Chemical processes in star forming regions

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This paper will review the basic concepts of gas–phase and grain surface chemistry of dense molecular clouds, where low mass and high mass stars form. The chemistry of cold pre-stellar cloud cores, where molecular freeze-out and deuterium fractionation dominate, will be presented. Then, following cloud evolution after protostellar birth, hot core and shock chemistry will be discussed in view of recent observations. A brief summary of the chemistry in protoplanetary disks will also be furnished. The aim is to identify important gas tracers in the various steps of the star formation process, pointing out the main problems still open in the field of astrochemistry.

Key words: astrochemistry; Stars: formation; ISM: clouds; ISM: molecules

1 Introduction

A good comprehension of the physical properties of molecular clouds and star forming regions implies a detailed radiative transfer analysis of molecular line data and their interpretation with chemical models, inclusive of gas–phase reactions as well as gas–grain and grain surface processes. In fact, molecular lines allow us to determine volume densities and temperatures (e.g. Evans 1999), independently from dust continuum emission and absorption measurements (e.g. Ward–Thompson et al. 1999; Bacmann et al. 2000; Visser et al. 2002). This is important to refine the results derived from the dust continuum observations, which are affected by (factor of a few) uncertainties due to the poorly known properties of dust grains (e.g. coagulation degree, thickness of icy mantles; Ossenkopf & Henning 1994; see also Bianchi et al. 2003) and the presence of dust temperature gradients (e.g. Evans et al. 2001; Galli et al. 2002; Pagani et al. 2004). Furthermore, molecular lines offer a unique way to study the kinematics of dense cores (e.g. Ohashi et al. 1999; Lee et al. 2001; Shinnaga et al. 2004).

The number of known interstellar molecules is continuously growing (see [http://astrochemistry.net] for a constantly updated list of interstellar molecules). Up to now, 137 molecules have been detected in the interstellar medium (205 including isotopomers) and about 50 in comets. The largest species so far observed contains 13 atoms (HC$_{11}$N; Bell & Matthews 1985).
The present paper will not be an exhaustive review of the whole field of astrochemistry. It has the aim of introducing the basic concepts of gas phase and surface chemistry (Sect. 2) and showing what are the main chemical processes in star forming regions (Sect. 3), from dark clouds to protoplanetary disks. The hope is to highlight the beauty of this field, which has become a crucial ingredient in all the areas of astrophysics. Interested readers are invited to see the following reviews: van Dishoeck & Blake (1998), Evans (1999), Ehrenfreund & Charnley (2000), van Dishoeck (2004). Useful books are “The chemically controlled cosmos” by Hartquist & Williams (1995); “Interstellar Chemistry” by Duley & Williams (1984); “The formation of stars” by Stahler & Palla (2004); “The Physics and Chemistry of the Interstellar Medium” by Tielens (2005).

2 Basic concepts in astrochemistry

The ingredients of astrochemical models are: atoms (with elemental abundances with respect to hydrogen nuclei reported in Tab. 1), molecular species, electrons, dust grains, cosmic rays and UV photons. Models of dark clouds typically neglect the action of UV photons (which is a good assumption when the visual extinction is larger than \( \sim 4 \) mag; e.g. McKee 1989), and start with all the elements in atomic form (although sometimes hydrogen is assumed to be in molecular form initially; e.g. Leung et al. 1984).

The first problem that chemists have to face concerns the elemental abundances. Four different values are listed in Tab. 1 for each atomic species, two measured and two typically adopted in chemical models: (i) the solar abundance, measured in the solar photosphere (from Anders & Grevesse 1989, but see Asplund et al. 2005 for recent revisions on these values); (ii) the cosmic abundance, slightly but significantly (factor between 1.5 and 2) lower than the solar values, measured in the direction of stars in the solar neighborhood (Snow & Witt 1996); (iii) the high metal abundances, used for diffuse cloud models, in which elements are depleted as found in diffuse clouds according to Morton (1975); (iv) the low metal abundances, used for dense cloud chemistry, where the elements S, Si, Na, Mg, and Fe are further depleted by two orders of magnitude. The low metal mix has been used to best reproduce the observed abundances of sulfur–containing species (Prasad & Huntries 1982), complex molecules (Herbst & Leung 1989), and the ionization balance of interstellar clouds (Graedel et al. 1982).

A better way to proceed would be to start with diffuse–cloud conditions and follow elemental depletion with time until dark cloud conditions are reached; however, this implies a knowledge of (i) the contraction time scale, which is still debatable (e.g. Palla & Stahler 2002; Hartmann 2003), (ii) the probability for each element to stick onto a dust grain (the so–called sticking coefficient, which is typically assumed of order unity, but see Jones & Williams 1985); (iii) the fraction of charged grains and their interaction
with positive ions (i.e. all those elements with ionization potential less than that of H in diffuse clouds, such as C, S, Si, Fe, Na, Mg; e.g. Ruffle et al. 1999; Weingartner & Draine 2001).

