

Chapter 7

Raman Spectroscopy

Course Code: SSCP 4473

Course Name: Spectroscopy & Materials Analysis

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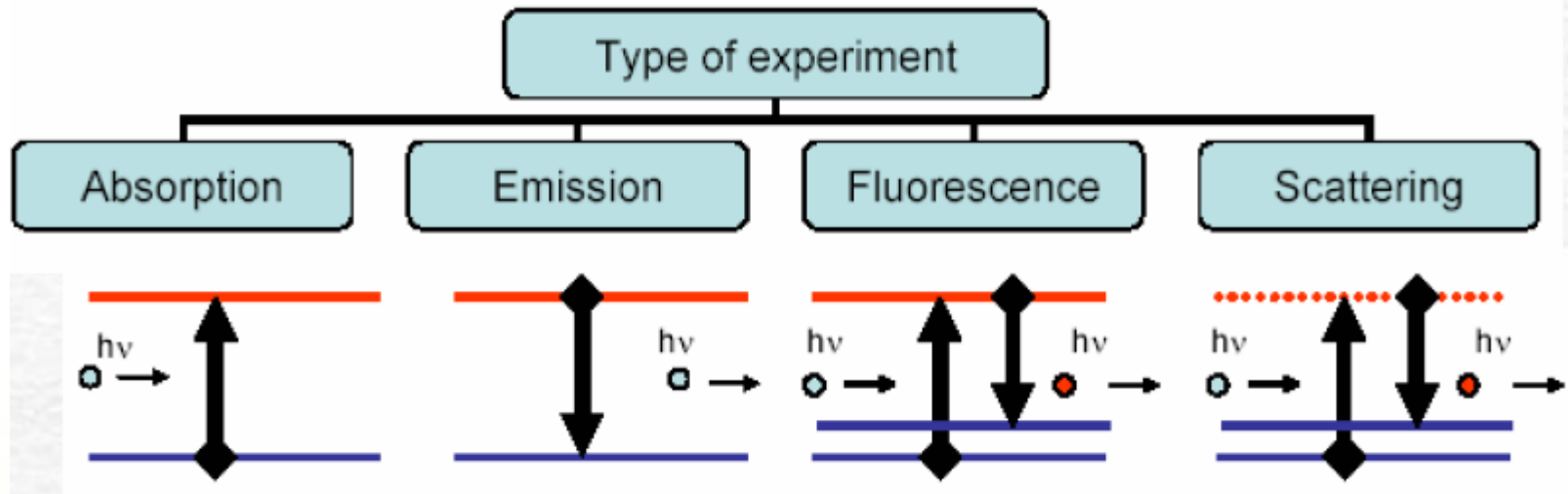
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Essence of Raman Spectroscopy: Based on Inelastic Scattering

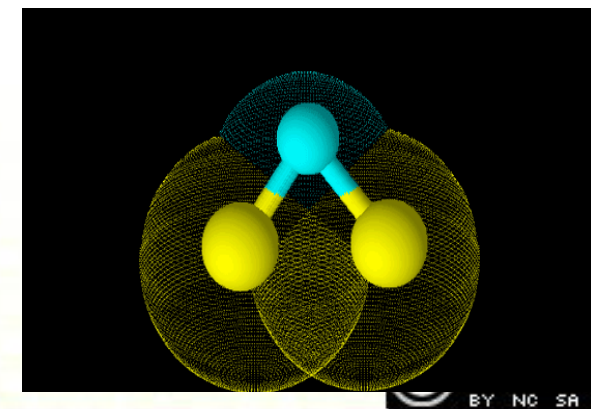
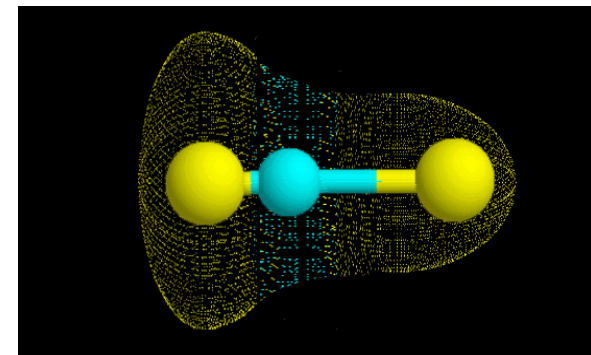
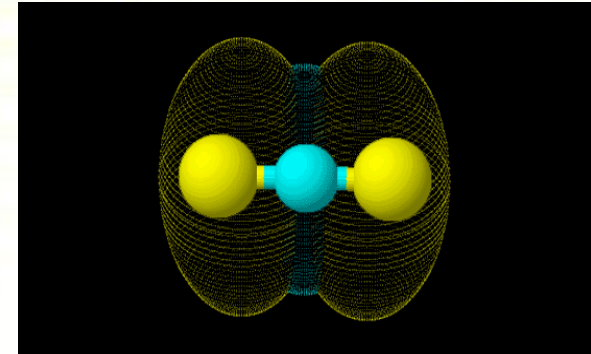
Only 1 in 10,000,000 (0.00001%) photons are scattered inelastically

Raman Effect is a 2-photon Scattering Process



- ✓ Why to select Raman for materials analyses?
- ✓ Fundamental importance
- ✓ What is the process?
- ✓ When and Where I should do?
- ✓ Instrumentation
- ✓ Basic theoretical concepts
- ✓ Challenges
- ✓ Spectral analyses
- ✓ Examples
- ✓ Conclusion

Typical frequencies of molecular vibrations range from less than 10^{12} to approximately 10^{14} Hz.



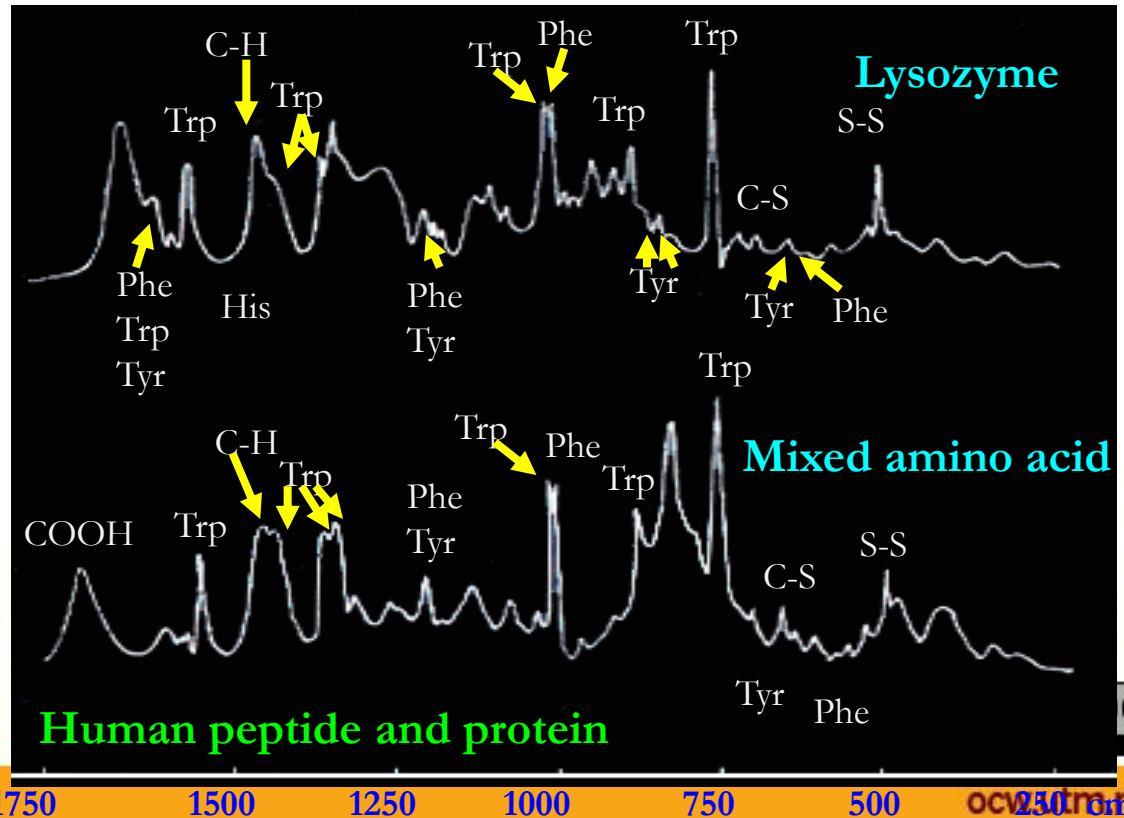
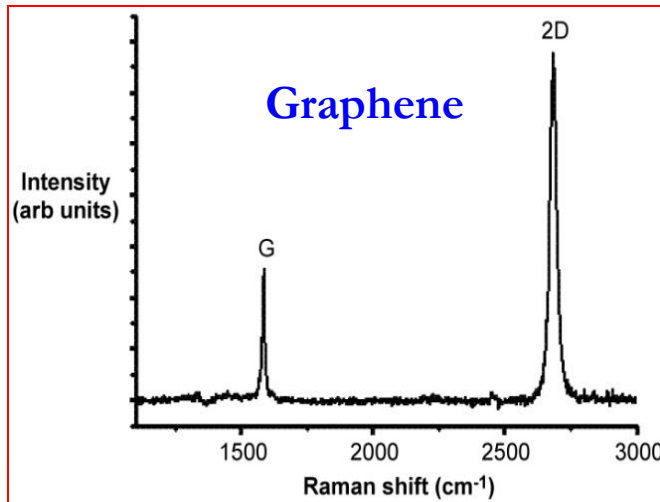
✓ A spectroscopic technique relies on **inelastic scattering** of **monochromatic light** (laser) in the visible, NIR, or NUV range.

What is it for?

✓ For determining vibrational, rotational, and other low-frequency modes (**fingerprints**) in a system (molecule to bulk).

