

Chemical Evolution of Protostars

Michiel R. Hogerheijde

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

Abstract. This review discusses the evolution of the chemical composition of the molecular gas throughout the process of star formation. It covers the initial stages of cloud-core formation, gravitational collapse and the formation of the star, the effects of stellar radiation and outflows on the surrounding cloud, and the composition of the circumstellar disk. A brief overview of relevant chemical processes sets the stage. The ensuing evolution of the chemistry is governed by several competing timescales and by energy input by the young star(s). Special attention is given to the role of molecular freeze-out on dust grains and to deuterium fractionation in cold gas.

Keywords: Star Formation, Astrochemistry, Molecular Astrophysics

1. Introduction

Molecular lines offer powerful probes of interstellar clouds and star-forming regions. Because excited energy levels are populated through collisions, relative line strengths of transitions of the same molecule provide measures of the gas density and temperature. The (emission or absorption) line profiles directly reflect the velocity field along the line of sight. And changes in the chemical abundances can signal specific processes such as shocks, heating, and photodissociation.

Full exploitation of these diagnostics requires understanding of the chemical processes that govern the molecular abundances. Ultimately, this may allow use of the chemistry as a clock or at least as a tool to assign a relative evolutionary ordering of objects. The following sections describe the basic chemical processes and sketch the evolution of the chemistry throughout star formation; more detailed reviews include van Dishoeck & Blake (1998), van Dishoeck & Hogerheijde (1999), and Langer et al. (2000).

2. Chemical Processes

At the low densities of interstellar clouds, chemical reactions in the gas phase involve only two bodies. Three-body reactions only play a role in shocks and the inner regions of protoplanetary disks, where H_2 densities exceed $\sim 10^{12} \text{ cm}^{-3}$. For two body reactions, the reaction rates (in $\text{cm}^{-3} \text{ s}^{-1}$) can be expressed as $k n(X) n(Y)$, where k is



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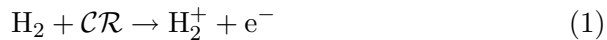
Table I. Formation and Destruction Reactions

Radiative association	$X + Y \leftrightarrow XY^* \leftrightarrow XY + \nu$
Photodissociation	$XY + \nu \rightarrow X + Y$
Associative detachment	$\begin{cases} X + e \rightarrow X^- + \nu \\ X^- + Y \rightarrow XY + e \end{cases}$
Dissociative recombination	$X^+ + e \rightarrow X + \nu$
	$XY^+ + e \rightarrow \begin{cases} XY + \nu \\ X + Y \end{cases}$
Gas-phase neutral-neutral reaction	$X + YZ \rightarrow XY + Z$
Gas-phase ion-neutral reaction	$X^+ + YZ \rightarrow XY^+ + Z$
Charge transfer	$X^+ + YZ \rightarrow X + YZ^+$
Grain-surface reactions	$X + \mathcal{G} : Y \rightarrow X : \mathcal{G} : Y \rightarrow \mathcal{G} : XY \rightarrow \mathcal{G} + XY$

the rate coefficient in $\text{cm}^3 \text{s}^{-1}$. Table I lists the main reactions (Dalgarno, 1987; van Dishoeck, 1988). On-line databases list the rates of all known reactions, e.g., the UMIST ‘rate99’ database which contains 4113 reactions between 396 species and 12 elements (Le Teuff et al., 2000).

Molecular bonds can either form through radiative association, where a photon carries off the excess energy, or on a grain surface, where the dust particle absorbs the released energy. Typical rates range from $< 10^{-17}$ to $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ with uncertainties as large as a factor 10. Ultraviolet radiation can easily break molecular bonds. In the unattenuated interstellar radiation field (Draine, 1978), molecular lifetimes are as short as 10^2 – 10^3 yr. Deep inside clouds ($A_V > 5$ mag), electrons released when cosmic-rays ionize H_2 can collisionally excite other H_2 molecules, which decay by emitting an ultraviolet photon. This secondary ultraviolet field photodissociates molecules at a rate 4–5 orders of magnitude lower than on the outside of clouds.

Existing molecular bonds can be rearranged through gas-phase reactions between neutral species or between an ion and a neutral species. The latter reactions are fast, with rate coefficients of 10^{-7} – $10^{-9} \text{ cm}^3 \text{ s}^{-1}$; the former reactions are generally slower by several orders of magnitude. Many ion-molecule reaction pathways are started by the formation of H_3^+ initiated by cosmic-ray ionization of H_2 ,



Cosmic rays penetrate deep into dark clouds, providing a ubiquitous source of H_3^+ . H_3^+ reacts rapidly with, e.g., CO or N_2 , producing HCO^+ and N_2H^+ , and allowing further ion-molecule reactions.