Once the set of initial abundances has been assumed, one needs to solve the “rate equations”, which govern the time variation of species both in the gas–phase and on the surface of dust grains (see e.g. Hasegawa et al. 1992). This involves quite often the assumption of uncertain rate coefficients for gas–phase reactions and the poorly known processes happening on grain surfaces. Nevertheless, chemical models are now reasonably able to reproduce observational data, thanks to the tight interaction between theorists, observers and experimentalists, fundamental for constraining models on the one side and guiding observations on the other. The next two subsections will treat gas–phase and surface chemistry separately, pointing out the basic concepts in both fields.

Table 1. Measured elemental abundances (with respect to total hydrogen) and those adopted in chemical models.

| Element | MEASURED | ADOPTED |
|---------|----------|---------|
|         | Solar    | Cosmic  |
|         | High Metal | Low Metal |
| C       | 3.6(-4)  | 7.3(-5) |
| N       | 9.3(-5)  | 2.1(-5) | 2.1(-5) |
| O       | 7.4(-4)  | 1.8(-4) | 1.8(-4) |
| S       | 1.9(-5)  | 8.0(-6) | 8.0(-8) |
| Si      | 3.6(-5)  | 8.0(-7) | 8.0(-9) |
| Fe      | 3.2(-5)  | 3.0(-7) | 3.0(-9) |
| Na      | 1.9(-6)  | 2.0(-7) | 2.0(-9) |
| Mg      | 3.8(-5)  | 7.0(-7) | 7.0(-9) |

Note: a(b) ≡ a × 10^b.

2.1 Gas–phase chemistry

The rate coefficient \( k(\text{cm}^3/\text{s}) \) of a generic reaction \( \text{A+B} \rightarrow \text{C+D} \) is given by:

\[
k = < \sigma v >
\]

where \( \sigma \) is the total cross section of the reactants, \( v \) is the relative velocity, and the averaging is performed over the thermal distribution. Most reactions have appreciable activation energy \( (E_a) \) even if exothermic (this is because chemical reaction typically involve the breaking of chemical bonds before the formation of new ones), and the rate coefficients \( k \) can be expressed by the simple Arrhenius formula (e.g. Herbst 1990):

\[
k = A(T) \exp(-E_a/k_B T)
\]
where $k_B$ is the Boltzmann constant, $T$ is the gas kinetic temperature and $A(T)$ is the “pre–exponential factor”, a weak function of the temperature, which depends upon the actual shape of the reaction potential surface. Activation energies of about 0.1–1 eV are normal, so that in dark clouds, where $k_B T \sim 0.01$ eV, even exothermic reactions may not proceed.

Particularly important for the chemistry of dark clouds are ion–molecule reactions (Herbst & Klemperer 1973), which do not possess activation energy because of the strong long–range attraction force, given by the potential:

$$V(R) = -\frac{\alpha e^2}{2R^4} \quad (3)$$

where $\alpha$ is the polarizability of the neutral species (cm$^3$), $e$ is the electronic charge in esu, and $R$ is the distance between the two species. For a sufficiently close encounter, so that orbiting or spiraling occurs ($R \leq (4e^2\alpha/\mu v^2)^{1/4}$, where $\mu$ is the reduced mass in the collision), the rate coefficient becomes:

$$k_L = 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2} \sim 10^{-9} \text{ cm}^3\text{s}^{-1}, \quad (4)$$

the so–called Langevin rate, independent of the temperature (Herbst 1990).

The main processes happening in the gas phase are listed in Tab. 2 along with their typical rate coefficients (see Tielens 2005 and Duley & Williams 1984 for details). Here it is worthwhile mentioning some examples, important for dark clouds and star forming regions.

### Table 2. Classes of gas–phase reactions

| Type                  | Process                      | Rate Coefficient |
|-----------------------|------------------------------|------------------|
| Ion–molecule          | $A^+ + B \rightarrow C^+ + D$ | $\sim 10^{-9}$ cm$^3$ s$^{-1}$ |
| Dissociative Recombination | $AB^+ + e \rightarrow A + B$ | $\sim 10^{-6}$ cm$^3$ s$^{-1}$ |
| Radiative Association  | $A + B \rightarrow AB + h\nu$ | $\sim 10^{-16}$–$10^{-9}$ cm$^3$ s$^{-1}$ |
| Neutral–neutral       | $A + B \rightarrow C + D$    | $\sim 10^{-12}$–$10^{-10}$ cm$^3$ s$^{-1}$ |
| Photodissociation     | $AB + h\nu \rightarrow A + B$ | $\sim 10^{-9}$ s$^{-1}$ |
| Charge–transfer       | $A^+ + B \rightarrow A + B^+$ | $\sim 10^{-9}$ cm$^3$ s$^{-1}$ |

NOTE: Photodissociation rate listed for no extinction only.

