

ISOTOPIC STUDIES FOR ORGANIC MOLECULES OF INTEREST IN ASTROBIOLOGY BY LIBS. ELUCIDATING THE ORIGIN OF MOLECULAR EMISSIONS IN LASER-INDUCED PLASMAS IN THE MARTIAN ENVIRONMENT. T. Delgado, L. García, L.M. Cabalín and J. J. Laserna. Departamento de Química Analítica, UMALASERLAB, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, España, e-mail address: laserna@uma.es.

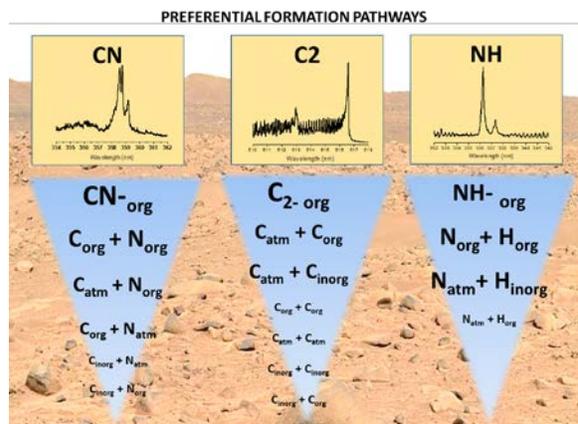
Introduction: Next spatial missions planned for Mars landing should significantly enlarge our long-expected insight into the Red Planet as a habitable environment. One of the focal purposes of such upcoming missions lies in the search for evidence of extant life [1]. Potential biosignature molecules include a series of organic compounds with their particular structures that can serve as diagnostic species [2]. In this sense, LIBS technique has gone a step further in the scope of molecular solids and its application in planetary exploration has become an effective tool for the detection of possible presence of organic extra-terrestrial materials [3]. However, to define a specific optical emission pattern for the identification of a particular organic residue is a very challenging practice due to the impact of other chemical reactions implied in the plasma plume development, mainly owing to the contribution of atmospheric components [4].

Goal: The present work aims at contributing to the preparedness to identify emissions features that may arise in the sampling and analysis of materials containing organic residues in Martian surrounding conditions, and on the other hand, to uncover the origin of such emission signals of molecular fragments registered in the LIBS spectrum. A home-made LIBS system coupled to a pressure chamber for simulating Martian environment was constructed and used to cope with these challenges.

Samples: To accomplish the goals of the work, a thorough experimental study was carried out in different background gas conditions and for different pure and modified selected compounds. Thus, we study emission features from LIBS spectra corresponding to model organic compounds of interest in astrobiology (benzamide, as an example of nitroaromatic compound; pyrene, as an example of polycyclic aromatic hydrocarbon; urea, as the case of a ring-less molecular substance) acquired in different atmospheres. In addition to this, several isotopically enriched molecules were also analysed, namely D-enriched urea, ^{13}C -enriched urea and ^{15}N -enriched benzamide. The materials used to support organic substances were both calcium sulfate and calcium carbonate matrices as they have been identified in both Gale Crater and Martian meteorites [5].

Routes in the formation of molecular fragments: For samples containing no carbon, the emission signal

corresponding to this element should be provided only by the surrounding gas and can be used to investigate the Martian atmosphere breakdown. When a C-containing substrate is ablated with laser excitation, the existence of two carbon sources affects the emission signal in different levels. Finally, in the case of a matrix doped with an organic compound, a third carbon source is involved in the mechanisms of ablation and additional possible pathways to generate emitting species can take place, thus turning the plasma chemistry into a more complex system under these conditions. In order to a better understanding of recombination pathways, experiments with isotopically enriched molecules were carried out for comparison with pure samples without isotopic modification. The challenge should be to elucidate the possible re-combination mechanisms - and ultimately, the dominant ones- for chief molecular fragments formation, namely CN, C_2 and NH species since, from an exhaustive examination of LIBS spectra, those emission bands were established as possible diagnostic tool for organic signals detection in martian ambient.



References:

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