GraphITA, l'Aquila, 16 May 2011

Tuning infrared phonon anomalies in optical conductivity of bilayer graphene: matching theory and experiments

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Phonon features in optical spectroscopy

analysis of phonon peak features in optics

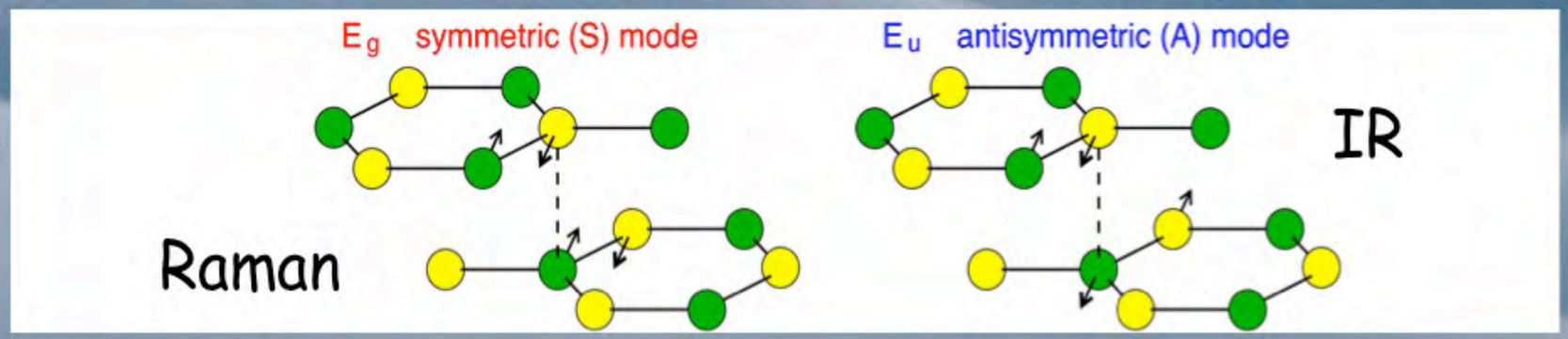
- characterization (N. layers, doping, disorder…)
- revealing of underlying many-body (el-ph) interactions
- investigation fundamental physics (Kohn anomalies, nonadiabaticity)

so far, most works mainly done using Raman spectroscopy

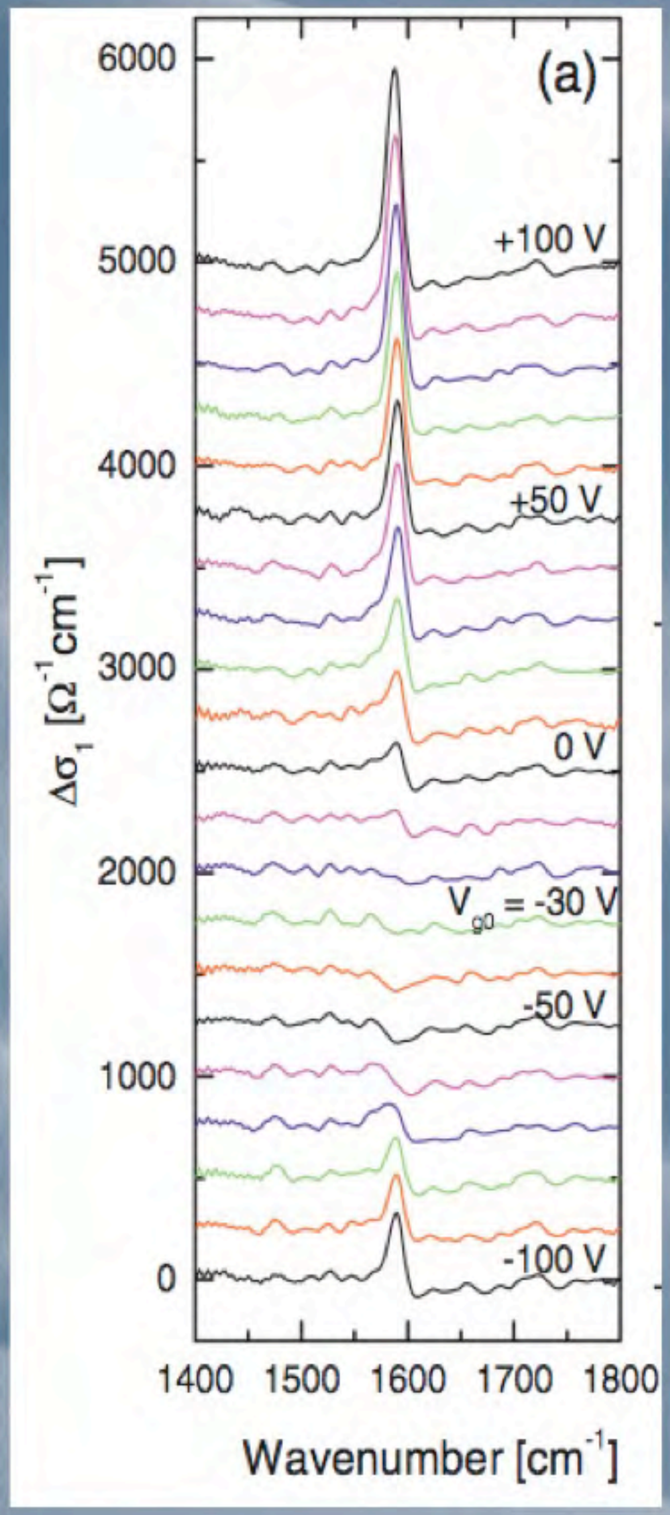
- phonon frequencies and linewidths
- absolute intensity G peaks not doping dependent

