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Introducing Students to Raman Spectroscopy as a Research Tool

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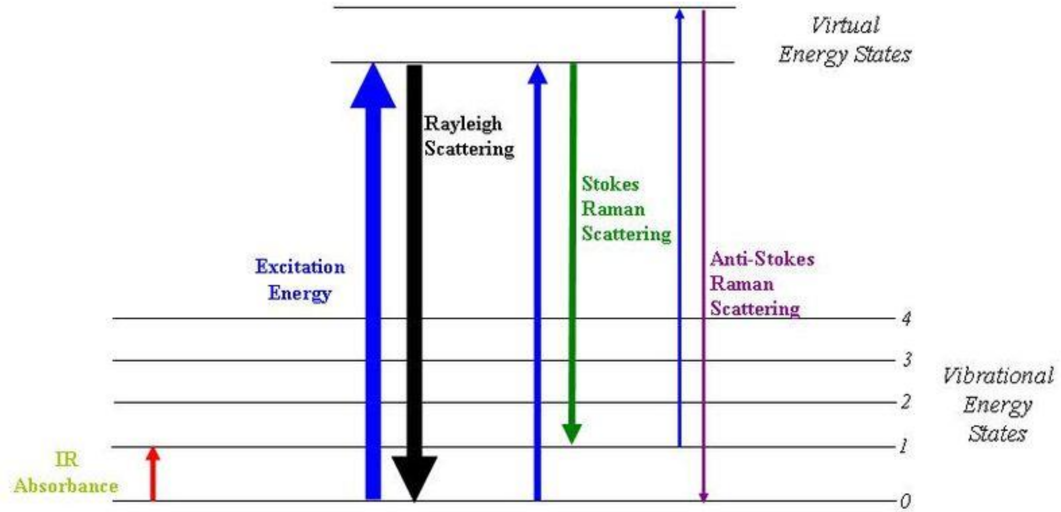
Outline

- **Introduction**
- **Raman Spectroscopy Overview**
- **Raman Spectroscopy of Si (100)**
  - **Model**: Polarization Analysis $ Raman Intensity
  - **Measurements**: Experimental Si Peak Intensity
- **Discussion and Summary**
- **Questions**

In Light Scattering “Sky is the limit”

Raman Scattering

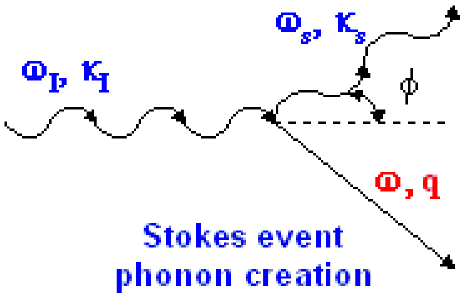


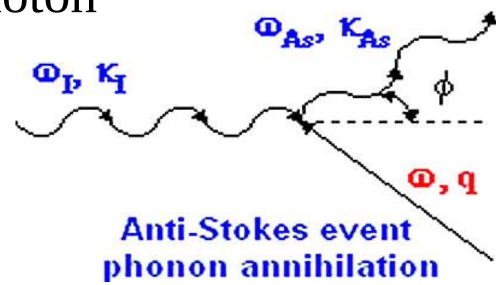
http://www.doitpoms.ac.uk/tlplib/raman/printall.php