Reactions that do not proceed effectively in the gas-phase can occur on grain surfaces, after the reagents have accreted onto a grain and diffused along the surface to the reaction site. The timescale for a gas molecule to stick on a grain is

$$t_{\text{accr}} \approx 2 \times 10^9 (n_{\text{H}} y_{\text{s}})^{-1}, \quad (3)$$

where $y_{\text{s}} = 0.1$ – 1.0 is the probability that the molecule sticks (see Williams, 1993 for a review). If the temperature of the dust is below the value at which the ice species evaporates (~ 20 K for CO, ~ 90 K for H₂O), it will remain on the grain until desorbed by processes such as cosmic-ray spot heating, grain-grain collisions, and exo-thermic chemical reactions (e.g., Schutte, 1997). Many reactions can proceed on grain surfaces because of the large time available (~ 1 day), even when reaction barriers are present. Because H is the most mobile species, surface chemistry leads to hydrogenated species such as CH₄, H₂O, and NH₃. Grain surfaces are the primary site for the formation of H₂.

An extensive literature exists on modeling the chemistry of interstellar clouds. The interested reader is referred to the reviews listed in § 1. Generally, one can distinguish models including only gas-phase reactions and those including also freeze-out, grain-surface reactions, and desorption. One can also distinguish time-dependent models, which follow the evolution over time, and depth-dependent models, which are calculated until chemical equilibrium is reached (10^5 – 10^7 yr). The dynamical timescales involved in star formation are comparable in magnitude, requiring that the chemistry is solved both as function of time and position. Current computational capabilities do not permit to do this efficiently for the thousands of reactions of the full networks. Ruffle et al. (2002), Wiebe et al. (2003), and Semenov et al. (2004) have developed reduced networks that make such calculations tractable.

3. Evolution of the Chemistry

3.1. DIFFUSE CLOUDS

Diffuse clouds have extinction up to a few magnitudes and H+H₂ densities less than a few thousand cm⁻³. These clouds are poorly shielded from the interstellar ultraviolet radiation field, which plays a significant role in their chemistry. In general, the abundances in these clouds are well explained by simple ion–neutral gas-phase chemistry; exceptions are the abundances of NH₃, H₂CO, and H₂S, which may be formed on grains and require a desorption mechanism. Meyer (1997) and Lucas & Liszt (1997) review observational aspects of diffuse-cloud chemistry.

3.2. DARK CLOUDS

Dark clouds have extinctions $> \text{few mag}$, and shield their molecules from the dissociating ultraviolet interstellar radiation field. H_2 and ^{12}CO exist in sufficient abundance that they can shield themselves against photodissociation; other species are shielded by dust. The densities of dark clouds are higher than those of diffuse clouds ($\gtrsim 10^4 \text{ cm}^{-3}$) and their temperatures lower (as low as 10 K). More complex species can survive here. Unsaturated carbon chains form through carbon insertion (e.g., $\text{C}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2$ or $\text{C} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H} + \text{H}$), condensation (e.g., $\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$ or $\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$), or radiative association ($\text{C}^+ + \text{C}_n \rightarrow \text{C}_{n+1}^+ + \nu$).

A classic example of a dark cloud is TMC 1, in the Taurus-Auriga cloud complex. This filamentary cloud shows prominent gradients in abundance along its length in species such as NH_3 and HC_7N (Ollano et al., 1988). Because of the similarity of dynamical and chemical timescales, explanations for this gradient invoke either a density slope along the ridge or a difference in evolutionary stage. The latter may be the result from turbulence affecting one side of the cloud and effectively resetting the chemical clock.

This dynamic interpretation of molecular clouds has been recently proposed by Hartmann et al. (2001), based on the distribution of pre-main-sequence stellar ages in Solar-neighborhood clouds. Bergin et al. (2004) has shown that convergent flows can indeed form H_2 and CO quickly once a sufficient column density has been accumulated for shielding to become effective. This underlines the relevance of time-dependent chemical models.

3.3. DEPLETION

Equation (3) shows that as the density of a cloud increases, molecules freeze out more rapidly. Inside pre-stellar cores, H_2 densities exceed 10^5 cm^{-3} , and $t_{\text{accr}} < t_{\text{dyn}}$. The pre-stellar core L1498 (Kuiper et al., 1996; Willacy et al., 1998) offers a clear example of molecular depletion through freeze out. C^{18}O , CS , and CCS emission form a ring around the core's center as traced by thermal continuum emission from dust.

