Paul Lauria
Physics 211A
Special Topics Paper

Shell-isolated nanoparticle-enhanced Raman spectroscopy

Raman spectroscopy is a technique in condensed matter physics involving the inelastic scattering of light. It is commonly used in many areas of science and industry, and is still studied and heavily used almost 100 years after its discovery. First experimentally realized in 1928 by the Indian physicist C.V. Raman, the technique was not widely used until the advent of the laser in the 1960s, due to its fundamentally weak signature.

To get some idea of the physics, we can say that Raman spectroscopy can, to first approximation, be explained entirely classically. In the basic Raman experiment, a high-intensity laser beam—typically in the optical to IR regime, since the UV lasers tend to cause heavy fluorescence—is back-scattered off the sample to be studied. After filtering out the laser line, the reflected light is then collected in a spectrometer. One might think that after such a filter, there would be nothing left except fluorescence. To a large degree, that is true; however, if fluorescence can be minimized through choice of laser, and the spectrometer made highly sensitive, another signal emerges: light frequencies shifted by hundreds or thousands of wavenumbers from the incident radiation.

These lines, or 'peaks' in the spectrum, result from photons scattering off the sample but having some of their energy absorbed into specific molecular vibrations. The reflected energy thus has energy 'missing' from it; this is called Stokes scattering. Another arrangement is possible, although it is less frequent and much less intense: should the light find some of the molecules already in an excited vibrational state, the laser will cause the stimulated emission of a photon at the energy of the molecular vibration. This is called anti-Stokes scattering. Qualitatively, the number of excited vibrations scales as the Boltzmann factor; at room temperature, this form of scattering is typically negligible.

We can make use of classical electrodynamics to quantify the discussion. The laser induces a

dipole moment in the material. This dipole moment can be expressed in a power series in the electric field, although we shall take just the first order term:

$$\mu^{(1)} = \alpha \cdot \mathbf{E}$$

where alpha is the polarizability tensor, expressing how easily a molecule can be polarized in the various spatial directions. Typically, the terms quadratic in E are 10 orders of magnitude weaker; at the strengths of the electric fields typically used (typically 0.1mW to 100mW), this is a reasonable approximation.

To proceed, we need to account for the polarizability. Ignoring rotational modes, the polarizability tensor can itself be expressed within the confines of a Taylor series; here we shall keep the 2nd order term:

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum_k \left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 Q_k$$

Here the Q's are the coordinates of the nucleus. It is reasonable to expect that the polarizability should depend on the nuclear coordinates, because the closer the nucleus is to the electrons, the less likely the electrons are to be influenced by a weak external electric field. Now insert the harmonic variation of the nucleus, with an arbitrary phase shift:

$$Q_k = Q_{k0} \cos(\omega_k t + \delta_k)$$

The expression for the polarizability becomes:

$$\alpha_k = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q} \right) Q_{k0} \cos(\omega_k t + \delta_k)$$

Plugging alpha into our expression for the dipole moment we finally have, after some algebra:

$$\mu^{(1)} = \alpha_k \cdot \mathbf{E}_0 \cos \omega_0 t = \alpha_0 \cdot \mathbf{E}_0 \cos \omega_0 t + \left(\frac{\upsilon \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos \omega_0 t \cos\left(\omega_k t + \delta_k\right) t =$$

$$\alpha_0 \cdot \mathbf{E}_0 \cos \omega_0 t + \frac{1}{2}\left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t + \omega_k t + \delta_k\right) + \frac{1}{2}\left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t - \omega_k t - \delta_k\right)$$

We know from classical theory that an oscillating dipole radiates—and the frequencies the spectrometer picks up are all here: Stokes (w0 + w), anti-Stokes (w0 - w), as well as the laser line itself. We thus see that, for Raman scattering to be observable, the polarizability must have a nonzero derivative with respect to the nuclear coordinates. Also, the laser line itself must be filtered out using sharp optical notch filters.

Thus we see the utility of the Raman scattering process: given an incident laser beam of any wavelength, we can probe a material to determine which vibrational modes are active. The vibrational mode energies depend critically upon the molecular structure; thus the presence or absence of certain bands relates to the corresponding presence or absence of particular functional groups in our sample. Thus the Raman profile is something of a unique fingerprint which identifies materials, and the amplitudes give clues as to the amount of a functional group in the material. This technique is used extensively to determine the crystallographic structure of a sample, for quality-control in industry, and for police and investigatory work in crime labs around the world.

