**Supporting Information**

# Shifted-Excitation Raman Difference Spectroscopy and Charge-Shifting Detection Coupled with Spatially Offset Raman Spectroscopy for Heritage Science

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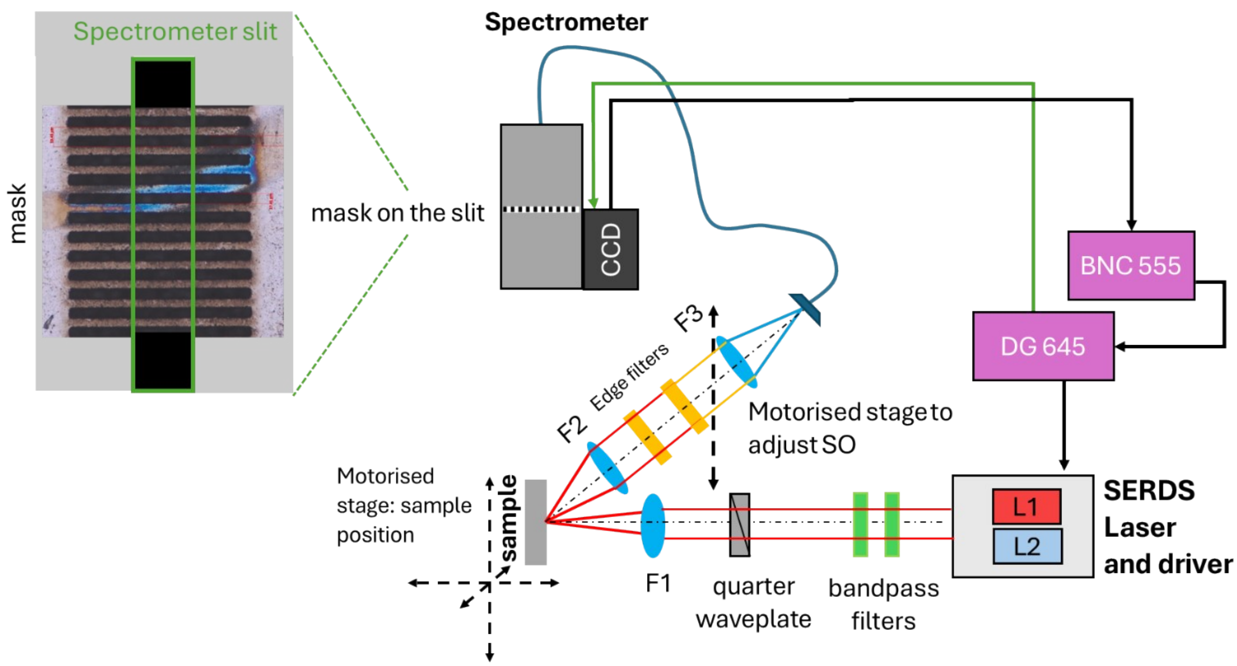


*Figure S1. A schematics of the charge-shifting SERDS setup used in this work. The excitation path is made of a dual-wavelength (L1, L2) laser and driver, bandpass filters around 830 nm, quarter waveplate, a 100 mm lens (F1) that focuses the laser on the sample surface. The collection path is assembled on a Thorlabs motorized stage defining the spatial offset (SO) consisting of 50 mm collection lenses (F2, F3), Raman edge filters, optical fibre bundle, spectrometer, and charge-shifting CCD. The DG645 digital delay generator and BNC model 555 digital delay generators connected to the laser driver and CCD allowed for the correct timing and synchronization of the charge-shifting detection. Top left insert, Sketch of the periodic mask placed in front of the second stage slit of a Raman spectrometer.*

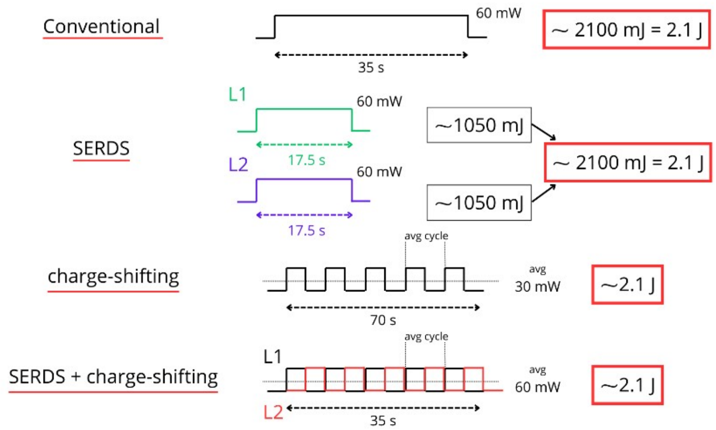


*Figure S2. Schematics of the laser intensity and acquisition time for the investigated methods.*