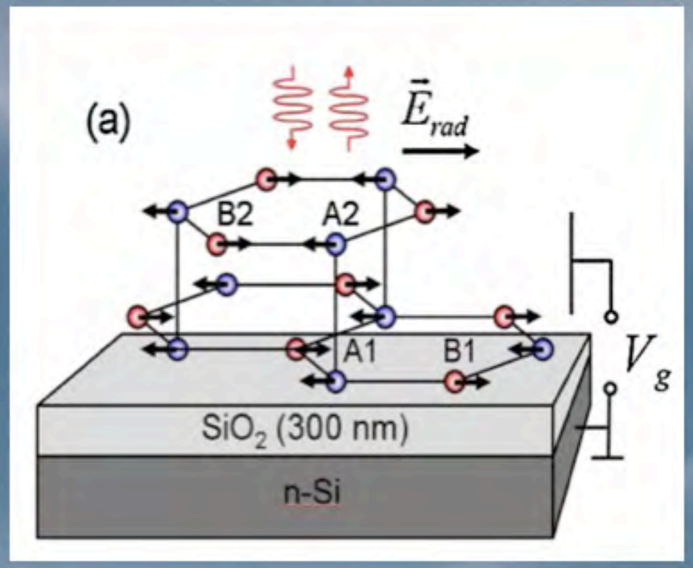
phonon features in infrared spectroscopy

- complentary information (different phonon symmetry)
- much sensible to n. layers/stacking (absent in 1 layer)
- further suitable properties (absolute intensity + lineshape asymmetry)