Raman Scattering Process

Incident Photon

Scattered Photon

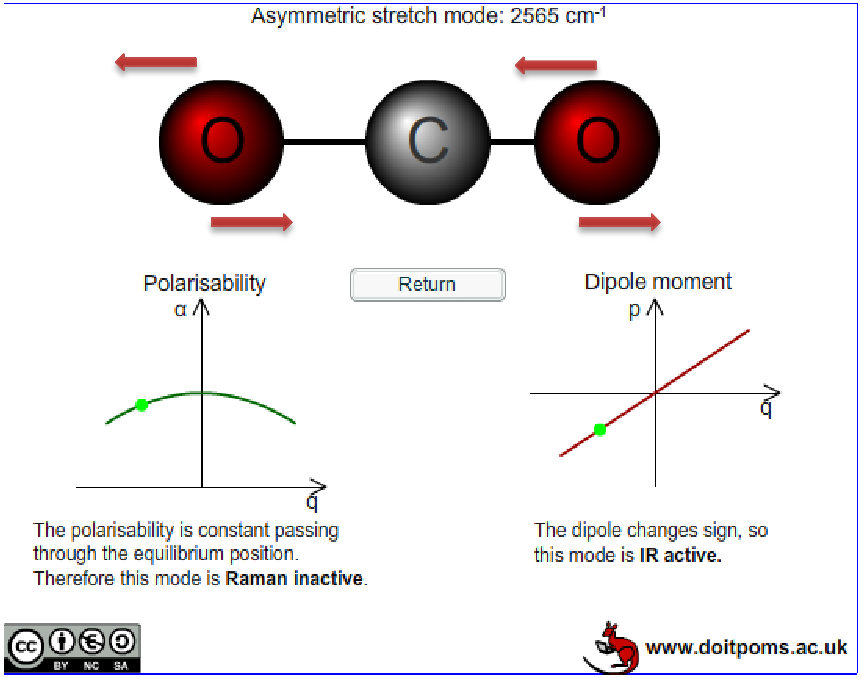


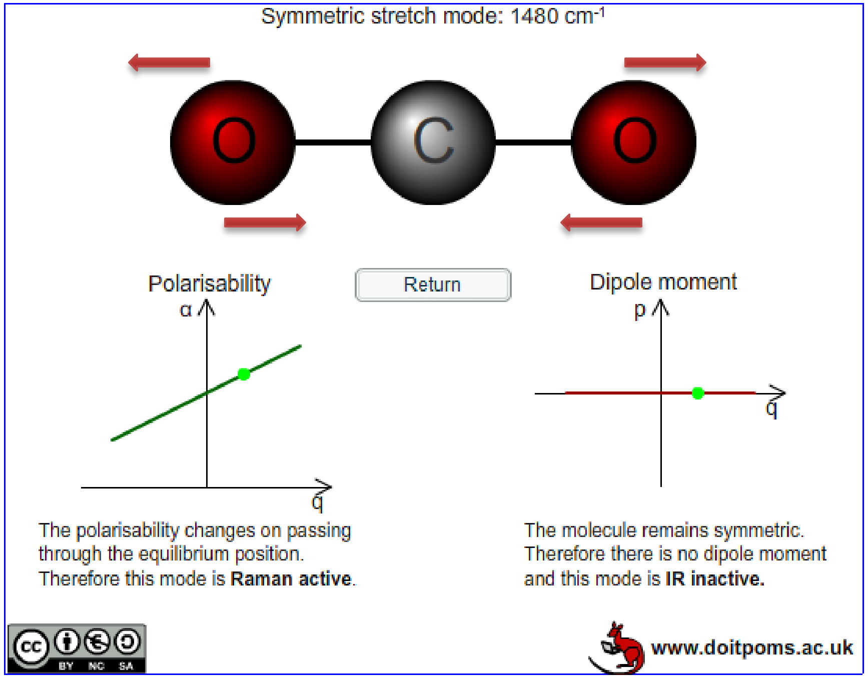


Phonon

Kinematic

Stokes event		Anti – Stokes event
$\hbar\omega_s = \hbar\omega_I - \hbar\omega$	(Energy)	$\hbar\omega_{As} = \hbar\omega_I + \hbar\omega$
$\hbar k_s = \hbar k_I - \hbar q$	(Momentum)	$\hbar k_{As} = \hbar k_I + \hbar q$

