The Chemical Evolution of Protoplanetary Disks

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In this review we reevaluate our observational and theoretical understanding of the chemical evolution of protoplanetary disks. We discuss how improved observational capabilities have enabled the detection of numerous molecules, exposing an active disk chemistry that appears to be in disequilibrium. We outline the primary facets of static and dynamical theoretical chemical models. Such models have demonstrated that the observed disk chemistry arises from warm surface layers that are irradiated by X-ray and FUV emission from the central accreting star. Key emphasis is placed on reviewing areas where disk chemistry and physics are linked, including deuterium chemistry, gas temperature structure, disk viscous evolution (mixing), ionization fraction, and the beginnings of planet formation.

1. **INTRODUCTION**

For decades, models of our own solar nebular chemical and physical evolution have been constrained by the chemical record gathered from meteorites, planetary atmospheres, and cometary comae. Such studies have provided important clues to the formation of the Sun and planets, but large questions remain regarding the structure of the solar nebula, the exact timescale of planetary formation, and the chemical evolution of nebular gas and dust. Today we are on the verge of a different approach to nebular chemical studies, one where the record gained by solar system studies is combined with observations of numerous molecular lines in a multitude of extrasolar protoplanetary disk systems tracking various evolutionary stages.

Our observational understanding of extrasolar protoplanetary disk systems is still in its infancy as the current capabilities of millimeter-wave observatories are limited by sensitivity and also by the small angular size of circumstellar disks, even in the closest star-forming regions (≤3–4″). Nonetheless, numerous molecules have been detected in protoplanetary disks, exposing an active chemistry (Dutrey et al., 1997; Kastner et al., 1997; Qi et al., 2003; Thi et al., 2004). Since the last Protostars and Planets review (Prinn, 1993) these observations have led to a paradigm shift in our understanding of disk chemistry. For many years focus was placed on thermochemical models as predictors of the gaseous composition, and these models have relevance in the high-pressure, and >10−6 bar (inner) regions of the nebula (e.g., Fegley, 1999). However, for most of the disk mass, the observed chemistry appears to be in disequilibrium and quite similar to that seen in dense regions of the interstellar medium (ISM) that are directly exposed to radiation (Aikawa and Herbst, 1999; Willacy and Langer, 2000; Aikawa et al., 2002).

In this review we focus on gains in our understanding of the chemistry that precedes and is contemporaneous with the formation of planets from a perspective guided by observations of other stellar systems whose masses are similar to the Sun. We examine both the observational and theoretical aspects of this emerging field, with an emphasis on areas where the chemistry directly relates to disk physics. Portions of this review overlap with other chapters, such as the observational summary of molecular disks, inner disk gas, and disk physical structure (see the chapters by Dutrey et al., Najita et al., and Dullemond et al., respectively). For this purpose we focus our review on the physics and chemistry of the outer disk (r > 10 AU) in systems with ages of
0.3–10 m.y. In support of our theory we also present an observational perspective extending from the infrared (IR) to the submillimeter to motivate the theoretical background and supplement other discussions.

2. GENERAL THEORETICAL PICTURE

2.1. Basic Physical and Chemical Structure of the Disk

Chemical abundances are determined by physical conditions such as density, temperature, and the incident radiation field. Recent years have seen significant progress in characterizing the physical structure of the disk, which aids in understanding disk chemical processes. Isolated disks can be quite extended, with $r_{\text{out}} \sim 100$ to a few hundred AU (Simon et al., 2000), much larger than expected from comparison with the minimum mass solar nebula (MMSN) (Hayashi, 1981). However, it should be stated that we have an observational bias toward detecting larger disks due to our observational limitations. The radial distribution of column density and midplane temperature have been estimated by observing thermal emission of dust; they are fitted by a power-law $\Sigma(r) \propto r^{-p}$ and $T(r) \propto r^{-q}$, with $p = 0$–1 and $q = 0.5$–0.75. The temperature at 1 AU is ~100–200 K, while the surface density at 100 AU is 0.1–10 g cm$^{-2}$ (e.g., Beckwith et al., 1990; Kitamura et al., 2002).

Fig. 1. Chemical structure of protoplanetary disks. Vertically the disk is schematically divided into three zones: a photon-dominated layer, a warm molecular layer, and a midplane freeze-out layer. The CO freeze-out layer disappears at $r \lesssim 30$–60 AU as the midplane temperature increases inward. Various nonthermal inputs, cosmic rays, UV, and X-rays drive chemical reactions. Viscous accretion and turbulence will transport the disk material both vertically and radially. The upper panels show the radial and vertical distribution of molecular abundances from a typical disk model at the midplane (Aikawa et al., 1999) and $r \sim 300$ AU (van Zadelhoff et al., 2003). A sample of the hydrogen density and dust temperature at the same distance (D’Alessio et al., 1999) is also provided. In upper layers ($\geq 150$ AU) the gas temperature will exceed the dust temperature by $\geq 25$ K (Jonkheid et al., 2004).
some deviation due to vertical temperature variations (see Fig. 1). As a whole the disk has a flared-up structure, with a geometrical thickness that increases with radius (Kenyon and Hartmann, 1987).

Based on such physical models, the current picture of the general disk chemical structure is schematically shown in Fig. 1. At \( r \geq 100 \) AU, the disk can be divided into three layers: the photon-dominated region (PDR), the warm molecular layer, and the midplane freeze-out layer. The disk is irradiated by UV radiation from the central star and interstellar radiation field that ionize and dissociate molecules and atoms in the surface layer. In the midplane the temperature is mostly lower than the freeze-out temperature of \( \text{CO} \) (~20 K), one of the most abundant and volatile molecules in the ISM. Since the timescale of adsorption onto grains is short at high density \( \begin{align*} &[-10(10^{10} \text{cm}^{-3}/\text{H}) \text{yr}] , \\
&\text{element species are significantly depleted onto grains.} \end{align*} \) At intermediate heights, the temperature is several tens of Kelvin, and the density is sufficiently high \( (\geq 10^6 \text{ cm}^{-3}) \) to ensure the existence of molecules even if the UV radiation is not completely attenuated by the upper layer (Aikawa and Herbst, 1999; Willicy and Langer, 2000; Aikawa et al., 2002). Here water is still frozen onto grains, trapping much of the oxygen in the solid state. Thus, the warm CO-rich gas layers will have C/O ~ 1, leading to a rich and extensive carbon-based chemistry.

These models provide a good match to observed abundances. Dutrey et al. (1997) found that in the DM Tau disk, molecular abundances are generally lower than in dense clouds, but the CN/HCN ratio is higher (see also Thi et al., 2004). The low molecular abundances are caused by depletion in the midplane, and the high CN/HCN ratio originates in the surface PDR (cf. Fig. 1), as seen in PDRs in the ISM (Rodriguez-Franco et al., 1998).

At \( r \leq 100 \) AU, the midplane temperature is high enough to sublimate various ice materials that formed originally in the outer disk radius and/or parental cloud core (e.g., Markwick et al., 2002). This sublimation will be species-dependent with the “snowline” for a given species appearing at different radii. For example, in the solar nebula the water ice snowline appeared near 3–5 AU, while the CO snowline would appear at greater distances where the midplane dust temperatures drop below ~20 K. Within these species-selective gaseous zones, sublimated molecules will be destroyed and transformed to other molecules by gas-phase reactions. In this fashion, the chemistry is similar to the so-called “hot core” chemistry, which appears in star-forming cores surrounding protostars (e.g., Hatchell et al., 1998; see chapter by Ceccarelli et al.). For example, sublimated CH \(_4\) is transformed to larger and less-volatile carbon-chain species, which can then accumulate onto grains (Aikawa et al., 1999).

