Chemistry in low-mass protostellar and protoplanetary regions

Ewine F. van Dishoeck*

Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

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When interstellar clouds collapse to form new stars and planets, the surrounding gas and dust become part of the infalling envelopes and rotating disks, thus providing the basic material from which new solar systems are formed. Instrumentation to probe the chemistry in low-mass star-forming regions has only recently become available. The results of a systematic program to study the abundances in solar-mass protostellar and protoplanetary regions are presented. Surveys at submillimeter and infrared wavelengths reveal a rich chemistry, including simple and complex (organic) gases, ices, polycyclic aromatic hydrocarbons, and silicates. Each of these species traces different aspects of the physical and chemical state of the objects as they evolve from deeply embedded protostars to pre-main sequence stars with planet-forming disks. Quantitative information on temperatures, densities, and abundances is obtained through molecular excitation and radiative transfer models as well as from analysis of solid-state line profiles. The chemical characteristics are dominated by freeze-out in the coldest regions and ice evaporation in the warmer zones. In the surface layers of disks, UV radiation controls the chemistry. The importance of complementary laboratory experiments and calculations to obtain basic molecular data is emphasized.

Methods

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Submillimeter Spectroscopy. At (sub)millimeter wavelengths, the pure rotational lines of gaseous molecules are seen in emission after collisional excitation of low-lying energy levels. The heterodyne detector technique naturally has very high spectral resolution, $R = \lambda/\Delta \lambda > 10^6$, so that the line profiles are fully resolved and also provide kinematic information on dynamical processes occurring in the protostellar environment such as outflows. The sensitivity of the data is very high: molecules with abundances as low as a few $10^{-12}$ with respect to $H_2$ can be seen. Detection of linear molecules is favored compared with heavy asymmetric rotors because their population is spread over fewer energy levels. Compared with the total reservoir of C, N, and O not locked up in refractory silicate or carbonaceous grain cores of $\sim 10^{-4}$ each, this implies that, except for CO, minor species in terms of overall abundances are observed in the coldest and densest parts, evaporation of ices in the warmer layers, high-temperature ion-molecule and neutral-neutral chemistry above 200 K forming complex molecules, and photo-dissociation, -ionization, and -desorption in regions exposed to radiation. This implies, on the one hand, that the chemistry must evolve as matter is transported from prestellar cores through the protostellar phase into disks. On the other hand, this variation in abundances offers the opportunity to use molecules as chemical diagnostics of the different evolutionary stages or of individual physical components. For example, the $N_2H^+$ ion and deuterated species are excellent tracers of the coldest cores, whereas CH$_3$OH and HCN are good probes of high temperature gas. Molecules are also accurate diagnostics of physical conditions because their energy levels are populated by collisions that in turn depend on temperature and density.

Previous astrochemical studies of star-forming regions focused on high-mass YSOs which have luminosities that are $10^4$ to $10^5$ times higher than those of our Sun (e.g., refs. 4 and 5). Only recently has it become possible to observe a wide variety of molecules, including complex organic molecules and ices, in solar-mass protostars and disks, owing to jumps in sensitivities at submillimeter and infrared wavelengths. This article presents an overview and synthesis of recent results from our group on both gas-phase and solid-state molecules. Other recent overviews include (6–8). The importance of the combination of observations with models and laboratory experiments, including quantum chemical calculations, is stressed.

Conflict of interest statement: No conflicts declared.

Abbreviations: AU, astronomical unit; PAH, polycyclic aromatic hydrocarbon; PDR, photon-ionization, and -desorption in regions exposed to radiation. This implies, on the one hand, that the chemistry must evolve as matter is transported from prestellar cores through the protostellar phase into disks. On the other hand, this variation in abundances offers the opportunity to use molecules as chemical diagnostics of the different evolutionary stages or of individual physical components. For example, the $N_2H^+$ ion and deuterated species are excellent tracers of the coldest cores, whereas CH$_3$OH and HCN are good probes of high temperature gas. Molecules are also accurate diagnostics of physical conditions because their energy levels are populated by collisions that in turn depend on temperature and density.

