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Phonon renormalisation and electron-phonon coupling in doped single-and by-layer graphene

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Phonon renormalisation and electron-phonon coupling in doped single- and by-layer graphene

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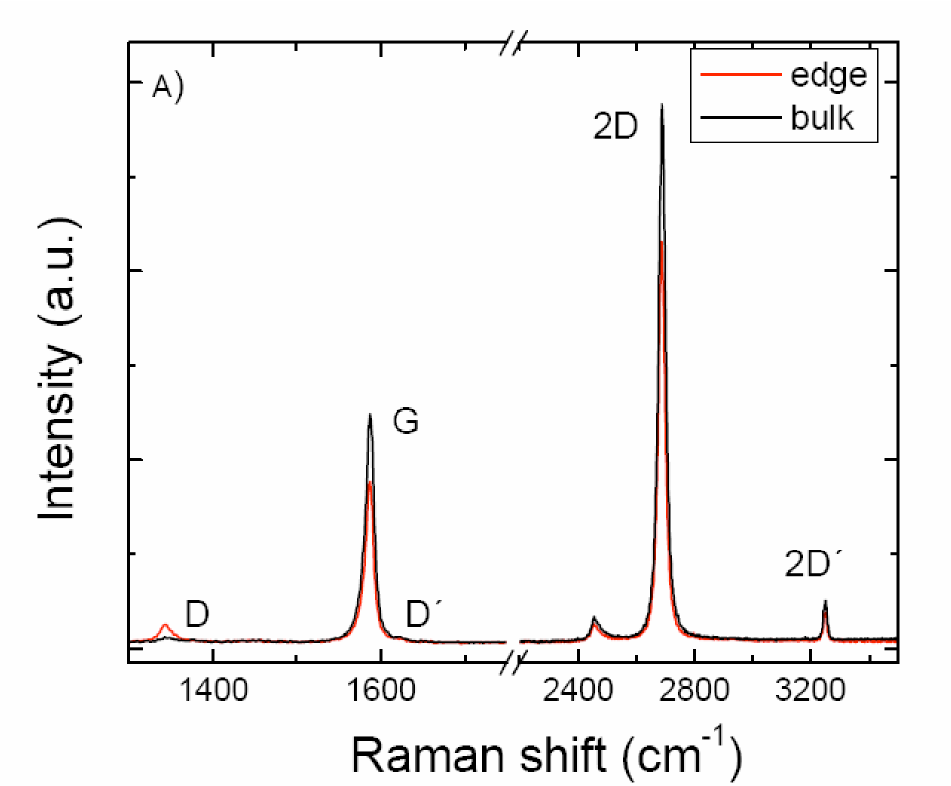
Outline

- Raman spectrum of graphene
- Evolution of the Raman spectrum with the number of layers
- Influence of doping on single-layer graphene
  - Effects of the electron-phonon coupling
  - Breakdown of the Born-Oppenheimer approximation
- Raman fingerprint of charge impurities in graphene
- Influence of doping in bi-layer graphene

Raman spectrum of graphene

G peak, D-peak, D'-peak and 2D peak



- G peak: very similar in graphite and graphene
- 2D peak: single peak (no structure) and **huge** intensity
- D peak: same dispersion as in graphite but different shape

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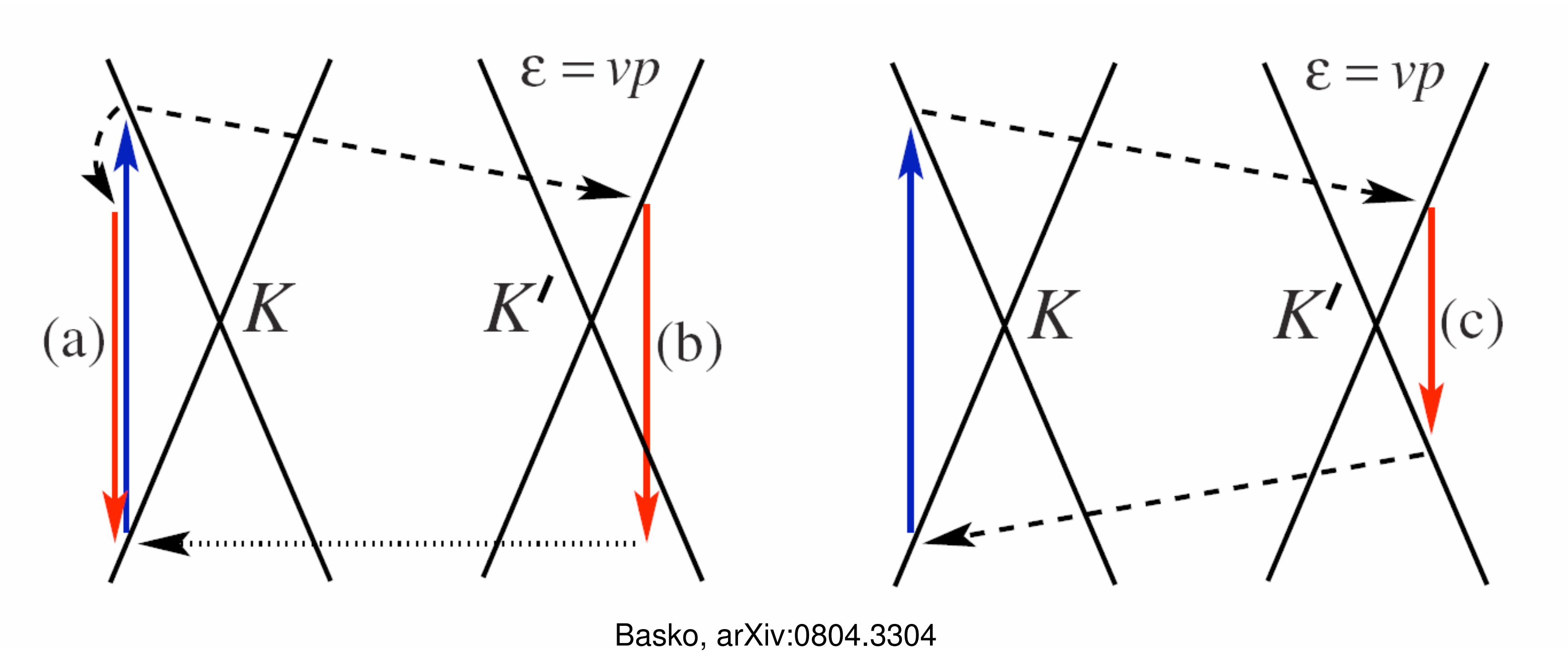
Origin of the G, D and 2D peaks

