Raman characterization of graphene-based materials

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Graphene Nanophotonics, Besnasque, Spain, March 05 2013

Departamento de Física - ICEX

Raman characterization of graphene-based materials:

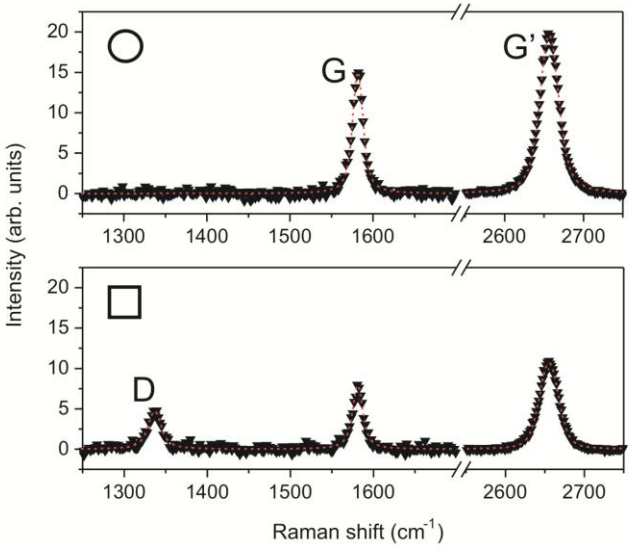
- Defect density
- Number of layers and stacking order
- Doping
- Strain
- Twist angle in superlattices

Raman spectrum of graphene:

One-phonon Raman bands:

$$\vec{k}_S = \vec{k}_0 - \vec{q}$$

$$q \sim 0$$



Two-phonon Raman bands:

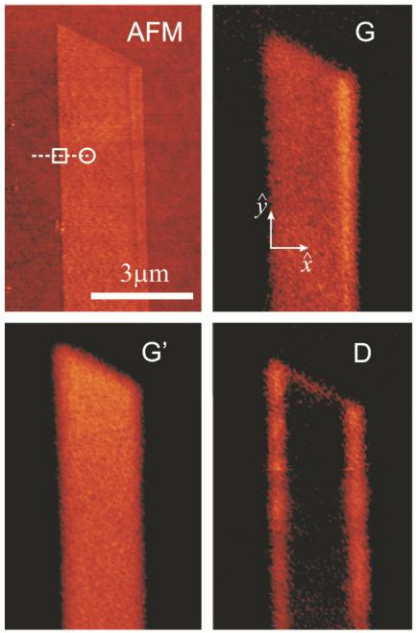
$$\vec{k}_S = \vec{k}_0 - \vec{q}_a - \vec{q}_b$$

$$\vec{q}_a \sim -\vec{q}_b$$

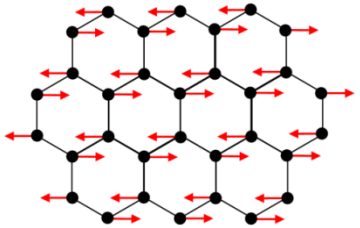
Disorder-induced one-phonon Raman bands:

$$\vec{k}_S = \vec{k}_0 - \vec{q} - \vec{d}$$

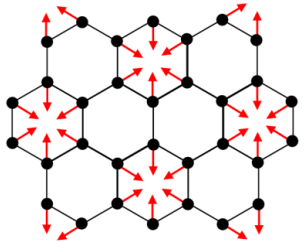
$$\vec{q} \sim -\vec{d}$$



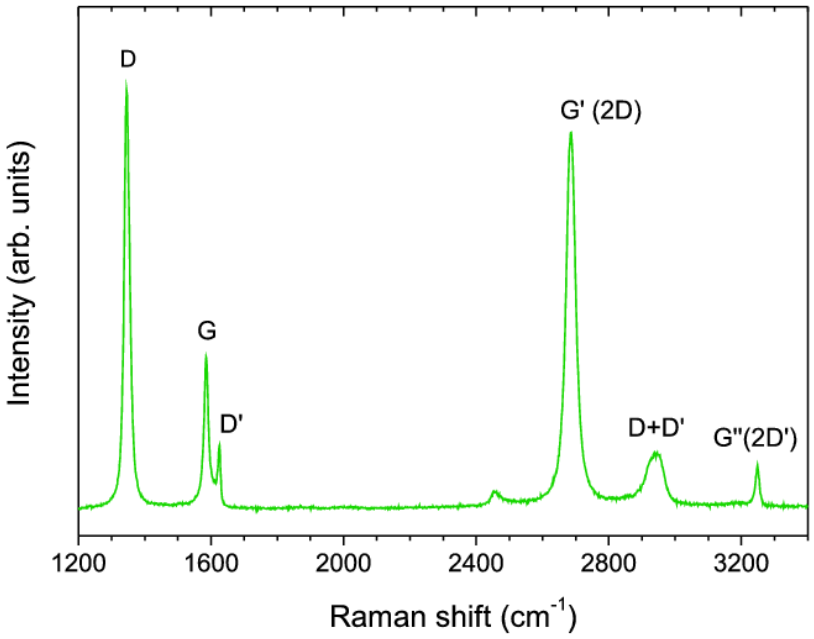
G band:



D and G' (2D) bands:

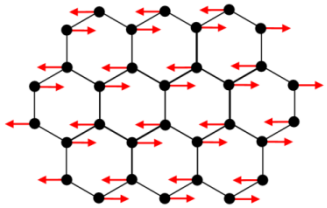


Raman spectrum of graphene:

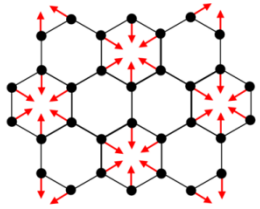


Tuinstra and Koenig. J. Phys. Chem. **53**, 1126 (1970).

G band:

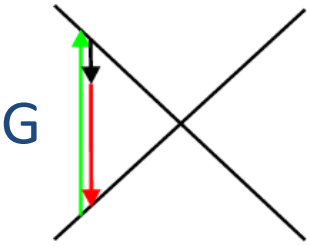


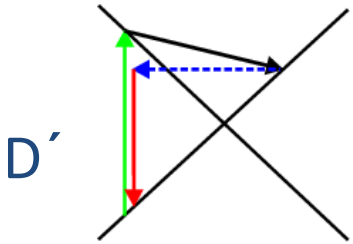
D and G' bands

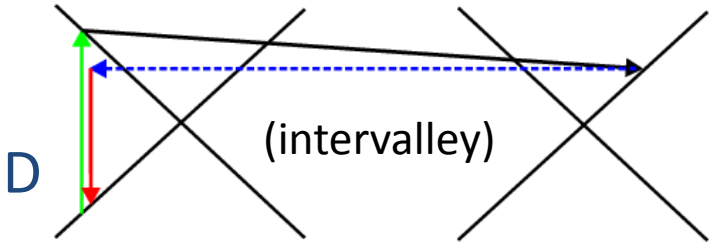


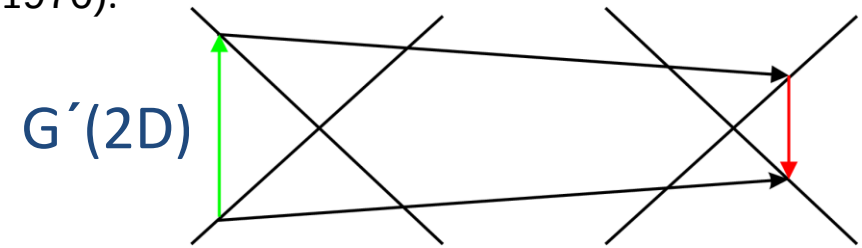
Thomsen and Reich, PRL **85**, 5214 (2000).
Saito et al., PRL **88**, 027401 (2002).

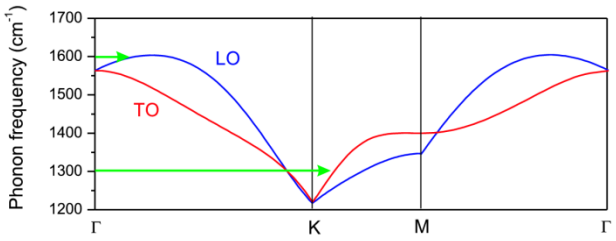
Venezuela, Lazzeri, and Mauri, PRB **84**, 035433 (2011).











Ion bombarded graphene

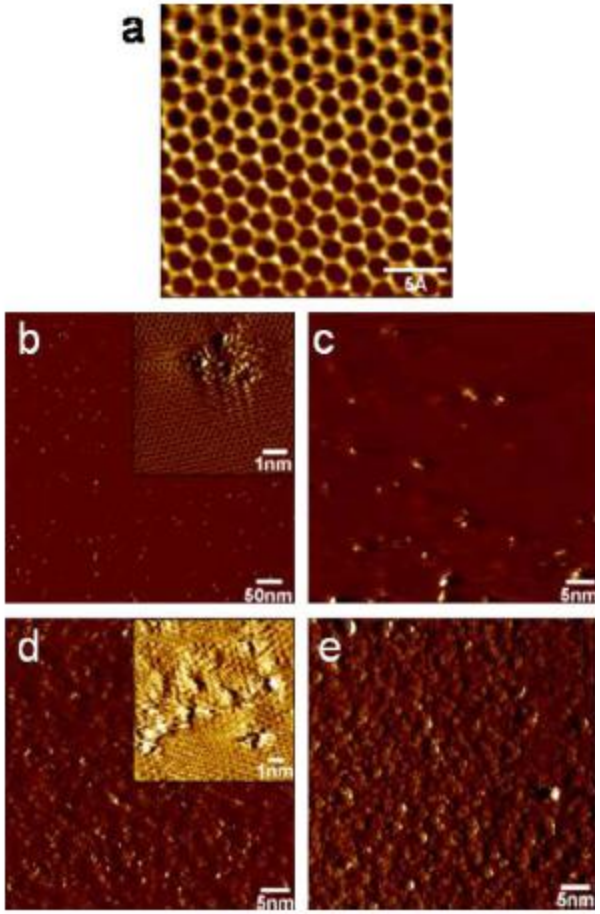
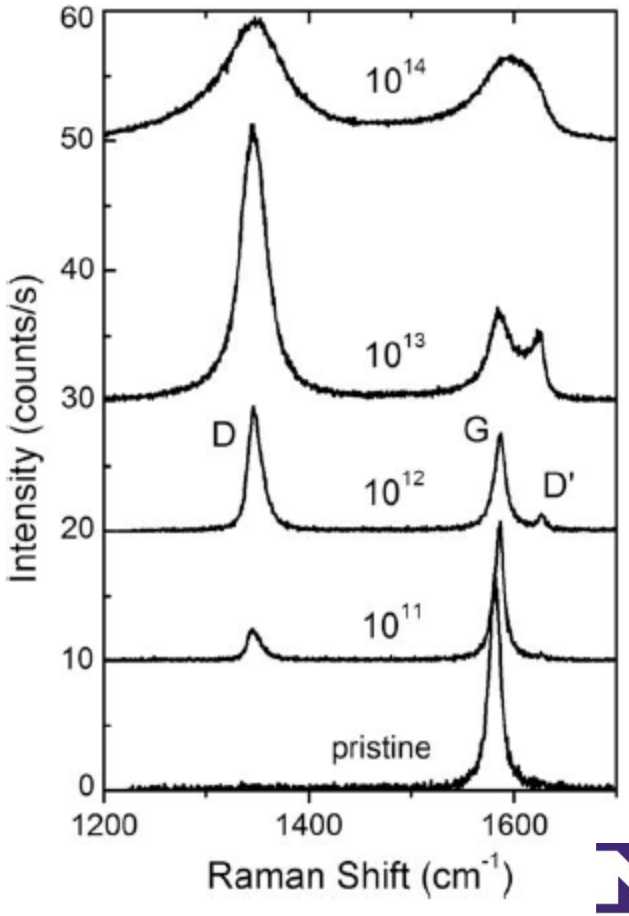


Fig. 1 – STM images of the surface of a bulk HOPG sample subjected to 90 eV Ar^+ ion bombardment. From (a–e) the panels display results at zero, 10^{11}, 10^{12}, 10^{13} and 10^{14} Ar^+/cm^2 ion doses. Insets to (b) and (d) show the detailed atomic structure of the defective areas at their respective ion doses.



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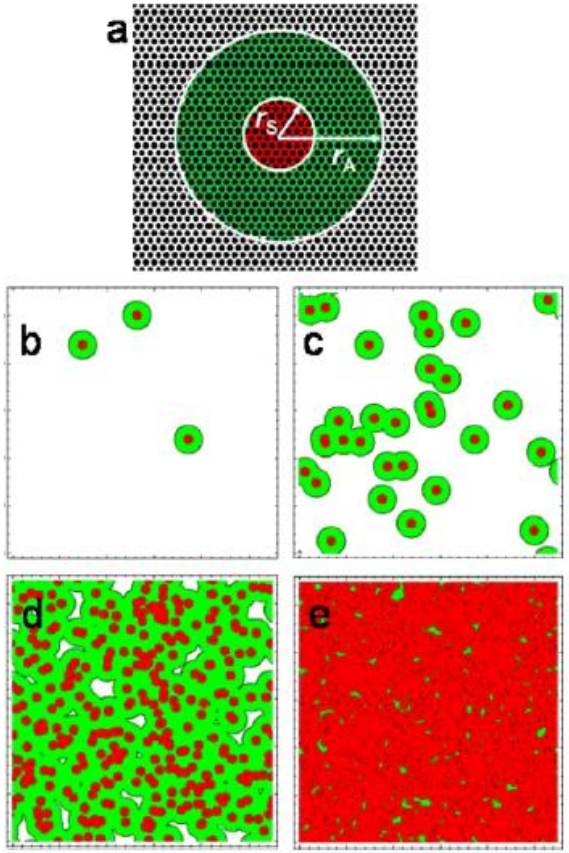
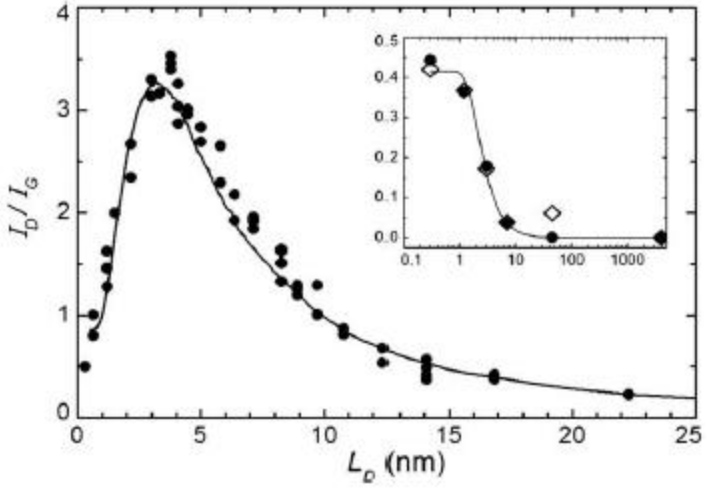
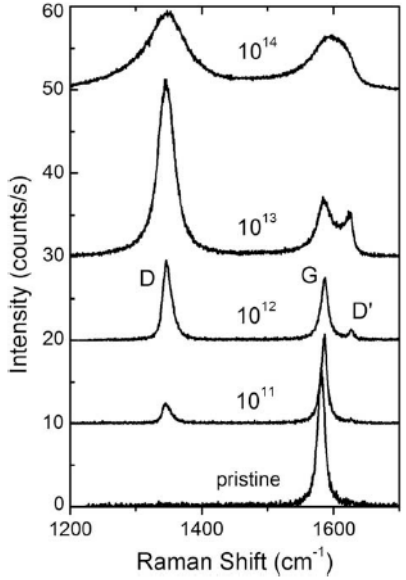
DE METROLOGIA, NORMALIZAÇÃO E
QUALIDADE INDUSTRIAL

Lucchese et al., Carbon, 48(5), 1592 (2010).

