# Astrochemistry and Star Formation: Successes and Challenges

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### Abstract

*The study of star formation has been helped immeasurably by the observation and analysis of molecules in various stages of the evolutionary process. Interpretation of molecular spectra reveals current physical conditions while an understanding of the chemical processes that form and destroy these molecules tells us much about both the present and the history of the sources. The use of chemistry to aid in our understanding of star formation will become increasingly powerful as a deeper comprehension of the exotic chemical processes occurring in such regions on interstellar dust particles becomes available.*

## 1 Introduction: The Science of Astrochemistry

Astrochemistry is the study of molecules in sources other than the earth. Since molecules exist in observable abundances in regions as close as the solar atmosphere and as far as the early universe, the field is a large one. Its interdisciplinary nature is revealed by the fact that astronomers, chemists, and physicists all contribute to progress. Among the important goals of this field are

- to probe the chemistry of exotic regions,
- to understand the extent of molecular complexity throughout the universe,
- to understand current and past physical conditions in different types of sources, both interstellar and circumstellar, galactic and extra-galactic, and in the early universe.

The first two goals are of great interest to chemists, and even to astrobiologists, while the third goal is clearly the province of astronomers, who use molecules as

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probes of physical conditions. Molecules have unique values as probes because (i) their spectra are so rich and diverse that they can be used to understand the details of their surroundings and even heterogeneities in these details, and (ii) chemical processes that both form and destroy molecules yield strong constraints on the history and lifetimes of the sources. Among the most important dynamical events probed by molecules and chemistry is star formation, a subject of this review.

Astrochemists can be divided into several classes depending on their field of inquiry and the tools at their disposal. Some are mainly observers who analyze molecular spectra from space with the help of detailed radiative transfer and collisional excitation codes, others are laboratory scientists or theoreticians who study relevant spectra and rate processes in the laboratory and by quantum mechanical calculations, and still others are modellers who simulate the chemistry occurring in assorted sources and predict abundances of molecules as functions of time and physical conditions. It is the modelers who are at the core of the field, since it is they who compare calculated and observational results to deduce details of the present and perhaps the past of the source.

Chemical models can be subdivided into those that are purely gas-phase and those that include the dust particles in some active manner (Herbst 2005a). Dust particles are important to chemistry for a variety of reasons; most crucially they provide a surface on which chemical reactions can occur. Taking account of this surface chemistry is extraordinarily difficult, however, and most modelers either use gas-phase codes or consider only the adsorption and desorption of particles onto and from grain surfaces without a detailed treatment of the surface chemistry. In addition to a classification of models by the type of chemistry, there is an additional classification by the manner in which time dependence is handled. Essentially there are three types of solutions to the chemical equations: steady-state solutions, in which there is no time dependence (Le Petit et al. 2004); pseudo-time-dependent solutions, in which the chemistry occurs with constant physical conditions (Hasegawa et al. 1992); and fully time-dependent solutions, in which both chemical and physical changes occur simultaneously (Aikawa et al. 2005). Finally, there is a third criterion: whether one considers homogeneous (even if time-dependent) physical conditions or one considers heterogeneous ones (Roberts et al. 2004). For example, one can consider a cold core inside a dense interstellar cloud as a homogeneous entity without changes in physical conditions, but in many situations it is more accurate to consider a heterogeneous entity that is collapsing, albeit slowly (Aikawa et al. 2005).

In trying to understand the chemistry of assorted interstellar and circumstellar objects and what it is telling us, astrochemists can study the concentrations of the many molecules that have been detected via a variety of spectroscopic techniques, both high-resolution and low-resolution, and in various regions of the electromagnetic spectrum. Over 130 different molecular species have been detected by the methods of high-resolution spectroscopy, ranging from the simplest and most abundant molecule – molecular hydrogen ($H_2$) – to a thirteen-atom species (see http://astrochemistry.net/). A convincing detection in space requires a close correlation between laboratory and observational results. Visible and ultra-violet spectroscopy can be used to study simple molecules in diffuse clouds with stars as the background sources (André et al. 2004). In denser clouds, there is sufficient dust so that visible and ultra-violet radiation does not penetrate, and longer wavelengths must be used. Infrared spectroscopy yields information on the vibrations of molecules, and is a workhorse technique in the laboratory, but infrared astronomy is often difficult from the ground, and only one satellite capable of high-resolution spectroscopy has been put into space in the last decade – the European ISO (Infrared Space Observatory; see, e.g., Whittet et al. 1996). Millimeter-wave spectroscopy yields information on the rotations of polar molecules, and can be done from the ground with radio telescopes. (There is sufficient $H_2$ that it can be detected via quadrupolar-allowed lines.) Indeed, ground-based measurements at radio wavelengths as short as 1/3 mm have been made at high desert sites (Comito et al. 2005). At still shorter wavelengths, non-ground-based telescopes are needed, and the German-American SOFIA airborne telescope and the ESA/NASA Herschel Space Observatory will soon be operational in what is known as the far infrared. Contour maps of individual rotational transitions of molecules are often made and, when combined with continuum maps of dust emission, yield detailed information about a source (Caselli et al. 2002).

Without discussing all of the interstellar molecules detected in loving detail, one can still mention a few salient features about them. First, all molecules in dense sources are trace constituents of the gas when compared with $H_2$; the second most abundant molecule – carbon monoxide (CO) – possesses at most an abundance of $10^{-4}$ with respect to $H_2$. Indeed, it is common to refer the abundances of molecules to either that of $H_2$ or that of the total hydrogen density, $n_{\mathrm{H}}$, defined as the sum of the density of atomic hydrogen and twice that of $H_2$. Even in cold diffuse clouds (Le Petit et al. 2004), there can be as much $H_2$ as atomic hydrogen. Second, most molecules are organic in nature; i.e., they are carbon-containing. This fact also holds on earth, and is probably due to the special reactivity of the carbon atom. Thirdly, there is no single source in which all of the molecules are found. Chemical concentrations are, of course, dependent on physical conditions, so that one would not expect different types of sources to have the same molecular abundances. There is a pattern to the abundances in dense interstellar sources that turns out to be critical to explaining their history: cold regions tend to have what are known as unsaturated, or hydrogen-poor species (Smith et al. 2004), whereas sources near to star-forming regions tend to have saturated, or hydrogen-rich species (Charnley et al. 1992). An example of the former is the largest interstellar molecule detected – $HC_{11}N$ – while an example of the latter is the common terrestrial molecule dimethyl ether ($CH_3OCH_3$). Fourthly, a large percentage of the molecules detected in the interstellar medium, especially the cold interstellar medium, are quite unusual by terrestrial standards even if they can be synthesized under unusual conditions such as pertain in gas discharges. One very interesting species, detected in infrared absorption from the ground, is the simplest polyatomic molecule: the molecular ion $H_3^+$ (Geballe & Oka 1996; McCall et al. 1998). Indeed, there is more controversy about some of the larger and more terrestrial-like organic molecules than about the exotic species. Particularly acute is the controversy about whether the simplest essential amino acid – glycine ($NH_2CH_2COOH$) – has been detected in a star-forming region (Kuan et al. 2003; Snyder et al. 2005).

Spectroscopy can also be used to study the chemical nature of dust particles. Broad features, mainly in the infra-red, indicate that there are a variety of general types of such particles (Whittet 2003). Emission features excited by photons from nearby stars indicate the existence of very tiny carbonaceous grains ($\leq 10$ nm), most often considered to be large individual molecules, known as polycyclic aromatic hydrocarbons (PAH's) consisting of arrays of bonded hexagons of carbon atoms (Allamandola et al. 1989). Other absorption and emission features indicate the existence of silicate grains, mostly amorphous, with a size distribution ranging from 10 nm to 10 $\mu$m (Li & Draine 2001). Another feature, a bump in the so-called UV extinction curve, is interpreted as being caused by a population of carbonaceous grains, possibly amorphous in nature. Crystalline silicate grains are also observed in space (with narrower spectral features) although mainly in circumstellar regions. The crystalline to amorphous conversion, which must occur as grains leave circumstellar regions where they are produced, remains poorly understood. Finally, absorption spectra through cold dense clouds show the existence of substantial mantles of ices, mainly water, carbon monoxide, and carbon dioxide, surrounding the cores of dust particles (d'Hendecourt & Dartois 2001). The mantles are thought to arise both by surface chemistry and by accretion from the gas (Hasegawa et al. 1992; Herbst 2005a).

