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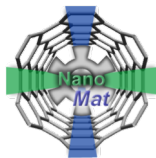
Microscopía Raman Confocal & Microscopia de Fuerza Atómica



UNIVERSIDAD
DE LA REPÚBLICA
URUGUAY

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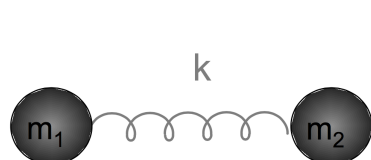
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Punteo

- ❑ Modos Vibracionales
- ❑ Reglas de Selección: IR vs Raman
- ❑ Microscopia Óptica y Confocal
- ❑ Microscopia Raman Confocal
- ❑ Aplicaciones de MicroRaman
- ❑ Microscopia de Fuerza Atómica
- ❑ Aplicaciones de MicroRamanAFM

1. Modos Vibracionales



$$V = \frac{1}{2} kx^2$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

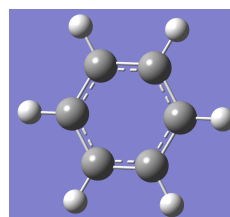
Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200
	stronger bond	$\bar{\nu}$ increases
Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
	heavier atoms	$\bar{\nu}$ decreases

1. Modos Vibracionales

□ Número de modos depende de los grados de libertad

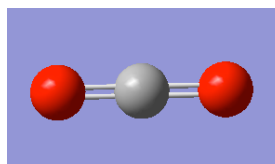
■ Moléculas no Lineales

- N° modos=3N-6
- Ejemplo: Benceno
 - 30 modos



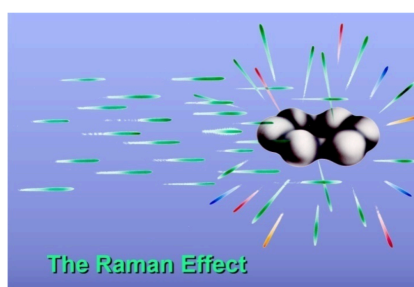
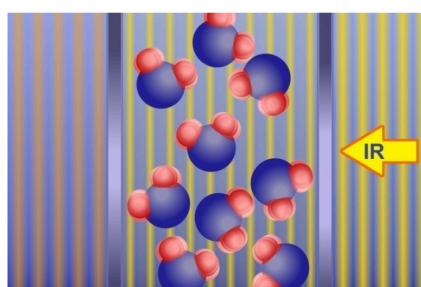
■ Moléculas Lineales

- N° modos=3N-5
- Ejemplo: CO₂
 - 4 modos

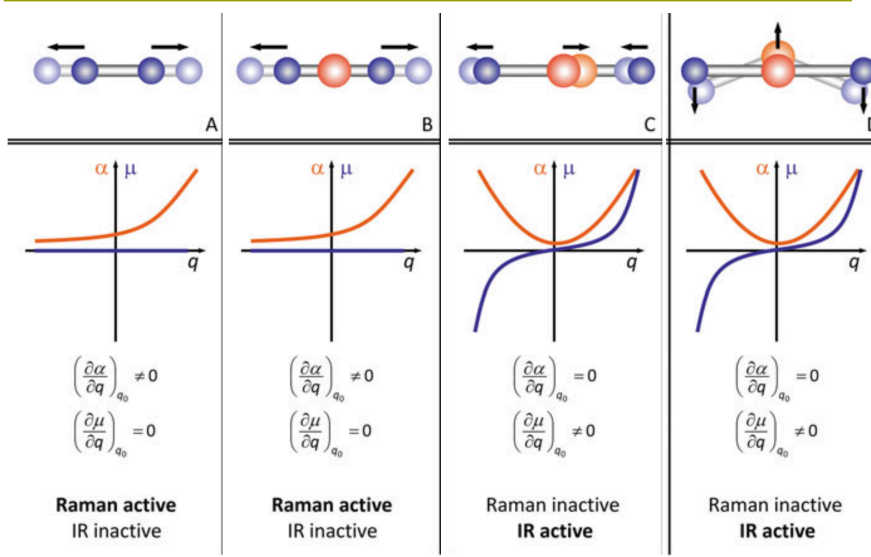


2. Reglas de Selección

- IR: Absorción de fotón por dipolo (μ) del modo normal de vibración.
- Raman: Dispersión inelástica mediada por momento dipolar inducido (polarizabilidad α) generado por la OEM.