Model and results:







$C_A = 4.56$

$C_S = 0.86$

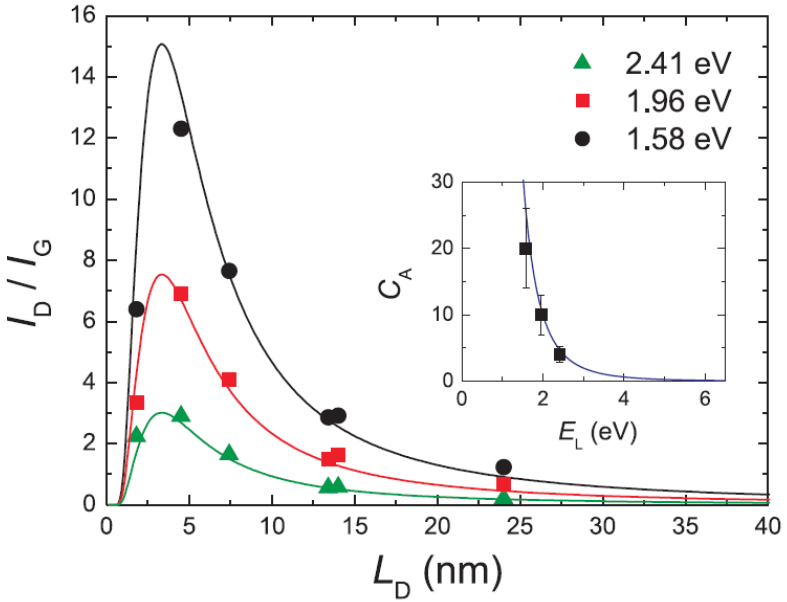
$r_A = 3$ nm

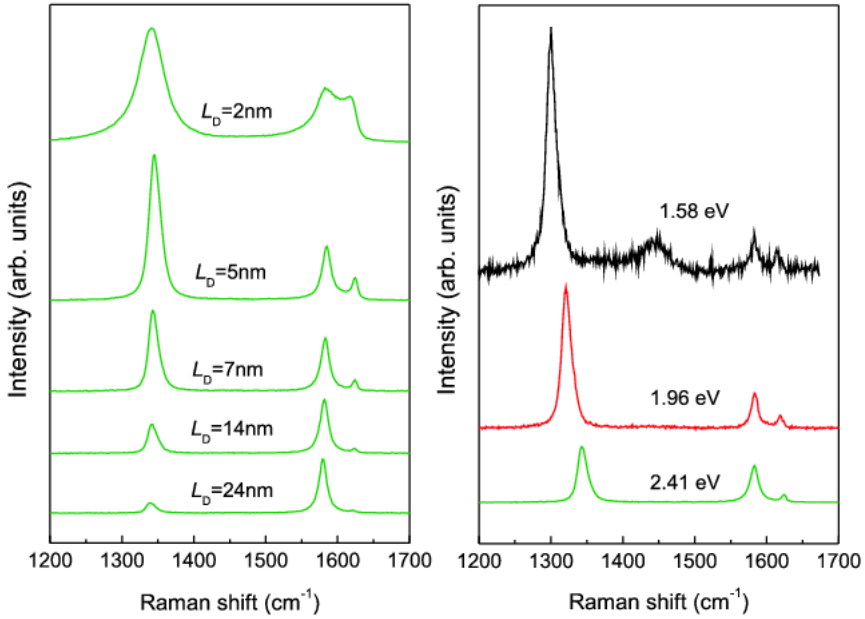
$r_S = 1$ nm

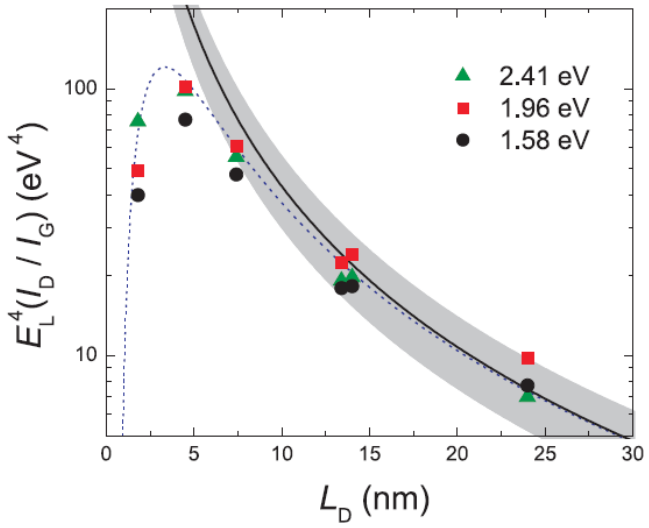
$$I_D/I_G = C_A \frac{r_A^2 - r_S^2}{r_A^2 - 2r_S^2}[\exp(-\pi r_S^2/L_D^2) - \exp(-\pi(r_A^2 - r_S^2)/L_D^2)] + C_S[1 - \exp(-\pi r_S^2/L_D^2)]$$

Lucchese et al., Carbon, 48(5), 1592 (2010).

Quantifying defects in graphene by Raman spectroscopy using diferent excitation laser energies





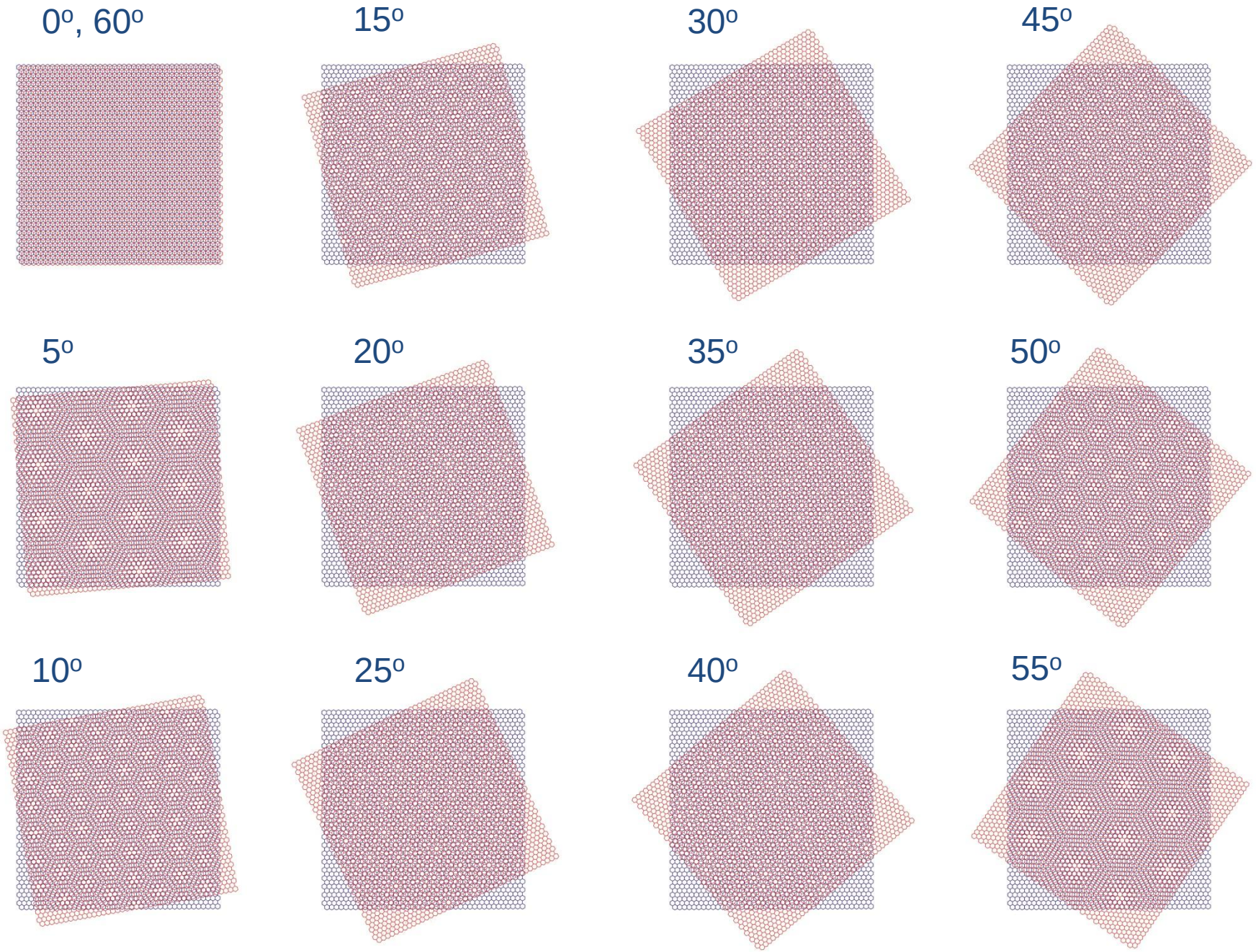


$$L_D^2\,(\mathrm{nm}^2) = \frac{(4.3 \pm 1.3) \times 10^3}{E_L^4} \left(\frac{I_D}{I_G}\right)^{-1}$$

$$n_D(\mathrm{cm}^{-2}) = (7.3 \pm 2.2) \times 10^9 E_L^4 \left(\frac{I_D}{I_G}\right)$$

Cançado et al., Nano Lett. 11(8), 3190 (2011).

Graphene superlattices: Moiré patterns



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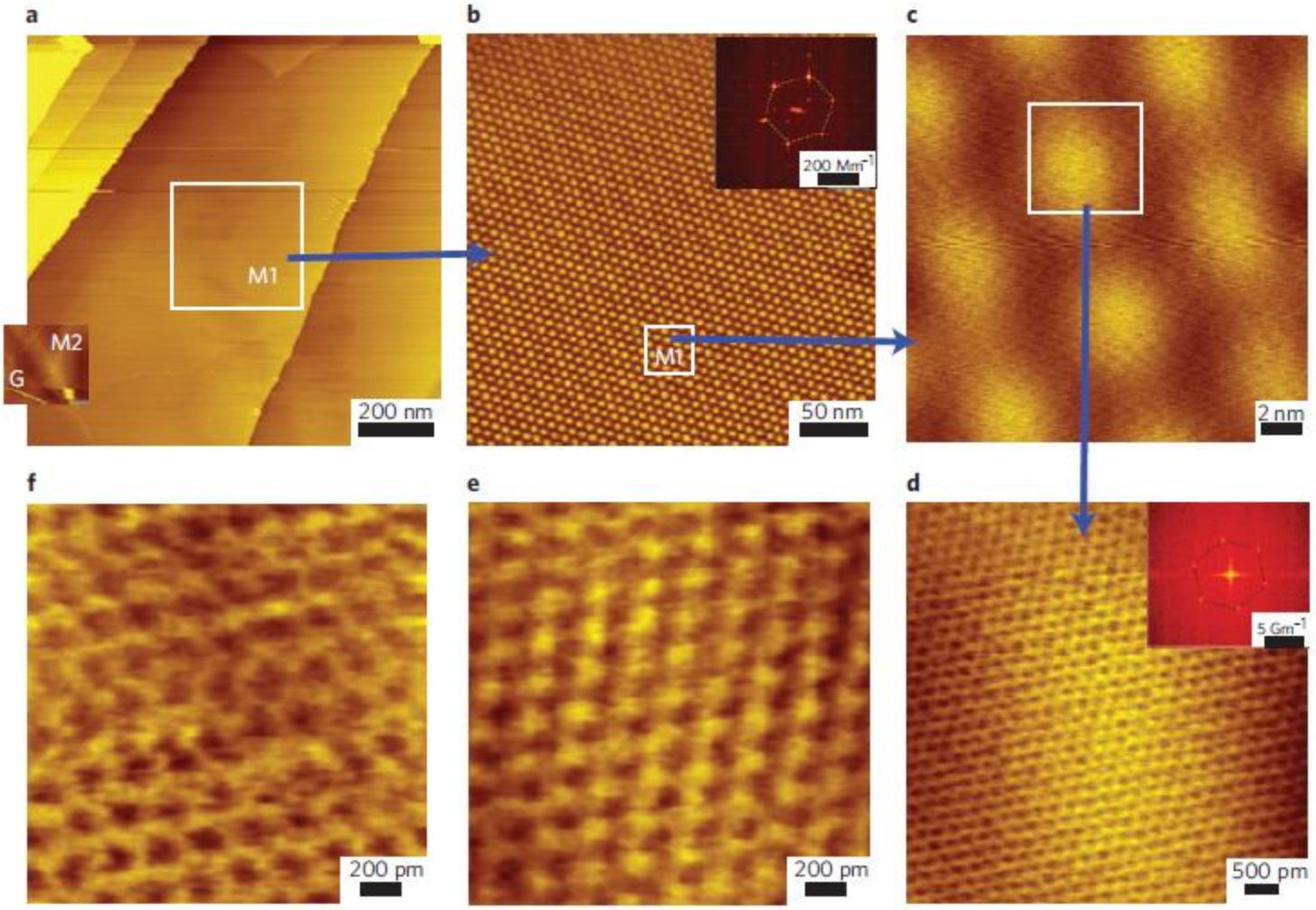
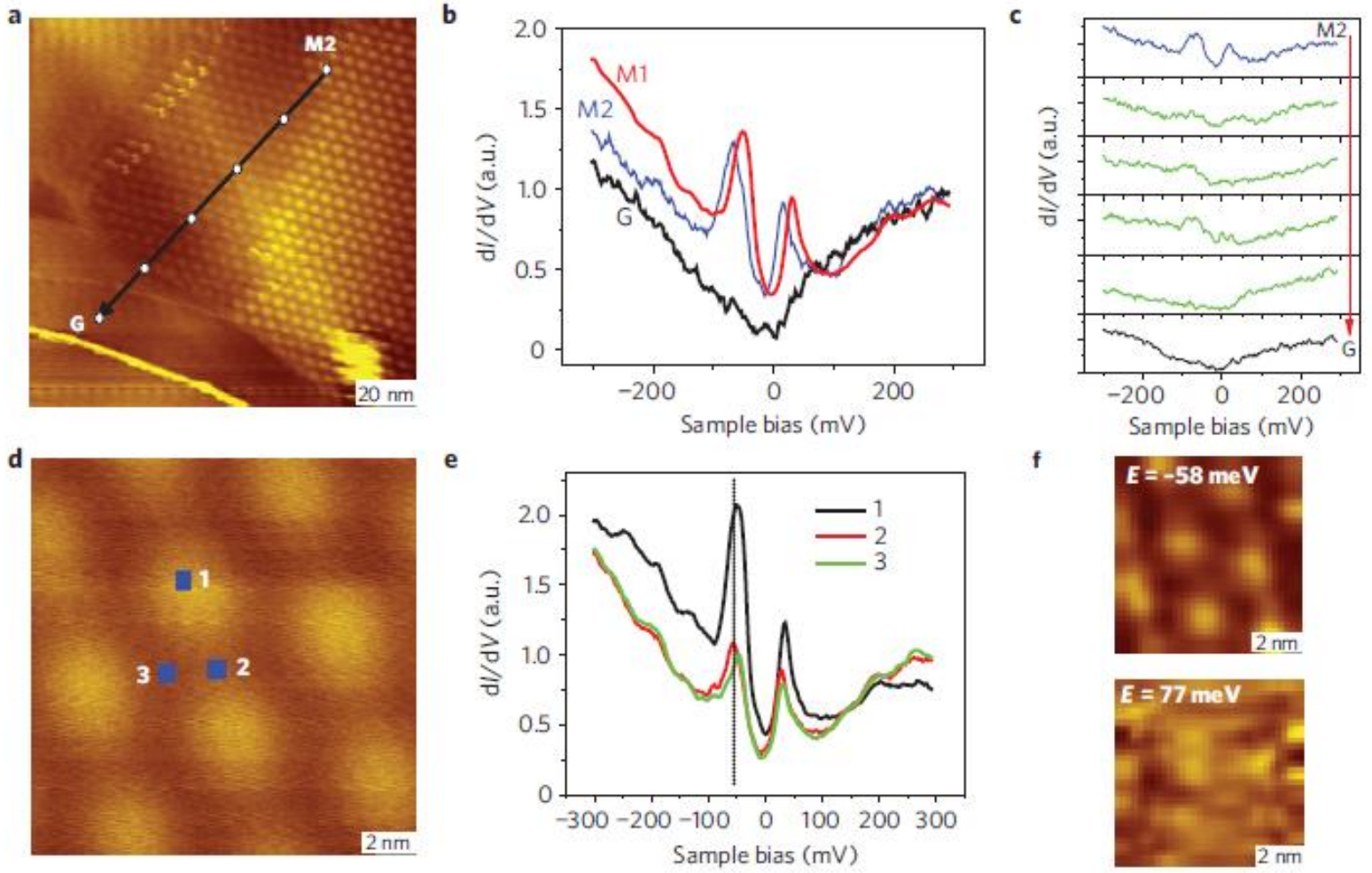
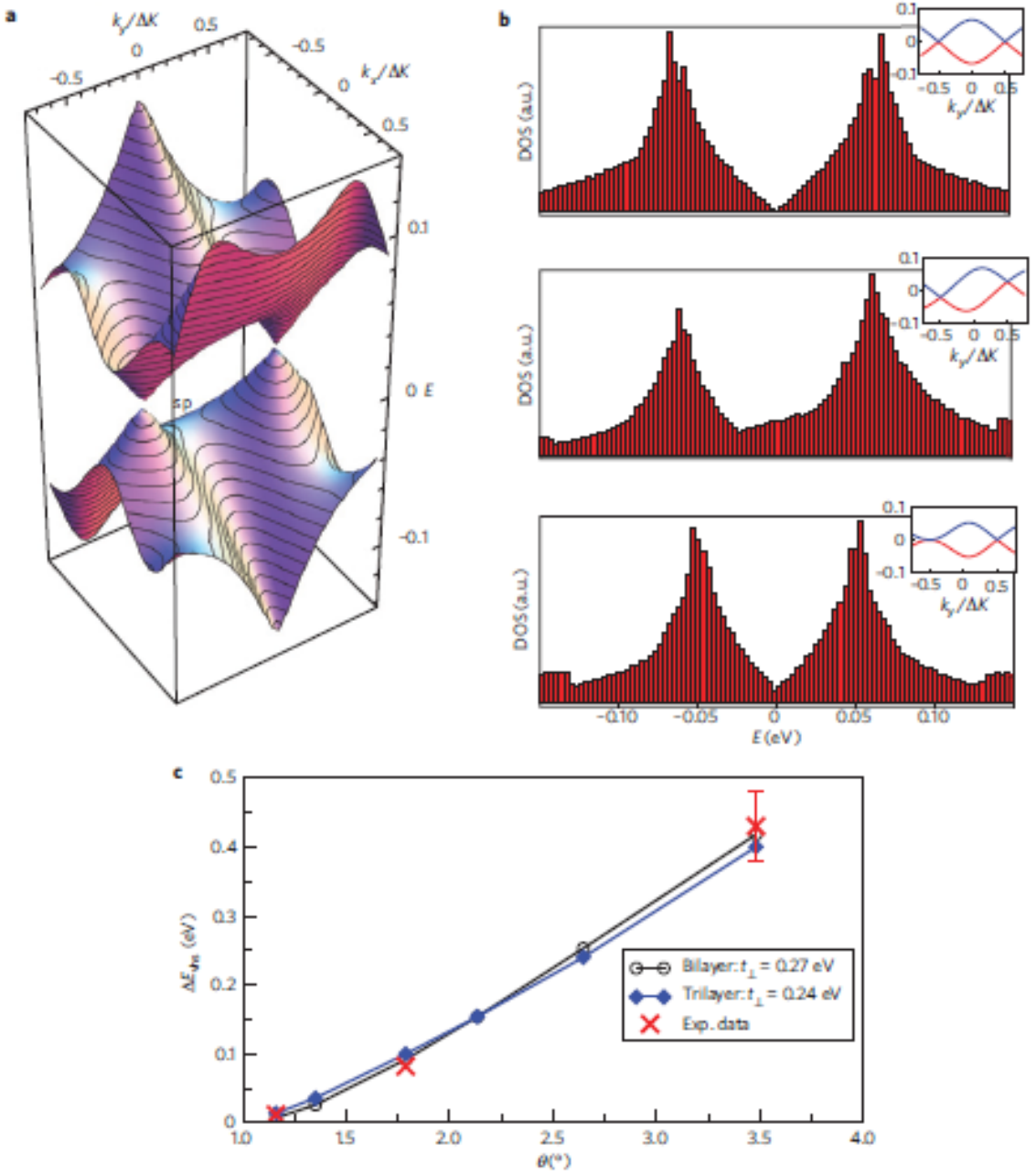
STM measurements