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in the submillimeter. Symmetric molecules like O$_2$ and N$_2$, which are predicted by models to be among the most abundant gaseous O- and N-bearing molecules in dense clouds, do not have strong rotational transitions.

An advantage of millimeter data is that the emission lines can be mapped so that the spatial distribution of the molecule can be obtained. However, the angular resolution of the most advanced single-dish telescopes such as the 15-m James Clerk Maxwell telescope and the 30-m Institut de Radioastronomie Millimétrique (IRAM) telescope is only $\approx$15$''$ (1$''$ = 1 arcsec = 1/3,600 of a degree of arc), which corresponds to a linear scale of a few thousand AU (1 astronomical unit = 1.496 x 10$^{13}$ cm = distance Sun–Earth) at the distances of the nearest star-forming regions of $\approx$150 pc (1 parsec = 206,265 AU = 3.086 x 10$^{19}$ cm). It is convenient to express spatial scales in AU, for easy comparison with our own solar system (distance Sun–Pluto is $\approx$40 AU). Typical sizes of protostellar envelopes are $\approx$3,000 AU. Thus, the single-dish beams are comparable to the sizes of the entire protostellar envelope and much larger than those of disks. This means that the different chemical and physical regimes are “blurred” together in a single spatial pixel.

There are two techniques to obtain information on smaller spatial scales. The first is millimeter interferometry, which can reach resolutions of a few $''$ or a few hundred AU. Pioneering interferometers have been developed over the last two decades, but their sensitivities are still limited, and large chemical surveys have not yet been feasible. The second method is to use multiline and multifrequency single-dish observations combined with detailed radiative transfer modeling to infer physical and chemical gradients on scales much smaller than the beam (9–11). This is the primary method used for most of the results reported in this article.

**Infrared Spectroscopy.** Infrared spectroscopy has the big advantage that both gas-phase and solid-state features can be seen, albeit usually at lower spectral resolution. In protostellar objects, broad bands of cold ices and silicates are detected in absorption superposed on the infrared continuum due to hot dust close to the protostar. Thus, a single pencil-beam line-of-sight is probed. For disks, features from silicates and polycyclic aromatic hydrocarbons (PAHs) are found in emission, originating in the warm surface layers. Fig. 1 illustrates these different types of spectra for a number of sources in the Serpens star-forming region.

A large part of the infrared wavelength range is obscured from Earth. The Infrared Space Observatory (1995–1998) provided the first opportunity to obtain complete mid-infrared spectra unhindered by the Earth’s atmosphere but was limited in sensitivity to systems 10$^4$ to 10$^5$ times more luminous than the Sun (5). The Spitzer Space Telescope, launched in 2003, has the sensitivity to obtain a complete inventory of solid-state molecules of solar-mass YSOs and disks through spectroscopy at 5–40 $\mu$m. Although the resolution of its InfraRed Spectrograph is only $R \approx$ 100–600, insufficient for detection of most gas-phase molecules, it allows a wide variety of features from ices, silicates, and PAHs to be observed (Fig. 1). The apertures are large, typically $>10''$, so that most emission is spatially unresolved.

The Spitzer data are complemented by ground-based spectra from 8- to 10-m-class telescopes such as the Keck Observatory (12) and the Very Large Telescope of the European Southern Observatory (13) in atmospheric windows at 3–5 $\mu$m. These facilities have two advantages: $R \approx$ 25,000 can be achieved and emission can be spatially resolved on subarcsec scales, comparable to those of disks.

**Importance of Radiative Transfer and Molecular Data.** The translation of the observed intensities to chemical abundances, temperatures, and densities requires sophisticated excitation and radiative transfer models to understand how the photon is produced in the cloud and how it makes its way from the cloud to the telescope. Significant progress has been made in recent years in the quantitative analysis of molecular line data through the development of rapid, accurate, and well tested radiative transfer codes that can be applied to multidimensional geometries (e.g., refs. 14 and 15).

To calculate the excitation of gas-phase molecules, information on the frequencies, radiative rates, and collisional rate coefficients with the main collision partner, H$_2$, is needed. In principle, state-to-state collisional rate coefficients are required for both para-H$_2$, $J = 0$ (cold clouds) and ortho-H$_2$, $J = 1$ (warm regions). In practice, such data are available for only a few molecules, and H$_2$, $J = 0$ is taken as the main collision partner. Much of the molecular data gathered over the last 30 years from laboratory experiments and quantum-chemical calculations have been summarized (16). For solid-state molecules, information on infrared band strengths and band profiles is needed (e.g., ref. 17).

