HIGH SPEED TIME-RESOLVED RAMAN SPECTROSCOPY FOR PLANETARY SURFACE EXPLORATION.

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Introduction: We present our progress in the development of a time-resolved Raman spectrometer for planetary exploration. The presented improvements of the laser and the detector are a first step towards a technological leap for the time-domain Raman spectroscopy technique, promising orders of magnitude improvements in signal-to-noise for the most challenging samples, e.g. dark samples and organics.

Raman spectroscopy is an optical, non-destructive, spectroscopic technique, currently under consideration for future *in situ* planetary exploration missions (i.e. NASA's 2020 Mars mission [1] and ESA's ExoMars [2]). The technique can be used to unambiguously identify mineral phases [3-5] and organic molecules [6] which provide information that can be used, for example, in the search for evidence of past life. The technique can be used with a small (<1 μm) spot size (i.e. interrogated area), making it possible to probe individual mineral grains. In addition, the measurements, which require no sample preparation, can be made in concert with microscopic imaging, providing, and preserving, the geological context.

The fluorescence problem: The Achilles heel of Raman spectroscopy is fluorescence, which may partially or completely obscure the spectroscopic signal from the weak Raman scattering process. Time-resolved Raman spectroscopy has been demonstrated as a successful way to overcome this problem [7-8]. This technique relies on the different time-scales involved in the different processes: Raman scattering is virtually instantaneous where as fluorescence is an exponentially decaying process (see figure 1). For minerals the fluorescence lifetime is relatively long (several ns to ms) where as organics are usually associated with shorter lifetimes (ps to ns). The rejection of shorter lifetime fluorescence is an important step that will allow us to identify minerals in the presence of organics as well as the organics themselves. We address the technical challenge posed by short lifetime fluorescence to the development of a highly capable miniaturized instrument for planetary exploration, based on time-resolved Raman spectroscopy.

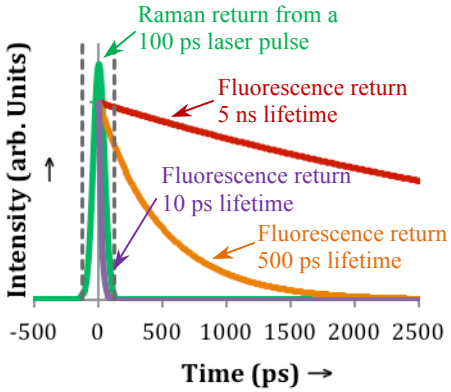

Figure 1. Illustration of the time-resolved Raman technique. The detector is only turned on (sensitive to light) during the short time when the instantaneous Raman signal arrives, as illustrated by the dashed lines. By rejecting light arriving later, all but the shortest (10 ps) lifetime fluorescence contributions are significantly reduced.

The dark sample problem: A second technical challenge is introduced by the time-resolved technique itself. The use of a pulsed laser, compared to a continuous wave (CW) laser as used in conventional Raman spectroscopy, increases the risk of damaging the sample as the peak power density (W/m^3) is far greater. For (semi-) transparent/translucent samples this is not a concern as the laser power is distributed over a larger volume. However, for highly absorbing (dark) samples much of the energy is absorbed closed to the surface, resulting in heating, and possibly ablation of the sample. Figure 2 illustrates the recorded spectra of silicon using our current state-of-the-art laser with a ~1 μm spot size. It is clear that in order to successfully employ the time-resolved Raman technique to investigate arbitrary samples, it is imperative to operate well below the ablation threshold for the darkest samples. Using a larger spot size and thereby reducing the peak power density can alleviate the problem but degrades spatial resolution. Reducing the pulse energy below the damage threshold requires a proportional increase in integration time to reach reasonable signal-to-noise ratios (SNR), due to the reduction in average laser power.

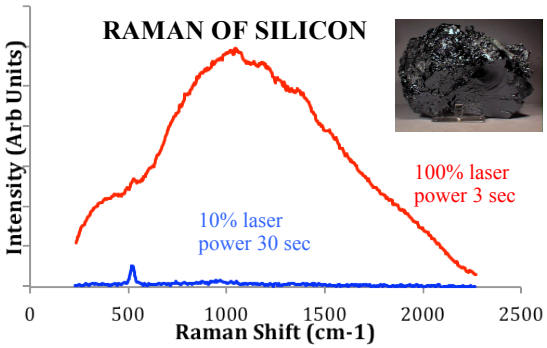

Figure 2. Raman spectra of silicon. At full laser power (532 nm, 40 kHz, ~500 ps pulse length, ~300 nJ/pulse laser), broadband emission associated with sample ablation overwhelms the spectroscopic (Raman) signal. Lowering the laser power below the ablation threshold the silicon Raman peak is clearly visible.

