Surface Enhanced Raman Spectroscopy (SERS)

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Outline

- What is SERS?
- What is Raman Scattering?
- How does SERS work?
- What information is obtained using SERS?
- Why use SERS?

What is SERS?

- SERS is a surface sensitive technique that results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces.

- The enhancement factor can be as much as $10^{14} – 10^{15}$, which allows the technique to be sensitive enough to detect single molecules.

What is Raman Scattering?

- Raman spectroscopy is concerned with radiation scattering from a sample.
- Scattering occurs when an incident photon interacts with the electric dipole of a molecule.
- This scattering process can be either elastic or inelastic.

What is Raman Scattering?

- Most incident photons are elastically scattered by the molecule (Rayleigh scattering).

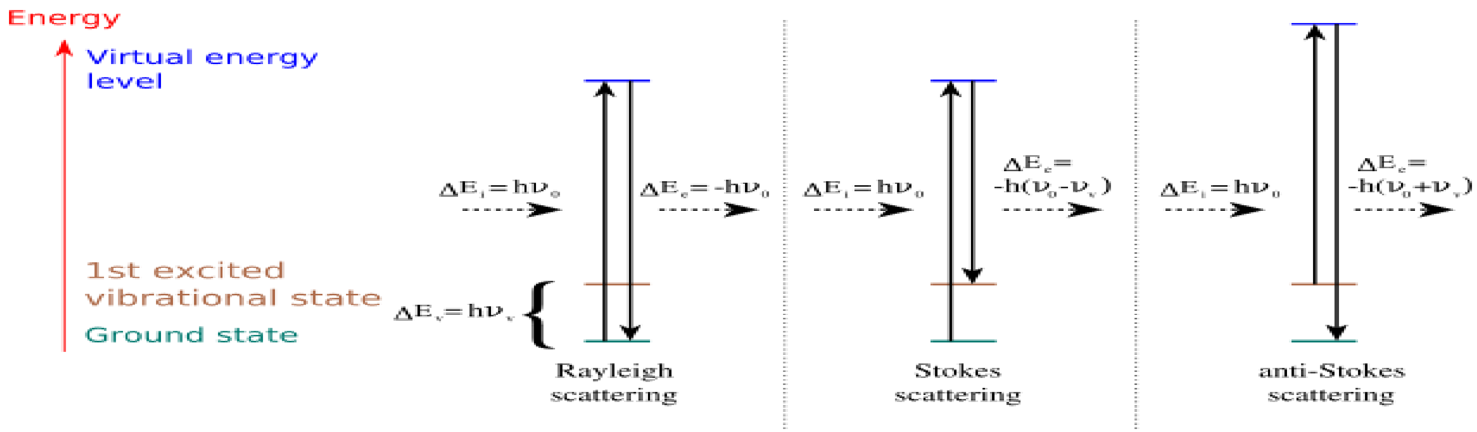
- In Rayleigh scattering the energy of the incident photons equals the energy of the scattered photons.

What is Raman Scattering?

- A small fraction of light is scattered at energies different than that of the incident photons (Raman effect).
- The Raman effect is an inelastic process and was first observed in 1928.
- Chandrasekhara Venkata Raman awarded Nobel prize in 1930.

What is Raman Scattering?

- Two situations arise with Raman scattering…
  - Scattered photons have a lower energy (Stokes scattering – phonon emitted)
  - Scattered photons have a higher energy (anti-Stokes scattering – phonon absorbed)



What is Raman Scattering?

- Conservation of energy and crystal momentum in a one-phonon process requires
  - $\hbar\omega' = \hbar\omega \pm \hbar\omega_s(\mathbf{k})$
  - $\hbar n\mathbf{q}' = \hbar n\mathbf{q} \pm \hbar\mathbf{k} + \hbar\mathbf{K}$
    - ω, **q** incident photon frequency, wave vector
    - ω', **q**' scattered photon frequency, wave vector
    - ω_s phonon frequency
    - n index of refraction of the crystal
    - **k** phonon wave vector ($k = 2nq \sin \frac{1}{2} \theta = (2\omega n/c) \sin \frac{1}{2} \theta$)
    - **K** reciprocal lattice vector (**K** = 0 since photon wave vector's small, 10^5 cm^{-1}, compared with dimensions of Brillouin zone, 10^8 cm^{-1})
    - \+ anti-Stokes (phonon absorbed)
    - \- Stokes (phonon emitted)

From Raman to SERS

- The energy of a vibrational mode depends on the molecule’s structure and environment.
  - Raman spectra of different molecules are unique
- Raman intensity lines are 0.001% (at most) of the source intensity.
- The intensity can be increased by $10^3 – 10^6$ orders of magnitude if the sample is adsorbed on the surface of colloidal metal particles.
  - Surface Enhanced Raman Scattering (SERS)

How does SERS work?

