Molecules in Space**

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Abstract: The distribution and nature of interstellar matter in the Galaxy is described. The chemical processes by which the rich variety of molecular species arise are briefly sketched. The importance of interstellar molecules in influencing the evolution of the Galaxy is emphasized.

Keywords: gas-phase chemistry · interstellar chemistry · ion–molecule reactions · star formation · surface chemistry

Space isn't empty! On a clear, dark night we can see in the sky, with the naked eye, a few thousand stars and perhaps several planets. If the Moon is up, then it is the most prominent night-sky object and its brilliance makes the night sky so bright that many of the fainter stars become invisible. We might also have the rare sight of a comet or of meteorites causing "shooting stars", reminding us that some astronomical phenomena are transient. That is the total of the universe that we can see with the naked eye. However, a moment's thought would convince us that this cannot be the whole story. The bright stars that we can see are emitting radiation at a high rate, and must use up their store of energy within a finite lifetime. The brightest of them can be shown to have a lifetime of a few *million* years, whereas we know from the geological record that the Earth is a few *billion* years old. So the inference is that stars have formed in the Galaxy in the very recent past, and—by implication—are forming now. The question is immediately raised in our minds: from what are the stars formed? There must be some source material available.

Telescopes operating in the visible and other regions of the spectrum reveal a much richer, more complex situation than that revealed by naked-eye observation. Optical photographs show that bright stars are often associated with clouds of gas and dust, suggesting that these clouds are the source of new stars. Precisely how this material is processed into stars is one of the great themes of modern astronomy, and, as we shall see, chemistry has a fundamental role to play in this process. Other optical photographs show that, at various stages of their lives, stars may return matter to interstellar space in steady winds, in jets, or in ejecta from stellar explosions such as novae or supernovae. This ejected material is rich in the "ashes" of the thermonuclear "burning" of hydrogen to heavier elements (especially carbon, nitrogen, oxygen, and elements up to iron), so the elemental composition of the interstellar gas is enriched as this return continues. New stars form from this enriched interstellar gas, and in their turn will enrich it further, so that each cycle of the process changes the chemical and physical properties of the gas, and of the stars and planets that may form from it (see Figure 1).

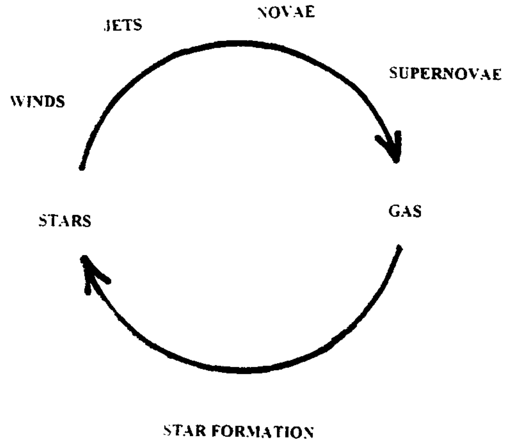

Figure 1. The cycle of material into and out of the interstellar medium.

Observations in other regions of the spectrum are more revealing than optical photography which, because of the obscuration caused by widespread interstellar dust mixed with the gas, is restricted to relatively nearby objects (a few thousand light years distant) in the plane of the Galaxy. Emission and absorption of hydrogen atoms at a wavelength of 21 cm is widespread in our Galaxy and in other galaxies, and shows that neutral hydrogen clouds are the most massive component of interstellar space. Observations in the millimetre wave region of the electromagnetic spectrum show that these hydrogen clouds contain an enormous variety of fairly simple molecules (see Table 1). Most of these species have been detected through their rotational emission spectra. For example, the CO 1–0 rotational transition corresponds to a wavelength of 2.6 mm, and the transition ener-

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Table 1. Molecules detected in interstellar and circumstellar regions (*n*: no. of atoms; *l*: linear, *c*: cyclic).

$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
H_2	H_2O	NH_3	HC_3N	CH_3OH	HC_5N	CH_3OCHO
OH	H_2S	H_3O^+	C_4H	CH_3CN	CH_3CCH	CH_3C_3N
SO	SO_2	H_2CO	CH_2NH	CH_3SH	CH_3NH_2	HC_7N
SiO	NH_2	HNCO	CH_2CO	NH_2CHO	CH_3CHO	CH_3OCH_3
SiS	N_2H^+	H_2CS	NH_2CN	CH_3NC	CH_2CHCN	CH_3CH_2OH
NO	HNO	HNCS	HOCHO	HC_2CHO	C_6H	CH_3CH_2CN
NS	HCN	C_3N	c-C_3H_2	C_5O		CH_3C_4H
HCl	HNC	c-C_3H	CH_2CN	H_2C_4		HC_9N
PN	C_2H	l-C_3H	H_2C_3			$HC_{11}N$
NH	HCO	C_3S	CH_4			CH_3C_5N
CH^+	HCO^+	C_3O	HC_2NC			$(CH_3)_2CO$
CH	OCS	C_2H_2				
CN	HCS^+	$HOCO^+$				
CO	C_2S	$HCNH^+$				
CS	C_2O					
C_2						
CO^+						

gy is equivalent to a temperature of about 5 K; therefore, if CO is present in interstellar gas, the 1–0 rotational transition may be excited collisionally even at very low gas kinetic temperatures.

