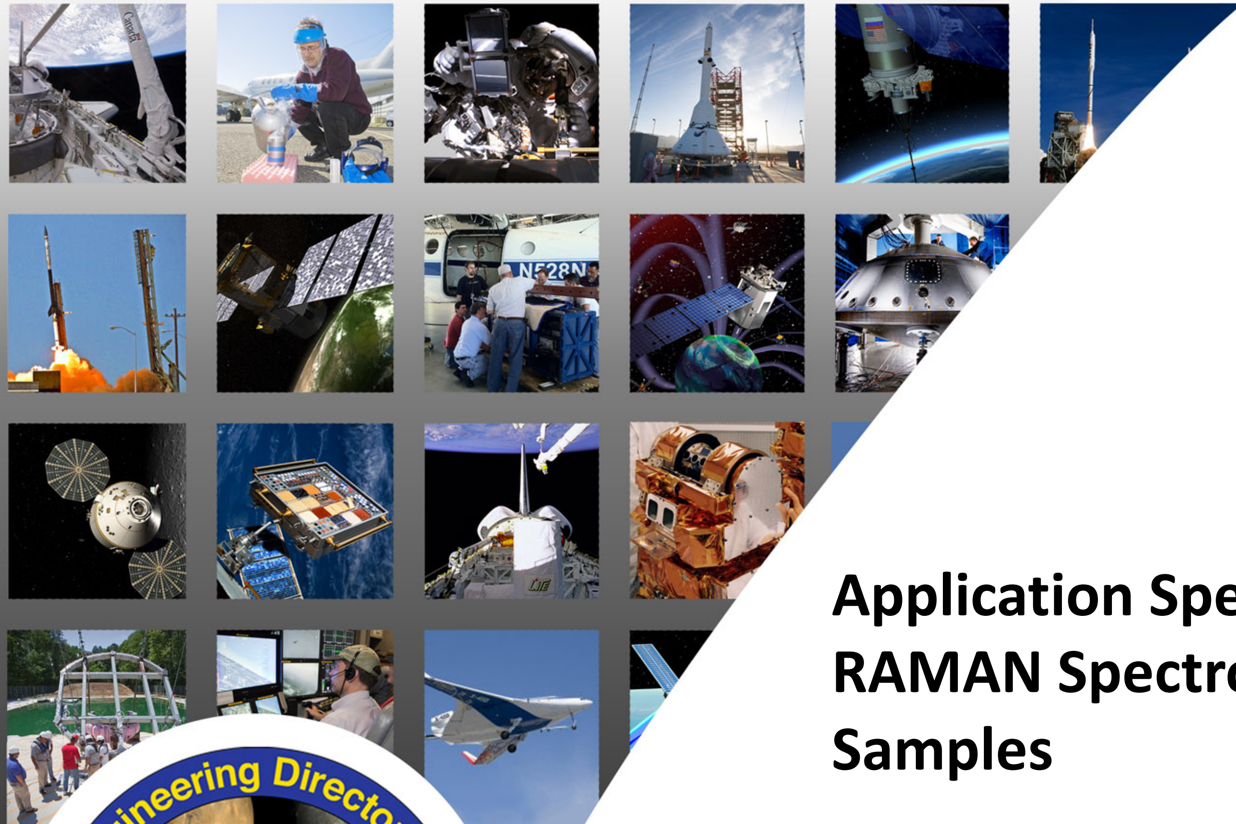

Application Specific Substrates for RAMAN Spectroscopy of NVR Samples

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11-06-2019

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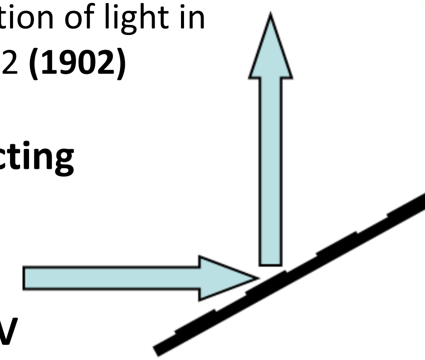
Background – Robert W. Wood's Anomaly

