2. The Early Universe: The Source of Chemistry – and of Our Guide

On March 30, 2010, an experiment called the Large Hadron Collider (LHC) succeeded in crashing together two beams of protons at the colossal energy of 7 million million electron volts. (An electron volt is the energy given to one electron passing through an electric field of 1 V.) This was energy 3½ times greater than anything achieved before, and made up for a nervous 18 months while scientists waited to see if the billions spent on the LHC were justified. This enormous particle collider is housed in a vast tunnel spanning the border between France and Switzerland at the European Nuclear Research Centre (CERN) near Geneva. Operating 100 m underground, the LHC is the latest in a long line of experiments designed to investigate the world at a sub-atomic level and is now the most powerful tool at the disposal of scientists who work in the area of particle physics. With it, particle physicists are attempting to recreate the conditions of the very early universe.

Immediately after its birth – at least, if the current theories are to be believed – the universe was a very energetic place. Protons and electrons ran around freely, along with neutrons – neutral particles with a mass very similar to the proton – while a zoo of other more exotic fundamental particles rushed to and fro like traders in a bear market. In addition to the particles of matter, there were also the particles of light known as photons, particles that have no mass of their own, and because the negatively charged electrons and positively charged protons interact strongly with light, photons were "trapped" in with the ordinary matter in a hot, vigorous soup.

This brief sketch – and it is just that – derives from the best theory that we currently have to explain the universe that we live in. Because it starts with an "explosion" of truly cosmic proportions,

S. Miller, *The Chemical Cosmos: A Guided Tour*,
Astronomers' Universe, DOI 10.1007/978-1-4419-8444-9_2,

it was nicknamed the "Big Bang" by people who did not believe in it, and who began to ridicule it. The Big Bang Universe is not just a whim, though, because it is strongly supported by scientific evidence – the expansion of the universe measured by galaxies and clusters of galaxies racing away from one another, the discovery of the afterglow of the initial explosion, and, crucially for our story, the chemical composition of the universe. Indeed, the Big Bang was initially proposed to explain the whole of cosmic chemistry.

The biologist J.B.S. Haldane was once asked if he could deduce anything about God from his study of the natural world. So the story goes, Haldane replied that if He did exist, the Creator had "an inordinate fondness for beetles" – they are everywhere, in species too numerous to name. Astronomers who were asked the same question might answer to the effect that God had "an inordinate fondness for Hydrogen". Hydrogen is the lightest and simplest of all atoms, comprised of just one positively charged proton orbited by one negatively charged electron. It, too, is everywhere; some nine out of ten of all atoms are Hydrogen atoms, and it makes up nearly three fourth of the mass of ordinary matter in the universe.

Although Hydrogen is the lightest and the most abundant of all elements, it is not alone in the universe, which is fortunate for Carbon-based life forms such as ourselves. It is joined by a 100+ series of heavier elements, the next heaviest and most abundant element being Helium, Element 2, which makes up 24% by mass of the ordinary matter of the universe. Carbon, Element 6 and 12 times as heavy as Hydrogen, makes up just half a percent of the ordinary matter mass; Oxygen, Element 8 and 16 times heavier than Hydrogen, makes up just 1%. In between them, Element 7, Nitrogen, contributes just a tenth of a percent to the mass of ordinary matter. As the element number and the mass increases, so the proportion found in the universe decreases, at least until the very heavy elements are reached.

In the immediate aftermath of World War II, with the images of the atomic explosions of Hiroshima and Nagasaki still fresh, George Gamow of George Washington University pointed out that one could explain the fact that there were fewer heavy chemical elements than light ones if the early universe were in a highly *unequilibrium* state – far out of energetic balance with itself – and was expanding and cooling rapidly following an initial explosive event. Since the nucleus of heavy elements would take longer to build out of the fundamental protons and neutrons that made it up, heavy elements would be rare if the time available to make them were short. And time *was* short for the expanding universe, product of the Big Bang explosion, was both rapidly cooling and getting less dense. So the chances of sufficient protons and neutrons coming together with enough energy to produce heavier and heavier elements got slimmer and slimmer as time went on. This was why, Gamow argued, the abundance of heavy elements would fall off dramatically as the element became heavier – which was exactly what astronomers observed as well.

