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Studying electrons and phonons in graphenes by resonance Raman scattering

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Studying electrons and phonons in graphenes by resonance Raman scattering

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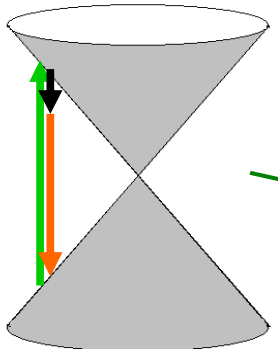
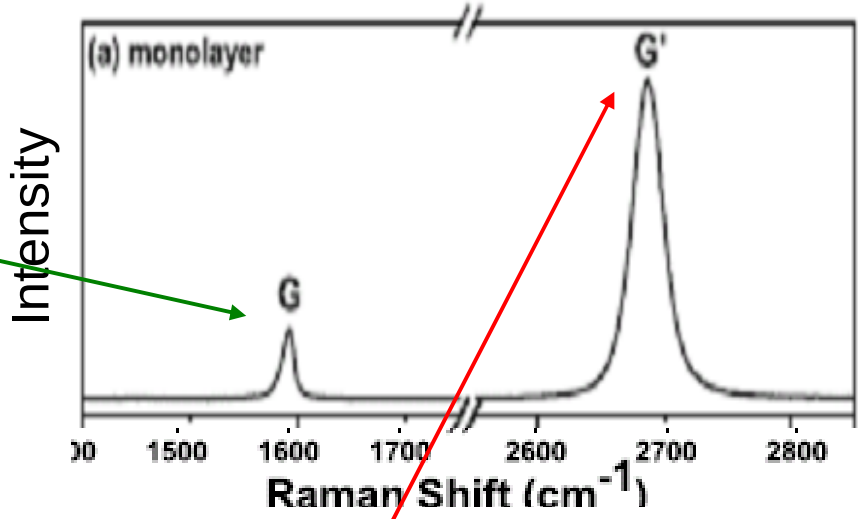
J. Nilsson - Universiteit Leiden
A. H. Castro Neto – Boston University

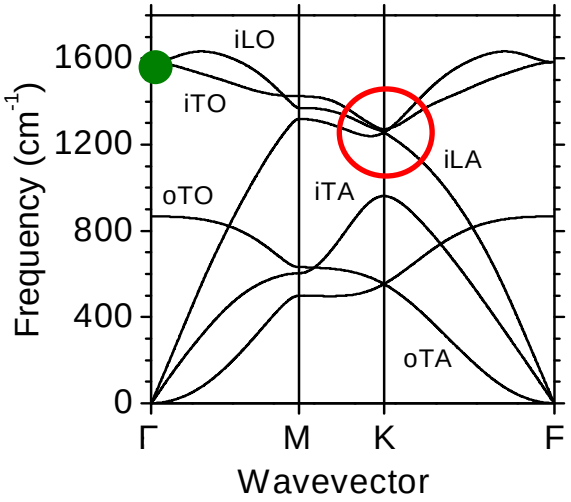
Outline

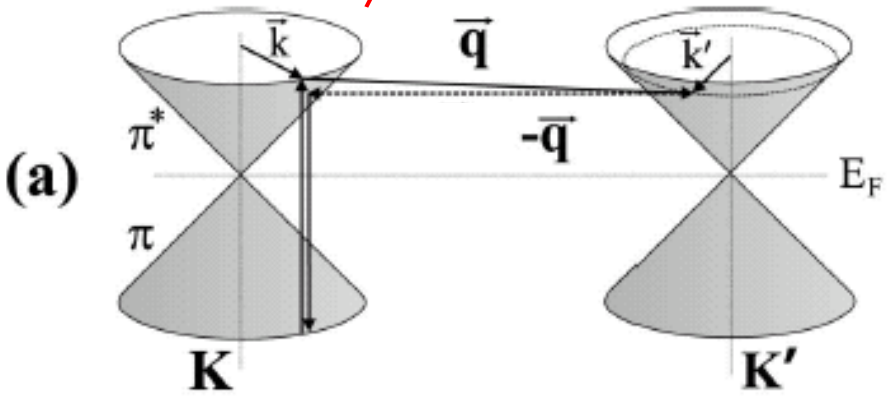
- Resonance Raman study of monolayer and bilayer graphene
- Raman investigation of back-gated bilayer graphene

Raman spectrum of exfoliated monolayer graphene





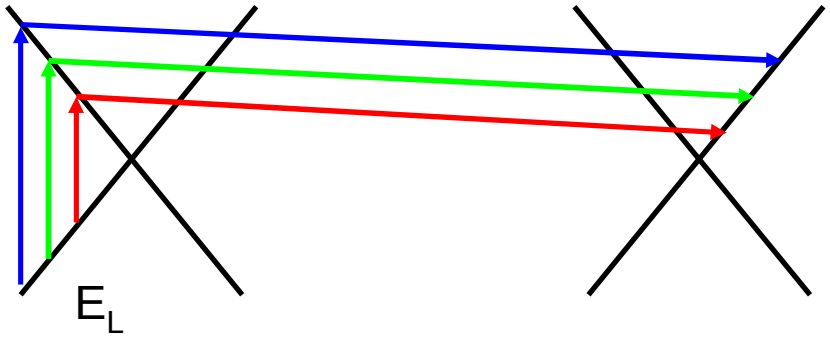


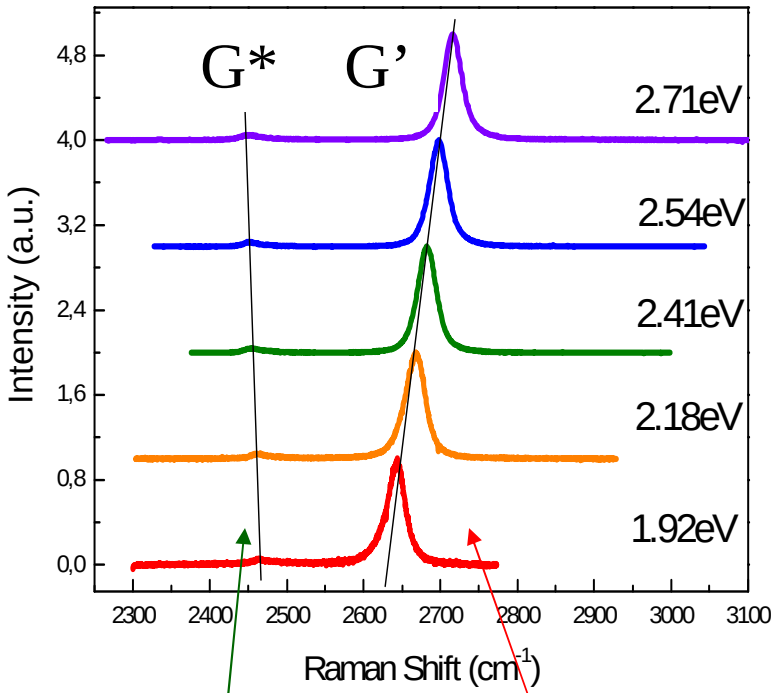


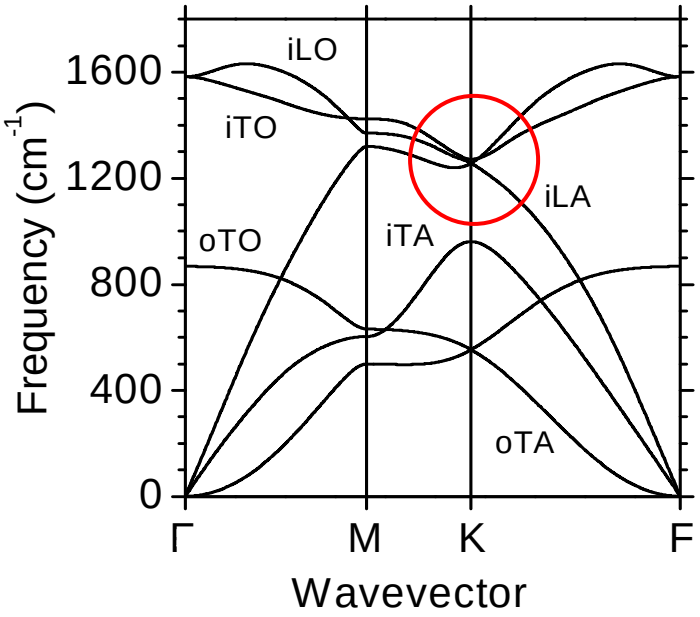
$$I(E_i) = C\left|\sum_{a,b,c}\frac{\langle f|H_{e-r}|c\rangle\langle c|H_{e-def}|b\rangle\langle b|H_{e-ph}|a\rangle\langle a|H_{e-r}|i\rangle}{(E_i - E_a - i\gamma)(E_i - E_b - i\gamma)(E_i - Ec - i\gamma)}\right|^2$$

Baranov et al., Opt. Spektrosk, 62, 612 (1987)
Thomsen and Reich, PRL, 85, 5214 (2000),
Saito et al, PRL, 88, 27401 (2002)

Measuring phonon dispersions near the Dirac point of graphene by resonance Raman scattering

