

EVALUATION OF CLOSE-UP REMOTE CW-RAMAN SPECTROSCOPY FOR IN-SITU PLANETARY EXPLORATION. S. Kubitza¹, S. Schröder¹, K. Rammelkamp¹, T. Hagelschuer¹, U. Böttger¹, P. B. Hansen¹, D. S. Vogt¹ and H.-W. Hübers^{1,2}, ¹Deutsches Zentrum für Luft- und Raumfahrt e.V., Institut für Optische Sensorsysteme, Berlin, Germany, simon.kubitza[at]dlr.de, ²Humboldt-Universität zu Berlin, Berlin, Germany.

Introduction: On Earth, Raman spectroscopy is widely used in geological and biological studies [1] for the identification of minerals and organic material. It allows for the detection of the lattice or molecular structure of samples and therefore to distinguish between variations of chemically similar materials by their specific vibration modes. Its sensitivity to functional groups enables the identification of organic complexes which could indicate the actual presence of current or past life in extraterrestrial environments and go beyond merely confirming habitability. The upcoming ESA mission ExoMars will have a Raman instrument aboard its rover [2] and NASA's Mars2020 mission launching in the same year will even carry two Raman instruments [3,4], showing the relevance of this technique for in-situ exploration of Solar System bodies.

One drawback of Raman spectroscopy that has impeded its application in space exploration so far is the low Raman signal intensity. A superimposed background signal, e.g. from fluorescence or sunlight can hide the Raman signal and saturate the detector. Approaches to suppress in particular the fluorescence are remote pulsed Raman spectroscopy [4] and a close-up configuration at a robotic arm with excitation in the deep UV range [3]. ESA's Raman Laser Spectrometer uses a microscope concept with continuous wave (cw) excitation in the dark interior of the rover body to avoid ambient light [2]. All three concepts impose additional constraints such as a rather heavy and energy consuming instrument for time-resolved detection, a robotic arm or a sampling system. In this study we explore the suitability and constraints of a cw-Raman concept over small distances (3 – 20 cm) for in-situ exploration of extraterrestrial surfaces in their natural environments, including ambient light, that could be realized with a small and lightweight instrument.

Considerations: For a fixed aperture of an instrument, larger sampling distances d result in a smaller detection solid angle and therefore a lower signal. This scales with $1/d^2$ and poses an upper limit onto the sampling distance. In addition, the detection foot print area (source area for background and noise) increases with d^2 , which compensates the smaller solid angle and keeps the signal from background illumination and the noise associated therewith constant. As a consequence, the signal-to-noise ratio (SNR) drops with $1/d^2$. With usual countermeasures like a close-up detection geometry and baffling against ambient light the instru-

ment would lose its remote capability and no longer be competitive with techniques like infrared or laser-induced breakdown spectroscopy.

Broadband fluorescence can be distinguished by its spectral shape and may allow identification of the Raman modes, as long as it does not saturate the detector before the Raman signal emerges from noise. While both the Raman and the fluorescence signal decrease similarly for larger sampling distances, the shot noise $\propto \sqrt{\text{signal counts}}$ related to the broad fluorescence will only reduce with $1/d$ and hence increase in relation to the signal, again limiting the maximum distance. Discrimination of fluorescence in the temporal regime is the most prominent approach but requires additional components together with control electronics and high voltage supply circuits, making the instrument less suitable for certain missions.

Experimental Setup: Since we aim for a particularly compact and lightweight instrument, the optical system we used in this study is kept as simple as possible. Excitation is realized with a compact ($12 \times 4 \times 4 \text{ cm}^3$) diode pumped Nd:YAG laser, frequency doubled to 532 nm and emitting 28 mW of optical power. The light is delivered through an optical fibre and afterwards collimated. After passing a short-pass beam splitter it shares the optical path with the detected light from the target. Single cemented achromatic doublets of different focal lengths are used to focus onto the sample in 3 to 20 cm distance. Light from the target is collected by the same lens doublet, diverted at the beam splitter, passing through a Rayleigh scattering suppressing long-pass edge filter, and focused into a 50 μm fibre using an $f = 60 \text{ mm}$ achromatic doublet. Finally, it is analysed by a commercial miniaturized spectrometer based on an uncooled CCD line detector with a 50 μm entrance slit and ranging from 530 to 700 nm. It offers 17 pixels per nm, but is limited to 0.78 nm linewidth due to the wide entrance slit.

Samples: Spectra were taken from a polycrystalline disk of silicon, pressed pellets of a (30:70) CaF₂-CaSO₄ mixture and a (70:30) CaSO₄-basalt mixture, a natural plagioclase sample collected from Mount Etna, Italy, and a piece of hematite provided by the Museum für Naturkunde, Berlin, Germany.

Results Under Laboratory Conditions: Figures 1 and 2 show spectra taken in the dark with a sampling distance of 3 and 20 cm, respectively. The close-up measurements show the silicon Raman mode at 520 cm⁻¹, the characteristic SO₄ symmetric stretching

mode v_1 around 1010 cm^{-1} , as well as a typical plagioclase spectrum for the sample from Mount Etna, and a hematite spectrum, already within short exposure times of only a few seconds. As expected from the considerations above, the signal decreases when moving away from the sample. This can be compensated with increased exposure times allowing unambiguous identification of most samples still within one minute (excluding dark measurement). For hematite, the phonon modes between 400 and 500 cm^{-1} ceased, leaving only the higher order peak around 1300 cm^{-1} for detection.

