EVALUATION OF CLOSE-UP REMOTE CW-RAMAN SPECTROSCOPY FOR IN-SITU PLANETARY EXPLORATION

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Raman spectroscopy for space exploration

Raman spectroscopy

- Inelastic scattering process
- Reveals information about molecules, structure, and functional groups
- Two options: excitation by continuous wave (cw) or pulsed laser for time-gated Raman spectroscopy
- cw-Raman is conceptually simple and could be realized in a small and light-weight instrument

Concepts of future Raman instruments in space

- **SuperCam** [1], Mars 2020 mission (NASA, 2020): pulsed laser, remote distances up to 12 m
- **RLS** [2], ExoMars mission (ESA, 2020): cw laser, measurements inside rover on crushed samples collected by a drill
- **SHERLOC** [3], Mars 2020 mission (NASA, 2020): UV cw laser, on rover's arm, sampling distance 48 mm

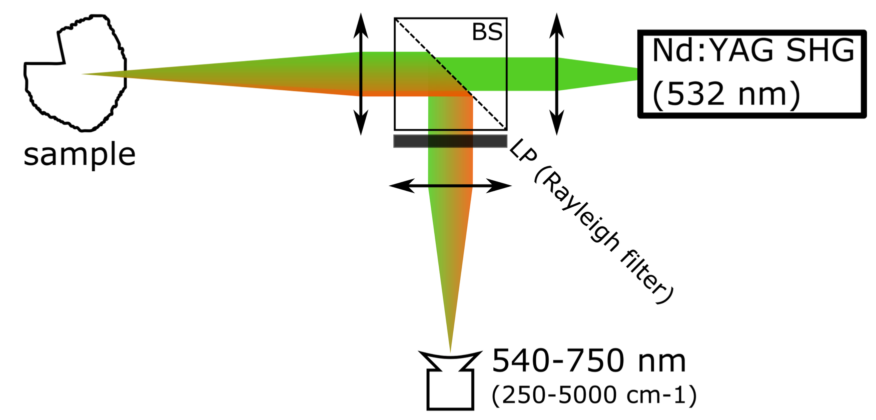
→ **Objective:** Investigate whether stand-off cw-Raman is possible for distances of up to 20 cm

Experimental setup

- Based on compact commercial-off-the-shelf (COTS) parts, flight instrument could be realized with ≤ 1.5 kg
- Frequency-doubled Nd:YAG laser (28 mW @ 532 nm) in compact design (12 × 4 × 4 cm^3)
- 3-20 cm fixed focus sampling distance with exchangeable lens
- OceanOptics Flame-T commercial miniature spectrometer, uncooled CCD detector, 50 µm entrance slit, resolution < 0.7 nm (25 cm^{-1})
- Avantes AvaSpec Mini commercial miniature spectrometer, uncooled CMOS detector, 10 µm entrance slit, resolution < 0.17 nm (6 cm^{-1})

Samples

- Pure samples of (30:70) CaF_2:$CaSO_4$, $CaSO_4$:basalt, silicon disk
- Natural samples of hematite and a plagioclase from Mt. Etna, Italy