**Results and Discussion**

The earliest stages of low-mass star-formation are identified by their spectral energy distribution, which peaks at far-infrared wavelengths for the most deeply embedded class 0 objects and shifts to mid- and near-infrared wavelengths for class I and class II objects, respectively, as the envelope is dispersed. Continuum surveys at
submillimeter and infrared wavelengths have identified a few dozen class 0 objects and a few hundred class I and II sources in the nearest star-forming clouds. In particular, large-scale maps obtained with Spitzer in the context of the "Cores to Disks" legacy survey provide an unbiased census of all YSOs in the nearest clouds with luminosities as low as 1% of that of our own Sun (18). From the statistics of the number of objects, rough time scales of each class can be obtained. Class 0 sources have ages of a few $\times 10^5$ yr, class I sources up to a few $\times 10^6$ yr, and class II sources up to a few $\times 10^6$ yr. One important result emerging from the Spitzer data is that time is not the only parameter determining the rate of evolution; environment and initial conditions are also important.

Chemically, the earliest stages are characterized by heavy freeze-out of molecules onto the grains in the prestellar cores and the cold outer envelopes. Once the protostar heats the dust in its immediate surroundings, the molecules start to return to the gas phase, roughly in a sequence according to their evaporation temperature (Fig. 2). When the envelope has been completely removed, strong UV radiation from the pre-main sequence star can reach the surface layers of the disk and dissociate and ionize atoms and molecules. In the following, these different evolutionary stages are systematically discussed; their characteristics are summarized in Table 1.

### Protostellar Envelopes: Gas-Phase Molecules

The first multiline chemical survey of low-mass YSOs (luminosities <50 times that of the Sun) has recently been completed at submillimeter wavelengths (10, 19–22). The sample consists of 12 class 0 protostars, 5 class I objects, and 2 prestellar cores. The distinction between class 0 and I YSOs is somewhat arbitrary, and it is even unclear whether they represent truly different evolutionary stages. In practice, a division in envelope mass at $\approx 0.5 M_{\odot}$ is taken (1 $M_{\odot}$ = 1.989 $\times 10^{33}$ g), but they do show chemical differences. In total, >40 lines of 16 species (CO, CS, HCO+, DCO+, $N_2$H+, HCN, HNC, DCN, CN, H$_2$N, SO, SO$_2$, SiO, H$_2$CO, CH$_3$OH, CH$_3$CN, and isotopes) were searched for. For linear molecules like CO, this involves the lower rotational transitions with energies up to 30 K. For (a)symmetric rotors like CH$_3$OH, transitions from energy levels up to 200 K have been detected in the frequency range covered. Note that the observed molecules are not necessarily the most abundant ones: they are chosen because they have strong transitions in the observed range. Nevertheless, many of these molecules turn out to be highly diagnostic of the physical and chemical processes in protostellar environments, even though they are only minor species.

#### Cold outer envelope: Freeze-out

The best-fit results show a clear trend of decreasing CO abundance with increasing $M_{\text{env}}$ if the abundance is taken to be constant with radius (10). The most likely explanation is freeze-out onto grains in the coldest and densest parts. Indeed, the best fit to the multitransition CO data are obtained with a so-called "drop" abundance profile (Fig. 2): here, the CO abundance $X = n$(CO)/$n$(H$_2$) is normal ($X_0 \approx 2 \times 10^{-4}$; i.e., most available carbon in CO) in the inner part of the envelope where the dust temperature $T_d$ is above the CO evaporation temperature ($>20–30$ K, and in the outermost part where the density is too low for significant freeze-out within the lifetime of the core. In the intermediate zone, the abundance $X_d$ is at least an order of magnitude lower. This chemical structure, inferred from spatially unresolved data, has been confirmed by millimeter interferometer

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**Table 1. Chemical characteristics of low-mass YSOs**