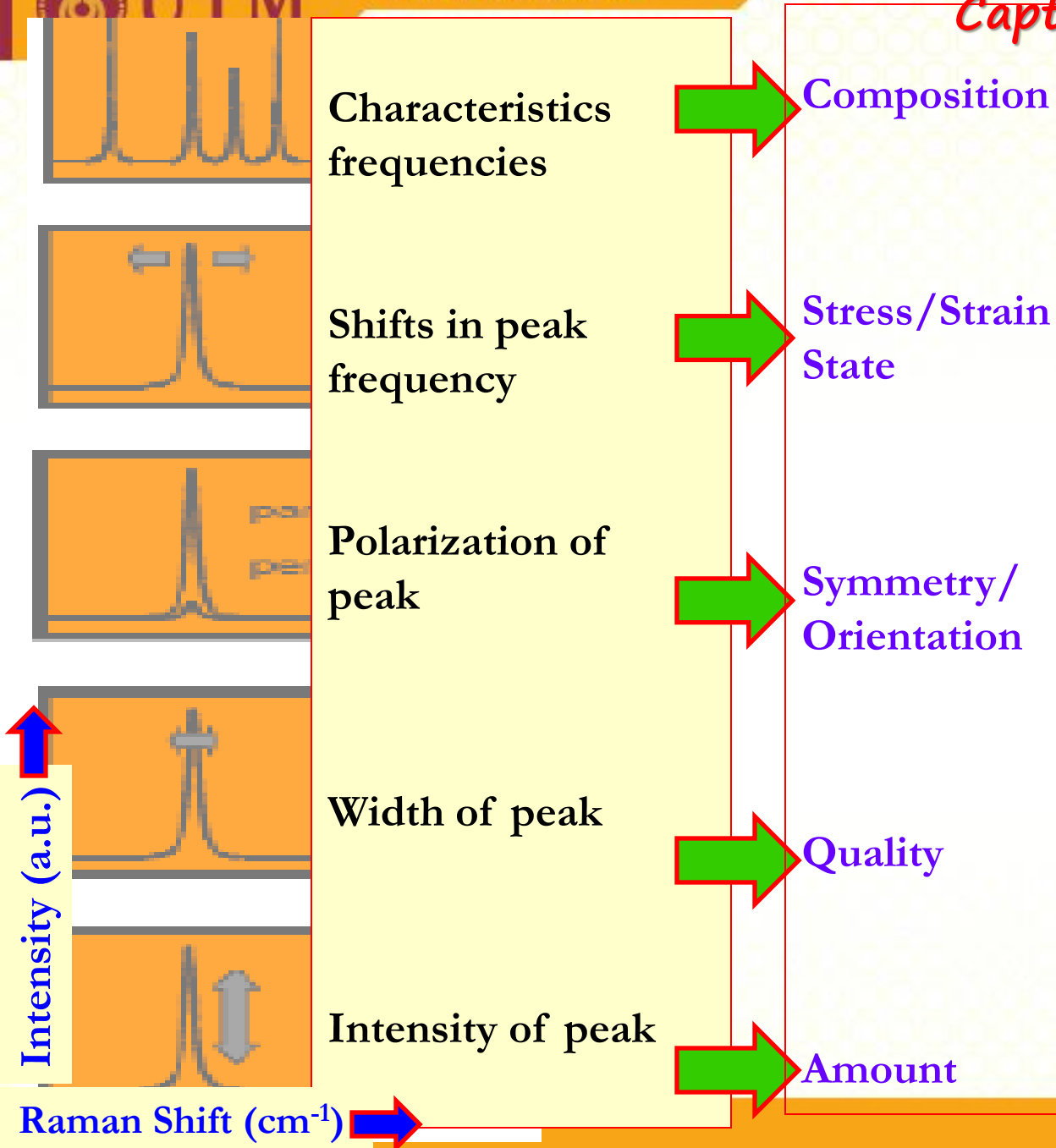
How Raman spectra looks like?

Lysozyme is a protein found in tears, saliva, and other secretions.



What information to extract??
Need Analyses!!

Analyses of Samples Fingerprints Captured by Raman Spectra



- ✓ Number of bands
- ✓ Band Intensities
- ✓ Band position
- ✓ Band symmetry
- ✓ Band polarization
- ✓ Band width
- ✓ Band shape

Spectrum:
Raman Shift (cm⁻¹)
Vs. Intensity (a.u.)

- ✓ **One broad band may be superposition of two or several peaks: Deconvolution is needed.**
- ✓ **Main peak may have shoulder or satellites.**

Why Raman to Use Spectroscopy?

- ✓ **Raman spectroscopy**: Important tool for characterization of **all** kinds of materials and interfaces, as **low frequency lasers** allow their excitations in the **infrared frequency** range by **minimizing** the effects of **fluorescence** (especially for polymers).
- ✓ Advances in Raman instrumentation have been dramatic, in many cases it is **preferred** method.
- ✓ **Raman spectroscopy** is **complementary to IR**, and due to differences in the nature of selection rules, yields **vibrational** information **not obtainable** from IR.
- ✓ **Raman** also is advantageous with **aqueous solutions** due to the low Raman scattering of water (biology, chemistry, forensic, pharmacology, etc.).

Exclusion Rule

If the molecule has a **center of symmetry**, then **no modes** can be both infrared and Raman active.



Why to Prefer Raman Scattering?

Notable Merits:

- ✓ Non-destructive to samples (**minimal** sample preparation)
- ✓ **Higher temperature** studies are possible (do not care about IR radiation)
- ✓ Easily examine **low wavenumber** region **$\sim 100 \text{ cm}^{-1}$** readily achievable
- ✓ Better microscopy: Using visible light so can **focus tightly**
- ✓ Easy sample preparation: **Water** is an excellent solvent for Raman
- ✓ Sample can be probed through **transparent containers** (glass or plastic)
- ✓ On top, **rich** in information contents

Prominent De-Merits:

- ✓ Very **low** sensitivity: Only 1 in $10^5 - 10^7$ photons suffers Raman shift
- ✓ Intense visible excitation source may **degrade** samples and cause fluorescence (**Raman efficiency $\sim \nu^4$**)
- ✓ More sophisticated (**expensive**) due to **laser** and other arrangements
- ✓ In solid state and on surfaces the **intensities vary** by **many orders** of magnitude according to substrate and preparation
- ✓ On top, in-depth knowledge is required for **interpretation**



FTIR Versus Raman: Information-wise

FTIR Spectroscopy (arise from change in the dipole moment)

- ✓ Lattice dynamics (phonons)
- ✓ Optical transitions (band structure)
- ✓ Absorption

Raman Spectroscopy (arise from change in the polarizability)

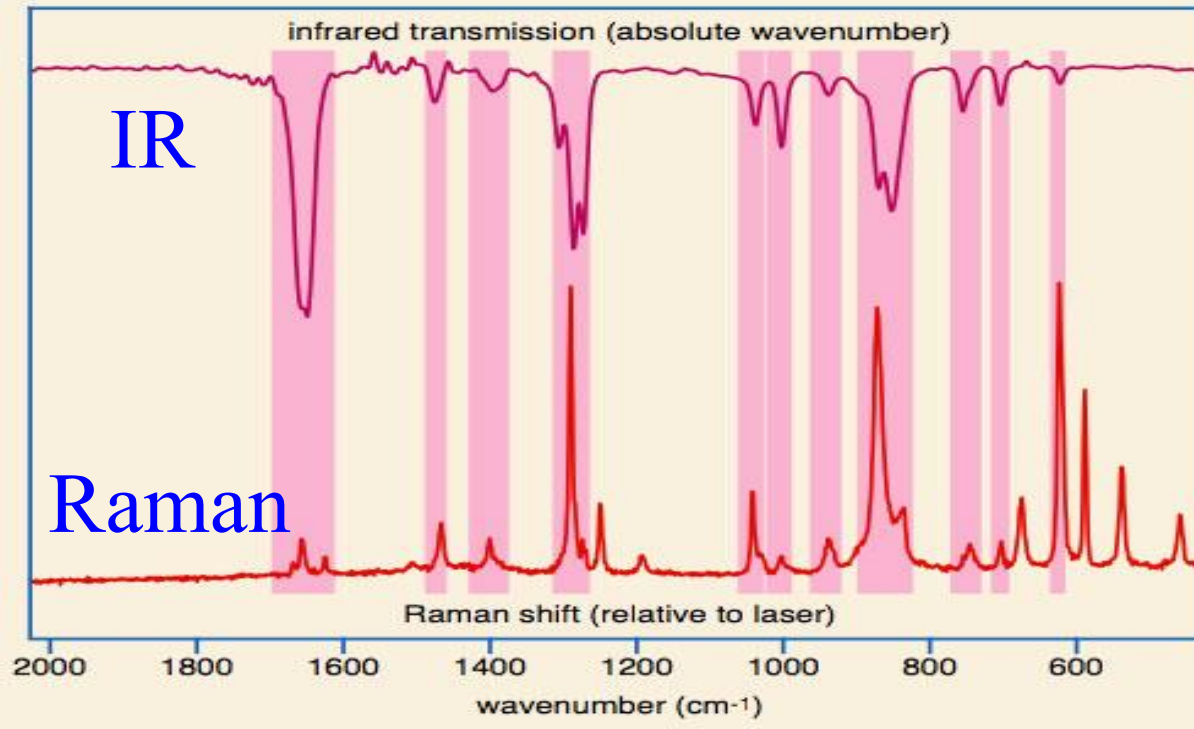
- ✓ Local structural information (symmetry, vacancies, dopants, etc.)
- ✓ Lattice dynamics (phonons)
- ✓ Electronic **excitations**, Magnetic excitations (energy, lifetime, symmetry)

Why Raman ?

- ✓ Non-destructive, contactless
- ✓ Informative
- ✓ Relatively painless
- ✓ Macro- to microscopic measurements possible
- ✓ Easy to **implement external parameters (T, B, P, etc)**
- ✓ No interference of water

Comparison of IR and Raman Spectra

Raman and IR spectra of PETN



Raman bands are much sharper than IR one

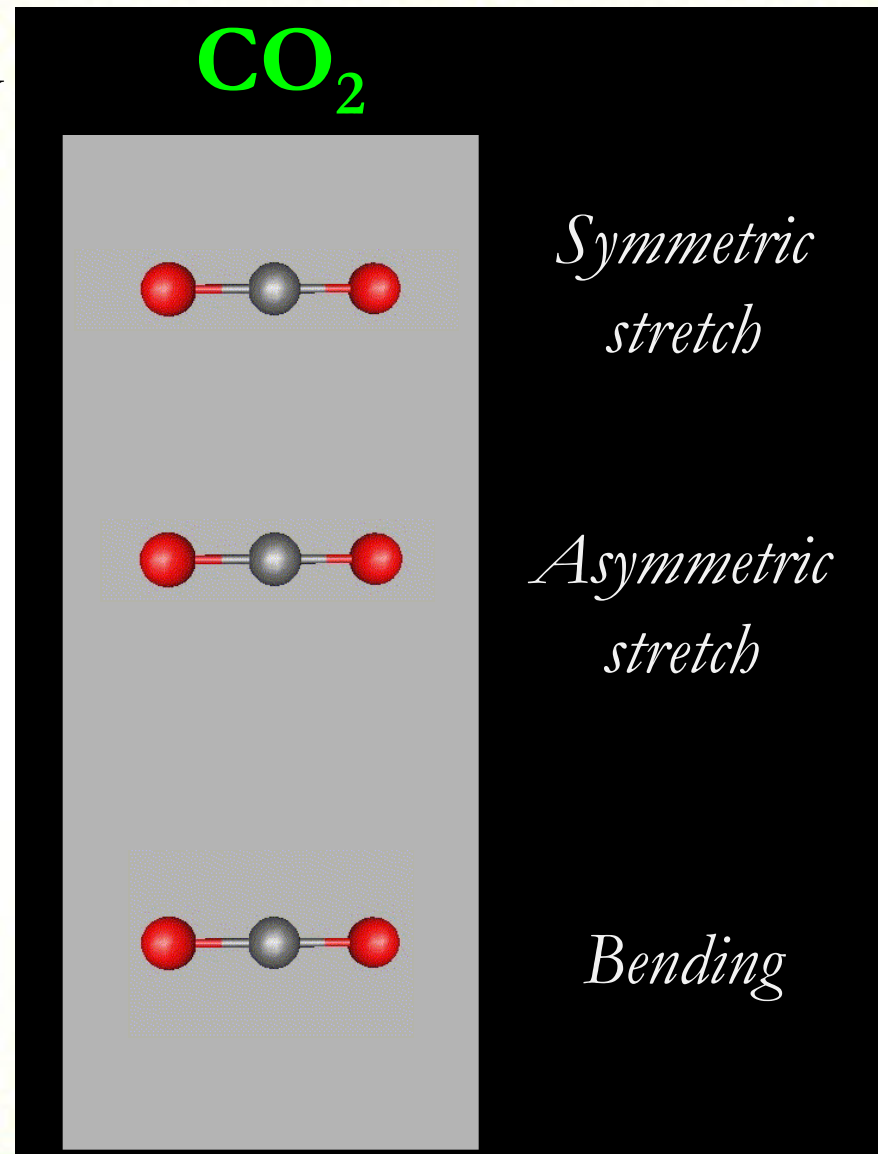
✓ **PETN** (Pentaerythritol tetranitrate) is one of the most powerful explosives and is difficult to detect. Because of its plastic nature, the explosive can easily pass metal detectors. Even bomb-sniffing dogs cannot detect it because of its low pressure molecules. (Airport Forensic!!)