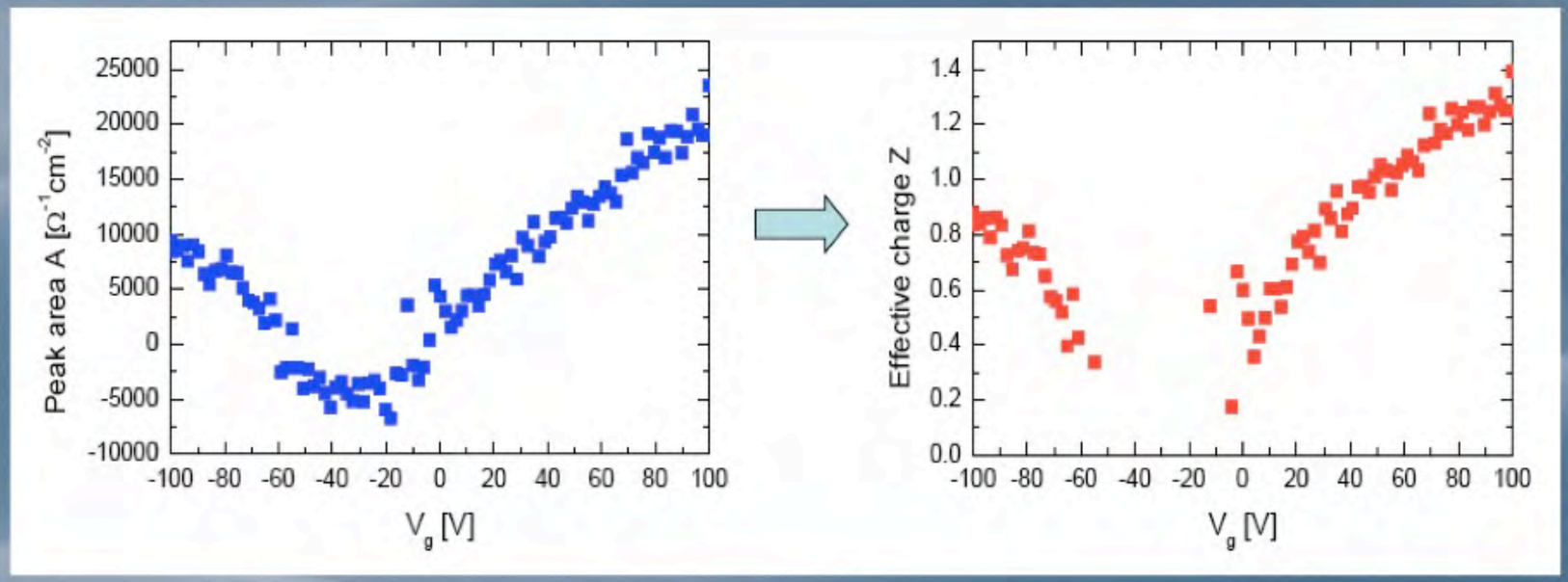
Exp. results: Geneve group





bilayer graphene

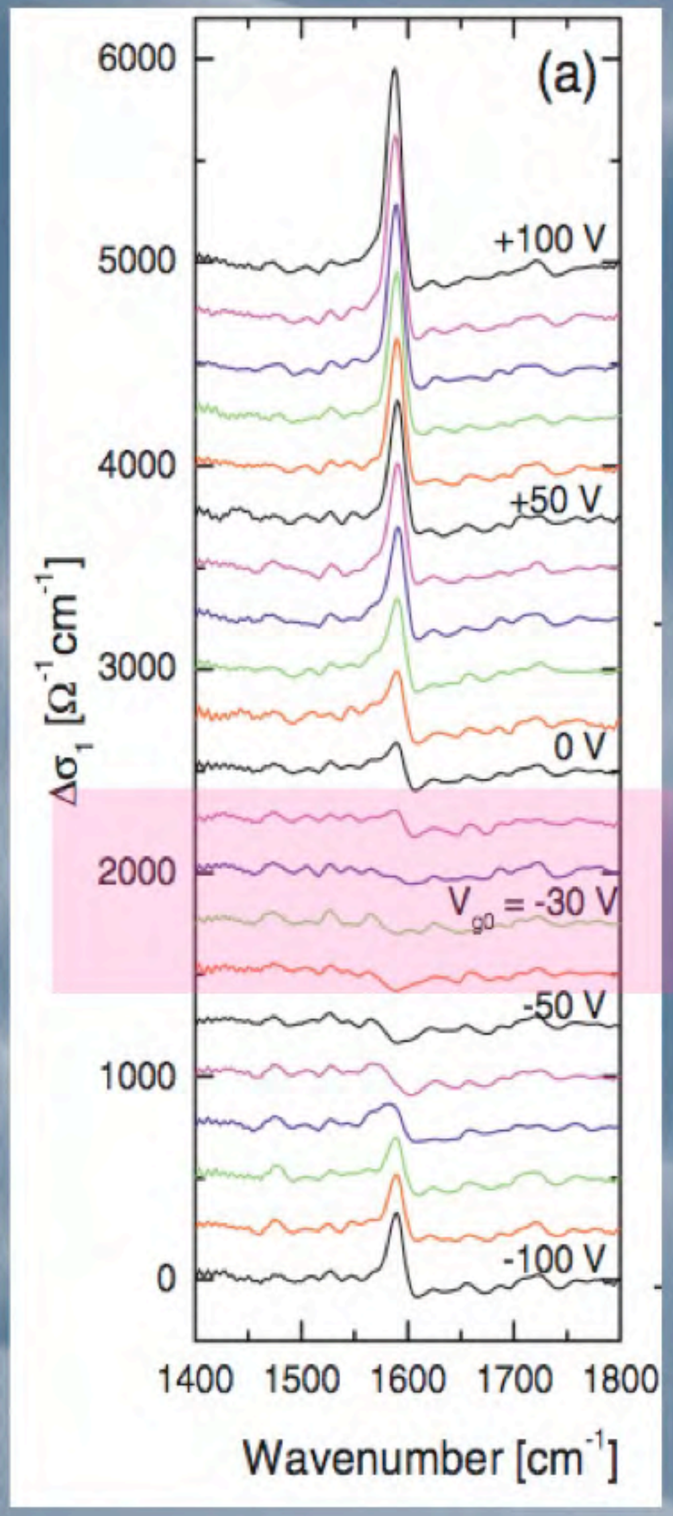
tunable phonon peak intensity

