SHIFTED EXCITATION RAMAN DIFFERENTIATED SPECTROSCOPY (SERDS) FOR PLANETARY SURFACE EXPLORATION.

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Planetary Raman Spectroscopy: pros and corns

Raman spectroscopy probes fundamental vibrations of molecules that produce finger-print spectral patterns with sharp peaks. Raman spectra can be acquired non-invasively, non-destructively and fast, thus is suitable for landed surface explorations on planetary bodies. On the other hand, Raman scattering phenomenon is intrinsically weak. It requires carefully crafted optical configurations with high Raman efficiency and robust optical-electronic-mechanical engineering, in order to provide the necessary science performances during a robotic planetary mission.

A major threat to Raman spectroscopy in terrestrial geological applications has been the fluorescence interference that appearing in some terrestrial rocks and regolith samples. Among those, the strongest fluorescence emissions are produced from bio-genetic species that were trapped in porous rocks or soils (e.g., clays). The bio-fluorescent emission has short life-time that is hard to be gated-out using a pulse Raman architecture. On the other hand, the fluorescence emissions by electronic transitions of rare earth elements (or sometimes from transition metals) are normally weak and have long life-time thus pulse Raman architecture may help.

IR- and UV-Raman architectures have been used in laboratories to address the bio-fluorescence issue for terrestrial geo-applications. Some units of this type were proposed for planetary applications. However, the Raman efficiency and the current TRL of IR- or UV-Raman systems are low. *More importantly, their values in planetary science have not been fully demonstrated and validated.*

A science team at Washington University in St. Louis and an engineering team at Jet Propulsion Laboratory have been developing a cw-green microbeam Raman architecture, i.e., MMRS & CIRS. It has reached TRL5-6, and *with its science values being fully demonstrating/validating through planetary science investigation since 1995 [1-26], and through field tests on Zoe rover in Atacama Desert in 2012-2015 [27].*

Furthermore, supported by MatISSE program, we have been conducting three sets of studies to address the potential bio-fluorescence issues. They are: (1). to evaluate the fluorescent properties and their potential threat to cw-green-Raman from a broad range of extraterrestrial materials, including lunar samples, Martian meteorites, variety of meteorites. This study ended with a contusion that *none-to-minimum fluorescence emission and none-threat to cw-green-Raman*, reported at 2015 LPSC [28]. (2). to compare Raman signal strengths generated by five laser wavelengths (785, 633, 532, 442, 325 nm), from a set of major rock-forming minerals and typical bio-markers, using a same Raman spectrometer (a state-of-art multi-wavelength Raman imager). This study ended with a conclusion that *532-Raman having the highest overall Raman efficiency*, reported at 2015 LPSC [29]. (3). to develop SERDS technology against the bio-fluorescence background, in case it appears during a planetary surface exploration. The primary results of the third study are to be reported here.

Shifted Excitation Raman Differentiated Spectroscopy (SERDS)

SERDS is a methodology based upon the difference in Raman signal generation and fluorescence signal generation.

Raman photons come from inelastic scattering emission of a molecule excited by a strong radiation beam (a laser). The Stokes Raman photons have longer wavelengths (λ_R) than that of laser (λ_0), with the wavelength difference ($\Delta\lambda=\lambda_0-\lambda_R$, i.e., Raman shift in cm^{-1}) corresponds the energy transitions among the vibrational states of that molecule. *The Raman scattering wavelength (λ_R) will change if the excitation laser wavelength (λ_0) changes, which will keep the $\Delta\lambda$ (Raman shift) unchanged.* This is the reason that the fundamental vibrational modes of a molecule can be observed using visible-, IR-, UV-lasers, and synchrotron X-ray for excitation (Fig. 1).

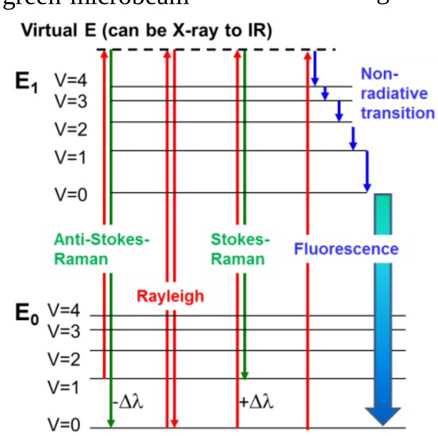


Fig 1. Raman & Fluorescence emissions

The same radiation may stimulate fluorescence emission from a sample (if it contains fluorescence centers, e.g., bio-genetic species or REE). However, *the wavelength of fluorescence emission would not change if the excitation laser wavelength (λ_0) changes.* Because the fluorescent emission comes only from the transition from an excited singlet electronic state to ground states, the extra-laser energy would convert to heat through *non-radiative* *transitions* (Fig. 1).

Based on above principle, SERDS uses (1) a wavelength shifted excitation laser to take Raman spectra from a sample, and then (2) to process the obtained spectra and re-generate Raman peaks without fluorescence interferences. *The laser wavelength shifting in CIRS unit has been realized at JPL by careful engineering.* At Washington University, we setup a SERDS system (Fig. 2) using three mini-lasers with slight different wavelengths (531.9, 532.3, and 532.5 nm), to validate SERDS applications on natural rocks.

