The chemistry of interstellar space

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Interstellar space is not empty, but contains gaseous and particulate matter that is concentrated into very large regions known as interstellar clouds. In the denser and cooler clouds, the gas is molecular and most of the molecules detected are organic in nature. The gas-phase molecules are synthesised from precursor atoms by rapid exothermic reactions in the gas and on the surfaces of tiny dust particles. Since dense interstellar clouds collapse to form stars and planetary systems, the molecules produced in the clouds may be eventually incorporated into solid bodies such as comets, meteors, and even planets.

1 Introduction

Matter in the universe is condensed into galaxies, each of which contains large numbers of stars. Although light from these stars dominates the night-time sky to a casual observer, there is also a significant amount of cool matter amongst the stars that cannot be detected easily by the naked eye. Interstellar matter is condensed into regions known as clouds, which can be many light years in extent and which contain material in the form of both gas and small dust particles approximately 0.1 μm in radius.[1] Although the dust particles contain only 1% of the matter, they scatter and absorb sufficient starlight that it is difficult if not impossible to see through the denser clouds in the visible.

Working in various regions of the electromagnetic spectrum, astronomers have measured the composition of the gas and, to a lesser extent, the dust particles.[2,3] In so-called diffuse clouds,

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which possess gas densities of 10–1000 cm^{-3} and temperatures of 50–100 K, the gaseous matter is probed by optical absorption spectroscopy with background stars as lamps. From the assigned absorption lines, astronomers have deduced that the gas is mainly atomic and neutral in nature, with a fractional ionisation on the order of 10^{-4}. The elemental abundances in the gas resemble those found in stars, where hydrogen dominates, helium has a concentration perhaps 10% of hydrogen, and the important elements carbon, nitrogen, and oxygen are 10^{-3}–10^{-4} of the hydrogen density. Some of the heavier elements found in stars are depleted strongly from the diffuse cloud gas; presumably these elements (*e.g.* silicon) are incorporated into the dust particles. As in most sources in the sky, there is more elemental oxygen than carbon. In addition to the assigned lines, there are several hundred unidentified absorption lines, many of which are broader than customary. These so-called 'diffuse interstellar bands' have remained unidentified for much of the last century, and are now thought to be caused by rather large and exotic organic molecules in the gas.[4] The widths of the broader lines in this hypothesis are due to internal conversion of electronic into vibrational energy. Although no definitive assignments have been made, tentative assignments of a few weak features to the bare carbon anionic chain molecule C_7^- and to the fullerene ion C_{60}^+ have provoked enthusiasm and controversy. In addition, the hypothesis that most of the stronger bands are due to a mixture of ionized polycyclic aromatic hydrocarbons has gained some plausibility although convincing laboratory evidence is not yet in hand.

Fig. 1 shows a small dense cloud known as the 'Black Cloud' Barnard 68. This cloud is sufficiently nearby (its distance is only 500 light years) that there are no stars in front of it to

Fig. 1 The 'Black Cloud', otherwise known as Barnard 68. This small cloud is sufficiently dense to extinguish almost all background starlight. Permission to reproduce the figure has been granted by ESO. Taken from web site http://antwrp.gsfc.nasa.gov/apod/ap990511.html

minimize the effect of strong extinction in the visible. Dense clouds such as Barnard 68 and its much bigger cousins obviously cannot be studied in the visible but must be observed at longer wavelengths, in particular the infrared and the

millimetre-wave, which have no difficulty in penetrating through the dust particles. Astronomers are particularly interested in the larger dense clouds because they are the birthplaces of stars; small portions of matter in the clouds gradually collapse and heat up to the point where nuclear reactions can begin and stars are born. The stars eventually blow away the interstellar matter surrounding them, although this can take millions of years, and astronomers are often able to study both star formation regions and newly-born stars within clouds. Except in regions surrounding newly formed and forming stars, the gas and dust in dense clouds is quite cold—temperatures of 10–30 K are common. Gas densities can be quite inhomogeneous; the denser matter in large clouds is found in regions known as 'cores', where the density can be 10^4 cm^{-3} or even more. Many cores are quiescent in nature, although many others are beginning the slow process of collapse to form stars. In the vicinity of young and forming stars (sometimes lumped together as 'young stellar objects'), a wide variety of manifestations can be detected depending upon the mass of the object. Particularly fascinating are dense 'protoplanetary' disks of gas and dust found to be surrounding very young low-mass stars and presumably the forebears of planetary systems, and very hot luminous regions of ionised matter (so-called H II regions) surrounding bright high-mass stars. Fig. 2 shows four protoplanetary disks serendipitously seen against the background light coming from an H II region in the Orion Nebula, a large dense interstellar cloud.
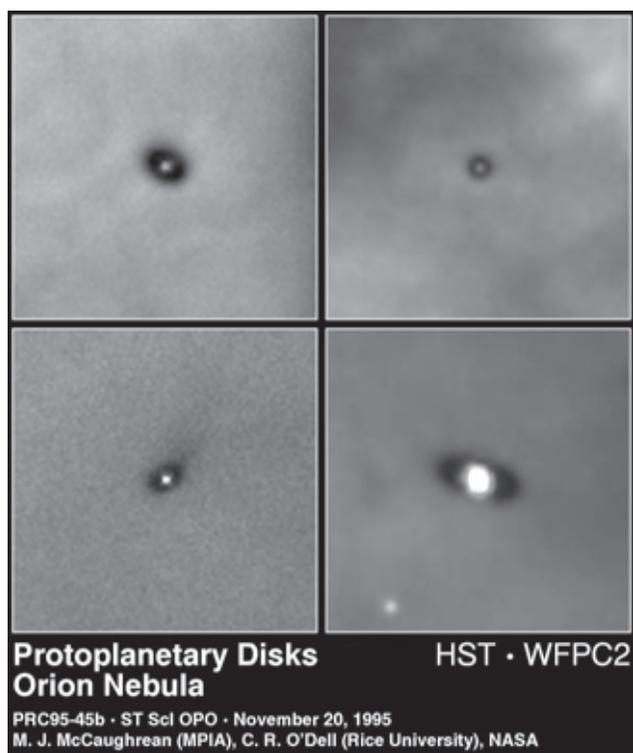

