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".

The title of this article needs some explanation. Clearly, the universe is not entirely made of molecules and we are exaggerating. In fact, most of the mass in the universe is probably not even made of familiar matter, i.e. the atoms and molecules of which we, the Earth, the solar system, and all the stars in our own and other galaxies are composed. "Dark matter" contains about 90% of the mass of the universe and is detected only by the gravitational effects it exerts. The composition of this matter is unknown. The remaining 10% or so of matter in the universe is the familiar "baryonic" material, mostly locked in stars. Only about 1% of all matter is gaseous and distributed between the stars. And of this 1%, perhaps half is molecular. Therefore only about 0.5% of the total mass of the universe is composed of molecules. Why then do we emphasize in the title of this article the importance of molecules? Surely this is a case of the tail wagging the dog?

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, as the gas from which these stars form becomes richer in dust, the opportunity to form planets as a by-product of star formation increases.

Many of the most interesting astronomical phenomena (e.g. the formation of galaxies, galactic collisions, formation of stars and planets and the injection of material into the interstellar medium through stellar winds and explosions) occur in (or are best traced through) matter that is at a higher-than-average density. For example, the average number density of the gas in the interstellar medium of the Milky Way is about one hydrogen (H) atom per cm^3 (i.e. a million per cubic metre), compared to 2.7×10^{19} molecules cm^{-3} in the air that we breathe on Earth. Processes that initiate star formation occur in clouds that are about one thousand times denser than this average interstellar density; in gas that is about a million times denser, star formation is inevitable; and the processes that control planet formation occur in gas that is about 10^{12} times denser 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. Molecules usually have electronic transitions in the optical/UV wavelengths, vibrational transitions in the infrared and rotational transitions in the radio. There is nearly always a suitable molecular transition to use to diagnose the conditions of a molecular region whether its temperature is as low as 10 K or as high as several thousand K. Emission in the radio regime is a particularly useful probe of dense and dusty regions that are opaque to UV and optical radiation. Often, the radiation emitted by the molecule represents an important loss of energy from the gas, so molecules can be important coolants. 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 – compared to those on Earth – seem extreme? (It is, of course, the conditions on Earth that are extreme.) Are other species, not yet detected, also likely to be present? Are there large molecules present, possibly of relevance to biology? To account for the hundred or so molecular species that we can detect in space, it is necessary to develop models of chemical networks that contain up to several hundred species interacting in several thousand reactions. 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_3C_7N) 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