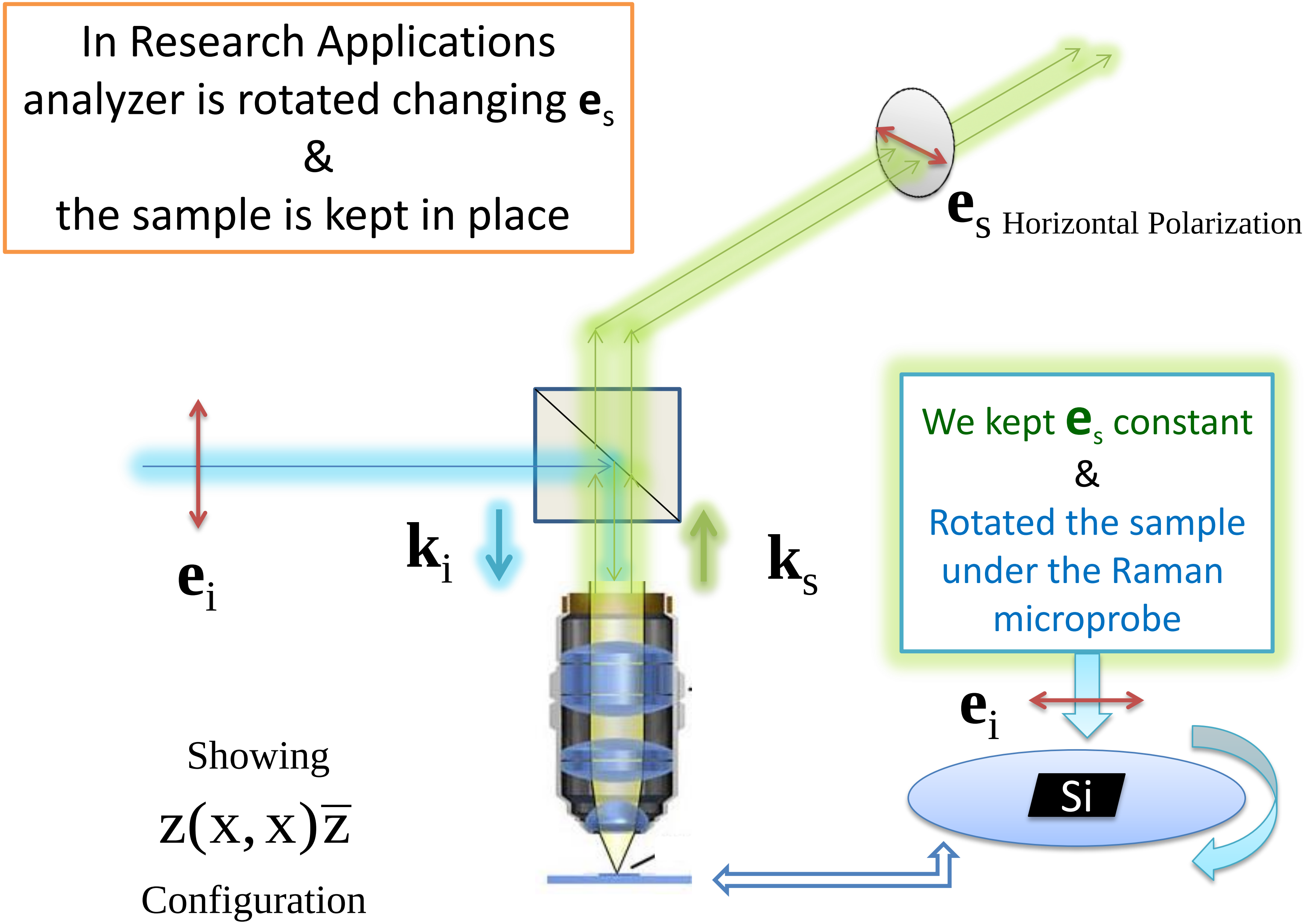




IR Active – Raman Inactive
Change in Dipole Moment Sign

Raman Active - IR Inactive
Change in Polarizability Sign

http://www.doitpoms.ac.uk/tlplib/raman/printall.php



In Research Applications
analyzer is rotated changing $\mathbf{e}_s$
&
the sample is kept in place
$\mathbf{e}_S$ Horizontal Polarization
$\mathbf{e}_i$
$\mathbf{k}_i$
$\mathbf{k}_s$
We kept $\mathbf{e}_s$ constant
&
Rotated the sample
under the Raman
microprobe
$\mathbf{e}_i$
Si
Showing
$z(x, x)\bar{z}$
Configuration

Si (100) Intensity:
Theoretical Model: 0° Rotation

$$R_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & b \\ o & b & 0 \end{bmatrix}, \quad R_y = \begin{bmatrix} 0 & 0 & b \\ 0 & 0 & 0 \\ b & 0 & 0 \end{bmatrix}, \quad R_z = \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$I \propto \left[e_i \ R_j \ e_s \right]^2$$

e.g., for x , y → Backscattering

$$I \propto \left[\begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \right]^2 = b^2$$

Polarization Configuration	Phonon modes (direction of atomic displacement)		
	LO (z-direction)	TO (x-direction)	TO (y-direction)
Z (x, x) $\bar{Z}$	0	0	0
Z (x, y) $\bar{Z}$	b^2	0	0
Z (y, y) $\bar{Z}$	0	0	0