- The mechanism of SERS is not completely understood.
  - Electromagnetic enhancement
    - Proposed by Jeanmarie and Van Duyne in 1977
  - Chemical enhancement
    - Proposed by Albrecht and Creighton in 1977

- Electromagnetic enhancement
  - Arises from the presence of surface plasmons on the substrate.
    - Surface plasmons are electromagnetic waves that propagate along the surface parallel to the metal/dielectric interface.

How does SERS work?

- Surface plasmons are generated when the incident light excites the electron gas of the metal.
- When a substrate is placed in the proximity of the plasmon, it experiences an enhanced electromagnetic field and produces an enhanced scattered Raman field.

- Chemical enhancement
  - Involves charge transfer between the chemisorbed species and the metal surface
    - This enhancement is generally less than a factor of 10

How does SERS work?

- The last decade has seen major advances in the application of SERS and Raman spectroscopy primarily because of the improvements made in Raman instrumentation--namely lasers, detectors and spectroscopic instrumentation.

- Raman instrumentation consists of lasers, spectrometers, optics and detectors.

How does SERS work?

- Lasers
  - The laser excitation frequency is the major determinant of the information content of a Raman spectral measurement
  - Both continuous and pulsed lasers are used

- Optics
  - Filters are used to remove the Rayleigh scattered photons

How does SERS work?

- Spectrometers
  - The purpose of the Raman spectrometer is to reject the intense Rayleigh scattered light and to disperse the Raman scattered light into its component frequencies for detection
  - If the Rayleigh light is allowed to enter the spectrograph unattenuated, it will obscure all or part of the much weaker Raman spectrum.

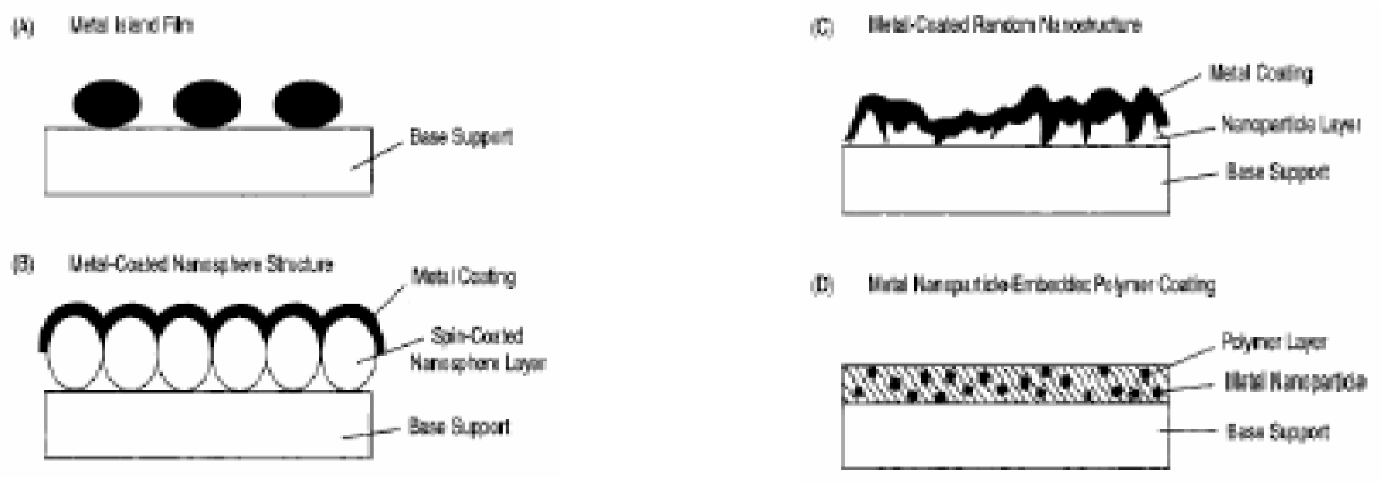
How does SERS work?

