

M5052
CHARACTERIZATION OF MATERIALS AND NANOMATERIALS

Graduate Program in Nanotechnology

RAMAN SPECTROSCOPY

(  **Espectroscopía Raman**)

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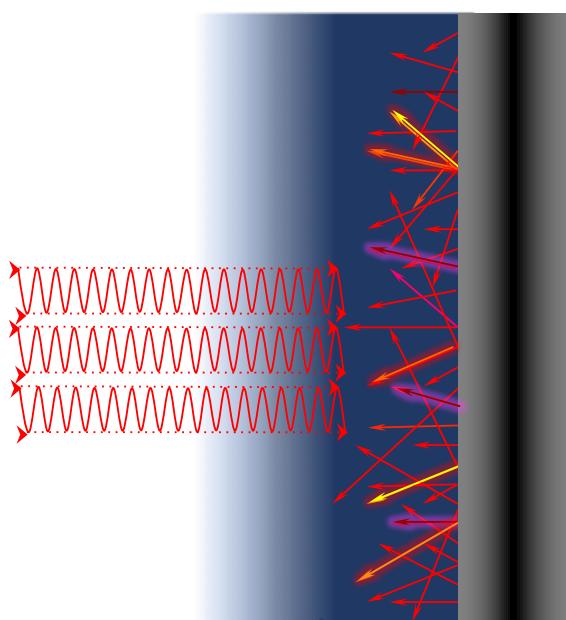


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LIGHT SCATTERING [**DISPERSIÓN DE LUZ**]

- Scattering: deviation of the trajectory of photons due to interaction (reflection, refraction) with matter
 - Absorption followed by re-emission (photoluminescence) is not really scattering
- Elastic Scattering (Rayleigh Scattering)
 - Scattered photons have the same energy as incident photons
 - Most of the scattered photons are elastically scattered
- Inelastic Scattering (Raman Scattering)
 - Scattered photons have a different frequency than the incident photons
 - Adolf Smekal predicted inelastic light scattering in 1923

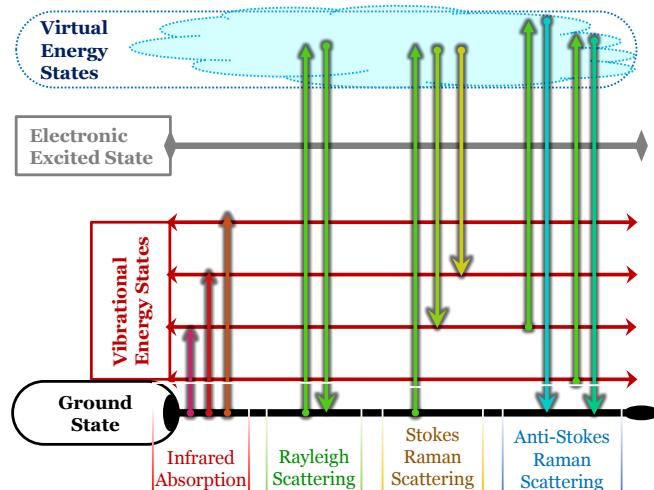


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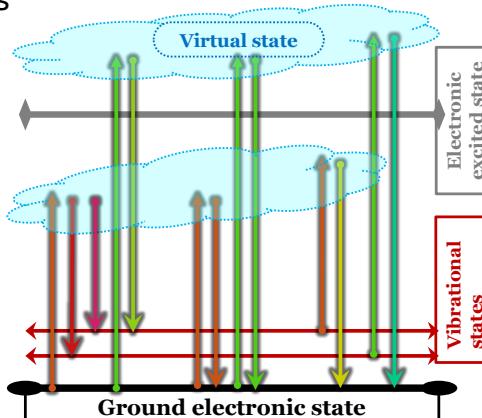
INELASTIC LIGHT SCATTERING

- Inelastic Scattering was first studied by Raman
 - 1923: First observation of inelastic scattering by C.V. Raman and K.S. Krishnan
 - G. Landsberg and L. I. Mandelstam made an independent observation of inelastic scattering by crystals
 - Stokes Raman Scattering: frequency of scattered light is lower than that of incident light
 - Anti-Stokes Scattering: scattered light has a higher frequency
- Ratio of Raman Scattering to Rayleigh Scattering is $\sim 1: 10^6$, up to $\sim 1: 10^8$
 - Not noticeable without highly monochromatic light (lasers)



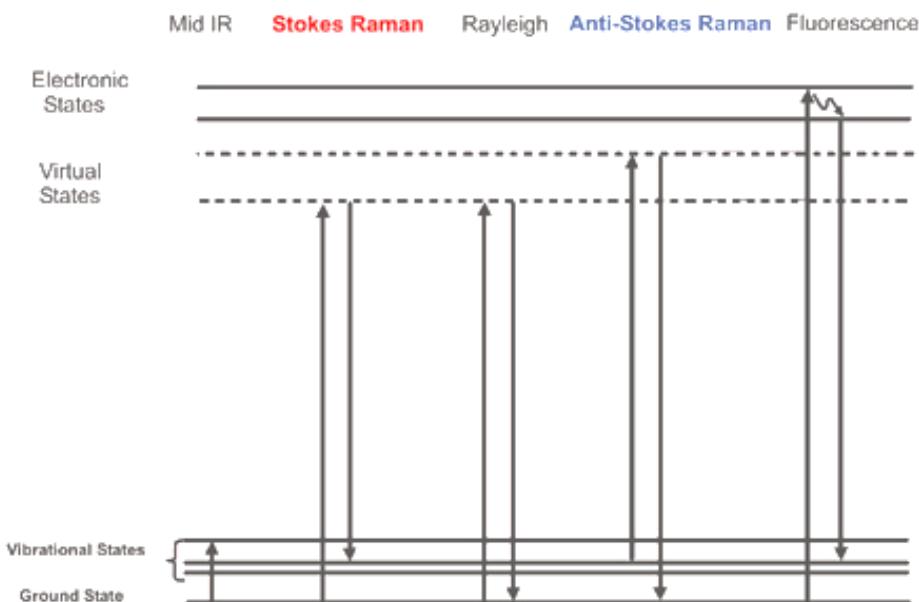
RAMAN SCATTERING

- Raman Spectroscopy is based on measuring the shifts in frequency of highly monochromatic light due to interaction with matter
 - Gives information related to the vibrational frequencies
- Stokes Raman Scattering:
 - Scattered photon loses energy (lower frequency)
 - Molecules end in vibrational states above the ground state
- Anti-Stokes Raman Scattering:
 - Photon has a higher frequency
 - Molecule was in an excited vibrational state and ends in the ground state
- Relative intensities of Stokes and Anti-Stokes scattering depend on the relative populations of the ground state and the vibrational states (this is related to temperature)



RAMAN SCATTERING VS. FLUORESCENCE

- In Raman scattering photons interact with the electron cloud (molecular orbitals) but do not have the exact energies required to promote electrons to an excited state

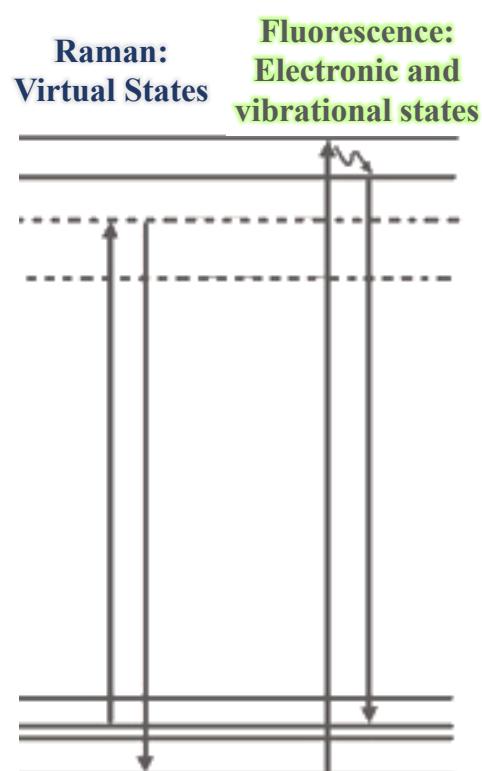


- Without any excited levels available in that energy range *there can be no photon absorption*
- Virtual States:** interaction between electric field of photons and the molecular orbitals



RAMAN SCATTERING VS. FLUORESCENCE

- In fluorescence photons have enough energy to excite electrons to higher energy levels
 - Absorption and photon re-emission processes
- Fluorescence intensity is almost always higher than for Raman scattering
 - If the photons can excite electronic transitions fluorescence may compete with Raman scattering
 - If the incident radiation does not have the energy to reach electronic states there will be no fluorescence



INTENSITY OF STOKES VS. ANTI-STOKES SCATTERING

- Usually most molecules/materials are in the ground state and Stokes scattering is much more intense
 - The higher the shift the lower the intensity of the anti-Stokes peak
 - Probability of molecule being in higher energy vibrational states is lower

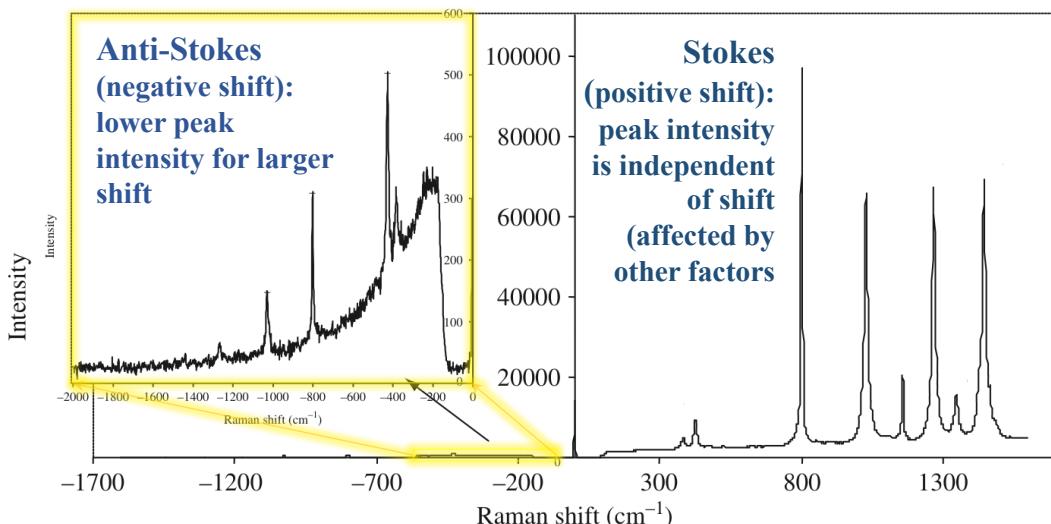


Figure 1.3. Stokes and anti-Stokes scattering for cyclohexane. To show the weak anti-Stokes spectrum, the y-axis has been extended in the inset.



