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Chemistry in Space Science

Existing chemical bonds are broken and new chemical bonds are being made every second on the surface of planet Earth, in its atmosphere, and on the surface of the Moon, in every other objects in the Solar System (irrespective of its size) and well beyond - the space between the solar systems - the interstellar medium (ISM). Although chemical changes are happening everywhere in the solar system, the reason behind the chemical changes that are observed on planet Earth or elsewhere could be different. However, there are circumstances that chemical reactions are accompanied with physical changes. So we have to also consider the physico-chemical changes while discussing chemistry that happens in the solar system bodies and in the ISM.

Although Copernicus' statement about Earth being at the centre of the Solar System wasn't factually true, if we look at this from the chemical perspective, then perhaps Earth can be considered as the epi-centre of a chemically rich Solar System being the only Solar System object that is, to-date, known to harbour life.

In this short course on chemistry in space science we will try to discuss the known and unknown realms of chemistry in different parts of the Solar System and in the ISM.

1. Chemical reactions in the subsurface of Earth

Before we move into the chemistry that is happening at 1 bar pressure, on the surface of our Earth, and even at lower pressures at much higher altitudes on Earth's atmosphere we shall see briefly on the chemistry that is happening below our feet. The pressure and temperature at the sub-surface varies with depth and, therefore, the chemical reactions may find their respective pathways. While looking at the chemistry in the near subsurface our attention is drawn to the nitrogen fixation which helps plant growth.

Please note a detailed explanation of this process is at present not in the scope of the discussion we are aiming at in this short course. However, I would like to point out the important chemical phenomenon happening in our near subsurface. Can we expect rich chemistry in the subsurface of other bodies in the Solar System?

2. Chemical reactions on the surface of Earth

We begin our discussion from the surface of the Earth where plenty of chemical reactions take place in front of us or even within us. Here are a few - we breathe in oxygen and exhale carbon dioxide, so definitely there is a chemical reaction that is taking place. But something that happens in front of us every day - the photosynthesis process where sunlight initiates the reaction between the ingredients that are from the planet Earth in bringing out a molecule as energy source for bio activity. How is the energy absorbed from the sunlight? And what wavelength range that reaches the Earth's surface is responsible for the photosynthesis?

The pigments that are present in the plants absorb energy at the wavelengths between 400 to 700 nm there by starting the reaction (equation 1) between water and carbon dioxide leaving the products (a) sugar molecule (glucose) and (b) six oxygen molecules.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

Note this chemical reaction is initiated by the absorption of solar photons in the visible wavelength (400 - 700 nm). What if we have the same reactants present on the surface of the surface of Mars - can we expect a similar product? Or would it be different?

The chemical reactions initiated by the photons from the Sun - photochemistry - can therefore be happening in other parts of planet Earth and not just on the surface. It is the solar photons that are responsible for photochemistry. But do all the wavelengths from the Sun reach Earth's surface or only a certain part of the electromagnetic spectrum? If only a certain part of the electromagnetic spectrum reaches the surface, then what about the rest of the wavelengths where they get stopped or absorbed and where that absorbed energy is spent? Maybe the molecules in the Earth's atmosphere hold the answer to this. As a thumb rule - wherever there are molecules and energy available then chemical reactions may be taking place.

Nevertheless, please note - the photons that strike a semiconductor (solar cell), at any altitude in Earth's atmosphere or even beyond Earth's atmosphere can generate electrons, electricity, without chemical changes on the target.

Similarly, if we take a plant to different altitudes in Earth's atmosphere and even beyond, do you think we will have the photosynthesis that is happening the same way as it was happening while the plant was on the Earth's surface? Certainly, the different conditions that we are about to experience at different altitudes are going to affect the chemical reaction initiated by the solar photons. The plant neither will be able to have the quantity of reactants nor the temperature that is needed to complete a photosynthesis if it were several kilometres up in the Earth's atmosphere. Do you think if we carry a plant to the highest summit on planet Earth, Mount Everest, we can expect photosynthesis to happen?

