The molecular universe

Helen J Fraser, Martin R S McCoustra and David A Williams present a simple guide to astrochemistry.

Abstract

Molecules play a fundamental role in many regions of our universe. The science where chemistry and astronomy overlap is known as astrochemistry, a branch of astronomy that has risen in importance over recent years. In this article we review the significance of chemistry in several astronomical environments including the early universe, interstellar clouds, star-forming regions and protoplanetary disks. We discuss theoretical models, laboratory experiments and observational data, and present several recent and exciting results that challenge our perception of the "molecular universe".

In fact it is not. This gaseous component is important because it is the reservoir of matter that remains to be processed into galaxies, stars and planets. For example, in the early universe protogalaxies were formed from gas clouds that contracted under their own weight to form galaxies of stars, but in the present era there is too little gas left in intergalactic space for galaxy formation to continue. Within any particular galaxy, star and planet formation continues while sufficient gas remains in the interstellar medium. However, when this reservoir is empty, a galaxy has little opportunity for further development and can only await the death of the stars that it contains. The interstellar medium of galaxies is replenished to some extent by material expelled from stars in winds and explosions, so the interstellar gas is continually enriched with heavy elements and dust that are the ashes of nuclear burning. Stars that form from the enriched interstellar gas will be richer in these heavy elements and dust than the mean interstellar gas. Material injected into the interstellar medium from stars is also, initially, very much denser than the interstellar medium. These are the kinds of regions that many astronomers wish to study. High density implies a high collision-rate in the gas between atoms, molecules, radicals and dust grains, stimulating a complex chemistry that produces a wide variety of new molecular species (see table 1). In fact, emission of electromagnetic radiation from (or sometimes absorption by) molecules is the most effective way of studying the properties of the denser-than-average gas, wherever it may be found. Cooling may prevent a cloud that is collapsing under its own weight from heating up, as gravitational potential energy is converted into heat. If the temperature remains sufficiently low, then the gas pressure will not rise enough to prevent the collapse. Something like this process must happen at the birth of both galaxies and stars. The chemistry that gives rise to the coolant molecules also tends to reduce the level of ionization in the gas, thereby reducing the ability of the magnetic field to support the gas against collapse. Consequently molecules play a key role in regions where much of the astronomical action takes place; through molecular emission we can trace the physical conditions during these events and this radiation may itself be important in modifying the physical conditions that allow these changes to continue. The motivation for studying astrochemistry is strong and although molecules are a minor component of the mass of the universe they exert a profound influence on its development because they affect and trace the transition to high density.

Routes to cosmic molecules

The list of detected cosmic molecules (table 1) represents a challenge for astrochemists. How are these molecules made under conditions that are similar to those on Earth? It is, of course, the conditions on Earth that dominate our thinking on the origin of molecules in the universe. Are these molecules made under conditions that prevail in the early universe, interstellar clouds, star-forming regions and protoplanetary disks? The latest version of the UMIST database (Le Teuff, Millar and Markwick 2000) provides the rate coefficients of 4113 gas-phase reactions among 396 species involving the elements H, He, C, N, O, Na, Mg, Si, P, S, Cl and Fe. Neutral molecules containing up to 12 atoms (CH$_2$C-N) are included; yet only a small number of these reactions have been studied in detail either theoretically or in the laboratory.

There are significant differences between...
results obtained with this UMIST database and that of the “New Standard Model” developed by astrochemists at the Ohio State University (Ruffle and Herbst 2000, 2001; Herbst, Terzieva and Talbi 2000). These differences are caused (inevitably) by the somewhat arbitrary selection of reactions to include in the database, the extent to which gas-grain processes are included in the models, and the uncertainty associated with many of the reaction-rate coefficients. Nevertheless, it is clear that very many species that have not yet been detected must be present in space. This might be because they are inherently difficult to detect (e.g. N$_2$ doesn’t have a dipole moment so its infrared and radio transitions are forbidden), or because the species only have a fleeting existence (e.g. CH$_3^+$ is rapidly destroyed because it is so chemically reactive), or because there is not a signature that is sufficiently specific to make an absolute identification (e.g. PAH [poly-aromatic hydrocarbon] molecules have generic spectra which can be measured but are difficult to assign to one particular PAH). Other families of large molecules, such as fullerenes and amino acids, have been detected in meteoritic samples and may also be present in the interstellar medium, although they have not yet been observed there. Just how far this complexity continues towards biological molecules is as yet unclear.

