Raman spectroscopy of graphene

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Outline

1. Raman scattering
   - Microscopic description of Raman scattering
   - Resonant Raman scattering
   - Higher order scattering
   - Symmetry selection rules
2. Raman spectroscopy of graphene
   - Raman spectrum of graphene
   - Characterization of graphene

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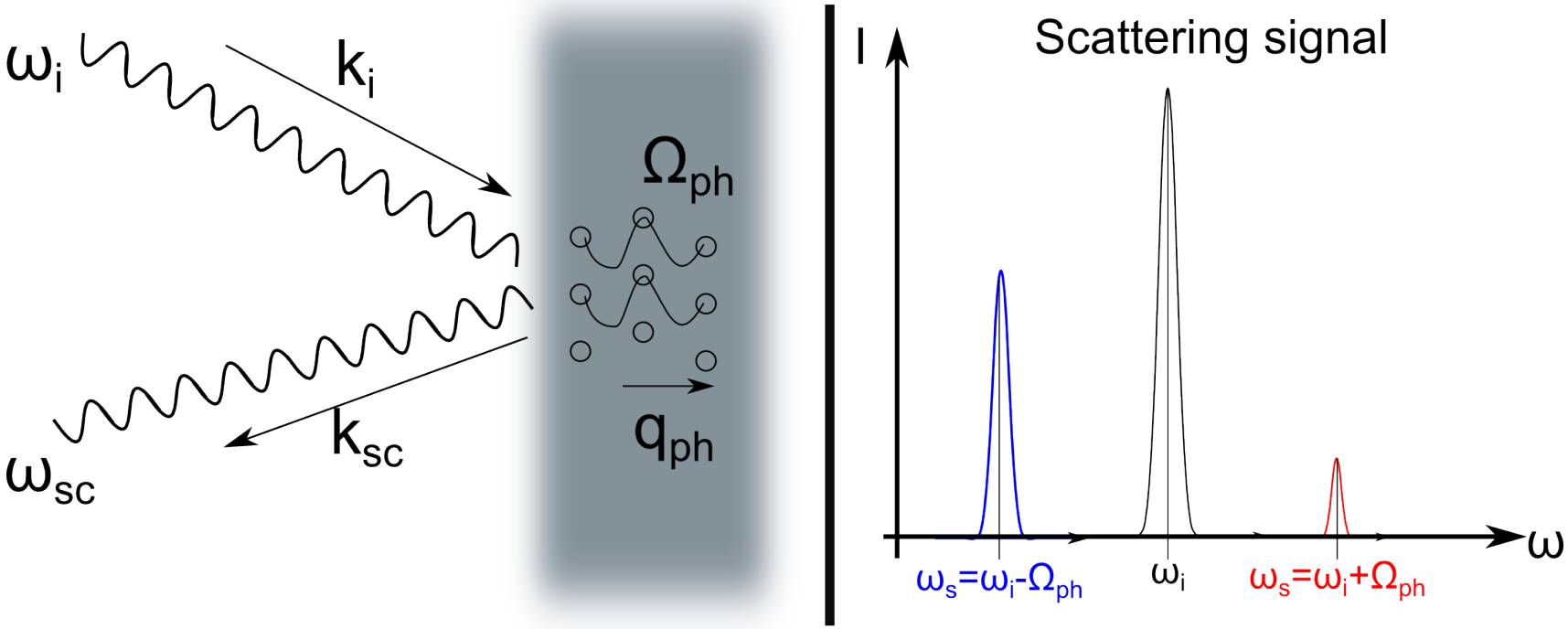
Visible light scattering on matter



Conservation requirements:

$$\hbar\omega_{sc} = \hbar\omega_i \pm \hbar\Omega_{ph}$$

$$\vec{k}_{sc} = \vec{k}_i \pm \vec{q}_{ph}$$

$\omega_{sc} = \omega_i$: Rayleigh

$\omega_{sc} = \omega_i - \Omega_{ph}$: Stokes

$\omega_{sc} = \omega_i + \Omega_{ph}$: Anti-Stokes

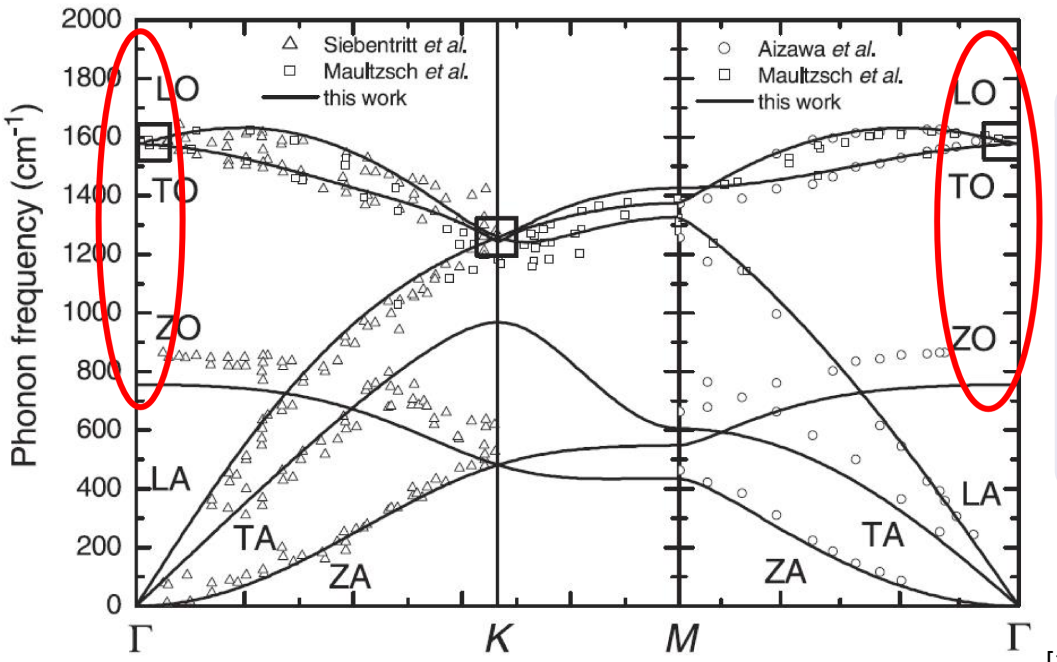
Fundamental Raman selection rule

Considerations for $\vec{q}_{ph}$

Maximal magnitude $|\vec{q}| = 2 \cdot |\vec{k}_i|$ for backscattering.

Visible light at 530 nm: $\mathcal{O}(|\vec{k}_i|) = 10^{-3}$ Å^{-1}

Phonon Brillouin zone(BZ) edge: $\mathcal{O}(|\vec{q}_{ph}|) = \frac{\pi}{a} =$ Å^{-1}

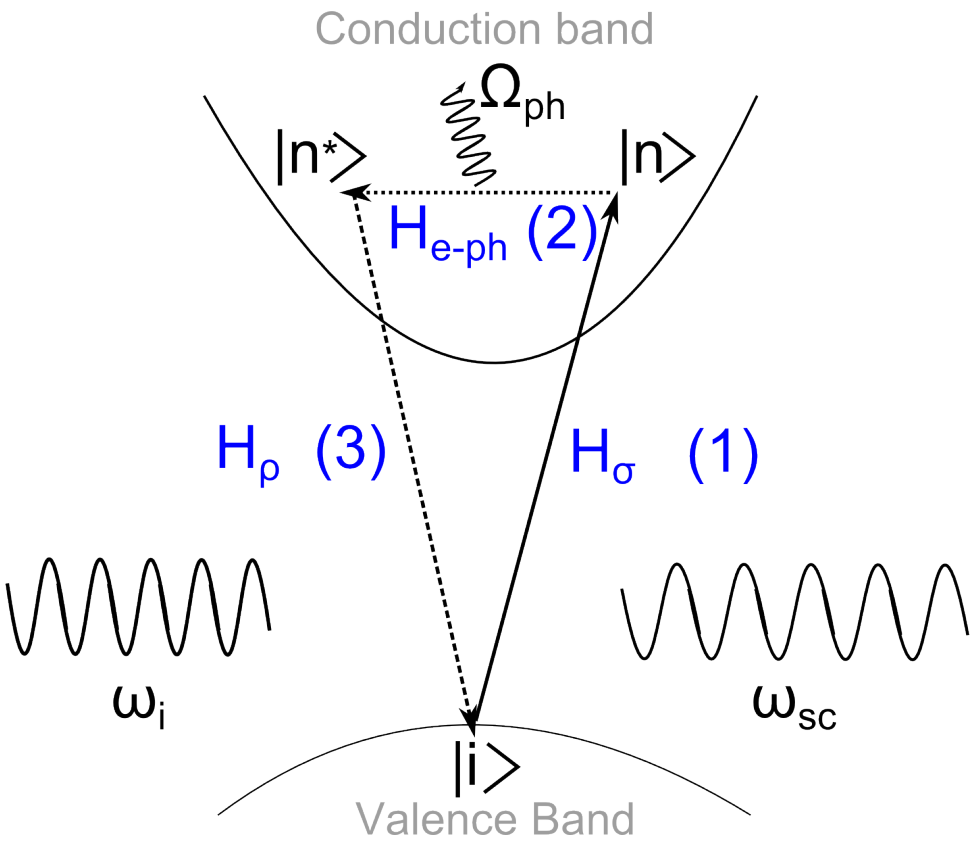


[1]

