University of Electronic Science and Technology of China

Surface Enhanced Raman Spectroscopy

Prof. Yongqi Fu

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- What is Raman Spectroscopy?
- What is SERS?
- A quick review on plasmons…

- Our Samples
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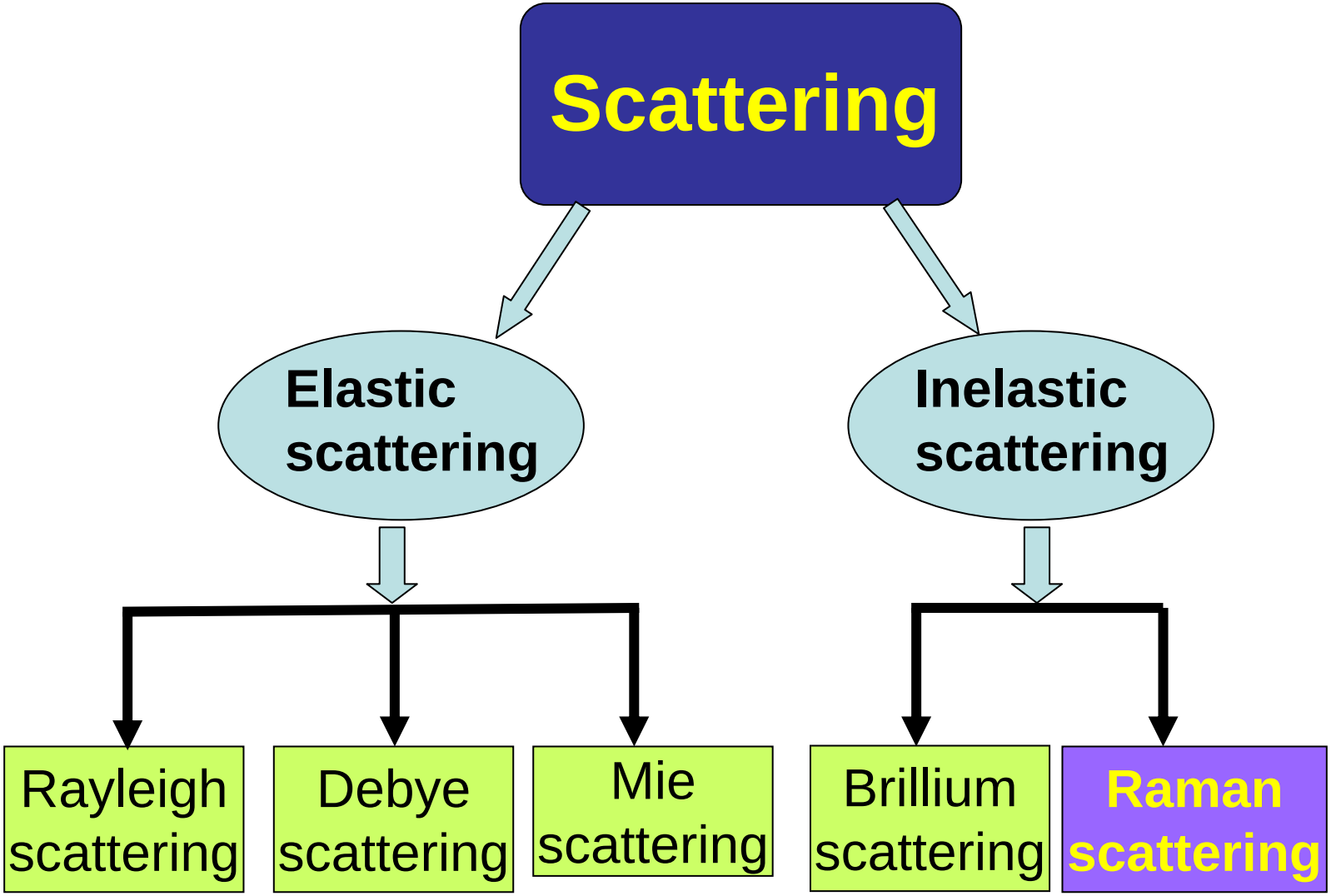
- Results so far

- Provisional Analysis & Conclusion


Scattering
Elastic scattering
Inelastic scattering
Rayleigh scattering
Debye scattering
Mie scattering
Brillium scattering
Raman scattering

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.

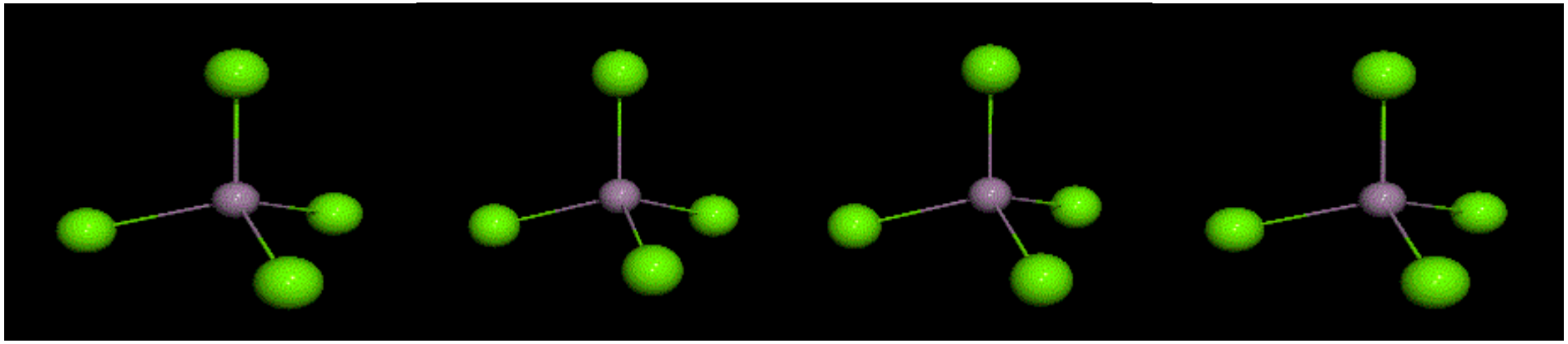
- By 'tailoring' the plasmonic properties of metals we can understand how to produce excellent reliable SERS signals.

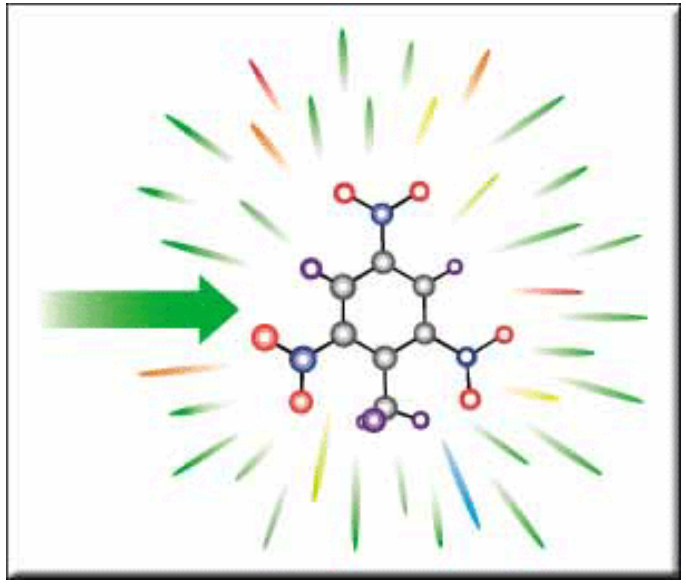
Sir Chandrasekhara V. Raman

Discovery year: 1928

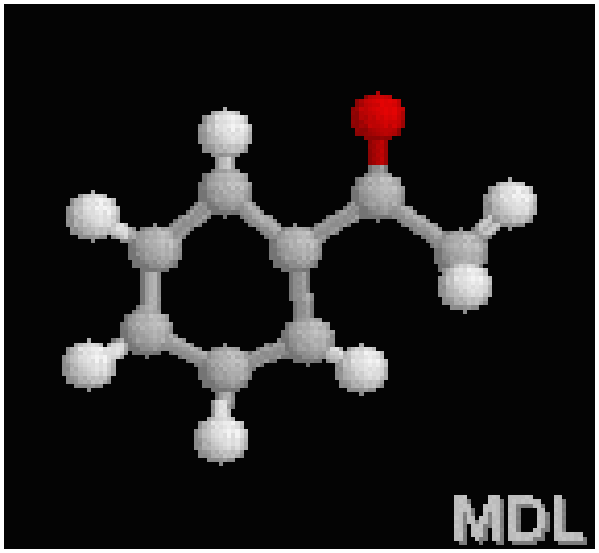
Raman won the Nobel Prize in Physics in 1930 for this discovery accomplished using sunlight, a narrow band photographic filter to create monochromatic light and a "crossed" filter to block this monochromatic light. He found that light of changed frequency passed through the "crossed" filter.

What Exactly Is Being Measured?

