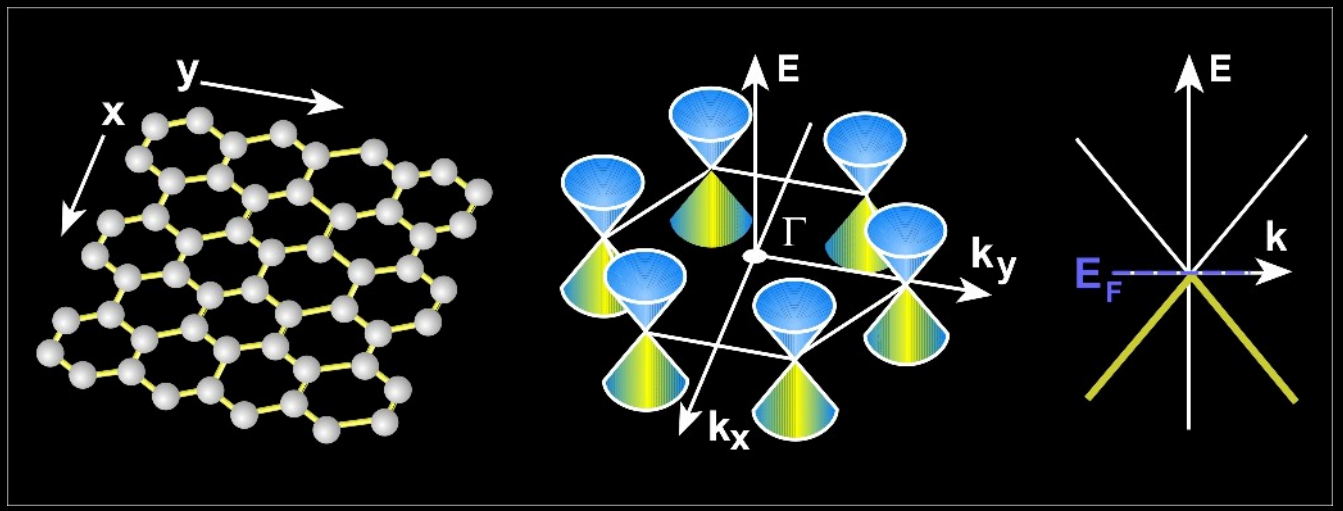
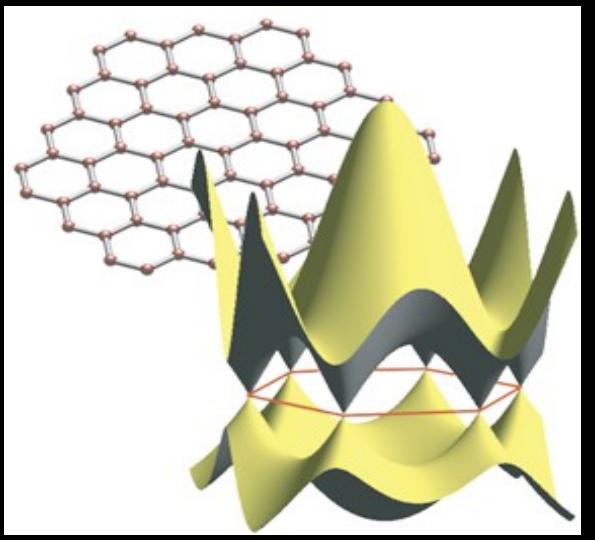
Graphene as tunable electron-phonon material

Claudio Attaccalite

Institut Neel, CNRS Grenoble (France)

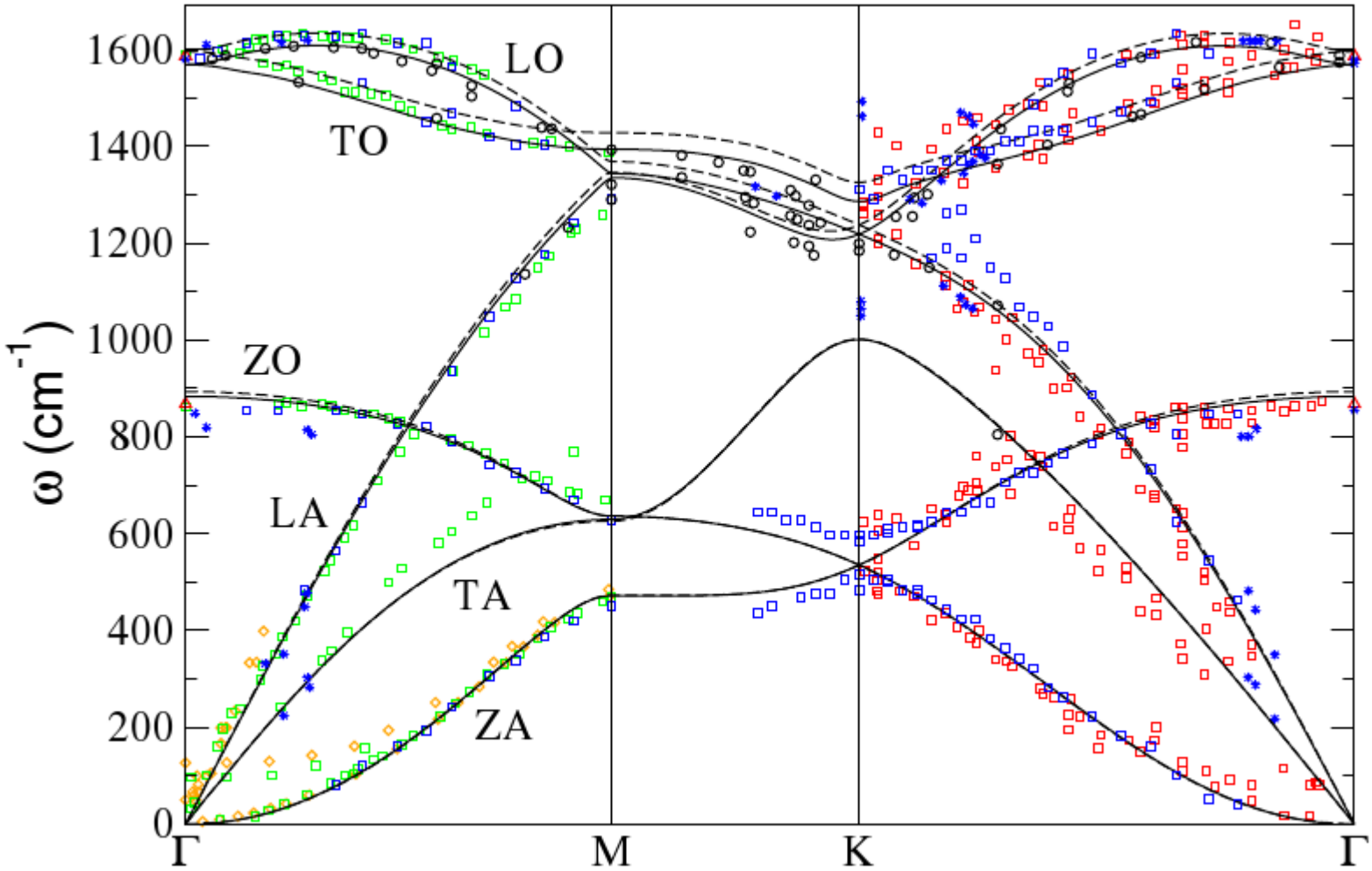




Outline

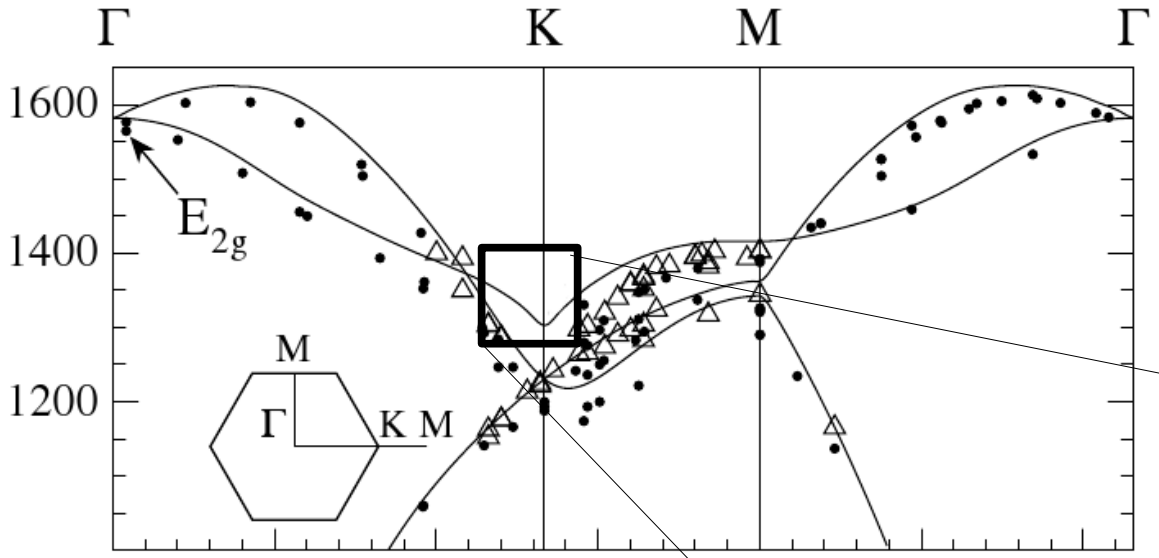
- DFT (LDA/GGA) fails to reproduce Electron-Phonon Coupling (EPC)
- It is possible to go beyond DFT and obtain an accurate description of the EPC within GW approximation
- Performance of hybrid functionals
- Correlation enhances the effect of doping on the EPC

Phonons dispersion of graphite

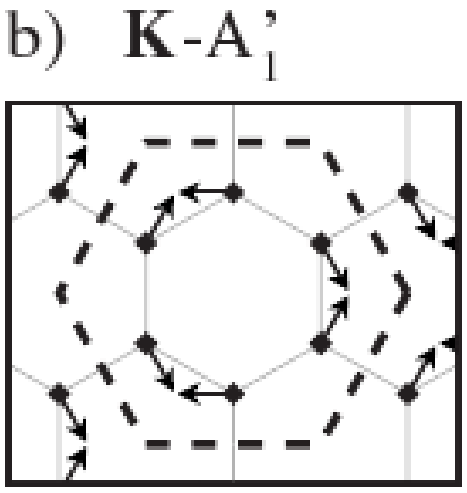


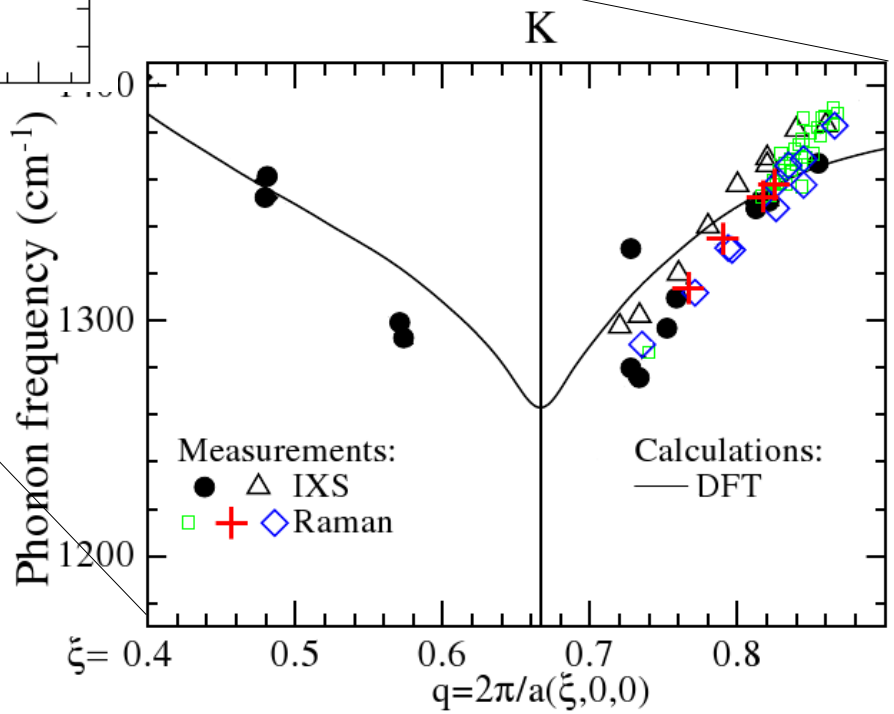
- M. Mohr et al. Phys. Rev. B **76**, 035439 (2007)
- J. Maultzusch et al. Phys. Rev. Lett. **92**, 075501 (2004)
- L. Wirtz and A. Rubio, Solid State Communications **131**, 141 (2004)