Where; x = < 1 0 0 >, y = < 0 1 0 >, and z = < 0 0 1 >

Si (100) Intensity:
Theoretical Model: 45° Rotation

$$I \propto \left[e_i \;\; R_j \; e_s\right]^2$$

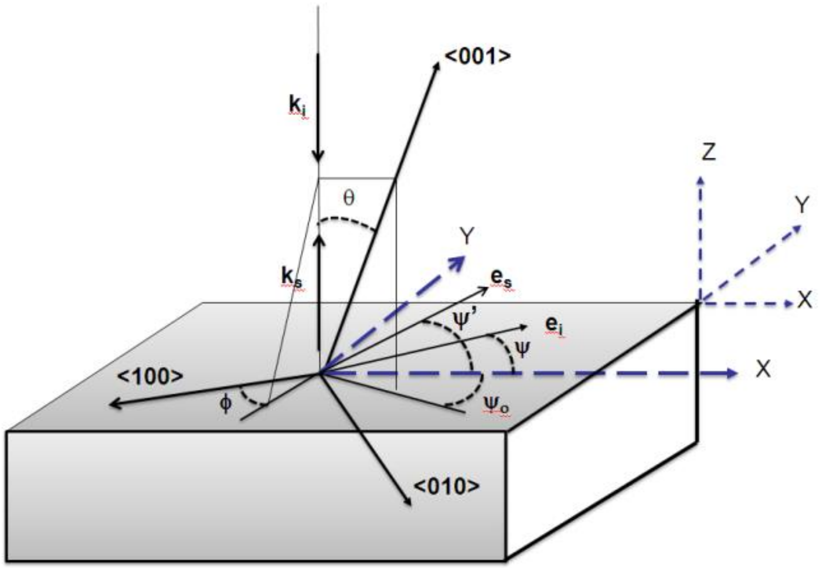
$$R_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & b \\ o & b & 0 \end{bmatrix}, \qquad R_y = \begin{bmatrix} 0 & 0 & b \\ 0 & 0 & 0 \\ b & 0 & 0 \end{bmatrix}, \qquad R_z = \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Polarization Configuration	Phonon modes (direction of atomic displacement)		
	LO (z-direction)	TO (x-direction)	TO (y-direction)
$Z\,(x', x')\,\bar{Z}$	b^2	0	0
$Z\,(x', y')\,\bar{Z}$	0	0	0
$Z\,(y', y')\,\bar{Z}$	b^2	0	0

Where $x' = \frac{1}{\sqrt{2}} < 1\ 1\ 0 >$, $\quad y' = \frac{1}{\sqrt{2}} < 1\ \bar{1}\ 0 >$, $\quad$ and $\quad z' = < 0\ 0\ 1 >$

General Configuration – Back Scattering Geometry

θ	Angle between <001> & the scattered wave vector $\mathbf{k}_s$,
ϕ	Angle between <100> & the projection of $\mathbf{k}_s$ onto the (001)
Ψ_o	Angle between the x-axis of laboratory coordinate and the projection of the <001> axis onto the x-y plane,
Ψ	Angle between the x-axis and unit polarization vectors $\mathbf{e}_i$
Ψ'	Angle between the x-axis and unit polarization vectors $\mathbf{e}_s$,



Incident polarization vector (e_i) & Scattered light polarization vector (e_s)

$$e_i^x = \cos\theta \ \ \cos\emptyset \ \ \cos[\psi + \psi_0] - \ \sin\phi \ \ \sin[\psi + \psi_0] \quad (3a)$$
$$e_i^y = \cos\theta \ \ \sin\emptyset \ \ \cos[\psi + \psi_0] + \ \cos\phi \ \ \sin[\psi + \psi_0] \quad (3b)$$
$$e_i^z = -\sin\theta \ \ \cos[\psi + \psi_0] \quad (3c)$$

And

$$e_s^x = \cos\theta \ \ \cos\emptyset \ \ \cos[\psi' + \psi_0] - \ \sin\phi \ \ \sin[\psi' + \psi_0] \quad (4a)$$
$$e_s^y = \cos\theta \ \ \sin\emptyset \ \ \cos[\psi' + \psi_0] + \ \cos\phi \ \ \sin[\psi' + \psi_0] \quad (4b)$$
$$e_s^z = -\sin\theta \ \ \cos[\psi' + \psi_0] \quad (4c)$$

Raman Intensity Calculations follows:

$$I \propto \left[e_i \ \ R_j \ e_s\right]^2$$

$$R_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & b \\ o & b & 0 \end{bmatrix}, \qquad R_y = \begin{bmatrix} 0 & 0 & b \\ 0 & 0 & 0 \\ b & 0 & 0 \end{bmatrix}, \qquad R_z = \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Si (100) Raman Tensors R_x, R_y & R_z

