Chemistry in the void

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Organic chemistry dominates in the voids between the stars. Could this be where the building blocks of life come from?

Atlas Image obtained as part of the Two Micron All Sky Survey (2MASS), for full credit see p641

Image of the Orion Nebula — an Atlas Image

In the past 30 years, we have discovered that the space between stars is not empty, as originally thought; rather it is filled by massive ‘clouds’ of gaseous molecules and small solid particles. These clouds contain enough mass to make millions of stars like our sun and are spread over vast areas of space — over 10^{15}m. It is in these ‘giant’ molecular clouds that new solar systems are being born, forever linking astrochemistry and molecular astronomy to star and planet formation. Today, the relatively new field of astrochemistry — the study of the ongoing chemical interactions between molecules found in interstellar space — has moved beyond the initial discovery phase and is investigating the tenuous clues linking the chemistry found in interstellar space to comets within our own solar system and, perhaps, to the origins of life itself.

The story of molecules in space began with Theodore Dunham and Walter Adams, astronomers at Carnegie Institution of Washington, who first detected interstellar cyanogen (CN) in 1936.[1] They achieved this not by direct observation, but by observing the effect that CN molecules had on the light of a background star shining through the molecules. In subsequent years, a few additional molecules were located in similar fashion; however, the true molecular revolution in astronomy waited for the technological advances driven by the Second World War.[2] This technology opened a new window for astronomers, that of the radio wavelength spectrum.

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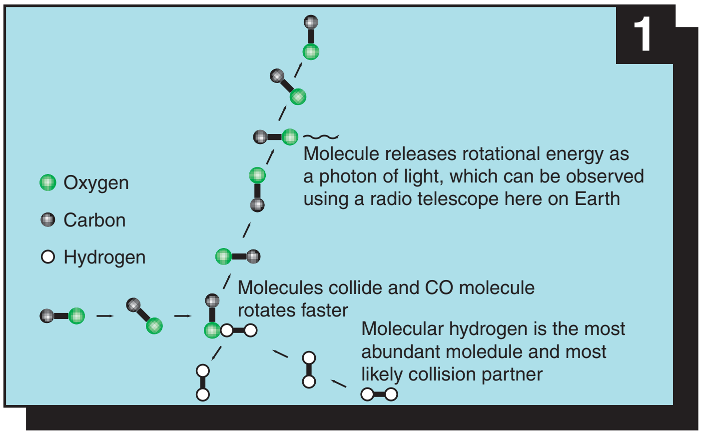
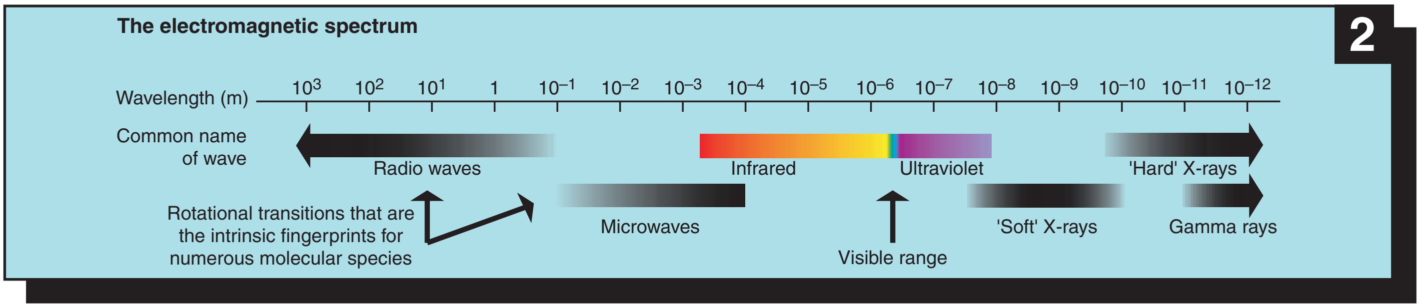


In molecular clouds energy is imparted to gaseous molecules through mutual collisions and this energy is transferred into rotational motion. The energies of molecular rotation are ‘quantised’ (see Glossary) according to the laws of quantum physics. When a rotating molecule slows down it will release a photon of light with a very specific energy and frequency (see Figure 1). This is somewhat similar to how a radio station can be identified by its frequency. In this fashion each molecule has its own fingerprint of ‘transitions’ with specified frequencies that can be used for identification.