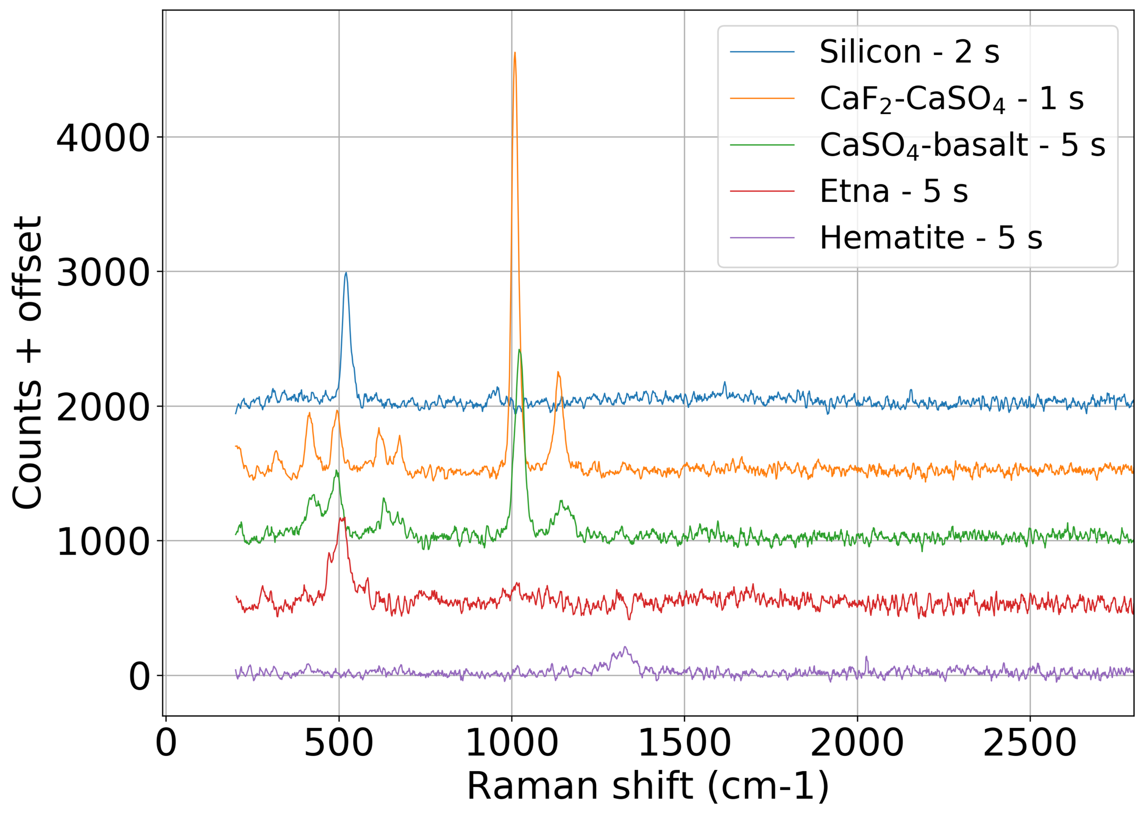


Raman signals of different samples

Experiment: Different samples at 20 cm sampling distance, average of 10 successive measurements, different exposure times, no ambient light

Observations:

- Exposure times adjusted to sample type
- Silicon (520 cm^{-1}) and sulfate (415, 495, 620, 670, 1010, 1135 cm^{-1}) modes are clearly visible within 2 and 1 s, respectively
- Natural plagioclases in Mt. Etna sample and hematite can be identified within 2 minutes including dark spectrum
- Hematite modes between 400 and 500 cm^{-1} detectable for shorter distances (not shown here) disappear, but higher order peak at 1300 cm^{-1} is still detectable



→ **cw-Raman spectroscopy** in darkness **is possible up to at least 20 cm** sampling distance

