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LIBS and Raman Data Fusion for in-situ Planetary Exploration

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1. Introduction

The combination of Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) is promising for in-situ planetary exploration. The first LIBS instrument in space, ChemCam, that is part of NASA's Mars Science Laboratory mission is analyzing Martian targets since 2012 [1]. The follow-up instrument, SuperCam, of NASA's Mars2020 mission joins LIBS with Raman spectroscopy [2]. Apart from these missions there exist several proposals for combined Raman/LIBS instruments in the context of in-situ extra-terrestrial research, e.g. [3]-[6].

We study LIBS-Raman data fusion strategies for optimized identification and quantification of minerals and salts that might be important for the SuperCam instrument as well as for other future missions. Data from both techniques is acquired with instrumentation that is built from miniaturized and prototype components.

2. Raman Spectroscopy and LIBS

LIBS uses high power laser pulses that are focused onto the surface of the target to create a luminous plasma. This plasma emits characteristic radiation corresponding to the elemental composition of the target. The Raman effect is non-destructive and based on inelastic scattering processes. These are initiated by laser radiation and the scattered light contains information about molecules and crystal structures in the target, due to vibrational and lattice excitations, respectively.

The two techniques have several advantages for planetary exploration as they are fast and need only optical access to the samples. Furthermore, hardware components such as the laser, focusing optics and the spectrometer can be shared allowing for a miniaturized instrument design. LIBS is capable of easily detecting alkalis, alkaline earth elements and metals that appear as cations but is challenged with anionic species, such as the halogens sulfur and chlorine. Raman spectroscopy on the other hand gives fingerprint spectra of minerals that contain strong features belonging to modes of anionic groups. But depending on symmetries there exist also minerals and salts without Raman active modes as for example halite (NaCl). Thus, LIBS and Raman data can complement each other and more information can be gained with a joint instrument of both techniques.

To obtain the maximum scientific output with regard to strong constraints on mass and energy in space applications the study of data fusion strategies is of great interest and gives input to the instrument design [6]. It has been shown in terrestrial applications that LIBS-Raman data fusion can improve the classification of explosives [7] or inks [8] and first attempts of data fusion for planetary exploration have been reported [9]. All of these examples use multivariate methods, which have already proven to be reliable tools for LIBS [10] and Raman [11] alone. We implement and compare different ways of combining the data from both techniques. Besides that, we investigate which wavelength regions from LIBS and Raman data, respectively, are most crucial for successful identification and quantification and which regions are redundant and could be left out or reduced in resolution. This can allow for a more miniaturized design.

3. Experimental

Raman and LIBS measurements were performed with different set-ups. For Raman measurements a frequency doubled Nd:YAG laser (532 nm, continuous wave, 50 mW output, Oxxius) is focused onto the sample and the light is spectrally analyzed with an Ocean Optics spectrometer. The LIBS laser is based on a Nd:YLF crystal (1053 nm, 4-5 ns pulse length, 3 mJ output). The plasma radiation is collected, split and guided to four different spectrometers (Avantes): UV (233-400 nm); VIS1 (360-515 nm),
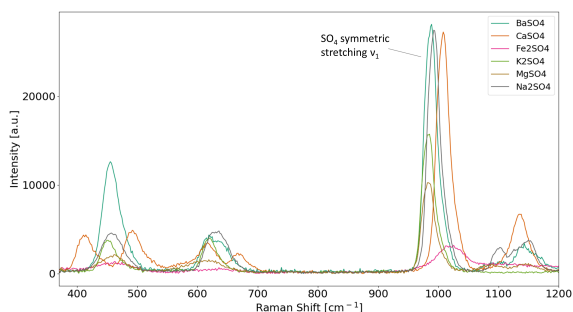
Figure 1: Raman spectra of the sulfates measured with a miniaturized set-up. The ν_1 mode is strong indicator for the presence of SO_4^{-2} ions.
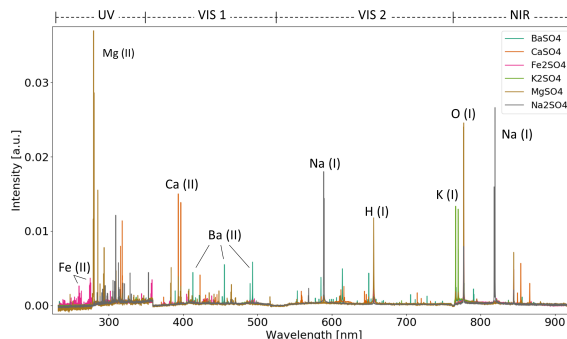

Figure 2: LIBS spectra of the sulfates measured with a miniaturized set-up. Besides the strong indicated cation emissions LIBS is also sensitive for hydrogen and oxygen detection.

VIS2 (530-760 nm), NIR (740-900 nm). For LIBS measurements each sample is measured in a small chamber under Martian atmospheric conditions, which means a pressure of 7 mbar and a CO_2 dominated gas. More details about the set-up can be found in [6].

4. Results

One set of samples that we studied with this set-up contains sulfate salts, in particular $MgSO_4 \times 7\,H_2O$, $CaSO_4 \times 2\,H_2O$, Na_2SO_4, Ba_2SO_4, K_2SO_4 and $Fe_2SO_4 \times n\,H_2O$. Sulfates and other hydrated salts as chlorides and perchlorates play an important role in the geological analysis of the Martian surface as they are linked to areas where liquid water has evaporated in the past [12]. The sulfate anion SO_4^{2-} has several Raman active modes with the strongest one ν_1 in the range 950 to $1100\,cm^{-1}$. We observed this peak in every Raman measurement, see Figure 1. The LIBS spectra do not indicate the presence of sulfur but show strong emissions of the cations, see Figure 2.

5. Summary and Outlook

The preliminary study of pure sulfates using miniaturized Raman and LIBS set-ups confirms the advantage of combining LIBS and Raman spectroscopy: The data is complementary and the substances can be better identified with both data. The sulfates can be identified by means of the Raman ν_1 mode and cation emissions in the LIBS data. For further investigations we will produce binary mixtures of the sulfates and additional chlorides, perchlorides and Martian regolith simulant JSC-1A. We will apply multivariate data analysis approaches and compare the results of single Raman and LIBS with the fused data.

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