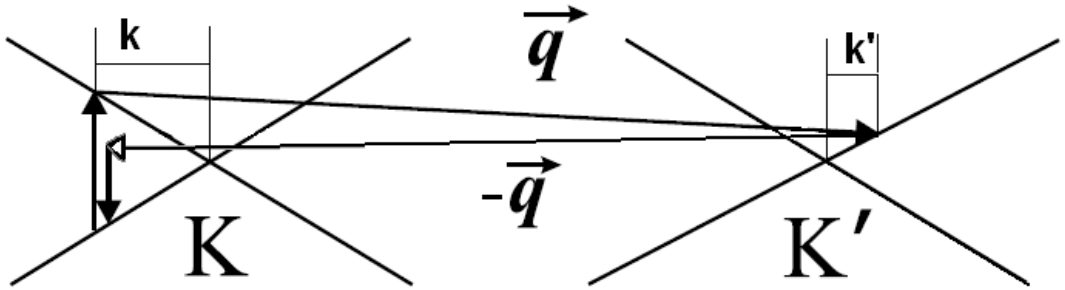


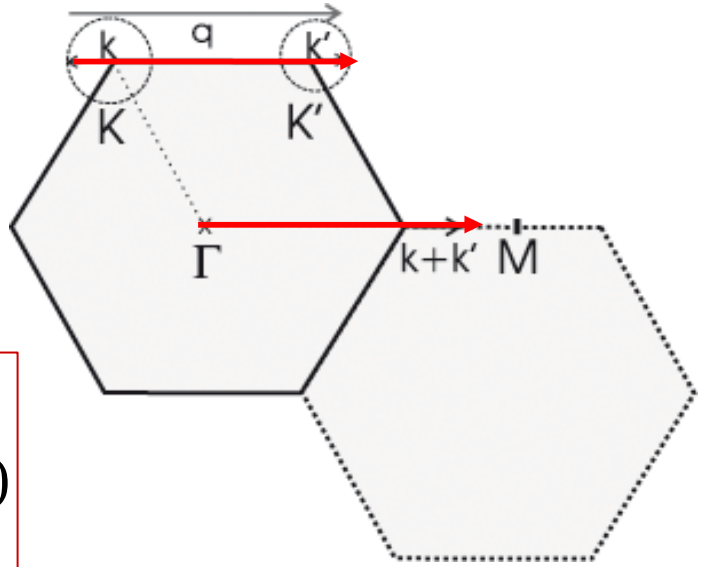


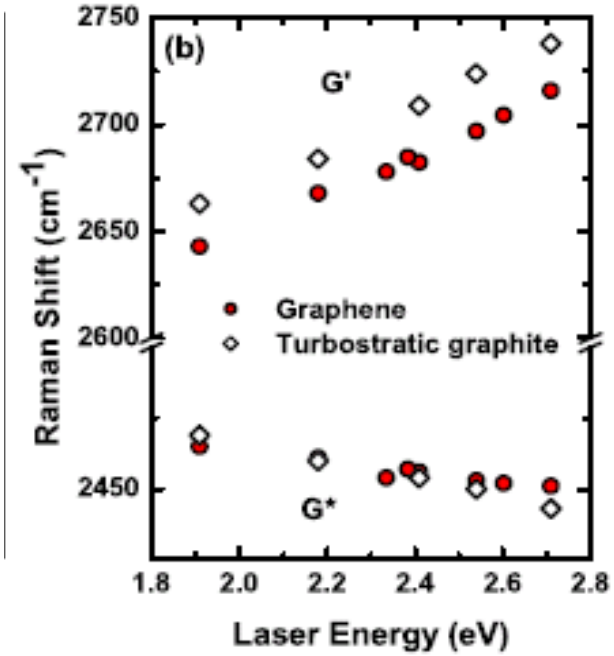


$$\omega_{TO} = \frac{\omega_{G'}}{2}$$

$$\omega_{LA} = \omega_{G*} - \frac{\omega_{G'}}{2}$$







$$E_{laser} = 2v_F\hbar k$$
$$E_{phonon} = v_F\hbar(k - k')$$
$$q = k + k'$$

ω_{ph} versus E_{laser} ⟶ ω_{ph} versus q

dG'/dω → 88 cm^{-1}/eV

$$v_{TO} = 5.47\times10^{-3}v_F$$

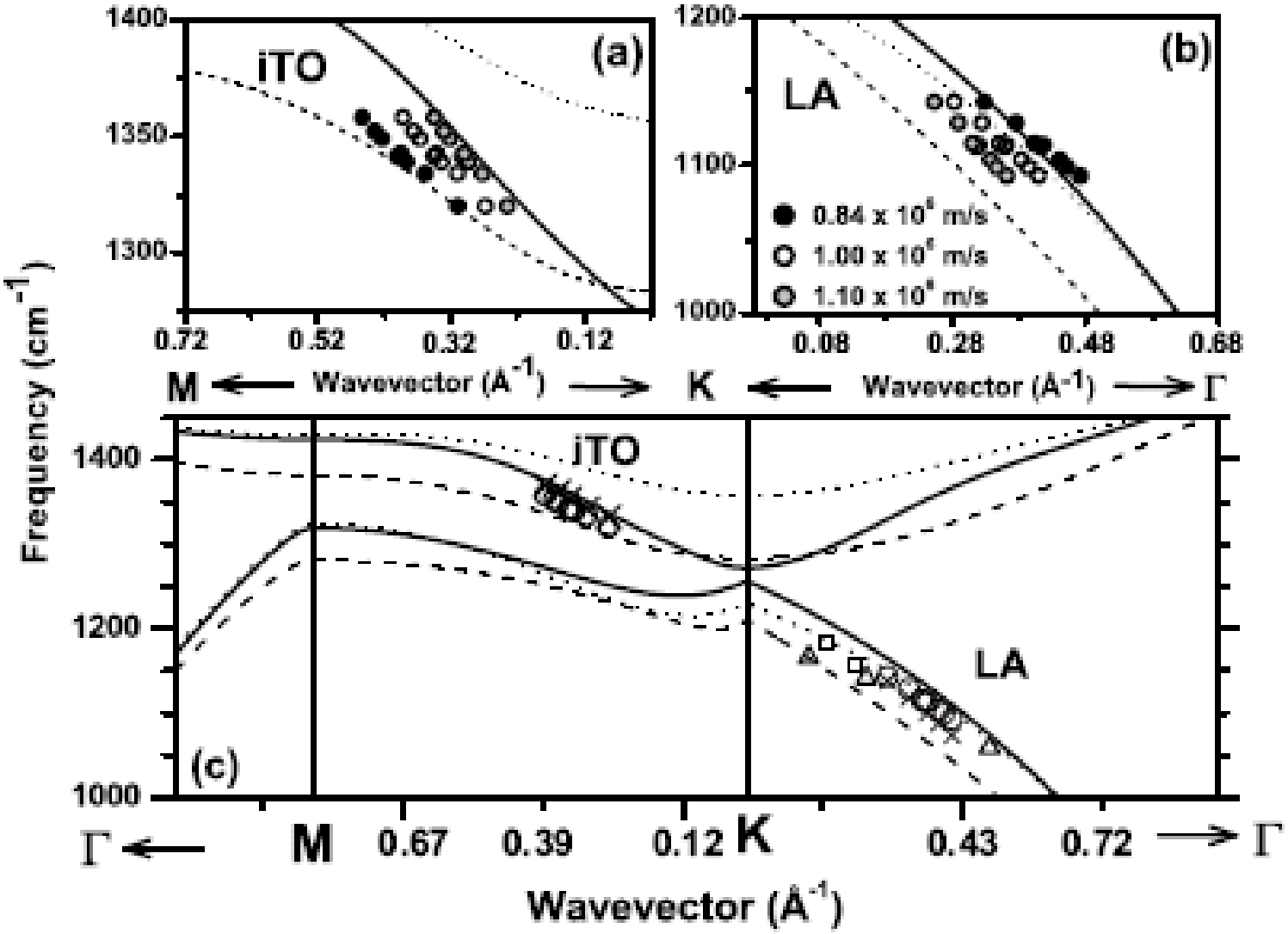
dG* /dω → -18 cm^{-1}/eV

$$v_{LA} = 7.70\times10^{-3}v_F$$

$$v_{LA} = (\frac{d\omega_{G^*}}{d\omega_l} - \frac{1}{2}\frac{d\omega_{G'}}{d\omega_l})v_F$$

$$v_{TO} = (\frac{1}{2}\frac{d\omega_{G'}}{d\omega_l})v_F$$

Measurement of the phonon velocities near the Dirac point as a function of v_F



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Maultzsch *et al* (2004)

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Dubay *et al.* (2003)

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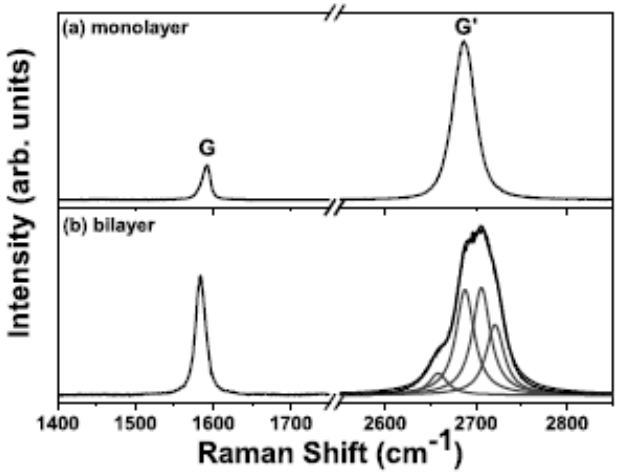
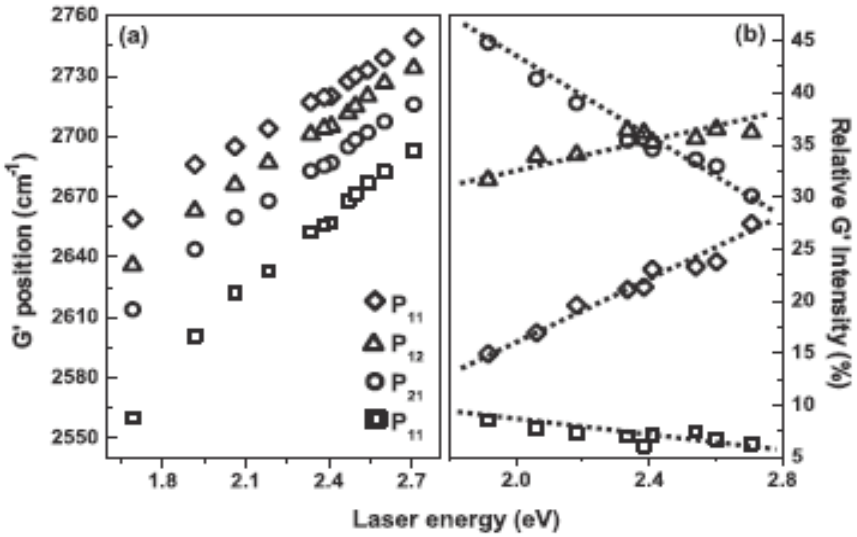
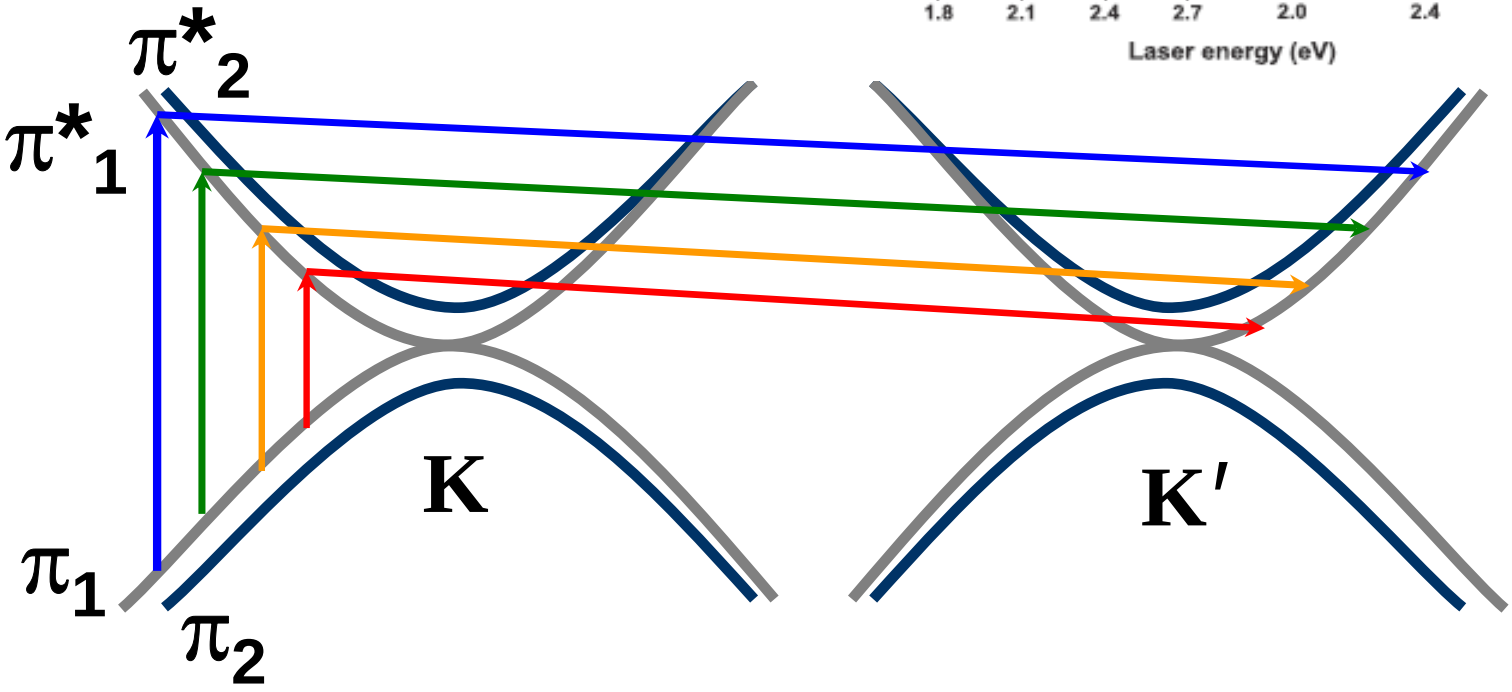
Popov and Lambin (2006)