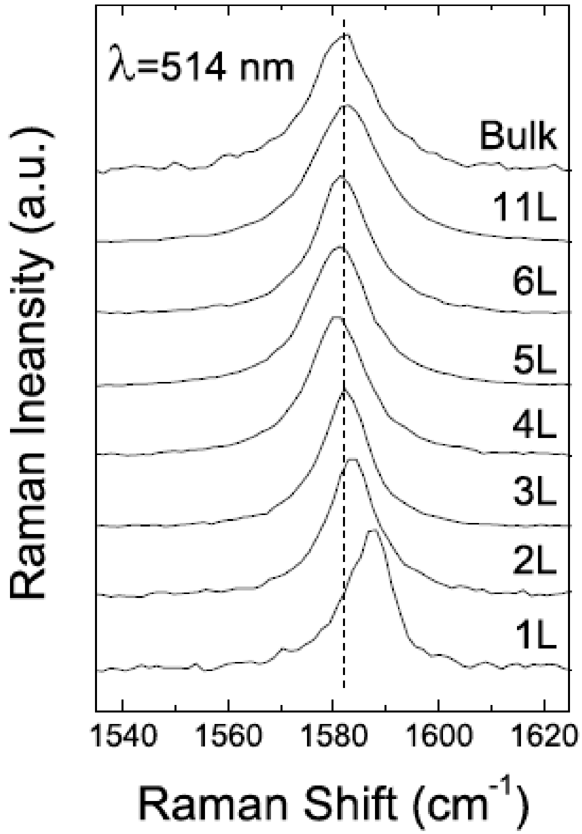


Basko, arXiv:0804.3304

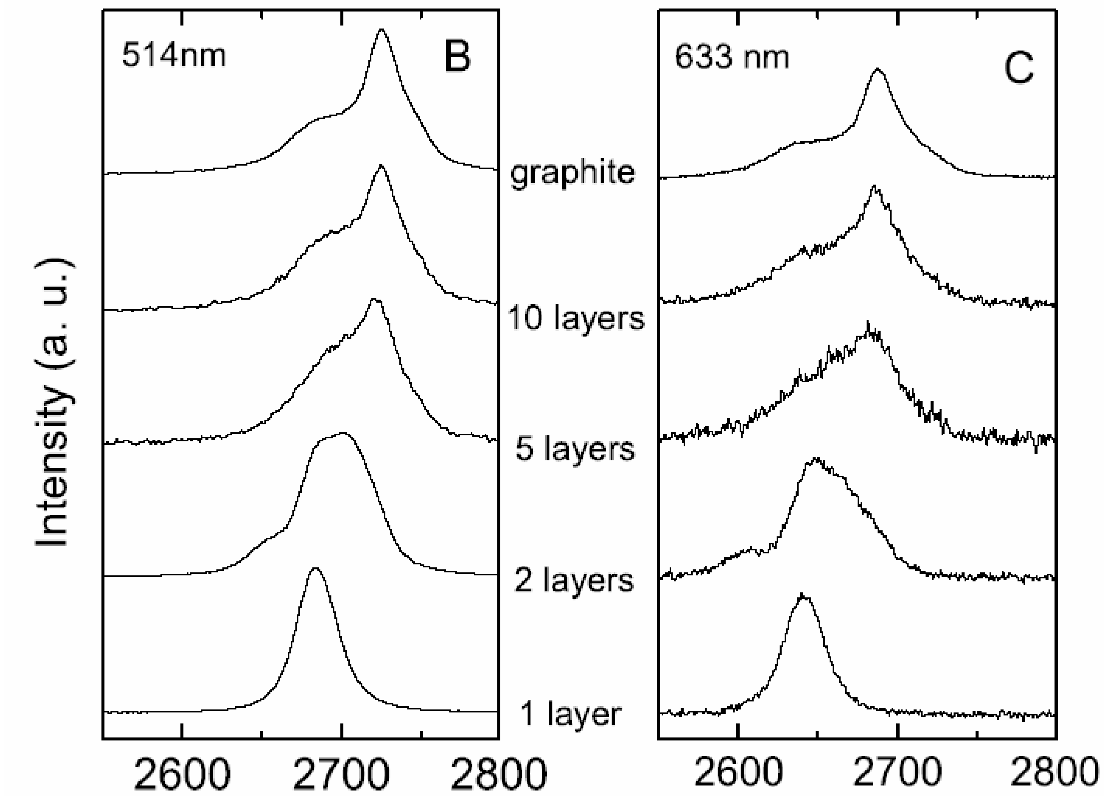
(a) Resonant process, q=0 → G peak
(b) Defect mediated double resonant process → D peak
(c) Two phonons fully resonant process → 2D peak

Spectrum evolution

G peak

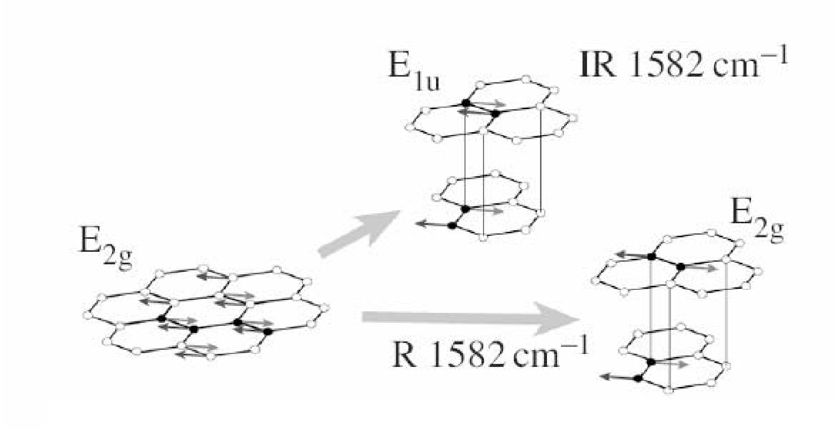


2D peak

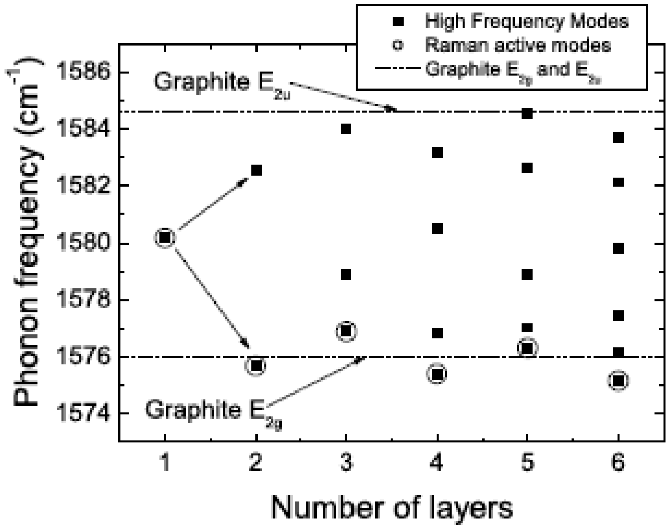


- We can count the number of layers!
- Most changes occur when moving from one to two layers

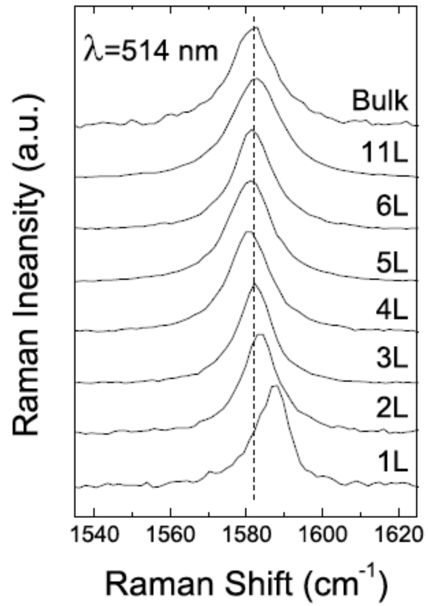
Evolution of the G peak



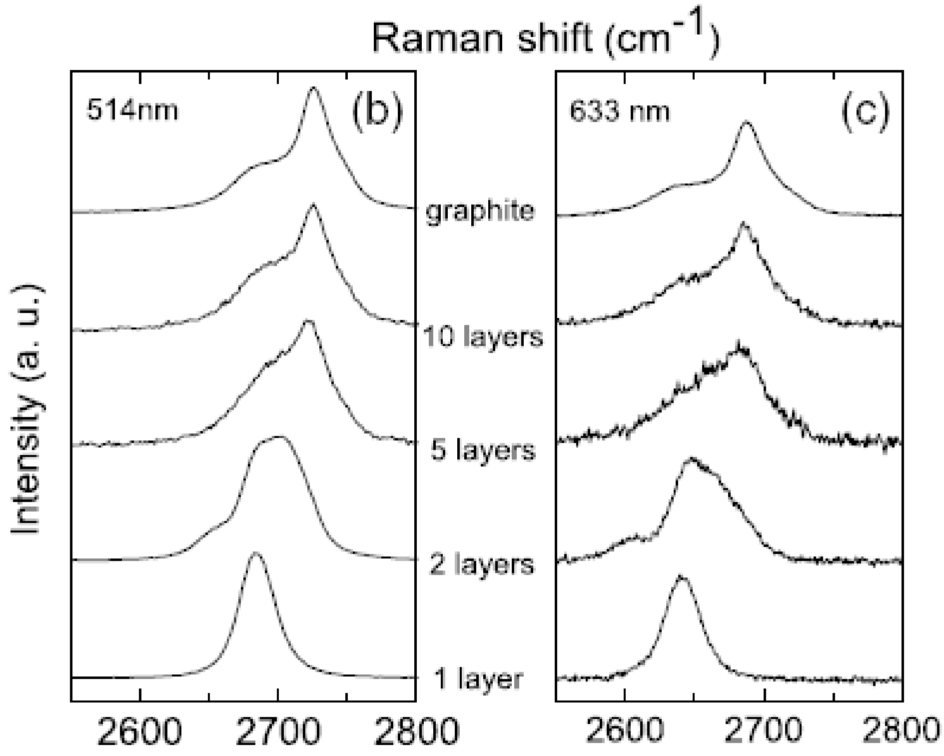
- 1Layer: E_{2g} mode at q=0
- 2 Layers: E_{2g} and E_{1u} at q=0