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<td>—</td>
<td>Silicates, hot gas (C$_2$H$_2$, HCN)</td>
<td>IRS 46, EC 82</td>
</tr>
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The freeze-out of CO is reflected in the abundances of many other species, either through correlations or anticorrelations (19). A striking example is the anticorrelation of CO with N2H+, whose abundance is enhanced when CO, its main destroyer, is removed from the gas. Also, the abundances of deuterated molecules are increased (24, 25). Deuterium fractionation in the gas is initiated by deuteron transfer from H2D+, whose abundance relative to H2+ is particularly enhanced at low temperatures when CO is frozen out (e.g., refs. 2 and 27). Indeed, the first detection of interstellar H2D+ was in a class 0 YSO with significant CO depletion (26). The abundances of most other observed molecules follow that of CO; see, for example, H2CO (20, 21). Based on these correlations, empirical reaction networks can be constructed against which chemical models can be tested.

The main difference between the class 0 and I sources is not in the absolute abundances but rather in the width of the freeze-out zone, which is significantly smaller for the class I objects and even vanishes for objects with $M_{\text{env}} < 0.1 M_{\odot}$. Quantitatively, the amount of freeze-out of a species can be derived by balancing the rates of desorption and freeze-out. The former depends exponentially on the ratio of the binding energy of the molecule and the dust temperature, $E_b/T_d$, whereas the latter scales linearly with density, $n$. The outer freeze-out radius can thus be used as a direct measure of the lifetime of the cores. A surprisingly short age of $\sim 10^5$ yr is inferred, with no significant difference between the class 0 and I objects. This suggests that the phase with heavy depletions (both in the pre- and protostellar stages) is short-lived (28).

Hot cores: Ice evaporation and complex organics. In regions where $T_d$ reaches 90–100 K, even the most strongly bound ices like H2O start to evaporate, resulting in a “jump” in the gas-phase abundances of molecules trapped in H2O ice. For the low-luminosity objects considered here, such “hot cores” have radii of $<100$ AU; i.e., less than 1" diameter. Thus, their emission is severely diluted in the $>10'$ single-dish beams. Other effects such as holes, cavities, and disks also start to become important on these scales (29, 30). Nevertheless, if the abundance enhancements are sufficiently large (typically more than a factor of 100), they become observable in the higher excitation lines.

Early submillimeter spectra of low-mass YSOs revealed strong lines of CH3OH and CH3CN from high excitation levels, implying enhanced abundances of these species in the inner warm envelopes (24, 31, 32) (Fig. 3). Subsequent deeper integrations with improved receivers have revealed surprisingly rich spectra for at least a few objects, rivaling the complex spectra seen for high-mass protostars (33). A multitude of features from large organic molecules such as CH3OCH3, HCOOCH3, and CH3CN have been detected and in some cases imaged (34, 35). The origin of these complex organic molecules is still under debate, in particular whether they are first generation molecules directly evaporated from the ices or whether they are second generation products of a “hot core chemistry” involving high-temperature gas-phase reactions between evaporated molecules (e.g., ref. 36). A related problem is that the time scales for crossing the hot core region are very short in a pure infall scenario, only a few hundred years, much shorter than the time scales of $\sim 10^4$ to $10^5$ yr needed for the hot core chemistry (32). Thus, unless some mechanism has slowed down the infall or unless the molecules are in a dynamically stable region such as a disk, there is insufficient time for the hot core chemistry to proceed.

Outflows and shocks. An alternative suggestion for the origin of the complex organics is local “hot spots” where the outflow impacts the envelope and sinters ices and grain cores (31, 37, 38). The SiO molecule is a good tracer of shocks: its abundance is greatly enhanced when Si atoms are liberated from the grains by the direct impact (39). Ices containing species like CH3OH can be released in the less violent, turbulent shear zones. Indeed, in outflow lobes offset from the central protostar [L1157 (39); NGC 1333 IRAS 2A (40)] CH3OH is enhanced by more than two orders of magnitude. The CH3OH line profiles for some sources are narrow, indicating a likely origin in the hot core, whereas in other cases they are so broad that they can only result from outflow interaction (20). Which of these two mechanisms dominates the observed emission depends on the relative filling factor of the thermal evaporation versus shocked zones in the observing beam.