**Ion–molecule reactions and dissociative recombination**

The production of ions in dark molecular clouds is initiated by cosmic rays (c.r.), which ionize $\text{H}_2$, the most abundant molecular species. The rate of this process, called $\zeta$, is typically of order $10^{-17}$ s$^{-1}$ (e.g. van der Tak & van Dishoeck 2000), and about 97% of the ionizations produce $\text{H}_2^+$:

$$\text{H}_2 + \text{c.r.} \rightarrow \text{H}_2^+ + e + \text{c.r.} \quad (5)$$
Once $\text{H}_2^+$ is formed, it reacts very quickly with $\text{H}_2$ to produce $\text{H}_3^+$, one of the most important molecular ions in astrochemistry:

$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \quad (6)$$

In general, if an ion can react with $\text{H}_2$, no other reaction need to be considered because $\text{H}_2$ is at least three orders of magnitude more abundant than the other species and the reaction rate is proportional to the abundance of the reactants. $\text{H}_3^+$ does not react with $\text{H}_2$ but it can easily transfer a proton, thus increasing molecular complexity. For example, if $\text{H}_3^+$ encounters an atomic oxygen, $\text{OH}^+$ is produced ($\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$). Then, successive “H atom” transfer (ion–$\text{H}_2$) reactions proceed until a saturated species (which cannot further react with $\text{H}_2$) is formed: $\text{OH}^+ \xrightarrow{\text{H}_2} \text{H}_2\text{O}^+ \xrightarrow{\text{H}_2} \text{H}_3\text{O}^+$. Upon dissociative recombination of the oxonium ion $\text{H}_3\text{O}^+$, water and OH form:

$$\text{H}_3\text{O}^+ + e \rightarrow \text{H}_2\text{O} + \text{H} \quad (7)$$

$$\rightarrow \text{OH} + 2\text{H} \text{ or } \text{OH} + \text{H}_2 \quad (8)$$

The fraction of $\text{H}_3\text{O}^+$ ions which will produce $\text{H}_2\text{O}$ and OH upon dissociative recombination is called the \textit{branching ratio} and it is measured in the laboratory (e.g., Geppert et al. 2004). Ion–molecule chemistry of larger species leads to mainly H–poor (unsaturated) species, unlike dust chemistry (see Sec. 2.2).

\subsection*{Neutral–neutral reactions}

Although they typically possess activation energy (and thus become important in high temperature regions; e.g., Sect. 3.2), some neutral–neutral reactions are especially crucial in dark clouds for nitrogen and sulphur chemistry, which starts with:

$$\text{CH} + \text{N} \rightarrow \text{CN} + \text{H} \quad (9)$$

$$\text{S} + \text{OH} \rightarrow \text{SO} + \text{H} \quad (10)$$

The reaction of CN with N will produce $\text{N}_2$ (also formed by NO + N), which can react with $\text{H}_3^+$ to form the easily observable $\text{N}_2\text{H}^+$. $\text{N}_2$ initiates the chemical path toward the production of another well known interstellar molecule: $\text{NH}_3$ ($\text{N}_2$ first reacts with $\text{He}^+$ to produce $\text{N}^+$, which is then successively hydrogenated by $\text{H}_2$ until the saturated $\text{NH}_2^+$ ion is formed; $\text{NH}_3$ is finally produced via $\text{NH}_2^+$ dissociative recombination). The common chemical origin between $\text{N}_2\text{H}^+$ and $\text{NH}_3$ explains the good correlation between the two species found in molecular cloud cores (Benson et al. 1998).

\section*{2.2 Surface chemistry}

The fundamental role played by dust grains in synthesizing molecular species is well known for about forty years, when they were invoked to explain the production rate of $\text{H}_2$ molecules in our Galaxy. Pioneer work in this field has
been done by Gould & Salpeter (1963) and Hollenbach & Salpeter (1971), who first derived the formation rate of \( \text{H}_2 \) on grain surfaces. From observations carried out by the Copernicus satellite, the derived rate of formation for \( \text{H}_2 \) in diffuse clouds is \( R \approx 3 \times 10^{-17} \text{ cm}^3\text{s}^{-1} \) (Jura 1975). Lots of theoretical and laboratory work has been done since then on this fundamental process (e.g. Pirrorello et al. 1999; Williams et al. 2000; Cazaux & Tielens 2004). Observations of the so–called HINSA (HI Narrow Self–Absorption) in cloud cores are also giving clues on the \( \text{H}_2 \) formation efficiency in regions where dust grains are covered by icy mantles (e.g. Li & Goldsmith 2005).

