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Recent Astrochemical Results on Star-Forming Regions

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Abstract. This review discusses recent results on the astrochemistry of (mostly high-mass) star-forming regions. After an introduction on the use of chemistry in astrophysics and some basic concepts of astrochemistry, specific results are presented. Highlighted areas are the use of chemistry in the search for massive circumstellar disks, the interaction of molecular clouds with cosmic rays, and the feedback effects of protostellar irradiation on the parent molecular cloud. The review concludes with a discussion of future observational opportunities.

1. The use of chemistry in astrophysics

There are several ways in which knowledge of chemistry is helpful to gain a better understanding of the Universe. The prime area of interest is the formation of stars and planets, which occurs in cold dark clouds which require observation at long (infrared and radio) wavelengths. The line radiation of molecules is an essential part of this effort, because it is the only probe of the kinematics of these clouds, and because it is the major way to determine their temperatures, volume densities, and other conditions. Successful use of molecular lines to derive physical parameters requires some understanding of chemistry to predict which molecules may be abundant under which conditions. This use may be called 'passive' astrochemistry.

A more active way to use chemistry in astrophysics makes use of the dependence of the molecular composition of the gas on parameters which are otherwise hard to estimate. This use involves the construction of chemical models typically containing thousands of reactions; Wakelam et al. (2006a) have studied the accuracy of such models. First, the chemical composition of the gas in such models usually depends on the time, so that observations of molecular lines may be used to estimate the ages of star-forming regions (Doty et al. 2006). Second, since the chemistry needs time to respond to changing conditions, molecular abundances often contain some memory of the source history. An example are the deuterium bearing molecules seen in hot molecular cores, which must be remnants of a previous cold phase. Third, the chemical composition of star-forming matter may give clues to the presence of (energetic) radiation which is difficult or impossible to observe directly. It is clear that chemistry is a significant help in the understanding of astrophysical processes.

More than 130 molecules are known to exist in interstellar space, of which 36 are known outside our Galaxy and 10 are known in the solid state (Gibb et al. 2004). The eight new discoveries of 2007 (see www.cdms.de for the latest updates) may be grouped in a few 'threads': (i) Complex organics (by which astronomers usually mean 4^+-atomic carbon chains), which probe gas-grain interactions and serve as a link to pre-biotic molecules; the most recent addition is C_3H_6 (Marcelino et al. 2007). (ii) Fluorine and phosphorus compounds (PO, HCP, CF^+), which help to determine elemental abundances and the composition of dust grains in dense clouds (Neufeld et al. 2006; Agúndez et al. 2007; Tenenbaum et al. 2007). (iii) Negative ions, which are useful to measure the electron fraction of molecular gas (§ 4.). (iv) Deuterated molecules, which are important as tracers of very early (cold and dense) phases of star formation (§ 3.).

Due to space limitations, this review is not comprehensive, but biased toward the interests of its author. For a recent general review of astrochemistry see the books edited by Lis et al. (2005) and Combes (2007). The physics and chemistry of regions of low-mass star formation are reviewed by Bergin & Tafalla (2007) and Ceccarelli et al. (2007). An overview of methods to derive molecular abundances from spectral line data can be found in Van der Tak & Hogerheijde (2007). The formation of high-mass stars is reviewed by Zinnecker & Yorke (2007) and Beuther et al. (2007), and is of course the topic of the current volume.

2. Basics of Astrochemistry

The chemical composition of interstellar molecular clouds depends strongly on the physical conditions, particularly the temperature and the radiation field. This discussion is restricted to dense interstellar clouds, defined theoretically as $n \gtrsim 10^4\,\mathrm{cm}^{-3}$ or observationally as $A_V \gtrsim 3$, so that photoprocesses can be ignored. In such clouds, four main types of environments can be distinguished:

Cold gas At $T \lesssim 100\,\mathrm{K}$, the main type of reactions occurring in the gas phase are ion-molecule reactions. An example is the proton transfer from H_2 to CO: $CO + H_3^+ \rightarrow HCO^+ + H_2$. This type of reaction usually does not have any activation barrier and usually proceeds at about the 'Langevin' rate of $\sim 10^{-9}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. The necessary ions are produced in the interaction of H_2 with cosmic rays (§ 4.). One major source of uncertainty are the rates and the branching ratios of dissociative recombination reactions of ions with free electrons (Florescu-Mitchell & Mitchell 2006).

