-ray photons showed measurable D

enrichments.<sup>430,431</sup> The process(es) responsible for the fractionations are not fully understood, but one possibility is that the conversion of aliphatic carbon into aromatic carbon, as was previously observed for residues subjected to X-ray radiation on a scanning transmission X-ray microscope (STXM),<sup>229</sup> may result in the loss of H atoms in higher proportions than D atoms via mass fractionation.

Interestingly, D enrichment can happen even in the absence of organic compounds. For example, the electron irradiation of thin films of amorphous silica, amorphous “serpentine”, and pellets of crystalline muscovite have been demonstrated to produce large H loss attended by moderate D enrichment of the solid residue.<sup>597</sup> The calculated fractionation factor is consistent with a kinetically controlled fractionation during the loss of hydrogen.

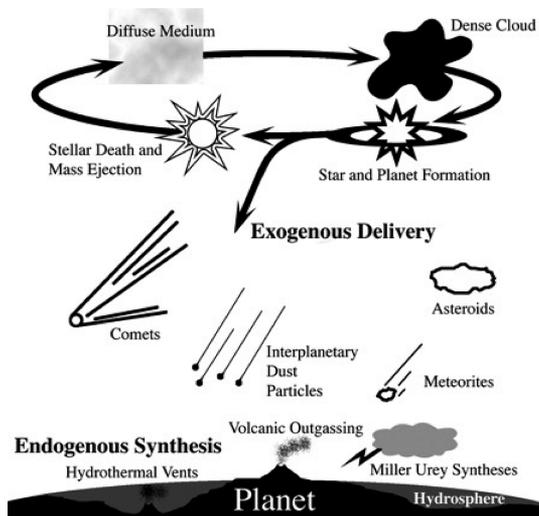
It is not currently known if the irradiation of interstellar ice analogues can result in the production of intrinsic <sup>15</sup>N/<sup>14</sup>N fractionations.

### 3. IMPLICATIONS FOR ASTROBIOLOGY

This review has shown that chemical processes in astrophysical environments result in the production of a wide variety of molecules, most of which are organic in nature and many of which are of direct interest for astrobiology, i.e., the study of the origins, evolution, distribution, and future of life in the universe.<sup>598</sup> Although gas-phase chemistry in these environments does take place and leads to the formation of small compounds, due to the very low densities in the ISM and the high radiation fields likely to photodissociate newly formed compounds, gas-phase chemistry is an inefficient process to make complex molecules, even at the time scales of the lifetime of molecular clouds. Chemistry of ices induced via ionizing radiation on the surface of small, cold grains thus appears like a more efficient way of forming new, more complex compounds because species are closer to each other and can thus react more efficiently with each other, and because ice matrices may behave like a shield to newly formed molecules. At the low temperatures of molecular clouds (typically, <20 K), reactions are slow and limited by the diffusion of species through the ice matrices. However, small species such as H hydrogen atoms, which are created from the photodissociation of icy components, including H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>3</sub>OH, are mobile enough even at these low temperatures to react with other species. Photoinduced ionization and bond breaking are also more efficient in ice matrices compared with the gas phase because, at low interstellar temperatures, some ions and radicals can survive long enough to participate in chemical reactions. Interactions with the ice matrix itself may help stabilizing those reactive species. In addition, the presence of radicals in ices does enhance the probability of forming more complex molecules, as radical recombinations are typically barrierless and thus can occur even at very low temperature without any additional energy input.

Therefore, processing of ices with energetic photons and/or particles is believed to be an important source for the organic molecules that are incorporated into the Solar System as well as probably in other planetary systems. Such organics are also subjected to harsh radiation during the formation of the Solar System, during the protosolar nebula stage. However, particles inside the nebula are subjected to turbulent movements, from the middle of the protoplanetary disk plane to the edges of the disk and from the close neighborhood of the forming star to the outskirts of the disk.<sup>29</sup> During this stage that lasts several

millions of years, particles experience a wide range of temperatures and radiation exposure, up to several orders of magnitude higher than the typical doses they are subjected to in the ISM, in which ices can condense, be irradiated, sublime away, expose newly formed species that are themselves irradiated, recondense, and so on. Those cycles may lead to the formation of robust, complex organic molecules that end up in asteroids and that can then be delivered to planets via meteoritic bombardment<sup>522–525</sup> (Figure 22).



**Figure 22.** Vast amounts of material are constantly cycled between various environments in our galaxy and the chemical processes in these environments can form a wide variety of organic materials, some of which are of astrobiological interest. Whenever a new star with a planetary system forms, a fraction of this material ends up being incorporated into solid bodies that ultimately end up being delivered to newly formed planets in the form of dust, meteorites, and large impactors. This feed stock material is then available to participate in additional planetary chemical processing and to play a role in the origin of life. Figure courtesy of Jason Dworkin.