- ✓ The region of the infrared spectrum which is of greatest interest to scientists is the wavelength range **2.5 to 15 μm** (In practice, units proportional to **frequency**, (**wavenumber** in units of cm^{-1}) rather than wavelength, are commonly used and the region 2.5 to 15 μm corresponds to approximately **4000 to 400 cm^{-1}**).
- ✓ Absorption of radiation in this region by a typical organic molecule results in the excitation of **vibrational, rotational** and **bending modes**, while the **molecule itself remains** in its **electronic ground state**.
- ✓ The frequencies at which there are absorptions of EM radiation ("**peaks**" or "**signals**") can be correlated directly to bonds within the compound in question.

Light inelastically scattered when there is spatial and temporal fluctuation or modulation in the polarizability.



- ✓ Atoms within a molecule are never still. They **vibrate** in a variety of ways (**modes**).
- ✓ Atoms may be considered as weights connected by springs.
- ✓ Each vibrational mode (**normal modes**) has its own **resonant frequency**.
- ✓ In Raman process **molecular bonds** interact with light.

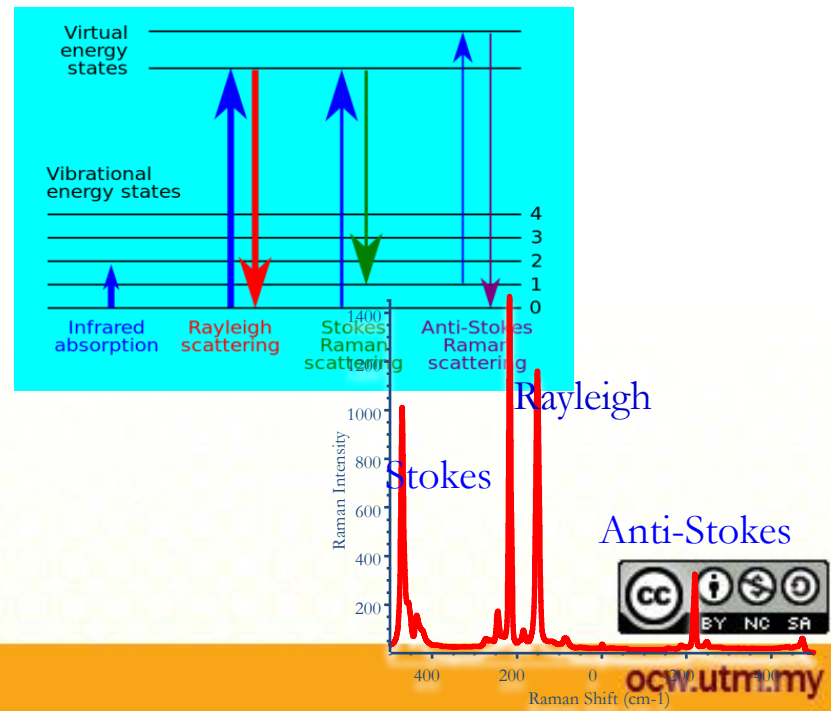
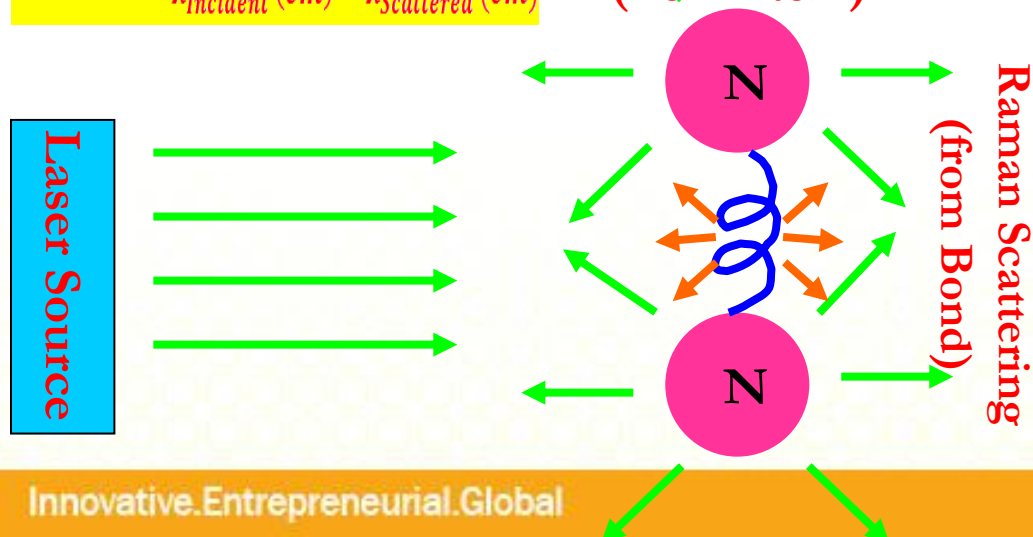


Origin of Raman Scattering & Raman Effect

- ✓ When light is scattered from a molecule **most photons** are **elastically** scattered (**Rayleigh**). The scattered photons have the **same energy** (frequency/wavelength) as the incident photons.
- ✓ However, a small fraction of light (approximately **1 in 10^7 photons**) is scattered at optical frequencies usually **lower than**, the frequency of the incident photons. The process leading to this **inelastic scattering** is termed the **Raman effect**. Raman scattering can occur with a change in **vibrational, rotational or electronic energy** of a molecule. Physicists/Chemists are concerned primarily with the **vibrational Raman effect**. The term **Raman effect** usually means **vibrational Raman effect** only.
- ✓ The difference in energy between the **incident photon** and the **Raman scattered photon** is equal to the energy of a vibration of the scattering molecule. A plot of **intensity of scattered light** versus **energy difference** is a **Raman spectrum**.

$$\Delta\nu(\text{cm}^{-1}) = \frac{1}{\lambda_{\text{Incident}}(\text{cm})} - \frac{1}{\lambda_{\text{Scattered}}(\text{cm})}$$

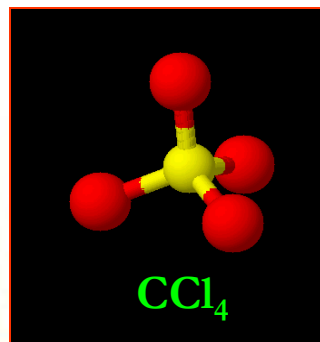
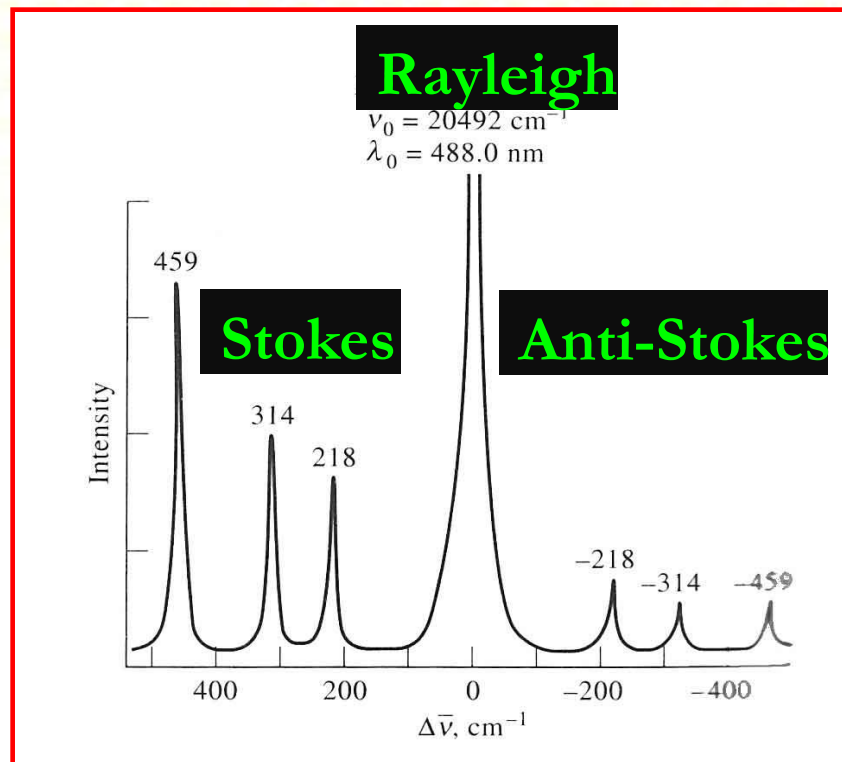
Rayleigh Scattering (from Atom)



How a Complete Raman Spectrum Appears?

A **complete** Raman spectrum consists of:

- ✓ A Rayleigh scattered peak (**high intensity, same wavelength** as excitation).
- ✓ A **series** of **Stokes**-shifted peaks (**low intensity, longer wavelength**).
- ✓ A **series** of **anti-Stokes** shifted peaks (**still lower intensity, shorter wavelength**).
- ✓ Spectrum is **independent** of excitation wavelength (488, 632.8, or 1064 nm)



Spectrum of CCl₄, using an Ar⁺ laser at 488 nm.

459 cm^{-1} - Symmetric stretching

314, 218 cm^{-1} - Asymmetric stretching



- ✓ The Raman effect arises when a photon is incident on a molecule and interacts with the **electric dipole (polarizability)** of the molecule.
- ✓ It is a form of electronic (more accurately, **vibronic**) spectroscopy, although the spectrum contains vibrational frequencies.
- ✓ In **classical** terms, the interaction can be viewed as a **perturbation** of the molecule electric field.
- ✓ In **quantum** mechanics the scattering is described as an excitation to a **virtual state** lower in energy than a real electronic transition with nearly coincident de-excitation and **a change in vibrational** energy.
- ✓ The **scattering event** occurs in **10^{-14} seconds or less**. Thus, the **virtual** state description of scattering works.