Warm gas Reactions between two neutral species occur if the gas is warm enough to overcome their activation barriers. The rates of these reactions and the heights of their barriers can be difficult to measure or predict, especially when radicals are involved. A classic case is the reaction $O + OH \rightarrow O_2 + H$ with a measured rate constant of $3.5\times10^{-11}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ at $T = 40\,\mathrm{K}$, well above the predicted value (Xu et al. 2007). This reaction determines the main oxygen reservoir in cold interstellar clouds, which is difficult to measure because the fine structure lines of O^0 do not probe cold gas and O_2 only has weak quadrupole lines. The abundance of O_2 recently measured with the Odin satellite towards the ρ Oph cloud (Larsson et al. 2007) is well below theoretical predictions. Laboratory data at $T < 40\,\mathrm{K}$ and observations with *Herschel* (§ 6.) are needed for further progress.

Cold dust In dense clouds, the surfaces of dust grains act as catalysts for reactions that would not take place in the cold gas phase. An important example is the formation of H_2CO and CH_3OH by successive additions of H atoms to CO molecules. Recent laboratory experiments indicate that this process is very efficient (Watanabe et al. 2004; Fuchs et al. 2007). One uncertainty in modeling such processes is the roughness of the surface which determines the mobility of the H and O atoms (e.g., Cuppen & Herbst 2005). Depending on this parameter, grain surface chemistry may operate at temperatures up to $\sim$100 K (Cazaux et al. 2005), but this remains subject of discussion (Herbst et al. 2005).

Warm dust When dust grains are heated by the radiation from young stars or by interstellar shock waves, any ice layers will evaporate. The evaporation temperature varies from $\approx$20 K for volatile species such as CO and N_2 to $\approx$110 K for the more refractive H_2O molecule which makes up the bulk of the ice mantle (Collings & McCoustra 2005).

Observations of dense molecular cores without embedded stars often show a differentiation between CO and N_2: in the core centers, CO appears depleted while N_2 (traced by N_2H^+ and NH_3) remains in the gas phase (e.g., Tafalla et al. 2002). This behaviour cannot be due to the difference in evaporation temperature between the two species which Bisschop et al. (2006) has shown to be very small. Alternatively, CO freeze-out removes the major destroyer of N_2H^+, so that its abundance rises toward the centers of pre-stellar cores (Aikawa 2007), but this effect does not quite explain the observations (Flower et al. 2006).

Significant rearrangement of the ice layers may occur during the warm-up phase of the ice before the actual evaporation, which may lead to the formation of more complex molecules (Garrod & Herbst 2006). This rearrangement is a more likely source of molecular complexity than gas-phase processes, the preferred model of the 1990's.

3. Chemical Filters

The rate coefficients of many chemical reactions depend on the temperature. If the dependence is very strong, a molecule may almost exclusively exist in warm or cold gas. In an astrophysical context, this behaviour may be used to trace regions of a particular temperature, a concept known as a chemical filter. Three particular cases are:

Cold gas: H_2D^+ The H_2D^+ molecule is produced in the gas phase by the reaction of H_3^+ with HD. At $T \lesssim 20$ K, the back reaction is very slow, and if in addition the density is high ($\gtrsim 10^5$ cm^{-3}), the main destroyers of H_2D^+, CO and O, will freeze out onto dust grains. Under these circumstances, the H_2D^+/H_3^+ ratio may approach or even exceed unity, and further reaction to D_2H^+ and D_3^+ may even occur (Roberts et al. 2003). High abundances of H_2D^+ measured in a few dense pre-stellar cores and of D_2H^+ in one confirm these predictions (Caselli et al. 2003; Belloche et al. 2006; Hogerheijde et al. 2006; Vastel et al. 2004). A survey of H_2D^+ in 12 dense molecular cores with and without embedded stars clearly shows a decrease of the H_2D^+ abundance as the young star warms up its surroundings (Caselli et al. 2007). The H_2D^+ molecule thus acts as a filter for the cold dense gas at the centers of pre-stellar cores where most other molecules are frozen onto dust, and is the only probe of the kinematics in this phase (e.g., Van der Tak et al. 2005).

Regions of high-mass star formation tend to have lower degrees of deuterium fractionation than their low-mass counterparts; see Fontani et al. (2006) for a recent example. The implication is that the cold pre-stellar phase for regions of massive star formation has a short duration compared with the low-mass case, or that the ambient gas is warmer in high-mass than in low-mass regions. The duration argument is supported by source counts (Garay & Lizano 1999).

