In this chapter we describe how elements have been and are still being formed in the galaxy and how they are transformed into the reservoir of materials present in protostellar environments. We discuss the global cycle of matter from stars, where nucleosynthesis produces heavy elements that are ejected through explosions and winds into the interstellar medium (ISM), through the formation and evolution of interstellar cloud material. In diffuse clouds, low-energy cosmic rays impact silicate grains, amorphizing crystals, and UV photons easily penetrate, sponsoring a simple photochemistry. In dense cold molecular clouds, cosmic rays penetrate, driving a chemistry where neutral-neutral reactions and ion-molecule reactions increase the complexity of molecules in icy grain mantles. In the coldest, densest prestellar cores within molecular clouds, all available heavy elements are depleted onto grains. Dense cores collapse to form protostars and the protostars heat the surrounding infalling matter and release molecules previously frozen in ices into the gas phase, sponsoring a rich gas-phase chemistry. Some material from the cold regions and from hot or warm cores within molecular clouds probably survives to be incorporated into the protoplanetary disks as interstellar matter. For diffuse clouds, for molecular clouds, and for dense hot cores and dense warm cores, the physiochemical processes that occur within the gas and solid state materials are discussed in detail.

1. GALACTIC INTERSTELLAR MEDIUM

1.1. Overview: Cycle of Matter from Stars through the Interstellar Medium to the Solar System

As with our Sun, new stars form in the dense cores of quiescent cold molecular clouds (Boss, 2004) from interstellar materials. To a minor extent, pre-main-sequence stars replenish the interstellar medium (ISM) with material through their bipolar outflows and jets. The ISM primarily becomes enriched with nucleosynthesized “metals”, i.e., elements heavier than H and He, through supernovae (SNe) explosions of high-mass stars (SNe type II) and of primary stars in a low-mass binary systems (SNe type I). Other sources of enrichment include the massive winds of low-mass asymptotic giant branch (AGB) stars and novae (e.g., Jones, 2001; Chiappini et al., 2003; Wheeler et al., 1989). Supernovae explosions (McKee and Ostriker, 1977), the UV photons from massive O and B stars (Wolfire et al., 2003), and, to a lesser extent, AGB stellar winds inject energy into the ISM. This energy is deposited in shocks and generates turbulence that acts on many different length scales to bring together, compress, and even shear apart enhancements in the interstellar gas density. Turbulent energy is degraded efficiently into thermal energy when turbulence is concentrated in small volumes such as in shocks and in small intermittent regions of velocity shear where viscous dissipation occurs (Vázquez-Semadeni et al., 2000). In the ISM, gas is processed rapidly through a wide range of temperatures, densities, and ionization stages, as given in Table 1, under the influence of turbulent and thermal processes, pressure gradients, and magnetic and gravitational forces. Interstellar clouds comprise definable structures in the ISM, but only represent two of five ISM components (section 1.2). Stars enrich the ISM (section 2) with the gas and dust that eventually contributes to the formation of new star systems after cooling and passing through interstellar cloud phases. Processes that contribute to increasing the complexity of solid-state and molecular materials are introduced by Irvine and Lunine (2004) and discussed here in detail; these processes primarily occur in interstellar clouds, i.e., in diffuse clouds (section 3) and molecular clouds (section 4), at low temperatures (≤100 K). In interstellar clouds, molecules and solid-state materials are more protected from the destruction mechanisms — UV irradiation, cosmic rays, fast electrons — prevalent in the highly energetic intercloud environment of the ISM of the galaxy. In the dense, hot high-mass and warm low-mass protostellar cores (section 5) that only comprise tiny fractions of the mass of molecular clouds, a rich gas-phase chemistry occurs that increases the complexity of the materials infalling onto
the protostellar disks. The increase in the complexity of molecules from diffuse clouds, through molecular clouds to star-forming cores, is demonstrated from left to right in Fig. 1. A fraction of these ISM materials survive to be incorporated into comets (Ehrenfreund et al., 2004).

1.2. Components of the Interstellar Medium

Of the total mass and volume of the galaxy, the ISM constitutes only ~10–15% of the mass but most of the volume. The mass of the ISM is concentrated within a thin disk that extends to ~25–30 kpc and has a vertical scale height of ~400–600 pc [cf. Ferrière (2001) for an extensive review on the galactic ISM]. About half the mass of the ISM is in discrete interstellar clouds that occupy ~1–2% of the interstellar volume. Interstellar clouds are concentrated along the spiral arms but also occur in interarm regions and in the galactic halo above and below the galactic plane.

Physical conditions in the ISM lead to the description of ISM as the coexistence and interaction of five components (included in Table 1): (1) the hot ionized medium (HIM), also called the coronal gas; (2) the warm ionized medium (WIM) containing ionized atomic hydrogen atoms (H\(^+\)), referred to in other works as the diffuse ionized gas (DIG); (3) the warm neutral medium (WNM), containing neutral atomic hydrogen atoms (H\(^0\) or H); (4) the atomic cold neutral medium (CNM), hereafter referred to as diffuse clouds, dominated by H but containing some molecular hydrogen (H\(_2\)); and (5) the molecular CNM, dominated by H\(_2\), hereafter referred to as molecular clouds or dark clouds.

The components of the ISM (Spitzer, 1985) characterized by significantly different temperatures — hot, warm,

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and cold — result from the balance between energy injected (primarily) by supernova shock waves and radiative losses (Spitzer, 1990; Ferrière, 2001; Wolfire et al., 2003). The gas atoms and ions are excited by collisions with electrons and other atoms and ions and by absorption of UV photons. The gas is cooled by electronic transitions of highly ionized heavy elements in the hot component, by electronic transitions of singly ionized and neutral atoms in the warm ionized and warm neutral components, and by vibrational and rotational modes of molecules in the cold atomic and cold molecular components of the ISM.

Ionized hydrogen (H II) gas constitutes the WIM, where gas temperatures of 10^4 K and higher pervade, and Lyα and Hα photons arise from the H^+ recombination cascade. Neutral atomic hydrogen (H I) gas and neutral (e.g., C, N, S) and singly ionized atoms (e.g., C+, S+) constitute the WNM, i.e., the low-density intercloud medium (n_H = 8 × 10^3–10^4 cm^-3, 6000 K ≤ T_g ≤ 10,000 K, A_V ≤ 0.1 mag). H I gas exists in diffuse clouds of rarefied atomic CNM (n_H = 20–50 cm^-3, 50 K ≤ T_g ≤ 100 K, 0.5 ≤ A_V ≤ 1 mag). The dominant heating process of both the WNM and the diffuse CNM is by cosmic rays, and at molecular cloud surfaces by grain photoelectric heating and collisions with excited H_2 molecules. Cooling is primarily by CO molecular line emission. Gas temperatures in molecular clouds also are affected by collisions with dust grains that either cool or warm the gas, depending on the density (Burke and Hollenbach, 1983) and on the freezing out of molecules (coolants) from the gas phase (Goldsmith, 2001).

Translucent clouds are intermediaries (1 < A_V < 5 mag) between the cold atomic diffuse clouds and cold molecular clouds, and are most easily distinguished in the galactic halo at high galactic latitudes (Hartmann et al., 1998) and by H_2, CH, CN, CO (Rachford et al., 2002), and H_2CO molecules (Magnani and Onello, 1995). We do not discuss these translucent clouds in detail; see Turner (2000) for a discussion of their properties and Ingalls et al. (2002) for recent modeling of heating and cooling processes. Figure 1 summarizes the fractional abundances of gas-phase ions, atoms, and molecules in four different components of the ISM. Note the increased complexity of molecules present in hot and warm dense molecular cloud cores.
1.3. Interstellar Medium Structures

A large fraction of the volume of the Milky Way is filled with the HIM, i.e., a tenuous, ionized coronal gas (McKee and Ostriker, 1977). Supernovae explosions generate the coronal gas (Spitzer, 1990) when their ejecta collide with and shock the surrounding medium. Expanding supernova ejecta sweep up ambient ISM material, compressing it into rapidly expanding shells that cool quickly due to their high densities, possibly becoming molecular gas after \( \sim 10^6 \) yr (McCray and Kafatos, 1987). Upon collision with a massive interstellar cloud the supernova remnant slows and breaks up into fragments, mixing with the interstellar clouds. Ions, primarily from H (87%), He (10%), \( \sim 1\% \) metals (C, N, O), and \( \sim 2\% \) electrons, are accelerated in supernova shocks and are the major source of relativistic particles in the ISM commonly referred to as cosmic rays. The cosmic-ray spectrum (1–1000 MeV) is the main energy source for ionizing the molecular gas (Cravens and Dalgaerno, 1978; Cesarsky and Völk, 1978). The low-energy cosmic-ray spectrum is not measured, because the solar wind with its magnetic field deflects these particles, but is instead inferred from the cosmic-ray ionization rate deduced from diffuse cloud chemical models (section 3.6). There is a high probability that 1-MeV cosmic rays will be absorbed close to their place of origin [within \( \sim 2 \) pc (Spitzer and Jenkins, 1975)]. In fact, the cosmic rays (E \( \leq 100 \) MeV) that ionize the WNM and CNM do not travel far from their supernova sources (Kulsrud and Cesarsky, 1971). EUV (13.6 eV \( \leq h \nu \leq 100 \) eV) and X-ray radiation dominate the ionization of the intercloud WNM. The gas in the WNM dominates the EUV and X-ray opacity. FUV (6 eV \( \leq h \nu \leq 13.6 \) eV) radiation dominates the heating of the WNM and the photoelectric heating of the CNM diffuse clouds and molecular cloud boundaries. The dust in the CNM clouds dominates the FUV opacity.

Massive stars often form in clusters, and their explosions supply enough of a continuum of energy to form supershells or superbubbles. The HIM that fills \( \sim 20\% \) of the galactic ISM local to the Sun is mostly seen as superbubbles (Ferrière, 1998). The expansion of superbubbles may extend beyond the local scale height of the galaxy and form chimneys, expelling HIM material into the galactic halo. As the expelled material gains height, the gas cools and forms high- and intermediate-velocity diffuse clouds in the halo (e.g., Richter et al., 2003). These diffuse clouds then fall back down onto the galactic disk and contribute even more energy to turbulent excitation of the ISM than supernovae; this convective cycle is called the galactic fountain (Shapiro and Field, 1976). Through H\( \alpha \) emission line studies, the WIM is observed to persist not only in the galactic plane in patches, filaments, and loops, but also in the galactic halo. The escape of UV photons from massive stars through superbubbles and chimneys accounts for the energy required to maintain the WIM in the halo (Dove et al., 2000). From the temperatures and densities determined for the ionized and neutral components, the thermal pressures of the HIM and the WIM exceed the WNM by factors of \( \sim 3 \)–\( 15 \) and \( \sim 2 \), respectively. The turbulence and thermal forces in the HIM and WIM, i.e., the shocks and pressures from ionized gas, can sweep up and compress WNM or shear apart CNM diffuse clouds. Hence, primarily supernovae, and to a lesser extent stellar winds, are responsible for the turbulent nature of the ISM, the multiple components of the ISM, and the structures of the interstellar clouds.

Diffuse clouds are thought to form when streams of WNM H\( I \) collide (e.g., Ballesteros-Paredes et al., 1999b). Widespread warm H\( I \) gas (WNM at 6,000–10,000 K) exists in the space between cold H\( I \) diffuse clouds (CNM at 50–100 K), as observed by H\( I \) 21-cm emission and absorption lines, respectively (cf. Ferrière, 2001). The density ratio between the WNM and diffuse clouds is approximately the inverse of the temperature ratio, supporting the view that the atomic WNM and CNM are in rough thermal pressure equilibrium (Boulahres and Cox, 1990; Wolfire et al., 2003). However, recent arguments have been made that diffuse clouds are not pressure confined by the WNM but rather result from turbulent density fluctuations in colliding gas streams (Ballesteros-Paredes et al., 1999b). Such nonthermal pressures due to turbulent motions, magnetic fields, and cosmic rays are required to produce the observed vertical scale height of the WNM component (Wolfire et al., 2003) and maintain sufficient pressures such that the neutral component of the ISM occurs in the galaxy as two phases — WNM and CNM. The balance between heating and cooling processes in the neutral medium, either through turbulent dynamics (Ballesteros-Paredes et al., 1999b) or in equilibrium conditions (Wolfire et al., 2003), generates a relationship between pressure and neutral hydrogen density that is double-valued for a range of pressures: The neutral two-phase ISM consists of either warm and rarefied (WNM) or cold and dense (CNM) material (Goldsmith et al., 1969). The two phases are in thermal equilibrium but not hydrostatic equilibrium. The kinematics of atomic gas and molecular gas are similar (Grabelsky et al., 1987), and the morphological distinction between WNM and CNM is often not clear: Warm H\( I \) gas is seen as an intercloud medium and diffuse clouds are seen to have H\( I \) halos. Massive stars form in molecular clouds that have diffuse cloud cocoons that are embedded within the intercloud WNM, so much of the mass of the CNM and the WNM is in photodissociation (PDR) regions illuminated by UV photons from massive stars (Hollenbach and Tielens, 1999).

Most of the mass of H\( I \) is in the CNM as diffuse clouds even though most of the volume of the ISM containing H\( I \) is in the rarefied intercloud WNM (Dickey and Lockman, 1990). Furthermore, most of the mass of CNM clouds is in molecular clouds. Specifically, most of the mass of gas in the ISM is in giant molecular clouds (GMCs) that each span tens to hundreds of parsecs and contain \( 10^5 \)–\( 10^6 \) M\(_\odot\) gas. GMCs with masses greater than \( \sim 10^4 \) M\(_\odot\) are gravitationally bound [e.g., for the outer galaxy (Heyer et al., 2001)]. By number, most molecular clouds are less massive than \( 10^4 \) M\(_\odot\) and have internal turbulent motions in excess of their gravitational binding energies (cf. Heyer et al., 2001). The formation and existence of these gravitationally unbound molecular clouds is thought to be a result of a highly
energetic turbulent ISM in which diffuse cloud material is compressed through supernova shocks, colliding H I streams, spiral density waves, and gravity. All molecular clouds including GMCs fill only 1–2% of the volume of the ISM.

1.4. Interstellar Cloud Lifetimes

The lifetimes of diffuse clouds and molecular clouds is a rapidly evolving subject. A couple of decades ago, concepts of molecular cloud formation were motivated to explain the formation of GMCs because that is where most of the molecular gas resides. The formation of molecular clouds by ballistic aggregation of smaller clouds on timescales of $4 \times 10^7$ yr was considered (Field and Hutchins, 1968). This view was superseded by the concept that large-scale magnetic Parker instabilities formed molecular clouds and produced lifetimes of $\sim 2 \times 10^7$ yr (Blitz and Shu, 1980). Based on the supposition that the entire GMC could form stars, the long lifetimes of GMCs were consistent with the observed slow rate at which molecular gas turns into stars. Mechanisms were evoked to delay the onset of star formation in GMCs, including ambipolar diffusion of magnetic flux (Shu et al., 1987) and turbulent cloud support (e.g., Nakano, 1998). We now know that only a small fraction of a GMC, or of any molecular cloud, has sufficient density to be protostellar cores (Boss, 2004; Elmegreen, 2000). Therefore the observed low star formation rate is a result of the small volume fraction of molecular clouds that are dense enough to be protostellar cores (Elmegreen, 2000).

