

To infinity and beyond ...

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Astronomical observations¹ have revealed the chemical richness of the interstellar medium. What are the molecules and species involved and how do they lead to the formation of stars?

OVER 120 DIFFERENT CHEMICAL SPECIES, from neutral atoms, through simple molecules, such as molecular hydrogen (H_2) and water (H_2O), to complex organic molecules with more than 10 atoms, have been observed by a combination of astronomical techniques capable of spanning the electromagnetic spectrum (see Box). The molecules are formed in most places in the universe that are colder than the Sun. In particular, observations have shown that molecules are abundant in molecular clouds: these dense regions are the nurseries of new stars and planets. Molecules can therefore be used to trace remotely and probe star and planet formation.

In fact molecules actively control star formation. Without molecules, especially small molecules like hydrogen, carbon monoxide, and water, the universe as we know it might not exist. The Big Bang produced a universe rich in atomic hydrogen, helium and a little lithium. When the universe cooled down enough for electrons and nuclei to combine, neutral atoms started to form. The appearance of neutral atoms led to the formation of molecular ions and simple molecules, such as H_2^+ and H_2 . However, the abundance of these simple molecular species remained small and constant as a consequence of their relatively slow rates of formation. So, how did the richness of molecules we see now come into being?

Star formation

The formation of the stars probably started with the gravitational collapse of a vast cloud consisting mainly of atomic hydrogen. Stars form when such clouds collapse and their density increases. Compression of this cloud heated the gas up

to very high temperatures – certainly to above 1000K. At these temperatures the motion of atoms in the gas begins to resist the force of gravity that is making the cloud collapse. Thus, for the star formation process to continue, the cloud had to cool. So how did this cooling occur?

At the same time as the cloud was collapsing, hydrogen atoms present in the cloud were reacting to form molecular hydrogen. This molecular hydrogen cooled the gas in the star-forming regions by emitting heat in the form of microwave and infrared radiation. Eventually, the temperature in the cloud cooled down to ca 300K. This is still an order of magnitude hotter than the molecular gas clouds that form stars today – we now have many more molecules and dust available to help cool the gas. Because of this, astronomers believe that the first generation of stars were massive and very short-lived. When these stars died, they exploded as supernovae dispersing heavy atomic elements and dust into space, thus contaminating other collapsing molecular clouds. Further generations of stars were then formed when such contaminated clouds started to collapse. Thus the star cycle as we know it came to be. The question remains – how is the vast array of molecules we see today formed in these molecular clouds?

The conditions in the star-forming regions of the interstellar medium are extremely harsh. Temperatures barely rise more than a few Kelvin above absolute zero and pressures are so low that it becomes the norm to think in terms of the few hundreds or thousands of atoms or molecules occupying a cubic centimetre (in comparison with 10^{19} particles cm^{-3} at atmospheric pressure). This means that almost all of the chemistry that we are familiar with in the laboratory does

not work.

Most chemical reactions have an activation barrier and thus energy must be put in to make them proceed. However, at the temperatures found in the interstellar medium, activated chemical reactions effectively stop, because the reactants do not have enough energy to get over the activation barrier. The low pressures in the interstellar medium also have an impact on reactivity. Many simple gas phase reactions occur as a result of collisions between the reacting species. At the low pressures found in the interstellar medium, the time between collisions is immense – 10^8 s compared with every 10^{-10} s for a collision at atmospheric pressure.

Nevertheless, there are some types of reactions that can occur in the harsh conditions of the interstellar medium. These reactions can be divided into three main 'groups' of molecular processes:

Formation

● Radiative association

$A \text{ atom} + B \text{ atom} \rightarrow AB \text{ molecule} + \text{photon}$

Destruction

● Photodissociation

$AB \text{ molecule} + \text{photon} \rightarrow A \text{ atom} + B \text{ atom}$

● Dissociative recombination

$AB^+ \text{ molecule} + e^- \rightarrow A \text{ atom} + B \text{ atom}$

Rearrangement

● Ion-molecule exchange

$A^+ + BC \text{ molecule} \rightarrow AB^+ \text{ molecule} + C$

In the beginning ...