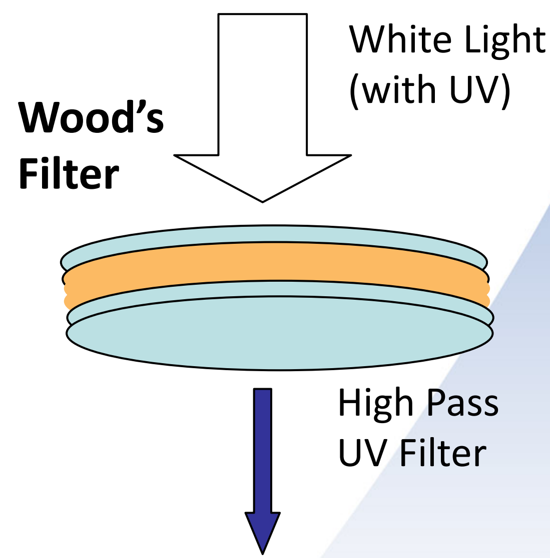
Light of certain wavelengths was not reflected for specific gratings (material, spacing and angle)

R.W. Wood, "On a remarkable case of uneven distribution of light in a diffraction grating spectrum." Philos. Mag. 4, 396–402 **(1902)**



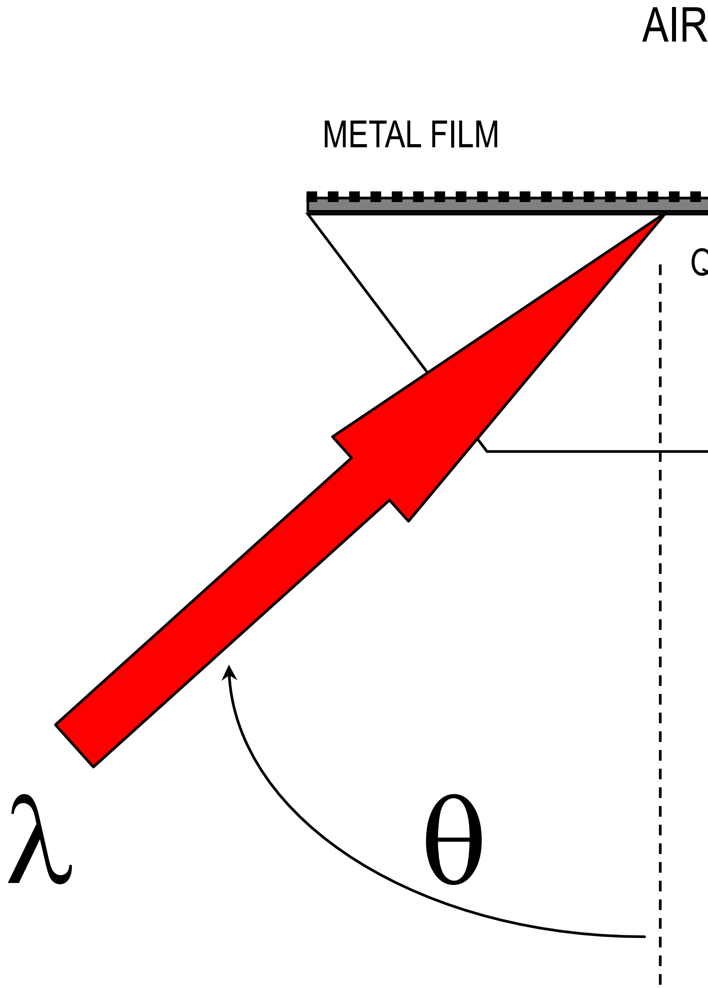
- **Early in the last century, an odd behavior was found in the light interacting with a grating**
- **"Wood's anomaly" is a surface plasmon effect resonance effect**
- **Another plasmon related development is a Wood's filter that allows UV light to pass by exploiting the metal's transparency above the plasmon resonance (which is in the UV for metals such as potassium).**
- **Our eyes cannot see light at the plasmon energy, so this behavior is outside of our everyday experience**

Metal	λ (expt)	λ $(2\pi c/\omega_P)$	Energy
Li	155 nm	155 nm	8.0 eV
Na	210 nm	209 nm	5.9 eV
K	315 nm	287 nm	3.9 eV
Rb	340 nm	322 nm	3.6 eV



UV Wavelengths at which a metal becomes transparent: table from C. Kittel Intro to Solid State Physics

ATR: Attenuated Total Reflection (Kretschmann Configuration)