Surface chemistry is also invoked to explain (i) the observed large abundances of complex species near star forming regions (Sect. 3.3); (ii) the orders–of–magnitude abundance enhancements of selected molecular species observed along molecular outflows (Sect. 3.2); (iii) dust grain mantles composed of complex icy mixtures, as deduced from ground–based and space – in particular, ISO, the Infrared Space Observatory – observations of background field stars or embedded protostars (e.g. Sellgren et al. 1994; Gibb et al. 2004; van Dishoeck 2004); (iv) the large amount of deuterium fractionation observed in low mass star forming regions (Sect. 3.1 and 3.3).

The main surface processes are illustrated in Fig. 1 (from Herbst 2000), which shows a portion of an idealized grain surface, with adjacent sites. Once a light atom (such as H) hits the dust surface, it is first adsorbed in a binding site. The species is physisorbed if it is linked to the surface by van der Waals forces, and binding energies are in the range 0.01–0.2 eV (100–2000 K). In this case, light species can quickly (<< 1 s) move across the surface, overcoming the energetic barriers via thermal hopping or quantum tunneling, depending upon the dust temperature (e.g. Tielens & Allamandola 1987). Indeed, surface chemistry is not limited by reaction rates but by the accretion rates of reactive species on grain surfaces (e.g. in a typical dark cloud, one H atom hits one dust grain approximately once every 10 days).

Surface chemistry based on diffusion is known as a Langmuir–Hinshelwood (LH) chemistry (see also Tielens & Hagen 1982). Here, hydrogenation is one of the main surface processes, so that O is transformed to H\( _2 \)O (the main ice component), C to CH\( _4 \), N to NH\( _3 \), S to H\( _2 \)S, and CO to H\( _2 \)CO and CH\( _3 \)OH. Hydrogenation of CO implies the overcoming of an activation energy barrier (Woon 2002), which slows down the process; in fact, CO is one of the major compounds of grain mantles observed in molecular clouds, second only to water (e.g. Chiar et al. 1995; Teixeira et al. 1998). There are still some doubts about the existence of solid NH\( _3 \) (e.g. Schutte et al. 2003) and H\( _2 \)S (see discussion in Wakelam et al. 2004). But solid OCS has been detected (Palumbo et al. 1997) and CO\( _2 \) absorption features are ubiquitous in the direction of background and embedded objects (e.g. Nummelin et al. 2001). Therefore, oxygenation is likely to be another important surface process, which competes with hydrogenation depending on the gaseous O/H ratio and the dust temperature (H being more volatile than O).
If the accreted species are strongly bound, or chemisorbed, with typical strengths of \( \sim 1 \) eV (10000 K), the Eley–Rideal (ER) mechanism dominates (see Fig. 1): a surface reaction only occurs when a gas-phase species lands atop or nearby the chemisorbed species. This type of chemistry, efficient only for high surface coverage, preferentially occurs at dust temperatures \( T_d \) below about 300 K (for a barrier between chemisorption sites of \( \sim 1 \) eV, S. Cazaux, priv. comm.), when the LH mechanism cannot proceed for chemisorbed species (see discussion in Habart et al. 2004 on the importance of the various mechanisms for H\(_2\) formation in photodissociation regions).

The return of surface species back in the gas phase can be driven by thermal desorption, with a time scale exponentially dependent on the dust temperature. At \( T_d = 10 \) K, only H and D can thermally evaporate with significantly large rates, whereas \( T_d > 90 \) K is needed to start H\(_2\)O evaporation. Thus, large abundances of water and other saturated species are expected in the gas phase in star forming regions where the dust has been heated above, say, 100 K by the protostellar radiation field (see Sect. 3.3). Among the main nonthermal desorption mechanisms, important in cold clouds, are: (i) cosmic-ray bombardment (especially by the heavier nuclei; Léger et al. 1985; Hasegawa & Herbst 1993), and (ii) the energy generated by chemical surface reactions, still debatable (Willacy & Millar 1998; Takahashi & Williams 2000). UV photons play a role in photodesorption of solid species in PDRs and diffuse clouds (although the yield of photodesorption is still not well constrained; e.g. Ruffle & Herbst 2001).

3 Astrochemistry in star forming regions

In this section, the main chemical processes in some of the regions of interest for star formation will be reviewed. For a more detailed description of the physical properties of molecular cloud cores the reader is encouraged to read Walmsley (this book), Myers (this book) and Tafalla (this book).
3.1 Pre–stellar cores