### 3.1. Compounds of Astrobiological and Prebiotic Interest

Among the wide variety of organic compounds produced from ices processed by energetic photons and/or particles, several of them constitute the fundamental building blocks of life on Earth. They include amino acids (the building blocks of proteins), nucleobases (the building blocks of the genetic material), sugars and their derivatives (which play several roles, from the building blocks of DNA, RNA, and cell walls, to energy storage), amphiphiles (the building blocks of cell membranes), and several other families of organic compounds. All of these compounds are found in meteorites, supporting a scenario in which they can form in astrophysical environments and then be incorporated into Solar System objects such as asteroids and comets. Laboratory experiments also support such a scenario, as most of the soluble organics identified in meteorites can form experimentally from the irradiation of ice mixtures with compositions similar to those observed in astrophysical environments.

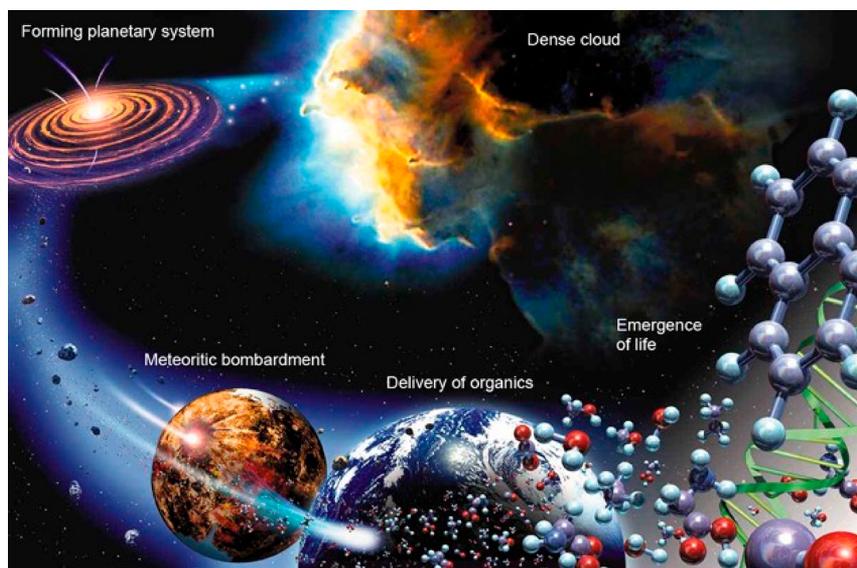
However, it must be noted that the variety of organics resulting from ice processing is much wider than the building blocks actually used in modern terrestrial life. Indeed, although only about 20 amino acids are used to build proteins in all life on Earth, more than 70 amino acids have been identified in primitive meteorites such as Murchison.<sup>443,448,599</sup> Similarly,

several isomers and variants of the nucleobases and sugars used in terrestrial life's genetic material are present in meteorites.<sup>123–126,469–471</sup> In addition, ice processing by energetic photons and/or particles in astrophysical environments is largely limited to only making the building blocks of biological structures and not the structures themselves. A mixture of amino acids, for example, does not spontaneously react to form functional proteins with a biological function, and sugars such as ribose do not spontaneously react with phosphoric acid and nucleobases to build RNA and DNA strands. The selection of which organics were useful to build such organized structures presumably happened at a later time in the history of our planet and the evolution of life.

### 3.2. Organic Inventory on the Primitive Earth

Despite the complexity of modern biological systems on Earth, even for the simplest microorganisms, it seems likely that life on our planet did not start with the same degree of complexity as we see now. Rather, it is believed that the first functional biological molecules were made of a smaller number of building blocks than what modern proteins and genetic materials are made of, and that some of the building blocks that were involved in these first functional molecules may have been abandoned by life along the way, as life evolved in a planetary setting into more and more complex forms.