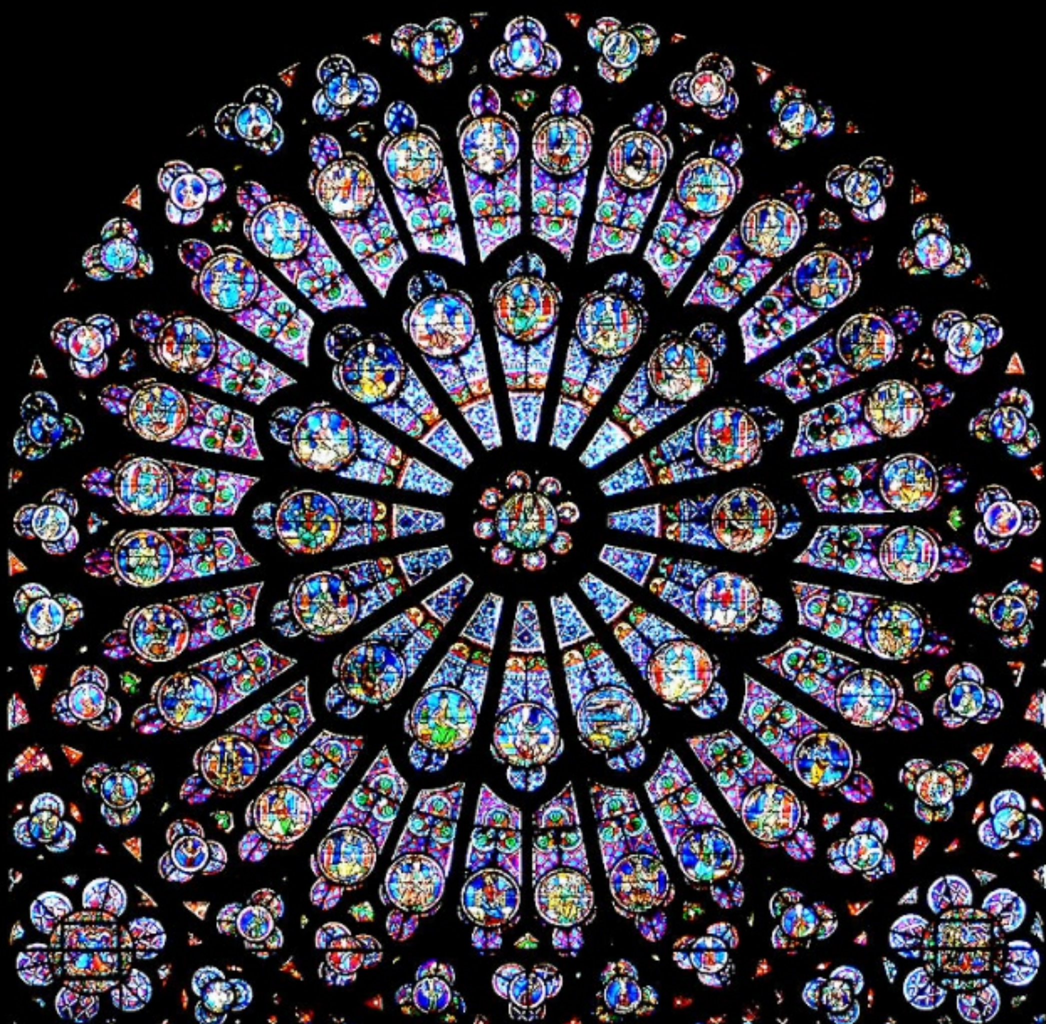
Direct photon excitation of a surface plasmon (S.P.) from vacuum is allowed because the phase velocity of the S.P. can equal the speed of light in prism.

$\omega_{SP} < c_{prism}$

$\omega_{SP} < c_{vac}$

Even Attenuated Total Reflection (ATR) Experiments with small HeNe lasers can produce enough Plasmon energy to destroy the metal film (usually silver because of low surface plasmon E).

2D & 3D Charge Density Waves: “Plasmons”



Plasmons are collective excitations of bound and free electron density in a solid and are a fundamental property of the material.