  - The most common and still most versatile Raman spectrometers utilize holographic dispersive gratings and CCD multichannel detectors. These spectrometers are useful from the UV to the near IR spectral region.

- Detectors
  - Photomultipliers were the standard detectors used until recently.
  - CCD (charge coupled detector) are now more commonly used.

How does SERS work?

- SERS substrates commonly used
  - Silver (Ag), gold (Au) and copper (Cu)
  - The energy required to generate plasmons matches the light sources typically used in Raman spectroscopy
- Surface preparations
  - Largest enhancements for rough surfaces of 10 – 100 nm



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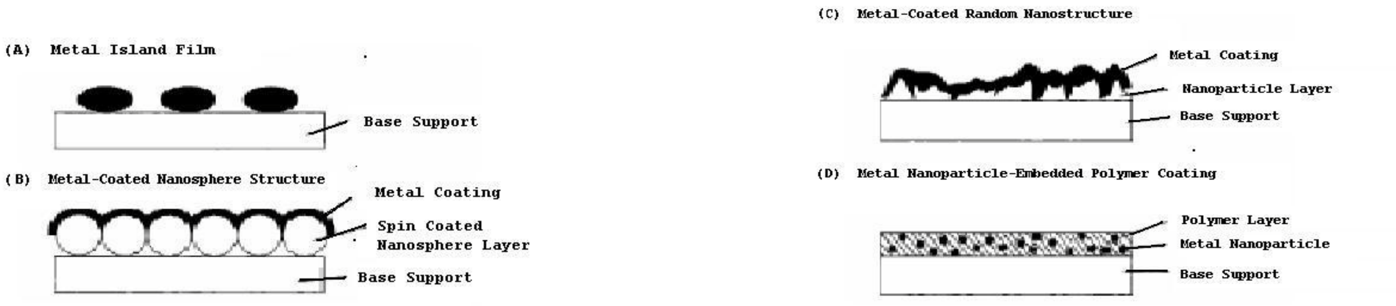

What information is obtained using SERS?

- SERS is used to investigate the vibrational properties of adsorbed molecules yielding structural information on the molecule and its local interactions.
- Uniquely identifies molecules.
- Enables the detection of individual molecules.

“Applications of Reproducible SERS Substrates for Trace Level Detection”
Netti and Stanford
(sic – 300 ppm should read 300 ppb)