### 2.2. Key Ingredients: Ultraviolet, X-Ray, and Cosmic-Ray

Thermochemistry and its consequences are described by Fegeley and Prinn (1989) and Prinn et al. (1993). In recent years nonthermal events such as cosmic rays, UV, and X-rays have been included in the disk chemistry models and are shown to play important roles.

In molecular clouds, chemical reactions are driven by cosmic-ray ionization (e.g., Herbst and Klemperer, 1973). Since cosmic-ray ionization has an attenuation length of 96 g cm\(^{-2}\) (Umebayashi and Nakano, 1981), in the disk it can be important, for \( r \geq \) several AU, in driving ion-molecule reactions and producing radicals that undergo neutral-neutral reactions (Aikawa et al., 1997). Although cosmic rays may be scattered by the magnetic fields within and around the protostar-disk system, detection of ions (e.g., HCO\(^+\) and H\(_2\)D\(^+\)) and comparison with theoretical models indicate that some ionization mechanisms, perhaps cosmic rays, is available at least for \( r \geq 100 \) AU (Semenov et al., 2004; Ceccarelli and Dominik, 2005) (see also section 4.3).

T Tauri stars have excess UV flux that is much higher than expected from their effective temperature of ~3000 K (e.g., Herbig and Goodrich, 1986). It is considered to originate in the accretion shock on the stellar surface (Calvet and Gullbring, 1998), with potential contributions from an active chromosphere (Alexander et al., 2005). For low-mass T Tauri stars, the strength of the UV field is often parameterized in terms of the local interstellar radiation field (Habing, 1968) (\( G_0 = 1 \)), and have values of \( G_0 \sim 300–1000 \) at 100 AU (Bergin et al., 2004). This radiation impinges on the flared disk surface with a shallow angle of incidence. Stellar and interstellar UV photons dissociate and ionize molecules and atoms in the flared disk surfaces and detailed two-dimensional radiative transfer models are required to quantitatively predict molecular abundances. van Zadelhoff et al. (2003) showed scattering of stellar UV at the disk surface significantly enhances the abundance of radical species in deeper layers, and examined the resulting chemical evolution for different wavelength dependencies of the stellar UV radiation field. Bergin et al. (2003) pointed out the importance of Ly\(\alpha\) emission, which stands out in the UV spectrum of T Tauri stars (Fig. 2) and is absent from the interstellar field. In the one case where the line is unaffected by interstellar absorption, TW Hya, Ly\(\alpha\) radiation carries ~85% of the FUV flux (Herczeg et al., 2004). Since photodissociation cross sections are a function of wavelength, species that absorb Ly\(\alpha\), such as HCN and H\(_2\)O, will be selectively dissociated, while others, such as CO and H\(_2\), are unaffected (van Dishoeck et al., 2006).

Most stars do not form in isolation, rather 70–90% stars are born in GMCs (which contain most of the galactic molecular mass) and are found in embedded stellar clusters (Lada and Lada, 2003). In this light there exists growing evidence that the Sun formed in a cluster in the vicinity of a massive star (see chapter by Wadhwa et al.; Hester and Desch, 2005). In this case the UV radiation field can be much higher, depending on the spectral type of the OB star, the proximity of the low-mass star to the source of energetic radiation, and the dissipation timescale of the surrounding dust and gas (which can shield forming low-mass disks from radiation). After gas/dust dissipation the external radiation has greater penetrating power, because it can impinge on the disk with a greater angle of incidence. The
primary effects of external radiation, if it dominates the stellar contribution, will be to magnify the chemistry (e.g., CO driven photochemistry) produced by the stellar radiation and increase the size of the warm molecular layer.

Strong X-ray emission is observed toward T Tauri stars (e.g., Kastner et al., 2005). It may originate in the magnetic reconnections either in the stellar magnetosphere, at the star-disk interface, or above the circumstellar disk (Feigelson and Montmerle, 1999, and references therein). X-rays affect the chemistry in several ways (Maloney et al., 1996; Stäuber et al., 2005): (1) They ionize atoms and molecules to produce high-energy photoelectrons that further ionize the gas. On the disk surface X-ray ionization produces a higher ionization rate than cosmic rays, and can even be the dominant ionization source if the cosmic rays are scattered by the magnetic field (Glassgold et al., 1997; Igea and Glassgold, 1999). (2) High-energy photoelectrons heat the gas. For example, at \( r = 1 \) AU, the gas temperature in the uppermost layer can be as high as 5000 K due to the X-ray heating together with mechanical heating such as turbulent dissipation (Glassgold et al., 2004; see chapter by Najita et al.). (3) Collision of the high-energy electrons with hydrogen atoms and molecules results in excitation of these species and then the emission of UV photons within the disk (Maloney et al., 1996; Herczeg et al., 2004). Recently Bergin et al. (2004) found \( \text{H}_2 \) FUV continuum emission caused by this mechanism. The high ionization rate and induced photodissociation of CO enhance the abundances of organic species such as CN, HCN, and HCO\(^+\) (Aikawa and Herbst, 1999, 2001).

Nonthermal particles and radiation can also drive the desorption of molecular species from the grain surface. Because of the high densities, gaseous species collide with grains on short timescales. In the low-temperature region in the outer disk the colliding molecules are adsorbed onto grains, and thermal desorption is inefficient except for very volatile species such as CO, \( \text{N}_2 \), and \( \text{CH}_4 \), depending on the temperature. Various gaseous molecules are still observable since they are formed from CO and \( \text{N}_2 \) via gas-phase reactions, which compensates for adsorption (e.g., Aikawa et al., 2002). However, observations may indicate the need for more efficient (thermal or nonthermal) desorption, especially for species mainly formed by grain-surface reactions. For example, Dartois et al. (2003) find evidence for gaseous CO in layers with a temperature below the CO sublimation temperature. Cosmic rays and X-rays can temporally “spot heat” the grains to enhance desorption rates (e.g., Léger et al., 1985; Hasegawa and Herbst, 1993). UV radiation can also desorb molecules, possibly by producing radicals within the ice mantle, which react with other radicals on the grain surface to release excess energies (Westley et al., 1995). It should be noted, however, that the nonthermal desorption rates are uncertain and depend on various parameters such as structure of the grain particle (Najita et al., 2001), UV flux, number density of radical species in grain mantle (Shen et al., 2004), and detailed desorption process.

![Fig. 2. UV spectra of T Tauri stars. Heavy solid lines and light solid lines represent the spectra of BP Tau and TW Hya, respectively. The spectrum of TW Hya is scaled by 3.5 to match the BP Tau continuum level. The long dashed line represents the interstellar radiation field of Draine (1978) scaled by a factor of 540. The region around the Ly\(\alpha\) line is enlarged in the right panel. Taken from Bergin et al. (2003).](image-url)
Mixing could also play a role in moving material from warmer layers to colder ones (e.g., section 4.4).