Simplified Version – Back Scattering Geometry

θ	Angle between <001> & the scattered wave vector $\mathbf{k}_s$,
ϕ	Angle between <100> & the projection of $\mathbf{k}_s$ onto the (001)
Ψ_o	Angle between the x-axis of laboratory coordinate and the projection of the <001> axis onto the x-y plane,
Ψ	Angle between the x-axis and unit polarization vectors $\mathbf{e}_i$
Ψ'	Angle between the x-axis and unit polarization vectors $\mathbf{e}_s$,

Simplified version assuming:

Lab z-axis || <001>

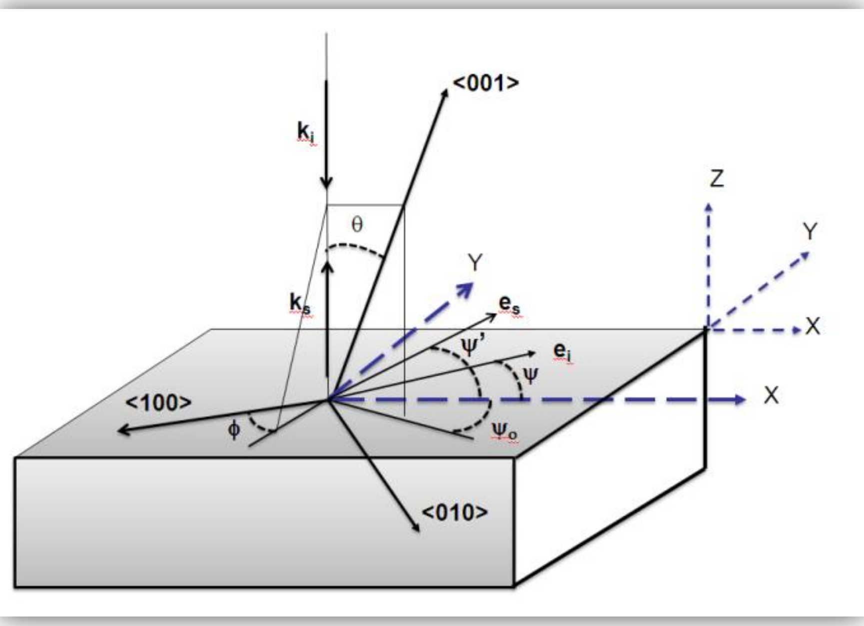
Thus,

$\theta = 0$

$\phi = 0$,

And, $\Psi_o = 0$

With Ψ and Ψ' as variable angles



General Case:

$$e_i^x = \cos\theta \;\; \cos\emptyset \;\; \cos[\psi + \psi_0] - \sin\phi \;\; \sin[\psi + \psi_0] \qquad (3a)$$
$$e_i^y = \cos\theta \;\; \sin\emptyset \;\; \cos[\psi + \psi_0] + \cos\phi \;\; \sin[\psi + \psi_0] \qquad (3b)$$
$$e_i^z = -\sin\theta \;\; \cos[\psi + \psi_0] \qquad (3c)$$

And

$$e_s^x = \cos\theta \;\; \cos\emptyset \;\; \cos[\psi' + \psi_0] - \sin\phi \;\; \sin[\psi' + \psi_0] \qquad (4a)$$
$$e_s^y = \cos\theta \;\; \sin\emptyset \;\; \cos[\psi' + \psi_0] + \cos\phi \;\; \sin[\psi' + \psi_0] \qquad (4b)$$
$$e_s^z = -\sin\theta \;\; \cos[\psi' + \psi_0] \qquad (4c)$$

Simplified Case:

$$e_i^x = \cos[\psi]$$

$$e_i^y = \sin[\psi] \qquad \text{Or,} \qquad \boldsymbol{e_i} = \begin{bmatrix} \cos\psi \\ \sin\psi \\ 0 \end{bmatrix} \qquad (5)$$

$$e_i^z = 0$$

And,

$$e_s^x = \cos[\psi']$$

$$e_s^y = \sin[\psi'] \qquad \text{Or,} \qquad \boldsymbol{e_s} = \begin{bmatrix} \cos\psi' \\ \sin\psi' \\ 0 \end{bmatrix} \qquad (6)$$

