Molecules in Space

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in

Chapter 14
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1 INTRODUCTION

The stars that twinkle brightly in the night sky are composed of ionized, often highly ionized, atoms. For many years, astronomical spectroscopy concentrated on atoms and atomic ions. Much of astrophysics still concerns itself with atomic processes. However, the increased sensitivity of telescopes and the opening up of other wavelengths than the visible has led to burgeoning of activity in molecular astrophysics. In particular, longer wavelengths such as the infrared and radio are sensitive to molecular transitions. Observations at these wavelengths has led to the realization that the Universe is substantially molecular. Indeed, although the discussion in the following text is largely confined to molecules in our own galaxy, the list of molecules detected in external galaxies is growing rapidly.[1]

The molecular composition of space is an active research area. This summary draws heavily on two multi-author books *The Molecular Astrophysics of Stars and Galaxies*[2] and *Molecular Processes in Astrophysics: Probes and Processes*,[3] which provide much more details than can be accommodated here.

2 MOLECULAR HYDROGEN

The Universe is 95% atomic hydrogen. This means that in nearly all molecular environments, molecular hydrogen is the dominant molecule. Thus, nearly all chemistry occurs in a hydrogen-rich or reducing environment, our own planet and our two nearest neighbours being obvious exceptions.

The preponderance of molecular hydrogen places a special emphasis on both its chemistry and its spectroscopy.[4] Indeed, the formation of hydrogen molecules in astronomical conditions has been a long running puzzle. In the interstellar medium (ISM), which is discussed further in the next section, even the so-called dense molecular clouds correspond to what, on Earth, would be considered an ultra-high vacuum. Typically, they contain a few tens of thousand particles per cubic centimetre and are cold with temperatures in the range 10 to 100 K. Under these conditions, the chances of three-body gas-phase reactions occurring are so small that they can be neglected. This leads to an entirely new chemistry.

Using only two-body reactions, it is difficult to form molecules directly from atoms: usually, a third body is required to carry off the excess energy. It is possible for this excess energy to be carried off by a photon, resulting in a process called *radiative association*. However, radiative association is an extremely inefficient process and even on astronomical timescales is rarely a major route for

neutral molecule formation. It is now generally accepted that in dense molecular clouds, molecular hydrogen forms on the surface of grains.[5] There is evidence that microscopic grains, usually referred to as dust, are widespread in cool astronomical environments. It is thought that these particles are largely silicates, possibly with coatings of ice.

However, the need to invoke dust to initiate molecule formation process raises the question of how molecules and hence grains formed in the first place. The early Universe, the chemistry of which is discussed in Section 4, contains essentially no elements beyond lithium. The heavier elements that form into grains in our galaxy have therefore been through at least one cycle of stellar processing in which hydrogen is burnt in nuclear reactions and heavier elements are produced. As molecule formation appears to be a necessary precondition for star formation, how were hydrogen molecules formed before there were any grains? This question remains an active area of research. Figure 1 presents the dominant reactions linking the gas-phase forms of hydrogen. Included in this scheme are methods of forming molecular hydrogen from hydrogen atoms. As can be seen, this involves excited H atoms in their $n = 2$ state. Note that the 2s state of atomic hydrogen is metastable or going via the weakly bound negative ion H^-.[6]

Direct detection of extraterrestrial hydrogen molecules relies on spectroscopy. Radio astronomy and more recently infrared telescopes have been the driving forces that have characterized the molecular nature of the Universe. As a homonuclear diatomic, the absence of permanent or vibrational induced dipoles means that standard means of molecular detection based, in particular, on strong rotational transitions should not apply to hydrogen. However, there is so much hydrogen present in the Universe that in fact its weak, quadrupole spectrum is well known. Quadrupole

transitions have been observed in the star-forming regions of Orion and elsewhere.[7] In practice, astronomical pure rotational spectra probe significantly higher levels of rotational excitation than what has so far been directly observed in the laboratory.[8]

Quadrupole transitions are very weak, typically a billion times weaker than standard dipole transitions. However, the density of H_2 is often many billion times more than other species that are routinely detected. Of course, hydrogen is light, which means that its rotational spectrum cannot be seen at radio frequencies. Instead, these low-lying lines lie in the far-infrared and higher transitions can be observed using ground-based telescopes in the mid-infrared through 'windows' in the Earth's atmosphere.[7]

The electronic emission spectra of molecular hydrogen can also be observed from active environments. Typical is the ionosphere of gas giants such as Jupiter where fast electrons, accelerated along magnetic field lines, collide with the atmospheric gas that is largely H_2. The resulting auroral emissions can be observed; the Hubble Space Telescope has been used to record a number of particularly beautiful and detailed images using these emissions.[9,10] H_2 fluorescence can also be observed from shocked[11] and diffuse[12] regions of the ISM, both of which are discussed in the next section.

3   THE INTERSTELLAR MEDIUM

The vast regions of space between the stars are largely empty. However, in this, near-vacuum matter still aggregates to form clouds that are the major feature of the ISM.

Figure 1. Key two-body reactions involved in the gas-phase production of a molecule of molecular hydrogen.[6]
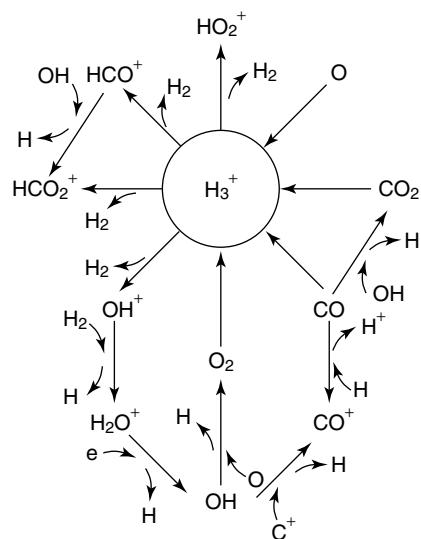
Figure 2. Chemical pathways starting from H_3^+ and involving oxygen molecules in diffuse interstellar clouds.[14]

These clouds are largely molecular.[5] The chemistry of the giant clouds that contain most of the matter in the ISM is now substantially established.[5,13] In discussing this, it is necessary to distinguish between two proto-typical types of clouds: the so-called dense clouds that contain 10 000 or more particles per cubic centimetre and diffuse clouds with typical densities of less than a 1000 particles per cubic centimetre.