3. OBSERVATIONS

Observational studies of the chemistry in extrasolar protoplanetary disks began only in the last decade thanks to improved sensitivity and spatial resolution at millimeter and IR wavelengths. At millimeter wavelengths, molecules other than CO have now been detected and imaged in a handful of disks with single-dish telescopes and interferometers. This technique has the advantage that molecules with very low abundances (down to $10^{-11}$ with respect to H$_2$) can be detected through their pure rotational transitions, and that the spatial distribution in the disk can be determined. With a spectral resolving power $R = \lambda/\Delta\lambda > 10^6$, the line profiles are fully resolved and kinematic information can be derived. Infrared spectroscopy has the main advantage that not only gas but also solid material can be probed through their vibrational transitions, including ices and silicates. Also, gas-phase molecules without dipole moments, including H$_2$, CH$_4$, C$_2$H$_2$, and CO$_2$, can only be observed at IR wavelengths. Finally, polycyclic aromatic hydrocarbons (PAHs) have unique IR features. For spacebased instruments, the resolving power is usually low, typically $R = 300$–$3000$, making it difficult to observe and resolve gas-phase lines.

3.1. Infrared Observations

3.1.1. Silicates, ices, and polycyclic aromatic hydrocarbons. The Infrared Space Observatory (ISO) opened up mid-IR spectroscopy of disks over the full 2–200-µm range unhindered by Earth’s atmosphere, revealing a wealth of features (see van Dishoeck, 2004, for a review). Because of limited sensitivity, ISO could only probe the chemistry in disks around intermediate-mass Herbig Ae/Be stars. The Spitzer Space Telescope has the sensitivity to obtain 5–40-µm spectra of solar-mass T Tauri stars, while large 8–10-m optical telescopes can obtain higher spectral and spatial resolution data in atmospheric windows, most notably at 3–4, 4.6–5, and 8–13 µm. The features are usually in emission, except if the disk is viewed nearly edge-on when the bands occur in absorption against the continuum of the warm dust in the inner disk. The amorphous broad silicate features at ~10 and 20 µm are the most prominent emission bands in disk spectra (e.g., Przygodda et al., 2003; Kessler-Silacci et al., 2005; 2006) (see Fig. 3). They arise in the superheated layers of the inner disk at <1–10 AU and are not representative of the outer disk. For at least half of the sources narrower features are seen as well, which can be ascribed to crystalline silicates such as forsterite, Mg$_2$SiO$_4$ (e.g., Malfait et al., 1998; Forrest et al., 2004). Silicates are discussed extensively in the chapter by Natta et al.; the main point for this chapter is that the shape and strength of the silicate features, together with the overall spectral energy distribution, can be used to determine whether grain growth and settling has occurred (e.g., van Boekel et al., 2005). This, in turn, affects the chemistry and heating in the disk (see section 4.1). Also, the presence of crystalline silicates may be an indication of significant radial and vertical mixing (see section 4.4).

Ices can only be present in the cold, outer parts of the disk where the temperature drops below 100 K. Thus, the strongest ice emission bands typically occur at far-IR wavelengths. Crystalline water ice has been seen in a few disks through librational features at 44 and 63 µm (e.g., Malfait et al., 1998, Chiang et al., 2001). The data can be reproduced in models assuming that 50% of the available oxygen is in water ice. Edge-on disks offer a special opportunity to study ices at mid-IR wavelengths in absorption. Examples are L1489 (Boogert et al., 2002), DG Tau B (Watson et al., 2004), and CRBR2422.8-3423 (Thi et al., 2002; Pontoppidan et al., 2005) (Fig. 3). Extreme care has to be taken in the interpretation of these data since a large fraction of the ice features may arise in foreground clouds. For the case of CRBR 2422.8-3423, a disk viewed at an inclination of ~70°, comparison with nearby lines of sight through the same core combined with detailed disk modeling has been used to constrain the amount of ice in the disk. H$_2$O ice has an average line-of-sight abundance of ~10$^{-4}$ relative to H$_2$, consistent with significant freeze-out. CO$_2$ and CO ice are also present, the latter only in the form where it is mixed with H$_2$O ice. The shape of the 6.85-µm ice band — usually ascribed to NH$_3$ (e.g., Schutte and Khanna, 2003) — shows evidence for heating to 40–50 K, as expected in the warm intermediate layers of the disk. Future studies of a large sample of edge-on disks can provide significant insight into the abundance and distribution of ices in disks, because the ice absorption depths, band shapes, and feature ratios depend strongly on the disk temperature structure and line of sight, i.e., inclination (Pontoppidan et al., 2005).

PAHs are important in the chemistry for at least three reasons: as absorbers of UV radiation, as a heating agent for the gas, and as potential sites of H$_2$ formation when classical grains have grown to large sizes. Since they require UV radiation for excitation, PAHs are also excellent diagnostics of the stellar radiation field and disk shape (flaring or flat). PAHs are detected in the spectra of at least 50% of Herbig Ae stars with disks through emission features at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.8 µm (Acke and van den Ancker, 2004). For T Tauri stars, the features are weaker and more difficult to see on top of the strong continuum, but at least 8% of sources with spectral types later than F7 show the 11.2-µm PAH feature (Geers et al., in preparation). Ground-based long-slit spectroscopy and narrow-band imaging at subarcsecond resolution has demonstrated that, at least for some disks, the PAH emission comes from a region of radius 10–100 AU (e.g., Habart et al., 2004). The inferred PAH abundance is typically 10$^{-7}$ with respect to H$_2$, assuming that ~10% of the carbon is in PAHs with 50–100 carbon atoms. PAHs have been detected in transitional disks, where there is evidence for grain growth to micrometer size, albeit at a low abundance of 10$^{-9}$ (Li and Lunine, 2003;
Jonkheid et al., 2006). This indicates that the PAHs and very small grains in the upper disk layer may be decoupled dynamically from the larger silicate grains and have a much longer lifetime toward grain growth and settling.

3.1.2. Gas-phase molecules. Vibration-rotation emission lines of gaseous CO at 4.7 µm are detected toward a large fraction (>80%) of T Tauri and Herbig Ae stars with disks (e.g., Najita et al., 2003; Brittain and Rettig, 2002; Blake and Boogert, 2004). The CO lines can be excited by collisions in the hot gas in the inner (<5–10 AU) disk as well as by IR or UV pumping in the upper layers of the outer (r > 10 AU) disk. Searches for other molecular emission lines have so far been largely unsuccessful except for the detection of hot H₂O toward one young star, presumably arising in the inner disk (Carr et al., 2004). A tentative detection of H₂ — a potential tracer of protoplanets — has been claimed toward one young star (HD141569) (Brittain and Rettig, 2002), but this remains unconfirmed (Goto et al., 2005).

Surprisingly, Spitzer has recently detected strong absorption from C₂H₂, HCN, and CO₂ at R = 600 toward one young star with an edge-on disk, IRS 46 in Ophiuchus (Fig. 3) (Lahuis et al., 2006). The inferred abundances are high, ~10⁻⁵ with respect to H₂, and the gas is hot, 300–700 K, with linewidths of ~20 km s⁻¹. The most likely location for this hot gas rich in organic molecules is in the inner (<few AU) disk, with the line of sight passing through the puffed-up inner rim. The observed abundances are comparable to those found in inner disk chemistry models (e.g., Markwick et al., 2002).