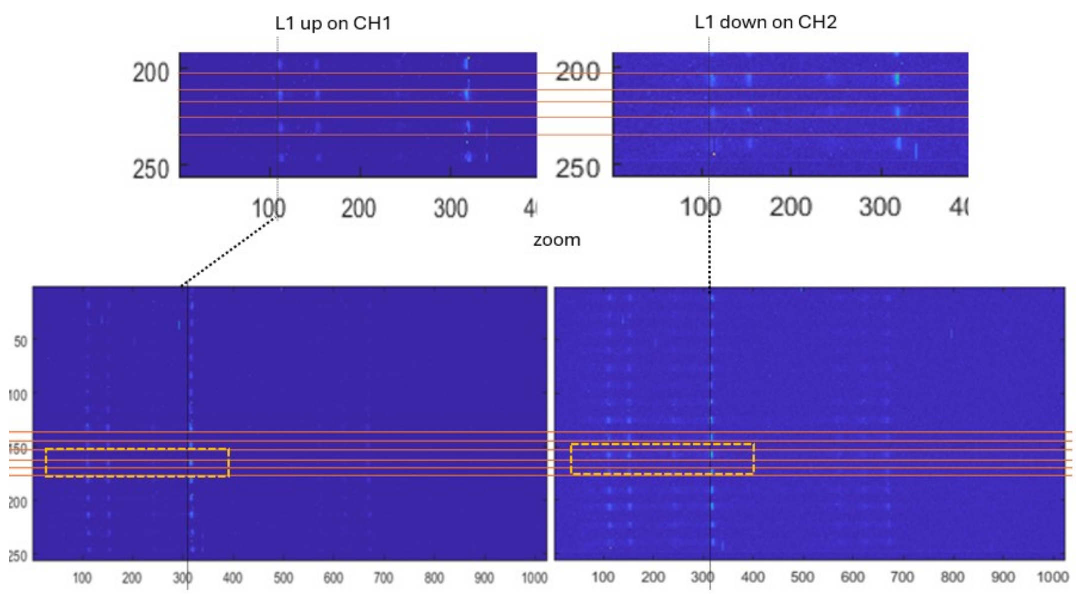


*Figure S3. CCD image during normal CS measurement (only one laser on).*

Regarding the choice of a high number of CS cycles, it is important to emphasize that this was an essential decision dictated by the nature of the samples and the set up rather than merely aiming to reduce the total number of acquisitions. This choice stems from the characteristics of the setup itself, particularly the "electronic control unit" which synchronizes the overall CS acquisition process (including L1 and L2 duration, delays, frequency, and CCD acquisition). As the CS acquisition begins, it is not possible to predetermine whether the first acquisition cycle will correspond to L1 (phase UP → channel 1, CH1) or to the 'blank background' measurement without any laser (in which case L1 corresponds to phase DOWN → channel 2, CH2). Both the scenarios are possible, and the phase can only be identified during the post processing stage, where the 2D image is converted into CH1 and CH2 (as described in the paper). An example is provided in the figure below, illustrating two different CS repetitions on the same sample that demonstrate this effect. On the left, the first cycle began with L1 and the Raman signal (from L1 excitation) was initially shifted up, therefore ended in CH1. On the right, the first cycle began with the laser off, resulting in the 'background' measurement being initially shifted up and ending in CH1, while the Raman signal (from L1 excitation) was stored in CH2.

Similarly in a SERDS-CS process, It is not possible to define if the process will start with L1 on phase UP, and L2 on phase down, or vice versa with L1 on phase down, and L2 on phase up. An equivalent example of CS-SERDS is provided in the figure below.