Molecules detected in the interstellar medium to date

Two atoms: H_2 , CO, CSi, CP, CS, NO, NS, SO, HCl, NaCl, KCl, AlCl, AlF, PN, SiN, SiO, SiS, NH, OH, C_2 , CN, HF, CO^+ , SO^+ , CH, CH^+

Three atoms: H_2O , H_2S , HCN, HNC, CO_2 , SO_2 , MgCN, MgNC, NaCN, N_2O , NH_2 , OCS, HCO, C_3 , C_2H , HCO^+ , HOC^+ , N_2H^+ , HNO, HCS^+ , H_3^+ , C_2O , C_2S , SiC₂, H_2D^+ , CH_2

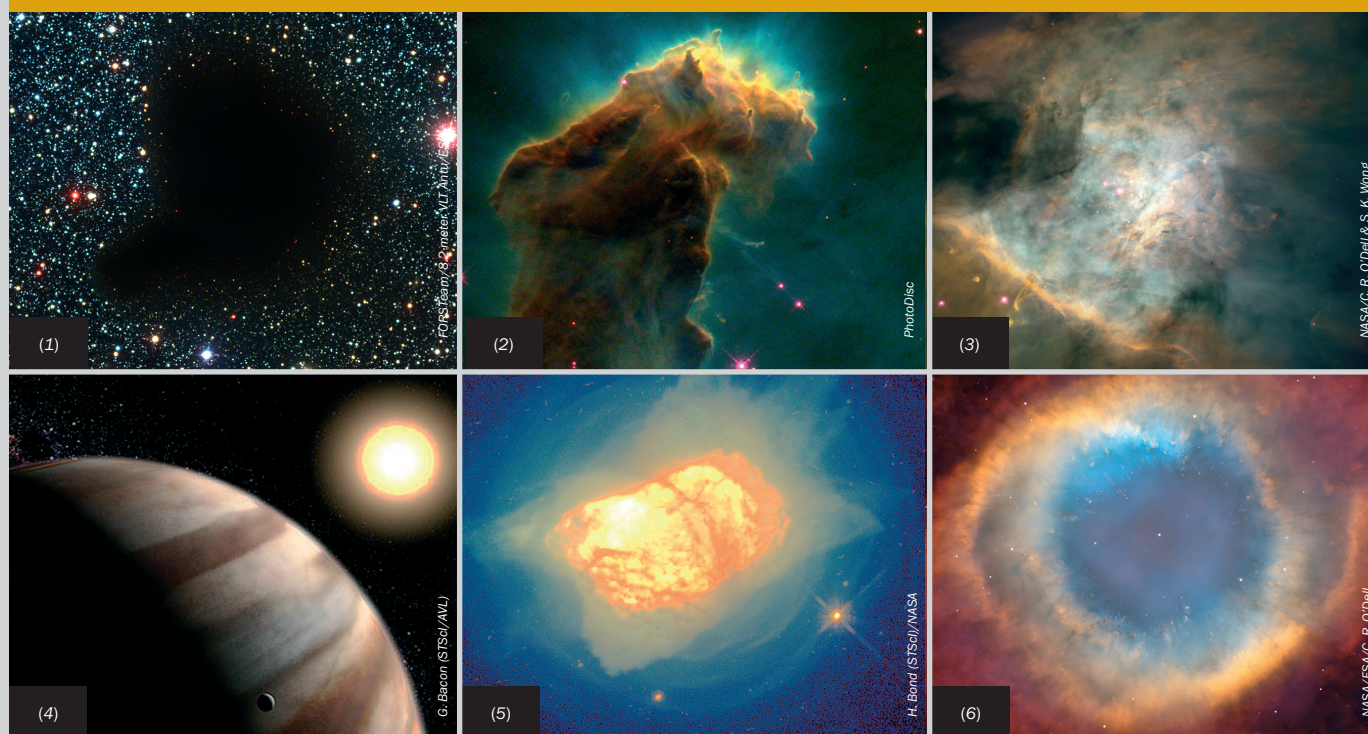
Four atoms: NH_3 , H_2CO , H_2CS , C_2H_2 , HNCO, HNCS, H_3O^+ , $HOCO^+$, C_3S , H_2CN , cyclic- C_3H , linear- C_3H , HCCN, H_2CO^+ , C_2CN , C_3O , $HCNH^+$, CH_2D^+

Five atoms: CH_4 , SiH_4 , CH_3NH , NH_2CN , CH_2CO , HCOOH, HC_2CN , HCCNC, cyclic- C_3H_2 , linear- C_3H_2 , CH_2CN , C_4H , C_4Si , C_5 , HNCCC

Six atoms: CH_3OH , CH_3SH , C_2H_4 , CH_3CN , CH_3NC , HC_2CHO , NH_2CHO , C_4H_2 , C_5H , C_5O

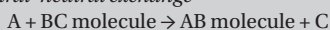
>Six atoms: CH_3C_2H , CH_3CHO , CH_3NH_2 , CH_2CHCN , HC_4CN , C_6H , CH_3COOH , $HCOOCH_3$, CH_3C_2CN , $(CH_3)_2O$, C_2H_5OH , C_2H_5CN , CH_3C_4H , HC_6CN , $(CH_3)_2CO$, $CH_3C_4N?$, NH_2CH_2COOH , HC_8CN , $HC_{10}CN$

Fig 1 The stellar cycle, whereby a star is born



(1) The starless core Barnard 68 which is probably on the verge of forming stars; (2) the Eagle Nebula where new stars are being formed; (3) close up views of 'proplyds', ie protoplanetary disks in the Orion Nebula; (4) an artist's impression of a planet around star HD 209458; (5) a pseudo-colour composite of two HST images of a Sun-like star (NGC 7026) nearing the end of its lifetime; (6) the Helix Nebula where stars towards the end of their lives return material from their outermost layers to the interstellar medium.