Gamow was right but the trouble was he was too right. Calculations on the Big Bang universe showed that the temperature and density of the early universe fell so rapidly that all that could be formed were the nuclei of Elements 1 through 3 – Hydrogen, Helium and Lithium – and Deuterium, a heavy form of Hydrogen that we will come across later. That made the early universe chemically simple, with just three chemical elements, but left unanswered how heavier elements, such as Carbon, Nitrogen and Oxygen and the other 100-plus elements, were formed. To answer that question, a subtle blend of astro-physics and astro-chemistry is required.

The early universe is clearly a product of what happens in the physical Big Bang and its immediate aftermath. It did not really start to be a *chemical* universe, though, until at least a hundred thousand years after the initial cosmic explosion, and probably more like 300,000 to 400,000 years. By that time, the temperature of the universe had fallen to a "mere" 4,000 degrees cooling to 3,000 degrees above absolute zero, still hot enough to melt almost anything except diamond (not that diamonds existed at this time, since there was no Carbon to form them) but cool compared with earlier times. (From now on, we will use the symbol K to denote "degrees above absolute zero". K stands for kelvin, and absolute zero is –273.15 degrees Centigrade. Note that a kelvin is the same temperature interval as a degree Centigrade. So temperatures expressed in kelvin, K, will always be 273.15 greater than temperatures expressed in degrees Centigrade.) Once the temperature got below about 3,000K, about 300,000 years after the Big Bang, positively charged protons – the nucleus of a Hydrogen atom – could (re-)combine with negatively charged electrons to form neutral Hydrogen atoms for the first time; electrons had teamed up with Lithium and Helium nuclei to form neutral atoms a "bit" earlier. Meanwhile, photons, the particles of light that had been trapped in the proton/electron soup of the very early universe, could escape and wander free. Matter and radiation were now no longer tightly coupled and could act independently of one another.

This period, extending from around 100,000 to 400,000 years after the Big Bang, is called the "Recombination Era," and more than 13 billion years later, we can still measure the light that first escaped at the time of the Recombination Era. Over time, and as the universe has expanded, the temperature of this all-pervasive background radiation has cooled from some 3,000K to just 2.73K and its wavelength has lengthened from (infra-)red to microwave, but it is there wherever we look out into space. This Cosmic Microwave Background Radiation, as it is known, was discovered in 1964 by American radio astronomers Arno Penzias and Robert Wilson, and for most astronomers that pretty much ended the argument about whether the universe started with a Big Bang or whether it had existed in a steady state from time immemorial.

So the Cosmic Microwave Background Radiation is the oldest radiation in the universe, and it carries in it the imprint of what the cosmos looked like and how it was structured in those early days. As well as allowing us to understand the universe at early times, however, it also acts as a veil; although we can derive theories about what went on before, and even try to simulate what happened in enormous particle accelerators such as the LHC, we cannot actually see further back in time than the time at which recombination happened, the time at which atoms started to form. The first few hundred thousand years of the universe are veiled off from direct observation, no matter how powerful our telescopes or how sensitive our instruments.

The Recombination Era produced the first electrically neutral atoms in the universe. It sounds easy enough; opposites attract and an electrically positive atomic nucleus and one or more negative electrons team up to form a neutral atom. The problem, however, is *excess* energy since free electrons and free atomic nuclei whizzing around the universe have enough energy to keep each other at arm's length. If they are to team up to form a neutral atom that is stable, they cannot keep all that energy; if they do, they will simply fly apart again. After all, in any relationship there has to be a bit of softening, a bit of accommodating to the partner's needs if things are going to work out. Just how depends on the fundamental structure of the atom itself.

