

CHAPTER 1

Astrochemistry: From Molecular Clouds To Planetary Systems

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1. Introduction

There are many different regions in the Cosmos - covering all regimes of physical conditions. What they all have in common, however, is that they are probed by observing molecules, and therefore, chemistry. Figure 1 shows schematically the life of cosmic material, which is recycled from the interstellar medium through stars and back again. Material processed during a star's life is subsequently ejected back into the interstellar medium when the star dies. All the atoms of heavy elements (e.g. carbon, oxygen etc.) in the Universe today, of which we too are made, were formed in stars. Studies of the various astrophysical regions depicted are almost separate disciplines today, but in reality they are all connected - by time. In this chapter I'll describe aspects of the chemistry in a subsection of the Figure, specifically in the transition between molecular clouds and planetary systems, and what we can hope to learn about this transition by studying chemistry.

2. The Interstellar Medium and Molecular Clouds

Many molecular species have been observed in the interstellar medium via ground-based and space-borne telescopes. The first molecule to be detected was CH, a simple diatomic, way back in 1937. The most abundant molecule in interstellar space after molecular hydrogen (H_2) is another diatomic, carbon monoxide (CO). At the other end of the molecular size scale, organic molecules such as ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3)

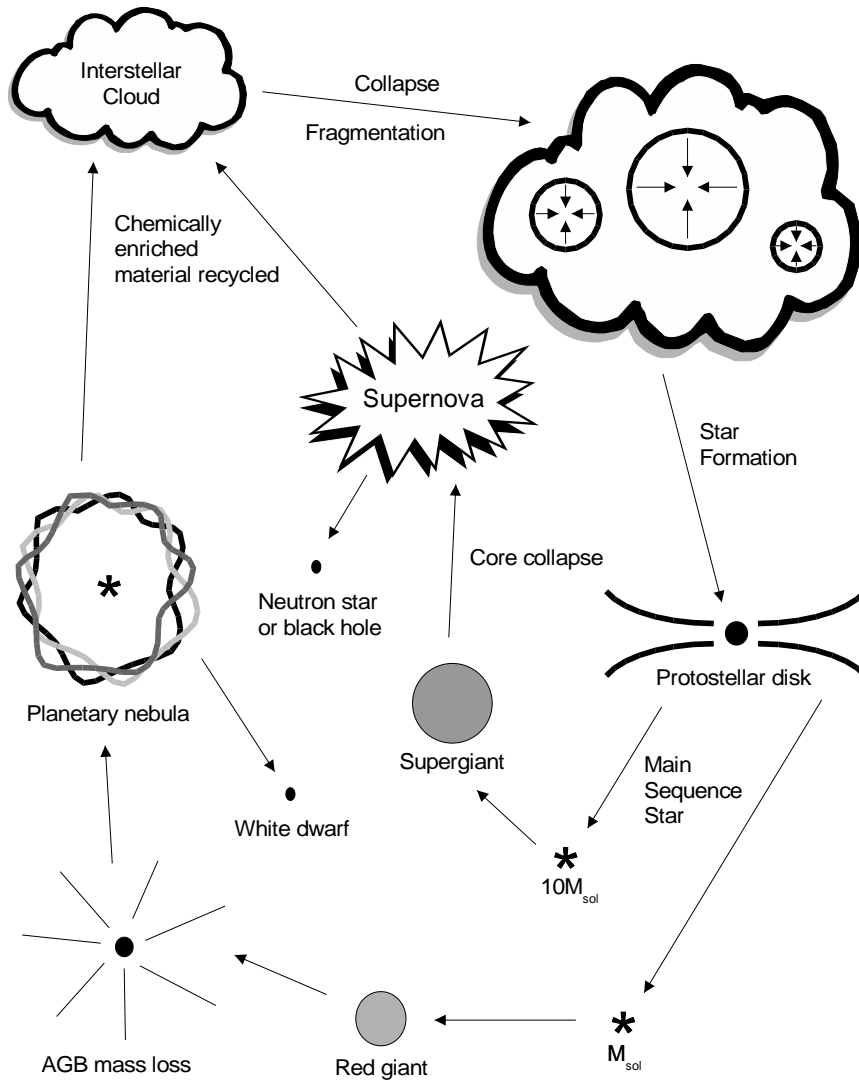


Fig. 1. Cosmic recycling. Material in the Universe is recycled through the interstellar medium, stars, and back again.

