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Unveiling the whole from its parts or to see the forest from the trees

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Abstract. In our quest for large organic molecules in the interstellar/circumstellar medium, the main difficulty is to disentangle their spectral signatures among the observed forest of bands. We propose a new approach to the problem, by defining a number of key transitions coming from parts of the whole molecule and that would characterize its fingerprint. If these key transitions are observed together in the same astrophysical target, it may be that we are detecting the whole from its part.

Key words. Astrobiology – Prebiotic molecules – Complex Organic Molecules – Detection of Complex Organic Molecules

1. Introduction

We live in a molecular universe. The more massive components of the Milky Way are the huge dust and gaseous molecular clouds that can be seen during a clear night, drawing the profile of our galaxy projected onto the sky. Carbon is the fourth more abundant chemical element in the Universe. Apart from the H_2 molecule and water, which are the first and second most common compounds in the universe, organic molecules are also rather abundant. They are the constituents of life as we know it on Earth. Many molecules used in biochemistry on Earth are found in comets, asteroids, in the interstellar medium, in circumstellar envelopes and atmospheres of evolved stars. It could be said that we live in an organic-friendly universe and a great number of organic compounds found are pre-biotic molecules.

2. Organic molecules in the interstellar medium

The interstellar molecular clouds, circumstellar envelopes and atmospheres of evolved stars are factories of complex molecular synthesis (Ehrenfreund et al. 2010). Complex organic molecules (COM) are thought to be formed on the surface of dust grains, pumped by ul-

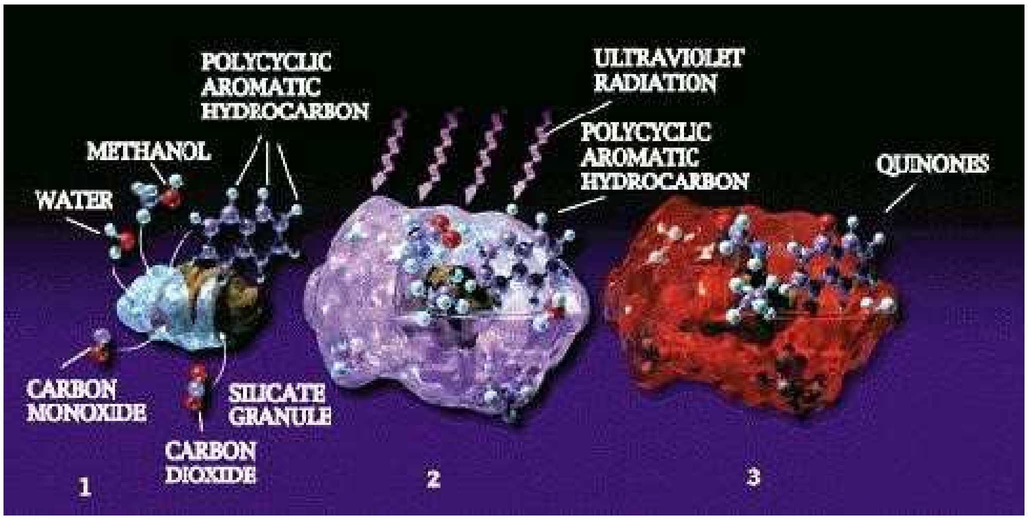


Fig. 1. Formation of complex organic molecules on the surface of grains pumped by UV radiation and/or cosmic rays (images.astronet.ru).

traviolet radiation and/or cosmic particles (see Figure 1).

An example of the wealth of organic molecules found in the interstellar medium is given in Figure 2.

3. The synthesis of nucleic acids

All living beings on Earth use de DNA molecule (deoxyribonucleic acid) as the informational code. The DNA of each species contains its genetic code. Primitive abiogenic reactions are supposed to have generated life building blocks. Inspired by a precursor work by Saladino et al (2004); Powner et al. (2009) showed that from cyanamide, cyanoacetylene, glycol-aldehyde, glyceral-dehyde and inorganic phosphate the relatively more complex amino oxazole molecule can be formed and from it, pyrimidines as cytosine and a RNA sugar (ribose) are finally synthetized (Fig. 3).