The notion that matter consists of atoms – literally "uncuttable" – goes back at least to the Greek philosophers Leucippus and Democritus, who lived in the fifth century BC. According to these philosophers, the properties of materials could be deduced from the properties of the atoms from which they were made. Atomic theory began to take on its modern form with the work of the nineteenth century Manchester chemist John Dalton, whose ideas included the notions that the atoms of any particular chemical element were identical, and that chemical reactions involved the rearrangement of atoms but could neither create nor destroy them. Once the nuclear reactions in the immediate aftermath of the Big Bang had ended, chemical reactions in the early universe might rearrange the atoms that had been produced but could not change the overall composition of elements. For some chemists like Dalton atoms were real; for others, however, they remained merely a "convenience", a way of keeping the chemical books straight whilst following the ever more complex reactions and sophisticated compounds that nineteenth century chemistry involved.

The year 1905 was a marvelous year for a young patent clerk called Albert Einstein, a man who would turn out to be one of the greatest minds of the twentieth century. It is best remembered as the year that he put forward his theory of special relativity, commencing what the London *Times* would later call a "revolution in science" that "overthrew" the classical mechanics of Sir Isaac Newton. (Einstein himself was far more modest in describing his achievements.) Less appreciated, however, is the work he did on what was called "Brownian motion".

Brownian motion was probably first described in writing in 60 BC by the Roman poet Lucretius in his *De rerum natura* (On the nature of things). Lucretius described the random "dancing" of particles of dust caught in a beam of sunlight as being due to "underlying movements of matter that are hidden from our sight" caused by the impetus of atoms, an idea that he inherited from Leucippus and Democritus. However, Brownian motion is actually named for the botanist Robert Brown who observed the same random dancing of pollen grains in water. What Einstein did was to show mathematically that the intuition of Lucretius was right, giving conclusive proof to chemists that the atoms that they had *proposed* as a chemical convenience really did exist.

The first real understanding of the structure of the atom is due to the New Zealand-born physicist, Ernest Rutherford. In the early 1900s, Rutherford and his colleagues were studying the newly discovered phenomenon of radioactivity in which atoms, such as Uranium that are unstable, break down and release a variety of "rays". These rays were labeled by the first three letters of the Greek alphabet, alpha, beta and gamma. The beta rays were negatively charged and quickly identified as electrons, themselves newly discovered in 1897 by Rutherford's mentor J.J. Thomson. Gamma rays had no electrical charge and were seen to be very energetic rays of the same sort as light – electromagnetic rays. So what were the alphas? Rutherford showed that they were Helium atoms that had lost their electrons. And he soon showed that these alpha particles could be used to probe the deepest structure of atoms.

Rutherford worked with his assistant Hans Geiger (for whom the Geiger counter that measures radioactivity is named) and student Ernest Marsden to measure the effect of firing a beam of alpha particles at very thin films of metal. Gold was the most suitable because it is very easily worked, and it is possible to produce thin films of gold that are only four millionths of a centimeter thick. Rutherford's expectation was that nearly all of the alpha particles, which were very energetic, would pass straight through the gold foil, but he and Geiger had already noticed that the image produced by alpha particles on a fluorescent screen became "fuzzy" after passing through even the finest of gold films. Clearly the alpha particles were not all passing straight through the film, but some were being deflected off course – by how much and how often though? Marsden was given the task of seeing if any particles were reflected back off the gold film: and there were!

About one in 20,000 or so of the alphas came back off the thin gold film at Marsden along the direction he had originally fired them. Rutherford was astonished: "It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you" he is reported to have said. It meant that the gold foil was not made up of evenly spread matter, but was a network of tiny, dense obstacles surrounded by almost empty space. Rutherford had put together the basic structure of the atom – a tiny, dense, positively-charged nucleus, surrounded by a space filled with Thomson's negative electrons. How, then, did the electrons "fill that space"?