$$e_s^z = 0$$

$$\boldsymbol{e_i} = \begin{bmatrix} \cos\psi \\ \sin\psi \\ 0 \end{bmatrix}$$

$$\boldsymbol{e_s} = \begin{bmatrix} \cos\psi' \\ \sin\psi' \\ 0 \end{bmatrix}$$

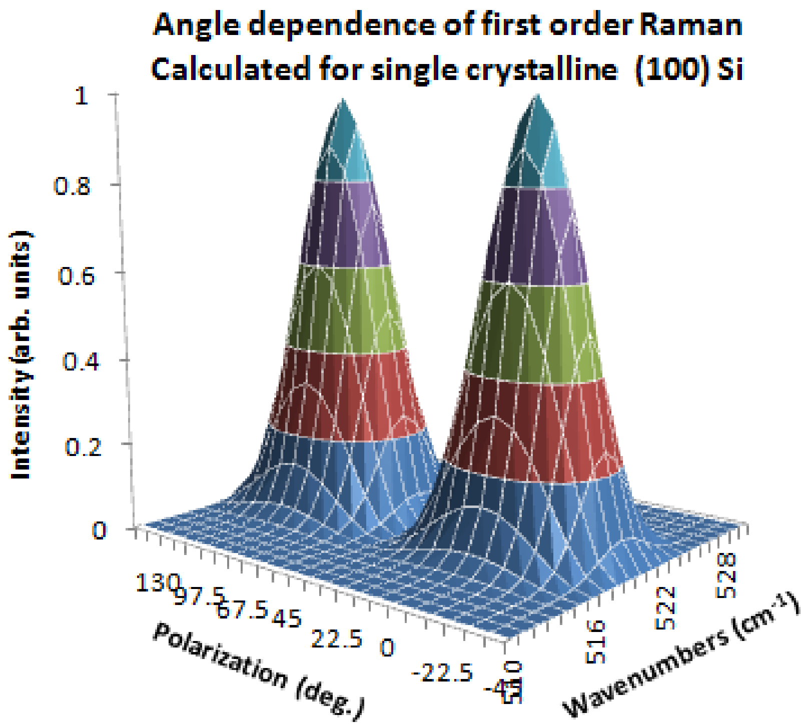
When Fixing The Analyzer Along The X-direction →

$$\boldsymbol{e_i} = \begin{bmatrix} \cos\psi \\ \sin\psi \\ 0 \end{bmatrix}, \text{ and, } \boldsymbol{e_s} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

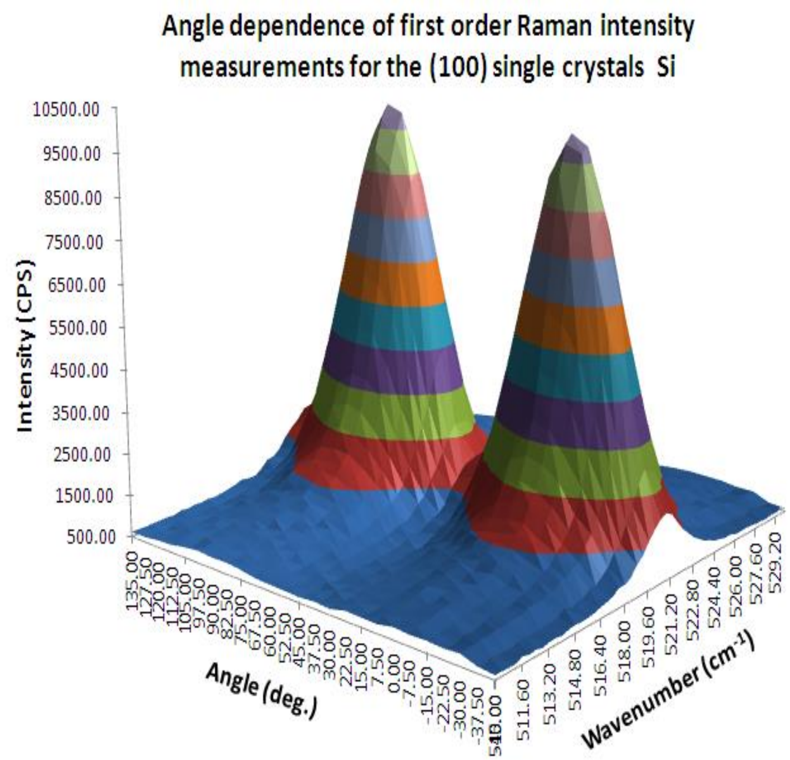
TO Mode: $$I \propto [e_i \ R_x \ e_s]^2 = \left[[cos\psi \quad sin\psi \quad 0] \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & b \\ 0 & b & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \right]^2 = 0 \qquad (7)$$

TO Mode: $$I \propto [e_i \ R_y \ e_s]^2 = \left[[cos\psi \quad sin\psi \quad 0] \begin{bmatrix} 0 & 0 & b \\ 0 & 0 & 0 \\ b & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \right]^2 = [b \ cos\psi]^2 \qquad (8)$$

LO Mode: $$I \propto [e_i \ R_z \ e_s]^2 = \left[[cos\psi \quad sin\psi \quad 0] \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \right]^2 = 0 \qquad (9)$$



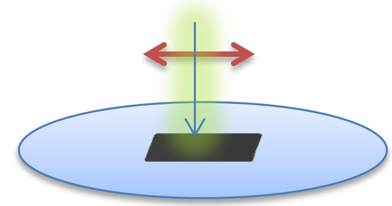
Three dimensional theoretical Raman intensity plot for backscattered signal from single crystalline Si from (100) plane is shown based on Raman intensity calculations.