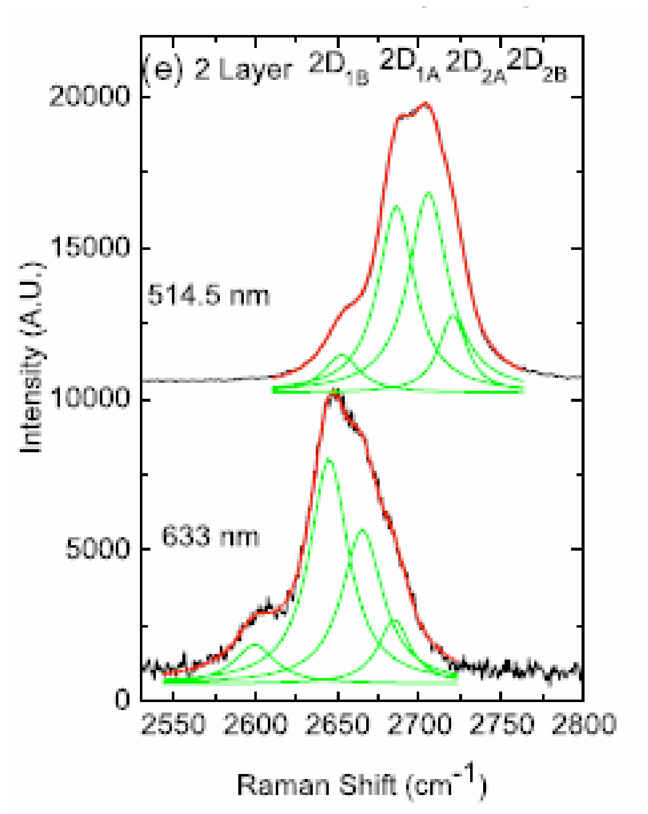


Phonon frequency: DFT
Raman tensor: TB



2D peak in graphene and bilayer





- Splitting of phonon branches → less than 1.5 cm^{-1} → No
- Splitting of electron bands

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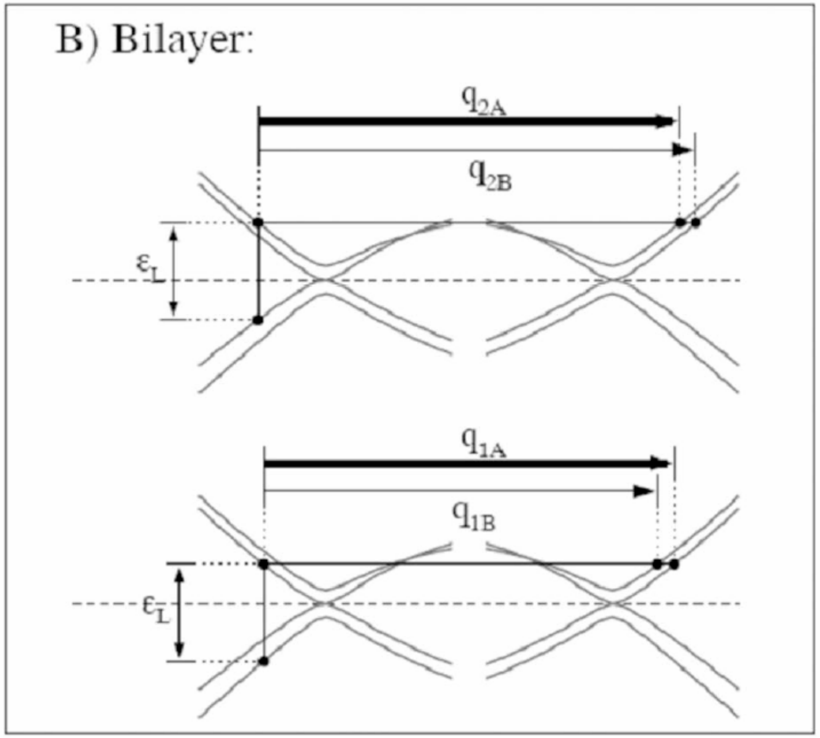
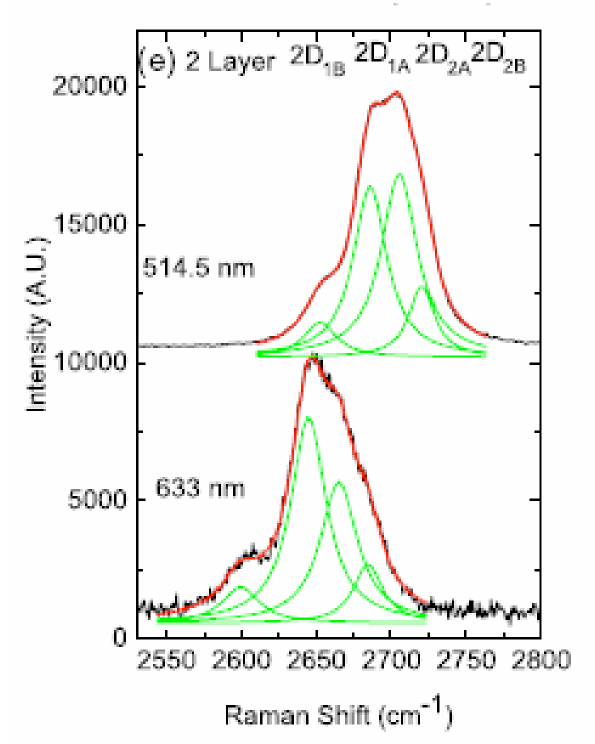
2D peak in graphene and bilayer





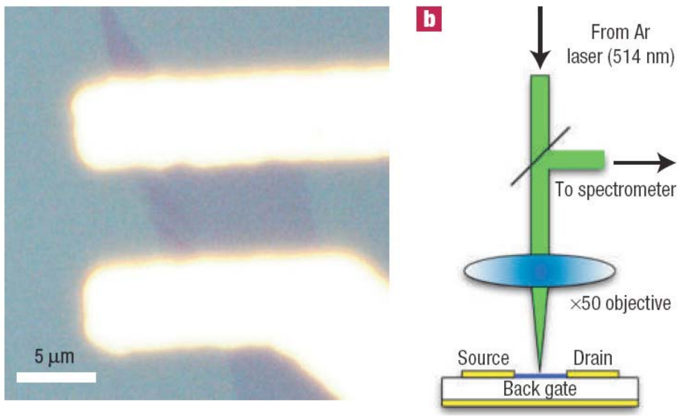
514.5 nm				
Experimental	−44	−10	+10	+25
Theory	−44	−11	+11	+41
633 nm				
Experimental	−55	−10	+10	+30
Theory	−44	−9	+9	+41