Stars form within the densest portions of molecular clouds, the “dense cores” (e.g. Myers 1999), upon gravitational collapse. Before the formation of a protostellar object, (starless) dense cores are characterized by low temperatures (∼ 10 K) and relatively high central densities (∼ 10⁵ cm⁻³). These conditions favour the freeze–out of gas phase species onto dust grains. This can be easily understood, comparing the freeze out and the dynamical time scales. The time for a gaseous species X to accrete onto a dust grain is given by:

\[
t_{\text{fo}} = \frac{1}{Sn_d \pi a_d^2 v_t} \ approximate 10^9 \sqrt{m_X/T} (n_H S) \^{-1} \text{ yr},
\]

where S is the sticking coefficient or the probability of a certain species to stick on the grain upon collision (about unity), \(n_d\) is the number density of dust grains, \(a_d\) is the grain radius, \(v_t\) is the thermal velocity of the gaseous species, \(n_H\) is the number density of hydrogen nuclei (it has been assumed that the gas–to–dust density ratio (by mass) is 100 and \(a_d = 0.1 \mu m\), and \(m_X\) is the mass of species X in amu. Therefore, in a cloud with number density \(n_H = 10^5 \text{ cm}^{-3}\), \(t_{\text{fo}} \approx 10^4 \text{ yr}\). The free–fall time scale, the shortest dynamical time scale, for a cloud with the same \(n_H\) value is (e.g. Spitzer 1978):

\[
t_{\text{ff}} = 4 \times 10^7 (n_H)^{-1/2} \text{ (yr)},
\]

or \(10^5 \text{ yr}\). Thus, freeze out is expected to be an important process in the evolution of cloud cores toward the formation of a star.

In fact, strong depletion of CO from the gas phase has been observed in a variety of molecular cloud cores (e.g. Caselli et al. 1999; Bergin et al. 2001; Tafalla et al. 2004). Tafalla (this volume) presents a detailed review of the observed chemical properties of starless cores. Here, I summarize the main observed properties of pre–stellar cores, which differ from starless cores in being more centrally concentrated and showing kinematic evidences of central infall (Ward–Thompson et al. 1999; Crapsi et al. 2005). Pre–stellar cores are thought to be unstable objects, on the verge of star formation, thus their study is crucial to unveil the initial conditions of the star formation process. Fig. 2 shows a schematic picture of the chemical structure of a “typical” pre–stellar core: (i) the core envelope (∼ 7,000–15,000 AU): CO is mainly in the gas phase, and the main molecular ion is HCO⁺; (ii) the core nucleus (∼ 2,500–7,000 AU): CO and other C–bearing species are highly depleted from the gas phase, unlike N–bearing species (e.g. Bergin & Langer 1987); thus, \(N_2H^+\) is a good tracer of these zones and the deuterium fractionation is very large (see below); (iii) the “molecular hole” (within ∼ 2,500 AU): all species heavier than helium are likely to be condensed out onto dust grains (the best tracer of this zone may be \(H_2D^+\)).
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Fig. 2. Schematic picture of the chemical structure of a typical pre–stellar core. The central density is around $10^6$ cm$^{-3}$ and it drops to $\sim 2 \times 10^4$ cm$^{-3}$ at the edge. In the outer shell, CO is mostly in the gas phase and HCO$^+$ is the main ion. Within about 7,000 AU, CO is mostly frozen onto dust grains whereas N$_2$ remains in the gas phase, so that a good probe of these zones is N$_2$H$^+$. In the central $\sim 2,500$ AU (the “molecular hole”), only light species survive in the gas phase. Here, the thick icy mantle may boost the coagulation of dust grains.

Freeze–out and deuterium fractionation
An important consequence of the depletion of gas phase species is the large enhancement in the deuterium fractionation of molecular species, which has been extensively observed in the past years (e.g. Caselli et al. 2002; van der Tak et al. 2002; Bacmann et al. 2003). This process involves the deuteron–proton exchange reaction (Watson 1974):

$$H_3^+ + HD \rightarrow H_2D^+ + H_2 + \Delta E,$$

with $\Delta E \approx 230$ K, which can only proceed from left to right in cold dark clouds. Here, in fact, the $H_2D^+/H_3^+$ abundance ratio increases well above the cosmic D/H ratio ($\sim 1.5 \times 10^{-5}$). $H_2D^+$ can react with CO, N$_2$ and other neutrals, transferring the deuteron in at least one third of its encounters, with the consequence of enhancing the deuterium fractionation in, e.g., HCO$^+$ and N$_2$H$^+$, as observed (e.g. Williams et al. 1998). In the case of CO (and other $H_3^+$ and $H_2D^+$ destruction partners) depletion, the $H_3^+$ abundance will increase and, consequently, the $H_2D^+$ production rate will raise (via reaction 14), further increasing the $H_2D^+/H_3^+$ abundance ratio and the deuterium fractionation. In pre–stellar cores, $N_2D^+/N_2H^+ \approx 0.2$ (Caselli et al. 2002; Crapsi et al. 2005) and $D_2CO/H_2CO \approx 0.05$ (Bacmann et al. 2003), orders of magnitude larger that the cosmic D/H ratio. The observed D–fractionation also correlates with the measured amount of CO depletion (Bacmann et al.
2003; Crapsi et al. 2005), as expected from theory (e.g. Dalgarno & Lepp 1984; Aikawa et al. 2005).