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INFRARED V. RAMAN

- Both techniques reveal vibrational states by interaction with light
- Many vibrational modes are active both in Raman and in IR spectroscopy
 - Some vibrational modes are active only on IR or Raman

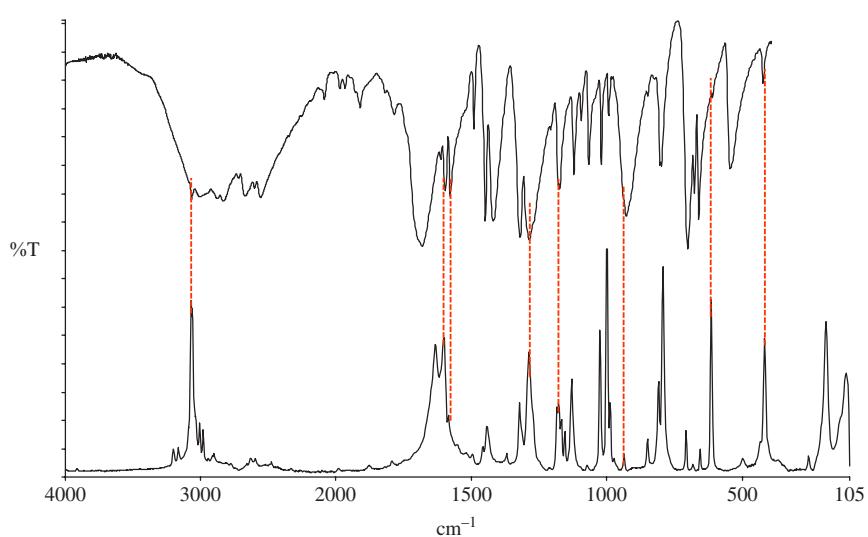


Figure 1.4. Infrared and Raman spectra of benzoic acid. The top trace is infrared absorption given in % transmission (%T) so that the lower the transmission value the greater the absorption. The lower trace is Raman scattering and the higher the peak the greater the scattering.



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RAMAN VS. FTIR

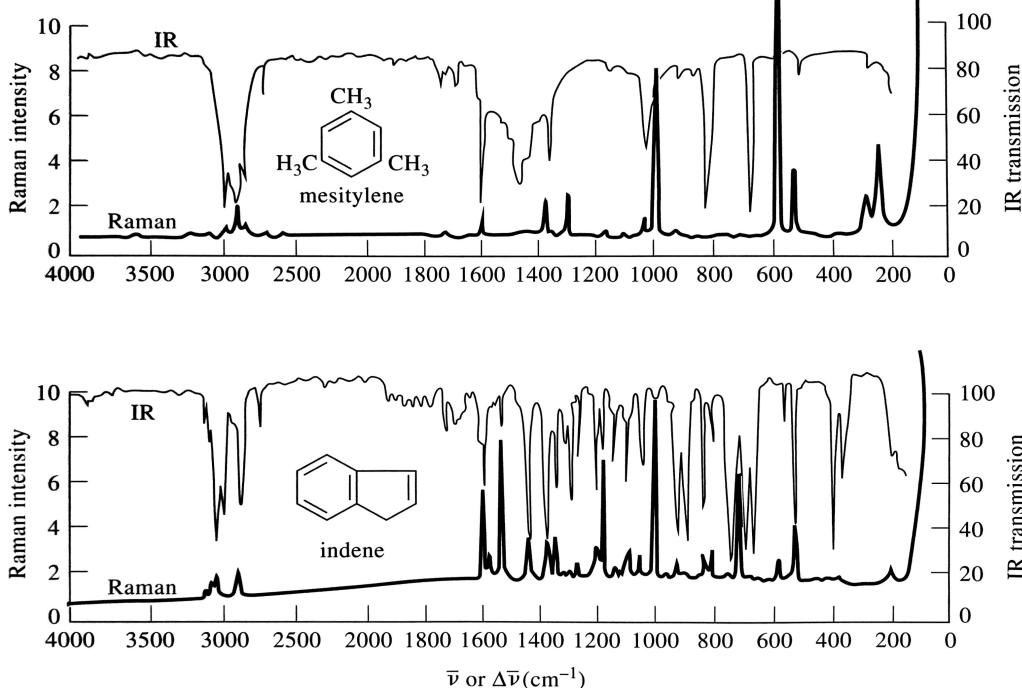


FIGURE 18-4 Comparison of Raman and IR spectra for mesitylene and indene. (Courtesy of Perkin-Elmer Corp., Norwalk, CT.)

- Relative intensities and active modes can be different between Raman and FTIR
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-



RAMAN EFFECT VS. INFRARED SPECTROSCOPY

- Raman effects is due to polarization of the electron cloud
 - Induced dipole
- Nuclei of atoms in the bond do not move
 - Orbital geometry changes depending on photon energy and electronic properties of molecules
- Virtual state
 - Unstable state with extremely short lifetimes
 - Energy of the virtual state depends on the energy of the laser photons
 - Virtual state can be considered as an “activated complex” of photons with the molecular orbitals
- IR absorption occurs by excitation of electrons to excited vibrational states
 - Infrared absorption occurs only if there is a change in dipole moment
 - Nuclei of atoms move (bond length changes in a vibration)
 - Orbital geometry changes due to movement of nuclei
 - Vibrational modes
 - Lifetimes in the nanosecond range



DIFFERENCES BETWEEN RAMAN AND INFRARED SPECTROSCOPY

- Differences between Raman and IR spectra can provide information about molecular structure
 - Knowing whether bond vibrations lead to polarization and/or to a change in dipole can provide some information about the structure of the molecule
 - Some vibrational modes are not active in IR but are active in Raman (and vice versa)
 - E.g. vibrational modes that result in larger bond polarizability but do not lead to a change in dipole moment are active only in Raman
 - Different relative intensities for the same peaks
 - Many practical differences are a consequence of the different origin of IR absorption and Raman scattering at the molecular level
 - *FTIR and Raman are complementary characterization techniques*



RAMAN VS. FTIR: S=C=S SPECTRUM

	V_a	V_{as}	δ_s
Vibration			
Dipole moment			
	$\partial\mu/\partial Q=0$	$\partial\mu/\partial Q \neq 0$	$\partial\mu/\partial Q \neq 0$
Polarizability			
	$\partial\alpha/\partial Q \neq 0$	$\partial\alpha/\partial Q = 0$	$\partial\alpha/\partial Q = 0$
IR spectrum			
Raman spectrum			

Figure 1.7. Dipole and polarization changes in carbon disulphide, with resultant infrared and Raman spectra.
 (Reprinted from A. Fadini and F.-M. Schnepel, Vibrational Spectroscopy: Methods and Applications, Ellis Horwood Ltd, Chichester, 1989.)

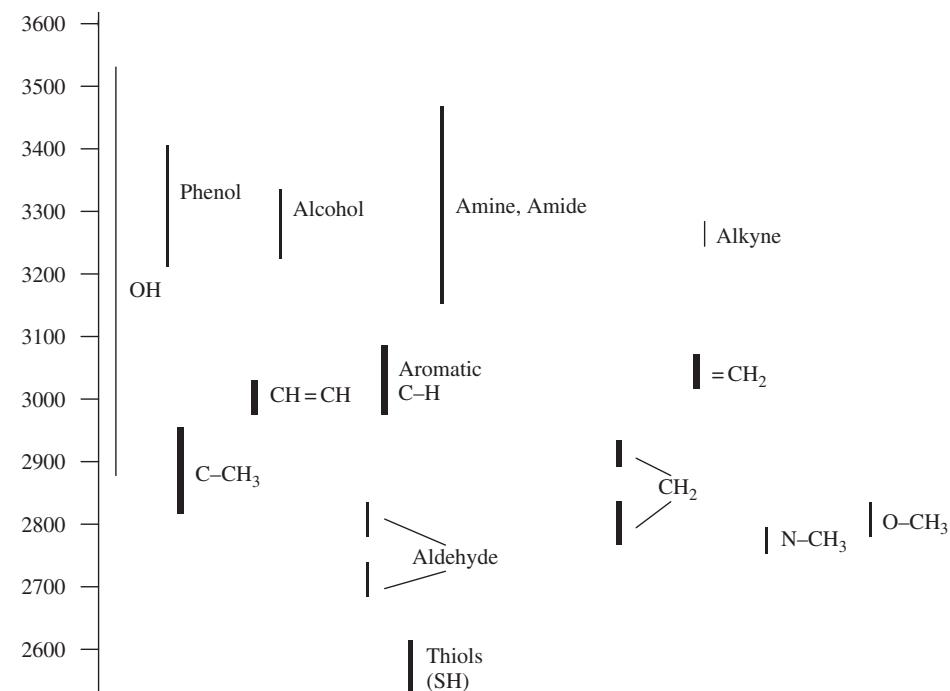
(This figure and figures “1.3” and “1.4” in previous slides from: E. Smith, G. Dent *“Modern Raman Spectroscopy – A Practical Approach”* (2005) John Wiley & Sons, Ltd)



RAMAN PEAK ASSIGNMENTS (1)

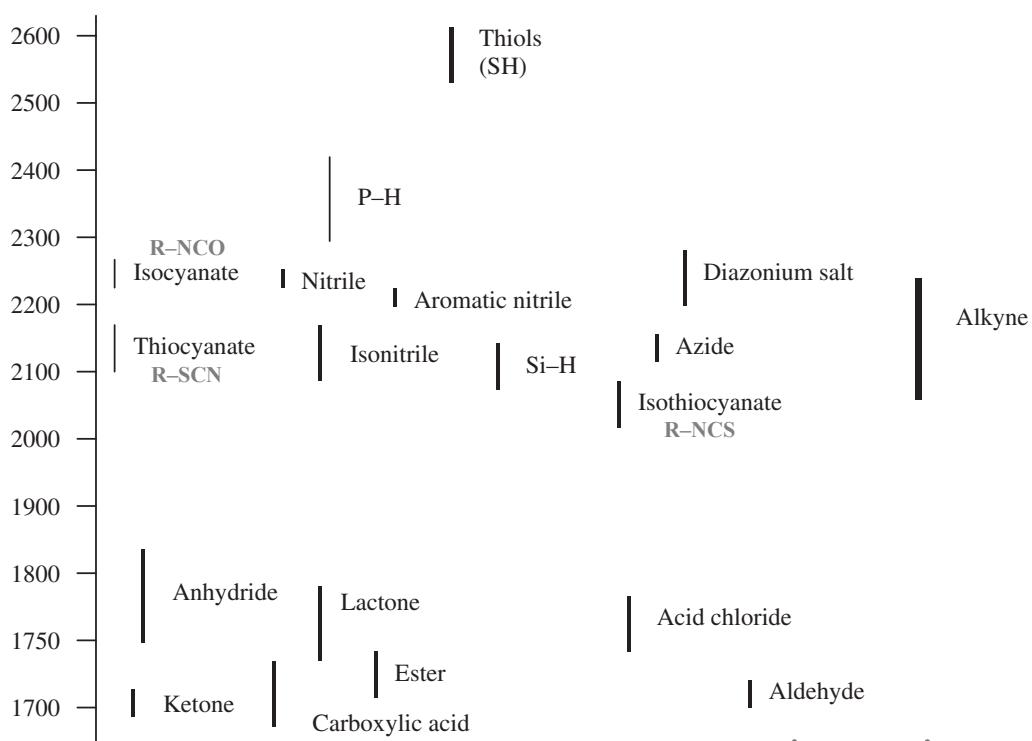
Length and thickness of lines represent range and intensity, respectively

[Tables from: E. Smith, G. Dent "Modern Raman Spectroscopy – A Practical Approach" (2005) John Wiley & Sons, Ltd.]