The types of reactions that play a role in cosmic chemistry are summarized in figure 1. This illustrates the breadth of chemistry that occurs

### Table 1: Molecules in space

Detected cosmic molecules in interstellar and circumstellar environments (adapted from Wootten 2001).

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1. The key reactions in astrochemistry: (a) radiative association; (b) three-body reactions; (c) neutral exchanges; (d) ion–molecule reactions; (e) recombination; (f) negative ion reactions; (g) condensation reactions; (h) surface reactions; (i) carbon insertion reactions; (j) aggregation of dust grains and large molecules.
in space by describing the different routes to molecule formation in a range of interstellar locations. In any astronomical environment, the most important reactions of all are those that convert hydrogen atoms (H) to hydrogen molecules (H₂). This is not only because H₂ is by far the most abundant molecule in the universe, but also because H₂ nearly always plays a key role in the formation of all the other molecular species. In the cool interstellar medium, this 2H→H₂ conversion occurs through surface catalysis (reaction h1 in figure 1), though other reaction mechanisms were important in the dust-free early universe (see below).

In high-density environments such as stellar photospheres and planetary atmospheres, three-body associations (figure 1b) dominate. At low temperatures, neutral atoms and molecules tend to be unreactive with H₂ and the chemistry is driven largely by ion–molecule reactions (figure 1d). The ionization sources are stellar UV radiation, cosmic ray impact, or X-rays from black holes or high-speed shocks in gas flows. In dark clouds, H₂ is ionized by cosmic rays to H₂⁺, which reacts rapidly with other H₂ molecules to form H₃⁺, a stable but reactive ion that easily donates its proton to almost any other species. This sets a rich chemistry underway, and provides one route for the formation of many common astronomical species (Geballe and Oka 1996).

However, the precise formation routes for most of the simpler molecules (say, up to a few atoms) are not completely understood. For example, the negative results obtained recently by the Submillimeter Wave Astronomy Satellite along many lines of sight for H₂O and O₂ (Bergin et al. 2000, Spaans and van Dishoeck 2001) took most astrochemists by surprise. Observational and theoretical upper limits on the concentrations of these molecules differ by orders of magnitude from each other. Apparently we are missing some of the key chemical routes by which these molecules might be created or destroyed, or the key physical routes by which the molecules may be trapped into ices or depleted from the gas phase. But, in general, our models of the chemistry in interstellar clouds, star-forming regions and circumstellar envelopes are now proving to be useful tools in interpreting observations and providing physical insight into these regions (as we will see in the final section of this article).

In contrast, our understanding of the formation processes for the larger molecules is poor. We can make educated guesses of the important reactions, but the results of our models do not agree well with observational evidence. For example, although we can devise appropriate networks of gas-phase reactions that provide interstellar methanol, CH₃OH, these networks fail to supply it in the quantities detected; and schemes to make the next member of the family, ethanol, C₂H₅OH, fail completely. We do know, however, that these molecules can be made in the laboratory by irradiating molecular ices, so it seems likely that surface processes and the processing of ices in the solid state are important. Large carbon-based molecules, such as the PAHs, may also be formed from the degradation of solid carbon grains in the hot gas behind interstellar shocks; in effect, these grains are probably like soot – assemblies of benzene-type derivatives and tiny pieces of graphic sheet, which are likely to reform into more stable fullerene and nanotube structures. Direct gas-phase synthesis of such large species is only feasible in the high densities found in stellar atmospheres. In fact, we observe that the envelopes of carbon stars are filled with smoke, puffing it out into space like factory chimneys.