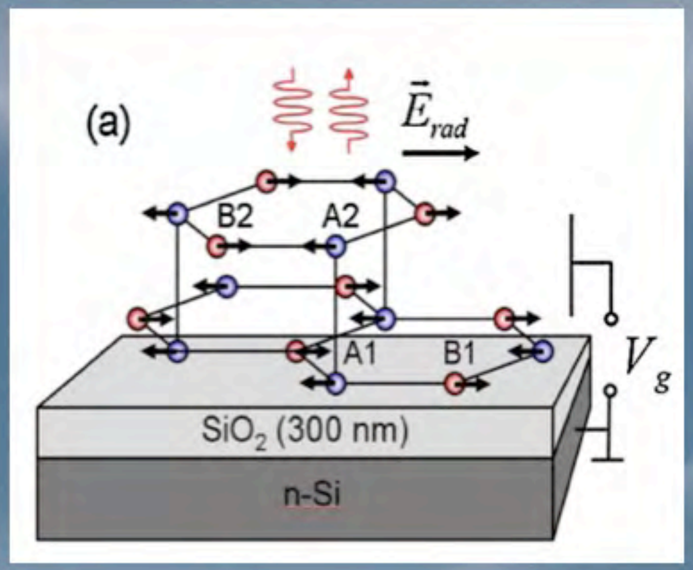


Z_{max} ~ 1.2!! huge!
as large as 1 electron over N=4 (sp^3) !!

AB Kuzmenko et al, PRL 103, 116804 (2009)