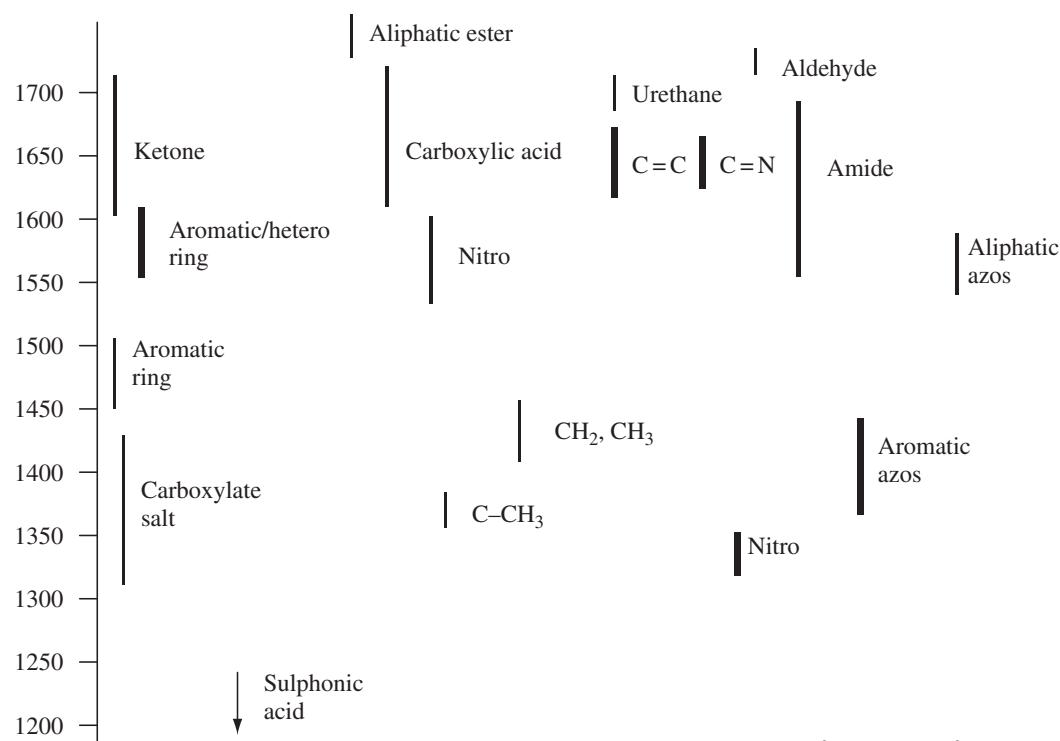


RAMAN PEAK ASSIGNMENTS (2)

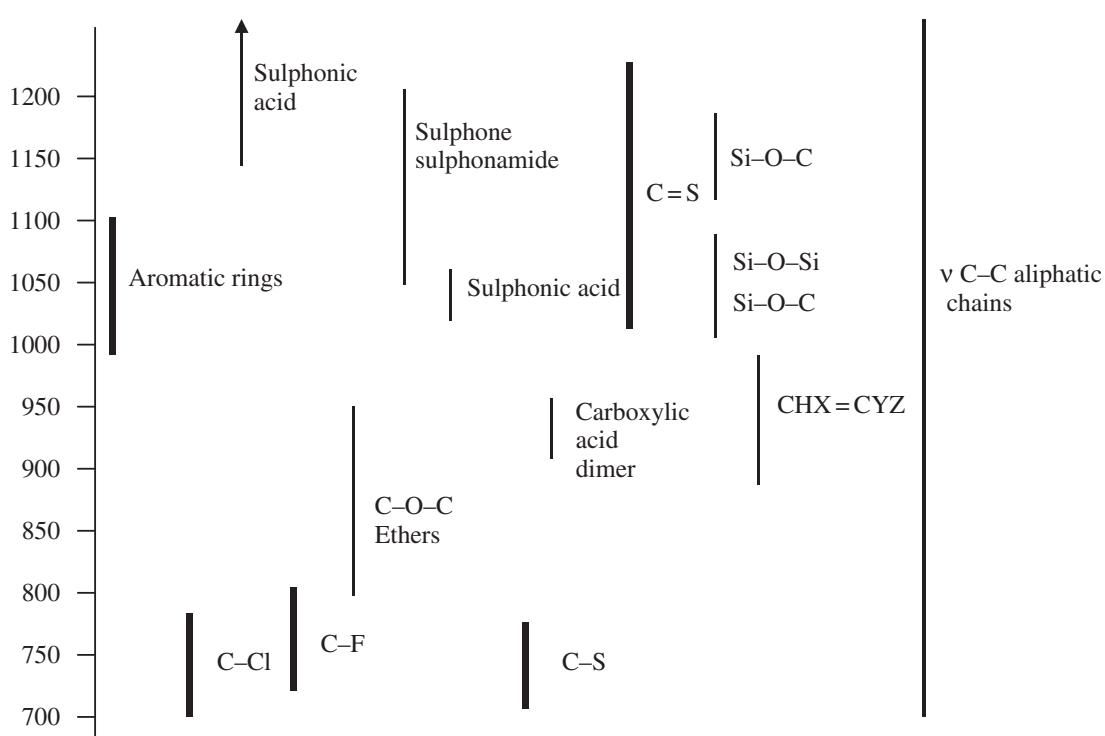
Table 1.2. Single vibration and group frequencies and an indication of possible intensities of peaks commonly identified in Raman scattering



RAMAN PEAK ASSIGNMENTS (3)

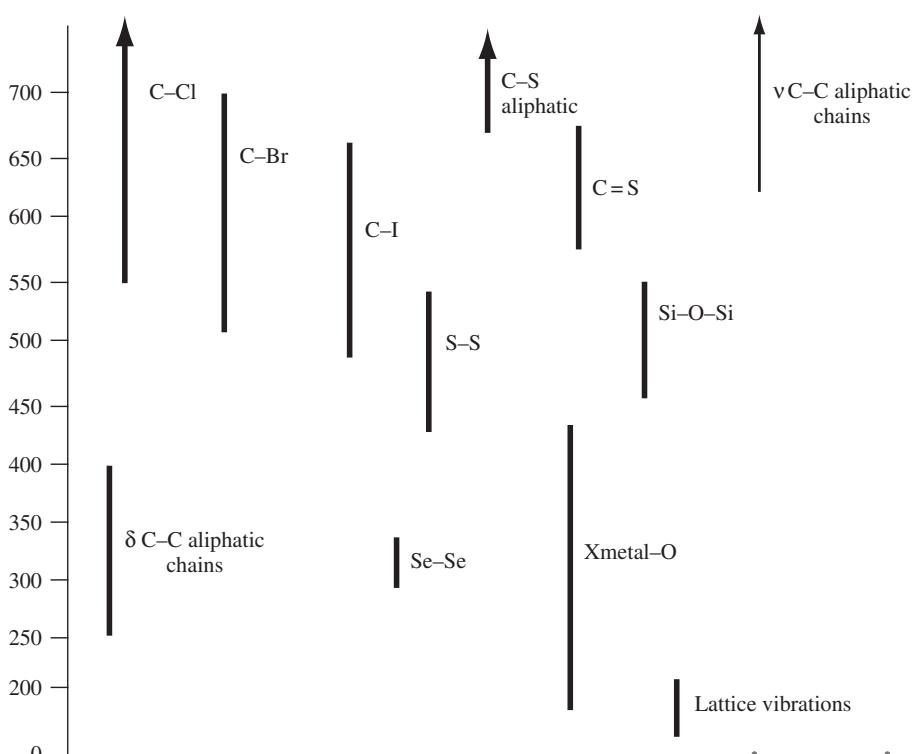


RAMAN PEAK ASSIGNMENTS (4)



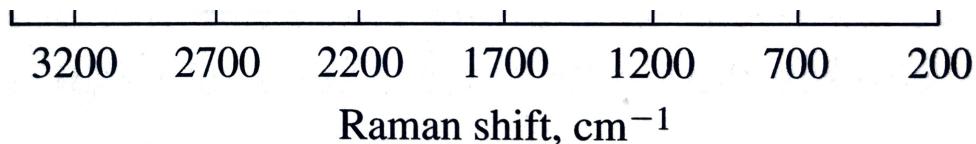
RAMAN PEAK ASSIGNMENTS (5)

Table 1.5. Single vibration and group frequencies and an indication of possible intensities of peaks commonly identified in Raman scattering



OTHER IMPORTANT POINTS ABOUT RAMAN SPECTROSCOPY

- Raman peaks are very low intensity, thus a high intensity light source is required
 - Raman spectroscopy became common only after the invention of the laser
- Raman shift frequencies correspond to wavelengths in the mid-infrared
 - The information of interest is usually in the range of $3600 - 400 \text{ cm}^{-1}$
 - Measuring Raman shifts down to $200 - 100 \text{ cm}^{-1}$ is possible
- In special instruments Raman shifts as small as 50 cm^{-1} can be measured
- High intensity light near the laser wavelength has to be filtered
- Measured signal is intensity of scattering (number of photons) as function of frequency shift of the scattered photons
- This shift is in units of Δcm^{-1}
 - In practice the x axis of spectra is shown with units of cm^{-1} not Δcm^{-1}



RAMAN SCATTERING V. WAVELENGTH

- Efficiency of Raman scattering increases in proportion to the fourth power of the frequency of incident light
 - Use of visible light is favorable
 - But visible range may produce fluorescence
 - Using a near IR laser reduces signal but avoids fluorescence
 - But high intensity of laser light may produce thermal degradation
- An FT-Raman instrument may increase sensibility allowing use of lower laser intensity
 - Laser intensity is regulated with neutral-density filters
- Using a UV laser can increase efficiency and reduce fluorescence, but increases possibility of sample degradation
 - Frequencies of UV photons may be above the energy that excites fluorescent modes
 - Energy of UV photons may be large enough to excite electrons to anti-bonding states

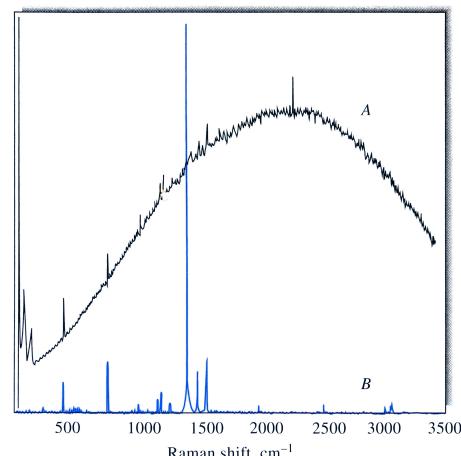


FIGURE 18-7 Spectra of anthracene taken with a conventional Raman instrument with an argon-ion laser source at 514.5 nm (A) and with an FT-Raman instrument with a Nd-YAG source at 1064 nm (B). (From B. Chase, *Anal. Chem.*, 1987, 59, 881A, DOI: 10.1021/ac00141a714. Copyright 1987 American Chemical Society.)