Spectroscopy was a second tool to probe the structure of the atom. Spectroscopy is to chemistry what fingerprinting is to criminology. Spectroscopy tells you what it is that you have in your test-tube and can claim the highest of scientific devotees - in the 1670s, Sir Isaac Newton used a glass prism to split up white light into its component rainbow of colors, eventually publishing his results many years later in his 1704 book *Opticks*. By the early 1800s, scientists had noted that while sunlight spanned the full spectrum of the rainbow, there were a number of dark lines or gaps that could be seen when precision instruments, much more sensitive than Newton's prism, were used. From 1814 onwards, the German physicist Joseph von Fraunhofer mapped nearly 600 such lines at different frequencies (or colors) in the Sun's spectrum. Many of the individual Fraunhofer lines, as they become known, were later shown to correspond to individual chemical elements, and a line in the red region with a wavelength of 656.3 nanometers (a nanometer, nm, is one billionth of a meter) was produced by Hydrogen. Hydrogen also produced lines in the blue-to-violet region of the spectrum, at 486.1 and 434.0 nm. Sodium produced two lines in the orange very close together, at 589.0 and 589.6 nm. Close by at 587.6 nm was a line that led to the identification of Helium, called so because it was first discovered in the Sun, or Helios in Greek. Some elements were extremely prolific such as Iron which was associated with ten strong Fraunhofer lines from the yellow-green through to the violet spectral regions.

As the nineteenth century closed, one of the major "revolutions" in our understanding of the physical world occurred. German physicist Max Planck proposed that energy could only come in discrete packets, called quanta. Unlike a dollar, which can be used to buy something for 27 cents and get you 73 cents back, quanta do not give you change. It is a quantum or nothing – a bit like a farmers' market where home-grown produce comes in one dollar packs, take it or leave it. Energy does not come in dollars, however, but in packets that are given by the frequency of the light corpuscles – photons – multiplied by a universal constant named for Planck, and given the symbol h. Again in his *annus mirabilis* of 1905, Einstein demonstrated that these packets of energy were real, and that light, which had the properties of a wave, was also composed of particles – again, photons.

Following Rutherford, the atom could then be described as a positively charged nucleus surrounded by "orbiting" negatively charged electrons. However traditional theory predicted that an electron in continuous motion about the nucleus of an atom would radiate away its energy and gradually spiral in until the two hit each other. Danish scientist Niels Bohr took Rutherford's atom together with Planck's quantum theory and simply proposed that this "spiraling in" would not happen if the electron were in an orbit around the nucleus with its angular momentum quantized. For a stable orbit, this angular momentum – given by the mass of the electron multiplied by the speed at which it orbited and its distance from the nucleus – should be a precise multiple of Planck's constant for the quantum of energy, h, divided by two times π, or pi; pi is given by dividing the diameter of any circle into its circumference and has a value of roughly 3.142.

As well as being the most abundant, Hydrogen is also the simplest of all atoms. Its nucleus is a single proton, and this is surrounded by a Rutherford "cloud" of just one electron. According to Bohr's model, the energy of stable electron orbits for Hydrogen would be given by a simple formula that depended simply on the level number, n, multiplied by itself to give n^2. This n^2 was then divided into Planck's constant, h, multiplied by the speed of light, c, and another fundamental constant, R, to get the energy of the level. R was a number known as the Rydberg Constant, and has a value of nearly 11 million inverse meters. The level number n was simply a number ranging from 1, 2, 3 … to as large as you like. The energy was measured from the point at which the Hydrogen atom would break up, or ionize, into a proton to become an H^+ cation, and a free electron. So the formula for the energy of Level n could be written simply as $-hcR/n^2$; the most stable orbits were furthest below the top of this energy "well", hence the minus sign in the formula.

The first energy level was produced when n was 1; in units of *hc*, it was –*R* units from the ionization point. (From now on, we will take the *hc* unit as a given.) The second level was at –*R* divided by two times 2, that is at –1/4 *R*. A spectral line of Hydrogen due to the electron "falling" from Level 2 to Level 1 has an energy of ¾*R*, in units of *hc*, and a wavelength given by 1 divided by that value, that is 4/3*R*. (This is why the Rydberg Constant is so useful; it leads directly to the wavelengths of Hydrogen lines.) This two-to-one line is actually measured in the ultraviolet part of the spectrum with a wavelength of 121.6 nm and is known as the Lyman-alpha line. The line of Hydrogen seen in the red part of the spectrum by Fraunhofer, known simply as H-alpha, corresponds to the electron changing its orbit from Level 3 to Level 2.