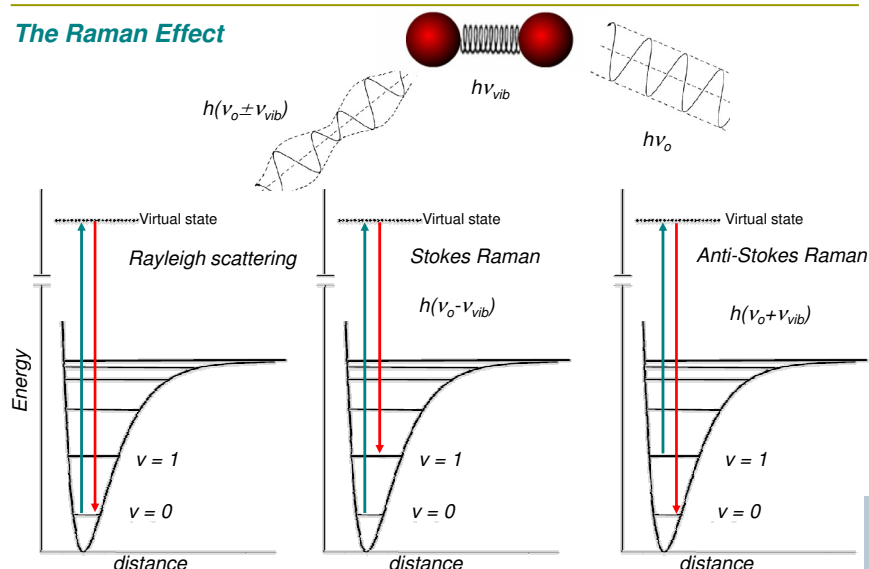


2. Reglas de Selección: IR vs Raman



2. El efecto Raman

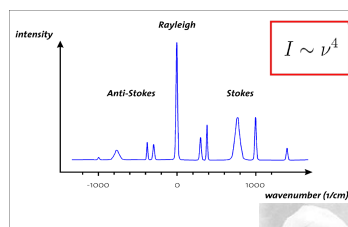
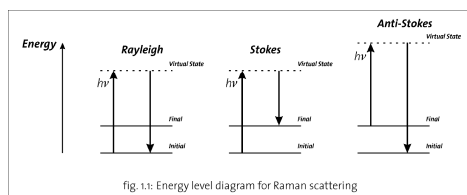
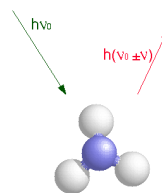
The Raman Effect



2. El efecto Raman

The Raman Effect

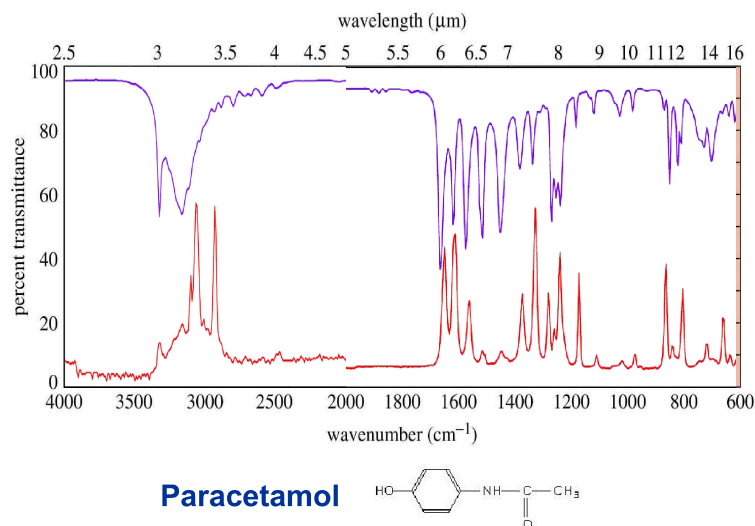
- non-resonant excitation (Stokes) or annihilation (Anti-Stokes) of a vibrational quantum
- energy shift between the exciting and scattered photon is characteristic for the molecules involved in the scattering process



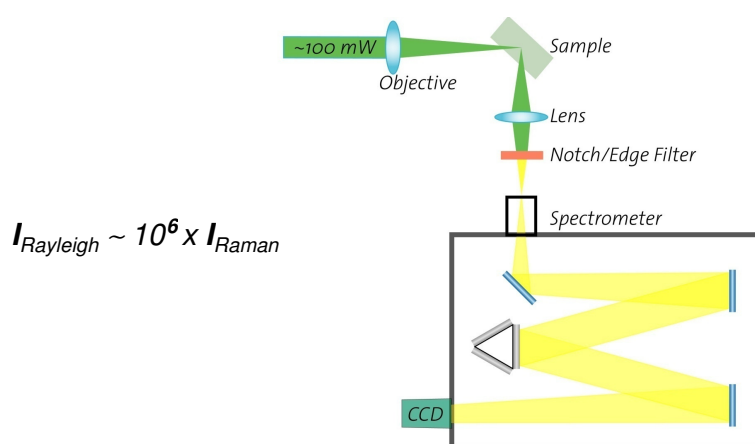
- theoretical prediction 1923 by A. Smekal
- experimentally discovered 1928 by Sir Chandrasekhara Raman, Nobel Prize 1930