## 2 The Dense Interstellar Medium and the Stages of Star Formation

Star formation occurs inside dense interstellar clouds, in which the gas phase is mainly molecular in nature. These objects are large and inhomogeneous, with relatively diffuse gas taking up much of the volume. Denser objects, known as cores, both form and dissipate. There is enough dust to make optical observations through the denser portions of these large objects impossible. The largest collections of gas and dust are also known as giant molecular clouds, the closest of which is the well-known Orion Molecular Cloud. Other, more loosely bound clumps of dense material, such as the Taurus Cloud, are better known as assemblies. It is the relatively dense gas in both types of objects that collapses to form stars, either singly or multiply. What starts the collapse is a matter of dispute, although the mechanism of nearby supernova action has gained some credibility.

For simplicity, let us consider the formation of a single low-mass star. The evolutionary stages mentioned here will be discussed in greater detail later in the text once the basic chemical processes have been considered. The process can be thought to start with a cold and dense portion of the cloud, known typically as a cold quiescent core, which possesses a gas density $n_{\rm H}$ of $2 \times 10^4$ cm$^{-3}$ and a kinetic temperature of 10 K. The best-studied such cores contain upwards of 50 molecules and show at most a little evidence of collapse. The polyatomic molecules tend to be hydrogen-poor. In other cores, some process, perhaps a nearby supernova burst, starts a gravitational contraction, which proceeds through a variety of stages. In the first stage of evolution, known as a pre-stellar core, the collapse remains largely isothermal, and a core within a core, at the center of the structure, begins to build up. Eventually the center reaches a density of $10^7$ cm$^{-3}$ or even higher. Observations show that some molecules heavier than helium tend to be depleted from the gas and onto the surfaces of dust particles in the densest regions (Tafalla et al. 2004).

As the central condensation becomes opaque, further collapse becomes adiabatic and the object, now known as a protostar, heats up (Stahler & Palla 2004). As the temperature rises, the spectral energy distribution shifts from the far-infrared to the infrared and visible. In addition to collapse, violent bipolar outflows of material occur, leading to shock waves. Even away from these violent events, the nearby portion of the envelope surrounding the center begins to warm up to temperatures of perhaps 100–200 K. Both shocked and more gently heated portions of the envelope show a chemistry rich in hydrogen-rich molecules such as methanol ($CH_3OH$) and more complex species. The more gently heated portion constitutes what is now known as a "hot corino" (Bottinelli et al. 2004; Ceccarelli 2006). The outer portion, on the other hand, remains at physical conditions similar to those of pre-stellar cores. Eventually, a disk of very dense gas and dust is formed in the equatorial plane perpendicular to the outflow, and becomes known as a protoplanetary disk as the protostar becomes a star. Such disks also possess gas-phase molecules (Thi et al. 2004), although a large portion of the gas-phase heavier than hydrogen and helium condenses onto the dust particles, which themselves agglomerate to form larger particles. Some unknown percentage of these protoplanetary disks eventually become systems of planets.

Although the above scenario seems reasonably well understood for low-mass stars such as the sun, the case of high-mass stars is not as well comprehended, mainly because the stages occur more quickly. There is considerable debate, for example, as to whether or not protoplanetary disks occur. Two well-known evolutionary stages are labelled "hot cores" and HII regions, the former containing large abundances of hydrogen-rich complex molecules as in the hot corinos of low-mass star formation (Friedel et al. 2004), and the latter containing no molecules at all since the gas surrounding the full-fledged hot star is ionized into a high-temperature plasma. Molecules may not exist in HII regions, but they do exist on their borders, in warm neutral gas known as photon-dominated regions (PDR's). The best-known PDR of this type is the Orion bar region, which abuts the Orion Nebula, a well-known HII region.

## 3 Interstellar Chemistry

Since the observation of polyatomic molecules in dense interstellar clouds more than thirty years ago, much work has been undertaken to elucidate the processes and pathways of the chemistry of molecules in these sources (Herbst 2005a). The chemistry is now known to occur both in the gas phase, even at temperatures as low as the 10 K values that pertain to cold quiescent and pre-stellar cores, and on the surfaces of the dust particles. The understanding of gas-phase chemistry is sufficiently well advanced to permit the construction of large gas-phase models, in which thousands of chemical reactions that form and destroy molecules are used to calculate molecular abundances as functions of time for assorted physical conditions (Le Teuff et al. 2000; Smith et al. 2004; see also the websites http://www.physics.ohio-state.edu/~ eric/ and http://www.rate99.co.uk/ for the osu.2003 and RATE99 networks, respectively). At present, it is even possible to estimate the uncertainties in the calculated abundances based on random uncertainties in the rate coefficients of the reactions utilized (Wakelam et al. 2005). So far, the determination of uncertainties has not been attempted for gas-grain models, in which grain-surface chemistry and processes leading to both the depletion of the gas onto the dust particles and the desorption of species from grains back to the gas are included (Hasegawa et al. 1992; Ruffle & Herbst 2000, 2001). Unfortunately, the chemistry that occurs on grain surfaces and physical gas-grain interactions are still poorly understood, and represent perhaps the major challenge mentioned in the title of this paper.

Other challenges remaining to be solved by astrochemists include a better integration of dynamics and chemistry, the simulation of actual spectral lines rather than the simple calculation of molecular abundances, a proper account of small-scale physical structure, and a better understanding of the past and future of interstellar objects. It is clear that the standard techniques of astrochemistry regarding the formation of molecules in dense clouds are insufficient. For example, the gas-phase chemistry of cold quiescent cores is typically studied by assuming a homogeneous object with time-independent physical conditions and starting materials that are largely atomic except for molecular hydrogen, which is assumed to have already been converted to its molecular state. Although, as will be discussed below, such a simple scenario leads to semi-quantitative agreement with observed gas-phase abundances, it does not produce 100% agreement (Smith et al. 2004). A more likely scenario is a rather complex set of physical changes occurring as the chemistry evolves. Unfortunately, the hydrodynamics of core formation from more diffuse gas is not sufficiently well understood to produce chemical models with a unique picture of collapse. Moreover, once the collapse to form a star commences, the challenges are even greater because the roles of dynamical change and heterogeneity assume significantly more importance.

Although the gas-phase chemistry occurring in cold portion of the interstellar medium is better understood than surface chemistry, let us start with the latter since it where the most important of all reactions takes place: the formation of molecular hydrogen (Hollenbach & Salpeter 1971). Molecular hydrogen cannot form efficiently in the gas at low temperatures from collisions of two neutral hydrogen atoms, because virtually all such collisions are just elastic in nature. There is a small possibility that, during the course of a collision, enough energy is emitted as electromagnetic radiation for the so-called collision complex to stabilize itself. But this possibility is too small to convert a significant portion of the atomic gas into molecular gas. In the early universe, on the other hand, molecular hydrogen can be formed by ionic processes, such as (Lepp et al. 2002)

$$\mathrm{H} + \mathrm{e}^- \longrightarrow \mathrm{H}^- + \mathrm{h}\nu, \tag{1}$$

$$\mathrm{H}^- + \mathrm{H} \longrightarrow \mathrm{H}_2 + \mathrm{e}^-. \tag{2}$$

## 3.1 Surface chemistry: a remaining challenge

The dominant process for the formation of $H_2$ in the cold interstellar medium undoubtedly occurs on the surfaces of dust particles, although the exact mechanism is still in some doubt (Herbst 2005b). The most likely scenario is the following. Two hydrogen atoms land on a cold dust particle and stick to it with a high probability. Unlike the situation when two H atoms collide with each other, the collision with a dust particle involves a thermodynamic entity with many modes of energy transfer to remove the kinetic energy of the striking H atom and raise the temperature of the grain. Sticking is followed by thermalization of the H atoms to the temperature of the dust particle and weak binding, with a typical potential well of five hundred K (0.05 eV), known as physisorption. Stronger bonds between adsorbate and surface ($\sim 1 - 2$ eV), known as chemisorption, can also occur, but there are typically barriers in the potential energy pathway so that the formation of strong bonds is favored by higher temperatures, such as occur in photon-dominated regions. Whether weak or strong, the binding does not occur uniformly along even a very smooth surface; rather, it occurs preferentially in potential wells separated by barriers (Cuppen & Herbst 2005). The weakly bound H atoms are able to move about the surface by either classical random-walk diffusion over the potential barriers or by quantum-mechanical tunneling under them. The atoms eventually find one another by landing in the same potential well, a mechanism known as the Langmuir-Hinshelwood process, after its originators. To form a stable $H_2$ molecule in the collision, the grain acts as a third-body and removes energy from the unstable H-H system. Finally, the molecule is ejected during the process of formation or, more likely, eventually evaporates. Note that for surface species heavier than $H_2$, evaporation is much less likely given greater binding energies. If the temperature is so low that H atoms cannot move, then another mechanism, known as the Eley-Rideal process, can come into play: here, a gas-phase H atom strikes a stationary surface H atom by landing directly atop it. A variant of this mechanism is known as the "hot atom" process; here the striking gas-phase atom lands near enough to a stationary adsorbate so that it can reach it before thermalization.