Trade-off cw sampling distance and exposure time

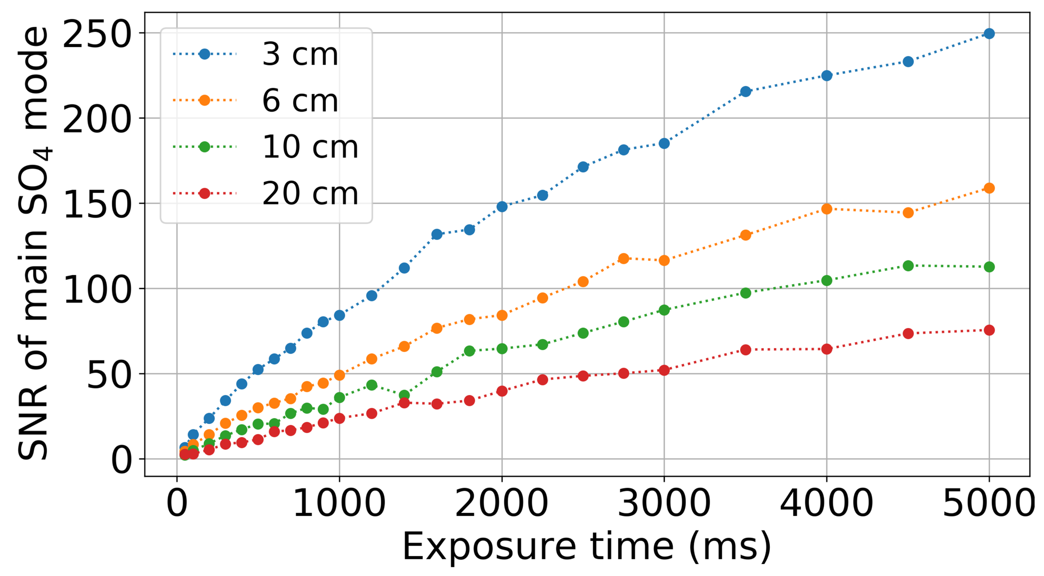
Experiment: CaF_2:$CaSO_4$ sample, no averaging and ambient light, exposure times **50—5000 ms**, sampling distances: **3; 6; 10; 20 cm**

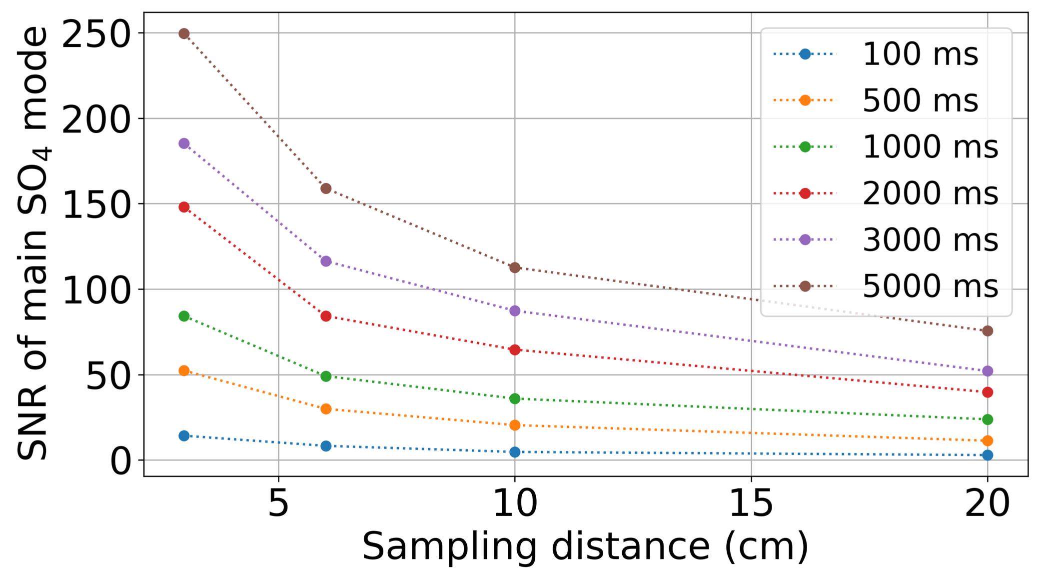
- Signal-to-noise ratio (**SNR**) estimation for SO_4 A_1 symmetric stretching mode at 1010 cm^{-1} by:
  1. removing background signal
  2. calculating signal height as height of Gaussian-fitted spectral line
  3. estimating the noise in a feature-free region

Observations:

- SNR increases quickly first, then slower for longer exposure times
- For longer sampling distances, SNR drops quickly first, afterwards moderately

→ **Longer exposure times** can compensate **for larger sampling distances** to some extent