Absorption (Excitation): 10^{-15} s

Internal Conversion and Vibrational Relaxation: 10^{-14} - 10^{-11} s

Fluorescence: 10^{-9} - 10^{-7} s; Phosphorescence: 10^{-3} - 10^2 s

- ✓ Light scattering technique for studying molecular vibrations
- ✓ Change in polarization is necessary for a vibration to be seen in Raman spectrum
- ✓ Implies change in distribution of electron cloud around vibrating atoms
- ✓ Polarization is easier for long bonds than for short bonds
- ✓ IR-inactive radiations are Raman-active

Principles

✓ Part of the radiation is scattered by molecules when the radiation passes through sample

Three types of scattering occurs

- ✓ Rayleigh scattering
- ✓ Stokes scattering
- ✓ Anti-Stokes scattering

Principles

Rayleigh scattering

- ✓ Result of elastic collisions between photons and sample molecules
- ✓ Energy is same as incident radiation

Stokes scattering

- ✓ Scattered photons have less energy than the incident radiation
- ✓ Results in spectral lines called Raman lines

Anti-Stokes scattering

- ✓ Raman lines result from photons scattered with more energy

Principles

- ✓ Stokes and anti-stokes are due to inelastic collisions
- ✓ The process is not quantized
- ✓ Raman lines are shifted in frequency from Rayleigh frequency
- ✓ Radiation measured is visible or NIR

Advantages over IR

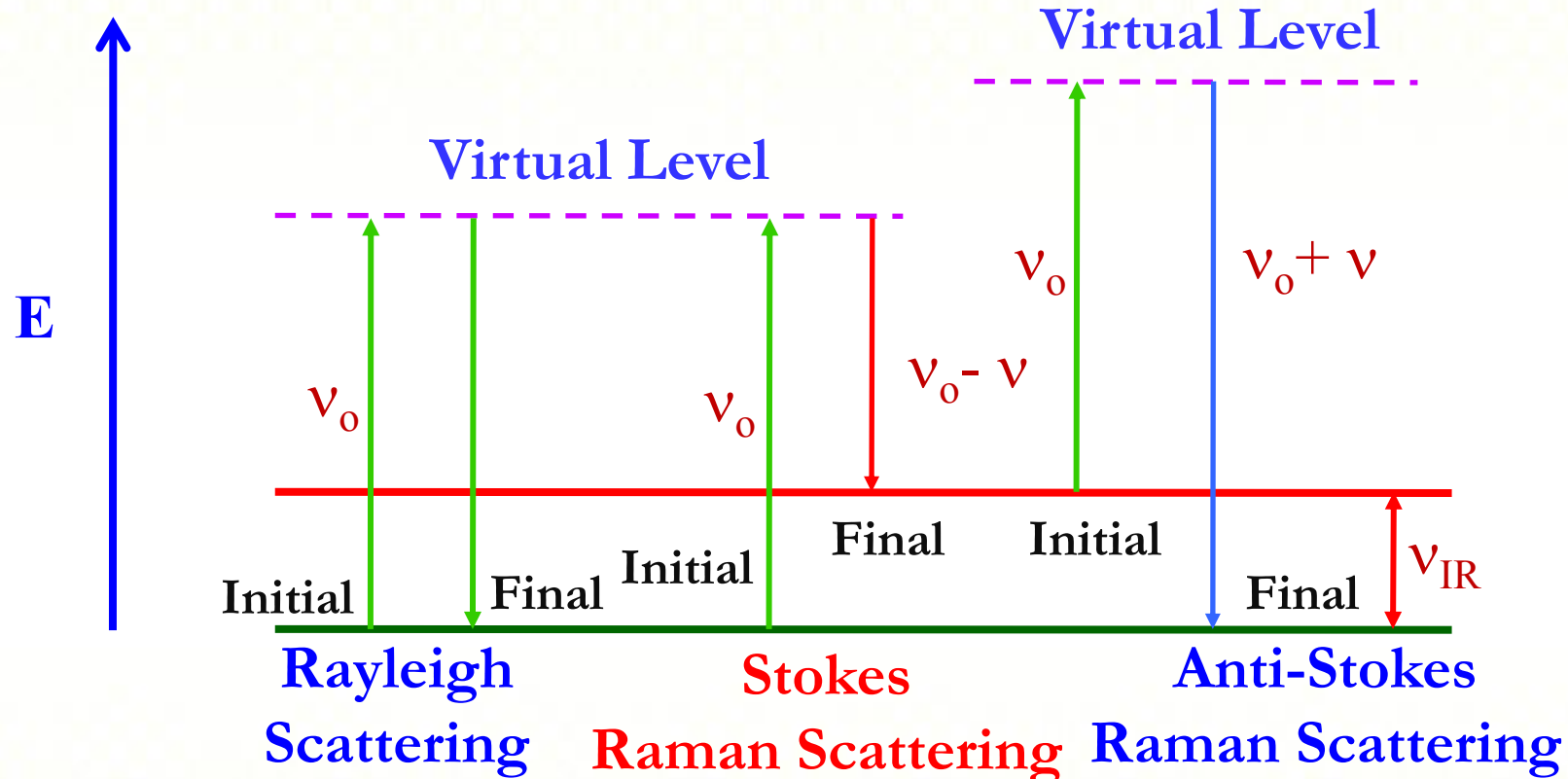
- ✓ Aqueous solutions can be analyzed
- ✓ Fewer and much sharper lines so better for quantitative analysis

Techniques

- ✓ Resonance Raman Spectroscopy
- ✓ Surface-Enhanced Raman Spectroscopy (SERS)
- ✓ Raman Microscopy

Raman Scattering & Raman Effect: Virtual Energy Level Diagram

Electronic Adsorption Level



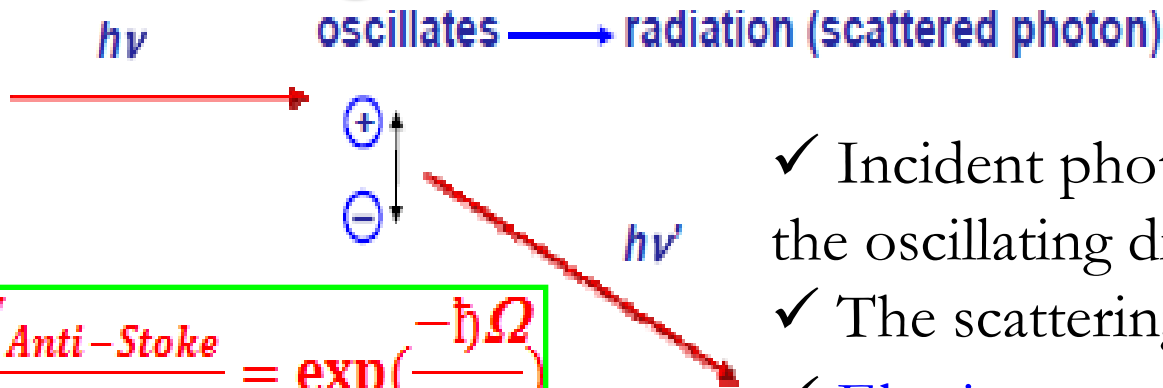
In Stokes Process: Phonon is **Emitted (+) Sign**

In Anti-Stokes Process: Phonon is **Absorbed (-) Sign**

$$\kappa_1 = \kappa_2 \pm Q$$

$$\omega_1 = \omega_2 \pm \Omega$$

Scattering



$$\frac{I_{\text{Anti-Stokes}}}{I_{\text{Stokes}}} = \exp\left(\frac{-\hbar\Omega}{k_B T}\right)$$

- ✓ Incident photon oscillates atoms and the oscillating dipoles radiate
- ✓ The scattering process is instantaneous
- ✓ Elastic scattering when $h\nu = h\nu'$
- ✓ Inelastic scattering when $h\nu \neq h\nu'$ (*Raman scattering*)

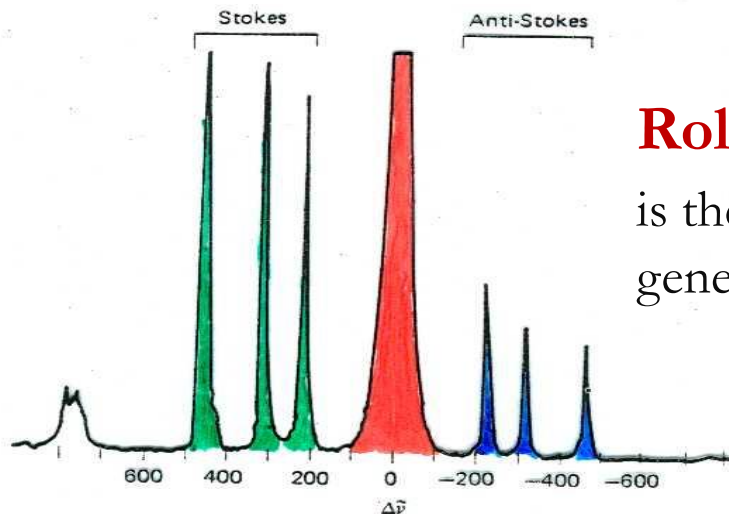


Figure 6-14 Raman spectrum of liquid CCl_4 scanned at $500 \text{ cm}^{-1}/\text{min}$ using a $3\text{-}\mu\text{l}$ sample with helium-neon 632.8 nm excitation. The strong signal at $\Delta\tilde{\nu} = 0$ is due to Rayleigh scattering of laser radiation. (*Journal of Chemical Education*,^(34*))

Role of Laser: The total spontaneous Raman signal is the **incoherent superposition** of the fields generated by an ensemble of **N oscillators**

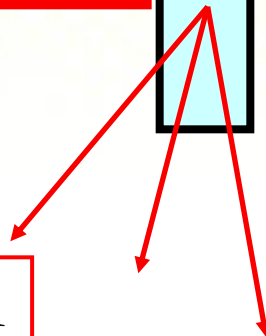
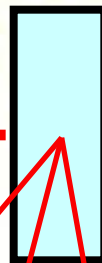
$$I_R \sim N I_L$$

Scattering of Photon from Optical Phonon

Goal & Challenges of Raman Spectroscopy?