Fig. 2 Four protoplanetary disks and their central stars in front of a bright region in Orion. Permission to reproduce the figure has been granted by ST Sci and by the author, C. R. O'Dell (currently at Vanderbilt University). Taken from web site http://oposite.stsci.edu/pubinfo/jpeg/OriProp4.jpg

Until recently, the main technique for studying dense interstellar clouds was 'radio astronomy', by which is really meant astronomy in the millimetre-wave and submillimetre-wave portions of the spectrum.[5] Radio telescopes can operate from the ground and peer through the atmosphere of the earth at wavelengths as short as 1 mm. At still shorter wavelengths, there are windows of transparency through the atmosphere, and ground-based observatories probing the sub-millimetre-wave sky exist. Supplementing these have been a number of airborne and satellite observatories. If a millimetre-wave telescope is aimed at a dense interstellar cloud and the radiation dispersed,

one sees a weak continuum in emission due to the dust particles and many thousands of individual sharp emission lines. The lines are produced by gas-phase molecules relaxing from higher to lower rotational energy levels with the concomitant spontaneous (and sometimes even the stimulated) emission of radiation. More recently, infrared astronomy has been increasingly utilised despite severe atmospheric attenuation. The role of the European satellite ISO has been especially prominent. (See the web page http://www.iso.vilspa.esa.es/science/publications.html for a list of publications.) Cool regions of dense interstellar clouds do not emit in the infrared, and it is necessary to perform absorption spectroscopy with infrared lamps that can consist of serendipitously situated background stars or even young warm stellar objects within the clouds themselves. In the infrared, one can detect sharp features due to gas-phase vibrational–rotational transitions of molecules superimposed upon broader features due to condensed phase material. In addition, near very hot ionised matter, one can detect rather warm neutral matter from regions known as 'photon dominated' material that is able to emit in the infrared.

In dense interstellar clouds, the gaseous matter is known to be overwhelmingly molecular from comparison of the high-resolution spectral lines in the millimetre-wave and the infrared with laboratory spectra. More than 120 different molecular species have been detected in dense clouds and similar clouds surrounding old low-mass stars.[2] In addition, a wide variety of isotopomers including elements such as D, ^{13}C, and ^{18}O have been seen. The molecules range in size from 2–13 atoms and are mainly organic in nature. About half of the molecules detected are common or easily synthesised terrestrial species, including water, ammonia, formaldehyde, and simple alcohols (methanol, ethanol). The other half consists of a witches' brew of molecular positive ions (*e.g.* H_3^+, HCO^+, H_3O^+), radicals (*e.g.* C_nH through $n = 8$), isomers (*e.g.* HNC, HCCNC, HOC^+), and unusual three-membered rings (*e.g.* C_3H, C_3H_2). Molecules containing second-row elements such as sulfur and silicon are also present. Molecular hydrogen is the dominant species, having a concentration roughly 10^4 times that of the second most abundant molecule—CO. This reflects to some extent the relative abundances of the elements. All polyatomic species are trace species in the sense that their fractional abundances with respect to H_2 are very small, yet the total amount of each molecular species is very large indeed.

The detection of interstellar molecules *via* high-resolution spectral features enables astronomers to understand the physical conditions in the sources where they are found.[6] In addition to what molecules are present and what their concentrations are, astronomers can determine temperatures by relative intensities of the lines from a given species. They can also determine the total gas density throughout dense interstellar clouds in an indirect manner since the rotational emission lines detected in such sources are excited by collisions, mainly with the dominant species H_2. Direct detection involves observation of the overwhelmingly dominant species H_2, which is non-trivial since it is non-polar. Nevertheless, detection of molecular hydrogen has been accomplished *via* its quadrupolar pure rotational and rotational–vibrational spectra, albeit in selected regions only because the emission lines are hard to excite and absorption can only be studied where a background lamp exists. To determine the total gas density indirectly from the emission lines of other species, one can, given knowledge of cross sections for rotationally inelastic collisions, compute a critical (minimum) density of excitation at which the collisional pump upwards is equal to the radiative rate downwards. Weakly polar molecules such as CO radiate slowly, especially from low-lying excited rotational states, and so their emission lines require only small critical densities and can be seen in lower density portions of dense clouds. Highly polar molecules, on the other hand, can only be detected in cores of high density. Using a variety of species and transitions, radio astronomers can map out accurate

density maps of clouds.[3,6] Fig. 3 shows a contour map of a core (TMC-2) in the Taurus dense molecular cloud as measured *via* the $J = 1 \rightarrow 0$ rotational emission line of the polar ion N_2H^+.
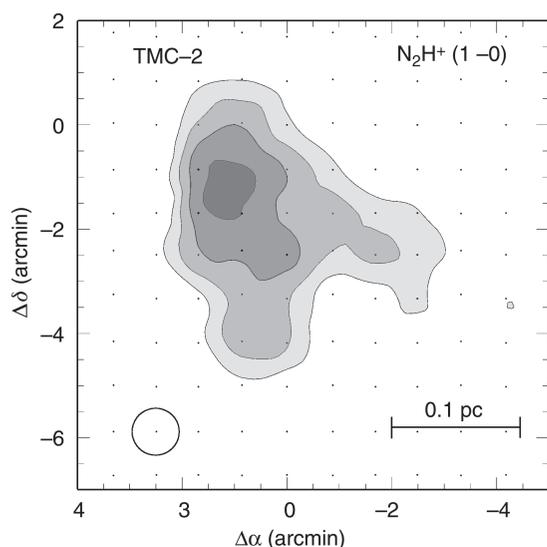

Fig. 3 A contour map of the TMC-2 core in the Taurus molecular cloud as measured *via* the $J = 1 \rightarrow 0$ rotational transition of the polar ion N_2H^+. The abscissa and ordinate are in units of minutes of arc along the sky. See text for more details. The author is kindly indebted to his collaborator Paola Caselli (Arcetri Observatory, Florence, Italy) for the figure.