In recent years, several multiply deuterated molecules have been detected toward dense molecular cores: D_2CO, D_2CS, ND_2H, D_2S, CHD_2OH, ND_3, CD_3OH, and D_2H^+(see Ceccarelli et al. 2007 for references). Th latest addition to this list, after extensive searches, is the discovery of interstellar D_2O (Butner et al. 2007). The low fractionation of H_2O compared with other molecules suggests that deuterium enrichment is primarily a gas-phase process. The likely origin of multiply deuterated molecules is transfer of deuterons from H_3^+ isotopologues at low temperatures ($\lesssim 20$ K), aided by transfer from deuterated CH_3^+ and $C_2H_2{}^+$ at higher temperatures (Roueff et al. 2007). The measured abundances of multiply deuterated molecules imply that the freeze-out of molecules onto grains is slow, suggesting grain growth in pre-stellar cores (Flower et al. 2005).

Warm gas: $\mathbf{H_2O}$ There are three formation routes for interstellar water. At low temperatures, H_2O is produced in the gas phase by dissociative recombination of H_3O^+, which itself derives from O by reactions with H_3^+ and H_2. However, H_2O is created much more efficiently on the surfaces of dust grains by H atom addition to adsorbed O atoms. The ice mantles may desorb from the grains if they are thermally heated to $T \gtrsim 100$ K by nearby young stars, or through photodesorption in regions with significant ultraviolet radiation (Hollenbach et al. 2007). At high temperatures ($\gtrsim 250$ K), H_2O is produced efficiently in the gas phase through the reactions of O and OH with H_2, which have significant barriers (Wagner & Graff 1987).

Far from embedded young stars, dense molecular cloud thus have a background level of H_2O originating in H_3O^+ recombination and photodesorption of H_2O ice; it is this H_2O which is picked up in large-scale maps of H_2O emission (Melnick & Bergin 2005) although excitation effects may complicate the picture (Poelman et al. 2007). Close to young stars, the H_2O abundance rises steeply because of thermal ice evaporation. Even higher H_2O abundances are reached in outflows, where gas is shock-heated to several 100 K and the neutral-neutral channel kicks in (Franklin et al. 2007). Because of these effects, H_2O acts as a filter for warm gas in star-forming regions.

One application of this filter is the search for massive circumstellar disks. High-mass stars may form through disk accretion like their low-mass counterparts, perhaps with an increased accretion rate. The alternative model where high-mass stars form through coagulation of lower-mass stars or pre-stellar cores probably only applies to a minority of cases, as extremely high stellar densities are required. However, positive evidence for accretion disks around young high-mass stars has been hard to find, as reviewed by Q. Zhang (this volume). The main problem is confusion of the molecular line emission from the disk with that from the surrounding envelope.

Observations of the $H_2^{18}O$ line at 203 GHz with the Plateau de Bure Interferometer have now revealed such a massive circumstellar disk (Van der Tak et al. 2006a). The disk radius is $\approx$400 AU, the mass of $\approx 0.8\,M_\odot$ is $\approx$5% of the mass of the central star, and the observed velocity gradient in the $H_2^{18}O$ line is consistent with the Keplerian rotation speed. Together with NGC 7538 IRS11 (Sandell et al. 2003) and IRAS 20126 (Cesaroni et al. 2005), this source is one of the more compelling cases for an accretion disk around a young high-mass star.

Shocked gas: SiO The star formation process entails gas parcels moving both inward and outward, and shocks occur frequently. The shocked gas has its own chemistry, because the gas is heated to $\sim$1000 K, grain mantles are disrupted, and even grain cores are shattered if the shocks are fast enough. The erosion of the grain mantles leads to observed enhancements of, e.g., CH_3OH (Bachiller et al. 2001), while the grain cores 'sputter' refractive atoms such as Si and Fe. Neutral-neutral reactions in the hot gas then transform these atoms into, e.g., SiO, which is widely used as tracer of outflows (Martín-Pintado et al. 1997), and the recently detected SiN and FeO molecules (Walmsley et al. 2002; Schilke et al. 2003).

4. Galactic Variations in Cosmic-Ray Flux

The ionization fraction of molecular clouds determines the efficiency of magnetic support against their gravitational collapse, and also sets the time scale for ion-molecule chemistry. In star-forming regions, the bulk of the matter is shielded against ultraviolet radiation, and cosmic rays are the main ionization source. Only very close to embedded stars, photo-ionization plays a role, as recent detections of CO^+ and SO^+ testify (Stäuber et al. 2007). Cosmic rays influence molecular abundances not only through their total flux, but also through their energy spectrum, in particular the ratio of H- to He-ionizing particles (Wakelam et al. 2006b).