D.L. Mafra et al. Phys. Rev. B 76, 233407 (2007)

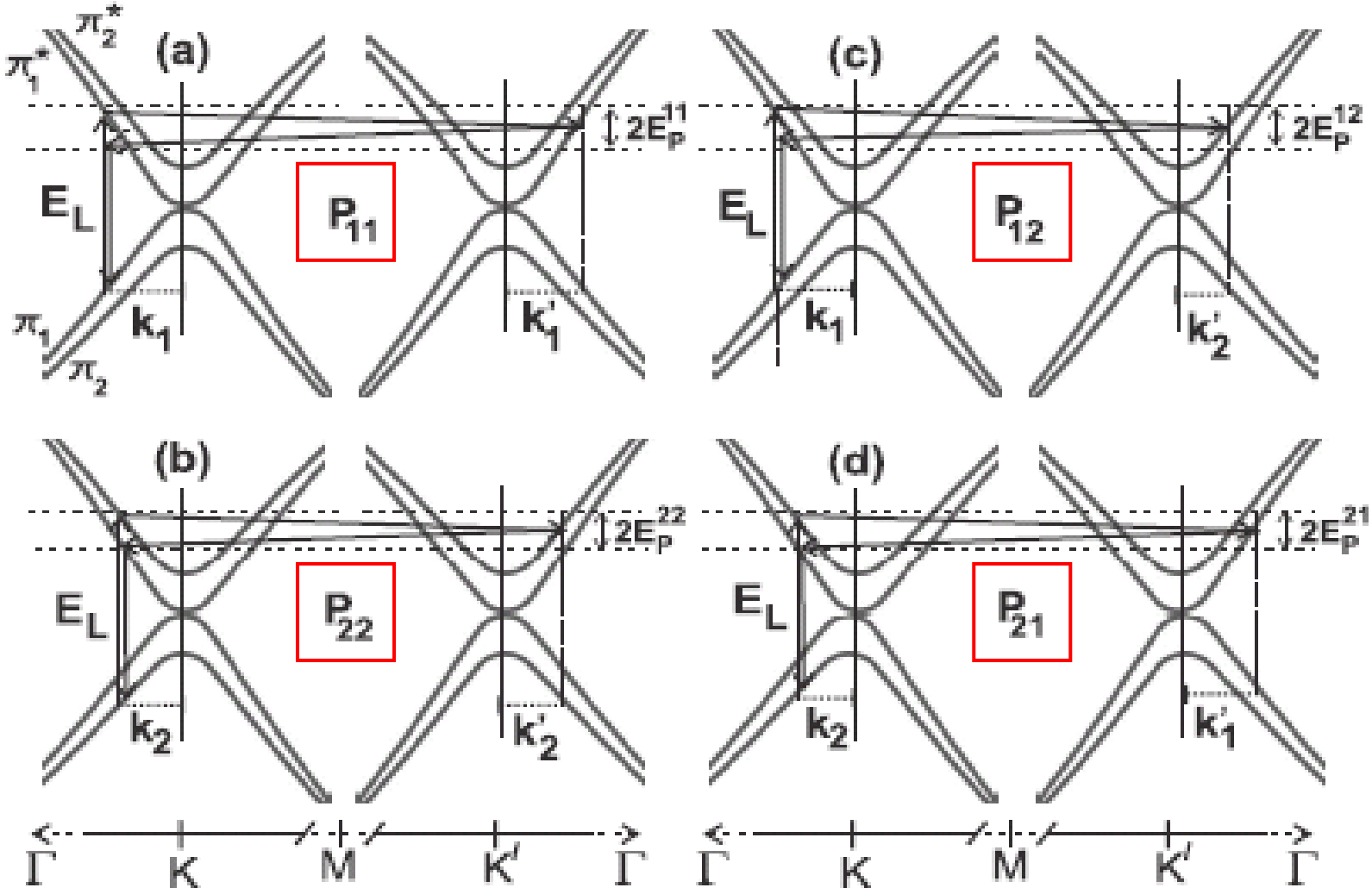
Probing the electronic structure of bilayer graphene by Resonance Raman scattering







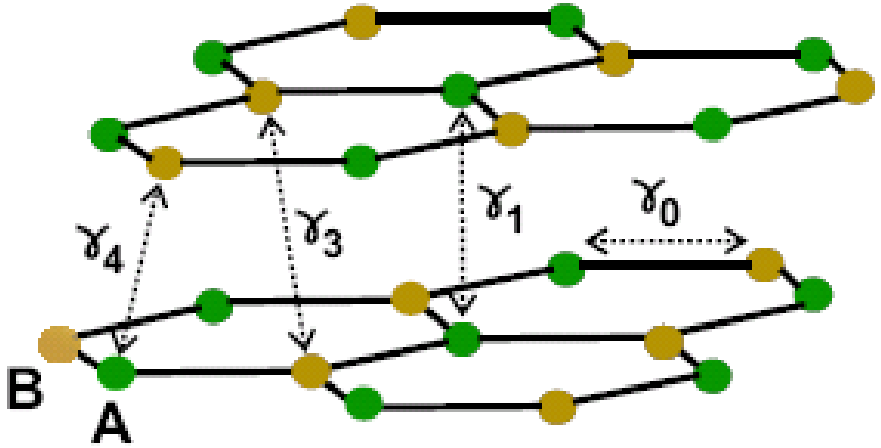
Four possible double resonance processes in bilayer graphene



Electronic structure of bilayer graphene

Slonczewski-Weiss-McClure (SWM) model for graphite

$$E_{\pi 2} = (-\gamma_1 - v_3\sigma - \xi_+)/2$$
$$E_{\pi 1} = (\gamma_1 + v_3\sigma - \xi_-)/2$$
$$E_{\pi^* 1} = (-\gamma_1 - v_3\sigma + \xi_+)/2$$
$$E_{\pi^* 2} = (\gamma_1 + v_3\sigma + \xi -)/2$$



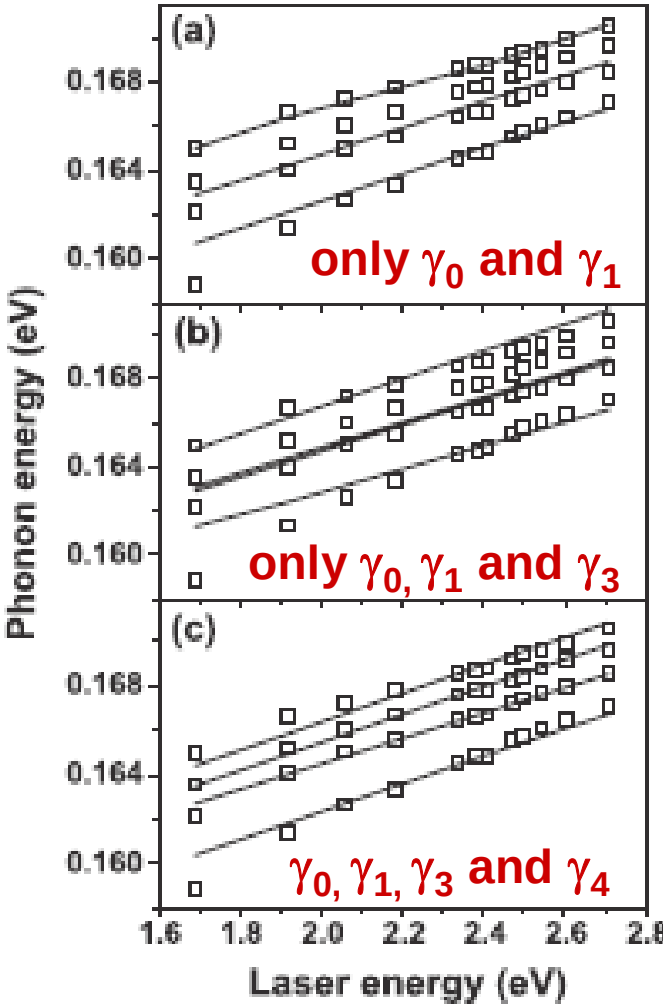
$$\sigma = \gamma_0[2\cos(2\pi/3 - ka\sqrt{3}/2) + 1]$$