Phonon dispersion close to K

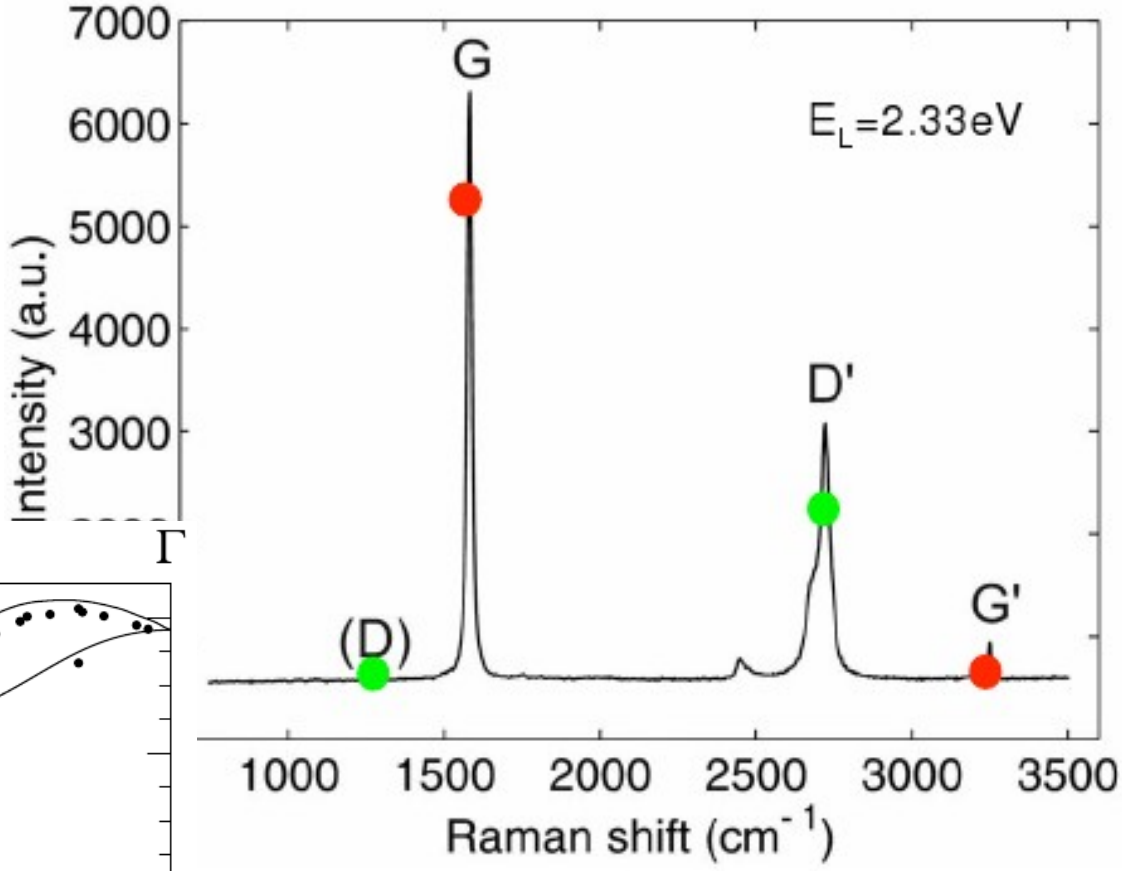


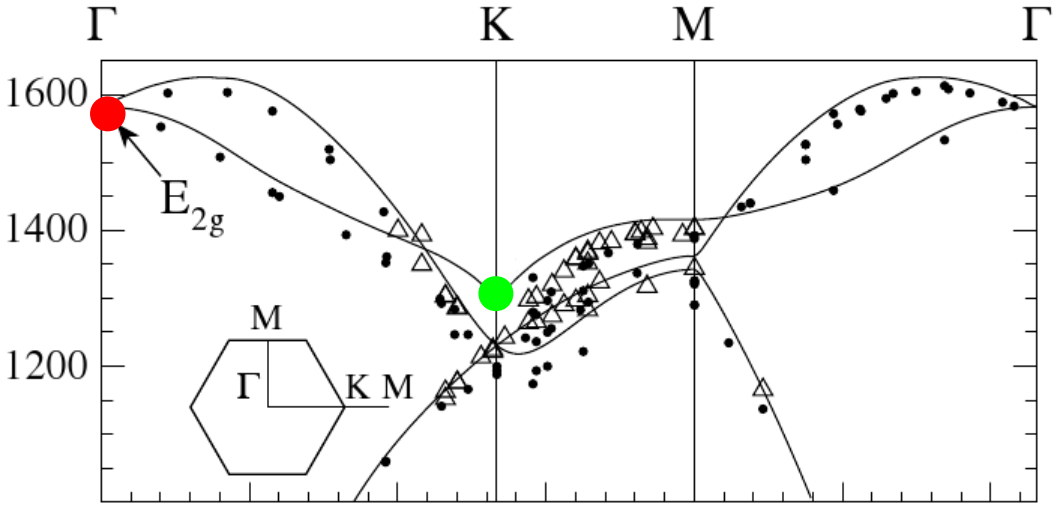
In spite of the general good agreement the situation is not clear close to **K**