The observations were made with the radio telescope at the Five College Radio Astronomical Observatory in Massachusetts. The size of the core is roughly 0.2 parsecs (1 pc = 3.09×10^{16} m). The abscissa and ordinate are plotted in terms of differences in astronomical longitude and latitude (right ascension and declination, respectively) in units of minutes of arc. The dots are the positions observed with the radio telescope. The contours range from 30% of peak intensity to 90% of peak intensity in steps of 20%. The spatial resolution of the telescope is indicated in the lower left, where the circle indicates the half-power beam width.

Unlike the gas phase, the nature of the dust particles is not yet well established.[7] From the scattering, polarisation, and absorption of radiation, one can deduce that the particles are non-spherical, and have a mean size of perhaps 0.1 μm. Whether they are fluffy or fractal in nature is uncertain although commonly assumed. From the depletion, relative to stellar abundances, of selected elements from the gas phase of diffuse clouds, one can deduce that heavy elements such as Si and Fe are important constituents of the dust but so are lighter elements such as O and C. Although the lighter elements are not as heavily depleted, their high abundances mean that even small depletions are important. Stronger clues to the chemical nature of the dust particles come from spectroscopic evidence in the ultraviolet and in the infrared. In the UV, there is a broad absorption feature in diffuse clouds at 217.5 nm that is commonly ascribed to carbonaceous particles. In the IR, there are features at 10 μm and 20 μm seen in emission in warm regions and in absorption in cold regions that are ascribed to silicates. Thus, it would appear that there are two grain populations—one carbonaceous and the other composed of metallic silicates. In addition, broad absorption features seen only in dense interstellar clouds are caused by ice mantles that develop around dust particle cores. The mantles consist mainly of water, CO, CO_2 and methanol ices, with water ice dominant. The relative proportions of these species in the ice mantles are source dependent. From detailed simulation of the ice features, laboratory astrophysicists can determine whether they arise from polar or non-polar environments.

A series of broad infrared emission features from warm regions of dense clouds near luminous areas has been assigned in terms of a mixture of neutral and ionised UV-pumped free polycyclic aromatic hydrocarbons (PAHs) with 10–50 C atoms, as well as PAH clusters and small dust particles composed of PAH sub-units.[8] The amount of carbon tied up in these molecules represents a substantial fraction of the carbon elemental abundance seen in stars. The dust particles composed of PAHs probably represent the small end of the distribution of sizes; larger carbonaceous particles may well be more graphitic in nature. It is not obvious that all dust particles are wholly carbonaceous or silicaceous; so-called interplanetary dust particles, collected above the earth but thought to have an interstellar origin, can contain both silicates and carbonaceous material within the same particle!

2 Interstellar chemistry: basic considerations

How are molecules synthesised in space? Perhaps a more basic question to ask is: where are molecule synthesised? There are literally two choices: they are produced within the clouds themselves or they are produced elsewhere and transported to the clouds. The problem with *in situ* production is that the physical conditions—low densities and low temperatures—are not normally associated with rapid chemistry. Consider a species A in a dense cloud. If we assume a collisional rate coefficient k_{coll} of 1×10^{-10} cm³ s⁻¹ and a gas density of 10^4 cm⁻³, the frequency of collision between A and other species is 1×10^{-6} s⁻¹. The corresponding time interval between collisions is 10^6 s or ≈2 weeks, and the mean free path assuming a speed of 10^4 cm s⁻¹ is 10^{10} cm = 100 000 km! Nor are the infrequent collisions necessarily reactive. Most chemical reactions have rate coefficients k that obey the Arrhenius law [eqn. (1)]:

$$k = A(T)\exp(-E_a/k_BT) \qquad (1)$$

where $A(T)$ is the pre-exponential factor, which may have a small temperature dependence, E_a is the activation energy, and k_B is the Boltzmann constant. This equation rules out all possible processes with an activation energy since, at a typical dense cloud temperature of 10 K, $E_a \gg k_BT$ and the exponent in eqn. (1) is very large and negative. The processes that do not occur efficiently include all endothermic reactions and most exothermic reactions.

As opposed to these negative considerations, conditions in stellar atmospheres, especially around very old stars which have huge atmospheres known as envelopes, appear to be more conducive to synthetic chemistry. In such atmospheres, temperatures range from thousands of K near the actual border of the star (the so-called photosphere) down to 10 K at the outer edge of the envelope, and densities are high enough so that dust particles can condense out in the inner regions. In addition to the dust particles, molecules are detected in the envelopes of old stars, especially in those rare instances in which there is more elemental carbon than elemental oxygen (so-called 'carbon-rich' sources).[9] Both the dust particles and the molecules are gradually expelled into space by strong winds from the star. Molecules and dust particles are also formed in explosive events such as supernovae, which come at the end of the lifetime of massive stars. Consequently, one might conclude that interstellar molecules are just remnants of earlier stellar material. But the conclusion is incorrect, at least for smaller molecules, because the ultraviolet radiation field in unshielded interstellar space is sufficiently strong to photodissociate small molecules within 100 years, which is an instant in astronomy.[10] That leaves dust particles and possibly large molecules such as PAHs that are relatively inert to strong radiation as the only candidates for a non-interstellar source. Thus, although stellar events, both massive explosions and gentler winds, result in the ejection of gaseous and particulate matter into the interstellar medium,

where they eventually form interstellar clouds under the influence of gravity, the gaseous matter is mainly atomic in nature. For all of the interstellar molecules detected *via* high resolution spectroscopy, it appears that their synthesis must occur within the clouds themselves. How is this possible?