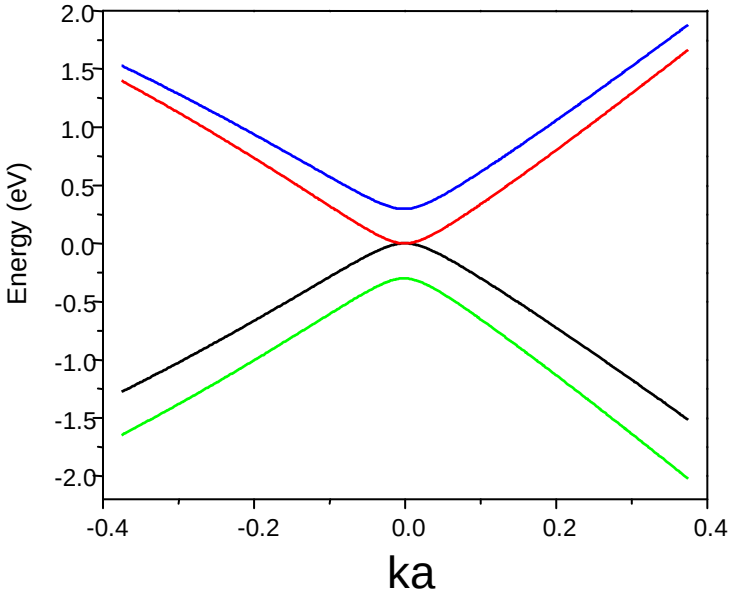
$$\xi_\pm = \sqrt{(\gamma_1 - v_3\sigma)^2 + 4(1 \pm v_4)^2\sigma^2}$$

$$v_j = \gamma_j/\gamma_0$$

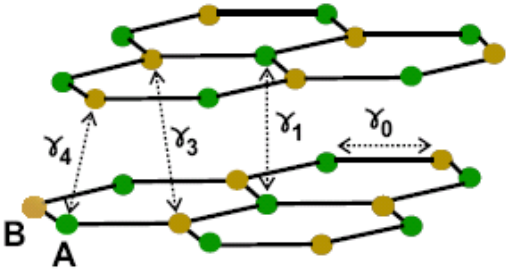
Double resonance conditions

$$E_L = E_{\pi_i^*}(k_i) - E_{\pi_i}(k_i)$$
$$E_p^{ij}(k_i + k_j') = E_{\pi_i^*}(k_i) - E_{\pi_j^*}(k_j')$$





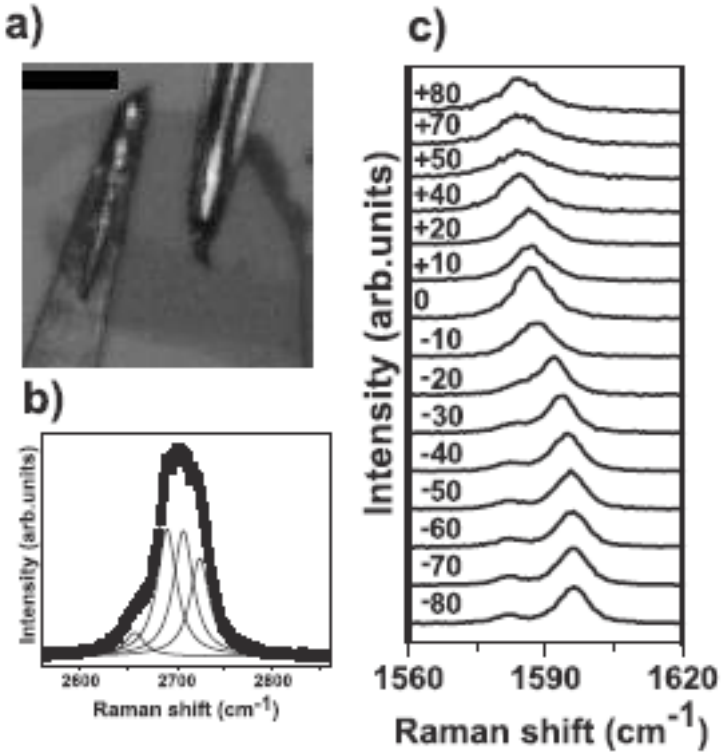
(eV)	γ_0	γ_1	γ_3	γ_4
BG – our fit	2.9	0.30	0.10	0.12
Graphite	3.16	0.39	0.32	0.04

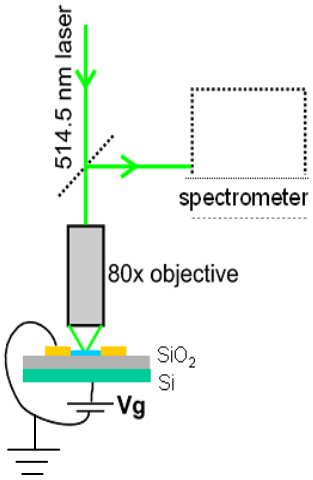


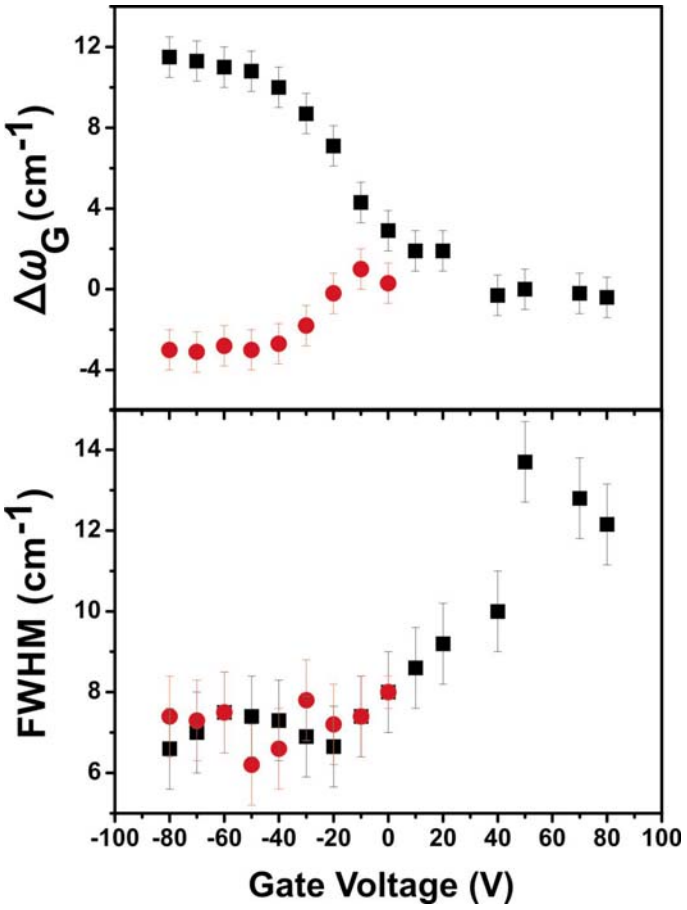
Asymmetry between the valence and conduction bands of bilayer graphene

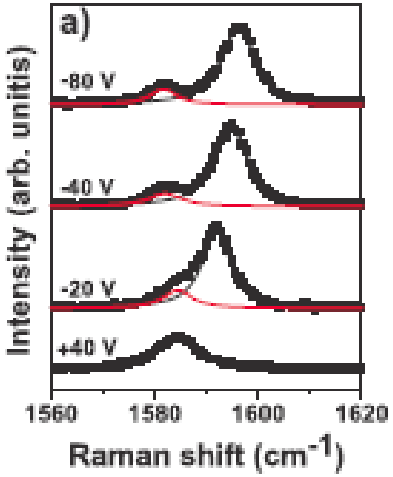
L. M. Malard et al. Phys.Rev. B 76, 201401 (2007)

Raman experiments on back gated bilayer graphene



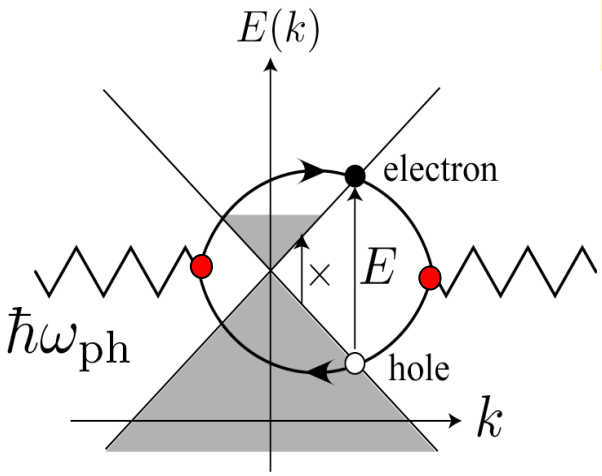






Splitting and narrowing of the G band of bilayer graphene for negative gate voltages

Renormalization of phonon energy in monolayer graphene: interaction of phonons with electron-hole pairs (Kohn anomaly)

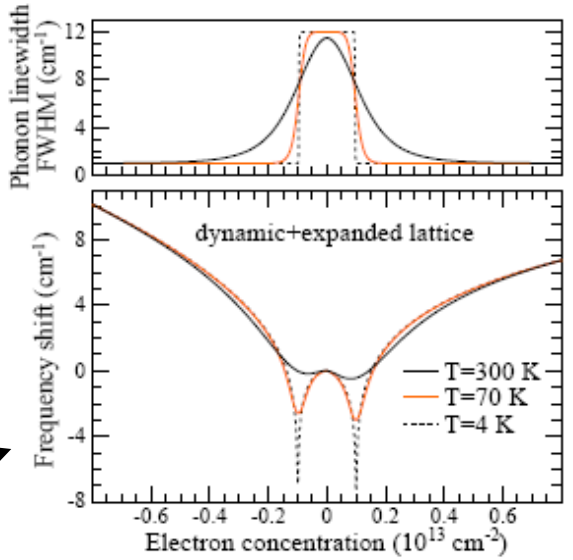


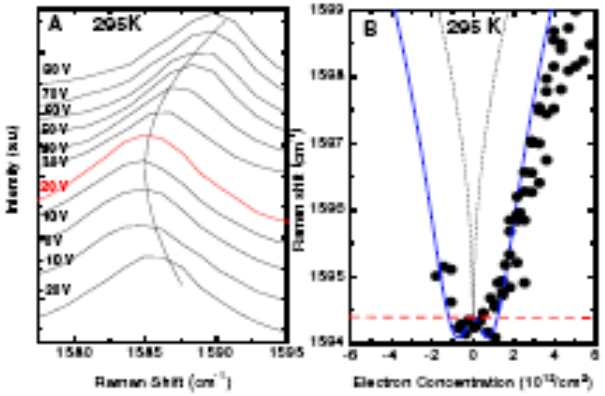
$$\hbar\omega = \hbar\omega^{(0)} + \hbar\omega^{(2)}$$