The distribution of interstellar gas: The interstellar gas is irregularly distributed. We can see this from optical photographs of nearby stars and gas in our Galaxy, but a general view is obscured by the dust grains that apparently always accompany the gas. This dust, composed essentially of soot and sand grains formed in the atmospheres of cool stars, acts like a fog that renders the denser clouds opaque in the visual region of the spectrum (see Figure 2). However, radiation of longer wavelengths readily penetrates these clouds and provides information about regions of molecular clouds where star formation is occurring. Most of the mass is in relatively dense, relatively cool clumps or clouds, embedded in a warm or hot and tenuous medium. The cooler, denser gas is rich in molecules and is mainly neutral. The hotter gas is almost completely ionized and is atomic. The situation is summarized in Table 2.[1] It is evident that most of the mass that is available to form stars is contained within the cool, mainly neutral molecular clouds, which are well traced by molecular rotational emissions. The interstellar clouds are largely molecular when the gas number density is greater than about 10^9 H atoms per m^3, and there are extensive regions of molecular clouds that have number densities of around 10^{10} H atoms per m^3 within which cores of even higher density are detected ($\approx 10^{12}$ H atoms per m^3). The molecular gas is almost always cold (≈ 10 K), except where the gas is heated dynamically and transiently, or by a nearby star. Some associations of molecular clouds form entities of masses approaching one million solar masses. These "giant molecular clouds" are the largest objects within the Galaxy, and are the sites where the brightest and most massive stars are formed. The total mass of gas in the interstellar medium is about 10% of the mass of all the stars, so the star formation process in the Galaxy can continue for some time yet. The star formation rate in the entire Galaxy is currently about one solar mass per year, so that the process could continue at this rate for as much as 10 billion years. In some other galaxies (particularly elliptical galaxies, as distinct from spiral galaxies like our own Galaxy) the fraction of mass in interstellar matter is very much smaller (<0.1%); so we may conclude that star formation has effectively ceased in them.

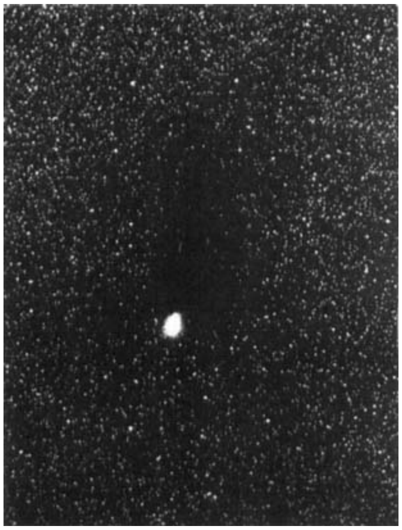

Figure 2. A photograph of a dark cloud silhouetted against a rich star background. The dust grains mixed with the gas in this dark cloud absorb and scatter starlight, making the cloud opaque at optical wavelengths (from P. Murdin and D. Allen, Catalogue of the Universe (photographs by D. Malin), Cambridge University Press, Cambridge, **1979**).

Table 2. The main types of region in interstellar space.

	T (K)	Number density (m^{-3})	Filling factor (%)	Mass fraction (%)
molecular clouds	10	10^{10}	<1	≈ 50
diffuse clouds	100	10^8	3	≈ 50
intercloud gas	10^3	10^6	≈ 50	–
"coronal" gas	10^6	10^4	≈ 50	–

The chemical composition of the interstellar gas: The variety of molecules that has been detected in interstellar clouds is illustrated in Table 1.[1] Most of the molecules have been detected in the denser molecular clouds (an H_2 number density of $n(H_2) \gtrsim 10^9\ m^{-3}$) by means of their rotational emission spectra excited in thermal collision with H_2 molecules. The different transitions of the various species trace different density and temperature régimes: for a given transition, too great a collision rate will cause collisional quenching of the upper state. So, for example, the CO $J=1-0$ emission tends to trace gas with $n(H_2) \approx 10^9\ m^{-3}$, while the similar transition in CS traces gas at $\approx 10^{11}\ m^{-3}$.

