

NANOSECOND TIME-RESOLVED RAMAN AND FLUORESCENCE SPECTROSCOPY: INSIGHTS FOR MINERAL AND ORGANICS CHARACTERIZATION. O. Beyssac¹, M. Gauthier¹, A. Fau¹, S. Bernard¹, K. Benzerara¹, M. Morand¹, P. Rosier¹, P.Y. Meslin², S. Maurice² and the SuperCam Science team, ¹ IMPMC, CNRS, Sorbonne Université, MNHN, Paris, France, Olivier.Beyssac@upmc.fr, ² IRAP, CNRS-UPS-OMP, Toulouse, France.

Introduction: Raman spectroscopy is an increasingly popular technique for surface exploration of planets, in particular Mars: Sherlock and SuperCam instruments for the Mars 2020 mission, RLS instrument for the Exomars mission. The SuperCam instrument will combine LIBS and time-resolved Raman and fluorescence spectroscopy in addition to IR, a microscope and advanced imagery.

In Paris, we have assembled an original customized experiment making possible time-resolved Raman and fluorescence spectroscopy analysis of materials, minerals and organics at the microscale (spot in the range 1-150 microns) with a time resolution on the order of the nanosecond. In the future, this experiment will provide mapping capabilities and remote analysis in a martian chamber following a design inspired by SuperCam [1]. Our main objective is to set up an experiment optimized to improve our knowledge of the techniques and physics of time-resolved Raman and fluorescence spectroscopy to better exploit data from *in situ* mission instruments (e.g. SuperCam).

Here, we present the main elements of our experiment and the first results obtained on various reference mineral phases and organics. We show how the technique can be powerful to separate the Raman signal from the fluorescence background using the temporal resolution even in the case of very short, nanosecond, fluorescence signals due to e.g. organics. We also investigate the information that can be retrieved from the combined acquisition of the Raman and fluorescence signals and we discuss some challenges for the SuperCam instrument.

Description of the experiment: Some laboratory-based time-resolved Raman and fluorescence experiments have been developed for planetary exploration, e.g. [2], [3]. Figure 1 depicts our experiments. The laser is a nanosecond pulsed DPSS laser operating at 532 nm with a 1.5 ns duration for the pulse, 10 to 2000 Hz repetition rate and up to 1 mJ output energy per pulse. The laser is focused at the sample surface through a microscope objective and the Raman signal collected in the backscattering geometry. A Notch filter cuts the Rayleigh scattering and spectra can be recorded in the range 70-4500 cm^{-1} range. The signal is collected in an optical fiber and sent into a modified Czerny-Turner spectrometer manufactured by Prince-

ton Instrument. This spectrometer has three motorized gratings that can be used depending on the chosen spectral window and spectral resolution necessary for the experiment. We use a PIMAX4 ICCD camera manufactured by Princeton Instrument with 500 ps gating capability. To reach sub-nanosecond time resolution, it is critical to have an excellent synchronization between the laser pulse and the ICCD gating through the delay (time elapsed between the laser pulse and its detection on the ICCD) and gate (time during which the intensifier of the ICCD is open) parameters.

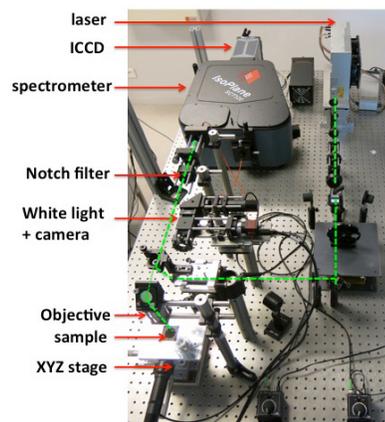


Figure 1. Overview of the time-resolved Raman and fluorescence experiment.

Our optical pathway is somewhat complex and is set on an optical breadboard for better stability. This optical design allows for choosing between two experimental pathways: microscope versus telescope (not yet operational). It allows an accurate control of the laser irradiance and polarization at the sample surface. We use a periscope to achieve a vertical illumination on an horizontal sample which makes possible analysis of raw mineral powders or grains without any sample preparation. On the microscope experiment, we have also a sample illumination with a white light and a camera to visualize axially the sample under the microscope with or without the laser. The sample is positioned on a XYZ motorized stage enabling XYZ profiles and basic mapping to be done in the near future owing to an homemade software controlling and syn-

chronizing the sample movement and the data acquisition with the Princeton lightfield software.