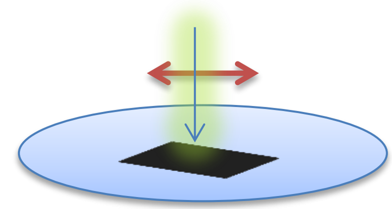
Three dimensional experimental Raman intensity plot for backscattered signal from single crystalline Si from (100) plane is shown based on Raman measurements.

Similarly For backscattering along <110> we have:

$$x_2 = <001> \qquad y_2 = \frac{1}{\sqrt{2}} <1\,\bar{1}\,0> \qquad z_2 = \frac{1}{\sqrt{2}} <1\,1\,0> \quad \leftrightarrow$$



$$x'_2 = \frac{1}{\sqrt{6}} <\bar{1}12> \qquad y'_2 = \frac{1}{\sqrt{3}} <1\,\bar{1}\,1> \qquad z_2 = \frac{1}{\sqrt{2}} <1\,1\,0> \quad \leftrightarrow$$



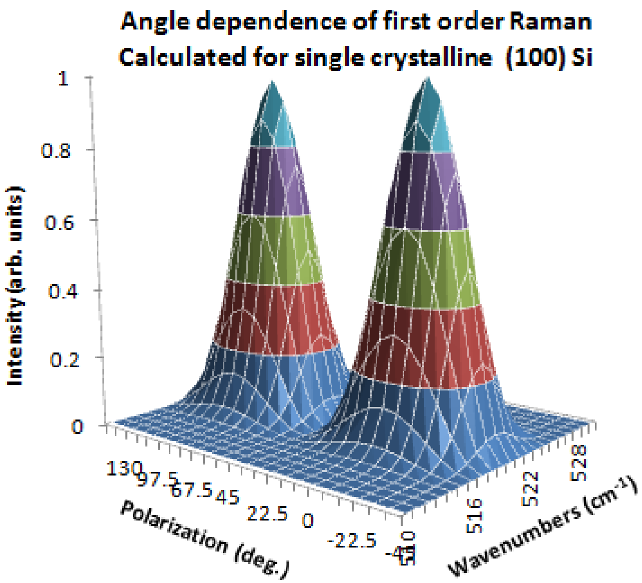
Raman tensors for x_2, y_2, and z_2 axes are:

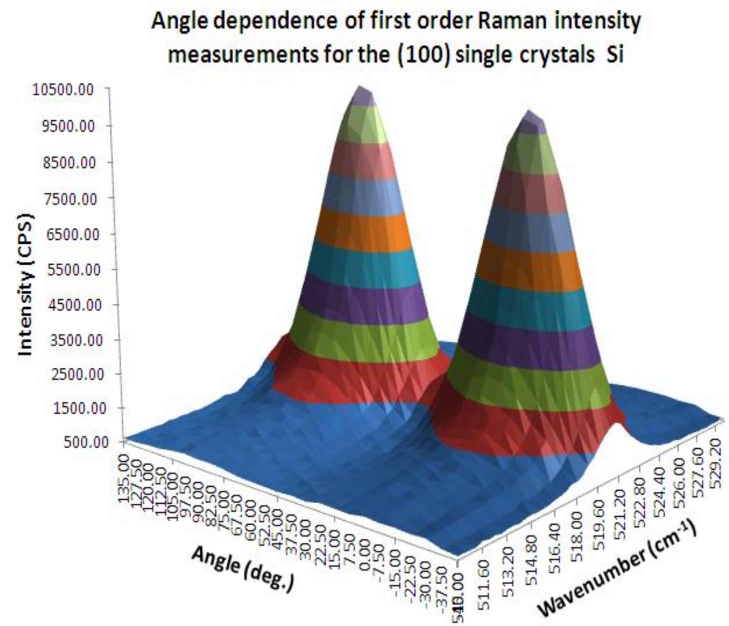
$$R_{x_2} = \begin{bmatrix} 0 & b & 0 \\ b & 0 & 0 \\ o & 0 & 0 \end{bmatrix}, \qquad R_{y_2} = \begin{bmatrix} 0 & 0 & -b \\ 0 & 0 & b \\ -b & b & 0 \end{bmatrix}, \qquad R_{z_2} = \begin{bmatrix} 0 & 0 & b \\ 0 & 0 & b \\ b & b & 0 \end{bmatrix}$$