S. Piscanec *et al.*, Phys. Rev. Lett 93, 185503 (2004).

T. Ando, J. Phys. Soc. Jpn. 75, 124701 (2006).

M. Lazzeri and F. Mauri, Phys. Rev. Lett. 97, 266407





S. Pisana, Nature Materials (2007)

Exp. observation in monolayer graphene

S. Pisana *et al.*, Nature Mater. 6, 198 (2007).

J. Yan *et al.*, Phys. Rev. Lett. 98, 166802 (2007).

A. Das *et al.*, Nature Nanotech. 3, 210 (2008).

Phonon renormalization in bilayer graphene

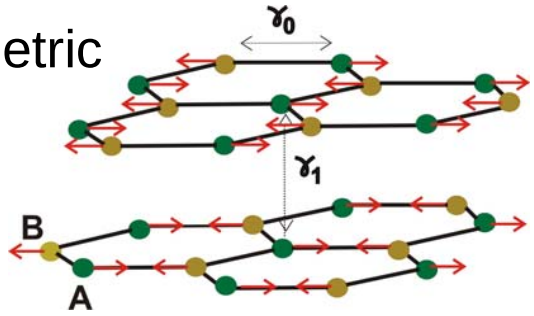
T. Ando, J. Phys. Soc. Jpn. 76, 104711 (2007).

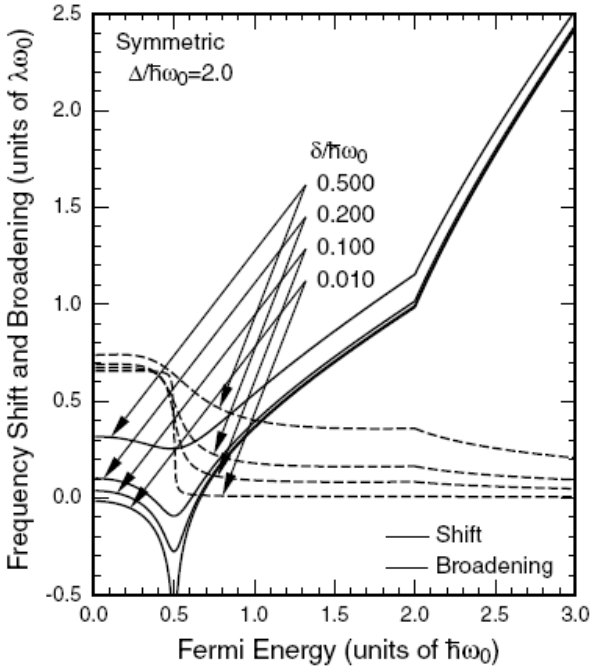
Phonon self energy

$$\Pi^{(\pm)}(\omega) = -\lambda \int_0^\infty \gamma^2 k dk \sum_{j,j'} \sum_{s,s'} \Phi^{(\pm)}_{jj'}(k) \times \frac{[f(\varepsilon_{sjk}) - f(\varepsilon_{s'j'k'})](\varepsilon_{sjk} - \varepsilon_{s'j'k'})}{(\hbar\omega + i\delta)^2 - (\varepsilon_{sjk} - \varepsilon_{s'j'k'})^2}$$

Symmetric

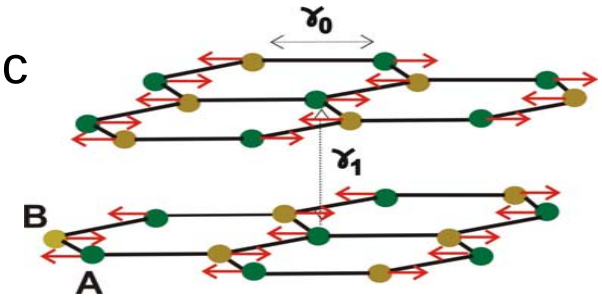
S

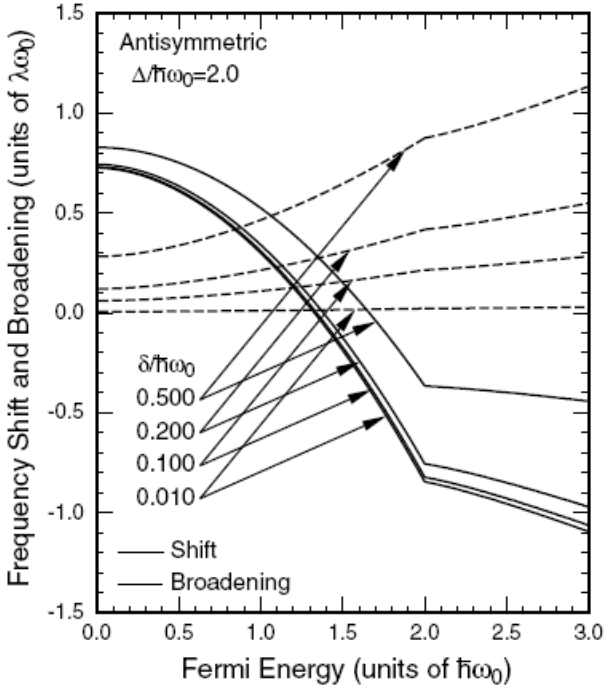




Anti-symmetric

AS





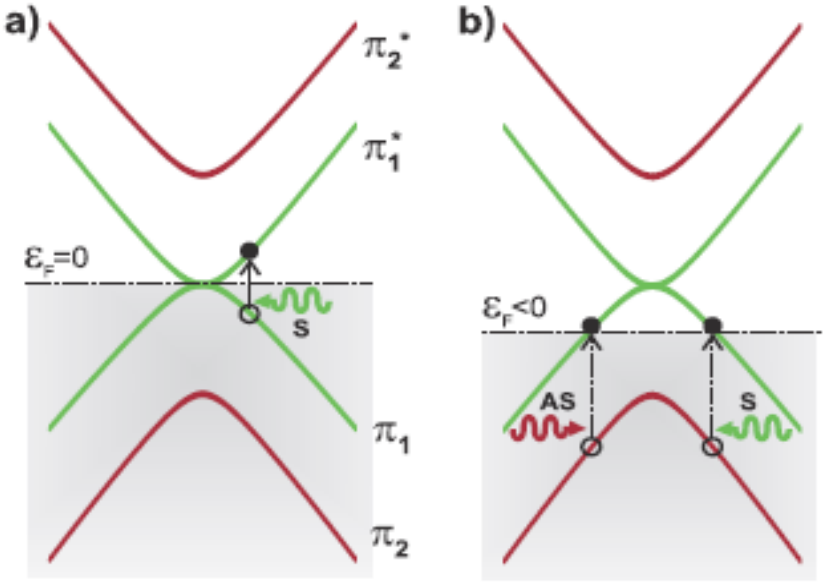
Selection rules for the interaction of S and AS phonons with intra-band and inter-band electron-hole pairs

Distinct electron-phonon couplings

S AS

$$\Phi^{+} = \frac{1}{2}\begin{pmatrix} sin^2\psi & cos^2\psi \\ cos^2\psi & sin^2\psi \end{pmatrix}, \Phi^{-} = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

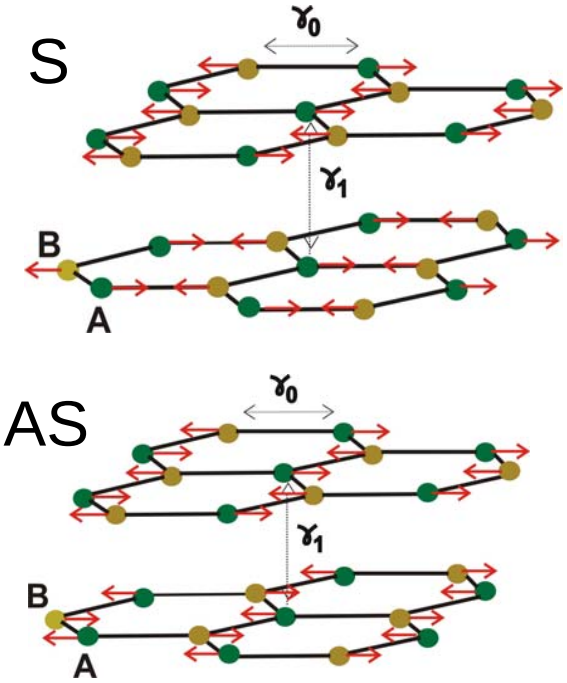
T. Ando, J. Phys. Soc. Jpn. 76, 104711 (2007)



- Hardening of the **S** phonon energy: main interaction of **S** phonons with **inter-band** electron-hole pairs

- Softening of the **AS** phonon energy: interaction of **AS** phonons with **intra-band** electron-hole pairs

Raman selection rules for S and AS phonons



D_{3d} C_{3v}

E_g (S) → E (S, AS)

E_u (AS) → E (S, AS)