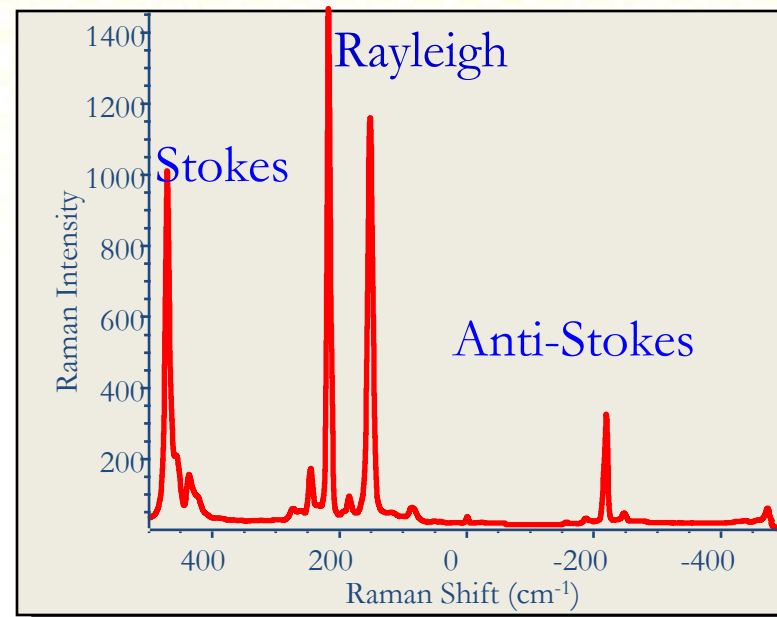
Detection & Analysis of Inelastically Scattered Radiation

Laser



Challenges

- ✓ Rejection of Rayleigh Signal
- ✓ Sensitive Detection
- ✓ High Resolving Power
- ✓ Strong Coherent Source



Raman Signal: Very Feeble !!!!

Rayleigh: No spectroscopic information

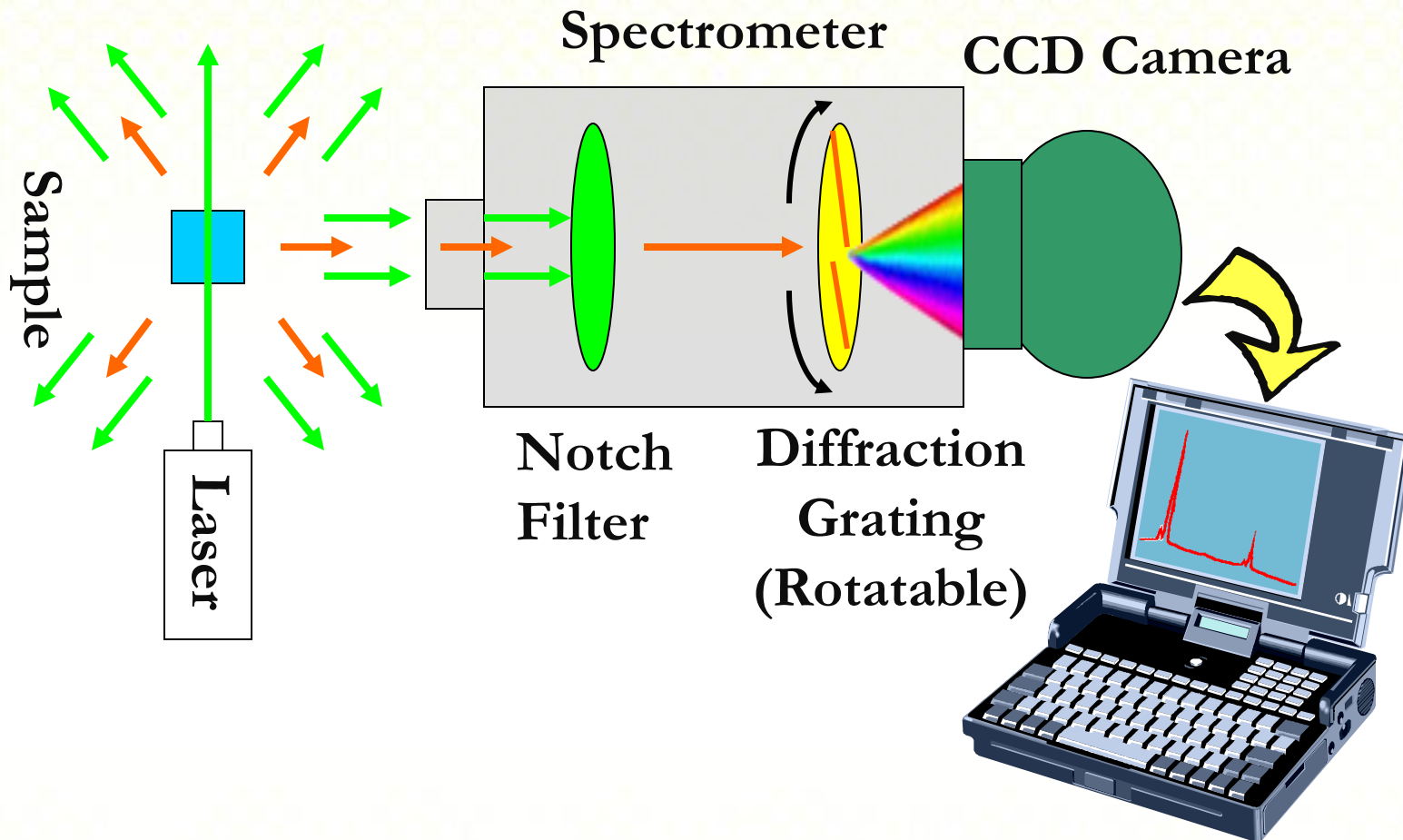
Stokes: Vibrational Excitation

Anti-Stokes: Vibrational De-excitation

Inelastic light scattering by **optical phonons** in materials, or more generally by other **elementary excitations** such as magnons, plasmons, polarons, excitons, electronic excitations, etc.



Instrument: Configuration Illustration



The Raman effect is **quite weak**. Rayleigh emission is 10^5 to 10^6 times more intense.

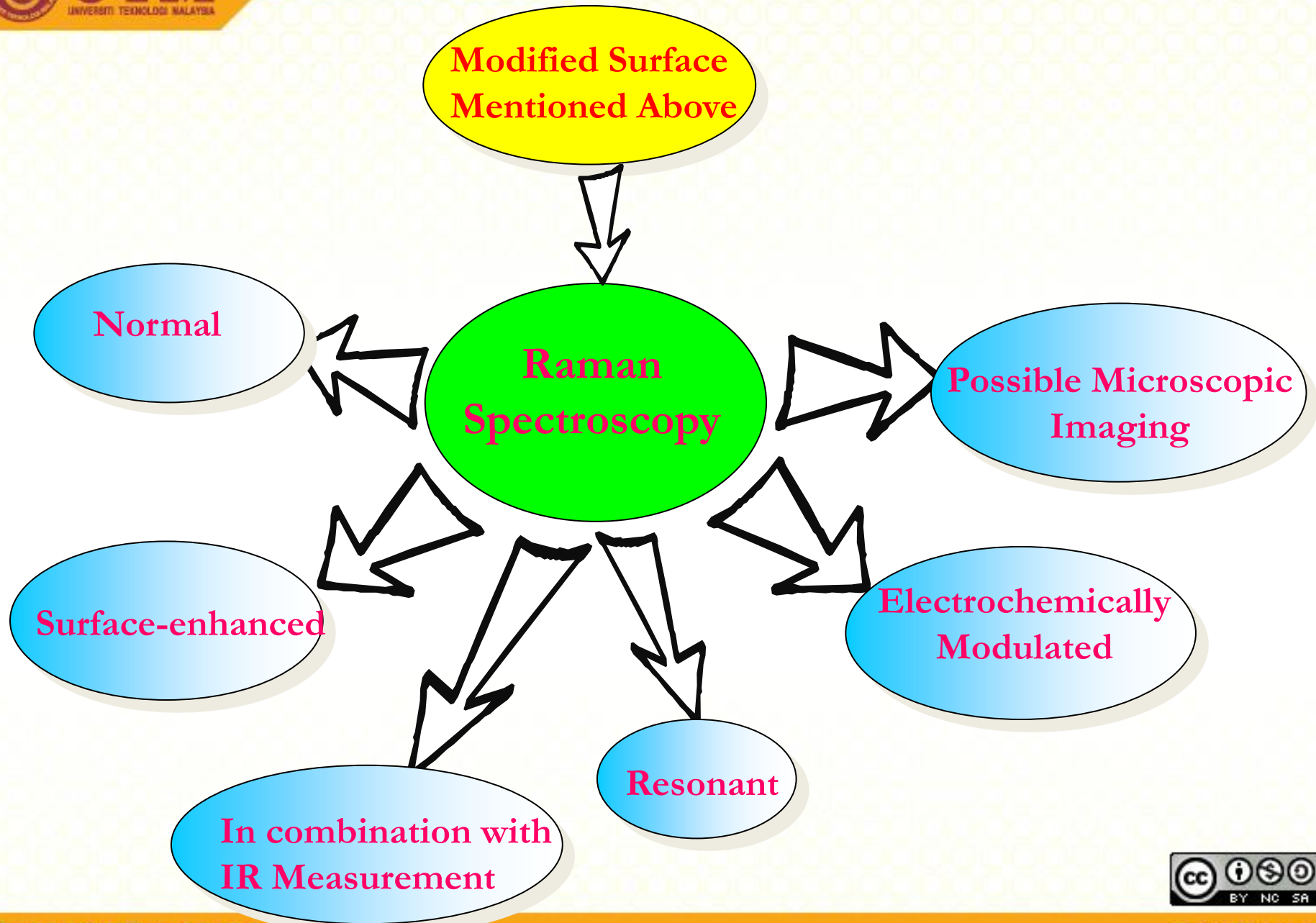
Advancements in Raman Spectroscopy

- ✓ FT-Raman
- ✓ Chemical Mapping
- ✓ Raman Imaging
- ✓ Tip-Enhanced Raman Spectroscopy (TERS)
- ✓ Spatially Offset Raman Spectroscopy (SORS)
- ✓ Surface-enhanced & Surface-enhanced Resonance Raman Spectroscopy (SERS & SERRS)
- ✓ Resonance Raman Scattering (RRS)
- ✓ Stimulated Raman Spectroscopy (SRS)
- ✓ Coherent anti-Stokes Raman Spectroscopy (CARS)
- ✓ Hyper-Raman Spectroscopy (HRS)
- ✓ Spontaneous Raman Spectroscopy (SR)
- ✓ Optical Tweezers Raman Spectroscopy (OTRS)