2. Infrarrojo vs. Raman

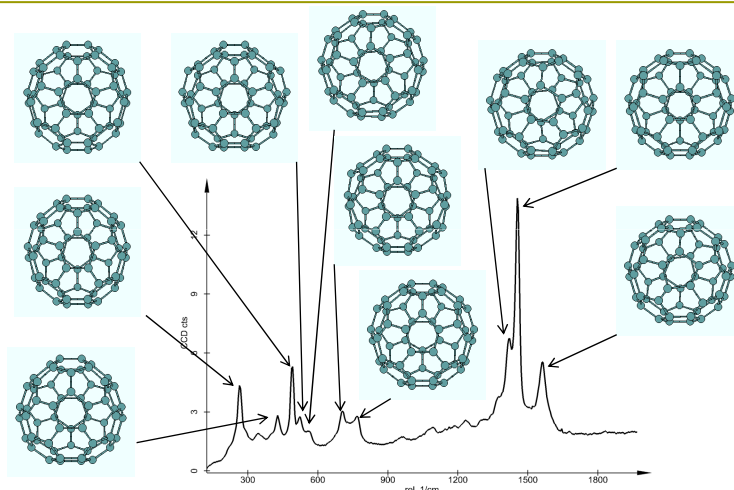


2. Esquema Típico de Experimento



- typical integration times: seconds - several minutes

2. Espectroscopia Raman



chemical, but NO spatial resolution

2. Identificación de Bandas

Functional Group/ Vibration	Region	Raman	InfraRed
Lattice vibrations in crystals, LA modes	10 - 200 cm^{-1}	strong	strong
$\delta(\text{CC})$ aliphatic chains	250 - 400 cm^{-1}	strong	weak
$\nu(\text{Se-Se})$	290 - 330 cm^{-1}	strong	weak
$\nu(\text{S-S})$	430 - 550 cm^{-1}	strong	weak
$\nu(\text{Si-O-Si})$	450 - 550 cm^{-1}	strong	weak
$\nu(\text{Xmetal-O})$	150-450 cm^{-1}	strong	med-weak
$\nu(\text{C-I})$	480 - 660 cm^{-1}	strong	strong
$\nu(\text{C-Br})$	500 - 700 cm^{-1}	strong	strong
$\nu(\text{C-Cl})$	550 - 800 cm^{-1}	strong	strong
$\nu(\text{C-S})$ aliphatic	630 - 790 cm^{-1}	strong	medium
$\nu(\text{C-S})$ aromatic	1080 - 1100 cm^{-1}	strong	medium
$\nu(\text{O-O})$	845 - 900 cm^{-1}	strong	weak
$\nu(\text{C-O-C})$	800 - 970 cm^{-1}	medium	weak
$\nu(\text{C-O-C})$ asym	1060 - 1150 cm^{-1}	weak	strong

$\nu(\text{CC})$ allicyclic, aliphatic chain vibrations	600 - 1300 cm^{-1}	medium	Medium
$\nu(\text{C}=\text{S})$	1000 - 1250 cm^{-1}	strong	weak
$\nu(\text{CC})$ aromatic ring chain vibrations	*1580, 1600 cm^{-1}	strong	medium
	*1450, 1500 cm^{-1}	medium	medium
	*1000 cm^{-1}	strong/medium	weak
$\delta(\text{CH}_3)$	1380 cm^{-1}	medium	strong
$\delta(\text{CH}_2)$ $\delta(\text{CH}_3)$ asym	1400 - 1470 cm^{-1}	medium	medium
$\delta(\text{CH}_2)$ $\delta(\text{CH}_3)$ asym	1400 - 1470 cm^{-1}	medium	medium
$\nu(\text{C}-(\text{NO}_2))$	1340 - 1380 cm^{-1}	strong	medium
$\nu(\text{C}-(\text{NO}_2))$ asym	1530 - 1590 cm^{-1}	medium	strong
$\nu(\text{N}=\text{N})$ aromatic	1410 - 1440 cm^{-1}	medium	-
$\nu(\text{N}=\text{N})$ aliphatic	1550 - 1580 cm^{-1}	medium	-
$\delta(\text{H}_2\text{O})$	~1640 cm^{-1}	weak broad	strong
$\nu(\text{C}=\text{N})$	1610 - 1680 cm^{-1}	strong	medium
$\nu(\text{C}=\text{C})$	1500 - 1900 cm^{-1}	strong	weak
$\nu(\text{C}=\text{O})$	1680 - 1820 cm^{-1}	medium	strong
$\nu(\text{C}\equiv\text{C})$	2100 - 2250 cm^{-1}	strong	weak
$\nu(\text{C}\equiv\text{N})$	2220 - 2255 cm^{-1}	medium	strong
$\nu(\text{-S-H})$	2550 - 2600 cm^{-1}	strong	weak
$\nu(\text{C-H})$	2800 - 3000 cm^{-1}	strong	strong
$\nu(\text{=C-H})$	3000 - 3100 cm^{-1}	strong	medium
$\nu(\text{=C-H})$	3300 cm^{-1}	weak	strong
$\nu(\text{N-H})$	3300 - 3500 cm^{-1}	medium	medium
$\nu(\text{O-H})$	3100 - 3650 cm^{-1}	weak	strong