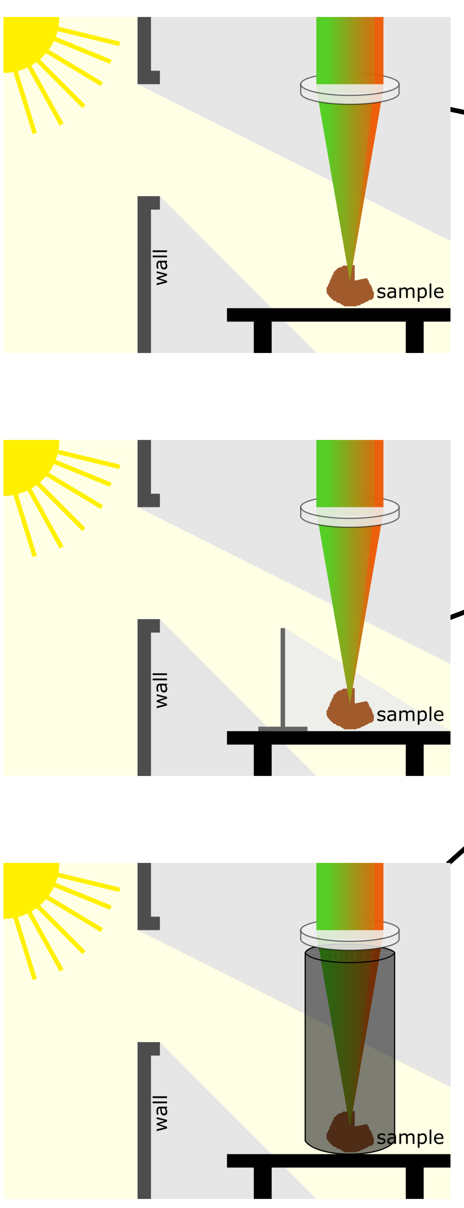


Influence of ambient light

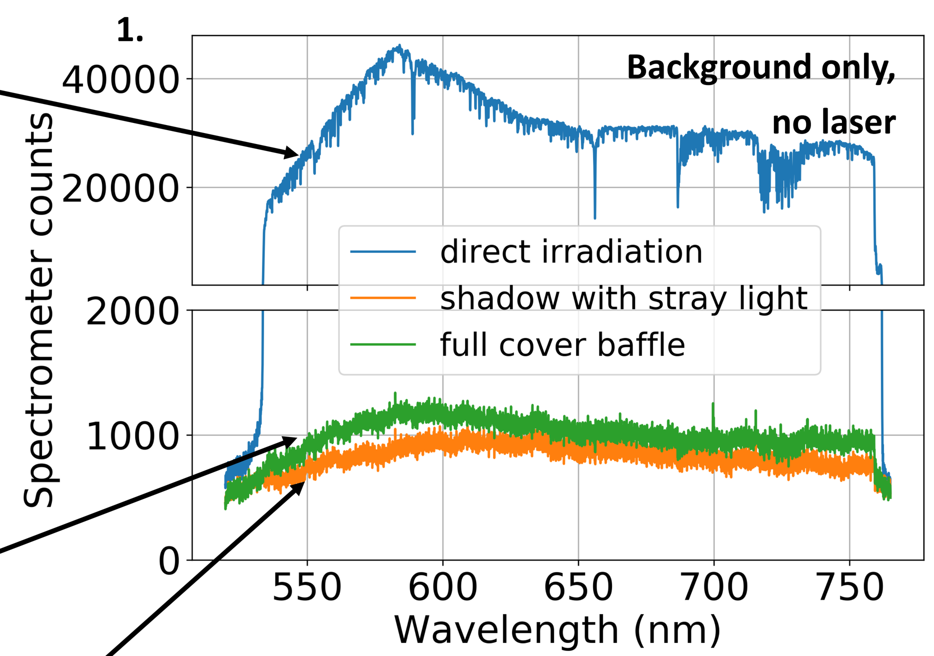
Motivation:

- Mission operation usually during daytime due to photovoltaic power supply and requirements towards operating temperature
  → **contribution of ambient light needs to be considered**
- E.g. in Mars orbit up to 240 µW/cm^2/nm (≈ 68 mW/cm^2 in the visible range) of solar radiation illuminate the targets

Experiment: Investigation of background signal (no laser) for Sun-illuminated, partly shadowed and completely covered sulfur sample **(1)**, and Raman spectroscopy of CaF_2:$CaSO_4$ sample for 6; 10; 20 cm sampling distance with simulated sunlight **(2)**



Observations:



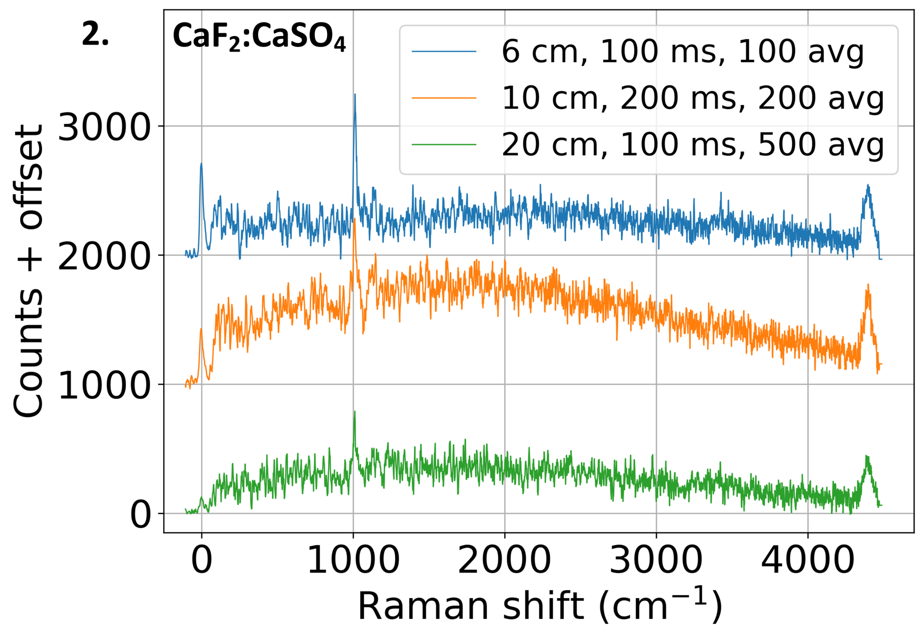
1. Background measurements in three configurations with sunlight on Earth

- Sunlight reflected from the sample saturates spectrometer within < 1 s
- Background signal changed up to approx. 10 % per second due to clouds and atmosphere movement (on Earth)
- Main contribution from direct irradiation, only little difference between atmospheric stray light and full baffle

→ cw-Raman measurements **in the shadow of or below the spacecraft** are feasible

2. CaF_2:$CaSO_4$ sample with illumination and different sampling distances

- Sunlight simulated with laser-driven light source (200-2000 nm output, power density adjusted to match solar flux near Mars in visible range)
- Strong signals like the main sulfate mode of $CaSO_4$ are still retrievable
- Displayed data was smoothened using boxcar average of width ±2 px



→ Strong Raman signals can still be identified in **up to 20 cm distance despite ambient light**

Conclusions

- In dark environment moderately strong Raman scatterers can be identified in up to 20 cm distance with a compact COTS-based instrument
- Longer exposure times can compensate for larger sampling distances
- Strong Raman signals can be detected despite direct sunlight
- Stray light is not critical as long as it is constant → measure in the shadow

→ Replace COTS components with optimized design for further improvement

References

[1] Wiens et al., 48th Lunar and Planetary Science Conference, LPI Contrib. no. 1964, id. 2600 (2017)
[2] Rull et al., Proc. SPIE 8152, 81520J (2011)
[3] Beegle et al., 11th International GeoRaman Conference, LPI Contrib. no. 1783, id. 5101 (2014)

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