

Pre-Biological Evolution of Organic Matter in the Universe

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In this contribution I present general considerations related to the non-biological evolution of the organic matter in the Universe. History of studies of interstellar molecules is briefly outlined. It is followed by discussion of the molecular evolution in interstellar clouds and protoplanetary disks.

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The title of this contribution may not be entirely proper as it sort of implies that the evolution of the material I am going to discuss necessarily predates the biological evolution, which is not the case. We do not know whether or not the molecules that I will be talking about play any role in the biological evolution here or maybe elsewhere in the Universe, so the proper title would be “Non-biological evolution of organic matter in the Universe”.

The second starting remark is to be related to the definition of organic matter. It looks like there is no commonly accepted definition of what the organic molecule is. It is generally accepted that, of course, an organic molecule should contain carbon, and probably it should also contain a carbon-hydrogen bond. So, CO molecule is not organic. Adding one hydrogen atom to it we obtain HCO radical, which does not have a name because as it does not occur too often on Earth. And if we get another hydrogen atom, we get formaldehyde, which contains a carbon atom, which contains H-C bonds, and which has a fancy name, so it is definitely organic.

Yet another definition, which is sometimes used in the astronomical literature, is related to the so-called complex organic molecules (COM). According to this definition, a complex organic molecule is a carbon-bearing molecule containing more than five atoms. Of course, this complexity stands nowhere close to the complexity of the biological world, and this should be kept in mind.

The existence of extraterrestrial molecules was first inferred back in the 19th century by William Huggins [1]. He observed wide emission bands in spectra of cometary tails and has related these bands to some carbon compounds. Now we know that some of these bands do belong to carbon-bearing molecules. But the idea that molecules can exist somewhere beyond the Solar System was not readily accepted until late 1930s. There is a famous quote from Eddington, “Atoms are physics, but molecules are chemistry” [2], implying that chemistry is something belonging purely to Earth.

But in the end of 1930s interstellar absorption bands had been discovered, which have been assigned to three molecules, CH, CN, and CH^+ , in early 1940s [3, 4, 5]. Note that these were again carbon compounds. The first chemical network to explain the presence of these molecules has been proposed in 1943, and it was argued that these molecules appear in the interstellar medium (ISM) due to reactions of radiative association [6, 7]. In general, it is no easy to bind two neutral atoms, but if they form a collisional complex that exists long enough, it may emit a photon which takes away the extra energy. The complex stabilizes itself into the molecule. Initially, it seemed that it is suffice to introduce reactions of radiative association to explain observed abundances of carbon-bearing molecules. But in 1951 rates of these reactions have been recomputed by Bates and Spitzer [8], and it turned out that these reactions are way too slow to explain the presence of even these three molecules. There have been other suggestions like the appearance of these molecules due to photodissociation of methane evaporating from dust grains. But at that time no one really cared much about the origin of these compounds. After all, these were only three compounds and very simple ones.

Everything changed once radioastronomy became a tool for studying the interstellar material. Molecules have rotational transitions which fall into the radio band, and emission related to these transition can be easily observed from Earth. The first interstellar molecule was discovered in the radio in 1963, and it was hydroxyl [9]. A few years later ammonia, water, and the first interstellar organic molecule, formaldehyde, were discovered [10, 11, 12]. Since that time every year adds a few molecules to the list, and as we go closer to present time, we see more and more complex

organic compounds [13]. The total list of known interstellar and circumstellar molecules comprises more than 200 names, and the largest molecule which is definitely known to exist in interstellar space is thirteen-atom molecule of benzonitrile [14, 15]. This is the first aromatic ring molecule to have been discovered in the interstellar medium. Apart from it, we have methanol, ethanol, acetonitrile, which is a precursor to glycine, the simplest amino acid, and many others.

Definitely, this diversity cannot be explained by any simple set of chemical reactions. We need something more elaborate, and we need these chemical reactions to work at very low temperatures, sometimes below 10 K, and at very low densities. All of this means that we should only account for two-body processes. Destructive processes in the general ISM imply that molecular clouds are the place to form most of these molecules. The specific explanation was proposed in 1973 in the two papers by William Watson [16], Eric Herbst, and William Klemperer [17]. They argued that the chemical diversity which was observed in molecular clouds was related to ion-molecular (or ion-neutral) chemistry.

It is not easy to bind two neutral atoms, to say nothing about two same charge ions. However, if one reactant is charged and another one is neutral then they react much more easily, and the idea is that initial ionization is caused by cosmic rays. It is either ionization of H_2 molecules, which leads to formation of H_3^+ ion, or cosmic ray-induced ionization of primary atoms. Then, a simple chain of chemical reactions is initiated, which starts either with the reaction of a neutral atom with H_3^+ or with the reaction between H_2 and an ion. Later, it turned out that this straightforward scheme only works in the simple way with oxygen. In the reactions of ionized oxygen with H_2 or neutral oxygen with H_3^+ ion, OH^+ , H_2O^+ , and H_3O^+ ions are produced. Then in the end we have the reaction of dissociative recombination, when the final ion in the chain recombines with an electron and is dissociated in the process into either hydroxyl or water.