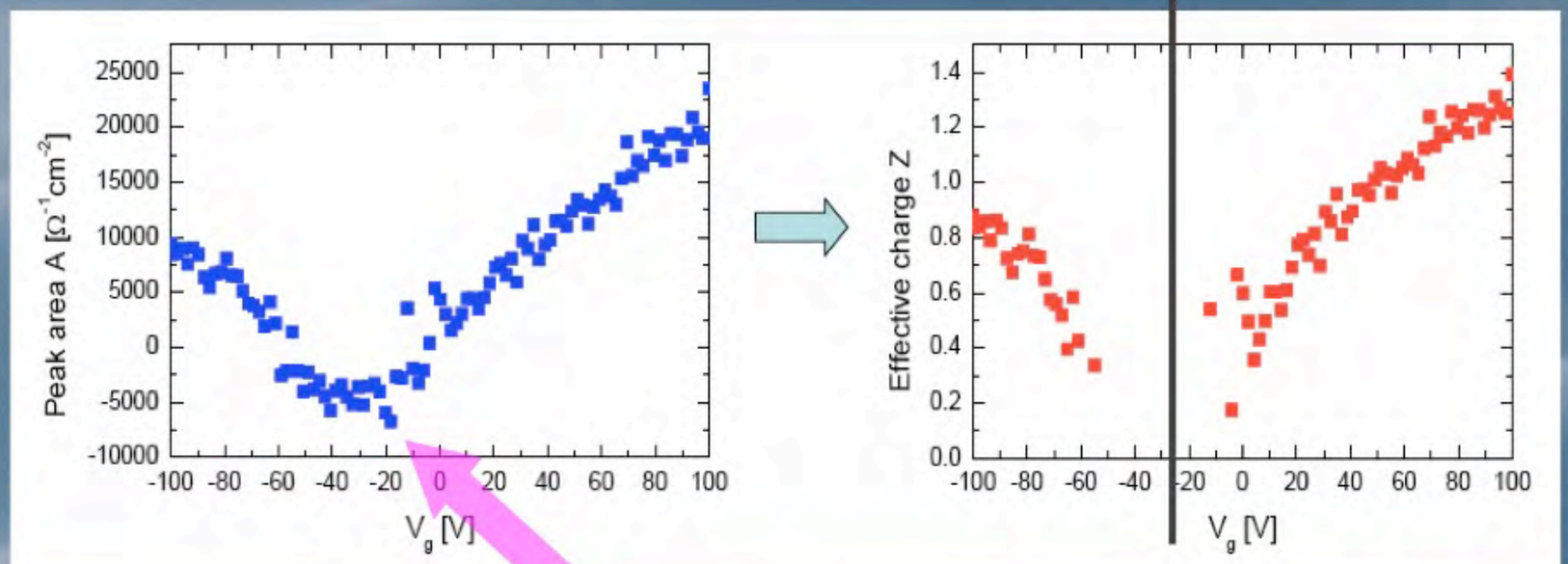
Exp. results: Geneve group





tunable phonon peak intensity

neutrality point (NP) n=0



also problem: negative peak area...
Z not defined...?

AB Kuzmenko et al, PRL 103, 116804 (2009)

Exp. results: Geneve group

- four independent parameter fit

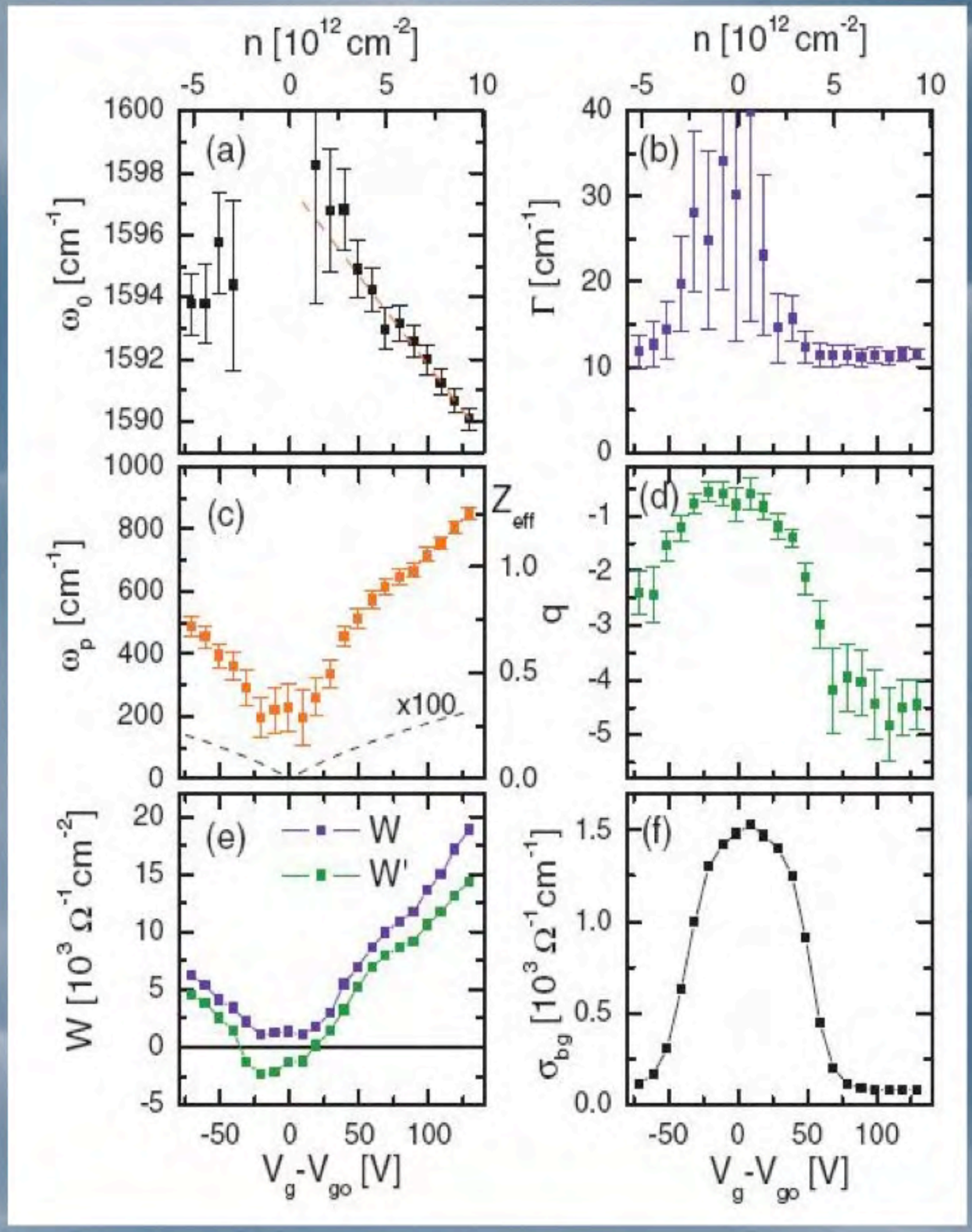
$$\sigma'(\omega) - \sigma'_{BG}(\omega) = \frac{\omega_p^2}{4\pi\Gamma} \frac{q^2 - 1 - 2qz}{q^2(z^2+1)}$$