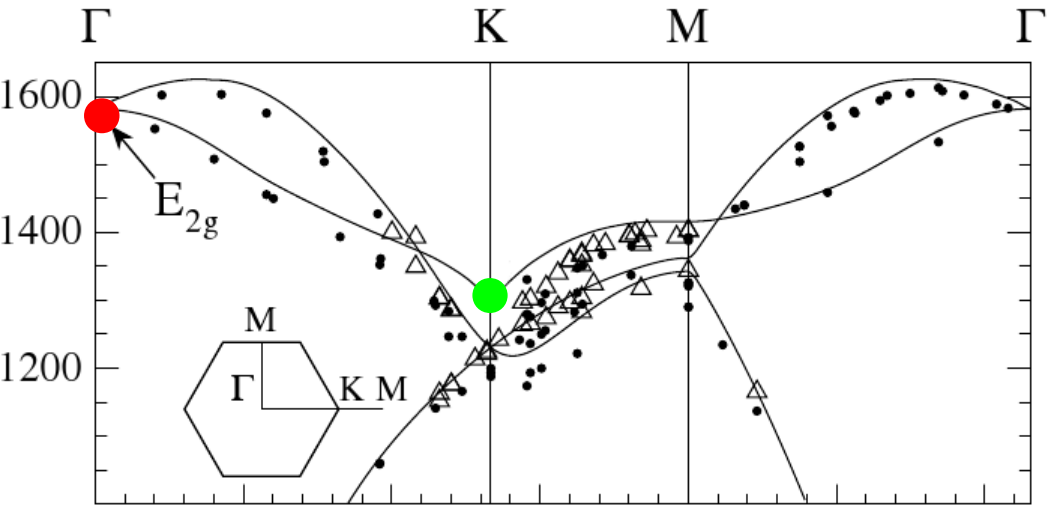


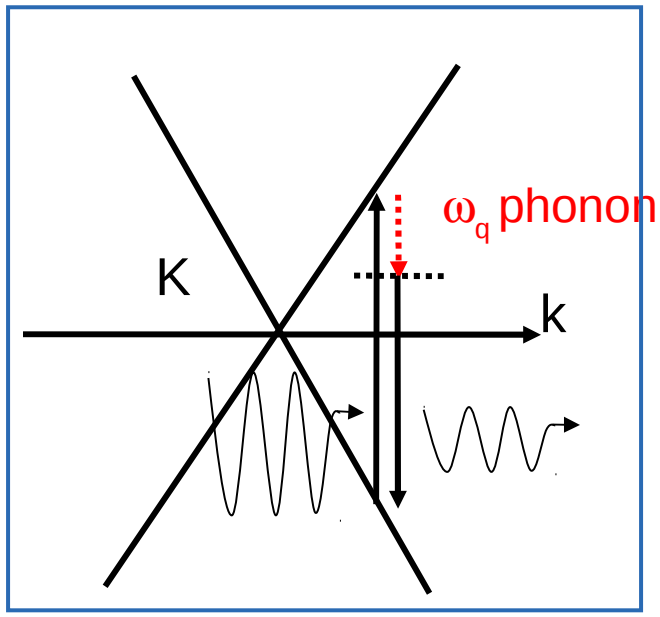
Raman Spectroscopy of graphene

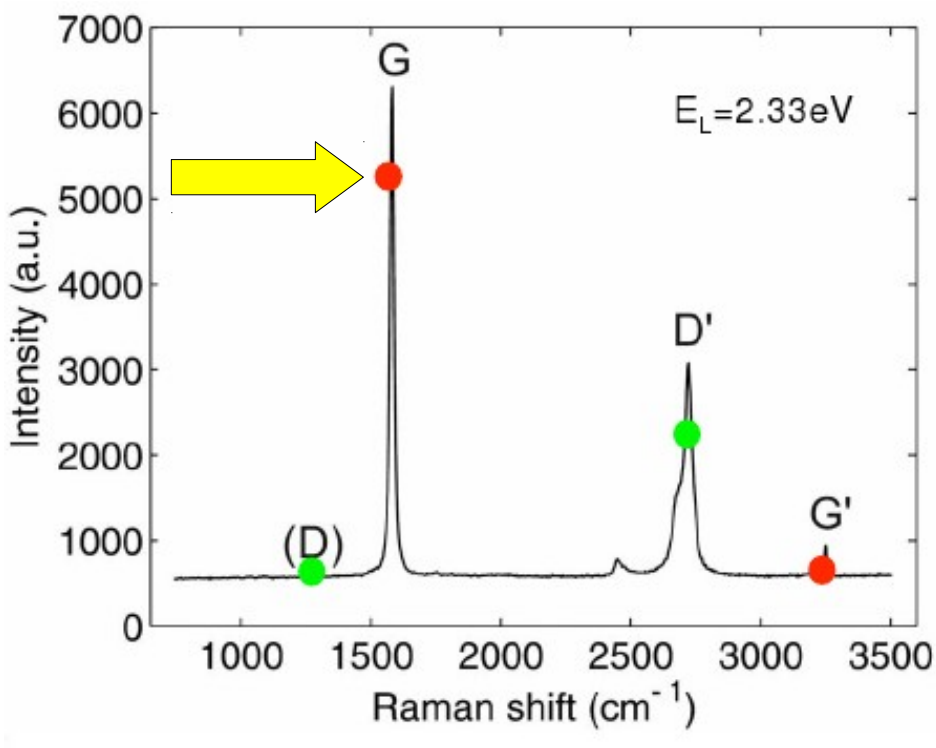




Raman G-line



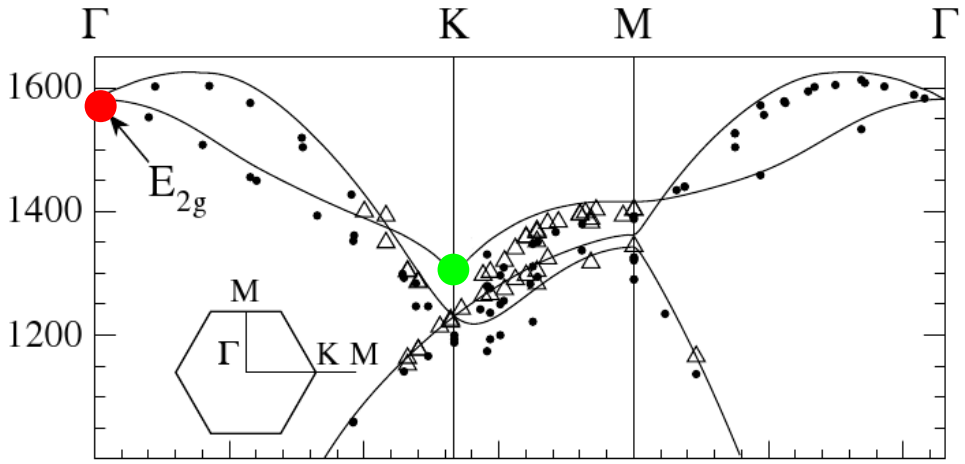




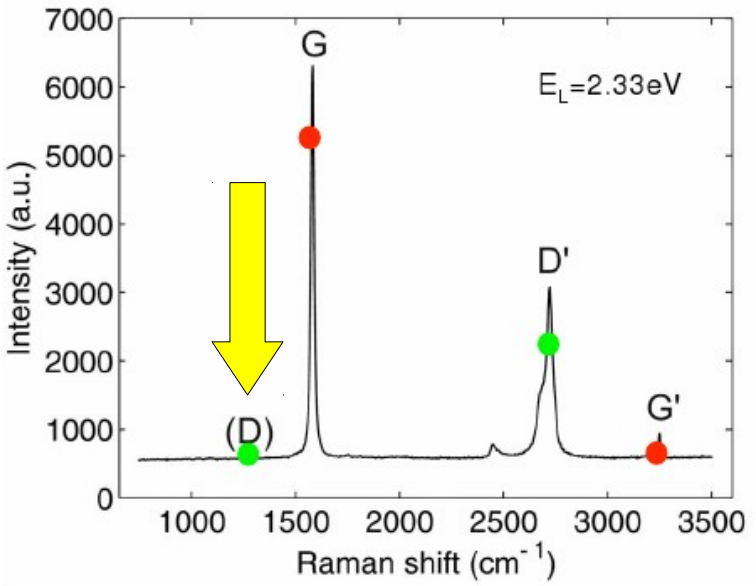
Single-resonant G-line

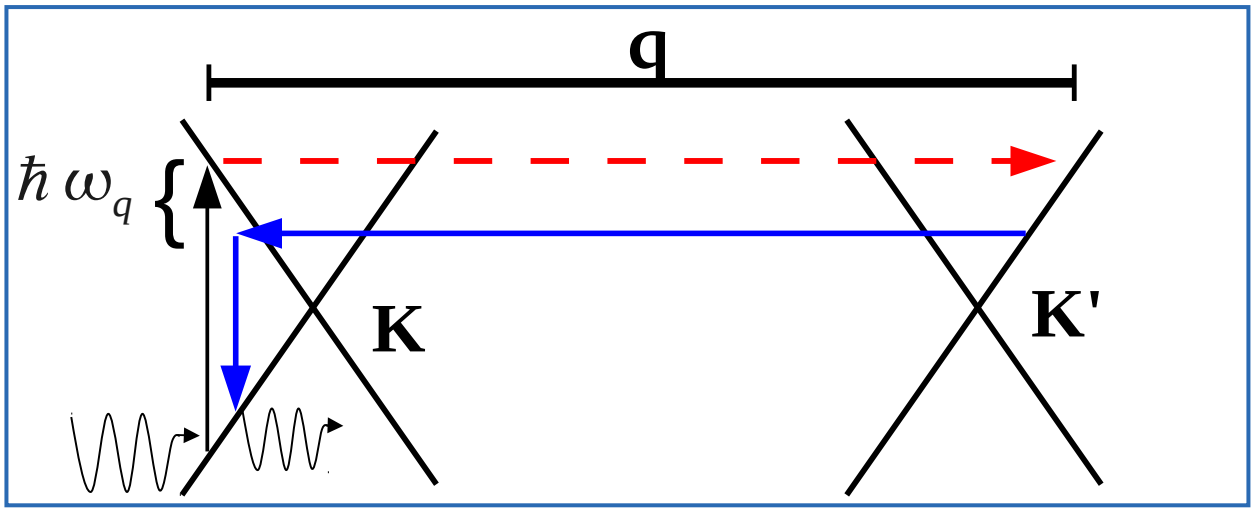
at Γ point, k~0
→ **G-line**

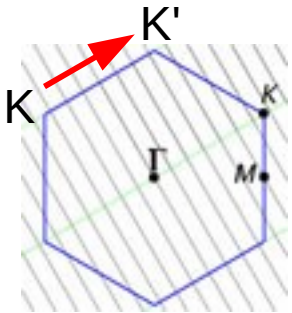
Raman D-line



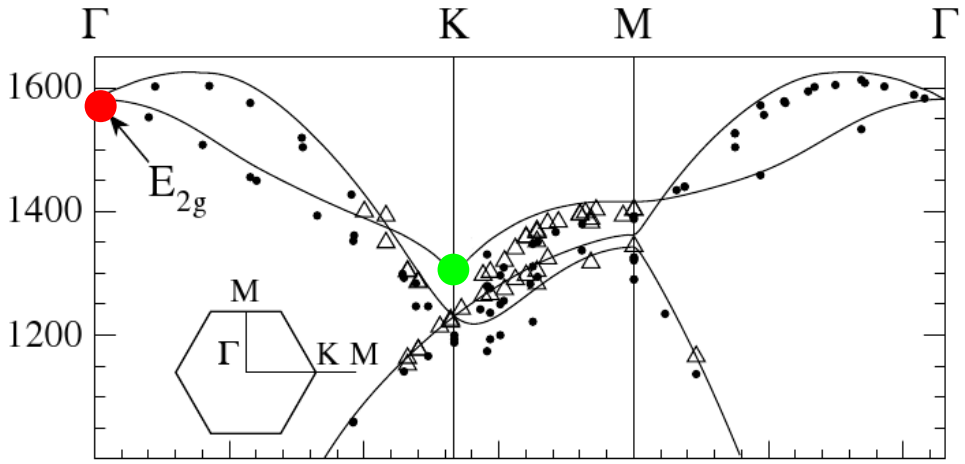
C. Thomsen et al., Phys. Rev. Lett. **85**, 5214 (2000)







Raman D-line



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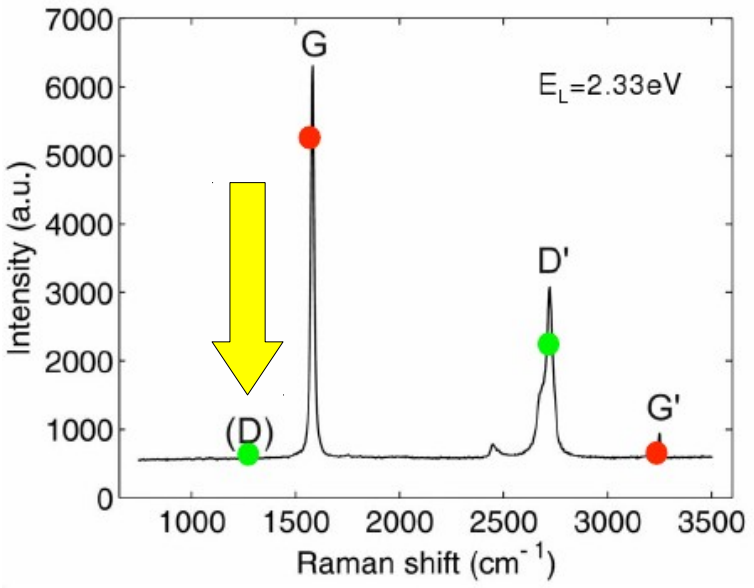
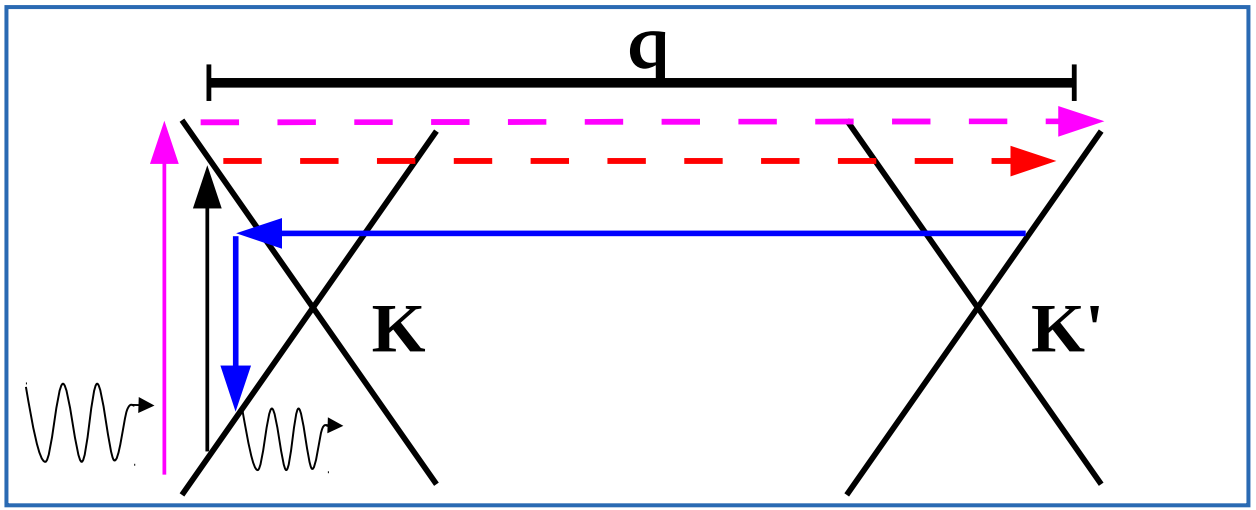
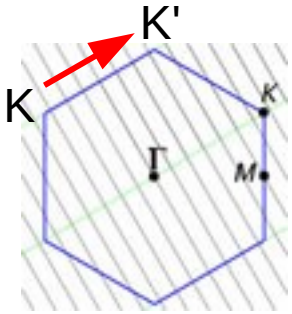
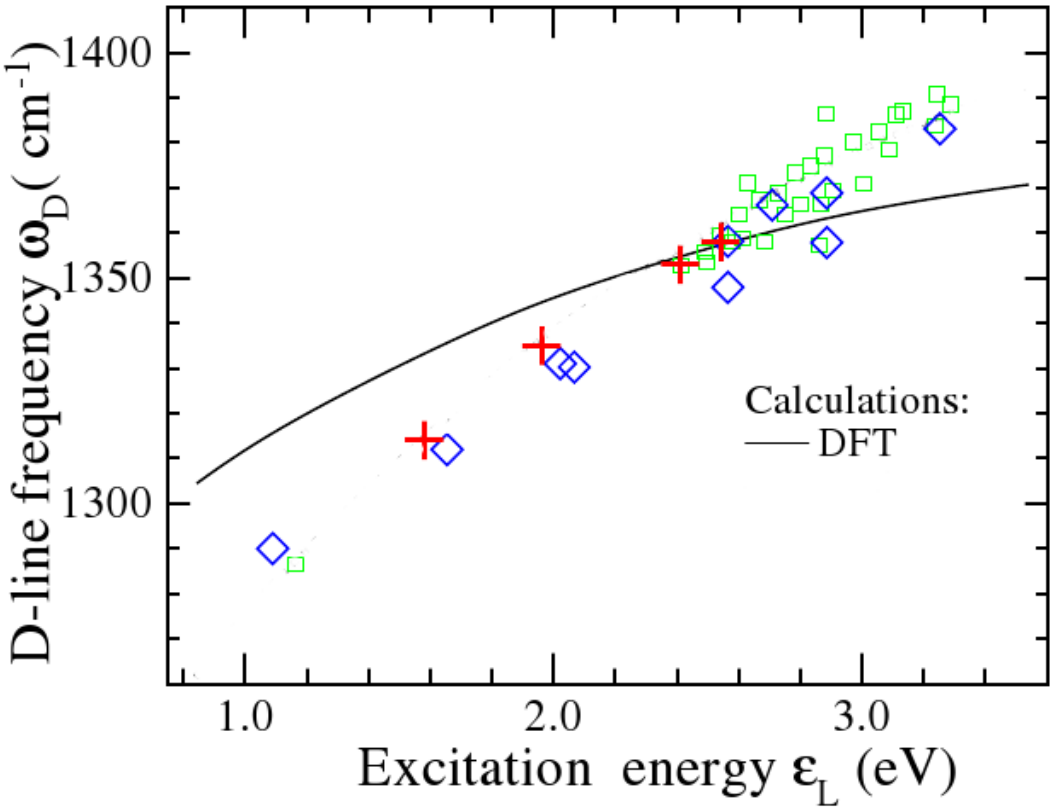






dispersive
Raman line

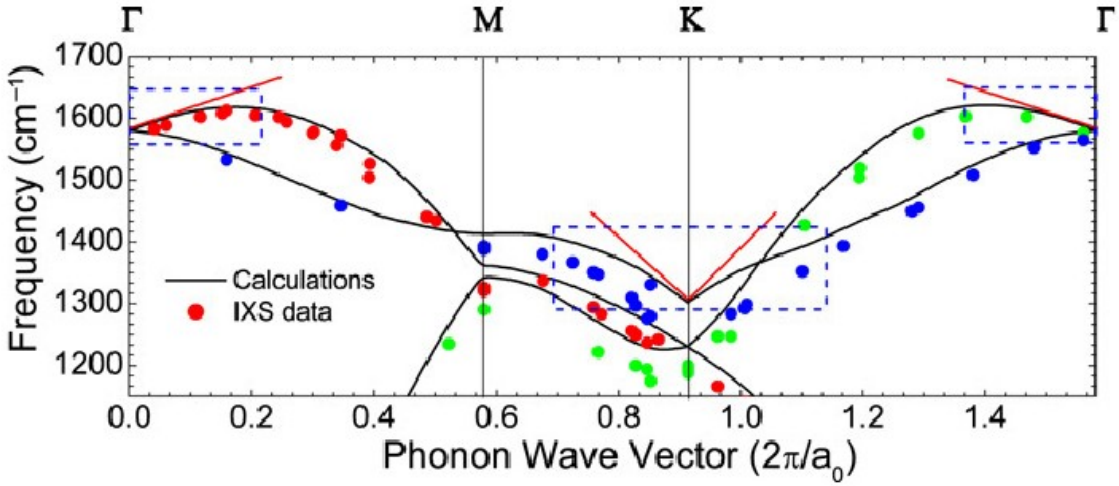
.... but also from Raman....



I. Pócsik et al., J. Non-Cryst. Solids **227**, 1083 (1998).
P. H. Tan et al., Phys. Rev. B **66**, 245410 (2002)
J. Maultzsch et al., Phys. Rev. B **70**, 155403 (2004).

Motivations

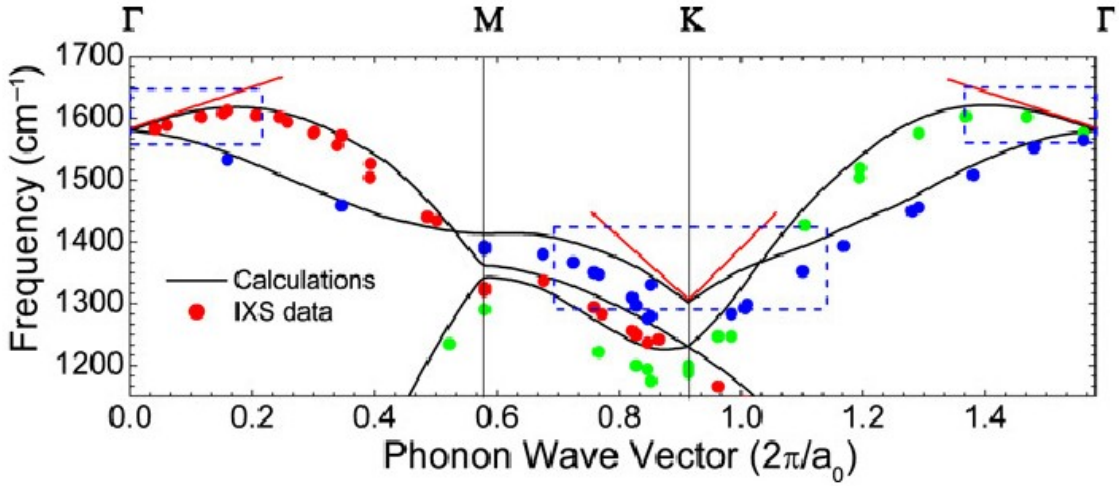
..phonons...



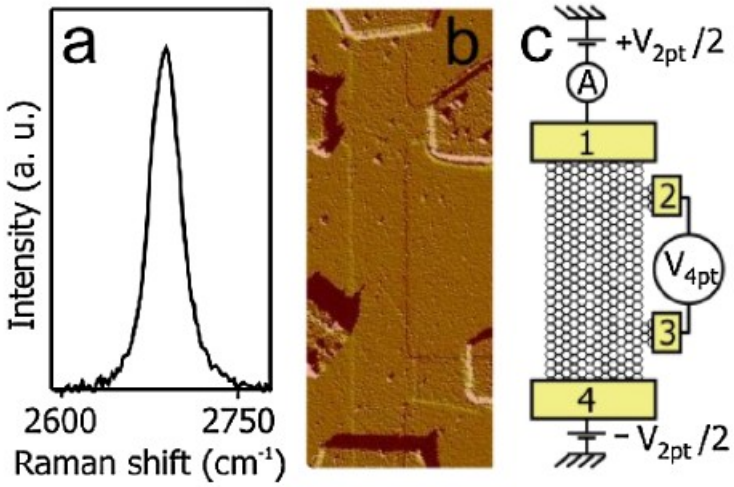
S. Piscanec et al . Phys. Rev. Lett. **93**, 185503 (2004)

Motivations

..phonons...