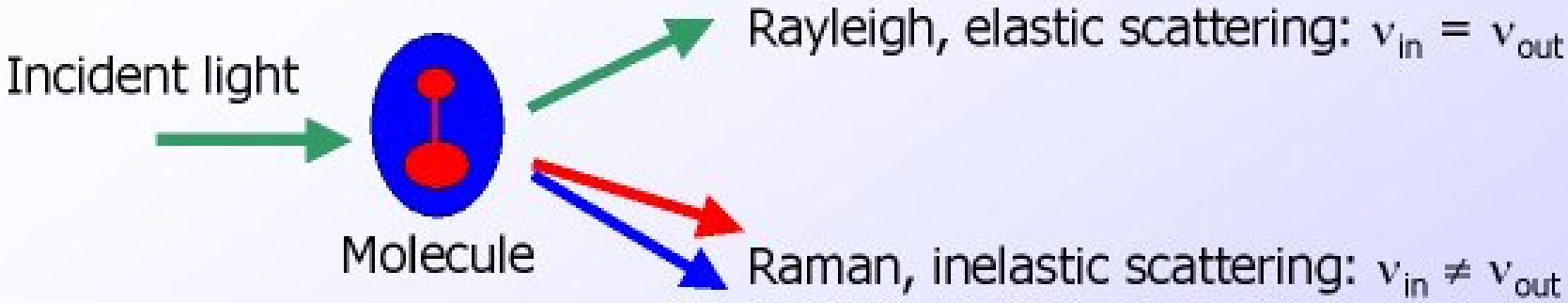


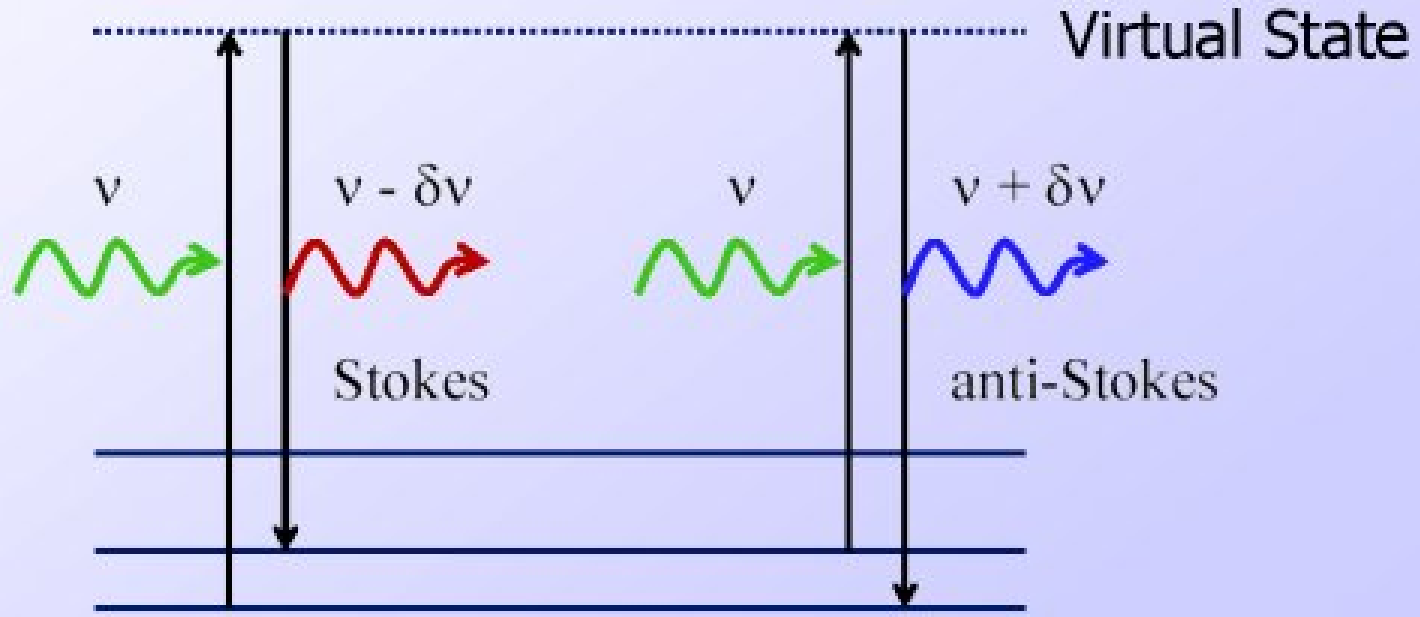


When Light hits a sample, It is **excited**, and is forced to vibrate and move. It is these vibrations which we are measuring.