For instance, it is commonly thought that the first genetic material was very different from the modern one. In particular, experiments showed that other polymeric structures such as peptide nucleic acids (PNAs),<sup>600,601</sup> threose nucleic acids (TNAs),<sup>602,603</sup> glycol nucleic acids (GNAs),<sup>604–606</sup> as well as a host of other possible candidates,<sup>607</sup> could have played the role of genetic backbone to which nucleobases were attached. Life could have then progressively replaced these backbones with other ones, either for stability/robustness reasons or because their properties made them more functional for genetic information storage or replication. Similarly, the nucleobases that store the genetic information in modern DNA and RNA may not have been all used in the first genetic material. Indeed, experiments have shown that the UV irradiation of pyrimidine in realistic astrophysical ice mixtures leads to the formation of uracil and cytosine, two of the three pyrimidine-based nucleobases used in modern life, but thymine is not as easy to form under the same conditions.<sup>407,408,521</sup> Interestingly, thymine is used only in DNA, while uracil is used in RNA. Furthermore, uracil was detected in carbonaceous meteorites such as Murchison, while thymine was not.<sup>124,608</sup> Therefore, if abundant amounts of uracil and cytosine, but not thymine, were delivered to the primitive Earth, this could have biased the formation of RNA first over that of DNA. While this hypothesis is difficult to verify, it is thought that the first functional genetic material and proteins were based on RNA (the “RNA world”), which supports such a scenario.<sup>526–528</sup> Similarly, experiments in which purine is embedded in realistic astrophysical ice mixtures led to the formation of adenine, one of the two purine-based nucleobases used in modern life, but guanine appeared to be difficult to form under the same conditions.<sup>245,246</sup> Instead, other purine-based nucleobase variants such as isoguanine and hypoxanthine were shown to form more efficiently than guanine, hypoxanthine being the most abundant oxidized purine among all photoproducts. It is interesting to note again that it was suggested that in primitive versions of the genetic material, hypoxanthine, which is efficiently formed from ice processing and found in



**Figure 23.** Schematic showing the formation of planetary systems from the condensation of a dense cloud, the bombardment of the forming planets by meteorites and the delivery of organics to these planets including the early Earth, and the plausible role of these organics in the emergence of life. Adapted with permission from ref 26. Copyright 1999 Springer Nature.

meteorites,<sup>126</sup> was used as a base-pairing substitute for guanine, which is not efficiently formed from ice photochemistry and has not been identified in meteorites to date.<sup>609–612</sup> These examples show that early proto-life had a variety of building blocks to choose from the inventory of organics that were delivered. These, mixed with additional compounds formed indigenously, provided early life with a host of materials for possible use.

Another family of molecules that are known to form in laboratory ice photochemistry experiments and present in primitive meteorites and may have played a critical role for the emergence of life is the amphiphiles<sup>409–411</sup> (see section 2.3.4.4). Indeed, these compounds spontaneously self-assemble into vesicles when they are put in a solvent. These vesicles were shown to possess an interior that is separated from the outside environment and able to encapsulate other molecules via successive wetting and drying cycles.<sup>409</sup> Such a mechanism of incorporation of compounds has been proposed as a mechanism via which primitive protocells could have captured impermeant molecules in prebiotic environments,<sup>511</sup> and thus, have significantly increased the probability for molecules to react and build more complex structures while being protected from the outside environment. Indeed, encapsulated molecules could react under chemical conditions (e.g., pH, temperature, salinity) that are different from outside and optimized for given reactions. The presence of amphiphilic molecules in the organic inventory of compounds that were delivered to the primitive Earth may have thus resulted in the formation of vesicles, playing the role of the first protocells in which the first biochemical reactions could occur.<sup>509</sup>

### 3.3. Life: A Universal Process?

Astronomical observations of dense molecular clouds and protoplanetary disks in our Galaxy as well as of other galaxies clearly show that these objects are made of similar materials. In particular, gases and ices condensed on cold grains are observed everywhere with similar compositions.<sup>4,10,33,310,613</sup> These observations therefore tend to highlight that the same materials are used and processed to make new stars and planets in the Universe. The processing of ices by energetic photons

and/or particles, and the resulting formation of complex organic molecules thus seem to be a universal process that should be ongoing wherever dense clouds and protoplanetary disks exist and lead to the formation of a wide variety of organic compounds, some of which are of astrobiological interest. A fraction of these materials survives the physical and chemical conditions of the protosolar nebula stage and end up being incorporated into small objects such as asteroids and comets. This implies that newly formed planetary systems likely possess an inventory of complex prebiotic organics that can, as discussed in section 2.4.5, be delivered to and seed newly formed planets, as was the case for the primitive Earth<sup>522–525</sup> (Figure 23).

Of course, the conditions on the host planets (temperature, luminosity received from the star, stability of the star, presence of an atmosphere, composition of the atmosphere, presence of water oceans or other stable liquids, frequency of meteor impacts, etc.) have a fundamental impact on whether life can or will emerge, even if a given planet has been abundantly seeded with many of the ingredients necessary for life. Some planets in the Universe may have met the right conditions to get life started at some point in their history, but life could not survive for some or many reasons. This applies to all kinds of life, and not only life as we know on Earth, as the variety and abundance of organics formed via prebiotic astrochemical processes and incorporated into planetary systems are large, and newly formed planetary systems are diverse, possibly leading to the emergence of life forms based on different basic building blocks.

