电子科技大学
University of Electronic Science and Technology of China

Surface Enhanced Raman Spectroscopy

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- What is SERS?
- A quick review on plasmons...

- Our Samples
- Experimental set-up
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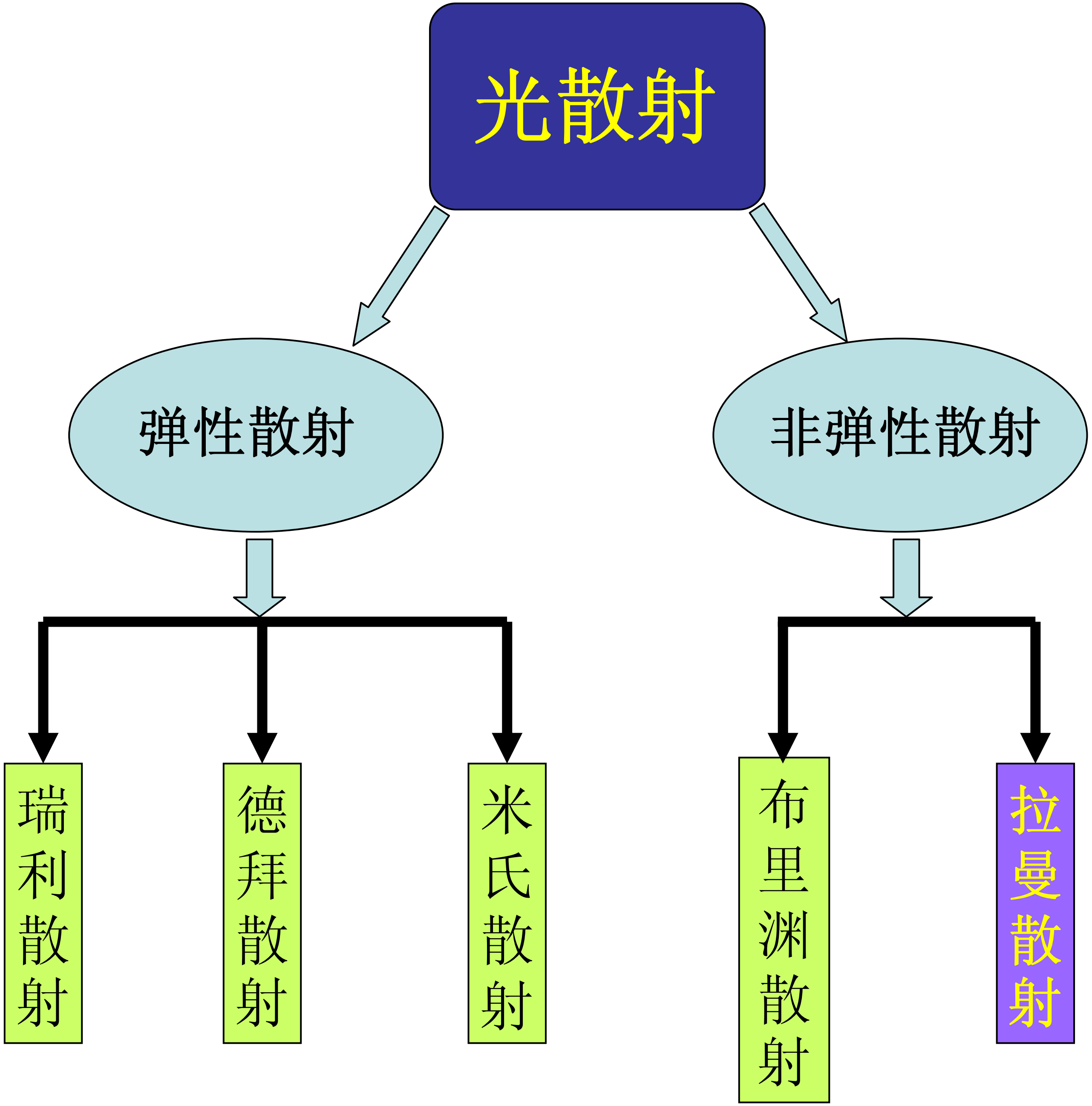


光散射
弹性散射
非弹性散射
瑞利散射
德拜散射
米氏散射
布里渊散射
拉曼散射

拉曼光谱定义

拉曼散射光谱: **1928**年**C.V.**拉曼实验发现，当光穿过透明介质被分子散射的光发生频率变化，这一现象称为拉曼散射，同年稍后在苏联和法国也被观察到。靠近瑞利散射线两侧的谱线称为小拉曼光谱；远离瑞利线的两侧出现的谱线称为大拉曼光谱。瑞利散射线的强度只有入射光强度的10^{-3}，拉曼光谱强度大约只有瑞利线的10^{-3}。小拉曼光谱与分子的转动能级有关，大拉曼光谱与分子振动-转动能级有关。分子能级的跃迁仅涉及转动能级，发射的是小拉曼光谱；涉及到振动-转动能级，发射的是大拉曼光谱。与分子红外光谱不同，极性分子和非极性分子都能产生拉曼光谱。

激光器的问世，提供了优质高强度单色光，有力推动了拉曼散射的研究及其应用。拉曼光谱的应用范围遍及化学、物理学、生物学和医学等各个领域，对于纯定性分析、高度定量分析和测定分子结构都有很大价值。

Introduction

- Raman Scattering is useful in 'fingerprinting' molecules. Unfortunately it is a very weak process.

- Surface Enhanced Raman Spectroscopy (SERS) uses metal to enhances the electric field.

- SERS gives a strong Raman signal but often has poor reproducibility.

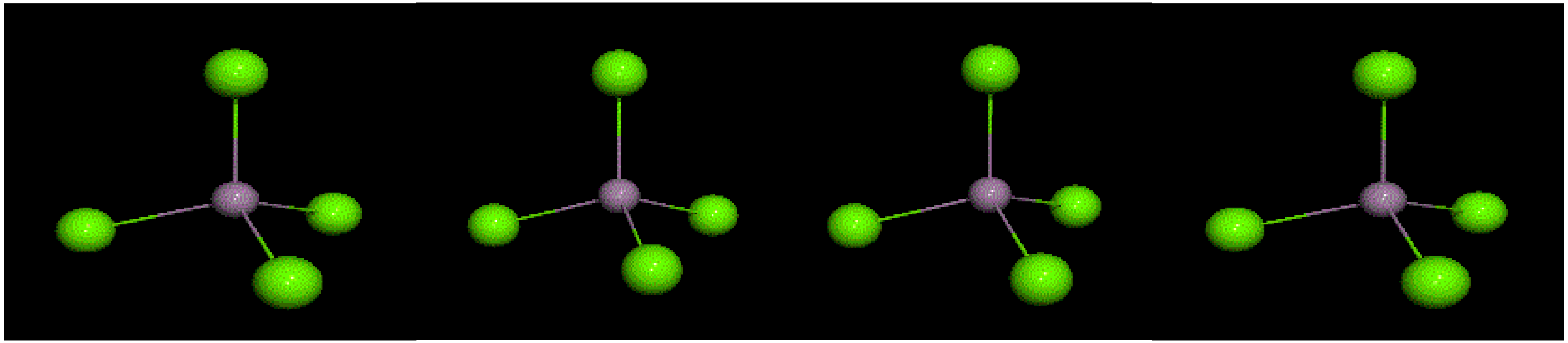
- By 'tailoring' the plasmonic properties of metals we can understand how to produce excellent reliable SERS signals.

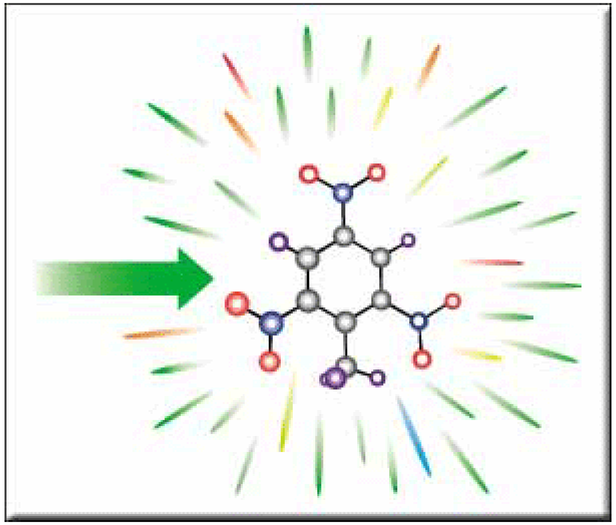
Sir Chandrasekhara V. Raman

Discovery year: 1928

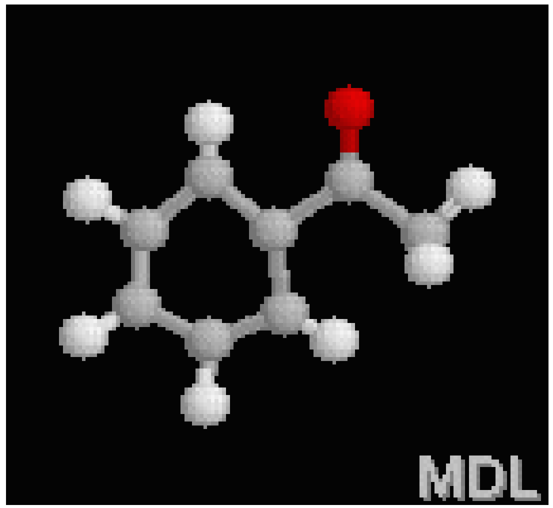
Raman won the Nobel Prize in Physics in 1930 for this discovery accomplished using sunlight, a narrow band photographic filter to create monochromatic light and a "crossed" filter to block this monochromatic light. He found that light of changed frequency passed through the "crossed" filter.