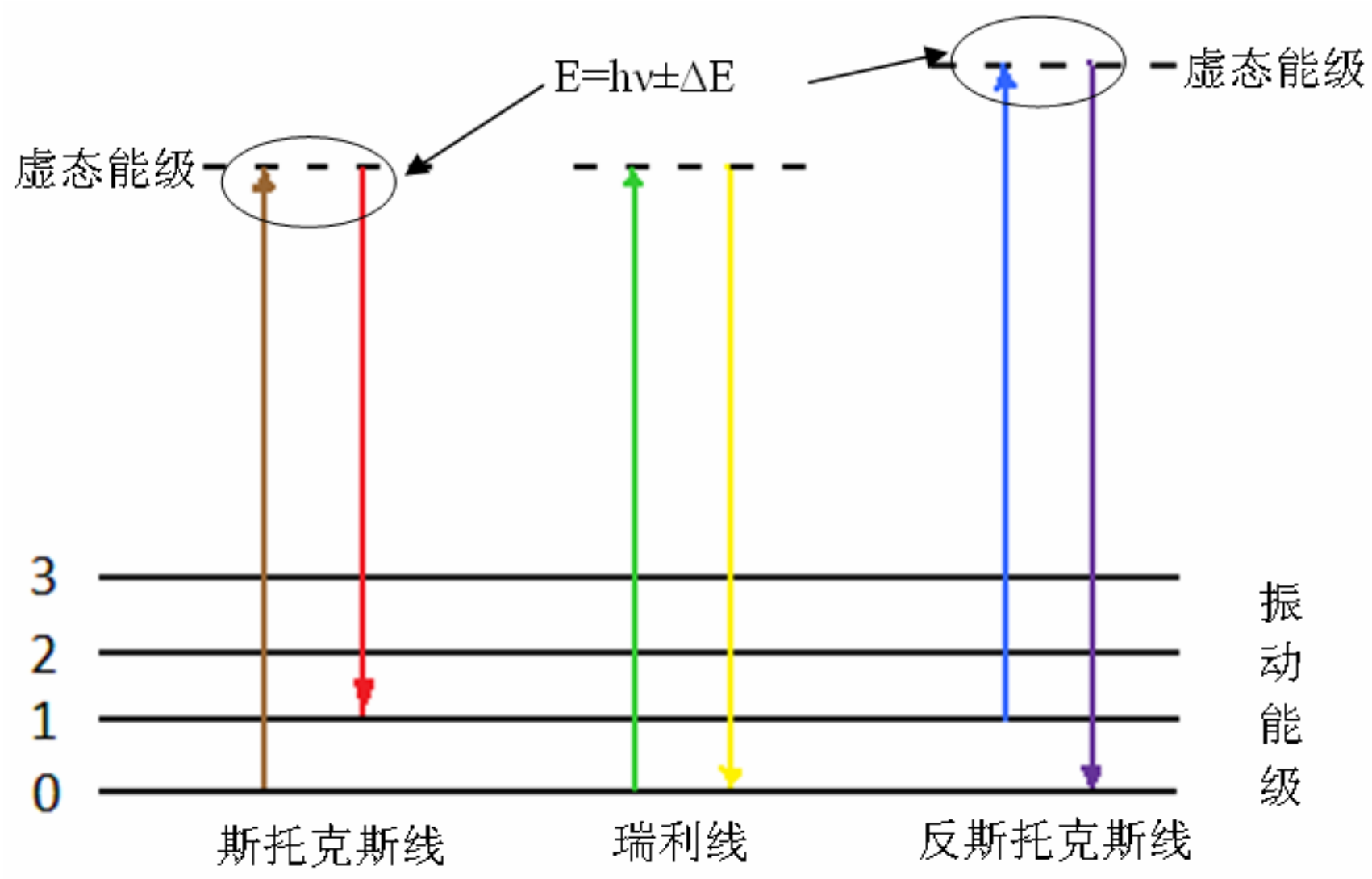


Raman Scattering



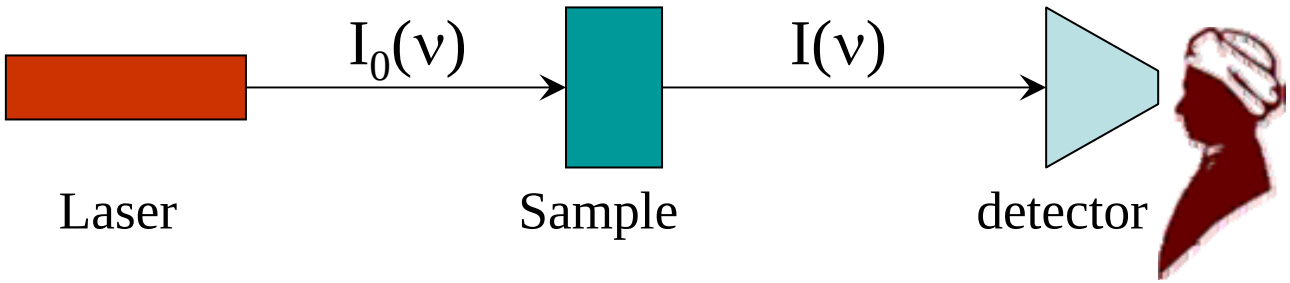


Energy Scheme for Photon Scattering

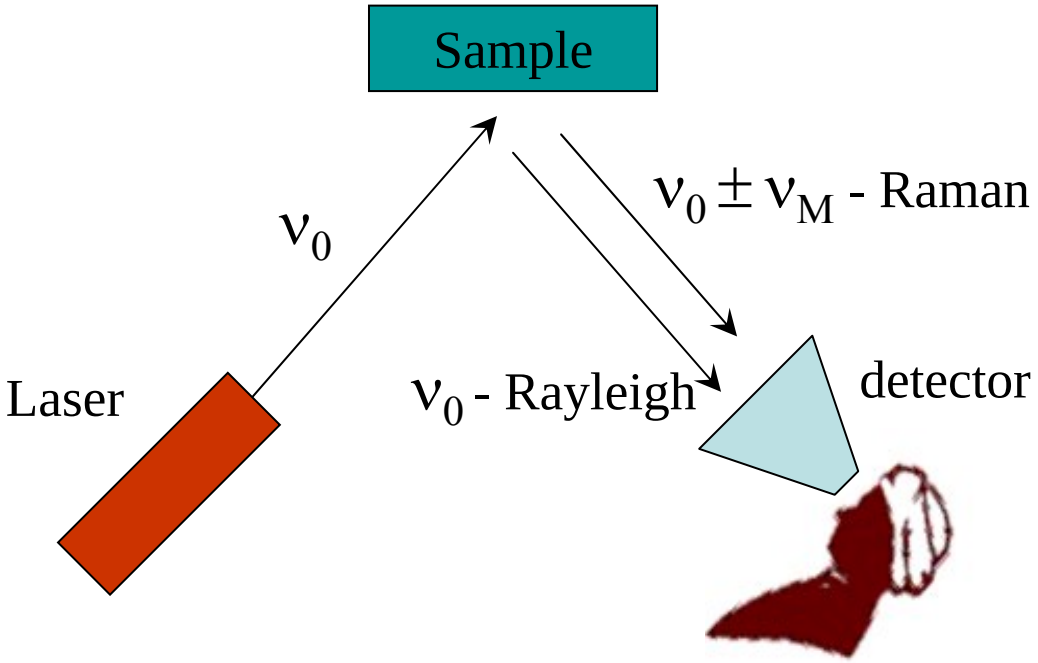


拉曼散射光谱示意图

IR Spectrography - Absorption

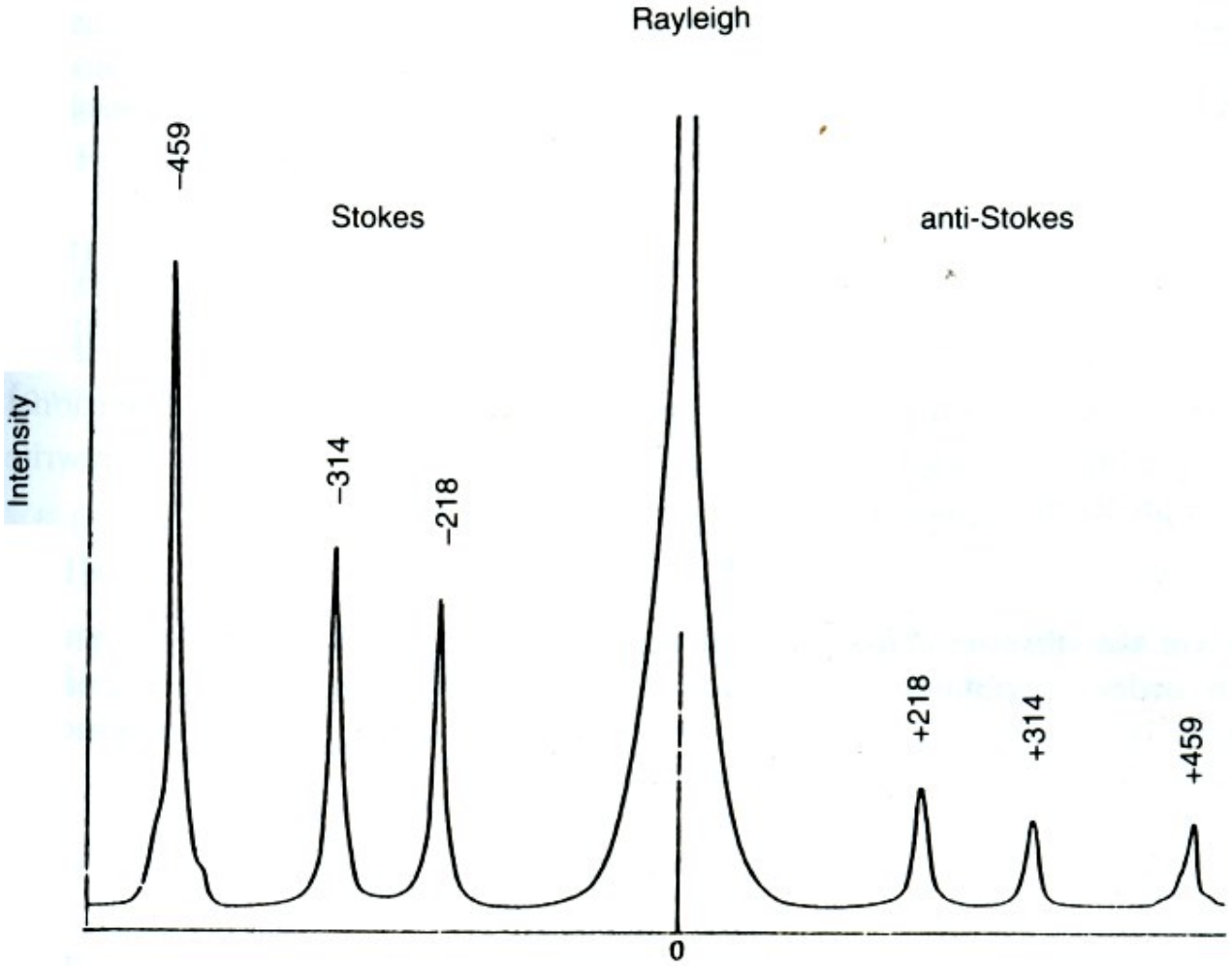


Raman Spectrography - Scattering



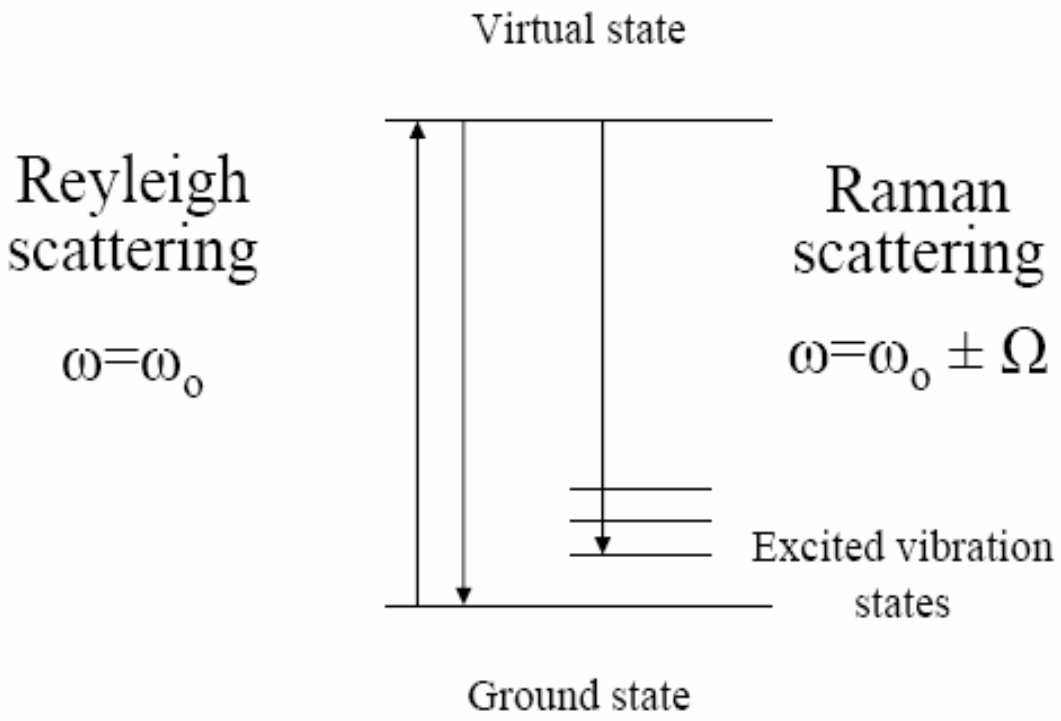
Raman Spectrum

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*.