Saladino et al (2004); Hudson et al. (2012) and Jeilani et al. (2018) using different approaches, showed that purines can also be synthetised from simple pre-biotic molecules (see Fig. 4). Finally, Ferus et al. (2017) showed that nucleobases and the RNA molecule are formed in a Miller and Urey experiment with a reduced atmosphere in the presence of formamide. This

c-H_2C_3O, H_2NCH_2CN, NH, C_3, C_2H, H_2C, HNC, HCO^+, NH_2, HCCN, HCNO, HNCO, HOCN, NH_3, c-C_3H_2, H_2CCN, H_2C_2O, H_2CNH, HC(O)CN, NH_2CN, c-H_2C_3O, e-HNCHCN, H_2CCNH, CH_3CN, HC_2CHO, c-C_2H_4O, CH_3CHO, $HCONH_2$, HC_2nN, CH_3C_2N, C_2H_3CN $H_2COHCHO$, HC(O)OCH_3, CH_3COOH, CH_2CHCHO, C_2H_5CN, $CH_3C(O)NH_2$, C_2H_5OH, $(CH_3)_2$ CO (CH_2OH)

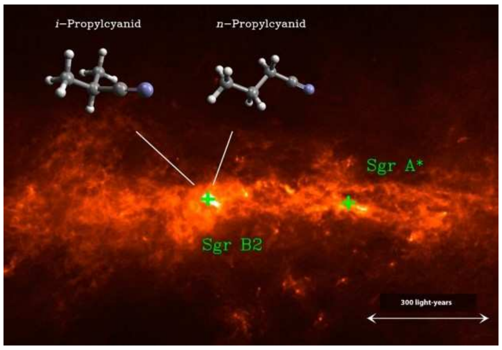
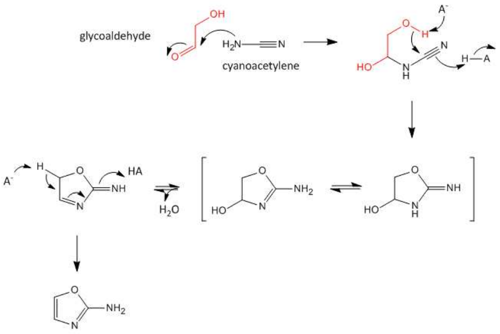


Fig. 2. Many organic molecules as listed above are found in the Sagittarius B2 interstellar cloud (images.destandard.at).



2-amino-oxazole 11

Fig. 3. The pyrimidine cytosine and an RNA sugar can be synthetized from simple molecules (Powner et al. 2009).

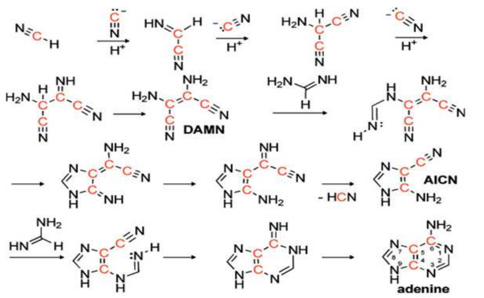


Fig. 4. Synthesis of adenine from simple prebiotic molecules (Hudson et al. 2012).

result represents a milestone in mankind efforts to synthesize molecules of fundamental importance for life in the laboratory.

4. Defining IR spectral signatures for nucleobases

Why is it so difficult to address the detection of COMs in astrophysical targets? There are multiple reasons for that:

1. as far as rotation transitions are concerned:
   (a) spectra of COMs show a crowded forest of lines, often quite difficult to identify;
   (b) we lack of a precise spectral signature;
   (c) the best appropriate wavelength range to collect spectra of complex molecules, the mid-IR, is only accessible through expensive cooled devices.

   About point *(a)* above, when the total mass of a molecule increases, its moment of inertia J also increases, the rotational molecular constants A, B, C (~inversely proportional to J) decrease and the difference between the levels of rotational energy (visible in the radio domain) quickly becomes unobservable. The spectra of big molecules is thus quite difficult to characterize (Andrews 2014). As for the vibrational transitions, visible in the infrared, a band does not characterize a molecule, but rather a functional group. Several bands observed in a correlated way can best characterize a family of molecules. The best example in astrophysics are the bands at 3.3, 6.7, 7.7, 8.6 and 11.3 microns that are attributed to PAHs. However, their precise assignment is still a subject of debate.
2. The situation is different for the vibrational transitions in molecules. Their frequency depends on the length force constant or on the bond angle that is deformed, weighted by the reduced mass of the atoms involved in the transition. This means that the vibrational frequencies are essentially independent of the size of the molecule but depend on the nature of the vibration. In any case, the number of vibrational modes increases by a factor of three with respect to the number of atoms in the molecule. Thus, the greater the molecule, the more entangled will be its spectrum and the more difficult to identify unambiguously its bands.