Protostellar Envelopes: Ices. The freeze-out can be probed directly by observations of the vibrational modes of the ices at infrared wavelengths. With Spitzer, several dozen low-mass YSOs have now been observed (41) (Fig. 1), including some of the most deeply embedded class 0 YSOs and sources of substellar luminosity. Fig. 1 also contains a spectrum of a background star that probes quiescent cloud material unaffected by star formation (42). The main features are the 9.7- and 18-μm Si–O stretch and bending modes of the silicate grain cores, and ice bands of relatively simple species. H2O ice has the largest abundance, $(0.5–1.5) \times 10^{-4}$ with respect to H2, whereas the combined contribution of CO and CO2 may be as high as that of H2O. Thus, the ices are a major reservoir of the heavy elements in cold clouds, containing up to 50% or more of the oxygen not locked up in refractory cores (see Table 2, which is published as supporting information on the PNAS web site). Solid CO may be even more abundant than gaseous CO, usually the second most abundant molecule in the gas after H2.

At first sight, all spectra look remarkably similar, not only to each other, but also to those of much more luminous YSOs obtained with the Infrared Space Observatory. This implies that most ices are formed before star formation, and that orders of magnitude higher luminosities do not result in major changes in the ice composition. However, on closer inspection, differences are found, both between different types of sources and within one class of objects. For example, the overall abundances of CO2 are a factor of two higher in low-mass compared with high-mass YSOs. Abundances of minor species like CH3OH and OCN− vary by more than an order of magnitude among the low-mass YSOs and even on spatial scales as small as 1,000 AU (43, 44). The line profiles of solid CO, CO2, and the carrier of the 6.8-μm feature [likely NH4+ (45)] show subtle changes that are related to heating of the ices up to at least 50 K (13, 46, 47) (Fig. 7, which is published as supporting information on the PNAS web site). Moreover, these profile changes always occur in concert (if one is found, so are the others) and are usually correlated with changes in the gas/solid ratios (Fig. 8, which is published as supporting information on the PNAS web site).

The presence of some features, for example that due to OCN− at 4.62 μm, is often cited as an indicator of “energetic” processing; i.e., changes induced in the ice composition due to UV or particle bombardment rather than thermal heating. There is a rich literature of laboratory studies (see, e.g., ref. 48)
formation routes. For example, a large fraction of the CO₂ ice must of the ice abundances with density provide critical clues about their in the coldest and densest regions (Fig. 2). Moreover, the variations analysis of the (sub)millimeter data that imply significant freeze-out of the models is summarized.

star-forming regions. Here, recent progress on some key aspects of freeze-out layer (C). Viscous accretion and turbulence will transport material both vertically and radially (based on refs. 85 and 86).

for UV and ref. 49 for particle bombardment), but no clear observational evidence has yet been found (44).

Spitzer and large ground-based telescopes have the sensitivity to observe many nearby lines of sight within a small region (see Fig. 1). This has opened up an important new development: maps of the ice abundances with the same spatial resolution (~1,000 AU) as those of gas-phase molecules (43, 50). Initial results show that both the H₂O and CO ice abundances have a clear jump at a density of ~10⁶ cm⁻³. These results confirm directly and quantitatively the analysis of the (sub)millimeter data that imply significant freeze-out in the coldest and densest regions (Fig. 2). Moreover, the variations of the ice abundances with density provide critical clues about their formation routes. For example, a large fraction of the CO₂ ice must be formed at low densities before the bulk of the CO ice freezes out. In the coldest and densest regions, CO freezes out as a separate, nearly pure (i.e., H₂O-poor) ice layer on top of the H₂O-rich ices accreted before collapse (13).

Protoplanetary Disks. Once the protostellar envelope has been dispersed, the pre-main sequence star becomes visible but it is still surrounded by a disk of gas and dust. Typical masses are ~0.01 M_J (~0.1 M_☉), sufficient to form a planetary system like our own (3). In the period between ~1 and 10 million years, the grains coagulate to larger particles, and most of the gas may be dissipated from the disk. Thus, studying young disks is highly relevant for constraining the initial conditions for exoplanetary systems because these systems are in the phase where they are actively forming planets.