$|\vec{q}_{max}| = 2 \cdot |\vec{k}_i| \approx 0$ at Γ-point of phonon BZ

At Γ: only optical phonons with $\Omega_{ph}(q = 0) \neq 0$ can contribute to *first order* Raman signal

Microscopic picture of Stokes process



Individual transition rates

(1) $|\omega_i, 0, i\rangle \Rightarrow |0, 0, n\rangle$:

$$k_1 \propto \sum_n \frac{\langle 0,0,n \mid H_\sigma \mid \omega_i,0,i\rangle}{\hbar\omega_i - (E_n - E_i)}$$

(2) $|0, 0, n\rangle \Rightarrow |0, ph, n^*\rangle$:

$$k_2 \propto \sum_{n,n^*} \frac{\langle 0,ph,n^* \mid H_{e-ph} \mid 0,0,n\rangle}{\hbar\omega_i - \hbar\Omega_{ph} - (E_{n^*} - E_n)}$$

(3) $|0, ph, n^*\rangle \Rightarrow |\omega_{sc}, ph, i\rangle$:

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Quantum state:
$|photon, phonon, electron\rangle$

Electronic: $|i\rangle \Rightarrow |n\rangle \Rightarrow |n^*\rangle \Rightarrow |i\rangle$

Electronic excitation mediates Raman scattering of photons

Electron remains unchanged after scattering:
Same final state $|i\rangle$ as before photon absorption

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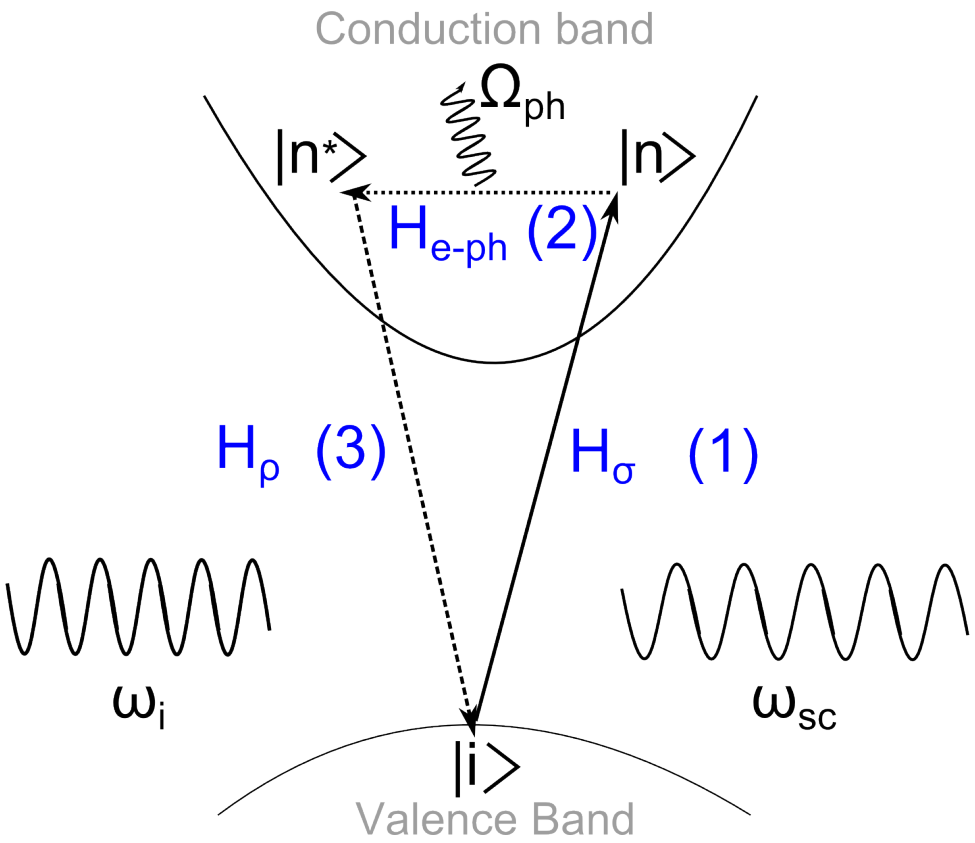

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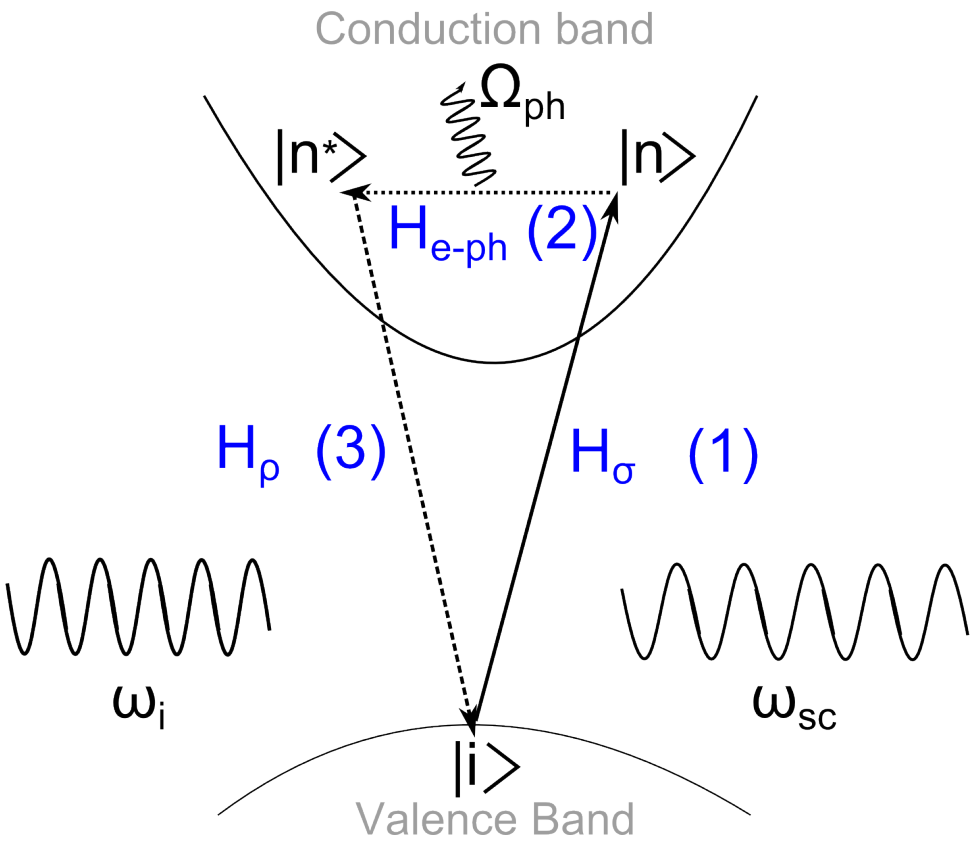

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Transition probability of first order Raman scattering