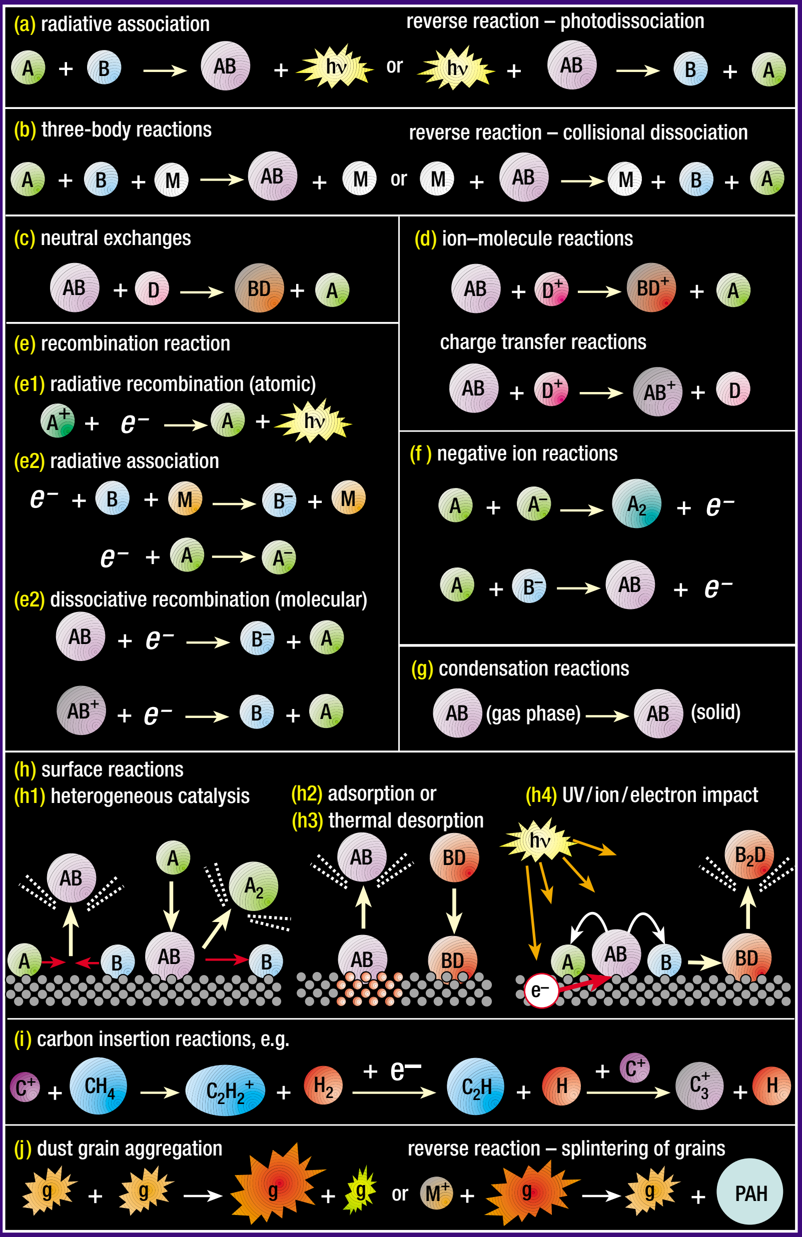
Table 1: Molecules in space

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

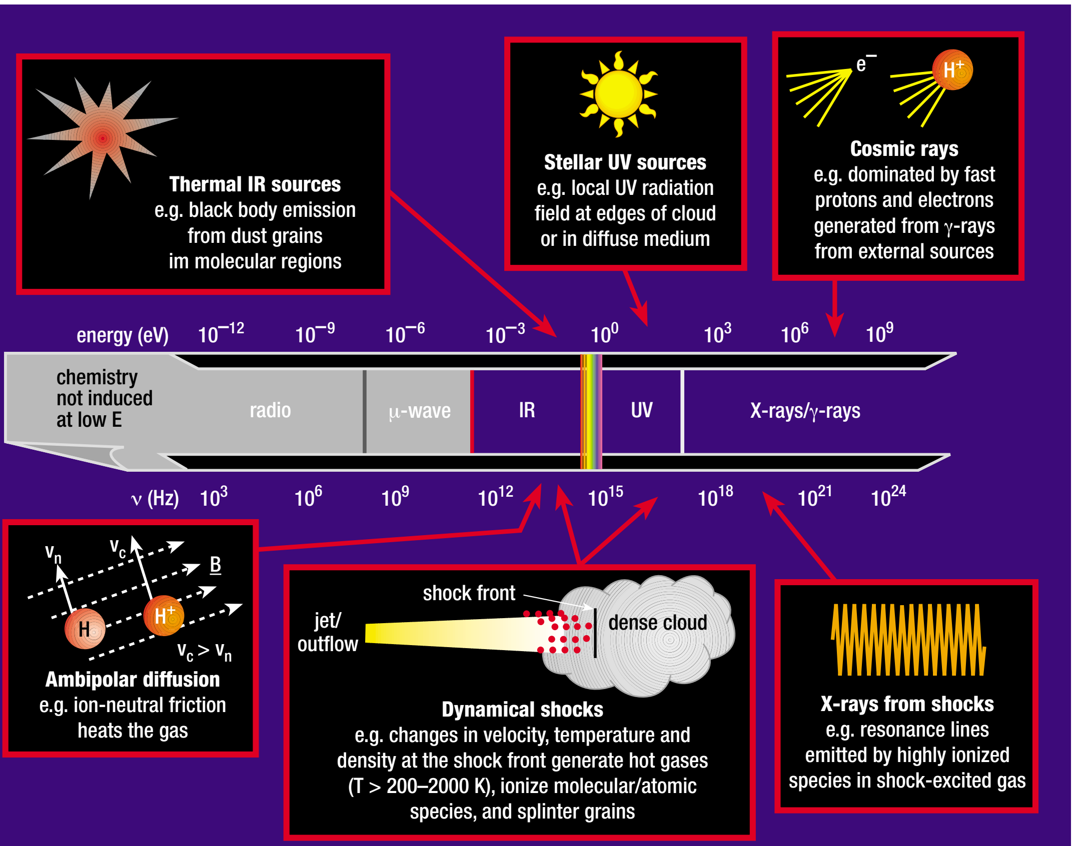
Diatomic	Triatomic	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	13 atoms
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$		
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	NH_2CH_2COOH		
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH			
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	CH_2OHCHO	HC_7N			
CH^+	HCN	C_2H_2	CH_2CN	CH_3OH	NH_2CH_3		C_8H			
CN	HCO	CH_2D^+	CH_4	CH_3SH	c-C_2H_4O					
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	CH_2CHOH					
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO						
CP	HOC^+	HNCO	HCOOH	NH_2CHO						
CSi	H_2O	HNCS	H_2CHN	C_5N						
HCl	H_2S	$HOCO^+$	H_2C_2O							
KCl	HNC	H_2CO	H_2NCN							
NH	HNO	H_2CN	HNC_3							
NO	MgCN	H_2CS	SiH_4							
NS	MgNC	H_3O^+	H_2COH^+							
NaCl	N_2H^+	NH_3								
OH	N_2O	SiC_3								
PN	NaCN									
SO	OCS									
SO^+	SO_2									
SiN	c-SiC_2									
SiO	CO_2									
SiS	NH_2									
CS	H_3^+									
HF	SiCN									
SH										

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



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.