have been detected. Recently, astronomers have also identified a simple sugar (glycolaldehyde; CH_2OHCHO), and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) - the simplest amino acid. Although molecules (and hence chemical processes) are observed in many astronomical sources, there are three main regions of differing physical condition in which interstellar molecules are prevalent. These are *cold dark clouds*, which are so-called because they are at a temperature of around 10 K (hence *cold*) and are dense enough that their interiors are shielded from UV radiation by H_2 and dust (hence *dark*). This is important because it means that many molecules can exist in them which would otherwise be *photodissociated*, that is, destroyed by radiation. Secondly, *hot molecular cores*, which range in temperature from 50-300 K and have density in excess of 10^6 hydrogen molecules cm^{-3} , are rich sources of molecular line emission. These objects are associated with very young stars, and many of the complex organic molecules detected have only been observed in them. Finally, many molecules are detected in the *circumstellar envelopes* of old (so-called *late-type*) stars. Several metal-bearing molecules such as magnesium cyanide and isocyanide (MgCN ; MgNC) have only been detected in these regions so far.

2.1. Observations of interstellar molecules

Table 1 shows an up-to-date list of molecules detected in interstellar space and comets, taken from astrochemistry.net. It is immediately apparent that interstellar space contains many *organic* (loosely, carbon-containing) molecules. There are difficulties associated with identifying molecules from their astronomical spectra, and therefore the organic molecules observed are not complex by terrestrial standards. Certain molecules are easier to detect than others, and so in observational astronomy there are *selection effects*. The energy level structure of linear carbon chain molecules, for example, is simple enough that for a given energy, there are not many ways for it to be distributed (the *partition function* is small), and so individual spectral lines can be quite strong. That is why the largest molecule unambiguously detected in space is HC_{11}N , a cyanopolyne species which was detected astronomically before it could be produced and identified in the laboratory. When we move to non-linear molecules, the energy level structure becomes vastly more complicated, so much so that an 11-atom non-linear molecule would need to be about 10 000 times more abundant than an equivalent 11-atom linear molecule to produce lines of similar strength. The astronomical detection of molecules is also hampered by the atmosphere, which is why

astronomers had to wait for space-based observatories like The Infrared Space Observatory (ISO) to detect carbon dioxide (CO_2). Table 1 is biased therefore towards diatomics, linear carbon-chains and simple non-linear organics. Many other molecules await detection - indeed new molecules are detected regularly - but some will remain undetected because their lines are too weak. Similarly, there are molecules which we know must be present, but which are impossible to detect because of their structure. The abundances of such molecules are inferred from observations of species which we think to be very closely related chemically. Also detected are many unidentified lines which have so far defied assignment, perhaps because their carrier's spectrum has not yet been measured or calculated. Table 1 lists only gas-phase detections, but some molecules have been observed in the solid-state - that is, as the ice component of interstellar dust grains. They were detected through their infrared absorption features and they include CO_2 , CH_4 , H_2O , H_2CO , NH_3 , CH_3OH and HCOOH .

2.2. Gas-phase astrochemistry

As more and more molecules are observed, theoretical astrochemistry has to evolve and adapt to explain how these molecules form and how they can persist. Making an astrochemical model which contains enough chemistry to form all of the molecules in Table 1 is at the bleeding edge of research in this discipline, but the underlying principles which make it possible to have a rich chemistry in the gas-phase have been understood for about 30 years and are fairly simple. Nearly all of the gas in a dark cloud is in the form of molecular hydrogen and because of this, we often measure the abundance of molecules *relative* to H_2 . The next most abundant molecule, CO , is present at a level of about 0.0001 relative to H_2 . It has a *fractional abundance* of 0.0001. Helium atoms are present in interstellar gas too, typically at a fractional abundance of 0.1. Cosmic rays are high energy protons which pervade space - they can penetrate the interior of dark clouds where other radiation cannot go, and ionise H_2 , H and He . Due to the low densities and temperatures in the interstellar medium, the only efficient chemical reactions between molecules are two-body processes which have small or no activation barriers. These are mainly *ion-neutral* reactions, which proceed at rates of around $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This rate is independent of temperature, so that room-temperature experimental data can be directly applied to low-temperature astrochemistry. Reactions between neutrals can also occur, but *neutral-neutral* reactions are about a hundred times slower than

Astrochemistry

Table 1. Detected interstellar, circumstellar and cometary molecules, by number of constituent atoms and ordered by mass. *Source: astrochemistry.net.*