A novel method to probe the chemistry in the outer (r > 10 AU) disk is through observations of narrow, low-velocity [O I] 1D–3P lines at 6300 Å showing signs of Keplerian rotation (Bally et al., 1998; Acke et al., 2005). The excited O 1D atoms most likely result from photodissociation of OH in the upper flaring layers of the disk out to at least 10 AU (Störzer and Hollenbach, 1998; van Dishoeck and Dalgarno, 1984). The OH abundance required to explain the observed [O I] fluxes is ~10⁻⁷–10⁻⁶, significantly larger than that found in current chemical models.

The main reservoir of the gas in disks is H₂, which has its fundamental rotational quadrupole lines at mid-IR wave-
lengths. Searches for these lines have been performed by Thi et al. (2001) with ISO, but tentative detections have not been confirmed by subsequent ground-based data (e.g., Richter et al., 2002; Sako et al., 2005), although H$_2$ vibrational lines have been detected (Bary et al., 2003). Constraining the amount of gas in disks is important not only for jovian planet formation, but also because the gas/dust ratio affects the chemistry and thermal balance of the disk as well as the dust dynamics.

3.2. Millimeter- and Submillimeter-Wave Spectroscopy

At long wavelengths, where the dust emission is largely optically thin, rotational line emission forms a powerful probe of the physics and chemistry in disks. Indeed, at a fiducial radius of 100 AU, with a temperature of 20–30 K, the disk radiates preferentially at (sub)millimeter wavelengths. Surveys of the millimeter-continuum and SEDs from disks (Beckwith et al., 1990) have confirmed the spatio-temporal properties of dust disks. However, only a handful of objects have been investigated by detailed imaging, with millimeter-wave interferometer observations of CO from disks around T Tauri stars providing among the earliest and most conclusive evidence for the expected ~Keplerian velocity fields (see Koerner et al., 1993; Dutrey et al., 1994).

From such studies a suite of disks have been identified that are many arcseconds in diameter, either because they are nearby (TW Hya) or are intrinsically large (GM Aur, LkCa 15, DM Tau). The age, large size, and masses of these disks make them important for further study since they may represent an important transitional phase in which viscous disk spreading and dispersal competes with planetary formation processes. Their large size makes them difficult, but feasible, targets for further chemical study. Work in this area began with the pioneering observations of DM Tau and GG Tau with the IRAM 30-m telescope (Dutrey et al., 1997) and TW Hya with the JCMT (Kastner et al., 1997). Further detections of the higher –J lines of high dipole moment species such as HCN and HCO$^+$, along with statistical equilibrium analyses, demonstrated that the line emission arises from the warm molecular layer with n$_{H_2}$ = 10$^6$–10$^8$ cm$^{-3}$, T $\geq$ 30 K (van Zadelhoff et al., 2001). The very deepest integrations have begun to reveal more complex species (Thi et al., 2004), although the larger organics often seen toward protostellar hot cores remain out of reach of existing single-dish telescopes.

At present, aperture synthesis observations can only sense the outer disk (r > 30–50 AU) (Dutrey and Guilloteau, 2004; see chapter by Dutrey et al.) for stars in the nearest molecular clouds. Thus, the chemical imaging of disks is rarer still, with studies concentrating on a few of the best characterized T Tauri and Herbig Ae stars. Imaging studies of LkCa 15, for example, have detected a number of isotopologues of CO along with the molecular ions HCO$^+$ and N$_2$H$^+$ and the more complex organics formaldehyde and methanol (Duvert et al., 2000; Aikawa et al., 2003; Qi et al., 2003). For this disk at least, molecular depletion of molecules onto the icy mantles of grains near the disk midplane is found to be extensive, but the fractional abundances and ionization in the warm molecular layer are in line with those seen toward dense PDRs (section 2.1). While the lines from the less-abundant species can be detected, they were too weak to image with good signal-to-noise. Thus, while millimeter-wave rotational line emission is a good tracer of the outer disk velocity field, it is not a robust tracer of the mass unless the chemistry is very well understood.

New observational facilities are poised to change this situation dramatically, as illustrated by the recent SMA results on the TW Hya disk presented in Fig. 4 (Qi et al., 2006, in prep.). At a distance of only 56 pc, observations of this source provide nearly 2–3× the effective linear resolution of studies in Taurus and Ophiuchus. Thus, channel maps such as those presented can be used to derive a great deal about the physical and chemical structure of the disk — its size and inclination (Qi et al., 2004), the run of mass surface density and temperature with radius, the chemical abundance ratios with radius in the outer disk, etc. Ongoing improvements to existing arrays such as the eSMA, PdBI, and CARMA will enable similar studies for a large number of disks in the near future, and will push the radii over which chemical studies can be pursued down to 10–20 AU. Resolving the chemical gradients discussed in section 4.3 and 4.4 and studying the chemistry in the 1–10-AU zone of active planet formation will require even greater sensitivity and spatial resolution, and awaits ALMA.

4. CHEMICAL AND PHYSICAL LINKS

Protoplanetary disks are evolving in many different, but connected, ways. Small micrometer-sized dust grains collide, coagulate, collisionally fragment, and settle in a process that ultimately produces planets (Weidenschilling, 1997). At the same time, the disk is viscously evolving, with indications that the disk mass accretion rate decreases with age (Hartmann et al., 1998). Finally, disks evolve chemically, with the eventual result that all heavy elements are frozen on grains in the midplane and, prior to gas dissipation, chemistry consists of H$_2$ ionization and the deuteration sequence to H$_2$D$^+$, D$_2$H$^+$, and D$^+$ (see section 4.3 and section 5). The interconnections between these types of evolution is, at present, poorly understood. Nonetheless, some physical and chemical connections have become clear, which we review here.

4.1. Grain Evolution

The onset of grain evolution within a protoplanetary disk consists of collisional growth of submicrometer-sized particles into larger grains; the process continues until the larger grains decouple from the gas and settle to an increasingly dust-rich midplane (Nakamura et al., 1981; Weidenschilling and Cuzzi, 1993; Beckwith et al., 2000). Evolving dust grains within irradiated disks reprocess stellar and accretion-gener-
lated UV and optical photons into the IR and submillimeter. Thus, the dust thermal emission spectrum bears information on the grain size distribution and spatial location. This, together with the spectral features discussed in section 3.1.1, is used to provide evidence for grain evolution in ~1-m.y. T Tauri systems (Beckwith et al., 2000; see chapter by Dullemond et al., and references therein).

Grain coagulation can alter the chemistry through the reduction in the total geometrical cross-section, lowering the adsorption rate and the Coulomb force for ion-electron grain recombination. Micrometer-sized grains couple to the smallest scales of turbulence (Weidenschilling and Cuzzi, 1993) and have a thermal, Brownian, velocity distribution. Thus, the timescale of grain-grain collisions is \( \tau_{\text{gr-gr}} \propto a_d^{5/2}/(T_d^{1/2}\xi n_H) \), where \( a_d \) is the grain radius, \( \xi \) the gas-to-dust mass ratio, and \( T_d \) the dust temperature (Aikawa et al., 1999).

In this fashion grain coagulation proceeds faster at small radii where the temperatures and densities are higher. Aikawa et al. (1999) note that the longer timescale for adsorption on larger grains leaves more time for gas-phase reactions to drive toward a steady-state solution; this involves more carbon trapped in CO as opposed to other, more-complex species.