Laser development: The laser source used in the time-resolved Raman instrument is the key to address the two challenges discussed above. However, limitations in current laser technology (i.e. Q-switched DPSS or fiber lasers) have impeded progress in this area, imposing limits to achievable pulse length and repetition rates. Fortunately, recent developments in Semiconductor Saturable Absorber Mirror (SESAM) Q-switching [9-10] suggest that miniature lasers with near ideal properties may be possible. The ideal laser should produce pulses shorter than the lifetime of the organics (e.g. <100 ps), with pulse energies well below the damage threshold (a few nJ/pulse for our current setup), at a high repetition rate (several MHz) to facilitate average powers around a few mWs. Further, Raman spectroscopy calls for excellent (close to diffraction limited) beam quality, and a narrow spectral line width (<0.1 nm at 532 nm). Finally, with applications towards planetary exploration in mind, the laser must be low power, low mass, and low volume, as well as rugged and resistant to radiation, shock, and temperature fluctuations.

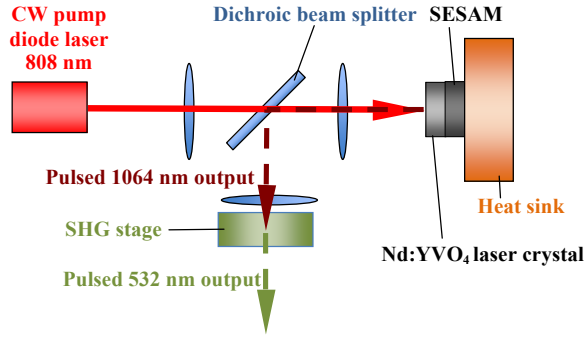

Figure 3. Schematic illustration of the SESAM Q-switched pulsed laser. Adapted from [9].

We present preliminary results using a SESAM Q-switched pulsed laser, implemented as a laboratory bench-top setup (schematically illustrated in figure 3). This laser offers 180 ps pulses with energies around 15 nJ (at 1064 nm, before the SHG stage), narrow spectral line width, and repetition rate variable from 100 kHz to 3 MHz.

Detector development: The time-resolved Raman technique relies on fast time-gated detection, synchronized with the pulsed laser. Our instrument uses a custom 1024x8 solid state Single-Photon Avalanche Diode (SPAD) detector array based on Complementary Metal-Oxide Semiconductor (CMOS) technology [8,11]. In order to utilize the potential in the new laser, we present improvements to the gating and readout electronics, enabling synchronization with the high repetition rate laser. The very low detector dark noise, even at room temperature, in combination with the absence of readout noise, ensures a significant gain in signal-to-noise ratio when moving towards a high repetition rate, low pulse energy laser, see Figure 4.

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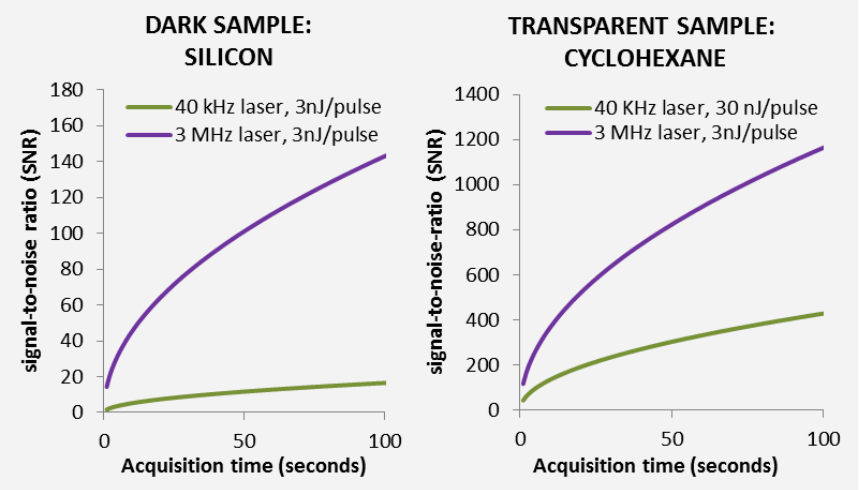

Figure 4. SNR vs. acquisition time curves for two different samples. The curves are calculated based on measured detector noise and Raman return. (Left) For dark samples the pulse energy is limited to prevent sample damage, resulting in a clear SNR advantage for the high-rep rate laser. (Right) For a transparent sample, the pulse energy is not an issue. However, the single-photon counting operation of the custom SPAD detector limits the pulse energy to avoid detector saturation. As a result, the high-repetion rate, low pulse energy laser offers a significant SNR advantage also in this case.