The microwave and radio portions of the wavelength spectrum coincides prominently with rotational transitions that are the intrinsic fingerprints for numerous molecular species (see Figure 2). This led to the detection of hydroxide (OH) in 1964 and, most importantly, carbon monoxide (CO) in 1970.[3,4] With these detections we have found a new component of our galaxy, one that consists almost entirely of molecules.

To date, 121 molecules have been detected in molecular clouds. The most abundant of these, by a large factor, is



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The electromagnetic spectrum

molecular hydrogen (H_2). The molecule with the second highest concentration, CO, is 10,000-fold less abundant than H_2. Beyond H_2 and CO the detected species range from simple molecules containing two atoms to molecules with 13 atoms. Examples are hydrogen cyanide (HCN), methanol (CH_3OH), methyl formate ($HCOOCH_3$), with ongoing searches for organic species thought to be the building blocks of life, such as the amino acid glycine (NH_2CH_2COOH). The richness of the molecular inventory suggests that interstellar chemistry is active and dominated by organic chemistry.

Interstellar molecules are not just cosmic curiosities. The light emitted from the molecules contains information about the conditions of the emitting or absorbing gas, and the abundance of the molecules themselves. For example, in 1940, analysis of the absorption of background starlight due to interstellar CN molecules by Andrew McKellar, an astronomer at the Dominion Astrophysical Observatory in Victoria, Canada, showed that the temperature of the absorbing gas is near three degrees above absolute zero (–273°C).[5] The significance of this result did not dawn upon astronomers until, in 1965, Nobel prize-winners Arno Penzias and Robert Wilson recorded that the fossil radiation left over from the big bang had a characteristic temperature of 3K.[6] This radiation pervades interstellar space, and heats all matter, including CN molecules, up to a temperature of 3K. Thus, the theorised cosmic background radiation had actually been revealed by molecular analysis over 20 years earlier. Today it is generally recognised that chemistry in molecular clouds plays an important and potentially controlling role in the formation of star and planetary systems. Indeed, some feel that astrochemistry may provide the molecular seeds for prebiotic (see Glossary) life on the Earth.

Of the numerous questions in this field, the intersection of astronomy and chemistry, the simplest is how can molecules exist in interstellar space at all? At first glance, astronomers thought that interstellar space would be an inhospitable place for the formation of molecules. There are over 100 billion stars in our galaxy. Each, like our sun, emits copious amounts of radiation into interstellar space. A molecule bathed in this radiation field would have a lifetime of only 300 years before being destroyed. Although this is quite long by human standards, it is far too short for astronomy where it takes well over a million years to assemble enough molecular gas to form a single star. The clear inference from this comparison is that there must be some method of reducing the molecular destruction rate due to interstellar radiation.

Over the past 50 years we have learned that this is indeed the case. Surprisingly, the answer has been in the night sky since the Earth formed 4.6 billion years ago. On a visit to the Southern Hemisphere, the night sky presents fantastic broad vistas of diffuse starlight arising from the high concentration of stars in the centre of our galaxy. Superimposed on this starlight are striking dark voids with little or no stars first characterised as 'dark nebula' by Sir William Herschel in the 18th century. An example of one such void, called Barnard 68, is shown in Figure 3. The nature of these voids remained a puzzle until the 20th century when Robert Trumpler, a pioneering scientist at Lick Observatory in California, determined that the space between stars is also filled with tiny, solid particles.[7] This interstellar 'dust' absorbs the light from stars in the visible and ultraviolet parts of the spectrum and re-emits the energy in the infrared as heat. For gaseous molecules this is important, as they are most susceptible to destruction from photons in the ultraviolet part of the spectrum. Thus, dark voids are regions where a high concentration of dust completely obscures starlight, blocking the destructive ultraviolet photons. It is here where we find both interstellar molecules and newly born stars.

It is now well understood that molecules can survive the harsh interstellar environment, thanks to the influence of dust, but how do molecules form in the first place?

Formation of molecules

It may seem difficult to determine which of the countless reactions that can occur in laboratories here on Earth could be active in regions so distant that it takes light from our sun 360 years to reach. Fortunately conditions in interstellar clouds are so severe that the number of possible reactions is curtailed significantly. For example, interstellar clouds have incredibly low pressures and particle densities (typically 1 molecule/m^3). For comparison the density of breathable air is over 100bn particles/m^3. Because of the low pressure and particle density, gas phase chemical reactions in molecular clouds are restricted to only two participants and not three or more. In addition, reactions must be quite rapid. After some searching, Eric Herbst and William Klemperer, theoretical chemists at Harvard University, demonstrated that reactions between molecular ions and neutrals, both of which have been observed, could easily drive a rich chemistry.[8] Chemical reactions are further limited by the extremely low temperatures only 10–30K above absolute zero. This restricts reactions to only those that are endothermic (see Glossary) in nature.