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ADVANTAGES

- No water interference
 - Raman spectra of aqueous solutions can be acquired
- Can analyze compounds and materials not active in the IR
- Less peak superposition than in IR
 - Excitation of overtones and of combined vibrational modes is less intense
- Allows use of glass or quartz vessels to confine samples
 - Glass has some small absorption below 2000 cm^{-1} but shows low scattering at other frequencies
- Facilitates use of fiber optics to collect signal
- No sample preparation required (in most cases)
- Fast Analysis
- Sample size as low as micrograms
 - When using Raman microscopes

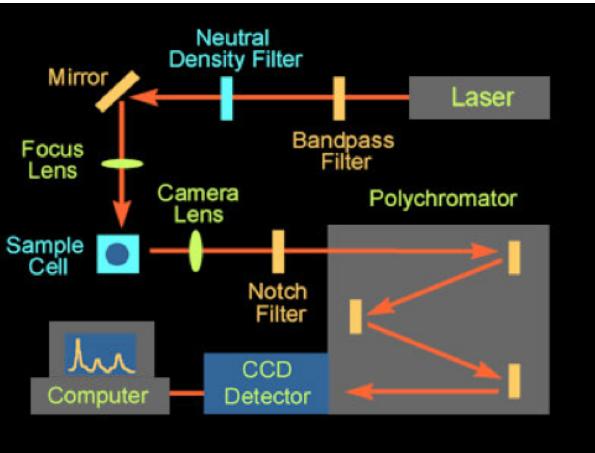
DISADVANTAGES

- Fluorescence Problems
 - Fluorescence of some impurities may be more intense than Raman scattering
- Samples can not be too diluted
 - Low intensity of signal does not allow analyzing very small amounts
- Instrumentation is more complicated than for FTIR
 - Equipment is more expensive
 - Calibration can be more complex than in FTIR
 - Detection in general is harder than in FTIR
- Use of laser may result in sample heating
 - Photochemical degradation may even happen, depending on the combination of laser and substance



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EQUIPMENT FOR RAMAN SPECTROSCOPY

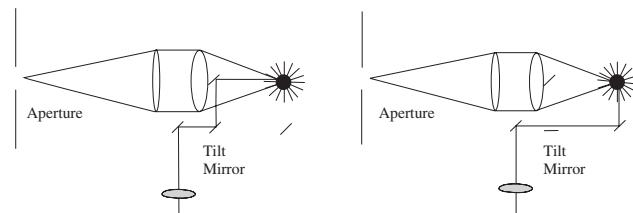
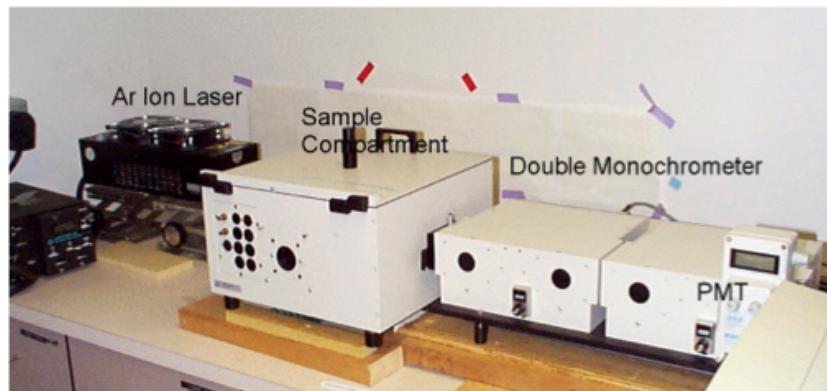


Figure 2.1. 180° (left) and 90° (right) scattering arrangements. The low beam is shown as arriving vertically through a lens and a set of mirrors onto the sample (the black dot) a cone of scattered light is then collected into the spectrometer.

- Initial Development used Dispersive Spectrometers
 - Two or more consecutive monochromators were necessary



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RAMAN INSTRUMENTATION

- Several Laser Options
 - Many samples (e.g. polymers) may present fluorescence, using a different laser line may minimize fluorescence
- Many commercial instruments include a microscope
 - Micro-Raman

Table 1: Excitation wavelength options



Application	Common excitation wavelengths ^a	Laser type
Near-IR spectroscopy	830 nm 785 nm	diode diode
Visible spectroscopy and 2-D imaging	633 nm 532 nm 514 nm 488 nm 442 nm	gas YAG ^b gas gas gas
UV spectroscopy	325 nm 244 nm	gas gas ^b

Notes

a Other wavelengths are available on request

b Frequency doubled



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EQUIPMENT:

MICRO-RAMAN

- Raman Spectrometer combined with microscope
 - Microscope lenses focus laser beam over sample
 - Small area analysis
 - Chemical Imaging and Mapping

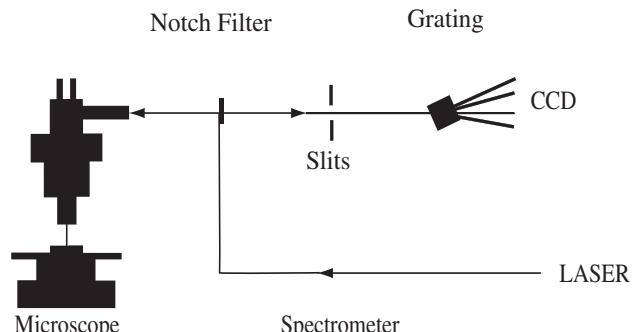
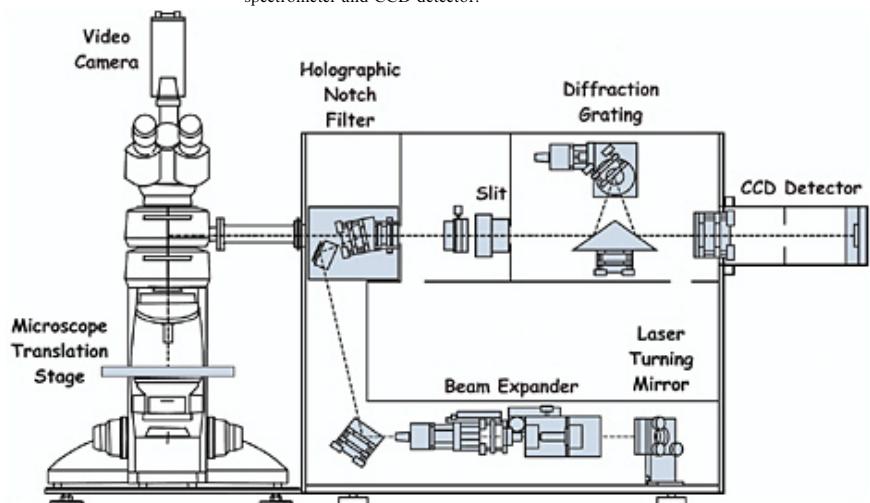


Figure 2.3. Raman spectrometer and microscope, using a visible laser, notch filter and CCD detector.



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RAMAN WITH FIBER OPTICS PROBE

- Sampling probe separate from spectrometer
 - Use in industrial monitoring
 - Allows remote monitoring of toxic or dangerous reactions
 - In portable instruments allows contacting probe to the sample independently of the position of the spectroscope body

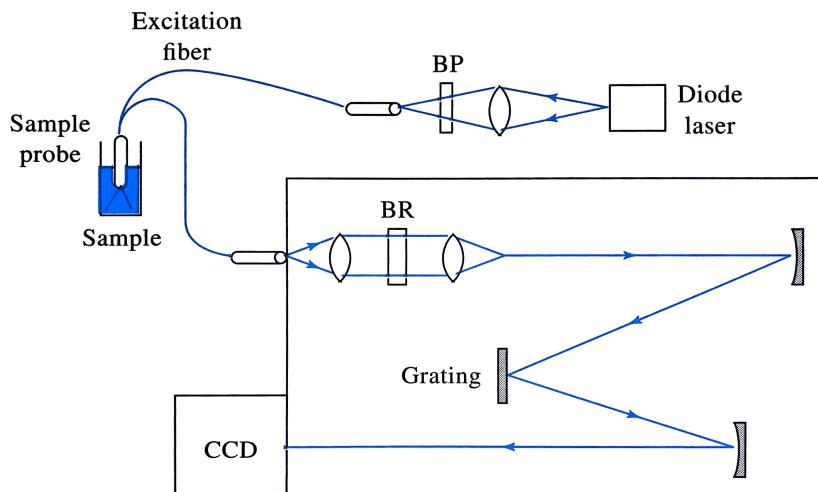


FIGURE 18-11 Fiber-optic Raman spectrometer with spectrograph and CCD detector. The bandpass filter (BP) is used to isolate a single laser line. The band-rejection filter (BR) minimizes the Rayleigh-scattered radiation.

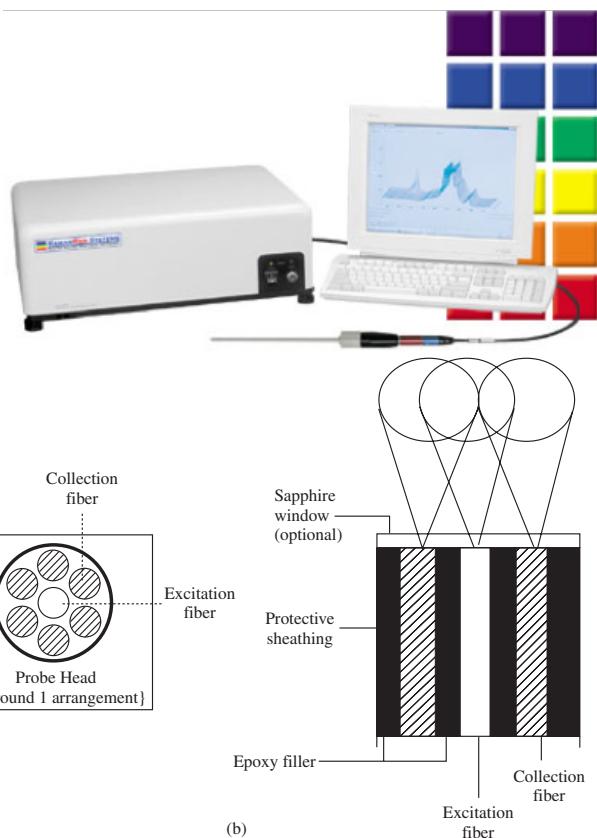


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RAMAN WITH FIBER OPTICS

- Sample probe can have many collection fibers to increase effectiveness of collection of scattered photons
- Potential problem: Raman scattering by the fiber optics material
 - This problem increases if the fiber is very long
 - Problems can be minimized using a “multimode fiber”
 - Laser beam guided by several fiber optics surrounding a collection fiber on the center
 - Use of filters right on the tip of probe can minimize scattering problem by removing Rayleigh scattered photons and reflected photons



FT-RAMAN

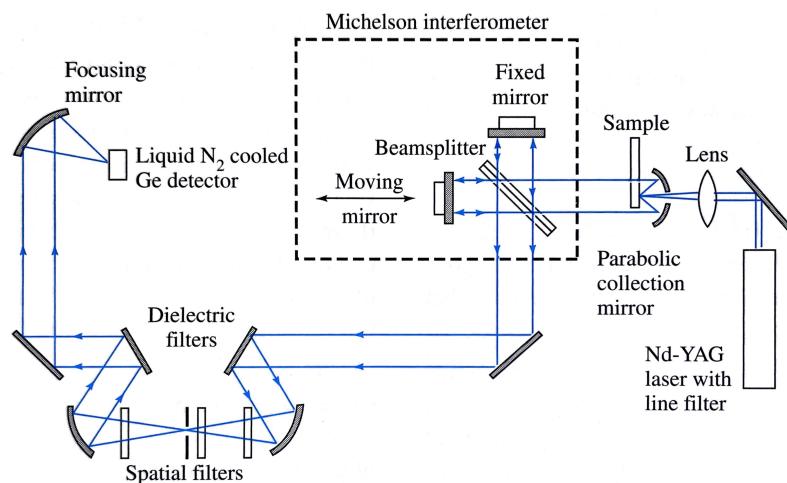


FIGURE 18-12 Optical diagram of an FT-Raman instrument. The laser radiation passes through the sample and then into the interferometer, consisting of the beamsplitter and the fixed and movable mirrors. The output of the interferometer is then extensively filtered to remove stray laser radiation and Rayleigh scattering. After passing through the filters, the radiation is focused onto a cooled Ge detector.