Let us look at some more examples for the chemistry at the surface of Earth without the involvement of photons. We will focus now on the internal combustion engines - the heart of our motor vehicles. The petroleum (hydrocarbon) that goes inside the engine combines with oxygen in the air to produce molecules in the gas phase (carbon dioxide, water, oxides of nitrogen and so on) and residues in the form of solid particles. These solid particles, blackish in colour, are a result of the combustion process that happens inside the engine. By looking at the residue that comes out of the exhaust in a vehicle we can guess that molecules made of carbon had clubbed together to form a solid particle. To be specific, the molecules that make up the soot from an internal combustion engine also contain polycyclic aromatic hydrocarbon (PAH) - aromatic carbon chains combined together. So the chemical reaction in this case is without photons. Figure 1, shows the Raman spectra of auto soot and it is compared to a spectrum obtained from the Orion bar. Does this mean we have similar auto exhaust somewhere in deep space?

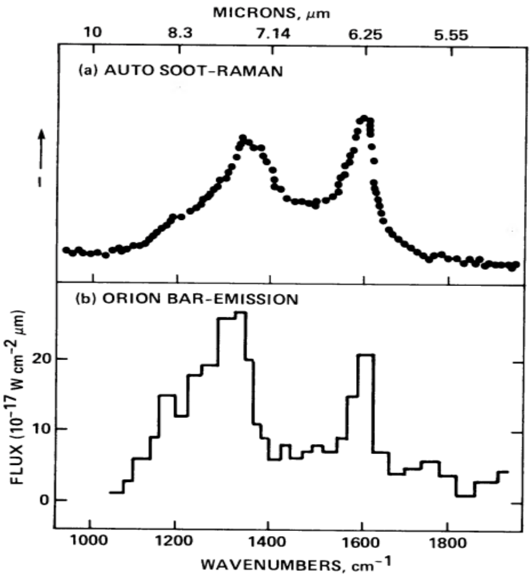

Figure 1 - From Allamandola et al., ApJ, 1985. Shows the similarity of carbon chain molecules that are from an auto exhaust and those along the milky way.

What about wood burning in air? At first it appears like oxygen atoms are consuming carbon atoms in the wood synthesising oxides of carbon and in addition, hydrogen reaction with carbon produces hydrocarbons. However, the carbon atoms can react among themselves and can also form allotropes of carbon, such as fullerene (C_{60}). Can you imagine how much of such carbon allotropes we could get by burning coal while extracting electricity? And by the way, how are we able to find the carbon allotropes present in the ashes from burning wood or coal?

How about the residue, the black smoke that emerges when we burn camphor? Does that contain similar hydrocarbons from wood and coal burning?

We can keep discussing several examples for the chemistry on Earth's surface. However, with these few examples we will now move to the Earth's atmosphere. Certainly, without doubt we can conclude that there will be a strong connection between the surface and the atmosphere - the coupling that is responsible for molecule recycling. By now we could also realise that the chemistry that takes place on Earth's surface, in the Earth's atmosphere at different altitudes and in deep space may have some similarities and differences.

While we talk about chemistry on Earth's surface, what comes to your mind when you hear the word "ice"? Eventually, it will be water ice that we go with. In addition, many also say "dry ice" - frozen carbon dioxide. Do you think the word ice in the Solar System or in deep space (ISM) refers to water and carbon dioxide ices or much more?

3. Chemical reactions in Earth's atmosphere

There are plenty of chemical reactions that happen in Earth's atmosphere depending on the altitude we look at. The day and night cycle, diurnal variations, the planet Earth undergoes has major effects to the chemistry that happens in its atmosphere. The combination of photochemistry and the presence of solid particles, aerosols, that are present in Earth's atmosphere are responsible for the necessary chemical cycle that is required to sustain life. In addition, a major chemical reaction (equation 2 & 3) leading to a molecule - very low in concentration, when compared to the major constituents of the Earth's atmosphere, is responsible for protecting the flora and fauna.

$O_2 \rightarrow O + O$ (2)
$O_2 + O + M \rightarrow O_3 + M$ (3)
Where, M is the third body. Note this two-step reaction happens in the stratosphere by absorbing the solar UV photons.