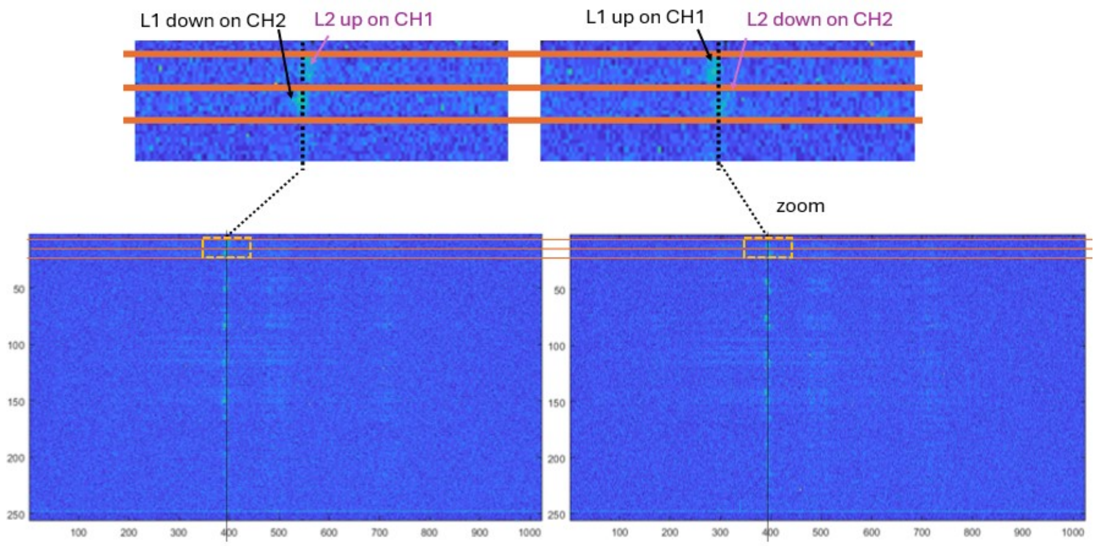


*Figure S4. CCD image of a SERDS+CS measurement (two lasers on).*

As previously explained, when adding different repetitions, it is crucial to correctly identify the phase of the CS cycle for each measurement (i.e., up or down for L1 and L2). The final CH1 and CH2 signals from different acquisitions must then be summed with the correct phase alignment (all L1 signals together and all L2 signals together). Failing to do so would mix the signals, resulting in a broader Raman band and rendering the sequential SERDS approach highly ineffective. In our case, the signal coming from the sample from a single acquisition at 1kHz with 5,000 repetitions (corresponding to a lower integration time) was at the noise level making it impossible to recognize the phase, and making the sequential addition of different repetitions with the correct phase alignment unfeasible.

Therefore, our choice of using a high number of cycles for the single accumulation is not only related to achieving the same power on the sample as the other techniques, but it is also tightly linked to the need of retrieving a stronger signal within a single 50,000 cycle acquisition. The extended accumulation time in a single acquisition (a factor of 10, going from 5,000 to 50,000 cycle) ensures that detected signal is sufficient for correct summation. Given the complexity of the samples and the nature of the setup, it would have been practically impossible to consistently detect such a signal across all individual 5,000-cycles acquisitions.

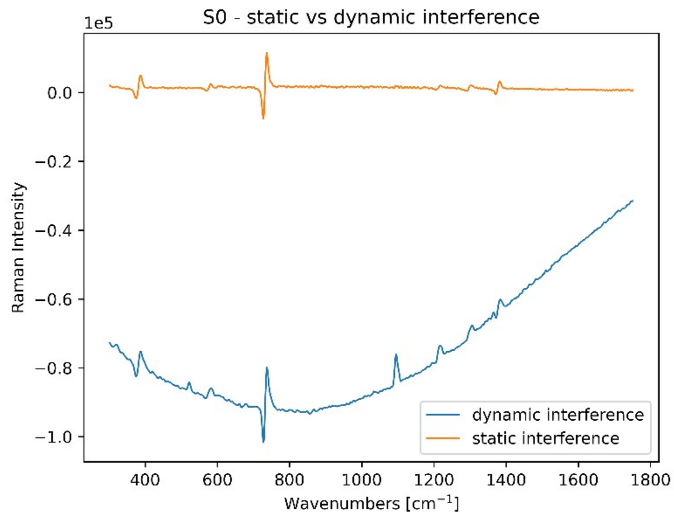


*Figure S5. Comparison of SERDS measurements of S0 with static or dynamic background interference. It is clear that in the latter case even SERDS struggles to provide an appreciable result.*