- Raman with Fourier Transform
 - Sample is illuminated *before* the interferometer
 - Use of FT-Raman with an IR laser (e.g. 1064 nm Nd:YAG) can provide good sensitivity while eliminating any fluorescence
- Disadvantages:
 - Water absorption in the 1000 nm region means that aqueous solutions can not be used
 - Optical filtering is necessary, otherwise Rayleigh scattered light can overwhelm the transducer
 - Cryogenically cooled detector is required



SEVERAL SAMPLE ILLUMINATION CONFIGURATIONS ARE POSSIBLE

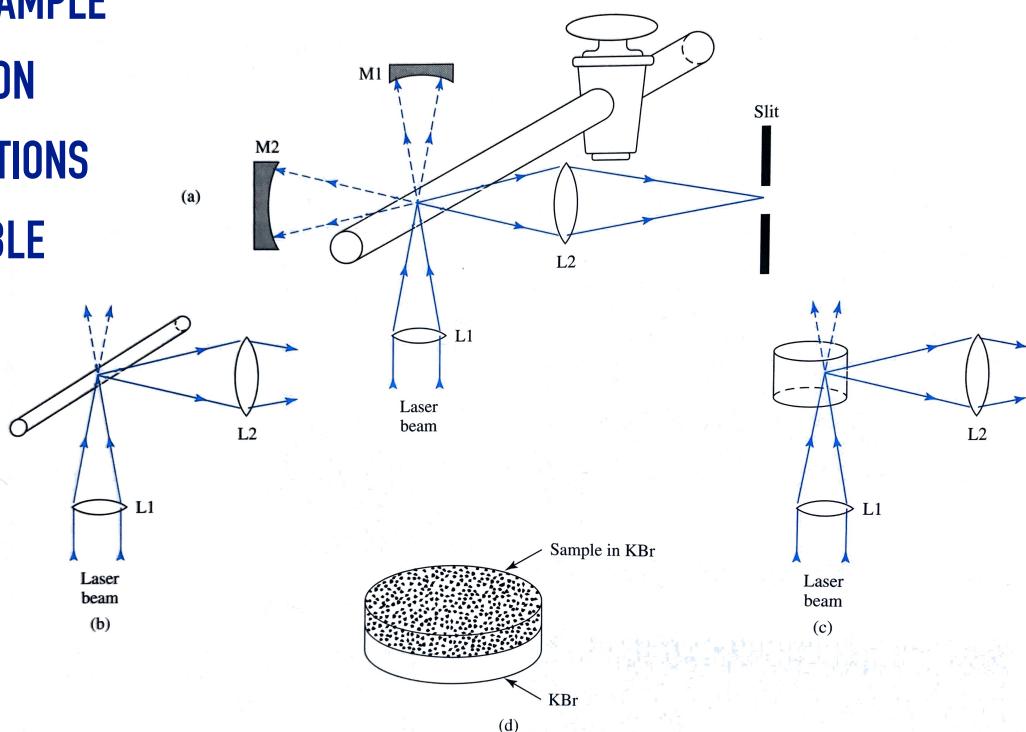


FIGURE 18-8 Sample illumination systems for Raman spectrometry. In (a), a gas cell is shown with external mirrors for passing the laser beam through the sample multiple times. Liquid cells can be capillaries (b) or cylindrical cells (c). Solids can be determined as powders packed in capillaries or as KBr pellets (d). (Adapted from J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003. Reprinted with permission.)



SOME APPLICATIONS OF RAMAN SPECTROSCOPY

- Inorganic species
 - Coordination Compounds
 - Information on composition, structure, coordination number
 - Ligands absorb in the $100\text{--}700\text{ cm}^{-1}$ (this region is very complex in IR)
- Minerals
- Study of *crystal lattice vibrations*
- Graphitic Carbon Materials
 - Including carbon nanostructures
- Organic Compounds
 - Similar applications than infrared spectroscopy
 - Allows identification of specific compounds (by comparing results to reference spectra)
- Polymers
 - Observation of vibrational modes (similar to FTIR)
 - Can be used to monitor progress of polymerization reactions
 - May present problems with fluorescence
- Determining configurational isomers
 - Due to differences in polarizability
- Analysis of moisture or air sensitive materials placing them in glass vessels
 - Glass absorbs below 2000 cm^{-1} , but produces little scattering in other frequency ranges



MORE APPLICATIONS OF RAMAN SPECTROSCOPY

- Microanalysis of particles, inclusions and fibers
 - Use of microRaman makes possible acquiring images with $\sim 1 \mu\text{m}$ resolution

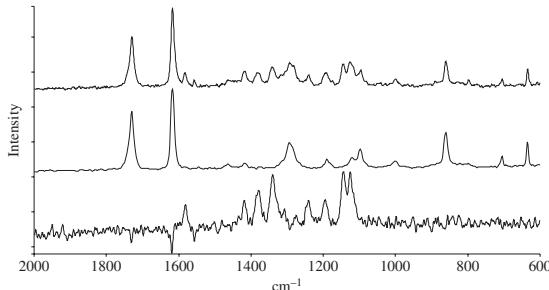


Figure 2.10. Raman spectra of dye in fibre. The top spectrum is from the dyed fibre, the middle one is from the fibre and the foot one is the difference.

- Study of substances and reactions in aqueous media
 - Water absorbs IR, but produces very low light scattering

- Biological Samples and Biomaterials
 - Without interference from aqueous media due to weak Raman signal of water
 - Good sensitivity for biomolecules allows analyzing small samples

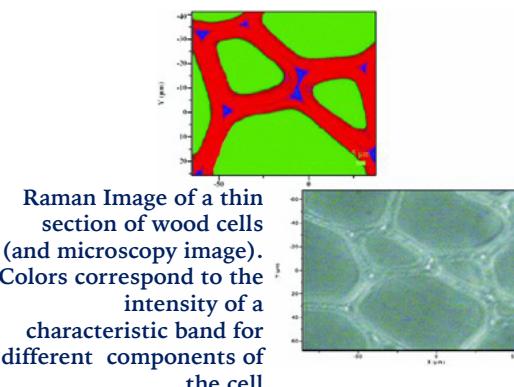


Image taken from: < <http://www.horiba.com/scientific/products/raman-spectroscopy/raman-imaging/image-gallery/thin-section-of-wood-cells/> >



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EXAMPLES

- Raman spectrum of a substance in aqueous solution

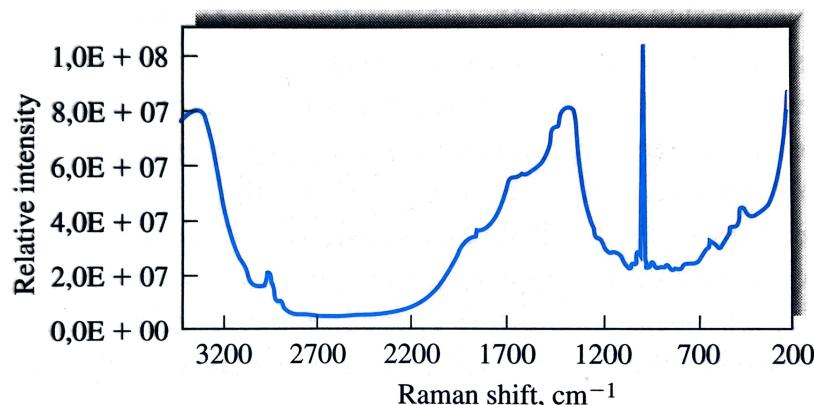


FIGURE 18-10 Raman spectrum of an aqueous solution containing aprotinin (100 mg/ml) and $(\text{NH}_4)_2\text{SO}_4$ (1.0 M) in 50 mM sodium acetate buffer at pH 4.5 and 24°C. A diode laser source at 785 nm was used with a CCD detector. (From R. E. Tamagawa, E. A. Miranda, and K. A. Berglund, *Cryst. Growth Des.*, 2002, 2, 511, DOI: 10.1021/cg025544m. Copyright 2002 American Chemical Society.)



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EXAMPLE: POLYMERIZATION ANALYSIS BY SPECTROSCOPY

- *Phenyl Triazine resin*
 - A thermoset plastic, curing reaction is trimerization of cyanate group (-OCN)
 - Raman Analysis (A, B, on top) is complemented by IR analysis (C, D, below)
 - Spectroscopy shows a decrease in intensity of peaks from reactants and an increase in intensity of peaks from the cross-linked polymer

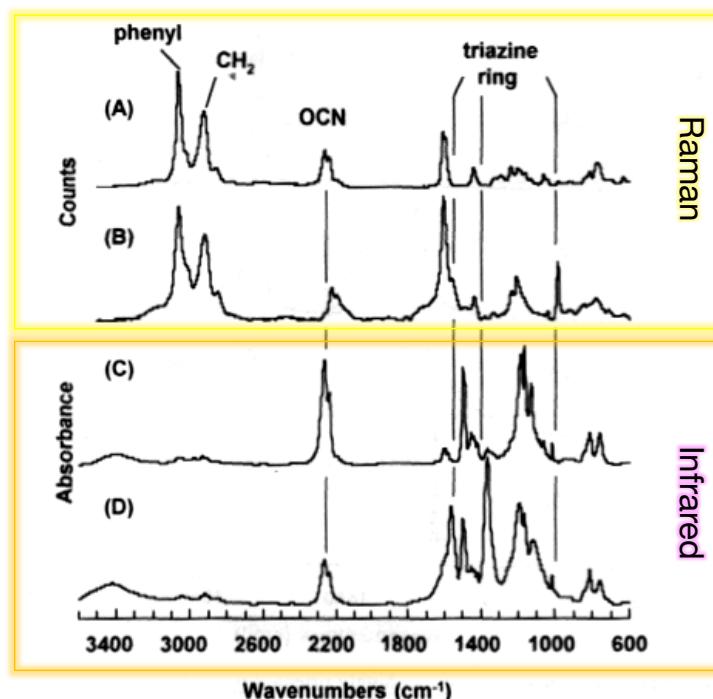
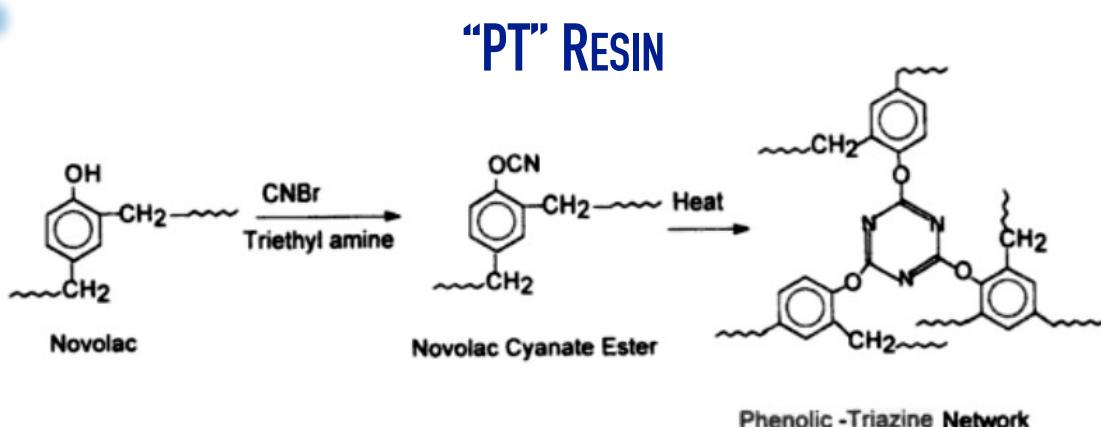


Figure 2.11. Raman (A, B) and IR (C, D) spectra of PT-resin. (A, C) refer to uncured samples; (B, D) are partially cured resin.



