

1. ABSTRACT

LIBS is a versatile analytical technique that can provide elemental and molecular information in real time. It is applicable to various fields, including planetary exploration [1,2], environmental analysis and materials science. The development of high-resolution LIBS (HR-LIBS) significantly improves the ability to resolve fine spectral details, including isotopic shifts. These shifts are of particular interest in astrobiological studies aimed at identifying biosignatures on Mars.

This work focuses on characterizing HR-LIBS spectra of isotopically labelled organic molecules, paying particular attention to the diatomic CN and C₂ fragments, which are potential molecular biosignatures. This study compares LIBS spectra obtained under two different environmental conditions - terrestrial air and a simulated Martian atmosphere (CO₂ at 7 mbar) - to evaluate the effect of surrounding gas composition on plasma formation and molecular emission.

Samples of urea and benzamide, as well as their enriched ¹³C and ¹⁵N isotopologues, were prepared in pellet form and analyzed using an Nd:YAG laser (1064 nm) and a high-resolution Echelle spectrograph. Isotopic shifts between the ¹²C¹⁴N-¹³C¹⁴N and ¹²C¹⁴N-¹²C¹⁵N isotopes were measured for the first time at high resolution.

The results reveal that molecular emission intensities are higher in air than in CO₂, due to the availability of atmospheric nitrogen in CN formation. The observed isotopic shifts in HR-LIBS spectra are in the order of picometers, which confirms the necessity of using high-resolution instrumentation to distinguish them accurately.

This study demonstrates the potential of HR-LIBS as a powerful analytical tool for isotopic and molecular analysis relevant to astrobiology and the search for life on other planets.

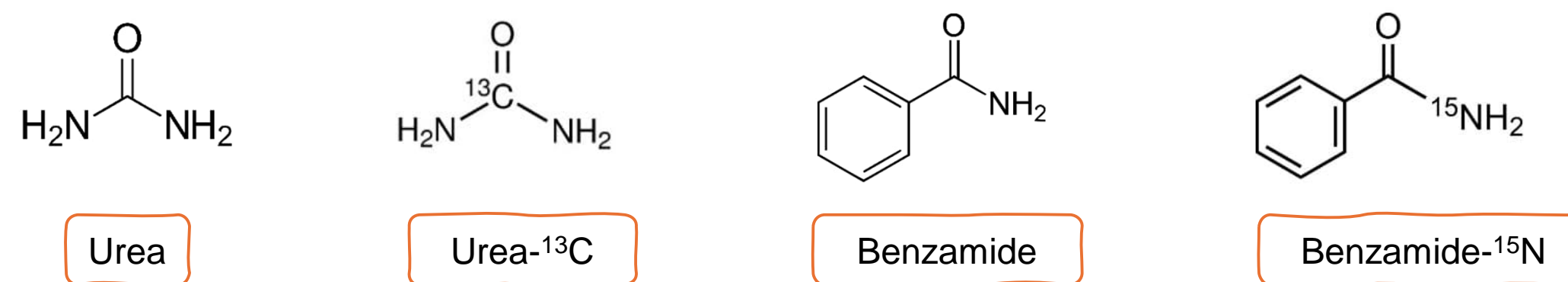
1. OBJETIVES AND METHODOLOGY

To investigate terrestrial analog compounds that may be present on other planetary bodies, specifically **Mars**.

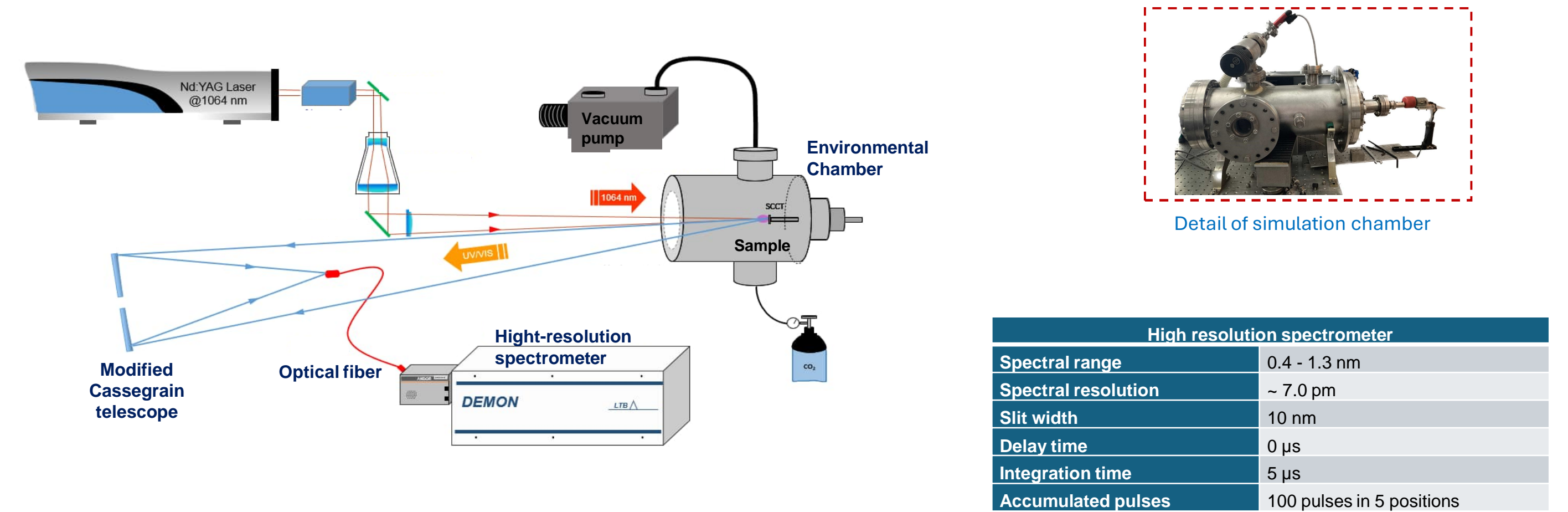
Atmospheric Influence: Evaluate the effect of the surrounding atmosphere (Earth vs. Mars) on CN and C₂ dimers.