Overall, the evolution of grains, both coagulation and sedimentation, can be a controlling factor for the chemistry. As grains grow the UV opacity, which is dominated by small grains, decreases, allowing greater penetration of ionizing/dissociating photons (e.g., Dullemond and Dominik, 2005). As an example, in the coagulation models of Dullemond and Dominik (2005) the integrated vertical UV optical depth at 1 AU decreases over several orders of magnitude, toward optically thin over the entire column (see also Weidenschilling, 1997). The chemical effects are demonstrated in Fig. 5b, where we show the C\(^+\) to CO transition as a function of vertical distance for two dust models, well-mixed and settled (Jonkheid et al., 2004). In the settled model the CO transition occurs at slightly smaller height, even though this model assumes that PAHs remain present in the upper atmosphere. Thus, as grains evolve, there will be a gradual shifting of the warm molecular layer deeper into the disk, eventually into the midplane. Because the grain emissivity, density, and temperature will also change, the chemical and emission characteristics of this layer may be altered (Aikawa and Nomura, 2006). These effects are magnified in the inner disk, where there is evidence for significant grain evolution in a few systems (Uchida et al., 2004; Calvet et al., 2005) and deeper penetration of energetic radiation (Bergin et al., 2004). A key question in this regard is the number of small grains (e.g., PAHs) present in the atmosphere of the disk during times when significant coagulation and settling has occurred (e.g., Dullemond and Dominik, 2005; D’Alessio et al., 2006).
It is worth noting that the penetration of X-ray photons is somewhat different than those at longer UV wavelengths. Absorption of UV radiation is dominated by the small grains, while X-rays are absorbed at the atomic scale by heavy metals predominantly trapped in the grain cores. Thus, coagulation will have a greater effect on UV photons. When the grain mass is distributed downward by settling, the X-ray penetration depth increases, eventually to the limit of total heavy element depletion where the opacity at 1 keV decreases by a factor of ~4.5 (i.e., the H and He absorption limit) (Morrison and McCammon, 1983).

4.2. Gas Thermal Structure

Models of disk physical structure have generally assumed that dust and gas temperatures are in equilibrium (Chiang and Goldreich, 1997; D’Alessio et al., 1998). However, the disk vertical structure is set by the temperature of the dominant mass component, hydrogen, which under some conditions in the upper disk atmosphere is thermally decoupled from dust (Chiang and Goldreich, 1997).

Irradiated disk surfaces are analogs to interstellar PDRs, which have a history of detailed thermal balance calculations (see Hollenbach and Tielens, 1999, and references therein). In the studies of the gas thermal balance in disk atmospheres (Jonkheid et al., 2004; Kamp and Dullemond, 2004; Nomura and Millar, 2005) a number of heating mechanisms have been investigated, including photoelectric heating by PAHs and large grains, UV excitation of H2 followed by collisional deexcitation, H2 dissociation, H2 formation, gas-grain collisions, carbon ionization, and cosmic rays. In decoupled layers, the gas cools primarily by atomic ([O I], [C II], [C I]) and molecular (CO) emission, with the dominant mechanism a function of radial and vertical distance.

Some of these results are shown in Fig. 5; note that the gas temperature can exceed that of the dust in the upper atmosphere (Fig. 5a), which has consequences for the gas phase emission (Figs. 5c,d). The inclusion of PAHs into the models has an effect as PAHs provide additional heating power and are strong UV absorbers. Thus, grain evolution can significantly alter the thermal structure (see Fig. 5) by
removing PAHs and small grains through coagulation and larger grains by settling, reducing photoelectric heating. In disks where grains have grown to micrometer size, and which are optically thin to UV radiation, other heating processes such as the drift velocity between the dust and gas may become important (see Kamp and van Zadelhoff, 2001).

One of the largest chemical influences for most of the disk mass is the freeze-out of molecular species onto grain surfaces. In general, the loss of gas coolants would produce a temperature rise, but in (midplane) layers dominated by freeze-out, the densities are high enough to thermally couple the gas to the dust (see, e.g., Goldsmith, 2001).

4.3. The Ionization Fraction

Over the past few years the disk fraction ionization has received a high degree of attention owing to the appreciation of the magneto-rotational instability (MRI) as a potential mechanism for disk angular momentum transport (e.g., Hawley and Balbus, 1991; Stone et al., 2000). The chemical evolution is linked to dynamics as the presence of ions is necessary to couple the gas to the magnetic field. As we will outline, most of the ionization processes are active at the surface and there exists the potential that accretion may only be active on the surface (Gammie, 1996; but see also Klahr and Bodenheimer, 2003; Inutsuka and Sano, 2005).

In equilibrium, the ion fraction, \( x_e = n_e / n_H \), can be expressed by

\[ x_e = \sqrt{\zeta / (\alpha_r n_H)} \]

where \( \zeta \) is the ionization rate and \( \alpha_r \) the electron recombination rate. In Table 1 we provide an overview of disk ionization. The top left panel in Fig. 6 also shows the electron abundance (equivalent to the ionization fraction) from a detailed model (Semenov et al., in preparation). This figure, along with Table 1, can be used as a guide for the following discussion. For a discussion of the validity of the equilibrium assumption see Semenov et al. (2004), while Ilgner and Nelson (2005a) provide a detailed comparison of ionization and MRI for a variety of reaction networks.

The observed FUV radiation excess produces high ion fractions, but only over a small surface column, with C\(^+\) as the charge carrier (the ionized hydrogen layer will be quite