Energy sources and timescales in cosmic reactions

Petrol does not spontaneously ignite. To make our cars go we need a spark to activate the chemistry, turning the hydrocarbon into water and carbon dioxide. It is similar in space: atoms of O, C and N, for example, do not spontaneously react with H₂. In fact they experience a barrier as they approach the H₂ molecule and usually “bounce off” rather than react. For reactions to occur, the atoms and molecules must approach with sufficient energy to overcome the reaction barrier – and this requires the gas to be heated to hundreds or thousands of Kelvin. Even then the chemi-
Ions often react easily with molecules, and radicals or in overcoming the reaction barriers. Without an input of energy, the chemistry may evaporate previously-formed ices and give a characteristic chemistry that we find in star-forming regions. The astrochemist needs to be aware of the competing or dominating energy source and to select the appropriate reaction network to describe astronomical observations and models.

It often turns out that the chemistry needs to be explored in a situation that is evolving dynamically, say, in a cloud collapsing under its own gravity, or in an expanding flow or wind from a cool star. If the chemistry is fast but the dynamical changes are relatively slow, then the chemistry may come to a quasi-steady state at any stage of the evolution. If so, this allows a great simplification. The timescales that are associated with some processes that occur in interstellar clouds and star-forming regions are given in table 2. This table shows that in diffuse clouds (at number densities around $10^6$ m$^{-3}$) the chemistry is fast compared to collapse under gravity and to the freeze-out of species on to dust grains. Therefore a chemical quasi-steady state can exist in such clouds. In gas with a density of around $10^{10}$ m$^{-3}$, typical of the dense cores within molecular clouds, all the timescales are comparable. One approach in such circumstances is to put all the processes into the computing pot and stir. Relating such results to observed conditions and laboratory experiments is one of the great challenges in astrochemistry!

So far, we have indicated what is needed to model the chemistry in astronomical regions. Below, we briefly describe regions where molecules are, or have been, important in astronomical terms.

## Molecules at high redshifts

About 300,000 years after the Big Bang, or at a redshift $z$ of about 1300 (for the Standard Big Bang Nucleosynthesis Model) the universe had cooled enough for the gas to become mainly neutral. Its composition was largely atomic hydrogen, with some helium, traces of deuterium and negligible amounts of other elements. Such a gas can cool from very high temperatures down to about 10,000 K by collisional excitation of the electronic states in atomic hydrogen. These states subsequently radiate, thereby removing thermal energy from the gas. A gas at 10,000 K has a high thermal pressure. How did the gas in the early universe cool further, so that gravity had a chance to overcome pressure and create a protogalaxy? We now know that the cooling agent was H$_2$, with some HD, and that the molecular species were created from reactions of atomic hydrogen with the remaining electrons and protons, (see figure 3). Of course, at that time H$_2$ could not be created from surface reactions on dust as there was no dust before the stars existed. The gas-phase processes initially converted about two in a million H atoms to H$_2$.

The great challenge in astrochemistry is to put all the processes into the computing pot and stir. Relating such results to observed conditions and laboratory experiments is one of the great challenges in astrochemistry!
This association is now being studied in observations of galaxies at high redshift. The detection of distant gas is not made directly with H$_2$, but through the tracer molecule, CO, where these elements of carbon and oxygen have been injected into the hydrogen cloud by the first stars. Warm CO has been detected in an object with redshift $z = 4.69$ (Ohta et al. 1996, Omont et al. 1996). More recently it has been shown that massive amounts of cold (and previously undetected) gas exist around a galaxy at $z = 3.91$ (Papadopoulos et al. 2001), as shown in figure 4. Such a massive reservoir of gas fuels star-formation and accretion on to Active Galactic Nuclei. These massive galactic halos of H$_2$ may even help to explain the curious rotation properties of spiral galaxies.

Molecules in interstellar clouds and star-forming regions

Our knowledge of astrochemistry grew out of observational and theoretical studies of interstellar clouds. Initially the emphasis was on diffuse clouds that are pervaded by stellar UV photons and consequently have rather low abundances of molecules. However, dark clouds, opaque to starlight, were soon found to be chemical factories; most of the molecules listed in table 1 have been detected in dark interstellar clouds. The attention given to dark clouds intensified when it became apparent that they were not only the sites of interesting chemistry but also the locations for the formation of stars with masses comparable to that of the Sun (the so-called “low mass stars”).