Unfortunately, Raman scattering has its drawbacks; as we have seen, it depends critically on the polarizability derivative. In many materials, this is vanishingly small. Furthermore, even if a material is highly Raman active, the signal might still be intolerably weak, since it depends on how *much* of a sample the beam probes, which is often determined by diffraction. For nanoparticles in particular, or discretely placed nanoparticle aggregates, narrowing the beam waist to include only signal from the nanoparticles is usually impossible. Furthermore, if there are any Raman-active layers beneath the sample, the laser will excite those as well, owing to the laser's finite depth of focus. Thus it becomes unsuitable for many thin-film measurements since the signal becomes contaminated and often

overwhelmed by vibrational modes of the substrate.

Despite its weaknesses, Raman spectroscopy has proved enormously useful, and many attempts have been made to enhance the signal. In the 1970s, it was discovered that a surprising enhancement of the Raman signal could be obtained: Fleishmann et, al.[i] discovered that by adsorbing a sample of pyrodine onto a substrate of roughened silver, the Raman signal was enhanced by a factor of 10^6. Intense research into the phenomena revealed the general nature of the effect, now called *surface-enhanced Raman spectroscopy (*SERS*)*, which occurs when one adsorbs their sample onto rough metal surfaces or by placement in a liquid of metal nanostructures. For many years thereafter, the precise cause of the enhancement was debated in the literature, but is now generally accepted that it arises mostly from large local electromagnetic field enhancements caused by the nanoparticular surfaces. The Raman effect depends on the fourth power of the electric field, as we shall see, and so this yields a large boost to the Raman signal.

A simple model of the electromagnetic enhancement is obtained by considering the effect a spherical gold nanoparticle would have on the local electric field. Proceeding in the long-wavelength ($a/\lambda < 0.1$, where a is the nanoparticle's radius) and quasi-static approximation, the electric field is constant over the surface of the nanoparticle. Thus, the solutions to the fields can be arrived at simply through Laplace's equation. Through a Jackson-level calculation, we arrive at the expression:

$$E_{out}(x, y, z) = E_0\hat{\mathbf{z}} - \alpha E_0 \left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5} \left(x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}} \right) \right]$$

Thus we see the enhancement dies off on the order of r^-3, requiring the sample to be in direct contact with the nanoparticles. Alpha is the usual polarizability and is expressed further as

$$\alpha = ga^3$$

and

$$g = \frac{\varepsilon_{in} - \varepsilon_{out}}{(\varepsilon_{in} + 2\varepsilon_{out})}.$$

where the epsilons are dielectric constants of the material inside and outside the nanoparticle.

The intensity immediately outside the nanoparticle can be given by squaring Eout and evaluating at *r=a*:

$$|\mathbf{E}_{\text{out}}|^2 = E_0^2[|1 - g|^2 + 3\cos^2\theta(2\mathrm{Re}(g) + |g|^2)]$$

where theta is the angle between the electric field vector and the position of the molecule on the surface. We can see the maximum enhancement approaches 4E^2|g|^2 when theta approaches 0 or pi. Assuming a typical g = 10 for a small sphere[ii], the Raman cross section—which goes as the fourth power of g[iii]—experiences a 10^4 enhancement of the Raman effect. Different nanoparticle geometries can produce enhancements as high as 10^8! Thus we see the utility of the SERS effect; with it, ultra-low detection limits are possible, capable of detecting single-molecule systems.

There are limitations even to SERS, however. Because the method's EM enhancement is highly localized, it is not possible to use SERS to study atomically flat single-crystal structures. Also, the substrate must be nanostructured of free-metal like atoms; mostly Au, Cu, and Ag and a handful of other elements. The making of these structures involves costly and time-consuming electro-chemical etching and thermal deposition. Furthermore, the low cohesive energy of Au, Cu and Ag means they quickly degrade under irradiation—they acquire kinetic energy and begin to spread, reducing the SERS effect and producing regions of "hot spots" that change position in time. This is unacceptable for many elements which, even with SERS, require minutes of exposure time to yield a usable signal. Thus we come to the innovation of the current paper: shell-isolated Raman spectroscopy, which addresses these concerns.