The energy of this line is given, once more, by the difference in energy between Level 3 and Level 2. As we have seen, Level 2 has an energy of 1 divided by two times 2, or ¼ R; Level 3 has an energy of 1 divided three times 3, or 1/9 R. So the energy of this line, again in units of *hc* is 1/4 minus 1/9 *R*, or 5/36*R*. This is equivalent to a wavelength of 656.3 nm. Spectral lines due to electrons in atomic Hydrogen changing their orbit occur right throughout the electromagnetic spectrum. For example, in the infrared region the line corresponding to a change from Level 5 to Level 4, and called Brackett-alpha, occurs at 4,053 nm with an energy equivalent of just a two-and-a-quarter percent of the Rydberg Constant.

One of the features of Bohr's atom is that the gap between adjacent energy levels gets less as the level number *n* increases. For example, the gap between Level 1 and Level 2 is 75% of a Rydberg. But the gap between Level 2 and Level 3 is less than 14% of a Rydberg, and between Level 3 and Level 4 is less than 5% of R. And, as we have seen, between Levels 4 and 5 the gap is just 2¼% of R. This makes the energy levels of the Hydrogen atom look like the branches of a Christmas tree – the higher up the tree you go the closer the branches are together, so it is just a small hop for a robin to get from the higher branches to ones just below. But if the robin at the top of the tree sees a worm on the ground at the bottom, it is a big jump to get down to it all in one go; maybe it is safer to hop down a branch at a time (Figure 2.1).

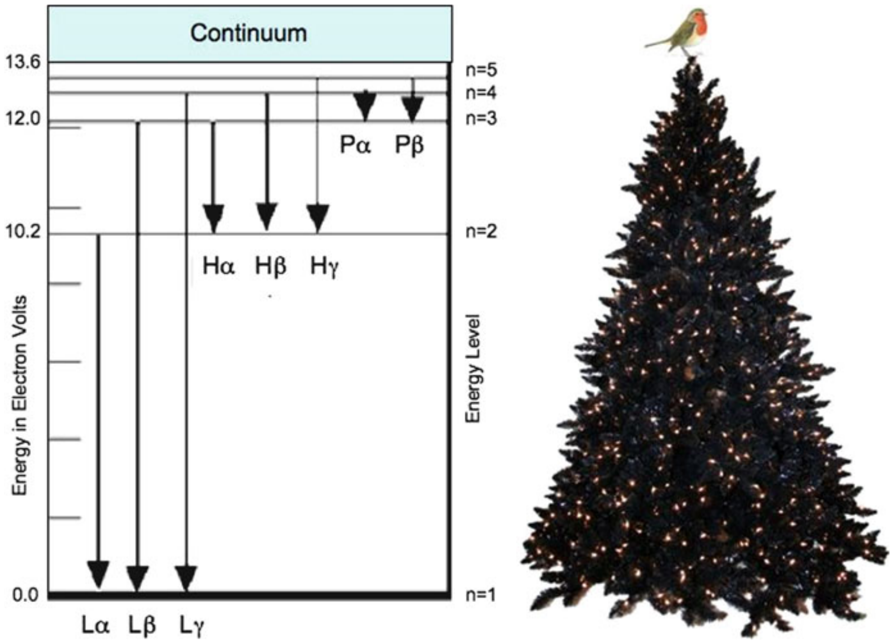

FIGURE 2.1 The energy levels of the Hydrogen Atom: a robin on an Xmas Tree can jump all the way to the lowest branch or hop down branch-by-branch, giving up much less energy per hop: *credit – Steve Miller.*