Neglecting other time orders[2], the Raman scattering probability is given by Fermi's rule:

$$P = \frac{2\pi}{\hbar} \cdot |k_1 \cdot k_2 \cdot k_3|^2$$

Total transition probability

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- Matrix elements depend on symmetries of $H_{\rho,\sigma,e-ph}$ and $|i\rangle, |n\rangle, |n^*\rangle$
  $\Rightarrow$ Symmetry selection rules
- Vanishing (or small) denominators increase scattering probability
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Resonant Raman scattering

Resonant transition probability at critical points[2]

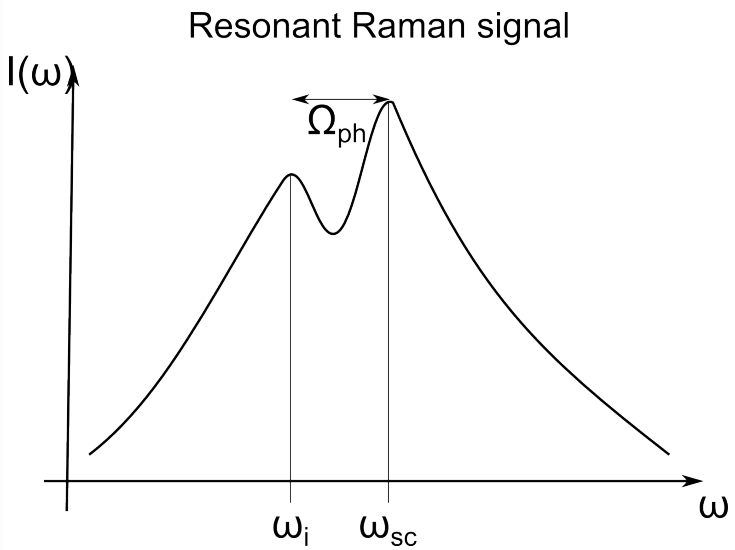
$$P_{res} \approx \frac{2\pi}{\hbar} \cdot \left| \frac{\langle i \,|\, H_\rho \,|\, n \rangle \cdot \langle n \,|\, H_{e-ph} \,|\, n \rangle \cdot \langle n \,|\, H_\sigma \,|\, i \rangle}{[\hbar\omega_i - E_n] \cdot [\hbar\omega_{sc} - E_n]} + C \right|^2 .$$

2 resonant processes

$\hbar\omega_i = E_n$: Incoming resonance

$\hbar\omega_{sc} = E_n$: Outgoing resonance

- Resonant Raman scattering can be used to determine Ω_{ph} and critical points of e^- bandstructure
- Scattering signal enhancement $\approx 10^5 - 10^7$



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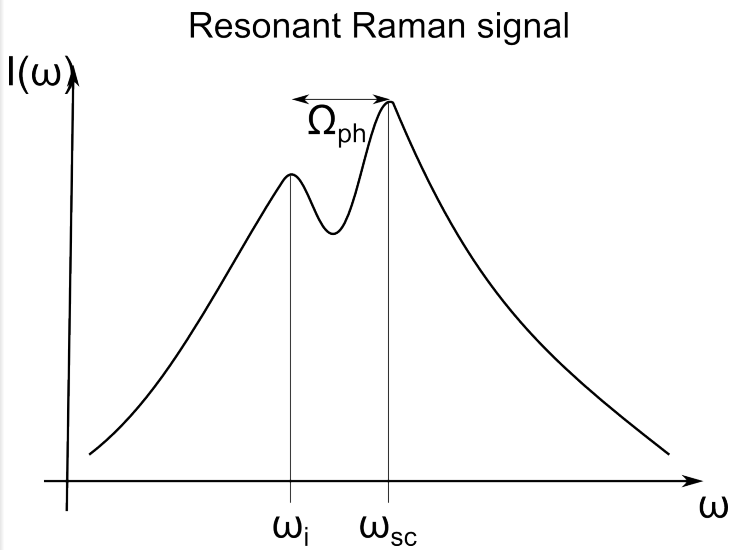
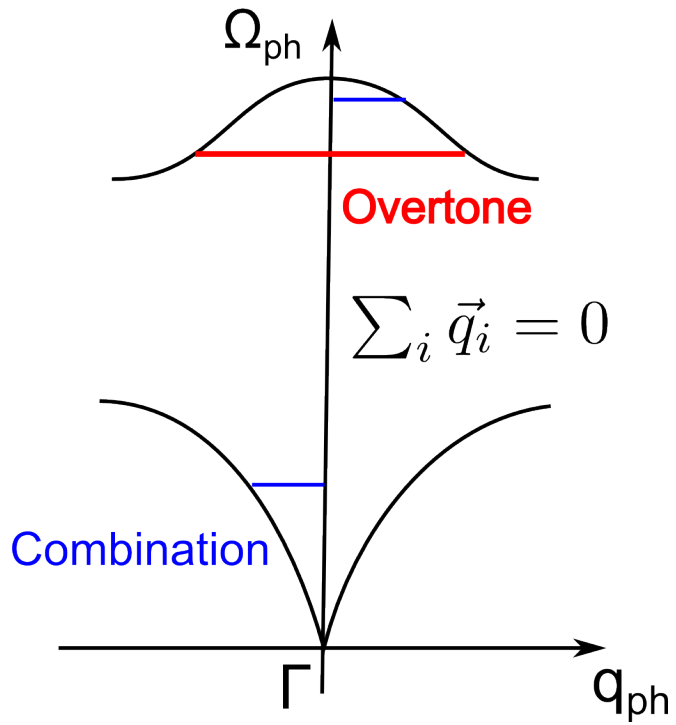


Higher order Raman scattering

Second order Raman scattering



Two-phonon scattering

Momentum conservation:
$\sum_i \vec{q}_i \approx 0$

Possible by exciting the same(overtone) or different phonon branches (combination)

$\Rightarrow$ Allows for study of phonon DOS in some materials

Other higher order processes

Electronic scattering on defects:
$\Rightarrow$ Important in graphene to study sample structure and quality

Higher order Raman scattering

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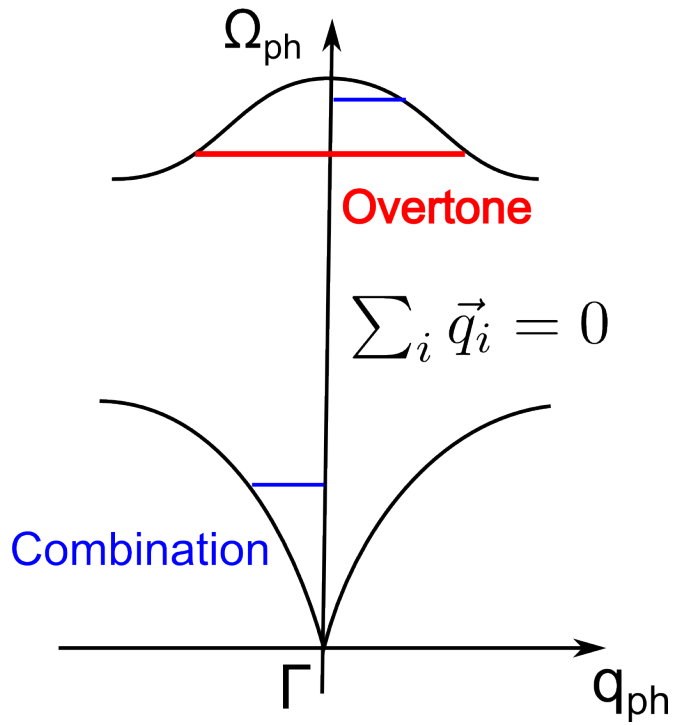

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Raman selection rules

Result of group theory

- *All* possible functions (electrons, phonons, physical properties) in a crystal transform uniquely under symmetry operations
  $\Rightarrow$ A defined symmetry (e.g. A_{1g}, B_{2u}) can be assigned to each state in the crystal
  $\Rightarrow$ Symmetry properties of a crystal and its functions are summarized in character tables

Symmetry of matrix elements

$$\mathcal{M} = \langle i \,|\, H_\rho \,|\, n^* \rangle \cdot \langle n^* \,|\, H_{e-ph} \,|\, n \rangle \cdot \langle n \,|\, H_\sigma \,|\, i \rangle$$