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

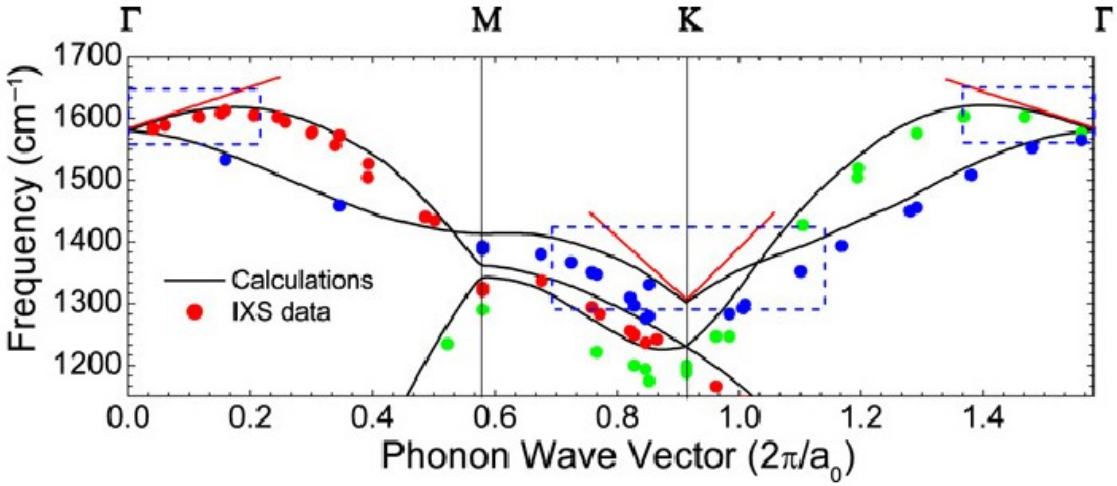


..transport...

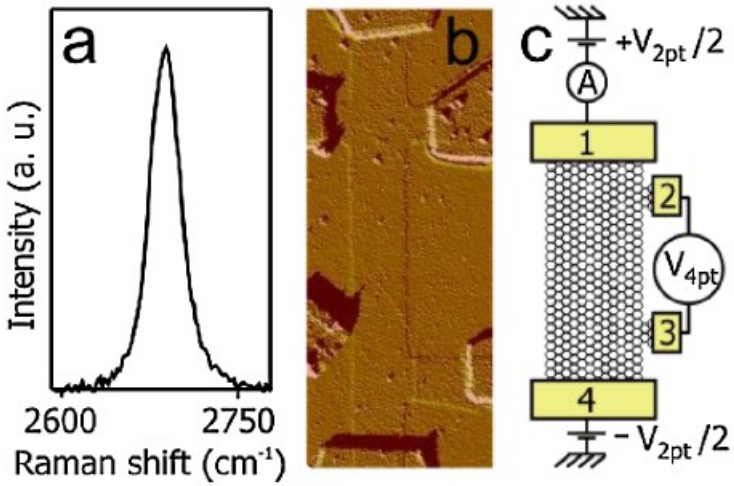
Amelia Barreiro et al. PRL **103**, 076601 (2009)

Motivations

..phonons...

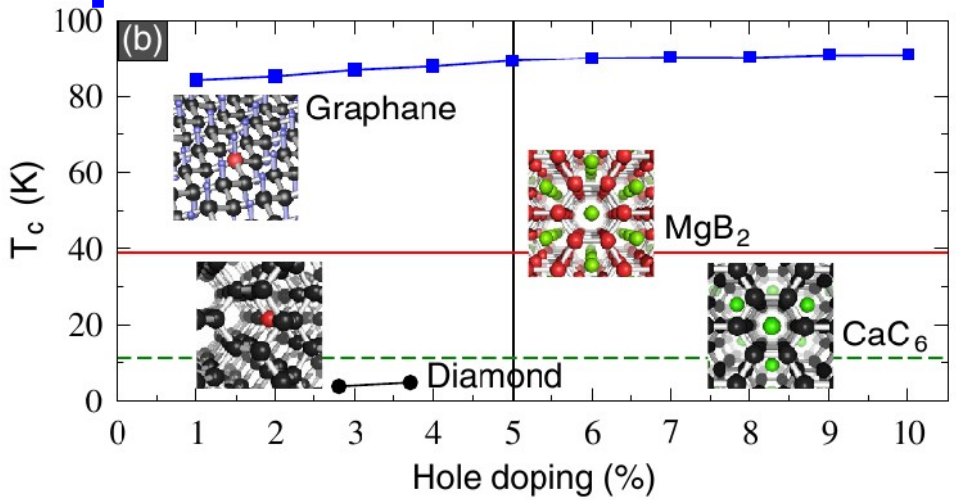


S. Piscanec et al . Phys. Rev. Lett. **93**, 185503 (2004)



Amelia Barreiro et al. PRL **103**, 076601 (2009)

..transport...



..superconductivity?...

G. Savini et al . PRL **105**, 037002 (2010)

J. L. McChesney et al. Phys. Rev. Lett. **104**, 136803 (2010)

A. Sanna, E. K. Gross, PSIK S6C4 contributed

How to calculate phonons and EPC ?

Phonon frequencies (squared) are eigenvalues of the dynamical matrix

$$D_{st}^{\alpha\beta}(q) = \frac{\partial^2 E}{\partial u_s^{*\alpha}(q)\partial_t^{\beta}(q)}$$

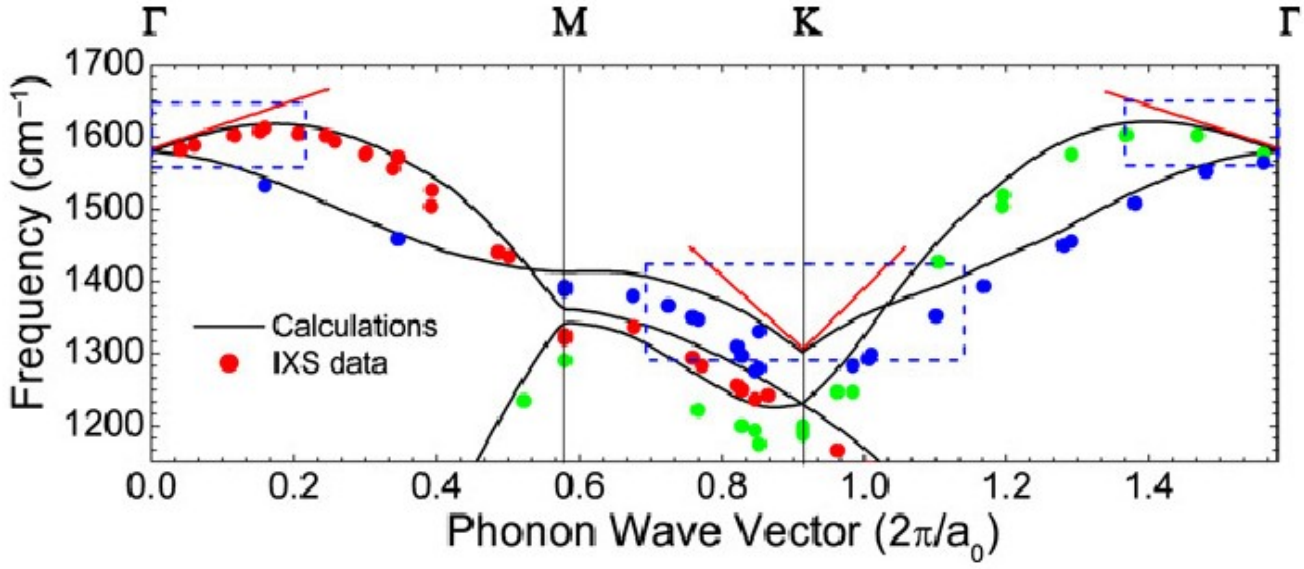
Ideal solution: calculate total energy and its derivatives

Problem: how to calculate total energy including quasi-particle effects (questions of self-consistence and of numerical feasibility)

Electron-Phonon Coupling and dynamical matrix

$$\omega_q = \sqrt{D_q / m}$$

$$D_q = B_q + P_q$$



π-bands self-energy

$$P_q = \frac{4}{N_k} \sum_k \frac{\left| D_{(k+q)\pi^*, k\pi} \right|^2}{\epsilon_{k,\pi} - \epsilon_{k+q,\pi^*}}$$

Electron-Phonon Coupling → $D_{(k+q)\pi^*, k\pi} = \langle k+q, \pi^* | \Delta V | k, \pi \rangle$

Frozen Phonons Calculation of the EPC

The electronic Hamiltonian for the π and π* bands can be written as 2x2 matrix:

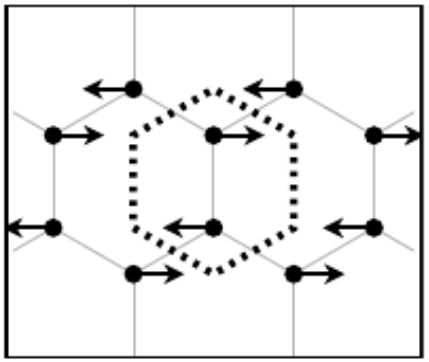
$$H(k,0)=\begin{pmatrix}\hbar v_f k & 0\\ 0 & -\hbar v_f k\end{pmatrix}$$

a distortion of the lattice according to the Γ-E_{2G}

$$H(k,u)=H(k,0)+\frac{\partial H(k,0)}{\partial u}u+O(u^2)$$

where: $$\frac{\partial H(k,0)}{\partial u}=2\sqrt{\langle D_\Gamma^2\rangle_F}\begin{pmatrix}a & b\\ b^* & -a\end{pmatrix}$$

a) Γ-E_{2g}



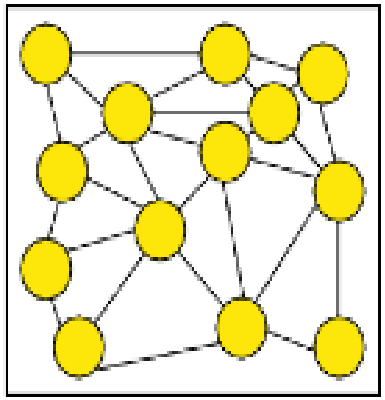
If we diagonalize **H(k,u)** at the K-point $\langle D_\Gamma^2\rangle_F=\lim_{d\to 0}\frac{1}{16}\left(\frac{\Delta E_\Gamma}{d}\right)^2$!!!!

We can get the EPC from the gap that is opened between the π bands for a given phonon mode!!!

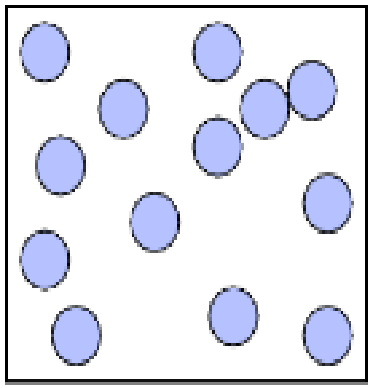
Quasi-Particles Band Structure

In GW the bandwidth is increased and consequently the Fermi velocity v_F is enhanced

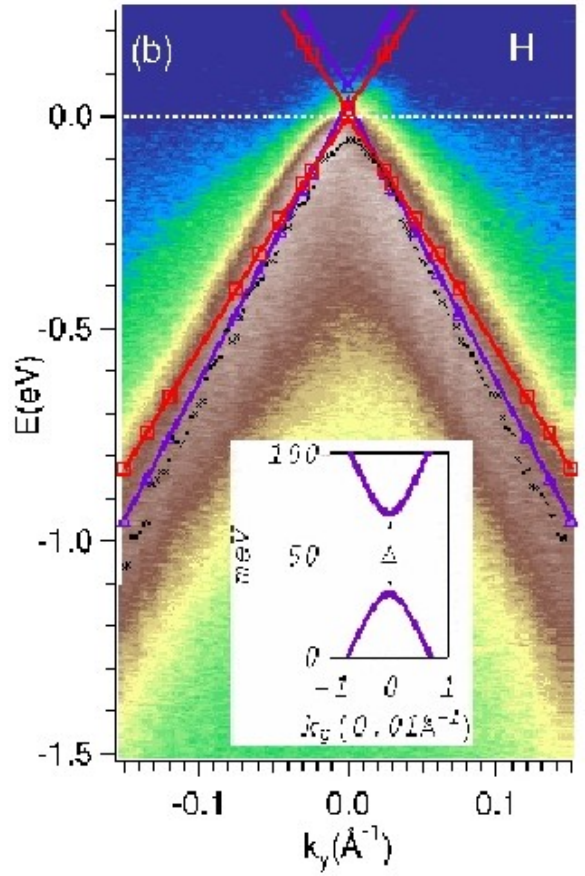
Full-Interacting



Quasi-particle



Particles experience a screened Coulomb Interaction (W)



$$[T+V_h+V_{ext}]\Psi_{n,k}(r)+\int dr'\,\Sigma(r,r';E_{n,k})\Psi_{n,k}(r')=E_{n,k}\Psi_{n,k}(r)$$

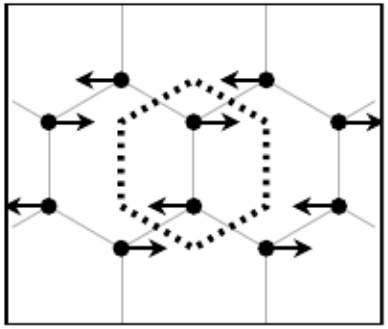
A. Gruenis, C.Attaccalite et al. PRL **100**, 189701 (2008)