The basic physical structure of protoplanetary disks is illustrated in Fig. 4 and has been derived from observations and analysis of the spectral energy distribution (e.g., ref. 63). In the innermost disk, accretion dominates the thermal balance but beyond a few AU the disk is mostly heated by UV radiation from
the young star. Thus, the temperature decreases not only in the radial direction outward, but also in the vertical direction toward the midplane. Densities in the inner disk and in the midplane are a few orders of magnitude higher than those found in the envelopes discussed above. Another key difference with envelope chemistry is the importance of UV radiation: for low-mass T Tauri stars, a flaring disk intercepts a substantial fraction of the stellar UV field.

**Protoplanetary Disks: Gas-Phase Molecules.** Disks are small with radii of a few hundred AU, and they contain a factor of 10–100 times less mass than the clouds from which they form. Thus, the emission from disks is easily overwhelmed by that from the surroundings unless the observations have high angular resolution and/or probe high density or temperature features not excited in the envelope. Chemical studies of disks are still scarce (7).

**Outer disk: Submillimeter observations.** Only a handful of disks have been studied in detail at (sub)millimeter wavelengths, with a heavy bias toward nearby (TW Hya at 56 pc) or intrinsically large (DM Tau, GG Tau, and LkCa 15 at 140 pc) disks (64–66) (Fig. 5). These data are only sensitive to the outer disk (>50 AU). The detection of ions like HCO$^+$ points toward ion-molecule chemistry, whereas the high abundances of CN compared with HCN are a testimony of photodissociation in the surface layers. Only simple molecules have been detected so far; the larger organic molecules seen toward “hot cores” are out of the reach of existing facilities. Interferometers have begun to reveal spatial gradients in disk chemistry (67, 68). For example, the HCN abundance peaks toward the inner disk, whereas that of CN is higher in the outer part.

The line ratios of high-dipole moment molecules like HCO$^+$ and HCN indicate that the emission arises from regions with densities of $10^6$ to $10^8$ cm$^{-3}$ and temperatures of $\gtrsim 30$ K (69), consistent with the warm molecular layer (Fig. 4). Detection of high-$J$ CO lines such as $J = 6–5$ provides further evidence for enhanced gas temperatures. Overall, the abundances are low, comparable to those found in the outer protostellar envelopes, suggesting that the heavy molecules are largely frozen out in the cold midplane. The absolute abundances of HCO$^+$ of $10^{-11}$ to $10^{-10}$ give a lower limit to the ionization fraction in the outer disk, which is sufficient to provide a source of turbulence and mixing in the disk to drive mass transfer.

Evidence for strong depletion also comes from deuterated molecules. DCO$^+$ has been detected toward TW Hya (Fig. 5) with DCO$^+$/HCO$^+$ = 0.035 ± 0.01, comparable to the deuteration ratios found in the outer protostellar envelopes (70). Hints of H$_2$O$^+$ have been seen toward two disks (71) but not toward others (66).

**Inner disk: Infrared observations.** Gaseous CO is readily seen through its vibrational emission at 4.7 $\mu$m, but searches for bands of other molecules have so far not been successful, except for the detection of hot H$_2$O toward one object (72). In contrast, surprisingly strong absorption lines of organic molecules, C$_2$H$_2$, HCN, and CO$_2$, have recently been found toward one young star, IRS 46 in Ophiuchus (see Fig. 6 and ref. 73). Comparison with submillimeter HCN data constrains the source size to <11 AU radius. The line of sight likely passes through the inner part of a near edge-on disk. The inferred abundances are high, high-3 with respect to H$_2$, three orders of magnitude higher than those found in the surrounding cloud, and the gas is very warm, of order 300–700 K. The large line widths and velocities suggest that this hot gas rich in organic molecules may actually arise in a disk wind. Regardless of their precise origin, these data provide the first probe of organic chemistry in planet-forming zones of disks.

**Surface layers: Optical observations.** [O I] $^1\text{D}$$^-$3$^\text{P}6$, 3 0 0Å lines with signs of Keplerian rotation have been detected from a number of disks around Herbig Ae stars (74). The excited O $^1\text{D}$ atoms are thought to result from photodissociation of OH in the upper flaring layers out to at least 10 AU. Cross sections and branching ratios for this process have been calculated (75).