What Exactly Is Being Measured?

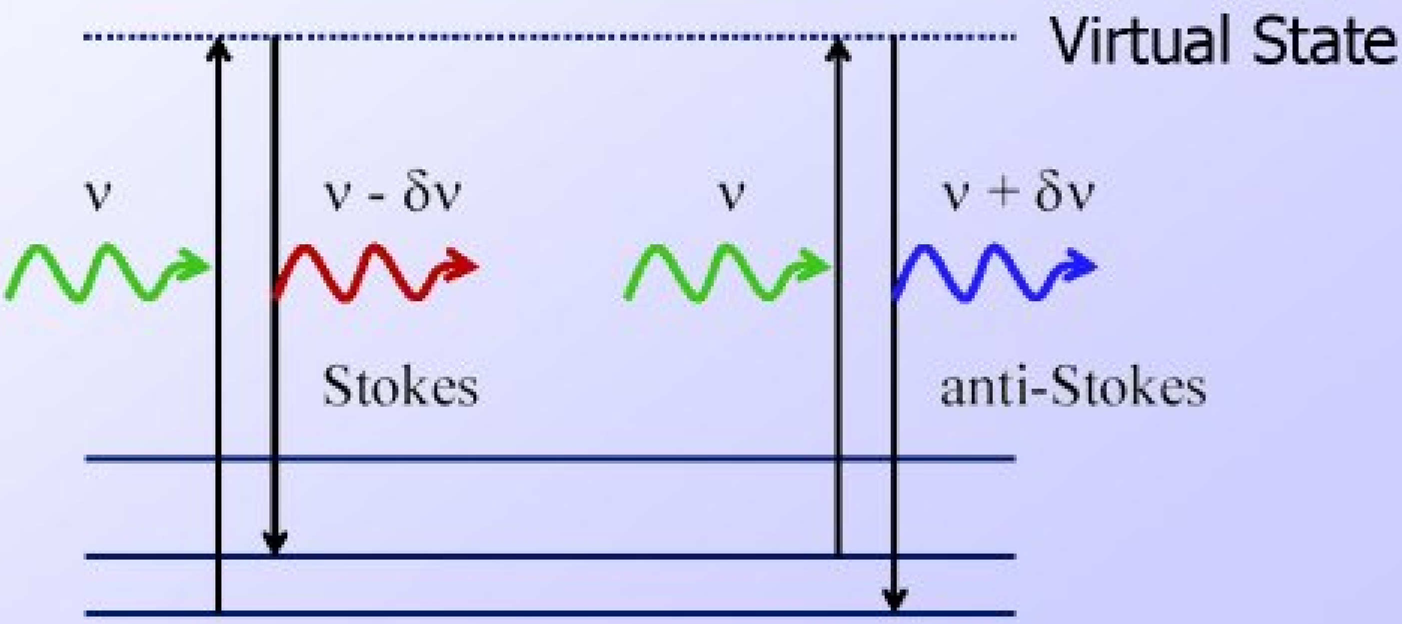




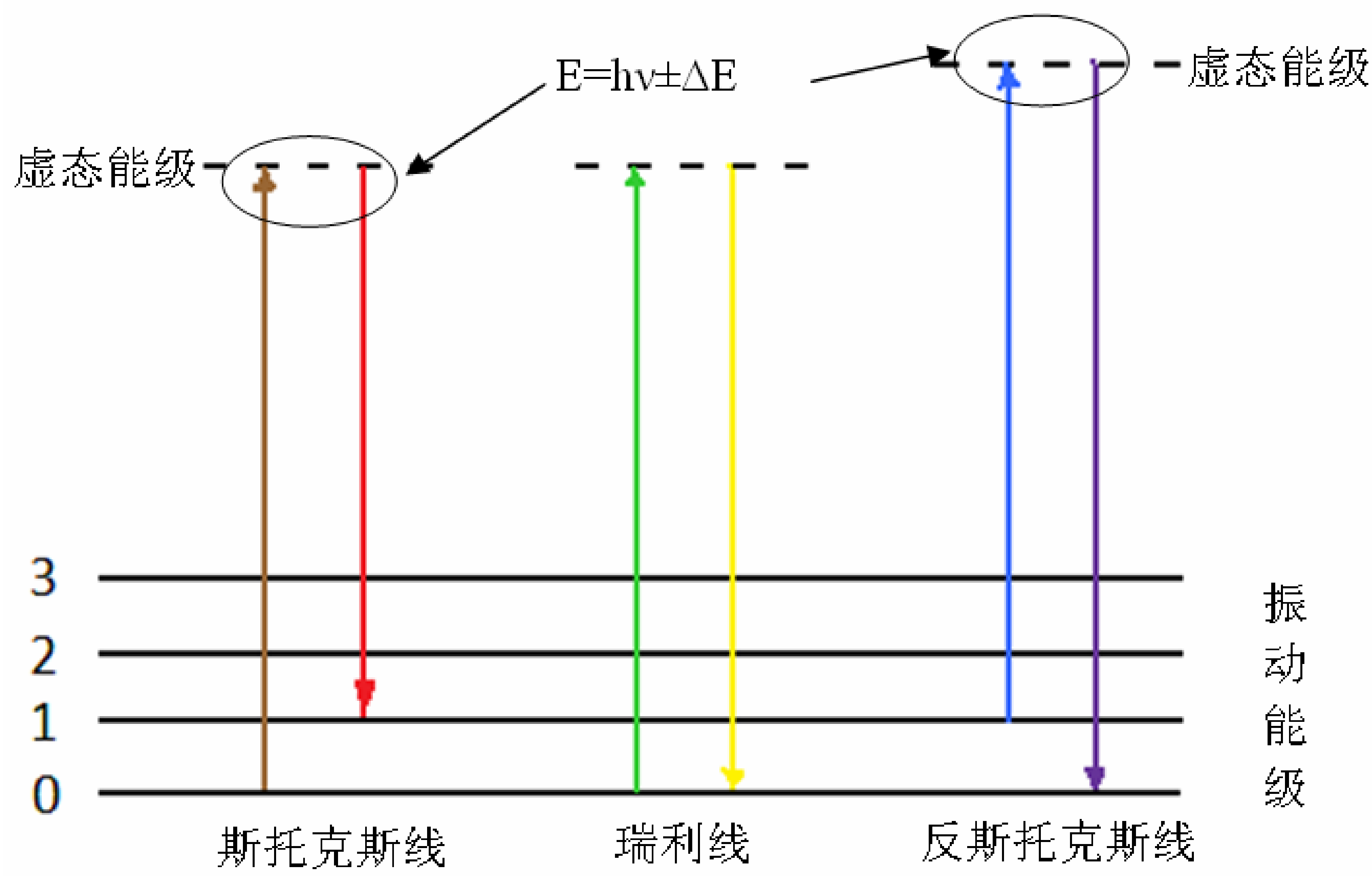
When Light hits a sample, It is Excited, and is forced to vibrate and move. It is these vibrations which we are measuring.