Let us look more carefully at the objections raised above to the *in situ* production of molecules in interstellar clouds. The long time intervals between collisions are long only by terrestrial standards; since clouds can live for hundreds of thousands of years or even longer, a chemistry based on collisions occurring every few weeks can still be rapid in an astronomical sense. Moreover, not all reactions occur with activation energy. For example, exothermic reactions between radicals are known to have large rates that possess very little if any temperature dependence. In addition, a small number of reactions involving an atom (*e.g.* C) or a radical (*e.g.* CN) and stable neutral species such as unsaturated hydrocarbons, have been found to proceed without activation energy and to have large rate coefficients at temperatures as low as 10 K.[11] More important in the interstellar context are exothermic reactions between positive ions and neutral molecules, known as ion–molecule reactions. Such processes tend quite frequently to have no activation energy barriers. Reactions involving ions and non-polar neutrals most often follow a very simple expression for the rate coefficient first derived by Langevin [eqn. (2)]:

$$k_{\text{ion–mol}} = 2\pi e(\alpha/\mu)^{1/2} \qquad (2)$$

where (in cgs units) e is the electronic charge, α is the polarisability, and μ is the reduced mass of the reactants.[12] This expression for the rate coefficient, which is totally independent of temperature, is based on the strong ion-induced dipole long-range force. It can be derived by the simple assumption that all collisions leading to capture or orbiting are reactive in nature. A typical value for $k_{\text{ion–mol}}$ is 10^{-9} cm^3 s^{-1}, which is 10–100 times as great as typical rate coefficients for neutral–neutral reactions without activation energy. The Langevin expression has been confirmed in experiments from room temperature and above down to temperatures below 10 K.[13] Moreover, exothermic ion–molecule reactions involving a polar neutral show an even more dramatic behaviour—they increase in rate coefficient as temperature is decreased, with a typical dependence of $T^{-1/2}$. By 10 K, rate coefficients for such reactions can be as large as 10^{-7} cm^3 s^{-1}![13] But how can interstellar ions be formed?

In diffuse interstellar clouds, ions can be produced by photoionisation caused by external UV photons since the density of dust particles is not sufficient to extinguish the interstellar radiation field to a great extent. But, these same photons photodissociate any molecules formed, so that the *in situ* gas-phase chemistry does not lead to high abundances of any molecules. In dense clouds, radiation does not penetrate deeply into the clouds, and the dominant source of ionisation is cosmic ray bombardment. Cosmic rays are bare nuclei travelling near the speed of light throughout the universe; such particles have a high penetrating power and can ionise atoms and molecules in their paths. The ionisation rate coefficient caused by cosmic rays can be estimated by actual measurement of the flux of such particles above the earth multiplied by the cross section for ionisation,[1] or by analysis of the abundances of selected ions in dense clouds.[14] For the case of H$_2$, one can derive a unimolecular rate coefficient for ionisation ζ of $\sim 10^{-17}$ s^{-1}. This small value leads only to a tiny fractional ionisation of $\sim 10^{-7}$–10^{-8} in dense clouds, but this fraction is enough to dominate the interstellar gas-phase chemistry.

Although we have seen that selected gas-phase processes can occur relatively rapidly under interstellar conditions, we have not seen how these processes can synthesis precursor atomic material into molecules as large as 13 atoms or more in size. The biggest roadblock in the path of synthesis is the conversion of atoms into diatomic molecules. Consider, for example, the conversion of H into H$_2$, which must occur in dense clouds since the gas is overwhelmingly molecular. If two H atoms collide with each other in the gas, they almost always separate shortly afterwards. There is a finite but exceedingly small possibility that a molecule of hydrogen can be formed; the system must rid itself of sufficient energy *via* emission of radiation to stabilize the H$_2$ chemical bond. This process, known as radiative association, is more efficient for larger sytems involving molecules, in which the collision complex can live for a long period of time and so increase the possibility that radiation is emitted. But it cannot convert atomic to molecular hydrogen under interstellar conditions.[15] Nor is the three-body associative process possible; the chance that a third body strikes the H$_2$ collision complex before it dissociates so as to stabilise it is nil under low density conditions. So, how does molecular hydrogen form?

One must remember that 1% of interstellar matter by mass is tied up in dust particles. The surfaces of these dust particles can provide a template (one hesitates to use the word 'catalyst') for chemical reactions.[15] Consider what happens when a hydrogen atom strikes a grain and, given the low temperatures, presumably sticks to it with high efficiency. If we assume that the atom is weakly bound, it can diffuse to other binding sites on the surface. The surface chemistry that ensues goes *via* the Langmuir–Hinshelwood, or diffusive, mechanism: a diffusing hydrogen atom eventually finds another such and they recombine to form a molecule by giving off sufficient energy to the dust particle, the temperature of which rises slightly. The nascent molecule can evaporate even at 10 K, or, as has been actually measured in recent experiments of the process, can desorb by utilising a portion of the reaction exothermicity as kinetic energy.[16] Although these recent experiments have shown that H$_2$ can be formed *via* a diffusive chemistry on assorted interstellar-type surfaces (olivine, amorphous carbon), they have also shown that the process may not be efficient enough to fully convert H into H$_2$ in dense clouds within reasonable astronomical time scales (10^5–10^6 yr).[16] Still, there does appear to be no alternative to the formation of H$_2$ in interstellar clouds.

Molecular hydrogen is clearly not the only species that can be produced *via* surface chemistry.[7] If weakly-bound hydrogen atoms can find one another *via* diffusion on grain surfaces, they can find heavier atoms stuck to the grains such as O, C, and N, leading to the production of the radicals OH, CH, and NH. Subsequent hydrogenation of these radicals leads eventually to the fully saturated species H$_2$O, CH$_4$, and NH$_3$ since reactions involving radicals do not possess any activation energy barriers. It is unclear if any of these species can be ejected from the surface during the process of formation; if not they cannot evaporate from cold grains since they are bound more strongly than H$_2$. Some non-thermal processes such as cosmic ray bombardment can slow the disappearance of the gas phase albeit with highly uncertain rates. Nevertheless, the inexorable result will be the slow development of mantles of ices, a result in agreement with observation. It is not known whether atoms heavier than hydrogen and radicals can diffuse rapidly enough on grain surfaces to react with one another, nor is it obvious that the products of such reactions are always simple addends. Indeed, the uncertainties in grain surface chemistry are sufficiently great that many investigators tend to avoid consideration of the subject except for the formation of H$_2$.