The dark clouds do not have uniform structure, but are clumpy, with different physical or chemical properties in different spatial regions. Stars appear to be forming right at the heart of the densest clumpy regions – the dense cores. Most of these new stars are still embedded in these dense cores of gas and dust and are consequently invisible at optical wavelengths, but can be detected in the infrared (see figure 5). The molecules are important in star-forming regions, firstly as coolants and secondly as...
tracers of the gas motion. The collapse under gravity of a gas cloud into a star (and its associated disk and envelope) releases enormous amounts of gravitational potential energy. This must be radiated away if the gas is not to heat up and arrest the collapse because of increased thermal pressure. The temperature of these clouds (around 10 K) is much too low for \( \text{H}_2 \) to be an effective coolant, as it was in pre-galactic gas clouds, so the most important coolant molecules are \( \text{CO} \) and its equivalents containing less abundant isotopes.

Figure 6 indicates how the CO emission that cools the cloud can also be used to trace the motions in the cloud. This figure shows that gas is still falling on to the new star, while orthogonal to that infall an outflow has been established with a continually widening angle. In about 10,000 years the outflow will have cut off the infall. The energy and momentum associated with these outflows are adequate to disperse the remnants of the dense core within which the new star was born and to rearrange the distribution of gas within the cloud. The cloud is not destroyed; rather this star formation process occurs in very localized dense clumps of the cloud, which then retains its overall integrity through several phases of star formation in different regions of the cloud.

The formation of a massive star is a much rarer and more energetic event. An external cause is apparently necessary to trigger the formation of the “high-mass” stars that are an order of ten times as massive as the Sun. This trigger might be the winds of a nearby massive star that are shocking and imploding gas in the vicinity. It is therefore particularly important to infer the nature of the collapse process that led to the formation of the massive star. At first sight this seems an impossible task since the newly formed massive star rapidly clears its birthplace of all the evidence. However, the clearing process leaves some transient debris behind, in the form of very dense and small knots of gas and dust that are warmed by the stellar radiation. The molecules that were in the pre-stellar collapsing core become frozen out on the dust and preserve in their composition a relic of the pre-stellar conditions.

These warm clumps, the so-called Hot Cores, enable astrochemists to decode the hidden memory of high mass star-formation. Figure 7 shows an example of a Hot Core, traced with emission features from CH$_3$CN molecules that were released from the warming ices. The emission contours about the ultra-compact HII region surrounding the newly formed star contain information about the chemistry and freeze-out in the pre-stellar phase as well as information about the warming process caused by the onset of stellar burning (Viti and Hatchell 2002).
Stellar and circumstellar molecules

Sufficiently cool stars (with surface temperatures of only a few thousand Kelvin) have atmospheres that are almost entirely molecular. In these atmospheres the densities and temperatures are relatively high in comparison to the interstellar medium. Consequently, atoms and molecules frequently collide with sufficient energy in three-body interactions that they rearrange themselves to form the most stable and strongly bound molecules. In carbon-rich stars, carbon takes up almost all the oxygen to form CO molecules and the residual carbon is in the form of simple hydrocarbons such as CH\textsubscript{2} and CH\textsubscript{3}. In oxygen-rich stars, oxygen takes up all the carbon in CO and the residual oxygen appears in metal oxides such as FeO, SiO, TiO and MgO. It is relatively straightforward to model the chemistry of these regions, as it is time-independent and depends only on known thermodynamic properties of the molecules involved. These stellar molecules have extremely rich spectra in the visible and UV, with large numbers of lines associated with the rotation-vibration band structure. Consequently, the atmosphere is almost totally opaque to radiation emerging from the star. This great stellar opacity effectively traps the momentum of the radiation and influences the structure of the star and its atmosphere. In these cases in particular, astrochemistry is directly influencing the astronomy of cool stars.

