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Infrared spectral investigations of UV irradiated nucleobases adsorbed on mineral surfaces

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Abstract

Spectroscopic studies of the effects of UV radiation on biomolecules such as nucleobases in heterogeneous environments are particularly relevant in prebiotic chemistry to unravel the role of minerals in the transformation/preservation of biomolecules in abiotic environments. Minerals may have a pivotal role in the prebiotic evolution of complex chemical systems, mediating the effects of electromagnetic radiation, influencing the photostability of biomolecules, catalyzing important chemical reactions and/or protecting molecules against degradation. Studies on the photodegradation of biomolecules adsorbed on minerals have applications also in the life detection context to identify potential biomarkers for future space mission and hence to develop suitable sample-extraction protocols for bioanalytical instruments [1]. Moreover, the characterization of the spectroscopic features of biomolecules-mineral complexes provides a support in remote sensing spectroscopy for detecting organic compounds on planetary surfaces or cometary grains and asteroid surfaces. In this context we will present laboratory results on UV photostability of nucleobases adsorbed on magnesium oxide and forsterite minerals and analysed with infrared spectroscopic [2,3].

1. Introduction

In the astrobiology context, the study of the interaction between electromagnetic radiation and bio-molecules in heterogeneous environments is particularly relevant to investigate the physico-chemical mechanisms that lead to the synthesis of complex chemical compounds in space.

Prebiotically relevant molecules to investigate are nucleobases, coding components of the informational macromolecules, i.e. nucleic acids DNA and RNA. The study of the adsorption of nucleobases on mineral surfaces may have important prebiotic implications in the RNA world model of the origin of life [4] and laboratory simulations of space-like conditions through UV irradiation experiments of such complexes may be very interesting to verify possible UV-induced polymerizations of nucleobases and/or catalytic effects of the mineral surfaces under space conditions. Investigations on the photostability of nucleobases, both pure and adsorbed on mineral surfaces, would be highly desirable also from the standpoint of the survival of biological systems in space conditions. Indeed, nucleobases are the cromophores of the nucleic acids and UV-induced DNA and RNA damage is the most dangerous for living organisms, because all the other components of the cells - proteins, fatty acids, coenzymes etc. - show a lower UV absorption compared with nucleic acids, i.e. a lower UV sensitivity, and are more abundant in the cells, so that their partial degradation would not affect their general biological functionality in the cell. We decided to focus our study on: 1) the characterization of the nature of the interaction between nucleobases and the surface of the minerals magnesium oxide and forsterite by infrared vibrational spectroscopy, providing also a support for the interpretation of astronomical data detecting organic compounds on planetary surfaces or cometary grains and asteroid surfaces; 2) investigation of the photostability of mid UV-irradiated nucleobases adsorbed on the surface of the minerals magnesium oxide and forsterite, to unravel the possible role of minerals in the transformation/preservation of such biomolecules under planetary conditions.

2. Results

IR-spectroscopy studies were carried out, using the diffuse reflectance infrared Fourier transform spectroscopy technique (DRIFTS), to understand at molecular level the interactions between the different nucleobases and the minerals magnesium oxide and forsterite, which is of interest in prebiotic processes. An important observation is that, comparing the IR spectra of the pure solid nucleobases with the ones of the nucleobases adsorbed on MgO, most of all the characteristic bands of pure bio-molecules disappeared when they adsorbed on the mineral. On the contrary, in the case of adenine and uracil adsorbed on forsterite, very intense nucleobase absorption peaks appeared. A possible interpretation of these spectroscopic features can be carried out considering that, in the case of nucleobases adsorbed onto MgO and forsterite, as established by the previous studies, a reversible physisorption occurs, thus the intramolecular bonds are only slightly perturbed, and the IR band intensities of the adsorbates are controlled predominantly by the surface selection rules, whereby the molecular orientation can be deduced. It is necessary to stress that many factors make very hard the interpretation of the IR spectra of molecules adsorbed on minerals. This aspect is important in remote sensing spectroscopy of planetary surfaces where low molecular coverage conditions are the most probable.

Then, we investigated the effects of UV radiation on the nucleobases adsorbed on magnesium oxide and forsterite, performing *in situ* UV irradiation experiments. The most remarkable changes in the IR spectra during irradiation were observed in the case of uracil, where molecular breakage seems to occur. In the case of adenine, the perturbation induced by UV irradiation caused only a different way of vibrating for this molecule, but it was not possible to assume real bond breaking. Experimental results confirmed the high intrinsic photostability of nucleobases, because a rather low probability of interaction with UV radiation was estimated, and furthermore indicated that with the exception of cytosine and hypoxanthine, which show a high photostability, magnesium oxide and forsterite have no protective effect against the UV radiation, instead they may be catalytic speeding up the degradation kinetics.

3. Summary and Conclusions

These results confirm that the nucleobases can survive limitative time to photodegradation in space and that only in planetary environments where they can be delivered by asteroids or comets or synthesized locally, they can survive and promote the formation of more complex prebiotic compounds. However, we showed that minerals do not promote the formation of new species. This is a confirmation that nucleobases are easily destructed after few hours on Martian surface where minerals on which they are supposed to be adsorbed, are exposed to Sun light. Unlike the Earth, Mars does not have a significant ozone level that can reduce the UV flux reaching the ground. The photochemical history of the planet was thus, exclusively determined by the increase in solar luminosity over time and change in the atmospheric carbon dioxide content.

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