Modern models of diffuse cloud formation involve gravitational instabilities and turbulence (e.g., Vázquez-Semadeni et al., 2000). The structure of the ISM is very fragmentary: Even on the largest scales, GMCs are seen as fragments inside H I clouds (Grabelsky et al., 1987). Structures inside GMCs are created by turbulence and are of similar fractal dimension to larger structures (Falgarone et al., 1991). It takes about a volume of WNM 1 kpc in diameter to make a CNM GMC. If this material is brought together within several tens of parsecs, the density of the gas is higher than average ($10^3$ cm$^{-3}$), but most of it is WNM. Gravity might pull this material together in a dynamical time ($G \rho^{-1/2}$) of $\sim 10^7$ yr (Elmegreen, 2000). However, turbulent processes stimulated by gravity, supernova shocks, collisions with supernova remnant shells, spiral density waves (e.g., Elmegreen, 1979), or collisions with other clouds can speed up this process. In this view, molecular clouds are an intermediate-scale manifestation of the turbulent cascade of energy from its injection into the HIM and WIM to small dissipative scales (Vázquez-Semadeni, 2004).

The lifetimes of diffuse clouds are not known. There is less mass in diffuse clouds than in molecular clouds, so under equilibrium conditions, the lifetimes of diffuse clouds would be shorter. In the local cloud containing the solar neighborhood, the fraction of ISM in molecular clouds is less than half. The self-gravitating or star-forming fraction of molecular clouds is significantly less than half. In the turbulent scenario, the diffuse clouds that are not dense enough or massive enough to be self-gravitating would have to live longer than the star-forming molecular clouds. That is, the rarefied CNM that takes the form of diffuse clouds could stay diffuse for a long time between its successive incorporations into dense CNM as GMCs or smaller molecular clouds. Each individual diffuse cloud is probably buffeted by turbulence and changed from diffuse cloud to molecular clouds in only a short time. Molecular clouds become diffuse clouds when dispersed by star formation or turbulent forces. Thus, much of the volume of the H I gas is retained in diffuse clouds.

The rapid formation of molecular clouds within diffuse clouds is thought to occur on the order of a few million years (Ballesteros-Paredes et al., 1999a, b; Hartmann et al., 2001). Most numerical simulations of diffuse cloud formation, however, are not followed to high enough densities ($100$ cm$^{-3}$) to confirm that a large fraction of the H I gas is turned to H$_2$ on timescales of $\sim 10^7$ yr (Ballesteros-Paredes et al., 1999b; Ostriker et al., 2001). The formation of H$_2$ (section 3) occurs when a sufficient column of H I shields the H$_2$ against UV dissociation [$A_{\text{H}_2}(\text{min}) = 0.5–1$ (van Dishoeck and Blake, 1998)] and when there is a sufficient concentration of dust on whose surfaces H$_2$ forms (cf. Richter et al., 2003). Molecular hydrogen formation can occur in diffuse clouds in the galactic halo with volume densities of only $n_{\text{H}} = 30$ cm$^{-3}$ because the UV field is not as intense as in the galactic plane (Richter et al., 2003). In the galactic plane, H$_2$ can form under equilibrium conditions in $\sim 10^6$ yr when both the densities are sufficient ($n_{\text{H}} = 100$ cm$^{-3}$) and the surrounding H I intercloud medium has sufficient H I column depth. These conditions occur for diffuse clouds that encompass $\sim 10^4$ M$_{\odot}$ of gas and are gravitationally bound (Hartmann et al., 2001). Many gravitationally unbound smaller molecular clouds exist, however, at densities of $n_{\text{H}} = 100$ cm$^{-3}$; these clouds contain H$_2$ and CO but are without massive H I cocoons. The conundrum is that timescales for H$_2$ formation appear to be faster than the timescales constrained by equilibrium processes (Cazaux and Tielens, 2002) at the densities observed for molecular clouds. Pavlovski et al. (2002) find that H$_2$ formation occurs in shock-induced transient higher-density enhancements more rapidly than expected from the average density of the gas. Three-dimensional computations of decaying supersonic turbulence in molecular gas show the complete destruction and the rapid reformation of H$_2$ in filaments and clumps within a diffuse cloud structure. These regions of turbulent compression then relax and the H$_2$ becomes relatively evenly distributed throughout the cloud. Therefore, molecular clouds may form out of diffuse cloud material several times faster in a turbulent ISM (Pavlovski et al., 2002), hence making the rapid formation and existence of gravitationally unbound molecular clouds of $\sim 10^5$ M$_{\odot}$, such as the Chameleon I–III and p Ophiuchi molecular clouds, theoretically realizable.

1.5. Rapid Star Formation

The rapid formation of molecular clouds, of stars within molecular clouds, and of molecular cloud dispersal, is a controversial issue. For detailed discussions on the subject,
see recent excellent reviews by Boss (2004), Mac Low and Klessen (2003), and Larson (2003). After a molecular cloud forms, star formation appears to proceed quickly in about a cloud crossing time, and the crossing time depends on the turbulent velocities in the cloud (Elmegreen, 2000; Hartmann et al., 2001; Vázquez-Semadeni, 2004). The duration of star formation corresponds to the size of the region: Spreads of less than \(4 \times 10^6\) yr in age are deduced for star clusters, the Orion region has a spread of ages of \(10^7\) yr, and the Gould’s Belt a spread of \(3 \times 10^7\) yr (Elmegreen, 2000). Careful application of pre-main-sequence theoretical stellar evolution tracks to stellar associations in Taurus shows that there is a \(10^7\)-yr spread in the ages of the association members, but the majority of stars are \(\leq 4 \times 10^6\) yr and the fewer older stars tend to lie on the cloud boundaries (Palla and Stahler, 2002). Many stellar associations do not show evidence for intermittent stellar formation activity in their derived stellar ages but do show over the past \(\sim 10^7\) yr an acceleration in the rate of stellar births during the most recent \(\sim 4 \times 10^6\) yr (Palla and Stahler, 2000). This is as expected because the rate of star formation accelerates as the cloud contracts (B. G. Elmegreen, personal communication, 2003). Thus the rapid-star-formation scenario is invoked to explain the absence of molecular gas from clusters more than \(\sim 4 \times 10^6\) yr in age, and the — still controversial (Palla and Stahler, 2002) — lack of an age dispersion in T Tauri stars of more than \(\sim 4 \times 10^6\) yr (Hartmann et al., 2001). Given the concept that small regions collapse to form stars and star clusters in \(1-3 \times 10^6\) yr during the lifetime of the larger complex, then rapid molecular cloud formation \((\sim 10^6\) yr\) is followed by rapid dissolution of molecular gas back to diffuse cloud material by the energy injected by young, newly formed stars or by turbulent motions. Shorter lifetimes of molecular clouds \((\sim 1-4 \times 10^6\) yr\) also help to resolve the many problems for interstellar chemistry posed by longer lifetimes \((\sim 10^7\) yr\) (section 4.3).

Molecular clouds are very inhomogeneous in density, containing density-enhanced “clumps” (approximately a few parsecs, \(10^3\) \(\mathrm{H}_2\) \(\mathrm{cm}^{-3}\)), and within these clumps contain smaller, particularly dense, self-gravitating “cores” \((\sim 0.1\) pc, \(\geq 10^5\) \(\mathrm{H}_2\) \(\mathrm{cm}^{-3}\)) (Larson, 2003). Clumps are thought to be the precursors of star clusters and small groups of stars, although most clumps are not as a whole self-gravitating (Gammie et al., 2003). In the view of rapid cloud formation, protostellar core masses result from a rapid sampling of existing cloud structures (clumps and cores) (Elmegreen, 2000). Evidence for this lies in the fact that the distribution of masses of newly formed stars, i.e., the initial mass function, is similar to the distribution of masses of protostellar cores in molecular clouds (Motte et al., 1998; Testi and Sargent, 1998; Luhrman and Rieke, 1999). Protostellar cores formed by turbulent processes are supercritical, i.e., their gravitational energies available for collapse are greater than their internal thermal and magnetic energies (Mac Low and Klessen, 2003). This concept is supported by the fact that the existence of a subcritical core has yet to be convincingly demonstrated (Nakano, 1998).

Most of the molecular mass is in GMCs; GMCs contain a wide range of core masses (Nakano et al., 1995) and are the birth sites of stellar clusters containing high-, intermediate-, and low-mass stars. By number, most of the low-mass stars form in regions of high-mass star formation. Low-mass stars also form in lower mass molecular clouds in the galactic plane, such as the \(\sim 10^5\)-M\(_\odot\) Taurus molecular cloud complex that spans \(\sim 30\) pc. The formation of our proto-Sun and the solar system is often thought to have formed in a Taurus-like cloud because T Tauri stars are proto-Sun analogs, although the high levels of radioactive isotopes in primitive bodies suggests the solar system formed in a region of high-mass star formation (Boss, 2004; Vahala and Boss, 2000). Complex gas phase chemistry occurs in protostellar cores because the reservoir of infalling material is rapidly made more complex: Gases trapped in the solid phase in icy grain mantles are warmed by the protostar and released into the gas phase. High-mass protostars are more luminous than low-mass protostars and therefore heat the surrounding infalling core material to a greater extent, producing hot cores, while low-mass protostars produce warm cores. In so far that this infalling core material has not yet passed through the protostellar disk, the rich gas-phase chemistry that occurs in hot and warm cores is considered part of the reservoir of interstellar cloud materials that contributes to the protoplanetary disk and the formation of cometary materials.

### 1.6. Cycling of the Elements through Diffuse Clouds and Molecular Clouds

Stars that form in quiescent dense cold molecular clouds heat and energize the ISM by ejecting matter. The ISM is continually enriched in newly nucleosynthesized heavy elements primarily through supernovae and AGB star winds (section 2.1). Much of the matter that is shed into the ISM occurs through the circumstellar envelopes (CSE) of late-type stars where the physical conditions are conducive to the condensation of dust grains (section 2.2–2.5). Dust grains are also thought to condense in supernovae and novae (e.g., Jones, 2000). Most of the heavy elements are therefore injected into the ISM as dust grains.

The dust grains in interstellar clouds, however, are not necessarily those produced by AGB stars and supernovae. Interstellar medium processes contribute to the rapid destruction of dust grains, including shocks produced by supernovae and turbulence, the same turbulence that can act to form interstellar clouds (section 1.4). Grain destruction processes are most efficient in the warm neutral component (WNM) of the ISM where gas densities are moderate \((\rho_{\mathrm{H}} = 0.25\) \(\mathrm{cm}^{-3}\)) and temperatures are high \((8 \times 10^{13}-10^4\) K) (Jones et al., 1996; McKee et al., 1987). In shocks, collisions occur between grains and gas atoms and ions, and between the dust grains themselves. Gas-grain collisions result in erosion and sputtering of grains. Grain-grain collisions result in fragmentation and, for the larger-velocity collisions, vaporization. From the passage through supernovae shocks, grain lifetimes are predicted to be shortened to \(6 \times 10^6\) and \(4 \times 10^6\) yr for carbonaceous and silicate grains respectively (Jones et al., 1996), about 50 times too short compared to a nominal grain lifetime of \(2 \times 10^{10}\) yr required to maintain
2. FORMATION OF THE ELEMENTS AND DUST GRAINS IN STARS

2.1. Nucleosynthesis

Beyond the large amounts of H, some He, and small amounts of Li created during the Big Bang, other elements that constitute cometary bodies, the planets, and our Sun were produced via nucleosynthesis in the interiors of stars or in the explosive nucleosynthesis of novae and supernovae. Nuclear burning sequences are subjects of detailed study (Clayton, 1983; Wheeler et al., 1989) and differ considerably for low- to intermediate-mass stars (Renzini and Voli, 1981) and high-mass stars (Woosley and Weaver, 1995; Thielemann et al., 1996).

In brief, during a star’s life on the main sequence, H fuses into He primarily through three temperature-dependent processes: two proton-proton reactions and the CNO bi-cycle. In the CNO cycle, He is a primary product and N is a secondary product formed at the expense of C and O already present in the stellar interior. After time on the main sequence, H is exhausted in the core and a He core is formed. This He core will begin nuclear burning into C through the triple-$\alpha$-particle reaction when the core has sufficiently contracted and heated to temperatures of $\sim 10^8$ K. During the time that H is burning only in a shell around the preignited He core, the stellar envelope expands and the star transits from the main sequence to the red giant branch of the luminosity-temperature or Hertzsprung-Russell (HR) diagram (Willson, 2000; Iben, 1974). The He core ignites and is later exhausted; the star expands again due to He shell burning and outer H shell burning as an asymptotic giant branch (AGB) star. During this AGB phase of low- to intermediate-mass stars when the expanded envelopes have low surface gravity, stars shed material through their winds and eject significant amounts of $^4$He, $^{12}$C, $^{13}$C, and $^{14}$N into the ISM. An AGB star is observed to undergo substantial mass loss in the form of a stellar wind. In cooler outer regions of the stellar atmosphere, elements form molecules, and these gas phase molecules condense into solid particles at temperatures lower than about 2000 K. The ratio of C to O (C/O) in the gas determines the mineralogy of the dust that forms (Tsujii, 1973), as will be discussed below (sections 2.2–2.4). Stellar radiation pressure on these dust grains drives them outward and gas-grain collisions drag the gas along with the dust. This leads to the existence of a massive circumstellar envelope (CSE) and a slow AGB stellar wind that enriches the surrounding ISM with molecules and dust.

The evolution of the stellar structure is critical to the yields of C and N (Busso et al., 1999; Chiappini et al., 2003). Carbon and N are primary products during the third dredge-up stage on the AGB if nuclear burning (“hot bottom burning”) at the base of the convective envelope is sufficient. During thermal pulses in $^{13}$C-rich pockets, slow neutron capture through the “s-process” leads to elements such as $^{14}$N, $^{22}$Ne, $^{28}$Mg, and rare-earth elements including Sr, Y, Zr, Ba, La, Ce, Nd, Pr, Sm, Eu, and in the presence of Fe seed nuclei slow neutron capture uniquely creates very heavy nuclei such as $^{134}$Ba, $^{153}$Ga, and $^{164}$Er. For a description of the dependence of nucleosynthesis in AGB stars on stellar structure and metallicity, see the review by Busso et al. (1999).

Iron is produced when long-lived white dwarf low-mass stars in binary star systems eventually explode as type Ia supernovae. Oxygen is produced when short-lived massive stars explode as type II supernovae (SNe II). In a SNe II all the burning shells (the star’s “onion skin structure”) are...
expanding at 2500–5000 km s\(^{-1}\), explosive nucleosynthesis forms. In the inner Si- and O-rich layers of the star that are
lar clouds (1996). Furthermore, dust grains probably reform in molecu-
ates from SNe II, the isotopically anomalous dust grains
have created the reservoir of elements of "solar composition." Even though GCE reveals that most of the O and Si origi-
metallicity with time; the spatial distribution of stars in the
stars of a given initial stellar mass; the increase of stellar
the history of star formation in the Milky Way; the
Galactic chemical evolution (GCE) is modeled by folding
formed is the result of the mixing of nucleosynthetic prod-
there are significantly fewer massive stars than low-mass
The reservoir of elements out of which the solar system
formed is the result of the mixing of nucleosynthetic prod-
products from many generations of stars of different masses.
Galactic chemical evolution (GCE) is modeled by folding
together the history of star formation in the Milky Way; the
initial mass function that describes the relative number of
stars of a given initial stellar mass; the increase of stellar
metallicity with time; the spatial distribution of stars in the
galaxy; and the nucleosynthetic yields as functions of stellar
mass, structure, and metallicity (Matteucci, 2001; Chiap-
pini et al., 2003). In the Milky Way 4.5 \times 10^9 yr ago, GCE had created the reservoir of elements of "solar composition." Even though GCE reveals that most of the O and Si origin-
ates from SNe II, the isotopically anomalous dust grains from SNe II are very few in number in meteorites (Yin et
al., 2002; Nittler et al., 1996). In fact, in interplanetary dust
particles (IDPs), O-isotopic anomalies are now being found
that are attributable to AGB stars (Messenger, 2000; Mes-
senger et al., 2002, 2003). This isotopically anomalous O
found in silicate grains within IDPs has a high (1%) abund-
dance by mass. Within the measurement errors, the other
99% of the IDPs are composed of approximately solar com-
position materials. Therefore, even the more primitive dust
grains in our solar system indicate that most of the heavy
elements locked in dust grains lost the isotopic signatures
of their birth sites prior to entering the solar nebula. It has
been hypothesized that dust grains are evaporated and re-
condensed in supernova shocks in the galaxy (Jones et al.,
1996). Furthermore, dust grains probably reform in molecu-
lar clouds (Dominik and Tielens, 1997). The evidence in the
most primitive interplanetary dust grains, of probable com-
etary origin, is that the material that came into the solar
nebula primarily was of approximate solar composition.