Experiments to understand the process of molecular hydrogen formation on surfaces that are good analogues of interstellar material have been undertaken by several different groups (Vidali et al. 2006; Hornekaer et al. 2006). The experiments use a technique known as temperature-programmed desorption (TPD), which involves the deposition ("irradiation") of atoms at a temperature so low that no motion on the surface occurs, followed by a gradual heating (Kolasinski 2002). One monitors the amount of gas-phase material coming off as a function of temperature. From the shape of this curve and its dependence on the time of irradiation, one is supposed to determine the mechanism of molecule formation as well as the energy barrier between binding sites for atomic H on a surface and the energy needed to desorb both H and $H_2$ (Katz et al. 1999). One of the two groups studying $H_2$ formation has pursued such as experiment on olivine, amorphous carbon, and amorphous low-density and high-density ice, with the finding that the Langmuir-Hinshelwood mechanism occurs via classical diffusion as the temperature is raised (Vidali et al. 2006). The other group, who studied the process on a type of amorphous ice only, finds that reaction occurs at the lowest temperature of the experiment, before the TPD is even begun, suggesting a rapid, tunneling-induced process (Hornaeker et al. 2003, 2006). So, at present, although experiments have shown that low-temperature surface formation of $H_2$ does indeed occur, the actual process may be a rather complex one that depends very strongly on fine details of the surface.

In addition to the formation of molecular hydrogen, other reactive processes are thought to occur on cold interstellar grain surfaces. Since atomic hydrogen is reactive, is abundant even in dense clouds and diffuses rapidly on surfaces due to its lightness and low binding energy, it is the most important surface reactant. In addition to reaction with itself, it can react with a variety of heavier atoms and reactive molecules ("radicals") to produce hydrogen-rich species (Hiraoka et al. 2002). For example, suppose an oxygen atom lands on a surface. Although it is bound sufficiently strongly to not move much, it can collide with a rapidly diffusing H atom to produce the radical OH, which can also react with atomic hydrogen, this time to form water. Water can add no further H atoms since it is totally saturated. The formation of water turns out to be very efficient (Ruffle & Herbst 2000), and it is not surprising that many monolayers of water ice have been observed to exist on cold grains in dense regions (Whittet 2003). In a similar manner, nitrogen atoms landing on grains can be converted into ammonia ($NH_3$) and carbon atoms converted into methane ($CH_4$). It has also been shown that CO, which can be produced copiously in the gas, can be partially converted into methanol via the sequence of reactions with H atoms (Hidaka et al. 2004):

$$\mathrm{CO} \xrightarrow{K_1} \mathrm{HCO} \xrightarrow{K_2} \mathrm{H_2CO} \xrightarrow{K_3} \mathrm{CH_3O}, \mathrm{CH_2OH} \xrightarrow{K_4} \mathrm{CH_3OH}. \tag{3}$$

The rate coefficients $K$ are discussed below. The first and third reactions of the sequence even involve what is known as " activation energy", a potential barrier to reaction common in chemical reactions involving neutral reactants that are not radicals (see below). The species CO and $H_2CO$ (formaldehyde) are rather stable and react slowly with H atoms because of potential barriers in the range of 1000–2000 K. Nevertheless, potential barriers for surface reactions are less debilitating than for gas-phase reactions because the reaction partners get many chances to undergo successful reactions while stuck near each other in a binding site. In any case, methanol ice has been observed via infrared observations (Pontoppidan et al. 2004). The situation regarding surface reactions involving two heavy species is far from clear because the diffusion of these molecules may not be sufficiently rapid to allow reaction at low temperatures, especially if there is in addition a chemical barrier to reaction. For example, the possible reaction

$$\mathrm{CO} + \mathrm{O} \longrightarrow \mathrm{CO_2} \tag{4}$$

may be the prime mechanism for the synthesis of large amounts of detected carbon dioxide ice, but if so, the reaction would have to occur despite a significant barrier.

In gas-grain models (Hasegawa et al. 1992; Ruffle & Herbst 2000, 2001), large numbers of surface reactions and gas-phase reactions are included along with adsorption and desorption processes. Although it is facile to write down rate expressions for the gas-phase reactions, it is less so for surface processes. Indeed, there is an additional challenge concerning interstellar surface chemistry: unlike the laboratory experiments, the interstellar reactions take place on small particles. This environment affects the rate of reaction in a subtle manner. When large numbers of reactive species exist on a surface, the rate of chemical reaction can be treated in an analogous manner to gas-phase reactions. If we consider the surface reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$, its rate in the limit of large numbers of reactants can be expressed by the equation

$$\frac{dN(\mathrm{AB})}{dt} = K_{\mathrm{A-B}} N(\mathrm{A})\mathrm{N}(\mathrm{B}), \tag{5}$$

where $N(\mathrm{I})$ stands for the number of species I on an average grain, and $K_{\mathrm{A-B}}$, the so-called rate coefficient, is simply the sum of the diffusion rates of A and B over a whole grain. The units used here are those of Caselli et al. (1998); often, surface abundances are instead expressed with respect to gas-phase molecular hydrogen (Hasegawa et al. 1992). The diffusion rate of species A for example is

$$K_{\mathrm{A}} = (\nu/N)\exp(-E_{\mathrm{diff}}(A)/T), \tag{6}$$

where $\nu$ is a frequency of vibration between A and the surface (typically $10^{12-13}$ $\mathrm{s}^{-1}$), $N$ is the number of binding sites per grain, $E_{\mathrm{diff}}(A)$ is the barrier against diffusion for species A in K, and $T$ is the temperature. For a reaction with activation energy, one must multiply the expression for the rate coefficient by a term that takes into account tunneling under this barrier or hopping over it (Hasegawa et al. 1992); the hopping case is discussed in the section on cold gas-phase reactions below. In the limit of small numbers of reactants, however, the rate law is unsuitable because the number of a given species must be treated as both discrete and capable of large fluctuations from one grain to another. To treat these manifestations, one must use a stochastic treatment of kinetics. In general, the rate equation approach yields too large a value for the formation rate of $H_2$ when the average number of hydrogen atoms per grain is unity or less.

The simplest stochastic treatment involves the so-called "master" equation, in which one replaces the average number of species on a grain with the probability $P(i)$ that a certain number of species is present (Biham et al. 2001; Green et al. 2001). The master equation for the formation of species AB from A and B refers to a series of differential equations containing the time derivatives $\frac{dP_{AB}(i)}{dt}$,with $i = 0, 1, 2, 3.....$ on the left-hand side, and terms for accretion, desorption, and reaction on the right-hand side involving $P_A(j)$ and $P_B(k)$. Integration of the coupled equations then yields values for the assorted probabilities, which can be used to determine average abundances via the equation

$$\langle N(AB) \rangle = \sum_{i=0}^{\infty} i \times P_{AB}(i). \tag{7}$$

Although the formal upper limit of the sum is set to $\infty$, the method works well only when it converges for small upper limits. Indeed, if large upper limits are needed, then the rate equation approach is probably valid anyway.

In using one chemical reaction as an example, however, we have simplified the procedure excessively, since when many reactions are occurring on a surface, the probabilities are correlated: one, for example, must compute the joint probability of finding $i$ molecules of species X, $j$ molecules of species Y, etc. The convergence problems become severe as the number of reactive species increases. So far, the master equation method has not been used for large gas-grain models that include many surface reactions, but approximation methods are improving and the method may eventually be suitable (Stantcheva & Herbst 2004; Lipshtat & Biham 2004). An alternative stochastic procedure for both surface and gas-phase reactions has been utilized by Charnley & Rodgers (2006).

The rate equation and master equation treatments discussed so far relate to "smooth" surfaces, on which there is only one type of binding site for a given adsorbate. In reality, interstellar grain surfaces are unlikely to be smooth in this sense, but rather to be rough; i.e., consisting of many different types of environments for binding. To handle such a situation, a stochastic treatment more complex than the master equation approach is preferable. The approach we have utilized for $H_2$ formation is known as the continuous-time random walk method (Chang et al. 2005; Cuppen & Herbst 2005). Here, one divides up a grain into lattice sites, and follows accretion onto the sites, diffusion from site to site, and desorption from the sites by suitable calling of random numbers. One can consider a finite number of different binding sites or even a continuous distribution of them. The net result is that the efficiency of $H_2$ formation is high over a much wider temeperature range than on smooth grains. We are currently collaborating with the experimental group of Vidali to see if this theoretical method agrees with laboratory TPD experiments of $H_2$ formation on rough olivine. We are also working on how the Monte Carlo treatment of rough surfaces can be used in a large gas-grain model.