Raman Scattering



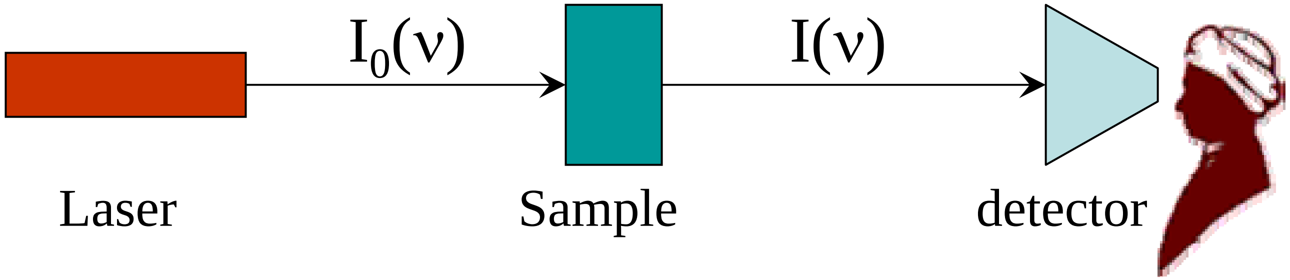
Energy Scheme for Photon Scattering



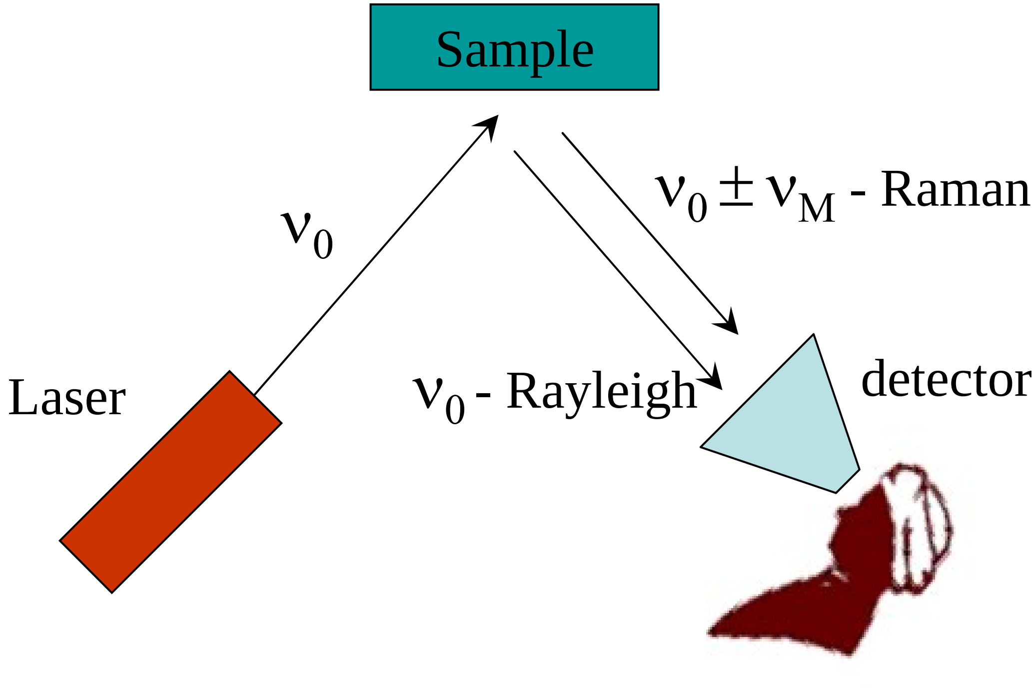
拉曼散射光谱示意图

Δν称为拉曼频率（或拉曼频移，通常用波数cm-1表示），是由散射系统本身的性质所决定，对应于物质的某两个能级(振动、转动或电子能级)之间的差值，即$h\Delta\nu=\Delta E$。它与入射光频率ν_0无关，仅取决于样品分子本身固有的振动和转动能级的结构及状态，选用不同频率的激发光都可以观察到相同的Δν值。拉曼光谱谱峰通常较狭窄，具有准确的特征标志，拉曼频移物质结构的任何微小变化都会非常敏感反映在拉曼光谱中，所以Δν可用来**对物质进行结构分析**。而拉曼强度反映了分子在不同能级上的分布和跃迁几率，而且正比于物质分子的浓度，可以用来**对分子含量进行定量分析**。

IR Spectrography - Absorption

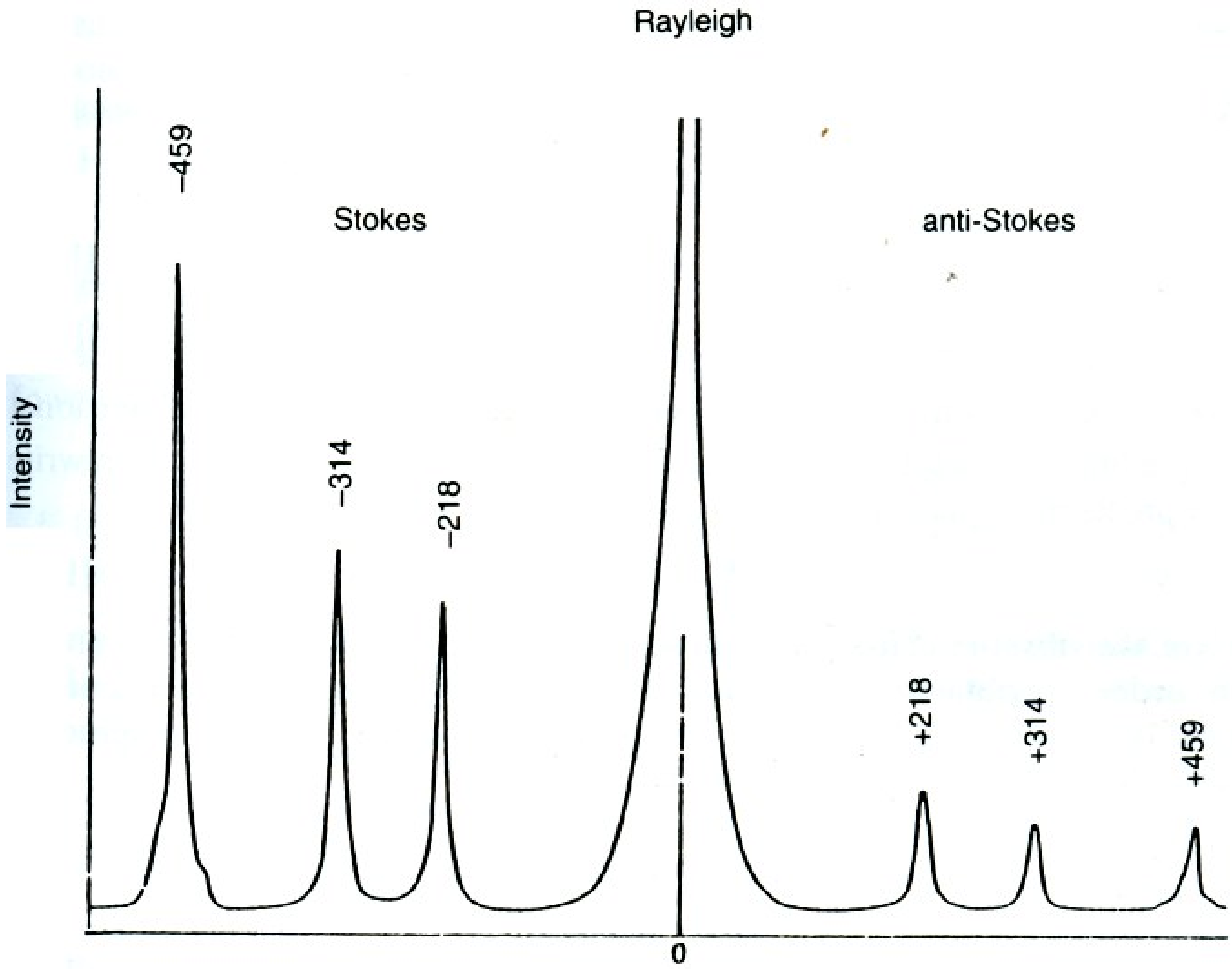


Raman Spectrography - Scattering



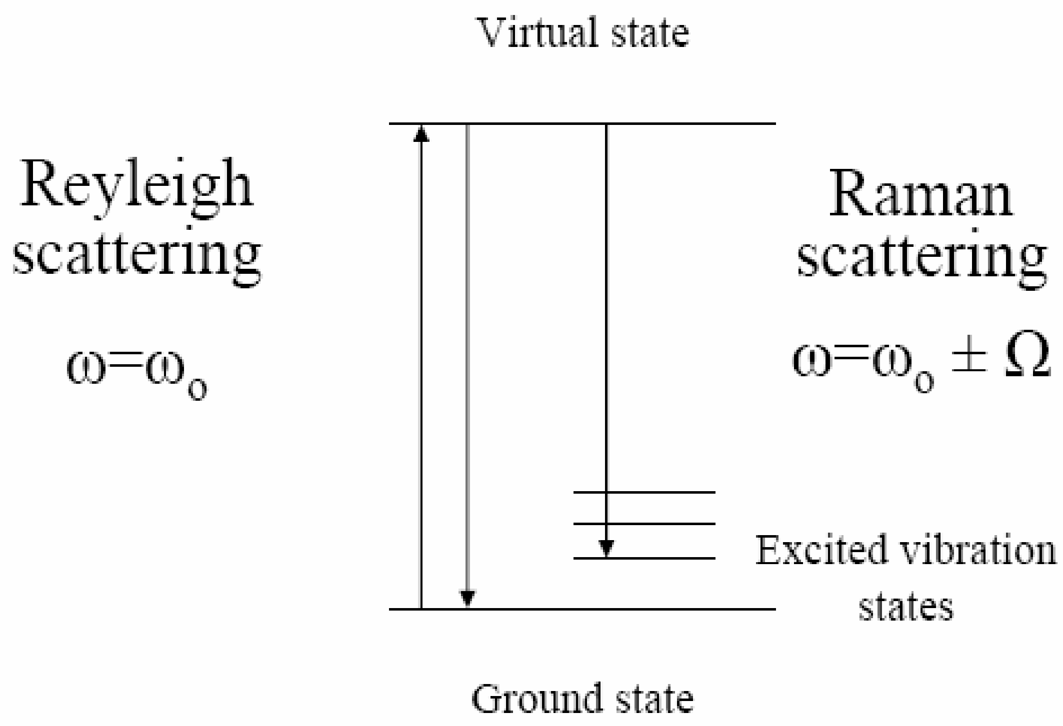
Raman Spectrum

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wavenumbers, cm^{-1}). This difference is called the *Raman shift*.