The oxygen molecules (O_2) absorbing the solar photons at certain wavelengths dissociate to atomic oxygen which eventually finds another oxygen molecule to make ozone (O_3) - a simple two-step process involving three atoms in a reaction. However, this reaction involves a third body to remove the energy from the reaction so that the product, ozone, is stabilised. For this the molecules in our Earth's atmosphere act as the third body. The ozone molecule thus formed will also absorb the solar photons at different wavelengths, one of those regions where it absorbs is very well known as the Hartley band. The region that absorbs the harmful UV photons (equation 4), which otherwise can interact with the molecules present in the cells of plants and humans and causing serious damages to the living cell.

O_3 $\rightarrow$ absorbs in the UV $\rightarrow$ 240 nm to 300 nm
(Hartley band) $\rightarrow$ absorption region of DNA (4)

The presence of nitrogen, oxygen, hydrogen, carbon and sulfur in the atmosphere combines in many ways via many reaction steps leading to several chemical products in the Earth's atmosphere. In fact, we have the advantage due to the formation of several molecules and also fight the reduction of several other molecules that affect us. Chemical pollutants due to human activities are also part of the chemistry in our planet's atmosphere.

While we say the molecules in the Earth's atmosphere are absorbing the photons of different wavelengths, emanating from the Sun, then what regions of the electromagnetic spectrum are absorbed by molecules in the Earth's atmosphere? In case if O_3 concentration is reduced to a significant level then we risk a good flux of UV photons reaching the surface of the Earth. Whilst visible wavelength is quite important for our survival, the longer wavelengths such as the infrared do reach the surface of the Earth. The thick atmosphere that shrouds the planet efficiently absorbs the vacuum ultraviolet and x-ray wavelengths thereby stopping the higher energy photons.

In fact, the absorption of vacuum ultraviolet photons, the solar wind particles (energetic electrons and protons), magnetospheric particles, and cosmic ray particles (high energy protons and atomic nuclei) ionises the atoms and molecules in Earth's atmosphere thereby resulting in the production of secondary electrons. These secondary electrons influence the chemical reactions in Earth's atmosphere.

If there is no atmosphere, then there will be a variety of energetic particles and a wide wavelength range of photons that will initiate chemical reactions - provided a good concentration of reactants are available. Moving away from the Earth's atmosphere, the immediate destination for an airless body which provides chemical reactors for reactions to occur is the surface of our own Moon.

4. Chemical reactions on the surface of our Moon

The major difference we will encounter will be the absence of an atmosphere for the Moon. Rather we call it an exosphere where molecules present won't be able to meet each other for a very long time - the molecules are separated by large distances - the density is so low and the molecules are bound by gravity. Also the surface temperature of the Moon varies from the equator to the pole especially if we consider the craters on the south and north pole of the Moon then we can locate many craters whose surface temperatures are very cold - at cryogenic temperatures (< 200 K) - due to the absence of sunlight. These places, called permanently shadowed craters, do not receive sunlight as the crater surface is deep enough. So the cold surface inside such craters are reservoirs for molecules to form an icy layer.

Recall the question we posted in Section 2 regarding the usage of the word "ice". Is it simply the water and carbon dioxide molecules that form the icy layers or could that be any molecule that is frozen. Well, while we consider the chemistry beyond Earth then the word "ice" refers to any molecule that is frozen.

There is no atmosphere, so all the Sun's electromagnetic radiation will be processing the surface of the Moon - hot and colder regions. So how does chemistry kick in? Let us look at how the key ingredient of life - water - is synthesised on the surface of the Moon and how it can form icy layers on the surface of the permanently shadowed craters. Please note - ISRO's Chandrayaan-1 mission discovered water in the lunar surface and exosphere.

The (mineral) particles on the surface of the moon are irradiated by the energetic photons and protons from the Sun. One of the products will be the formation hydroxyl radical, OH, that reacts with a hydrogen atom to form water. The water molecule thus formed will hop from the hotter parts of the Moon's surface towards the polar regions where the cold reservoirs inside the permanently shadowed craters are cold enough for the hopping molecules to stick and form an icy layer. However, the cometary delivery of water molecules, along with other molecules, are also among the source of water for airless bodies.