2: The key energy sources for chemical reactions in interstellar and circumstellar regions.

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 (H_2). This is not only because H_2 is by far the most abundant molecule in the universe, but also because H_2 nearly always plays a key role in the formation of all the other molecular species. In the cool interstellar medium, this $2H \rightarrow H_2$ conversion occurs through surface catalysis (reaction h1 in figure 1), though other reaction mechanisms were important in the dust-free early universe (see below).

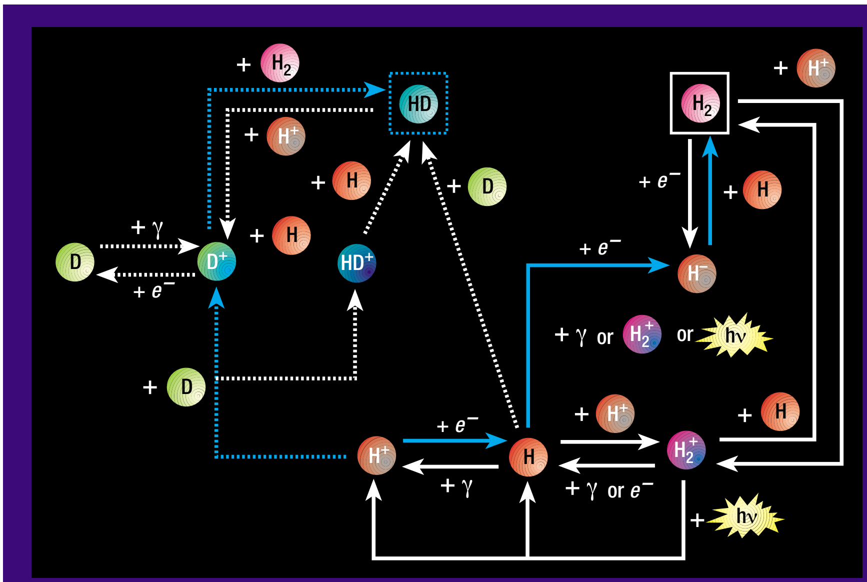
In high-density environments such as stellar photospheres and planetary atmospheres, three-body associations (figure 1b) dominate. At low temperatures, neutral atoms and molecules tend to be unreactive with H_2 and the chemistry is driven largely by ion–molecule reactions (figure 1d). The ionization sources are stellar UV radiation, cosmic ray impact, or X-rays from black holes or high-speed shocks in gas flows. In dark clouds, H_2 is ionized by cosmic rays to H_2^+, which reacts rapidly with other H_2 molecules to form H_3^+, 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 H_2O and O_2 (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, CH_3OH, these networks fail to supply it in the quantities detected; and schemes to make the next member of the family, ethanol, C_2H_5OH, 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 graphitic 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 H_2. In fact they experience a barrier as they approach the H_2 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-



3: Chemical routes to H_2 (right) and HD (left) formation in the early universe. Hydrogen chemistry was significantly more important to the evolution of the early universe than deuterium chemistry. Gas phase processes converted about 1% of the atomic H into H_2 (solid blue arrows). Competing mechanisms and intermediate steps in H_2 chemistry are shown by white arrows. A tiny amount of the H_2 was further processed to HD, via D^+ ions (dotted blue arrows). Hydrogen and deuterium chemistry are linked (dotted white arrows). Reagents are shown over arrows: $+e^-$, electrons; $+\gamma$, cosmic rays; $+h\nu$, photons; +H, H^+, H_2^+ atoms and ions.

Table 2: Timescales in interstellar clouds and star-forming regions

Process	Mechanism	Timescale[1, 2, 3] (yr)	Timescale (yr) in ISM where $n=10^{10}$ m^{-3}
chemistry	cosmic-ray ionization	$\approx 3\times10^5$	$\approx 3\times10^5$
freeze-out	gas–grain collisions	$\approx(3\times10^5)/n$	$\approx 3\times10^5$
cooling	radiative emission	$\approx 10^6$	$\approx 10^6$
collapse	gravity	$\approx 10^{11}/\sqrt{n}$	$\approx 10^6$
ambipolar diffusion	ion-neutral drift	$\approx 4\times10^5\,[X^{(i)}/10^{-8}]$	$\approx 4\times10^5$