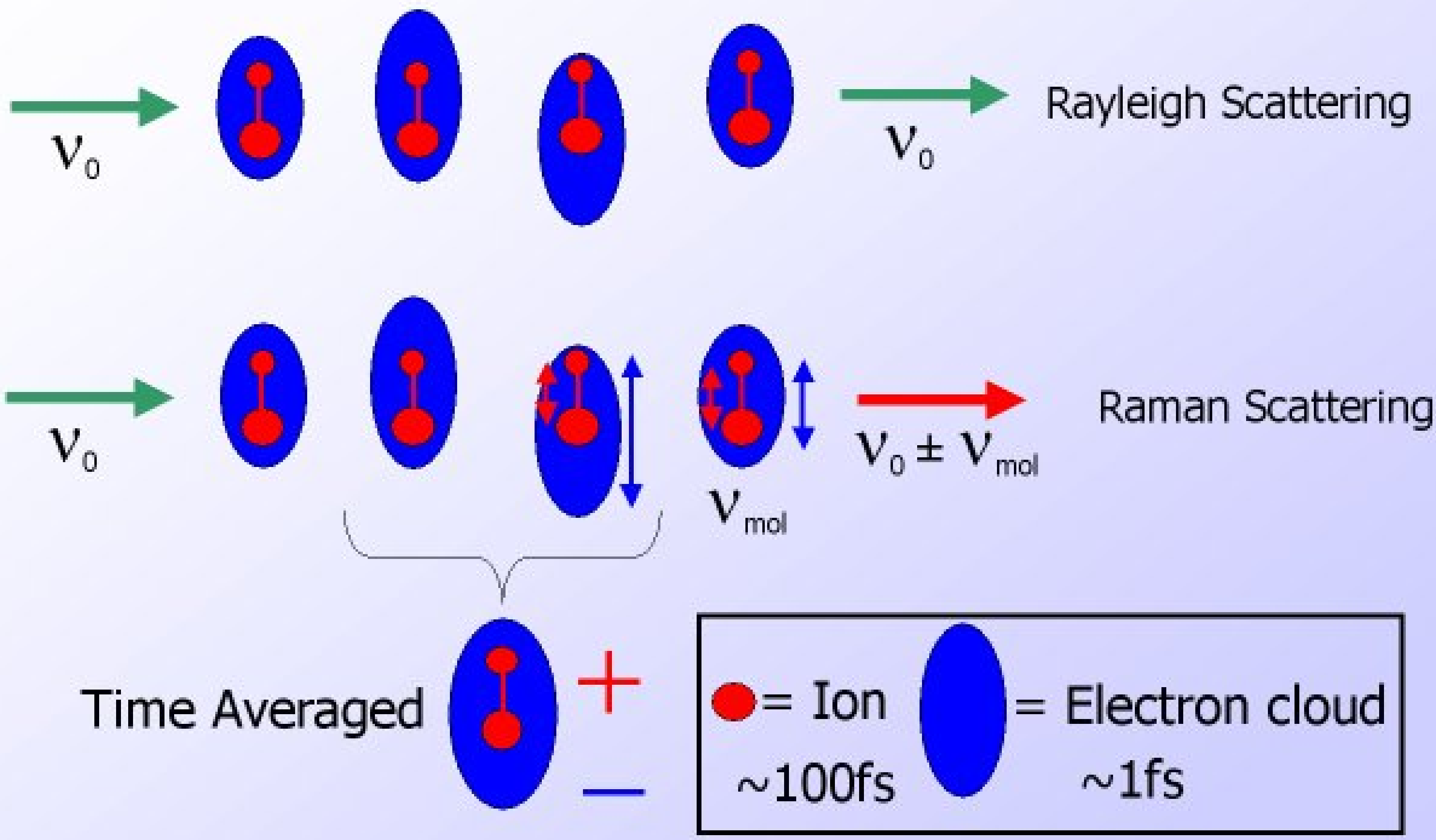
Raman Spectrum of CCl_4

What is Raman scattering?

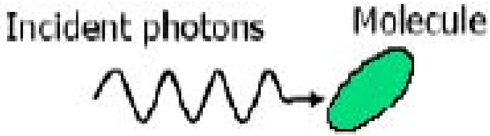


Frequencies of the incident and scattered photons are different due to the energy loss caused by molecular vibration.

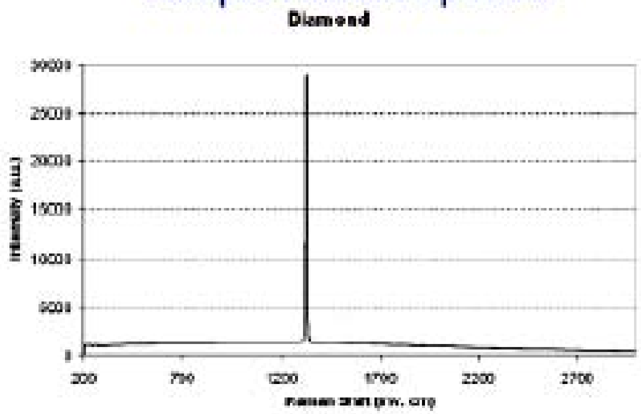
Raman Scattering



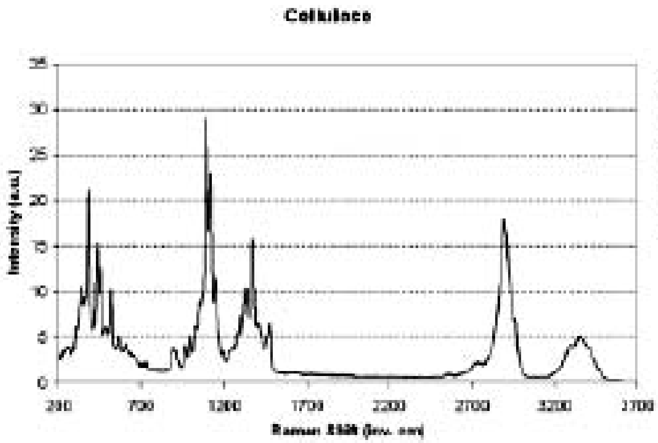
Raman scattering



Sample Raman Spectra

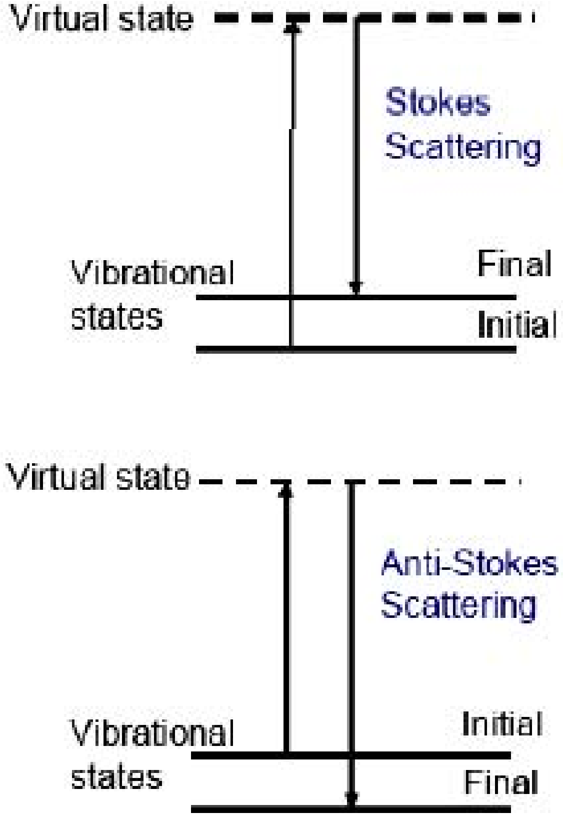


Diamond:
- C-C lattice
- Only one bond type
- One Raman band



Cellulose ($C_6H_{10}O_5$):
- Organic molecule
- Many bond types
- Several Raman bands

Raman Scattering Energy Diagrams



Raman scattering

- Raman scattering is a weak effect
  - Raman scattering cross section ~10^{-30} cm^2
- If we can increase the local fields we can obtain a larger *effective* scattering cross section
  - More Raman scattering (higher signal)
  - Lower detection limits
- How can we increase the local fields?
  - Plasmon excitation produces induced fields
  - Fields can be localized and intense
  - Raman scattering scales with E^4
  - Surface-enhanced Raman scattering (SERS)

Raman scattering

Applications:

Insulin Analog Detection

- Millions of diabetics, many who must use insulin daily
- Insulin (Humulin) is slow-acting, while Humalog is fast-acting
- Humulin and Humalog are very hard to distinguish from each other

Protein Binding Detection

- Binding responsible for many processes in the body
- Key for diagnostics
- Drug development research

Issues to address with plasmonic bio-sensing

Fabrication
Lithography
Integration in larger units
High yield

Stability
Can it be used over and over again, even after long time?

Specificity
Recognizable sensing?

Multifunctional capability?
(use of shape/size)

Big issue in high protein concentration environments.

Chemistry
Biocompatibility

Understanding of protein-surface interactions.

Surface Enhanced Raman Spectroscopy

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.