In molecular holes, volume densities are large enough to allow an “extreme” depletion of gaseous species heavier than helium. This seems to be supported by the detection of a strong $\text{H}_2\text{D}^+$ line in the direction of L1544 (Caselli et al. 2003). The estimated $\text{H}_2\text{D}^+$ abundance cannot be reproduced by standard gas–grain chemistry unless CO is mainly in solid form (e.g. Roberts et al. 2003; Walmsley et al. 2004). If this is the case, the only tracer of the chemical composition of this region may be $\text{H}_2\text{D}^+$. Also $\text{D}_2\text{H}^+$ has been observed in another pre–stellar core (Vastel et al. 2004), with abundances similar to $\text{H}_2\text{D}^+$, which further pointed out the importance of including multiply deuterated species in chemical models of pre–stellar cores.

3.2 Outflows

In their youngest phase, protostars are called Class 0 sources (André et al. 1993) and one of their main characteristics is the presence of powerful and collimated outflows (e.g. Bachiller 1996; see also Beuther & Shepherd, this book and Bacciotti, this book). Outflows shock the material along their path, raising the gas temperature and partially destroying dust grains. In the presence of magnetic fields, if the electron fraction is sufficiently low (as in the dense material surrounding Class 0 sources), and if the shock velocity is below about 50 km s$^{-1}$ (Draine et al. 1983), a discontinuity in the hydrodynamical variables (e.g. density and temperature) is not present and the shock is named “C–type” (“C” stays for “continuous”). In all the other cases, a “jump front” is formed, and the shock is called “J–type” (see Draine 1980).

In “C–type” shocks, molecular species (in particular $\text{H}_2$) do not dissociate. In these conditions, and if the gas temperature raises above $\sim 200$ K, some important endothermic reactions become fast and quickly convert most of the free oxygen into water ($\text{H}_3\text{O} \rightarrow \text{OH} \rightarrow \text{H}_2\text{O}$), and sulphur mainly into SO and SO$_2$ (e.g. Hartquist et al. 1980; Pineau des Forêts et al. 1993). In dissociative shocks, as soon as the post–shocked gas temperature has fallen to a few hundred degrees, $\text{H}_2$ molecules are reformed and shock chemistry proceeds as in C–type shocks (e.g. Neufeld & Dalgarno 1989).

The presence of magnetic fields in C–type shocks implies different velocities for neutrals and charged particles, including dust grains which are negatively charged and linked to the magnetic field lines. In these conditions, the collisions between (especially) $\text{H}_2$ molecules and dust grains may cause the return of mantle and refractory species in the gas phase. This process is called grain sputtering (e.g. Flower & Pineau des Forêts 1995; Schilke et al. 1997) and it is thought to be responsible for the observed enhancement of SiO and saturated molecular species such as $\text{H}_2\text{O}$, $\text{NH}_3$, and $\text{CH}_3\text{OH}$ along protostellar outflows (e.g. Bachiller & Perez Gutiérrez 1997; Jørgensen et al. 2004). Dust grains with different sizes will also have relative velocities because
of the different mass and charge (entering the gyrofrequency expression), so that grain–grain collisions are also quite efficient in vaporising mantle and refractory material (Caselli et al. 1997).

Once icy mantles and part of the refractory material are released in the gas phase, shock chemistry proceeds until the gas temperature drops to the pre–shock values. This happens in a short time scale (a few hundred years), because of the efficient gas cooling mainly due to H$_2$, water and CO (e.g. Kaufman & Neufeld 1996). Then, the post–shocked gas will experience again the “cold chemistry”, including freeze–out (e.g. Bergin et al. 1998). This mechanism (shock+freeze–out) has been suggested by Bergin et al. (1999) as a way to explain the large abundance ($\sim 10^{-4}$ w.r.t. H$_2$) of water in solid form in molecular clouds.

### 3.3 Hot Cores

The newborn protostar eventually heats up the surrounding material with its radiation, raising the dust temperature above the sublimation value for grain mantles, and forming the so–called “Hot Cores” (HCs). HCs are typically associated with high mass star forming regions and represent a stage earlier than ultracompact HII regions. They have diameters of $<0.1$ pc, H$_2$ number densities of $\geq 10^7$ cm$^{-3}$ and gas temperatures $\geq 100$ K (e.g. Kurtz et al. 2000). Their chemical signatures are: (i) large abundances of saturated species, such as H$_2$O, NH$_3$, H$_2$S, CH$_3$OH (e.g. Pauls et al. 1983; Menten et al. 1986), suggestive of an active surface chemistry (Sect. 2.2); (ii) large abundances of complex organic H–rich molecules, in particular HCOOCH$_3$ (methyl formate), CH$_3$COOH (acetic acid), CH$_3$CH$_2$CN (ethyl cyanide), CH$_3$CH$_2$OH (ethanol), (CH$_3$)$_2$CO (acetone) (e.g. Millar et al. 1995; Mehringer & Snyder 1996; Remijan et al. 2004), hard to form in the gas phase; (iii) relatively large deuterium fractionations (e.g. Olofsson 1984; Turner 1990), a record of an early cold phase (Sect. 3.1). Interestingly, these regions show a strong chemical differentiation, especially evident in the nearby Orion KL (e.g. Blake et al. 1987; Wright et al. 1996) and also in the W3(OH) region (Wyrowski et al. 1997), when millimeter interferometry is used.