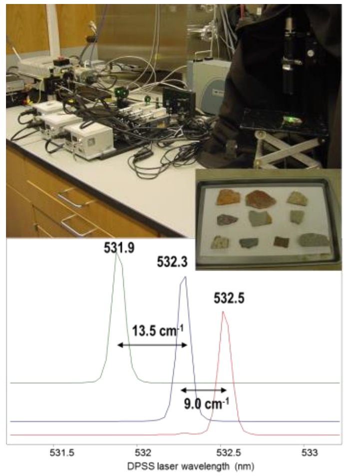


Fig 2. SERDS experiment setup at WUSTL

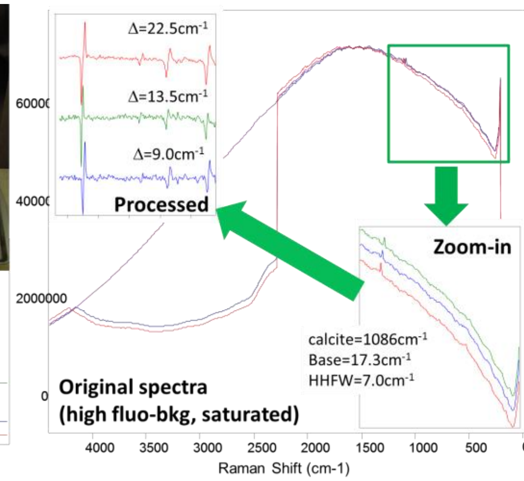
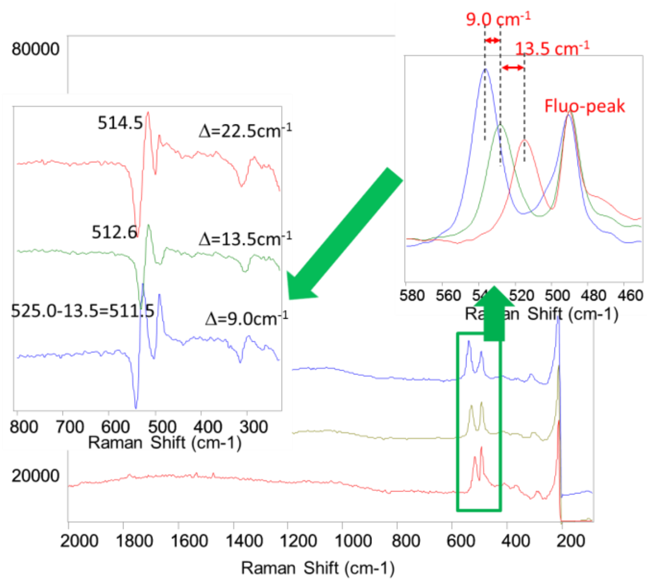


Fig 3. SERDS measurements and data process of rock AKB

We selected ten terrestrial rocks for SERDS test. They all show high level of fluorescence emission during the preliminary check using a cw-532 nm-Raman system (HoloLab5000-532, Kaiser Optical Systems Inc. KOSI). In our SERDS setup, we use a KOSI Mark-II Raman probe. The cw-green laser beam from a mini-laser was guided into the excitation fiber of that probe. We use a set of mirrors and pinholes to ensure the beams from different mini-lasers fall on to the same spot on a rock. The collected Raman photons from the rock sample were sent through a collection fiber bundle to a KOSI NEXUN-E Raman spectrometer.

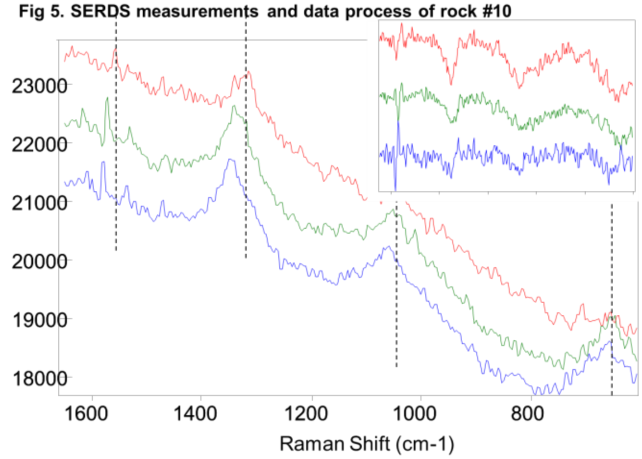
Fig 4. SERDS measurements and data process of rock #4



SERDS experimental results

Our SERDS measurements from real rocks can be described in three groups: (1) sharp Raman peaks on wide fluorescence background (Fig. 3); (2) sharp Raman peaks with sharp fluorescence peaks (Fig. 4); (3) sharp and wide Raman peaks (Fig. 5). Based on these data, we understood that the standard SERDS data processing would end with the results with different reliabilities. A practical procedure to process mission data from the non-predictable rocks is under development.

Fig 5. SERDS measurements and data process of rock #10



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References: [1] Wang et al., 1995, JGR, 100, 21189-21199; [2] Haskin et al., 1997, JGR, 102, 19293-19306; [3-18] Wang et al., 1998, 1999a, b, 2001, 2003, 2004a, b 2006, 2009, 2011, 2012, 2013, 2014, 2015a, b, c [19] Kuebler et al., 2006, GCA, 70, 6201-6222; [20] Freeman et al., 2007, Can Min. 46, 1477-1500; [21-23] Ling & Wang, 2010, Icarus, 209, 422-433; 2011, 211, 101-113; 2015, JGR, 120, 1141-1159; [24-25] Kong et al., 2011,JRS, *doi10.1002/jrs.2790.*, 2013 Icarus; [26] Liu & Wang, 2015 JRS, DOI: 10.1002/jrs.4655; [27] Wei et al., 2015, JRS, DOI: 10.1002/jrs.4656; [28-29] Wei and Wang, 2014a, b, LPSC abs. #2168 & #2448.