### 2.2. Asymptotic Giant Branch Star Circumstellar Envelopes

The circumstellar envelope (CSE) of an AGB star pro-
vides the ideal environment for complex silicates and car-onaceous material to grow and polymerize (see Draine,
2003, for a review). The chemistry of the dust that con-
denses depends on the C/O ratio. The molecule CO is very
tightly bound and consumes all available C or O, whichever
is less abundant. If there is C left over after the formation of
CO, then a C-based dust chemistry occurs. Conversely, if
there is leftover O, O-rich silicate dust forms. Early in the
AGB phase, when C/O ratios are less than unity, silicate
dust forms, as is widely observed in the dust shells around
these stars (Molster et al., 2002a,b,c). The chemistry of the
O-rich dust follows condensation pathways for silicates,
aluminum oxides, and alumino-silicates. Later in the AGB
phase, sufficient newly synthesized C is dredged up from
the stellar interior to increase the atmospheric C/O ratio
above unity. In this case, carbonaceous dust is formed. The
chemistry of C-dust formation is believed to be similar to
that which produces soot in terrestrial combustion, and im-
portant chemical intermediates are the PAH molecules
(Frenklach and Feigelson, 1989; Tielens and Charnley,
1997). Distinctive IR emission bands from hydrocarbon
grains are detected in C-rich AGB stars, but the aromatic
infrared bands (AIBs) from PAHs are not detected prob-
![Fig. 2. PAH emission (arrows) in different lines of sight through the ISM. (a) Mon R2 IRS2 depicts a line of sight toward a mas-
ive protostar, exhibiting dust grains with ice mantles (H_2O, CO_2),
and a UV-illuminated region where the gas is photodissociated and
PAH emission is evident. (b) Orion Bar, which is a photodisso-
ociation region; the chemistry is dominated by UV and the PAH
emission dominates the IR spectra. (c) PAH emission is also seen
in the environs of the reflection nebula NGC 2023. Figure cour-
tesy of J. Keane and E. Peeters.]
ably because AGB stars are too cool to produce the UV photons that excite the PAHs. In the global cycle of matter in the galaxy, PAHs are small enough to survive supernovae shocks (Papoular, 2003) and UV exposure in the WIM component of the ISM, thereby enabling them to be the carriers of the AIB features (see Fig. 2; section 3.4) in protostellar regions (e.g., Mon R2 IRS2), photodissociation regions around massive stars (e.g., the Orion Bar), and reflection nebulae (e.g., NGC 2264). Thus, stellar mass loss during the AGB phase is an important source of silicate and C-rich dust for the ISM (Willson, 2000).

2.3. Oxygen-rich Asymptotic Giant Branch Silicate and Oxide Dust

Oxygen-rich dust grains in the ISM are recognized to be primarily Fe-bearing amorphous, i.e., disordered, silicate dust grains (Li and Greenberg, 1997). Oxygen-rich AGB stars are recognized through their IR spectra to be the main producers of these amorphous silicates. Silicates largely fall into two mineral families: olivine (Mg,Fe)2SiO4 and pyroxene (Mg,Fe)SiO3 (cf. Hamner and Bradley, 2004). The Mg-rich end members of the olivine group and pyroxene group are forsterite and enstatite respectively. The “ISM” 9.7-µm silicate absorption band is attributed to Fe-bearing amorphous olivine (Li and Greenberg, 1997) or to Fe-bearing olivines and pyroxenes in a ratio of ~5 : 1 (Kemper et al., 2004). In the past five years, analysis of IR spectra of O-rich AGB stars obtained with the short wavelength spectrometer (SWS) onboard the Infrared Space Observatory (ISO) reveals other amorphous forms and crystalline forms of silicates and oxides. In particular, O-rich AGB stars also produce Mg-rich crystalline olivine and Mg-rich crystalline pyroxene grains in varying abundance ratios (Molster et al., 2002a,b,c). The high Mg-content of the crystalline silicates is confirmed by the wavelengths of the resonant peaks (Fabian et al., 2001a). In O-rich AGB stars characterized by high mass loss rates of ~10^{-4} M⊙ yr^{-1}, i.e., the OH/IR stars, at most a few percent of the total mass of dust ejected can be crystalline silicates, while the preponderance is amorphous silicates (Kemper et al., 2001). In O-rich AGB stars with low mass-loss rates of ~10^{-6} M⊙ yr^{-1} and CSEs that are less optically thick in their IR continuum than the OH/IR stars, i.e., the Mira variable stars, the ISO SWS detection limits constrain the crystalline silicates to be ~40% or less of the total mass ejected (Kemper et al., 2001). More stringent limits will be determined for Miras by Spitzer Space Telescope observations. The crystalline silicates are not seen, however, in the diffuse ISM: Constraints of <5% and <0.5% are determined from the ISM 9.7-µm feature and the 9.7-µm feature toward the galactic center by Li and Draine (2002) and Kemper et al. (2004) respectively. Silicate crystals are efficiently transformed to amorphous silicate structures in the ISM, probably through cosmic-ray impacts during their residence in diffuse clouds (section 3.3).

Oxygen-rich AGB stars with more rarefied CSEs than Miras show emission features of either amorphous silicates, or oxides, or both (Cami, 2002). The spectrally broad amorphous silicate bands (with central wavelengths at ~9.7 µm and spanning ~8–12.5 µm) are the most common bands seen in O-rich AGB stars, with the 13-µm feature being second. Postulated carriers for the 13-µm feature include corundum (e.g., Onaka et al., 1989), silica (Speck et al., 2000), and spinel (Posch et al., 1999; Fabian et al., 2001b). Spinel (MgAl2O4) can account for the rather common 13-µm feature, as well as the 16.8-µm and 32-µm features in the ISO SWS spectra (Cami, 2002). Alumina (Al2O3), in the case of G Her, matches the profile of 11-µm feature. Magnesiowüstite (Mg0.1Fe0.9O) is identified as the carrier of the 19.5-µm feature (Posch et al., 2002; Cami, 2002).

The silicates and the Al oxides follow two distinct condensation pathways because Si is much more abundant than Al. These thermodynamic condensation sequences were developed for the solar nebula (Grossman, 1972). In an AGB outflow that originates at the stellar photosphere and expands and cools, the first grains to condense are those with the highest condensation temperature: corundum (Al2O3) at 1760 K. After corundum condenses, aluminosilicates condense, including Ca-bearing gehlenite (Ca2Al2SiO7). Gehlenite then reacts with the Mg in the gas at about 1550 K to form spinel (MgAl2O4) (Speck et al., 2000). Isotopically anomalous presolar spinel grains from AGB stars are found in meteorites (Nittler et al., 1997).

In the same parcel of gas, the silicates condense: Magnesium-rich olivine condenses first as forsterite at about 1440 K. By reactions with SiO molecules in the gas phase, cooling of the forsterite leads to the formation of enstatite. At high temperatures the incorporation of Fe into crystalline silicate minerals is inhibited thermodynamically (Grossman, 1972). When the gas temperatures drop below the crystallization temperature of ~1000 K, conditions prevail where Fe can be incorporated into the minerals and amorphous forms of silicates can grow. This is the mechanism suggested for the formation of Fe-bearing amorphous silicates in AGB stars (Tielens et al., 1997). Iron is present in the gas phase and condenses as pure Fe grains at temperatures of about 900 K (Gail and Sedlmayr, 1999), significantly cooler than the Mg-rich silicates. Pure Fe grains, even though spectrally featureless, have been invoked to explain the hot near-IR continuum in AGB stars (Kemper et al., 2002).

Not all minerals appear to follow a thermodynamic sequence. Magnesiowüstite (MgFeO) is not expected to form, yet it is seen in spectra of O-rich AGB stars (Cami, 2002). Similarly, the preponderant amorphous silicates in the CSE of AGB stars are not a consequence of a thermodynamic condensation sequence. A quantitative explanation of their formation will probably require the application of a kinetic condensation theory that includes surface exchange processes (Gail and Sedlmayr, 1999).

2.4. Asymptotic Giant Branch Carbon-rich Dust

The extended convective envelopes of AGB stars evolve from O-rich to C-rich during the third dredge-up phase when C is nucleosynthesized at the base of the CSE and brought to the stellar surface. In the CSE of C-rich AGB stars, a com-
plex carbon chemistry occurs that is analogous to carbon soot formation in a candle flame or in industrial smoke stacks. An active acetylene (C_2H_2) chemistry appears to be the starting point for the development of hexagonal aromatic rings of C atoms, the structure of which mimics the cross-section of a honeycomb. These aromatic rings probably react further to form large aromatic networks such as soot. The kinetic theory for PAH and soot formation is a subject of current astrophysics research (Cherchneff et al., 1991; Cadwell et al., 1994; Hudgins et al., 2001). These soot particles also contain aliphatic bonds, i.e., nonaromatic C–C, C≡C, C≡C, and C–H bonds. At intermediate radii in the AGB CSE a transient photochemistry occurs (Glassgold, 1996), but by the time the CSE edge is reached, all small volatile molecules that formed in this region, as well as at the photosphere (e.g., HC_3N, SO_2, H_2CO, CO, H_2, C_2H_2, SiO), are completely destroyed and hence play no part in interstellar cloud chemistry. The solid particles from AGB CSE, upon entering the warm ionized and warm neutral components of the ISM, can be structurally altered by large fluxes of UV photons (Mennella et al., 2001) and fast H atoms (Mennella et al., 1999) present there (Chiar et al., 1998; Pendleton and Allamandola, 2002). After many thermal pulses the AGB star has shed much of its extended envelope and transitions to the protoplanetary nebula phase. The white dwarf central star begins to be revealed, its strong UV radiation field dissipating and revealing a carbon chemistry that is dominated by aliphatic carbon materials (Chiar et al., 1998). The aliphatic bonds emit through the 3.4-µm feature (e.g., Chiar et al., 1998; Goto et al., 2003). The 6.9-µm band is also observed, which is characteristic of aliphatic-aromatic hybrid compounds containing methylene (–CH₂) substructures (Hrivnak et al., 2000). As the CSE is becoming rarefied and excited by the wind and the UV photons of the hot white dwarf stellar core, UV photons destroy the aliphatic bonds (Menella et al., 2001). Some of this aliphatic material formed in AGB CSE may survive the intense galactic UV field and interstellar shocks to be incorporated into the diffuse clouds, as evidenced by the strong similarities between the shapes and substructures in the 3.4-µm features in the protoplanetary nebula CRL 618 and in the line of sight to the galactic center (Chiar et al., 1998, 2000). In the mere few thousand years during which a planetary nebula emerges, however, the hydrocarbon dust becomes dehydrogenated and the aliphatic bonds are transformed to aromatic bonds. The greatest evolution of the PAH features occurs in the rapid post-AGB protoplanetary nebula phase (cf. Mennella et al., 2003). Ultraviolet light from AGB stars is insufficient to excite the PAHs, and so the PAHs are not directly observable at their birth sites in the AGB CSE. In addition to soot (hydrocarbon grains containing aromatic and aliphatic bonds), silicon carbide (SiC) forms in the C-rich AGB CSE. Silicon carbide grains have two primary crystallographic forms: α-SiC and β-SiC. Only β-SiC is spectroscopically detected in C-rich AGB stars (Speck et al., 1999). Silicon carbide grains are only a minor component of the ISM, constituting less than 5% of the submicrometer dust that contributes to the interstellar extinction curve (Whittet et al., 1990). All solid grains larger than a few micrometers lack spectroscopic signatures, so large SiC grains may be present in the ISM but are not spectroscopically detected. Presolar SiC grains constitute all the β-SiC structure (Daulton et al., 2002), have isotopic anomalies indicative of AGB CSEs, and are typically larger than 1 µm in size (Amari et al., 2001). Perhaps only the largest SiC grains survive their journey through the ISM to be incorporated into meteorites.

3. PHYSIOCHEMICAL PROCESSES IN DIFFUSE CLOUDS

3.1. Overview

In this section we summarize the composition of and the important chemical processes operating in diffuse clouds of gas and dust. (Note that the lines of sight to background stars frequently sample many diffuse clouds, so diffuse cloud matter often is called the diffuse interstellar medium, or DISM.) Cosmic dust forms in the atmospheres of evolved stars (sections 2.2–2.4). Subsequent complex evolution of dust and gas is driven by interactions with gas and by processes such as heating, UV radiation, shocks, and cosmic-ray (energetic ion) bombardment. However, during this journey only the most refractory compounds survive, while most of the simple species are destroyed. Supernova remnants are a source of galactic cosmic rays, and these play an important chemical role throughout all phases of the ISM, including diffuse clouds. Diffuse interstellar clouds are subject to dynamical phenomena such as supernovae-driven shocks and cloud–cloud collisions. As the interstellar plasma is highly compressible, sound waves and magnetohydrodynamic waves readily steepen into shock waves; the energy available from these shocks opens up many pathways in a high-temperature chemistry (Flower and Pineau des Forêts, 1998). The dissipation of interstellar turbulence has also been considered as potentially important for driving chemical reactions that cannot take place at the low average kinetic temperature of the diffuse medium (Falgarone et al., 1995; Joulain et al., 1998).

Diffuse clouds have temperatures of around 70–100 K that are the result of the thermal balance between heating and radiative cooling. Diffuse cloud gas is heated through photoelectron emission (section 1.2) from dust grains, PAHs (section 2.1), and C atoms. Cooling is predominately through radiation from fine-structure transitions of C⁺ and O; these are excited by collisions with H atoms and with the electrons produced from the photoionization of C atoms.

A diffuse cloud is characterized by a density of ~1–100 H atoms cm⁻³, a gas temperature of ~100 K, and an active photochemistry that forms, destroys, and shapes interstellar matter. As they have optical depths less than unity, diffuse clouds are almost unshielded from the UV radiation produced by massive O and B stars. These UV photons can easily penetrate almost the entire extent of a diffuse cloud and lead to a gas phase composition that is dominated by photochemical reactions, and this, in turn, only permits the
formation of fairly simple molecules. Spectroscopy from the UV to radio wavelengths reveals a diversity of solid-state species and gas molecules that exist in the diffuse clouds. Several diatomic molecules such as CO, CH, CN, CH+, and H₂ have been identified in diffuse clouds (Lucas and Liszt, 2000). Simple polyatomic species such as hydrogen cyanide (HCN), formylium (HCO+), H₂CO, and cycloprenylidene (C₃H₂) are observed in diffuse clouds and in translucent clouds (section 1.2) (Turner, 2000), which are interstellar clouds of a slightly higher extinction and density than diffuse clouds. In contrast, dense molecular clouds whose interiors are shielded from the ISM UV radiation field are the sites where more complex molecules form (see Fig. 1; section 4).