These oscillations run as **longitudinal waves** of charge density through the crystal volume or along the surface…

“For hv < hωp there is little coupling of the electron to the photon field. Bulk plasmons cannot be excited because of energy conservation. Surface plasmons do not couple to the photon field because of momentum conservation. [Surface roughness, though, can provide enough momentum transfer to see light emission due to surface plasmons as an extrinsic effect…]”

W. Drube, F. J. Himpsel & P. J. Feibelman
‘Inverse of the Photoelectric Effect in Al’
PRL, 60, 2070 (1988).

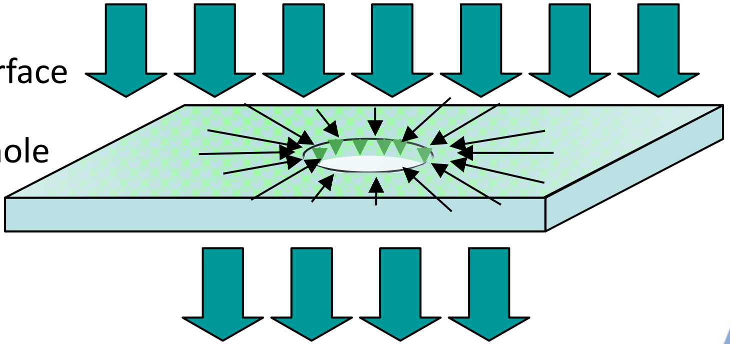
2D Metal Films Exhibit these plasmon behaviors:

Extraordinary Optical Transmission is Such a Process

Transmission of UV light can occur through holes in a metal film,
despite the holes being smaller than the diffraction limit for that wavelength of light

UV Light excites Surface Plasmons on a metal film surface

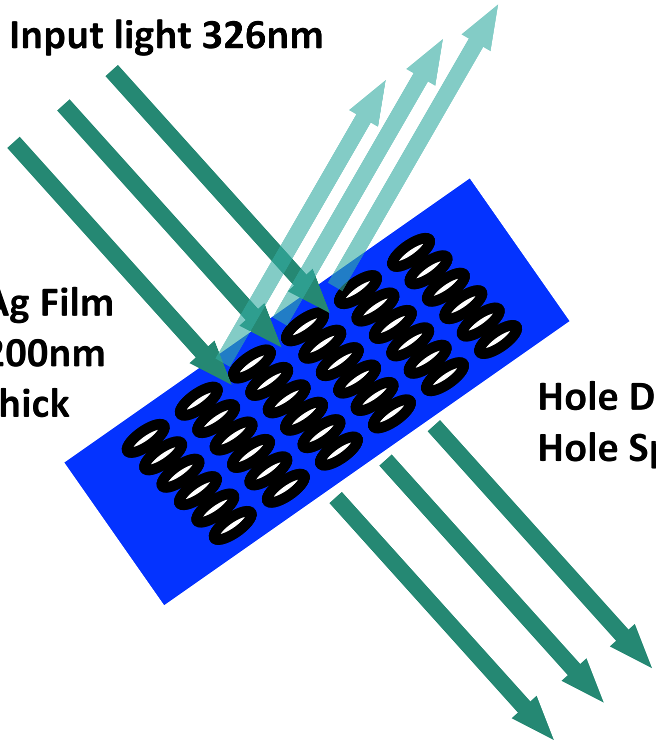
Surface Plasmons Move on the surface & through the hole



UV Light is emitted when the Surface Plasmons radiatively decay on the back surface

Input light 326nm

Ag Film 200nm thick



Hole Diameter 150nm
Hole Spacing 900nm

T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio & P. A. Wolff, **Nature**, vol 391, pp 667–669 (1998)

Review of SERS Substrates for Chemical Sensing
Nanomaterials (Basel) 2017 Jun; 7(6): 142 Pamela A. Mosier-Boss
doi: 10.3390/nano7060142

Most common substrates are Ag, Cu & Au

- Good: Narrow peaks (high resolution, multicomponent analysis possible)
- Bad: Substrates – In intimate contact with analyte; lifetimes; reusability
- Ugly: Results – sample homogeneity; data reproducibility

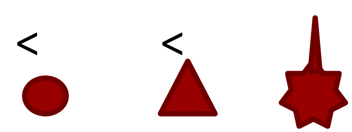
Lessons Learned for SERS

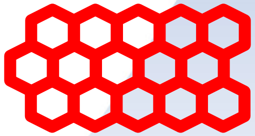
- Surfaces: roughened; good wetting; relatively SERS high cross-section for analyte; watch for substrate SERS response changes over time
- Process: control excitation intensity (avoid surface photochemistry); avg. enough samples to limit reproducibility & homogeneity issues