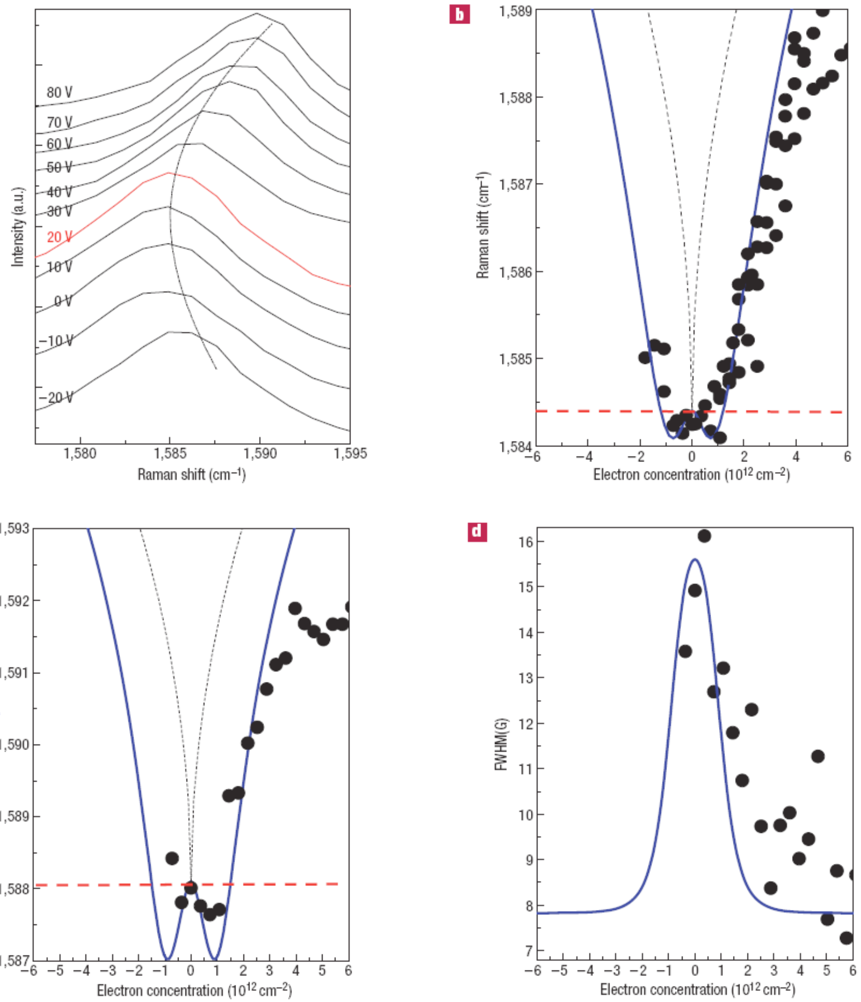
The possible transitions are determined by:
- Dipole transition matrix elements
- Electron-phonon coupling matrix elements
- Trigonal warping

Ferrari et al. PRL 2006

Effects of doping on the G-band of graphene

Si-oxide back gate





The Fermi energy of graphene can be shifted by applying a gate voltage

Electrical doping →
- **Stiffening** of the G peak
- **Reduction** of the FWHM

Pisana et al. Nature Materials 2006

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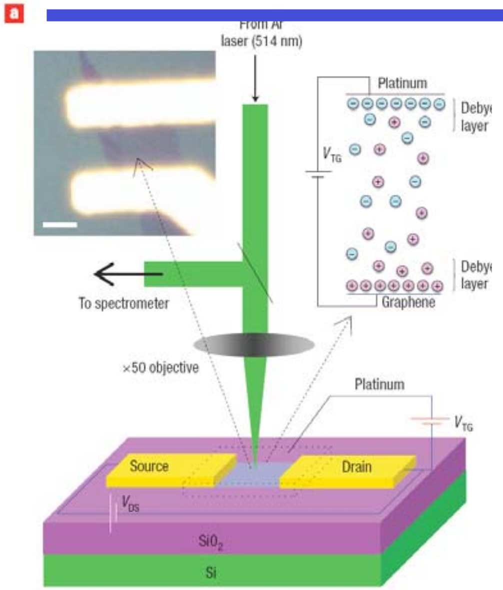
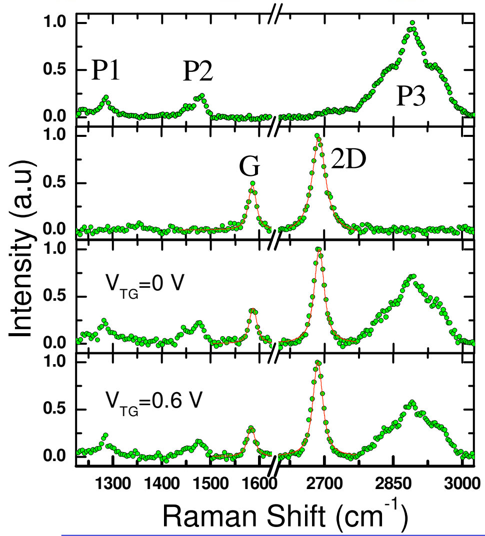
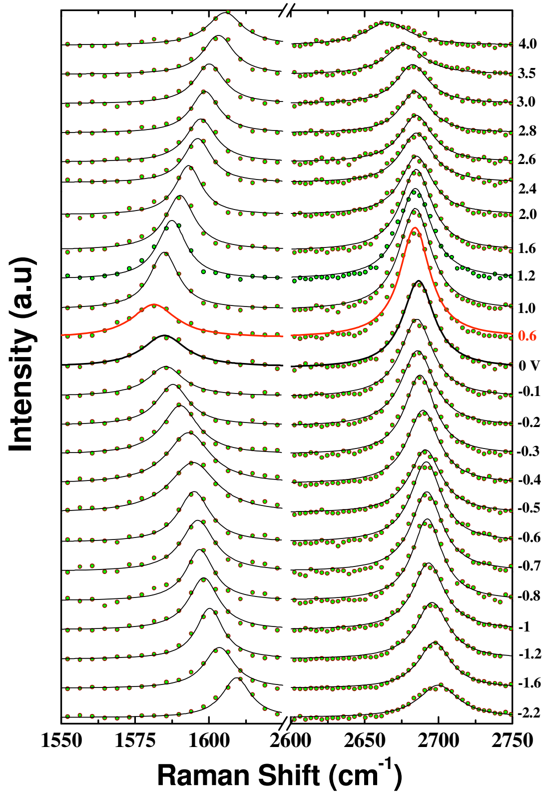
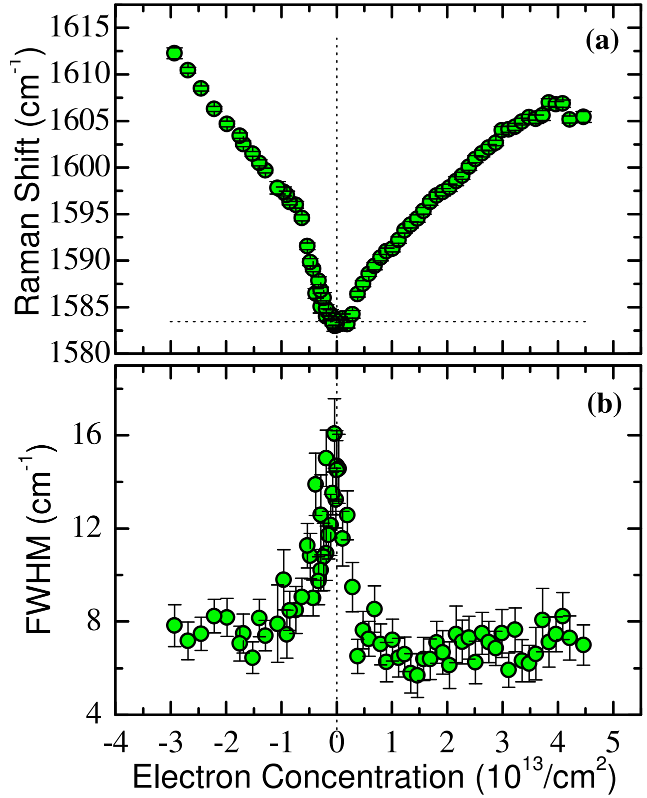
Polymer electrolyte top-gate: higher doping









Electrical doping → solid polymer electrolyte: $LiClO_4$ + PEO 0.12:1 + platinum electrode in the polymer layer

Raman peaks of graphene and polymer do not overlap

Das et al. Nature Nanotechnology 2008

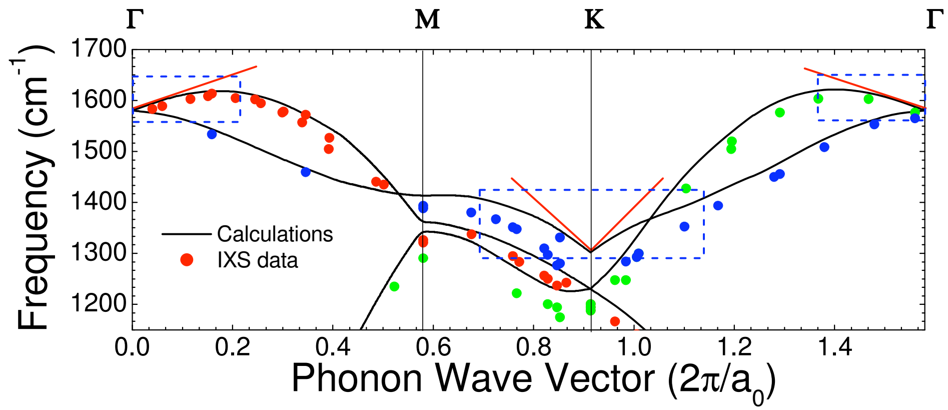
Effects of doping on the G-band of graphene