- $\mathcal{M} \neq 0$ only if $\Gamma(H_\sigma) \otimes \Gamma(H_\rho) \otimes \Gamma(H_{e-ph}) \neq 0$
- Dipole approximation: H_σ and H_ρ have the same symmetry as the polarization coordinates of the photons.
- H_{e-ph} transforms like the phonon with symmetry Γ_{ph}

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Symmetry conditions on matrix elements

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Excited phonon has to have the same symmetry as the product of the respective polarization coordinates of H_ρ and H_σ

$\Rightarrow$ Determination of phonon symmetry via polarization dependent Raman signal

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Example: graphene, D_{6h} group

Character table for D_{6h} point group

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Linear, rotations	Quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2

[3]

H_σ, H_ρ along $\vec{x}$ direction (polarizers)

$\Rightarrow$ Phonon with A_{1g} symmetry could be measured since it transforms like x^2

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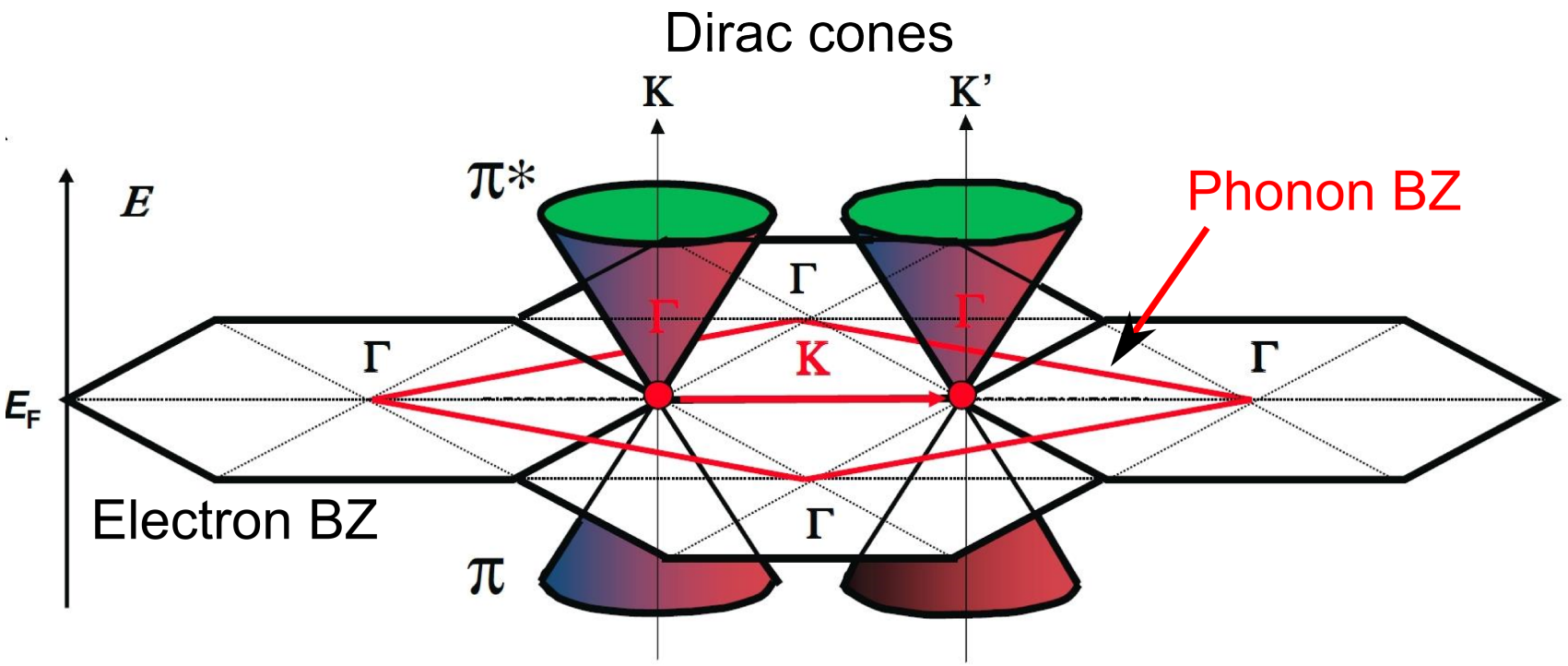
1. Raman scattering
2. Raman spectroscopy of graphene
   - Raman spectrum of graphene
   - Characterization of graphene

Graphene recap



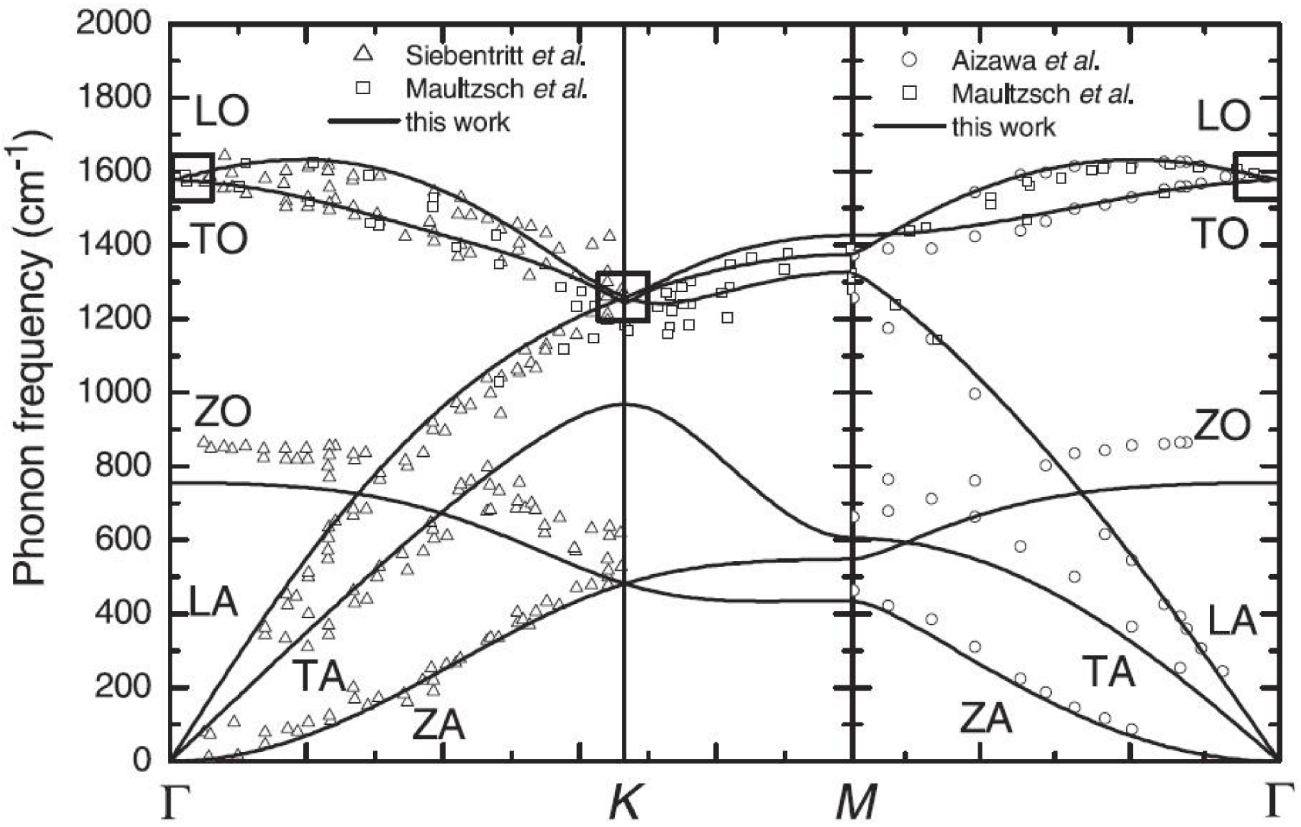
[4]

Crystal properties

- 2-dimensional material with hexagonal symmetry (D_{6h} space group)
- 2 carbon atoms per unit cell

Phonon dispersion of graphene

[1]