Dense molecular clouds are the main molecule-forming regions, and their chemistry is well documented.[5] These clouds contain sufficient material to become self-shielding from ultraviolet radiation. That is, any photons of energy greater than the ionization potential of atomic hydrogen, 13.65 eV, are absorbed. This means that molecules, including molecular hydrogen, whose ionization potential is greater than that of H do not get ionized. However, as will be discussed when considering reaction schemes in the following text, the clouds are not entirely neutral. This is because there are some low ionization potential species present, particularly atomic carbon, and also because very energetic γ rays, usually called *cosmic rays*, do penetrate.

Ionization of molecular hydrogen by cosmic rays is followed rapidly by formation of the triangular H_3^+ molecule

$$H_2 + H_2^+ \longrightarrow H_3^+ + H \qquad (1)$$
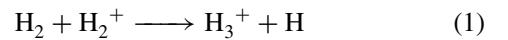
This exothermic reaction occurs at essentially every collision. H_3^+ is a strong protonating agent and the starting point for much of interstellar chemistry. Figure 2 gives an example of the reaction networks that can follow the formation of H_3^+. As can be seen from the large array of molecules that have been observed in the ISM, (see Tables 1 and 2), the reaction networks become extensive.

Table 1. Neutral molecules identified in the ISM and in circumstellar environments up to the end of year 2000. Molecules marked with an asterisk have only been detected in the circumstellar envelopes of carbon-rich stars. Unconfirmed detections are denoted with a ?. This tabulation is based on one by Wootten [1] which is regularly updated.

Molecules with two atoms							
AlF*	AlCl*	C_2	CH	CN	CO	CP*	CS
CSi*	HCl	H_2	KCl*	NH	NO	NS	NaCl*
OH	PN	SO	SiN*	SiO	SiS	HF	SH
SiH							
Molecules with three atoms							
C_3	C_2H	C_2O	C_2S	CH_2	HCN	HCO	H_2O
H_2S	HNC	HNO	MgCN	MgNC	N_2O	NaCN	OCS
SO_2	c-SiC_2	CO_2	NH_2	SiCN*			
Molecules with four atoms							
c-C_3H	l-C_3H	C_3N	C_3O	C_3S	C_2H_2	HCCN	HNCO
HNCS	H_2CO	H_2CN	H_2CS	NH_3	SiC_3	CH_3	
Molecules with five atoms							
C_5^*	C_4H	C_4Si^*	l-C_3H_2	c-C_3H_2	CH_2CN	CH_4	HC_3N
HC_2NC	HCOOH	H_2CHN	H_2C_2O	H_2NCN	HNC_3	SiH_4^*	
Molecules with six atoms							
C_5H	C_5O	$C_2H_4^*$	CH_3CN	CH_3NC	CH_3OH	CH_3SH	HC_3NH^+
HC_2CHO	$HCONH_2$	l-H_2C_4	C_5N				
Molecules with seven atoms							
C_6H	CH_2CHCN	CH_3C_2H		HC_5N	$HCOCH_3$	NH_2CH_3	c-C_2H_4O
Molecules with eight atoms							
CH_3C_3N	$HCOOCH_3$	CH_3COOH?		CH_2OHCHO		H_2C_6	C_7H
Molecules with nine atoms							
CH_3C_4H	CH_3CH_2CN	$(CH_3)_2O$		CH_3CH_2OH	HC_7N	C_8H	
Molecules with ten atoms							
CH_3C_5N?		$(CH_3)_2CO$		NH_2CH_2COOH?			
Molecules with eleven atoms							
HC_9N							
Molecules with thirteen atoms							
$HC_{11}N$							

Table 2. Molecular ions identified in the ISM.[15]

Ions with two atoms
CH^+ CD^+ CO^+ SO^+

Ions with three atoms
HCO^+ DCO^+ HCS^+ HOC^+ N_2H^+ $H_3{}^+$ H_2D^+

Ions with four atoms
CH_2D^+? $HCNH^+$ $HOCO^+$ H_3O^+

Ions with more than four atoms
H_2COH^+ HC_3NH^+

Table 3. Chemical reactions important in the ISM.[16]

Bond formation	
Radiative association	$A + B \rightarrow AB + h\nu$
Grain surface formation	$A + B : g \rightarrow AB + g$
Associative detachment	$A^- + B \rightarrow AB + e^-$
Bond breaking	
Photodissociation	$AB + h\nu \rightarrow A + B$
Dissociative recombination	$AB^+ + e^- \rightarrow A + B$
Collision dissociation	$AB + M \rightarrow X + Y + M$
Rearrangement reactions	
Ion–molecule exchange	$A^+ + BC \rightarrow AB^+ + C$
Charge transfer	$A^+ + B \rightarrow A + B^+$
Neutral collisions	$A + BC \rightarrow AB + C$