## 3.2 Cold gas-phase chemistry: a success

In analogy with the surface processes discussed in the last section, the rate of gas-phase processes can be written in terms of concentrations and a rate coefficient. Suppose that the gaseous reactants A and B react to form species C and D. The rate of formation of C (or D) is then given by the expression

$$\frac{dn(\mathrm{C})}{dt} = k_{\mathrm{A-B}}(T)n(\mathrm{A})n(\mathrm{B}), \tag{8}$$

where $k_{\mathrm{A-B}}$(T) is the rate coefficient (cm$^3$ s$^{-1}$), which is a function of temperature, and the symbol $n$ refers to concentration (cm$^{-3}$). In order for chemical reactions to occur in the gas at low temperatures, they must be exothermic and possess little or no activation energy barriers. The exothermicity criterion is more subtle than for surface reactions because most gas-phase reactions produce more than one product, and whether or not they are exothermic cannot be determined by inspection. Since most reactions in chemistry between neutral species do possess significant amounts of activation energy, they cannot occur rapidly at low temperatures even if exothermic. This assertion can be understood from the so-called Arrhenius formula for the reaction rate coefficient (Herbst 1996):

$$k = A(T)\exp{(-E_a/T)}, \tag{9}$$

where $E_a$ is the activation energy (K), and $A(T)$ is the so-called pre-exponential factor, which can be weakly temperature dependent. The simplest expression for $A(T)$ comes from collision theory, which relates it to the cross section $\sigma$ determined by long-range forces via the relation

$$A(T) = \langle \sigma \times v \rangle, \tag{10}$$

where $v$ is the relative collision speed and the average is over thermal distributions of translational energy and internal quantum numbers. For neutral reactants, which do not possess strong long-range forces, the simple assumption that collisions occur with a geometric cross section leads to a pre-exponential factor on the order of $\approx 10^{-11}$ cm$^3$ s$^{-1}$ at room temperature with a temperature dependence of $T^{1/2}$. A more complex picture is given by activated complex theory (ACT), a statistical picture in which the reactants are approximated to be in thermal equilibrium with a so-called transition state, which lies somewhere along the reaction potential, typically at a saddle point if it exists (the height of the least steep path over the mountain range, closely related to the activation energy; see Steinfeld et al. 1999).

If one puts into the Arrhenius equation even a rather small activation energy of 0.1 eV (1000 K), one can immediately see that at a temperature of 10 K, the value of $k$ is very low compared with $A(10K)$. Consequently, those reactions that do not have to surmount significant barriers are the only to be rapid at low temperatures. Years of research have shown that the following classes of reactions are most important (Herbst 2005a):

- (i) Ion-molecule
- (ii) radiative association
- (iii) dissociative recombination
- (iv) radical-radical
- (v) radical-stable.

Ion-molecule reactions involve collisions between one charged and one neutral atom or molecule. The strong long-range forces tend to lead to potential surfaces in which there is an intermediate well rather than a maximum, so that no activation energy is typically found for exothermic processes (Herbst 1996). For non-polar neutrals, the rate coefficient most often obeys the result of a very simple theory based on long-range forces. In the so-called Langevin theory, the rate constant $k_{\mathrm{i-m}}$ in cgs-esu units (cm$^3$ s$^{-1}$) is given by the equation

$$k_{\mathrm{i-m}} = A(T) = 2\pi e \sqrt{\alpha/\mu}, \tag{11}$$

where $e$ is the electronic charge, $\alpha$ is the dipole polarizability of the neutral reactant, and $\mu$ is the reduced mass. In these units, the rate constant is typically on the order of $10^{-9}$ cm$^3$ s$^{-1}$, a number that possesses no temperature dependence at all. For polar neutral reactants, the physics of long-range attraction becomes more complex and non-central since the charge-dipolar force now depends on the orientation of the reactants. Nevertheless, experiments and theory indicate that the rate coefficients tend to get larger as temperature is reduced, with a typical dependence on temperature of $T^{-1/2}$ (Herbst & Leung 1986). Thus, at 10 K, the rate coefficient can be approximately 5–6 times larger than at room temperature (Rowe & Rebrion 1991).

Given their large rate coefficients, ion-molecule reactions are dominant in low-temperature chemistry if there is a source of ions. The ubiquitous source in the universe consists of cosmic rays, although there are additional local sources such as X-rays. The rate of ionization $\zeta$ is typically expressed as an inverse time for the ionization of hydrogen atoms, and results based both on measurements of the local cosmic ray flux in the solar system as well as isolated aspects of the chemistry of diffuse and dense interstellar clouds (see, e.g., Hartquist et al. 1978) lead to values of $\zeta$ in the wide range $10^{-15}-10^{-17}\ \mathrm{s}^{-1}$, with the higher value probably more pertinent to diffuse material, which low-energy cosmic rays are able to penetrate (McCall et al. 1998; Le Petit et al. 2004), and the lower value more pertinent to dense clouds (Herbst & Klemperer 1973).

If an ion-molecule reaction is endothermic or possesses an activation energy barrier, it is useful to consider radiative association processes, in which the ion and neutral combine to form a collision complex that stabilizes itself by the emission of radiation. This process was discussed previously for the case of $H_2$ formation in the gas, a case in which it is totally inefficient. But, as the collision complex increases in size, it lives for longer periods of time, increasing the probability of stabilization. Although simple statistical theories of the rate constants of these processes are often available, there are few experimental measurements to test the theories (Bates & Herbst 1988). One reasonably well-studied process is the reaction

$$\mathrm{CH_3^+ + H_2 \longrightarrow CH_5^+ + h\nu}, \tag{12}$$

although both experiments and theories show widely varying values for the rate coefficient, which is significantly smaller than the Langevin value (see, e.g., Gerlich & Horning 1992).

As ion-molecule and radiative association reactions build larger positive ions, dissociation recombination reactions with electrons convert the ions into somewhat smaller neutral species. These reactions have been known to be quite rapid for some time, and their rate coefficients possess an inverse temperature dependence that typically goes as the inverse square root of the temperature. Until recently, however, the branching ratios of the assorted neutral products had not been measured unambiguously. In the last decade, the use of storage rings to study this class of reactions has resulted in an explosion of knowledge concerning the neutral products (Geppert et al. 2005; Larsson 2005; Mitchell et al. 2005). In these experiments, positive molecular ions and electrons are directed into a ring at high translational energies in the laboratory frame but low relative collision energies. Neutralization leads to products that leave the ring at high energy. Detection of the neutral products is made by particle detectors coupled with partially transmissive filters to give a sense of how many individual species arrive for each mass detected.

As one example of a dissociative recombination reaction, consider the process

$$\mathrm{H_3O^+ + e^- \longrightarrow H_2O + H; OH + H_2; OH + 2H; O + H + H_2}, \tag{13}$$

where the four possible exothermic sets of products are shown. The dominant product appears to be the three-body channel OH + 2H, with the $H_2O$ + H channel only about 30% of the total (Jensen et al. 2000). In general, three-body channels have been found by storage ring experiments to be far more salient than had been thought. As an example, the dissociative recombination of $CH_5^+$ leads mainly to the methyl radical ($CH_3$) and two hydrogen atoms. Thus, these reactions not only produce normal species such as water and methane, but also radicals such as OH and $CH_3$.