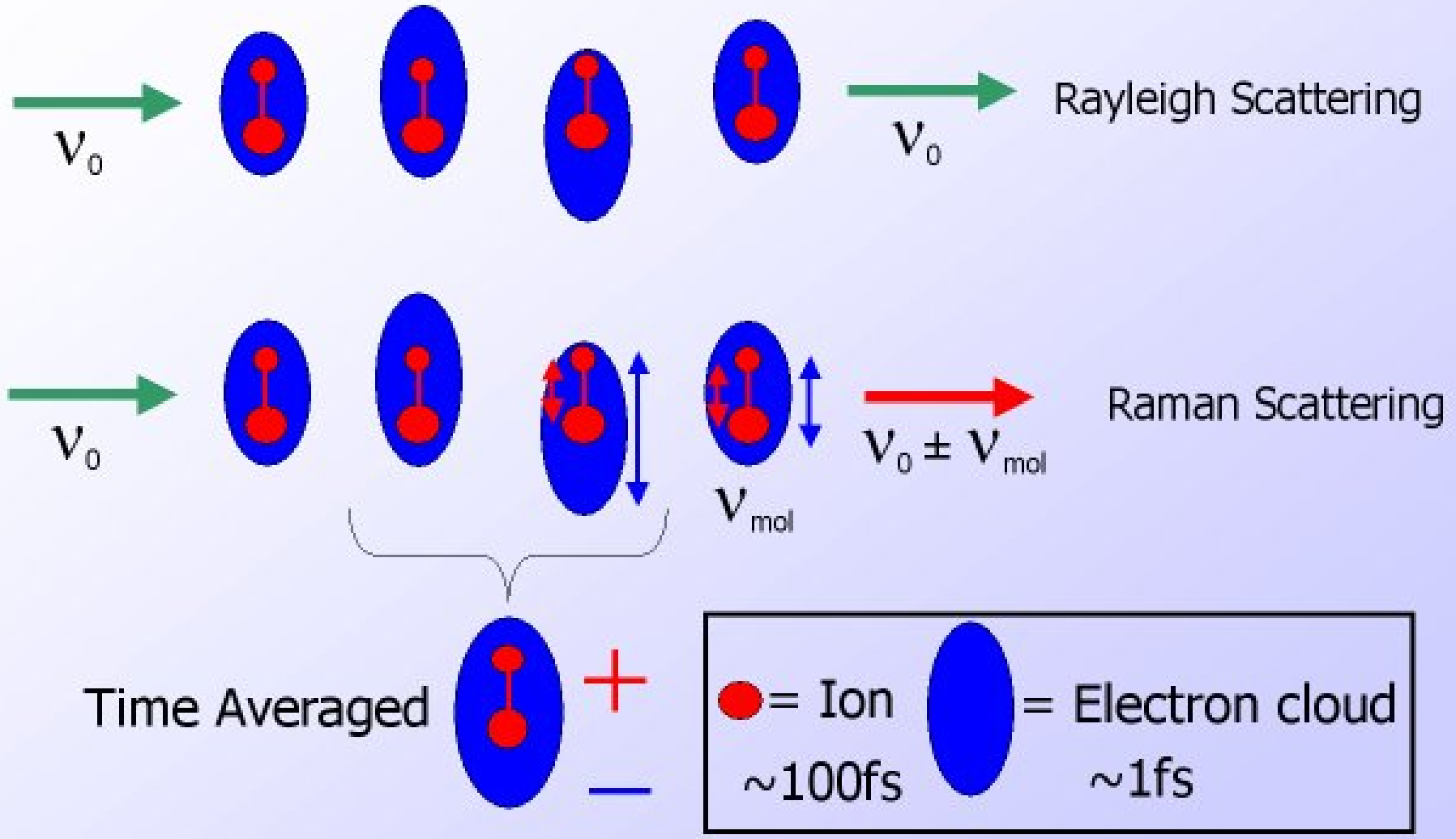
Raman Spectrum of CCl_4

What is Raman scattering?

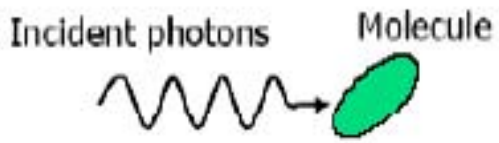


Frequencies of the incident and scattered photons are different due to the energy loss caused by molecular vibration.

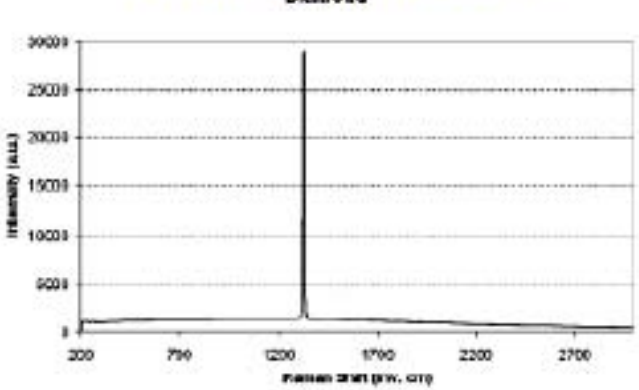
Raman Scattering



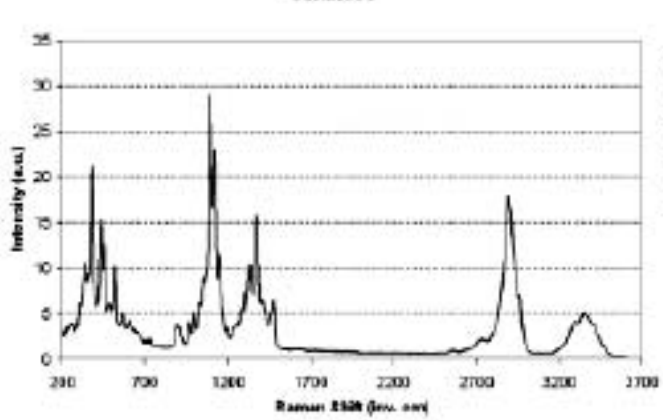
Raman scattering



Sample Raman Spectra

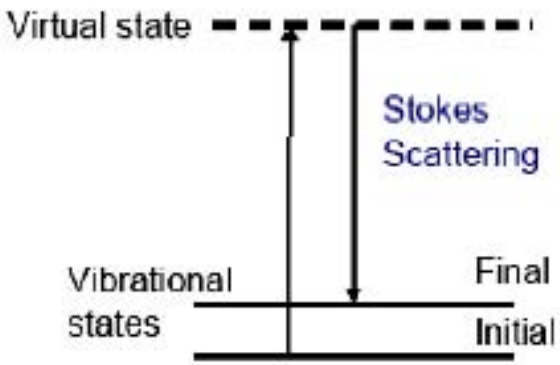


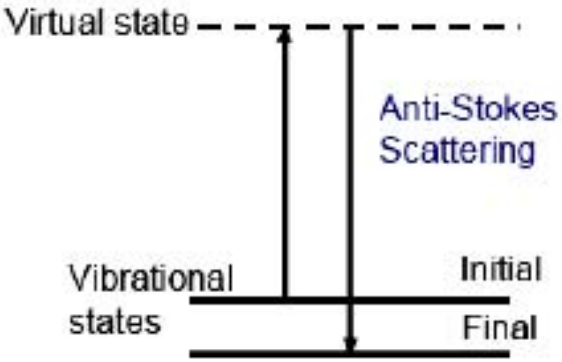
Diamond:
- C-C lattice
- Only one bond type
- One Raman band