	2	3	4	5	6	7	8	≥ 9
H ₂	SiN	H ⁺	CH ₃	CH ₄	C ₂ H ₄	CH ₃ NH ₂	CH ₃ CH ₃	CH ₃ CH ₂ OH
CH	CP	CH ₂	NH ₃	NH ₄ ⁺	CH ₃ CN	CH ₃ CCH	CH ₂ OHCHO	CH ₃ OCH ₃
CH ⁺	CS	NH ₂	H ₃ O ⁺	CH ₂ NH	CH ₃ NC	c-C ₂ H ₄ O	CH ₃ COOH	CH ₃ CH ₂ CN
NH	SiO	H ₂ O	C ₂ H ₂	H ₃ CO ⁺	NH ₂ CHO	CH ₃ CHO	HCOOCH ₃	CH ₃ COCH ₃
OH	PN	H ₂ O ⁺	H ₂ CN	CH ₃ OH	CH ₃ SH	CH ₂ CHCN	CH ₃ C ₃ N	CH ₃ C ₄ H
OH ⁺	AlF	C ₂ H	HCNH ⁺	SiH ₄	H ₂ CCCC	C ₆ H	C ₆ H ₂	NH ₂ CH ₂ COOH
HF	NS	HGN	H ₂ CO	c-C ₃ H ₂	H ₂ CCCC	HC ₅ N	HC ₆ H	C ₆ H ₆
C ₂	SO	HNC	c-C ₃ H	H ₂ CCC	HCCCGH	HC ₃ N ⁺	C ₇ H	C ₈ H
CN	SO ⁺	HCO	l-C ₃ H	CH ₂ CN	H ₂ C ₃ N ⁺	HC ₂ CHO	HC ₇ N	HC ₉ N
CN ⁺	NaCl	HCO ⁺	HCCN	H ₂ CCO	C ₅ H	C ₅ H	HC ₉ N	HC ₁₁ N
CO	SiS	N ₂ H ⁺	HNCO	NH ₂ CN	C ₅ N			
CO ⁺	AlCl	HOC ⁺	HNCO ⁻	HCOOH				
N ₂	S ₂	HNO	HOCO ⁺	C ₄ H				
SiH	FeO	H ₂ S	H ₂ CS ⁺	HC ₃ N				
NO	KCl	H ₂ S ⁺	C ₃ N	HCCNC				
HS		C ₃	C ₃ O	HNCCC				
HS ⁺		C ₂ O	HNCS	C ₅				
HCl		CO ₂	SiC ₃	SiC ₄				
SiC		CO ₂ ⁺	C ₃ S					

ion-neutral reactions, and they often possess activation barriers. In general it is not easy to determine whether a neutral-neutral reaction will proceed under interstellar conditions, so experimental or theoretical data is required in this case. One rapid reaction type is *dissociative recombination*, where an ion (e.g. HCO^+) is broken apart by an electron. These reactions typically occur at a rate of $10^{-6} \text{ cm}^3 \text{ s}^{-1}$, but they are temperature dependent and so in general experimental data is required. Experiments are particularly important for this class of reactions because they can determine the *branching ratios* of the reaction. As an example, the dissociative recombination of N_2H^+ has three possible exit channels: $\text{N} + \text{N} + \text{H}$, $\text{N}_2 + \text{H}$ and $\text{N} + \text{NH}$. Before the reaction was measured in the laboratory, astrochemists assumed that the reaction always produced $\text{N}_2 + \text{H}$. Recent measurements have found that this only happens 35% of the time, whereas 65% of the time the exit channel is $\text{N} + \text{NH}$, so our models have to be adjusted accordingly, and the consequences examined. There is a close interaction between observation, theory and laboratory experiment in astrochemistry, and the cycle between them is one of the field's most attractive features.

For many molecules, their formation in the gas-phase is via the dissociative recombination of a precursor ion. That is, if you want to form a particular molecule by gas-phase chemistry, you first form its *protonated* counterpart, and recombine it. Molecular hydrogen is so abundant that anything that can react with it does so very efficiently, so for simple examples involving species like water, ammonia or methane, the problem reduces to initiating the chemistry, or, creating the initial ion. As an example, consider the gas-phase formation of water. The last step is the recombination of H_3O^+ (protonated water) with an electron, producing H_2O and H . We can form H_3O^+ by successive reaction of O^+ with H_2 : $\text{O}^+ \longrightarrow \text{OH}^+ \longrightarrow \text{OH}_2^+ \longrightarrow \text{OH}_3^+$, where each reaction also produces a hydrogen atom. The problem therefore reduces to forming either O^+ or OH^+ . Since H_2 is the dominant form of hydrogen in a dark cloud, the product of its cosmic ray ionisation, H_2^+ , will react straight away with H_2 again to form H_3^+ , the simplest molecular ion. A given ion will transfer a proton to anything which has a *proton affinity* greater than it. For H_3^+ , that is most things, the notable exceptions being atomic nitrogen and molecular oxygen. For the formation of water, this means that OH^+ can be produced by reaction of H_3^+ with atomic oxygen. The fact that H_3^+ is so abundant explains why molecular ions like HCO^+ and N_2H^+ are readily observed - they are the products of proton transfer between H_3^+ and CO and N_2 . In essence it is the low proton affinity of H_2 which drives interstellar chemistry. The interstellar detection of

H_3^+ was finally made in 1996 with the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea, Hawai'i. This was an important event because it confirmed that our understanding of the chemistry in dark clouds is largely correct, as the molecule was observed at an abundance predicted by models. Subsequently, however, it was detected in diffuse clouds with an unexpected abundance, indicating that our understanding of the chemistry in those objects is incomplete.