Back in our early universe, the simplest way to get rid of excess energy is for the combining free electron and atomic nucleus simply to hand it over to just one independent photon. For a Hydrogen atom forming from a free electron and a free proton, and ending up with the electron in the first – and lowest – energy level, that would mean producing an energetic photon with an energy equivalent to R. What goes down can also go up again, however; absolute dictators, for example, know that it is unwise to name a successor who will inherit all that personal power because it is a surefire way of getting yourself assassinated. Much better to groom a stable of acolytes each of whom can inherit only some of your powers, and to make sure that they never quite get it together enough to make it worth their while to kill you off. Similarly a Hydrogen atom that had settled down to a comfortable existence with its electron in Level Number 1 might suddenly find its peace shattered by bumping into a photon with an energy equal to R, emitted by a neighboring atom, and ending up re-ionized back into a free proton and a free electron. And if it and all other Hydrogen atoms did likewise and gave up all their ionization energy in one go, stable atoms would not form, and there would be no *Chemical Cosmos* – we would be back to square one.

Although Bohr's structure for the Hydrogen atom is now considered primitive and has been superseded by more detailed modern Quantum Mechanical models, it does, however, serve to demonstrate that recombination does not have to be an all or nothing process. Instead, the recombining atom can proceed from its free-nucleus, free-electron state down to its lowest – Level 1 – energy level by two or more stages, giving off two or more photons each of which has energy less than the Rydberg Constant. So each of these photons is unable to re-ionize its neighbors on its own. Even the largest and final jump – from Level 2 to Level 1 – only has an energy equivalent to ¾ *R*, a quarter of a Rydberg too little to re-ionize another atom. By the end of the Recombination Era, the universe was sufficiently spread out that the chances of several photons all ganging up on one poor Hydrogen atom to re-ionize it were very few and far between. Neutral atoms could form safely!

Immediately after the Big Bang, the universe was hot and energetic, but very uniform. Even at the end of the Recombination Era, the universe was so "smooth" that only small differences of about one thousandth of a percent show up in the Cosmic Microwave Background Radiation. Nonetheless, by the time that the universe was about 100 million years old – 1,000 times older than it was at the start of the Recombination Era, but very young by comparison with its current 13½ billion years – gas clouds vast enough and dense enough to form 100,000 or even one million stars the size of our Sun were quite common. These enormous gas clouds had been "seeded" by halos of dark matter, cold material composed of exotic particles that interact so weakly with "normal" matter – the kind that we, our planet Earth and our Sun are made of – that they have never been detected. These vast, dense gas clouds are known as proto-galaxies. Although they are very large, these very first galaxies are small in comparison with our own galaxy; the Milky Way is more than a million times more massive than the earliest proto-galaxies. And unlike the Milky Way, or other galaxies that we can see today, such as those in the constellation of Andromeda, proto-galaxies did not yet have stars.

So the task was to form the very first stars. Stars would be the next step towards the rich Chemical Cosmos that we enjoy today.

Stars are themselves huge balls of gas. But even a fairly middling star like our Sun has a density greater than that of the water we drink, and more than a thousand times more dense than the air that we breathe. The gas clouds that formed in the early universe, however, were a hundred billion billion times *less* dense than air. To form the first stars, therefore, meant forming dense clumps within the individual clouds, clumps that would eventually become a trillion trillion times denser than the original cloud. Unfortunately, gas heats up as it condenses, and hot gas tends to expand rather than contract. To have clumps dense enough to make stars meant cooling the gas down sufficiently and rapidly so that gravity had enough time to pull everything together before it became hot enough to fly apart. That, in turn, meant the gas temperature had to get down to just 1,000K or 2,000K. Something had to cool it.