### 3.2. Depletion of Heavy Elements into Dust Grains in Diffuse Clouds

Dust grains form in the cool CSE of AGB stars, in novae, and in supernovae ejecta (e.g., Draine, 2003; Jones, 2001) (sections 2.2–2.4). Fragmentation and sputtering of dust grains in low- and high-velocity shocks in the HIM and WIM release heavy elements into the gas phase and selectively enhance the abundances of very small grains (e.g., Zagury et al., 1998). In diffuse clouds, however, the heavy elements (except N and S) primarily reside in dust grains as deduced from the observed depletion of the heavy-element abundances from the gas phase relative to cosmic abundances (for a review, see Savage and Sembach, 1996). Thus dust destruction in the hot and warm components of the ISM is followed by reformation and aggregation in diffuse clouds (Jones, 2001), and the grains quickly become chemically and isotopically homogenized (Jones, 2000). Interstellar medium grain size distribution ranges from 0.001- to 0.05-μm grains (PAHs, HACs, amorphous carbons) up to 1-μm grains (amorphous silicate). To account for the larger grains in the ISM grain size distribution, grain growth and aggregation is inferred to occur in diffuse clouds, molecular clouds, and dense cores. Grains aggregated in diffuse clouds are likely to be highly porous and fractal in structure because coagulation processes do not make highly compact grains (Weidenschilling and Ruzmaikina, 1994). Evidence for coagulation into fluffy aggregates in a translucent (Aᵥ = 4) filamentary cloud in the Taurus region is shown through analysis of mult wavelength emission data (Stepnik et al., 2001). Grains may coagulate at larger grains at the boundaries of diffuse and molecular clouds (Miville-Deschênes et al., 2002) and within dense molecular clouds (Bianchi et al., 2003).

Dust grain compositions are measured through the depletion studies of diffuse clouds, and grain mineralogical types are then deduced from the relative ratios of the depleted elements. Depletion measurements indicate four groups of dust-forming elements in the following order, where each group represents about a factor of 10 drop in abundance 

(Jones, 2000): (1) C and O; (2) Mg, Si, and Fe; (3) Na, Al, Ca, and Ni; and (4) K, Ti, Cr, Mn, and Co. Oxygen is not measured along the lines of sight of the halo clouds, but it is assumed that O resides in the dust. Of the rare earth elements, over 70% are contained in the dust. The patterns of elemental depletions for different diffuse cloud lines of sight also show that the more depleted the element, the higher the condensation temperature of the dust species that the element constitutes. There are two chemically distinct grain populations. Some investigators refer to these dust populations as “core” and “mantle” (Savage and Sembach, 1996), or “more-refractory” and “less-refractory” dust components (Jones, 2000). Only the more-refractory dust grains survive in the harsher environments of high-velocity clouds in the galactic halo. These more-refractory grains are primarily composed of O, Mg, Fe, and Si with smaller amounts of Ni, Cr, and Mn. The deduced mineralogic composition of the grains depends on the relative abundances of the elements, which in turn depends on the abundances taken as solar or cosmic. Currently, there are three different references for cosmic abundance: (1) meteorites (Anders and Grevesse, 1989; Grevesse and Noels, 1993), (2) B stars in the solar neighborhood (Snow and Witt, 1996, and references therein), and (3) that deduced for the ISM (Snow and Witt, 1996). Depending on the three different cosmic abundance references, Jones (2000) deduces the more-refractory dust component in the diffuse medium to be either (1) an Fe-rich olivine-type silicate, (2) a mixed silicate and oxide, or (3) an Fe oxide. Savage and Sembach (1996) deduce the more-refractory dust component to be a combination of olivine-type silicate (MgₓFeₙ₋ₓ)₂SiO₄ oxides (MgO, Fe₂O₃, Fe₃O₄), and pure Fe grains. Both more- and less-refractory grains appear to exist in the diffuse clouds in the galactic disk. By subtracting the abundances of the more-refractory component from the total, the less-refractory grain component is deduced to consist of Mg-rich olivine-type grains (Jones, 2000; Savage and Sembach, 1996).

Moreover, not all Si appears to be bound in silicates and oxides (Jones, 2000). This can be interpreted to mean that Mg and Fe exists in forms independent of Si (Sofia et al., 1994; Savage and Sembach, 1996). On the other hand, a continuous evolution of the chemistry of the grains may occur by the preferential erosion of Si with respect to Mg, and the further erosion of both Si and Mg with respect to Fe (Jones, 2000). The erosion of Mg with respect to Fe is expected for sputtering (Jones et al., 1994, 1996; Jones, 2000). The enhanced erosion of Si with respect to Mg may occur with low-energy (~4 KeV) cosmic-ray bombardment (Carrez et al., 2002) in diffuse clouds (section 3.3).

For a given level of depletion in different diffuse clouds, the elemental variations are small. Perhaps the relative elemental abundances are established early in the life of the dust grain and are not significantly altered. The maintenance of grain composition over the lifetime of a grain is surprising because theoretical models predict that shocks of only ~100 km s⁻¹ are required to release enough material from grains to explain the abundances derived for the halo clouds (Sembach and Savage, 1996), and this in turn suggests significant reprocessing. Dust grain recondensation following the passage of supernova shocks (Jones et al., 1994, 1996) and formation of grains in molecular clouds (Dominik and Tielens, 1997) are suggested mechanisms to account for the
long lifetime of interstellar dust grains. If significant fractions of ISM dust are destroyed and reaccreted, it is difficult to see how pure silicates, uncontaminated by C, could form (Jones, 2000). In diffuse clouds, grains may form in non-thermal-equilibrium conditions because temperatures and pressures are low compared to AGB CSEs. In higher-density regions, accretion onto preexisting grains is faster than in lower-density regions, and grain mantles can form under conditions far from thermodynamic equilibrium. Grain formation may occur through kinetic processes (e.g., Gail and Sedlmayr, 1999). Low-temperature grain-formation processes have also been suggested (Sembach and Savage, 1996), but the details of these processes are as yet unknown.

Only the most refractory materials, i.e., minerals that have high condensation and vaporization temperatures, appear to have survived intact through the hot and warm components of the ISM to the CNM. These presolar grains are identified by their anomalous isotopic ratios and are found in meteorites and in IDPs (Hammer and Bradley, 2004; Sykes et al., 2004). Dust grains that have isotopically anomalous presolar signatures of their birth sites include diamonds (Lewis et al., 1987) and TiC grains (Nittler et al., 1996) that condensed in the ejecta of SNe II, SiC grains that primarily formed in AGB CSE (Lewis et al., 1994), graphite grains that formed in the CSEs of massive stars (Hoppe et al., 1992), oxide grains that formed in the O-rich CSE of red giant stars and AGB stars (Nittler et al., 1997), and silicates from AGB stars (Messenger, 2000; Messenger et al., 2003). Presolar silicate grains currently are not found in meteorites, and are <1% by mass of IDPs. Out of more than 1000 subgrains measured in 9 IDPs, 6 subgrains have extreme isotopic $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios: Three are of unknown origin, two are amorphous silicates [glass with embedded metal and sulfides, or GEMS (Bradley, 1994; Hammer and Bradley, 2004)], and one is a Mg-rich crystalline olivine (forsterite) (Messenger et al., 2003). The dust grains mentioned above that are known to be presolar by their isotopic signatures do not represent the typical grains in the ISM that are composed primarily of silicates, metal oxides (from depletion studies), amorphous C, and aromatic hydrocarbons. At this time, the only link that exists between presolar grains and the silicates deduced from diffuse clouds depletion studies are the GEMS (Bradley, 1994). Recall that of the nine IDPs measured by Messenger et al. (2003), 99% of the mass falls in an error ellipse centered on solar composition, albeit the measurement errors on these submicrometer samples are still large, and this supports the suggestion by Jones (2000) that grain materials are rapidly homogenized through destruction-formations processes in the ISM.

3.3. Cosmic-Ray (Ion) Bombardment of Silicate Dust in Diffuse Clouds

Oxygen-rich AGB stars produce a fraction of their silicate dust in crystalline forms (~4–40%) (sections 2.2–2.3). In the ISM the fraction of crystalline silicates is very low, however [<5%; Li and Draine (2002); <0.5%, Kemper et al. (2004)], and is insufficient to account for the fraction of crystalline silicates deduced for comets (Hammer and Bradley, 2004; Ehrenfreund et al., 2004). Therefore silicate crystals are efficiently amorphized in the ISM. Laboratory experiments demonstrate the bombardment of crystalline silicates by energetic ions amorphizes the silicates, which simulates cosmic-ray impacts in ISM shocks (Demyk et al., 2001).

When cosmic rays impact grains, significant processing occurs. Most cosmic rays are H$^+$ and He$^+$ ions. Recent laboratory measurements show that the following changes occur to Fe-bearing olivine crystals when bombarded by 4-KeV He$^+$ ions (Carrez et al., 2002): (1) The crystalline structure changes to a disordered, amorphous structure; (2) the porosity is increased; (3) Fe is reduced from its original stoichiometric inclusion in the mineral lattice to embedded nanophase Fe; and (4) Si is ejected, changing the chemistry from olivine to pyroxene. When higher-energy He$^+$ ions of 50 KeV are used, similar changes occur to the structure of the mineral as occurred with the 4-KeV He$^+$ ions, but the chemistry [i.e., (4) in the above list] is unaltered (Jäger et al., 2003). Through depletion studies of diffuse clouds we know that less Si (more Mg and Fe) in the grains exists than is consistent with silicate mineral stoichiometry. Cosmic-ray bombardment of silicate grains by ~4-KeV He$^+$ ions is a feasible explanation for the observed preferential ejection of Si from the grains (section 3.2). Cosmic-ray bombardment of Fe-bearing silicate minerals also serves to reduce the Fe from its incorporation in the mineral lattice to nanophase Fe grains embedded within a Mg-rich silicate (Carrez et al., 2002). This reduction mechanism explains the presence of nanophase Fe in GEMS in IDPs (section 3.2) (Bradley, 1994; Brownlee et al., 2000). Thus cosmic-ray bombardment of silicates in diffuse clouds may be a viable process for explaining the lack of crystalline silicates in the ISM, the observed properties of the more- and less-refractory grains in diffuse clouds (section 3.2), and the amorphous silicate component of cometary IDPs (Hammer and Bradley, 2004; Ehrenfreund et al., 2004; Wooden, 2002).

The cosmic-ray energies that are utilized in the laboratory to change the properties of silicates only penetrate the diffuse clouds. It is the higher-energy cosmic rays (1–100 MeV, section 1.3) that penetrate the dense molecular clouds and ionize the gas, contributing to the coupling between the gas and the magnetic field and to ion-molecule chemistry (Goldsmith and Langer, 1978). Thus it is the lower energy (1–100 keV) cosmic rays that penetrate diffuse clouds that can amorphize silicates, and therefore change the composition of the silicates in a manner necessary to explain the depletion studies of the diffuse clouds (Jones, 2000).

3.4. Carbonaceous Dust and Macromolecules in the Diffuse Clouds

By observing the “extinction” of starlight toward stars we can trace the nature of interstellar dust particles. The so-called interstellar extinction curve samples the spectroscopic absorption and emission features of interstellar dust.
from the UV to IR wavelengths. Two of the most relevant signatures of interstellar dust are observed at 217.5 nm [called the “ultraviolet extinction bump” (e.g., Fitzpatrick and Massa, 1990)] and 3.4 µm (Pendleton et al., 1994). The 217.5-nm feature is well modeled by UV-irradiated nanosized amorphous carbon (AC) or hydrogenated amorphous carbon (HAC) (Mennella et al., 1998) or by a bimodal distribution of hydrocarbon particles with a range of hydrogenation and a dehydrogenated macromolecule corone (a compact PAH C_{20}H_{12}) (Duley and Seahra, 1999). Other materials such as carbon black of different composition, fullerenes, and PAHs do not show a good match with the UV extinction bump (Cataldo, 2002). Due to constraints on the abundance of elemental C in the ISM (Sofia et al., 1997; Gacinski, 2000), C atoms in sp^2 bonds and C atoms in C–H bonds in the same hydrocarbon grains may be responsible for the 217.5-nm and 3.4-µm features respectively. The 3.4-µm stretching band and the 6.85- and 7.25-µm bending modes [e.g., toward the galactic center (Chiar et al., 2000)] are attributed to the C–H bonds in hydrocarbon grains that occur in –CH_{2} (methylene) and –CH_{3} (methyl) aliphatic groups. Carriers of the interstellar 3.4-µm absorption feature exist in material ejected from some C-rich evolved stars, i.e., the protoplanetary nebula CRL 618 (Chiar et al., 1998). The intense galactic UV field (Mennella et al., 2001) and cosmic rays (Mennella et al., 2003), however, rapidly destroy aliphatic bonds. The aliphatic bonds in hydrocarbon grains are probably formed primarily in diffuse clouds (section 3.5).

Carbonaceous dust in the diffuse medium appears to be highly aromatic in nature, consisting of aromatic hydrocarbon moieties bonded by weak van der Waals forces and aliphatic hydrocarbon bridges (cf. Pendleton and Allamandola, 2002). Among the most abundant C-based species in diffuse clouds are PAHs (see Puget and Léger, 1989). Polycyclic aromatic hydrocarbons contain 1–10% of the total C in the Milky Way, and are the next most abundant molecules after H_{2} and CO. They play a vital role in the heating and cooling of the WNM, diffuse clouds, and surfaces of molecular clouds (Salama et al., 1996; Wolfire et al., 1995, 2003). Ultraviolet photons more energetic than 13.6 eV ionize H and produce energetic electrons that, in turn, heat and ionize the gas in photodissociation regions. Ultraviolet photons less energetic than 13.6 eV would pass practically unattenuated through space if it were not for the PAHs. When PAHs absorb UV photons, both energetic electrons are ejected that collisionally heat the gas (Bakes and Tielens, 1994), and energy retained by the molecules is transferred to vibration modes that then radiate through strong thermal-IR emission bands. These aromatic infrared bands (AIBs) result from C–H stretching and bending modes and C–C ring-stretching modes (Tielens et al., 1999) and have characteristic wavelengths (see Fig. 2): 3.3 µm, 11.3 µm, and 12.5 µm for the C–H bonds on the periphery of the PAH, and 6.2 µm, 7.7 µm, and 8.6 µm for the PAH skeletal C–C bonds. The relative band strengths depend on the size of the PAH macromolecule and on its negatively charged, neutral, or positively charged ionization state (Bakes et al., 2001a,b).

The AIBs are ubiquitous in the diffuse ISM in locations where UV photons can excite them. Polycyclic aromatic hydrocarbon emission arises from photodissociation regions (PDRs) where UV light ionizes and excites the gas and dust (e.g., the Great Nebula in Orion) and in reflection nebulae (e.g., NGC 2023), and where massive stars are illuminating the edges of molecular clouds, as shown in Fig. 2. The AIB bands also are found in external galaxies. Only PAHs in the gas phase provide the necessary properties for internal energy conversion after absorbing a photon, in order to emit at this wavelength range. Though little is known about the exact PAH species present in those environments, their abundance and size distribution can be estimated (Boulanger et al., 1998). Laboratory experiments and theoretical calculations of PAHs have revealed important details about their charge state and structural properties (Allamandola et al., 1999; Van Kerckhoven et al., 2000; Bakes et al., 2001a,b).