<table>
<thead>
<tr>
<th>Layer/Carrier</th>
<th>Ionization Mechanism</th>
<th>( \Sigma_{\tau = 1} ) (g cm(^{-2}))(^*)</th>
<th>( \alpha_r ) (cm(^{-3}) s(^{-1}))(^\dagger)</th>
<th>( x_e ) (^\ddagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Upper Surface</strong></td>
<td>UV photoionization of H(^+)</td>
<td>6.9 × 10(^{-4})</td>
<td>2.5 × 10(^{-10})T(^{-0.75})</td>
<td>&gt;10(^{-4})</td>
</tr>
<tr>
<td>H(^+)</td>
<td>k(_{H^+}) \sim 10(^{-4}) s(^{-1})</td>
<td>1.3 × 10(^{-3})</td>
<td>1.3 × 10(^{-10})T(^{-0.61})</td>
<td>&gt;10(^{-4})</td>
</tr>
<tr>
<td><strong>Lower Surface</strong></td>
<td>UV photoionization of Cl</td>
<td>0.008 (1 keV)</td>
<td>1.6 (10 keV)</td>
<td>3.3 × 10(^{-5})T(^{-1})</td>
</tr>
<tr>
<td>C(^+)</td>
<td>k(_{C^+}) \sim 4 × 10(^{-8}) s(^{-1})</td>
<td>96 (CR)</td>
<td>( \alpha_{H^+} = -1.3 \times 10^{-8} + 1.27 \times 10^{-6}T^{-0.48} )</td>
<td>10(^{-11} \rightarrow -6)</td>
</tr>
<tr>
<td>Warm Molecular</td>
<td>Cosmic-ray(^*) and X-ray(^\dagger\dagger) ionization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_3^+), HCO(^+)</td>
<td>( \zeta_{CR} = \frac{\zeta_{N_1,0}}{2} \left( \exp \left( -\frac{\Sigma_1}{\Sigma_{CR}} \right) + \exp \left( -\frac{\Sigma_2}{\Sigma_{CR}} \right) \right) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \zeta_X = \frac{\sigma(kT_X)}{\sigma(1 \text{ keV})}L_{29}J(r/\text{AU})^{-2} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid-Plane</td>
<td>Cosmic-ray(^*) and Radionuclide(^\ddagger\ddagger)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal(^+)/gr</td>
<td></td>
<td>( \alpha_{N^+} = 1.4 \times 10^{-10}T^{-0.69} )</td>
<td>&lt;10(^{-12})</td>
<td></td>
</tr>
<tr>
<td>(r &lt; 3 AU)</td>
<td></td>
<td>( \alpha_{gr} ) (see text)</td>
<td>10(^{-13} \rightarrow -12)</td>
<td></td>
</tr>
<tr>
<td>HCO(^+)/gr</td>
<td></td>
<td>( \alpha_{D^+} = 2.7 \times 10^{-8}T^{-0.5} )</td>
<td>&gt;10(^{-11})</td>
<td></td>
</tr>
<tr>
<td>(3 &lt; r &lt; 60 AU)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_3^+) – D(_3^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r &gt; 60 AU)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( * \) Effective penetration depth of radiation (e.g., \( \tau = 1 \) surface).
\( \dagger \) Recombination rates from UMIST database (Le Teuff et al., 2000) except for H\(_3^+\), which is from McCall et al. (2004), and D\(_3^+\), from Larson et al. (1997).
\( \ddagger \) Ion fractions estimated from Semenov et al. (2004) and Sano et al. (2000). Unless noted values are relevant for all radii.
\( \ddagger \ddagger \) Estimated at 100 AU assuming 10\(^{41}\) s\(^{-1}\) ionizing photons (Hollenbach et al., 2000) and \( \sigma = 6.3 \times 10^{-19} \text{ cm}^2 \) (H photoionization cross-section at threshold). This is an overestimate as we assume all ionizing photons are at the Lyman limit.
\( \ddagger \ddagger \) Rate at the disk surface at 100 AU using the radiation field from Bergin et al. (2003).
\( \ddagger \ddagger \) Taken from Semenov et al. (2004). \( \zeta_{N_1,0} = 1.0 \times 10^{-1} \text{ s}^{-1} \) and \( \Sigma_1(r, z) \) is the surface density above the point with height \( z \) and radius \( r \) with \( \Sigma_2(r, z) \) the surface density below the same point. \( \Sigma_{CR} = 96 \text{ g cm}^{-2} \) as given above (Umebayashi and Nakano, 1981).
\( \ddagger \ddagger \) X-ray ionization formalism from Glassgold et al. (2000). \( \zeta_{X_0} = 1.4 \times 10^{-10} \text{ s}^{-1} \), while \( L_{29} = L_X/10^{29} \text{ erg s}^{-1} \) is the X-ray luminosity and \( J \) is an attenuation factor, \( J = A_0e^{-B_0} \) with \( A_0 = 1.6 \) (10 keV).

TABLE 1. Disk ionization processes and vertical ion structure.
small). Deeper inside the warm molecular layer is reached, where primary charge carriers are molecular ions produced by X-ray ionization of H$_2$ (Glassgold et al., 1997) and, when this decays, cosmic-ray ionization. It is worth noting that X-ray flares are observed in T Tauri systems (e.g., Favata et al., 2005), after which there will exist a burst of ionization on the disk surface that will last for $\tau_r \sim 1/(\alpha r_n e)$.

An important question is whether cosmic rays penetrate the inner disk. Within our own planetary system, the solar wind excludes ionizing cosmic rays. Estimates of mass loss rates from young star winds significantly exceed the solar mass loss rate (Dupree et al., 2005), and may similarly exclude high-energy nuclei. In the case of cosmic-ray penetration, primary charge carriers range from metal ions and/or grains at small radii (~1 AU) to molecular ions for $r >$ few AU with $x_e \sim 10^{-13}$ near the midplane. If ionizing cosmic rays are excluded, radionuclides can produce

$$x_e \sim 10^{-3}(T/20 \text{ K})^{-0.5/\sqrt{n_H}}$$

(assuming H$_2^+$ as the dominant ion and $^{26}$Al is present; if $^{26}$Al is not present, the prefactor is $10^{-8}$). The presence or absence of metal ions in the midplane can also affect MHD-driven dynamics (Ilgner and Nelson, 2005b). Metal ions have recombination times longer than molecular ions or the diffusive timescale and, if present, can be important charge reservoirs.

In dense protostellar cores models and observations now suggest near total freeze-out of heavy species that results in D$_3^+$ and other forms of deuterated H$_3^+$ becoming important charge carriers (Roberts et al., 2004; Walmsley et al., 2004). The disk midplane should present a similar environment. The recent detection of H$_2$D$^+$ by Ceccarelli et al. (2004) in the outer disks of TW Hya and DM Tau supports this view.

In the midplane one issue is the electron sticking coefficient ($S_e$) to grains. Sano et al. (2000) assume $S_e = 0.6$ based on the work of Nishi et al. (1991), while Semenov et al. (2004) assume a strong temperature dependence with $S_e$ essentially zero at high temperatures. Thus in the inner disk the primary charge carrier differs between these two models, with grains dominating in the Sano et al. (2000) model and molecular/metal ions in the Semenov et al. (2004) model [for a discussion of electron sticking coefficients see Weingartner and Draine (2001)]. If grains are the dominant charge carrier the recombination rate $\alpha_{gr}$ is the grain collisional timescale with a correction for long-distance Coulomb focusing: $\alpha_{gr} = \pi \alpha_{gr} n_e v (1 + e^2/k_a T_g)$. At $T_g = 20$ K Draine and Sutin (1987) show that for molecular ions, grain recombination will dominate when $n_e/n_H < 10^{-7} (a_{min}/3 \AA)^{-3/2}$. Grains can be positive or negative and carry multiple charge: Sano et al. (2000) find that the total grain charge is typically negative, while the amount of charge is $1-2e^-$, varying with radial and vertical distance. Since the criteria for the MRI instability include the mass
of the charged particles, it is important to determine whether grains or molecules are the primary charge carriers.

4.4. Mixing

Chemical mixing within the solar nebula has a long history due to important questions regarding the potential transport of material from warm, thermochemically active regions (either inner solar nebula or jovian subnebula) into colder inactive regions (Lewis and Prinn, 1980; Prinn and Fegley, 1981). It is clear that some movement of processed material is likely; for example, the detection of crystalline silicates in comets (Crovisier et al., 1997; Bockelée-Morvan et al., 2002) and the chondritic refractory inclusions in meteorites (MacPherson et al., 1988) imply some mixing. However, the mixing efficiency has been a matter of debate (Stevenson, 1990; Prinn, 1990, 1993).