## 3 Gas-phase interstellar chemistry: reactions and models

Once H$_2$ is formed on grains and desorbed into the interstellar gas, it can be ionised by reactions with cosmic rays.[14] The dominant process is single ionisation [eqn. (3)]:

$$H_2 + \text{cosmic ray} \rightarrow H_2^+ + e^- + \text{cosmic ray} \qquad (3)$$
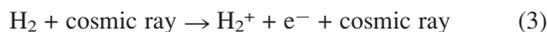
which occurs with a unimolecular rate coefficient ζ. The H_2^+ ion produced is reactive with ubiquitous molecular hydrogen, and reacts quickly to form H_3^+ [eqn. (4)]:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (4)$$
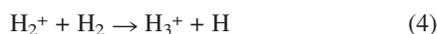
The H_3^+ ion, detected *via* infrared absorption, is relatively abundant because it does not react with H_2.[14] The ion can react with other primary neutral atoms and is the precursor for much of the gas-phase chemistry that occurs in dense interstellar clouds.[17] For example, the reaction with atomic oxygen initiates a chain of well-studied reactions leading to the oxonium ion:

$$H_3^+ + O \rightarrow OH^+ + H_2 \qquad (5)$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H \qquad (6)$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H \qquad (7)$$
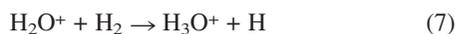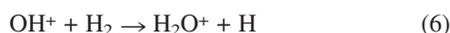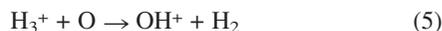
The oxonium ion, detected *via* millimetre-wave emission, eventually is destroyed by dissociative recombination with electrons. Such reactions are quite rapid, with rate coefficients on the order of 10^{-6} cm^3 s^{-1}.[18] The branching fractions of the possible exothermic products of the reaction, $H_2O + H$, $OH + H_2$, $OH + 2H$, and $O + H_2 + H$, have been studied in both a benchtop 'flowing afterglow' apparatus and in two large Scandinavian storage rings named ASTRID and CRYRING. The agreement among the three experiments is far from ideal— for the water channel, the storage ring results are 18% and 24%, while at most 5% water is detected in the flowing afterglow experiment.[17] Most independent observers tend to support the storage ring results. In any case, the production of water by gas-phase reactions serves as a paradigm of ion–molecule syntheses: chains of such reactions lead to polyatomic molecular ions which eventually recombine with electrons to form smaller neutral products.

As another example, consider the chain of reactions resulting from the initial reaction of atomic C and H_3^+:

$$H_3^+ + C \rightarrow CH^+ + H_2 \qquad (8)$$

$$CH^+ + H_2 \rightarrow CH_2^+ + H \qquad (9)$$

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H \qquad (10)$$
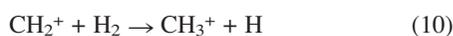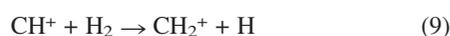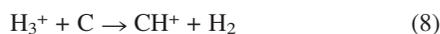
An analogous H-atom transfer reaction between CH_3^+ and H_2 does not occur because it is endothermic. Instead, a radiative association reaction has been measured to occur [eqn. (11)]:

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \qquad (11)$$
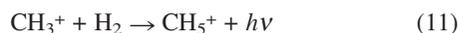
with a rate coefficient of $\sim 10^{-13}$ cm^3 s^{-1} at low temperatures.[19] Although the rate coefficient is small, the reaction is competitive because of the large abundance of molecular hydrogen. The dissociative recombination between CH_5^+ and electrons that follows has been studied in one storage ring, and the major product is methyl (CH_3) rather than methane. Methane is produced *via* a competitive reaction with abundant CO [eqn. (12)]:

$$CH_5^+ + CO \rightarrow CH_4 + HCO^+ \qquad (12)$$

The CO molecule is itself formed *via* a wide variety of reactions including processes such as:

$$O + CH_3^+ \rightarrow HCO^+ + H_2 \qquad (13)$$

$$HCO^+ + e^- \rightarrow CO + H \qquad (14)$$
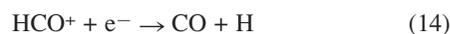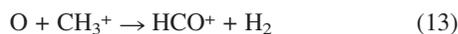
An alternative initiating reaction for hydrocarbon synthesis to reaction (8) involves C^+, which at times can be as abundant as neutral C. In particular, C^+ undergoes a slow radiative association reaction with H_2:

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \qquad (15)$$
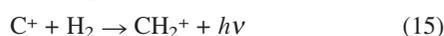
which is measured to occur with a rather small rate coefficient of $\sim 10^{-15}$ cm^3 s^{-1} at interstellar temperatures.[19]

Once simple hydrocarbons such as methyl and methane are formed, more complex hydrocarbons can be produced *via*

several classes of reactions,[20] the most important of which is carbon insertion, in which either C^+ or C inserts itself into a smaller hydrocarbon to form a larger one; *viz.*,

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H, C_2H_2^+ + H_2 \qquad (16)$$
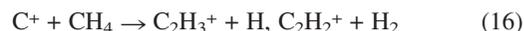
Another important class of reactions is labelled condensation. Here a hydrocarbon ion and a hydrocarbon neutral react to form a larger product, *viz.*:

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H, C_4H_2^+ + H_2 \qquad (17)$$
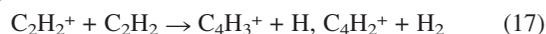
Yet a third class of reactions important in hydrocarbon synthesis is radiative association, although here experimental evidence is often lacking and theory must be used.[21] For example, reactions of the type

$$C^+ + C_n \rightarrow C_{n+1}^+ + h\nu \qquad (18)$$
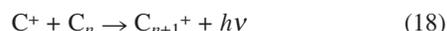
have been calculated to be efficient in building bare carbon chains once n is larger than 3 or 4. As another example, the C_3H^+ ion, formed in the ion–molecule reaction between C^+ and C_2H_2, is thought to associate with H_2 to form a precursor to the cyclic species C_3H_2:

$$C_3H^+ + H_2 \rightarrow c\text{-}C_3H_3^+ + h\nu \qquad (19)$$
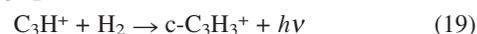
Hydrocarbon neutrals are produced *via* dissociative recombination reactions between hydrocarbon ions and electrons, although experimental evidence of the exact products and their branching fractions is often lacking.