Table 3 summarizes the important type of reactions that contribute to the chemistry of the ISM. It is possible to form quite large molecules by a series of ion–molecule reactions that can then be terminated to yield neutral species by dissociative recombination. Thus, for example, it is thought that both water and HCN are dominantly formed from the protonated species:

$$H_3O^+ + e^- \longrightarrow H_2O + H \qquad (2)$$

$$HCNH^+ + e^- \longrightarrow HCN + H \qquad (3)$$

In fact, reaction (3) can also produce the metastable, linear isocyanide isomer HNC. Anomalously, high quantities of the HNC are observed in the ISM with concentrations sometimes exceeding that of HCN.[17] Thermodynamics would suggest that the ISM is much too cold to support this high-energy alternative but, as with other processes found in the ISM, it is kinetics and not thermodynamics that dictates what actually occurs. HNC is not the only metastable isomer detected in the ISM, as can be seen from Table 1. Indeed, it appears that not only does thermodynamic equilibrium not prevail in the ISM but the chemistry of clouds never reaches a steady state in the lifetime of the cloud even though it is many, many millions of years![18]

An understanding of the chemistry of the ISM therefore relies on the construction of detailed reaction pathways.[5]

Rates, at low temperatures, for each of the key steps in these pathways need to be determined. For example, the UMIST database,[19] which is the most widely used, links approximately 130 species, nearly 400 if deuterated isotopomers are counted separately, using about 5000 reaction pathways. The UMIST database contains reactions involving molecules made from H, He, N, O, C, S, Si, Fe, Na, Mg, P, and Cl, which are the most abundant atoms in the ISM. Use of such databases accounts successfully for about 80% of the observed molecular abundances in dense molecular clouds.[20]

One problem with chemical models of the ISM is that much of the rate information used must be regarded as the best available rather than highly accurate. Performing laboratory measurements at ISM temperatures is difficult, but not impossible.[21,22] Similarly, theoretical studies have shown that new reaction mechanisms can come into play at very low temperatures,[23] which means that the extrapolation of reaction rates from high-temperature determinations is often dubious. Indeed, these studies suggest that two-body reactions between neutral species may be quite rapid at very low temperatures when at least one of the species is strongly dipolar.

Mature molecular clouds have a significant quantity of material in the condensed phase in the form of grains or dust.[24] These particles generally have cores composed of various silicates that, at low temperatures, develop mantles of other molecules. For example, water ice condenses onto grains at temperatures below 150 K. Besides water, the polar mantles that form about the silicate core also contain CO, N_2, O_2, and possibly CO_2.[25] Further, apolar grain mantles containing molecules such as methane form at very low temperatures. Grain surfaces provide the route by which atomic hydrogen combines to form H_2. Other chemistry occurs on the grain surfaces.[24,26] Molecular hydrogen is presumed to be volatile enough to be immediately returned to the gas phase upon formation, a situation that may be true for other species formed on grain surfaces.[27,28]

It should be noted that many, indeed most, of the larger molecules detected in the ISM (see Table 1) are strongly dipolar. Of course, these molecules are also easier to detect at radio frequencies because they display very strong rotational spectra, which can allow even very small column densities to be observed. Figure 3 gives a typical portion of a radio spectrum of the ISM. As is usual in ISM radio spectra, the most prominent features are seen in emission. Although many of the lines are assigned to particular rotational transitions, most surveys find lines of unknown origin, generally designated as 'U'. Absorption features are sometimes observed but the species in Figure 3 not
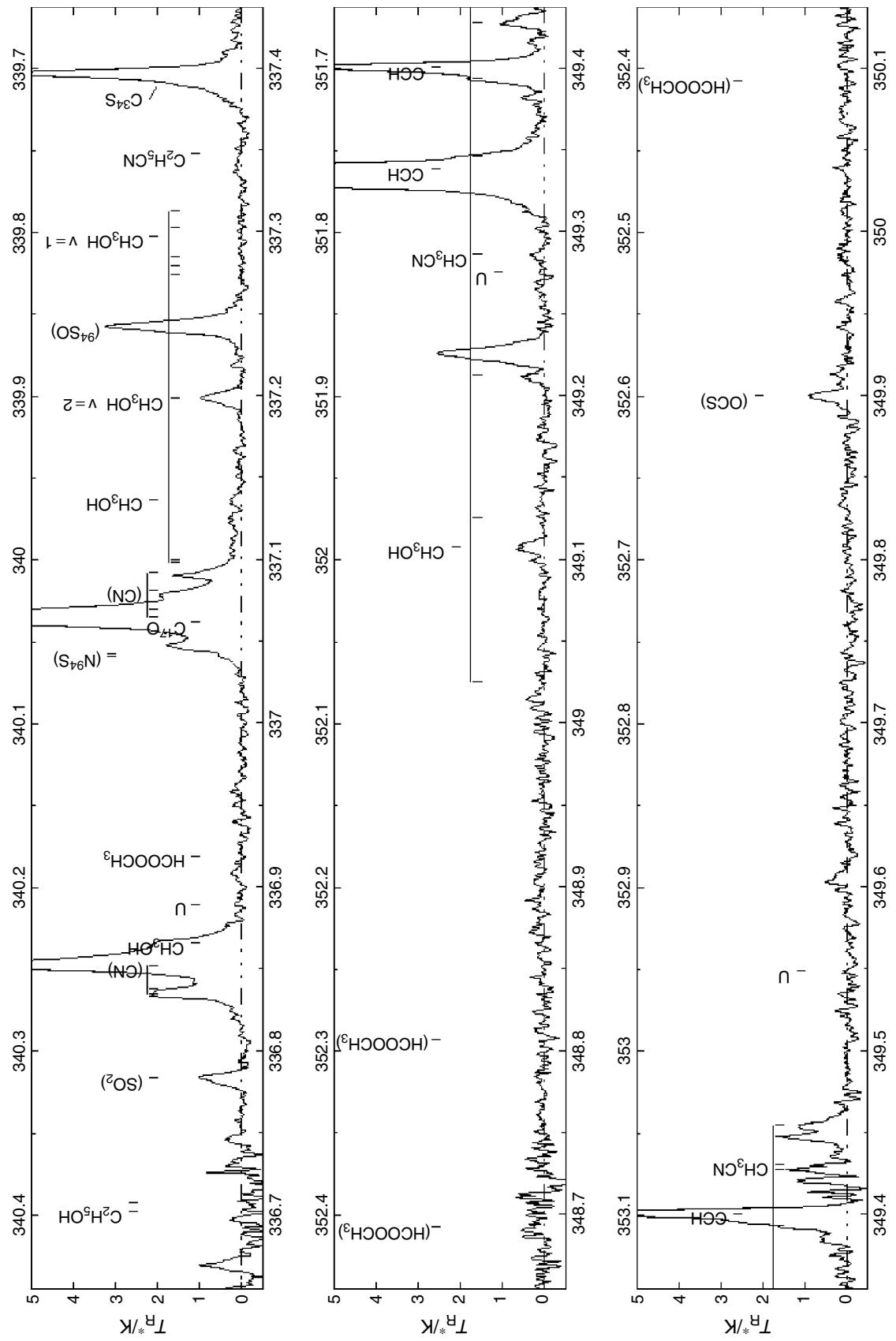
Figure 3. A radio frequency spectrum of the molecular hot core in G5.89. This hot core is a remnant left over from formation of a massive star. Hot cores such as this are known to be particularly rich in molecules. The spectrum shown, which plots frequency in GHz against antennae temperature in K, is only part of a detailed survey by Hatchell *et al.*[29] The lower frequency scale is the main band and the upper scale a side band displaced by 3 GHz.