A long-standing spectroscopic mystery in the diffuse medium is the diffuse interstellar bands (DIBs). More than 300 DIBs, narrow and broad bands, and many of them of weak intensity, can be observed toward hot stars throughout the diffuse interstellar medium. Substructures detected in some of the narrow, strong DIBs strongly suggest a gas-phase origin of the carrier molecules. Consequently, good candidates are abundant and stable C-bearing macromolecules that reside ubiquitously in the diffuse cloud gas (Ehrenfreund and Charnley, 2000). Polycyclic aromatic hydrocarbons are therefore among the most promising carrier candidates (Salama et al., 1996). The same unidentified absorption bands are also observed in extragalactic targets (Ehrenfreund et al., 2002).

The harsh conditions in the diffuse component of the ISM, e.g., a UV radiation field of 10^{8} photons cm^{-2} s^{-1}, determines the chemistry in such a way that large stable species may either stay intact, change their charge state, become dehydrogenated, or get partially destroyed. Small unstable species are rapidly destroyed. Small amounts of cosmic C probably are incorporated into species such as carbon chains, diamonds, and fullerenes (Ehrenfreund and Charnley, 2000). The presence of such small species in the diffuse clouds, including short carbon chains, thus indicates an efficient formation mechanism. Grain fragmentation by shocks and subsequent release of subunits into the gas phase can also provide a source of relatively large and stable gas-phase species (e.g., Papoular, 2003). Among those, fullerenes have not been unambiguously identified. Recently it has been shown that UV radiation and γ-radiation cause the oligomerization or polymerization of fullerenes in the solid state. Continuous ion irradiation causes the complete degradation of the fullerene molecules into carbonaceous matter that resembles diamond-like carbon (Cataldo et al., 2002). This raises doubts as to whether fullerenes can ever be observed as an interstellar dust component. In contrast, PAHs have large UV cross-sections and can survive in harsh UV environments. Due to their high photostability, PAHs are among the only free-flying gas-phase molecules that can survive passage through the harsh UV environment of the
WIM and WNM components of the ISM to the diffuse clouds.

3.5. Ultraviolet and Cosmic-Ray Processing of Hydrocarbon Dust in the Diffuse Clouds

The 3.4-µm absorption bands are seen along many lines of sight through the diffuse medium (Pendleton et al., 1994; Rawlings et al., 2003). The 3.4-µm feature was well measured in emission in the protoplanetary nebulae CRL 618 (Chiar et al., 1998) and shown to match the 3.4-µm absorption feature toward the galactic center, suggesting that at least some of the hydrocarbons in diffuse clouds originate as stardust (Chiar et al., 1998, 2000). Some AGB hydrocarbon dust grains are likely to survive ISM shocks and the transition to diffuse clouds (Jones et al., 1996; Papoular, 2003), where, if they maintain or regain their degree of hydrogenation, they will contribute to the 3.4-µm aliphatic feature. Grain destruction is so efficient in the ISM (section 1.6), however, that most AGB carbonaceous grains probably readily lose the memory of their birth sites and a new equilibrium for the formation of aliphatic hydrocarbon bonds is set up in diffuse clouds (Mennella et al., 2002).

A long history of laboratory studies exists on the formation of organic residues from the UV photolysis of ices deposited at low temperatures. These organic residues have aliphatic bonds and so the carriers of the 3.4-µm feature in the diffuse clouds were thought to be the products of energetic processing of icy grain mantles within dense molecular clouds (e.g., Greenberg et al., 1995). Several lines of evidence show that the carriers of the 3.4-µm feature are more consistent with plasma-processed pure hydrocarbons than with energetically processed organic residues: (1) The 3.4-µm feature toward the galactic center is unpolarized (Adamson et al., 1999), while the 9.7-µm silicate feature is polarized, so the 3.4-µm feature is not a mantle on silicate cores; (2) the 3.4-µm feature is not observed in dense clouds, requiring that at least 55% of the C–H bonds seen in diffuse clouds be absent from dense molecular clouds (Muñoz Caro et al., 2001), the presumed sites of their formation; and (3) by comparison with laboratory analogs, carriers of the 3.4-µm feature have little O and N, which is uncharacteristic of organic residues.

The carrier of 3.4-µm aliphatic bonds in diffuse clouds plausibly is a consequence of the equilibrium between destruction of C–H bonds via UV photons and cosmic rays and the rapid formation of C–H bonds by the collisions with abundant atomic H atoms. The C–H bond destruction rates for diffuse clouds environments are deduced from experiments of UV irradiation and 30-KeV He⁺ ion bombardment of hydrocarbon grains. Competition between the formation and destruction results in saturation of C–H bonds in ~10⁴ yr, i.e., short times compared to the lifetime of material in diffuse clouds (Mennella et al., 2002, 2003).

Assessment of formation and destruction rates of C–H bonds in different CNM environments provides an explanation for the observed presence of the 3.4-µm feature in the diffuse medium and its absence from the dense medium (Mennella et al., 2003). Between the two destruction mechanisms, UV photons dominate over cosmic rays in diffuse clouds while cosmic rays dominate over UV photons in dense molecular clouds. In molecular clouds, the same cosmic rays (1–100 MeV) that ionize the gas also break C–H bonds. C–H bonds are destroyed and not readily formed: C–H bond formation is stifled by the absence of H atoms in the gas (hydrogen is in H₂ molecules) and by ice mantles on grains that inhibit C–H bond formation. The C–H bond destruction rates in molecular clouds are estimated from the cosmic-ray ionization rates deduced from molecular cloud chemical models (section 4).

3.6. Gas-Phase Chemical Reactions in the Diffuse Clouds

Here the key reaction processes occurring in interstellar chemistry are summarized in the context of diffuse clouds (e.g., van Dishoeck and Black, 1988). Many of the basic chemical processes that operate in diffuse clouds also operate, to a greater or lesser extent, in other regions of the ISM and in protostellar environments. Additional processes are described below where appropriate. Diffuse cloud chemistry predominantly forms simple molecules as a direct consequence of the high UV flux, as shown in Fig. 1. In diffuse clouds most of the nitrogen is present as N² and N³; in dense molecular clouds nitrogen is mostly in the form of N₂. Recent observations indicate the presence of several polyatomic species in diffuse clouds, the origin of which is uncertain at present (Lucas and Liszt, 2000).

Molecular hydrogen plays a key role in the gas-phase chemistry but cannot be produced from it since the low densities and temperatures of the diffuse clouds mean that three-body reaction pathways to H₂ are excluded. Such reactions can form H₂ in dense, high-energy environments such as the early universe or in the winds of novae and supernovae (Rawlings et al., 1993). Instead, in diffuse clouds interstellar H₂ is produced when H atoms collide, stick, migrate, and react on the surfaces of dust grains (Hollenbach and Salpeter, 1971). This catalytic process releases about 4.6 eV of energy, so the H₂ formed is ejected into the gas and also contributes to heating the gas. Experimental studies of H₂ formation on surfaces analogous to those believed to be present in the diffuse clouds indicate that H⁺ recombination appears to be slower (Pirronello et al., 1997, 1999) than predicted by theory (Hollenbach and Salpeter, 1971). This may raise difficulties for producing H₂ in diffuse clouds. Nevertheless, the H/H₂ ratio that is obtained in diffuse clouds is a balance between H₂ formation on dust and UV photo-destruction; the latter is controlled nonlinearly by H₂ self-shielding. Although NH formation by grain-surface chemistry has been suggested (Crawford and Williams, 1997), the role of surface catalysis for other interstellar molecules is highly uncertain at present.
The forms in which the major heavy elements are present are based largely on their ionization potentials and the energy spectrum of the interstellar UV field. Atoms with ionization potentials less than 13.6 eV are readily photoionized, i.e.,

\[ \text{C + } \nu \rightarrow \text{C}^+ + \text{e} \]

Thus, whereas C, S, and various refractory metals (e.g., Fe, Mg, Na) are almost completely ionized, there are insufficient photons energetic enough to ionize O and N. Cosmic-ray particles can ionize H and H₂, and He atoms, to H⁺, H₂⁺, and He⁺. The H₂⁺ ions can subsequently react rapidly with H₂ molecules to produce H₃⁺ and this ion readily transfers a proton to other atomic and molecular species with greater proton affinities than H₂. The electrons produced in these ionizations are lost through radiative recombination reactions such as

\[ \text{C}^+ + \text{e} \rightarrow \text{C} + \nu \]

or in dissociative recombination reactions such as

\[ \text{H}_2^+ + \text{e} \rightarrow \text{H}_2 + \text{H}, \text{ or 3H} \]

The charge transfer process

\[ \text{H}^+ + \text{O} \rightarrow \text{O}^+ + \text{H} \]

followed by

\[ \text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H} \]

initiates a sequence of exchange reactions with H₂ that ends with the dissociative recombination of H₂O⁺ producing OH and H₂O. Ion-molecule reactions also partially contribute to CO production in diffuse clouds through

\[ \text{C}^+ + \text{OH} \rightarrow \text{CO}^+ + \text{H} \]

\[ \text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H} \]

\[ \text{HCO}^+ + \text{e} \rightarrow \text{CO} + \text{H} \]

The precise value of the appropriate rate coefficient for \( \text{H}_2^+ \) recombination is at present controversial (McCall et al., 2002). Exothermic ion-molecule processes typically proceed at the Langevin (collisional) rate. It should be noted, however, that a large population of PAH molecules can qualitatively alter the chemistry of interstellar clouds. In diffuse clouds, where a substantial abundance of PAHs is required to heat the gas through the photoelectric effect (e.g., Bakes and Tielens, 1994, 1998), positive atomic ions are destroyed more efficiently by PAHs than by electrons (Lepp et al., 1988; Liszt, 2003). If a substantial PAH population exists in molecular clouds, then atomic and molecular cations are lost primarily through mutual neutralization with PAH anions (Lepp and Dalgarno, 1988).

Radiative association can initiate a limited hydrocarbon chemistry starting from

\[ \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+_2 + \nu \]

and leading to CH and C₂. Neutral-neutral exchange reactions can also be important for producing simple molecules

\[ \text{C} + \text{OH} \rightarrow \text{CO} + \text{H} \]

\[ \text{N} + \text{CH} \rightarrow \text{CN} + \text{H} \]

The \textit{in situ} production of complex molecules within diffuse clouds is inhibited by the efficient photodestruction of diatomic and triatomic molecules, e.g.,

\[ \text{OH} + \nu \rightarrow \text{O} + \text{H} \]

Of course, other chemical reactions have to occur, and we now discuss these in the context of the so-called “CH⁺ problem” (Williams, 1992; Gredel, 1999). Chemical models of the diffuse interstellar medium can reproduce the observed column densities of many species (van Dishoeck and Black, 1988). However, to date no model has been able to reproduce the observed abundance of CH⁺ while obeying all the other observational constraints. The obvious formation reaction is highly endoergic by 4640 K

\[ \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H} \quad (1) \]

and will not proceed at normal diffuse clouds temperatures. When diffuse interstellar gas is heated and compressed by shock waves, many chemical reactions that are endothermic, or possess activation energy barriers, can occur in the post-shock gas (e.g., Mitchell and Deveau, 1983). For example, the reaction above (equation (1)) and

\[ \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \]

\[ \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H} \]

However, hydrodynamic shocks have not been shown to be able to resolve the CH⁺ issue without violating the constraints on, e.g., the observed OH abundance and the rotational populations of H₂ (e.g., Williams, 1992).

As interstellar clouds are magnetized and only partially ionized, slow shock waves can exhibit more complex structures than simple shock discontinuities (e.g., Roberge and Draine, 1990). The fact that some magnetohydrodynamic waves can travel faster than the sound speed in these plasmas means that there is a substantial difference in the velocities of the ions and neutrals. This effect gives rise to C-shocks in which all variables are continuous across the shock structure (see Draine, 1980). C-shocks also have been pro-
posed to produce CH+ (Pineau des Forêts et al., 1986; Draine and Katz, 1986) but with mixed success when compared to observation (Gredel et al., 1993; Flower and Pineau des Forêts, 1998; Gredel et al., 2002).

Finally, while dissipation of interstellar turbulence occurs in shocks, it also occurs intermittently in small regions of high-velocity shear (Falgarone et al., 1995), and the associated heating has been suggested as important for driving the reaction shown in equation (1) (Joulain et al., 1998). In both cases, the high heating efficiency occurs because the energy available from dissipation of turbulence is degraded to thermal energy within a small volume. At present, the CH+ problem remains unsolved, but it is clear that solving the origin of CH+ will significantly impact the study of the physics and chemistry of diffuse clouds.

4. PHYSIOCHEMICAL PROCESSES IN COLD DENSE MOLECULAR CLOUDS

4.1. Overview

In this section we describe the gaseous and solid-state composition of dark, dense molecular clouds, the regions where high- and low-mass stars form. Considering an evolutionary chemical sequence originating from AGB envelopes and the diffuse ISM, molecular clouds are the point where interstellar chemistry starts to have direct relevance for cometary composition (e.g., Langer et al., 2000). Specifically, molecular ice mantles (see Table 2) can form on siliceous and carbonaceous dust grains, and processing of these ices opens up many more chemical pathways (see Fig. 3).

Molecular clouds possess higher densities of gas and dust than diffuse clouds, their presumed precursors. Cosmic rays penetrate into the deepest cloud interiors and produce H$_3^+$, He$,^+$, and electrons that heat the gas. This results in a rich gas phase chemistry (van Dishoeck et al., 1993). Dust grains shield the inner regions of the cloud from external UV radiation and most of the photons capable of dissociating H$_2$ (and other molecules) are absorbed at cloud surfaces. Hence, grain catalysis can convert almost all the available H to H$_2$ (section 3.6). As most of the gas phase C is present as CO, these clouds cool principally by molecular rotational emission from CO molecules excited by collisions with H$_2$ and He. The gas and dust temperatures are tightly restricted to lie in a range around 10 K (Goldsmith and Langer, 1978).

At lower densities, the gas and dust are not thermally well coupled and depletion of coolant species may increase the gas temperature (Goldsmith, 2001). Although external UV photons do not significantly penetrate these clouds, there probably exists a weak UV flux throughout molecular cloud interiors. This flux derives from excitation of H$_2$ by energetic electrons produced in primary cosmic-ray impacts. The

**TABLE 2. Ice composition* toward interstellar sources †.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>W33A High-Mass Protostar</th>
<th>NGC7538 IRS9 High-Mass Protostar</th>
<th>Elias 29 Low-Mass Protostar</th>
<th>Elias 16 Field Star</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>CO</td>
<td>9</td>
<td>16</td>
<td>5.6</td>
<td>25</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>14</td>
<td>20</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2</td>
<td>2</td>
<td>&lt;1.6</td>
<td>—</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>22</td>
<td>5</td>
<td>&lt;4</td>
<td>&lt;3.4</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>1.7–7‡</td>
<td>5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>OCS</td>
<td>0.3</td>
<td>0.05</td>
<td>&lt;0.08</td>
<td>—</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>15</td>
<td>13</td>
<td>&lt;9.2</td>
<td>&lt;6</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>—</td>
<td>&lt;0.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HCOOH</td>
<td>0.4–2‡</td>
<td>3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>OCN–</td>
<td>3</td>
<td>1</td>
<td>&lt;0.24</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>HCN</td>
<td>&lt;3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Abundances by number relative to water ice.
†Adapted from Ehrenfreund and Charnley (2000).
‡Abundances with large uncertainties are shown as a range of values.
subsequent UV emission spectrum can photodissociate and photoionize interstellar molecules (Prasad and Tafrađar, 1983), and can significantly influence the abundances of some species (e.g., atomic C) (Gredel et al., 1987).