1 Assuming ζ (cosmic-ray ionization rate) $=10^{-17}$ H-atoms s^{-1}
2 n = number density of H nuclei (atomic and molecular H) measured in units of 10^{10} m^{-3}
3 $X^{(i)}$ = total number density of ions/n

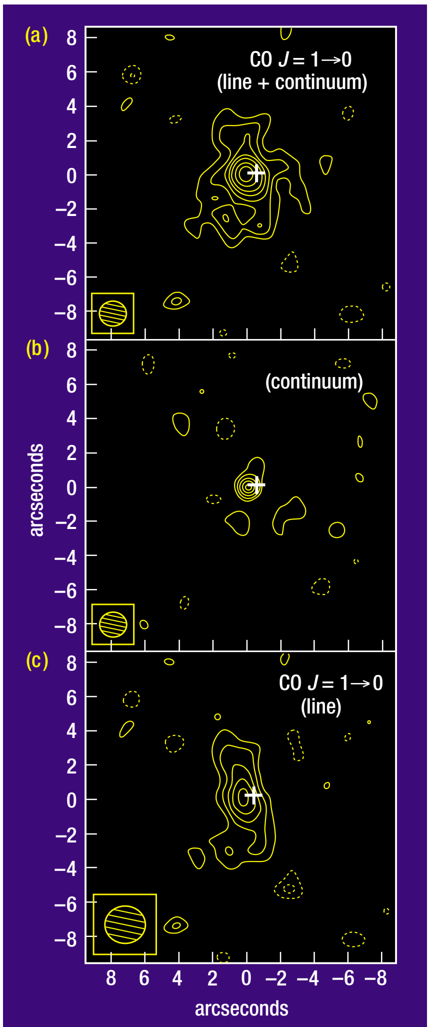
cal kinetics are complicated further by steric factors; the orientation between the reacting parties can be crucial in determining whether or not a reaction occurs, even if there is sufficient energy to overcome the reaction barrier. Reactions may occur if some ions are created, because ions often react easily with molecules, without having to overcome a reaction barrier. In each case, energy is required to drive the chemical network, either in generating ions and radicals or in overcoming the reaction barriers. Without an input of energy, the astronomical chemical engine would simply grind to a halt. So what are the possible sources of energy to drive the cosmic chemical engine? These are shown in figure 2. Each has its own specific effect and generates a characteristic chemistry. It is like the difference between diesel and petrol engines. In the diesel engine, the initial energy is generated by the rapid adiabatic compression of the fuel–air mixture, while in the petrol engine it is the spark that ignites the reactions. The outputs are chemically different, as any commuter knows. In cosmic chemistry, for example, chemistry in shock-heated gas produces molecules (such as some sulphur-bearing species) that are rarely formed in chemistry driven by slow cosmic-ray ionization. Direct thermal effects can come from direct heating of gas and dust by light from a nearby star; this heating may evaporate previously-formed ices and give a characteristic chemistry that we find in high-mass 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 10^8 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.