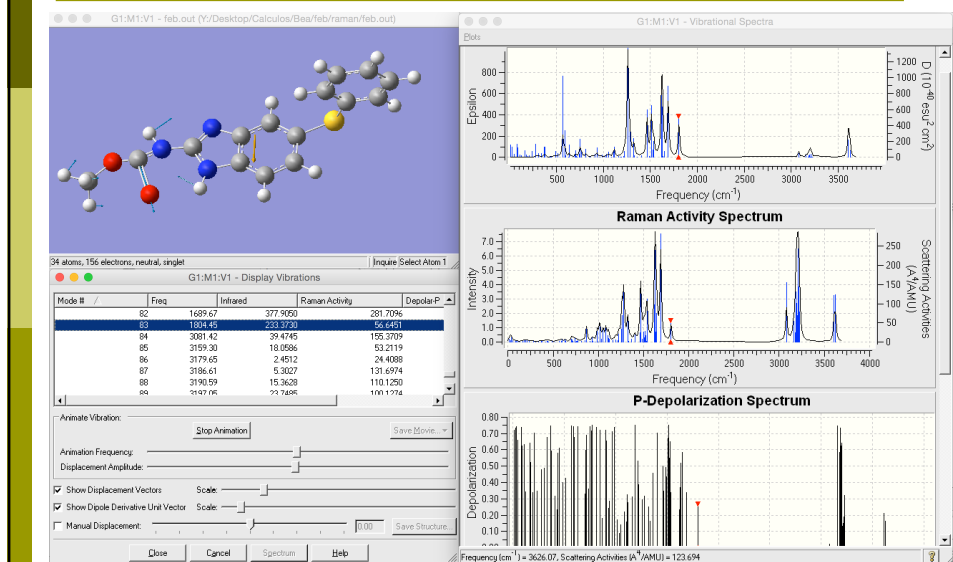
2. Métodos Teóricos

▣ Cálculos *ab initio* o *Primeros Principios*

▣ *DFT*

■ *Gaussian*

2. Simulación de IR y Raman

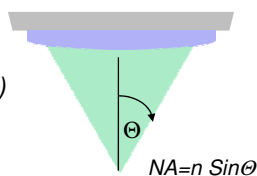


3 Microscopia Óptica Clásica

What is the resolution limit of a classical optical microscope?

Ernst Abbé (1840-1905): diffraction theory

$$\Delta x \geq 0,61 \times (\lambda / NA)$$

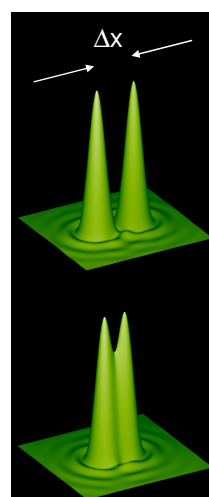


air: $NA \leq 0,95$ (340nm @ 532nm exc.)

water: $NA \leq 1,2$ (270nm @ 532nm exc.)

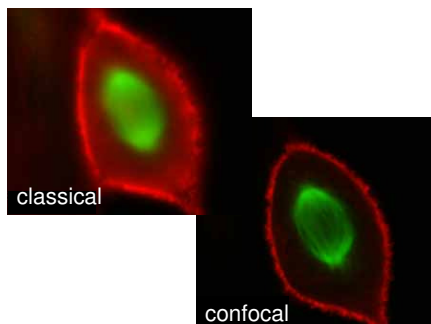
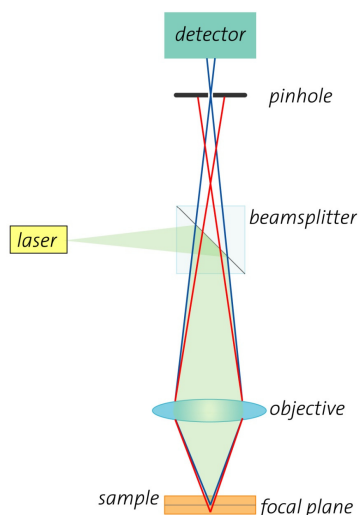
oil: $NA \leq 1,4$ (230nm @ 532nm exc.)