GW results for the EPC

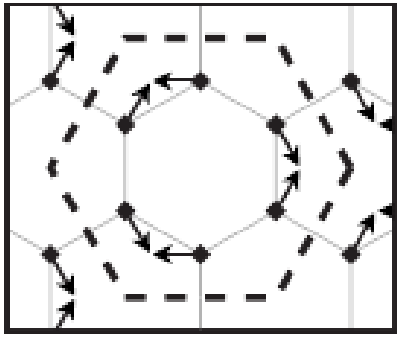
To study the changes on the phonon slope we recall that P_q is the ratio of the square EPC and band energies

$$P_q = \frac{4}{N_k} \sum_k \frac{\left| D_{(k+q)\pi^*, k\pi} \right|^2}{\epsilon_{k,\pi} - \epsilon_{k+q,\pi^*}}$$

a) Γ-E_{2g}



b) **K**-A_1'



we studied also:

$$\alpha_q = \langle D_q^2 \rangle_F / \Delta\epsilon_g$$

	<D^2>	α	ω_Γ
LDA	44.4	11.0	1568
GW	62.8	12.8	-

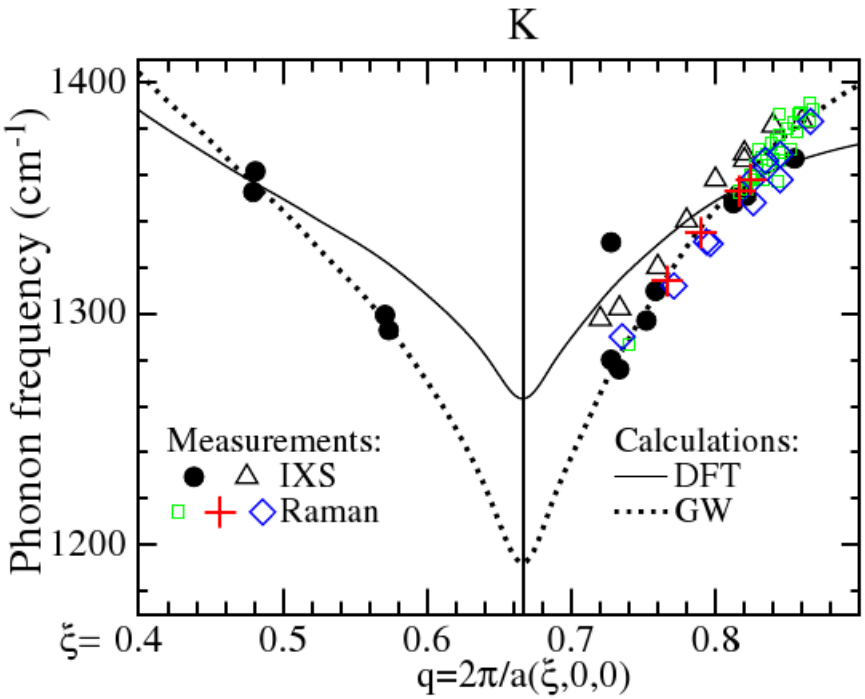
Graphene	<D^2>	α	ω_K
LDA	89.9	22.3	1275
GW	193	39.5	-

Graphite	<D^2>	α	ω_K
LDA	88.9	21.8	1299
GW	164.2	35.9	(1192)

M. Lazzeri, C.Attaccalite, L. Wirtz and F. Mauri
PRB **80**, 081406(R) (2008)

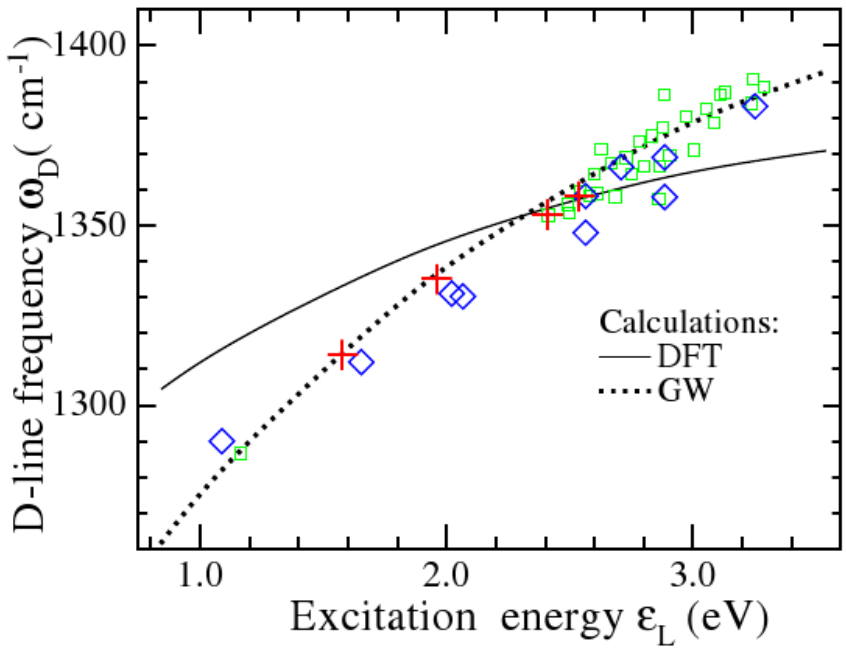
Comparison with experiments

Phonons around K



J. Maultzsch et al., Phys. Rev. Lett. **92**, 075501 (2004).
M. Mohr et al., Phys. Rev. B **76**, 035439 (2007).

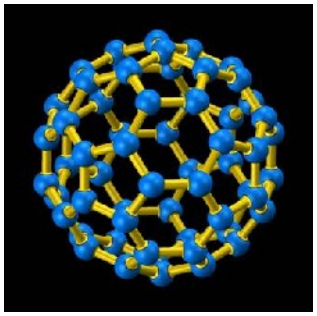
Raman D-line dispersion



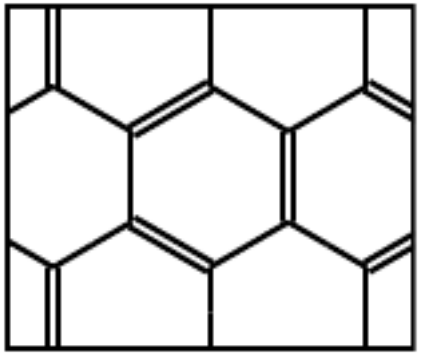
I. Pócsik et al., J. Non-Cryst. Solids **227**, 1083 (1998).
P. H. Tan et al., Phys. Rev. B **66**, 245410 (2002).
J. Maultzsch et al., Phys. Rev. B **70**, 155403 (2004).

The resulting K A′ phonon frequency is **1192 cm^{-1}** which is our best estimation and is almost 100 cm^{-1} smaller than in DFT.

Hybrids functionals and EPC



J. L. Janssen, M. Cote, S. G. Louie and M. L. Cohen
Phys. Rev. B **81**, 073106 (2010)



Hartree-Fock equilibrium structure

	Graphene:					
	$D^2_{\Gamma}\rangle_{\mathrm{F}}$	α_{Γ}	ω_{Γ}	$\langle D^2_{\mathbf{K}}\rangle_{\mathrm{F}}$	$\alpha_{\mathbf{K}}$	$\omega_{\mathbf{K}}$
$\mathrm{DFT_{LDA}}$	44.4	11.0	1568	89.9	22.3	1275
$\mathrm{DFT_{GGA}}$	45.4	11.1	1583	92.0	22.5	1303
GW	62.8	12.8	–	193	39.5	–
B3LYP	82.3	13.4	1588	256	41.7	1172
HF	321	26.6	1705	6020	498	$960\times i$
	Graphite:					
	$\overline{D^2_{\Gamma}\rangle}_{\mathrm{F}}$	α_{Γ}	ω_{Γ}	$\overline{\langle D^2_{\mathbf{K}}\rangle}_{\mathrm{F}}$	$\alpha_{\mathbf{K}}$	$\omega_{\mathbf{K}}$
$\mathrm{DFT_{LDA}}$	43.6	10.7	1568	88.9	21.8	1299
$\mathrm{DFT_{GGA}}$	44.9	11.0	1581	91.5	22.5	1319
GW	58.6	12.8	–	164.2	35.9	(1192)

Tuning the B3LYP

The B3LYP hybrid-functional has the form:

$$E_{xc} = (1-A)(E_x^{LDA} + B\,E_x^{BECKE}) + A\,E_x^{HF} + (1-C)\,E_c^{VWN} + C\,E_c^{LYP}$$

B3LYP consists of a mixture of Vosko-Wilk-Nusair and LYP correlation part E_c and a mixture of LDA/Becke exchange with Hartree-Fock exchange

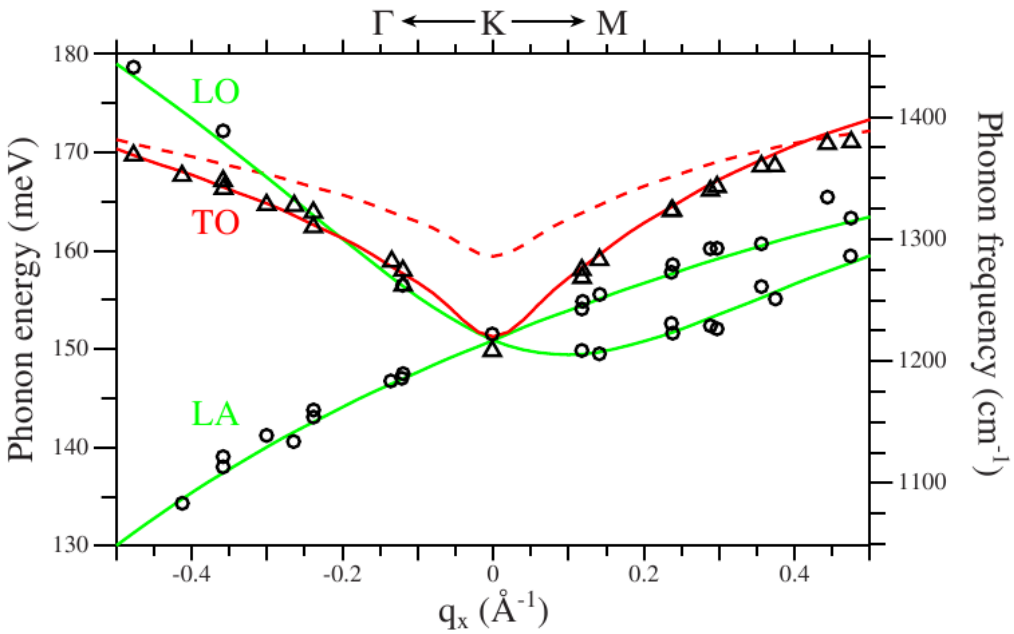
The parameter **A** controls the admixture of HF exchange in the standard B3LYP is 20%

A(%)	$\langle D_K^2 \rangle$	M gap	α_K
12%	176.96	5.547	31.93
13%	185.50	5.662	32.99
14%	194.39	5.695	34.13
15%	203.65	5.769	35.30
20%	256.03	6.140	41.70
GW	193	4.89	39.5

It is possible to reproduce GW results tuning the non-local exchange in B3LYP !!!!!

Recent Experimental evidences

Phonon dispersions around the K point of graphite by inelastic x-ray scattering

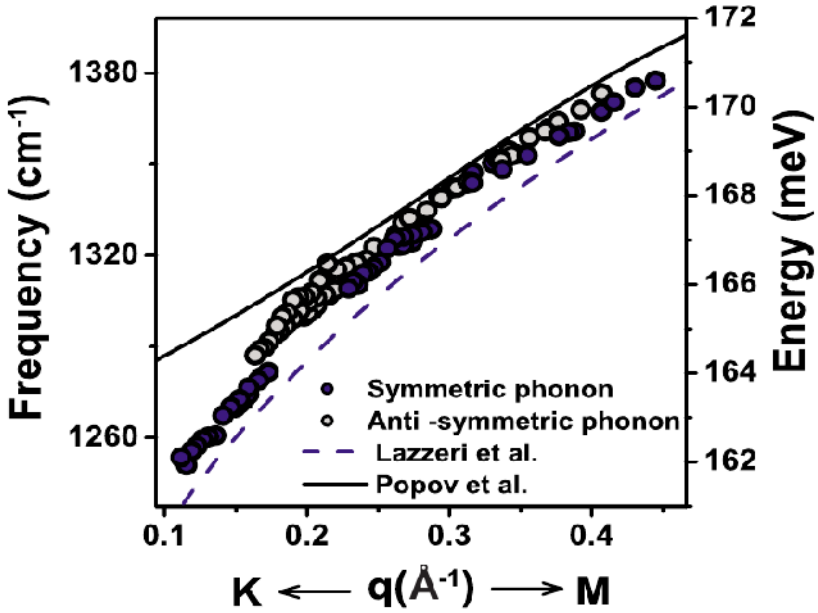


A. Grüneis et al . Phys. Rev. B **80**, 085423 (2009)

$\langle D_K^2 \rangle_F = 166 (eV/\mathring{A})$ inelastic x-ray

$\langle D_K^2 \rangle_F = 164 (eV/\mathring{A})$ GW

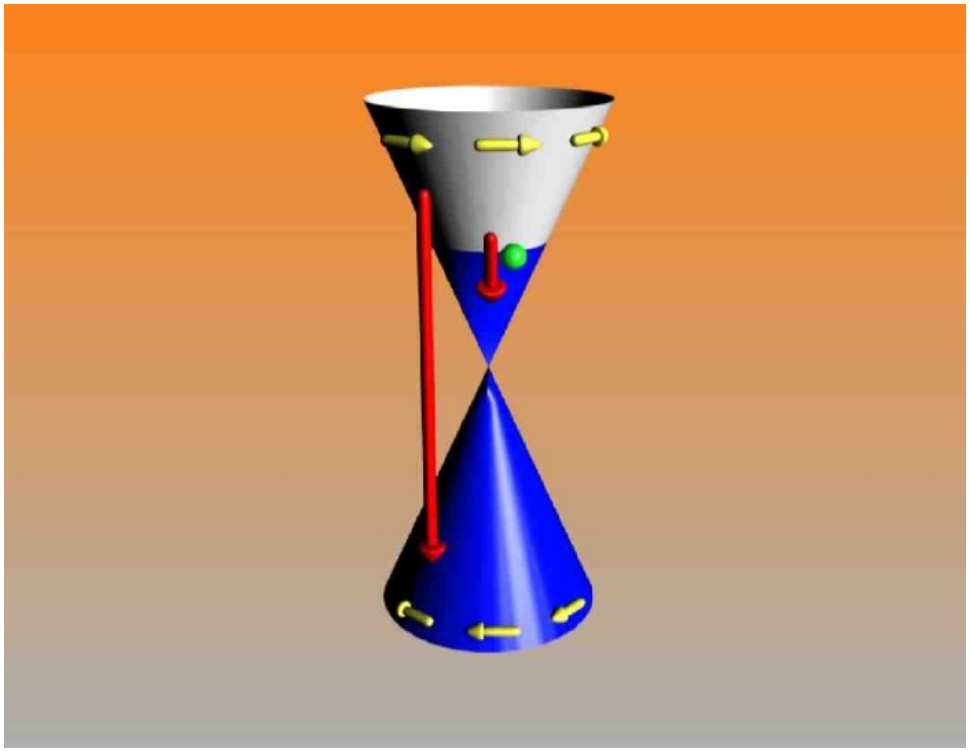
Experimental phonon dispersion in bilayer graphene obtained by Raman spectroscopy