The existence of the molecules listed in Table 1 implies that other species must also be present. For example, although interstellar O_2 and N_2 have not been detected (as their rotational spectra are strongly forbidden), nevertheless the detection of species such as N_2H^+ and of OH seems to imply that the homonuclear diatomics are present. In addition, there is strong evidence that polycyclic aromatic hydrocarbons (PAH's) are present. A series of spectral features in the infrared, between wavelengths of about 3 and 12 µm, is suggestive of PAH's, though no precise identifications have been made. It is speculated that cage molecules such as C_{60} or the derivatives $C_{60}H_m$ ($0<m<60$), etc., are present in the interstellar medium, and there is a suggestion that the ion, C_{60}^+, is detected. Therefore, although the conditions in interstellar molecular clouds appear hostile (low temperature, low density, particle and electromagnetic irradiation), nevertheless a rich chemistry incorporating some species not previously well studied (e.g. the linear chain HC_nN, $n = 3, 5-11$) has developed.

The large molecules present may be regarded as the tail of the size distribution of the dust grains from sizes of the order of a micron into the microscopic regime. The dust is well-mixed with the gas, and plays a variety of roles that affect the chemistry. For the present discussion, chief among these are the shielding against starlight of cloud interiors, inhibiting the photoprocessing of molecules; surface catalysis; ice mantle formation and chemical processing of the ices. It seems likely that the source of the PAH molecules, if their existence in the interstellar medium is confirmed, is in the erosion of dust grains of amorphous carbon in shocks and other regions of high excitation.

Interstellar chemistry: The gas in molecular clouds is almost entirely molecular hydrogen. The ratio of H atoms to He atoms is 10:1. The elements C, N, and O together comprise around 0.1 %, with magnesium, silicon, sulfur and other species comprising around 0.01 % by number. The cloud interiors are generally dark, being shielded from starlight by interstellar dust. What is the chemistry by which the remarkable variety of species in Table 1 is brought about?

Reactions between the neutrals in the low-temperature gas are generally inhibited by energy barriers. However, ionization by cosmic rays (mainly ≈ MeV protons and electrons) permits a sequence of fast ion–molecule reactions to occur. When the sequence is completed, then recombination will create a neutral species. Figure 3 illustrates schematically how these ion–molecule schemes may be driven by the creation of the proton-donor H_3^+ from the cosmic-ray ionization of H_2, and simple molecules involving C and O may be formed. Larger species may be formed by similar schemes, by radiative association (for which the efficiency rises very rapidly with complexity), by carbon insertion, or by condensation reactions (see Figure 4).[1]

a) Cosmic ray ionization of H_2:
$H_2 \rightarrow H_2^+ + e^-$

b) Formation of H_3^+:
$H_2^+ + H_2 \rightarrow H_3^+ + H$

c) Reactions of H_3^+:
$O + H_3^+ \rightarrow OH^+ + H$

d) Ion–molecule reactions with H_2:
$OH^+ + H_2 \rightarrow H_2O^+ + H$
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$

e) Dissociative recombinations:
$H_3O^+ + e^- \rightarrow H_2O + H;\ OH + H_2$

f) Neutral exchange reactions:
$OH + C \rightarrow CO + H$

Figure 3. Dark-cloud chemistry: schematic representation of how the ionization (a) of interstellar H_2 molecules caused by cosmic-ray particles creates (b) the reactive ion, H_3^+, which drives (c) a sequence of ion–molecule reactions (d). The product molecular ions recombine dissociatively (e) to form a variety of neutral hydride species. Further reactions (f) between these species form molecules with more than one heavy atom.

a) $CH_3^+ + H_2O \rightarrow CH_3{\cdot}H_2O^+ + h\nu$
$CH_3{\cdot}H_2O^+ + e \rightarrow CH_3OH + H$

b) $C^+ + C_nH_m \rightarrow C_{n+1}H_{m-1}^+ + H$

c) $CH_3^+ + C_2H \rightarrow C_3H_3^+ + H$

Figure 4. More complicated interstellar species may be formed through a) radiative associations of polyatomic species, b) carbon insertion reactions, and c) condensation reactions. Examples of these are given here.

All of these gas phase schemes depend on the presence of molecular hydrogen. However, gas phase routes for H_2 formation are not efficient. The existence of H_2 in regions penetrated by stellar UV radiation at wavelengths ≈ 100 nm (which dissociates H_2) requires a more efficient mechanism. This is proposed to be surface catalysis on interstellar dust, in either Eley–Rideal ($H(gas) + H(ads) \rightarrow H_2$), or Langmuir–Hinshelwood ($H(ads) + H(ads) \rightarrow H_2$) modes. The requirement of the astronomical observations of interstellar H_2 is that the probability of an H atom arriving at a grain and leaving as part of an H_2 molecule is high, in the range (0.1–1.0).