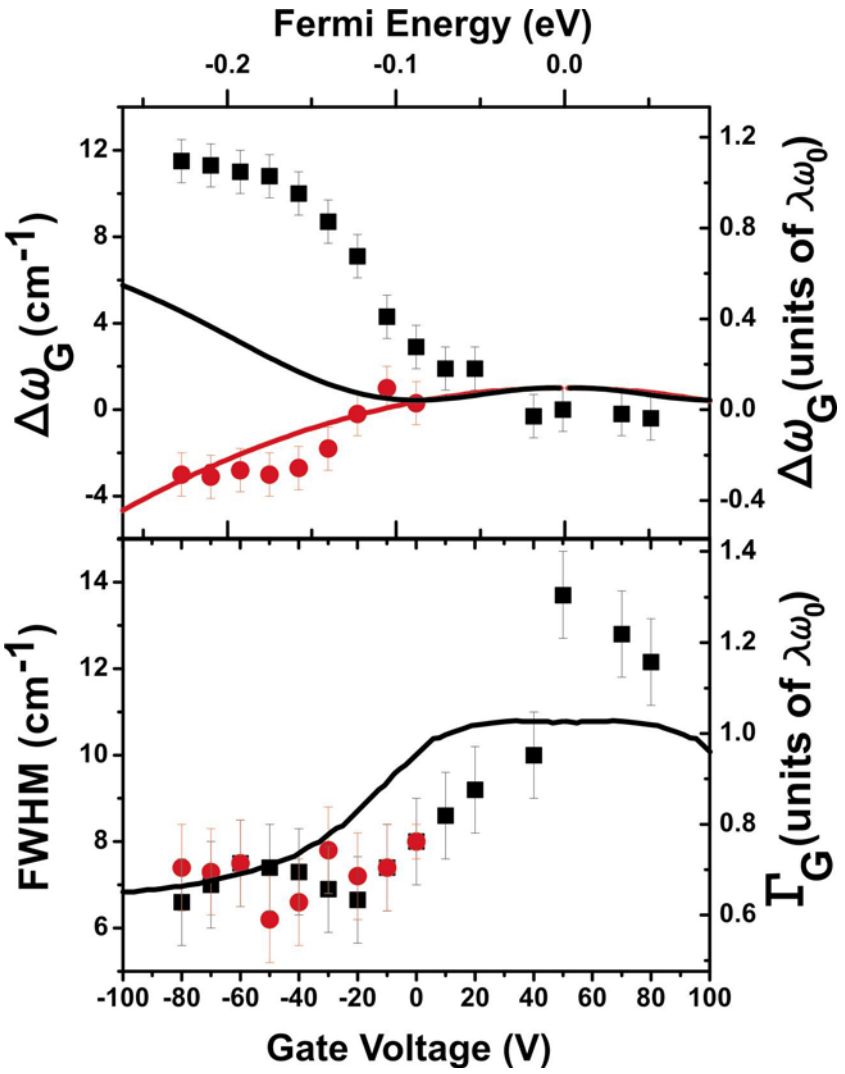
The breaking of inversion symmetry allows the observation of the anti-symmetric (AS) mode.

- **Interaction of the BL with the SiO_2 and the indium wire contact.**
- **Non-homogeneous charge distribution on the top and bottom layers**

Can the two peaks be associated with the S mode of the bottom and top layers?

- The low frequency peak is five times less intense than the other one.
- The low frequency peak softens for $E_F > \hbar\omega_0 / 2$

Comparing the experimental and theoretical results



Converting the vertical scale

$$\lambda = 0.16 \times 10^{-3} (\text{Å}^2 eV^{-2}) [\frac{\partial \gamma_0}{\partial b}]^2$$

$$\frac{\partial \gamma_0}{\partial b} = 6.4 eV \text{A}^{-1}$$

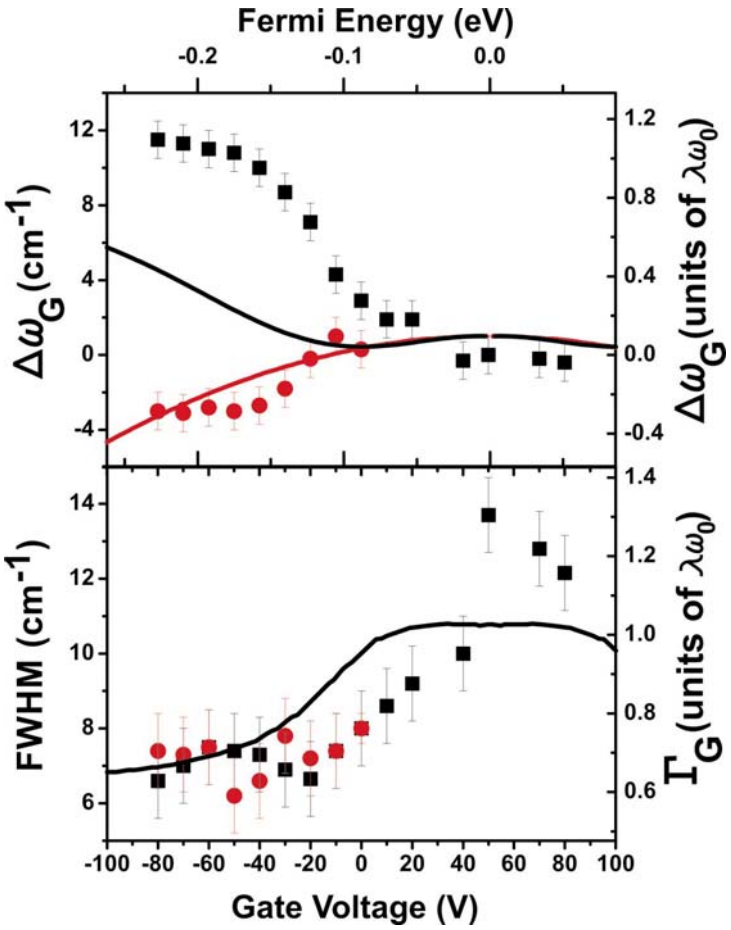
Converting the horizontal scale

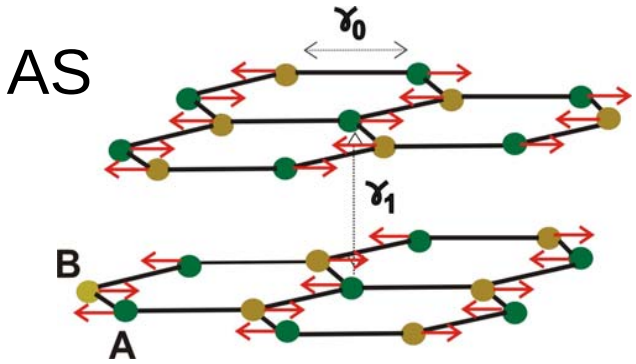
$$|\varepsilon_F| = \frac{1}{2}(-\gamma_1 + \sqrt{4n\pi\gamma^2 + \gamma_1^2}),$$

$$n = 7.2 \times 10^{-10} cm^{-2} V^{-1} (V_G - V_D)$$

$V_D = 50\ V$ $\gamma_1 = 0.35\ eV$ $\delta = 0.1\ eV$

Observation of Distinct Electron-Phonon Couplings in Bilayer Graphene





Good qualitative agreement between the experimental results and the theoretical prediction for distinct *el-ph* couplings.

- Simple model of a parallel capacitor with homogeneous carrier concentrationin in the two layers.
- Model doesn't take into account the angular dependence of the electron-phonon coupling.
- The strength $\partial\gamma_1/\partial b$ might be relevant for the coupling between electrons and AS phonons.
- A more detailed model is needed to improve the fitting of the experimental data.

Conclusions

♦ Resonance Raman scattering probes electrons and phonons near the Dirac point of graphene.

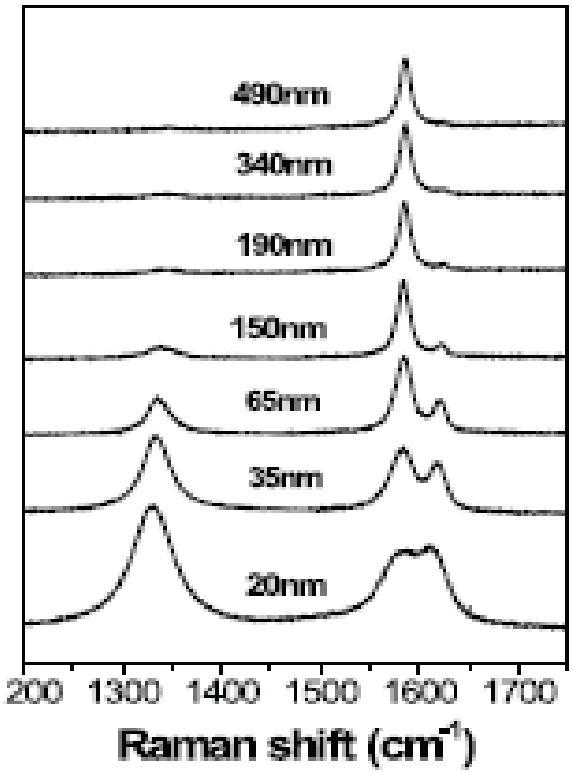
♦ Determination of phonon velocities for monolayer graphene and the SWM parameters of bilayer graphene.

♦ Asymmetry between valence and conduction electron bands in bilayer graphene.

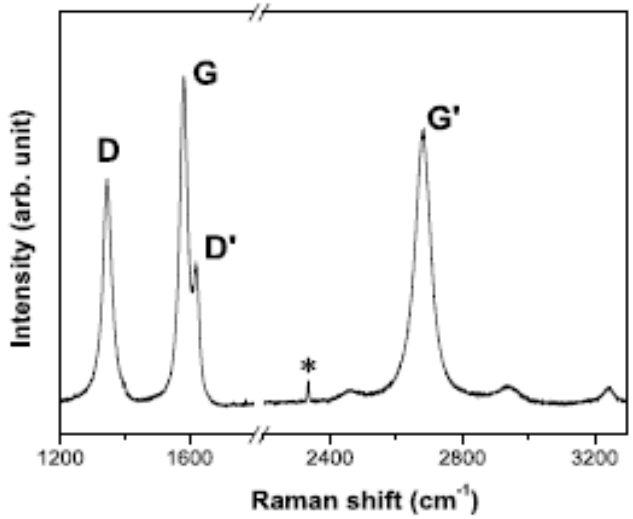
♦ Observation of anti-symmetric AS phonons in gated bilayer graphene on the top of a SiO_2 substrate.