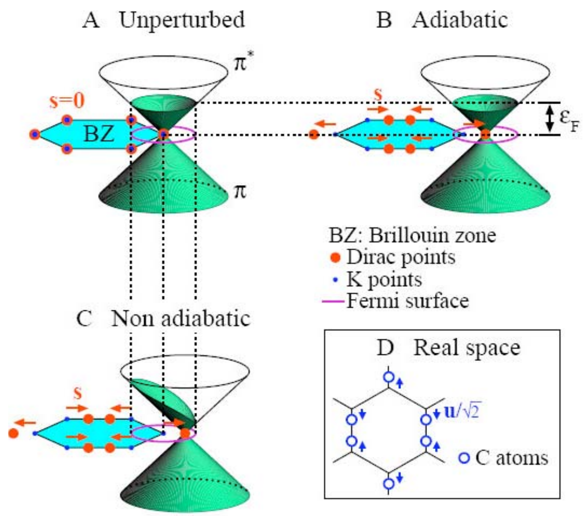
1. bond strength changes
2. lattice constant changes
3. Born-Oppenheimer fails

Adiabatic or "static" effects (1, 2)

$$\frac{\Delta\omega}{2\pi c} = -2.13\sigma - 0.0360\sigma^2 - 0.00329\sigma^3 - 0.226|\sigma|^{3/2}$$

Non-adiabatic or "dynamic" effects (3)





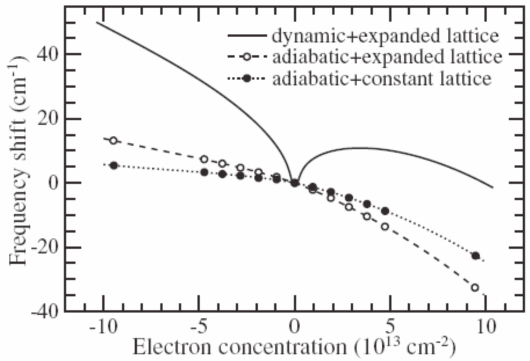
- Kohn anomalies in the phonon dispersion @Γ and @**K**
- Static Born-Oppenheimer approach ok for undoped graphene
- This approach fails for doped graphene

Electrons cannot follow adiabatically the motion of the nuclei!

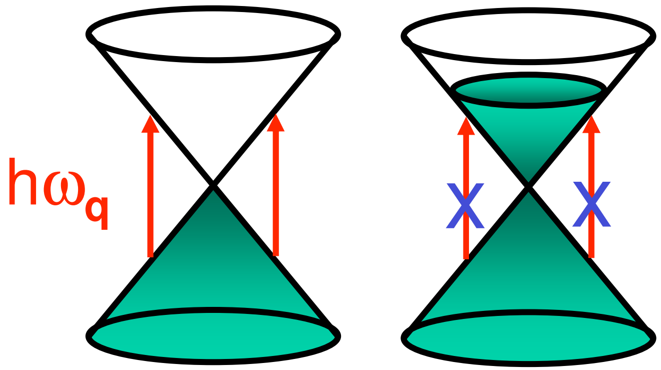
Pisana et al. Nature Materials 2006 / Lazzeri and Mauri PRL (2007)

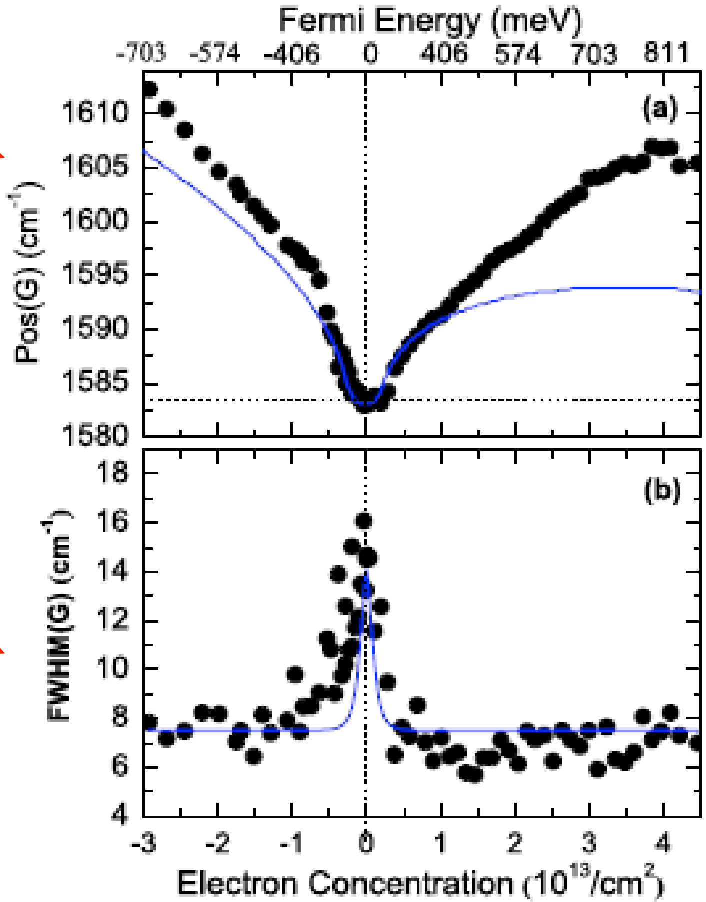
Effects of doping on the G-band of graphene

Sum of static and dynamic effects explain the G-peak position



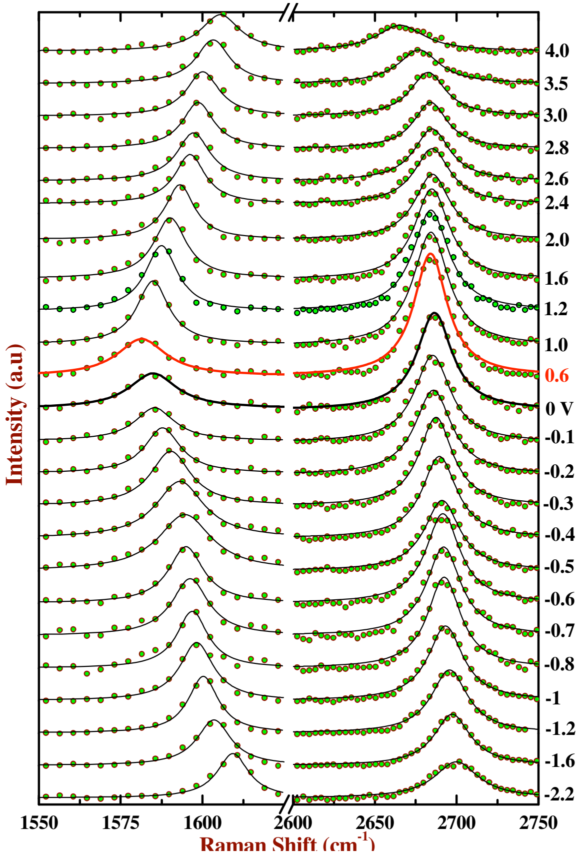
Suppression of electron-phonon decay channel explain the FWHM



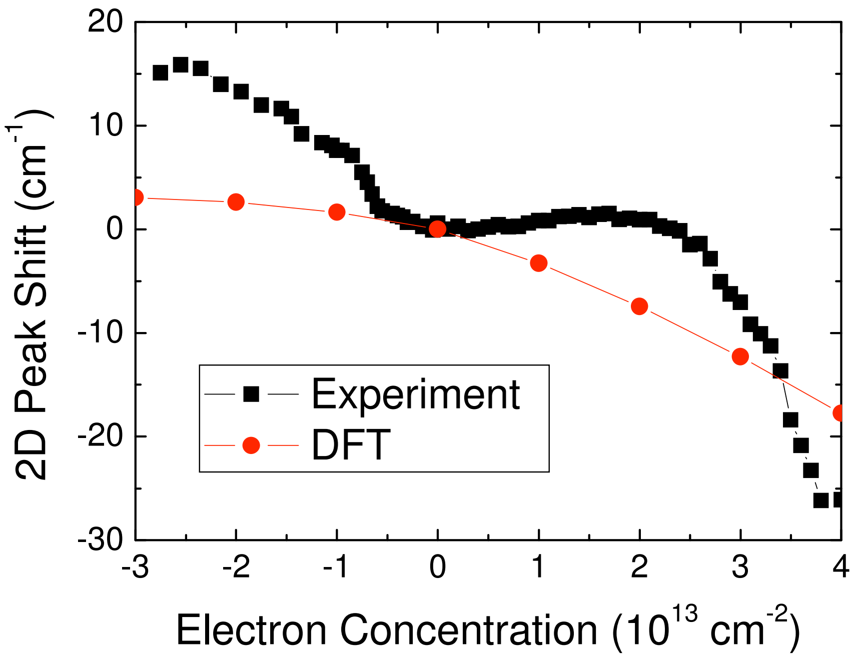


Pisana et al. Nature Materials 2006 / Lazzeri & Mauri PRL 2006 / Das et al. Nature Nanotechnology 2008

Influence of doping on the 2D band



Different behaviour for electrons and holes!