Scheme 8. Synthesis and curing of cyanate novolac

- “PT” (“*Phenyl Triazine*”, “*Phenolic Triazine*”)
 - Cures via trimerization of cyanate groups (-OCN) forming a cross-linked network
 - This provides higher thermo-oxidative resistance
 - Curing reaction does not form volatile byproducts, avoiding formation of pores
 - This is important for thermoset composite materials

Figure from C.P. Reghunadhan Nair, Dona Mathew, K.N. Ninan, "Cyanante Ester Resins, Recent Developments" in M. Biswas (Editor) "New Polymerization Techniques and Synthetic Methodologies"; Springer-Verlag, Berlin, 2001 (via books.google.com) (Adv. Poly. Sci. (2001) Vol. 155, p. 21)

ANALYSIS OF POLYMER MORPHOLOGY

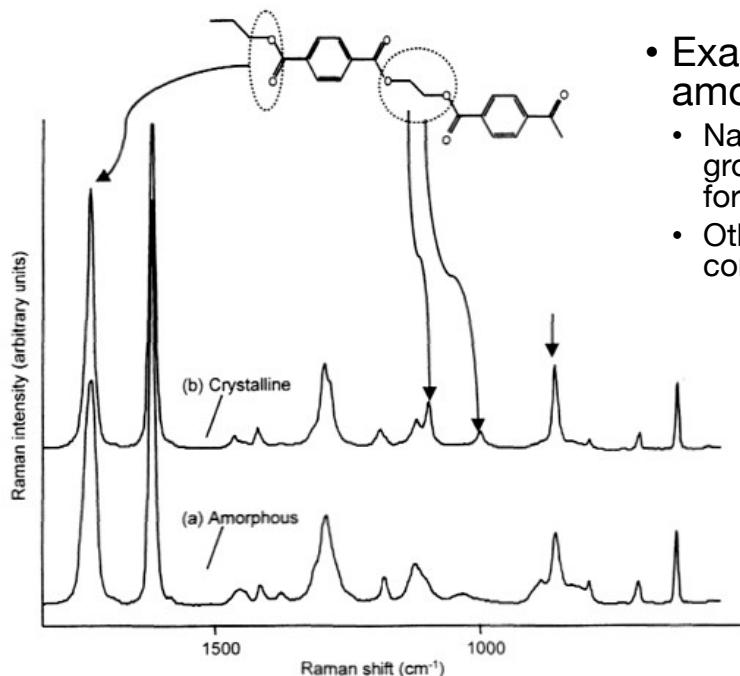


Figure 4.19 Raman band changes occurring when PET crystallizes. The narrowing of the carbonyl band near 1730 cm^{-1} is the only true crystallinity indicator, the others are due to conformational changes. Data recorded using Kaiser Optical Systems fiber-coupled Holoprobe spectrometer, 532 nm excitation.

- Example: crystalline PET vs. amorphous PET

- Narrowing of band from carbonyl group stretch ($\sim 1730\text{ cm}^{-1}$) in crystal form due to lower mobility of bonds
- Other differences are due to conformational changes

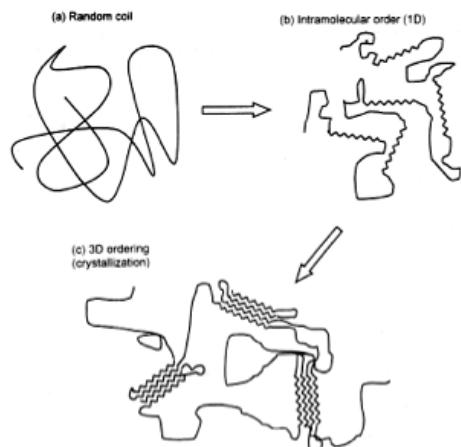


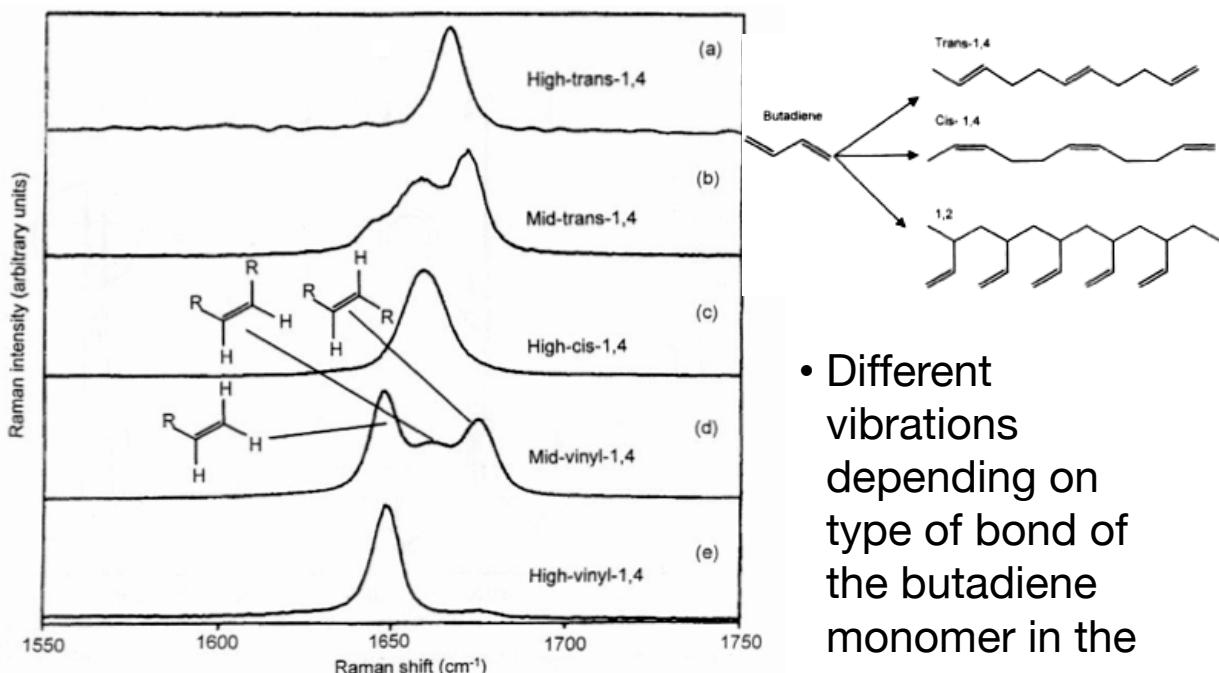
Figure 4.18 Schematic illustration of crystallization of a polymer.



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POLYMER MORPHOLOGY: CONFIGURATION



- Different vibrations depending on type of bond of the butadiene monomer in the polymer

Figure 4.15 Raman spectrum of poly(butadiene) showing the $\text{C}=\text{C}$ stretching bands for *cis*, *trans*, and vinyl isomers. (Redrawn from Figure 1 of reference 16.)



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PROBLEMS WITH FLUORESCENCE

- Fluorescence may occur depending on the sample conditions or due to impurities

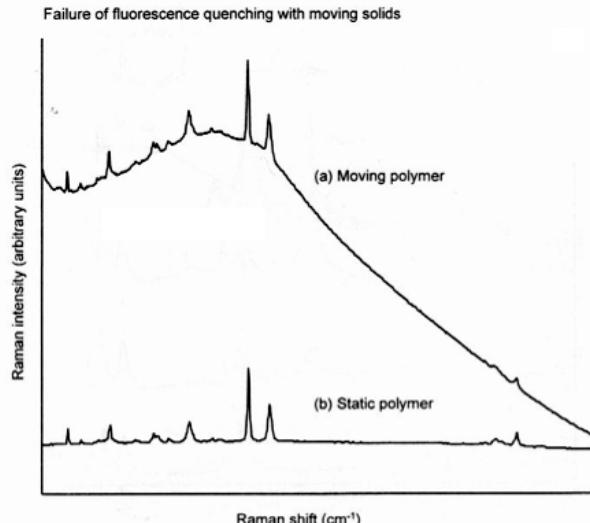


Figure 4.29 Effect of sample motion on fluorescence. A stationary sample is fluorescence free, but the moving polymer fluoresces strongly owing to failure of fluorescence quenching. Data acquired using Kaiser Optical Systems fiber coupled process Raman analyzer, 532 nm excitation, 50 m fiber cable.

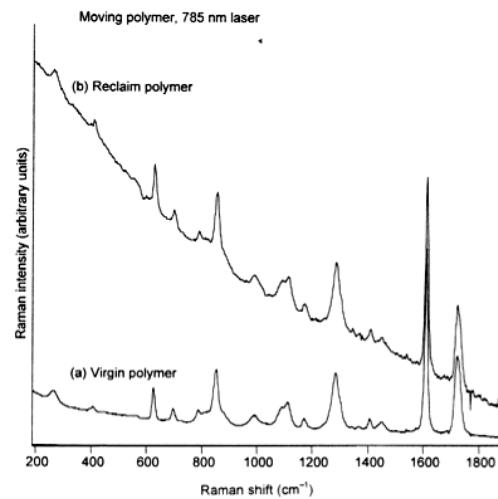


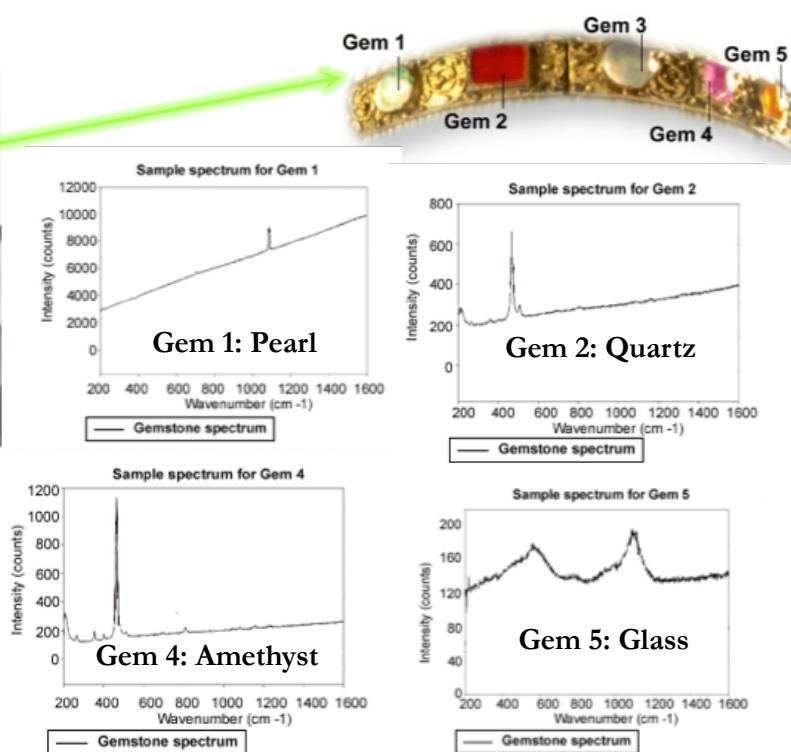
Figure 4.30 Effect of reclaim polymer on fluorescence. Use of a 785 nm laser with moving, virgin polymer yields good fluorescence-free data (a), but incorporation of recycled polymer in the stream causes fluorescence (b). Data acquired using Kaiser Optical Systems fiber coupled process Raman analyzer, 785 nm excitation, 50 m fiber cable.