Neutral–neutral reactions involving atomic C are also efficient in synthesis.[11] For example, the well-studied reaction (20)

$$C + C_2H_2 \rightarrow C_3H + H \qquad (20)$$

is known to be efficient at low temperatures and to produce the cylic and linear forms of the C_3H radical, both of which are observed in dense clouds. Interestingly, only ion–molecule reaction chains lead efficiently to the more saturated three-membered ring species C_3H_2. Neutral–neutral condensation reactions such as

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \qquad (21)$$
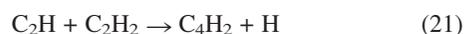
are also important. Neutral–neutral reactions can lead to the production of complex species other than hydrocarbons as well. The radical CN can react with acetylene efficiently at low temperatures to produce cyanoacetylene, a well-known interstellar species:

$$CN + C_2H_2 \rightarrow HCCCN + H, \qquad (22)$$

and analogous reactions with larger alkynes can lead to more complex members of the cyanopolyyne family, of which HC_9N is the most complex detected in dense clouds. Ion–molecule reactions can also lead to these species *via* reactions such as

$$N + C_3H_3^+ \rightarrow HC_3NH^+ + H \qquad (23)$$

followed by dissociative recombination.

Ion–molecule and neutral–neutral pathways for many molecules have been included in large networks used in model calculations.[22] In these 'purely' gas-phase models, chemical reactions in the gas both produce and destroy molecules with the exception of H_2, which is produced on grain surfaces. Photodestruction and cosmic ray processes must also be considered. For each species i in the model, the concentration $n(i)$ as a function of time is given by a differential 'rate' equation of the type shown in eqn. (24):

$$dn(i)/dt = \Sigma k_j n(j) + \Sigma k_{jl} n(j) n(l) - n(i) \Sigma k_{ij} n(j) - k_i n(i) \quad (24)$$

where formation and destruction terms include both bimolecular chemical reactions and unimolecular processes involving photons and cosmic rays. Solution of a model requires the integration of many coupled rate equations of this type as a function of time and possibly changing physical conditions. Initial conditions are somewhat uncertain but are normally assumed to be atomic or, for dense clouds, to resemble diffuse cloud concentrations. The elemental abundances used are also uncertain, especially in dense cloud calculations. It is important

to note that chemical equilibrium is not achieved, so that abundances cannot be calculated by minimising the Gibbs free energy.

In diffuse cloud models, photodestruction is typically much more efficient than chemical destruction. In models of the cores of dense clouds, photodestruction is significantly slower and is dominated by internal UV photons produced *via* cosmic ray excitation processes. Here, chemical destruction is somewhat more rapid than photodestruction, although the latter must be included. An additional destruction process, not often considered, is sticking to the surfaces of dust grains. The time scale for such sticking in a dense cloud is in the order of 10^6 yr. In the absence of adsorption onto grains and under constant physical conditions, the coupled equations lead eventually to steady-state (*not chemical equilibrium)* abundances although the time required to reach steady-state can be as long as 10^7 years. With certain non-standard choices of elemental abundances and under restricted physical conditions, more than one solution of the concentrations is possible at steady state. In addition to the standard one, known as the 'low ionization phase,' there is an unusual one known as the 'high ionization phase'.[23] This bistability may or may not be an artifact of the models.

The time scale to reach steady-state is not only longer than the adsorption time in dense cloud cores, but is also longer than the lifetime of cores of dense clouds against gravitational collapse in the simplest collapse scenarios. So, some practitioners of gas-phase models prefer to use times before steady state is reached to compare results with observations of cores. Others prefer to include grain adsorption but also to consider the highly uncertain effect of non-thermal grain desorption terms. The most common non-thermal desorption mechanism included is cosmic ray heating of the grains followed by evaporation. A few intrepid investigators, such as the author and his colleagues, consider desorption mechanisms and also try to follow the complex chemistry occurring on the grain surfaces.[24] In general, steady-state abundances are not reached in these calculations, where the eventual outcome is that all matter (with the exception of H_2 and He) becomes solid state in nature if one waits long enough.

In the simplest model calculations, the physical conditions are chosen to be uniform and time invariant. Such calculations can be applied to cores of dense clouds. At the next higher level of complexity, time-independent variations in the physical conditions are included. For simplicity, one can assume a cloud to be composed of slabs of material, each with a given density and temperature. In such models, the radiative transfer of external photons through at least the outer slabs must be carefully considered. Diffuse cloud models are often of this type, as are models of photon-dominated regions that are near bright stars within dense clouds. Models of disks surrounding young stars now include spatial inhomogeneities in two dimensions—distance from the star, and height above the disk plane. Finally, there are models with both changing and inhomogeneous physical conditions, such as occur during star formation. The changing physical conditions can be treated *via* simple approaches such as free fall collapse or *via* complex approaches such as hydrodynamics in one or even more dimensions.

What gas-phase chemical reactions are included in networks? For networks in which the largest molecules are roughly of the same size as the largest species detected *via* high resolution spectroscopy (13 atoms), networks now include approximately 4000 chemical reactions involving 400 species composed of a dozen different first- and second-row elements.[22] Most of the reactions are of the ion–molecule variety, although there is a significant fraction of neutral–neutral reactions. Many but by no means all of the important reactions have been studied in the laboratory. It is the extent of the neutral–neutral chemistry that is most uncertain, because the number of possible reactions between atoms/radicals and stable molecules at low tem-

peratures is poorly understood. So, in our group, we maintain three chemical networks.[25] Our so-called standard one has the minimum number of neutral–neutral reactions of this type, essentially containing only systems measured in the laboratory and their very close cousins, while the other two networks contain many more reactions with rate coefficients based on the studied systems and on chemical intuition. In general, the model results using these three networks differ mainly for the larger species in the models.

4 Results of gas-phase chemical models

Gas-phase models have been utilised for a variety of interstellar objects in which molecules are found. Table 1 contains some of these sources along with their salient physical characteristics.[2] The sources associated with star formation in this table are far enough away from the young stellar objects that molecules can still exist. The results of the assorted models are often successful, but point to a variety of continuing problems, as can be seen in the discussion below concerning various sources.