Isotopic Analysis: Estimate the isotopic shifts of CN (¹³C and ¹⁵N) using HR-LIBS within the $\Delta v=0$

Analog compounds



3. LIBS EXPERIMENTAL

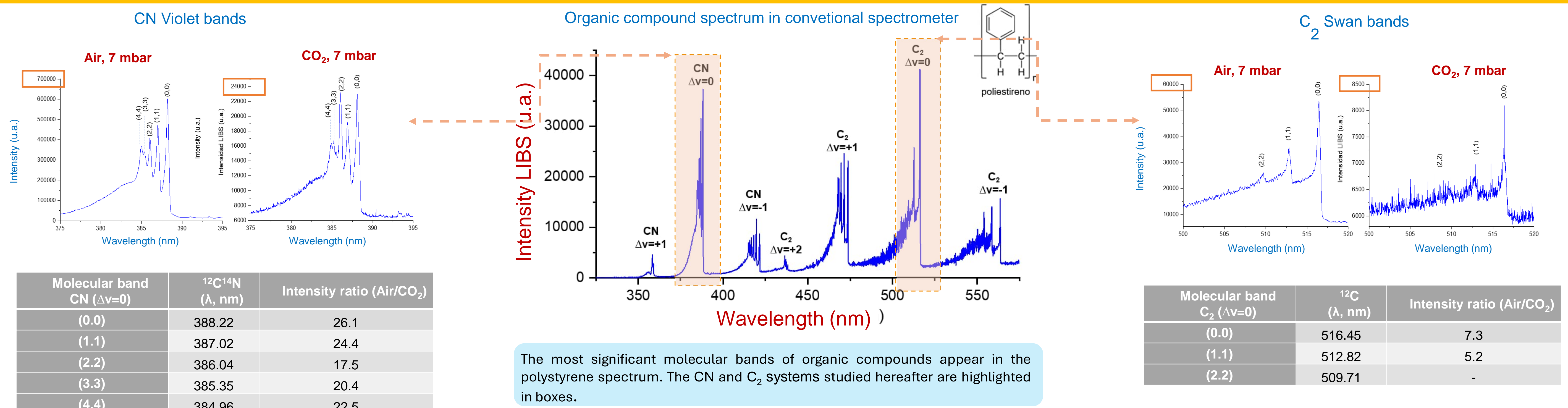


High resolution spectrometer	
Spectral range	0.4 - 1.3 nm
Spectral resolution	~ 7.0 pm
Slit width	10 nm
Delay time	0 μs
Integration time	5 μs
Accumulated pulses	100 pulses in 5 positions

To carry out the experiment, a laboratory LIBS system was coupled to a pressure chamber. Samples of urea and benzamide, as well as their enriched ¹³C and ¹⁵N isotopologues, were prepared in pellet form and analysed using an Nd:YAG laser (1064 nm) and a high-resolution Echelle spectrograph. This spectrograph is a DEMON model, manufactured by LaserTechnik Berlin (LTB). It has a double dispersion system containing two monochromators, a CaF₂ prism and an Echelle grating. According to the manufacturer, it offers high spectral resolution with a full width at half maximum (FWHM) of ~7.0 pm. This spectrograph was coupled to an intensified CCD camera for signal processing.