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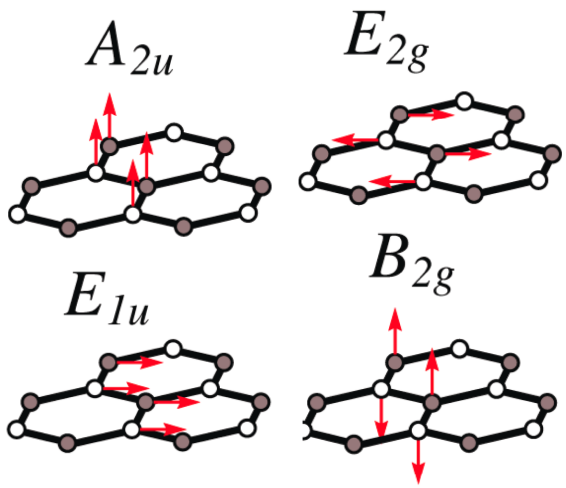

6 phonon branches

- 4 different symmetries

D_{6h} character table

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Linear, rotations	Quadratic
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A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
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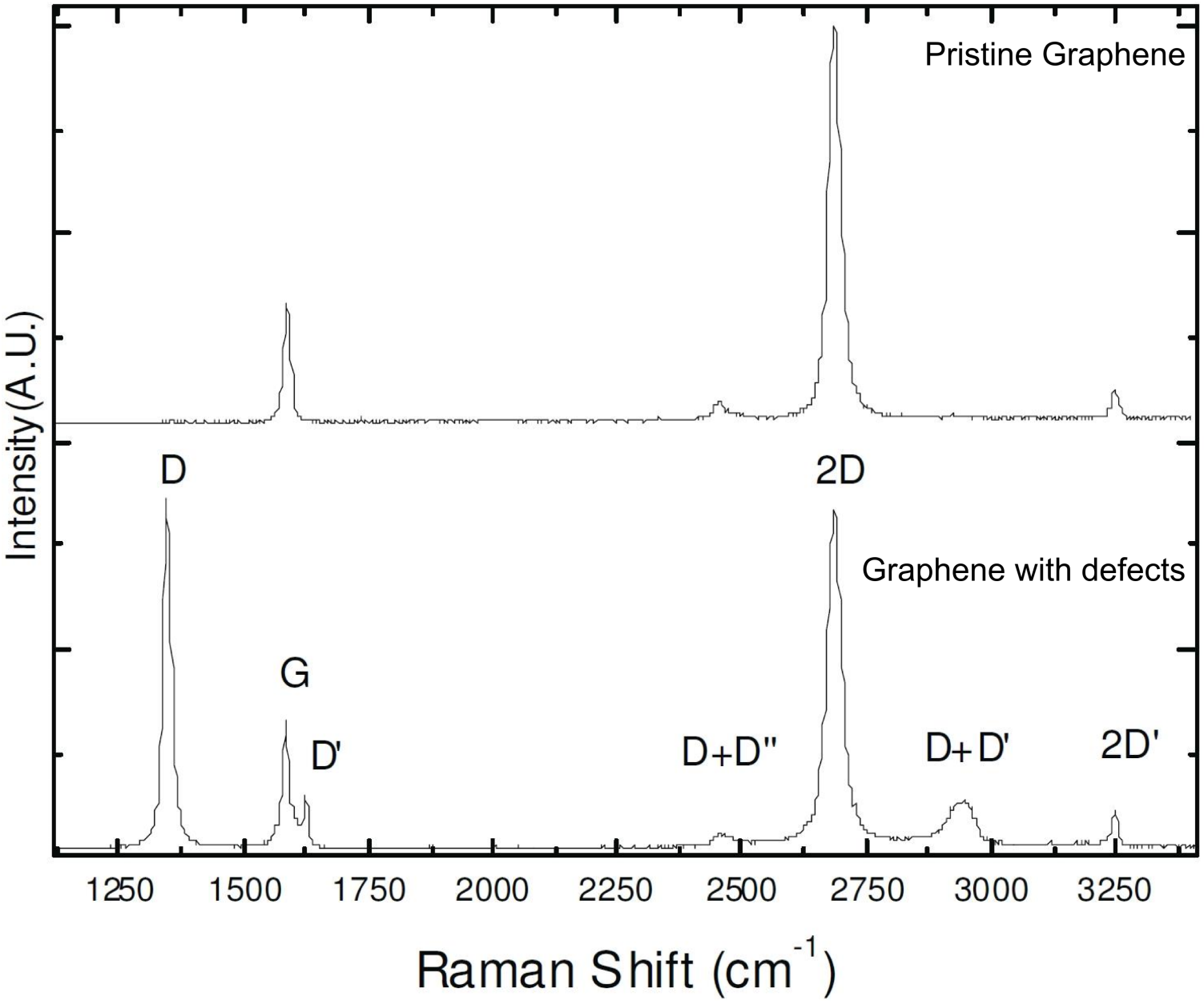
First order Raman active mode

[3]

Raman spectrum of graphene



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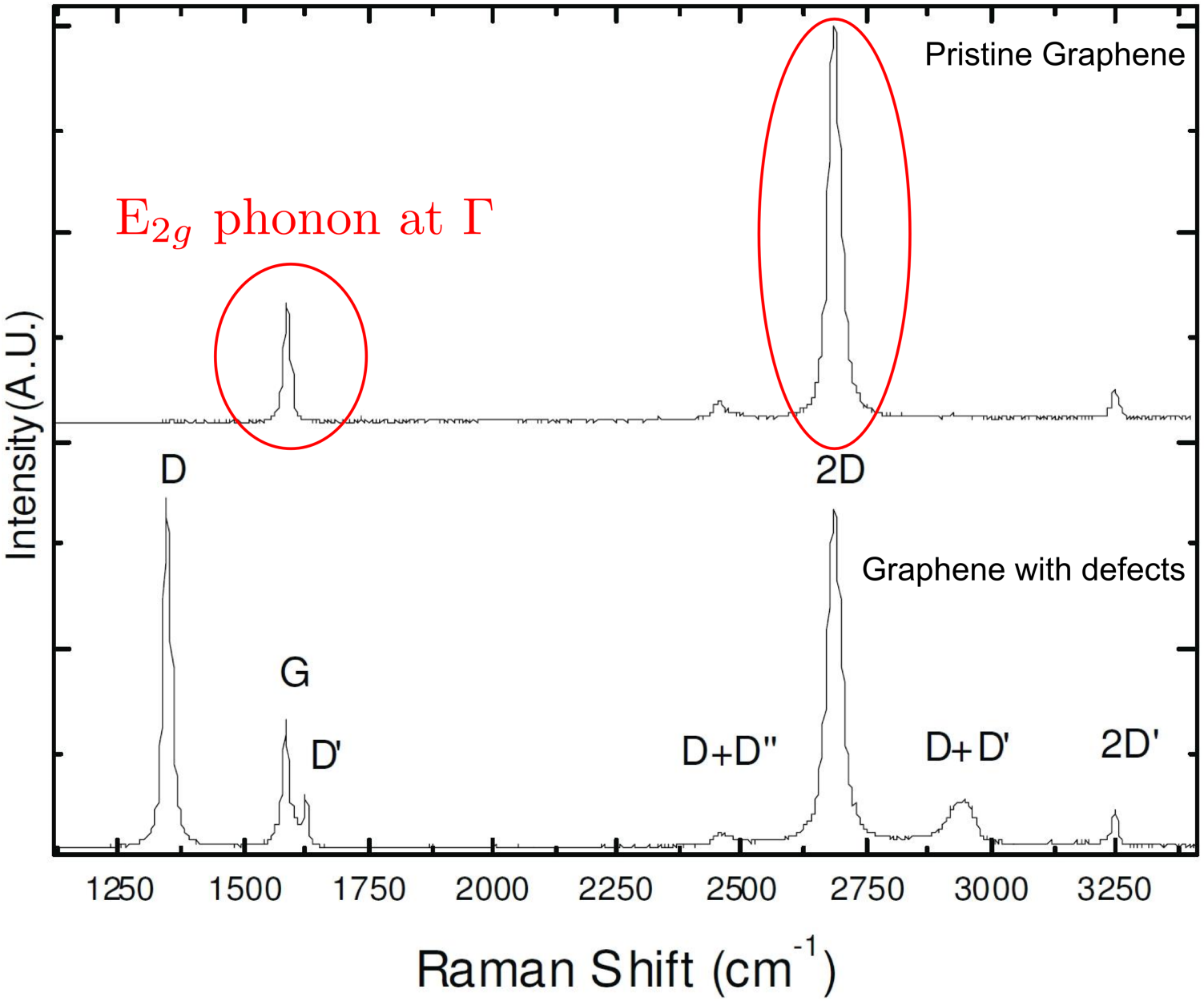
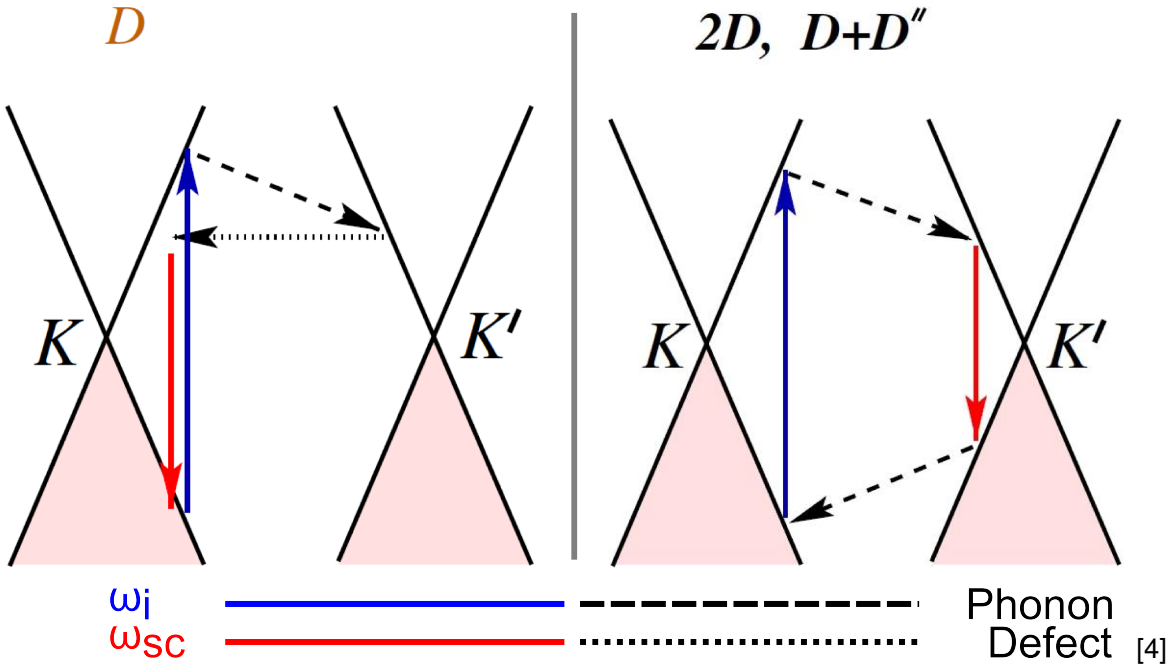