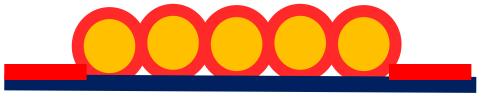
Common Designer Substrate Schemes

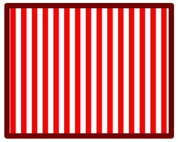
Tian F., Bonnier F., Casey A., Shanahan A.E., Byrne H.J. SERS with Au Nanoparticles: Effect of Particle Shape. Anal. Methods. 2014;6:9116–9123. doi: 10.1039/C4AY02112F

- Deposited metal nanostructures;
- Soft Lithography (nano-hexagons ?)
- NanoSpheres coated with metal
- eBeam structures



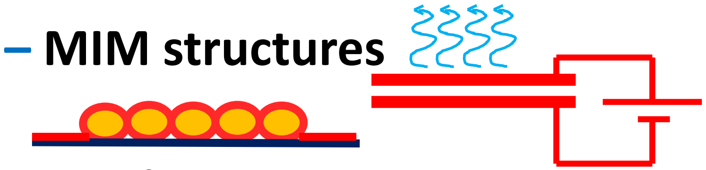






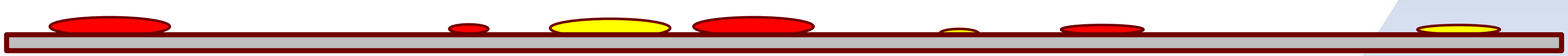
The Key Problem in Using Surface Enhanced Raman Spectroscopy is coupling into the Substrate

- Wood's 1905 solution - **make a grating structure on metal film**
- Whitesides et al – **use soft lithography to make periodic structures**
- Chemistry, Photochemistry or Electrochemistry – **make metal nanoparticles**
- J Lambe & SL McCarthy PRL 37, 923 (1976) – **MIM structures**
  "Light emission from Inelastic Tunneling"

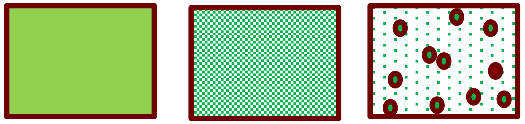


- Kretschmann - **Dovetail Prism (more used in FTIR)**
  - Photochemistry? (John Hemminger)

- **Still need to pick the best substrate (cross-section & stability/lifetime)**
  - Au, Ag, Cu
  - Have known surface wetting issues
  - Also have complicating effects (e.g. mixed Au & Ag islands can be tuned to 2 resonances)



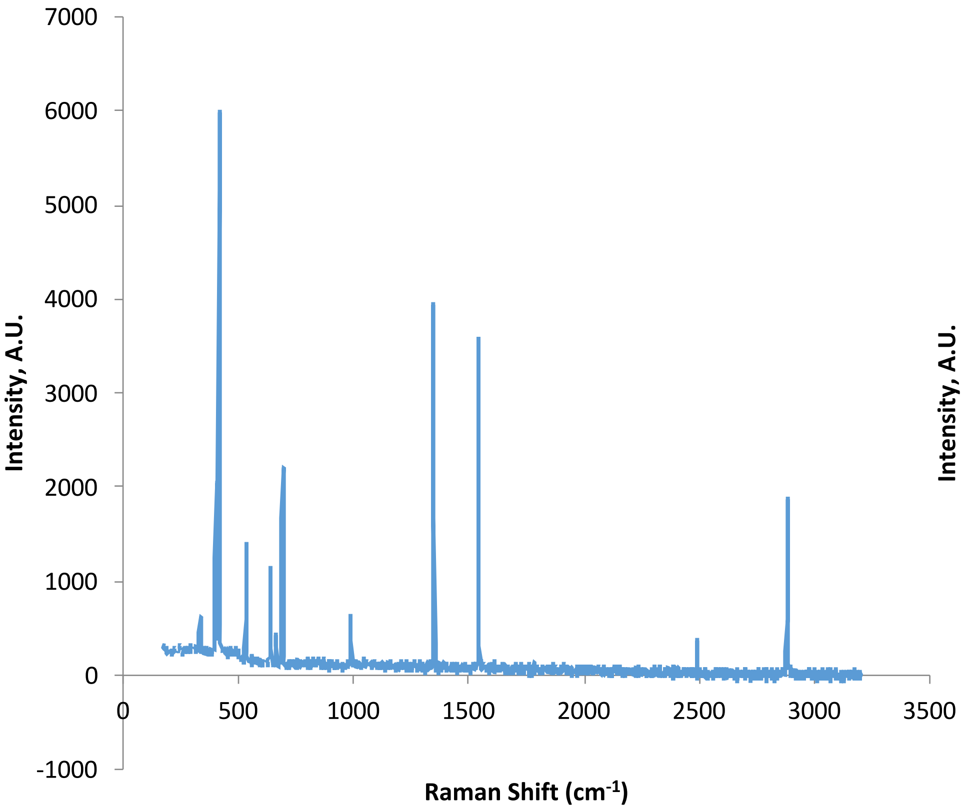
- **Reconsider solvent – analyte issues**