$$\left[z = \frac{\omega - \omega_0}{\Gamma} \right]$$

- ω_0 : phonon frequency
- Γ : phonon linewidth
- ω_p : related to intensity
- q : Fano asymmetry

$$W' = \frac{\omega_p^2}{8}\left(1 - \frac{1}{q^2}\right) \qquad W = \frac{\omega_p^2}{8}$$

"bare" intensity (in the absence of Fano)



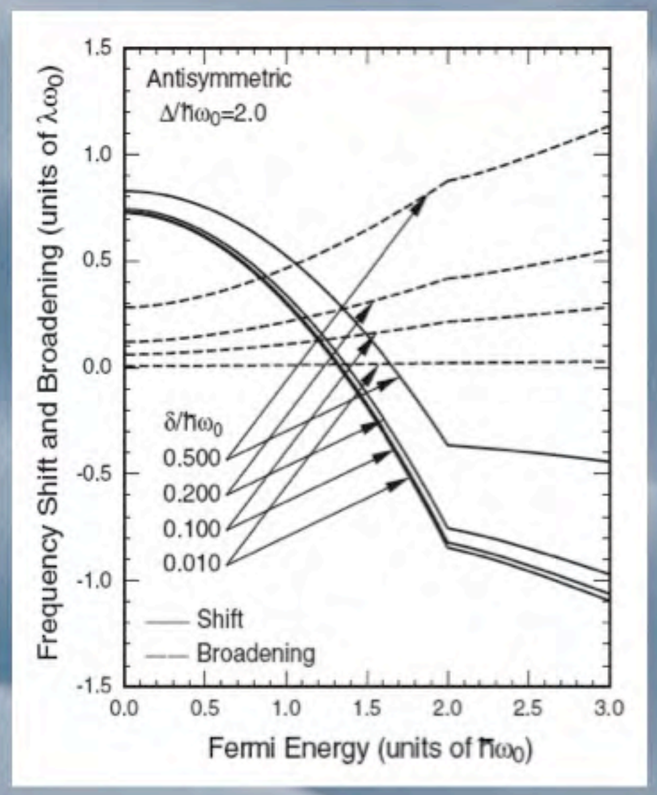
AB Kuzmenko et al, PRL 103, 116804 (2009)