Now we can combine the types of reactions discussed to show gas-phase interstellar syntheses of water, OH, methyl, and methane in dense interstellar clouds. The initial reaction is the cosmic ray ionization of molecular hydrogen, which produces in the main $H_2^+$:

$$\mathrm{H_2 + CRP \longrightarrow H_2^+ + e^- + CRP,} \tag{14}$$

where CRP stands for a cosmic ray proton. The $H_2^+$ ion reacts quickly with neutral $H_2$ to form the well-known interstellar ion $H_3^+$, a species with the structure of an equilateral triangle:

$$\mathrm{H_2^+ + H_2 \longrightarrow H_3^+ + H.} \tag{15}$$

This triatomic ion can react with a variety of heavy atoms. Let us follow what happens when reactions with the atoms O and C occur:

$$\mathrm{O + H_3^+ \longrightarrow OH^+ + H_2,} \tag{16}$$

$$\mathrm{OH^+ + H_2 \longrightarrow OH_2^+ + H,} \tag{17}$$

$$\mathrm{OH_2^+ + H_2 \longrightarrow H_3O^+ + H,} \tag{18}$$

$$\mathrm{C + H_3^+ \longrightarrow CH^+ + H_2,} \tag{19}$$

$$\mathrm{CH^+ + H_2 \longrightarrow CH_2^+ + H,} \tag{20}$$

$$\mathrm{CH_2^+ + H_2 \longrightarrow CH_3^+ + H,} \tag{21}$$

$$\mathrm{CH_3^+ + H_2 \longrightarrow CH_5^+ + h}\nu. \tag{22}$$

Following the formation of $H_3^+$, the simple ions $OH^+$ and $CH^+$ are produced. These quickly react several times with ubiquitous molecular hydrogen to form the more hydrogenated forms $H_3O^+$ and $CH_3^+$; the former is saturated with hydrogen and can only react with electrons to produce water and OH (see above), while the latter ion cannot react in a normal way with $H_2$ because the reaction to produce $CH_4^+$ + H is endothermic. The radiative association then occurs competitively to produce the saturated ion $CH_5^+$ which, as we have already seen, then reacts with electrons to form species such as methyl and methane ($CH_4$).

More complex species can then be produced by a variety of ion-molecule processes, one of which is an insertion reaction, in which a $C^+$ ion reacts with a hydrocarbon to form a more complex hydrocarbon while ejecting one or more hydrogen atoms. A well-known example is:

$$\mathrm{C^+ + C_2H_2 \longrightarrow C_3H^+ + H.} \tag{23}$$

The product ion can then add molecular hydrogen or react with electrons. Another class of synthetic reactions is known as a condensation; here a hydrocarbon ion and neutral react to form a more complex species; viz.,

$$\mathrm{C_2H_2^+ + C_2H_2 \longrightarrow C_4H_3^+ + H.} \tag{24}$$

In addition to reactions involving ions, there are classes of neutral-neutral reactions that are important even at low temperatures because, unlike most systems in this class of reactions, they do not possess activation energy barriers. The first class of such reactions is the better known and involves collisions between two radicals, which can be defined formally as molecules with an odd number of electrons so that their spins cannot all be paired (see the database http://kinetics.nist.gov/index.php). These molecules, which tend to lie in doublet electronic states, are unusually reactive. One can also regard many individual atoms as radicals, if one extends the definition to include all species with non-singlet ground electronic states, even if they contain a spin multiplicity different from two. Atom-radical reactions can be more important than radical-radical reactions in the interstellar medium, if they involve an abundant atom such as C or O, both of which have ground triplet states. As an example of a rapid atom-radical reaction, consider the process

$$\mathrm{O} + \mathrm{OH} \longrightarrow \mathrm{O}_2 + \mathrm{H}, \tag{25}$$

which produces interstellar molecular oxygen, a molecule that has proven difficult to detect. This reaction has been studied in a special jet known by the French acronym CRESU down to about 35 K, and is still quite rapid by the standards of neutral-neutral systems ($k \approx 2 \times 10^{-11}$ cm$^3$ s$^{-1}$) with a minimal temperature dependence, showing that there is no activation energy barrier (Sims 2006).

The final class of important reactions consists of neutral-neutral systems in which one of the reactants is an atom or radical and the other is a rather standard molecule in a ground singlet electronic state. Such systems were quite unusual until work with a CRESU apparatus over the last decade showed that they can play a prominent role in interstellar chemistry (Sims & Smith 1995; Sims 2006). In general, these reactions not only do not obey the Arrhenius equation since they have zero activation energy, but their pre-exponential factors tend to increase with decreasing temperature. Two critical interstellar reactions in this class, both involving acetylene as the standard reactant, are

$$\mathrm{CN} + \mathrm{C_2H_2} \longrightarrow \mathrm{HC_3N} + \mathrm{H} \tag{26}$$

and

$$\mathrm{C} + \mathrm{C_2H_2} \longrightarrow \mathrm{C_3H} + \mathrm{H}; \mathrm{C_3} + \mathrm{H_2}. \tag{27}$$

In the first reaction, the well-known interstellar molecule cyanoacetylene is formed, while in the latter the radical $C_3H$, which has two isomeric structures – a linear and a cyclic form – is produced. The evidence that there is an additional channel leading to $C_3$ is still ambiguous. Note that the second reaction produces more complex hydrocarbons from simpler ones, in the sense that the products possess more carbon atoms. This type of neutral-neutral reaction competes with a variety of ion-molecule processes discussed above to produce greater molecular complexity.

# 4 Networks and Models

In order to explain the abundances of molecules through approximately 10–15 atoms in size in various regions of the interstellar medium associated with star formation, it is necessary to follow the gas-phase chemistry of a significantly higher number of species, since only a small percentage of molecular ions thought to be important intermediates have been detected. For most species, there are a variety of reactions leading both to their formation and to their destruction. Current gas-phase networks used in the community contain about 4000 reactions, but only up to perhaps one-third of these have actually been measured in the laboratory or studied by assorted theoretical methods (see http://www.physics.ohio-state.edu/~ eric/ and http://www.rate99.co.uk/). Suppose, as an example, we consider the molecular ion $\mathrm{OH}^+$, mentioned above. Its so-called kinetic equation (or "rate law") is given by

$$\frac{dn(\mathrm{OH}^+)}{dt} = k_{16}n(\mathrm{O})n(\mathrm{H}_3^+) - k_{17}n(\mathrm{OH}^+)n(\mathrm{H}_2), \tag{28}$$

where there is both a gain and a loss term.

Solution of gas-phase chemical models consists of integrating the simultaneous kinetic equations as a function of time from given initial conditions, consisting of density, temperature, and atomic and molecular concentrations. A model in which the physical conditions are homogeneous is known as a a one-point model, while one in which slabs of material with different physical conditions are considered is known as a multi-point model. If, as mentioned in the Introduction, the physical conditions are independent of time, the model is known as a pseudo-time-dependent one, since only the chemical abundances change with time. If the integration is performed until no subsequent changes result, it is known as a steady-state calculation.

If a modeler wishes to consider gas-phase and grain-surface chemistry simultaneously, the simplest solution is to use rate equations for both types of chemistry (see above). For a gas-phase species A, the kinetic equation for its concentration would have additional terms on the right-hand side; these would contain accretion onto grains and desorption (via various mechanisms) from grains. For a surface species, the kinetic equation would have to contain formation and destruction terms via surface chemistry as well as the desorption and accretion terms. The rate of adsorption onto a grain surface for a gas-phase species A is given by the expression

$$\frac{dn(A)}{dt} = -k_{ads}n(\mathrm{A})n(gr), \tag{29}$$

where $n(\mathrm{A})$ is the gas-phase concentration and $n(gr)$, the grain concentration. The adsorption rate coefficient is

$$k_{ads}(cm^3s^{-1}) = f \times \sigma \times \langle v(A) \rangle, \tag{30}$$

where $\sigma$ is the geometrical cross section of the grain and $f$ is the sticking efficiency, which is close to unity for most species at low temperatures and falls off with increasing temperature. For a surface species A, the accretion rate law would have a positive sign. The rate of thermal desorption (evaporation) of a surface species B is given by the rate law

$$\frac{dN(\mathrm{B})}{dt} = -k_{des}N(\mathrm{B}), \tag{31}$$

where the rate coefficient is given the expression

$$k_{des}(s^{-1}) = \nu \exp(-E_{des}/T). \tag{32}$$

Here, the trial frequency $\nu(s^{-1})$ is a typical adsorbate-lattice frequency encountered earlier when diffusion was considered, while the energy of desorption (binding energy to the surface), $E_{des}$, is typically three times as great as the barrier against diffusion (Hasegawa et al. 1992). For cold sources, evaporation is only important for very light species such as hydrogen and helium, which possess very small energies of desorption. Unless these sources are younger than the time scale for accretion, there must be some non-thermal desorption mechanisms to maintain the gas-phase detected by radio observations. A variety of possible mechanisms have been suggested, but there is as yet no clear evidence in the laboratory for any of them. In our current gas-grain code (Garrod et al. 2006), we include mechanisms based on cosmic ray bombardment and on conversion of some of the excess energy gained by exothermic chemical reactions when greater than the surface binding energy of the product. The latter appears to be the far more efficient, if our estimation is correct. Experiments are planned.