With this information, astrochemists have constructed theoretical chemical networks that involve over 400 species linked through a network of over 4000 reactions.[9,10] These reactions are inputs into computer programs that predict chemical abundances that subsequently are compared with observations. Such networks have proven quite successful in reproducing the observed abundances of numerous molecules.

Oxygen-bearing molecules

Despite these advances in our understanding of interstellar chemistry, only three years ago there still remained large gaps in

Glossary

Quantised	In quantum theory, the division of the energy of a system into discrete units (quanta) to exclude infinitesimal changes
Prebiotic	The very different conditions existing on earth before the appearance of life, which provided an environment in which the first living organisms could evolve from non-living molecules
Endothermic	A chemical reaction accompanied by the absorption of heat (ΔH-positive)
Interstellar medium	The matter present between stars

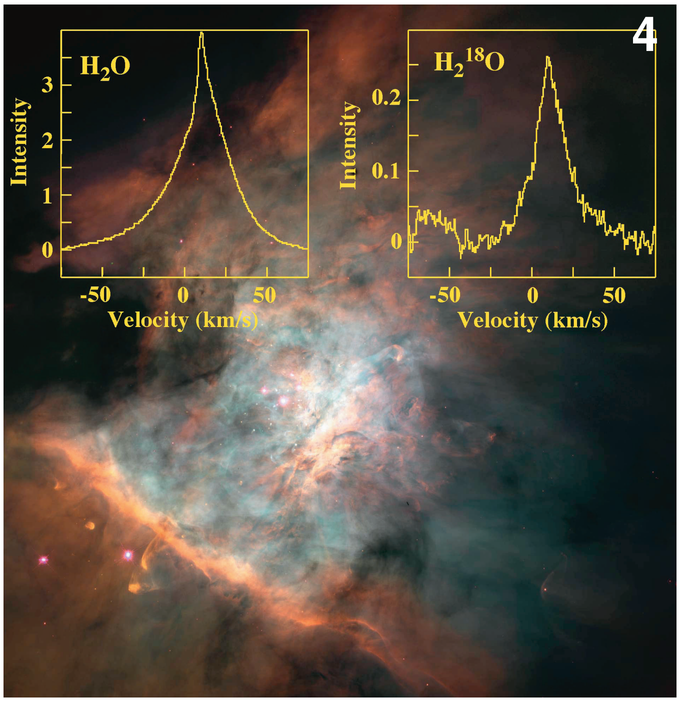
our knowledge. Foremost among these has been the chemistry of oxygen-bearing molecules. Oxygen is the third most abundant element in the universe after hydrogen and helium. Chemical models have long predicted that two of the simplest oxygen-bearing molecules, water and molecular oxygen, would be important and abundant components of the interstellar medium (the matter present between stars).[11] Unfortunately, the intrinsic radiation from interstellar H_2O and O_2 does not penetrate the Earth's atmosphere, due to the simple — and quite useful — fact that the Earth's atmosphere is rich in both of these species. Moreover, the reactions thought to form water and molecular oxygen involve oxygen atoms reacting with hydrogen-bearing ions and occur quite early in the reaction chain (just a few steps beyond the initiating reactions). Thus, information about two molecules, crucial to our understanding of the entire chemical reaction network, remained the largest single gap in our knowledge of molecular chemistry. Beyond their importance to interstellar chemistry, it is generally accepted that the presence of liquid water is a prerequisite for the origin of life on Earth, and it is certain that molecular oxygen is required for our own life. Thus, it would seem to be important to search for the ingredients necessary for life, wherever they may be.

This remained the situation until 5 December, 1998 when NASA launched the Submillimetre Wave Astronomy Satellite or SWAS. The SWAS mission is operated from the Harvard–Smithsonian Centre for Astrophysics in Cambridge, Massachusetts, with Gary Melnick as the principal investigator. Its primary goal is to search the interstellar medium for evidence of gaseous water and molecular oxygen. This enables astronomers to test the 20 year old chemical theories and also to search for the molecules of life in space. Like a radio station, SWAS is pre-tuned to specific frequencies characteristic of H_2O and O_2 emission.