showing strong emission features are ones that have not been detected.

The search for new species in the ISM is a continuing one.[30] A standard technique is to synthesize candidate species in the laboratory, record their spectrum, and then search for its signature at radio frequencies. As many of the species now being discovered in the ISM are not stable, this requires special techniques. A good example of this procedure is the recent laboratory analysis of the radio frequency spectra of a number of Si containing radicals.[31] Of these, SiCN was found to have the large permanent dipole and therefore was considered to be the best candidate for detection by radio astronomy techniques. The clear spectroscopic signature of SiCN was rapidly found in the envelope of a carbon-rich star.[32]

One consequence of the non-thermalized nature of much of the ISM is the presence of maser transitions that have been observed, usually for several different transitions, in a number of molecules including water, OH, SiO, methanol, and ammonia.[33,34] Maser transitions can arise because collisions, typically with dominant species H_2, preferentially populate certain excited states resulting in population inversion and maser action. Models of masers can be used as detailed probes of the collision processes in the ISM.[35]

Table 1 shows a preponderance of small organic molecules. In fact, there is a strong body of evidence for a significant presence of larger organic species.[26] Polyaromatic hydrocarbons, usually known as PAHs, comprise several linked aromatic rings. Pyrene, which has the chemical composition of $C_{16}H_{10}$, is an example of a smaller PAH. Molecules containing up to 50 carbon atoms have been considered. Structures and some properties of 'standard' PAHs are given by Clemett *et al*.[36] It is harder to obtain positive spectroscopic confirmation of these species although features characteristic of standard function group analysis used for analysing infrared spectra of hydrocarbons in the laboratory are common in astronomical infrared spectra from a number of carbon-rich sources. Quantum chemical calculations are now being used to resolve problems with PAHs by synthesizing spectra,[37] considering formation mechanisms[38] and possible chemical reactions under astronomical conditions.[39]

One interesting development in the astrochemistry of PAHs is the laboratory identification of a number of them in the meteorite ALH84001.[40] This meteorite is of martian origin and the detection of PAHs led to speculation that they are the signature of life on Mars.[36,40]

Even more controversial is the association of PAHs with the diffuse interstellar bands. These features that are ubiquitous in optical spectra of the ISM[41] have been studied for 70 years.[42] Their origin is almost certainly molecular but which molecule or class of molecules exactly

remains a subject of considerable debate [2]. However, the most likely explanations suggest carbon-containing or organic molecules as the source of these features.[43]

An aspect of chemistry particular to the giant molecular clouds in the ISM is the fractionation effect, which is particularly prominent for deuterium. As on earth, deuterium is a trace species in the ISM present typically at an abundance of only a few times 10^{-5} that of H.[44] However, D is often found to be significantly over-represented in ISM molecules. This is because D exchange reactions such as

$$H_2 + D \longrightarrow HD + H \qquad (4)$$

$$H_3{}^+ + HD \longrightarrow H_2D^+ + H_2 \qquad (5)$$

$$HCO^+ + D \longrightarrow DCO^+ + H \qquad (6)$$
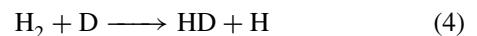
are all exothermic because of vibrational zero point energy effects. Thus, for example, the zero point energy of HD is less than that of H_2. In the case of $H_3{}^+$, this situation is exacerbated by the fact that for $H_3{}^+$, but not H_2D^+, the $J = 0$ rotational state of the vibrational ground state also cannot be occupied as a consequence of the Pauli principle.[45] The exothermicity of reaction (5) is equivalent to a temperature of 227 K.[46] Exothermicities of this magnitude are too small to have a significant effect on the isotopic composition of molecules at room temperature, but at 10 K the effect can be profound. This effect, known as *fractionation*, can increase the concentration of deuterated species by many orders of magnitude.[17] In the extreme case of H_2D^+, abundances up to 10^4 times that which might be expected from the D/H ratio have been predicted.[47,48] Other isotopes, such as ^{13}C and ^{18}O, show similar but less extreme effects due to fractionation.[49]