## 5 Cold Starless Cores: Successes and Challenges

The best-known cold cores with little or no evidence for collapse are TMC-1 and L134N (Ohishi et al. 1992). The former is actually a set of probably 6 or more cores, with the best-studied known as TMC-1(CP) where the letters CP stand for "cyanopolyyne peak." Until recently, these were treated mainly by pseudo-time-dependent gas-phase model calculations with atomic initial abundances except for $H_2$, based on sets of elemental abundances with heavy elements depleted by various amounts from stellar values to account for the dust particles (see, e.g., Smith et al. 2004). The most commonly used set of abundances is known as the "low-metal" case, where some of the heavier elements are depleted by several orders of magnitude (Graedel et al. 1982; Leung et al. 1984). With standard homogeneous physical conditions ($n_{\rm H} = 2 \times 10^4$ cm$^{-3}$, $T$ = 10 K), the calculated abundances come closest to observation at times of $10^{5-6}$ yr, well before steady-state conditions set in ($10^{7-8}$ yr) and somewhat before the gas-phase is lost to the grains if accretion is included.

Although simplistic, these models get much of the observed chemistry correct and have had much predictive power for observers searching for new molecules in space. In particular, the models have had the following successes:

- prediction of the dominant observable molecular ions
- explanation of the many unusual neutral molecules present, including radicals and isomers (species with unusual structures corresponding to local but not global potential minima)
- prediction that as molecules grow in size, they become hydrogen-poor even though hydrogen is the dominant element by four orders of magnitude.
- reproduction of the severe deuterium isotopic fractionation.

The prediction of observable molecular ions stems from the basic ion-molecule chemistry, and has been more than verified by the many ions detected. The explanation of unusual radicals and isomers stems partially from the products of dissociative recombination reactions. We have already seen, for example, that the radicals OH and $CH_3$ are produced preferentially over the stable molecules water and methane. In addition, it is most likely that isomers are also produced in such processes, the best known of which is the recombination of the observed molecular ion $HCNH^+$ to produce both HCN and its isomer HNC:

$$\mathrm{HCNH^+ + e^- \longrightarrow HCN + H; HNC + H; CN + H + H.} \tag{33}$$

Isomers can also be produced via neutral-neutral reactions; the reaction between C and $C_2H_2$, mentioned above, is known to produce both linear and cyclic forms of the radical $C_3H$ (Kaiser et al. 1997).

The prediction of hydrogen-poor ("unsaturated") larger molecules arises from the fact that carbonaceous ions with more than 3–4 carbon atoms tend not to react significantly with molecular hydrogen. In particular, reactions of the type

$$\mathrm{C_nH_m^+ + H_2 \longrightarrow C_nH_{m+1}^+ + H} \tag{34}$$

rarely occur rapidly due to either a barrier or endothermicity for $m \geq 2$, and even association reactions are rarely observed. The combination of difficulties in hydrogenating these ions significantly and their subsequent dissociation via recombination with electrons makes for a very unsaturated chemistry in which species with zero or one hydrogen atom can dominate; e.g., the carbon clusters $C_n$, the radicals $C_nH$, and the cyanopolyynes $HC_{2n}CN$. Of these, only the last two classes of molecules have permanent dipole moments and strong rotational spectra for facile millimeter-wave detection. Nevertheless, the carbon cluster $C_3$ has been detected in the far infrared, infrared, and visible (see, e.g., Maier et al. 2001; Giesen et al. 2001) but not in a cold core environment, while $C_5$ has also been detected in the infrared.

The study of deuterium fractionation has received much attention lately (e.g. Roberts et al. 2003, 2004), although the initial work was done thirty years ago (Watson 1974; Guélin et al. 1977). The basic idea is that the repository of deuterium in cold dense clouds is HD, formed mainly on grains, with a typical abundance ratio with respect to $H_2$ of $2 \times 10^{-5}$. Trace species show a much higher abundance ratio between singly deuterated "isotopomers" (e.g. $DCO^+$) and normal species; a typical ratio in cold cores is 0.01–0.10, three-to-four orders of magnitude greater than the $HD/H_2$ ratio. The explanation of this dramatic effect, known as fractionation, has to do with the importance of the exothermic direction of deuteron exchange reactions, in particular with the critical reaction system

$$\mathrm{H_3^+ + HD \rightleftharpoons H_2D^+ + H_2,} \tag{35}$$

in which the exothermic direction is the left-to-right one, with an exothermicity of 230 K. Assuming that the pre-exponential factor in the Arrhenius equation is the same for both forward and backward reaction, and that the backward one possesses an activation energy of 230 K, we obtain that the ratio of $H_2D^+$ to $H_3^+$ is given by the expression

$$\frac{n(\mathrm{H_2D^+})}{n(\mathrm{H_3^+})} = \exp(+230/T)\frac{n(\mathrm{HD})}{n(\mathrm{H_2})} \tag{36}$$

where we have assumed that the system is at steady-state so that the rate of the forward and backward reactions are equal.

For 10 K and an HD/$H_2$ ratio of $2 \times 10^{-5}$, we obtain that the abundance ratio of the deuterated to normal $H_3^+$ is far greater than unity, an obviously incorrect result. The basic problem with our analysis is that $H_2D^+$ is destroyed very slowly by reaction with $H_2$ but much more quickly by dissociative recombination with electrons and by reactions with heavy neutral species; viz.,

$$H_2D^+ + CO \longrightarrow DCO^+ + H_2; HCO^+ + HD. \tag{37}$$

The latter type of reaction spreads the enhanced deuteration around while at the same time diluting it. If, for example, we assume that $H_2D^+$ is destroyed only by CO, which has a fractional abundance with respect to $H_2$ of $\approx 10^{-4}$, we obtain a reduced abundance ratio between $H_2D^+$ and $H_3^+$ of $\sim 0.1$, assuming that the reaction with CO occurs at the Langevin rate. The analogous ratio $DCO^+$/$HCO^+$ is about 1/3 of this value since the reaction with CO produces $HCO^+$ on 2/3 of the collisions, in excellent agreement with observation.

So far, we have discussed the successes of rather simple models. When it comes to a quantitative determination of how successful the models are, the picture changes and we are faced with continuing challenges. Specifically, if one uses a simple gas-phase, pseudo-time-dependent, homogeneous picture with initial atomic abundances except for hydrogen (initially $H_2$), and the standard oxygen-rich elemental abundances, one cannot reproduce all of the observed abundances in the well-known sources TMC1-CP and L134N. (This inventory excludes deuterated and other isotopomers.) Until recently, the criterion used by our group was that the calculated and observed abundances for a molecule had to be within an order of magnitude of one another. With our osu.2003 network and this criterion (Smith et al. 2004), we found that at early-times ($\approx 10^5$ yr), even the best agreement for TMC-1CP reaches only about 60% of the observed 52 molecules (including upper limits). Increasing the elemental carbon-to-oxygen ratio helps somewhat, but it is clear that the simple treatment fails quantitatively. This conclusion has been buttressed with a new statistical approach to the comparison of theory and observation, in which random uncertainties in rate constants are used to derive uncertainties in calculated abundances (Wakelam, Selsis, and Herbst, in preparation). Although the number of molecules now calculated to be in agreement with observation in TMC1-CP (and L134N) improves at early times, the fraction of such molecules is still significantly under 100% − 80% for L134N and 70% for TMC-1CP.

This discrepancy is not surprising, since even quiescent cores are far from homogeneous, and it is certainly unclear that the physical conditions have remained the same for the time during which chemical evolution has been occurring. In addition, there is the possibility that surface chemistry can account for some of the poorly reproduced molecular abundances. We have recently used our gas-grain network with a new non-thermal desorption mechanism: utilization of the exothermicity of chemical reactions to drive reaction products off of grains if the energy available exceeds the binding energy to the surface (energy of desorption). The results for TMC1-CP show that we can do at least as well as the purely gas-phase models and indeed somewhat better (80%) since saturated (hydrogen-rich) molecules found in cold sources can be explained with the aid of surface processes (Garrod et al. 2006). In addition, the optimum chemical age is more than an order of magnitude larger (3–30 Myr) than obtained with gas-phase species.

Although the gas-grain model contains a great deal of uncertainty in its treatment of surface processes, it is probably true that the remainder of the molecules with poorly understood abundances cannot be understood without a proper consideration of dynamics and heterogeneity. An ambitous attempt along these lines considers the role of MHD waves in the desorption of organic molecules for grain mantles (Markwick et al. 2000). These waves reach different cores in the TMC-1 assembly of six cores at different times, and help account for the apparent differences in chemical age among the cores.