Unexpectedly, early detections of water emission placed SWAS results in direct conflict with existing theory. Theory had predicted a water abundance of 1ppm with respect to molecular hydrogen, however, SWAS observations revealed that the true abundance is 1ppbn.[12] To date, molecular oxygen has not been detected. However, current observational limits are at least 100-fold less than the predicted abundance.[13] An example of SWAS observations is provided in Figure 4.

Dark nebula Barnard 68. Note how stars behind the cloud appear redder than stars beyond the cloud edge. This is due to the dust grains preferentiallly absorbing the shorter wavelength light or the blue portion of the visible spectrum, which makes the stars appear red. Taken at the European Southern Observatory

*Alves, Lada & Lada (Nature, 2001, **409**, 159–161)*



Emission from rotating water molecules in the Orion molecular cloud. Here two SWAS spectra of H_2O and its lesser abundant isotopic variant $H_2{}^{18}O$ are shown superposed on a picture of the Orion Nebula from the Hubble Space Telescope. These 'spectra' are typical examples of how radio astronomers probe molecular clouds. The emission is shown as intensity against velocity (or equivalent frequency) and the strength of these lines depends on the abundance of the molecule

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These results present quite a quandary for astrochemical theory, one that remains a focus of current worldwide research efforts. The most likely solution is that the water is actually present in molecular clouds, but in the form of water ice, which is unobservable by SWAS.[14] Frozen water has been observed in interstellar space by other techniques. It is likely that this ice formed through an entirely different chemistry, one that occurs on the surfaces of small solid particles that are also present. By mass, about 1% of molecular clouds are actually tiny solid particles. These are the same solid particles that, by reducing the destructive powers of the interstellar radiation field, allow molecules to exist. We believe that when an oxygen atom collides with a 'dust' grain it will attach and, eventually, react with any hydrogen atoms that are also on the grain. In this fashion, the oxygen atom will quickly saturate in the form of water ice. Thus, water ice is formed not by gas phase chemistry, but rather by solid-state chemistry, which is catalytic in nature. Catalytic chemistry, or chemistry facilitated by solid surfaces, occurs in laboratories on Earth and, by inference, in space as well. The water ice created by solid-state chemistry will remain frozen until the temperatures rise far above the observed values of 10–30K. Thus, the gas phase chemistry that should form water vapour and gaseous molecular oxygen in abundance is deprived of its primary fuel — oxygen atoms — and is essentially slowed down to match observations.[14]

This is quite an elegant solution since the theory accounts for both forms of water found in interstellar space: gas and solid. However, there are broader implications that relate to the formation of our own solar system, comets, and even to the Earth itself. Over the past decade the Earth has seen the appearance of two bright comets, Hyakutake in 1996 and Hale-Bopp in 1997. Because comets were present in the cold, dark, outer reaches of the solar system they are believed to have been the least chemically altered during the formation of the solar system. Studies of comets therefore probe a 'fossil' record of conditions that existed in the molecular cloud that collapsed to form our sun a little over 4.6 billion years ago.

Comets themselves are composed mostly of water ice and solids, and the primary theory for their origin is that they are agglomerates of the much smaller ice-coated dust grains found in the interstellar medium. Recent observations of Hyakutake and Hale-Bopp have increased support for the interstellar origin of comets.[15]

The evolution of the solar system has, in large part, been one dominated by collisions between various solid bodies. Today the odds for a collision between the Earth and, for example, asteroids, are quite small. Early in solar system history this was not the case as collisions occurred much more frequently. Indeed, due to this fact it is possible that part of our oceans was delivered to the forming Earth by numerous collisions with icy cometary bodies. Another theory, one that is very much in debate, is that comets themselves could have delivered organic molecules that served as the molecular seeds for prebiotic life on Earth. These suggestions point to tenuous connections between the Earth's oceans and life itself, with comets, which are themselves linked to chemistry seen today in interstellar space. If these theories are true, this would strengthen the case for life elsewhere in the galaxy as the necessary ingredients are found in abundance in space itself!

Despite these advances in our understanding, the complexities of these problems (origins of solar systems, life . . .) suggest the answers will remain elusive. Moreover, astronomers will always be limited by man's capabilities to remotely explore distant regions, both within our own solar system and beyond. However, the quest for origins is an important undertaking that is, and will remain, a major focus of research for years to come. In the future, astronomers will continue to investigate connections between comets and interstellar space clouds, search for the signs of life on Mars and, through missions such as SWAS, gain a greater understanding of the chemistry and physics of the parent molecular clouds. Ultimately we hope that these efforts will result in greater understanding of how solar systems are currently being born and, by inference, our own.

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