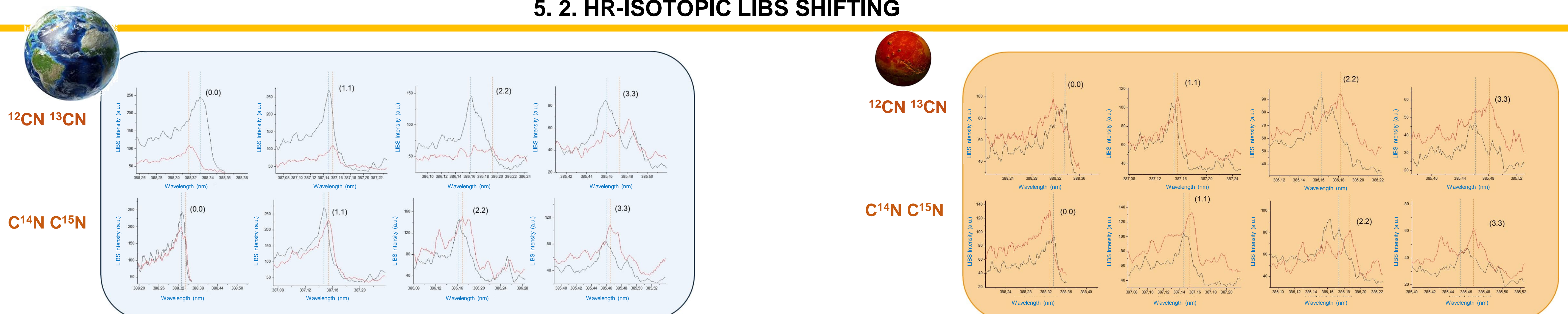
5. RESULTS AND DISCUSSION

5.1. ATMOSPHERIC INFLUENCE ON CN AND C₂ MOLECULAR SPECIES



The most significant molecular bands of organic compounds appear in the polystyrene spectrum. The CN and C₂ systems studied hereafter are highlighted in boxes.

5.2. HR-ISOTOPIC LIBS SHIFTING



LIBS spectra of CN vibrational transitions ($\Delta v = 0$) for pure benzamide and benzamide isotopically labelled with C-13 and N-15, measured in an air atmosphere at 7 mbar

Molecular Band CN ($\Delta v=0$)	¹² C ¹⁴ N	¹³ C ¹⁴ N	Isotopic shift (nm)
(0.0)	388.3307	388.3182	-0.0124
(1.1)	387.1469	387.1540	0.0071
(2.2)	386.1634	386.1929	0.0295
(3.3)	385.4572	385.4722	0.0150

Molecular Band CN ($\Delta v=0$)	¹² C ¹⁴ N	¹² C ¹⁵ N	Isotopic shift (nm)
(0.0)	388.3307	388.3282	-0.0025
(1.1)	387.1469	387.1540	0.0071
(2.2)	386.1634	386.1693	0.0059
(3.3)	385.4587	385.4647	0.006

Wavelengths and isotopic shifts calculated for ¹³C¹⁴N benzamide and ¹²C¹⁵N benzamide in the CN region ($\Delta v=0$) measured in an air atmosphere at 7 mbar. Negative displacement marked in blue and positive displacement marked in red.

LIBS spectra of CN vibrational transitions ($\Delta v = 0$), measured in a CO₂ atmosphere at 7 mbar, from pure benzamide and benzamide isotopically labelled with C-13 and N-15.

Molecular Band CN ($\Delta v=0$)	¹² C ¹⁴ N	¹³ C ¹⁴ N	Isotopic shift (nm)	Molecular Band CN ($\Delta v=0$)	¹² C ¹⁴ N	¹² C ¹⁵ N	Isotopic shift (nm)
(0.0)	388.3357	388.3158	-0.0199	(0.0)	388.3357	388.3158	-0.0087
(1.1)	387.1498	387.1555	0.0057	(1.1)	387.1498	387.1555	0.0071
(2.2)	386.1634	386.1826	0.0192	(2.2)	386.1634	386.1826	0.0133
(3.3)	385.4602	385.4813	0.0211	(3.3)	385.4602	385.4813	0.0135

Wavelengths and isotopic shifts calculated for ¹³C¹⁴N benzamide and ¹²C¹⁵N benzamide in the CN region ($\Delta v=0$) measured in a CO₂ atmosphere at 7 mbar. Negative displacement marked in blue and positive displacement marked in red.

6. CONCLUSIONS

- LIBS is a viable technique for identifying potential biomarkers in planetary exploration.
- The surrounding atmosphere significantly affects LIBS spectra.
- For isotopic shifts in the picometer range a high-resolution spectrometer is required
- All the isotopic shifts of the CN dimer for the $\Delta v=0$ sequence follow the same trend.

7. REFERENCES

- T. Delgado, L. García-Gómez, L.M. Cabalin, J.J. Laserna. *Investigation on the origin of molecular emissions in laser-induced breakdown spectroscopy under Mars-like atmospheric conditions of isotope-labeled compounds of interest in astrobiology*. Spectrochim Acta Part B. 179 (2021) 106114. <https://doi.org/10.1016/j.sab.2021.106114>
- T. Delgado, F.J. Fortes, L.M. Cabalin, J.J. Laserna. *The crucial role of molecular emissions on LIBS differentiation of organic compounds of interest in astrobiology under a Mars simulated atmosphere*. Spectrochim Acta Part B. 192 (2022) 106413. <https://doi.org/10.1016/j.sab.2022.106413>

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