Li et al. Nature Physics **06**, 109 (2010).

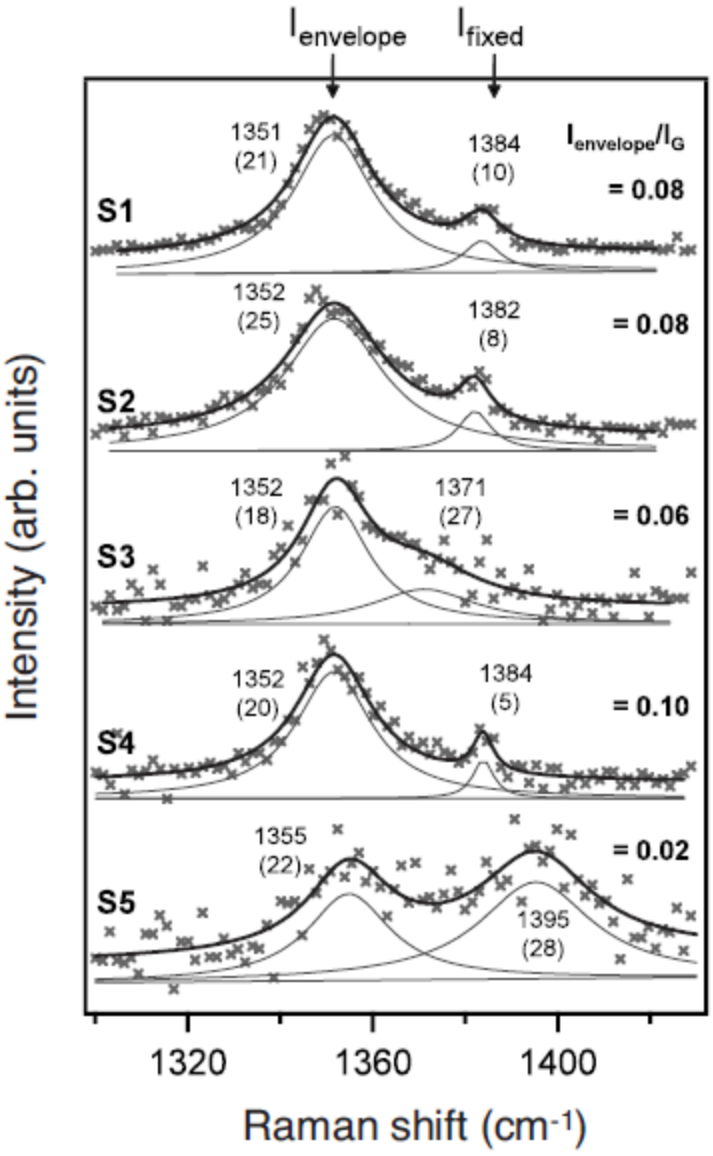


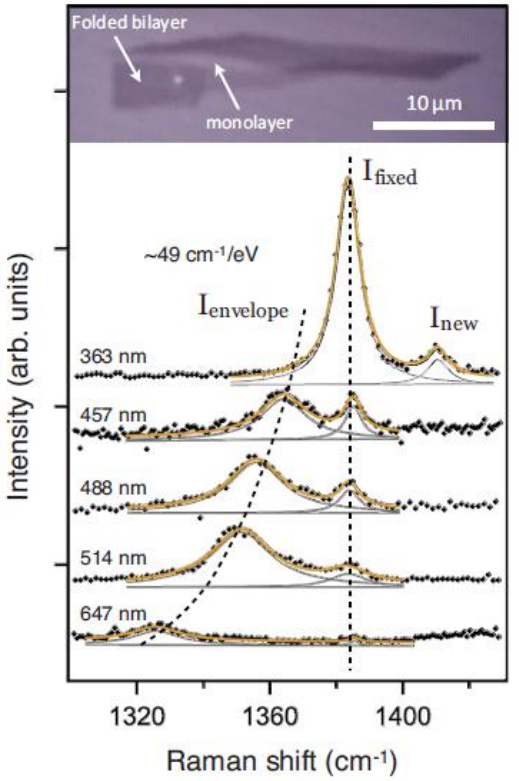
Li et al. Nature Physics **06**, 109 (2010).

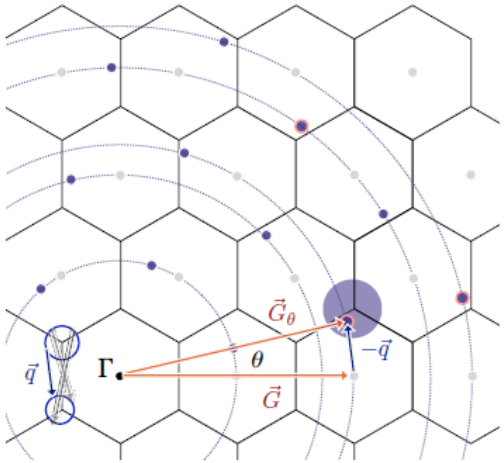


Li et al. Nature Physics **06**, 109 (2010).

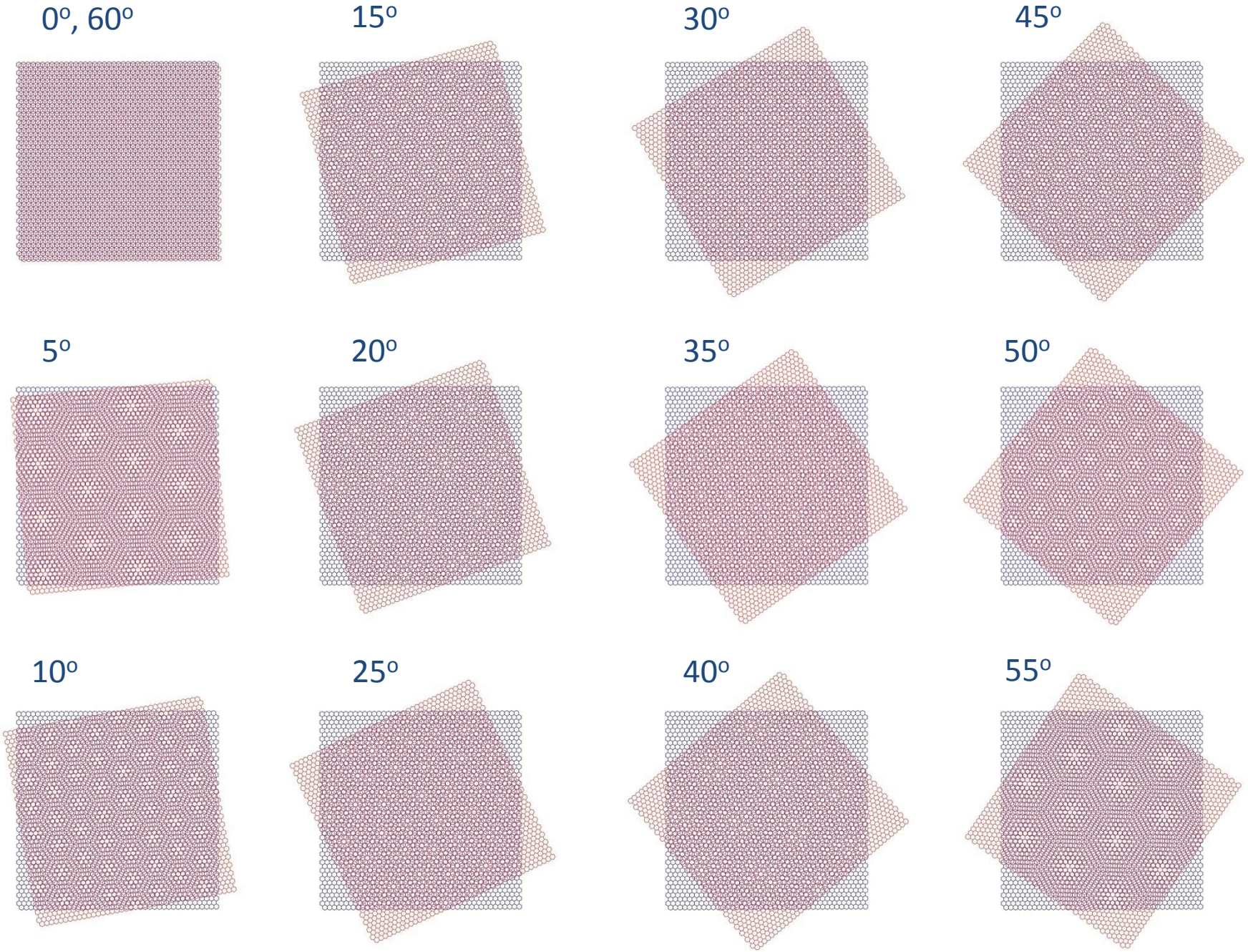
Raman spectrum of folded graphene:

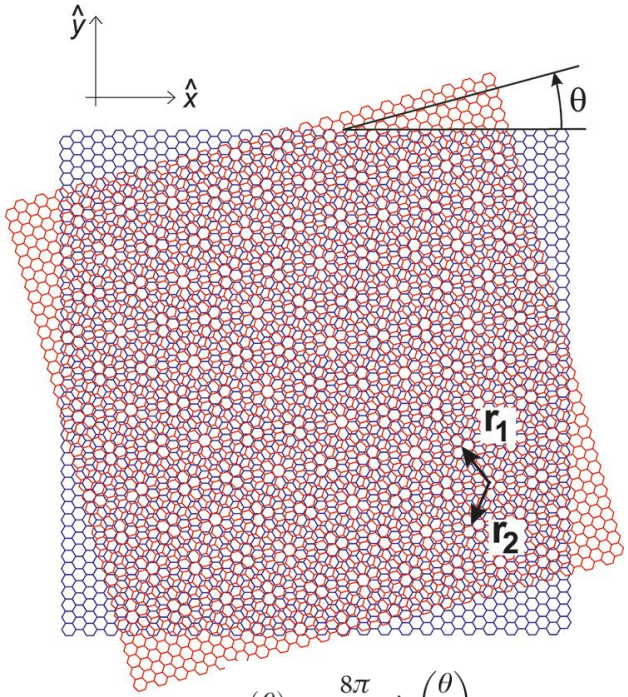




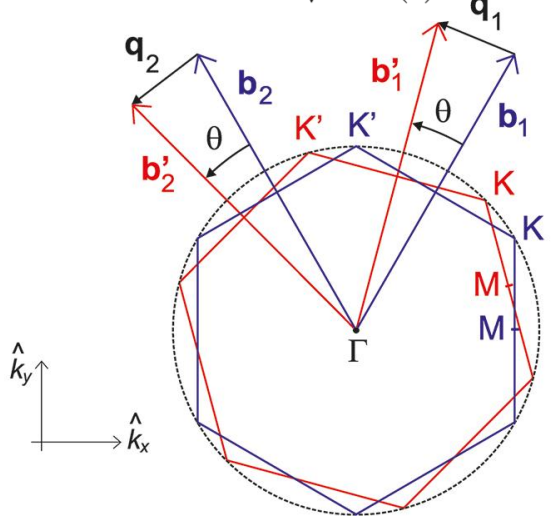


Gupta et al. PRB(R) **82**, 241406 (2010).