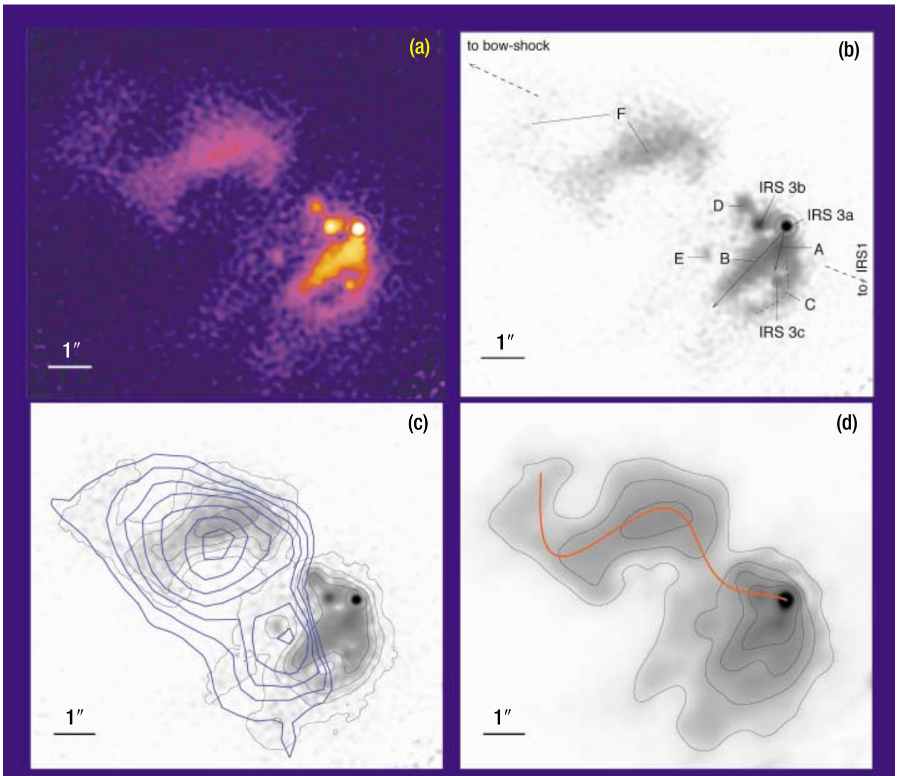
Molecules at high redshifts

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 and a tiny amount of this H_2 was further processed to HD. Molecular hydrogen possesses low-lying energy levels (much lower than the atomic species) associated with rotational and vibrational molecular motion. Collisional excitation of these levels, followed by radiative relaxation, cooled the gas to about 100 K. H_2 in the early



4: The detection of molecular gas beyond our own galaxy. These images show molecular gas stretching across about 30kpc in and around APM08279+5255, a galaxy at $z = 3.912$, as traced by CO $J = 1 \rightarrow 0$ and continuum emission from the active nucleus. (a) Naturally weighted maps at observed frequency 23.4649 GHz corresponding to CO $J = 1 \rightarrow 0$ (rest frequency 115.2712 GHz). (b) Observed frequency 23.3649 GHz, corresponding to the adjacent continuum emission. The beam, identical in both maps, is shown bottom left. Contours are at −3, −2, 2, 3, 4, 5, 6, 8, 10 times 40 microJy/beam. (c) Naturally weighted map of CO $J = 1 \rightarrow 0$ with the continuum source subtracted. Contours this time are at −3, −2, 2, 3, 4, 5, 6. Reproduced by permission from *Nature* (Papadopoulos *et al.* 2001 **409** 58) © 2001 Macmillan Magazines Ltd.

universe was therefore able to cool the gas, reducing the pressure by a factor of about 100 compared to that at $z = 1300$, and the resulting gravitational collapse led to protogalaxy formation by about 400 million years after the Big Bang (redshift of about 10). Once the first stars were formed, stellar winds and explosions created a much more complex environment, in which H_2 and its effects were even more pronounced. Therefore, H_2 should be associated with the most distant galaxies.



5: The embedded structure within a dense molecular core in which a star of about one solar mass has just formed. These images are of S140 IRS3. In all images north is up and east is to the left.
(a) Colour representation of K-band (about 2μ) speckle image of S140 IRS3. Blue areas are 40 times fainter than the peak intensity.
(b) Greyscale representation of the K-band speckle image with embedded structure indicated. The dashed-lined arrow near the right edge of the image indicates the direction towards S140 IRS1.
(c) Greyscale representation of the K-band speckle image. The black contour lines show a smoothed representation of this image in order to pronounce the structure of the faintest diffuse emission features. Thick blue contours show the continuum-subtracted H_2 emission line image. Contours are drawn at 8, 10, 12, 14, 17, 20 and 22 times the rms noise level above the median in the continuum-subtracted image.
(d) Greyscale and contour representation of the K-band speckle reconstructed with a reduced resolution to show the fainter details.
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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

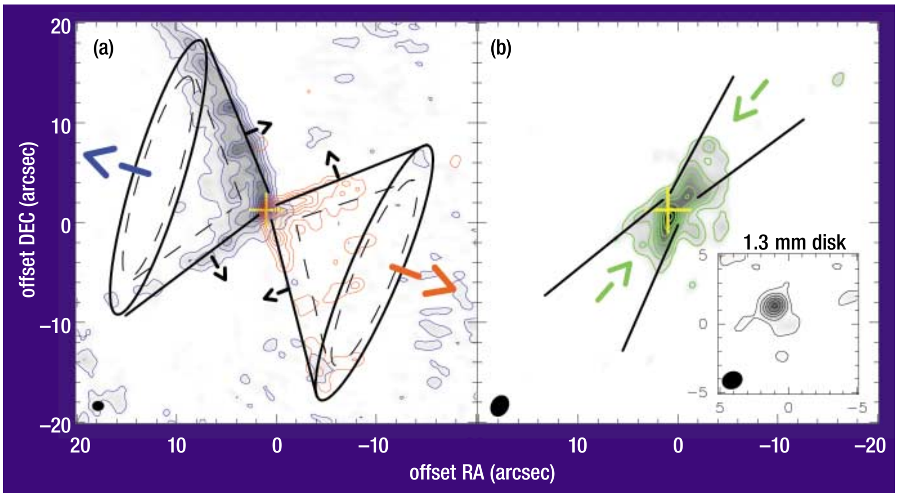
Our knowledge of astrochemistry grew out of observational and theoretical studies of interstellar clouds. Initially the emphasis was on diffuse clouds that are pervaded by stellar UV photons and consequently have rather low abundances of molecules. However, dark clouds, opaque to starlight, were soon 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 H_2 to be an effective coolant, as it was in pre-galactic gas clouds, so the most important coolant molecules are 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_3CN 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).