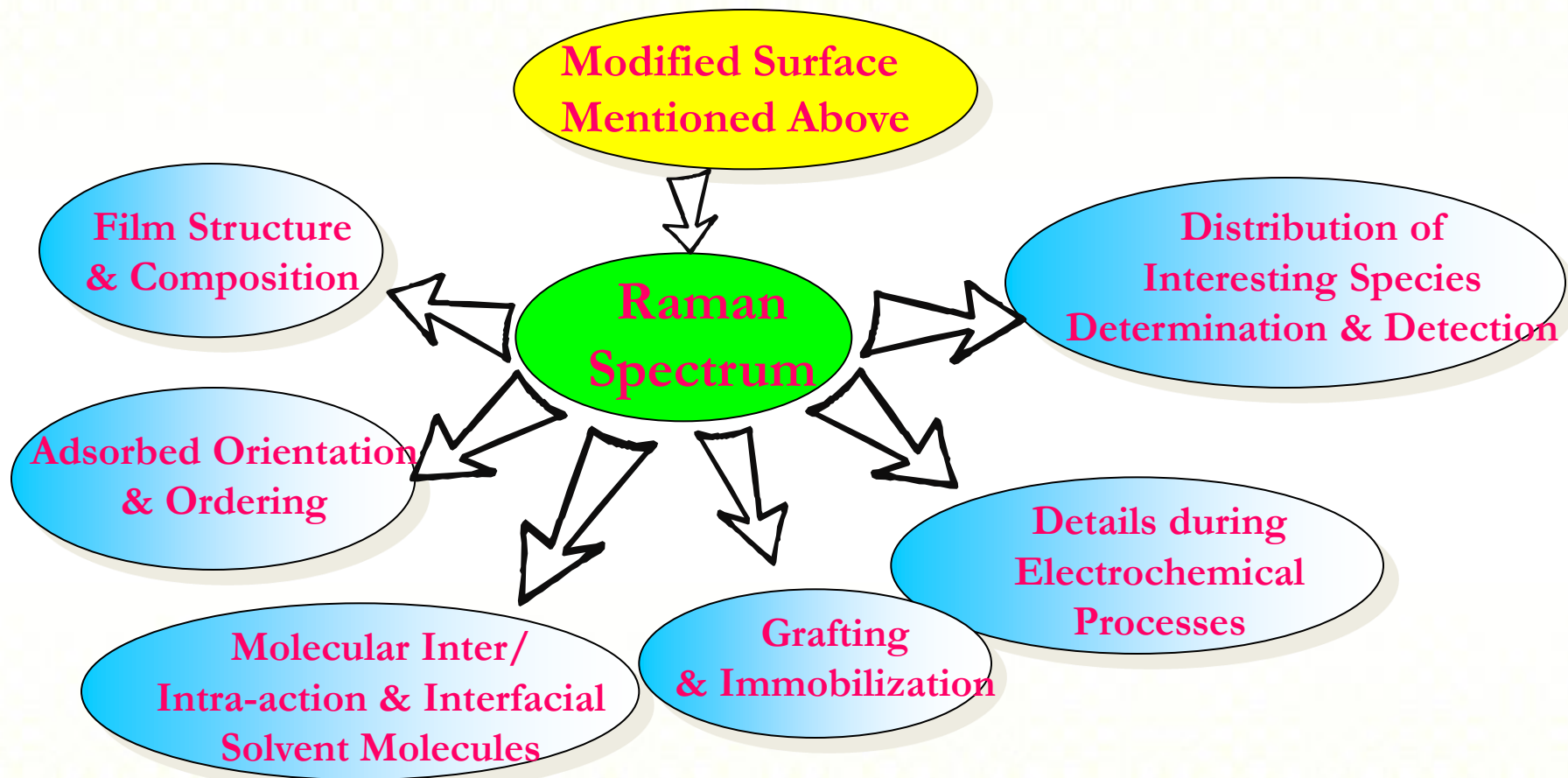
✓ Raman spectroscopy is conventionally performed with green, red or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as assumed by scattering theory.

✓ The situation changes if the wavelength of the exciting laser within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases by a factor of 10^2 - 10^4 . This resonance enhancement or resonance Raman effect can be quite useful.

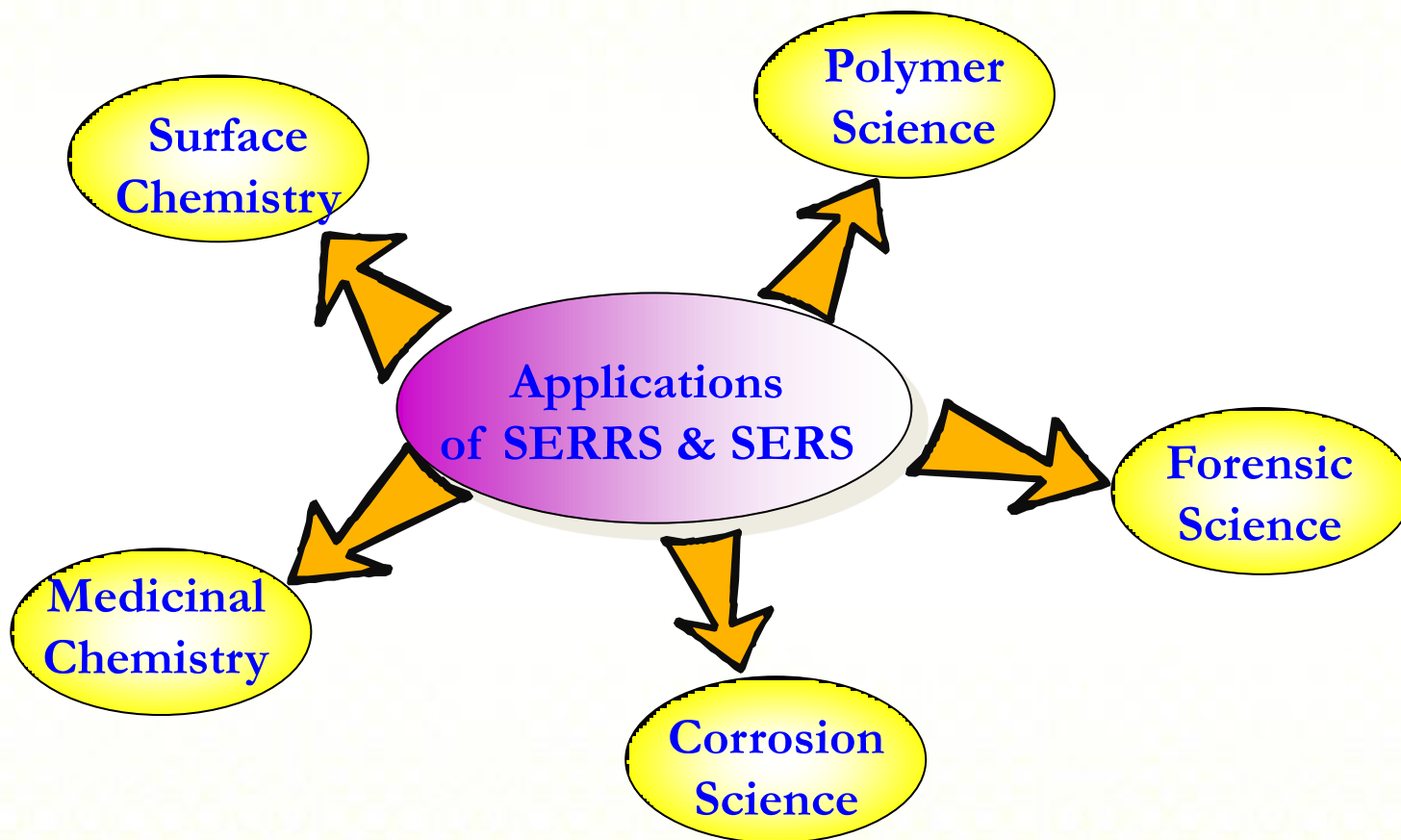




Information Obtained in Combined Electro-physical-chemistry



Surface Enhanced and Surface Enhanced Resonance Raman Scattering: Applications



- ✓ The electric field E_i of the light wave acts on the charges in the material
- ✓ Induced dipole moment P_i of a molecule (vector)

$$P_i = p_i + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \dots$$

Raman effect
Hyper Raman effect

p_i – Permanent dipole moment

α_{ij} – Polarizability (tensor)

i, j, k, l – Subscripts running over directions x, y, z

Power radiated by \mathbf{P}_{ind}

$$I \propto \omega^4 |\mathbf{P}_{ind} \cdot \mathbf{e}_s|^2 \propto \omega^4 \left| \mathbf{e}_i \cdot \frac{\partial \vec{\chi}}{\partial \mathbf{Q}} \Big|_0 \cdot \mathbf{Q}(\mathbf{q}, \omega_0) \cdot \mathbf{e}_s \right|^2$$



Material polarization

$$P_i = p_i + \alpha_j E_j + K \quad \text{Taylor expansion}$$

$$= p_{oi} + \sum_n \left(\frac{\partial p_i}{\partial q_n} \right)_{q=0} q_{0n} \cos(\omega_n t) + \alpha_{oij} E_{0j} \cos(\omega_L t) \\ + \sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n} \right)_{q=0} q_{0n} \cos(\omega_n t) \times E_{0j} \cos(\omega_L t) + K$$

IR absorption

Rayleigh scattering

$$= p_{oi} + \sum_n \left(\frac{\partial p_i}{\partial q_n} \right)_{q=0} q_{0n} \cos(\omega_n t) + \alpha_{oij} E_{0j} \cos(\omega_L t)$$

$$+ q_{0n} E_{0j} \sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n} \right)_{q=0} \{ \cos(\omega_L - \omega_n)t + \cos(\omega_L + \omega_n)t \} + K$$

Raman scattering (Stokes & anti-Stokes)

Classical Macroscopic Theory of Polarizability

An oscillating dipole radiates energy at the frequency of its oscillation (e.g. a broadcast radio antenna, 60 Hz emission from transmission lines)

$$E = E_0 \cos(\omega_{ex} t)$$

The oscillating electric field of the excitation light.

$$\mu_{induced} = \alpha E = \alpha E_0 \cos(\omega_{ex} t)$$

The **induced** dipole moment from this oscillating field.

$$\alpha = \alpha_0 + (r - r_{eq}) \frac{d\alpha}{dr}$$

The molecular polarizability usually **changes with bond length**.

$$r - r_{eq} = r_{max} \cos(\omega_{vib} t)$$

The bond length oscillates at the **vibrational frequency**.

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dr} \right) r_{max} \cos(\omega_{vib} t)$$

$$\begin{aligned} \mu_{induced} &= \left[\alpha_0 + \left(\frac{d\alpha}{dr} \right) r_{max} \cos(\omega_{vib} t) \right] E_0 \cos(\omega_{ex} t) \\ &= \alpha_0 E_0 \cos(\omega_{ex} t) + E_0 r_{max} \left(\frac{d\alpha}{dr} \right) \cos(\omega_{ex} t) \cos(\omega_{vib} t) \end{aligned}$$



Substituting the identity

$$\cos x \cos y = \frac{1}{2} [\cos(x + y) + \cos(x - y)]$$

Rayleigh Component

$$\mu_{induced} = \alpha_0 E_0 \cos(\omega_{ex} t) +$$

$$\frac{E_0 r_{max}}{2} \left(\frac{d\alpha}{dr} \right) [\cos((\omega_{ex} + \omega_{vib})t) + \cos((\omega_{ex} - \omega_{vib})t)]$$

Anti-Stokes Component

Stokes Component

Here Raman Selection Rules Comes In

Raman Selection Rules for Intensities

- ✓ **C**lassical EM field description of Raman band intensities: The dipole moment in terms of polarizability of the molecule (α) is $\mathbf{P} = \alpha\mathbf{E}$
- ✓ **P**olarizability measures the *ease* with which the electron cloud around a molecule can be *distorted*. The induced dipole emits or scatters light at the optical frequency of the incident light wave.
- ✓ **R**aman scattering occurs because a molecular vibration can **change the polarizability**.
- ✓ The *change* is described by the polarizability derivative, $\partial\alpha/\partial Q$, where Q is the normal coordinate of the vibration.
- ✓ The **selection rule** for a **Raman-active vibration** requires that there be a change in polarizability during the vibration $\partial\alpha/\partial Q \neq 0$



Raman Selection Rules for Intensities

- ✓ **Infrared-active** vibration requires that there must be a **net change** in **permanent dipole moment** during the vibration.
- ✓ From **Group Theory** one can show that if a molecule has a **center of symmetry** then **Raman-active** vibrations will be **silent** in the infrared, and vice versa.
- ✓ **Scattering intensity** is proportional to the square of the induced dipole moment, that is to the square of the polarizability derivative, $(\partial\alpha/\partial Q)^2$.