0º, 60º
15º
30º
45º
5º
20º
35º
50º
10º
25º
40º
55º



$$q(\theta) = \frac{8\pi}{\sqrt{3}a}\sin\left(\frac{\theta}{2}\right)$$



$$\mathbf{b}_1 = (2\pi/a)\left[(\sqrt{3}/3)\hat{\mathbf{k}}_\mathbf{x} + \hat{\mathbf{k}}_\mathbf{y}\right]$$

$$\mathbf{b}_2 = (2\pi/a)\left[-(\sqrt{3}/3)\hat{\mathbf{k}}_\mathbf{x} + \hat{\mathbf{k}}_\mathbf{y}\right]$$

$$\mathbf{b}'_1(\theta) = \frac{2\pi}{\sqrt{3}a}\left[\left(\cos\theta - \sqrt{3}\sin\theta\right)\hat{\mathbf{k}}_\mathbf{x} + \left(\sqrt{3}\cos\theta + \sin\theta\right)\hat{\mathbf{k}}_\mathbf{y}\right],$$

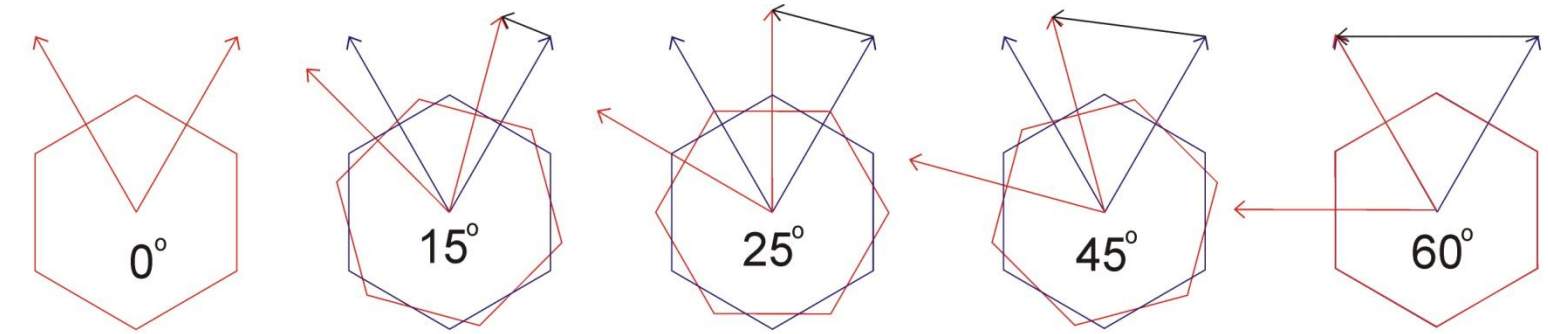
$$\mathbf{b}'_2(\theta) = \frac{2\pi}{\sqrt{3}a}\left[\left(-\cos\theta - \sqrt{3}\sin\theta\right)\hat{\mathbf{k}}_\mathbf{x} + \left(\sqrt{3}\cos\theta - \sin\theta\right)\hat{\mathbf{k}}_\mathbf{y}\right].$$

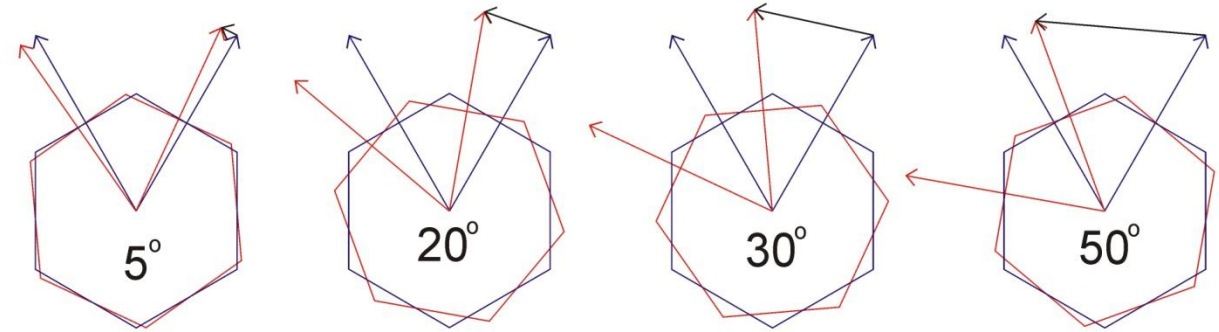
$$\mathbf{q}_1 = \mathbf{b}'_1 - \mathbf{b}_1 \qquad \mathbf{q}_2 = \mathbf{b}'_2 - \mathbf{b}_2$$

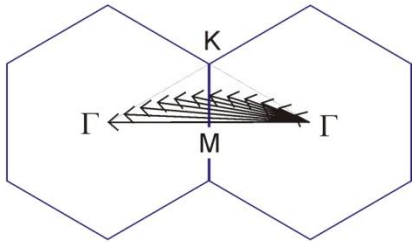
$$\mathbf{q}_1(\theta) = \frac{2\pi}{\sqrt{3}a}\left\{\left[-(1-\cos\theta) - \sqrt{3}\sin\theta\right]\hat{\mathbf{k}}_\mathbf{x} + \left[-\sqrt{3}(1-\cos\theta) + \sin\theta\right]\hat{\mathbf{k}}_\mathbf{y}\right\},$$

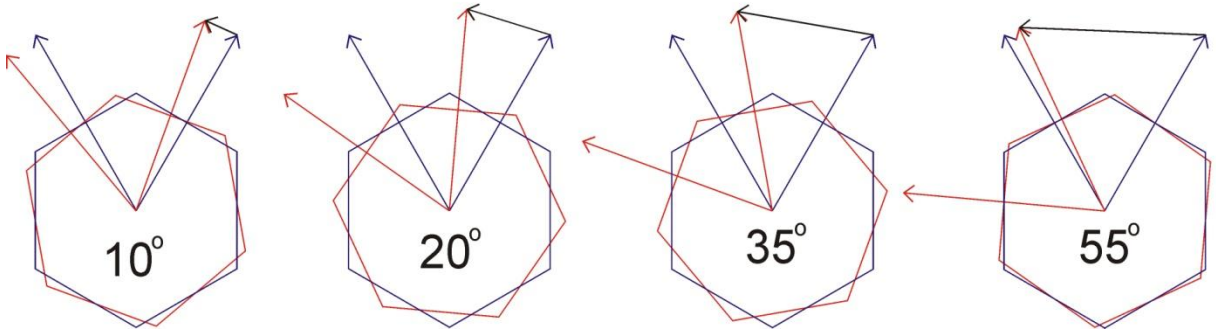
$$\mathbf{q}_2(\theta) = \frac{2\pi}{\sqrt{3}a}\left\{\left[(1-\cos\theta) - \sqrt{3}\sin\theta\right]\hat{\mathbf{k}}_\mathbf{x} + \left[-\sqrt{3}(1-\cos\theta) - \sin\theta\right]\hat{\mathbf{k}}_\mathbf{y}\right\}.$$

Carozo et al., Nano Lett. **11**, 4527 (2011).





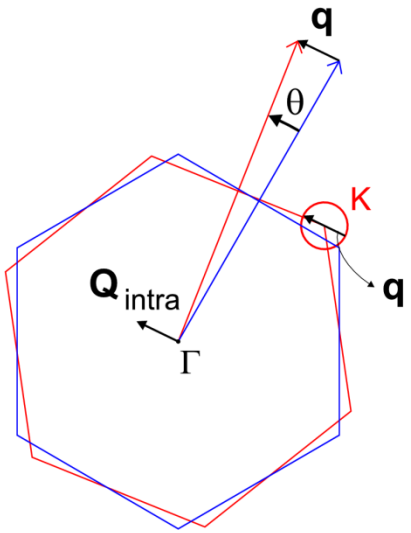


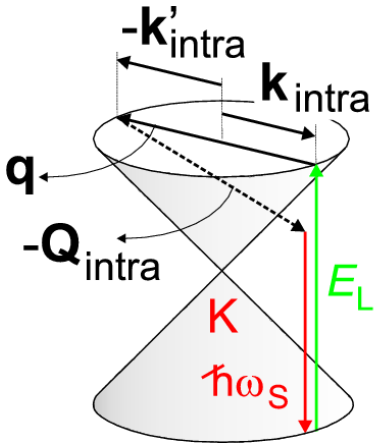


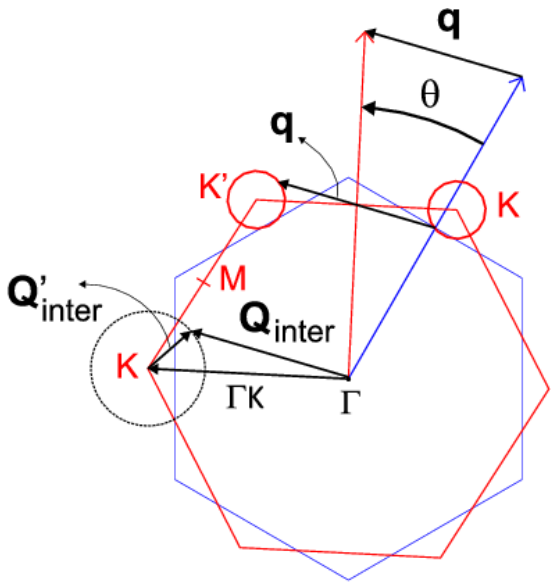
$$q(\theta) = \frac{8\pi}{\sqrt{3}a}\sin\left(\frac{\theta}{2}\right)$$

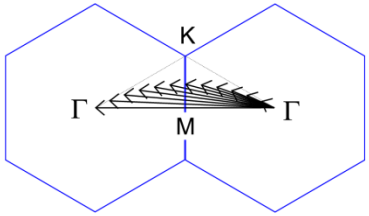
$$\mathbf{q}_1(\theta) = \frac{2\pi}{\sqrt{3}a}\left\{\left[-(1-\cos\theta) - \sqrt{3}\sin\theta\right]\hat{\mathbf{k}}_\mathbf{x} + \left[-\sqrt{3}(1-\cos\theta) + \sin\theta\right]\hat{\mathbf{k}}_\mathbf{y}\right\}$$

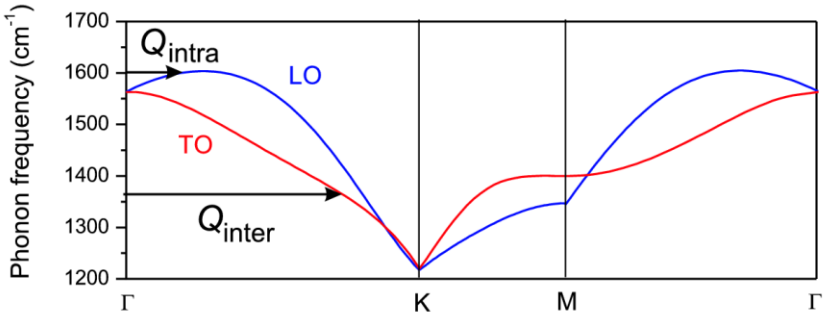
Rotation-induced intravalley and intervalley resonance scattering:

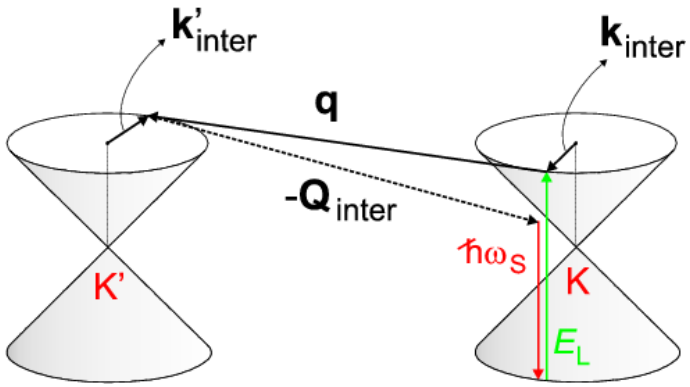








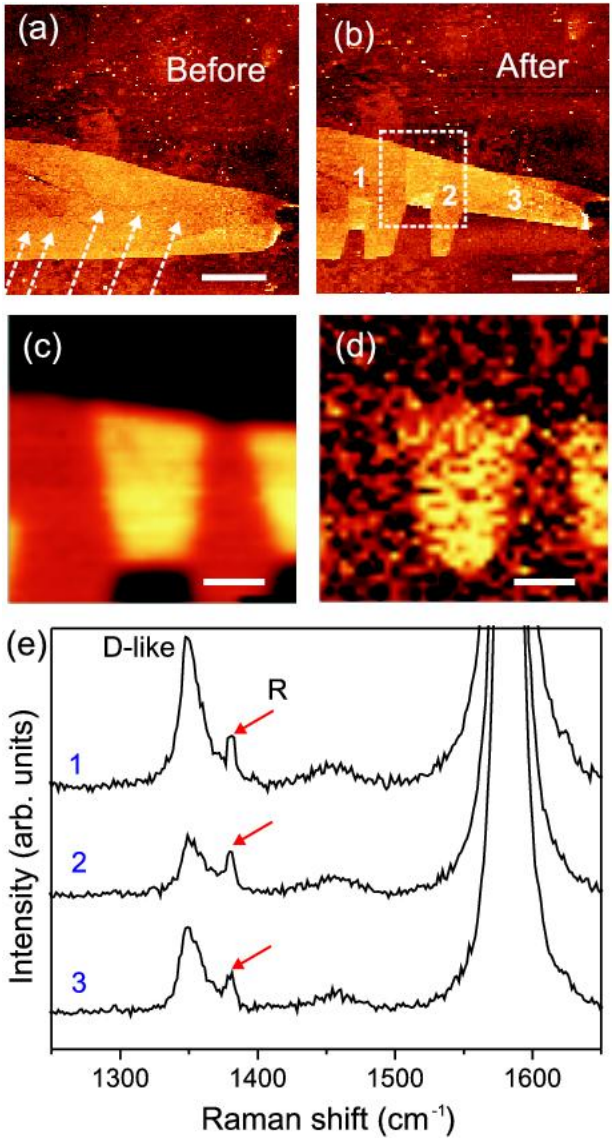




Venezuela, Lazzeri, and Mauri, PRB **84**, 035433 (2011).

Carozo et al., Nano Lett. **11**, 4527 (2011).