Of course, molecules are not only formed, they are also destroyed. Reaction with H_3^+ partly returns a species to its protonated form from where it can recombine again, but the reaction can also dissociate the molecule. The reaction of a species with He^+ is even more destructive, because it isn't possible for a species to react with He^+ to produce the protonated form and therefore the reaction is always dissociative (incidentally, He^+ does not react with H_2). This means that the cosmic ray ionisation of helium (which produces He^+) is a critical reaction for interstellar chemistry. If the rate of this reaction is changed even by a factor of 2 - a small error for astronomers - the calculated abundances of nearly all species are significantly affected. In fact studies have shown that this is the reaction to which the overall abundances of species are most sensitive. As well as destruction by chemical reactions, molecules can also be destroyed by radiation, and they can even be removed completely from the gas-phase by sticking to a grain surface, a process known as adsorption or more informally, *freeze-out*.

To build a model of gas-phase chemistry in a dark cloud, one obviously needs a source of reactions and their *rate coefficients*. The main source used by the community is the publicly available UMIST Database for Astrochemistry, which resides online at udfa.net. This database contains reaction data for around 4200 chemical reactions involving around 400 atomic and molecular species, and includes all the processes discussed above and many more besides. Once the reaction network is specified for the given problem, software exists which can translate the network into a system of coupled ordinary differential equations describing the rate of change of the abundance of each species. Since the rate coefficients depend on temperature, density, the amount of UV radiation (for photoprocesses) and on the cosmic ray ionisation rate, these parameters must be given. Once the initial abundances of species are determined, the system of ODEs can be integrated in time using library routines, and the chemical evolution of the object be found. It is a remarkable feature of such a system that after around a million years (for a dark cloud model at least) the chemistry approaches a *steady state*, where the abundances of all the species in the model remain constant. If one

is only interested in these abundances, the integration can be done away with and a non-linear system of algebraic equations solved instead. This is usually done using a generalisation of Newton's root finding algorithm.

2.3. *Gas-grain and solid state astrochemistry*

Some of the molecules in Table 1 are difficult to form via gas-phase reactions. H_2 , in fact, is one such molecule, but there are other more complex ones too. These include formaldehyde (methanal; H_2CO) and methanol (CH_3OH). The observed abundances of these molecules in certain regions of the interstellar medium are greater than those that can be produced by gas-phase chemistry alone, and so reactions on grain surfaces are needed to form these species. We know for certain that these species are present in ice mantles, because they have been observed directly. It has been demonstrated experimentally that they can form by successive hydrogenation of CO molecules, so that $\text{CO} \rightarrow \text{HCO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$. This process is most efficient at a temperature of 15 K, while at 20 K, the process is inefficient. Hence, in regions where larger abundances of methanol and formaldehyde are observed, we assume that they were made on grains and then some process returned the ice mantle species to the gas phase. This process can be thermal desorption, or a non-thermal process like cosmic-ray heating or grain mantle explosions. The simultaneous calculation of realistic solid-state and gas-grain chemistry is currently slightly out of reach - we expect such models to be forthcoming within a few years. The reason for this is that in order to model this chemistry properly, the stochastic nature of gas-grain interaction has to be considered. In pure gas-phase models, the chemical abundances are found in a deterministic way using differential equations, as described above. In grain surface chemistry though, the limiting factor is the accretion of gas-phase species onto grains, which is inherently stochastic. Initial attempts to include this chemistry in gas-phase models forced the gas-grain interaction into the framework of deterministic kinetics, which is unrealistic. Of course, it may turn out that this is a reasonable approximation to the full calculation in some cases.