In Raman spectra there are few things to look at:

- ✓ Number of bands
- ✓ Band Intensities
- ✓ Band position
- ✓ Band symmetry
- ✓ Band polarization
- ✓ Band width
- ✓ Band shape

Vibrational Modes of Molecules: Number of Bands

- ✓ A **linear** molecule of N atoms has $3N-5$ normal modes of vibration.
- ✓ **Nonlinear** molecule has $3N-6$ normal modes.

Normal Modes:

- ✓ Stretching motion between two bonded atoms
- ✓ Bending motion between three atoms connected by two atoms
- ✓ Out-of-plane deformation modes

Remember Q is the normal coordinate of the vibrational modes

Fundamental Vibrations

Degrees of freedom	linear	non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

N = number of atoms in molecule



Number of bands in the Raman spectrum for an N-atom non-linear molecule is seldom $3N-6$, because:

- ✓ Polarizability **change is zero** or small for some vibrations
- ✓ Bands **overlap**
- ✓ Combination or **overtone** bands are present
- ✓ Fermi **resonances** occur
- ✓ Some vibrations are highly **degenerate**; etc...

Raman Spectroscopy is a method of determining **modes of molecular motions**, especially **vibrations**. It is predominantly applicable to the qualitative and quantitative analyses of covalently bonded molecules.

Spontaneous Raman spectroscopy is used to among other things, **characterize materials**:

- ✓ Measure **temperature**.
- ✓ Find the **crystallographic** orientation of a sample.
- ✓ Determine Crystal **stress**: through E_2^h mode
- ✓ Determine **carrier concentration**: through $A_1(\text{LO})$ mode and LPP-
- ✓ Can be used to observe other low frequency **excitations** of the solid, such as plasmons, magnons, and superconducting gap excitations.
- ✓ Obtain information on the **population** of a given phonon mode in the ratio between the Stokes intensity and anti-Stokes intensity.
- ✓ In **nanotechnology**, a Raman microscope can be used to analyze nanowires to better understand the **composition of the structures**.

Illegal drug inspection

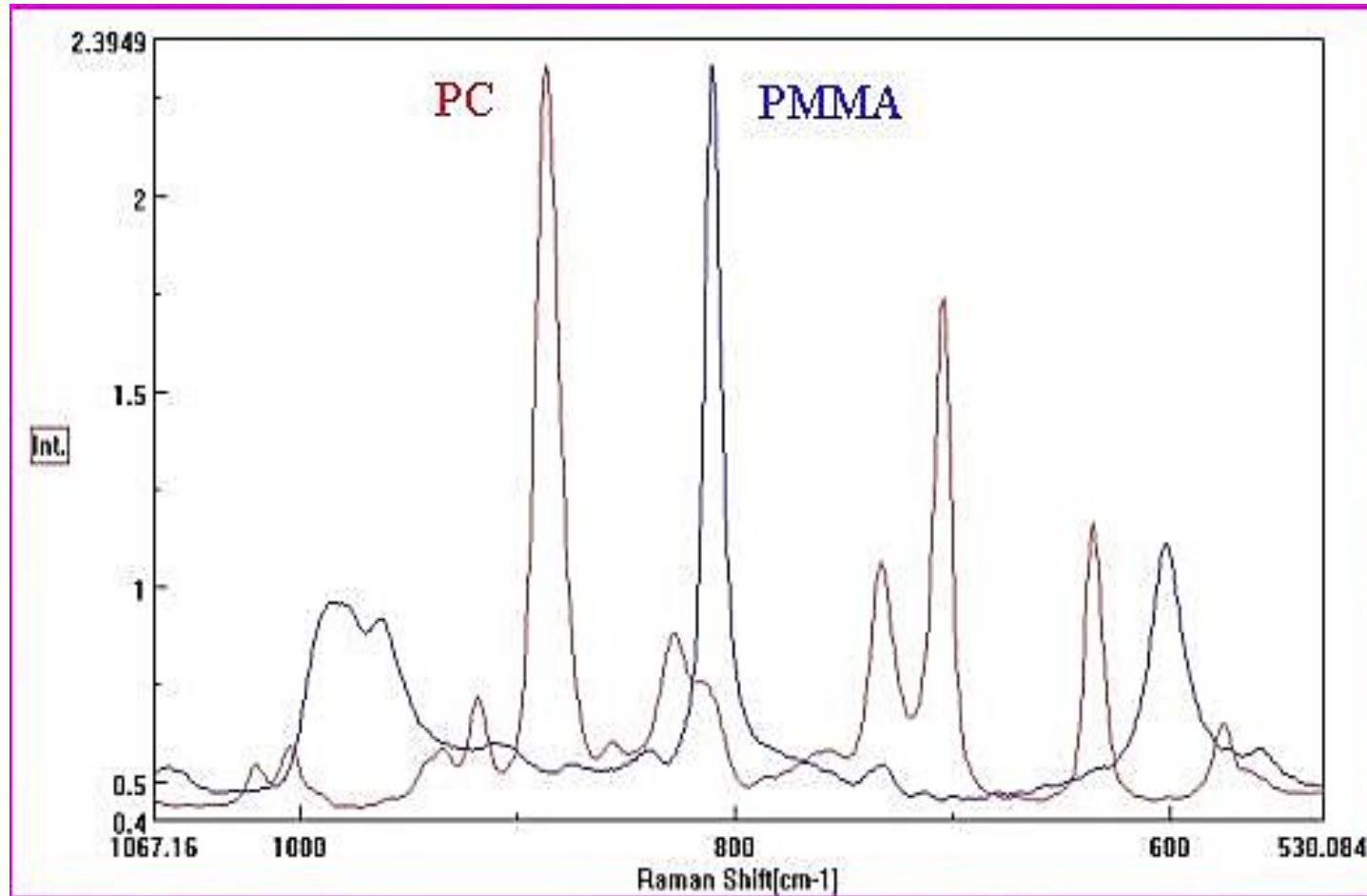
Mixture of **cocaine** and **sugar**. **Bright** spots are **cocaine**.

This is a **drug tablet**. The **yellow** corresponds to the **active** ingredient. Particles are in the 10's of μm range.

Paint Chips : Car Accident Investigation

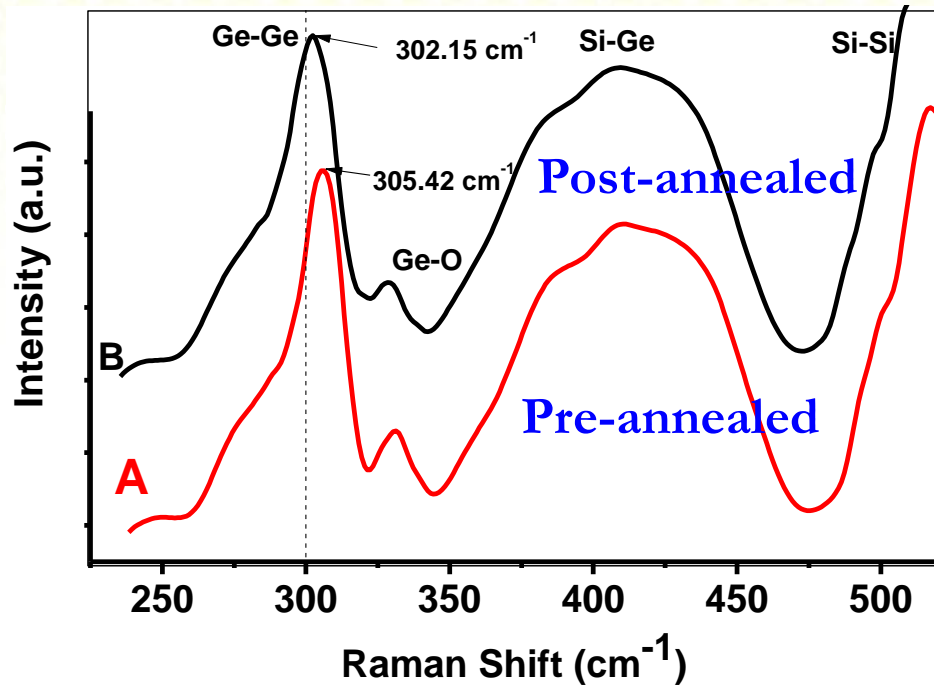
Forensic analysis of paint chips in vehicle accidents. Often multiple layers. Can analyze with IR by stripping successive layers. Image edge with micro-Raman.

Layers 1 and 3 turned out to be rutile phase TiO_2 - a white paint. Layer 2 was a Goethite, a red pigment and corrosion inhibitor. Layer 4 was molybdate orange, a common red paint in the 70's in North America and still used in the U.K. today. Layer 5 was a silicate based paint. Data arising from a case investigated by Los Angeles Police Department



Identify poly(carbonate) from poly(methylmethacrylate). Both used for shatter-proof glass

Ge Nanoislands on Si Substrate

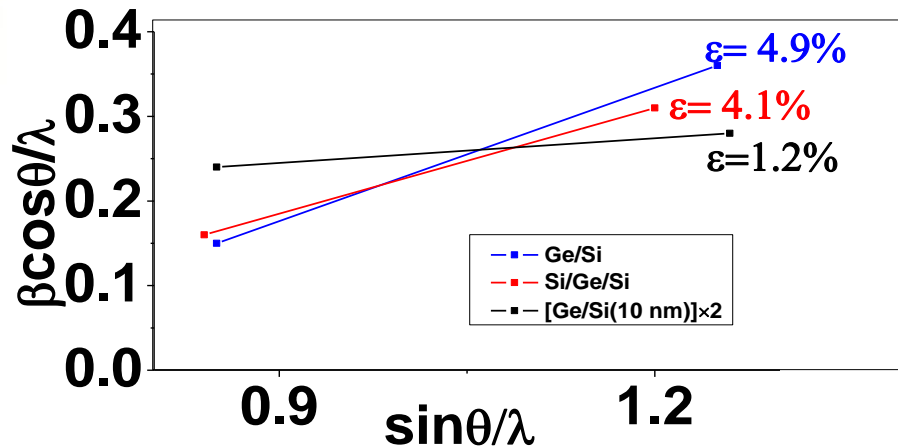


- ✓ The Raman shift is related to evolution of shape, size and Ge composition in dots
- ✓ Ge-Ge optical phonon for pre-annealed and post-annealed (650 °C) samples and their position **matching** to the bulk crystalline Ge (300 cm⁻¹).