4.2. Gas-Phase Chemistry

Most of the chemical reactions described for diffuse clouds (section 3.6) also play a role in molecular cloud chemistry. Cosmic-ray ionizations drive a chemistry where ion-molecule and neutral-neutral reactions convert an appreciable fraction of the heavy elements to molecular forms. Thus, one finds that most C exists as CO, although a significant fraction of atomic C is present (C/CO = 0.1). The dominant form of O is not well determined in these sources but is understood to be atomic, from chemical models and the observed lack of O2 (Goldsmith et al., 2000, 2002). Based on observed N2H+ abundances, almost all the available nitrogen is in N2. Sulfur constitutes a puzzle, as its elemental depletion with respect to the diffuse ISM, and its major form, are unknown (e.g., Charnley et al., 2001a; Scappini et al., 2003). Many S-bearing molecules are detected and this suggests that atomic S is probably the major repository of this element. Molecules containing refractory metals (e.g., Fe, Mg, Na) are not present and metals are understood to be completely depleted on/in dust grains.

Proton transfer reactions produce many molecular ions and observations of these (HCO+, DCO+) can be used to estimate the electron density or the abundances of undeveloped molecules (e.g., N2H+ to trace N2). It appears that many neutral-neutral reactions have significant rate coefficients at low temperatures (Chastaing et al., 2001). Reactions involving various hydrocarbons (e.g., C2H2 acetylene) with C atoms and with the CN radical are particularly important in producing many of the long carbon-chain compounds (Cherchneff and Glassgold, 1993), e.g., cyanoacetylene

\[
\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}
\]

These reactions can generate many of the higher cyanopolynes [i.e., HC6N, HC5N (Dickens et al., 2001), HC4N, and HC3N] as well as various hydrocarbon chains (e.g., C6H, C5H, C4H, C3H), that are detected in molecular clouds, such as TMC-1 in Taurus (Pratap et al., 1997; Markwick et al., 2000) (Fig. 1). Several important species are known in star-forming clouds but are not shown in Fig. 1 (e.g., atomic O and CO2). Some species, undoubtedly present in molecular clouds, are difficult or impossible to detect directly in sources like TMC-1 (e.g., S, O, N2, CO2 and C2H2). It is worth noting that significant compositional differences are found among molecular clouds. For example, L134N does not contain large abundances of carbon-chain molecules (Pagani et al., 2003; Dickens et al., 2000) and may be more typical than TMC-1 (Dickens et al., 2001).

The extremely cold temperatures in these dense clouds mean that molecular zero-point energies can be an important factor in the gas-phase kinetics. Molecular clouds are there-

\[
\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2
\]

is very slow at 10 K. Similar reactions also occur for some hydrocarbon ions such as CH3+ and CH5+. The H2D+ ions formed can initiate the distribution of D atoms throughout the molecular chemistry (e.g., Millar et al., 1989, 2000). Isotopic exchange involving 13C+ and 12CO leads to enhancements of 13C in CO (Langer et al., 1984) and a general decrease of 13CO/12CO in other molecules. Chemical fractionation of 13N also occurs in ion-neutral reactions (Terzieva and Herbst, 2000) but the highest 15N/14N ratios theoretically possible in interstellar molecules may require special conditions apart from very low temperatures [such as CO depleted but N2 not depleted in the gas phase (Charnley and Rodgers, 2002)]. The extreme sensitivity of these fractionation reactions to the gas temperature is further strong evidence of the importance of cold cloud chemistry for understanding the origin of the enhanced isotopic fractionation found in primitive solar system material such as comets and meteorites.

4.3. Gas-Grain Interactions

Siliceous and carbonaceous micrometer- and submicrometer-sized dust particles that are produced in the outflows of late-type AGB stars provide a catalytic surface for a variety of reactions to occur when they are dispersed throughout molecular clouds. Atoms and molecules strike and stick to the surfaces of these cold dust grains and this process leads to the formation of an amorphous, mixed, molecular ice mantle covering the siliceous/carbonaceous grains. Table 2 shows the observed composition of interstellar ices. The forming ice mantles consist of molecules directly accreted from the gas (e.g., CO) and molecules formed through chemical reactions at about 10 K. These ices are susceptible to various kinds of energetic processing: cosmic-ray impacts, heating near protostars, and perhaps UV photolysis.

At typical molecular cloud densities, particles are accreted from the gas at the rate of about one per day. The sticking coefficients for most of these species at 10 K are calculated to be close to unity (e.g., Leitch-Devlin and Williams, 1985). On the surface, heavy particles such as CO are relatively immobile. Atoms can diffuse and react with the immobile species, as well as among themselves. Hydrogen atoms can rapidly explore the surface by quantum-mechanical tunnelling. Experiments show that, once a monolayer has formed, quantum diffusion by H atoms is very rapid (Manico et al., 2001). An H atom can therefore scan the entire surface to find any available co-reactants. Heavy atoms (e.g., C and O) can diffuse by thermal hopping (e.g., Tielens and Allamandola, 1987). Slowly, the accreted atoms react chemically, are converted to various molecules, and as a result, ice mantles are formed.
Unabated accretion, i.e., in the absence of an efficient means of returning molecules to the gas, would completely remove the heavy element component from the molecular gas on an accretion timescale of $3 \times 10^9 n_{\text{H}}^{-1}$ yr, i.e., about $10^5$ yr at a density of $n_{\text{H}} = 10^4$ cm$^{-3}$ (e.g., Brown and Charnley, 1990). Hence, if molecular clouds are dynamically much older than this, there must be some desorption from the grain surfaces to prevent this “accretion catastrophe.” However, the precise nature of the putative desorption mechanism (or mechanisms) is not yet unambiguously identified. Several candidate mechanisms have been proposed, including evaporation following grain heating by cosmic rays, mantle explosions, and ejection upon molecule formation (see Willacy and Millar, 1998). As molecular clouds are also regions of star formation, dynamical events also have been proposed for removing and reforming the molecular ices within the accretion timescale; these include sputtering in low-velocity shock waves (Bergin et al., 1998; Charnley et al., 2001a) and grain-grain collisions induced by clump collisions or wave motions (Markwick et al., 2000; Dickens et al., 2001).

The “accretion catastrophe” is most evident in a dynamical scenario where molecular clouds are long-lived ($\sim 10^7$ yr), and where low-mass star formation is controlled quasi-statically by ambipolar diffusion, the relative drift between ions and neutrals in partially ionized plasma. Ambipolar diffusion leads to interstellar cloud material losing magnetic support against gravity on characteristic timescales of $\approx 5 \times 10^6$ yr that are determined by the electron density. The electron density is set by the ionization rate that is, in turn, determined from the chemistry of molecular cloud material (e.g., Shu et al., 1987, 1993). An enormous effort has been made over the past two decades to reconcile observed molecular abundances and the results of chemical models with such long cloud lifetimes, i.e., to reconcile the apparent “chemical youth” of objects many millions of years old. However, when viewed in the context of the more recent dynamical scenario (section 1.4) where molecular cloud formation and star formation are controlled by supernovae-driven supersonic turbulence (e.g., Mac Low and Klessen, 2003; Larson, 2003), and the shorter cloud lifetimes ($\sim 1-3 \times 10^6$ yr) inferred from observations (Elmegreen, 2000; Hartmann et al., 2001), the accretion catastrophe problem may be resolvable. In this picture, most interstellar cloud materials are in a low-density, primarily atomic phase as diffuse clouds and hence can have accretion timescales longer than the molecular cloud lifetimes. The long lifetimes of diffuse cloud material will not greatly affect the molecular composition of molecular clouds.

Dense prestellar cores evolve roughly on free-fall timescales and have shorter lifetimes than the molecular clouds in which they lie. The fact that substantial selective depletions (e.g., CO relative to $N_2$) are observed in these regions (Bergin et al., 2002) indicates that a viable surface desorption mechanism is still needed. However, this mechanism eventually should be overwhelmed in the most dense, coldest regions. It is very likely that the central regions of prestellar cores pass through a phase where all the available heavy atoms have been incorporated into molecular ices. Short cloud lifetimes (section 1.4), and the inference that molecular clouds are indeed chemically young, could also provide a natural explanation for other astrochemical problems, such as the high $C/O_2$ ratio that is observed to be widespread in galactic clouds (Goldsmith et al., 2000). However, the existence of small-scale ($\sim 0.01$ pc) molecular differentiation in dense clouds still presents a major challenge for chemical models (Dickens et al., 2001; Takakuwa et al., 2000).

Observations of dense cores within molecular clouds show strong evidence for substantial depletions (Bergin et al., 2002); this suggests whatever desorption mechanism operates at lower densities is overwhelmed in dense cold cores.

### 4.4. Observations of Astronomical Ices

The protostars that form in molecular clouds are natural IR background sources, which can be utilized to perform solid-state spectroscopy on the column of gas along the line-of-sight. Ground-based observations performed since the 1970s demonstrated the presence of abundant water ice as well as CO ice (e.g., Whittet, 1993) (see Fig. 2a). The absorption features of water ice and silicates observed at 3 µm and 10 µm, respectively, dominate the spectrum toward stars in dense molecular clouds. Those bands are broad and often saturated and are the reason why the inventory of ices will never be complete. Many species, in particular NH$_3$ and CH$_3$OH as well as species with a C=O group, are either blended or masked by those dominant spectral bands. This strongly biases abundance determinations.

Other species remained undetected until sophisticated IR satellites provided the full range of spectral data from 1 to 200 µm. The ISO provided us with very exciting spectra that allowed us to compile an inventory of interstellar ice species and measure their abundances in various interstellar environments [for reviews on ISO data, see Ehrenfreund and Schutte (2000) and Gibb et al. (2000)]. ISO identified two distinct ice layer compositions: hydrogen-rich ices (“polar” H$_2$O-dominated with traces of CO, CO$_2$, CH$_3$, NH$_3$, CH$_3$OH, HCOOH, and H$_2$CO) and the more volatile “apolar” CO-dominated ices (with small admixtures of O$_2$ and N$_2$). The build up of apolar ice layers occurs at successively lower temperatures than polar ice layers on grain mantles. Abundances and inventories of ice species toward low- and high-mass protostars can be found in Table 2.

The solid CO band at 4.67 µm can be well studied by groundbased observations. Laboratory studies reveal that the CO band profile is strongly influenced by neighboring species in the ice and acts therefore as a good tracer of the overall grain-mantle composition (Ehrenfreund et al., 1996). Recent high-resolution measurements of CO using 8-m class telescopes reveal a multicomponent structure. Boogert et al. (2002a) observed the M-band spectrum of the class I protostar L1448 IRS in the Taurus molecular cloud. The CO band profile showed a third component apart from CO in “polar” ices (CO mixed with H$_2$O) and CO in “apolar” ices (see above). The high-spectral-resolution observations show that the apolar component has two distinct components, likely
due to pure CO and CO mixed with \( \text{CO}_2 \), \( \text{O}_2 \), and/or \( \text{N}_2 \). \( \text{Pontoppidan} \text{ et al.} \) (2003a) conclude from recent ground-based observations of more than 40 targets that the CO band profile can be fitted with a three-component model that includes pure CO, CO embedded in water ice, and a third component that is attributed to the longitudinal component of the vibrational transition in pure crystalline CO ice (appearing when the background source is linearly polarized). This three-component model applied in varying ratios provides an excellent fit to all bands observed, and indicates a rather simple universal chemistry in star-forming regions with 60–90% of the CO in a nearly pure form (\( \text{Pontoppidan} \text{ et al.} \) 2003a). The freezeout of CO in a circumstellar disk around the edge-on class I object CRBR 2422.8-3423 has been recently observed with the ISAAC instrument on the Very Large Telescope (VLT) by \( \text{Thi} \text{ et al.} \) (2002) with the highest abundance observed so far.

In high-spectral-resolution spectra, \( \text{Boogert} \text{ et al.} \) (2002a) detected toward the massive protostar NGC 7538 IRS 9 a narrow absorption feature at 4.779\( \mu \text{m} \) (2002.3 cm\(^{-1}\)) attributed to the vibrational stretching mode of the \( ^{13}\text{CO} \) isotope in pure CO icy grain mantles. This is the first detection of \( ^{13}\text{CO} \) in icy grain mantles in the ISM. A ratio of \( ^{12}\text{CO}/^{13}\text{CO} = 71 \pm 15 \) (3\( \sigma \)) was deduced, in good agreement with gas-phase CO studies (\( ^{12}\text{CO}/^{13}\text{CO} = 77 \)) and the solid \( ^{12}\text{CO}/^{13}\text{CO} \) ratio of 80 \( \pm \) 11 found in the same line of sight (\( \text{Boogert} \text{ et al.} \) 2002b). The ratio is confirmed by the ratio observed in the low-mass star IRS 51, namely a \( ^{12}\text{CO}/^{13}\text{CO} \) ratio of 68 \( \pm \) 10 (\( \text{Pontoppidan} \text{ et al.} \) 2003a).

The abundance of \( \text{NH}_3 \) in interstellar grain mantles has been a hotly debated subject for a long time (e.g., \( \text{Gibb} \text{ et al.} \) 2001). The reported abundances for \( \text{NH}_3 \) relative to \( \text{H}_2\text{O} \) range from 5–15%. The most recent VLT data confirm abundances on the lower end of this scale. \( \text{Dartois} \text{ et al.} \) (2002) report \( \approx 7\% \) for the \( \text{NH}_3/\text{H}_2\text{O} \) ratio toward the evolved massive protostars GL 989 and GL 2136, derived from a band at 3.47\( \mu \text{m} \) attributed to ammonia hydrate. \( \text{Taban} \text{ et al.} \) (2003) observe the 2.21\( \mu \text{m} \) band of solid \( \text{NH}_3 \) and provide only an upper limit toward W33A; their limit is \( \approx 5\% \) for the \( \text{NH}_3/\text{H}_2\text{O} \) ratio.

The lines of sight toward star-forming regions consist of regions with strongly varying conditions. Temperatures are low in molecular cloud clumps but can be very high in hot core regions close to the star, where ices are completely sublimated. The spectra that sample the different regions in the line of sight toward star-forming regions need to be deconvolved using additional information about the gas phase composition and geometry of the region. For example, Fig. 2a shows spectra of material in the line of sight to a massive protostar that intercepts both cold cloud ices and UV-illuminated PAHs. In the past few years, ground-based telescopes of the 8–10-m class have allowed us to observe some ice species with unprecedented spectral resolution. The spectral resolution also enables us to study lines of sight toward low-mass protostars, which usually were too faint to be observed with the ISO satellite. VLT and KECK II, equipped with the ISAAC and NIRSPEC spectrographs, respectively, have delivered exciting new data on ice species such as CO (and \( ^{13}\text{CO} \)), \( \text{NH}_3 \), and \( \text{CH}_3\text{OH} \) (\( \text{Thi} \text{ et al.} \) 2002; \( \text{Boogert} \text{ et al.} \) 2002b; \( \text{Dartois} \text{ et al.} \) 2002; \( \text{Pontoppidan} \text{ et al.} \) 2003a,b; \( \text{Taban} \text{ et al.} \) 2003). The \( \text{CH}_3\text{OH} \) abundance relative to water ice measured in star-forming regions lies between 0% and 30%. Two high-mass protostars have been identified with very large \( \text{CH}_3\text{OH} \) abundances, namely up to 25% relative to water ice (\( \text{Dartois} \text{ et al.} \) 1999). New VLT data of the 3.52-\( \mu \text{m} \) band (C-H stretching mode of \( \text{CH}_3\text{OH} \)) also show abundances up to 20% toward low-mass stars in the Serpens cloud (\( \text{Pontoppidan} \text{ et al.} \) 2003b).