The chances of the permanently shadowed craters to harbour a variety of molecules (in addition to water) in the ice phase are at large because of two reasons - [1] the cometary delivery of molecules via the micrometeorite bombardment and [2] the energetic electrons and the cosmic ray particles that reach the surface of the permanently shadowed craters.

Now we are entering into another realm of chemistry that is initiated by energetic electrons, cosmic ray particles and micrometeorite bombardment, which we did not pay much attention to while looking at the chemical changes on Earth's surface and atmosphere. While molecules are frozen at cryogenic conditions, well below their sublimation temperature, the energy provided to break and make new chemical bonds can result in a variety of products following many chemical pathways that are not efficient for reactions when molecules are present in the gas phase. For example, in such permanently shadowed craters, along with water molecules, if we have molecules containing carbon (methane - CH_4), sulfur (sulfur dioxide - SO_2) and nitrogen (ammonia - NH_3) are present, then the reactions initiated will result in the synthesis of hydrocarbons, organosulfur compounds and oxides of nitrogen. However, the reaction does not stop there; the products thus formed can also react to form many other complex molecules such as large hydrocarbons, nitriles and thiols etc. So apart from water molecules, we can expect a plethora of molecules in the icy reservoirs. In the event of a good concentration of water and carbon dioxide mixed molecular ices, the energetic processing will lead to the formation of carbonic acid (equation 5) to be present in the cold regions of the lunar surface, this has been demonstrated in laboratory conditions.

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (5)$$

The synthesis of carbonic acid in an icy mixture of water and carbon dioxide is very efficient, even at 10 K.

Is there anything special about these icy reservoirs in the inner solar system? If we cannot reach the outer Solar System objects, then can we use the icy reservoirs of our own Moon to understand the chemical evolution in such colder conditions?

5. Chemical reactions in the icy inner solar system

There are only a handful of large Solar System objects we have within our inner Solar System. The number of smaller bodies are plenty; the asteroid belt still has many yet to be found asteroids. Within the large Solar System objects, we encounter from hot to cold objects with varying chemical composition. However, we will focus on something special about the presence of ices within the inner solar system object.

It will be surprising to note if one says that the planet Mercury, the first planet from the Sun, also harbours molecular ices on its surface. Well, such a scenario is quite possible if it is possible on our own Moon, yet, Mercury being too close to the Sun, the presence of molecular ice is a bit surprising. However, the permanently shadowed craters on the Mercury provide the low temperature zones, cryogenic reservoirs, that can harbour a variety of molecules similar to that we have discussed for our own Moon. But for Mercury, the source of molecules could be from the Sun grazing comets, comets that are on collision course with the Sun, and also the left over molecules / refractory dust from other comets. And these molecular ices can be processed by the energetic electrons and cosmic ray particles.

So, in terms of processing the molecular ices, do you think we have a good similarity between our own Moon and Mercury?

And what about Mars? Mars is neither an airless body nor containing the atmospheric structure like Earth. The atmosphere is quite thin dominated by the carbon dioxide molecule. So the initiation towards chemical reactions are quite unique at Martian conditions. Though ozone can be formed in the martian atmosphere, via a series of reactions given in equation (6) from the breaking CO2 molecules by absorbing UV photons, the ozone concentration is localised which does not form a blanket of ozone as seen in the Earth's atmosphere. So the UV radiation is quite harsh at the Martian surface.

$$CO_2 \rightarrow CO + O$$
$$O + O \rightarrow O_2$$
$$O_2 + O \rightarrow O_3 \quad (6)$$

How about the asteroids? Can they make water and ozone molecule with the molecular ingredient that is present on their surface? Well the answer is yes, if we have protons irradiating the surface of asteroids then the combination of atomic hydrogen with OH radical, similar to the reaction we discussed for water synthesis on the lunar surface, results in the formation of water molecules on the surface of the asteroid. For the synthesis of ozone, from the equation we can infer that oxygen rich molecules can contribute enough oxygen atoms to build a significant molecular oxygen concentration so that ozone molecules can be synthesised. Therefore, if the asteroid surface harbours a significant amount of carbon dioxide ice then we have strong chances of the ozone synthesis via the energetic processing (electrons, photons, cosmic ray particles).