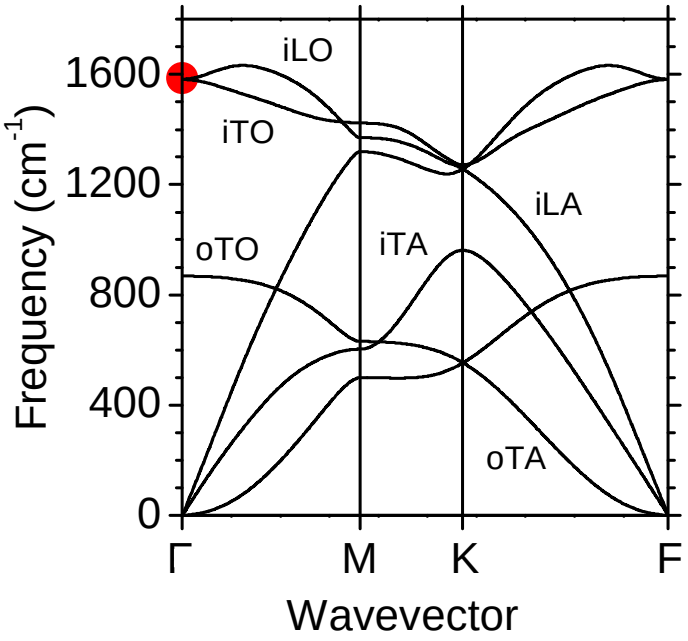
♦ Hardening of the S phonon and softening of the AS phonon (different electron-phonon selection rules for intra-band and inter-band electron hole pairs)

Raman spectra of nanographites

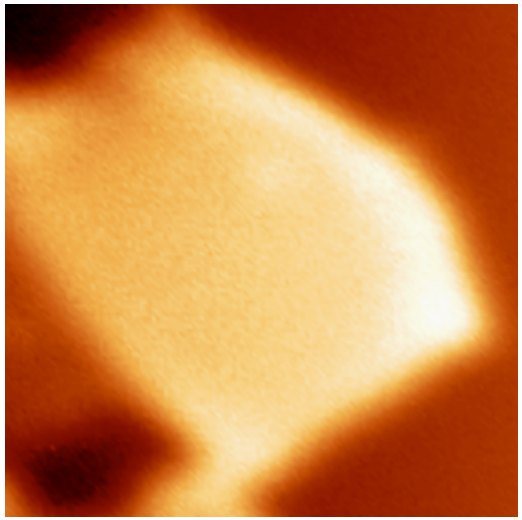


M. A. Pimenta et al., PCCP (2007)

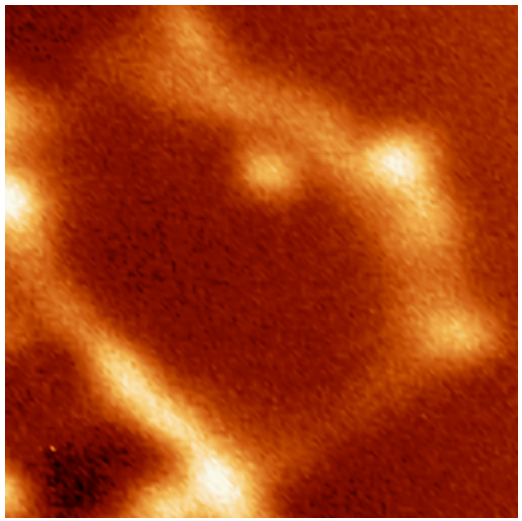




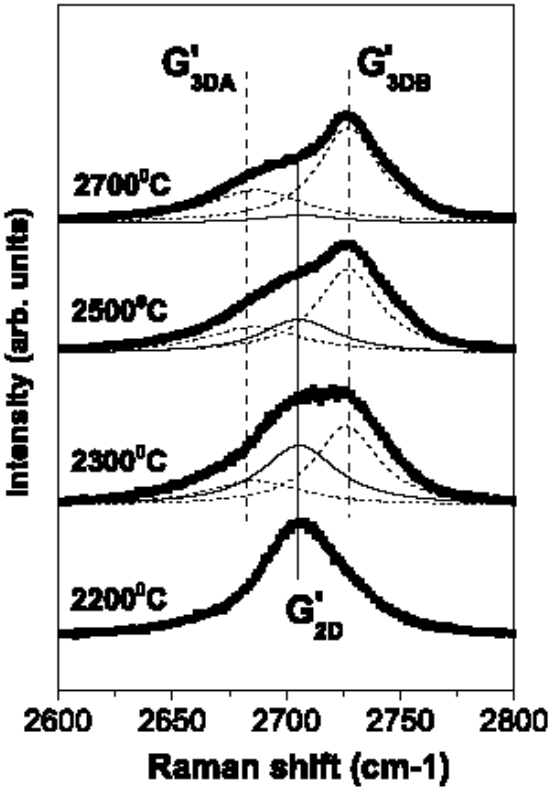
G-band image

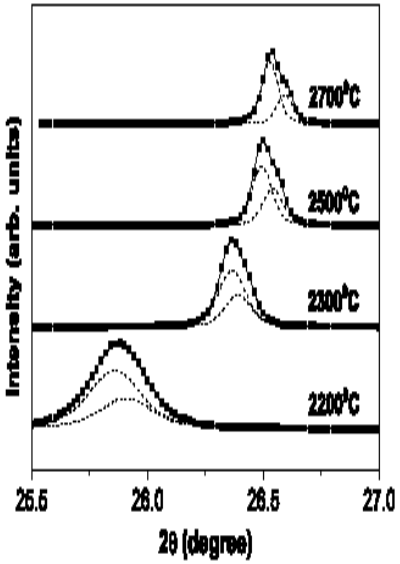


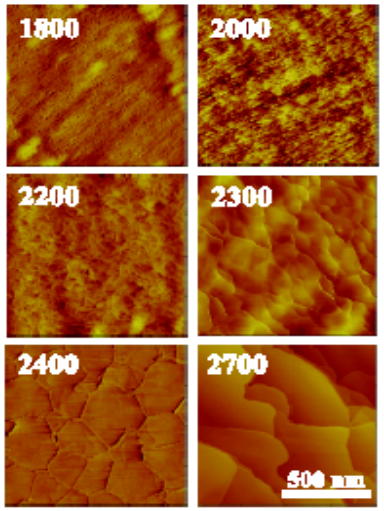
D-band image



Measuring stacking order in graphite by Raman

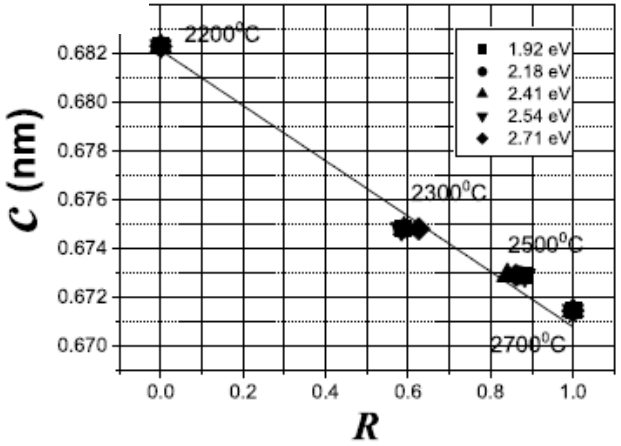


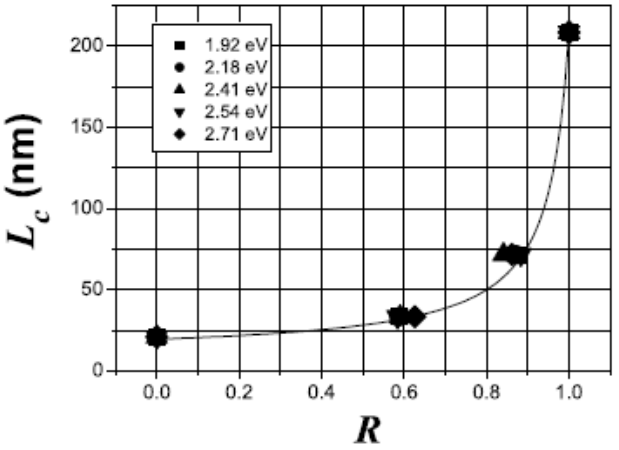




L. G. Cançado et al , Carbon (2008)

$$R = \left| \frac{I_{G'_{3DB}}}{I_{G'_{3DB}} + I_{G'_{2D}}} \right|$$



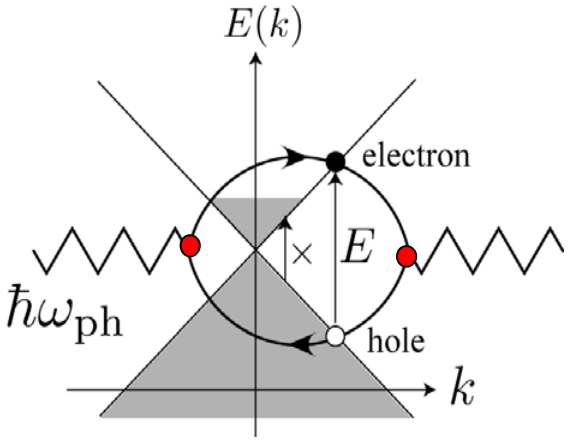


Renormalization of phonon energy in monolayer graphene: interaction of phonons with electron-hole pairs (Kohn anomaly)

S. Piscanec *et al.*, Phys. Rev. Lett 93, 185503 (2004).

T. Ando, J. Phys. Soc. Jpn. 75, 124701 (2006).

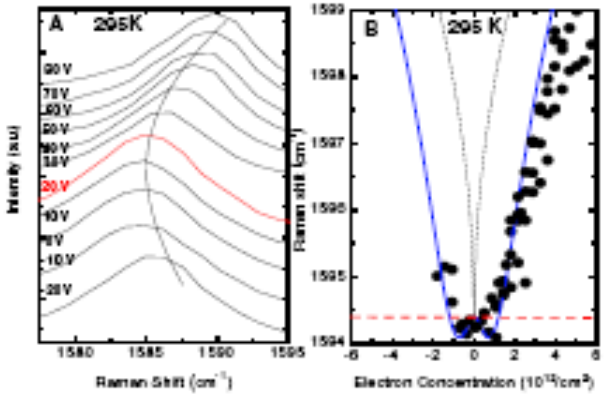
M. Lazzeri and F. Mauri, Phys. Rev. Lett. 97, 266407



$$\hbar\omega = \hbar\omega^{(0)} + \hbar\omega^{(2)}$$

$$\hbar\omega^{(2)} = \sum_{\mathbf{k}} \frac{|\langle \mathrm{eh}(\mathbf{k})|\mathcal{H}_{\mathrm{ep}}|\omega\rangle|^2}{\hbar\omega^{(0)} - (E_e(\mathbf{k}) - E_h(\mathbf{k})) + i\Gamma} (f(E_h(\mathbf{k}) - E_{\mathrm{F}}) - f(E_e(\mathbf{k}) - E_{\mathrm{F}}))$$