Not all species drop in abundance. Volatile molecules such as H_2 and N_2 do not stick on the grains. Following reactions (1–2), H_3^+ can react with N_2 to form N_2H^+ and NH_3 . The main destruction reactions of N_2H^+ are with CO and H_2O , both of which are depleted inside cloud cores, and N_2H^+ can retain significant abundances. The pre-stellar cores L1498 and B68 (Bergin et al., 2002) show NH_3 and N_2H^+ emission peaks at their center. At the very center of B68, however, N_2H^+ too decreases, suggesting that even N_2 ultimately depletes.

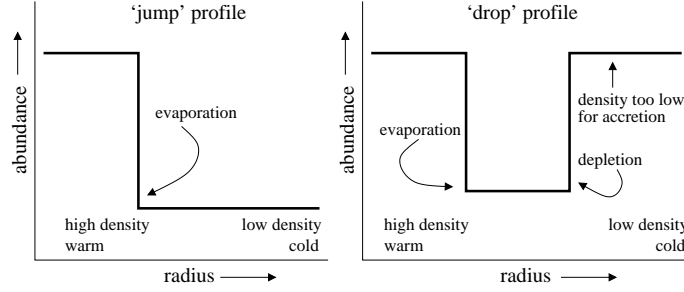
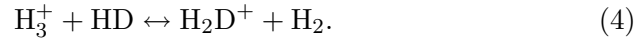


Figure 1. ‘Jump’ (left) and ‘drop’ (right) abundance profiles, after Van der Tak et al. (2000) and Jørgensen et al. (2004).

Studying the velocity fields in pre-stellar cores is critical to understand the earliest phases of collapse. The depletion of so many molecules poses a challenge to our ability to trace these earliest stages of collapse. Only H_3^+ and its isotopes (§3.4) may offer observational access.

3.4. DEUTERATION

The cosmic abundance of deuterium is $[\text{D}]/[\text{H}] \approx 1.6 \times 10^{-5}$, but deuterated forms of many molecules are observed at much higher relative abundance. Deuterium fractionation starts with the exchange reaction



Below ~ 20 K the forward reaction is favored because of the lower zero-point vibrational energy of H_2D^+ . This drives much of the atomic D into H_2D^+ or even HD_2^+ , inserting D into the ion–neutral chemical network. In regions of high depletion the main destruction partner of H_3^+ (and isotopes), CO, is underabundant, increasing the likelihood of H_2D^+ reacting with other species and further boosting the deuterium fractionation of the products. Detections of singly, doubly, and even triply deuterated forms of, e.g., H_3^+ , H_2CO , NH_3 , and CH_3OH imply deuterium fractionation by up to four (!) orders of magnitude (Lis et al., 2002; van der Tak et al., 2002; Bacmann et al., 2003; Caselli et al., 2003; Ceccarelli et al., 2004; Parise et al., 2004).

3.5. JUMP AND DROP PROFILES

Once a star has formed at the center of the collapsing core, it will start to heat the infalling material. In ice mixtures, species can segregate and evaporate at their respective T_{evap} , or the inclusions can evaporate together with the CO or H_2O matrix.

The resulting abundance distributions follow so-called ‘jump’ or ‘drop’ profile (Fig. 3.5; van der Tak et al., 2000; Jørgensen et al., 2004).

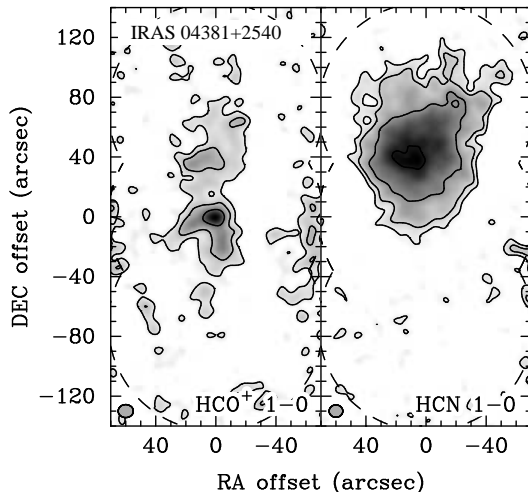


Figure 2. HCO^+ (left) and $\text{HCN } J=1-0$ (right) emission image of the outflow driven by the young stellar object IRAS 04381+2540 [at (0, 0)] obtained with the BIMA interferometer by Hogerheijde (2001). The emission, especially of HCN in the northern outflow lobe, is strongly enhanced, suggesting significant abundance increases.