● Neutral-neutral exchange



Reactions of this type account for the formation of many of the molecules that have been observed to date.

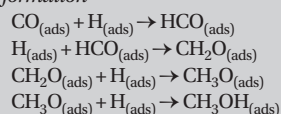
However, some molecules, including the most abundant molecule, molecular hydrogen, are present in quantities that cannot be accounted for by only gas phase reactions. Astronomers have therefore suggested that these molecules may instead be formed by reactions which take place on the surface of dust grains.

Surface reactions

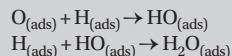
Catalytic processes occurring on the surface of grains have long been thought to be responsible for the formation of molecular hydrogen,² but it is only in the past few years that chemists have begun to investigate this process in detail in the laboratory.³ When hydrogen atoms hit a grain, they stick to its surface. If two hydrogen atoms are stuck near to each other on the surface of the grain, they can combine to form a molecule – this is the so-called Langmuir-Hinshelwood mechanism. An alternative way for H₂ to form is through the reaction of a H atom in the gas phase with a H atom bonded to the grain surface – the so-called Eley-Rideal mechanism. For these processes to occur, it is important that one H atom is retained on the surface long enough for a second H atom to arrive nearby; this requires that the rate at which H atoms stick to the surface is higher than the rate that they evaporate off. Once the H₂ molecules are formed, they then leave the surface and pass into the gas phase. The large amount of energy, released when a bond is formed between the two H atoms, leads to excitation of the H₂ molecule which is observed in the form of vibrations and rotations of the molecule as it comes off the grain surface.

In addition to molecular hydrogen, other small molecules such as water, ammonia (NH₃), methanol (CH₃OH) and carbon dioxide (CO₂) are also thought to form on the surface of dust grains.

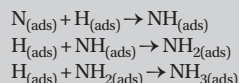
● CH₃OH formation



● H₂O formation



● NH₃ formation



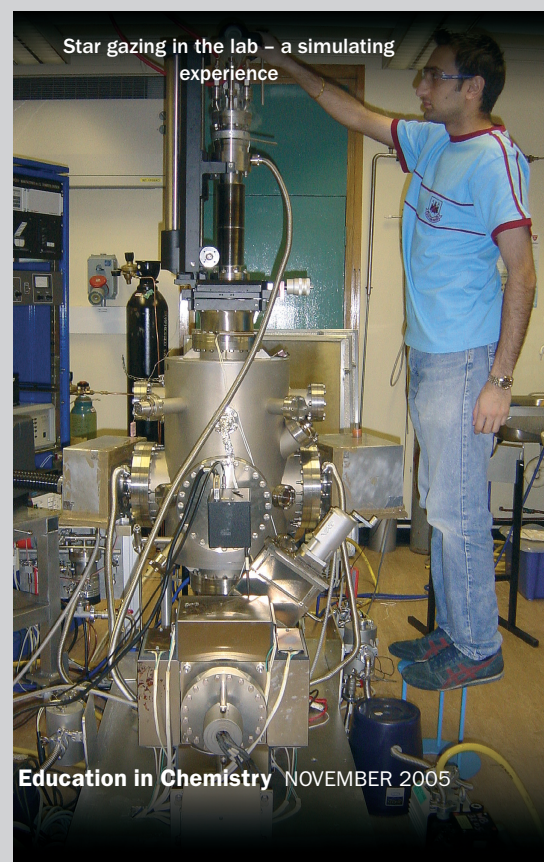
Note that (ads) indicates that the species is stuck (adsorbed) on the grain surface.

These molecules are found as icy mantles that freeze out on the surface of the grains at the very low temperatures (10–20K) found in the interstellar medium. As for molecular hydrogen, the abundances of the molecules found in these interstellar ices can only be accounted for if catalytic processes, occurring on the surface of dust grains, form them.