[4]

Raman D peak in graphene



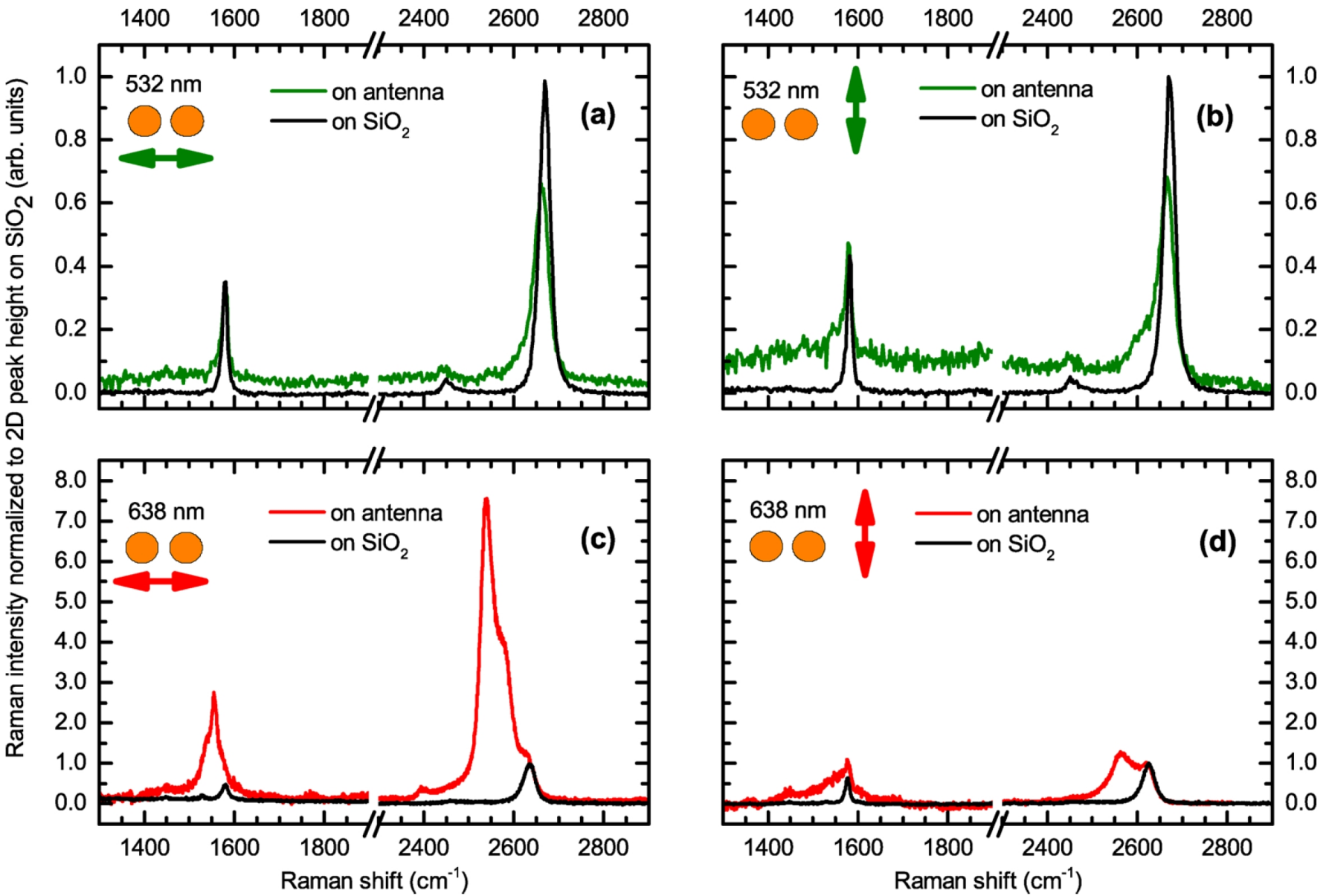
D

- Intervalley scattering with TO phonon at K-point, $\vec{q}_{ph} \neq 0$
- D peak requires defect scattering to conserve momentum

2D

- Double-resonant, intervalley scattering[5] requires no defects
- Strong e^--ph coupling: 2D peak is more intense than G

Determination of defects and number of layers

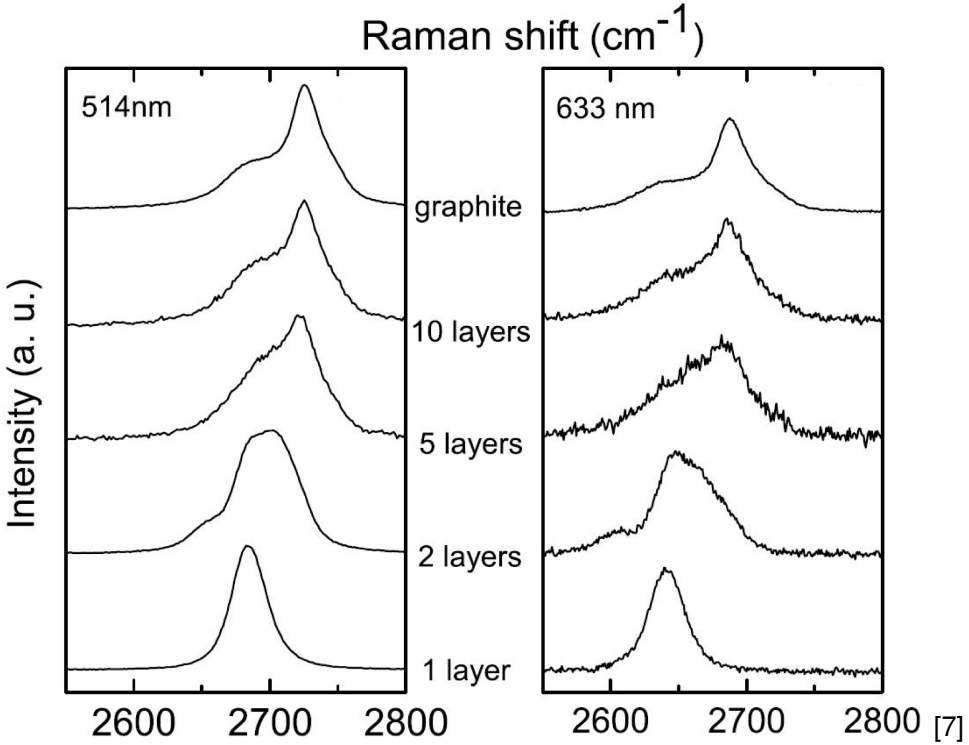


[6]