So far, it has been assumed that dense molecular clouds are always cold. In fact, there are regions that are significantly warmed by shocks, due to a number of causes,[50] passing through the cloud. The presence of shocks can have a profound effect on the chemistry because they allow reactions with small barriers or ones that are weakly exothermic to proceed.[51] For example, at low temperatures, water is made in the ISM by dissociative recombination of H_3O^+, (equation 2). At temperatures above 300 K, water can be made much more efficiently and directly by[52]

$$H_2 + O \longrightarrow OH + H \qquad (7)$$

$$H_2 + OH \longrightarrow H_2O + H \qquad (8)$$
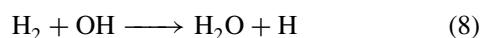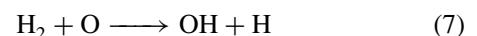
Similarly, carbon chemistry also changes. At low temperature, hydrocarbons are built by radiative association:

$$H_2 + C^+ \longrightarrow CH_2{}^+ + h\nu \qquad (9)$$

$$H_2 + CH_3{}^+ \longrightarrow CH_5{}^+ + h\nu \qquad (10)$$
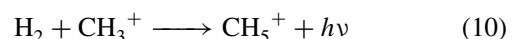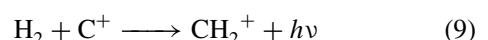
This is a very inefficient process and the quoted reactions occur only for one in every 10 000 or less collisions.[51] The ion molecule reaction

$$H_2 + C^+ \longrightarrow CH^+ + H \qquad (11)$$
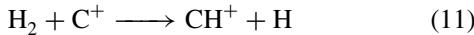
is exothermic by about 0.4 eV and again only occurs in shocks.[51] Similarly, at higher temperature, neutral reactions such as

$$C + H_2 \longrightarrow CH + H \qquad (12)$$
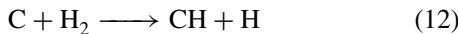
can occur much more efficiently and such reactions predominate.[51]

Diffuse molecular clouds, as their name suggests, occur with much lower density, typically a 100 or so particles per cubic centimetre. Diffuse clouds are generally larger, of similar total mass, than dense clouds. Because ionizing radiation penetrates to the heart of these clouds, their chemistry is greatly simplified[13] but some molecules, such as H_2, CO, OH, CH, HCO^+, and CH^+, can still form. The recent observation of the key molecular ion H_3^{+}[53] in diffuse molecular clouds, contrary to accepted models, is forcing a revaluation of the chemistry of these objects, which may prove to be richer than what had previously been thought.

4 THE EARLY UNIVERSE

Just as the chemistry of the ISM is very different from terrestrial or standard laboratory chemistry, the chemistry of the Early Universe is very distinctive and needs to be considered in its own right. To give an extreme example, there was an epoch, lasting for a million or so years from about 10 000 years after the Big Bang[6] when all molecules contained the inertest of all the noble gases – helium!

The elemental composition of the early Universe was very different from that found in our solar system or indeed our galaxy. This is because elements heavier than H and He, often referred to by astronomers as 'metals', which are abundant in our local environment, are the product of the nuclear reactions that power the stars. Thus, our very existence is predicated on a phase of stellar processing. The heavier elements are ejected into space if the star concerned undergoes an explosive death. Indeed, elements heavier than iron are only produced during supernova explosions, the most violent of the stellar cataclysms.

The early Universe was composed of H, ^{4}He, D, ^{3}He, a small amount of ^{7}Li, one atom in 10^7, and even smaller traces of Be and B.[6] The exact elemental abundances resulting from the original Big Bang is a key cosmological parameter that may be extractable from studies of chemistry

of the ISM.[44] Stars can only form and start nuclear synthesis if matter is cool enough to undergo gravitational collapse. For matter formed in the primordial Universe to cool sufficiently to form stars, it is necessary to invoke molecules. This is because the prime method of cooling is radiative and the energy levels in atoms, specifically in H and He, are too well separated to allow cooling down to the temperatures required. However, forming molecules in a hot environment that is too diffuse for more than two-body collisions is difficult.

The chemistry of the early Universe has been extensively studied by Dalgarno *et al.*[6] Their models suggest that the earliest molecules formed were He_2^+ and HeH^+. These can be produced even before the protons and electrons formed in the post Big Bang plasma recombine to form H atoms.

A more significant phase of molecule formation occurred about three million years after the Big Bang and led to the formation of molecular hydrogen and LiH.[54] Because of the small amounts of Li, LiH is only a trace species but it is important since its large permanent dipole moment, and closely spaced rotational and vibrational energy levels, makes it an efficient radiator of energy.

There are a number of means by which molecular hydrogen can be formed (see Figure 1). The most direct route, radiative association between two ground state H atoms does not occur because of the absence of appropriate transition dipoles. However, even the small, non-Born–Oppenheimer permanent dipole moment introduced by replacing one of the H atoms with deuterium can be important since the molecule HD has weak dipole-allowed rotation and vibration-rotation spectra. Although the dipoles involved are very small, the effects of these spectra can be significant.[55]

As can be seen from Table 4, radiative association is never particularly rapid but the rates for forming molecular ions tend to be faster than that for neutrals. In the case of H_2, it is possible to form it from H atoms provided one of the atoms is electronically excited, thus allowing the molecule to be stabilized by emission of an ultraviolet photon. It should be noted that this process proceeds at a similar rate to the competing associative ionization reaction[56]

$$H(2\ell) + H \longrightarrow H_2^+ + e^- \qquad (13)$$
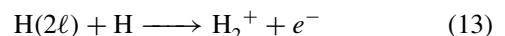
which results in the formation of the H_2^+ molecular ion.