## 6 Pre-stellar Cores: Cold Collapse

Within the last decade, a new class of objects known as pre-stellar cores has been elucidated (Ward-Thompson et al. 1999; Caselli et al. 2002; Bergin et al. 2002; Tafalla et al. 2004). These objects, which probably represent the next evolutionary stage in single star formation after quiescent cores, are both cold ($\approx 10$ K)and collapsing; the central condensations are typically at densities of $10^{6-7}$ cm$^{-3}$. At these densities the time scale for accretion of heavy species onto dust particles is about $10^{3-4}$ yr, and given the rate of collapse, it is likely that depletion is heavy if not total except for light species such as hydrogen and helium, which can evaporate. Some depletion of heavy species such as CO towards the center has been detected even though the columns of material seen traverse the envelope as well as the central condensation. That the depletion is much more severe than these averaged observations indicate is made clear by the strong deuterium fractionation seen. If one considers the reaction system given by eq. (35), one can assume that in the absence of heavy species such as CO, the $H_2D^+$ ion can only be depleted by slow reaction with $H_2$ or by dissociation recombination reactions with electrons. But, at high densities, the electron density is also quite low, and the system comes near the condition of chemical equilibrium, in which only the forward and backward reactions need be considered. The large abundance of $H_2D^+$ that is predicted (Roberts et al. 2003) is in agreement with observations towards perhaps the best-studied pre-stellar core, L1544 (Caselli et al. 2003). But, efficient deuteration does not stop at this stage. Rather, subsequent reactions can produce $D_2H^+$ and finally $D_3^+$ (Roberts et al. 2003):

$$\mathrm{H_2D^+ + HD \rightleftharpoons D_2H^+ + H_2}, \tag{38}$$

$$\mathrm{D_2H^+ + HD \rightleftharpoons D_3^+ + H_2}, \tag{39}$$

both of which reactions are exothermic left-to-right. Although it is difficult to detect $D_3^+$ in small pre-stellar cores because it does not possess a permanent dipole and must be seen in infrared absorption, the doubly deuterated species $D_2H^+$ does possess a dipole moment, just like $H_2D^+$, and has been detected with a high abundance, confirming the picture of deuteration presented here (Vastel et al. 2004). Once doubly and triply deuterated ions are present, the deuteration of the few remaining heavy neutral species in the gas near the center of a pre-stellar core becomes much more efficient. If we take the deuterating ion $D_3^+$ as an example, we see that it is three times as efficient as is $H_2D^+$ as a deuterator. Consider its reaction with CO:

$$\mathrm{CO} + \mathrm{D}_3^+ \longrightarrow \mathrm{DCO}^+ + \mathrm{D}_2. \tag{40}$$

In comparison with eq. (37), here there is only one set of products, and these lead to deuteration. The result of the more efficient deuteration is to produce multiply deuterated species such as $D_2CO$ and $ND_3$ with reasonably high relative abundances compared with their non-deuterated isotopologues, especially in regions near but not quite at the center, where there is still a significant residue of gaseous heavy species.

To model the chemistry of pre-stellar cores accurately, one cannot use a purely gas-phase model since accretion is very important towards the center of the cores. Although simple homogeneous models with accretion have been advocated for the central condensations, it is perhaps better to consider a shell model, with shells of increasing density towards the center. We have published such a shell model, which considers static shells in which gas-phase chemistry and accretion onto and desorption from grains occur (Roberts et al. 2004). One then integrates through the shells and compares columns at a reasonable time with observations. We obtain very good agreement with molecules and their deuterated isotopomers for several pre-stellar cores for which there is significant observational information. An even more advanced model contains hydrodynamic collapse and surface chemistry (Aikawa et al. 2005). The importance of surface chemistry lies in the fact that once the central condensation begins to heat up, the material on grain mantles will evaporate into the gas, leading to chemical consequences.

Surface chemistry can also cause deuterium fractionation via the following mechanism (Tielens 1983; Stantcheva & Herbst 2003). The dissociative recombination of ions such as $H_3^+$ and its deuterated isotopologues produces deuterium atoms (Roberts et al. 2003). These atoms adsorb onto grains and react in a similar manner to the reactions involving hydrogen atoms. For example, CO landing on a grain can be the precursor for totally deuterated methanol via the reactions

$$\mathrm{CO} \xrightarrow{K_1'} \mathrm{DCO} \xrightarrow{K_2'} \mathrm{D_2CO} \xrightarrow{K_3'} \mathrm{CD_3O}, \mathrm{CD_2OD} \xrightarrow{K_4'} \mathrm{CD_3OD}. \tag{41}$$

in analogy with eq. (3). Note that the primed rate coefficients are not exactly the same as for the hydrogen case; deuterium atoms are heavier than hydrogen atoms and probably diffuse more slowly (Watanabe 2006). Of course, both H and D atoms land on the grain surfaces, and there is a complex competitive chemistry to determine the relative abundances of the assorted deuterated isotopologues of methanol (Watanabe 2006). Whether or not non-thermal desorption can then lead to some gas-phase consequences in the pre-stellar core evolutionary stage is unclear, and we are presently using our gas-grain code to study this problem. Although doubly deuterated formaldehyde has been detected in pre-stellar cores, deuterated forms of methanol have not. Moreover, doubly deuterated formaldehyde can possibly be produced in sufficient abundance in the gas (Osamura et al. 2005).

# 7 Protostars: Hot cores and corinos

Once the central condensation becomes opaque and commences to heat up, the physical picture changes dramatically, as mentioned previously. First, the envelope, especially the material closest to the center, begins to warm up to an eventual temperature of $\approx 100 - 200$ K. Now known as a "hot corino," the warmed portion of the envelope becomes chemically quite different from the cooler outer part, which remains similar chemically to pre-stellar cores, especially in deuterium fractionation (Bottinelli et al. 2004; Ceccarelli 2006). Secondly, matter in the form of jets comes out in a bipolar flow and interacts with the envelope, causing local shock waves and violent sputtering of material off of dust particles. Perhaps the best studied protostellar object goes by the unromantic name of IRAS 16293-2422.

The gas-phase of hot corinos has recently been studied by Ceccarelli and coworkers (see Ceccarelli 2006), who found these sources to be smaller and somewhat cooler versions of so-called hot cores, which are located around young high-mass stars (Friedel et al. 2004). In both the hot corinos and hot cores, saturated (hydrogen-rich) molecules are detected; the molecules are either found only in these types of regions or found at higher abundance than in colder sources. Methanol is a very important indicator of hot core-like behavior. Found in cold sources at a low fractional abundance of $\approx 10^{-9}$, the abundance of methanol jumps two-to-three orders of magnitude in hot cores and corinos, presumably because its efficient formation on dust surfaces is followed by near total evaporation into the gas. In addition to methanol, far more complex saturated species are found, including ethyl alcohol ($CH_3CH_2OH$), methyl formate ($HCOOCH_3$), dimethyl ether ($CH_3OCH_3$), ethyl cyanide ($CH_3CH_2CN$), and others. These are only detected in warm sources. The production of the complex molecules is still poorly understood. Although dimethyl ether can be produced by a gas-phase synthesis in the warm gas starting from methanol (Millar et al. 1991; Charnley & Rodgers 2006):

$$\mathrm{CH_3OH + H_3^+ \longrightarrow CH_3OH_2^+ + H_2}, \tag{42}$$

$$\mathrm{CH_3OH_2^+ + CH_3OH \longrightarrow CH_3OHCH_3^+ + H_2O}, \tag{43}$$

$$\mathrm{CH_3OHCH_3^+ + e^- \longrightarrow CH_3OCH_3 + H}, \tag{44}$$

other species such as methyl formate cannot be (Horn et al. 2004). Of course, storage beam techniques have not yet been used to study the products of dissociative recombination reactions with ions more complex than protonated methanol, so it is possible that the products are dominated by three-body channels. It is thus probable for several reasons that surface chemistry produces some of these larger species, possibly during the very act of heating up the grain mantles since at low temperatures, the surface chemistry is dominated by reactions with H atoms, which lead to saturated species but not much complexity. At higher temperatures, H atoms may not remain on grains long enough to react, while heavier radicals may diffuse more rapidly and react with one another. The three stages of the chemistry are shown in Fig. 1. Both the initial and final stages have been studied, but the middle one remains to be understood (Charnley et al. 1992; Caselli et al. 1993).

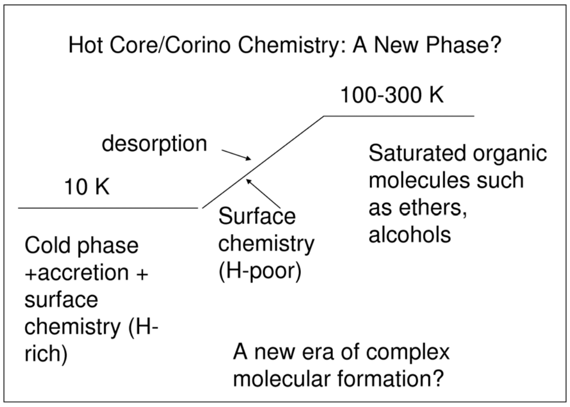

**Figure 1:** The stages of the chemistry of hot corinos and hot cores, including the heating-up phase, which has so far not been treated in chemical models.