Table 1 Some interstellar sources of molecules

Source	Density/cm^{-3}	T/K	Salient molecular feature
Diffuse clouds			
Typical conditions	100	50–100	Some diatomic
Shocked regions		≤4000	CH$^+$
Translucent clouds	1000	10–50	Some polyatomic
Dense clouds			
Inter-core material	1000	10	Some polyatomic
Quiescent cores	10^4	10	Many polyatomic
Low mass young stellar objects			
Starless cores (collapse starting)	10^4–10^6	10	Many polyatomic
Collapsing cores (central object present)	10^4–10^6	10	Depletion onto grains
Protoplanetary disks	≤10^{10}	30	Depletion onto grains
High mass young stellar objects			
Hot molecular cores	10^6	100–300	Saturated molecules
Shocked regions	10^4	≤4000	Sputtering
Photon-dominated regions	10^4	100–1000	PAH's

Steady-state slab models of the gas-phase chemistry of diffuse clouds reproduce the small abundances of most but not all of the diatomic molecules detected *via* optical absorption studies.[26] Two poorly understood molecules are the radical NH and the molecular ion CH$^+$, the observed abundances of both of which are larger than calculated. The CH$^+$ problem is particularly acute.[26] One possibility is that this species is produced by the reaction

$$C^+ + H_2 \rightarrow CH^+ + H \qquad (25)$$

which is, however, endothermic by 0.4 eV. For CH$^+$ to be produced in this manner, the temperature must be quite high. To achieve such a temperature, the presence of shock waves has been advocated to raise temperatures as high as 4000 K for relatively brief instances of time. Shock waves are common in the interstellar medium but are most often associated with star formation. Their detailed properties are very sensitive to the existence and direction of small magnetic fields. Regarding diffuse clouds, shock models can almost reproduce the CH$^+$ abundance but the evidence for shocks in diffuse clouds is ambiguous and, moreover, the inclusion of shocks often tends to worsen the agreement with observation for other species. More recent hypotheses include areas of intermittent turbulence, which can also achieve high temperatures in rather small portions of the clouds.[27] In all high temperature models,

investigators must add a large number of endothermic reactions and exothermic reactions with activation energy. Often these reactions have only been studied under thermal equilibrium conditions. In the interstellar medium, on the other hand, it is likely that following the passage of a shock wave or during periods of turbulence, the translational temperature cools much more slowly than internal molecular degrees of freedom. In shock waves, it is also possible that sputtering of species from interstellar grains will occur. Sputtering of large molecules from dust particles in diffuse clouds may produce the exotic molecules that are the carriers of the diffuse interstellar bands.

Gas-phase chemical models of quiescent cores in dense clouds can be highly successful. This can be seen *via* qualitative as well as quantitative considerations. Qualitatively, the models reproduce the odd assortment of molecules seen: ions are formed by ion–molecule reactions, radicals and isomers are produced by dissociative recombination reactions, and mainly unsaturated hydrocarbons are synthesised since H_2 is not reactive with most complex hydrocarbon ions. In addition, isotopic fractionation regarding the deuterium : hydrogen ratio is well understood by including ion–molecule exchange reactions at low temperature into the models. The deuterium : hydrogen abundance ratio is roughly 10^{-5} and stems from the Big Bang era. Yet, the observed and calculated abundance ratios of singly deuterated isotopomers to normal species can be as high as 0.1 and even some doubly deuterated isotopomers have been detected![28]

To analyse the quantitative agreement possible between models and observations, one must look at individual sources. One of the best-studied quiescent cores is known as TMC-1 (Taurus Molecular Cloud-1), which is inside a giant association of dense matter in the constellation Taurus. In this source, over 50 molecules have been studied, with observed abundances accurate to perhaps factors of 3–10. Our purely gas-phase chemical models with homogeneous physical conditions (gas density of 10^4 cm^{-3}, temperature of 10 K) are capable of reproducing 80–90% of these observed abundances over a variety of times starting at 10^5 years and depending on the exact elemental abundances chosen.[25] In particular, with the standard oxygen-rich abundances ($O > C$) found in stellar atmospheres, agreement is good only at so-called early-times of 10^5–10^6 years from the onset of the chemistry. With increasing amounts of carbon, the duration of the agreement increases. In general, the standard model works better, for reasons unknown, than models with more neutral–neutral reactions. Incorporation of adsorption onto grains, desorption from grains and surface chemistry neither vitiates nor improves the agreement until very late times, when the gas phase is lost.[29]

The fact that the model does not reproduce 100% of the observed abundances in this and other quiescent dense cloud cores can be ascribed to both chemical and astronomical uncertainties. In the latter category, we can include the problem that star formation is beginning to occur in TMC-1 (and other cores) so that the assumption of homogeneous and temporally invariant physical conditions is an oversimplification.

Gas-phase chemical models of a variety of regions affected by star formation have also been attempted (see Table 1). One type of region that has attracted much interest is known as a hot molecular core, which is found in the vicinity of young and bright stellar objects of high mass and which has a density (10^6 cm^{-3}) and temperature (100–300 K) somewhat higher than the ambient dense interstellar gas. In hot cores, the molecular composition of the gas is much more saturated than in the ambient material—molecules such as water, ammonia, H_2S, and methanol become much more abundant, and larger molecules such as methyl formate, dimethyl ether, and ethanol are seen only in such regions. Although opinions differ on the cause of the change in chemical composition, the dominant view is as follows.[30] Before star formation occurs, both gas-

phase and surface chemistry occur at low temperature and ice mantles build up on the grain surfaces. The ice mantles contain methanol, possibly produced by the hydrogenation of CO by successive addition of H atoms landing on grains. During star formation, the temperature increases to 100–300 K, which is sufficient to result in the evaporation of the ice mantles. The composition of the gas is now much more saturated than before, but a gas-phase chemistry ensues which can alter the abundances significantly within a period of 10^4–10^5 years. In particular, molecules such as methyl formate and dimethyl ether can be synthesised by ion–molecule reactions from precursor methanol. In fact the abundances of these and other species can be used to estimate the age of the hot core. In standard gas-phase models, one assumes an initial composition of the gas following desorption. Although the current generation of such models appears to be successful in reproducing abundances of some hot core molecules, it must be noted that some of the suggested gas-phase synthetic processes have not been studied in the laboratory. In more detailed models, one actually tries to follow the gas-phase and grain-surface chemistries of the previous cold era and current warm era simultaneously.