Model calculations[57] suggest that in this epoch, the so-called recombination era, hydrogen molecules were indeed formed by direct radiative association collisions involving an excited H atom. At later stages, when the proportion of H_2 grew, the dominant mechanism involved the formation of H_2^+ by radiative association followed by charge

exchange[6]

$$H_2^+ + H \longrightarrow H_2 + H^+ \qquad (14)$$
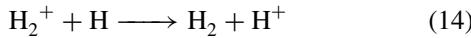
This process dominated up to about 10 million years after the Big Bang. At this time, recombination was essentially complete and significant amounts of the H^- ion were formed. Molecular hydrogen was then formed by associative detachment[6]

$$H + H^- \longrightarrow H_2 + e^- \qquad (15)$$
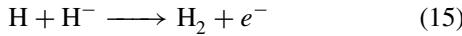
which tends to form H_2 in vibrationally and rotationally excited states.

5 CIRCUMSTELLAR PROCESSES

The chemistry of supernova explosions bears some similarity to that of the early Universe in that molecule formation occurs from a cooling hot plasma.[58] However, supernova remnants are denser than the post-recombination era early Universe and the timescales for molecule formation are months rather than millions of years. Of course, the composition of these remnants is also significantly different because they are rich in heavy elements.

Nearby supernova explosions are rare. In 1987, a supernova exploded in a neighbouring galaxy – the small Magellanic cloud. Supernova SN1987a provided an opportunity, unique in modern times, to study at close hand a supernova explosion as it evolved. Molecule formation was detected and monitored for the first time in the ejecta from SN1987a.[59,60] So far, spectroscopic signatures for CO, SiO, CS, and H_3^+ have been detected.[58] A tentative detection of HeH^+ has been claimed.[61]

Table 4. Radiative association rates, $\alpha(T)$ in $cm^3 s^{-1}$, for the formation of key species in the early Universe.[56] Species are assumed to be in their electronic ground state unless otherwise stated. (Numbers in parenthesis denote powers of ten.)

Molecule	Channel	$\alpha(T = 100K)$	$\alpha(T = 1000K)$
H_2^+	$H + H^+$	1.6(−20)	7.9(−20)
He_2^+	$He + He^+$	7.2(−21)	5.8(−19)
HD	$H + D$	8.3(−27)	2.2(−26)
LiH	$Li + H$	3.2(−20)	2.1(−20)
HeH^+	$He^+ + H$	9.8(−16)	4.1(−16)
LiH^+	$Li^+ + H$	1.3(−20)	2.4(−23)
LiH^+	$Li + H^+$	5.5(−15)	1.8(−15)
H_2	$H(2s) + H$	2.2(−14)	1.2(−14)
H_2	$H(2p) + H$	1.2(−14)	3.4(−14)
O_2	$O + O$	1.3(−26)	2.9(−23)
O_2^+	$O + O^+$	2.6(−19)	4.2(−18)

It is not just exploded supernovae that are surrounded by gas in which molecules can form. Up to 90% of the starting mass of a star may be lost during its lifetime in the form of winds and molecular outflows.[62] It is thus common for the circumstellar environment to have an interesting chemistry.[63] It has already been mentioned that organic molecules are particularly prevalent in regions about carbon-rich sources. The source IRC + 10 216 is the standard astrophysical laboratory for studying carbon chemistry while a separate chemistry predominates in and around oxygen-rich stars.[64] Table 1 distinguishes those molecules and have only so far been observed in circumstellar environments.

There are other regions about stars with an altogether different, photon-rich chemistry called *planetary nebulae*. Apart from yielding many of the most spectacular astronomical images, planetary nebulae provide a harsh environment for molecules to survive in.[15] Typically they comprise a hot central star or stars surrounded by a cloud of gas that can often be observed glowing. This gas, the outer layer of which cools down to usual ISM temperatures, is constantly irradiated by ultraviolet photons from the central star(s). This radiation is ionizing but is also progressively absorbed so that layers further from the star(s) are shielded from the harsher effects. The result is a photodissociation region (PDR) about the star; this region is currently sometimes referred to as a photon-dominated region, which has the same acronym and a unique chemistry.[65]

Figure 4 shows a typical cross section of a planetary nebula giving the dominant levels of ionization of various species. The interface between O and O_2 should be regarded as speculative since molecular oxygen has yet to be observed anywhere outside our solar system.[66] However, this interface represents the boundary beyond
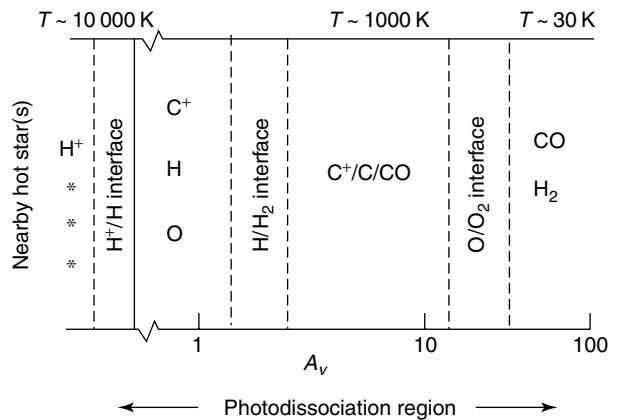

Figure 4. Schematic structure of a typical planetary nebulae. A_v represents the total visible absorption on a logarithmic scale such that by $A_v = 10$ the stellar flux is reduced by a factor of approximately 10^4.

which most carbon is in neutral, generally molecular, form.

Because carbon has a relatively low ionization potential, 11.26 eV,[67] it can remain ionized in so-called HI regions where the hydrogen is neutral. Under these circumstances, the carbon provides a source of electrons. The PDR is the HI region where carbon is ionized and its chemistry is strongly influenced by photons from the central star.

A number of molecules, and molecular cations (see Table 2), have been observed in this relatively harsh environment of a PDR.[68] Indeed, the warmer temperature makes many chemical processes much more facile, and a number of molecules have only been observed in circumstellar envelopes. Particularly popular for molecule spotting is the nearby planetary nebula NGC7027,[69] which has a particularly hot and vigorous central star.