Atoms can cool by radiating photons as their electrons jump down from higher energy levels to lower ones. As hot atoms fly about in the gas with great energy, they can crash into one another. The outcome can be that one atom has its electrons changed so that they hop up to a higher energy level, while its colliding partner looses steam and cools down. The now very excited atom can then cool back down by firing a photon off into deep cold space, where its energy can no longer heat the gas cloud; cooling has been effected. For atomic cooling to work, the colliding atoms have to have enough energy so that at least one of them can have its electron excited. Hydrogen atoms need energy equivalent to a temperature of about 12,000K to push an electron from Level 1 to Level 2, and it turns out that the atoms formed in the early universe are only good at cooling things down for temperatures above 8,000K. That still leaves the gas needing to drop another 6,000K in temperature. Something else is needed – the chemical combinations of atoms known as molecules.

Molecules mean that you really do have a Chemical Cosmos. Starting simple, molecules can grow into more complex creatures. Eventually, they can grow as complicated as the DNA that holds the genetic code for life, so for chemists, the Recombination Era marks the start of the good times. Back then, however, with just a few types of atoms – Hydrogen, Helium, Lithium and Deuterium – there is only so much chemistry you can do, especially when 90% of those atoms are Hydrogen and almost all of the rest are Helium. And making molecules is easier said than done; close to its source, the river of cosmic chemistry is a rather narrow, rocky stream.

By the middle of the Recombination Era, some 200,000 years after the Big Bang, most of the Helium had recombined to form neutral atoms. Much of the Hydrogen, on the other hand, was still in the form of positive nuclei (protons) without their neutralizing electron. Therefore one of the first molecules to form up was a molecular ion, not our chemical guide H_3^+, but a Hydrogen-Helium combination of just one Helium atom and a Hydrogen nucleus, Helium-Hydrogen-plus, denoted HeH^+. This reactive, little molecule then tagged onto whatever Hydrogen atoms had been able to "go neutral", eventually forming our diatomic Hydrogen molecule, H_2, the most fundamental of all molecules.

Unfortunately for these first cosmic attempts at making molecules, the background temperature of the universe was still hot enough to cause them to break up again. Almost as soon as molecules formed, they shook themselves apart, disintegrating too soon for them to play any real part in cooling down the gas clouds to the point where they could start to form stars. To create significant amounts of diatomic Hydrogen molecules meant waiting until more or less the end of the Recombination Era, when both positive and negative Hydrogen ions, H^+ and H^-, could combine directly with neutral Hydrogen atoms to start the formation of H_2, rather than using Helium as a matchmaker.

Even so, astronomical amounts of time were required to convert the gas in the universe from atoms to molecules; making just one Hydrogen molecule per cubic centimeter took over a week. As a result, some 100 million years after the Big Bang, Hydrogen molecules still only made up one part in 400,000 of the Chemical Cosmos. A network of over 40 chemical reactions, involving Hydrogen, Deuterium, Helium, and Lithium, and a variety of positive and negative ions, still only managed to produce ten other molecules at vanishingly small concentrations. Nonetheless, it is at this very early stage of the Chemical Cosmos that our guide,

H_3^+, made its first appearance. At a concentration of just one part in a billion billion, it came in right in the middle of the batting order at Number 6 out of the 11 molecules to be found.

They may be vanishingly small, but even at these concentrations molecules have a significance way beyond their numerical abundance. Once molecules form up, the Chemical Cosmos begins, and the universe can make a start to become the universe we have today, with stars and the possibility of planets, with clusters of stars, and the vast clusters of star clusters that we call galaxies, and even clusters of galaxies! Molecules can accomplish what atoms fail to do.

Like atoms, molecules may also give off photons as a result of changes in the motion of the electrons that surround their constituent atomic nuclei, and also like atoms they can use these changes in electronic motion to cool down to a few thousand degrees. Unlike atoms, however, molecules are made up of several atomic nuclei held together by chemical bonds that can be thought of as little springs, vibrating as a result. As they move through space, molecules can also tumble about like nanoscale circus performers; molecules have spectra that are caused by the motions of the atomic nuclei from which they are made, vibrations and rotations. These motions are, like the electronic motions, quantized; the vibrational and rotational energy of a molecule can only have a certain set of values.