Surface Enhanced Raman Spectroscopy

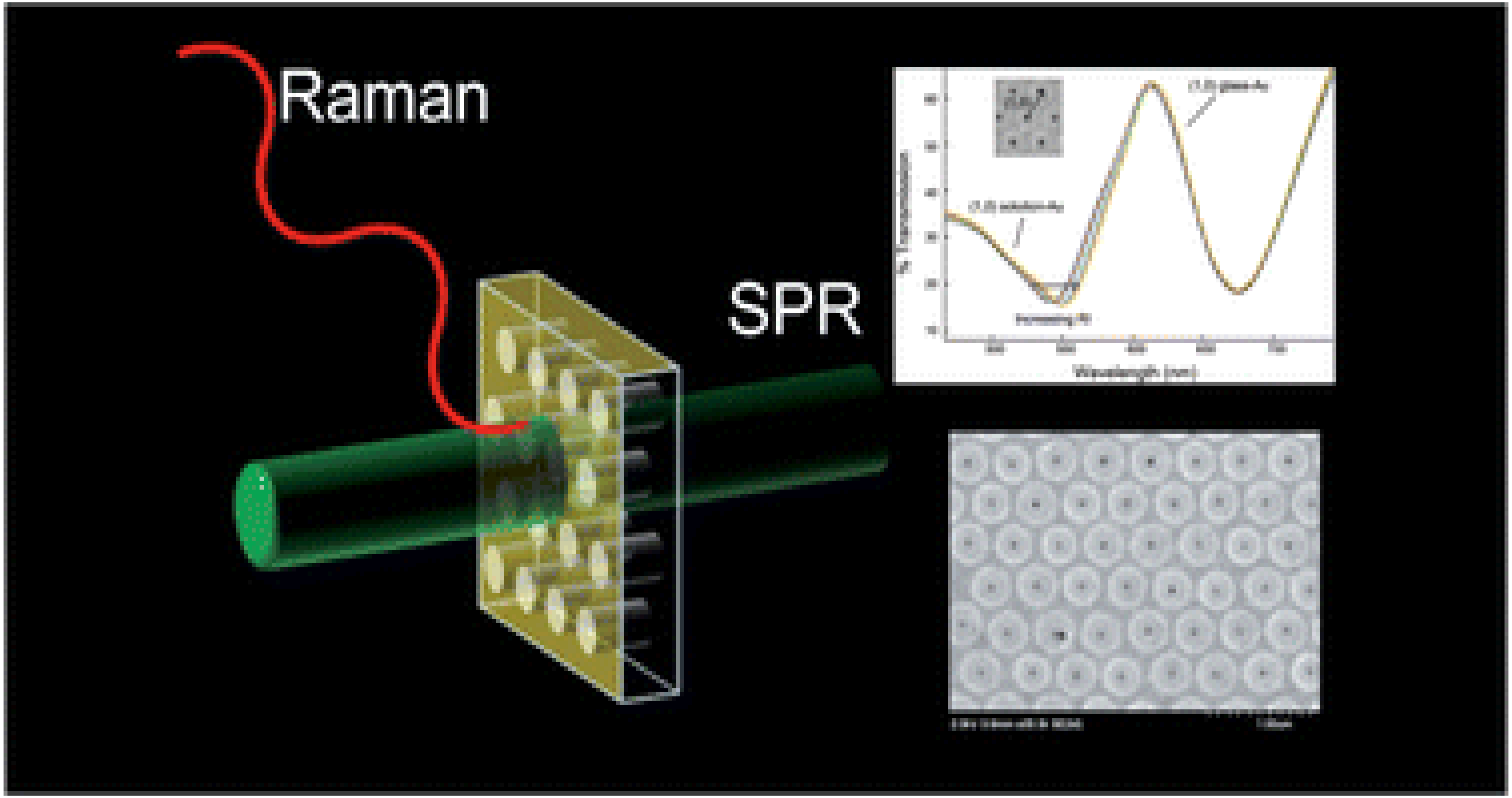
- Raman molecules are placed on a rough metallic surface.

- Surface acts an antenna, greatly increasing the local electric field, increasing signal by up to 1 million times.

- Mechanism not fully understood.

- Most SERS surfaces are essentially rough metal – signal intensity is very variable and lacks consistency.

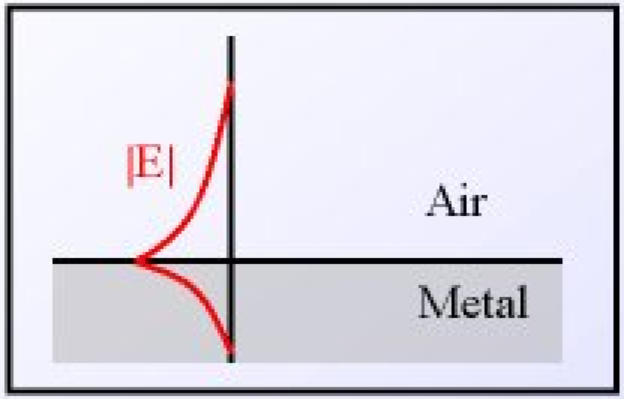
Schematic diagram of SERS

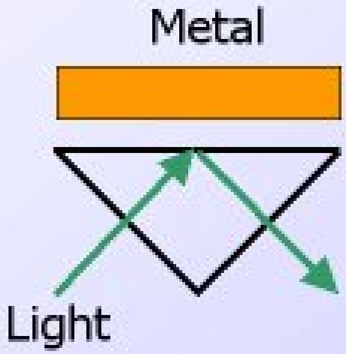


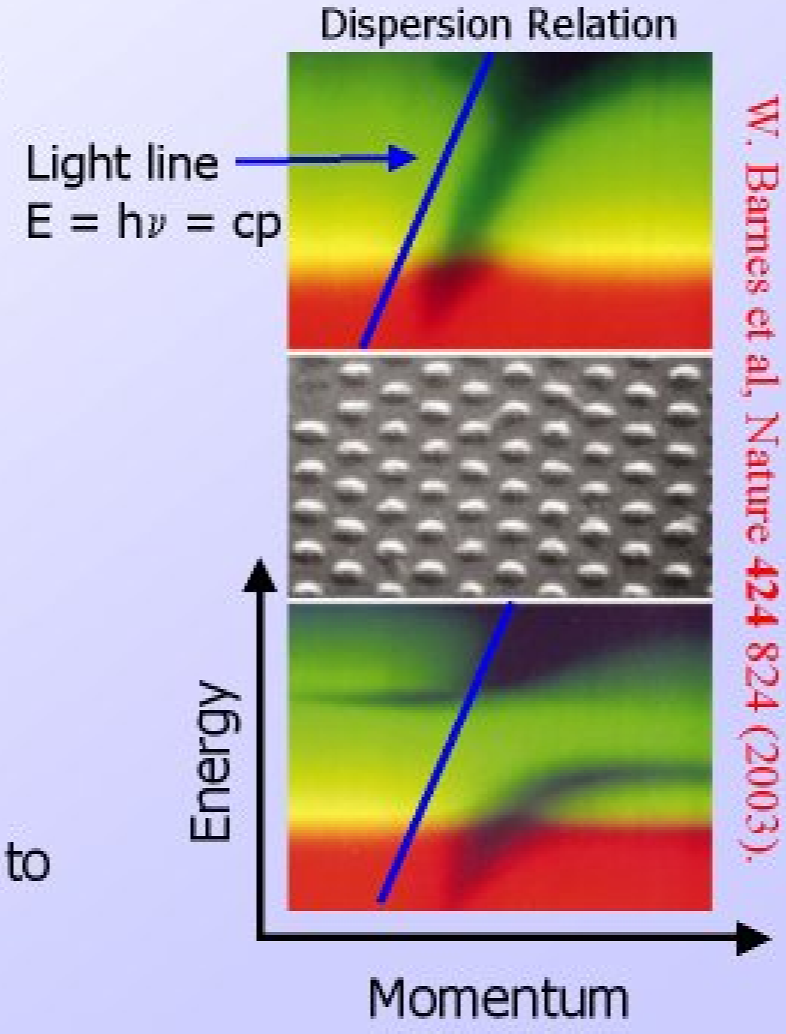
Minireview of the applications and challenges in nanohole arrays

Surface Plasmons

- A plasmon is an oscillation of electrons.
- A surface plasmon is pinned to the surface of a metal
- Reflection off smooth and structured metal:

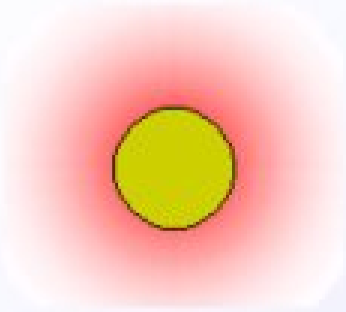






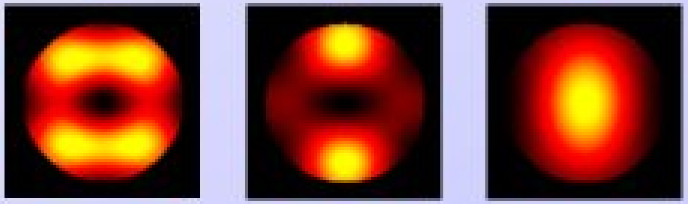
- A surface plasmon polariton is a surface plasmon coupled to an optical field
- Grating gives momentum to light - couple to SP