There are some surprises too. The Sun has a photospheric temperature of nearly 6000 K, which is considered too high for molecules to survive. However, in sunspot regions, absorption from solar H\textsubscript{2} in the Lyman and Werner bands has been detected (Jordan et al. 1977, Jordan et al. 1978, Bartoe et al. 1979) and more recently some high excitation lines of H\textsubscript{2}O were also observed (Polyansky et al. 1997, Zobov et al. 2000). Can the Sun possibly be wet? No, it cannot; the existence of these molecules is only fleeting, but their presence in detectable amounts indicates that the temperature in sunspots is much less than the photospheric temperature. Molecular hydrogen has also been detected in the atmospheres of other stars (Johnson et al. 1983).

Towards the ends of their lives, cool stars of moderate mass develop huge envelopes that extend so far that stellar gravity cannot prevent them from drifting out into space. This mass-loss is an important mechanism through which stellar processed material is returned to interstellar space. Matter in the stellar atmosphere is accelerated, possibly in stellar pulsations, to join the flow. Initially, the flow conditions are very dense and warm compared to the interstellar medium and chemical timescales are measured merely in minutes rather than in thousands of years. In a nucleation process that is not yet understood, this rapid chemistry leads to the formation of dust particles. These are soot-like grains in carbon-rich envelopes and sand-like grains in oxygen-rich envelopes. Radiation pressure on these tiny particles (which are perhaps only a few tenths of a micron to microns in size) help to drive the outward flow of the envelope.

As this flow continues, the number density of the gas and dust falls, so that radiation from interstellar space can penetrate the envelope, ionize the species present and promote a transient population of envelope molecules. Ultimately, the same radiation will destroy those molecules as they enter interstellar space. Thus, molecules emerging from the stellar atmosphere into the envelope, the so-called parent molecules, form new molecules, the daughters, as the material travels outward to interstellar space and becomes exposed to the interstellar radiation field. A simple example is shown in figure 8 where the parent molecule, HCN, is concentrated on the star, while the daughter species, CN, is in a shell with a cavity at the centre. Observations of chemistry in circumstellar envelopes provide the severest tests of astrochemical models and the observational/theoretical interaction has made this area of astrochemistry one of the most accurate, as illustrated by Aikawa and Herbst (2000) and Millar et al. (2000). However, even these accurate models still do not account for the detected abundances of the larger species, such as H\textsubscript{2}C\textsubscript{18}O, where n = 1–5.

Cool stars with molecular envelopes evolve ultimately into the dramatic but short-lived objects called planetary nebulae. The cool envelope then detaches from the star, which contracts, heats up and generates a fast wind. Molecules are observed either in the residual
envelope, now subject to intense radiation from the central star, or from the complex interaction zone of the fast wind and the envelope (Howe and Williams 1998). Eventually the star becomes a white dwarf, cools slowly and fades from sight. Other stars approach the end of their lives more dramatically, as novae or as supernovae. In both cases molecules are observed, although the environment is apparently hostile to chemistry. The fact that observable amounts of molecules can form rapidly in novae and supernovae ejecta places severe constraints on physical parameters in these regions (Rawlings 1998, Liu 1998).

Molecules in planetary systems

Planetary systems are reservoirs of molecules and dust. Outside the Sun and the central cores of planets, almost every component is made of molecules and dust: planetary atmospheres, comets, meteorites and interplanetary dust.

The study of planetary atmospheres is regarded as separate from that of astrochemistry and is beyond the scope of this article. However, the connection between planetary atmospheres and astrochemistry is close, since planetary atmospheres result from the outgassing from planetesimals as the planets were formed, and from the impact of comets and asteroids on the early planet. The planetesimals and the comets were most probably conglomerates of interstellar dust. In the outer reaches of a newly forming solar system, the icy molecular mantles that coat dust grains in dark interstellar clouds survive the collapse of the cloud and appear in the protoplanetary disk. Closer to the newly forming protostar, the temperatures are so high that the ices evaporate into the gas phase and the chemical signature of the interstellar medium is lost, as the gases and dust grains are heavily processed by radiation from the new star.