The trick that molecules have is that the energy levels and jumps associated with vibrations and rotations are much less formidable than those associated with electronic motions. If our robin had to jump from branch to branch on the atomic Christmas tree, it only has to hop from twig to twig on the molecular pine. So that means that molecules can still be excited even when the surrounding gas only has a temperature of a few thousand, a few hundred, and even just a few tens of degrees above absolute zero. An atom or molecule hitting another molecule with too little energy to make the electrons jump can still cause the molecule as a whole to change its vibrational or rotational states. Relaxing once more, these hot molecules can then radiate a photon out into space. The vibration-rotation lines of molecules show up all the way from the visible part of the spectrum, at temperatures equivalent to a few thousand degrees, all the way to the microwave, at temperatures of only a few degrees. That means that they can cool at temperatures well below the 8,000K cut-off for atoms.

The question for the early universe was: are there enough molecules? As we have seen, at an age of 100 million years, the universe still only had one Hydrogen molecule, H_2, for every 400,000 Hydrogen atoms. Moreover, on its own, the Hydrogen molecule is actually not a very good radiator, taking something over 10 days to emit a single photon once it has been excited in the first place. So collapsing a cloud of gas to make a star in the early universe was a slow process; with a density of just ten million Hydrogen atoms in each cubic meter of gas (the air we breathe has more than a billion billion times as many) cloud collapse took 15 million years. For nearly the whole of these 15 million years, the gas temperature slowly cooled from about 1,000K to less than 200K, photon by painful photon. Its density increased by a factor of 1,000; now there were ten billion Hydrogen atoms for every cubic meter of gas. Then things started to warm up again; the gas density was high enough that hot atoms could pass on their energy to cooler atoms or molecules before the Hydrogen molecules could radiate it away in the form of photons. The last few thousand years, while the clump got dense enough to form a star, were a constant battle between gravity pulling the gas cloud together and the heating trying to push things apart again.

And what a battle it was.

In the last 10 years during which the gas cloud underwent its final gravitational collapse to form a star, the density had risen to ten billion billion molecules per cubic meter – still over a million times fewer than in the air that we breathe, but a trillion times denser than when the cloud started to collapse all those 15 million years previously. Fighting this collapse, the temperature had now increased again to over 1,000K. Hydrogen molecules worked hard to keep the gas cool, but during this final 10 years only one in every two Hydrogens managed to emit a single solitary photon. With six billion billion Hydrogen molecules in every cubic meter of gas, shortly before the first stars "turned on" the cooling rate was a miniscule one billionth of a watt. Tens of cubic kilometers of gas were only giving out as much energy as a single household light bulb!

Yet it was enough and stars did form. Once formed they could enrich the Chemical Cosmos as never before.

So if Hydrogen molecules are not very good coolers, one might ask if there was anything else. The answer is not really. The fact that Hydrogen molecules were so much more abundant than any other molecule meant that they dominated the cooling of the gas cloud. They were not entirely alone, though; a Hydrogen atom can team up with an atom of heavy Hydrogen, called Deuterium, to form a molecule denoted HD instead of our normal Hydrogen molecule, H_2. HD is a much better cooler per molecule than H_2, and if the gas became shocked and compressed faster than the speed of sound, it could contribute considerably to the subsequent cooling. There was also a critical period of some 10,000 years while the density of our collapsing gas cloud increased from around 10 billion to more than 100 billion atoms per cubic meter; the temperature was rising sharply, and our cosmic guide, H_3^+, showed what it could do. Although there was only one H_3^+ molecule for every billion of H_2, it managed to contribute more than 1% of the total cooling. With that effort, each H_3^+ molecule showed it is at least ten million times more effective at cooling as its neutral parent, a property that will be important later on in our guided tour.

For now, however, along with our guide, we are on our way downriver to the stars.

Springer

http://www.springer.com/978-1-4419-8443-2

The Chemical Cosmos
A Guided Tour
Miller, S.
2012, XII, 236 p. 25 illus., 22 illus. in color., Softcover
ISBN: 978-1-4419-8443-2