6: An overview of the outflow–infall interaction in IRS1, a young protostar in a dense core in B5.
(a) Integrated ^{12}CO J = 2→1 emission in the wings of the high-velocity line traces the limb-brightened molecular outflow cones. The values of the first contours and contour intervals are 0.45 and 0.9 Jy km s^{-1} per beam for the blue lobe, and 1.2 and 2.4 Jy km s^{-1} per beam for the red lobe. The red and blue arrows denote red- and blue-shifted lobes, and the widening of the outflow cones is indicated by the short black arrows.
(b) The central low-velocity C^{18}O J = 2→1 emission traces the infall region. The values of the first contour and contour interval are 0.24 Jy km s^{-1} per beam. The infall is confined to a flared disk (approximately) 30° wide, as indicated. The diameter of the disk is (approximately) 3500 AU and its thickness varies from 850 AU at the centre to 1700 AU at the edge. The inset in (b) shows the 1.3 mm continuum emission which traces the central pre-protoplanetary disk; the first contour and contour interval are 5 mJy per beam.
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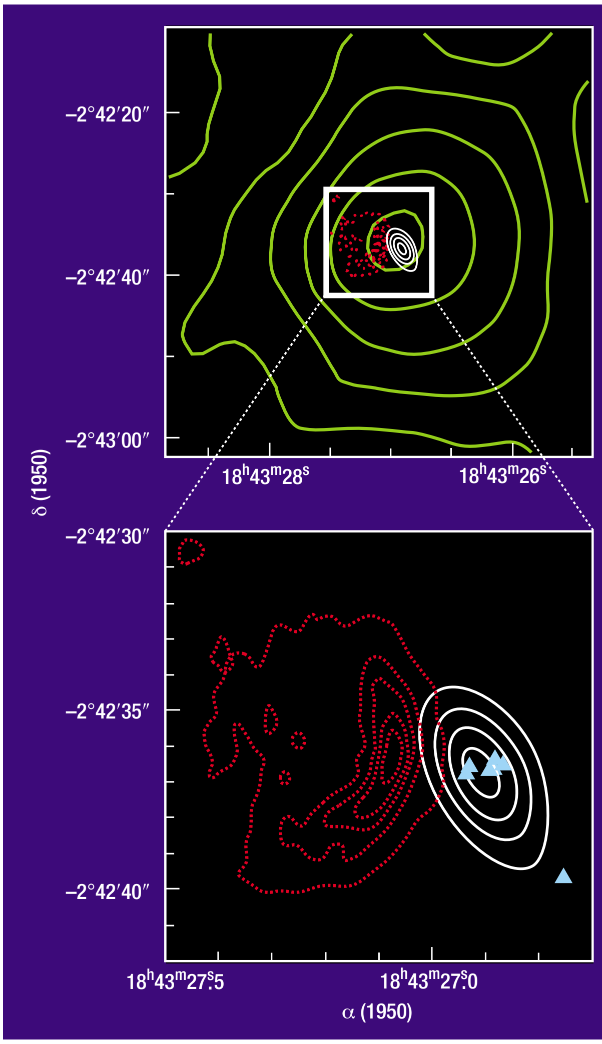
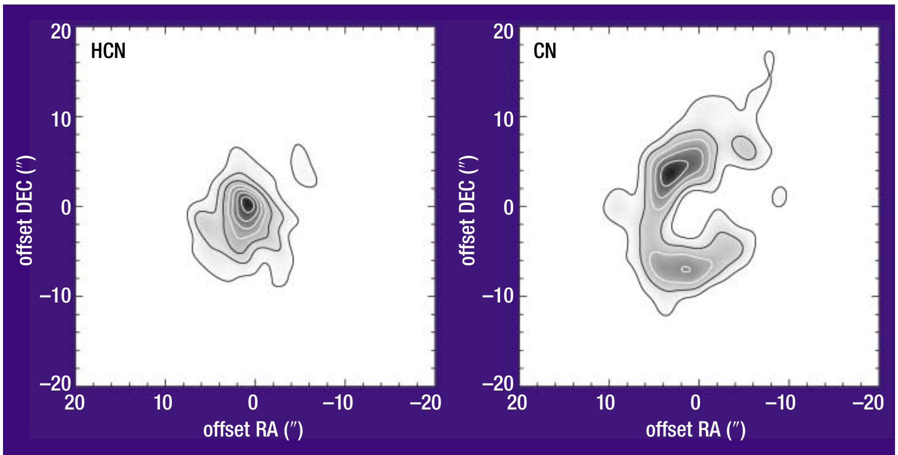