To understand the gas phase composition in HCs, surface chemistry is needed, because gas phase routes appear to be too slow. In particular, saturated species can be efficiently formed on grain surfaces before or during the earliest stages of protostar evolution, when the dust temperature is low enough ($\leq 20$K) to allow hydrogenation and produce solid H$_2$O, NH$_3$, CH$_3$OH and H$_2$S (see Sect. 2.2). Once the dust is heated to temperatures larger than the sublimation values for icy mantles (about 100 K), these saturated species will enrich the gas phase and start a hot gas phase chemistry (e.g. Brown et al. 1988; Charnley et al. 1992). A way to reproduce the observed chemical differentiation in the Orion KL region, where N–bearing and O–bearing species are spatially segregated, is to take into account the temperature and density gradients of the circumstellar cloud (Caselli et al. 1993).
In general, different routes are invoked for complex O–bearing and N–bearing species: the former are produced after the evaporation of solid methanol (CH$_3$OH) and formaldehyde (H$_2$CO) (the complexity is increasing in the gas phase); the latter are formed on grain surfaces (e.g. ethyl cyanide, CH$_3$CH$_2$CN) and, once evaporated, they form simpler daughter species (e.g. vinyl cyanide, CH$_2$CHCN). However, as recently found in the laboratory (Horn et al. 2005), some key reactions in the chain to form the HC–ubiquitous methyl formate from evaporated methanol do not proceed. Thus, surface chemistry is also needed to produce complex O–bearing species. This is all to be explored! In fact, current chemical models neglect surface chemistry, although they are very sophisticated in treating the physical structure of the molecular clouds (e.g. Doty et al. 2002; Rodgers & Charnley 2003; Nomura & Millar 2004; Viti et al. 2004).

In the past few years it has been realized that HCs are not only a signature of high mass star formation, but they are also found in low mass star forming regions, during the earliest (Class 0) protostellar phase (Cazaux et al. 2003; Bottinelli et al. 2004a,b; Kuan et al. 2004), and in one intermediate mass Class 0 source (Fuente et al. 2005). Low–mass HCs, called “hot corinos”, are a “scaled” version (n(H$_2$) $\sim$ 10$^7$ cm$^{-3}$, T $\sim$ 50–100 K, size $\sim$ 150 AU) of the massive HCs. Nevertheless, they show rich spectra at millimeter wavelengths, with complex organic molecules, which is challenging current theory (see e.g. Rodgers & Charnley 2001). Outside these “hot corinos”, the gas and the dust still maintain the pre–stellar–core characteristics, including freeze–out (e.g. Belloche & André 2004). In the well–studied case of IRAS 16293-2422, the deuterium fractionation is very large (especially for H$_2$CO and CH$_3$OH; e.g. Parise et al. 2004) compared to high mass HCs, probably suggesting a different chemical evolution, such as lower dust temperatures during the pre–stellar phase, which favour surface deuteration, or different chemical time scales.

### 3.4 Protoplanetary Disks

Protoplanetary disks around T Tauri and Herbig Ae/Be stars, which are contracting toward the main sequence and have ages of a few hundred years, are an important link between molecular clouds and protoplanetary systems (see Markwick & Charnley 2004 for a recent review). Understanding their chemical composition and the chemical processes is in fact one of the major challenge for astrochemistry, although the next generation of telescopes (in particular ALMA, the Atacama Large Millimeter Array) is needed to put stringent constraints on the models. So far, observations of species such as CO, CS, CN, HCN, HCO$^+$, N$_2$H$^+$, and H$_2$CO have shown that molecular abundances are typically lower than those in dense interstellar clouds, suggesting that molecular freeze–out is at work (e.g. Dutrey et al. 1997; Goldsmith et al. 1999; Qi et al. 2003; Thi et al. 2004). Moreover, DCO$^+$ has also been detected and the derived deuterium fractionation is comparable to that
Chemical processes in star forming regions observed in dense cloud cores \((\text{DCO}^+ / \text{HCO}^+ \sim 0.04; \text{van Dishoeck et al. 2003})\). Ceccarelli et al. (2004) have detected \(\text{H}_2\text{D}^+\), known to be abundant in highly depleted regions (see Sect. 3.1). There is also observational evidence that photon–dominated chemistry is significant (because of the relatively large abundance of CN and \(\text{C}_2\text{H}\), e.g. Dutrey et al. 1997). Theoretical work has pointed out the importance of X–rays in the ionization (e.g. Glassgold et al. 1997) and thermal (e.g. Glassgold et al. 2004) balance. Thus, many ingredients participate in the chemistry of protoplanetary disks.