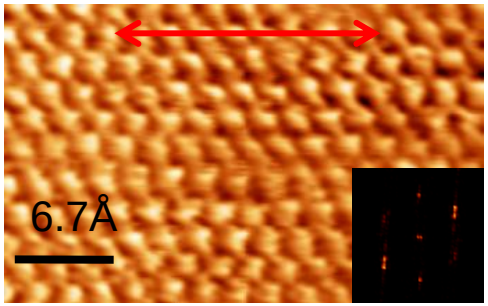
Production of folded graphene:



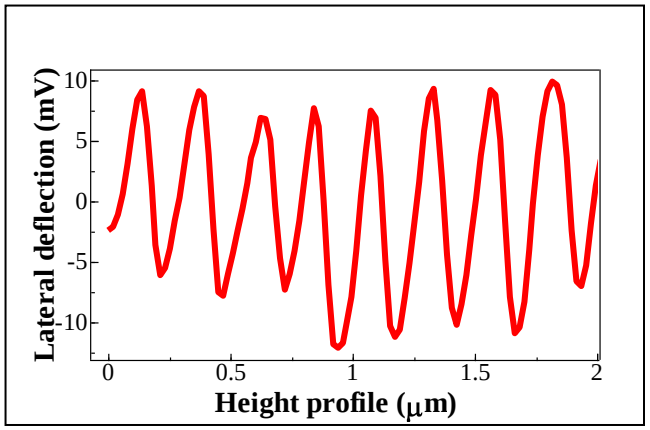
Carozo et al., submitted.

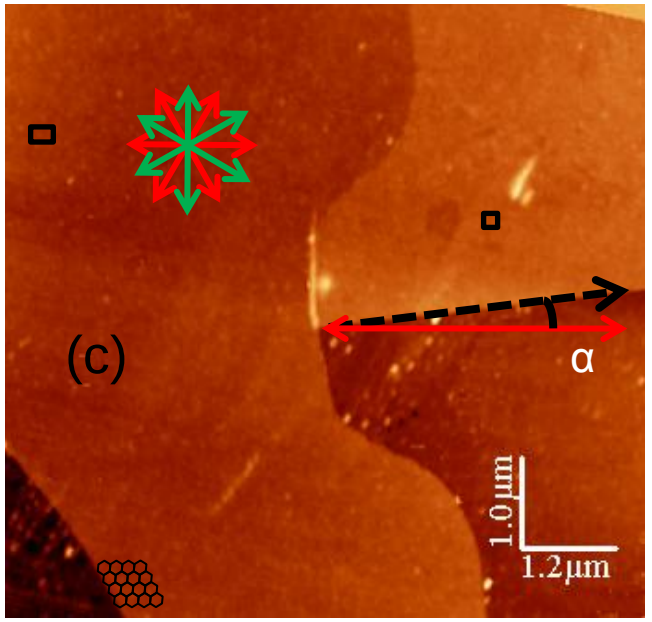
Lattice-resolution AFM characterization

(a)

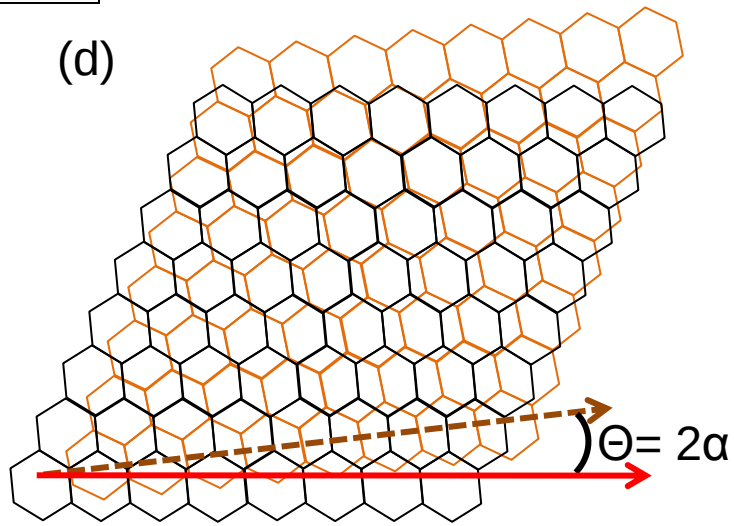


(b)

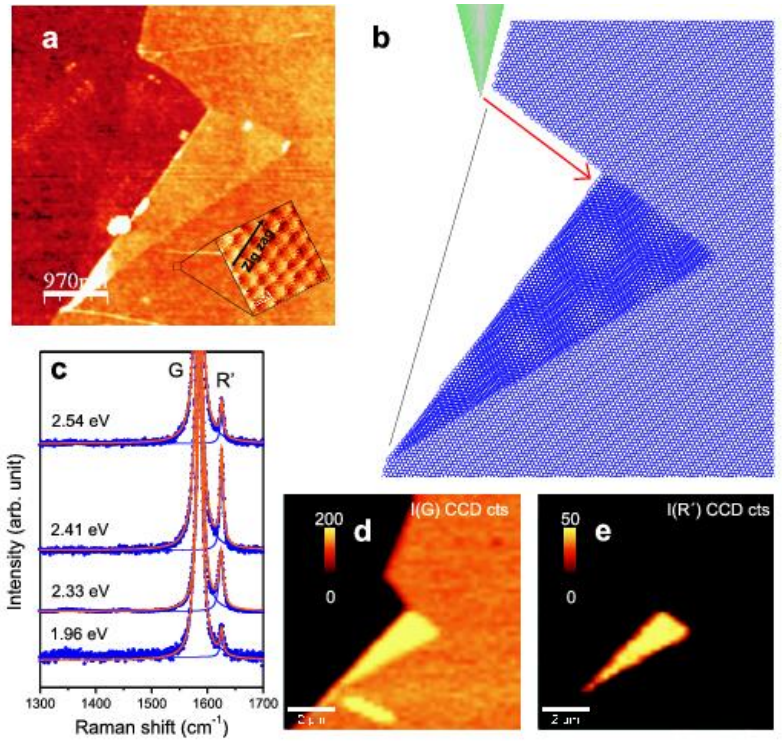


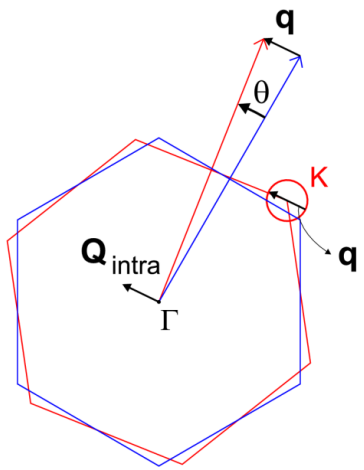


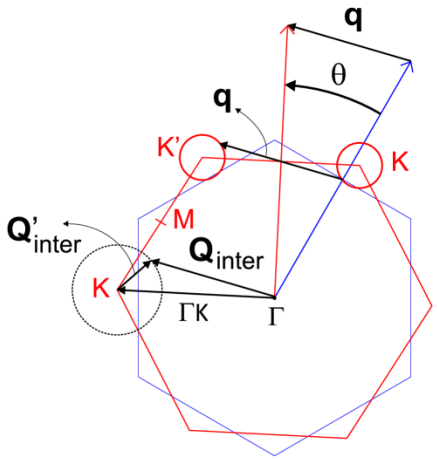
(d)



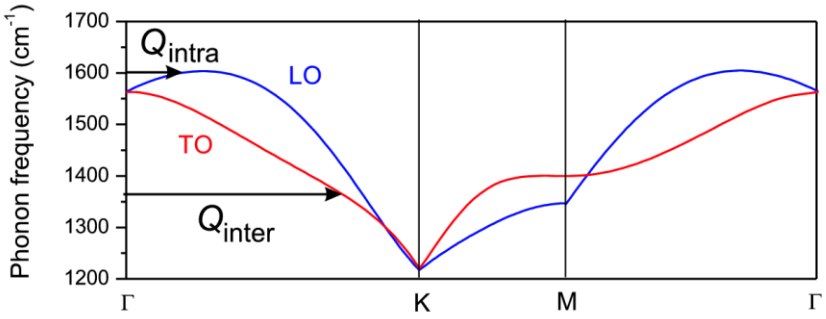
C. Ameida et al. JAP **110**, 086101 (2011).







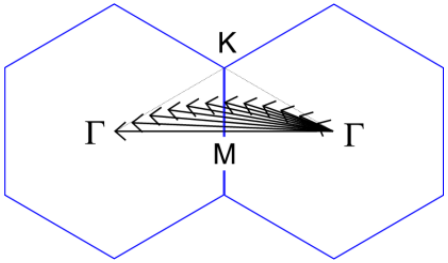
Carozo et al., Nano Lett. **11**, 4527 (2011).

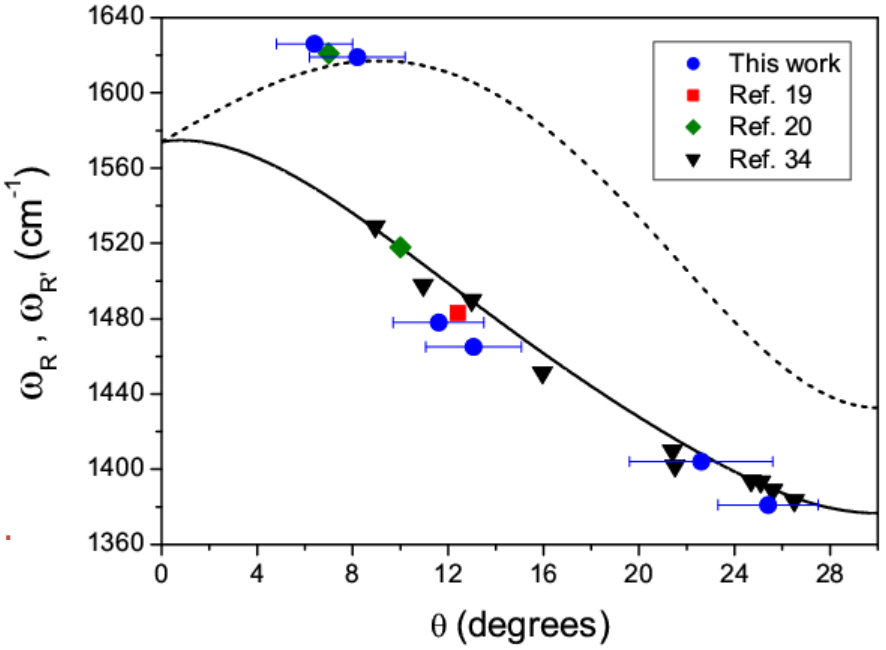


Venezuela, Lazzeri, and Mauri, PRB **84**, 035433 (2011).

$$\boldsymbol{q} = \frac{2\pi}{\sqrt{3}a}\{[-(1-cos\theta) - \sqrt{3}sin\theta]\hat{k}_x + [-\sqrt{3}(1-cos\theta) + sin\theta]\hat{k}_y\},$$

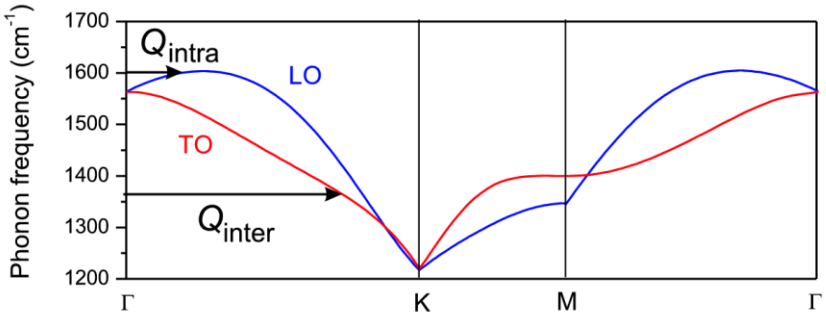
Carozo et al., Nano Lett. **11**, 4527 (2011).





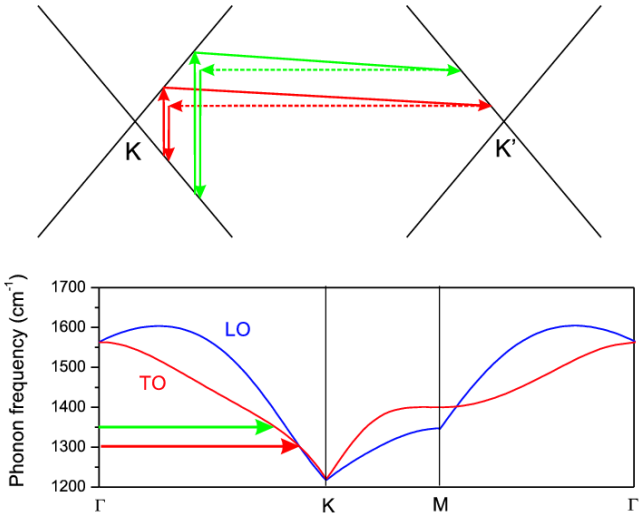
Carozo et al., submitted.

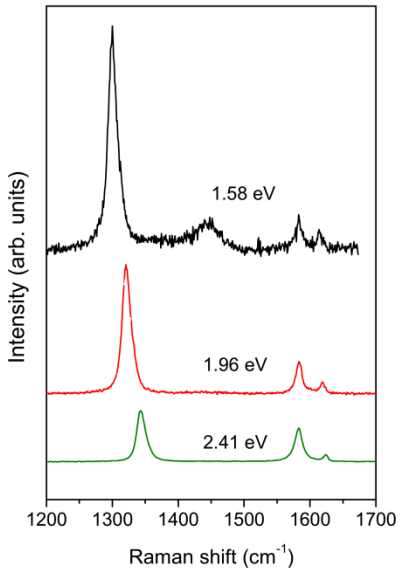
◇ Kim et al., PRL **108**, 246103 (2012).
□ Havener et al., Nano Lett. **12**, 3162 (2012).
▽ Wang et al., arXiv:1301.4488v1 (2013).



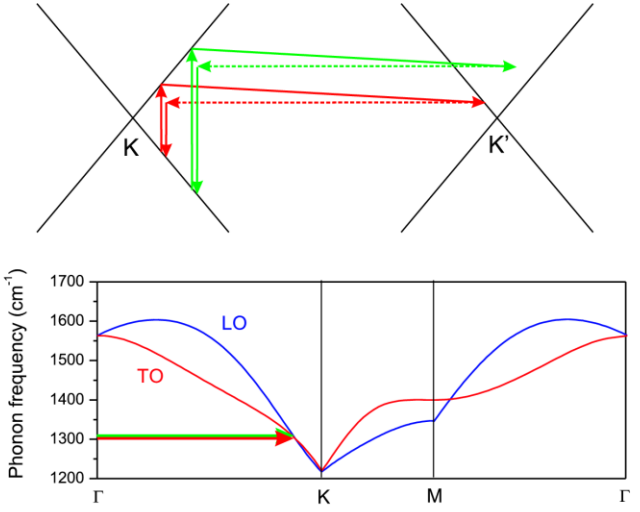
Venezuela, Lazzeri, and Mauri, PRB **84**, 035433 (2011).

