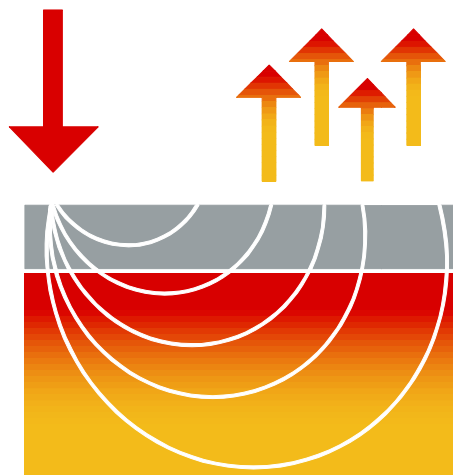


## Spatially Offset Raman Spectroscopy (SORS)



**Conventional Raman spectroscopy tends to be limited to near-surface regions or reliant on transparency to enable analysis of sub-surface composition. SORS is a new technique that permits measurement at depths of many millimetres, allowing accurate chemical analysis of materials inside opaque objects.**

Many analytical applications require a highly chemically specific method capable of non-invasive analysis of samples through opaque layers or containers. Examples include non-invasive diagnosis of bone disease, detection of concealed explosives and the identification of counterfeit drugs through packaging. Until recently, only shallow penetration depths (for example, with biological tissue of a few hundred microns) were possible using conventional Raman spectroscopy. This limitation arises as the majority of systems use backscattering collection geometries, which is popular for its instrumental simplicity and ease of use.

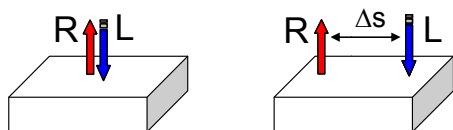


Figure 1: Conventional backscattering Raman spectroscopy (left) and SORS (right).

Recently, a substantial increase in penetration depth was achieved using the diffuse component of scattered light – Spatially Offset Raman Spectroscopy or SORS.

### SORS

Spatially Offset Raman Spectroscopy<sup>i,ii</sup> is capable of isolating the Raman spectra of *individual sub-layers* within a stratified diffusely scattering system using

relatively low power lasers. The SORS method is based on the acquisition of Raman spectra from regions spatially offset on the sample surface from the laser beam excitation point (see Fig. 1).

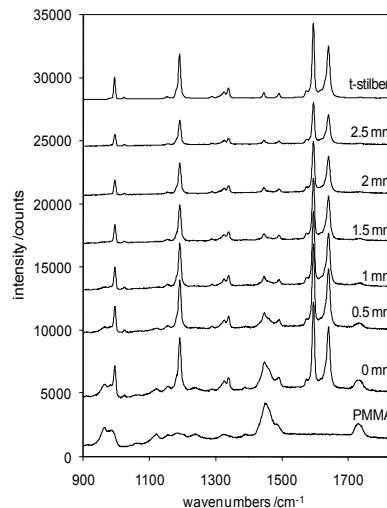


Figure 2: SORS spectra from a two-layer system of 1mm-thick PMMA 20µm-diameter spheres and a 2mm sub-layer of *trans*-stilbene powder.

Raman spectra observed at increasing spatial offsets contain increasing relative contributions from deeper layers due to the spreading of photons at the surface. Since Raman and fluorescence components (from the same layer) have identical spatial distributions SORS also effectively discriminates fluorescence generated from the surface layer.



The Raman spectra at different offsets have varying degrees of surface and subsurface components, which enables the separation of Raman spectra of individual layers via simple numerical methods. Separation can be achieved using multivariate techniques such as band target entropy minimization (BTEM)<sup>iii</sup> or, for a two-layer system, a simple scaled subtraction of spectra acquired at two different spatial offsets.<sup>i</sup> This is in contrast with conventional backscattering Raman spectroscopy where only a single Raman spectrum is available and no such separation is possible.

Figure 2 shows the first demonstration of SORS performed on a two-layer sample of a 1mm thick PMMA powder layer located on top of a *trans*-stilbene powder sub-layer.<sup>i</sup> The conventional Raman spectrum corresponds to the SORS spectrum obtained with zero spatial offset. The introduction of a non-zero spatial offset leads to a more rapid decrease of the surface-generated Raman signal (PMMA) relative to that of the sub-layer (*trans*-stilbene); at a spatial offset of 2mm, the surface-to-subsurface relative Raman intensity was diminished by an order of magnitude.<sup>i</sup> The dependence of SORS on variables such as layer depth, sample absorption and scattering parameters was analysed using Monte Carlo simulations by Matousek *et al.*<sup>ii</sup>

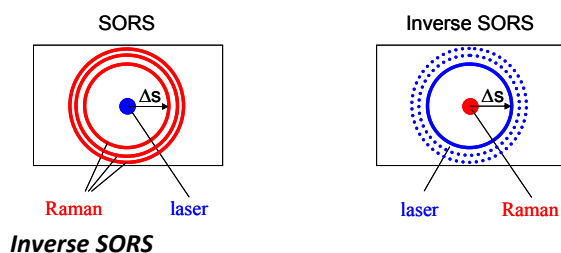


Figure 3: Schematic diagram of SORS and inverse SORS geometries.

Where illumination intensity limits have to be strictly adhered to, e.g., to avoid sample heating or to stay within exposure limits for the illumination of human skin *in vivo*, inverse SORS permits the use of higher overall laser powers by reducing power density at the sample surface.

Inverse SORS,<sup>iv,v</sup> in contrast to standard SORS, relies on the collection of Raman light contained within the centre of a probed area defined by a ring shaped laser beam (see Fig. 3). The radius of the ring, which defines the spatial offset, can be tailored to match the size and parameters of each sample. This is not possible with conventional ring SORS probes where the ring radii are fixed.

The ring-shaped beam is typically generated using a conical lens (axicon) where the radius of the ring, and hence the spatial offset, is continuously adjustable.<sup>iv</sup>

### Application Areas

Applications of SORS are wide ranging and steadily increasing. They include the non-invasive Raman spectroscopy of bones,<sup>vi</sup> development of cancer diagnostic tools,<sup>vii</sup> detection of counterfeit drugs through diffusely scattering plastic bottles<sup>viii</sup> and the detection of liquid and solid explosives.<sup>ix</sup>

### Conclusions

The combination of the advantages of Raman spectroscopy with the ability to probe deeply hidden layers holds great promise in a variety of fields. Several new exciting applications, including the diagnosis of bone disease and breast cancer, the authentication of pharmaceutical products through packaging, the detection of powder and liquid explosives and illicit drugs through containers are made possible. This is a direct result of the flexibility and straightforward adaptability of SORS.

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