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

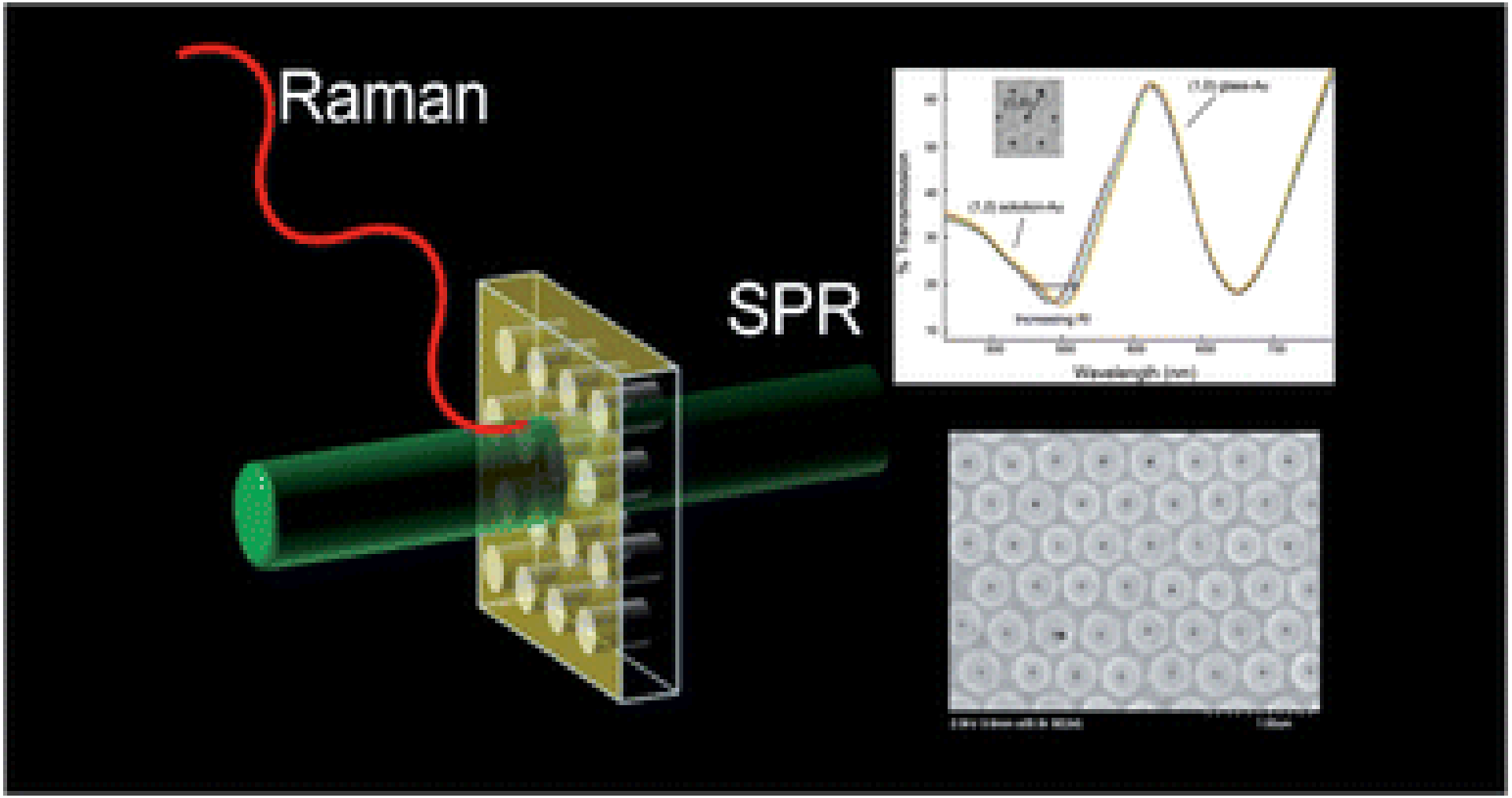
Why use SERS?

- 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.

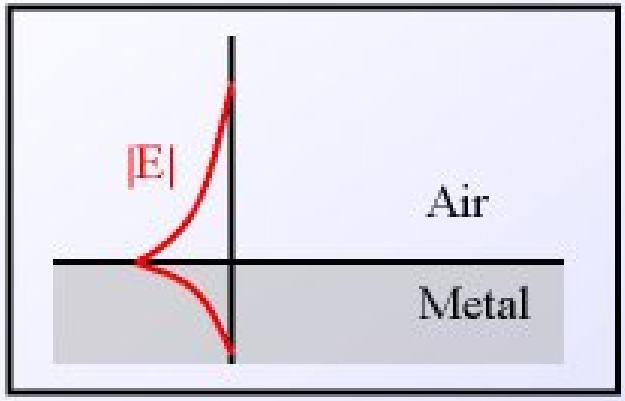
Schematic diagram of SERS

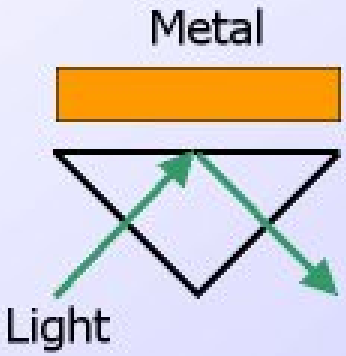


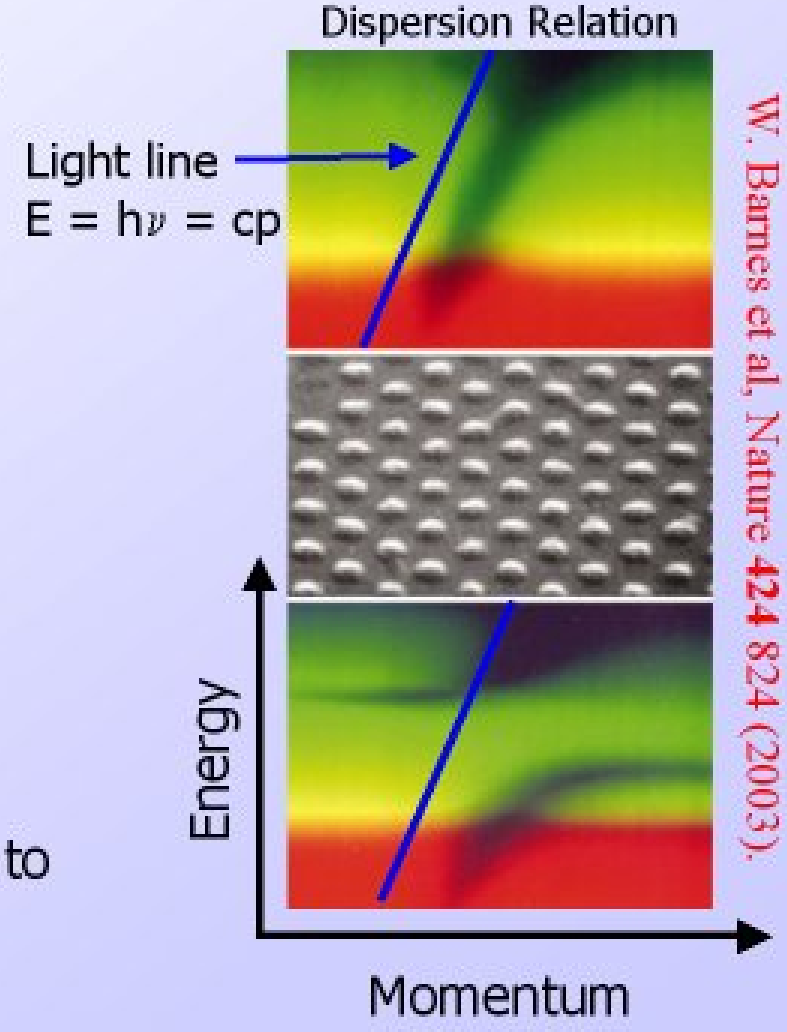
Minireview of the applications and challenges in nanohole arrays

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:



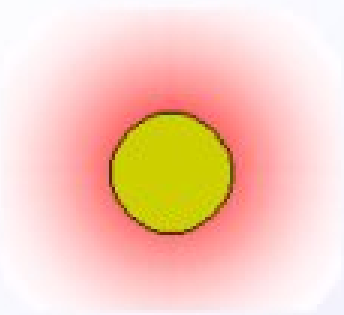




W. Barnes et al, Nature **424** 824 (2003).

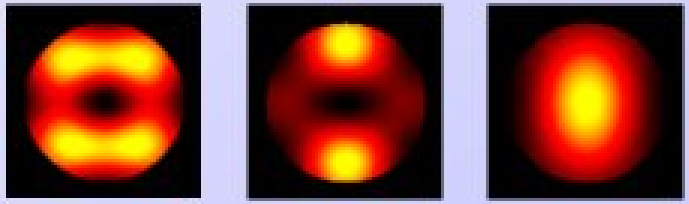
- A surface plasmon polariton is a surface plasmon coupled to an optical field
- Grating gives momentum to light - couple to SP