In terms of the dynamical movement of gas within a protoplanetary disk and its chemical effects, a key question is whether the chemical timescale, $\tau_{\text{chem}}$, is less than the relevant dynamical timescale, $\tau_{\text{dyn}}$, in which case the chemistry will be in equilibrium and unaffected by the motion. If $\tau_{\text{dyn}} < \tau_{\text{chem}}$, then mixing will alter the anticipated composition. These two constraints are the equilibrium and disequilibrium regions (respectively) outlined in Prinn (1993). What is somewhat different in our current perspective is the recognition of an active gas-phase chemistry on a photon-dominated surface. This provides another potential mixing reservoir in the vertical direction, as opposed to radial, which was the previous focus.

It is common to parameterize the transfer of angular momentum in terms of the turbulent viscosity, $v = \alpha c_s H$, where $v$ is the viscosity, $c_s$ the sound speed, $H$ the disk scale height, and $\alpha$ is a dimensionless parameter (Shakura and Sunyaev, 1973; Pringle, 1981). Hartmann et al. (1998) empirically constrained the $\alpha$-parameter to be $\leq 10^{-2}$ for a sample of T Tauri disks.

The radial disk viscous timescale is $\tau_v = r^2/v$ or

$$\tau_v \sim 10^4 \text{ yr} \left(\frac{\alpha}{10^{-2}}\right)^{-1} \left(\frac{T}{100 \text{ K}}\right)^{-1} \left(\frac{r}{1 \text{ AU}}\right)^2 \left(\frac{M_*}{M_\odot}\right)^{1/2}$$

The diffusivity, D, is not necessarily the same as the viscosity, $v$ (e.g., Stevenson, 1990), even though some treatments equate the two (Ilgner et al., 2004; Willacy et al., 2006). In the case of MRI, Carballido et al. (2005) estimate $v/D \sim 11$, i.e., turbulent mixing is much less efficient than angular momentum transport [but see also Turner et al. (2006), where $v/D \sim 1$–2]. With knowledge of the $v/D$ ratio, the above equation for $\tau_v$ serves as an estimate of the dynamical timescale for diffusion.

Recent models that include dynamics with chemistry generally can be grouped into two categories: ones that include only advection (Duschl et al., 1996; Finocchi et al., 1997; Willacy et al., 1998; Aikawa et al., 1999; Markwick et al., 2002) and ones that investigate the effects of vertical and/or radial mixing including advection (Wehrstedt and Gail, 2003; Ilgner et al., 2004; Willacy et al., 2006; Semenov et al., in preparation). The effects of advection on the chemical evolution are dominated by migration of icy grains toward the warmer inner disk where the volatile ices evaporate. Most of the species that desorb are processed via the active gas phase and/or gas-grain chemistry into less-volatile species that freeze out (e.g., Aikawa et al., 1999). For instance, N$_2$ evaporates at $T > 20$ K ($\ddot{O}$berg et al., 2005) and is converted to HCN, and other less-volatile species, via ion-molecule reactions. This would predict a strong temporal dependence on the chemistry in the accreting material within the evaporative zones.

As an example of more complex dynamical models, Fig. 6 shows results from Semenov et al. (in preparation) (see also Willacy et al., 2006). For these models, radial and vertical mixing is incorporated into a disk model that also includes all other relevant physical/chemical processes described in section 1.2. The model assumes a traditional $\alpha$-disk that is fully dynamically active with $v/D = 1$. This model reproduces the basic structure shown in Fig. 1, with the presence of a warm molecular layer and a drop in abundance toward the midplane (most dramatically seen in CS). When vertical transport and/or radial transport is included the essential features of the basic structure are preserved, in the sense that the warm molecular layer still exists, although it may be expanded (Willacy et al., 2006). This is readily understood as the chemical timescales driven by photo-dissociation, $\tau_{\text{chem}} \leq 100–1000/(r/100 \text{ AU})^2$ yr, are less than the dynamical timescale at all radii, thus the photochemical equilibrium is preserved. The effects of radial mixing and advection are mostly important for the upper disk atmosphere. Two results stand out: (1) The electron abundance structure shows little overall change, thus ionization equilibrium is preserved throughout the disk. (2) There is clear evidence for abundance enhancements of key species (such as H$_2$CO) in models with vertical mixing. The molecules with the largest abundance enhancements in the vertical mixing models are those that are more volatile than water, but are also major components of the grain mantle. This suggests that observations of these species may ultimately be capable of constraining disk mixing. However, all predictions are highly uncertain. If MRI powers accretion, and cosmic rays do not penetrate to the midplane, then the bulk of the disk mass will not participate in any global mixing. Moreover, the outer disk may be actively turbulent while the inner disk may be predominantly quiescent (excluding the surface ionized by X-rays). Thus, while current models are suggestive of the importance of mixing for the disk chemical evolution, significant questions remain.

5. DEUTERATED SPECIES IN DISKS AND COMETS

Isotopic fractionations are measured in primordial materials in comets and meteorites, and considered to be good tracers of their origin and evolution. Here we review recent progress on deuterium fractionation in relation to comets.
In contrast to the millimeter observations of gas in the outer disk, comets carry information on ice (rather than gas) at radii of 5–30 AU (e.g., Mumma et al., 1993). The similarity in molecular D/H ratios between comets and high-mass hot cores has been used to argue for an interstellar origin of cometary matter, but the D/H ratios in low-mass star-forming regions (e.g., TMC-1) are higher than those in comets, casting questions as to the interstellar origin scenario (e.g., Irvine, 1999). In recent years hot cores are found around low- or intermediate-mass protostars (see IRAS 16293-2422). In addition, temporal and spatial variation in molecular D/H ratios are found in low-mass dense cores, where the bulk of ices formed (e.g., Bacmann et al., 2003; Caselli, 2002). Hence, what one means by “interstellar” is ambiguous. Eventually, molecular evolution from cores to disks and within disks should be investigated.

Aikawa and Herbst (1999) calculated molecular abundances and D/H ratios in a fluid parcel accreting from a core to the disk, and then from the outer disk radius to the cometary matter. However, the D/H ratio in the disk; initially high D/H ratios of H2O and HCN are lowered by mixing with the poorly deuterated material.