6 ATMOSPHERES OF COOL STARS

The stars that are visible to the naked eye in the night sky are substantially composed of atomic ions. These bright stars are too hot for complicated molecules to form, although stars such as our sun are cool enough for some diatomic molecules to form in their atmosphere.

The night sky also contains many fainter stars that can only be seen with specially adapted telescopes. Many of these are distant hot stars, but there are also a substantial number of cool stars. Indeed, it is believed that these small, cool stars are the most abundant in the universe.

Figure 5 gives the schematic of molecular formation in the atmosphere of these cooler stars as a function of temperature. Stars whose atmosphere is below about 4000 K show strong features owing to molecular absorptions in their atmosphere. Indeed, they are the dominant spectroscopic features in these atmospheres. As molecular spectra

appear as broad bands, because of the unresolved rotational structure, these absorption features are usually extensive, making it difficult to estimate a stellar temperature by the standard technique of fitting its light curve to a black body form.[70]

The molecular composition of stellar atmosphere divides neatly into two classes: oxygen-rich M-stars and the less common carbon-rich C-stars.[71] Table 5 lists molecules observed in each class of cool star as well as our own sun, which is oxygen rich but hotter than a typical M-star. Included in Table 5 is information on rare S-stars that have a C to O ratio of approximately unity. Table 5 only lists molecules that have been detected with confidence; Jorgensen[72] also gives tentative detections.

Unlike much of the astrochemistry discussed in the preceding text, the chemistry of stellar atmospheres is that of thermodynamic equilibrium. Under these circumstances, the carbon and oxygen rapidly combine to form the strongly bound CO molecule. The characteristics of the star are then determined by whether there is oxygen (M-stars), carbon (C-stars), or neither (S-stars) left over after CO formation.[71]

The chemistry of M-stars is relatively simple with water, the most important source of molecular opacity.[70,73] However, various rather surprising transition metal oxides, and particularly TiO, are also found to have prominent spectra.[70,73] These molecules are important since they possess a dense forest of vibronic transitions in the mid- or near-infrared where the black body curve of the cool stars peaks. Grains, sometimes also referred to as dust, can also form in an atmosphere of cooler M-dwarfs. The exact composition of these micro-particles remains a matter of speculation.[70]

Carbon stars have a rather richer chemistry, and polyatomic molecules such as HCN, C_3, and acetylene are found
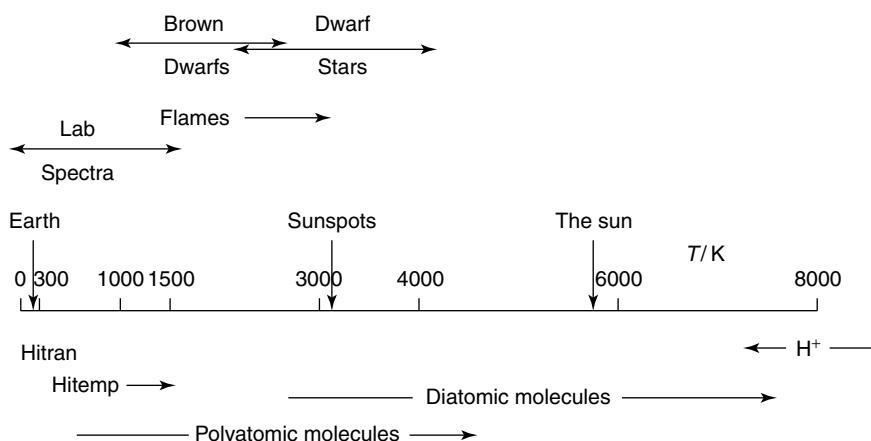
Figure 5. Schematic molecular thermometer displaying the approximate temperature range in which molecules are found in different bodies and possible sources of spectroscopic data.

Table 5. Molecules observed in the atmosphere of cool stars.[72] See text for a description of the star types.

Molecule	Sun	M	S	C
AlH	x	x	x	x
CaH	x	x		
CrO		x		
CH	x	x	x	x
CS				x
GeH				x
HCl	x		x	
MgO		x		
OH	x	x	x	
SiH	x	x	x	x
SnH				x
TiS			x	
YS			x	
ZrS			x	
C_2H				x
CaOH		x		
SiC_2				x
AlO		x		
CaCl				x
CrH	x			
CN	x	x	x	x
CuH	x			x
H_2	x	x	x	x
LaO		x		
NH	x	x		x
ScO	x	x	x	
SiN		x		
TiH	x	x		
VO		x	x	
ZnH				x
SiH^+	x			
C_2H_2				x
HCN				x
BO		x		
CeO			x	
C_2	x			
CO	x	x	x	x
FeH	x	x	x	
HF	x	x	x	x
MgH	x	x	x	
NiH	x			
SiF		x		
SiO	x	x	x	
TiO	x	x	x	
YO		x	x	
ZrO	x	x	x	
CH^+	x			
C_3				x
H_2O	x	x		

in significant abundances. Even the presence of micro-diamonds is considered.[74] The role of the dense spectra of molecules in determining the properties of these cool stars is neatly illustrated by studies of the role of HCN.[75]

Models that added eight vibrational bands of HCN to the then standard cool star atmosphere increased the size of the stellar photosphere by a factor of 5![76]

It is now usual to include large amounts of molecular data in models of cool stellar atmospheres.[70,73] Such calculations require detailed spectroscopic information on a line-by-line, molecule-by-molecule basis to construct stellar opacities as a function of wavelength, temperature, and chemical composition. The starting point for constructing such information are databases compiled for models of hot stars, such as those given by Kurucz,[77,78] augmented by data from standard molecular spectroscopy databases such as HITRAN[79] or GEISA.[80] However, these latter compilations, which are geared largely towards studies of radiative transport through the earth's atmosphere, do not contain sufficient information for studies of 'cool' stars (see Figure 5). It has therefore become standard to use theoretical (ab initio) calculations to generate large lists of molecular transitions.[81−84]

