Standoff Raman spectroscopy of extended targets

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A coded-aperture spectrometer provides higher-throughput measurement of an extended source than a slit-based instrument: our initial experiments show a gain of 1.9x in SNR.

Standoff Raman spectroscopy provides a method for identifying chemicals in a sample located a distance away. This distance can vary from a few centimeters, for monitoring chemicals in a manufacturing process, to tens of meters when examining potentially-dangerous samples like explosives. One of the greatest challenges inherent to Raman spectroscopy is the extremely-weak intensity of the Raman signal measured by the spectrometer. We have developed a spectrometer that is optimized for this kind of signal and provides solutions to some of the major challenges of standoff Raman spectroscopy.

Basic standoff Raman spectroscopy systems combine a spectrometer, light-collecting optics (a telescope), and a monochromatic excitation source. To make a measurement, the sample of interest is illuminated with monochromatic light from a laser. A small fraction of the input photons (on the order of one in $10^{-5}$ to $10^{-9}$) are inelastically, or Raman, scattered. These Raman scattered photons exhibit a unique signature for a particular molecular configuration—essentially a ‘fingerprint’ than can be used to detect the presence of chemicals in the sample.

The Raman photons generated by the excitation source are isotropic so, in a standoff system, the fraction of photons collected is equivalent to the solid angle subtended by the aperture of the collection optics, as seen by the target. For a 254mm-diameter telescope and a target distance of 30m, the fraction is $3 \times 10^{-6}$. Since the signal measured by a standoff Raman system is many orders of magnitude lower than the power input by the excitation laser ($10^{-11}$ to $10^{-13}$ for our example case), system designers frequently use pulsed lasers to achieve power densities on the order of $10^6$W/cm$^2$ on the target. Even in cases where the standoff distance is just a few centimeters, achieving measurement times on the order of a second can require power levels that will damage the target.

Figure 1. Microphotograph of a coded aperture.

To maintain Raman signal strength without causing damage, one can increase the size of the laser spot. This has the added advantage of increasing the interrogation region, or area sampled in one measurement; consider the time difference required to scan a target surface with a 1mm$^2$ versus a 100cm$^2$ region. Unfortunately, increasing the interrogation-region size presents a problem for a typical slit-based spectrometer where spectral resolution and slit width are coupled. The interrogation must be small enough so that the collection optics can focus light from the entire region through the slit. Increasing the slit width allows the use of a larger region at the cost of spectral resolution. Our solution to this problem is a coded aperture spectrometer, where the slit at the input is replaced with a two-dimensional series of openings: an example coded aperture is shown in Figure 1.

The spectral resolution of a coded aperture is based on the size of an individual opening, while light throughput is based on the size of the entire two-dimensional pattern. The best comparison between a slit and coded aperture is expressed in terms

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of étendue, which measures total light throughput as the product of the entrance aperture area and entrance solid angle. For a standoff Raman system, the entrance solid angle is limited by the collection optics: spectrometers typically have much lower f-numbers than large-aperture telescopes. This means that when we compare étendue for a slit- and coded-aperture spectrometers using the same telescope, we simply compare aperture area. The largest coded aperture used in our proof-of-concept system was based on a 40 row mask with 50% throughput, yielding 20× the aperture area of a slit with equivalent spectral resolution.

Our proof-of-concept system is based on our coded aperture Raman spectrometer with a 5.5W laser at 532nm and an f/6.3 Schmidt-Cassegrain telescope with a 254mm aperture. The spectrometer is designed with f/6.3 optics to match the telescope and a set of removable apertures, to compare the performance of a slit with several different sizes of coded aperture. Both the coded apertures and slit have a feature size of 36μm. In our initial experiments, we used varying concentrations of isopropanol and water as a target. We measured a signal-to-noise ratio gain \((\text{SNR}_{\text{coded aperture}}/\text{SNR}_{\text{slit}})\) of 1.9×, for the 40-row mask.2 This is about a factor of two less than theory predicts, caused by aberrations in our optical system.

Coded-aperture spectrometers show great utility when measuring the spectra of high étendue sources. These are frequently encountered in standoff Raman spectroscopy, especially when measuring large-area sources. Future work includes using our proof-of-concept system to measure some more interesting chemicals as well as exploring different aperture-coding schemes.

References