7: The desorption of complex molecules from icy grains in Hot Cores. This figure shows a comparison between emission features from C^{34}S ($J = 5 \rightarrow 4$) (green contours), CH_3CN ($J = 6 \rightarrow 5$) (white contours), and the 1.3 mm continuum (dotted contours) towards the ultra-compact HII region G29.96–0.02. The lower plot shows an enlargement of the Hot Core region. The triangles indicate the positions of the H_2O masers. These clumps are around 1 pc across. Reproduced by permission of University of Arizona Press from *Hot Molecular Cores and the Earliest Stages of High-Mass Star Formation* by S Kurtz, R Cesaroni, F Churchwell, P Hofner and C M Walmsley, from *Protostars and Planets IV*, edited by V Mannings, A P Boss and S S Russell, © 2000 The Arizona Board of Regents.



8: The spatial separation of 440 pc between parent and daughter molecules in circumstellar envelopes of cool stars. These are emission maps of the circumstellar envelope around the C-star CIT6 for the parent molecule HCN ($J=1\rightarrow0$) on the left, and the daughter molecule CN ($N=1\rightarrow0$) on the right. The maps show that HCN is concentrated in the photosphere of the central star, whereas CN (the photodissociation product of HCN) is concentrated in a shell around the star.
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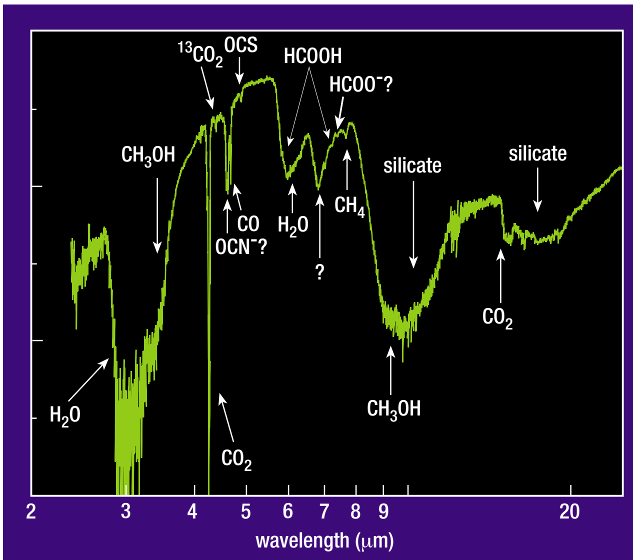

9: The detection and identification of solid-state features in interstellar clouds. This image shows the complete SWS flux-spectrum of W33a, a deeply embedded object. Those features which have been identified with the assistance of laboratory studies are highlighted – key unassigned features are also indicated.
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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 C_2H_2 and C_2H. 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_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_2O 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 $HC_{(2n+1)}N$, 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

Table 3: Molecules in ice

A comparison of molecular abundances in interstellar ices and cometary systems (adapted from Crovisier 1998).

Molecule	Cometary ices Hale-Bopp	Other comets	Interstellar ices Dark clouds (Elias 16)	Embedded YSOs Low Mass (Elias 29)	High Mass (W33a)
H_2O	100	100	100	100	100
CO	20	6–30	25	5.6	9
CO_2	6–20	2–10	18	22	14
CH_4	0.6	0.7	1–2	<1.6	2
CH_3OH	2	1–7	<3	<4	22
H_2CO	1	0.2–1	2–6?	–	1.7–7
OCS	0.5	0.1	0.2	<0.08	0.3
NH_3	0.7–0.18	0.5	<10	<9.2	15
C_2H_6	0.3	0.4	–	–	–
HCOOH	0.06	–	3?	–	0.4–2
OCN^-/XCN	–	–	<2	0.24	3–10
HCN	0.25	0.05–0.2	0.5–10	–	<3
HNC	0.04	0.01	–	–	–
HNCO	0.06–0.1	0.07	–	–	–
C_2H_2	0.1	0.5	–	–	–
CH_3CN	0.02	0.01	–	–	–
$HCOOCH_3$	0.06	–	–	–	–
HC_3N	0.02	–	–	–	–
NH_2CHO	0.01	–	–	–	–
H_2S	1.5	0.2–1.5	–	–	–
H_2CS	0.02	–	–	–	–
SO	0.2–0.8	–	–	–	–
SO_2	0.1	–	–	–	–
O_3	–	–	<2	–	–
H_2	?	?	1	?	?
N_2	?	?	?	?	?
O_2	?	?	?	?	?

Note that all abundances are expressed as a percentage as compared to the abundance of H_2O ice. – indicates a current lack of information. ? indicates ice expected to be present but not observable.

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 repositories 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.