Determination of defects and number of layers

Seminar paper[6]

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



[7]

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

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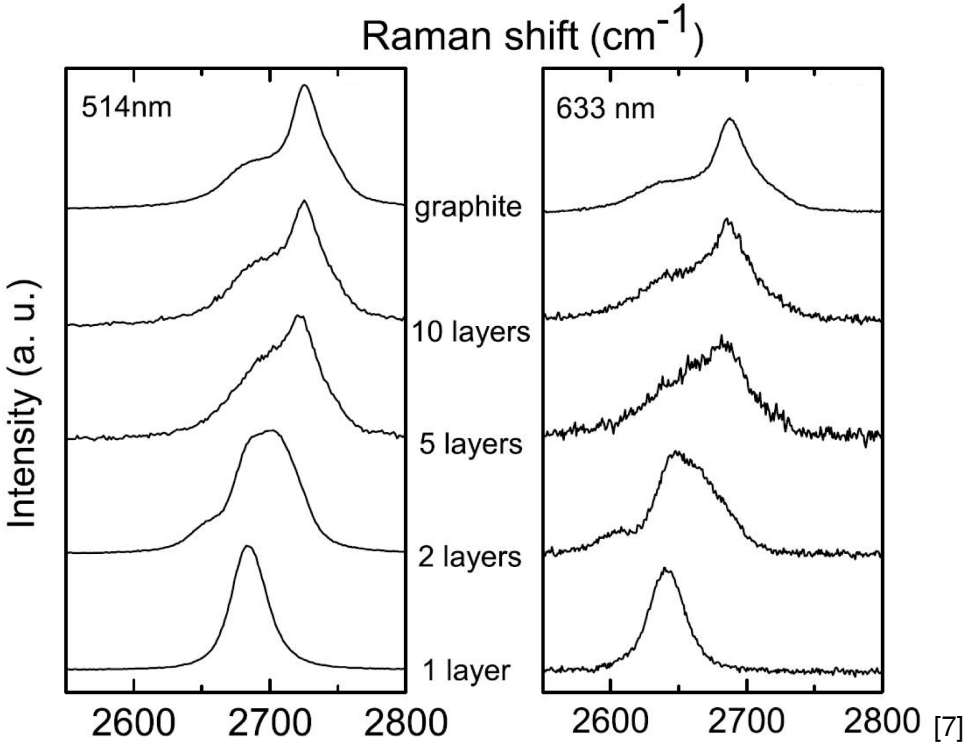

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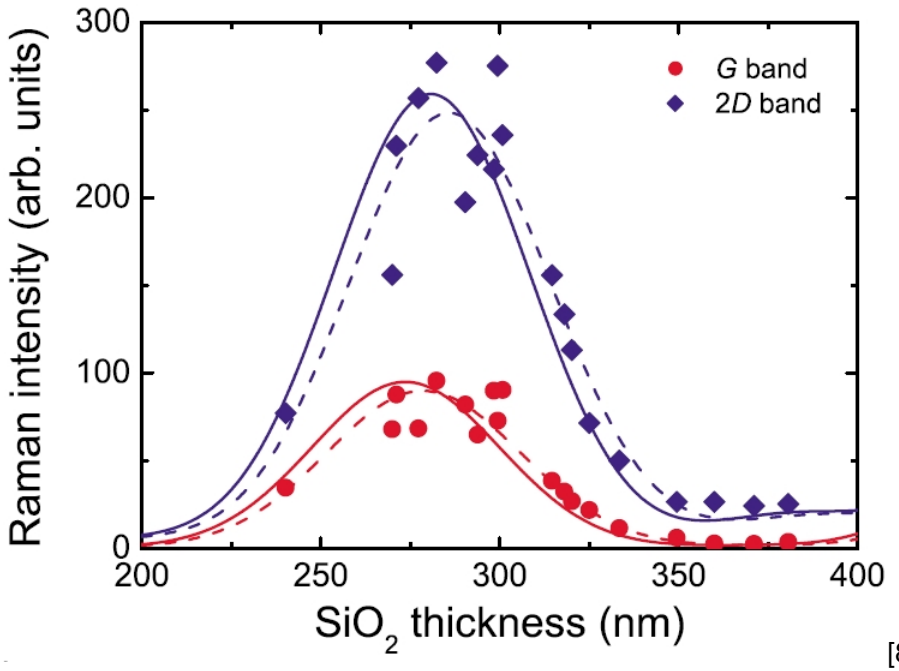
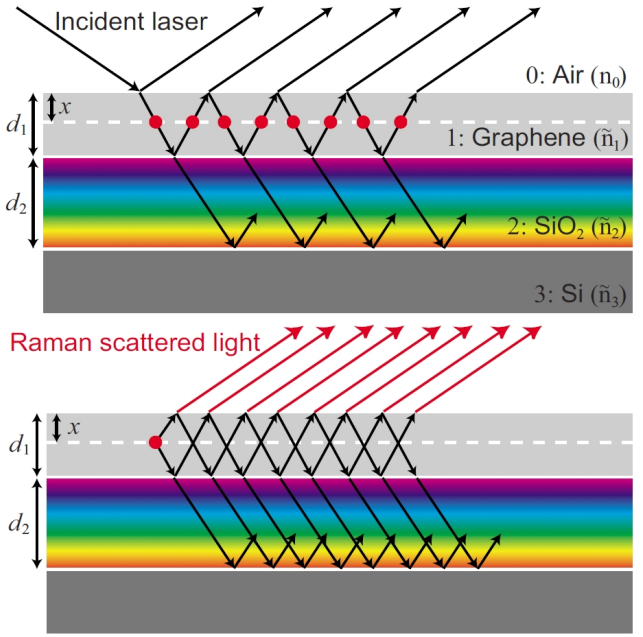
Interference with substrate

Seminar paper[6]

"This is supported by a peak height ratio 2D/G of 2.8 which [indicates](...)an oxide layer of 300 nm thickness"



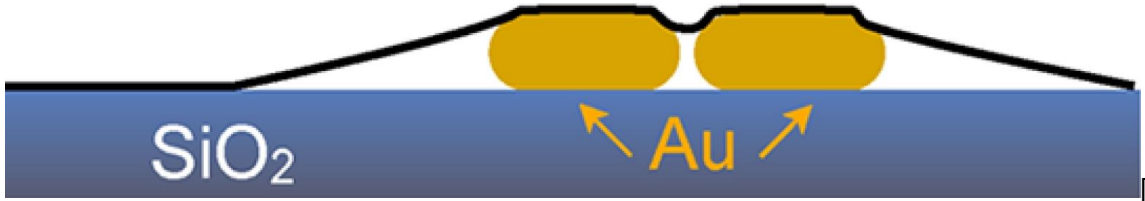
[8]



[8]

Interference effects of Raman signal and substrate allow for determination of layer thickness from peak ratio 2D/G

Determination of strain components



[6]