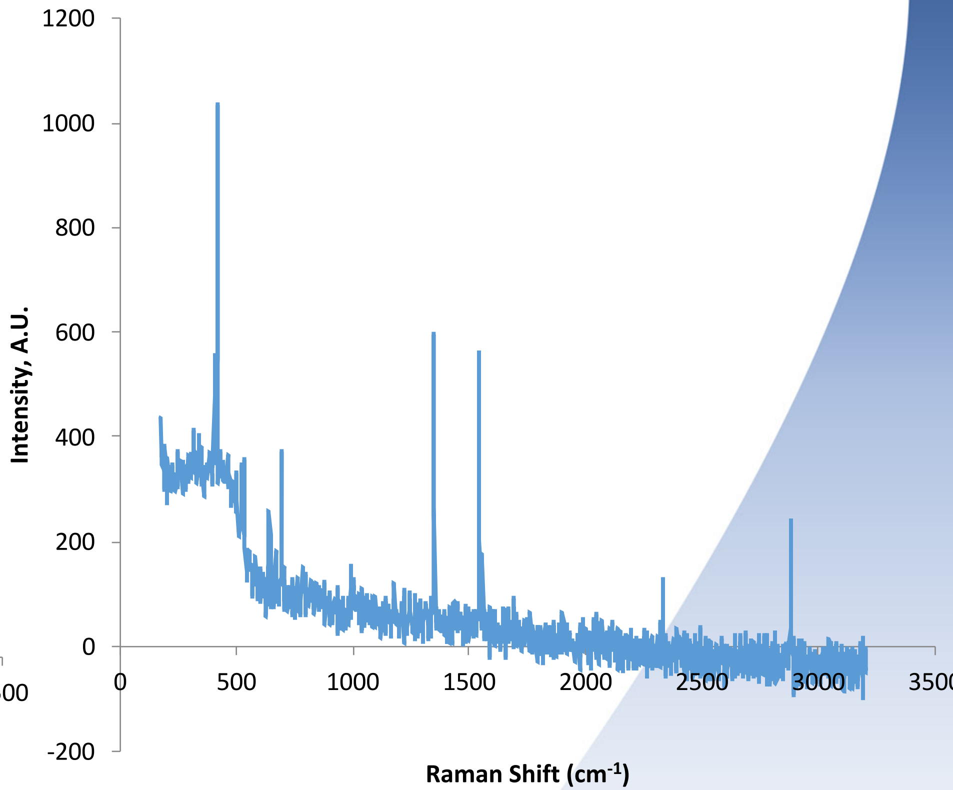
SERS of a Model Contaminant
DC704

Comparison of the same sample on an Aluminum and Gold Substrate

Sample Al_785nm_Sample S4_Raman



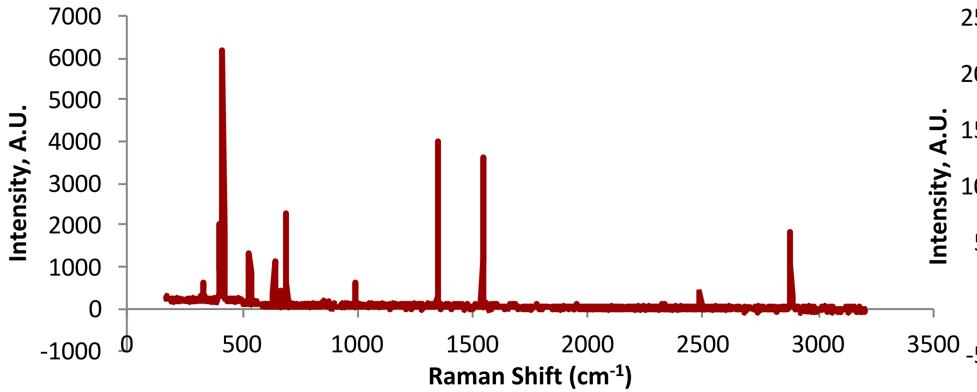
Au_785nm_Sample_S4 Raman



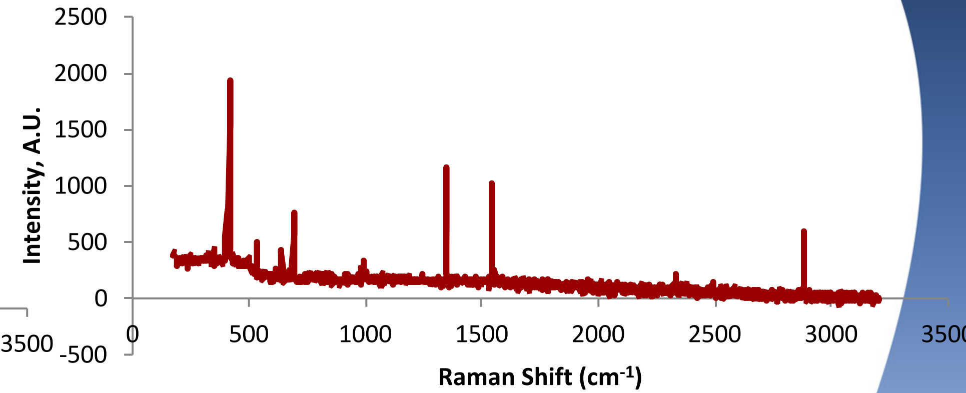
Aluminum is a better substrate material than Gold for this analysis