Since surface chemistry is invoked for H_2 formation, it is possible that surface chemistry also plays a part in the formation of other species.[2] Evidence for this is in the detection of the radical, NH, along several lines of sight towards bright stars. Nitrogen atoms are expected to be neutral in such regions, and their reaction with H_2 is strongly inhibited at low temperatures; hence, gas phase routes to form NH seem to be excluded. On the other hand, the assumption that N atoms are converted to NH and then to NH_3 with reasonable efficiency at dust grain surfaces can readily satisfy the observational requirement.

In darker regions in the interior of dark clouds, dust grains accumulate mantles of ice, mostly H_2O, but also containing CO, CH_3OH, and possibly NH_3 and a variety of other species. The water (and possibly the ammonia) molecules are probably formed in situ by hydrogenation of atoms incident on grain surfaces and then retained, whereas the other species may simply freeze-out from the gas phase. These ice mantles represent a considerable store of molecular species that can in some circumstances, e.g. the formation of a nearby star, be released back into the gas phase, creating a transient overabundance.[2] This situation is, apparently, observed in dense packets of gas heated by newly formed stars: these are called "hot cores".

The irradiation of ice particles by UV, X-ray or energetic particles may initiate a solid state chemistry, and there have been many studies of laboratory analogues of this process. For example, in an ice consisting mainly of H_2O with a minor component of CO, irradiated by UV with a dose sufficient to give each H_2O one UV photon, a range of product species is produced: CO_2 (37 %), CH_3OH (0.8 %), H_2CO (4 %) and HCOOH (4 %). These species could be released to the gas phase either on formation or at some stage where the ice mantles are evaporated. Astronomical evidence suggests that in some situations the sequential hydrogenation of CO to CH_3OH may be occurring.

The role of molecules in astronomy: Molecules provide important tracers of gas in regions that are obscured from study by interstellar dust. The rotational emission spectra from the variety of species present, and the various rotational levels populated in collisions, ensure that there is always an appropriate tracer available for the temperature and density conditions under which molecules exist. By using several tracers, we can build up a detailed picture of the density and temperature structure of a particular region.

However, molecules play a more fundamental role than simply passively tracing the interstellar material. The energy emitted in their rotational spectra is often the dominant cooling mechanism for regions undergoing dynamical change. Thus, in the gravitational collapse of tenuous gas clouds (typically $n(\mathrm{H}_2) \approx 10^9\,\mathrm{m}^{-3}$) to dense cores (typically $n(\mathrm{H}_2) \approx 10^{12}\,\mathrm{m}^{-3}$) where gravity is dominant, the gravitational potential energy released will appear as heat and must be removed radiatively, otherwise the consequent pressure increase will arrest the collapse. Since the gas is cool (≈ 10 K) the most effective radiators at these temperatures are molecules whose rotational transitions can be thermally excited even at these low temperatures. Hence, important coolants in gravitationally collapsing molecular clouds are the abundant species that possess dipole moments, namely, carbon monoxide (in its various isotopic forms: $^{12}\mathrm{C}^{16}\mathrm{O}$, $^{13}\mathrm{C}^{16}\mathrm{O}$, $^{12}\mathrm{C}^{18}\mathrm{O}$, etc.), $\mathrm{H_2O}$, OH, etc.

Gravitational collapse is resisted not only by thermal and turbulent pressure but also by magnetic pressure. The coupling between the magnetic field and the gas is determined by the ionized fraction of the gas, through ion–neutral collisions. The timescale over which magnetic support can be significant is called the ambipolar diffusion timescale and is about 4×10^5 years for molecular cloud gas in which the fractional ionization is typically around 10^{-8}. This timescale is comparable to the gravitational collapse time for molecular clouds; so the extent to which magnetic fields can inhibit the collapse is controlled by the level of ionization, which itself is determined by the chemistry through recombination, especially the fast dissociative recombination of molecules.[3]

The various timescales associated with processes occurring in the collapse of molecular clouds in the early stages of star formation are listed in Table 3. We see that these processes tend to have similar timescales and that chemistry controls all these processes, apart from gravitational collapse. Chemistry is, therefore, central to the evolution of our universe.[4]

Table 3. Approximate timescales, in years, associated with processes occurring in the collapse of molecular clouds in the early stages of star formation [a].

gravitational collapse	$10^{11}/n^{1/2}$
ion–molecule chemistry driven by cosmic-ray ionization	10^6
freeze-out of molecules on to dust grains, forming icy molecular mantles	$10^{16}/n$
cooling through molecular emission at low temperature	$10^{15}/n$
ambipolar diffusion, magnetic support	$4 \times 10^5(x/10^{-8})$

[a] n represents the number density of hydrogen molecules (m^{-3}) and x the fractional ionization in the cloud. Typical values of these parameters in molecular clouds are $n = 10^{10}\,\mathrm{m}^{-3}$, and $x = 10^{-8}$.

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