2.4. *Interstellar Organic Chemistry*

Many complex organic molecules are observed in regions known as *hot molecular cores*. These objects are associated with high-mass star formation, and are hot enough (around 200 K) that the species in ice mantles on dust grains have been returned to the gas by sublimation. In regions

where ice mantles have been removed from their parent dust grains, we have conditions where we can expect both gas-phase and solid-state chemistry to contribute to the organic complexity in the gas. Instead of relying on solid-state astrochemistry to produce *every* species we can't explain by pure gas-phase chemistry, we can rely on the former to produce a few simpler *precursor* species which may then react in the warm gas to produce the more complex molecules. These simpler species are precisely those which are known to exist and be efficiently formed on grain surfaces, including methanol and formaldehyde. Models which evaporate appropriate quantities of these species from dust grains produce much higher abundances of more complex organics (e.g. ethanol) than pure gas-phase models, bringing the models into closer agreement with observations. Methanol, when protonated, can transfer an alkyl cation to other simple evaporated neutral species to form species like methyl formate, acetic acid and dimethyl ether, all of which are observed in hot cores. The proposed formation mechanism for interstellar glycine is that the precursor molecule NH_2OH (hydroxylamine) is desorbed from grain surfaces and, when protonated, reacts with acetic acid to form protonated glycine, which then recombines. Of course, to confirm the theory, the precursor molecule should be observed as well, and these observations are currently underway.

2.5. *Isotopic fractionation chemistry*

We also see many isotopically-substituted species in interstellar gas. For example, hydrogen cyanide (HCN) has been detected in its ^2H (deuterium), ^{13}C and ^{15}N forms as well as the main isotopomer $^1\text{H}^{12}\text{C}^{14}\text{N}$. Such observations can provide further information about the physical conditions in the interstellar medium, but are also useful for identifying chemical processes via isotopic labelling. Deuterium fractionation is especially useful in this regard due to its high sensitivity to temperature. The cosmic abundance of deuterium is about 0.00002 relative to hydrogen, but some molecules in interstellar clouds are observed to have D/H ratios orders of magnitude bigger than that. For example, the DCN/HCN ratio in a typical dark cloud may be around 0.01. This enhancement is a chemical effect which relies on low temperature to work. The deuterium is brought out of its reservoir in HD (the deuterated form of molecular hydrogen) by the reaction of HD with H_3^+ . The products of that reaction are H_2D^+ and H_2 . From there, the deuterium is propagated around the chemical network via ion-neutral reactions. The crucial fact is that the back-reaction between H_2D^+ and H_2 ,

which returns deuterium to HD, has an activation barrier. This means that at low temperatures ($T < 30$ K), the deuterium is permanently out of its reservoir and so the chemistry is *fractionated*.

Recently, multiply-deuterated species have also been detected. Amazingly, the fractionation ratio of fully-deuterated ammonia (ND_3/NH_3) was measured to be 0.0009 - almost 12 orders of magnitude higher than the expected value based on the cosmic D/H ratio! This, together with observations of D_2CO and various isotopomers of methanol and ammonia, has put real pressure on astrochemical models.

3. Prestellar and protostellar cores

Prestellar cores are regions of interstellar clouds which are in the first stage of low-mass star formation. They are collapsing, and so the density of the gas increases towards the centre, but there is as yet no star, so they are cold, still at the temperature of the cloud, around 10 K. The rate of 'freeze-out' of molecular species from gas to dust grain surface depends on the number of collisions of gas with dust, which depends on the velocity of the gas (and therefore the gas temperature) and the density. So as the density of the gas increases, the freeze-out rate increases too, and molecular material is removed from the gas-phase, in a specific order which depends on the binding energy of each species (see also the chapter by Malcolm Gray in this volume). In prestellar cores therefore, the opportunity exists to directly observe different stages of the core collapse by using observations of different species, and thereby work out how the collapse proceeds. Regions in the centres of such cores have been found where the CO abundance indicates that it has frozen out, and likewise CS, but there is still N_2 (inferred from N_2H^+) and ammonia.

One interesting aspect of observations of prestellar cores is that the level of deuterium fractionation in D_2CO , for example, is correlated with the amount of CO which is frozen out of the gas-phase. The $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratios observed in these sources range from 0.01 to 0.1 (remember, the cosmic D/H ratio is about 0.00001), with the higher ratios observed towards sources with greater CO depletion. It has been known theoretically since 1989, when the first deuterium fractionation models were constructed, that the fractionation increases with increasing gas-phase CO depletion, i.e. with increasing density. (In the following discussion, it may help to refer to Figure 2). This is because H_3^+ and H_2D^+ are mainly destroyed by neutral molecules like CO, but in cold, dense regions, this destruction diminishes