Localised Plasmons



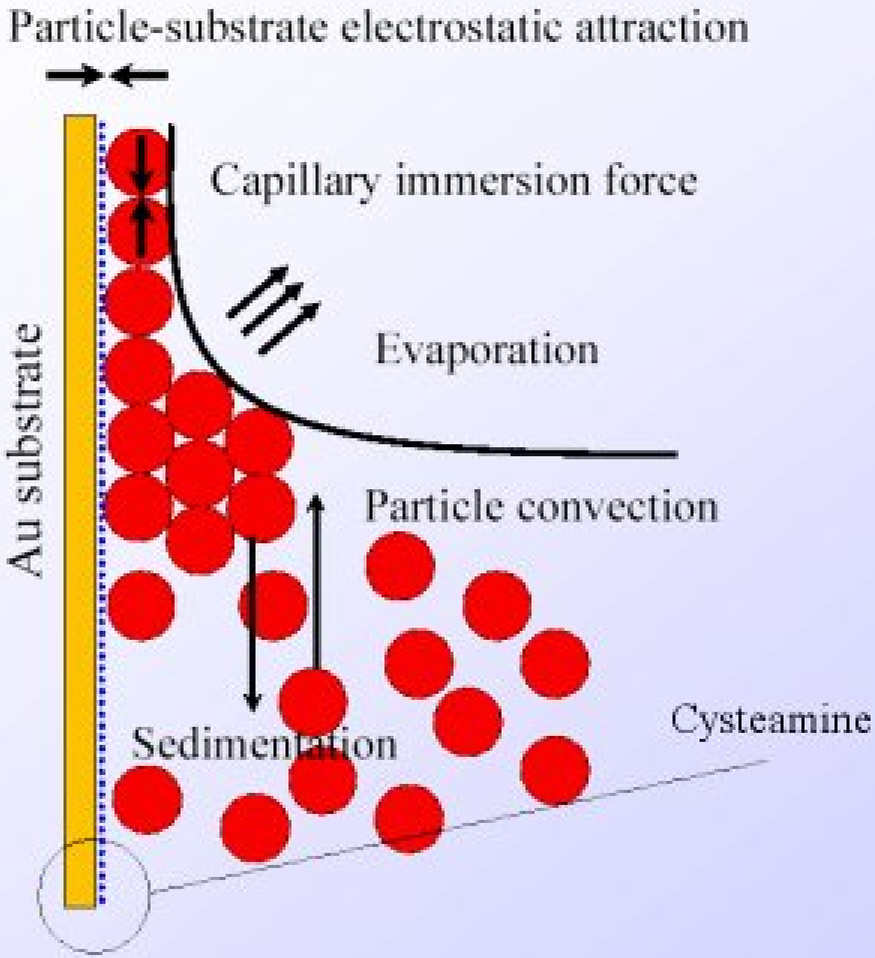
Halas

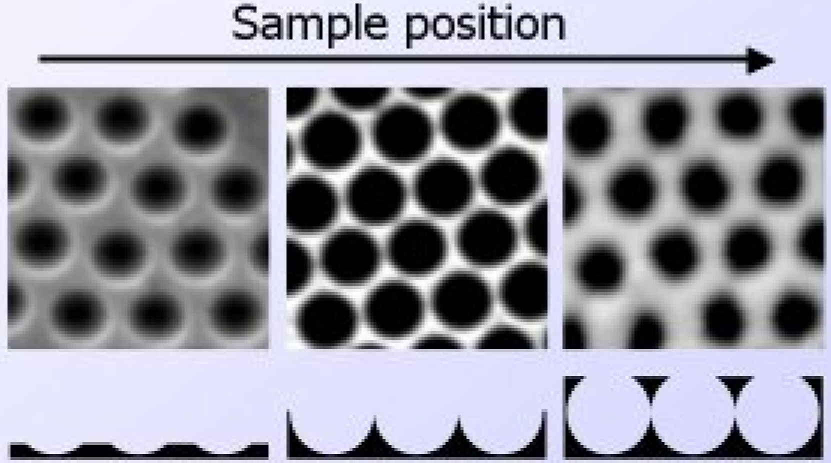
- Localisation of electric field within the nano structures.
- Depends on void geometry.

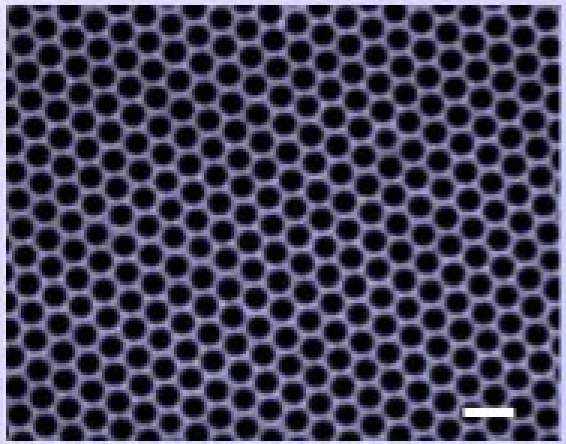


Sample Preparation

1. Produce Template, left
2. Electro-plate metal, below
3. Remove Template

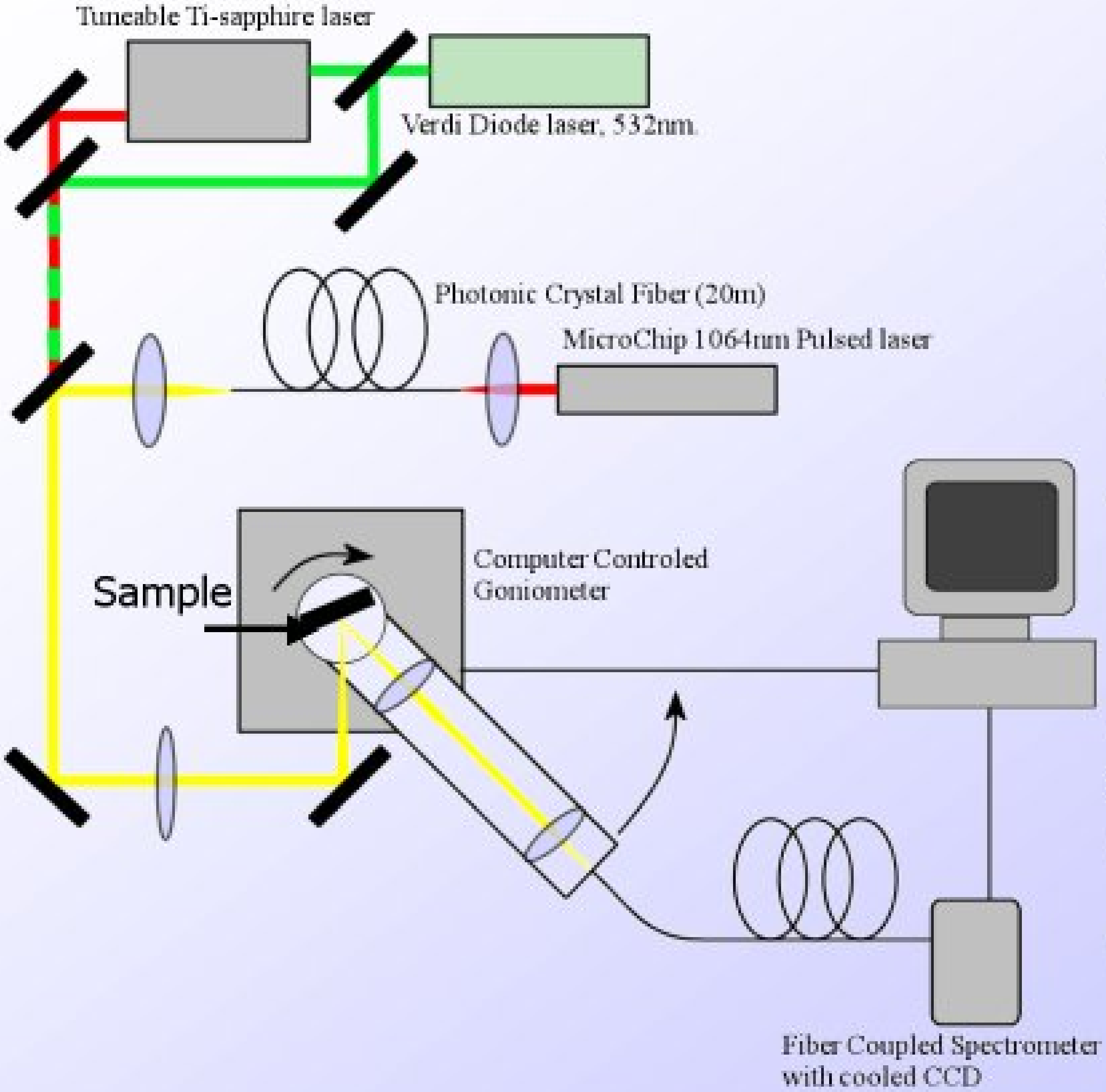






SEM. Pore diameter = 700nm.

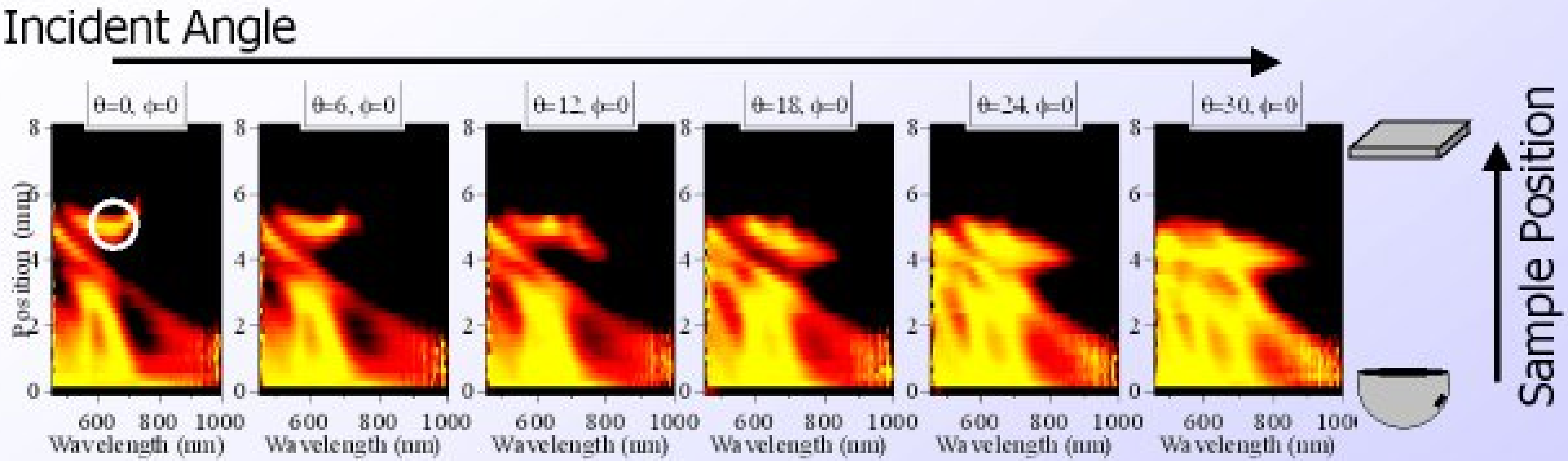
Experimental Set-up



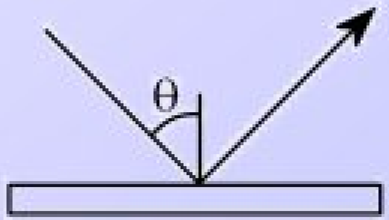
Lasers:

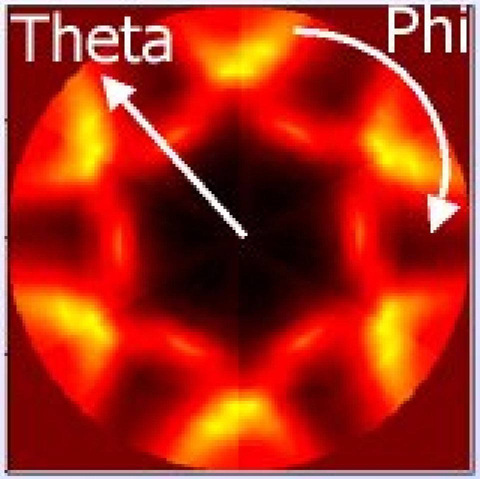
- White light continuum for sample reflectivity characterisation
- Green for luminescence
- Tuneable ~800 for SERS
- Sample can be moved in x and y planes along with ϕ and θ angles.
- All totally automated!