$$\text{resolution limit} \approx \lambda / 2$$



3. Microscopia Confocal

confocal microscopy



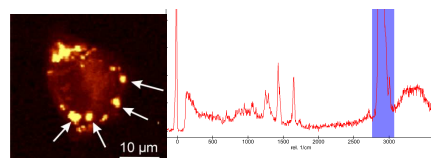
- much smaller background
- 3-D information
- slightly higher resolution possible

spatial, but NO chemical information

3. Microscopio Confocal + Espectroscopia Raman

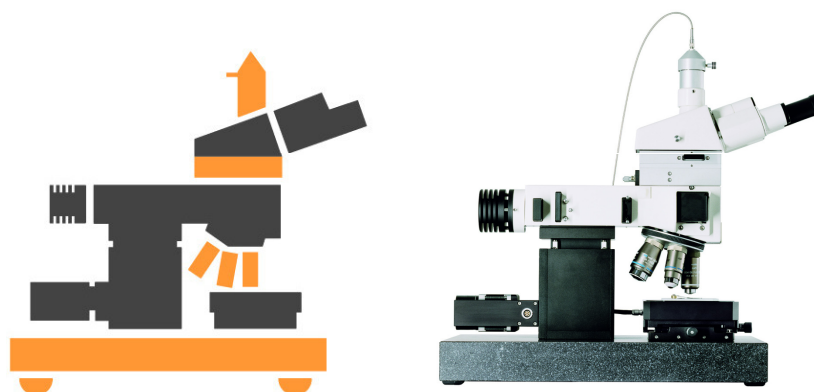
3-D Imaging with chemical sensitivity

- take a complete Raman spectrum at every image pixel
- extract the relevant information (peak intensity, width, position etc.)
- display this information as image



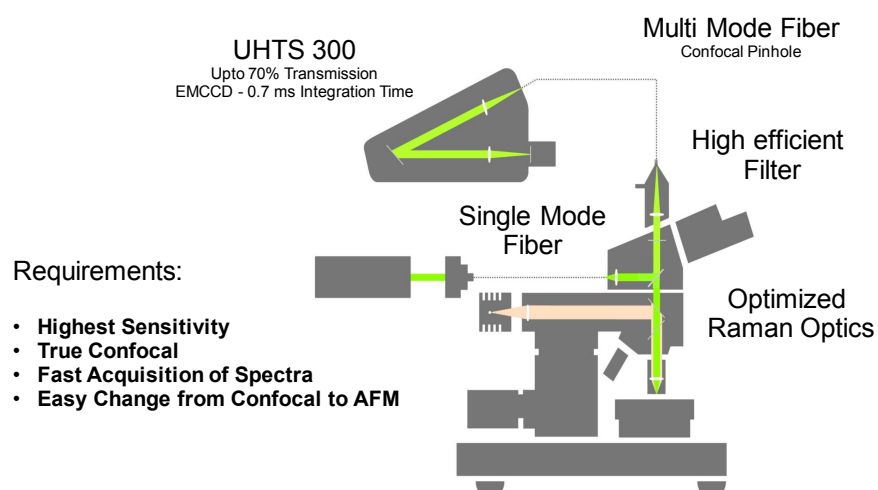
Parque Científico y Tecnológico de Pando (PCTP) /
Instituto Polo Tecnológico de Pando (IPTP)
ANII- Proyecto EQC_X_2012_1_14

3. Microscopio Confocal + Espectrómetro Raman



Imaging with chemical sensitivity

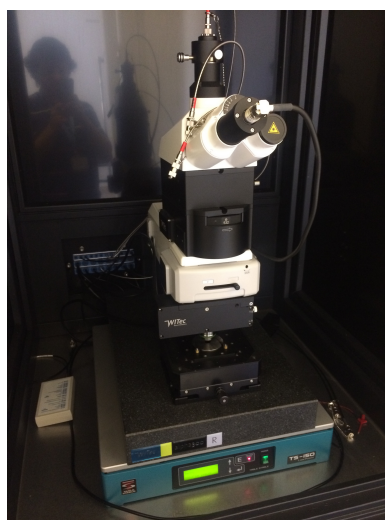
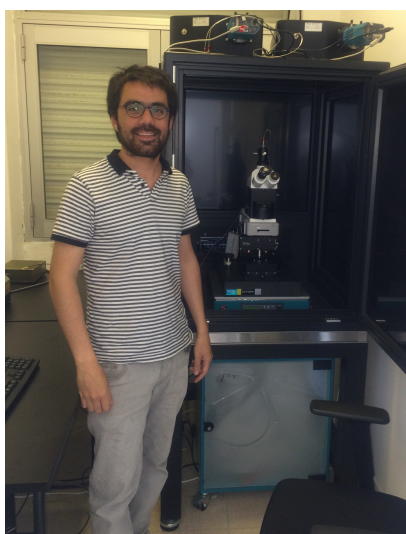
3. Esquema