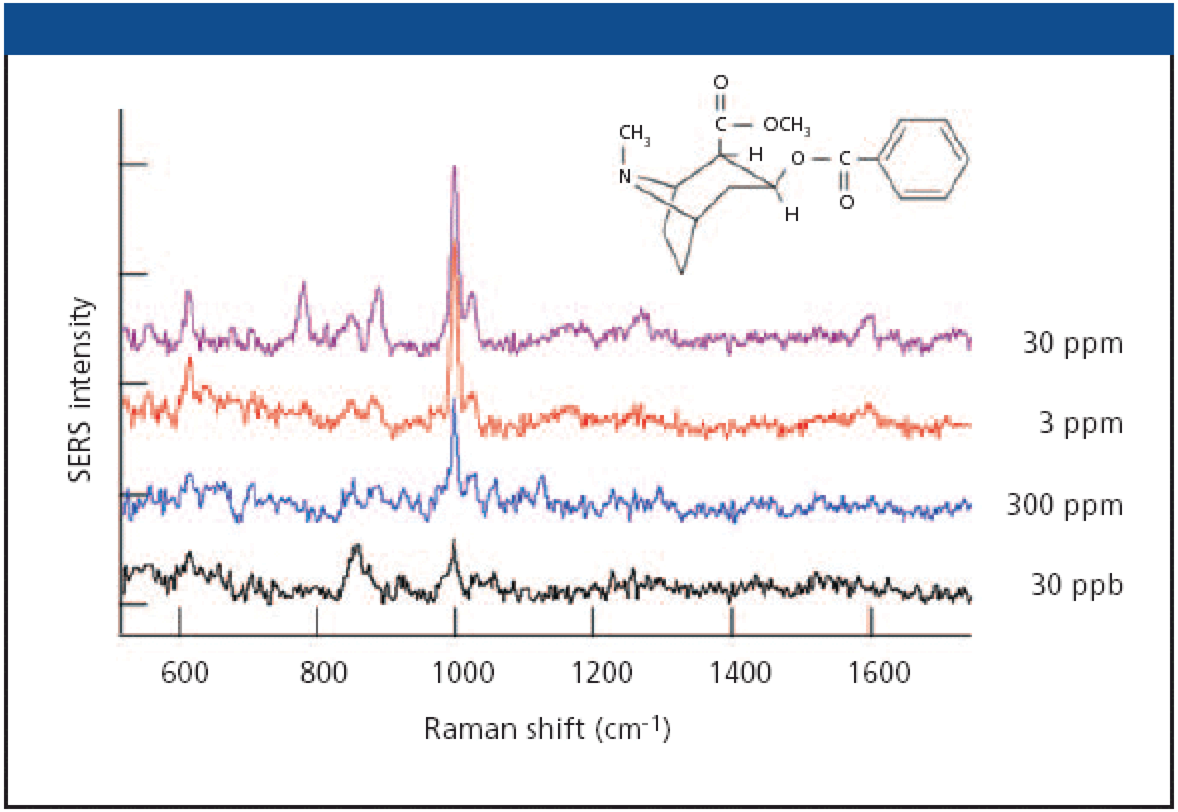

Figure 4: SERS spectra of cocaine aqueous solutions for concentration ranging from 30 ppm (30 μg/mL) to 30 ppb (30 ng/mL). The spectra were acquired with an analytical-grade Raman system with a 10-s exposure at 785 nm.

“Applications of Reproducible SERS Substrates for Trace Level Detection”
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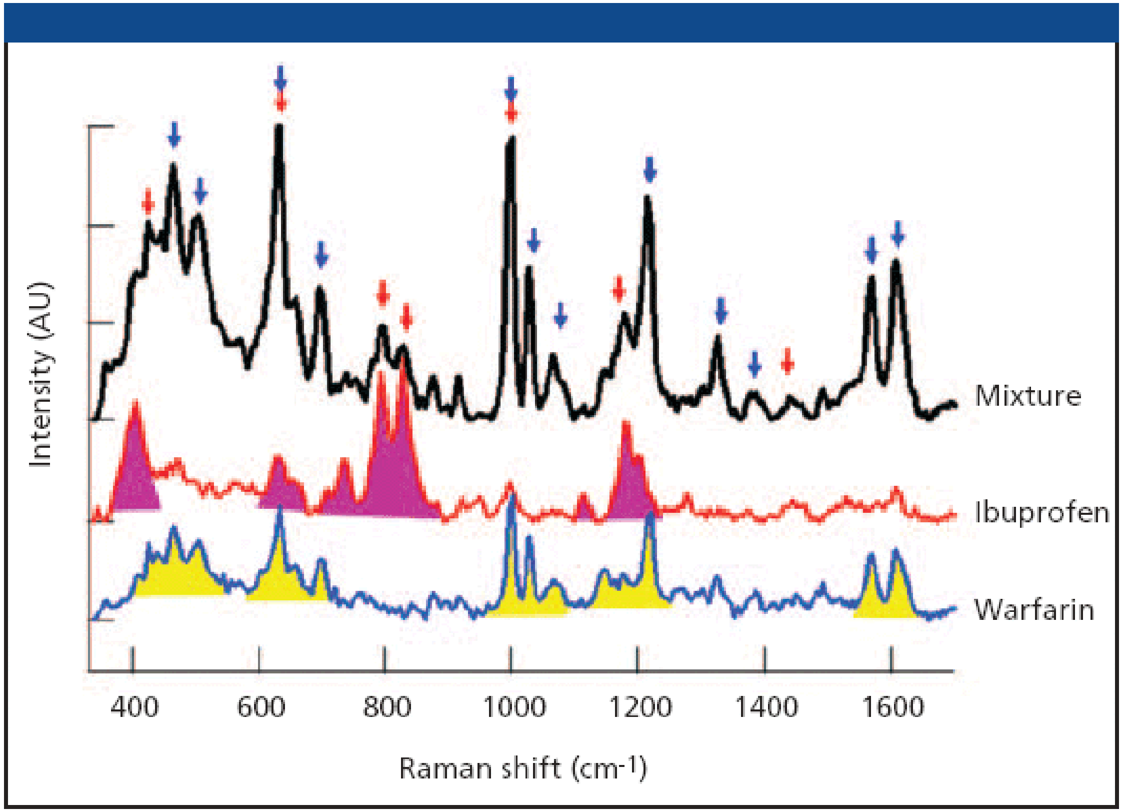