Localised Plasmons



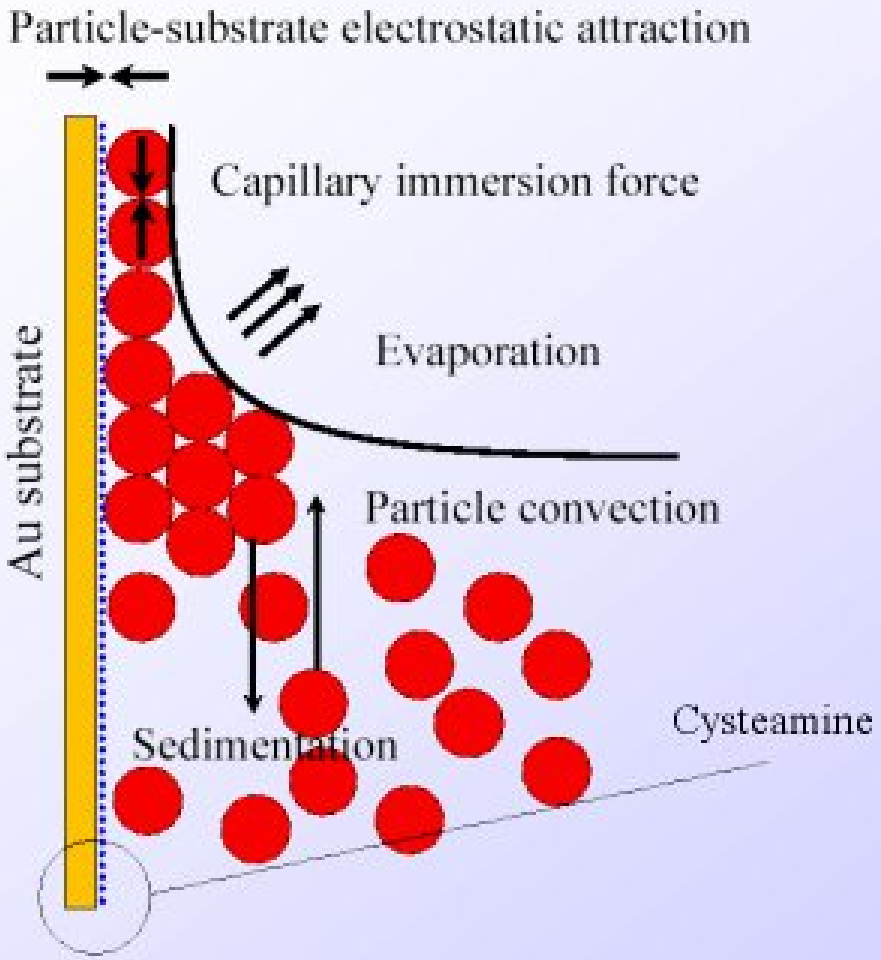
Halas

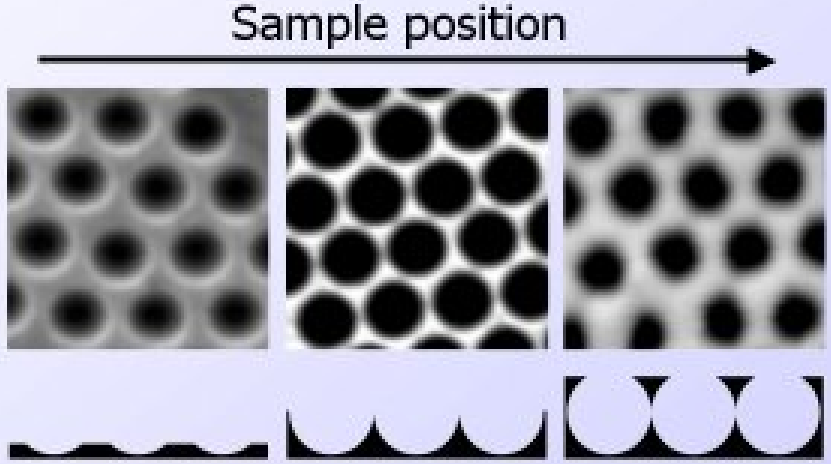
- Localisation of electric field within the nano structures.
- Depends on void geometry.

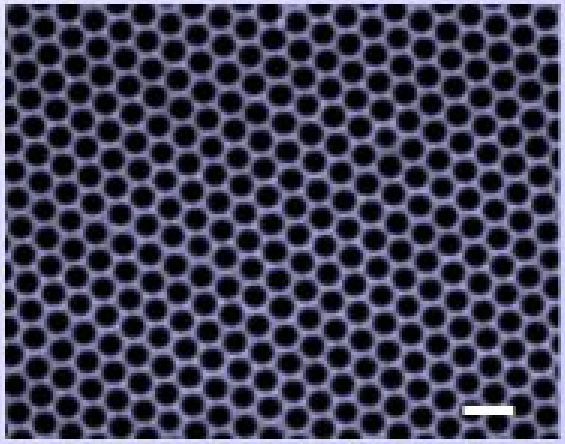


Sample Preparation

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

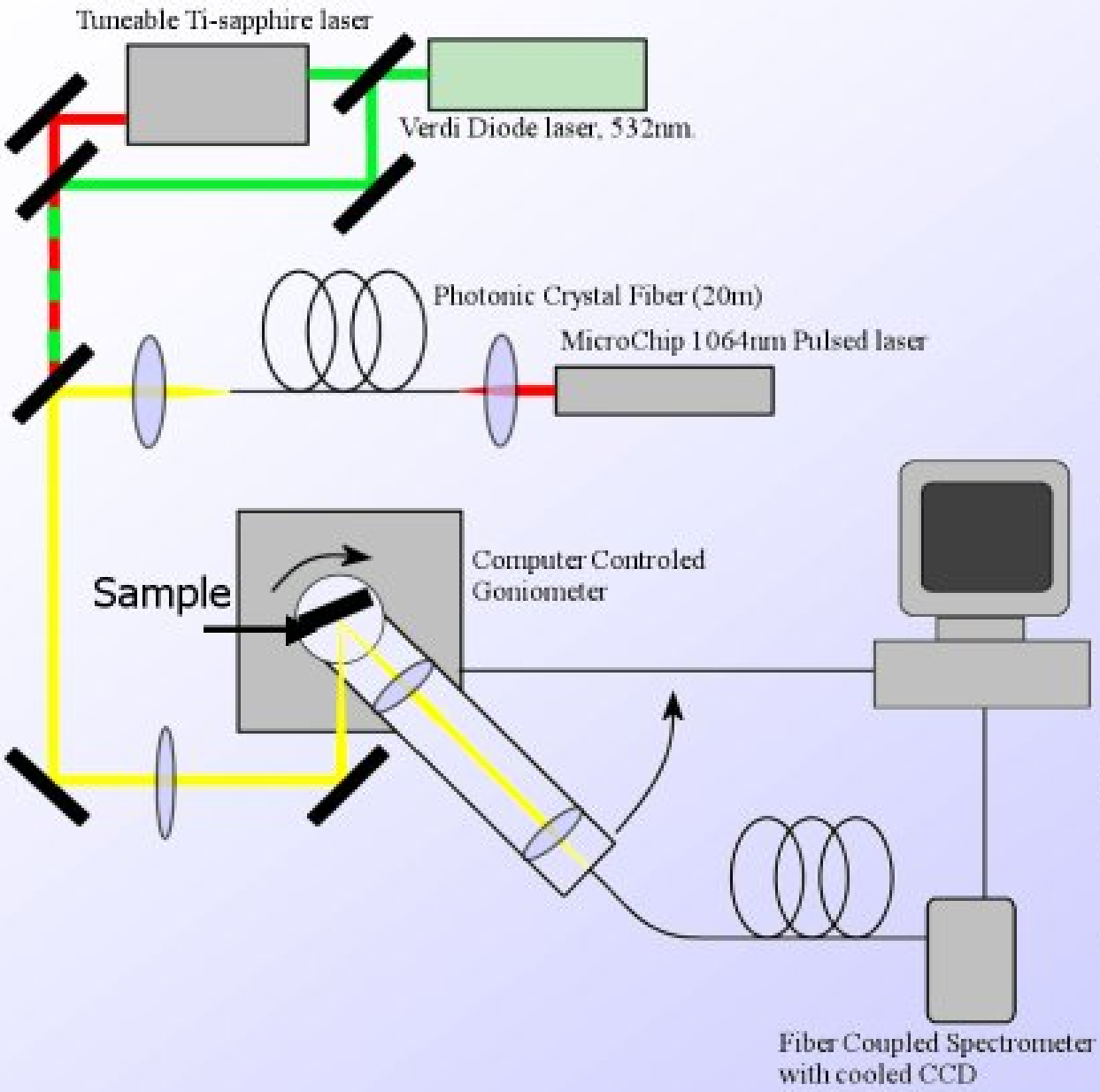






SEM. Pore diameter = 700nm.

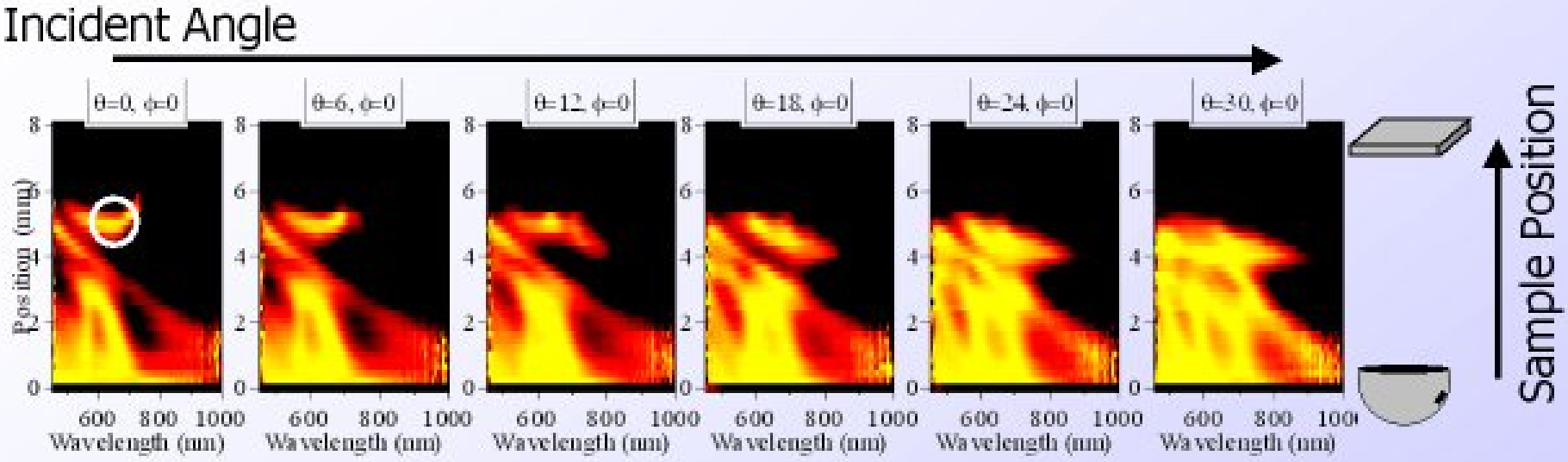
Experimental Set-up



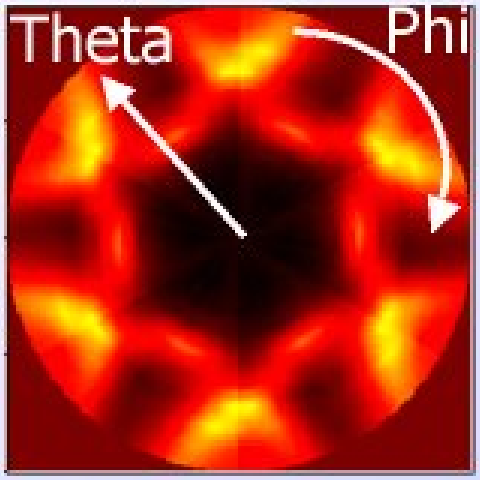
Lasers:

- 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!