3. Características de la Técnica

- ❑ No Destructivo
- ❑ Identificación Química Directa
- ❑ Identificación de Propiedades de Materiales
- ❑ Fácil o nula preparación de muestra
- ❑ Sólidos cristalinos, sólidos amorfos y Líquidos
- ❑ Detección 3-dimensional
- ❑ Variación de Temperatura (Linkam)
- ❑ Combinación de detección química con AFM (EFM & MFM)

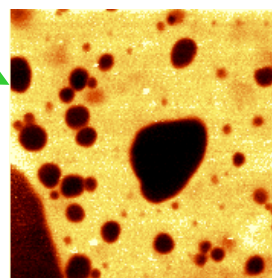
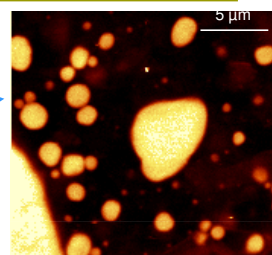
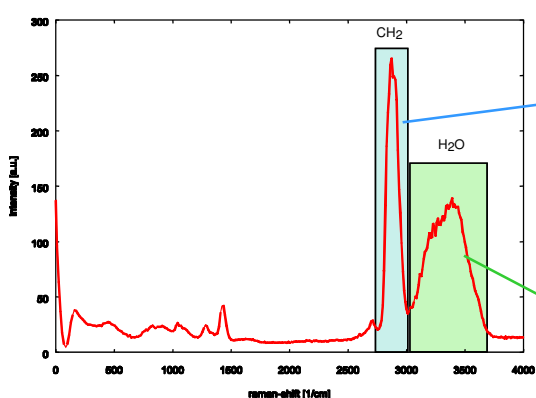
3. Disposición



Aplicaciones

Microscopia Raman Confocal

Imagen Raman: dispersión agua-aceite



Body lotion, imaging parameters:

2 mW excitation @ 532nm, 100x oil, NA=1,25

20 x 20 μm, 180 x 180 pixels (= 32400 spectra)

50ms/spectrum

Reconstrucción Imagen Raman 3D

Sample: Oil/Water Emulsion

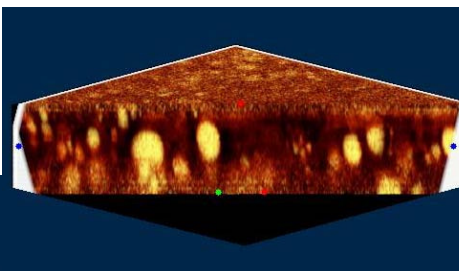
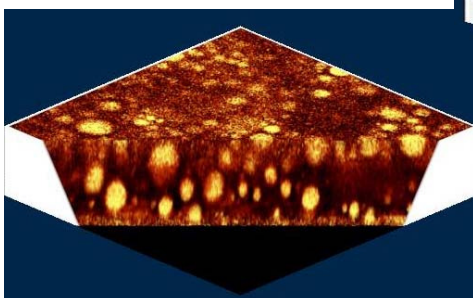
3-D Reconstruction

Evaluated Band: CH-Stretching

Excitation: 532nm

Scan Range XY: 100x100 μm

Scan Range Z: 30 μm /32 layers



Total number of Spectra: 517 500

Total Acquisition Time: 23 min

Geociencias

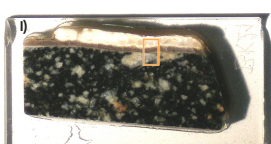


Fig. 1: I) Orange rectangle indicates scan position on polished rock section.

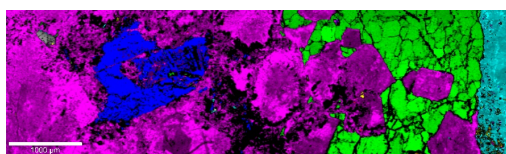


Fig. 2: I) Combined false color image and the corresponding color-coded spectra.