Observations of molecular ions show significant variations in the cosmic-ray ionization rate ζ within our Galaxy. Submillimeter emission data of HCO^+ toward a sample of seven high-mass star-forming regions at distances of 1–4 kpc indicate $\zeta \sim 3 \times 10^{-17}\,s^{-1}$ (Van der Tak & van Dishoeck 2000). This number is in good agreement with measurements of low-energy cosmic ray fluxes by the Voyager and Pioneer spacecraft (Webber 1998). However, observations of DCO^+ in nearby (0.1 kpc) starless molecular cores indicate an ionization rate reduced by a factor of $\sim$10 from this value (Caselli et al. 2002). On the other hand, 10× larger ionization rates are found from H_3^+ absorption data on the nearby (0.3 kpc) ζ Per cloud (McCall et al. 2003; Le Petit & Roueff 2006), and especially toward the Sgr A region near the Galactic center (Oka et al. 2005). Enhanced ζ-values near the Galactic center are also reported from H_3O^+ observations of the Sgr B2 cloud Van der Tak et al. (2006b), but the derived ionization rate is lower than that from H_3^+.

At least two effects appear responsible for the observed variations. First, the cosmic-ray flux appears to decrease by a factor of ∼10 from the inner to the outer Galaxy, as corroborated by synchrotron, X-ray and γ-ray data (Yusef-Zadeh et al. 2007). Second, scattering of cosmic rays off plasma waves appears to cause the difference between diffuse and dense clouds. This process is more efficient in denser clouds with stronger magnetic fields, in agreement with the observations. However, other mechanisms may also play a role. Observational estimates of ζ in regions with known magnetic field strengths will help to make progress on this front.

The recent detections of interstellar and circumstellar C_4H^-, C_6H^- and C_8H^- mark the discovery of negative ions in space (McCarthy et al. 2006; Remijan et al. 2007; Cernicharo et al. 2007; Brünken et al. 2007; Sakai et al. 2007). The large electron affinities of hydrocarbon chains makes the anionic species almost as abundant as the neutral species (Herbst 1981; Millar et al. 2007). The total abundances only imply a small shift of negative charge, so that the above estimates of the ionization rates of star-forming regions are not affected. The negative ions are useful though, because combined with measurements of the H I 21 cm line, the abundance ratios C_nH^-/C_nH may be used to estimate the electron abundances in dark clouds (Flower et al. 2007).

5. Effects of Protostellar Irradiation

During their main sequence phase, high-mass stars emit $\sim 10^{-7}$ of their luminosity in the form of X-rays, which originate in wind shocks. X-ray observations of star-forming regions mainly probe the low-mass population, which emits X-rays due to magnetic and accretion activity (see review by Feigelson et al. 2007). The onset of X-ray emission from high-mass stars is hidden from our view, because of obscuration by the surrounding material. However, the protostellar X-ray emission may be probed indirectly through its effect on the chemistry of its molecular envelope.

Benz et al. (2007) have imaged the CS and SO submillimeter line emission from the young high-mass star AFGL 2591 with the SubMillimeter Array. The data show a pronounced 'jump' in the SO abundance by a factor of ∼100 at a radius of ∼1000 AU. Model calculations by Stäuber et al. (2005) show that such a jump is evidence for protostellar X-ray emission. Models with ice evaporation but without X-rays do not fit the data. The derived L_X is $\sim 10^{-6}$ of the total luminosity of AFGL 2591, which is somewhat higher than for main sequence objects. Possibly the stellar winds of high-mass protostars are stronger than those of main sequence stars, or additional X-ray emission is generated in the interaction of the wind with the surrounding envelope.

6. Prospects

The year 2008 will see the launch of ESA's *Herschel* satellite, and first data are expected in early 2009. Unhindered by the Earth's atmosphere, this mission will make a major and unique contribution to astrochemistry, especially with its spectrometer HIFI which covers the 480–1250 and 1410–1910 GHz ranges at a resolution better than 1 km s^{-1}. The highlights of HIFI science will be, from an astrochemical point of view:

- unbiased spectral surveys of several Galactic star-forming regions, which provide inventories of their molecular composition;
- large-scale maps of the H_2O emission from dense clouds, and detailed multi-line studies of the H_2O abundance distribution in star-forming regions;
- precise measurements of the O_2 abundance in dense clouds, PDRs and other environments;
- measure the abundances of interstellar hydrides such as NH, a cornerstone of nitrogen chemistry (which is poorly known because N^0 does not have fine structure lines and N_2 has no rotational lines.);
- make an inventory of the major carbon and oxygen species in external galaxies, to study chemistry under more extreme conditions (including metallicity) than our Galaxy offers.

And just when the Herschel data will have been digested, ALMA operations will get in full swing. One byproduct will be lots of 'accidental' astrochemists, who find their submillimeter spectra full of unexpected spectral lines around the line they were interested in. This reviewer hopes that these researchers will evolve one day into 'active' astrochemists.

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