Raman Scattering rules for Backscattering from <110> Si:

Polarization Configuration	**Phonon Modes**		
	TO (x_2)	**TO(y_2)**	**LO(z_2)**
$z_2(x_2, x_2)\overline{z_2}$	**0**	**0**	**0**
$z_2(x_2, y_2)\overline{z_2}$	**0**	**b^2**	**0**
$z_2(y_2, y_2)\overline{z_2}$	**b^2**	**0**	**0**
	TO (x'_2)	**TO(y'_2)**	**LO(z'_2)**
$z_2(x'_2, x'_2)\overline{z_2}$	$\frac{2}{3}b^2$	$\frac{1}{3}b^2$	**0**
$z_2(x'_2, y'_2)\overline{z_2}$	$\frac{1}{3}b^2$	**0**	**0**
$z_2(y'_2, y'_2)\overline{z_2}$	**0**	$\frac{4}{3}b^2$	**0**

Discussion and Summary:



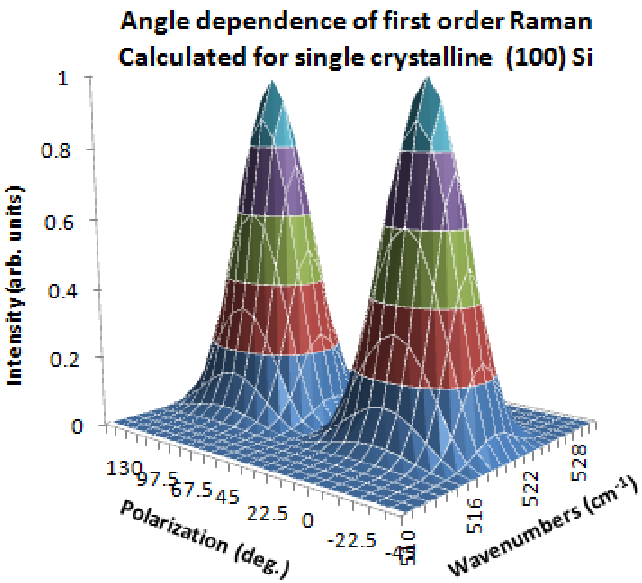


Model **Si (100) samples** **Experiment**

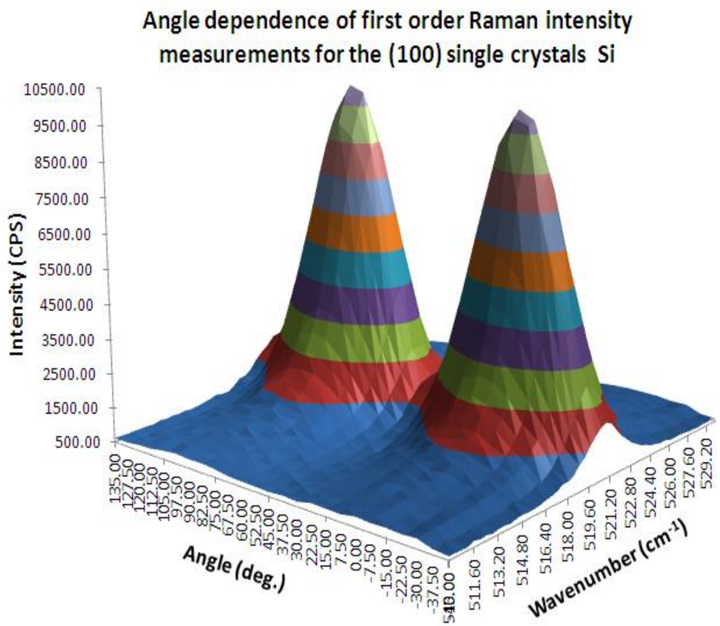
Close agreement between theory and experiment
Same analysis could be done for other Si samples; (110), (111), etc.
Same analysis could be done for any single crystalline samples

An effective approach for introducing students to Raman Spectroscopy applications in scientific research!

Questions?



Model



Experiment

Thank you for your attention!

> *"For the things we have to learn before we can do them, we learn by doing them."*
>
> *— Aristotle*