**Protoplanetary Disks: Solid-State Species. Ices.** The strongest ice emission bands at <100 K occur at far-infrared wavelengths. So far, only crystalline water ice has been seen in a few disks through librational features at 44 and 63 $\mu$m (76, 77). The data can be reproduced in models assuming that 50% of the available oxygen is in water ice at low temperatures, confirming the heavy freeze-out.

**Silicates: Grain growth and crystallization.** The amorphous broad silicate features at $\approx$10 and 20 $\mu$m are the most prominent emission bands in the infrared spectra of disks (see Fig. 1).
Spitzer and new ground-based facilities allow studies of large samples of solar mass T Tauri stars for the first time (79). The silicate features arise in the superheated layers of a few hundred kelvins in the inner disk at <1–10 AU and are therefore not representative of the outer disk. For at least 30% of the sources, narrower features are seen as well, which can be ascribed to crystalline silicates such as forsterite, Mg$_2$SiO$_4$ (76, 79). The shape and strength of the silicate features relative to the continuum are a measure of grain size: most T Tauri disks show evidence for grain growth from 0.1 to a few micrometers. Even larger sizes, up to a few centimeters, can be inferred from the spectral slope at millimeter and centimeter wavelengths, which probes the bulk of the grains in the outer disk (80). In combination with the shape of the spectral energy distribution, evidence for grain settling toward the midplane can be found. The presence of crystalline silicates may be an indication of significant radial and vertical mixing (81). Both grain growth and settling affect the chemistry in disks: larger grains have much smaller absorption cross sections for UV radiation and smaller surface areas for molecule formation (keeping the total mass in grains fixed).

**PAHs.** PAHs are detected in the spectra of at least 50% of Herbig Ae stars with disks through their characteristic infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.2, 12.8, ..., μm (82). For T Tauri stars, the features are weaker and more difficult to see on top of the strong continuum, but at least 8% show the 11.2-μm PAH band. Ground-based long-slit spectroscopy and narrow-band imaging at subarcsec resolution have demonstrated that the PAH emission comes from a region of radius 10–100 AU for at least some disks (83, 84). PAHs are excited by optical and UV radiation, so they are observed much further out in the disk than the silicates. Where detected, the inferred PAH abundance is typically 10$^{-7}$, indicating that a few percent of the carbon is in PAHs with 50–100 carbon atoms. PAHs are important in the chemistry for at least three reasons: as absorbers of UV radiation providing significant extinction at the shortest wavelengths, as a heating agent of the gas, and as potential sites of H$_2$ formation when classical grains have grown to large sizes.

**Protoplanetary Disks: Chemistry. Overall structure.** The basic chemical structure of a disk consists of three layers: the photon-dominated region (PDR), the warm molecular layer, and the cold midplane with heavy freeze-out (7, 85, 86) (Fig. 4). In the PDR layer, molecules are photodissociated and atoms ionized by the intense UV radiation from the central star. At intermediate heights, the dust temperatures are still high enough (>20 K) to prevent CO freeze-out, and the UV radiation is somewhat attenuated but still large enough to drive an active ion-molecule chemistry. In the midplane, the temperatures fall below the freeze-out temperature of CO. Thus, most of the active chemistry occurs in the intermediate warm molecular layer.

In the inner disk (∼50 AU), the midplane temperature is high enough that ices evaporate back into the gas phase. Because the various ices have different sublimation temperatures, the radius at which they come off the grains is species-dependent. For example, in the standard disk model for our own solar nebula, the CO “snow line” appears at ∼20 AU, whereas the H$_2$O “snow line” is at ∼5 AU, near the orbit of Jupiter.

Once all ices have evaporated in the inner disk, the chemistry becomes similar to the “hot core” chemistry and complex molecules can form. The main differences with protostellar envelopes are the much higher densities (>10$^{10}$ cm$^{-3}$) and temperatures (up to a few thousand kelvins) and the intense UV and x-ray radiation. Thus, in the densest regions, three-body reactions start to become important and the chemistry approaches that found in thermodynamic equilibrium in a gas of cosmic composition, including large abundances of C$_2$H$_2$ and HCN (87, 88), consistent with the observations toward IRS 46 described above (Fig. 6).