4.5. Solid-State Chemical Reactions on Dust

Astrochemical theories suggest that only a few classes of reactions appear to be necessary to form most of the molecules observed in ices (\( \text{Herbst} \), 2000). Several exothermic \( \text{H} \) atom additions to \( \text{C}, \text{O}, \text{N} \), and \( \text{S} \) produce methane (\( \text{CH}_4 \)), water, ammonia (\( \text{NH}_3 \)), and hydrogen sulphide (\( \text{H}_2\text{S} \)). Atom additions to closed-shell molecules such as CO possess substantial activation-energy barriers. However, due to their small mass, \( \text{H} \) and \( \text{D} \) atoms could saturate these molecules by tunnelling through this barrier (\( \text{Tielens} \) and \( \text{Hagen} \), 1982; \( \text{Tielens} \), 1983). Hydrogenation of CO has been suggested to be the source of the large abundances of solid methanol (\( \text{CH}_3\text{OH} \)) seen in many lines of sight toward protostars (e.g., \( \text{Tielens} \) and \( \text{Charnley} \), 1997; \( \text{Charnley} \), 1997; \( \text{Caselli} \text{ et al.} \) 2002), and the enormous D/H ratios observed in both formaldehyde (\( \text{H}_2\text{CO} \)) and methanol in protostellar cores where CO ices have been sublimated to the gas phase (\( \text{Loinard} \text{ et al.} \) 2000; \( \text{Parise} \text{ et al.} \) 2002). Additionally, \( \text{CO}_2 \) could form by \( \text{O} \) atom addition to CO at 10 K (\( \text{Tielens} \) and \( \text{Hagen} \), 1982). Based on these mechanisms many large organic molecules may form on grains (e.g., \( \text{Charnley} \), 1997b).

Thermal processing close to the protostar leads to molecular diffusion, structural changes within the ice matrix, and subsequently to sublimation. Ice segregation, and possibly even clathrate formation, has been observed in dense clouds (\( \text{Ehrenfreund} \text{ et al.} \) 1998). Simple thermal processing of ice mixtures can itself produce new molecules. In the laboratory, it has been shown that the heating of ice mixtures containing formaldehyde \(( \text{H}_2\text{CO}, \text{also called methanal})\) and ammonia \(( \text{NH}_3 \)) results in polymerization of the formaldehyde into polyoxymethylene (POM, \(-\text{CH}_2\text{-O}-\)) \(( \text{Schutte} \text{ et al.} \) 1993). Extensive and detailed laboratory studies have been undertaken to study the chemistry of interstellar ice analogs (\( \text{Cottin} \text{ et al.} \) 1999). For many years these studies were restricted to either UV photoysis (e.g., \( \text{Allamandola} \text{ et al.} \) 1997) or proton irradiation (e.g., \( \text{Moore} \) and \( \text{Hudson} \), 1998) of bulk ices; in both cases the effects of warming the ices are usually considered (“thermal chemistry,” Fig. 3). The strongly attenuated UV flux in such dense environments strongly limits photolysis processes. In contrast, cosmic rays can penetrate dense molecular clouds and effect the structure and composition of the ices, including sputtering of icy grain mantles (\( \text{Cottin} \text{ et al.} \) 2001).

Atom addition reactions on grain surfaces are necessary to initially form water ice mantles, as gas phase ion-molecule reactions cannot produce large quantities of water. How-
ever, it is only recently that atom reactions on analog surfaces have come to be studied in detail (e.g., Hiraoaka et al., 1998; Pironello et al., 1999; Watanabe and Kouchi, 2002). From the existing laboratory data it is possible to make comparisons of the relative efficiency of each chemical process (photolysis, radiolysis, and atom additions) in producing the major observed mantle molecules from CO. Both radiolysis (i.e., proton irradiation) and photolysis easily produce CO$_2$. Recent experiments show that, although oxidation of CO by O atoms has a small activation energy barrier, this reaction can form CO$_2$ (Roser et al., 2001). However, in these experiments CO$_2$ is only produced efficiently when the reacting CO and O atoms are covered by a layer of H$_2$O molecules and warmed. This appears to increase the migration rates in the ice and suggests that the longer migration times available on grain surfaces in dense clouds, times much longer than can reasonably be studied in the laboratory, may make this reaction the source of the observed CO$_2$. Also, cold H additions in ices containing acetylene (C$_2$H$_2$) have been proposed as the origin of the ethane (C$_2$H$_6$) found in comets (Musman et al., 1996) and experiments support this idea (Hiraoaka et al., 2000). As yet, ethane is not detected in the ISM but these experiments suggest it has an interstellar origin (see Ehrenfreund et al., 2004).

Ultraviolet photolysis of ice mantles produces radicals that may migrate and react (see Fig. 3). However, experiments show that UV processing of H$_2$O/CH$_4$ mixtures is very inefficient at producing methanol (CH$_3$OH) (d’Hendecourt et al., 1986). In fact, experiments show that methanol is readily decomposed to formaldehyde under photolysis (Allamandola et al., 1988). By contrast, radiolysis of dirty ice mixtures can produce methanol in astronomically interesting amounts (Hudson and Moore, 1999). Initial reports that cold H atom additions to CO could produce methanol at low temperatures were positive (Hiraoka et al., 1994, 1998) but were not supported by more recent experiments by the same group (Hiraoka et al., 2002). However, recent laboratory experiments (Watanabe and Kouchi, 2002; Watanabe et al., 2003) strongly argue for CH$_3$OH production via this mechanism.

Experiments involving H$^+$ irradiation (radiolysis) are designed to simulate cosmic-ray bombardment (see Fig. 3). Radiolysis proceeds by ionization of H$_2$O to H$_2$O$^+$, from which a proton then transfers to water to form protonated water, H$_3$O$^+$. Subsequent dissociative electron recombination of protonated water produces a population of energetic, reactive H atoms and hydroxyl (OH) molecules in the ice (Moore and Hudson, 1998). Experiments show that radiolysis of H$_2$O/CO ice mixtures can produce high abundances of H$_2$CO and CH$_3$OH (Hudson and Moore, 1999), although formic acid (HCOOH, also called methanoic acid) is over-produced relative to the HCOOH/CH$_3$OH ratio observed in interstellar ices. Radiolysis of ice mixtures containing CO and C$_2$H$_2$ also produces ethane, as well as several other putative mantle molecules such as CH$_3$CHO and C$_2$H$_5$OH (Hudson and Moore, 1997; Moore and Hudson, 1998).

One interstellar molecule that certainly originates in energetically processed ices is the carrier of the so-called “XCN” 4.62-µm absorption feature, observed in the diffuse clouds (Pendleton et al., 1999), toward protostars (e.g., Tegler et al., 1995), and, most recently, in the nearby dusty starburst AGN galaxy NGC 4945 (Spooner et al., 2003). Laboratory experiments indicate that “XCN” is produced both by photolysis (Lacy et al., 1984; Bernstein et al., 2000) and by radiolysis (Hudson and Moore, 2000; Palumbo et al., 2000). At present, the best candidate for the identity of this carrier appears to be the OCN$^-$ ion, formed in a solid-state acid-base reaction between NH$_3$ and isocyanic acid (HNCO) (see Novozamsky et al., 2001, and references therein).

4.6. Theoretical Modeling of Solid-State Reactions

There have been many attempts to model low-temperature grain-surface chemical reactions (e.g., Allen and Robinson, 1977; Tielens and Charnley, 1997; Herbst, 2000). Heterogeneous catalytic chemistry on grain surfaces occurs primarily through the Langmuir-Hinshelwood mechanism. Here reactive species arrive from the gas, stick to the surface, and then migrate until they encounter another species with which they can react (section 4.3); the product molecule may either remain on the surface or be desorbed. In deterministic theoretical models it is relatively straightforward to quantitatively treat the accretion and desorption of surface species (e.g., Charnley, 1997c). However, to correctly model surface diffusion and reaction, a fully stochastic treatment involving solution of the associated master equation for the surface populations is necessary (Charnley, 1998). A number of recent papers have modeled surface chemistry in this way, although the adopted methods of solution have differed considerably (Charnley, 2001; Biham et al., 2001; Green et al., 2001; Stantcheva et al., 2002; Caselli et al., 2002). However, in marked contrast to the amount of effort expended in trying to model surface reactions, there has been almost no theoretical modeling of the kinetics associated with the photolysis or radiolysis of the bulk ice mantle (however, see Ruffle and Herbst, 2001; Woon, 2002).

5. Physicochemical Processes in Dense Star-Forming Cores

5.1. Overview

Understanding the physics and chemistry of low-mass star formation is most relevant for solar system studies. Modeling well-studied sources at various evolutionary stages enables us to understand how much processing interstellar material experienced as it became incorporated into the nascent protosolar nebula (van Dishoeck and Blake, 1998; Ehrenfreund and Charnley, 2000).

Star formation occurs rapidly in molecular clouds, probably within a million years (section 1.4). The mass scale and
the occurrence of isolated stars, binaries, stellar clusters, and associations are determined by the local and global competition between self-gravity and the turbulent velocity field in interstellar clouds. Massive stars may form from a single isolated core (Stahler et al., 2000), or may grow in stellar clusters through coalescence of two or more low-mass and intermediate-mass stars (Clark et al., 2000; Bonnell and Bate, 2002). Formation of single and binary low-mass stars can proceed from collapse and fragmentation of less-massive regions of lower density (Mac Low and Klessen, 2003).

The chemistry of its surroundings is dramatically influenced by the protostar. A central aspect in understanding the chemical evolution prior to and following star formation appears to be the prestellar accretion of molecules onto grains and their subsequent removal, which occurs in a hot (or warm) dense core of the molecular cloud surrounding the accreting protostar. Due to the higher intrinsic line fluxes, and stronger IR emission, most previous studies of protostellar gas and solid-phase compositions have focused on high-mass star-forming hot cores, such as Orion A and Sagittarius B2 (Johansson et al., 1984; Cummins et al., 1986; Blake et al., 1987; Turner, 1991; Smith et al., 1989). However, it is now becoming clear that low-mass protostars also pass through a warm core phase (e.g., Schoier et al., 2002; Cazaux et al., 2003). In this section we present an overview of the chemistry, and associated molecular morphology that develops around an accreting protostar.

### 5.2. Hot Cores Around Massive Protostars

Hot molecular cores are most commonly identified with the earliest phases of massive star formation (Churchwell, 2002). Hot cores contain a young protostar embedded within its dense cocoon of gas and dust and the most sophisticated chemical models have been developed to account for the observations of these massive hot cores (Doty et al., 2002; Rodgers and Charnley, 2003). The elevated temperatures and densities in these small regions (<0.1 pc, see Table 1) produce a chemical composition markedly distinct from other regions of the ISM as shown in Fig. 1. Note that in Fig. 1 the abundances listed for IRAS 16293 are for the warm inner component as determined by Schoier et al. (2002) except for CO, HCO+, CN, HCN, C_2H, C_2H_2, and CS. The C_2H_3CN entry and the remarkably high abundances of HCOOC_2H_5, CH_3OCH_3, and HCOOH are taken from Cazaux et al. (2003). Many large organic molecules are also detected in hot molecular cores but have been omitted from Fig. 1; these include ethanol, glycolaldehyde, ethylene glycol, acetone, acetic acid, and glycine (Ohishi et al., 1995; Hollis et al., 2000, 2002; Snyder et al., 2002; Remijan et al., 2003; Kuan et al., 2003). It is now understood that hot core chemistry is mainly the result of the volatile contents of the ice mantles being deposited into the gas via desorption. Evidence for this are the high abundances of saturated molecules (water, ammonia, methane) and enhanced D/H ratios, both of which could only have been set in much colder conditions (section 4). Similar chemical processes also can be expected to play a key role in low-mass star-formation environments, and so here a brief overview of chemistry in massive star formation is given.

The basic chemistry of massive star formation can be best described by distinguishing between processes that occur in a cold prestellar phase and those that occur in a hot phase after a protostar has formed (Brown et al., 1988). The cold phase includes the quasistatic chemical evolution in molecular clouds (section 4) and eventually an isothermal gravitational collapse to a small, cold (10 K), dense core. Rapid protostellar heating of the core to hot core temperatures (100–300 K) induces thermal evaporation (sublimation) of icy grain mantles and hot core chemistry.

During the isothermal collapse, gas-grain collision times become so short that most of the heavy atoms and molecules in the center of the cloud core are in the solid state (section 4). There is recent observational evidence for the disappearance of CO and N_2 molecules in the central region of dense cores (e.g., Bergin et al., 2002; Baczmann et al., 2002; Caselli et al., 2003). Subsequent protostellar heating returns the volatile ices to the gas phase. Radioastronomy permits the ice composition to be studied in more detail when in the gas phase than is possible by direct IR absorption studies of the solid phase using field stars behind molecular clouds, or toward embedded protostars (e.g., Charnley et al., 2001b). For example, the recently discovered gas-phase organics, including vinyl alcohol (Turner and Apponi, 2001), glycolaldehyde (Hollis et al., 2000), and ethylene glycol (Hollis et al., 2002), are inferred to be present in the solid-phase on grains only in trace amounts.

In the collapse phase, the warming and subsequent release of the grain material can be used to constrain the nature of grain-surface reactions. Identifying the origin of specific molecules (and classes of molecules) can provide important information on the composition of the prestellar core and on the nature of grain-surface chemistry. There are three ways in which the molecules observed in hot cores can originate: First, molecules produced in the cold prestellar phase (e.g., CO) that accreted on grains and formed ices can simply be returned to a hot environment. Second, other atoms and radicals can stick to grains and take part in grain-surface reactions to form mixed molecular ices (section 4). However, not all the complex molecules observed in hot cores are products of grain-surface chemistry. It transpires that a highly transient chemistry can also occur in the gas during the hot core phase, and therefore the third formation pathway for hot core molecules is in situ molecule formation (Charnley et al., 1992; Caselli et al., 1993). For example, alkyl cation transfer reactions involving surface-formed alcohols can produce many larger organic molecules, such as ethers (e.g., Charnley et al., 1995; Charnley, 1997b). Hot core chemistry is more accurately described than that of warm cores because the initial conditions (i.e., the grain mantle composition) are constrained better, and because the evolution lasts less than ~10^5 yr or so.
Between individual cores, a strong chemical differentiation is observed between O-bearing and N-bearing molecules. This chemical differentiation is modeled and attributed to differences in temperature and evolutionary state of the core: Hotter cores tend to have higher abundances of N-bearing molecules (Rodgers and Charnley, 2001). Models of the hot-phase chemistry have been constructed for the chemistries of second-row elements (P, Si, S), which are particularly sensitive to the temperature in the hot gas (Charnley and Millar, 1994; Mackay, 1995; Charnley, 1997a). Observations of S-bearing molecules may be particularly useful as molecular clocks for star-formation timescales (Hatchell et al., 1998; Buckle and Fuller, 2003; Whisnant et al., 2003). Ice mantles also can be sputtered in shock waves, and postshock chemistry could play a role in either initiating, or contributing to, hot core chemical evolution (Charnley and Kaufman, 2000; Viti et al., 2001). ISO SWS observations of solid and gaseous CO$_2$ toward many protostars indicate that shock processing may be common (Boonman et al., 2003). Finally, hot cores surrounding massive protostars eventually evolve into ultracompact HII regions (Churchwell, 2002) and photodissociation regions where the strong UV field and X-rays rapidly destroy molecules (Tielens and Hollenbach, 1985; Maloney et al., 1996).