5. Question: are we seeing the forest for the trees?

Maybe only partial transitions coming from big molecules have been identified, but we are not able to interpret them correctly. Although nucleic acids may be there, perhaps that we are only seen parts of the whole. Within the "spectral forest" of IR or radio spectra, parts of a complex molecule can be due to simpler compounds, as for the HNCO molecule inside a DNA (see Fig. 5), since we do not know the spectral signature of the larger molecule.

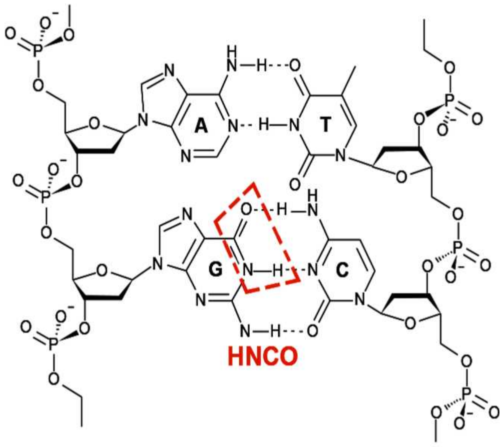


Fig. 5. A portion of a DNA molecule showing its main components: ATPs, phosphates and nucleobases for each side of the double helix. A HNCO molecule is highlighted (see text).

Fig. 6. The pyrimidine family.

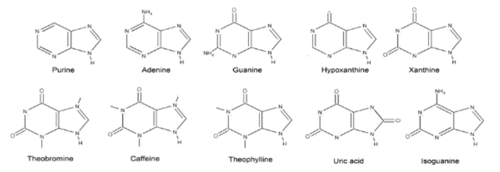


Fig. 7. The purine family.

5.1. The proposition:

To define spectral signatures for families of the nucleobases purine and pyrimidines, instead of a single component. This approach is envisaged to enhance possible signal detection, once the signature will be assigned for multiple members. In order to search for a number of infrared transitions from DNA nucleobases that should be detected together and at the same target we propose to define spectral signaturse for nucleobases (purines and pyrimidines). We propose to do this by selecting a number of local transitions within the molecules. In order to enhance the signal, the chosen transitions should be present in all types of nucleobases (there are 5 types of pyrimidines and 10 types of purines). Five transitions are proposed preliminarily for each family shown in Figures 6 and 7. If they are detected together at the same astronomical target, we are perhaps seeing the forest (the nucleobases) through detection of the trees (local transitions within these nucleobases).

5.1.1. Proposed spectral signatures for the pyrimidine family.

Out-of-plane ring vibration ("chair" movement): 3 lines between 43.10 51.54 μm; 2) $C^5 - C^6$ in-ring double bond: lines at 5.94 and 6.19 μm; 3) N^1 – r C^6 in-ring single bond: line at 6.79 μm; 4) $C^2 - N^1$ in-ring bond: lines at 6.79 and 13.18 μm; 5) C^2 – O double bond: lines between 5.62 and 5.88 μm;

5.1.2. Proposed spectral signatures for the purine family.

In-plane ring vibration ("breathing" movement): 9 lines between 14.4 and 6.7 μm; 2) out of plane ring vibration ("butterfly movement"): lines at 43.47 and 34.96 μm; 3) $N^7 - C^5$ in-ring bond: line at 8. 10 μm; 4) $N^7 - C^8$ in-ring double bond: 5 lines between 6.75 and 8.40 μm; 5) $C^4 - C^5$ in-ring double bond: 3 common lines at 6.37, 6.25 and 5.93 μm.

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References

Andrews, D.L. 2014, in Molecular Photophysics and Spectroscopy, by D. L. Andrews (IOP Publ., Bristol, UK), 7

Ehrenfreund, P., & Cami, J. 2010, Cold Spring Harb Perspective Biol., 2, a002097

Ferus, M., et al. 2017, PNAS 114, 4306

Hudson, J. S., et al. 2012, Angewandte Chemie Int. Ed., 51, 5134

Jeilani, Y. A., et al. 2018, J. Phys. Chem A., 122, 2992

Powner, M. W., Gerland, B. & Sutherland, J. D. 2009, Nature, 259, 239

Saladino, R., et al. 2004, ChemBiochem, 5, 1558