Of course, the atmospheres that we now find on planets are not necessarily the primitive atmospheres that were chemically related to interstellar ices. The atmospheres have been heavily processed, most notably, in the case of Earth’s atmosphere, by living organisms that converted a largely chemically reducing CO2 atmosphere to a chemically oxidizing one of O2 and N2.

The composition of interstellar ices has been inferred by matching spectra recorded with the Infrared Space Observatory (ISO) Short Wave-length Spectrometer (SWS) to laboratory-based spectra. Molecules in very cold ices can vibrate, but rotation is hindered, so that against a background source of radiation the molecules in the dust absorb in pure vibrational transitions, easily distinguishable from the rotation-vibration structure of free-flying gas-phase molecules. These transitions occur in the near infrared. Figure 9 shows the spectrum of embedded young stellar object W33a, with absorption features of interstellar ices along the line-of-sight, as identified from laboratory spectra. The composition of this ice is rather similar to that of several cometary bodies in our own solar system (see Table 3) and, although differences exist, bears some resemblance to the composition of interstellar gas.

In regions where the interstellar ice is exposed to UV photons, cosmic rays and electron or ion bombardment, then the ice can be processed to other solid phases, and chemical reactions can be induced within the solid state. Such processing generates radicals, secondary electrons and ions in the ices, which then react further to produce more complex species such as CH4, OH and CH3 (Ehrenfreund and Schutte 2000). These ice-coated grains are the raw material for the formation of the solid bodies that we believe were present in a protoplanetary system – dust, planetesimals, comets and planets, formed from the protoplanetary disk.

However, inside dense molecular clouds and in the dense equatorial planes of protoplanetary disks, UV photons are unable to penetrate, so the ices are predominantly processed by thermal heating, or cosmic rays. In recent years it has been realized that the techniques of modern ultrahigh-vacuum science can be applied to understanding the complex surface physics and chemistry that occurs on grains. Illustrative of such studies is recent work by the laboratory astrophysics group at the University of Nottingham. Using a custom-designed ultra high voltage chamber and some surface probes (Fraser et al. 2002), this group has investigated a range of gas-dust interactions that are directly relevant to the interstellar medium. Early experiments on the thermal evolution of H2O ice under interstellar conditions showed that it was possible for such ices to remain in the solid state to much higher temperatures and over longer timescales than had previously been assumed (Fraser et al. 2001).

More recently, as figure 10 shows, these studies have revealed the complex interplay between adsorption, diffusion, and desorption when CO is deposited on H2O ice, revealing that the spectroscopy and desorption kinetics of such systems are even more complex than we thought previously (Collings et al. 2002).
Astrochemistry

Between 15 and 25 K, solid CO undergoes the competing processes of sublimation and diffusion into the porous H$_2$O film.

Interstellar models imply.

Both experiments suggest that the formation and behaviour of interstellar ices is more sophisticated and more diverse than current interstellar models imply.

In addition to dust, gas from the interstellar cloud is also abundant in such disks. In a recent remarkable observation, highly forbidden rotational transitions were detected towards β-Picoris, 49 Ceti, and HD135344 debris disks, taken with the Infrared Space Observatory. The dashed vertical line depicts the rest wavelengths of CO transitions, and the solid curve illustrates the range of potential wavelength shifts induced by grating repositioning errors or pointing offsets of the spacecraft.

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Conclusion

Astrochemical research is a tool that enables astronomers to explore and understand some of the most interesting problems in modern astronomy; in particular those in which the densities are relatively high and the “small scale” structure of the universe is still evolving. The effects of chemistry on star formation, dense-cloud evolution and planetary formation, in particular, are profound. However, to keep this tool sharp, we need a vast supply of fundamental data on atomic, molecular, surface and solid-state physics and chemistry.

The “new” research area of laboratory astrophysics is now growing rapidly, particularly in the UK. Alongside these advances, the theoretical modelling community is developing newer, more sophisticated models of all regions of the “molecular universe”, enhancing our understanding and interpretation of astronomical objects, as well as providing laboratory astrochemists with interesting challenges to investigate. Finally, the next generation of space telescopes, satellites and exploratory missions, ensures that we will be able to observe and marvel at our molecular universe for many years to come.

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