Species that form in the ice mantles on dust grains have ‘jump’ profiles, where the abundance is negligible for radii outside the location where $T_d(r) = T_{\text{evap}}$, and high inside this radius. Species that were present in the gas-phase in the original cloud (e.g., CO), have a depleted (‘drop’) abundance for radii $r_{\text{evap}} < r < r_{\text{accr}}$, where r_{evap} is the radius within which $T_d(r) > T_{\text{evap}}$, and r_{accr} the radius where $t_{\text{accr}} < t_{\text{age}}$. Outside r_{accr} the density is too low to accrete significant amounts of the molecule within the life time of the core (eq. 3).

3.6. OUTFLOWS

The bipolar jets that many young stars drive also affect the abundances in the surrounding cloud material by heating and shocking the gas, reviewed by Bachiller (1996). In shocks with speeds of $v_s \approx 25 \text{ km s}^{-1}$ grains are destroyed or sputtered, and large columns for SiO rapidly form from the released Si (Schilke et al., 1997).

Weaker shocks at the sides of the flow can still evaporate the ice mantles of grains, releasing species such as CH_3OH and HCN (Fig. 3.6; for another recent example see, e.g., Jørgensen et al., 2004). Large quantities of H_2O are also released or formed (Bergin et al., 1998). As a result, species such as N_2H^+ that are abundant in the unperturbed cloud are destroyed through reactions with water and absent from the shocked regions (Jørgensen et al., 2004).

3.7. MASSIVE STAR FORMATION

The formation of massive stars is less well understood than that of lower mass objects. Massive stars are less common and often located at larger distances; much of their early evolution occurs deep in dense clouds; and massive stars often form together with many lower mass objects, complicating the interpretation of (unresolved) observations. Evans (1999) gives a comparison of low vs. high-mass star formation.

Nevertheless, the chemical evolution of sites of massive star formation is understood qualitatively. While governed by the same processes as lower mass objects, the much larger luminosity of massive stars greatly affects the outcome. The earliest observable state is that of a ‘hot core’, where the star has started to heat a sizeable fraction of its surrounding gas, evaporating many ice species. This is followed by an ultra-compact H II region (UCHII), where the ultraviolet radiation of the star has begun to photo-ionize part of its surroundings. In time, this will develop into a H II region. Space limitations preclude more details here; the interested reader is referred to the reviews of Kurtz et al. (2000) and Churchwell (2002).

3.8. PROTOPLANETARY DISKS

Many young stars are surrounded by circumstellar disks (Beckwith & Sargent, 1996). The chemistry in these disks follows the same processes as described above: In the disk midplane, where densities are high and temperatures low, molecules are frozen out. At larger heights in the flared disk, molecules can exist in the gas-phase. At the surface of the flared disk, the ultraviolet radiation from the star dissociates and ionizes the material. Although low mass stars emit little ultraviolet radiation, mostly from accretion, the disk material is sufficiently close to the star that the ultraviolet radiation field at 100 AU still equals 300–3000 times the interstellar field (Bergin et al., 2003).

Observations of molecular lines from disks have confirmed the picture sketched above: large depletions are inferred, and many molecules typically trace the warm gas at intermediate heights (e.g., Dutrey et al., 1997; van Zadelhoff et al., 2001). Signatures of photoprocessing such as the CN radical are present at large heights (Qi, 2001).

Current observations only have a few resolving elements across the disk, and no in-depth comparisons to theory can be made (yet). Open questions are the extent to which material mixes radially and vertically, which would expose a larger fraction of the disk material to different temperatures and radiation regimes. At the current relatively poor resolution, observations only trace material > 50 AU which may never make it into a planetary system.

4. Summary and Outlook

The chemistry in star-forming regions is governed by four competing processes: gas-phase chemistry, depletion (and grain-surface chemistry), evaporation, and photodissociation.

The differences in luminosity and ionizing flux between low mass and high mass objects causes large variations in the chemistry of the surrounding material, although the basic processes are the same.

The chemistry in disks also follows the same processes, but densities are higher, and even weak ionizing fluxes from the central star are important because of the small distances.

Much of what we know about this chemistry has been learned with single-dish telescopes like CSO and JCMT; and interferometer arrays like PdBI, OVRO, and BIMA. In the coming years, our understanding will greatly benefit from observations with APEX, the SMA and its link-up with JCMT and CSO, the merger of OVRO and BIMA into CARMA, and ultimately ALMA. These instruments will be complemented at shorter wavelengths by the Spitzer, Herchel, and SOFIA.

Together these observational possibilities will allow access to higher excitations, tracing warmer and denser material; and higher spatial resolutions, allowing to separate the different regions that are still confused around high-mass stars and in protplanetary disks. Paired with increased modeling capabilities, the foreseen observations will greatly increase our understanding of the chemical evolution of protostars.

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