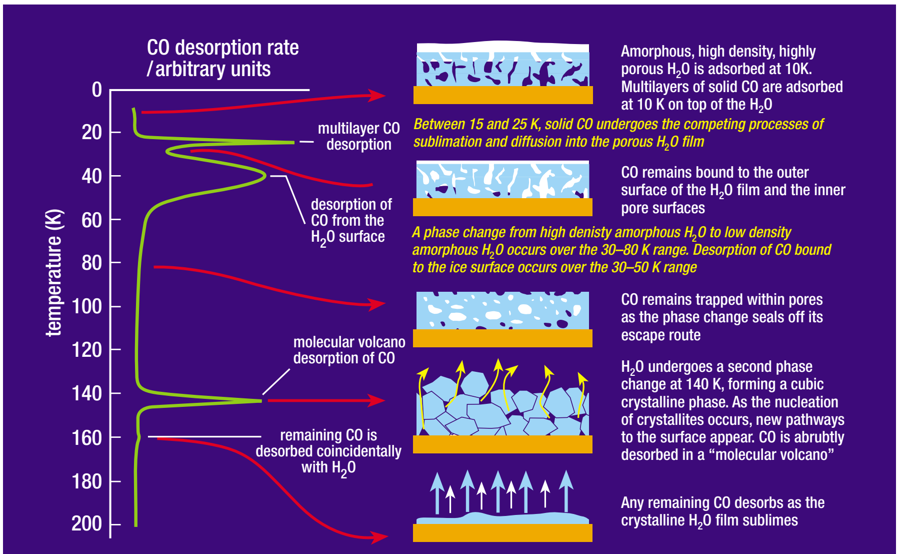
Of course, the atmospheres that we now find on planets are not necessarily the primitive atmospheres that were chemically related to interstellar ices. The atmospheres have been heavily processed, most notably, in the case of Earth's atmosphere, by living organisms that converted a largely chemically reducing CO_2 atmosphere to a chemically oxidizing one of O_2 and N_2.

The composition of interstellar ices has been inferred by matching spectra recorded with the Infrared Space Observatory (ISO) Short Wavelength 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.

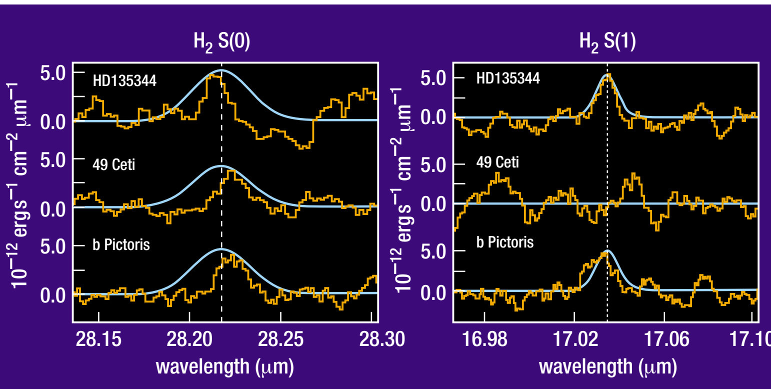
In regions where the interstellar ice is exposed to UV photons, cosmic rays and electron or ion bombardment, then the ice can be processed to other solid phases, and chemical reactions can be induced within the solid state. Such processing generates radicals, secondary electrons and ions in the ices, which then react further to produce more complex species such as CH_3OH and CH_4 (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 H_2O 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 H_2O ice, revealing that the spectroscopy and desorption kinetics of such systems are even more complex than we thought previously (Collings *et al.* 2002).



10: The adsorption, diffusion and desorption behaviour of CO on H_2O ice under laboratory "pseudo interstellar" conditions (adapted from Collings *et al.* 2002). Cyan is H_2O, white CO and purple empty.



11: The high gas densities in protoplanetary disks. This figure shows spectra of the lowest pure rotational molecular hydrogen transitions towards β-Pictoris, 49 Ceti, and HD135344 debris disks, taken with the Infrared Space Observatory. The dashed vertical line depicts the rest wavelengths of the H_2 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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Both these 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 the disk. In a recent remarkable observation, highly forbidden rotational transitions were detected towards β-Pictoris, 49 Ceti and HD135344, with the implication that large amounts of gas are present in those disks (see figure 11). The implication of this is that there is enough molecular hydrogen present to form giant planets that apparently are abundant in extrasolar planetary systems (Thi *et al.* 2001). The study of these protoplanetary disks is one of the newest areas of astrochemistry. Deep inside the disks, most material more massive than H_2 will be frozen on to the dust, but closer to the protostar and nearer the surface of the disk, stellar radiation will warm the dust, evaporate the ices and promote an active photon-driven chemistry. It is one of the aims of astrochemistry to identify tracer molecules from such processes that will, with the next generation of telescopes, help to solve the problem of planet formation.

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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