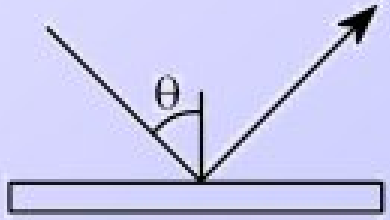
Reflectivity Results

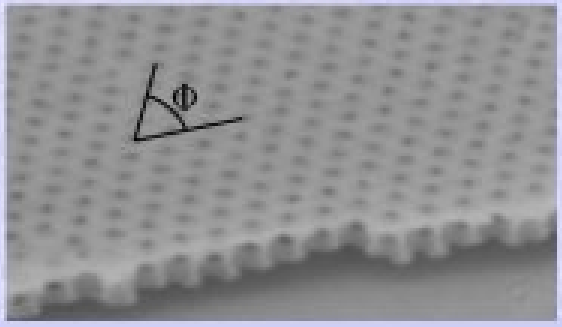


[All data other than below is for $\phi = 0$]



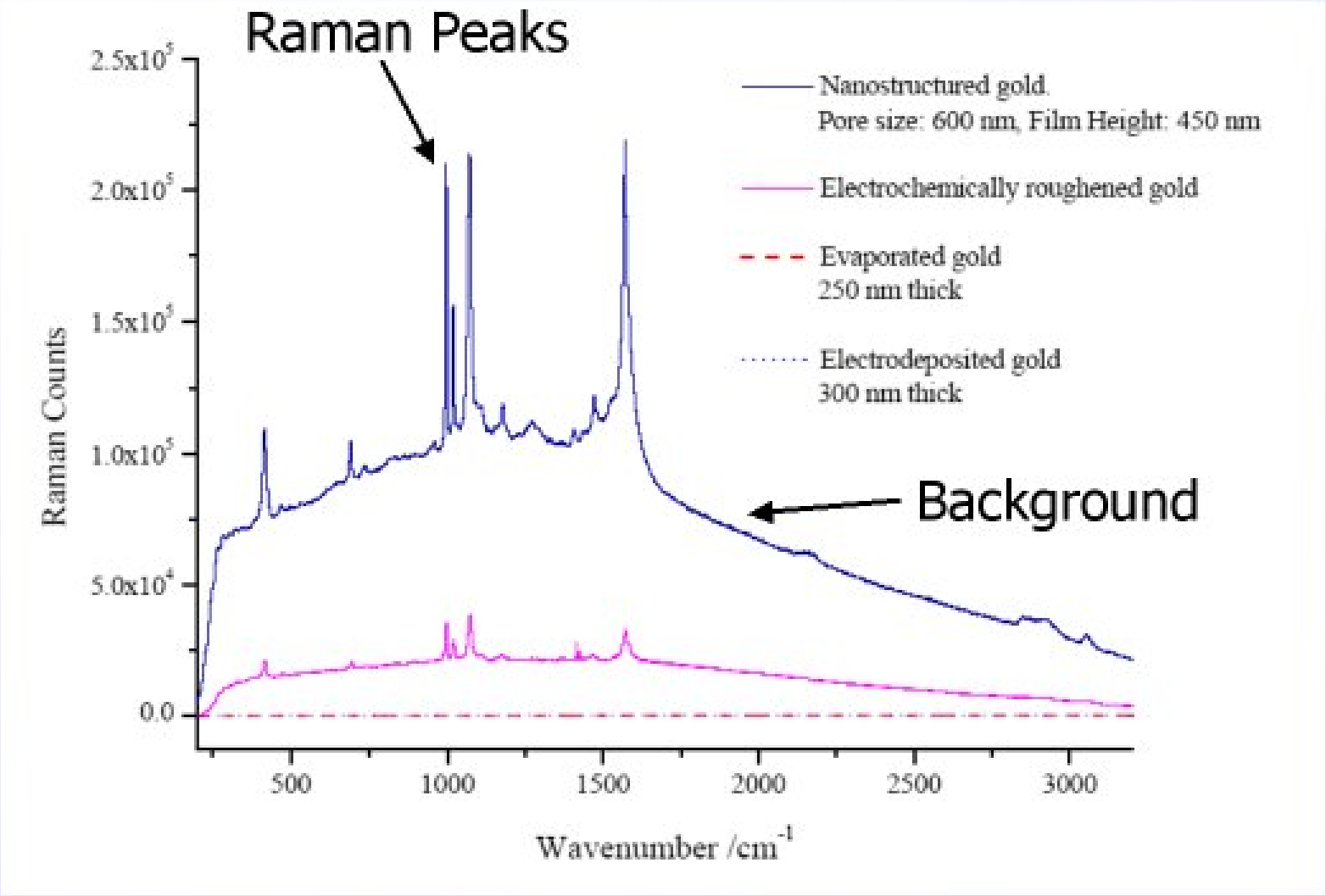
& 700nm
1 Point on sample





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)

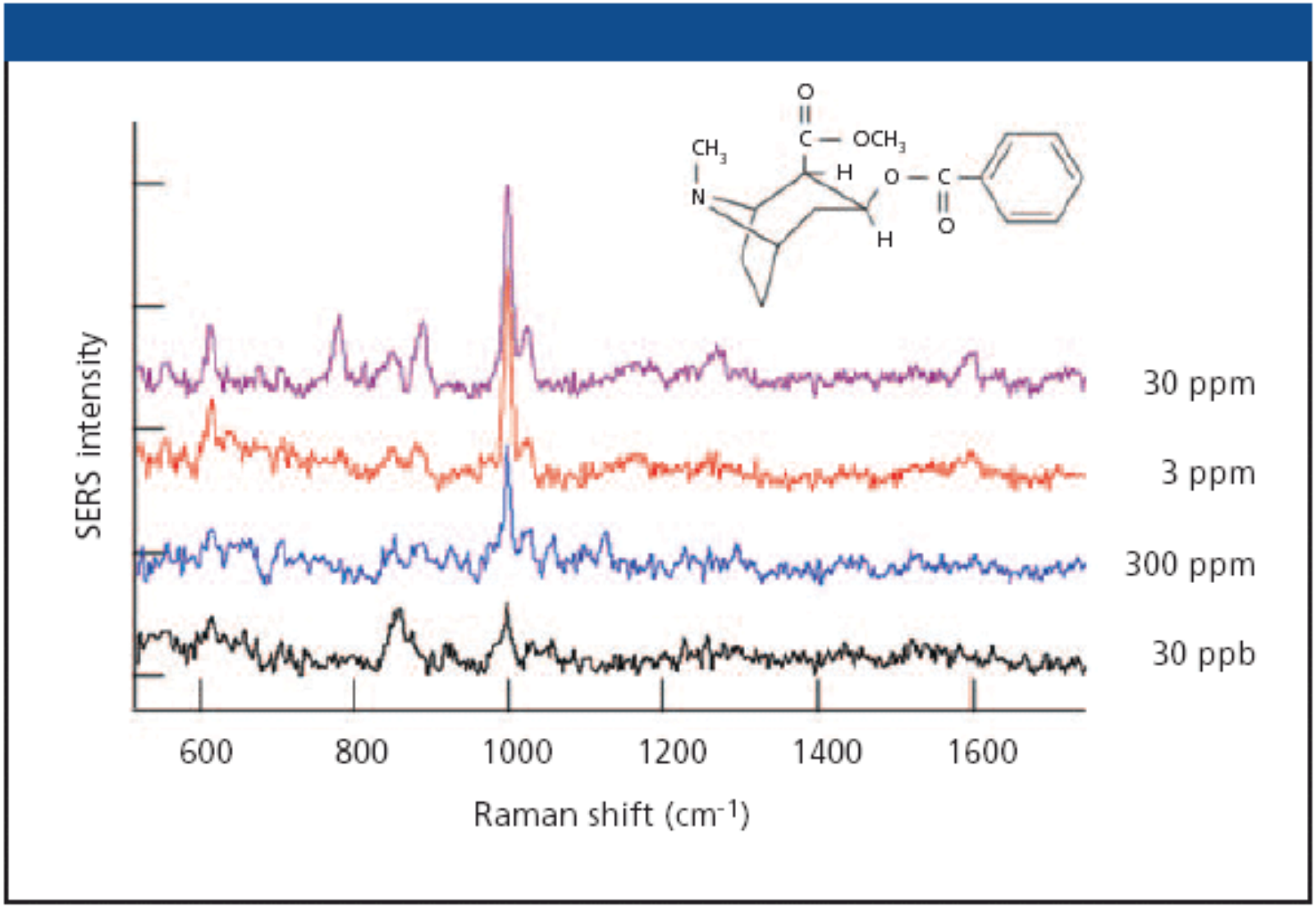


Figure 4: SERS spectra of cocaine aqueous solutions for concentration ranging from 30 ppm (30 µg/mL) to 30 ppb (30 ng/mL). The spectra were acquired with an analytical-grade Raman system with a 10-s exposure at 785 nm.