ANALYSIS OF GEMSTONES



- Raman is a Non-destructive Technique: can be used in archaeological artifacts and relics



RAMAN OF CARBON MATERIALS

- Carbon presents characteristic vibrational modes in Raman that are not detected in IR
- G peak ($\sim 1582 \text{ cm}^{-1}$)
 - sp^2 carbon (“Graphitic”)
- D peak ($\sim 1332 \text{ cm}^{-1}$)
 - sp^3 carbon (“Disorder”)
- Ratio of intensity of D/G peaks is related to graphitization and crystallinity of the sample
- Chemical functionalization of carbon nanomaterials increases intensity of D peak

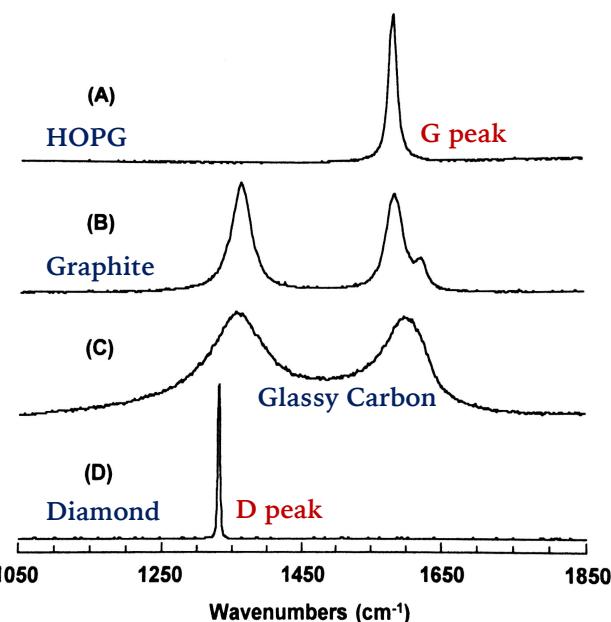


Figure 2.10. Raman spectra of (A) highly oriented pyrolytic graphite, (B) polycrystalline graphite, (C) glassy carbon, and (D) diamond.



RAMAN OF CARBON NANO-MATERIALS

- “Breathing” Mode of Single Walled Carbon Nanotubes (SWCNT) is different depending on diameter and chirality

424 TERRONES

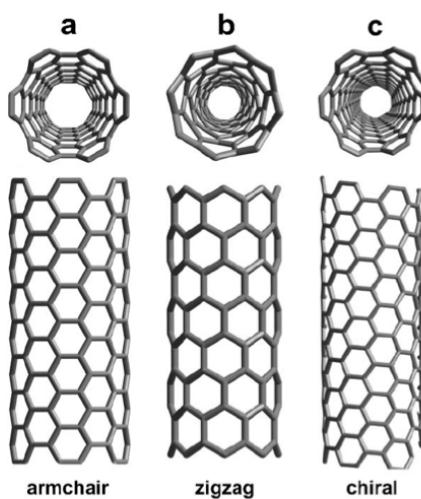
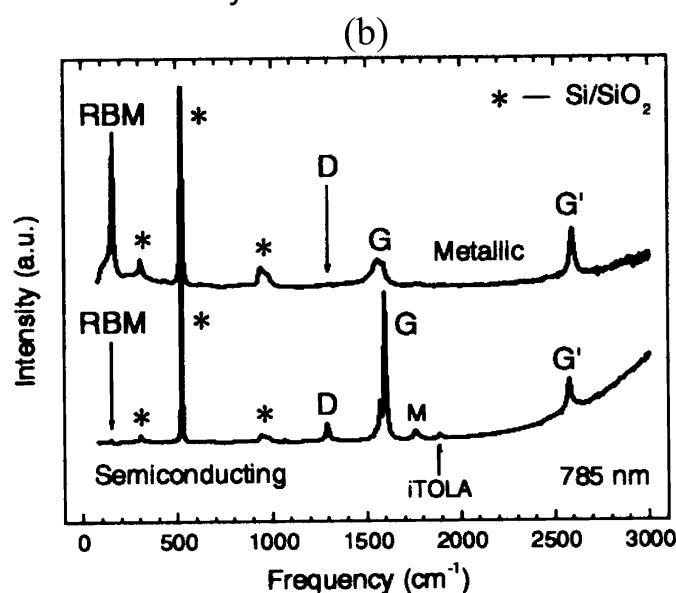


Figure 4 Molecular models of SWNTs exhibiting different chiralities: (a) armchair configuration, (b) zig-zag arrangement, and (c) chiral conformation.



EFFECT OF LASER WAVELENGTH ON RAMAN SPECTRA

EXAMPLE: SINGLE-WALLED CARBON NANOTUBES

- SWCNT show a very notorious effect of changing the laser line
- Effects of wavelength in peak position and intensity can occur with other substances too
- It is important to always report which laser was used when a Raman spectrum is presented*

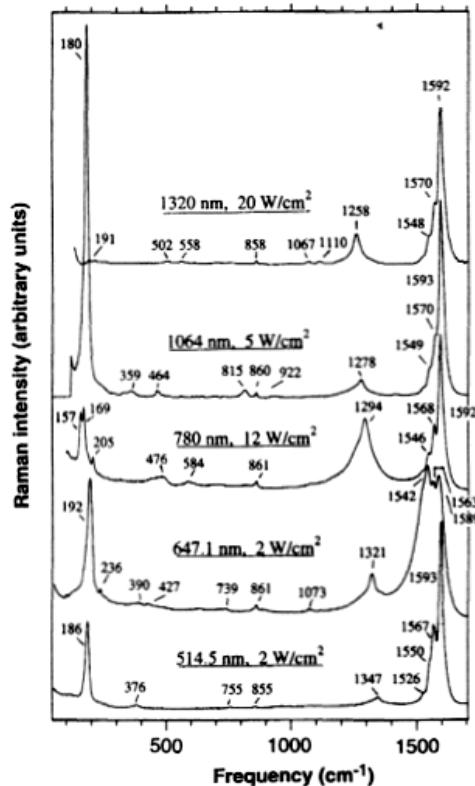


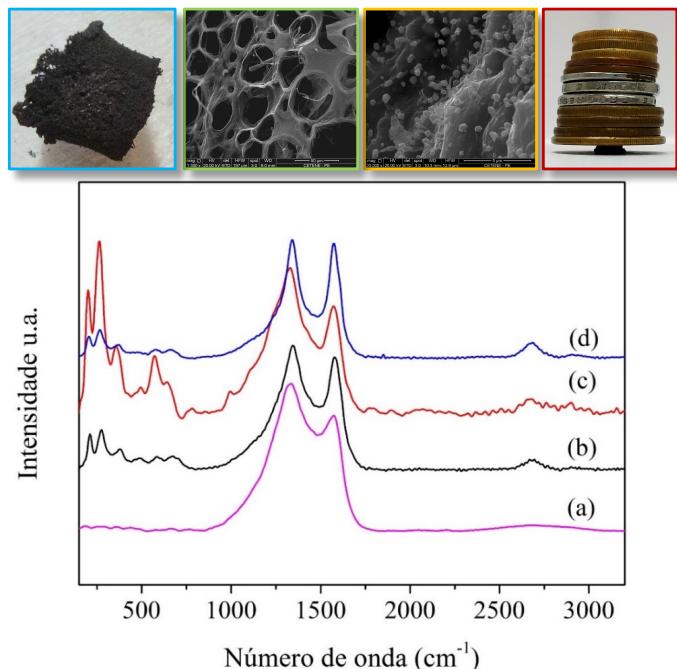
Figure 9.40 Experimental room temperature Raman spectra for purified single-wall carbon nanotubes excited at five different laser excitation wavelengths. The laser wavelength and power density for each spectrum are indicated, as are the vibrational frequencies (in cm^{-1}). The equivalent photon energies for the laser excitation are: 1320 nm \rightarrow 0.94 eV; 1064 nm \rightarrow 1.17 eV; 780 nm \rightarrow 1.58 eV; 647.1 nm \rightarrow 1.92 eV; 514.5 nm \rightarrow 2.41 eV. (Reproduced with permission from reference 61.)



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EXAMPLE: CARBON-CARBON COMPOSITES

- Raman of Carbon Nanomaterials with Iron Oxides
 - Simone da Silva Simões, “Produção e Caracterização de Compósitos Carbono-Carbono Baseados em Aerogel de Gelatina e Nanotubos de Carbono Dopados com Nitrogênio”, Masters Thesis (Graduate Program in Materials Science), Universidade Federal de Pernambuco, Sept. 2017
- Thesis project using iron nanoparticles over carbon nanotubes to catalyze growth of carbon for a carbon-carbon composite
- Relative intensities of D and G peak (I_D/I_G ratio) is used as a way to estimate how graphitic is the carbon deposit over the nanotubes



Four samples processed at different temperatures
Peaks at 517 cm^{-1} , 656 cm^{-1} , 672 cm^{-1} and 709 cm^{-1} are related to $\gamma\text{-Fe}_2\text{O}_3$, all other peaks in the region below 700 correspond to $\alpha\text{-Fe}_2\text{O}_3$



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M5052 - Characterization of Materials

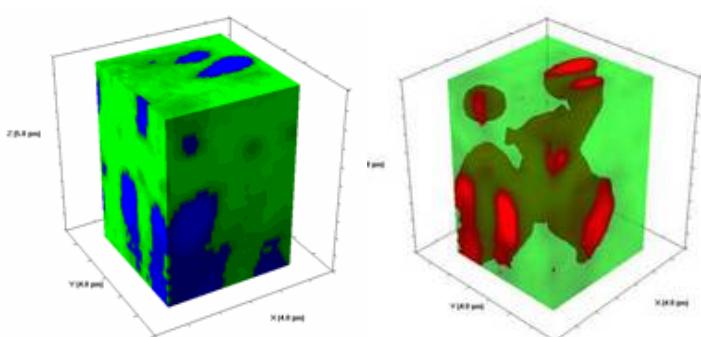
SOME SPECIAL APPLICATIONS OF RAMAN SPECTROSCOPY



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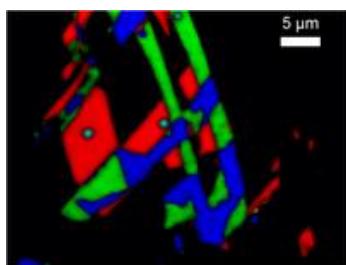
M5052 - Characterization of Materials

COMPOSITION MAPPING WITH MICRORAMAN

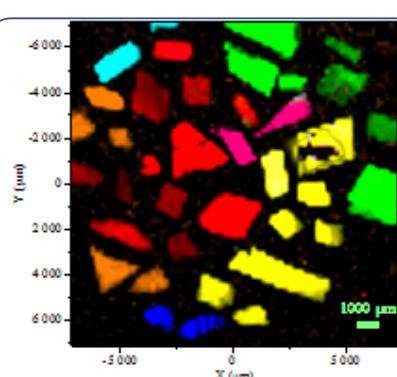


BaSO₄ particles in HDPE matrix, 3D Raman image acquired using a confocal microscope

Graphene over Si
Colors indicate if
graphene is a
monolayer, or 2 or 3
layers



Examples from <http://www.horiba.com/scientific/products/raman-spectroscopy/raman-imaging/image-gallery/>



Samples of Carbonate Minerals (polished rock)

- Red: Mg Siderite ($\text{FeCO}_3\text{-MgCO}_3$ solid solution)
- Yellow: Calcite (CaCO_3)
- Green: Dolomite ($\text{CaMg}(\text{CO}_3)_2$)
- Dark blue: Aragonite (CaCO_3)
- Light blue: Siderite (FeCO_3)
- Orange Magnesite (MgCO_3)
- Pink: Rhodocrosite (MnCO_3)



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M5052 - Characterization of Materials

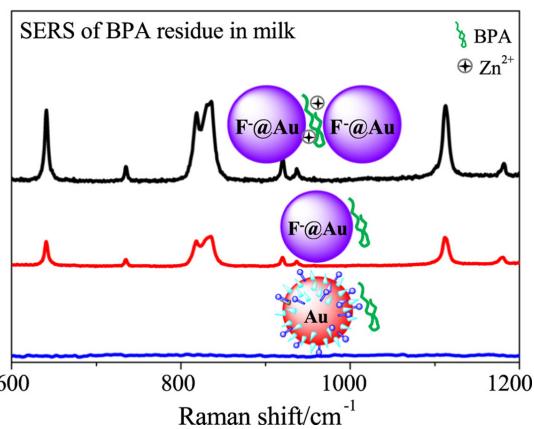
SERS: SURFACE ENHANCED RAMAN SPECTROSCOPY