• Phonons involved are away from KAs → no "dynamic" effects are expected

• Static effects can be computed as for G-peak

Das et al. Nature Nanotechnology 2008

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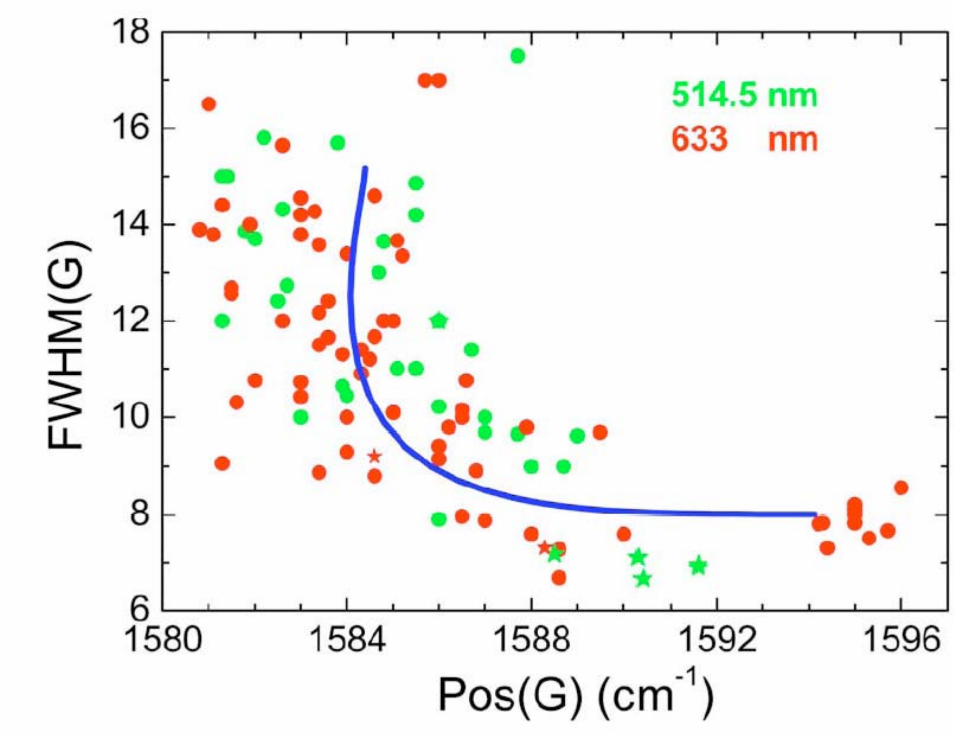
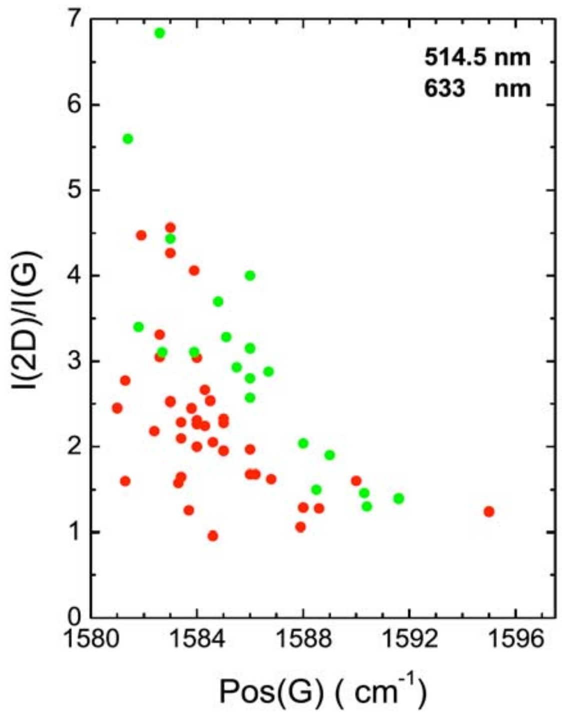
Charged impurities in graphene



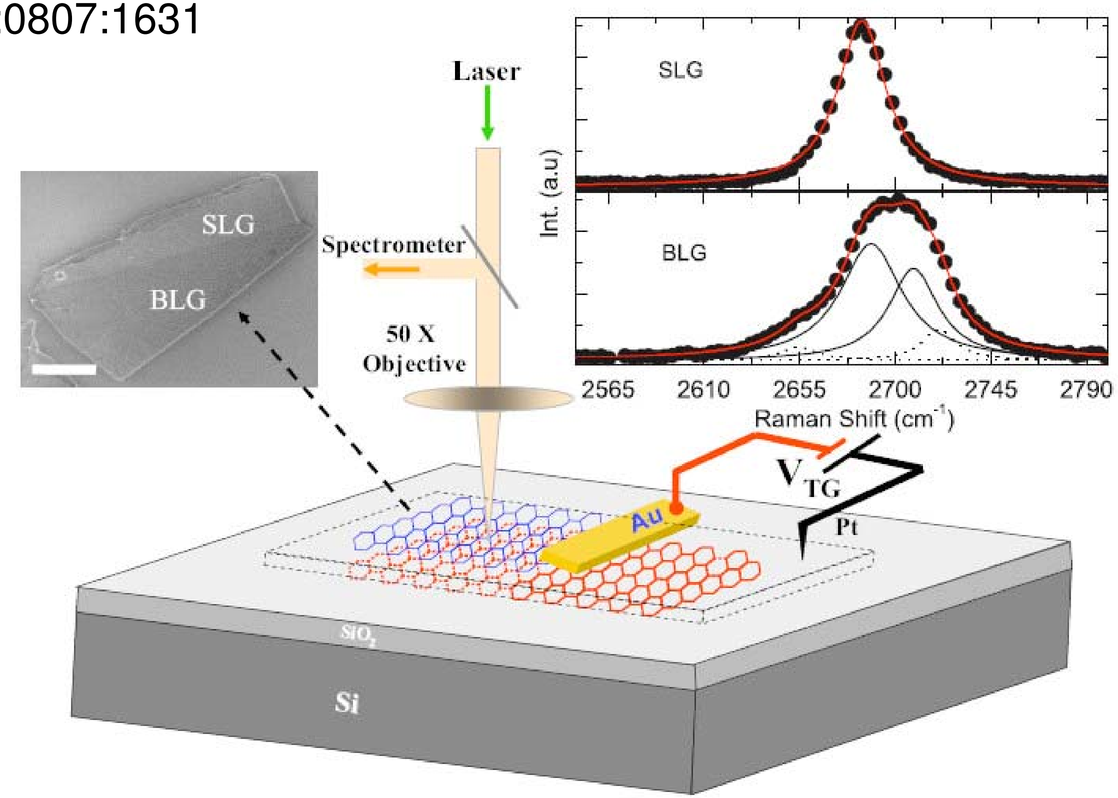


- Position and FWHM of G peak vary on different graphene samples or within different regions of the same sample → inhomogeneous distribution of charged impurities