In hot stars, atomic opacities depend on electronic transitions between atoms at various stages of ionization. The physics underlying molecular opacities can be rather different. For stable polyatomic molecules such as water or HCN, the dominant process that needs to be understood are vibration−rotation transitions of hot molecules. The sheer number of possible vibration−rotation transitions between thermally excited levels of these molecules leads to almost blanket absorption over important parts of the spectrum of cool star such as the near-infrared. Opacities for transition metal diatomics such as TiO, VO, ZrO and FeH have been actively considered;[70] in this case the important transitions are electronic ones. These molecules have open shell structures and many low-lying electronic states leading to complicated and dense electronic spectra that can blanket much of the visible region of the spectrum.

Molecules are not the only source of opacity in the atmospheres of cool stars. The H^- anion is an important opacity source in a number of cool stars including our own Sun. One class of cool stars not considered in Table 5 are the 'metal-free' stars that consist entirely of hydrogen and helium. The original stars in the Universe must have been of this form and it is still possible to observe examples. H^- forms the major opacity source in these stars although electrical neutrality dictates that there must also be cations present. Models show[85] that for cool metal-free stars it is the H_3^+ molecular ion that plays this role.

There is a class of substellar objects that are so faint that their spectra are only just beginning to be extensively studied. These 'stars' that are not massive enough to undergo hydrogen burning nuclear reactions are called *brown dwarfs*. Studies[86,87] have shown that brown dwarfs,

Table 6. Molecules identified in comet Hale-Bopp, C/1995O1,[93] see also Wootten [1].

Simple species							
H_2O	HDO	CO	CO_2	H_2S	SO	SO_2	OCS
CS	Na	NH_3					
Molecular ions							
H_2O^+	H_3O^+	HCO^+	CO^+				
Hydrocarbons, nitriles, and acetylene derivatives							
HCN	DCN	CH_3CN	HNC	HC_3N	HNCO	C_2H_2	C_2H_6
CH_4	NH_2CHO						
Aldehydes, alcohols, esters, ketones, amides, and related molecules							
CH_3OH	H_2CO	HCOOH	H_2CS	CH_3OCHO			
Radicals							
OH	CN	NH_2	NH	C_3	C_2		

with atmospheric temperatures below 1500 K, show prominent features due to both water and methane. Indeed, spectral analysis suggests that at about this temperature there is a switch from carbon being predominantly in CO, as found in the hotter stars, to forming methane,[87] as found in the atmospheres of the gas giant planets.

So far, stellar spectra have been discussed as if they are isotropic for the whole surface of the star. However, our own Sun has long been known to have cool features or spots on its surface. The chemical composition of sunspots differs somewhat from the rest of the Sun's atmosphere owing to the lower temperature: 3200 K as against 5800 K. At these lower temperatures, water is observed to be a prominent component.[88] The hydroxyl radical is well known in the solar spectrum. However, as the atmosphere cools in the penumbra around a sunspot (an 'umbra'), OH turns to water. Under solar conditions, OH and water populations are approximately equal at 4000 K.

7 COMETS

Comets can be thought of as large, dirty ice-balls.[89,90] They are substantially composed of water. Indeed, it is conjectured that comets are responsible for much of the water on Earth replenishing the hydrogen that was lost from our primordial planet. It is also thought that comets are formed far out in space and therefore provide a direct link with the ISM. Such ideas can be tested using isotopic abundances and, in particular, D to H ratios, and it should be noted that the terrestrial D/H ratio differs significantly from that generally observed in the ISM. Recent spectroscopic observations of comets tend to confirm ISM composition of comets but, in consequence, argue against comets being the main source of hydrogen on earth.[91]

Spectroscopic studies of cometary tails allow the volatile material that is ejected as the comet passes close to the

Sun to be studied. Recent comets such as Hyakutake and Hale-Bopp have passed close to the earth and have greatly increased the knowledge of comet chemistry.[92] Table 6 summarizes the molecules observed in Hale-Bopp, the most intensively studied of these comets.[93] Spectroscopy gives information on the gas-phase molecules in the comets' tails. Table 6 includes ions detected in comet Hale-Bopp although the ions are produced by photoionization, and possibly subsequent chemistry, in the tail.

8 SUMMARY

Molecules are widespread throughout the Universe, where the differing local conditions lead to different chemistries. A great variety of molecules, whose number is still steadily increasing, have been identified in space. At present by terrestrial standards, only relatively small molecules have been firmly identified outside our solar system. It would be a mistake to assume from the lack of positive detections that larger molecules do not occur naturally in space. The spectroscopic techniques that have proved so adept at characterizing small molecules in a wide range of locations are not so clear cut for large molecules. For larger molecules, the spectra suffer from not being fully resolved even using high-resolution studies and not being completely characteristic, especially if the molecules exist in close proximity with several similar species.

This summary has not considered the molecular composition of the planets in our solar system. Spectroscopic techniques have been extensively applied to these objects, and all the planets with atmospheres have also been visited by unmanned satellites. The discovering of a large number of planets orbiting other stars has put an emphasis on trying to determine the molecular composition of these newly identified bodies. Such studies hold the key to determining whether we are the sole occupants of our galaxy. It can

thus be assumed that the study of molecules in space will remain a lively one for the foreseeable future.

NOTES

[1] Wootten, A.,   *http://www.cv.nrao.edu/~awootten/all-mols.html*.

[2] see General Discussion in (1998) Faraday Discuss. **109**, 217.

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