It works somewhat differently in the case of carbon because carbon has a low ionization potential. So in most volume of the interstellar space it is ionized, and the reaction between C^+ and H_2 is very slow because it turned out to be radiative association reaction, and the reaction between C and H_3^+ does not proceed efficiently because neutral carbon abundance is quite low. And because of that another branch of chemical reactions starts with the reaction of ionized carbon with hydroxyl, and it ends with the formation of CO, the most abundant molecule after H_2 . A complicated situation is also typical for nitrogen reactions, again the two reactions $N + H_3^+$ and $N^+ + H_2$ are slow, and atomic nitrogen prefers to react with hydroxyl with the final formation of N_2 molecule.

Of course, all the intermediate products of the above reaction chains are free to react with each other. For example, HCO^+ ion can react with H_2 forming formaldehyde, H_3^+ can react with a CN radical producing isomers HCN and HNC. C^+ can react with CH initiating another reaction chain, which ends with the acetylene formation. You may notice that some of these reactions are neutral-neutral reactions. These reactions are slow when atoms are involved, but when you already have some molecules, neutral molecules react with each other more efficiently.

It was long believed that farther organic synthesis is based on reactions with CH_3^+ ion [18]. It reacts with less complex organic molecules forming more complex organic molecules, and then situation develops farther and farther. But experiments have shown that in one case this logic fails. It was believed that the main production channel for methanol is formation of protonated methanol followed by its dissociative recombination. But experiments have shown that for some reasons this reaction is, first, very slow, and then, protonated methanol prefers to break somewhere in between

producing not methanol but CH_3 and OH [19]. So, gas-phase reactions turned out to be insufficient to explain at least high abundance of methanol in the interstellar medium. But actually this is not the major problem. The major problem is molecular hydrogen, which makes molecular clouds “molecular”. There are no gas-phase reactions which effectively form H_2 molecules in the modern Universe. Of course, this is the only way to produce H_2 in the early Universe. But now it is believed that surface chemistry plays a major role in formation of molecular hydrogen.

When two hydrogen atoms recombine to form a molecule, you need some sink for the energy, and a dust grain plays a role of this sink. And, of course, if we allow molecular hydrogen to form on dust surfaces, we need to consider other surface processes as well. The simplest chain is a subsequent addition of hydrogen atoms to CO molecules, and it ends up with a methanol molecule. Some other branches are also possible, which lead to formation of methanol, ethanol, dimethyl ether. All these reactions proceed in low density cold dark environments. As a star formation proceeds, additional sources of energy appear. Icy mantles of dust grains can be further processed with formation of even more complex molecules.

To study this process, that is, to reproduce it in numerical models we need to write down the kinetic rate equations, which account for two-body processes and for the interaction of each molecule with some external factors like radiation, cosmic rays, and so on. There are some generally adopted parametrizations for coefficients in these reactions, and the relevant reaction parameters are available in various astrochemical databases like the Kinetic Database for Astrochemistry [20]. Farther, we need to adopt an element set along with a set of molecules which we want to consider. We also need to set physical conditions: density, temperature, cosmic ray flux, radiation, and extinction if the considered location is embedded deep into a molecular cloud.

To test the astrochemical model, there ought to be an etalon object rich in molecular gas. Fortunately, such a region is available nearby in the Taurus Molecular Cloud. The entire region is called the Molecular Ring, and it is very rich in organic molecules [21]. When you run a model with some typical physical conditions, and then you can compare your results with observations of various molecules in this object, which is often used as a testbed for astrochemical models. The various tests have shown that for most molecules we find a reasonable agreement with observations. Reasonable, in this case, means an order of magnitude in both directions, which is quite generous but taking into account all the uncertainties related both to observations and to simulations, this is reasonable. I would like to point out that with the modern models we can simultaneously explain abundances of very abundant molecules like CO and molecules with very low abundances. The range of abundances is six orders of magnitude, and we can explain it in a single model. It all concerns with gas-phase molecules. The situation is less clear with ices, as they should be observed in the infrared, in absorption, and for that we need a good source of infrared emission, which are quite rare. For now securely identified ice species only contain six molecules, and the most complex molecule in this list is again methanol. But even in this case we have some numerical constraints to our model.