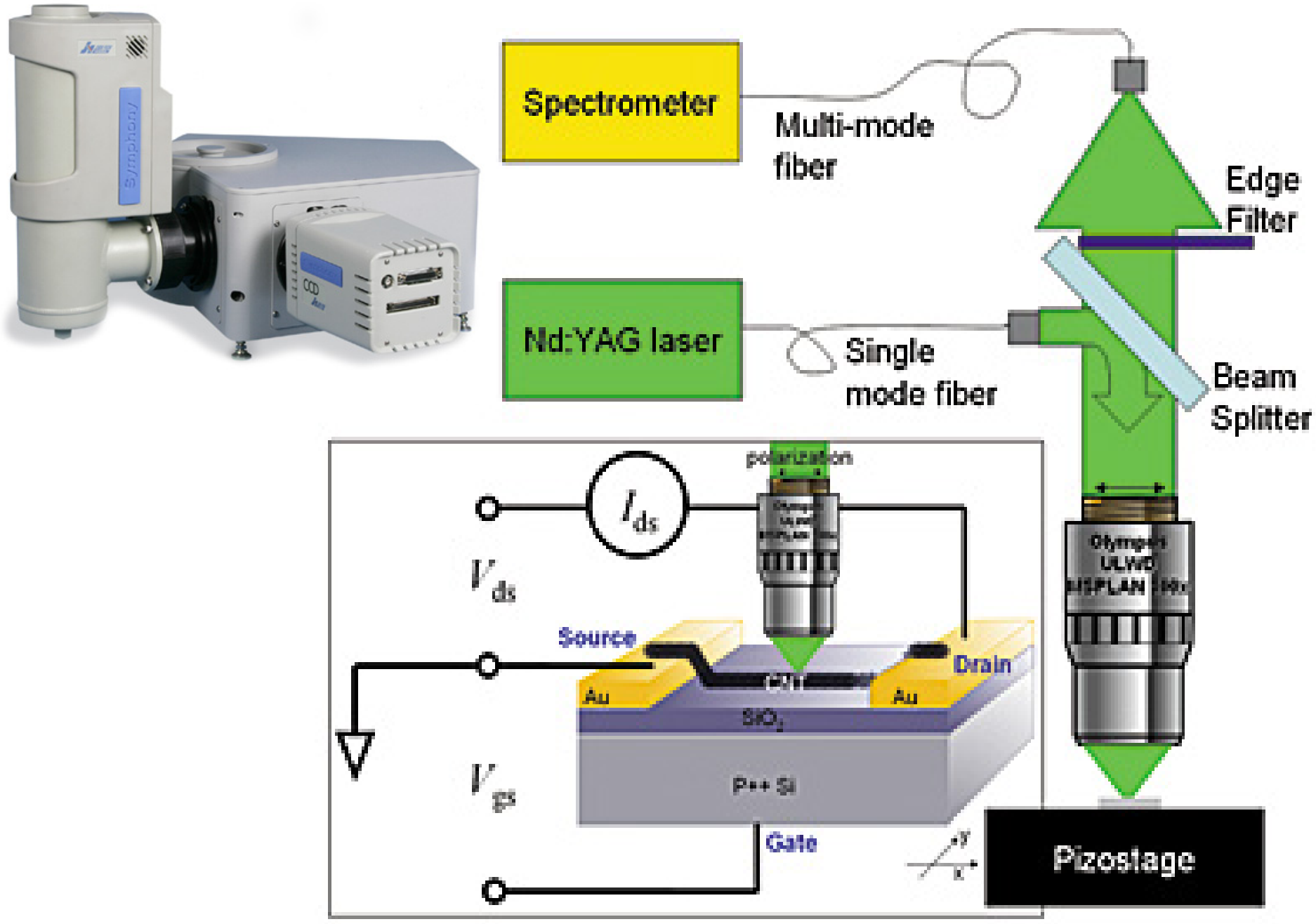
SERS mechanism

1. Electromagnetic induced mechanism

- ✓ Lightning rod effect model
- ✓ surface mirror field model
- ✓ **Surface plasmon resonance model**

2. Chemical induced mechanism

- ✓ mobile moving model
- ✓Charge transportation model


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

Nanonics
Renishaw
NSOM/Raman
Combination
12.01.2003

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™

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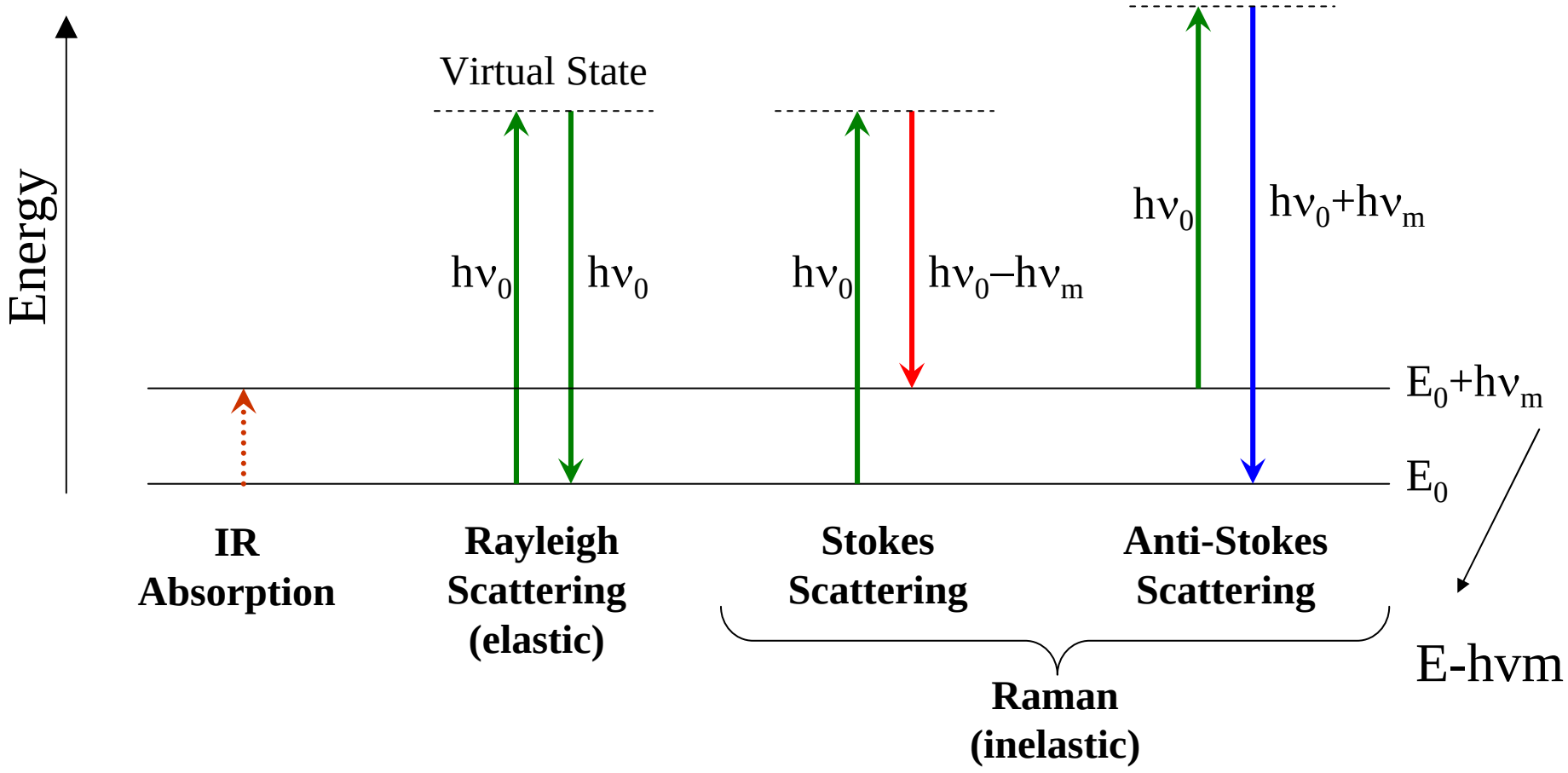
Conclusions

- 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.

THE END