There is another possibility: that radiation from the star actually drives a photochemistry on the surfaces of dust grains that produces complex molecules. Experiments have shown that such phenomena occur in the laboratory; however, it must be remembered that a hot core differs from the laboratory in three fundamental ways: the photon flux is much lower, the time scale for processes to occur is much longer, and the atmosphere (the gas phase) is full of reactive species such as hydrogen atoms that can accrete onto grains and re-hydrogenate any species formed by photodissociation of parent neutrals (Ruffle & Herbst 2001). Detailed modeling of surface photochemical effects is needed, as well as modeling of the analogous effects of bombardment of grains by high energy particles (cosmic rays). Even if the star does not drive a photochemistry, it heats up nearby regions in a heterogeneous manner (Staüber et al. 2004) and might even heat up some material to temperatures as high as 800 K or so. It will be interesting to understand the chemistry of such hot regions.

Methanol is also a tracer of the interaction between the jets of material pouring out of a protostar and the ambient material. Presumably the methanol derives from grain mantles, but here the ejection is more violent and leads to significant sputtering from the inner parts of the grain, which presumably ejects the molecules SiO and FeO, which are not typically found in the gas phase (Walmsley et al. 2002).

## 8 Other Sources: PDR's and Protopanetary Disks

Photon-dominated regions are warm, neutral sources where the interstellar medium abuts against either newly formed stars or the HII regions surrounding such stars (Sternberg 2006; Hollenbach & Tielens 1997). Perhaps the two best-known objects in this class are both in Orion: the Orion Bar and the Horsehead Nebula. PDR's are typically treated via gas-phase models under steady-state conditions with a careful attention to radiative transfer. Far from homogeneous, PDR's require slabs of differing density and temperature; the outer slabs possess low density and high temperature while the inner slabs possess high density and low temperature (see, e.g., Le Petit et al. 2002). Most common are one-dimensional treatments in which the radiation either streams in from one or both sides towards the center, but weakens as it traverses the PDR, both due to extinction by the dust particles and self-shielding by molecular hydrogen and, to a lesser extent, CO. The radiation field can be treated as a diluted stellar field, but is more commonly treated as a factor greater than unity multiplying the standard interstellar radiation field. The outermost layers are dominated by neutral atomic hydrogen and ionized carbon ($C^+$); as one traverses inward, the hydrogen is soon converted into its molecular form. Farther inward, the ionized carbon is neutralized, but shortly thereafter is converted into CO. Unfortunately, the simple $C^+$/C/CO picture has never been verified by observations, probably because geometries are always more complex than in the one-dimensional picture.

One surprise concerning PDR's is the detection of unsaturated hydrocarbons (e.g. $C_2H$, $C_3H_2$, $C_4H$) in the outer regions of the Horsehead Nebula, in disagreement with steady-state gas-phase models, which predict much lower abundances for these species. This discrepancy might be caused by photoablation of carbonaceous dust particles, especially PAH's, or by time-dependent effects not included in the current models (Gerin et al. 2006). The association with PAH's stems from the high intensity of the infra-red emissive bands normally associated with these molecules detected in the outer regions of the nebula.

Protoplanetary disks are even more complex than one-dimensional PDR's since they can be thought of in essense as two-dimensional versions. These disks are formed in the final stages of star formation, when the young star has not yet settled down on the main sequence. They are dense assemblages of gas and dust in Keplerian rotation around young stars in the plane of the equator. Although visual images of protoplanetary disks seem to indicate planar structures, these objects are known to flare out with increasing distance from the central star so as to capture radiation from the star. The disks are subjected to ultra-violet and X-ray radiation from the new stars as well as ultra-violet radiation from the interstellar field since much of the material surrounding them has been blown off. A schematic diagram of a protoplanetary disk and the radiation incident on it is shown in Fig. 2. If we assume that the objects are cylindrically and top-bottom symmetric, there are two coordinates to consider: the distance from the star along the so-called midplane and the height off the midplane, both of which can extend for hundreds of AU. Along the midplane, the temperature decreases signficantly as the distance from the star increases, reaching typical interstellar-cloud values by 100 AU. With increasing height from the midplane, the density of gas and dust decreases analogously to the barometric formula while the temperature increases somewhat. At high elevations, the material becomes a typical PDR. Radio observations detect gas-phase molecules in these objects, mainly at fractional abundances much lower on average than seen in cold cores, possibly because of accretion of heavy molecules onto the dust grains (Thi et al. 2004). The heavy accretion is confirmed by strong deuterium fractionation (Ceccarelli et al. 2005), as in pre-stellar cores and the outer regions of protostellar sources.

Chemical models of complete disks should include the division of the disk into a number of slabs with differing height and distance from the star. Radiative trans-

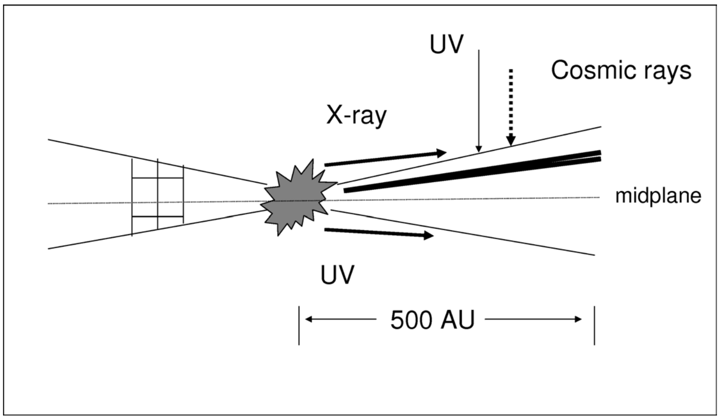

**Figure 2:** A schematic figure of a protoplanetary disk. The large black band is where gas-phase molecules are predicted to be at their most abundant. The hatches on the left show division into slabs.

fer from two directions should be considered, and either accretion or accretion and surface chemistry added to the standard gas-phase treatment. If one starts from typical molecular abundances in cold sources, after a million yr the chemistry evolves to the stage where the gas-phase molecules are predicted to be found in regions of intermediate height because on the midplane (except very near to the star) the high density and low temperature leads to almost instant accretion, while at large heights, the high flux of photons dissociates much of the molecular inventory (Willacy & Langer 2000; Aikawa et al. 2002). Whether or not this prediction is accurate awaits the millimeter-array known as ALMA, which will be able, unlike current interferometers, to probe such spatially small structures as protoplanetary disks.

The next stage of evolution converts the protoplanetary disk to a so-called debris disk, with gaps appearing possibly due to the formation of planets, as well as the comets, ateroids, and meteors with which we are all well acquainted. Chemical models of the solar nebula take us out of our realm and will not be pursued here.

## 9 The Future of Astrochemistry

The field of astrochemistry is approximately thirty years old, having started with the first large wave of molecular detections in the early 1970's. In the early years, most of the effort was directed at understanding the low-temperature chemistry occurring in the interstellar medium (Herbst & Klemperer 1973). As the years passed and computing power grew, more complex gas-phase models began appearing, with large reaction networks and integration of many simultaneous differential equations (Graedel et al. 1982; Leung et al. 1984). The chemistry occurring on grain surfaces began to join gas-phase processes in models (Hasegawa et al. 1992), and new generations of experiments concerning surface chemistry helped to constrain the models (Vidali 2006). Eventually, the simplification of homogeneous and stationary physical conditions began to give way. The study of PDR's (Sternberg 2006) led astrochemists to consider heterogeneity, albeit in a rather regular manner. Subsequent models of protoplanetary disks took the PDR hypothesis one step further by increasing the number of dimensions. Meanwhile, an appreciation not only of heterogeneity but of the actual temporal change in physical conditions took hold (Aikawa et al. 2005; Shematovich et al. 2006). Especially for the case of pre-stellar cores, chemistry and hydrodynamics have begun to march hand in hand. There seems to be no end to the increase in complexity, a trend which is alarming to some, but we must remember that observations are showing us a more and more complex universe, in which phenomena occur over much shorter ranges than realized heretofore. As the power of observations increases, so will the need to confront complexity and complex phenomena, and this confrontation will require increasingly complex chemical models to understand what is happening.

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