Modern experiments

Although it has long been suggested that molecules can be formed on the surface of dust grains, little is known about the exact mechanisms of the surface reactions that take place. Experiments⁴ are therefore underway to try to understand how molecules such as H₂, and those found in interstellar ices (H₂O, NH₃, CH₃OH and CO₂), could be formed on the surface of dust grains. The experiments use complex laboratory apparatus to simulate the conditions in a cold, dense cloud in the interstellar medium. Ultrahigh vacuum apparatus is used to reproduce pressures close to those observed in the dense regions where stars and planets are being formed. Helium refrigerators are then used to cool a model surface down to 10–20K, to reflect the temperatures in such environments. Beams of atoms and molecules are then directed onto the cold surfaces and surface infrared spectroscopy is used to identify the molecules that are formed. In parallel, a technique called temperature programmed desorption (TPD) is used to give infor-

mation (energetics) about the strength of binding of the molecules to the grain surfaces. Essentially, in TPD a surface is heated at a constant rate and the desorbing molecules are monitored with a mass spectrometer. The key aims of these experiments are to determine whether H₂, and other small molecules, can be formed on surfaces which are suitable models of dust grains, and to establish the mechanism by which these molecules are formed. The experiments also aim to determine the way in which the nature of the surface affects the formation of these molecules and how strongly these molecules are retained on the cold grains. The strength of the interaction between the molecule and the grain is what ultimately determines the temperature at which the molecules are





Star search – the Hubble Space Telescope

released into the gas phase during the star formation process. Even this relatively simple process of molecular desorption from the grain was, until recently, poorly understood.⁵

Molecules clearly have a crucial role to play in the universe today. Without them, there is little doubt that the formation of the small, long-lived stars necessary for the evolution of life would have been unlikely. Fifty years ago scientists realised that many of the key small molecules found in the universe are formed on the surface of dust grains. Today, this is inspiring chemists to apply sophisticated modern experimental and theoretical tools to investigate molecular formation and desorption processes on surfaces, which are suitable models of dust grains. The results of these investigations will lead to a greater understanding of the universe in which we live. They may even provide information about the origin of life itself since there is increasing evidence, from both astronomical observations and laboratory experiments, that the building blocks of life can be formed through reactions initiated by cosmic radiation that occur in the icy mantles around dust grains.

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4. For further information about experiments investigating molecular formation on dust grain surfaces see www.chem.ucl.ac.uk/cosmicdust/; www.chem.ucl.ac.uk/astrosurf/; or www.nottingham.ac.uk/~pczfj.
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Newton. Within three years Graham had made considerable savings in gold and silver coinage by introducing new weighing machines and more experienced staff, which reduced waste. He replaced copper coins with new, harder bronze ones still used today, which brought much profit to the British Crown. In addition to producing coins and medals for Britain and its colonies, he proposed the adoption of metric weights and measures, decimal coinage, and an international coinage.⁴ In 1870, after Graham's death, which occurred from pleuropneumonia at the age of 63 on 16 September 1869, the post of Master of the Mint was combined with that of Chancellor of the Exchequer.

Honours

Graham's extremely varied studies included the absorption of gases by charcoal, the solubility of gases, the glow of phosphorus and phosphorus compounds, including spontaneously flammable phosphine, an early theory of metal-amines, the aurora borealis, the adulteration of coffee, and the production of ethanol during bread-making.¹⁴

Among his honours are the Royal Society's Royal Medal (twice, 1837 and 1863), the Royal Society's Copley Medal (1862), and the Paris *Académie des Sciences' Prix Jecker* (1862). He was made a Doctor of Civil Law of Oxford University, Honorary Member of the Royal Society of Edinburgh, Corresponding Member of the French Institute and of the Academies of Berlin and of the National Institute of Washington. In 1878 the Graham Medal and Lecture Fund was established by the leading manufacturing chemists of Glasgow.^{2b} The Royal Society of Chemistry is located in Thomas Graham House, in Cambridge and the University of Strathclyde's department of pure and applied chemistry is housed in the Thomas Graham building, completed in 1964. Much of Graham's apparatus is preserved in the National Museum of Science and Industry in South Kensington.¹⁵

Robert Angus Smith summarised Graham's personality:

As a private man, Graham led an uneventful life; but no man has passed through the world more uniformly respected. Too retired, too quiet, his life appears to have a deep tinge of melancholy in it, notwithstanding its eminent success. Very intimate friends he had few out of the circle of the family of brothers and sisters, who were strongly attached to him, and to whom he was much devoted, being himself unmarried.^{2a}

Although Thomas Graham taught chemistry to thousands of students, including medical students, women, and mechanics, unlike Robert Wilhelm Bunsen, Justus von Liebig, August von Hofmann, and other leading luminaries of 19th century chemistry, he left behind few disciples, and consequently few biographical reminiscences of him are available.

Graham investigated the spectacle that is the aurora borealis

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