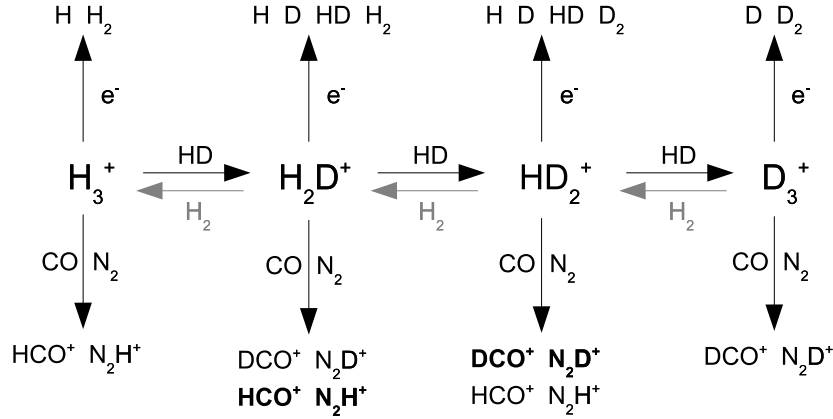


Fig. 2. Reactions involving H_3^+ and its deuterated isotopomers. They are formed by successive reaction with HD. At temperatures less than 30 K, the back-reactions with H_2 (grey arrows) do not happen, so the gas becomes fractionated. The main destructions of the ions are through dissociative recombination with electrons and ion-neutral reactions with abundant species.

due to the freeze-out of these species. The conversion from H_3^+ to H_2D^+ does not change however, and so there is relatively more deuterium in molecules. The problem is that the enhancements in multiply-deuterated species observed in prestellar and protostellar sources are too large for conventional models to reproduce even in light of this consideration. This is exacerbated in prestellar cores because they are not hot enough for ice mantles to have been evaporated, so grain surface chemistry cannot be relied upon to 'save us' by producing the high ratios in the solid-state. This prompted some researchers to reconsider the theory of gas-phase deuterium fractionation by adding the multiply-deuterated forms of H_3^+ (HD_2^+ and D_3^+) to their models. The results were impressive: the D_2CO ratios now agree much better with observations, while some ratios in other molecules now exceed those observed! Although it is no doubt still not the end of the story, this change represents a leap in our understanding of deuterium chemistry in cold gas. Given the importance of H_3^+ to interstellar chemistry in general, it may seem obvious in hindsight that the inclusion of these ions makes such a difference. Why then were they not included in models before? Normally, that is under normal interstellar cloud conditions, the dominant destruction of all the forms of H_3^+ is by recombination with electrons. We have to add a deuterium atom to an ion by reacting HD with it, and normally we

can expect these reactions to be uncompetitive compared to the dissociative recombination. In the case of dense gas however, the electron fraction is lower, and eventually the gas will reach a density where the recombination reaction is not dominant. In that special case, a cascade occurs from H_3^+ to D_3^+ (see Figure 2). Model calculations show that in fact D_3^+ will be the dominant (most abundant) ion in these dense regions. In the same way that H_3^+ readily donates a proton to most other species, D_3^+ donates a deuterium atom and this is how the fractionation in molecules gets so large. The fact that the deuterated forms of H_3^+ are abundant offers observational astrophysicists a unique probe of an otherwise hidden part of star formation - the very centre of the prestellar core. The density is so high that all molecules are completely frozen-out, but H_2D^+ and HD_2^+ will still be abundant in the gas (D_3^+ is harder to detect), and can be used to trace the physical conditions.

Another consequence of including these ions in models is that they increase the gas-phase atomic D/H ratio. This is important because of the deuterated forms of methanol and formaldehyde observed in protostellar sources. These are objects which are in the next stage of low-mass star formation after the prestellar phase. There is now a young star at the centre of the object, and the heat from it removes the ice mantles from dust grains. Since the deuterated forms of methanol observed are highly fractionated, and that these species are not formed efficiently in the gas-phase (see above), we need a way of fractionating them on the grain surface. The same is true of hydrogen sulphide (D_2S) which has also been observed with a high ratio. It turns out that the critical number for achieving high fractionation on grain surfaces is the accreting (freezing) gas-phase atomic D/H ratio. The accretion occurs during the prestellar phase, and those models with multiply-deuterated H_3^+ produce the ratio which models of the solid-state fractionation require to make the ratios in methanol agree with those observed in protostellar sources.

4. Protoplanetary Disks

As the molecular cloud core undergoes gravitational collapse, it is rotating. The enhanced centripetal effects flatten the protostellar object into a disk. The observational evidence is that most pre-main sequence objects have disks, and it is now widely accepted that planetary systems form from these disks by the agglomeration of particles. A simple study of our Solar System lends credence to the argument that planetary systems form out

of disks: first, all the planets' orbits are in roughly the same plane, and second, all the orbits are in the same sense. It is difficult to imagine how these criteria could be satisfied if not because the planets formed out of a rotating disk.