### Table 2. D/H ratios in comets, disks, and cores.

<table>
<thead>
<tr>
<th>Region Type</th>
<th>Object</th>
<th>Species</th>
<th>D/H ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot cores</td>
<td>various</td>
<td>HDO</td>
<td>3.0 × 10^{-4}</td>
<td>Gensheimer et al. (1996)</td>
</tr>
<tr>
<td></td>
<td>various</td>
<td>DCN</td>
<td>0.940 × 10^{-3}</td>
<td>Hatchell et al. (1998)</td>
</tr>
<tr>
<td>Low-mass protostars</td>
<td>IRAS 16293-2422</td>
<td>HDO</td>
<td>3.0 × 10^{-2}</td>
<td>Parise et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>IRAS 16293-2422</td>
<td>CH3OD</td>
<td>2.0 × 10^{-2}</td>
<td>Parise et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>IRAS 16293-2422</td>
<td>CH3DOH</td>
<td>3.0 × 10^{-1}</td>
<td>Parise et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>various</td>
<td>HDO</td>
<td>5.0–7.0 × 10^{-2}</td>
<td>Roberts et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>various</td>
<td>NH3D</td>
<td>1.0–2.8 × 10^{-1}</td>
<td>Roueff et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>various</td>
<td>DCO+</td>
<td>1.0 × 10^{-2}</td>
<td>Class 0 average; Jørgensen et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>various</td>
<td>DCN</td>
<td>1.0 × 10^{-2}</td>
<td>Class 0 average; Jørgensen et al. (2004)</td>
</tr>
<tr>
<td>Dark Cores</td>
<td>L1554</td>
<td>DCO+</td>
<td>4.0 × 10^{-2}</td>
<td>Caselli et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>L134N</td>
<td>DCO+</td>
<td>1.8 × 10^{-1}</td>
<td>Tiné et al. (2000)</td>
</tr>
<tr>
<td></td>
<td>TMC-1</td>
<td>DCN</td>
<td>2.3 × 10^{-2}</td>
<td>van Dishoeck et al. (1995)</td>
</tr>
<tr>
<td>Disks</td>
<td>TW Hya</td>
<td>DCO+</td>
<td>3.5 × 10^{-2}</td>
<td>van Dishoeck et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>LkCa 15</td>
<td>HDO</td>
<td>6.4 × 10^{-2}</td>
<td>Kessler et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>DM Tau</td>
<td>HDO</td>
<td>1.0 × 10^{-2}</td>
<td>Ceccarelli et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>LkCa 15</td>
<td>DCN</td>
<td>&lt;0.002</td>
<td>Kessler et al. (2003)</td>
</tr>
<tr>
<td>Comets</td>
<td>Halley</td>
<td>HDO</td>
<td>(3.2 ± 0.3) × 10^{-4}</td>
<td>Eberhardt et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>Hyakutake</td>
<td>HDO</td>
<td>(2.9 ± 1.0) × 10^{-4}</td>
<td>Bockelée-Morvan et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>Hale-Bopp</td>
<td>HDO</td>
<td>(3.3 ± 0.8) × 10^{-4}</td>
<td>Meier et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>Hale-Bopp</td>
<td>DCN</td>
<td>2 × 10^{-3}</td>
<td>Blake et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Hale-Bopp</td>
<td>DCO+</td>
<td>(2.3 ± 0.4) × 10^{-3}</td>
<td>Meier et al. (1998)</td>
</tr>
</tbody>
</table>

HDO has only been tentatively detected in disks, whereas H2O has not. In these cases (Ceccarelli et al., 2005; Kessler et al., 2003) the D/H ratio is estimated by model calculation and is therefore highly uncertain.

(see the chapter by Yurimoto et al. for a discussion of oxygen fractionation). In Table 2 we list molecular D/H ratios, defined as n(XD)/n(XH), observed in protoplanetary disks, comets, and low-mass cores.

The two-dimensional (r–z) distributions of deuterated species at r ≥ 26 AU have been calculated in models of Aikawa and Herbst (2001) and Aikawa et al. (2002). At low temperatures D/H fractionation proceeds via ion-molecule reactions; species such as H3D+ and CH3D are enriched in deuterium because of the difference in zero-point energies between isotopomers and rapid exchange reactions such as H3D+ + HD → H3D2+ + H2 (e.g., Millar et al., 1989). Since CO is the dominant reactant with H3D+, CO depletion further enhances the H2D+/H+ ratio. The deuterium enrichment propagates to other species via chemical reactions (see chapters by Ceccarelli et al. and Di Francesco et al.). Hence the D/H ratios of HCN and HCO+ tend to increase toward the midplane with low temperature and heavy molecular depletion, while their absolute abundances reach the maximum value at some intermediate height. The column density D/H ratios of HCO+, HCN, and H2O integrated in the vertical direction are 10^{-2} at r ≥ 100 AU and 10^{-3} at 26 AU ≤ r ≤ 100 AU in Aikawa et al. (2002). H3D+ and its deuterated families (H3D2+, HD3H+, and D3H), on the other hand, are abundant in the midplane, and the D/H ratio can even be higher than unity. At present, the data on D/H ratios in disks (with both deuterated and hydrogenated species observed) is limited to the detection of DCO+ (van Dishoeck et al., 2003), which is in agreement with models (Aikawa et al., 2002).
from the smaller radii. This model, however, considered only thermal reactions. In reality deuterium fractionation (or backward reactions) via ion-molecule reactions would proceed within the disk depending on the local ionization rate, temperature, and density of molecular depletion, while the vertical and radial diffusion will tend to lessen the spatial gradient of D/\ H ratios. Inclusion of deuterated species in the recent models with nonthermal chemistry and two-dimensional diffusion is desirable.

6. OUTSTANDING ISSUES AND FUTURE PROSPECTS

Significant gains have been made in our observational and theoretical understanding of the chemical evolution of protoplanetary disks in the decade since the last review in this conference series. We now recognize the importance of the irradiated surface, which at the very least contains an active chemistry and is responsible for most observed molecular emission lines. The gross characteristics and key ingredients of this surface are roughly understood. How the varied effects (grain evolution, UV/X-ray radiation dominance, etc.) play out on the chemical evolution in terms of X-ray/UV dominance and the dependence on other evolutionary factors is one of the challenges for future models. Given the observed chemical complexity, a detailed understanding of the chemistry is a prerequisite for the interpretation of ongoing and future observations of molecular emission in protoplanetary disks.

Disk surface processes may dominate the observed chemistry, but it is not certain how much of a role this chemistry plays in altering the chemical characteristics within the primary mass reservoir, the disk midplane. Thus one of the main outstanding questions for disk chemistry remains the question of how much material remains pristine and chemically unaltered from its origin in the parent molecular cloud. We now have observational and theoretical evidence for active chemical zones; it is thus likely that the most volatile species, which are frozen on grains in the infalling material (e.g., CO, N$_2$), do undergo significant processing. This will trickle down to other, less-abundant molecules that form easily from the “parent species” (e.g., H$_2$CO, HCN, and the deuterated counterparts). Disentangling these effects will be complicated because the chemistry in the outer disk (r > 30 AU), which through advection feeds the inner disk, is quite similar to that seen in dense regions of the interstellar medium. For the least-volatile molecules, in particular water ice, sublimation and subsequent gas-phase alteration is less likely, unless there is significant radial mixing from the warmer inner disk to colder outer regions.

In part, our recognition of the warm molecular layer and the importance of photochemistry is driven by our current observational facilities, which are unable to resolve the innermost regions of the disk (e.g., planet-forming zones), coupling better to the larger surface area of the outer disk. Within r < 10–30 AU, the midplane and surface are both hot enough to sublime even the least-volatile molecules (e.g., H$_2$O), eventually producing an active chemistry that is described by the earlier Protostars and Planets III review (Prinn, 1993) and in the chapter by Najita et al. The transition between these layers, the so-called “snowline,” and the chemistry within the planet-forming zone will be species specific and should be readily detectable with upcoming advances in our capabilities, in particular the eagerly awaited ALMA array.

In summary, we stand on the cusp of the marriage of a rapidly emerging new field, studies of extrasolar protoplanetary disk chemical evolution, and an old one, the cosmochemical study of planets, meteorites, asteroids, and comets. In this review we have outlined broad areas where the evolving chemistry can be altered through changes induced by vertical and horizontal temperature gradients, the evolution of grain properties, and disk dynamics (mixing). Thus studies of active chemistry in extrasolar disks offers the promise and possibility to untangle long-standing questions regarding the initial conditions, chemistry, and dynamics of planet formation, the origin of cometary ices, and, ultimately, a greater understanding of the organic content of gas/solid reservoirs that produced life at least once in the galaxy.

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