Did you notice the difference in the size of the object we had ended up with where a similar chemistry can take place? Asteroids aren't that big as the Moon and Mercury that we have discussed.

6. Chemical reactions in the icy outer solar system

The icy outer solar system is so magnificent that each planet with its moons is a Mini-Solar System. This region has some interesting features on how the chemistry occurs on the surface of the icy moons. This region of the Solar System is the cryogenic zone where most of the molecules are frozen forming an icy crust (Table 1). Each planet, Jupiter and Saturn etc, contain many icy moons of which only a few moons are embedded in the magnetosphere of their own planets.

Table 1 - Typical ices found in the outer solar system

Planet	Satellite	Ice
Jupiter	Io	SO_2, SO_3, H_2S?, H_2O?
	Europa	H_2O, SO_2, CO_2, C_xH_y, XCN, H_2O_2, H_2SO_4
	Ganymede	H_2O, SO_2, CO_2, C_xH_y, XCN, O_2, O_3
Saturn	Enceladus	H_2O
	Dione	H_2O, C_xH_y, O_3
	Rhea	H_2O, C_xH_y, O_3
	Titan	H_2O, CH_4 C_2H_6 , CO, NH_3
Neptune	Triton	N_2, CH_4, CO, CO_2, H_2O
Pluto	Charon	N_2, CH_4, CO, H_2O, NH_3, NH_3 hydrate
Kuiper Belt objects	Quaoar	H_2O, CH_4, CH_3OH, NH_3, NH_3 hydrate

For example, in the Jupiter (Galilean) system, the moons Io, Europa, Ganymede and Callisto are well embedded in the magnetosphere of the planet. This adds another pathway in the chemical enrichment, the magnetosphere picks up the ions and accelerates it (Figure 2). If the ions are picked from Io, which is the rich source for sulfur, then the sulfur ions can be implanted on the surface of the other moons. The chemical ingredient can be transferred from one moon to the other.

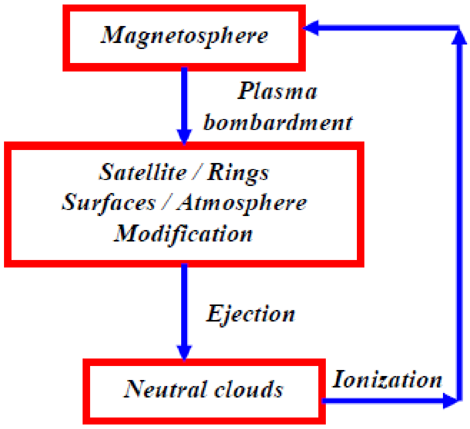

Figure 2 - Energetic ions supply chain for a satellite embedded in a planetary magnetosphere. (Adapted from Johnson 1990).

Similarly, magnetospheric implantation of reactive ions also takes place in the Saturnian system, where the nitrogen rich Titan atmosphere supplies the nitrogen atoms (in form of ions) that is carried away by the magnetosphere to chemically enrich the other moons within the Saturnian magnetosphere. If you consider the moons Rhea and Titan that are close to each other (approximately twice Earth-Moon distance) in the Saturnian system, the moon Titan is suspected to have supplied a large amount of nitrogen / nitrogen containing molecules to the moon Rhea in geological times scales. Such good concentration of chemical ingredient transfer can influence the surface chemistry of the other moon. In the case of Titan-Rhea the presence of hydrazine monohydrate ($N_2H_4.H_2O$) on the surface of Rhea is thought to be the outcome of a combined process of chemical transfer and irradiation.

There is another energetic process that must be considered, the hypervelocity impacts of micro and macro bodies onto the surface of these icy moons. The icy moons contain many craters which are an outcome of the impact events. The impact event inflicts physical damage to the surface, whilst the energy deposited is used to alter the chemical composition at the molecular and micron (or even slightly larger) sized particles.