Shell-isolated nano-particle enhanced Raman spectroscopy (SHINERS) was introduced in 2010[iv] to address the limitations of SERS. The essential process of SHINERS is to coat Au nanoparticles in a dielectric material—silicon, in this case, but other dielectrics, such as aluminum dioxide, have been

used as well. This nanoparticle is then dusted over the surface of a sample—no particular substrate or morphology is necessary—and the Raman signal read out. The dielectric is physically inert, preventing interactions with the sample under study that might distort the vibrational results. It also allows the nanoparticle dust to conform to whatever surface is under examination. Illustration 1 shows the process pictorially.
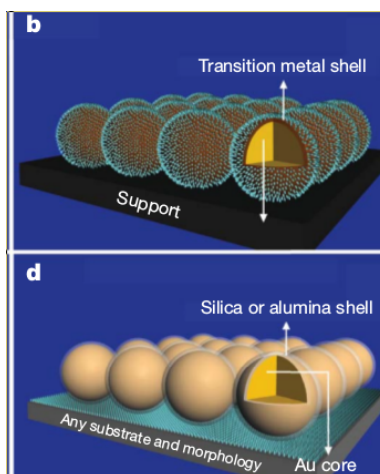
Illustration 1: Illustration of SHINERS technique. The material to be probed clings to the nanoparticle on its surface.

In their initial study, Ling et. al. used the technique to demonstrate the capturing of the Raman spectra of hydrogen adsorbed onto single-crystal surface. Hydrogen adsorption is an important measurement in surface science and industry, and the signal had never been seen before due to its low Raman cross section. They also show its application to biological systems, directing their focus on the cell walls of yeast. Illustration 2 shows their result and the difference the approach makes. Finally, they show the technique's utility in food safety, examining an orange that has been contaminated by pesticide. A normal Raman scan shows only the vibrations of the molecules always found in citrus fruits, while the SHINERS technique distinctly shows the pesticide's presence as a lump in the spectra at the characteristic frequency of the pesticide.
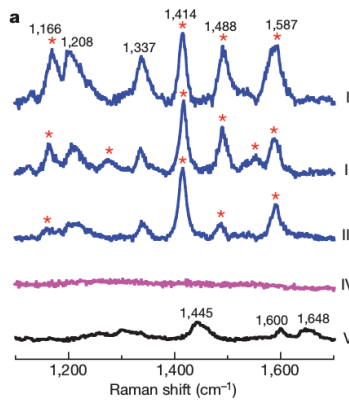
Illustration 2: SHINERS spectroscopy of yeast cells. Curves I, II, and III are spectra from different spots on the wall of a yeast cell. IV is the substrate only. V is the usual (non-SHINERS) Raman spectra.

The biological and chemical sciences make up the bulk of the technique's users. For instance, it has been used to study bipyridine, a chemical in certain herbicides, overturning previous Raman spectra that had been occluded with noise.[v] It has been used to detect cyanide, a deadly poison, below the 1 microgram/liter threshold.[vi] On the national security front, it has seen use as highly sensitive detector of trinitrotoluene (TNT).[vii] Protocols have been recently published so that use of the technique can spread to less specialized labs.[viii] In general, due to its high detection sensitivity it is expected that the SHINERS method will find its way into cancer research in examining biopsy tissue, skin surface measurements, or industrial control surface measurements.

i Fleischmann M., Hendra P. J., McQuillan A. J. *Chem. Phys. Lett.* **1974**. 26 163–166.
ii P. Stiles et. al., *Annual Review for Analytic Chemistry*. **2008**. 1:601-626.
iii *Ibid*.
iv J. Ling et. al. Nature Letters. **2010** 464.
v D. P. Butcher et. al. *Journal of Physical Chemistry C.* **2012** *116* (8), 5128-5140
vi J. Gao et. al. Journal of Raman Spectroscopy. **2014** 45 (8) 619-626.
vii J. Li et, al. Nature Protocols, **2013** (8) 52-65.
viii K. Qian. et. al. Analyst, **2012** (137) 4644-4646