The situation becomes more favorable for modeling and for observations when a young star appears nearby, and this star warms up dust grains, evaporates icy mantles, and all the molecules which had been synthesized on dust surfaces appear in the gas-phase where they can be observed. Actually, many molecules in the list presented in [13] have been observed in one single object, which is called Large Molecular Heimat and is located right next to the Galaxy center. This is where

numerous organic and non-organic molecules are observed in a quite compact region, and one can in principle study the spatial distribution of these molecules and compare these distributions with numerical models. In more sensitive observations it was shown that a similar situation is seen not only around massive young stellar objects but also around low mass young stellar objects, which are called hot corinos. What is interesting, complex organic molecules are now observed in dark pre-stellar cores like the prototypical pre-stellar core L1544 [22]. It is assumed to be very cold, and still it is rich in various organic molecules, which may imply that we are missing some desorption mechanism. The situation may not be that simple in this specific core. These are interferometric observations of methanol emission presented by [23], and they show that methanol emission is observed on one side of the core. This may imply that there is some illumination from this side.

Anyway, once these molecules are evaporated from icy mantles in hot cores, they can farther react with each other in the gas-phase, producing even more complex molecules and even maybe some amino acids. There were several claims that glycine was detected in interstellar space, but every time these claims have later been disputed. But this should be merely a technical problem, as there are no obstacles to form glycine in the interstellar medium. There are problems of observations, problems related by identification to the lack of laboratory data about many molecules. Because of that, many spectral lines which have already been observed are still unidentified, so we can wait for further discoveries as well.

There is still an open question whether or not this has any relation to the biological evolution. In the current paradigm of star formation, planetary systems definitely form out of the material which has passed through the molecular cloud stage into the pre-stellar core stage, so it should contain initially all these rich molecular inventory. But the question is whether or not these organic molecules are preserved during the formation of a protoplanetary disk.

Fortunately, we now have a possibility to observe such objects directly. At first, they were only observed in the optical, but now thanks to ALMA and other similar facilities we can observe protoplanetary disks in the radio band, and probably the nearest future will allow us to answer the question, whether or not this quite a complicated path of the pre-stellar core material to the terrestrial planet forming zone allows preserve the organic inventory which has been accumulated during the pre-stellar stage.

Some answer can be deduced from the analysis of meteorites. Meteorites are known to contain complex organic molecules, which sometimes possess quite significant anomalies in some isotopes, and the most prominent anomalies are observed for deuterium. The excessive deuterium (along with ^{15}N) fractionation is believed to be a signature of the interstellar origin of the meteorite organics. It does not mean that all these molecules have been synthesized on the pre-stellar stage, but they have been synthesized out of the moieties inherited from the interstellar stage. Direct modeling is also possible, and this is what we are trying to do in our group.

The list of molecules which are now observed in protoplanetary disks is not that rich, but it already includes some simple organic molecules. We can compute some typical structure of a protoplanetary disk in terms of density, temperature, and radiation field. Then, on top of this structure we can compute the molecular evolution, trying to answer the question, whether or not the initial molecular inventory is preserved during the evolution of a protoplanetary disk. The problem is that most molecules can be frozen-out in real disks, so that it is not a straightforward task to infer their presence. Only in the very inner hottest region of the disk do complex molecules

evaporate from icy mantles and may participate in further gas-phase processing. Beyond the so-called ice line, methanol and other complex organic molecules are preserved untouched; or would be preserved untouched during the protostellar disk evolution if there were no luminosity outbursts.

We observe luminosity outbursts in some protostellar systems, and they may be an inevitable stage of evolution of any protoplanetary disk. On one hand, these outbursts move all ice lines farther out from the star. If during the outburst the luminosity is raised to about 200 solar luminosities, all the disk up to one hundred AU is heated up to temperatures which would evaporate most organic molecules. On the one hand, this allows us to make observations and to see whether or not abundances of these organic molecules are consistent with our prediction for molecular clouds and disks. On the other hand, these outbursts initiate new chemical processes, which may essentially change the initial inventory of molecules, especially close to the star, in the region where terrestrial planets form. What are the conclusions of these calculations remains to be seen.

My final comment is about an alternative scenario, which is now also being considered. This is a “top-down scenario”. We know that the interstellar dust partially consists of organic compounds, and some organic molecules which are observed in regions of star formation may be products of the destruction of these organic dust grains rather than products of synthesis out of simpler compounds.

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DISCUSSION

DIEGO MOLINARI QUESTION: How do these complex molecules evolve with the evolution of the protoplanetary disk? Do they survive the formation of planets?

DMITRI ANSWER: The disk structure I have shown is a stationary disk structure. It does not account for any motion of gas within a disk. And when we do the chemical simulation with this structure, we see that molecular composition changes significantly within few AU from a star where terrestrial planets form. It remains mostly unchanged farther out in the stationary model, but if there are some flows, meridional flows, for example, then changes may encompass a more significant part of the disk.