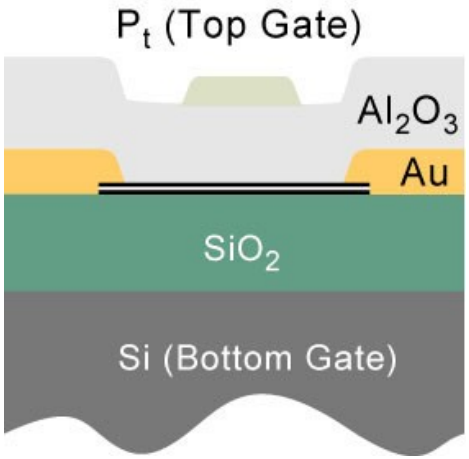
D. L. Mafra et al. Phys. Rev. B **80**, 241414(R)(2009)

Doped graphene

With doping graphene evolves from a semi-metal to a real metal.

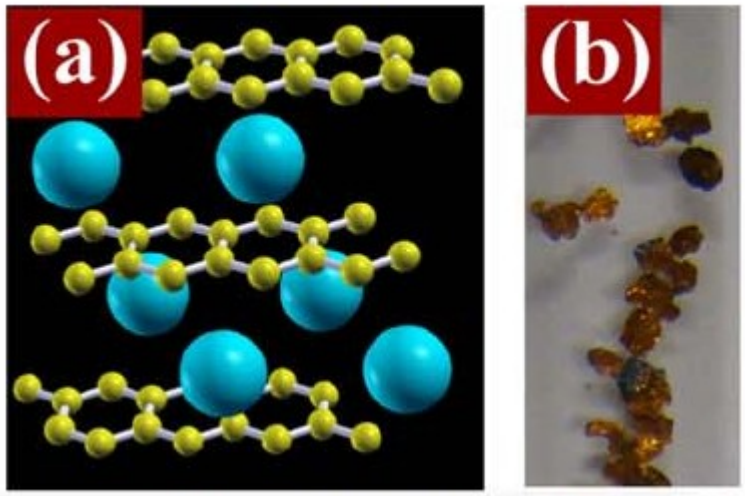


Doped graphene



Top gated graphene

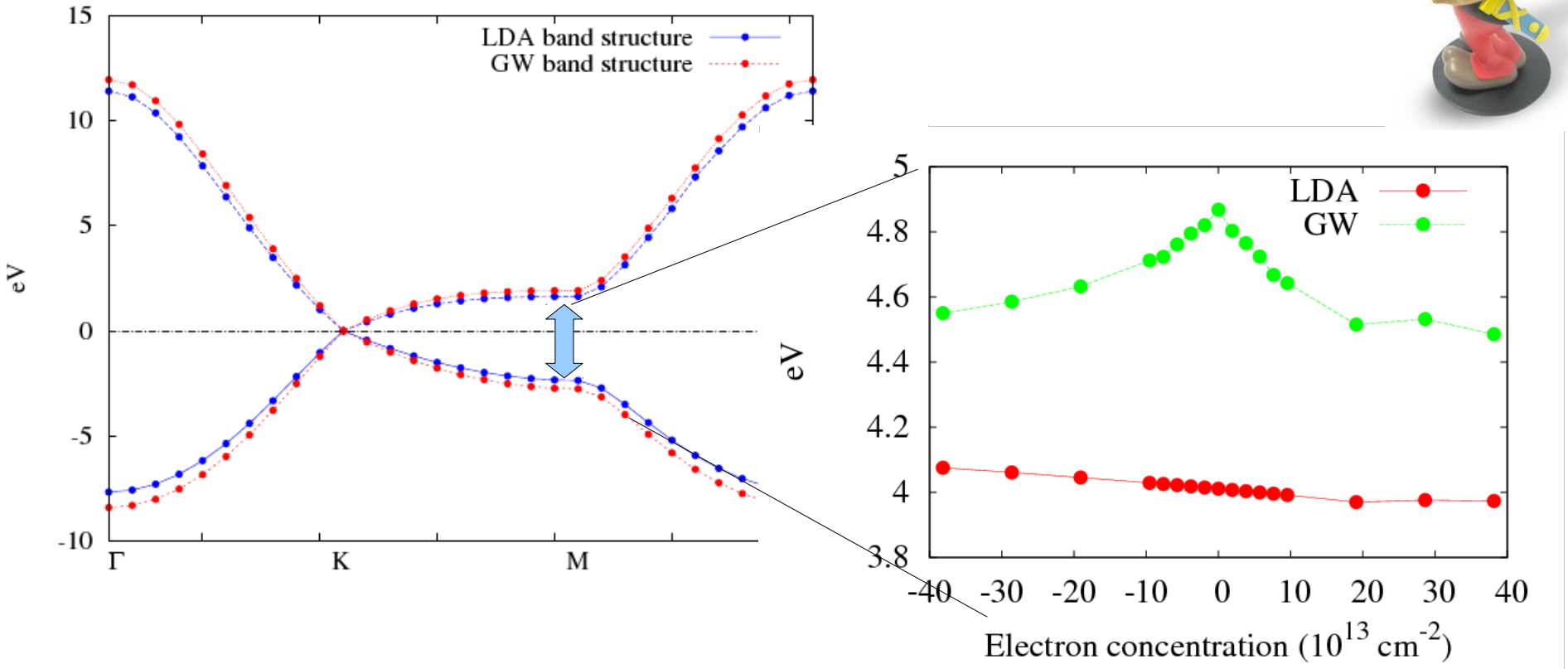
A. Das et al. Nature Nanotechnology **3**, 210 - 215 (2008)



Intercalated Graphite

A Gruneis, C. Attaccalite et al. Phys. Rev. B **80**, 075431 (2009)

Quasiparticle band structure of Doped Graphene



The effective interaction experienced by the electrons becomes weaker due the stronger screening of the Coulomb potential.

M. Polini et al. Solid State Commun. **143**, 58(2007)

C. Attaccalite et al. Phys. Status Solidi B, **246,** 2523(2009)

Electron-phonon coupling and doping

$$\lambda_{\boldsymbol{q}\nu} = \frac{2}{\hbar \omega_{\boldsymbol{q}\nu} N_\sigma(\epsilon_f)} \int_{BZ} \frac{d\boldsymbol{k}}{\Omega} \sum_{i,j} \left| g^{\nu}_{\boldsymbol{k}\boldsymbol{i},(\boldsymbol{k}+\boldsymbol{q},j)} \right|^2 \delta(\epsilon_k - \epsilon_k)\, \delta(\epsilon_{k+q} - \epsilon_f)$$

..where the electron-phonon matrix element..

$$g^{\nu}_{\boldsymbol{k}\boldsymbol{i},(\boldsymbol{k}+\boldsymbol{q},j)} = \langle \boldsymbol{k}+\boldsymbol{q}, j | \Delta V_{\boldsymbol{q}\nu} | \boldsymbol{k}, i \rangle$$

describe the scattering of an electron from the band i to band j due to the phonon ν

Has been always considered a constant with respect to the electron/hole doping

Electron-phonon coupling and doping

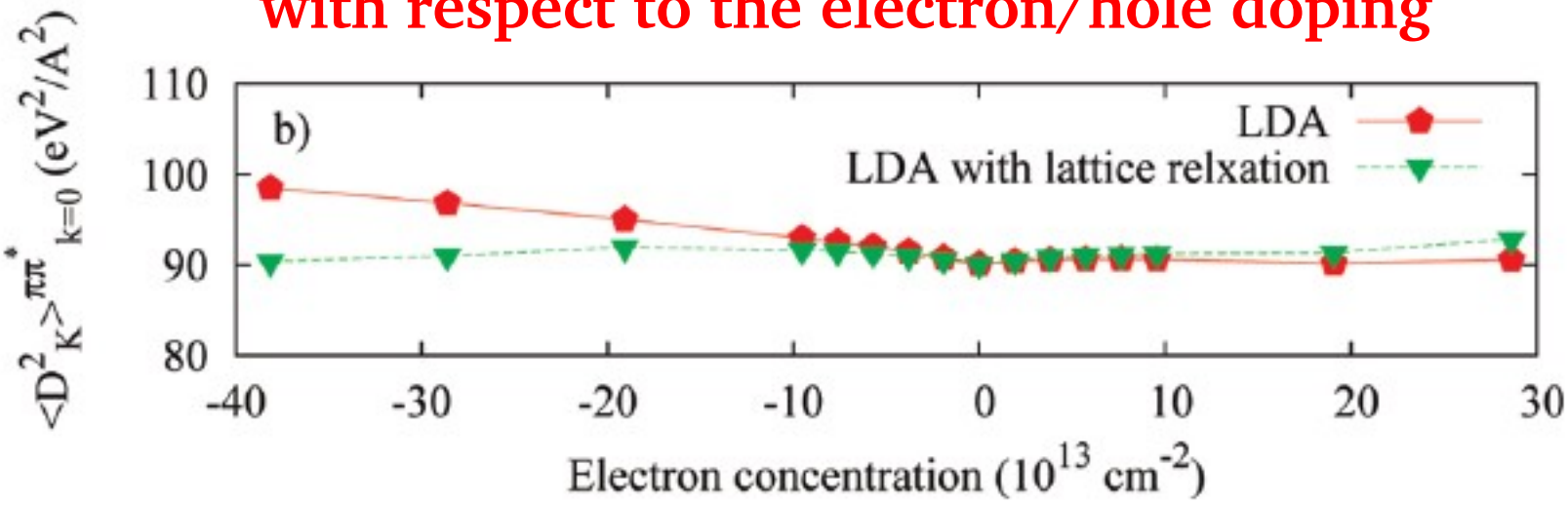
$$\lambda_{q\nu}=\frac{2}{\hbar\omega_{q\nu}N_{\sigma}(\epsilon_f)}\int_{BZ}\frac{d\,\boldsymbol{k}}{\Omega}\sum_{i,j}\left|g^{\nu}_{\boldsymbol{ki},(\boldsymbol{k}+\boldsymbol{q},j)}\right|^2\delta(\epsilon_k-\epsilon_k)\,\delta(\epsilon_{k+q}-\epsilon_f)$$

..where the electron-phonon matrix element..