The life of a protoplanetary accretion disk can be divided into three phases. In the *formation phase*, the disk is built up by the infall of matter from the cloud core on a timescale of around 100 000 years. The mass of the disk at this stage is comparable with the mass of the resulting stellar system, because not much accretion onto the central object has taken place. In this phase all the infalling material encounters the accretion shock as it falls onto the disk. Next comes the *viscous phase*, where the supply of external matter is greatly reduced and mass accretion proper, that is, accretion onto a central object, starts. Angular momentum is expelled and the disk spreads. Now the mass of the disk is less than the mass of the central object, and a small amount of mass carries a large proportion of the angular momentum. This phase lasts for a few hundred thousand years, and it is in this phase that planet formation starts by agglomeration of microscopic interstellar particles into macroscopic objects. What remains in the disk is nearly unprocessed material from the molecular cloud (except any processing by the accretion shock). In the final *clearing phase*, the gaseous component of the nebula is dispersed, perhaps by strong pre-main sequence stellar winds.

Detailed high-resolution observations of disks around stars are at least a few years away yet, and the community awaits results from the SMA and ALMA interferometers to provide more data. Several molecules have been detected in disks by current telescopes though - these include CO, CN, CS, H₂CO, HCN and HCO⁺. The only deuterated molecules detected so far are DCO⁺ and HDO. These observations are sensitive to the outer regions of the disks, at radii of a few hundred A.U. from the centre (an Astronomical Unit is the mean distance between the Earth and the Sun, and is equivalent to about 149598 million metres).

Originally, the chemistry in protoplanetary disks was investigated using equilibrium calculations, which just consider thermodynamics and do not explicitly include chemical reactions. Equilibrium is a valid approximation for the region extremely close to the central object where the temperature and density are high, but it is unrealistic in the cooler, less dense outer disk. The chemistry occurring there has to be calculated kinetically. Figure 3 shows schematically some of the processes affecting chemistry which should be included in a model. These include sources of ionising radiation as well as mass transport processes. Most researchers working in this field

adopt an approach where a complex dynamical code is obtained and values of density, temperature and so on are used as inputs to a stand-alone chemical model. The disadvantage with this approach is that the dynamics and chemistry are treated as if they are independent, which is certainly not the case, but the (significant) advantage is that both sides of the model (dynamics, chemistry) can be as complex as possible. Recently, some progress has been made in the direction of coupling chemistry and dynamics in disk models - in a model where diffusive transport is included, significant effects on the distribution of molecules are found.

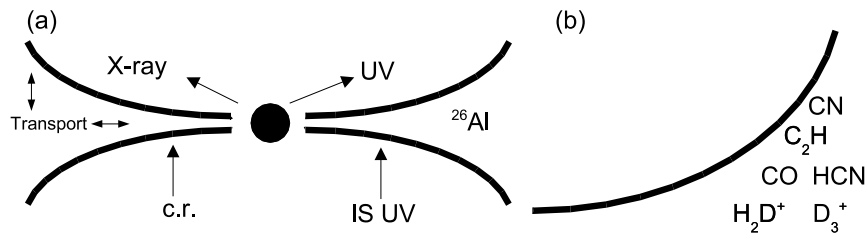


Fig. 3. (a) Schematic showing the important physical processes affecting chemistry in a protoplanetary disk. These include ionisation by UV, X-rays and cosmic rays, ionisation due to the decay of extinct radionuclides and mass transport processes. (b) Blow up of one quadrant of the disk, showing the positions of molecules: C_2H , CN and dissociation products are most abundant near the surface, while molecular ions like H_2D^+ dominate the gas in the cold midplane where other species are frozen out. The warm intermediate layer contains most of the observed abundant molecules.

One-dimensional chemical kinetic models have been calculated to study the chemistry in the midplane of the disk. In this region, irrespective of the physical model chosen, the temperature is low (10-15 K) in the outer part of the disk ($r > 100$ A.U.). There is also not much ionisation due to the amount of material above the midplane which blocks radiation. Molecular species are therefore totally frozen onto grain surfaces. This is a problem, because the observations clearly show a rich gas-phase chemistry in the outer regions of the disks, but in midplane models there isn't any at these radii. This situation changed when models were calculated in 2D using physical models which included the UV irradiation of the disk by the central star. This radiation creates a warm layer of gas above the midplane, and it is therefore from that layer that the molecular line emission comes. Due to the high level of ionisation at the surface, this region is abundant in molecules

which are photodissociation products. These include CN and C₂H, which are the products of HCN and C₂H₂ photodissociation respectively.