As we move further away towards the Pluto system - we notice that the presence of nitrogen bearing molecules tends to appear along with other molecules that we have discussed so far. This is due to the reason that the temperatures drop further into the low orders. The average temperature of the surface of Pluto is 30 K - 35 K. So the molecules known as super volatiles, nitrogen / carbon monoxide / methane play a major role in this region of the Solar System. Even, molecular oxygen is considered a super volatile as the sublimation temperature (~ 30 K) is quite equivalent to that of carbon monoxide. The chemistry that happens at such low temperatures and at such large distances from the Sun (semi-major axis ~ 39 AU, 39 times the Sun-Earth distance) can be attributed to the solar photons as well as to the cosmic ray irradiation. The moons of Pluto also experience a similar irradiation environment and no magnetospheric ions. So do you think Pluto has a magnetosphere?

Did you notice the phase of molecular nitrogen as we move from the Saturnian system to Pluto? It is in the gas phase in Titan and as a frozen solid on Pluto's surface.

7. Chemical reactions in the Kuiper belt system

The Kuiper belt system is well beyond the orbit of Pluto. To-date from the New Horizons spacecraft we have visualised and closely examined a Kuiper belt object, Arrokoth (semi-major axis ~ 44.5 AU). Though the temperatures are low there is no dearth for chemical reactions in this region. Arrokoth displayed a rich chemical composition (methanol with organic material) on its surface, however, no evidence for water ice is known on Arrokoth. It is considered that water molecules might have been consumed in reactions with other simple molecules such as methane making methanol and organic compounds. The Kuiper belt is known to be the most pristine region on the icy Solar System so the chemical reactions by the impact of silicate grains or other grains has to be considered.

By now, you may have come to the conclusion that the icy bodies in the Solar System have unique chemical composition with a variety of sources that can initiate chemistry as we move away from the Sun.

8. Chemical reactions in the interstellar medium

The interstellar medium, commonly denoted as ISM, is a very active place for molecular synthesis and for the birth of new stars. There are many regions of the ISM in which temperatures range from 10^6 K to 10 K. Two types of interstellar clouds are defined according to their physical properties and the chemical constitution, 'diffuse' and 'dense' molecular clouds (Table 2). Diffuse clouds have low density and high temperatures whereas dense molecular clouds have higher density and are the coldest (10 K) region of the ISM. Do you think, one of the famous equations $PV = nRT$, in our school text books will helps us to deduce the ISM conditions?

Table 2 - Typical characteristics of cool interstellar nebulae.

Type of nebula	Number density	Temperature (K)	Pressure (atm)
Diffuse	0050	80	5×10^{-19}
Dense	5000	10	7×10^{-18}

Table 3 - Interstellar abundance of elements relative to hydrogen.

Element	Abundance
H	1.00
He	0.09
O	7×10^{-4}
C	3×10^{-4}
N	9×10^{-5}

In the ISM, interstellar dust particles provide the surface for molecules to stick on and accumulate to form ice layers (Figure 3). *How big and chemically diverse is an interstellar dust particle? where chemical reactions are taking place.* Interstellar dust particles are identified to be made of silicates, graphite, and amorphous carbon or hydrogenated amorphous carbon, with varying sizes from 10 – 30000 Å. To date more than 200 molecules (including isotopic composition) have been identified in the ISM and the list grows with the recent identification of phosphorous containing species. The list of molecules ranges from diatomics to those containing 13 atoms. Relative to hydrogen (H), elements like helium (He), oxygen (O), carbon (C) and nitrogen (N) are found to be most dominant elements in the ISM (Table 3). Figure 4, shows the temporal growth in the identification of new molecules in the ISM until the discovery of fullerene (C_{60} and C_{70}). Since

2010, several new molecules were discovered in the ISM. In the year 2021, a total of nearly 41 new molecules were reported to be present in the ISM. This adds to the chemical complexity which we try to understand through laboratory experiments by recreating the ISM conditions in the laboratory.