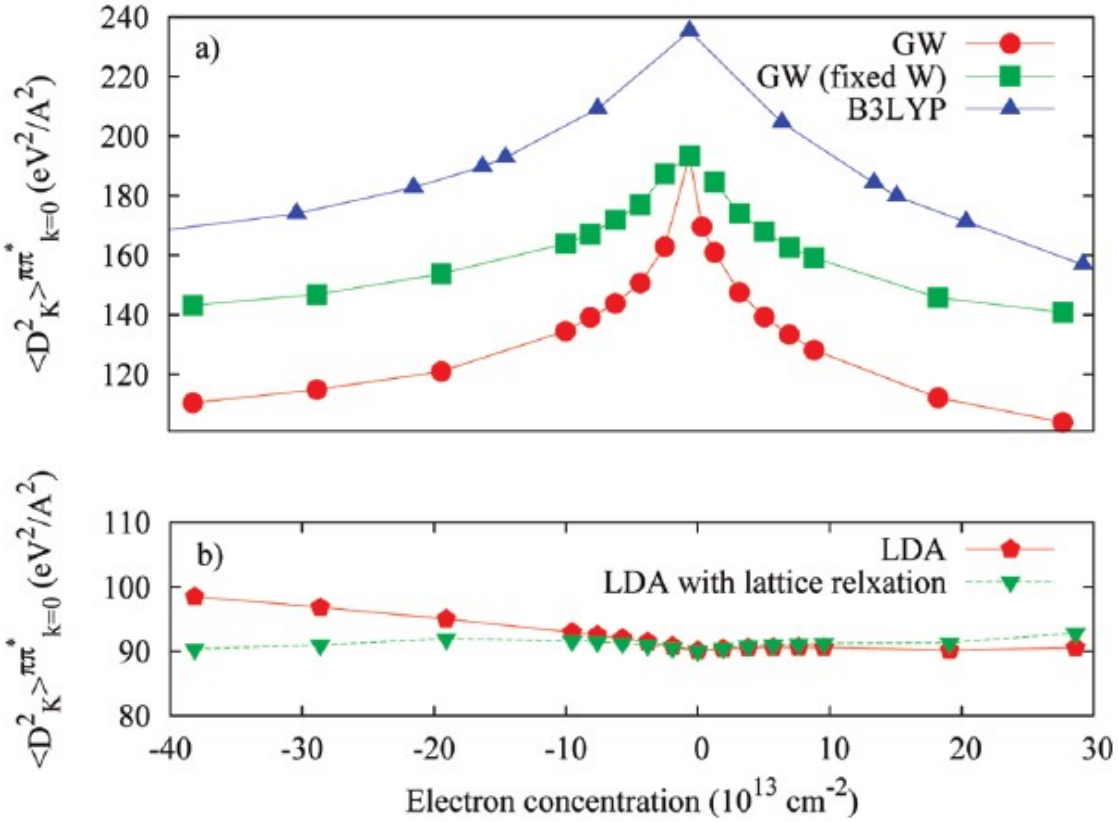
$$g^{\nu}_{\boldsymbol{ki},(\boldsymbol{k}+\boldsymbol{q},j)}=\langle \boldsymbol{k}+\boldsymbol{q},j\left|\Delta V_{q\nu}\right|\boldsymbol{k},i\rangle$$

describe the scattering of an electron from the band i to band j due to the phonon ν

Has been always considered a constant with respect to the electron/hole doping



Electron-phonon Coupling at K

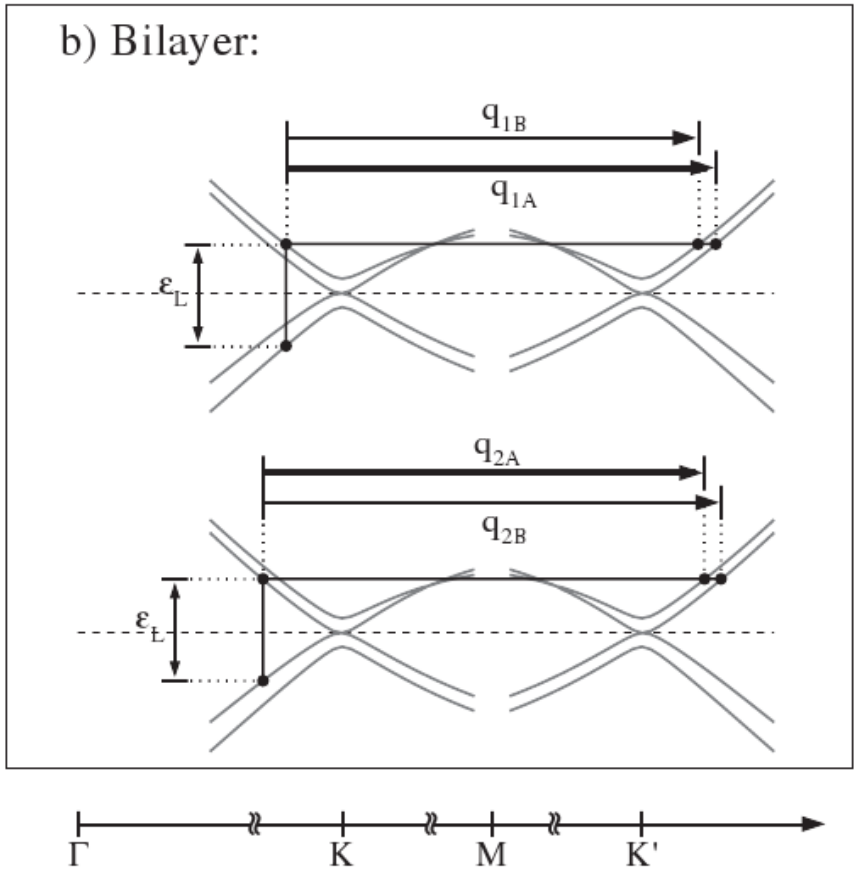


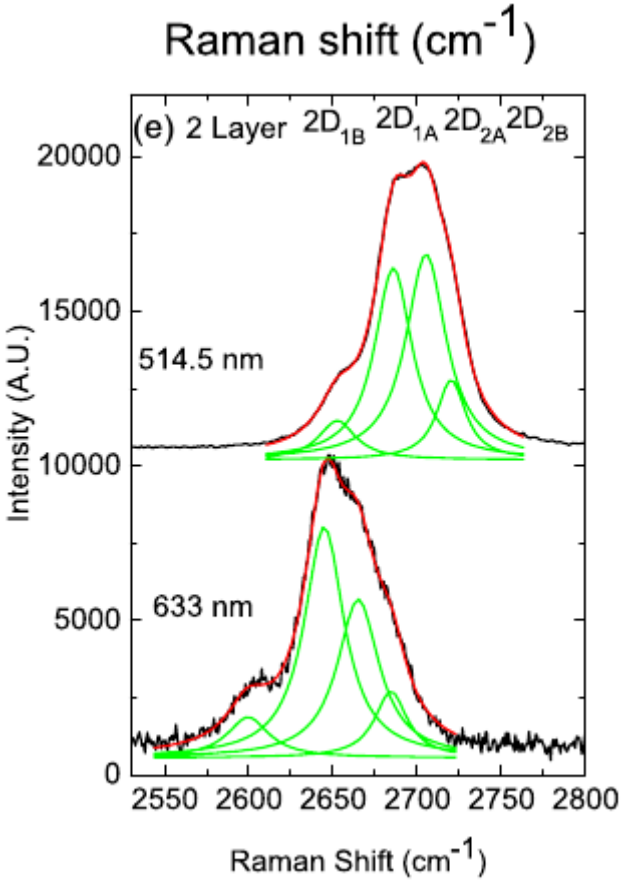
$\langle D_K \rangle$ changes by more than 40%

Squared deformation potential for the K-A1′ phonon between the π bands $\langle D^2 \rangle_{\pi\pi^*}$ in different approximations.

C. Attaccalite et al. Nano Letters, **10**(2) 1172 (2010)

Raman 2D peak splitting in bilayer graphene



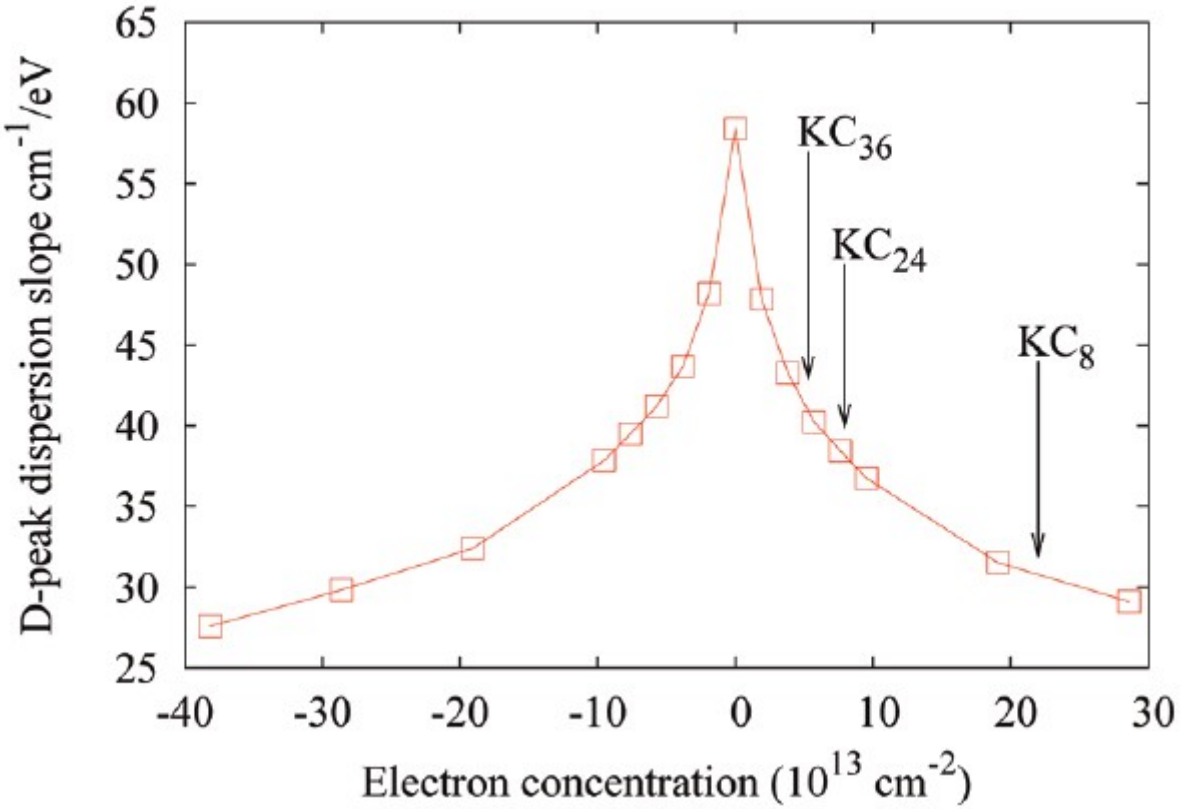


A. C. Ferrari et al. Phys. Rev. Lett., **97** 187401(2006)

Introduce a doping dependence in the slitting of the 2D peak in multilayer graphene

C. Attaccalite et al. Nano Letters, **10**(2) 1172 (2010)

Raman D-peak dispersion



Change of slope of the Raman D peak dispersion versus doping. Arrows indicate the equivalent doping level for the KC_8, KC_{24}, and KC_{36} intercalated graphite.

C. Attaccalite et al. Nano Letters, **10**(2) 1172 (2010)

Conclusions

- Quasi-particle effects are important in the calculation of the EPC
- In graphene and graphite DFT(LDA and GGA) underestimates the phonon dispersion of the highest optical branch at the zone-boundaries
- It is possible to reproduce completely *ab-initio* the Raman D-line shift
- Correlation effects induce a doping dependence in the EPC at K that can be measured in experiments

Acknowledgment

My collaborators:

M. Lazzeri, L. Wirtz, A. Rubio, F. Mauri

The codes:

YAMBO ©

QUANTUMESPRESSO

CRYSTAL — a computational tool for solid state chemistry and physics

The support from:

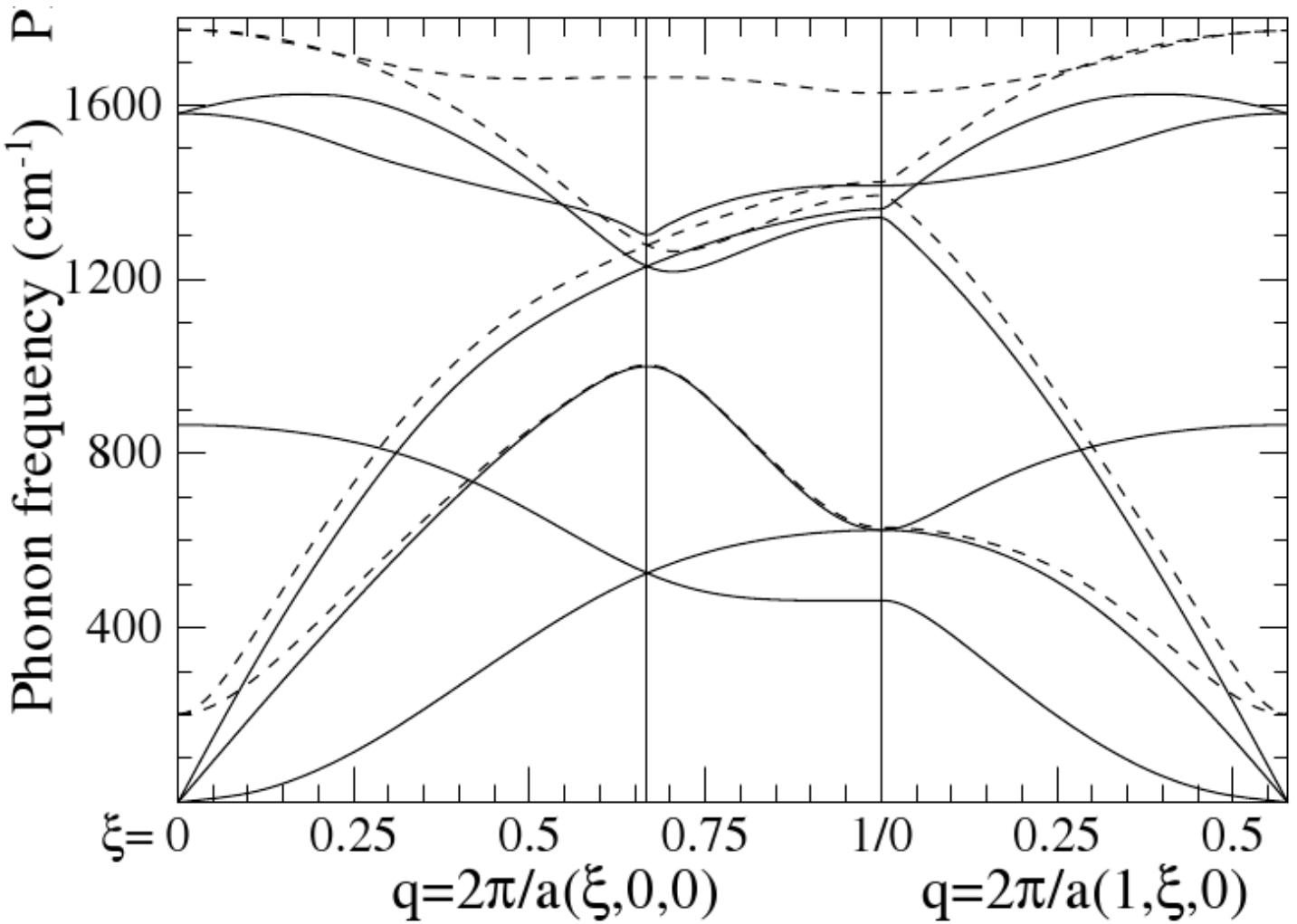
NÉEL institut

cnrs — advancing the frontiers

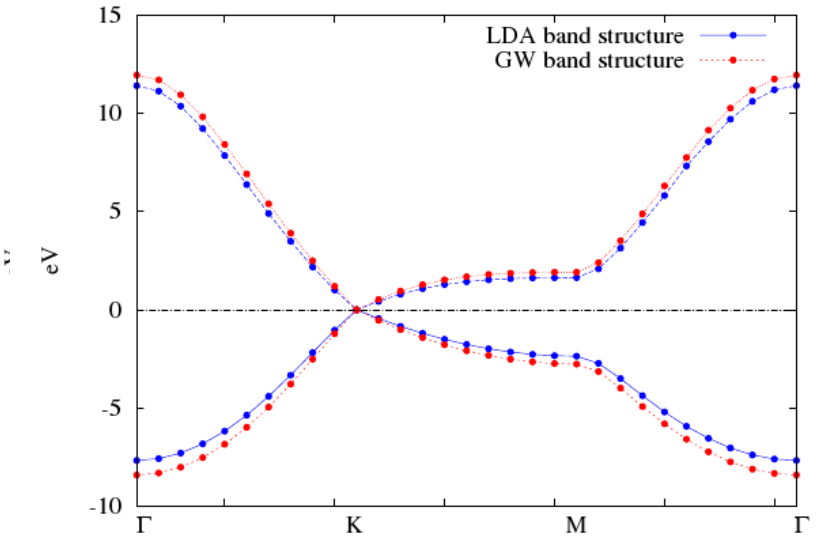
ETSF — European Theoretical Spectroscopy Facility