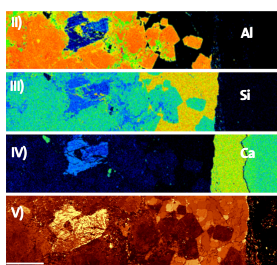
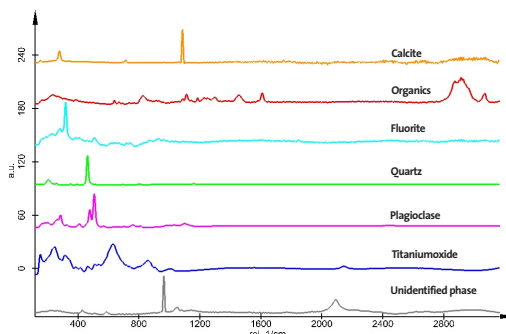
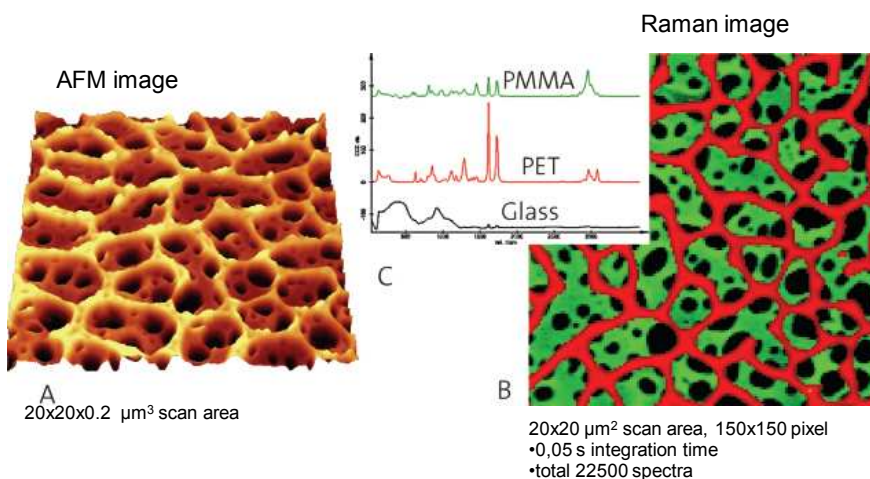


Fig. 3: II-IV) EMP maps showing elemental distribution; V) corresponding Raman image, integrated intensity 140-300 $\text{rel.}/\text{cm}$.



Polímeros

Thin Film of PMMA - PET



Blend PMMA+SBR

Fig. 5: Overview AFM image of a PMMA-SBR blend.

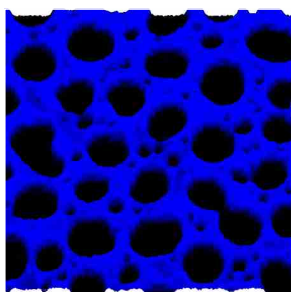
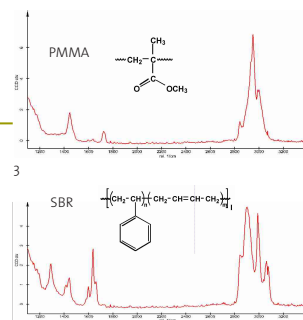
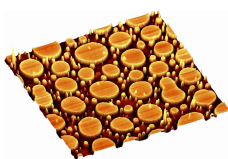


Fig. 9: Color coded Raman image of SBR resulting from the integral intensity of each spectrum.

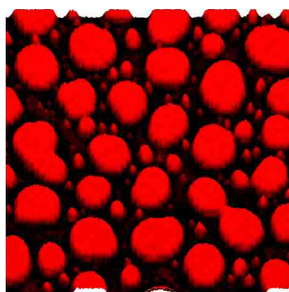


Fig. 10: Color coded Raman image of PMMA resulting from the integral intensity of each spectrum.

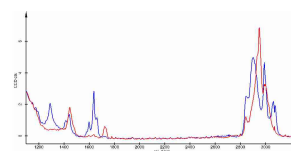
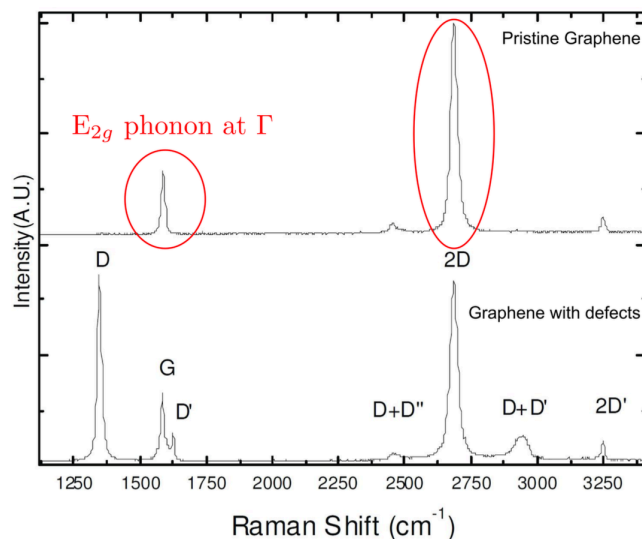


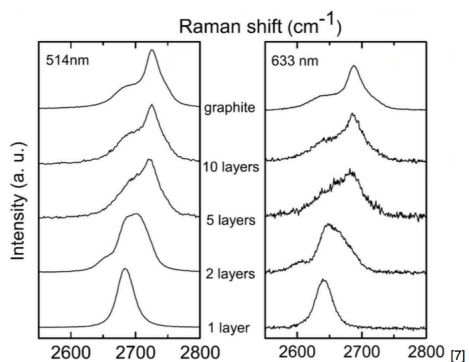
Fig. 11: Corresponding spectra: SBR (blue) and PMMA (red).