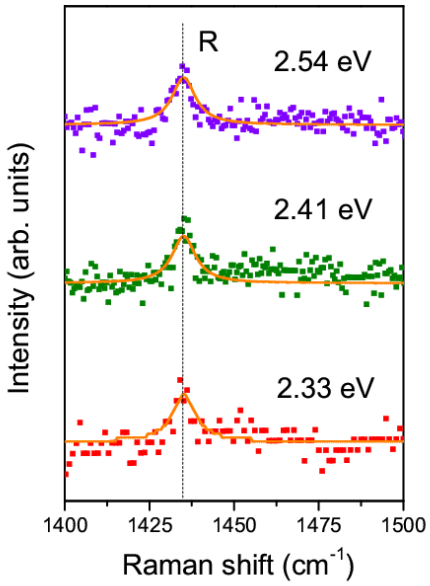
D band dispersion

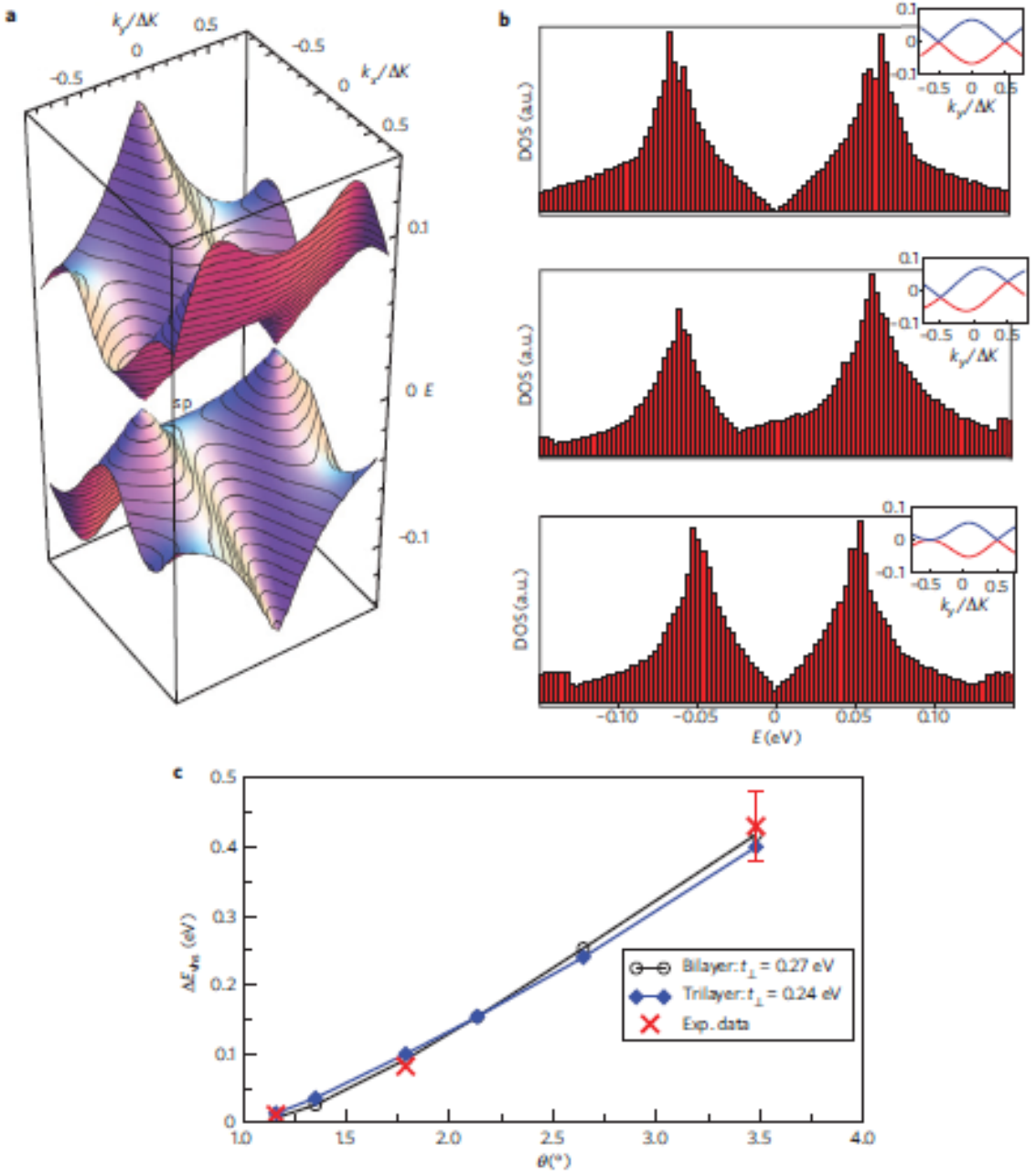




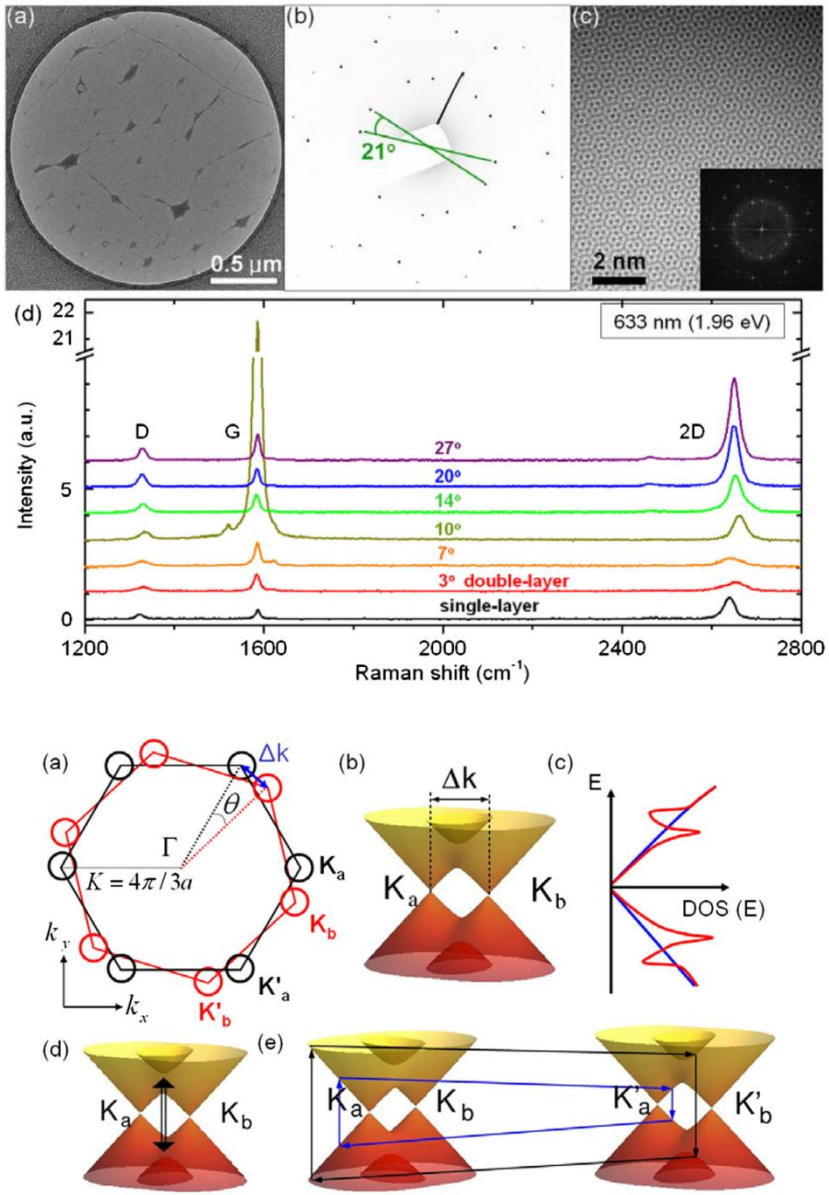
R and R' bands are not dispersive



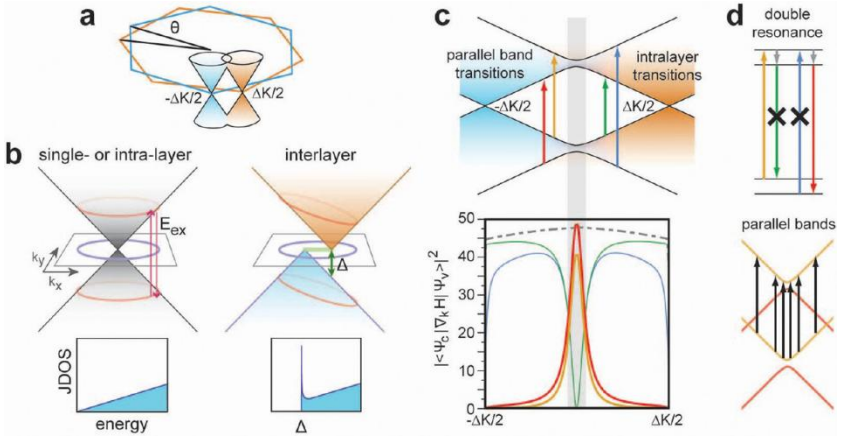


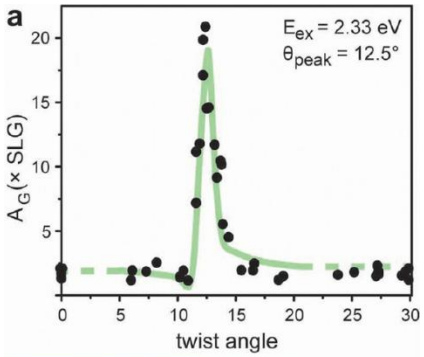


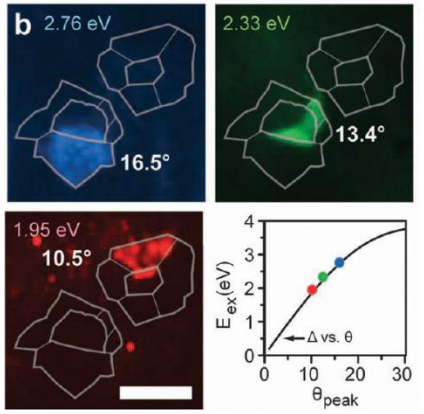
Li et al. Nature Physics **06**, 109 (2010).



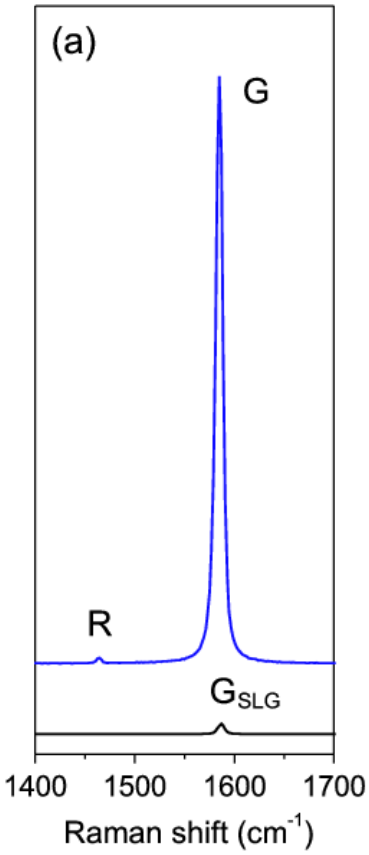
Kim et al., PRL **108**, 246103 (2012).

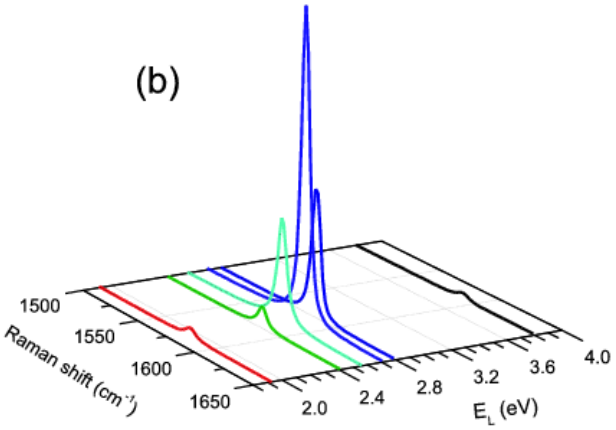


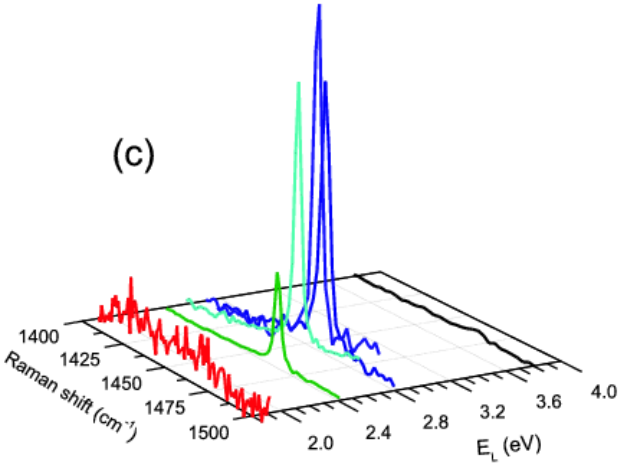


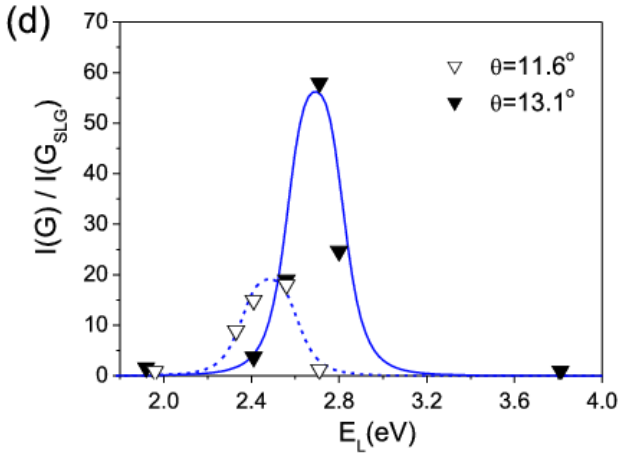


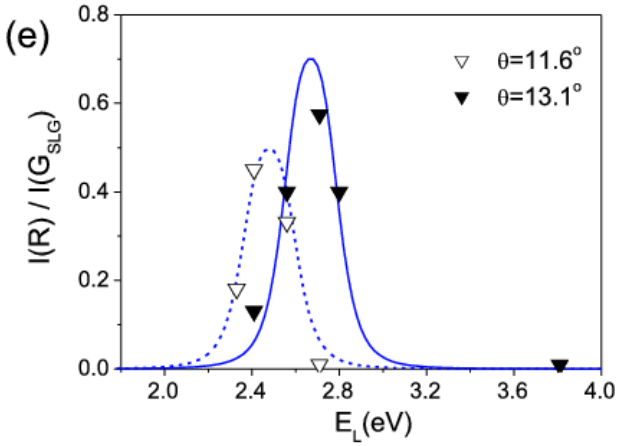
Havener et al., Nano Lett. **12**, 3162 (2012).