Insofar as astrochemistry may play an important role in the formation and delivery of the organic materials necessary for life to the surfaces of planets, and the delivery of these materials could play a significant role in the emergence and early evolution of life, this suggests that life may be relatively common in the Universe. Whether life on other planets is based on similar compounds as those found in terrestrial life or is based on different building blocks will likely depend more on the different physical and chemical conditions on the planets in question than on the materials delivered to them.

## 4. CONCLUSIONS

Chemistry in space takes place under an extremely wide variety of environments and environmental conditions and proceeds via a multitude of chemical processes that include gas-phase reactions, gas–grain surface reactions, and solid-state reactions mediated by ions and radicals generated by ionizing radiation. These processes yield a wide range of chemical products, some of which are not stable under normal terrestrial conditions.

The chemical processes that occur in dense interstellar molecular clouds and protostellar disks are of particular interest because they support rich and varied chemistries and because materials made and altered in these environments can ultimately be delivered to the surfaces of planets. Because H, C, O, and N are the most common reactive elements in space, it is not surprising that many of these materials are organic in nature. Indeed, some of the products are of clear astrobiological interest and they may play key roles in the origin of life on planets. The chemical processes are universal in nature and should occur in these environments wherever they are found. Thus, abiotically produced organic materials should be widely distributed and routinely delivered to new planetary systems. Insofar as they may play key roles in the origin of life, this suggests life may be relatively common where local conditions are favorable.

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### Notes

The authors declare no competing financial interest.

### Biographies

Scott Sandford is currently NASA's Senior Laboratory Astrophysicist and works in the Astrochemistry and Astrophysics Laboratory at NASA's Ames Research Center in Moffett Field, CA. Dr. Sandford received a Bachelor of Science in Mathematics and Physics from the New Mexico Institute of Mining and Technology in 1978 and an M.A. and Ph.D. in Physics from Washington University in St. Louis in 1981 and 1986, respectively. His research includes astronomical infrared spectroscopy, laboratory astrochemistry, and astrophysics, and the study of extraterrestrial materials (interplanetary dust, meteorites, and samples returned to Earth by spacecraft), with an emphasis on organic materials, particularly those of astrobiological interest. He serves as a

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Michel Nuevo is a Bay Area Environmental Research Institute research scientist at NASA Ames Research Center in Moffett Field, California, where he has been working since October 2007. Dr. Nuevo received his Master Degree in Molecular Physico-Chemistry from the Université Paris-Sud in Orsay and the Université Pierre et Marie Curie in Paris (France) in 2001 and his Ph.D. Degree in Astrophysics from the Université Paris-Sud in 2005. His research interests are strongly connected to Astrochemistry and Astrobiology and include experimental studies of the formation and evolution of organic compounds under astrophysical conditions using a broad variety of analytical techniques, their connection with solar nebula and Solar System materials, as well as the analysis of extraterrestrial materials such as meteorites. He is a member of the American Chemical Society (Physical Chemistry Division, Astrochemistry Subdivision) and the American Astronomical Society (Laboratory Astrophysics Division).

Partha P. Bera is a research scientist at the Bay Area Environmental Research Institute and works at the Space Science and Astrobiology division of the NASA Ames Research Center. Prior to this, he was a postdoctoral fellow from 2008 to 2011 at Ames with the NASA Postdoctoral Program (NPP). Dr. Bera received his Ph.D. degree in quantum chemistry and electronic structure theory from the Center for Computational Quantum Chemistry at the University of Georgia. Dr. Bera received his B.Sc. and M.Sc. degrees in chemistry from the Presidency College and University of Calcutta. He investigates novel chemistry of evolution of complex organic molecules towards becoming biogenic in astrophysical environments, and the spectroscopy and atmospheric chemistry of gas phase molecules using the techniques of ab initio quantum chemistry. Dr. Bera is a member of the American Chemical Society and is currently serving as the Chair-Elect of the Astrochemistry Subdivision of the Physical Chemistry Division of the ACS.

Timothy J. Lee is a senior research scientist in the Space Science & Astrobiology Division at NASA Ames Research Center and was previously the Division Chief for 10 years. He has been a civil servant at NASA Ames since 1989, and prior to that he was a NATO/NSF postdoctoral researcher at Cambridge University. Dr. Lee received his Ph.D. in Theoretical/Computational Chemistry from the University of California, Berkeley. His research interests include the development of methods in electronic structure theory and rovibrational spectroscopy, with applications in astrochemistry, astrobiology, astrophysics, atmospheric chemistry, and generally molecular physics. Dr. Lee was awarded the 1998 Dirac Medal of WATOC, and is a Fellow of the American Physical Society and the American Association for the Advancement of Science. He has been a member of the American Chemical Society for more than 35 years, and was previously the Chair of the Astrochemistry Subdivision of the Physical Chemistry Division.

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