**Importance of UV radiation.** At 100 AU, the UV radiation from a T Tauri star is enhanced compared with the local interstellar radiation field by up to a factor of 300–1,000 (89), whereas that from a Herbig Ae star can be as large as 10$^3$. At the outermost radii, the interstellar field dominates. Because the stellar radiation impinges on the disk at a shallow angle, anisotropic scattering needs to be taken into account to calculate its penetration depth (86).

The chemistry in the surface layers resembles that of traditional PDRs at the edges of dense clouds studied extensively over the past two decades but with some important differences (90). First, the spectrum of a typical 10,000-K Herbig Ae star has orders of magnitude fewer photons than the standard interstellar radiation field in the critical 912–1,100 Å region where H$_2$ and CO are photodissociated and C is photoionized. This difference is even more extreme for a 4,000-K T Tauri star, unless it has excess UV emission above the stellar photosphere. Thus, the wavelength dependence of the cross sections needs to be taken into account (91), and the regions where hydrogen and carbon are transformed from atomic to molecular form (H → H$_2$ and C$^+$ → C → CO) are shifted closer to edge of the disk than in a traditional PDR.

Second, specific resonance lines like Lyman α can dominate the stellar spectra (89). Some molecules, like H$_2$O, OH, and HCN, can readily be photodissociated by Lyman α, but others, such as H$_3$, CO, CN, and N$_2$, cannot (90, 92). Third, the grain sizes can be much larger than those found in molecular clouds resulting in much smaller UV extinction cross sections. For molecules that are not self-shielding (i.e., all species except H$_2$, CO, and C), this implies that the PDR and warm layers shift deeper into the disk. Fourth, the gas/dust mass ratio can differ significantly from the interstellar value of 100. Fifth, ices may be mixed up from the midplane into the warm layer and be evaporated or photodesorbed. The presence of enhanced gaseous H$_2$O can modify the PDR chemistry, in particular the CN/HCN ratio (59). X-rays and cosmic rays also affect the chemistry of disks, with processes similar to those discussed for protostellar envelopes. They are particularly important in the high-density regions, where the UV photons cannot penetrate. Finally, the gas temperature may be significantly higher than the dust temperature in the surface layers, affecting both the chemistry and excitation (93–95).

**Conclusions**

Through combined submillimeter and infrared spectroscopy, an inventory of both the gas and the solid-state material associated with solar-mass protostars has been obtained. Systematic variations in the gas-phase and ice abundances occur as the system evolves from the precollapse stage to the phase where the young star emerges from its envelope. Diagnostic species of each of these stages can be identified; solid-state line profiles are particularly powerful probes of heating, gas–solid interactions, and other processes like grain growth. The chemistry is dominated by heavy freeze-out in the coldest phases and evaporation when the protostar heats up its surroundings, with the size of the freeze-out zone decreasing with time. The evaporation of CO-rich ice around 20–30 K and of H$_2$O-rich ice around 90–100 K control the chemistry of many other species. The Herschel Space Observatory, to be launched in 2008, will provide a unique opportunity to observe gaseous H$_2$O with the same level of detail as currently possible for CO.

Chemical studies of disks are just starting and are largely limited to simple molecules in the outer disk because of poor spatial resolution and sensitivity. Edge-on disks offer a unique opportunity to obtain a first glimpse of the hot inner disk chemistry. UV radiation from the central star dominates the chemistry of the disk surface layers.

Despite the recent progress, there are many unanswered questions. In particular, what is the origin of the complex...
species like H₂O and CH₃OH proceed under interstellar conditions? What is the role of organics in hot cores: are they formed in ices or are they second generation products of hot core chemistry? How does the chemistry of the inner disk evolve? Future submillimeter- and infrared facilities, in particular the Atacama Large Millimeter Array (ALMA) and the James Webb Space Telescope (JWST), will be able to address these and other questions in an unprecedented way and will be able to zoom in with orders-of-magnitude-increased sensitivity and spatial resolution on the chemistry in planet-forming zones.

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