The fact that the molecular emission comes from the warmer upper layers of the disk means that we have to look for a different tracer of the conditions in the midplane. If we could measure the dominant ion there, we could use that information to deduce the electron fraction. Furthermore, if the ion contained deuterium, we could also use it to probe the temperature profile. Since H₃⁺ doesn't freeze out, we could use H₂D⁺ or HD₂⁺ for this purpose. The same arguments presented in Section 3 apply though, and D₃⁺ is likely to be the dominant midplane ion at some radii. Our best chance to probe the midplane may therefore be to observe H₂D⁺ and/or HD₂⁺ and interpret the results with a chemical model.

5. The Solar System

Between the evolution of the protoplanetary disk and the formation of the Solar System, the key question for astrochemistry is: how much processing did pristine interstellar material undergo in the disk before it became incorporated into Solar System bodies like comets and meteorites? Since Hale-Bopp, our knowledge of molecular abundances and particularly deuterium fractionation ratios in comets (specifically cometary *comae*) has increased significantly. Comets are made of dust and ice, but as a comet nears the Sun, the ice starts to sublime which produces the coma of gas which we see easily with the naked eye in some cases. As the desorbing *parent* molecules are photodissociated by radiation from the Sun, chemistry occurs which produces many *daughter* species. Using models of the chemistry in the coma we can attempt to work backwards from the observed molecules and deduce the abundances of solid-state molecules in the comet nucleus. To date, there are around 50 molecules detected in cometary comae, and they are almost all seen in interstellar clouds as well, which although not proof that the nucleus is composed of pristine interstellar material, is certainly suggestive. The types of molecules observed, coexisting reduced and oxidised species, and the D/H ratios observed are similar to those seen in interstellar hot cores, the gas in which also originated from sublimation of ice mantles. By comparing cometary gas with interstellar gas we can at least conclude that the molecules formed under interstellar *conditions*. Approximately the same story is true for meteoritic material in the Solar System as well. Many organic molecules have been found in meteorites, including but not limited to amines and amides, alcohols, aldehydes, ke-

tones, aliphatic and aromatic hydrocarbons, amino acids, carboxylic acids, purines and pyrimidines. Enrichments in deuterium and ^{15}N fractionation are also observed, again signifying at least similar formation conditions for the molecules, if not that they are in fact unprocessed interstellar material. Comets are split into two families based on their period. The short period, Kuiper Belt comets are thought to have formed at roughly the same radius from the protosun as where they are today (~ 40 A.U.), while the long period, Oort Cloud comets formed closer to the protosun (~ 10 A.U.) and were ejected into much larger orbits ($\sim 50\,000$ A.U.) possibly by gravitational interaction with the giant planets. There are some chemical differences observed between the two families, and one can suppose that this is either because they were formed differently or that they have had different processing histories. In fact, using a midplane protoplanetary disk model, it was found that over the 5-40 A.U. comet-forming region the solid-state chemical composition changes very little, suggesting the latter explanation.

Astrobiology is a relatively new field of research which is basically concerned with the origins of life on Earth and in the Universe. Observations of biologically significant molecules in the interstellar medium attract much attention largely because of the implied connection between interstellar and Solar System material. The detection of glycine (the simplest amino acid) in the ISM for example, strengthens the thesis that amino acids were already present in the early Solar System and that perhaps the first *prebiotic* material was delivered to Earth by comets. The detection of glycine in the coma of a comet would be even more significant.

6. Bibliography and further reading

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About the author

Andrew Markwick was born in Middlesbrough in north-east England. He was educated at Stokesley School and Sixth Form College, following which he did a degree in Mathematics with Astrophysics at UMIST in Manchester. After that he stayed at UMIST to do a PhD in Astrophysics supervised by Prof. Tom Millar, which was finally entitled “*Chemistry in dynamically evolving astrophysical regions*”. He received his doctorate in October 2000, by which time he had already taken up a PPARC funded post-doc (PDRA) position. In January 2003 he decided it was time to leave UMIST and so he took a 2 year NRC (National Research Council) Research Associateship to NASA Ames Research Center in California. His research interests are varied - he has published papers describing aspects of the chemistry in protoplanetary disks, AGB circumstellar envelopes and dark interstellar clouds, and a few observational papers using infrared and radio data. His many other interests include walking (especially in the North York Moors), playing music (guitar, keyboards, drums), football (he supports Middlesbrough FC) and all aspects of technology. You can contact him by email (ajm@ajmarkwick.com) or find out more by visiting www.ajmarkwick.com.



Fig. 4. Andrew Markwick (centre), with Helen Roberts (left) and Tom Millar (right) above Zermatt, Switzerland, September 2003.