K. Sasaki, R. Saito et al., *(2008)*

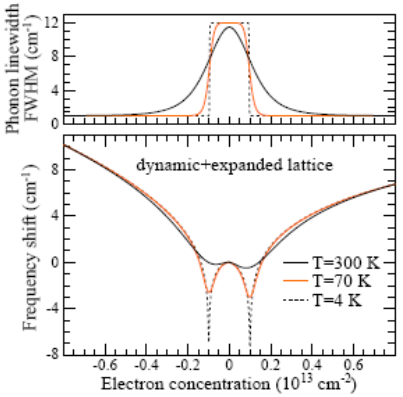


Exp. observation in monolayer graphene

S. Pisana *et al.*, Nature Mater. 6, 198 (2007).

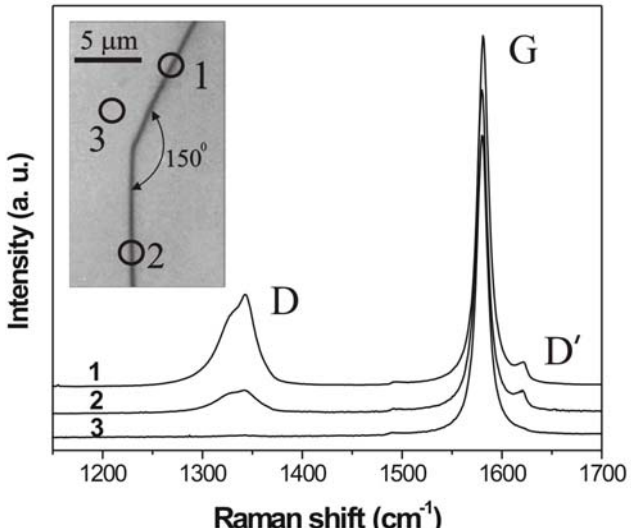
J. Yan *et al.*, Phys. Rev. Lett. 98, 166802 (2007).

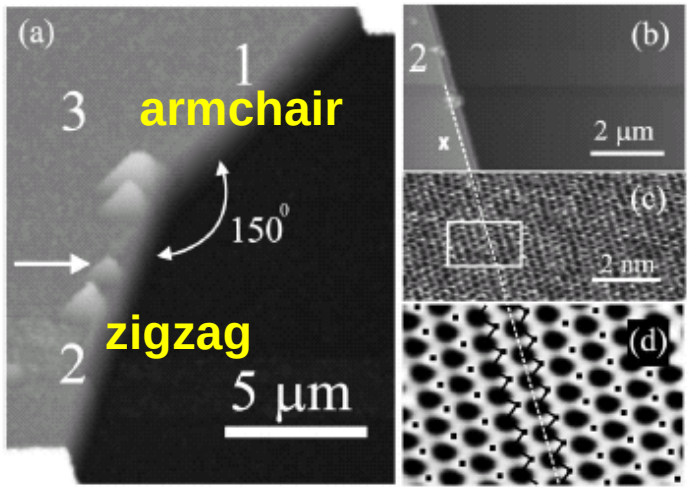
A. Das *et al.*, Nature Nanotech. 3, 210 (2008).

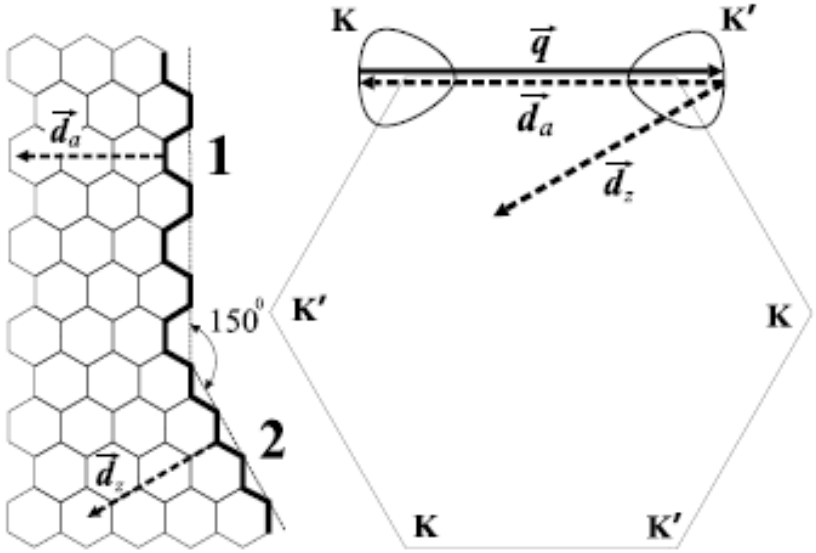


S. Pisana, Nature Materials (2007)

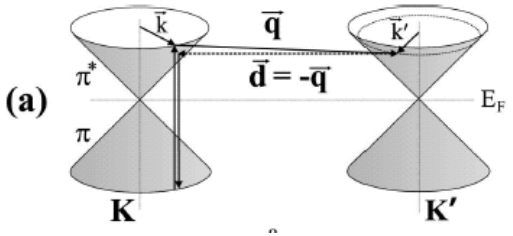
Raman scattering in graphites edges





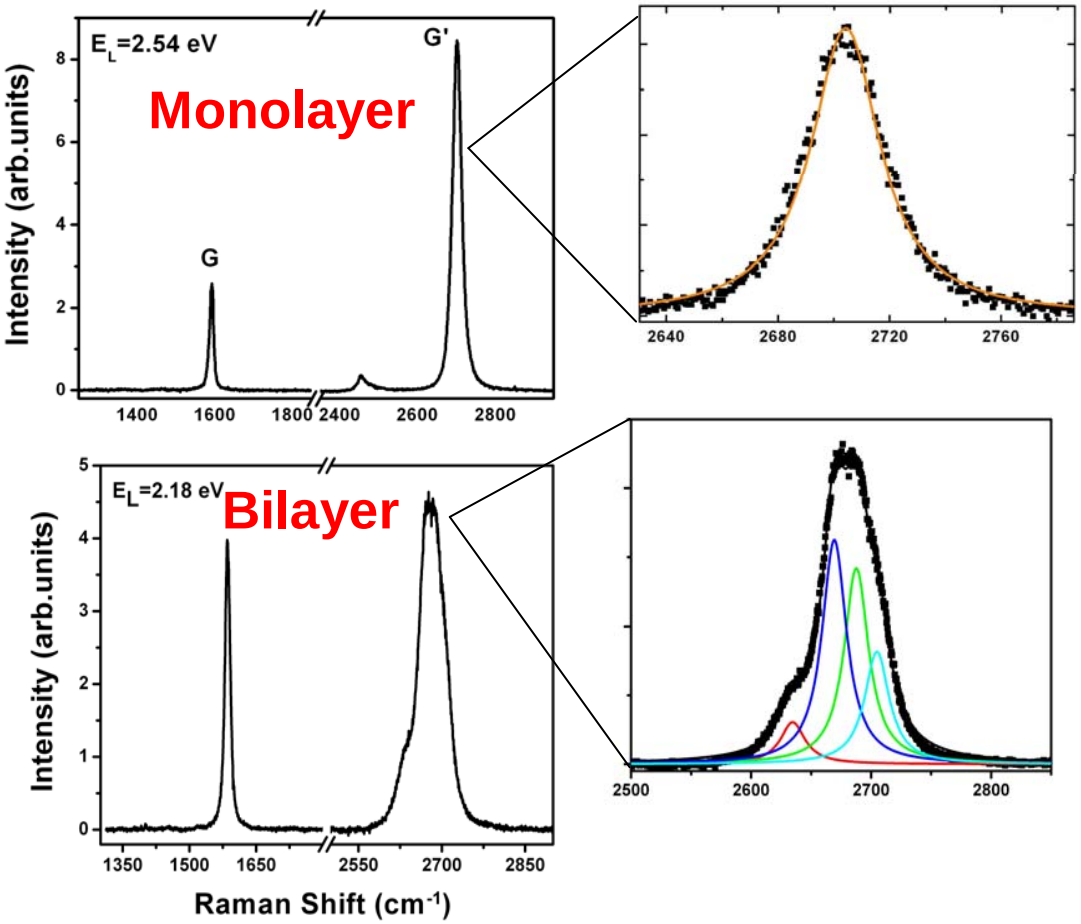


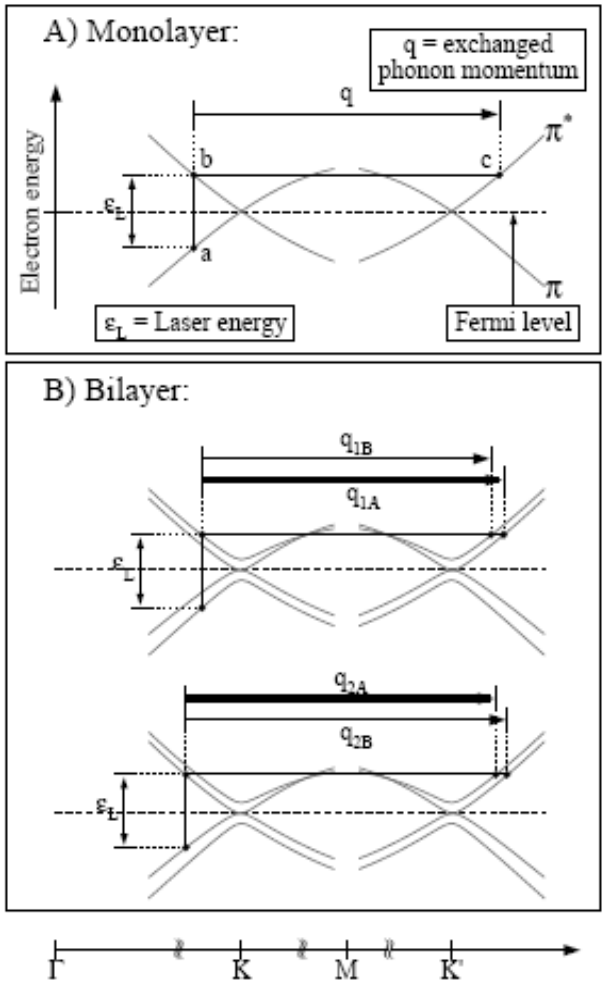
Raman scattering can distinguish zig-zag and armchair edges of graphite



L. G. Cançado, et al. Phys. Rev. Letters, 93, 247401 (2004)

Raman spectra of monolayer and bilayer graphene





The number of layers in graphene is easily determined by Raman

A. C. Ferrari et al. Phys. Rev. Lett. (2007)