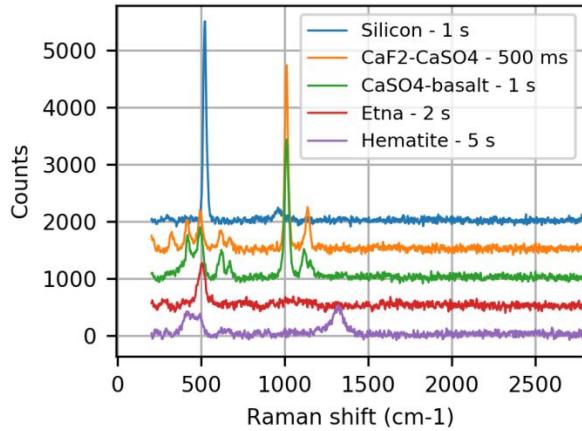


Figure 1: Raman spectra taken in the dark at a sampling distance of 3 cm. For each sample 10 acquisitions have been averaged with exposure times given in the legend.

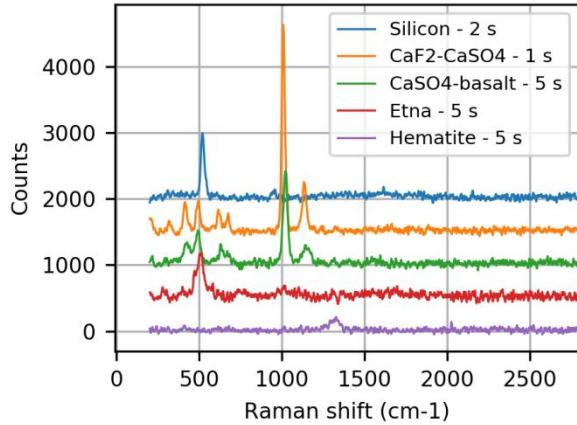


Figure 2: Raman spectra for 20 cm sampling distance. The sulphate mixtures and silicon still produce good signals, while the hematite is becoming difficult to identify.

Measurements With Ambient Light: A laser driven light source was used to simulate the solar irradiation in proximity to the Mars orbit. The spot size was chosen to match approximately the power density of the solar spectrum in the detected spectral range. Due to the broadband output of the light source, the UV part was a factor of 1.4 to 2 stronger than estimated

for the sun and could have induced additional fluorescence or other effects.

Backscattered light saturated the detector within 200 to 1000 ms, depending on the sample and sampling distance, setting an upper limit for the exposure times. Only for the sulphur-comprising samples with the strong sulphate main mode it was possible to extract the Raman signal from the inherent shot noise generated by the high background signal at all distances. The raw data has an SNR of only ~ 3 for 20 cm. Smoothing the data with a moving average, the main sulphate mode could be recovered from the data. The raw and smoothed data are shown in Figure 3. For 6 cm sampling distance the SNR of the same mode increases to 8, allowing the direct identification. Further studies indicate that shadowing the direct irradiation is sufficient to reduce the background signal by more than one order of magnitude.

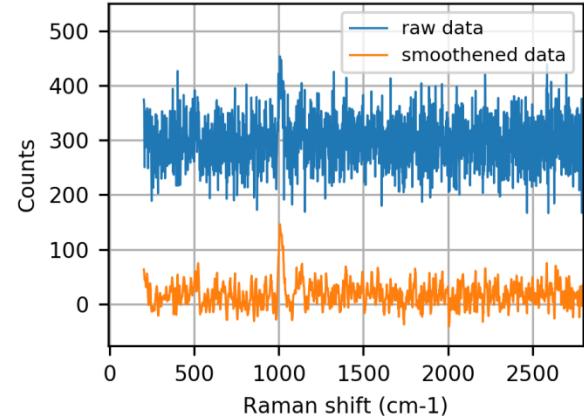


Figure 3: Sulphate signal measured in the presence of ambient light at 20 cm sampling distance, averaged across 200 spectra of 50 ms exposure time. Additional smoothing reveals the main Raman mode.

Conclusion: Despite the minimalistic instrument approach we were able to reliably identify sulphates, silicon and also natural samples in up to 20 cm distance. It has been shown that strongly Raman-active materials can even be detected under direct sun irradiation. However, measuring in the dark, for example in the shadow of the spacecraft or at night, would significantly improve the quality of the data. An optimized spectrometer design where the signal is confined to fewer pixels would likely improve the sensitivity as well.

References: [1] Schmitt M. and Popp J. (2006) *J. Raman Spectrosc.*, 37, 20–28. [2] Rull F. et al. (2017) *Astrobiology*, 17, 627–654. [3] Beagle L. et al. (2015) *IEEE Aerospace Conf. 2015, INSPEC 15215591*. [4] Wiens R.C. et al. (2017) *Spectroscopy*, 32, 50–55.