Figure 5: SERS spectra of Ibuprofen (red line) and Warfarin (blue line) acquired with analytical-grade Raman systems. The main modes of each component are highlighted in the graph. The SERS spectrum of a mixture of equal volumes (0.1 mL) of Ibuprofen (2 mg/mL) and Warfarin (3 mg/mL) is also reported (black line). The blue and red arrows mark the vibrational modes of the warfarin and ibuprofen components, respectively.

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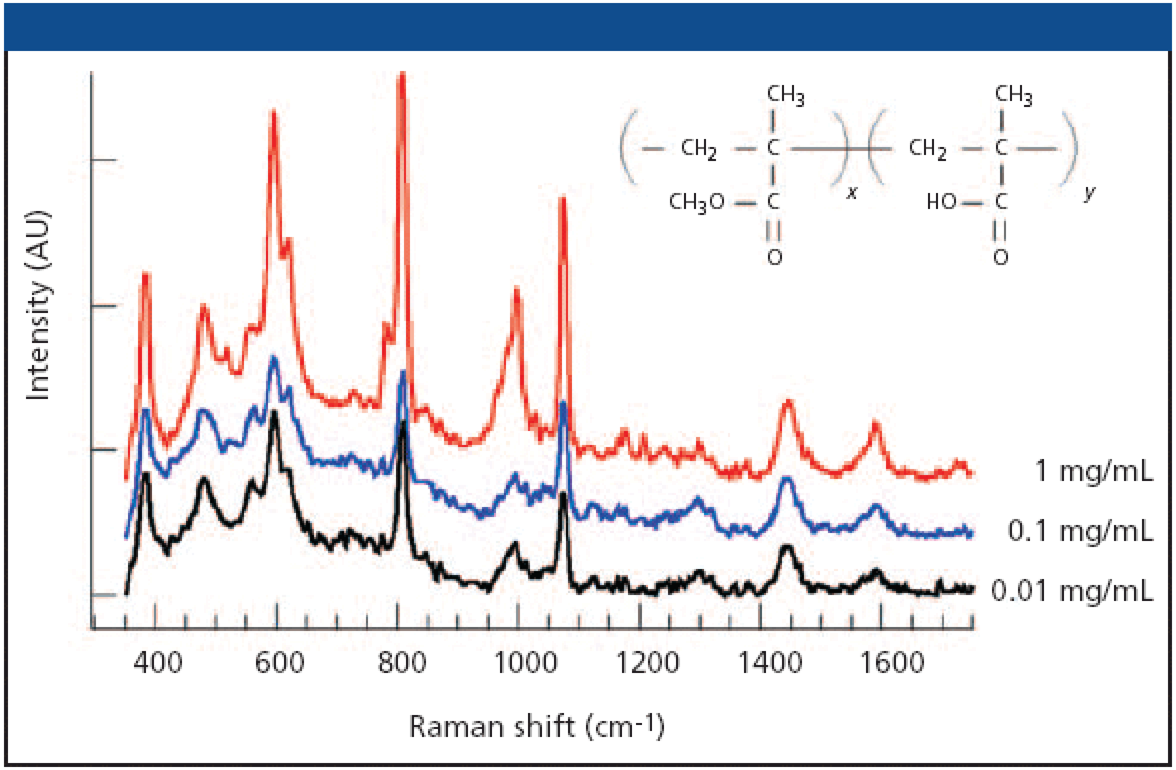

Figure 6: SERS spectra of copolymer toluene solutions – poly(methyl methacrylate–co-ethyl acrylate) – at three different concentrations (1, 0.1, and 0.01 mg/mL).

Why use SERS?

- High sensitivity
- Specificity
- Valuable tool for analyzing mixtures
- Low-power lasers and low magnification optics are suitable to acquire SERS spectra in very short acquisition times (typical ~10 s).
- Many applications—biochemistry, chemical manufacturing, environmental detection, forensics.

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