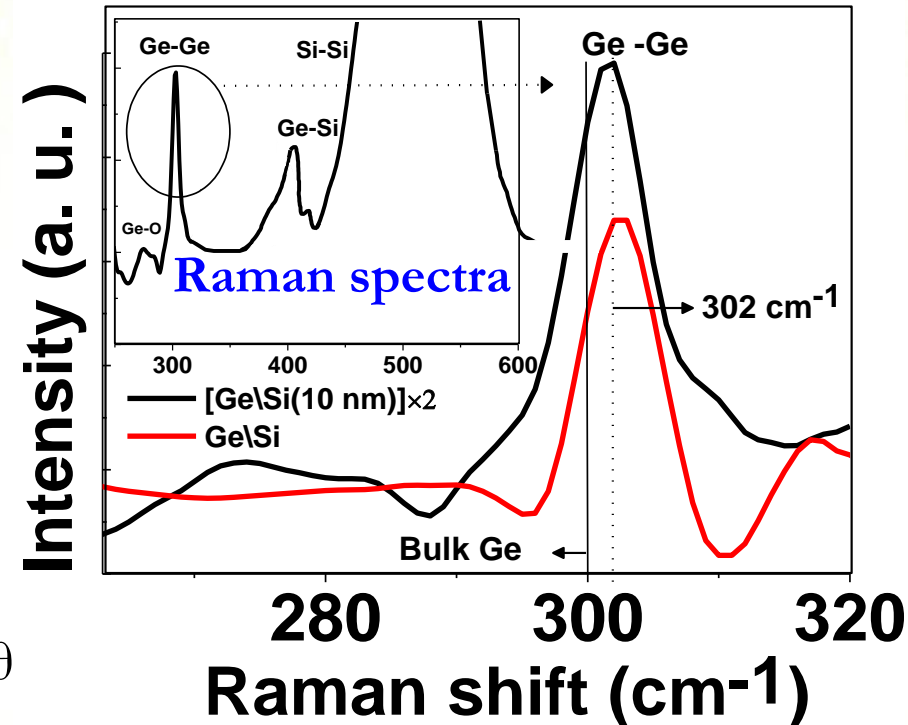
✓ Some phonons and vibrational modes are **restricted** in the low dimensional system. This restriction labeled as quantization is displayed in different behaviors such as changes in the symmetry of the vibration peaks, vibrations that shift to different energies and variation in the peak intensity that can be vanished or even enhanced.

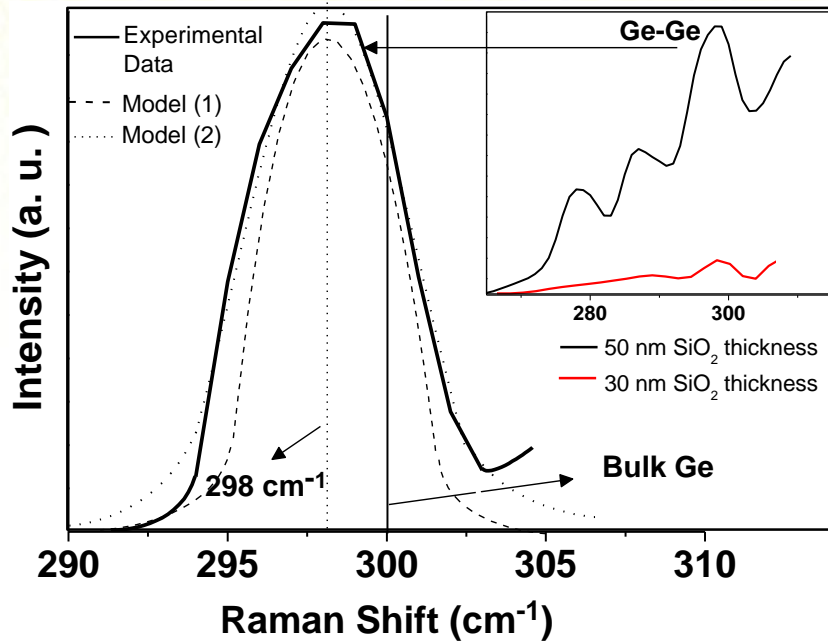
Williamson-Hall Plot and Raman Analysis for Ge Nanoislands Bilayer on Si Substrate

Williamson-Hall plot



- ✓ A linear relation between $\beta \cos \theta$ and $\sin \theta$
- ✓ Decrease of strain through bi-layering
- ✓ Ge-Ge optical phonons are **shifted** slightly to higher frequencies
- ✓ Shift is originated from the competitive effect of **phonon confinement** and **strain**
- ✓ The signature of the **intermixing** is pronounced as Ge-Si peak





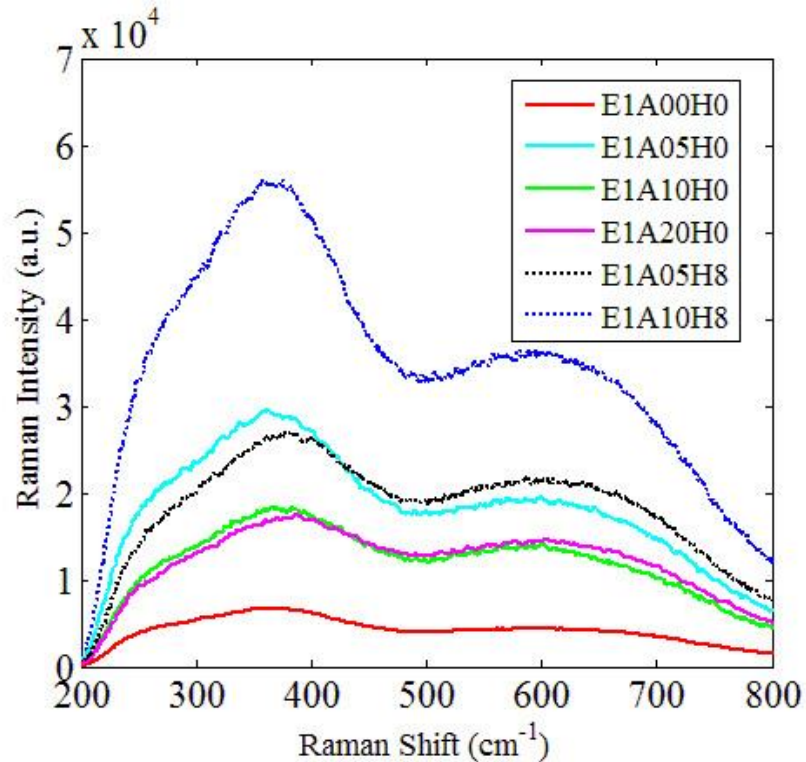
Model 1

$$I(\omega) = \int \frac{4\pi q^2 |C(0, q)|^2}{[\omega - \omega(q)]^2 + \left[\frac{\Gamma_c}{2}\right]^2} dq$$

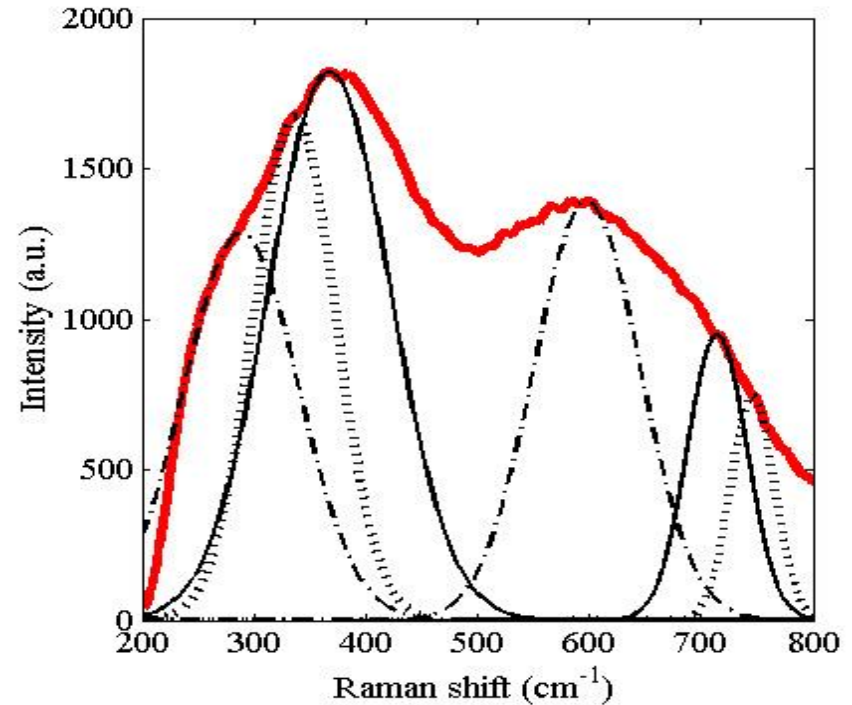
Model 2

$$I(\omega) = \int \rho(L) dL \times \int \frac{4\pi q^2 |C(0, q)|^2}{[\omega - \omega(q)]^2 + \left[\frac{\Gamma_c}{2}\right]^2} dq$$

- ✓ Emission at 2.9 eV can be explained by Ge-nanoislands/SiO₂/Si interface model.
- ✓ Peak at 298 cm⁻¹ is assigned to the first order transverse optical (TO) phonon mode of Ge nanoisland



Actual Raman spectra in the range of 200-800 cm^{-1}



Spectral de-convolution

- ✓ The **D-band** is known as the **disorder band** or the defect band. It represents a **ring breathing mode** from sp^2 carbon rings. The band is the result of a one phonon lattice vibrational process, which is typically **weaker in graphite** and **weak in graphene**.
- ✓ Prominent D-band indicates the presence of lot of **defects** in the material. The intensity of the D-band is directly proportional to the level of defects in the sample.
- ✓ The **G-band** is the primary mode in **graphene** and graphite. It represents the planar configuration sp^2 **bonded carbon** that constitutes graphene.

- ✓ **Justice** cannot be given through a single presentation to a field like RS where the advancements are too rapid.
- ✓ Lasers scientists and engineers are working together to meet the requirements of **laser source** and related optics.
- ✓ Continue to **predominate** over other techniques especially in biology, medicine, polymers, drugs, surface science, forensic, electro-chemistry, memory and sensor materials, photovoltaics, cosmetics, space exploration, environmental science, ...etc.
- ✓ It simultaneously probes **lattice dynamics** (energy, symmetry, impurity, damping), **electronic degrees of freedom** (spin, energy, lifetime, symmetry) and **excitations** and their **interactions** (magnons, excitons, plasmons, ...).
- ✓ Extremely powerful in **low-dimensional materials** for probing various excitations
- ✓ Possibility of “single molecule detection.”

Thanks