In current chemical models, protoplanetary disks can be divided in three layers (see Fig. 3): the surface layer, where photochemical processes are important because of the exposure to the UV flux from the star and the interstellar radiation field; the intermediate layer, where the extinction is large enough that the chemistry resembles that of dense clouds; the midplane, where the density is so large that the majority of gas phase species are frozen onto dust grains (see, e.g., Aikawa et al. 2001; Willacy & Langer 2000; Markwick et al. 2002; van Zadelhoff et al. 2003; Semenov et al. 2004).

**Fig. 3.** Schematic picture of a protoplanetary disk, where three chemically distinct zones can be recognized: the midplane, where freeze–out is dominant; the intermediate zone, where dense cloud chemistry is appropriate; the surface, where photochemistry is important (courtesy of Y. Aikawa).

### 4 Conclusions

Tab. 3 summarizes the main processes for the chemistry of star forming regions, in the three phases (pre–stellar cores, Class 0 protostars and protoplanetary disks) briefly illustrated in this review. Question marks in the table follow not–yet–proved statements, mostly based on model predictions.

Here, I would like to point out some of the main problems still open in the field of astrochemistry of star forming regions. Many uncertainties are present especially regarding surface chemistry (e.g. Stantcheva & Herbst 2004; Chang et al. 2004) and gas phase reactions at high temperature (e.g. Wakelam et al. 2004), which in particular affect our interpretation of the observations toward molecular outflows and hot cores. Some important problems to solve
Table 3. Main processes and molecular gas tracers in star forming regions

| Region               | Gas Tracer                  | Main Processes                          |
|----------------------|-----------------------------|-----------------------------------------|
| Pre–stellar cores:   |                             |                                         |
| envelope             | CO, HCO⁺, CS               | ion–molecule                            |
| nucleus              | N₂H⁺, N₂D⁺, NH₃            | freeze–out, D–fractionation             |
| molecular hole       | H₂D⁺, D₂H⁺, D₃⁺?           | freeze–out, grain coagulation?          |
| Class 0:             |                             |                                         |
| envelope             | N₂H⁺, NH₃                  | ion–molecule, freeze–out                |
| outflow              | H₂O, SiO, CH₃OH, SO₂       | grain sputtering, neutral–neutral       |
| hot cores            | H₂O, complex organics      | mantle evaporation, neutral–neutral     |
| Protoplanetary disks:|                             |                                         |
| surface layer        | CO, CN, C₂H                | photochemistry, ion–molecule            |
| intermediate layer   | HCN, DCO⁺, N₂H⁺            | freeze–out, D–fractionation             |
| midplane             | H₂D⁺, H⁺?, D₂H⁺?, D₃⁺?    | freeze–out, grain coagulation           |

are: (i) after recent laboratory work (Horn et al. 2004; Luca et al. 2004), we are left with the non–trivial problem of producing HCOOCH₃ and CH₃OH in the gas phase. It seems that the formation on grain surfaces (not yet explored for methyl formate) followed by desorption is the only possible route. (ii) Grain mantle composition is expected to change during cloud evolution and contraction; thus, binding energies (and consequently freeze–out rates) are a function of time. Nevertheless, current models simply neglect this. (iii) There are still quite large uncertainties regarding the chemistry of Oxygen (e.g. how much atomic O is left in the gas phase in pre–stellar core?), and Sulphur (where does S go in dense clouds and what is its form in icy grain mantles?). (iv) How good is the approximation of assuming a constant cosmic ray ionization rate (ζ) throughout the core? A large value of ζ (∼ 10⁻¹⁵ s⁻¹) has been deduced for diffuse clouds (McCall et al. 2003). But this value drops to 1–3×10⁻¹⁷ s⁻¹ in dense clouds; does it continue to drop within pre–stellar cores, with a consequent variation of the fractional ionization and the chemistry in cloud core nuclei? A synergy of laboratory, theoretical, and observational work, as well as the new generation of telescopes and interferometers (ALMA, SMA, CARMA, Herschel, SOFIA, APEX), are sorely needed to advance our understanding of astrochemistry.

Acknowledgements

I thank all my collaborators, who keep feeding my enthusiasm about astrochemistry. A special thank to Eric Herbst and Malcolm Walmsley to have had the patience of going through this review and giving me important input. Finally, I thank all the organizers of this meeting and, in particular, Nanda Kumar for all his hard work, needed to make the C2C a very successful (and enjoyable) meeting.
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