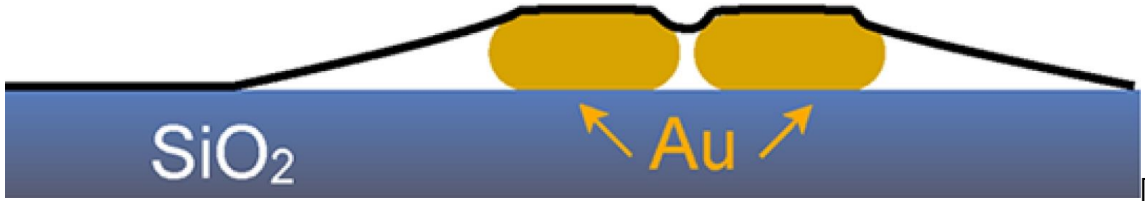
Phonon frequencies change under strain[9]

$$\Delta\omega^{\pm} = \Delta\omega^{h} \pm \frac{1}{2}\Delta\omega^{s}$$
$$= -\omega^{0} \cdot \gamma \cdot \epsilon_{h} \pm \frac{1}{2}\omega^{0}\beta \cdot \epsilon_{s}$$

- Hydrostatic strain $\Delta\omega^{h}$ shifts phonon frequency
- Degenerate phonon modes split due to shear strain $\Delta\omega^{s}$
- Frequency shift allows for determination of strain tensor $\bar{\bar{\epsilon}}$

$\Rightarrow$ Raman signals sensitive to sample strain and relative orientation

Determination of strain components



[6]

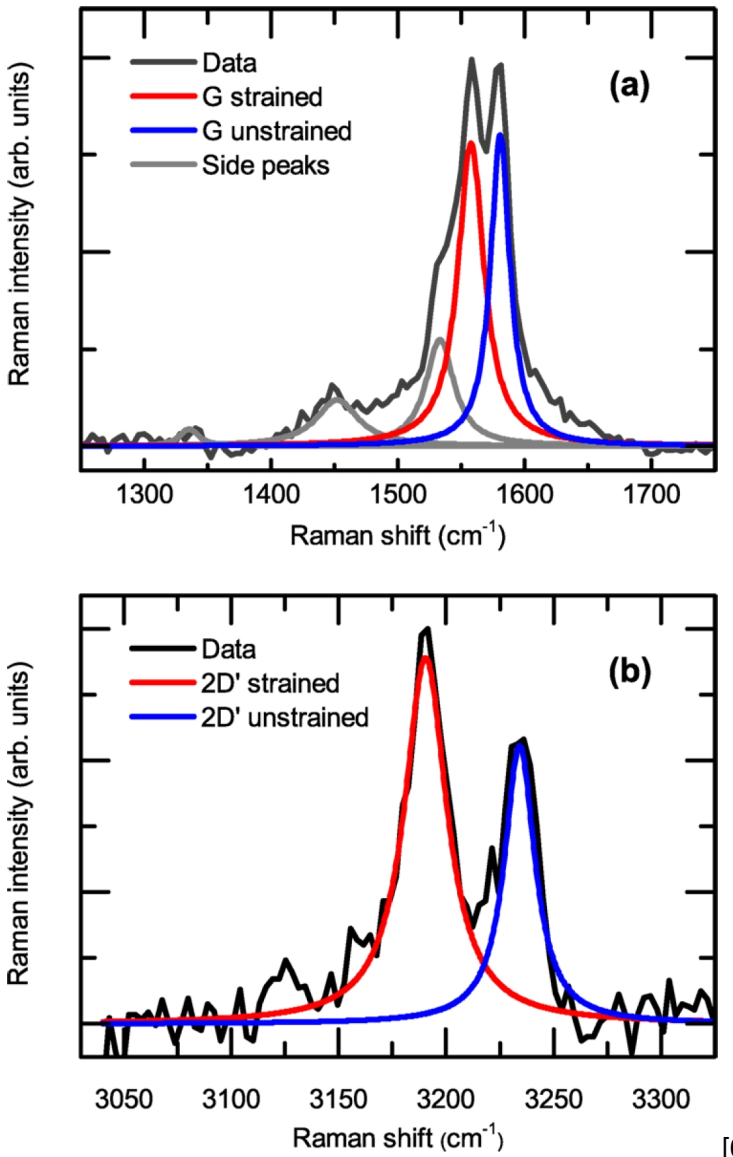
Phonon frequencies change under strain[9]

$$\Delta\omega^{\pm} = \Delta\omega^{h} \pm \frac{1}{2}\Delta\omega^{s}$$
$$= -\omega^{0} \cdot \gamma \cdot \epsilon_{h} \pm \frac{1}{2}\omega^{0}\beta \cdot \epsilon_{s}$$

- Hydrostatic strain $\Delta\omega^{h}$ shifts phonon frequency
- Degenerate phonon modes split due to shear strain $\Delta\omega^{s}$
- Frequency shift allows for determination of strain tensor $\bar{\bar{\epsilon}}$

$\Rightarrow$ Raman signals sensitive to sample strain and relative orientation

Determination of strain components



[6]

Seminar paper[6]

"In areas of plasmonic enhancement the graphene is under strain with a hydrostatic component ≈0.8% and a shear component <0.4%"

- Frequency shift of peaks on Au nanostructure
- Modes broadened but not split in areas of strain

⇒ Calculate hydrostatic strain, approximate shear strain

⇒ Plasmonic signal enhancement in areas under strain

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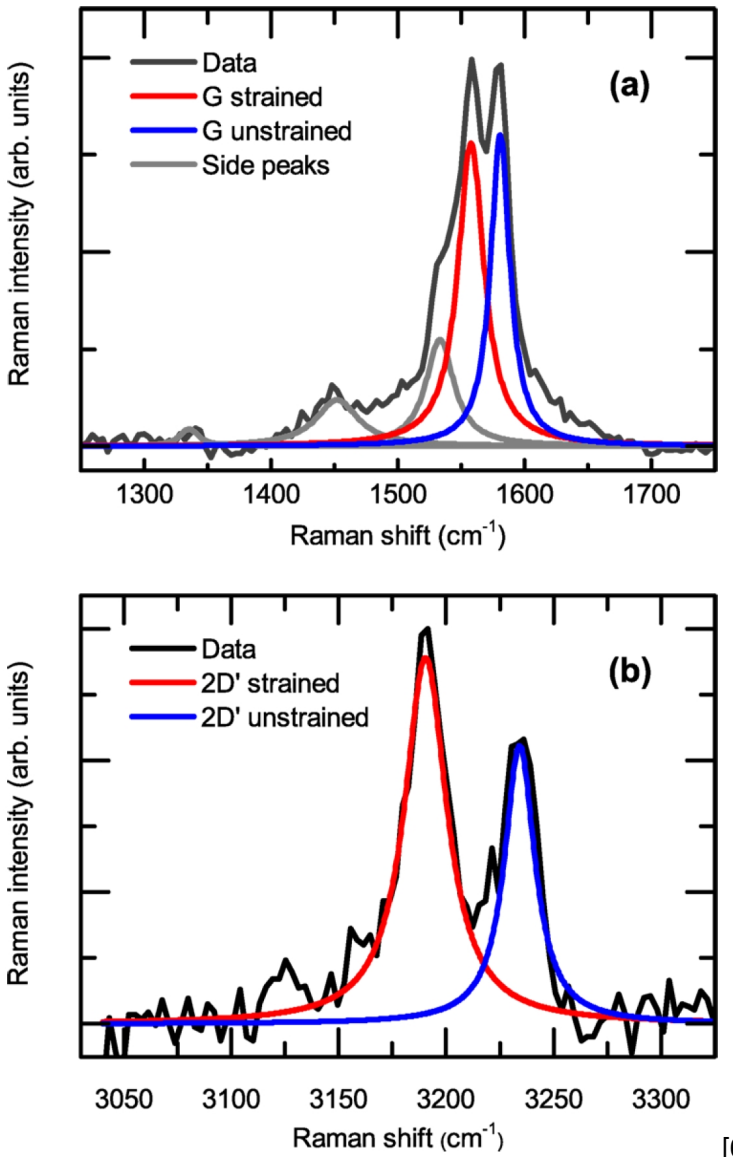

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Summary

Raman scattering

- Non-destructive technique to determine both electronic and vibrational properties
- Identification of phonon symmetry and energy
- Allows study of samples with both spatial and frequency resolution

Raman spectroscopy of graphene

- Identification of defects, substrate thickness and number of layers
- Resolution of regions under strain and determination of strain components
- Study electron-phonon and electron-electron interactions
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