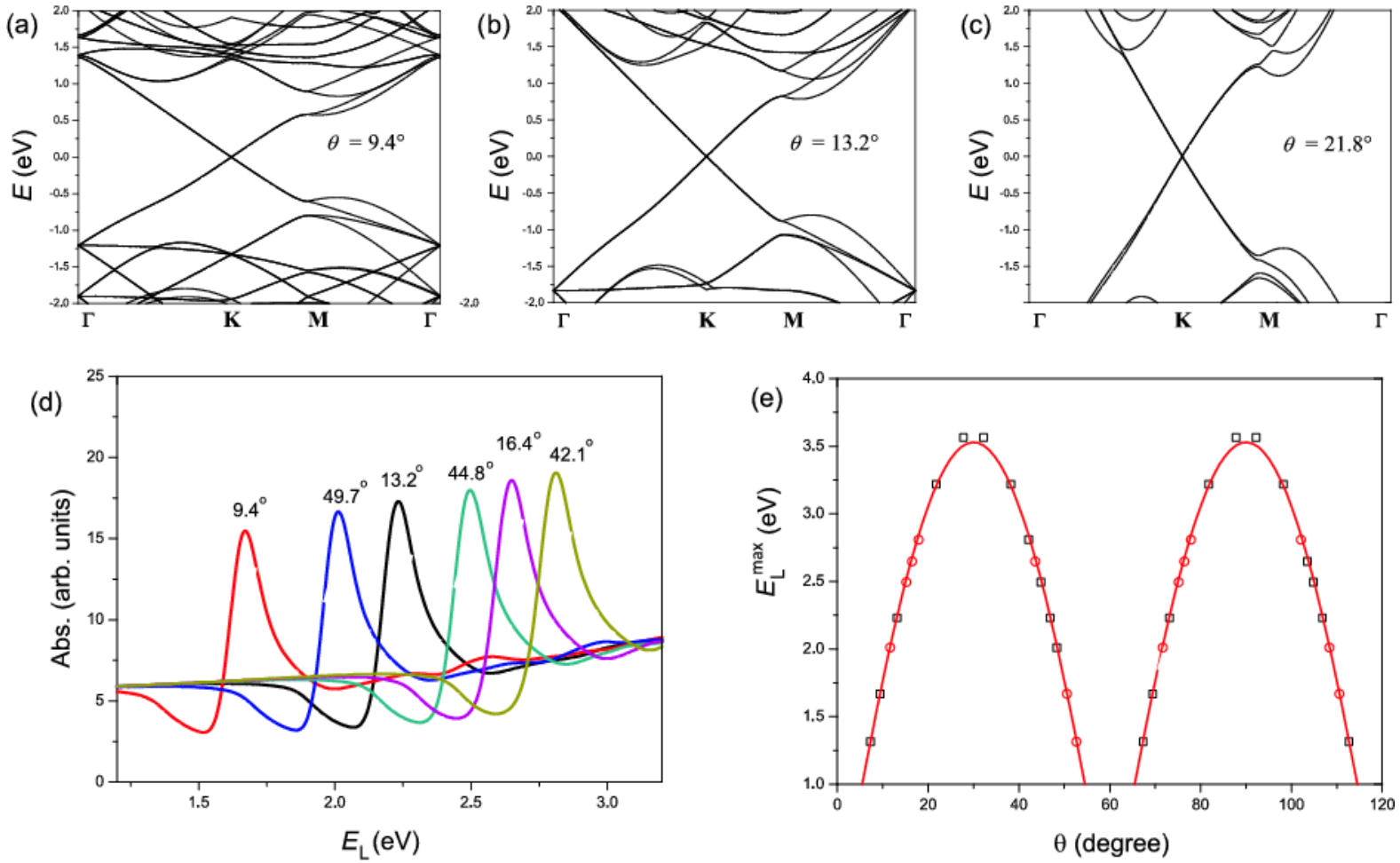
$$\frac{I(G)}{I(G_{\mathrm{SLG}})} = \left| \frac{M}{(E_{\mathrm{L}} - E_{\mathrm{vHs}} - i\gamma)(E_{\mathrm{L}} - E_{\mathrm{vHs}} - \hbar\omega_{\mathrm{G}} - i\gamma)} \right|^2$$

$\gamma = 0.12\,\mathrm{eV}$

$$\frac{I(R)}{I(G_{\mathrm{SLG}})} = \left| \frac{M'}{(E_{\mathrm{L}} - E_{\mathrm{vHs}} - i\gamma)[E_{\mathrm{L}} - E_{\mathrm{eh}}(k+q) - i\gamma](E_{\mathrm{L}} - E_{\mathrm{vHs}} - \hbar\omega_{\mathrm{R}} - i\gamma)} \right|^2$$

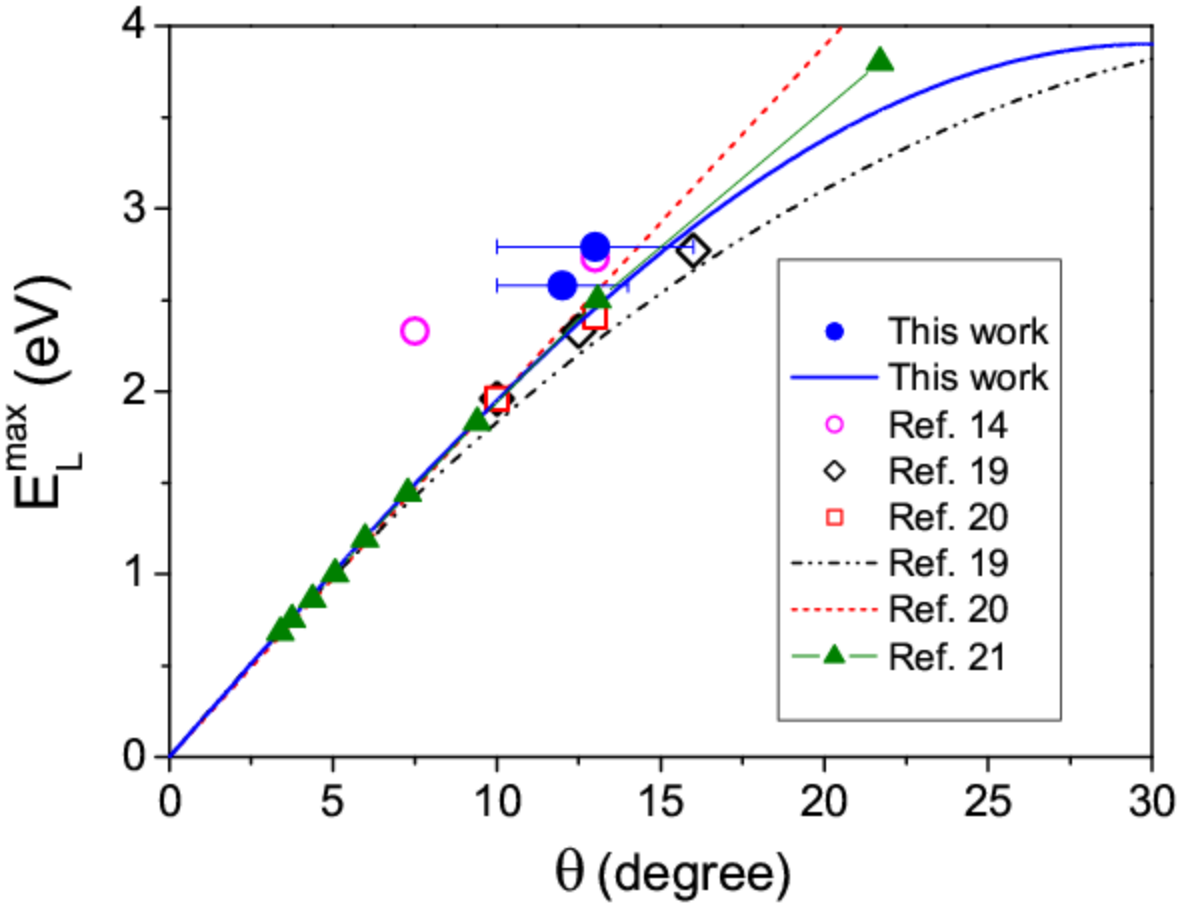
Carozo et al., submitted.

Ab-initio calculations



$$E_{\mathrm{L}}^{\max} = E_0 |\sin(3\theta)|$$

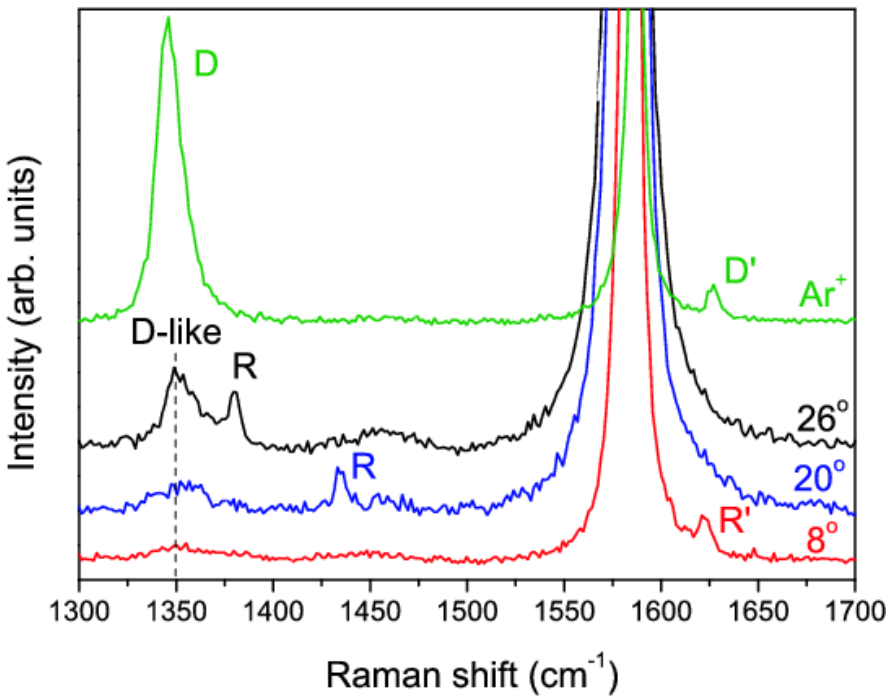
Carozo et al., submitted.

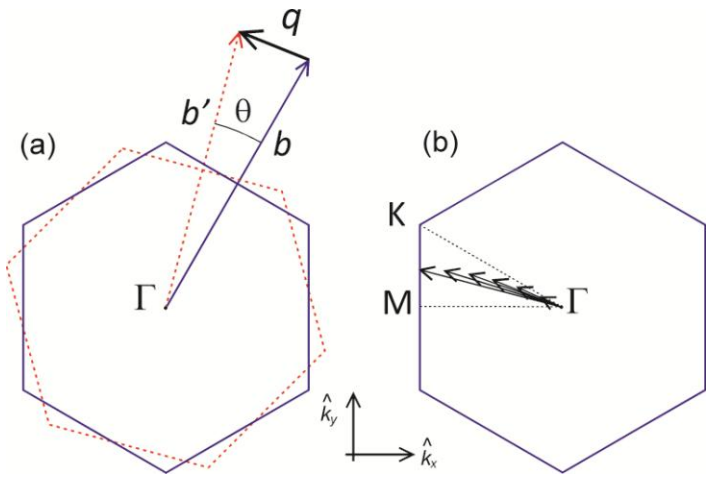


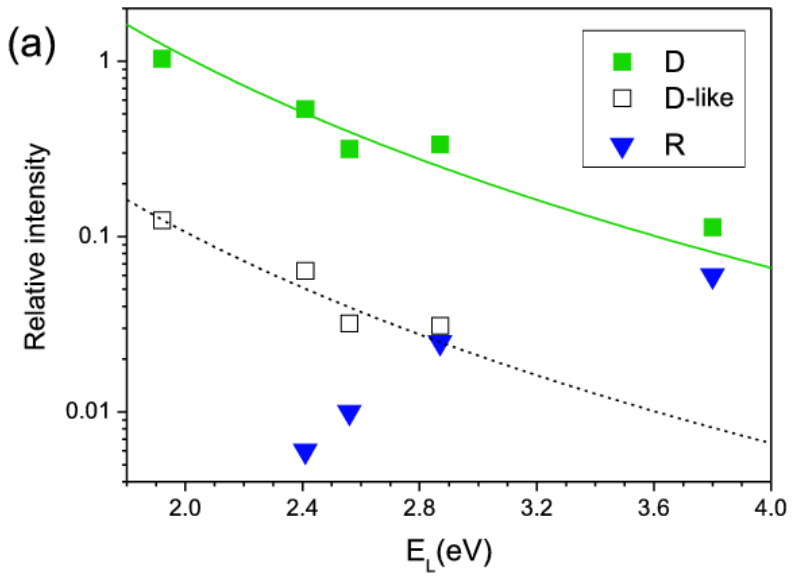
Carozo et al., submitted.

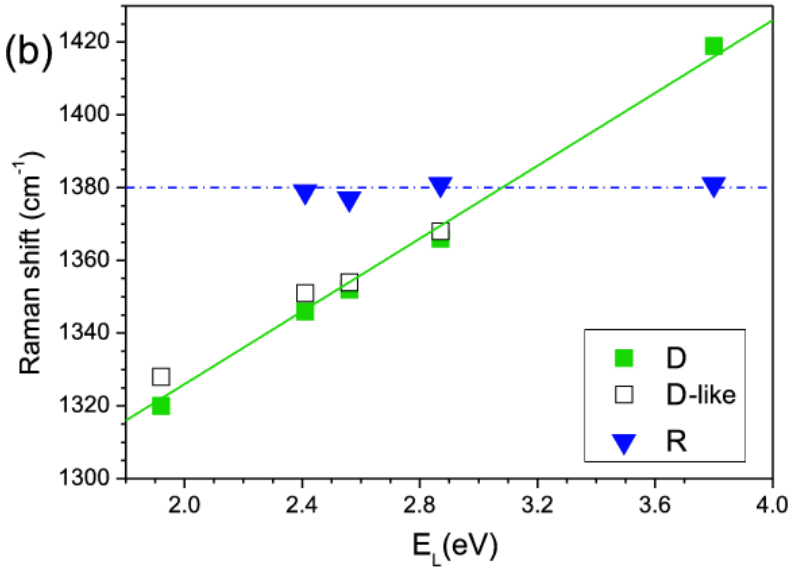
◊ Havener et al., Nano Lett. **12**, 3162 (2012).
□ Kim et al., PRL **108**, 246103 (2012).
▲ Sato et al. , Phys. Rev. B **86**, 125414 (2012).
○ Ni et al. Phys. Rev. B 80, 125404 (2009).