Reflectivity Results

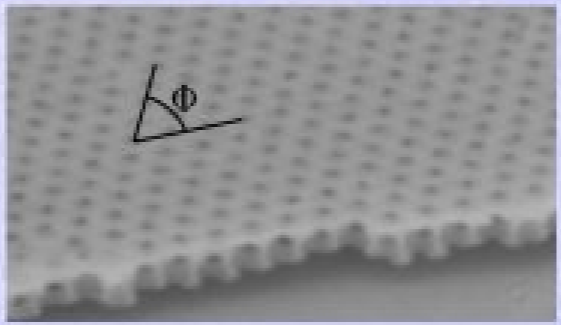


[All data other than below is for ϕ = 0]



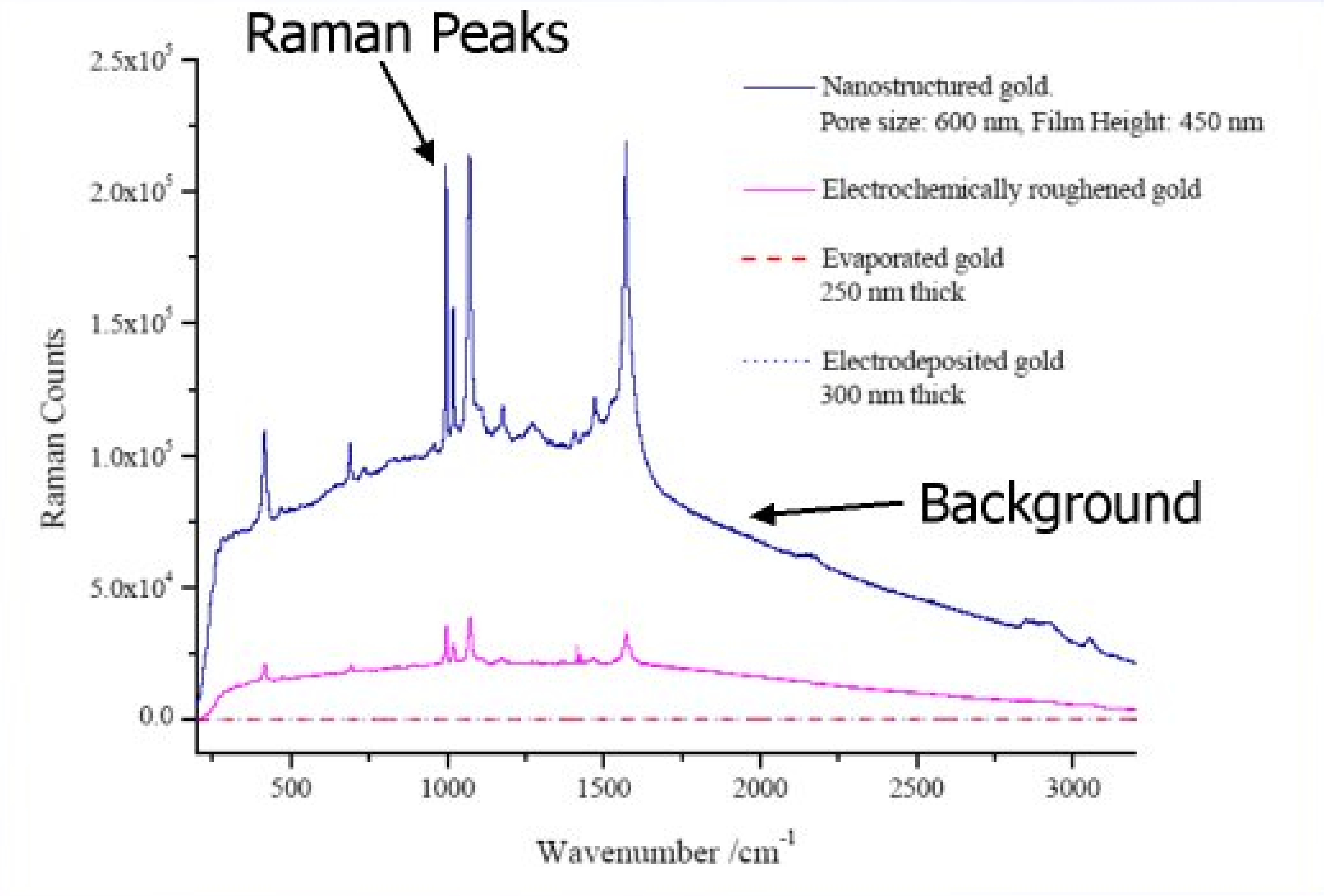


& 700nm
1 Point on sample



Raman Data From Surfaces

- Use benzene thiol to get Raman signal.



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

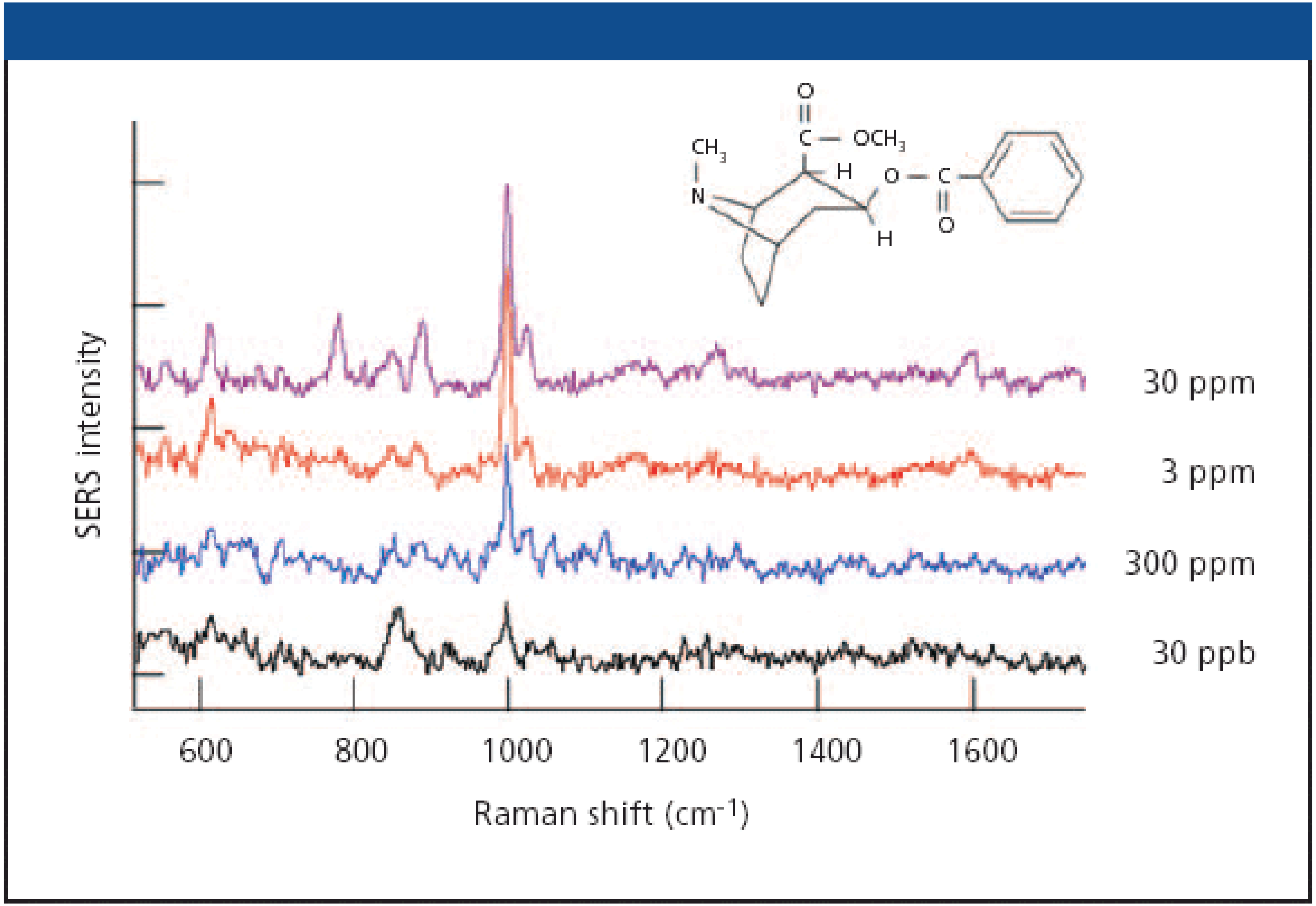


Figure 4: SERS spectra of cocaine aqueous solutions for concentration ranging from 30 ppm (30 µg/mL) to 30 ppb (30 ng/mL). The spectra were acquired with an analytical-grade Raman system with a 10-s exposure at 785 nm.