Casiraghi et al. APL 2007

Doped bi-layer graphene

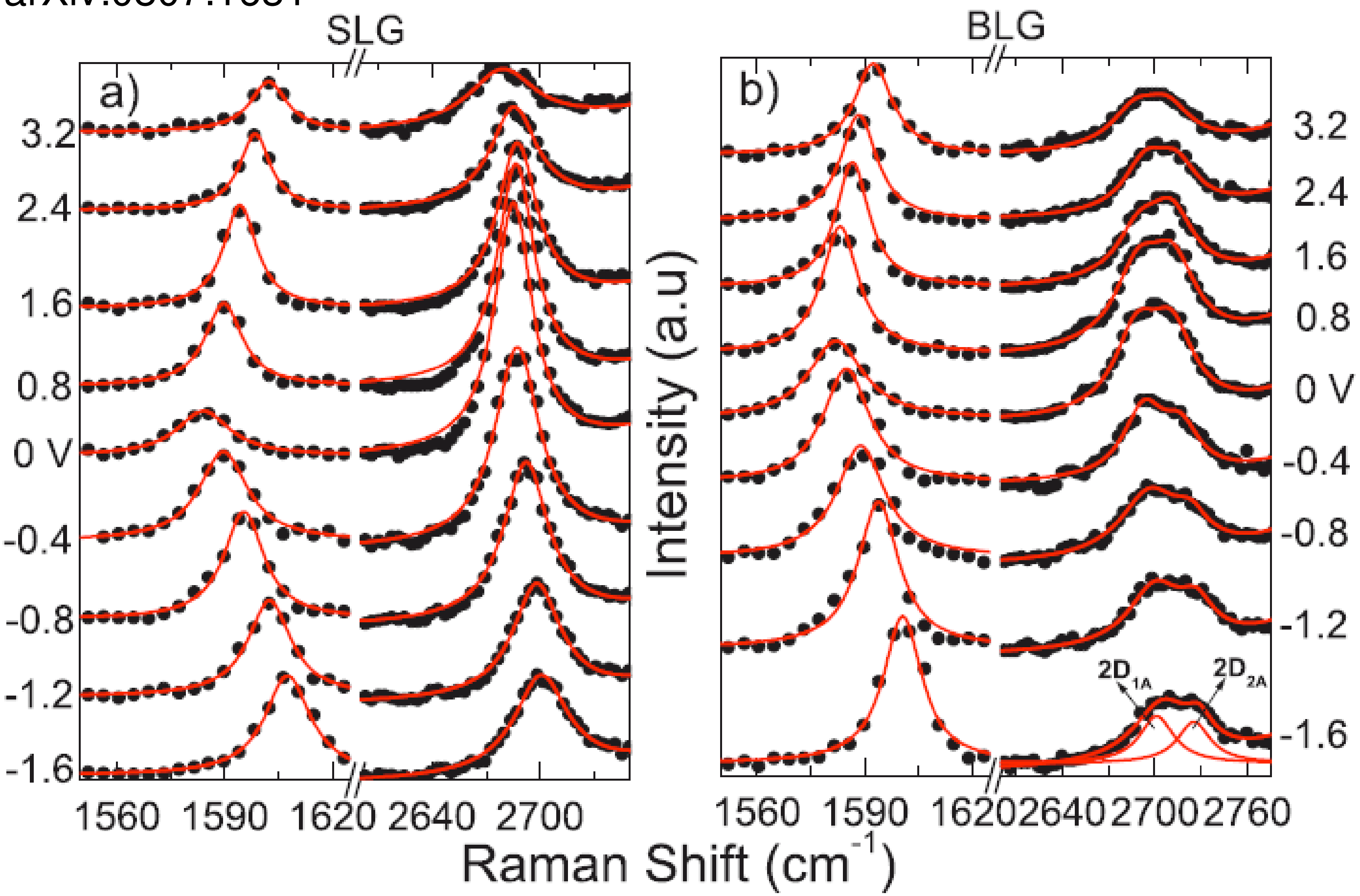
Das et al. arXiv:0807:1631



- A single layer graphene protruding from a doble layer
→ We can measure SLG and BLG under the same conditions!
- Top gating with polymer electrolyte → high level of doping can be reached

Evolution of the spectra with doping

Das et al. arXiv:0807:1631



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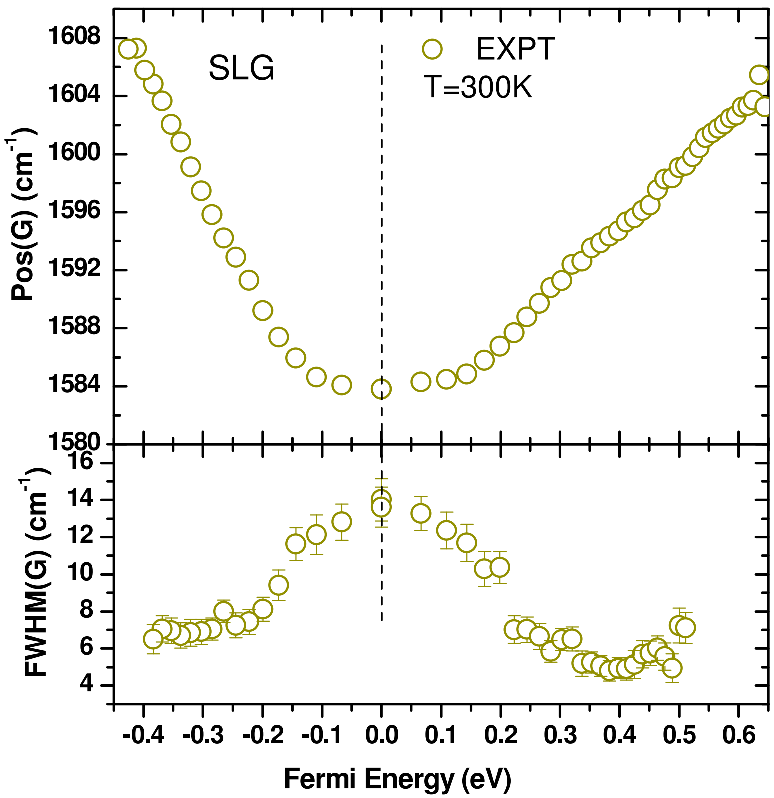
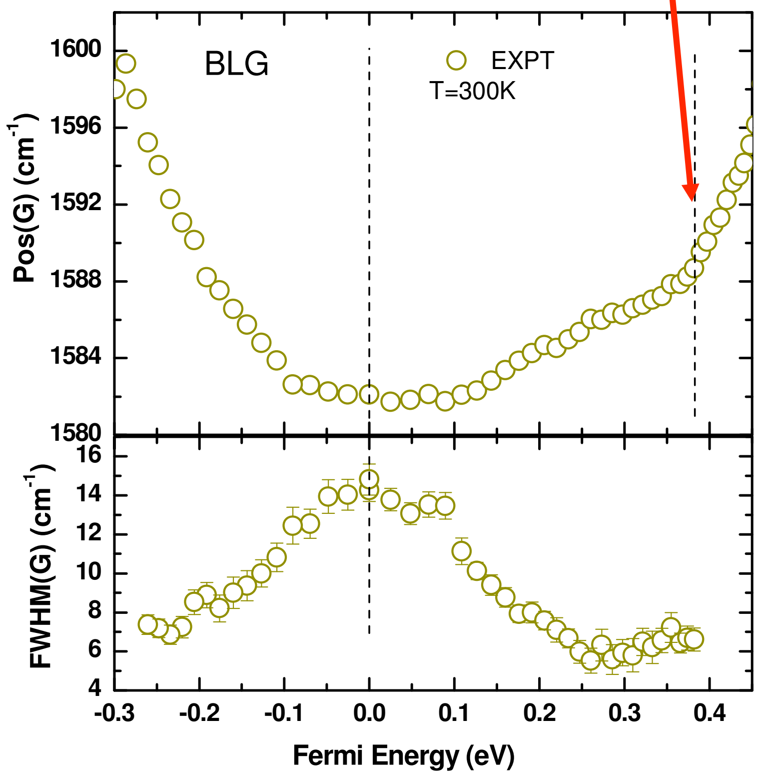
Single-layer Vs bi-layer

Bilayer graphene has a kink

It is most likely due to the filling of the second subband





Das et al. arXiv:0807:1631

Theoretical approach

$$\Pi(E_F)^{BLG} = \alpha' \int_0^\infty \gamma^2 k dk \sum_{s,s'} \sum_{j,j'} \phi^+{}_{jj'} \times \frac{[f(\epsilon_{sjk}) - f(\epsilon_{s'j'k})][\epsilon_{sjk} - \epsilon_{s'j'k}]}{(\epsilon_{sjk} - \epsilon_{s'j'k})^2 - (\hbar\omega_0 + i\delta)^2}$$