Some complementary continuous wavelength (CW) Raman analyses were performed using a Renishaw InVia Reflex spectrometer.

Results and discussion: In the case of SuperCam the high-energy laser is collimated on a relatively large surface, whereas in our microscope configuration it is focalized at the sample surface which may induce severe damage. After precise measurements and by comparison with CW Raman, we assume that an irradiance of 10^{10} W.m⁻² is acceptable for our experiment to avoid laser-induced damages on the selected samples.

Figure 2 illustrates the results obtained in the case of a ruby synthetic crystal of as a proof of concept. Ruby has a well-known intense fluorescence emission at ca. 690 nm due to Cr³⁺ that makes any Raman analysis using visible light notoriously difficult. This fluorescence emission is easily measured with our system as well as its decay rate over ms timescale. By closing the ICCD gate to 4 ns and by synchronizing it perfectly with the laser pulse, our experiment enables the measurement of the Raman spectrum of ruby.

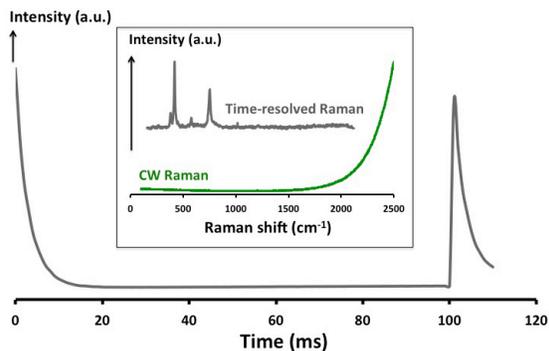


Figure 2. Decay of Cr³⁺ fluorescence in ruby on ms timescale. The inset shows continuous (green) and time-resolved (dark grey) Raman spectra of ruby. Fluorescence overwhelms the Raman signal in the CW and is removed using time-resolved spectroscopy.

Phosphates are possible hosts for phosphorous on Mars [4]. We have performed analyses of various Ca-phosphate apatites. Figure 3 presents the results obtained on a crystal of the Durango apatite which is a reference for many geochemical purposes. CW Raman at 532 nm clearly shows an intense fluorescence background with several large bands mainly due to the presence of REE in the crystal structure. The Raman signal is barely detected in the CW mode. Using the time-resolved experiment at 532 nm, closing the gate to a few ns and synchronizing it with the laser pulse, the Raman signal can be completely separated from the

high fluorescence contribution. The decay rate of this mineral fluorescence is again on ms timescale. More data obtained on other mineral phases observed on Mars will be discussed.

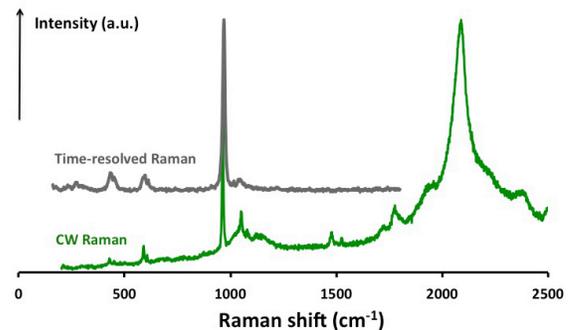


Figure 3. Continuous (green) and time-resolved (dark grey) Raman spectra of the Durango apatite. The fluorescence signal is absent in the time-resolved spectrum.

Detection of organics and tracing life at the surface of Mars is one of the main challenges for the forthcoming exploration missions. In that purpose, Raman spectroscopy is considered as one of the most promising techniques. Among several technical challenges, organic compounds may be very sensitive to laser radiation and may exhibit short lifetime fluorescence on ns timescale that makes difficult the separation of the Raman signal by time-resolved spectroscopy. Using appropriate biomineralization samples with organics included in a mineral matrix, we show that our experiment allows the extraction of good quality Raman spectra of the host mineral from the organic fluorescence background.

Conclusion: Our results confirm that time-resolved Raman and fluorescence spectroscopy is a very promising method for the exploration of planetary surface, in particular for the characterization of alteration and/or bio-related samples (phosphates, carbonates, sulfates, clays) and the detection of organics.

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References: [1] R.C. Wiens et al. (2016) LPSC Abstr #1322, [2] S.K. Sharma et al. (2009) *Spectrochim. Acta Part A*, 73, 468-476, [3] V. Blacksberg et al. (2016) *Applied Optics* 55, 739-748, [4] O. Forni et al. (2015) *GRL* 42(4) 2014GL062742