Ejemplo: Grafeno



Ejemplo : Grafeno

"Position and fwhm of the G and 2D peak(...)confirm presence of single-layer graphene"

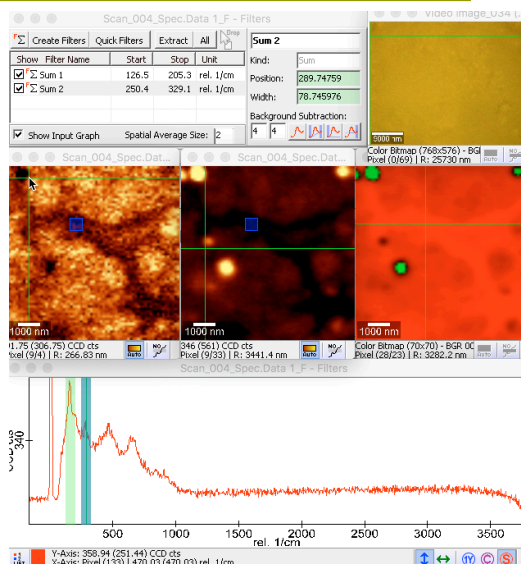


- Position of 2D peak depends on number of layers
- Additional layers increase FWHM of 2D peak (more e^- states for resonant scattering)
- Occurrence of peaks at 1350 cm^{-1} (D) and 1620 cm^{-1} (D') reveal defects of graphene sample

Ejemplo: Caracterización de NT

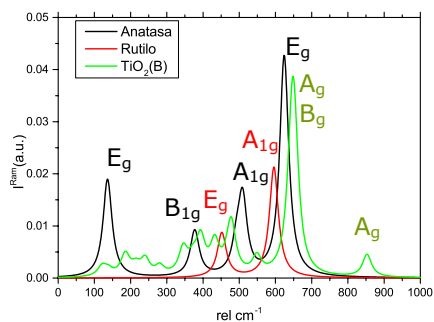
Ejemplo de Funcionamiento:

- Muestra de NT calentados a $T=200^{\circ}\text{C}$.
- Presencia de Nanopartículas de Anatasa en muestra de NT.



Modelado: Espectros Raman de polimorfos de TiO_2

Espectros Raman Calculados

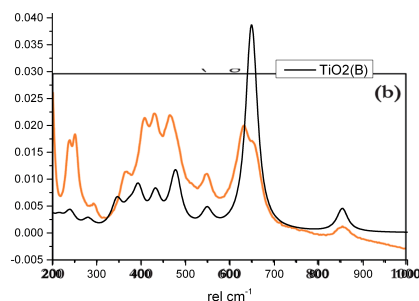


Cálculos DFT: Código VASP

Ecut=400 eV

Ondas Planas

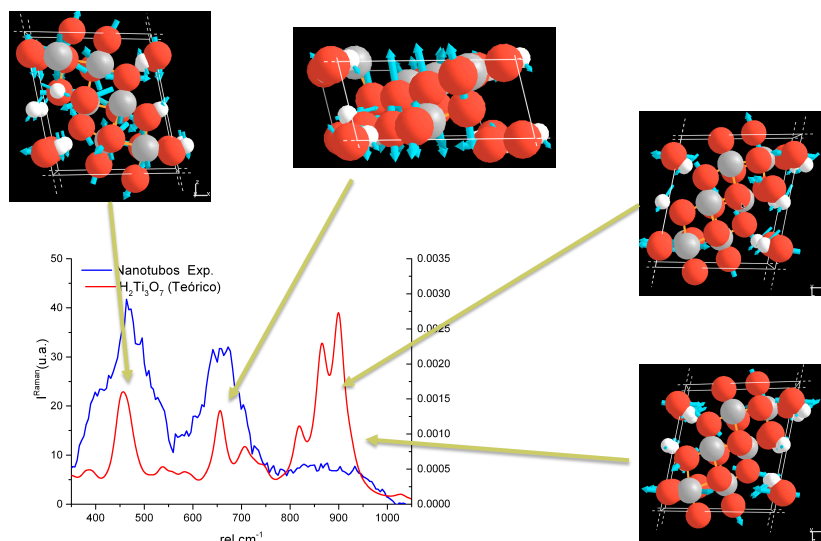
DFPT fonones



Espectros Raman Calculados y Experimental:

Dylla et al, J. Phys. Chem. Lett. 2012, 3, 2015 2019

Modelado: Espectros Raman de Titanatos de H y Na (Teóricos)



Resumen: Micro Raman Confocal

- ▣ No Destructivo
- ▣ Identificación Química Directa
- ▣ Identificación de Propiedades de Materiales
- ▣ Preparación sencilla de muestra
- ▣ Sólidos y Líquidos
- ▣ Detección 3-dimensional
- ▣ Combinación de detección química con AFM
- ▣ Variación de Temperatura (Linkam)