The chemistry of 'protoplanetary' disks that surround newly formed low-mass stars known as T Tauri objects is also of great interest since these disks will eventually become solar-type planetary systems, and the dust particles will eventually coagulate into comets, meteors, and planets.[31] Much but not all of the material in disks (typically 0.1–0.01 of the mass of the sun) is located in a thin cylindrical volume that rotates around the star in Keplerian fashion with the density of gas and dust decreasing with increasing radial distance from the central star. The disks can extend outwards for distances up to 800 astronomical units (1 astronomical unit = mean distance between the earth and the sun). But there is also matter above and below the midplane, with density decreasing with increasing distance from the midplane. The temperature of a protoplanetary disk can be quite low until the material is rather close to the star so that the chemistry for much of the outer disk is similar to that of normal interstellar clouds although the densities are much higher.

Although gaseous molecules in disks can be detected by single-dish radio astronomical observations, interferometric observations with a number of dishes are needed to get the high spatial resolution necessary for studying the positional dependence of the molecular concentrations. The general observational result from single-dish work is that average molecular abundances in a fractional sense (with respect to H_2) tend to be lower than in normal dense cloud cores although the effect is greater for stable molecules such as HCN than it is for radicals such as CN. This result is understood using current-generation models in which at each radial distance from the star, the material as a function of height is divided into a number of slabs and the radiative transfer of external radiation from both the central star and the general intestellar medium is treated. As T Tauri stars can emit much X-ray radiation, the effects caused by this radiation must be included. The general picture of the chemistry is that in the midplane most of the gas-phase molecules adsorb onto dust particles by the time of a typical age of a T Tauri star (10^6 years) so that the bulk of the observed gas-phase molecular concentrations are above and below the midplane, where initial densities are lower and collisions with dust particles more rare. But in regions sufficiently far removed from the midplane, radiation from the star and the interstellar medium can be intense and result in the photodissociation of stable molecules into radicals. So, on average, radicals have higher relative abundances. Detailed model predictions of the radial dependence of molecular concentrations are available, but the necessary observations will be difficult to perform until a new large array of millimetre-wave telescopes, currently under construction in the Chilean Andes, becomes available in perhaps a decade.

Other types of regions associated with star formation have also been studied with suitable chemical models. High-mass stars are often born with shock waves emanating from them, and the chemistry of shocks includes sputtering of material off dust particles leading to the production of unusual gaseous species such as SiO. Star-less cores are regions in which, although collapse has started, there is no evidence of even a warm object at the centre. Gas-phase chemical models of these objects can lead to predictions of the radial dependence of molecular abundances that can be compared with observations.

This discussion of a few types of sources is hardly inclusive, but serves to show some of the many manifestations of star formation and how a study of the chemistry in such regions adds to our understanding of what is happening.

5 Interstellar surface chemistry

Perhaps by the end of this decade, astrochemists will be able to include surface chemical processes into their models with some assurance that the chemistry is sufficiently well understood that the model results are reliable. Despite much effort in the laboratory, especially on the formation of H_2,[16] current uncertainties regarding grain chemistry are so great that all but the most basic model results are in question. There are six main problems and uncertainties that afflict attempted treatments of grain surface chemistry. First, the size distribution and topology of the grains are poorly constrained. Secondly, the chemical nature of the grain surface is uncertain and likely to be time-dependent since ice mantles build up over time in dense clouds that remain cold. Thirdly, there are at least two mechanisms for surface chemistry—the diffusive (Langmuir–Hinshelwood) mechanism, which dominates for weakly-bound adsorbates at temperatures high enough for motion to occur, and the Eley–Rideal mechanism, in which a gas-phase species strikes a stationary adsorbate—and which dominates for a given set of reactants depends on the grain surface, temperature, and size. Fourthly, the products of surface reactions are often unknown. In particular, it is customarily assumed (without much evidence) that association reactions dominate in all cases where a strong chemical bond can be formed between the reactants even though competitive exothermic product channels with more than one product exist. Fifthly, there are mathematical problems associated with diffusion on small particles. In the limit of large numbers of adsorbates diffusing on a surface, the rate equations for diffusively-controlled reactions are quite similar to the gas-phase rate equations [eqn. (24)] except that the rate coefficients reflect a two-dimensional random walk rather than straight-line trajectories, as in the gas. But on interstellar dust particles, there are at most a few reactive particles on a given grain at any time, and rate equations, which yield averages rather than integers, are not exact. A variety of other methods, including Monte Carlo and master equation approaches, have been proposed and utilised for simple systems, but none has yet been incorporated into a real time-dependent chemical model with both gas-phase and grain surface reactions. Lastly, as mentioned previously, the rate and mechanisms of non-thermal desorption of heavy species from grain surfaces are poorly understood. Without some mechanisms for non-thermal desorption, the gas-phase of dense interstellar clouds would exist only for 10^6 years or so, and many investigators believe this number to be too small.

The result of all these uncertainties is that modellers must make many simplifications and assumptions in their treatments. In current models, results confirm that grain mantles of ices containing saturated species do indeed grow on grain cores in cold, dense regions, but the actual observed abundances of the major species in the ice are not easily reproduced in some cases.[29]

6 Summary

Since the first detection of polyatomic molecules in interstellar clouds more than thirty years ago, the role of molecules in astronomy has grown remarkably. Molecules are detected in both interstellar and circumstellar sources; they are even present in our own Sun, which appears to have large amounts of water vapor! Molecules are detected in our galaxy, the Milky Way, as well as external galaxies. Indeed, molecules have been detected in galaxies in the most distant regions of the universe hurtling away from us at near the speed of light. The study of molecules, especially H_2, in the era immediately following the Big Bang is well advanced—here H_2 is formed by high-temperature gaseous processes involving the ions H^+ and H^-.

To astronomers, molecules are useful as probes of physical conditions while to chemists, the growth of molecules, especially organic molecules, throughout the universe is inherently interesting and worthy of study. The field of interstellar chemistry is a young one, and our knowledge of the chemistry of interstellar clouds in our galaxy and elsewhere is still imperfect. Still, much has been learned in the last thirty years and, given the attention paid to interstellar chemistry by chemists, including kineticists and spectroscopists, as well as astronomers working in all regions of the electromagnetic spectrum, the field will remain a major subject of investigation.

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