SERS 785 nm of DC704 on Aluminum

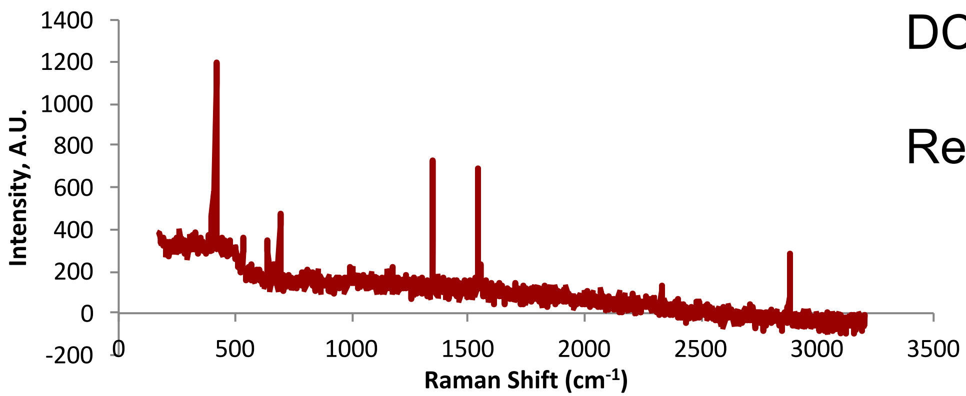
Sample Al DC704 S400 Raman Data



Sample Al DC704 S200 Raman Data



Sample Al DC&04 S100 Raman Data

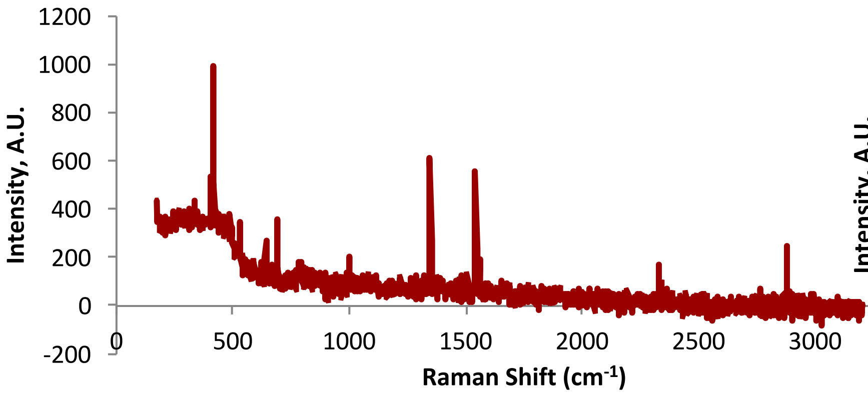


DC704 on Al response is ~ linear

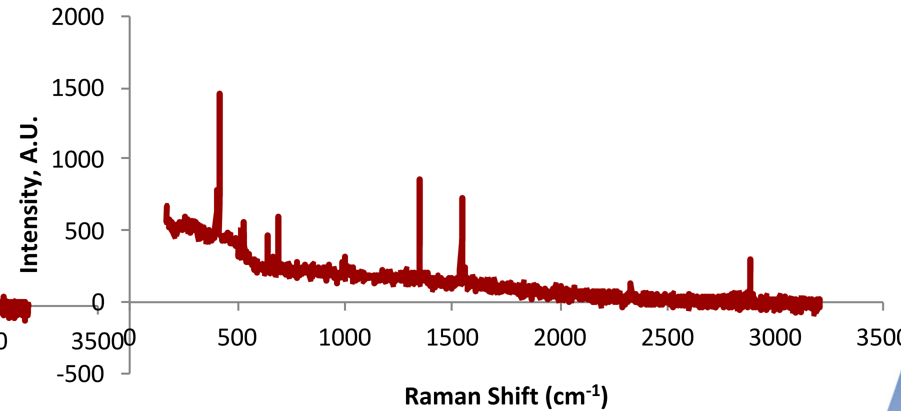
Repeatability is OK (with caveats)

SERS 785 nm of DC704 on Gold

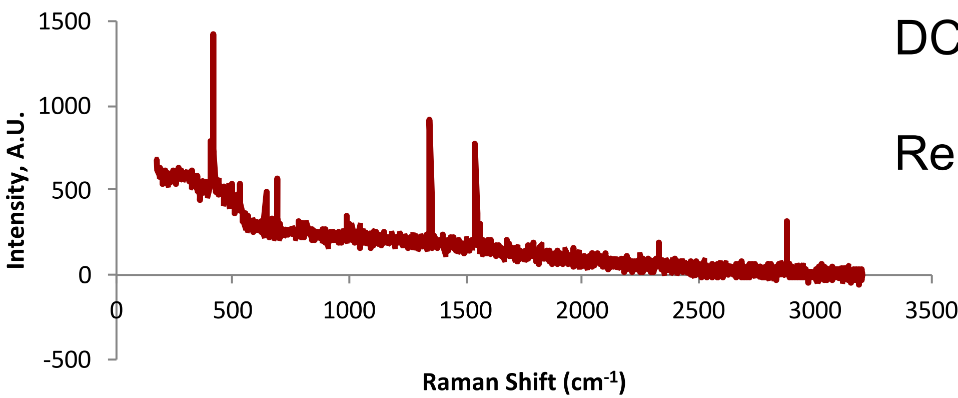
Sample Au DC704 S400 Raman Data



Sample Au DC704 S100 Raman Data



Sample Au DC704 S050 Raman Data



DC704 on Gold response is variable

Repeatability is bad (with caveats)

Observations

- **The (laser excitation and sample detection) focus position contributes a lot to the SERS response.**
  - Focus position seems more important when the Raman coupling is weak
  - Will try to employ an internal standard – although that has problems too
- **The relative SERS cross-section is very important**
  - Raman Laser excitation wavelength
  - Sample response
  - Substrate response
  - Surface issues
- **While the SERS approach can offer multicomponent information, quantitative measurements on multiple components are suspect**

Conclusions… So Far

- **I never got to the “designer” SERS substrates in this work.**
  - Quite a few are available commercially.
  - There are some promising avenues to improve the results
  - However, the most basic exploration of relative SERS response takes time and is a necessary prerequisite for “designer” substrates
- **SERS requires method development**
  - This is true both as a qualitative and quantitative method
  - One size does not fit all – not wavelengths, substrates, or analytes
- **If a workable basic SERS approach has been found,**
  - It should be possible to tailor the technique for rapid sample analysis with specificity
  - Refining the technique to perform a multiple component analysis can be considered, but SERS is likely to be one of several methods employed.