Phonon self energy in bilayer graphene

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

Blue →: positive contribution to Π

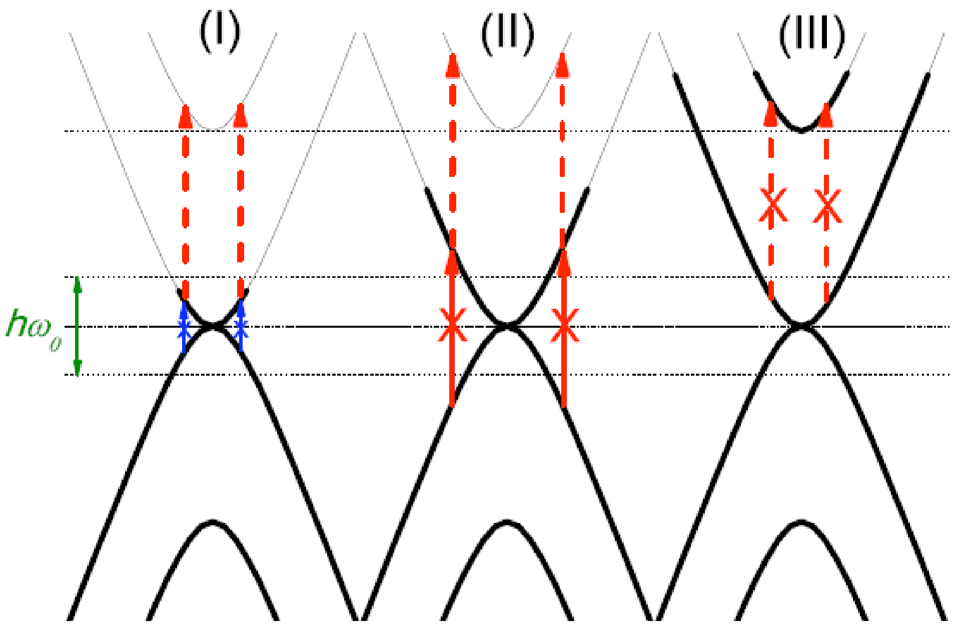
Red → negative contributions to Π

Solid → intraband process

Dashed → interband process

3 regions can be distinguished:

1. $E_F < h\omega$
2. $hw < E_F < \gamma_1$
3. $\gamma_1 < E_F$



Softening Hardening Stronger Hardening

Das et al. arXiv:0807:1631

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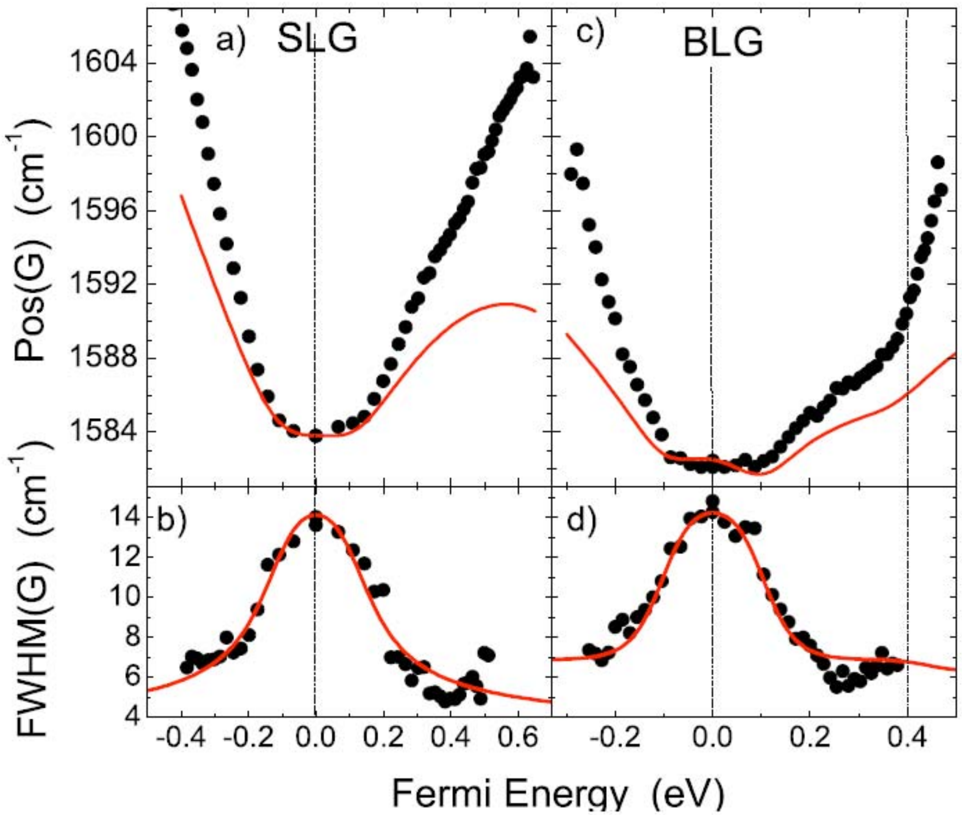
Theory Vs Experiment

Dynamic effects from the phonon self-energy + static corrections



The kink is a direct measure of γ_1

Das et al. arXiv:0807:1631

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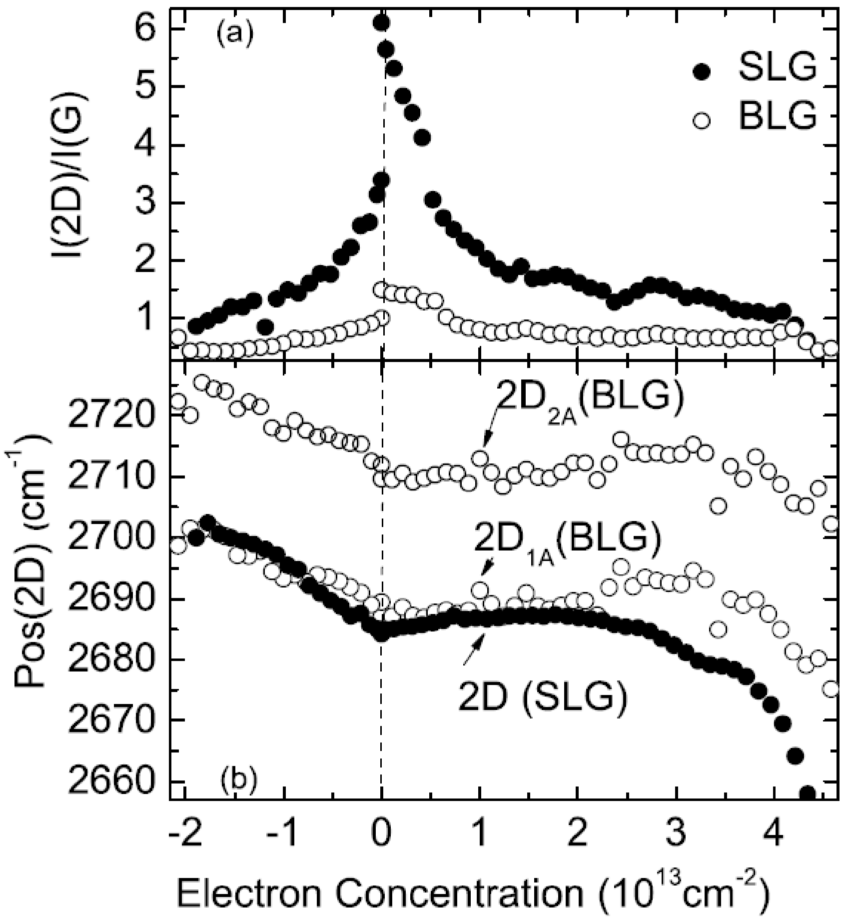
Intensity of the peaks in SLG and BLG



Das et al. arXiv:0807:1631

Conclusions

• The number of layers of graphene is reflected in its Raman spectrum

• The structure of the 2D band is due to the splitting of the electronic bands close to the Fermi energy

• The dependence of the G-peak position on doping is explained by effects beyond the Born Oppenheimer approximation

• An inhomogeneous distribution of charged impurities is normally present on graphene samples

•Non adiabatic effects also explain the doping dependence of the G peak in bilayer graphene and allow the experimental determination of γ_1

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