"D-like" band:

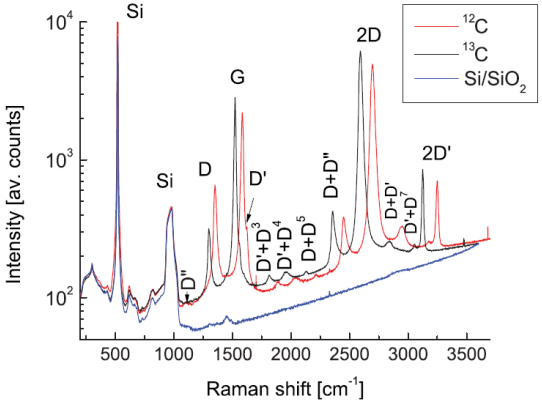




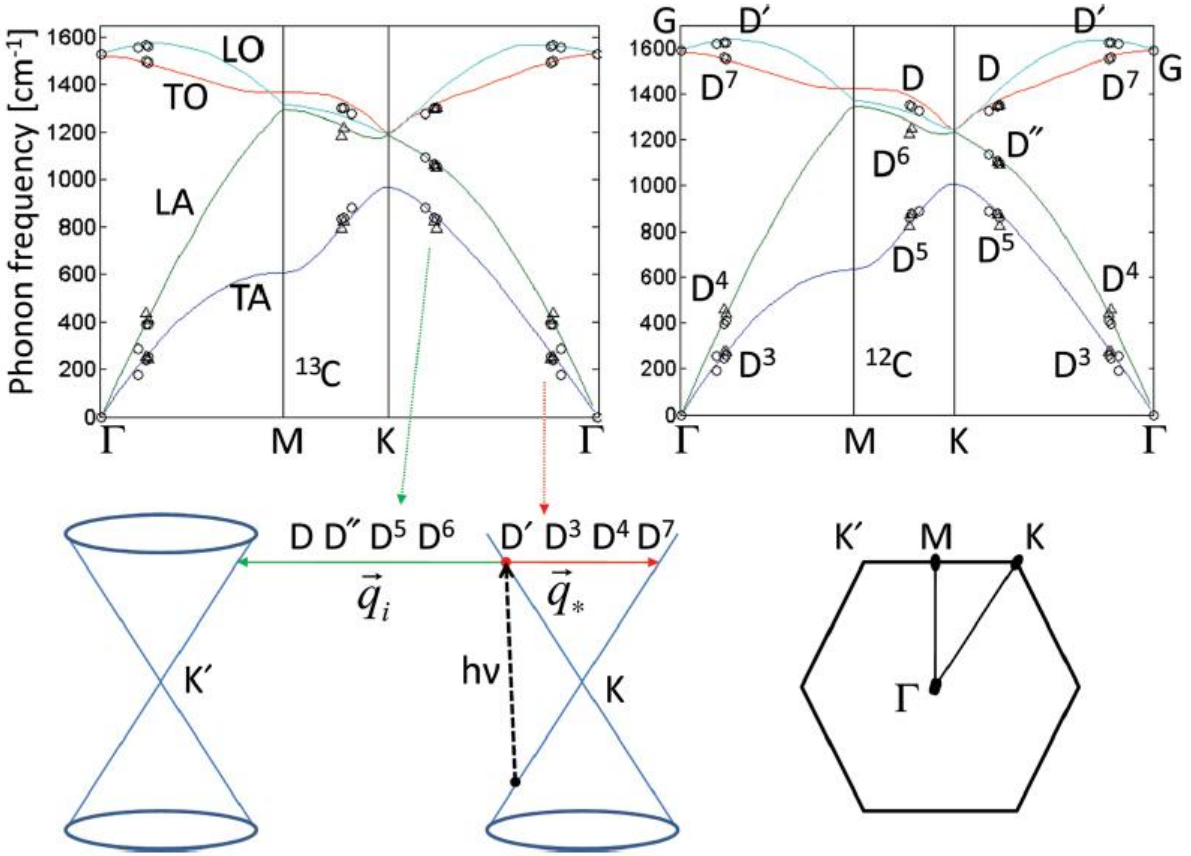




Carozo et al., submitted.

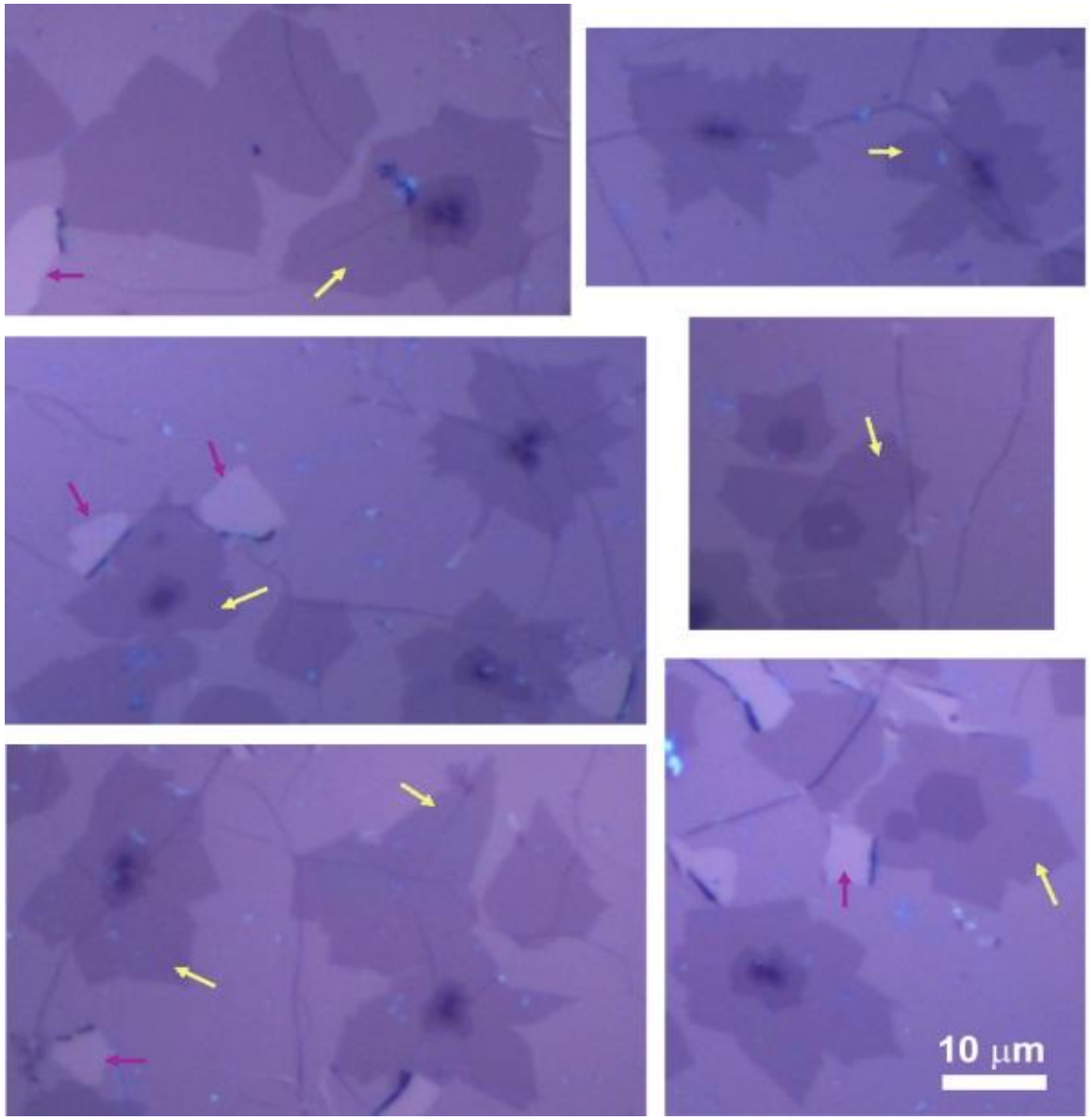


Phonon dispersion of graphene



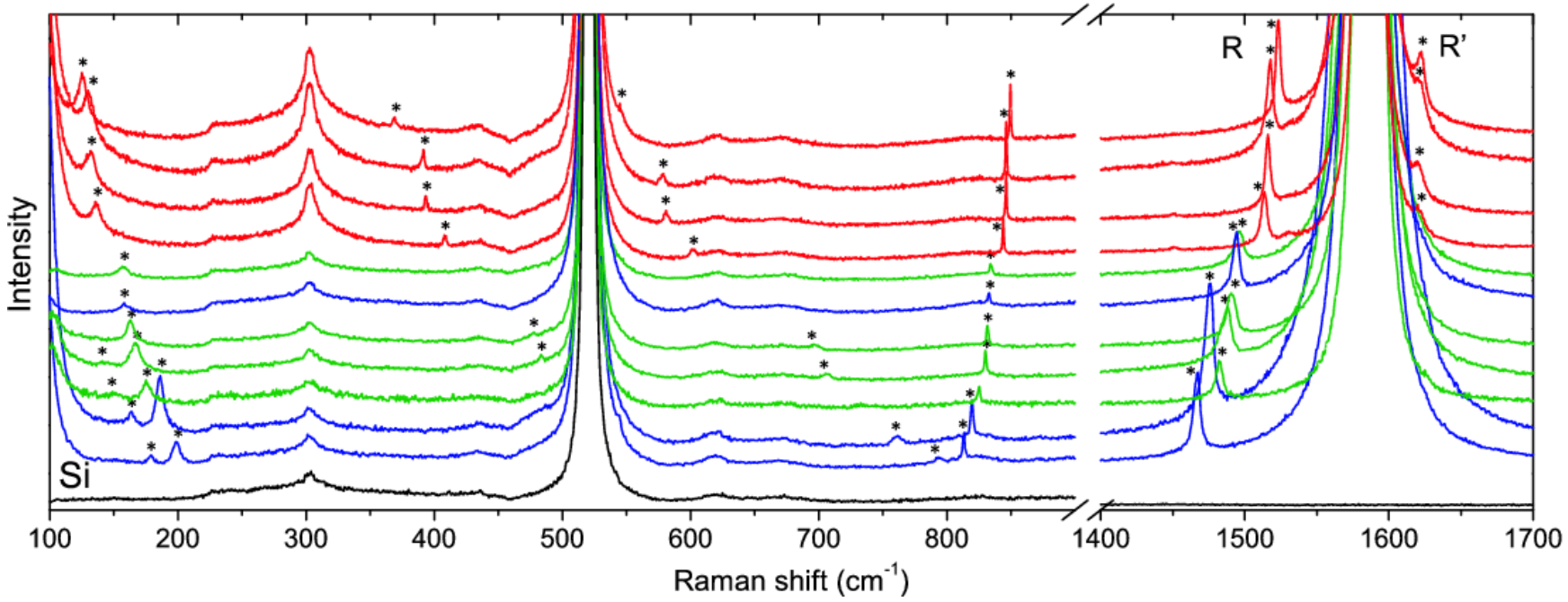
S. Bernard et al., PRB **86**, 085409 (2012).

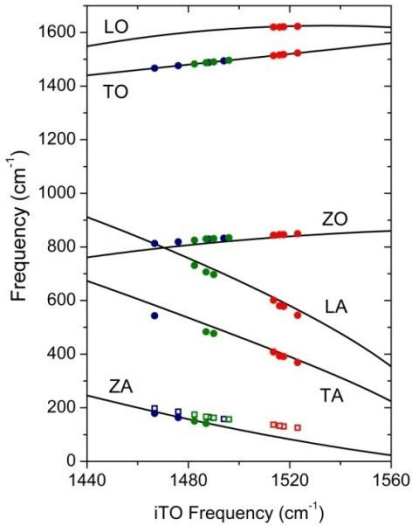
CVD-grown graphene



Jessica Campos-Delgado et al., submitted.

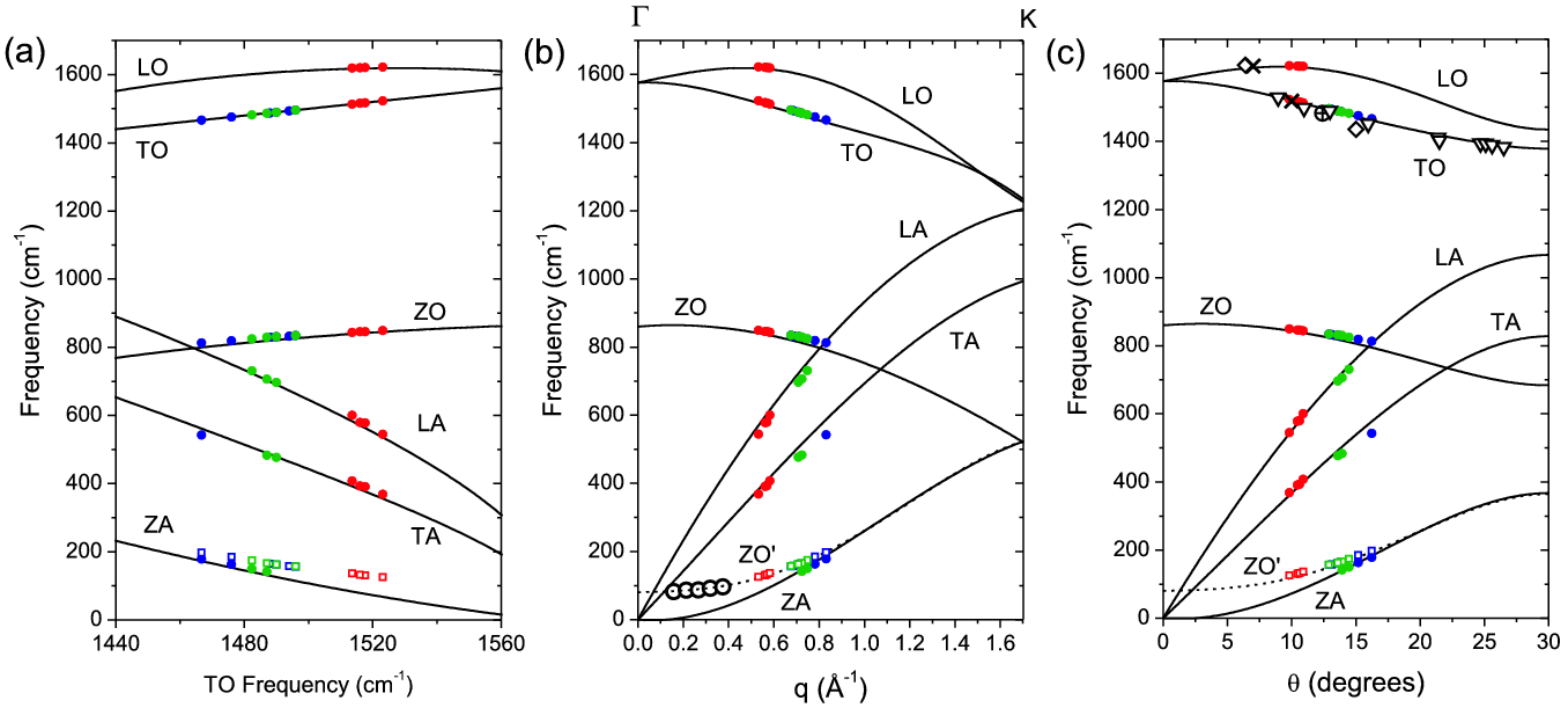
Phonon dispersion of tBLG



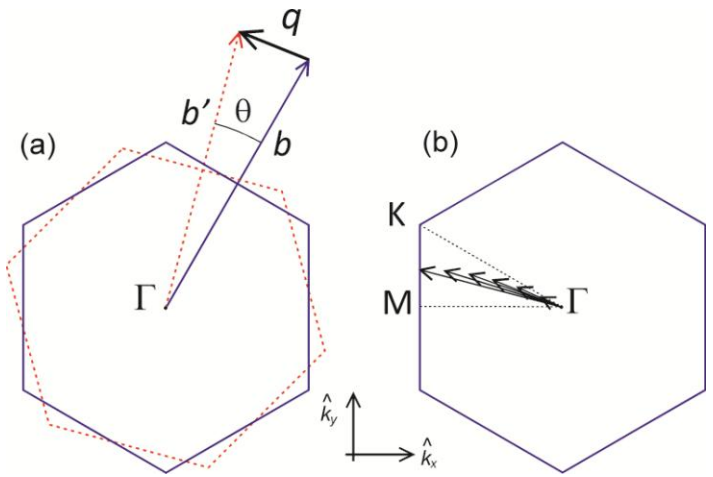


J. Campos-Delgado et al., submitted.

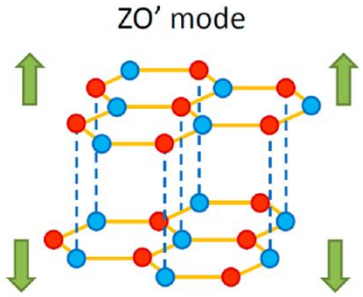
Phonon dispersion of tBLG



J. Campos-Delgado et al., submitted.



X Kim et al., PRL **108**, 246103 (2012).
⊕ Havener et al., Nano Lett. **12**, 3162 (2012).
◊ Carozo et al., Nano Lett. **11**, 4527 (2011).
∇ Wang et al., arXiv:1301.4488v1 (2013).



Lui et al.,Nano Lett. **12**, 5539−5544 (2012).

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FAPEMIG

CAPES

PÓS GRADUAÇÃO FÍSICA UFMG

INMETRO INSTITUTO NACIONAL DE METROLOGIA, NORMALIZAÇÃO E QUALIDADE INDUSTRIAL