Phonon dispersion without dynamical matrix of the π bands

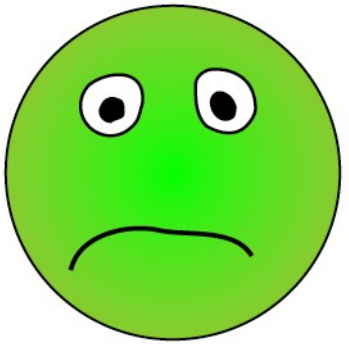
$$\tilde{\omega} = \sqrt{B_q / m}$$



..but using quasi-particle band structure provides a worse result



$$\omega_q = \sqrt{(B_q + P_q)/m}$$



where $$P_q = \frac{4}{N_k} \sum_k \frac{\left| D_{(k+q)\pi^*, k\pi} \right|^2}{\epsilon_{k,\pi} - \epsilon_{k+q,\pi^*}}$$

In fact the GW correction to the electronic bands alone results in a larger denominator providing a smaller phonon slope and a worse agreement with experiments.

How to model the phonon dispersion

to determine the GW phonon dispersion we assume

$$\omega_q^{GW} \simeq \sqrt{(B_q^{GW} + r^{GW} P_q^{DFT})/m}$$

where

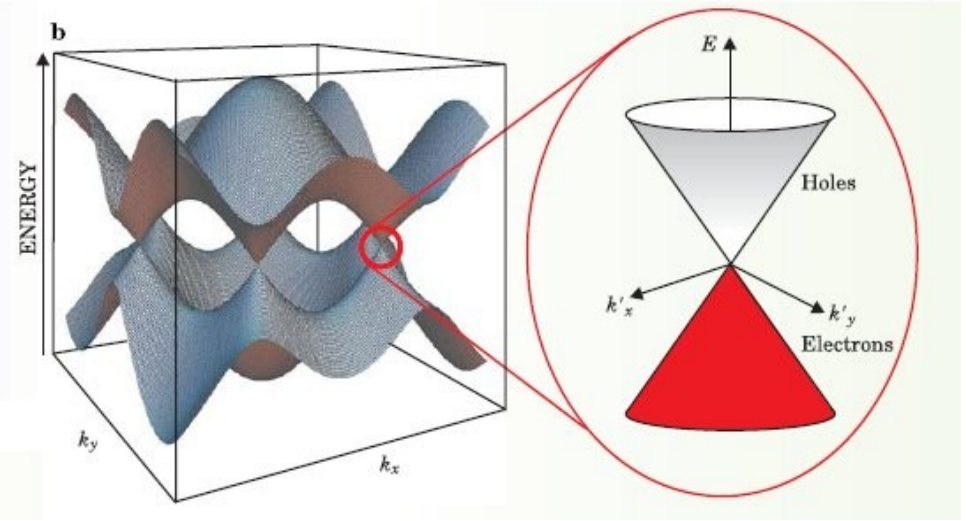
$$r^{GW} = \frac{\alpha_K^{GW}}{\alpha_K^{DFT}} \simeq \frac{P_K^{GW}}{P_K^{DFT}}$$

$$B_q^{GW} \simeq B_K^{GW}$$

We assume B_q constant because it is expected to have a small dependence from q and fit it from the experimental measures

The resulting K A′ phonon frequency is **1192 cm^{-1}** which is our best estimation and is almost 100 cm^{-1} smaller than in DFT.

...the same result ...
but with another approach



Dirac massless fermions
+
Renormalization Group

D. M. Basko et I. L. Aleiner
Phys. Rev. B **77**, 0414099(R) 2008

Electron and phonon
renormalization
of the EPC vertex

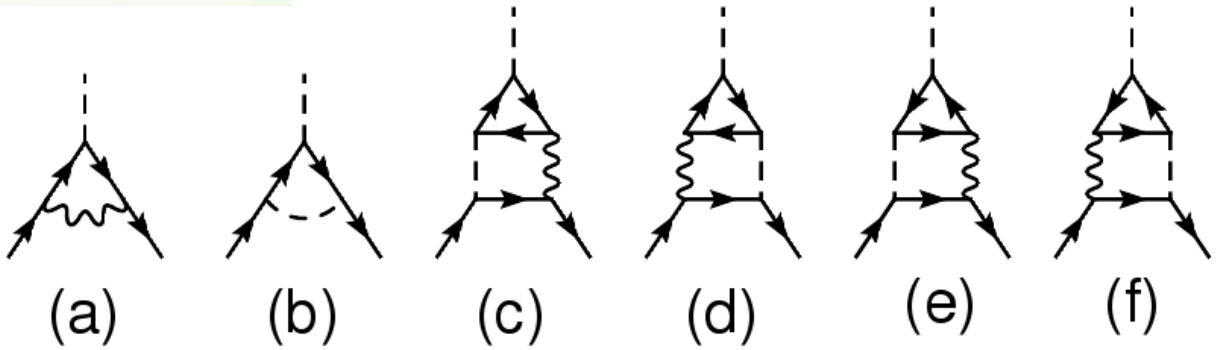


FIG. 4: Logarithmic corrections to the EPC vertex F_μ of the order $O(1/\mathcal{N}, \lambda_\mu^2)$. Diagrams (c)–(f) vanish.

Density Functional Theory

The ground state energy is expressed in terms of the density and an unknown functional E_{xc}

$$E[n]=T_0[n]-\frac{e^2}{2}\int\frac{n(r)n(r')}{|r-r'|}dr\,dr'+E_{xc}[n]-\int n(r)v_{xc}(r)dr$$

Kohn-Sham eigenfunctions are obtained from

$$\left(\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial r^2}+V_{SCF}(r)\right)\Psi_n(r)=\epsilon_n\Psi_n(r)$$

Usually E_{xc} in the local density approximation (LDA) or the general gradient approximation (GGA) successfully describes the ground state properties of solids.

Beyond DFT: Many-Body Perturbation Theory

Starting from the LDA Hamiltonian we construct the Quasi-Particle Dyson equation:

$$[T+V_h+V_{ext}]\Psi_{n,k}(r)+\int dr'\,\Sigma(r,r';E_{n,k})\Psi_{n,k}(r')=E_{n,k}\Psi_{n,k}(r)$$

Σ: Self-Energy Operator; $E_{n,k}$: Quasi-particle energies;

... following Hedin(1965): the self-energy operator is written as a perturbation series of the screened Coulomb interaction

$$\Sigma = i\,G\,W+\cdots$$

$$W=\epsilon^{-1}v$$

G: dressed Green Function

W: in the screened interaction

Many-Body perturbation Theory 2

Approximations for G and W (Hybertsen and Louie, 1986):

- Random phase approximation (RPA) for the dielectric function.
- General plasmon-pole model for dynamical screening.

we use the LDA results as starting point $G \approx G^{LDA}$

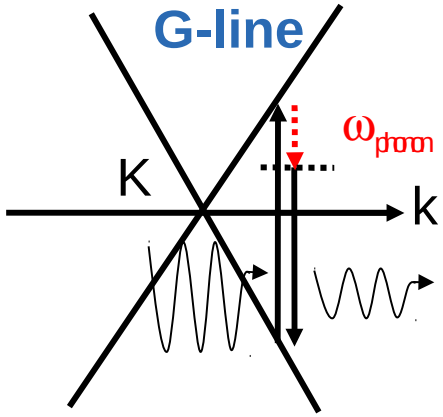
and so the Dyson equation becomes

$$\left(T + V_h + V_{ext} + V_{xc}\right)\Psi_{n,k} \int \Sigma'\left(r, r'; E_{n,k}\right)\Psi_{n,k} = E_{n,k}\Psi_{n,k}(r)$$

$$\Sigma'\left(r, r'; E_{n,k}\right) = \Sigma'\left(r, r'; E_{n,k}\right) - \delta\left(r, r'\right)V_{xc}(r)$$

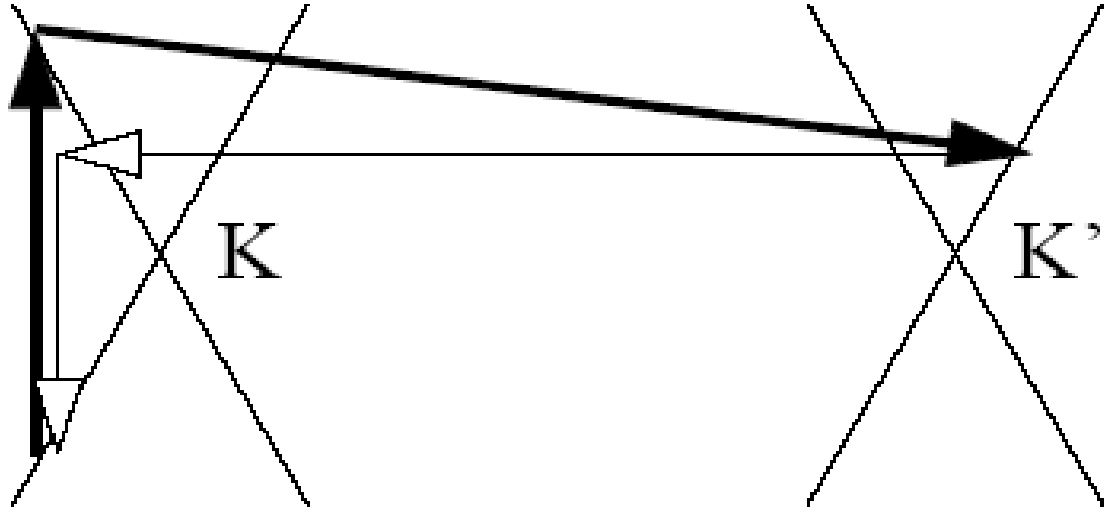
Raman spectroscopy of graphene

Single-resonant G-line



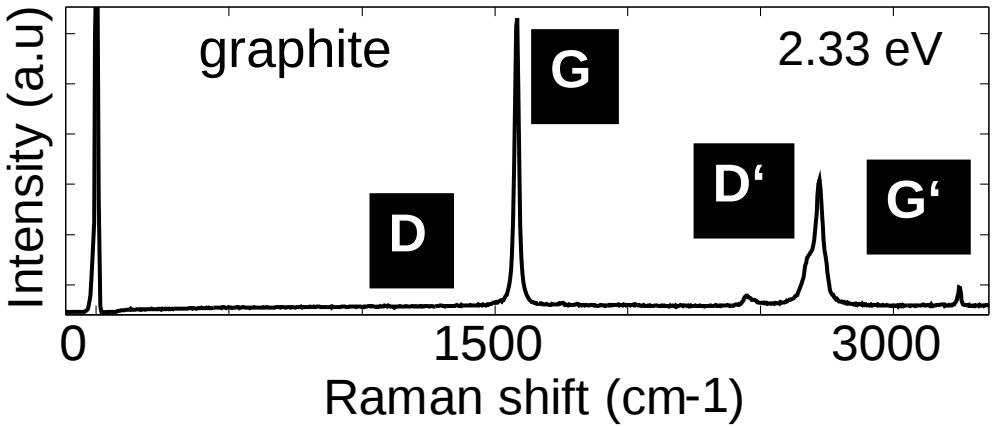
at Γ point, k~0
→ **G-line**

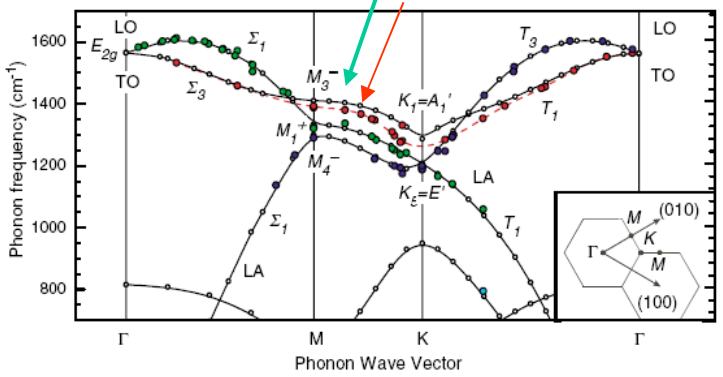
D-line



dispersive

TO mode between K and M





Ref.: S. Reich, C. Thomsen, J. Maultzsch, Carbon Nanotubes, Wiley-VCH (2004)