- Surface Plasmons from metallic nanoparticles intensify Raman scattering signal
 - Surface plasmons are collective oscillations of free electrons in a metal
 - Thin metal films can also show the SERS effect due to nanoscale rugosity on the surface
 - Nanoscale metal films also show the effect
 - E.g. “core/shell” particles ($\text{SiO}_2@\text{Ag}$ or $\text{SiO}_2@\text{Au}$)
 - Au and Ag are commonly used
 - Functionalization of metal NP with organic molecules can be monitored by SERS
 - Modification of NP to give them affinity to specific analytes can be used to detect those analytes at small concentrations
- • •
- Factors that lead to surface enhanced Raman scattering
 - Distance to metal surface
 - Signal enhancement drops off with distance
 - Molecule of interest must be close to surface for signal enhancement
 - Surface morphology and roughness
 - Rougher surfaces or the presence of nanoparticles increases surface area
 - More surface area means more molecules can be close to metal surface
 - Properties of the metal
 - Larger enhancement if excitation wavelength is close to the plasmon resonance frequency of the metal
 - Relative orientation of molecule to the surface
 - Polarizability of molecular bonds is affected by electrons in surface of metal



SERS

- *Electromagnetic Enhancement* of signal
 - When surface plasmon resonance increases intensity of electromagnetic field in specific points (hot spots)
 - Molecules adsorbed near the hot spots experience higher intensity of light, which increases intensity of scattering
 - Signal increased by a factor of 10^5 or larger
- *Chemical Enhancement* of signal
 - Surface-molecule Interactions generate states that are more effective at scattering in the adsorbed molecules
 - Technical term “larger effective cross-section” for scattering
 - Energy transfer between electrons in the Fermi level of the metal and the molecular orbitals (HOMO, LUMO) of adsorbed molecules increases probability of Raman scattering
 - Signal increases by 1-2 orders of magnitude



- SERS allows detecting extremely small amounts of substances
 - Example above: surface modification of Au NP with fluoride allows detecting bisphenol A at the nm (10^{-9}) level
 - Figure from: Talanta 179 (2018) 37–42

How small a concentration can SERS help detect, you may wonder....



....THIS IS HOW SMALL THE DETECTION LIMIT CAN BE WITH SERS



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Single-Molecule Surface-Enhanced Raman Spectroscopy

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Keywords

SERS, single-molecule detection, hot spot, enhancement factor

Abstract

A general overview of the field of single-molecule (SM) surface-enhanced Raman spectroscopy (SERS) as it stands today is provided. After years of debates on the basic aspects of SM-SERS, the technique is emerging as a well-established subfield of spectroscopy and SERS. SM-SERS is allowing the observation of subtle spectroscopic phenomena that were not hitherto accessible. Examples of the latter are natural isotopic substitutions in single molecules, observation of the true homogeneous broadening of Raman peaks, Raman excitation profiles of individual molecules, and SM electrochemistry. With background examples of the contributions produced by our group, properly interleaved with results by other practitioners in the field, we present some of the latest developments and promising new leads in this new field of spectroscopy.



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SORS: SPATIALLY OFFSET RAMAN SPECTROSCOPY

- Allows analysis of samples behind the walls of containers or behind layers of opaque materials
- Two detection points:
 1. Near the illumination point, to get background spectrum of container
 2. Away from laser beam to detect signal coming mostly from behind the barrier
- Sample spectrum obtained subtracting spectrum 1 from spectrum 2
- SORS minimizes problems with strong signal from packaging surface or from fluorescence of surface compounds

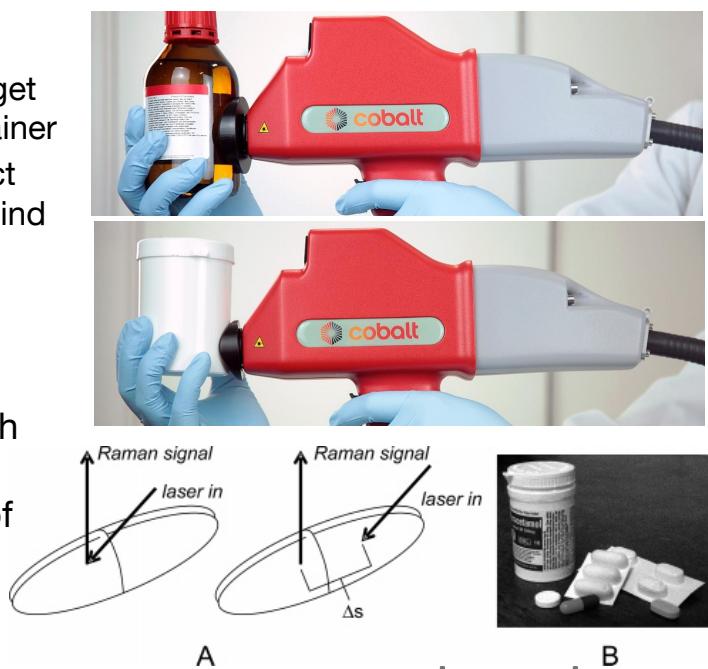


Image taken from:
Anal. Chem. 2007, 79, 1696-1701



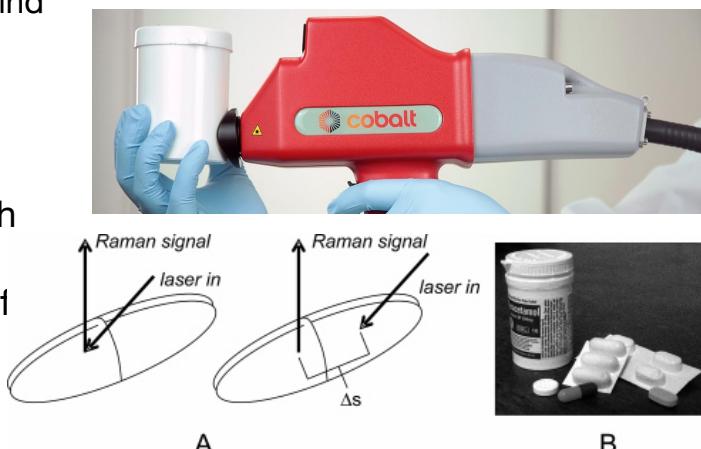
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Image taken from:
Anal. Chem. **2007**, 79, 1696-1701



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EXAMPLE: CNT-PS COMPOSITE

- C.G. Espinosa-González, F.J. Rodríguez-Macías, A.G. Cano-Márquez, J. Kaur, M.L. Shofner, Y.I. Vega-Cantú. "Polystyrene Composites with Very High Carbon Nanotubes Loadings by *in situ* Grafting Polymerization". Journal of Materials Research, **28**(8), 1087-1096 (2013).
 - DOI: 10.1557/jmr.2013.38

TABLE II. I_D/I_G ratios and peak shifts for the composites from Raman spectroscopy (633 nm laser excitation).

MWCNT loading (wt%)	I_D/I_G	ΔD	ΔG
22	1.353	-21.3	+3.54
42	1.471	-7.39	+0.88
67	1.434	-9.24	+5.31
75	1.757	-5.54	-1.77
80	1.498	-22.2	+0.88
100	0.492

- Peak positions shift due to functionalization and due to interactions with the polymer matrix
- I_D/I_G ratio increases as the CNT are functionalized with more polymer
 - But it does not show the expected trend of increasing with degree of functionalization

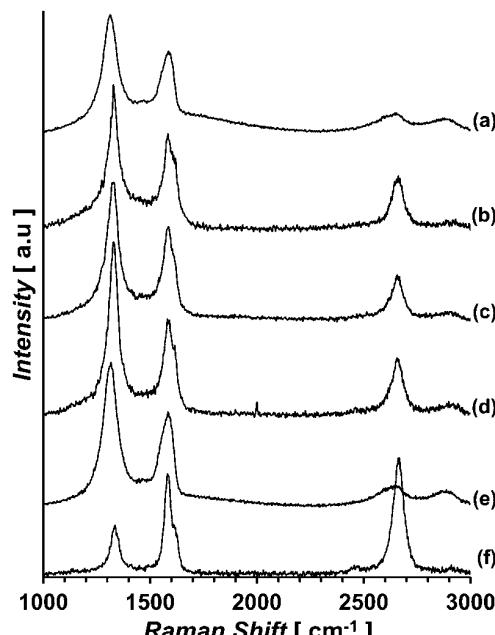


FIG. 7. Raman spectra of PS-g-MWCNTs nanocomposites with decreasing fractions of PS, (a) 22 wt% MWCNT, (b) 42 wt%, (c) 67 wt%, (d) 75 wt%, (e) 80 wt%, and (f) purified MWCNTs.

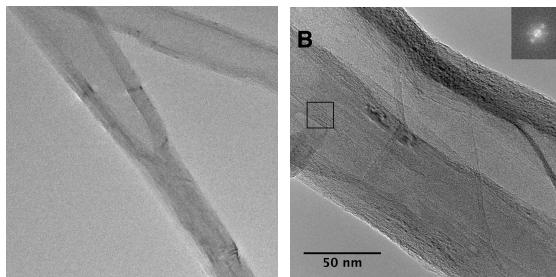
- Deviation from trend is because the functionalization process leads to partial opening of CNT due to intercalation of lithium and exfoliation during composite processing



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EXAMPLE: EX-MWNT GRAPHITIC NANO RIBBONS



- ex-MWNT: GNR made by splitting open Multi-Walled Carbon Nanotubes after an intercalation-exfoliation process
 - Method was found as side effect of lithium catalyzed functionalization of MWCNT
- I_D/I_G ratio shows that more sp^3 carbon is present in open nanotubes
 - Degree of opening changes with different treatments
 - Process starts by cutting MWCNT by sonication in oxidizing acids, which removes impurities and reduces I_D/I_G
- Shifts in peak position due to treatment are also observed
- Raman spectroscopy shows partial annealing of defects after final thermal treatment
- Higher I_D/I_G ratio than original material due to edges

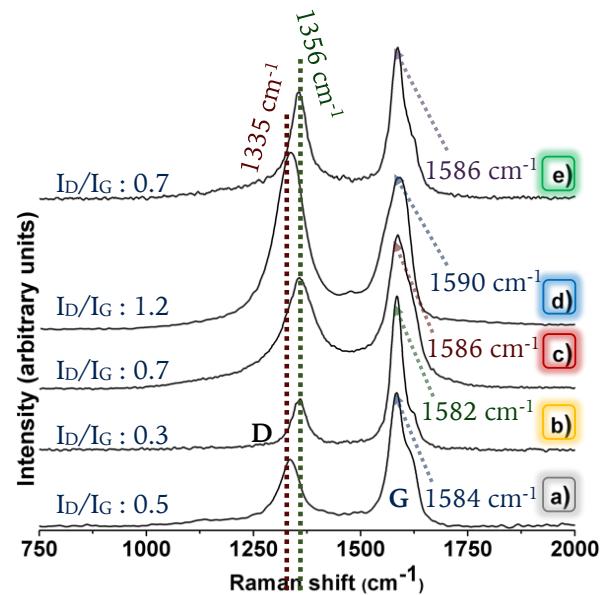


Figure 6. Raman spectra for MWNTs: (a) as synthesized; (b) cut- MWNTs; (c) cut-MWNTs treated only with NH_3 ; (d) Li- NH_3 intercalated, exfoliated with HCl solution only; (e) HCl exfoliated material after thermal treatments.