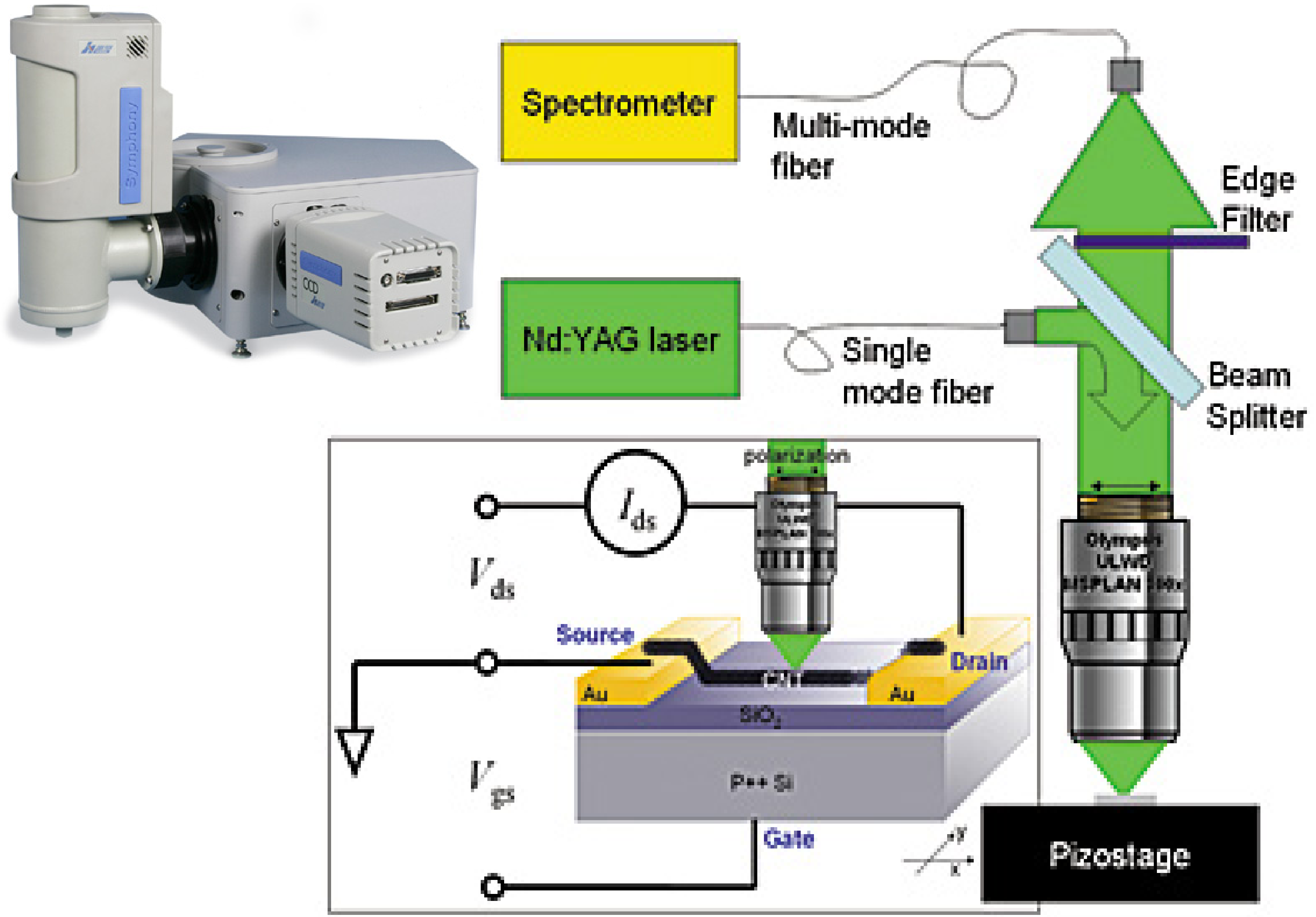
SERS增强机理

1. 电磁增强机理

- ✓ 避雷针效应模型
- ✓ 表面镜像场模型
- ✓ **表面等离子体子共振模型**

2. 化学增强机理

- ✓ 活位模型
- ✓ 电荷转移模型



Spectrometer
Multi-mode fiber
Edge Filter
Nd:YAG laser
Single mode fiber
Beam Splitter
polarization
I_{ds}
V_{ds}
V_{gs}
Source
Drain
Au
Au
SiO_2
P++ Si
Gate
Pizostage
Olympus ULWD MSPLAN

Designed for Transparent Integration: Renishaw Raman Microscope Combination

On-line AFM/Raman Advantages:

- •AFM Z Adjustment permits intensity comparison without sample topography artifacts
- •AFM Z Adjustment reduces point spread function of Raman microscope providing 170 nm confocal Raman resolution
- •Transparent application of surface enhanced protocols
- •Allows new protocols such as Shadow NSOM™

Conclusions

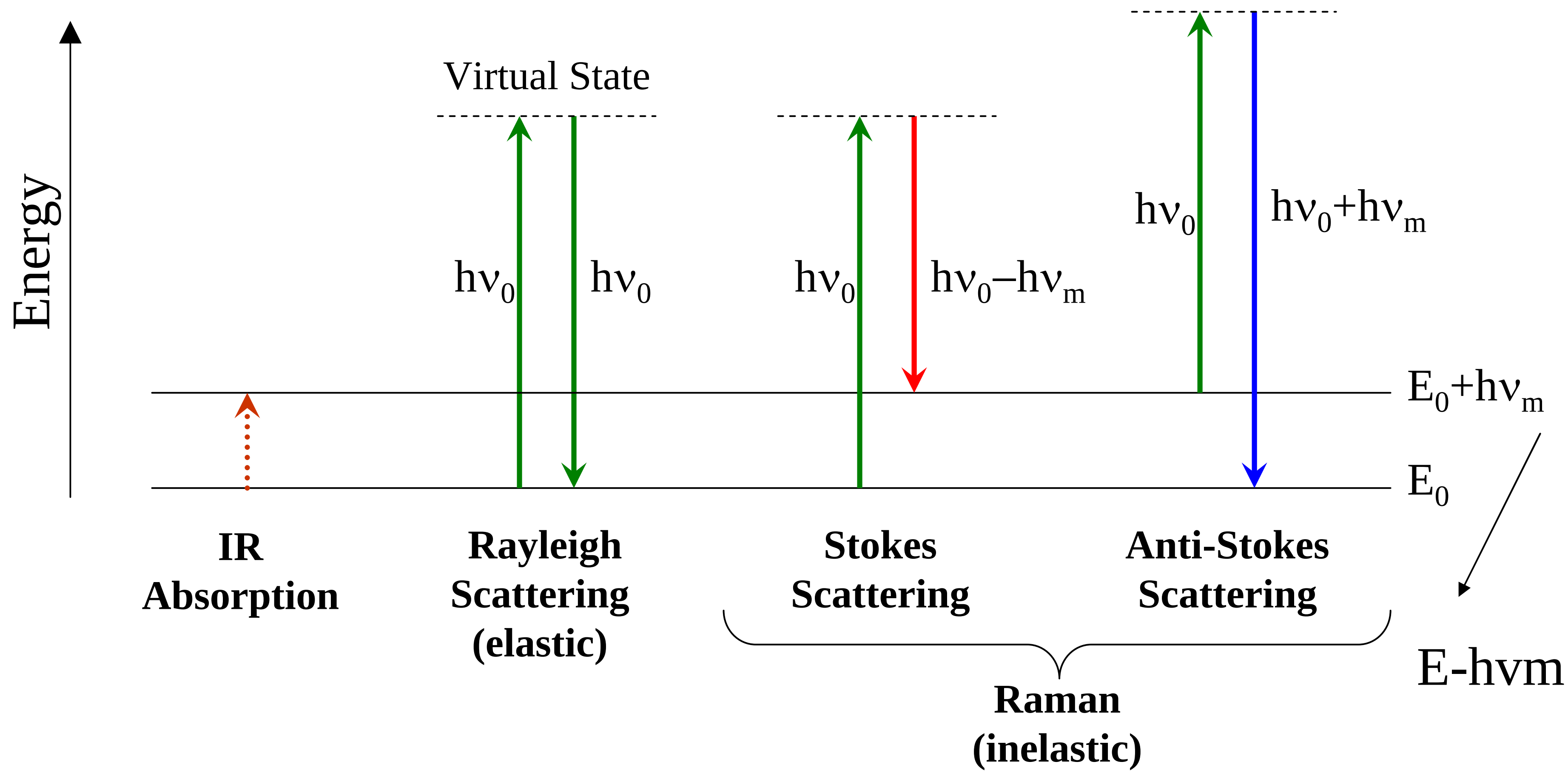
- Raman scattering is useful for molecular characterisation.

- We have demonstrated High power, reproducible SERS spectra.

- Starting to take data for angle/wavelength/sample geometry/sample material to optimise effect.

- Hopefully soon understand the SERS-plasmon coupling.

Energy Scheme for Photon Scattering



The Raman effect comprises a very small fraction, about 1 in 10^7 of the incident photons.