5.3. Warm Cores Around Low-Mass Protostars

At the heart of a low-mass star-forming core lie the protostar and its surrounding disk, from which comets, asteroids, and planets eventually form. Observations show that many of the chemical characteristics seen in hot cores — small-scale differentiation, shock tracers, high D/H ratios, and the presence of putative mantle organic molecules — are also present toward low-mass sources (Fig. 1) (van Dishoeck et al., 1993; McMullin et al., 1994; Langer et al., 2000; Loinard et al., 2001; Schoier et al., 2002; Cazaux et al., 2003). Many of the chemical processes described above (section 5.2) should come into play in determining the overall chemical morphology and evolutionary state of these regions. Hence, elucidating the major physiochemical processes that occur around massive protostars may allow us to determine the likely chemical structure of the low-mass protostellar core in which the Sun formed. Figure 4 shows schematically the main physical regions in the environment of a low-mass accreting protostar (see Mumma et al., 1993; Lunine et al., 2000). Several regions exist where the local physical conditions will drive a specific chemical evolution. Interstellar materials from the ~0.1-pc dense core, and in particular from the innermost core heated by the protostar, may become incorporated into the protoplanetary disk after passing through the accretion shock at the boundary between the disk and the infalling core. However, the innermost core regions including accretion shock, which are most important for understanding the processing/connection of interstellar and cometary materials, have not yet been observed directly in great detail; this will become possible with the Atacama Large Millimetre Array (ALMA) (Wootten, 2001). Below we discuss the physiochemical properties of each of the six regions identified in Fig. 4 around a low-mass protostar.

Region I: Cold cloud. The chemistry in this region is essentially that which is outlined for cold, dense molecular clouds (section 4). Molecular tracers of the cold cloud include HCO$^+$ and N$_2$H$^+$.

Region II: Infall. The initial density structure and the precise details of the subsequent collapse are the subject of current debate (Larson, 2003; Mac Low and Klessen, 2003). It is clear, however, that when gravity dominates over support by thermal, turbulent, and magnetic pressures, a dynamic core collapse will occur and cold material from the infalling envelope will become incorporated into the protostar and its accretion disk. These infall motions can be detected spectroscopically from molecular line observations (Evans, 1999; Myers et al., 2000). Chemical models utilizing various collapse scenarios (Shu, 1977; Larson, 1969; Pensiot, 1969) have been constructed (Rawlings et al., 1992; Aikawa et al., 2001, 2003; Rodgers and Charnley, 2003). A common molecular tracer of infall is N$_2$H$^+$. 

Fig. 4. Chemistry around a low-mass protostar. In the environment of a low-mass protostar, physical processes determine the chemistry of distinct regions in the protostellar core. Distinct physical regions are characterized by different molecular tracers and include Region I — cold cloud, HCO$^+$ and N$_2$H$^+$; Region II — infall, N$_2$H$^+$; Region III — sphere of thermal influence, (CH$_3$)$_2$O; Region IV — bipolar outflow (CO); Region V — wind-cloud bow shock, H$_2$S, SO, SO$_2$, SO, CH$_3$OH, D$_2$CO; and Region VI — accretion shock at the disk surface, CS. Details of the chemical processes active in each region are discussed in the text (section 5). Artwork by J. Woebcke.
Region III: The “sphere of thermal influence.” As material approaches the protostellar disk, the accretion luminosity of the disk heats the infalling dust and gas. The dust and gas temperatures at any radii are controlled by the mass accretion physics (Adams and Shu, 1985; Ceccarelli et al., 1996) and this should therefore be reflected in the chemical evolution of the core. The chemistry is strongly radial dependent in the protostellar cocoon since the molecular desorption rate depends exponentially on the local dust temperature, as well as on the abundances and binding energies of molecules present in the grain mantles (see Ehrenfreund et al., 1998; Rodgers and Charnley, 2003). As interstellar gas and dust falls down toward the protostar, initially only the most volatile molecules are efficiently desorbed (CO, N₂, O₂, CH₄) and the chemistry is similar to that of molecular clouds (Brown and Charnley, 1991). Eventually, those remaining molecules with binding energies less than water and ammonia (e.g., CH₃OH, H₂CO, C₂H₂) are desorbed. In the inner regions, all the volatile mantle molecules have been removed and water, methanol, and ammonia are present in the gas at high abundances (see van der Tak et al., 2000). In these innermost regions the chemical evolution should most strongly resemble that of massive hot cores (section 5.2). A molecular tracer of the sphere of thermal influence is (CH₃)₂O.

Region IV: Bipolar outflow. Accretion of infalling interstellar material onto the protostellar disk appears to be intimately connected with the presence of atomic jets and bipolar molecular (i.e., CO) outflows (Konigl and Pudritz, 2000). Low-velocity bipolar flows (less than about 25 km s⁻¹) are believed to be molecular gas entrained from the ambient cloud by the higher velocity jets (typically 150–400 km s⁻¹). The jets themselves are probably driven through magnetohydrodynamic processes in the accretion disk (e.g., Konigl and Pudritz, 2000; Shu et al., 2000). Although hydrogen in the jets is primarily atomic, some molecule formation can proceed within jets (Glassgold et al., 1991) and this, for example, could be the origin of some of the high-velocity CO in the outflows. Alternatively, as ambient cloud material is entrained, atomic material from the jet can turbulently mix with surrounding molecular gas and an active chemistry can occur along the jet edge (Taylor and Raga, 1995).

Region V: Wind-cloud bow shock. Bipolar outflows drive strong shock waves into the surrounding natal cloud material. The associated high temperatures and compression permit many endothermic chemical reactions to occur. Nonthermal sputtering of icy grain mantles by neutral atoms of He and H and H₂ removes icy grain mantles and erodes refractory grain cores (Draine et al., 1983; Flower and Pineau des Forêts, 1994). Silicon-bearing molecules are observed to be highly depleted in cold molecular clouds (Herbst et al., 1989) so common chemical signposts of shock activity in star-forming regions are the greatly enhanced abundances of gaseous SiO, produced by the sputtering of silicate grains (Schilke et al., 1997; Garay et al., 2002). The shocked outflow lobes of low-mass protostars, such as L1157, are observed to exhibit a particularly rich chemical composition — a mixture of sputtered solid material and the products of high-temperature reactions in the postshock gas (Bachiller et al., 2001). Molecular tracers of the wind-cloud bow shock include H₂S, SO, SO₂, CH₃OH, D₂CO, and, as mentioned above, SiO.

Region VI: Disk accretion shock. Gravitational collapse of a rotating core will generally lead to the formation of an accretion disk (Cassen and Moosman, 1981; Terebey et al., 1984; Boss, 2004). Infalling material is decelerated in an accretion shock at the disk surface where interstellar chemistry effectively ends. Shock chemistry and other processes associated with disk accretion begin to dominate the chemistry of the material first entering the nebula (Lunine et al., 1991; Chick and Cassen, 1997). Neufeld and Hollenbach (1994) have modeled the disk accretion shock as a dissociative “J-shock” and determined the regions of the disk where various interstellar materials (refractory metals, refractory and volatile organics, and ice) would be vaporized. The smallest accretion shock speeds and preshock densities favor the survival of the most volatile materials; this occurs in the outermost region of the disk. Apart from a few CS observations (Blake et al., 1992; Walker et al., 1994; Velusamy et al., 2002), thus far there have been no detailed observational studies of this critical region, and so the chemical composition of the (interstellar) material in this phase is relatively uncharacterized.

6. SUMMARY

The ISM is turbulent and interstellar cloud structures are very filamentary and fragmentary. Stars that form in relatively quiescent cold dense molecular cloud cores then inject energy into the ISM at the ends of their lives via explosions or winds. Supernovae-driven shocks accelerate cosmic rays and generate turbulence. Gas is rapidly processed from very high temperatures (10⁶ K) and rarefied densities (≤1 cm⁻³) to low temperatures (≤10² K) and moderately high densities (n_H > 10–10² cm⁻³) as turbulence concentrates matter into shocks and small intermittent regions of high-velocity shear where viscous dissipation and heating and cooling processes occur. Turbulent compression of H I in the WNM, driven by supernova shocks, colliding H I streams, spiral density waves, or gravity, leads to the rapid formation of cold H I diffuse clouds. Turbulence may also speed up the formation of H₂ on grain surfaces in intermittent shock-induced density enhancements (n_H > 10⁵ cm⁻³), enabling the formation of molecular clouds on short timescales (~10⁶ yr). Most of the galaxy’s molecular gas is in giant molecular clouds that fill only 1–2% of the volume of the ISM. Rapidly, stars form out of molecular cloud cores that encompass only a small fraction of the volume of a molecular cloud. Massive stars only live a few million years, so molecular cloud material is dispersed in ~4 × 10⁶ yr from the energy injected by the winds and jets of young stars or by turbulence. Diffuse cloud material is converted to molecular clouds and back to diffuse
clouds on relatively short timescales. Physiochemical processes in diffuse clouds and molecular clouds increase the complexity of solid-state and molecular materials, a fraction of which survives the protostellar collapse to be incorporated into comets.

Stars enrich the ISM with nucleosynthesized elements: SNe II contribute O, SNe Ia contribute Fe, and AGB stars contribute C and N. Supernovae also provide the energy for the turbulence in the ISM. Most of the heavy elements are deposited into the ISM as dust grains. In particular, O-rich AGB circumstellar envelopes (CSE) produce silicates, oxides, and aluminosilicates, and C-rich AGB CSEs produce amorphous carbon, hydrocarbons with aromatic moieties (i.e., PAHs) and aliphatic bonds, and silicon carbide. However, dust grains are rapidly destroyed in the ISM by supernovae shocks and recondense in postshock gas or form in diffuse clouds by processes that as yet are unknown. Furthermore, most aliphatic bonds in hydrocarbon dust from AGB stars are destroyed by interstellar UV photons or by UV photons from hot white dwarf stellar cores when AGB stars become planetary nebulae over the course of a few thousand years. Aliphatic bonds probably are reformed in diffuse clouds when H atoms impinge on carbonaceous dust grains. Cosmic-ray bombardment of silicate grains in diffuse clouds selectively removes primarily Si and secondarily Mg from the grains, and efficiently converts silicate crystals to amorphous silicates. Only a minor fraction of the most refractory stardust grains survive their passage through the ISM to be incorporated as presolar grains in meteorites and cometary IDPs.

Galactic UV photons also destroy all small volatile molecules formed in the AGB CSE and thus simple molecules must be reformed in diffuse clouds. The only molecules to survive the passage through the WIM and WNM to diffuse clouds are PAHs. Photoelectric heating of the diffuse clouds and molecular cloud boundaries occurs when UV photons are absorbed by PAHs.

Diffuse clouds are unshielded from UV and photochemistry only permits the formation of fairly simple molecules. Many major heavy elements that are not depleted into grains are singly ionized: C⁺, S⁺, Fe⁺, Mg⁺, and Na⁺; only O and N are neutral. This means that many neutral-neutral chemical reactions that occur in dense clouds are not viable in diffuse clouds, as exemplified by the “CH⁺ problem.” Neutral H₂ reacts with C⁺ to form CH and C₂. Cosmic rays ionize H and H₂ that can then subsequently react rapidly to produce other ions and species such as OH. Ion-molecule reactions also contribute to the formation of CO in diffuse clouds.

Cosmic rays penetrate dense molecular clouds where UV photons do not, ionizing and heating the gas, promoting ion-molecule chemistry, and affecting the composition of icy mantles on dust grains. Ion-molecule and neutral-neutral reactions convert an appreciable fraction of the available heavy elements into molecules. This process begins with the freezing out of atoms from the gas onto silicate and carbonaceous grain surfaces. Ices are observed along the lines of sight through molecular clouds to protostars: CO-rich ice mantles with O₂ and N₂ and H₂O-rich ice mantles with traces of CO, CO₂, methane (CH₄), ammonia (NH₃), methanol (CH₃OH), formic acid or methanoic acid (HCOOH), and formaldehyde or methanal (H₂CO). A few classes of reactions are needed to form most of the molecules observed in ices. Reactions beginning with simple hydrocarbons such as acetylene (C₂H₂) form long C-chain molecules. Furthermore, many large organic molecules can form on grain surfaces. Low kinetic temperatures favor the fractionation of isotopes of H, C, and N. In order to maintain molecules in the gas phase, desorption from grain surfaces must occur, possibly due to grain heating by cosmic rays, mantle explosions, sputtering in low-velocity shocks, or grain-grain collisions.

Ice mantles consisting of molecules accreted from the gas are made more complex by energetic processing by cosmic rays, heating in protostellar cores, and perhaps UV photolysis. Although UV photons cannot penetrate deep into molecular clouds, UV photons are created in molecular clouds by H₂ excited by energetic electrons produced by primary cosmic-ray interactions. In particular, the carrier of the “XCN” band is produced by photolysis and/or radiolysis (proton irradiation). The complex molecules formed on cold grain surfaces are revealed in hot and warm protostellar cores when these molecules are returned to the gas phase via desorption.

In a collapsing molecular cloud core the protostar dramatically influences the chemistry of its surroundings. Hot cores and warm cores surround high-mass and low-mass protostars respectively. Molecules are evaporated from icy grain mantles, react on grain surfaces to form mixed molecular ices, and participate in a highly transient chemistry in which molecules form through gas-gas reactions. A strong chemical differentiation occurs between O-bearing and N-bearing molecules with temperature and time: Hotter cores tend to have high abundances of N-bearing molecules. The chemical processes occurring in hot cores are discussed, and many of the same processes apply to warm cores. The chemistries that delineate six different regions around a low-mass protostar are described and shown in Fig. 4. The molecular cloud core collapses (N₂H⁺) and heats the surrounding material as traced by (CH₃)₂O. Bipolar CO outflows and jets shock the ambient cloud core material as traced by H₂S, SO, SO₂, CH₃OH, SiO, and D₂CO. Interstellar material falling onto the protoplanetary disk passes through an accretion shock traced by CS emission. The physical conditions of the accretion shock region in the outer disk will become better constrained by future high-spatial-resolution, high-sensitivity observations using ALMA.

Interstellar chemistry, i.e., physiochemical processes in diffuse clouds and molecular clouds, sets the chemical boundary conditions on the composition of the material that was initially available for incorporation into the protosolar nebula, and thereafter into cometary matter. Understanding the degree of modification of these pristine interstellar molecules and solids as they passed through the accretion
shock in the outer disk, to subsequently take part in nebular chemistry, will permit detailed comparison of the composition of comets with ISM material, and hence an appreciation of the chemical diversity among comets (Ehrenfreund et al., 2004).

Acknowledgments. The authors collectively thank P. Goldsmith, W. Irvine, and an anonymous reviewer for their time and comments on this chapter. Discussions with B. Elmegreen (D.H.W.) and L. Allamandola (S.B.C.) are gratefully appreciated. Studies at NASA Ames (D.H.W.) of dust in comets and pre-main-sequence stars are supported by NASA's Planetary Astronomy and Origins of Solar Systems Programs. Studies of theoretical astrochemistry at NASA Ames (S.B.C.) is supported by NASA's Planetary Atmospheres and Origins of Solar Systems Programs through funds allocated by NASA Ames under Interchange No. NCC2-1412 and by the NASA Astrobiology Institute. Laboratory astrochemistry and astrobiology (P.E.) is supported by NWO (VI), SRON, and ESA. We are grateful to S. Rodgers for preparation of Fig. 1. We thank E. Peeters and J. Keane for the ISO reduced data and preparation of Fig. 2.

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