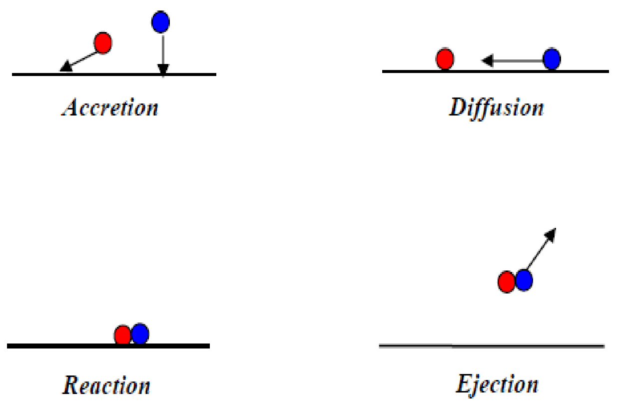

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Figure 3 - Formation of new molecules on cold grain surfaces.

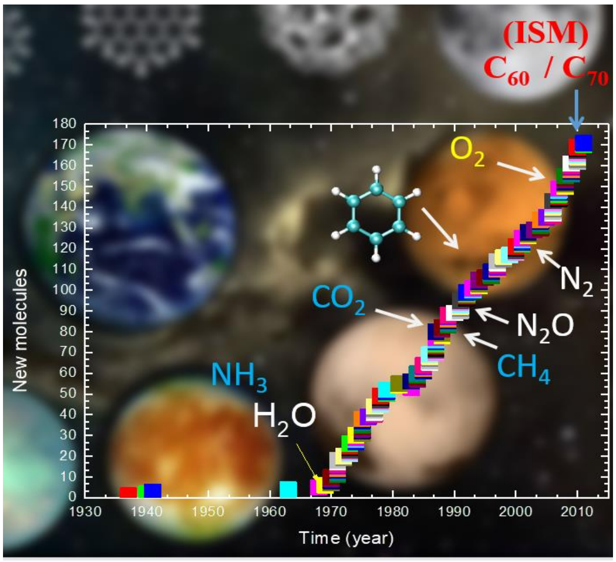

Figure 4 – Temporal evolution of the discovery of many new molecules in the ISM. The plot ends at 2010 when fullerenes were discovered in the ISM.

The production of simple molecules such as O_2 and N_2 on the interstellar dust or grain mantle is restricted due to the abundance of H atoms. When H atoms are consumed in a reaction to form molecular hydrogen during the increase in cloud density then the formation of molecules like O_2 and N_2 are enabled. In regions where H dominates then the production of H dominated species (eg. H_2O, NH_3 and CH_4) is more likely. Apart from reactions that take place by diffusion of molecules or atoms, reactions are also enabled by the action of radiation. For diffuse clouds starlight can induce chemistry but in the case of dense clouds, which are opaque to starlight, molecules are formed by the energetic cosmic ray particles.

The irradiation of dense clouds by the action of cosmic rays leads to the liberation of electrons due to ionization of molecular hydrogen (Equation 7.1). In a diffuse cloud, electrons become available by photoionisation (Equation 7.2). Such secondary electrons can then in turn induce chemistry in the ice. There is no limitation to the variety of chemical reactions that can take place in the extreme conditions of a chemically rich ISM.

H_2 + cosmic ray → $H_2^+ + e^-$ (7.1)

A + photon → $A^+ + e^-$ (7.2)

Chemistry is happening only at cold temperatures in the ISM or are there high temperature chemical processes too? Is there a source for the ISM particles to experience a sudden jump in temperature from few 100’s of K to a few 1000’s of K within a second? In such a case, will it bring only chemical changes to the interacting medium or physico-chemical changes?

9. Astrochemistry and its significance in astrobiology

From the discussion so far, we now know that ISM and the Solar System are chemical reactors that are capable of making complex molecules. If the basic ingredients of the molecules of life (amino acids, nucleobases and sugars), are provided then we will eventually end up making those via a set of chemical reactions. These molecules of life await identification in the ISM, but are already known to be present in the Solar System via studying the molecules on the meteorites (the left over material that made the planets). Nevertheless, the laboratory experiments carried out by recreating the ISM conditions, strongly suggest the presence of the molecules of life in the ISM, so definitely it is a matter of time before we confirm its presence in the ISM. Though many unknown molecules are present in the vastness of the ISM and the Solar System, with the available information, to-date, on the molecular complexity we may arrive at a conclusion that life is not confined only to the planet Earth. Can we say that the presence of complex molecules is where astrobiology begins? What is astrobiology – making the first cell?