Exp. results: Geneve group

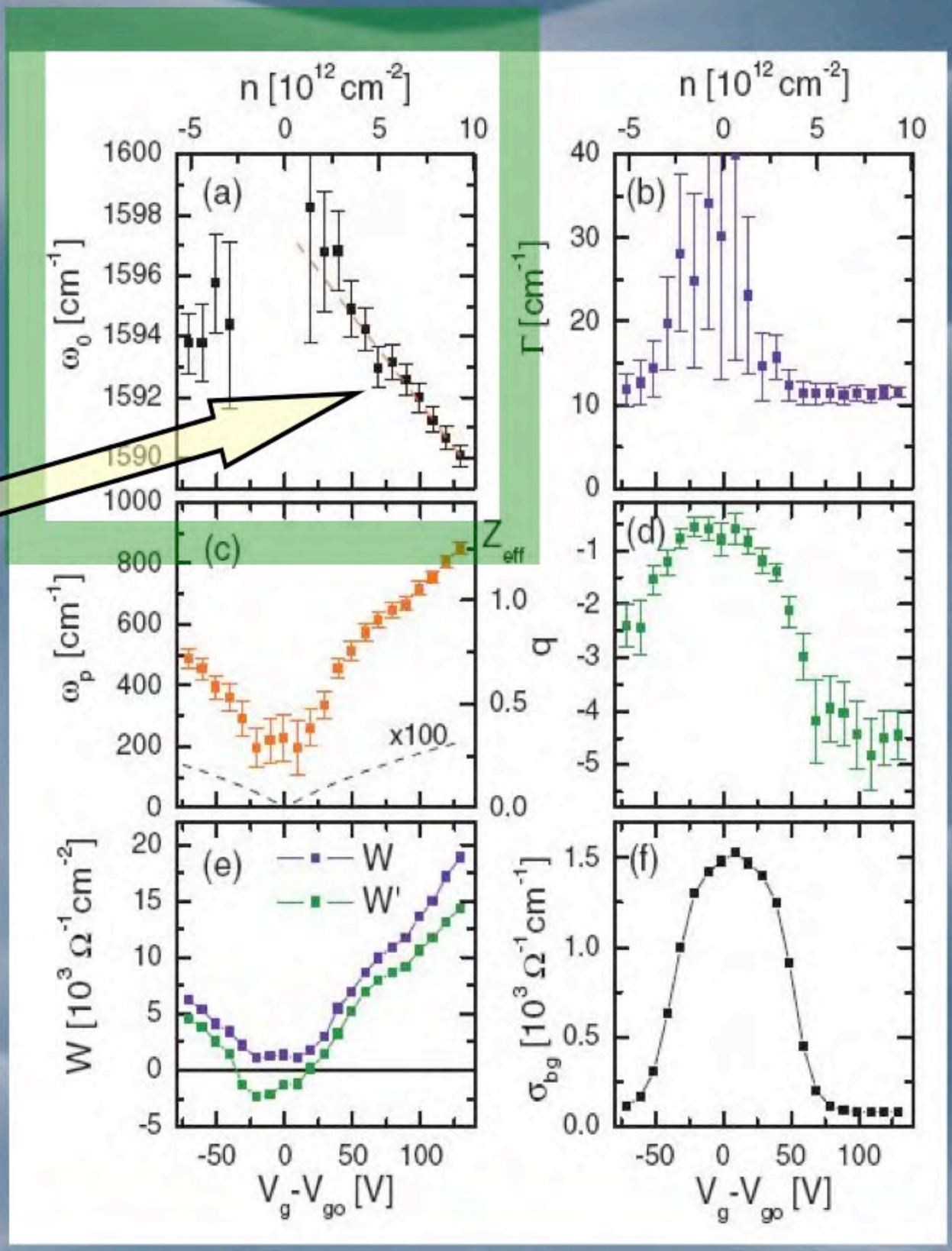
- phonon softening with doping: ok with LDA and TB theory

~~E_g (S) mode~~

E_u (A) mode



T Ando, JPSJ 76, 104711 (2007)

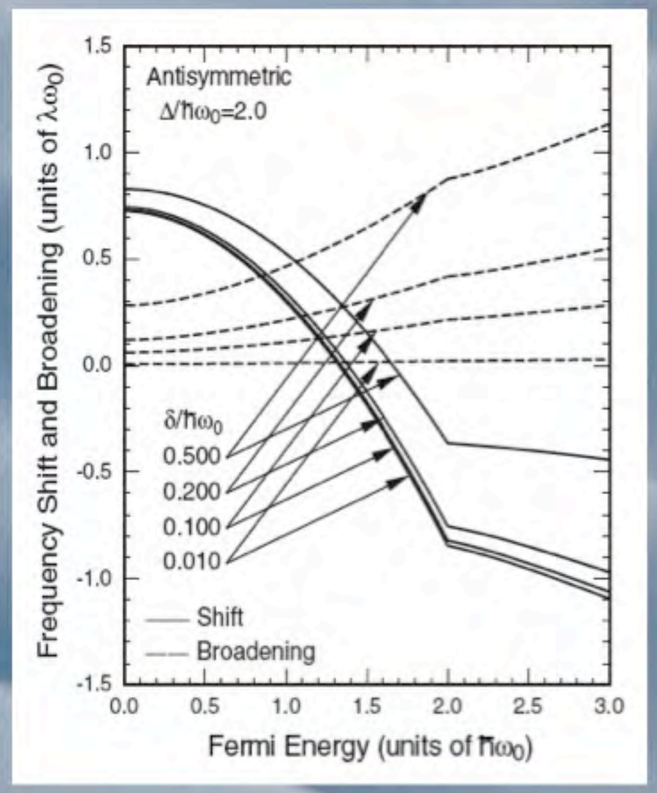


AB Kuzmenko et al, PRL 103, 116804 (2009)

Exp. results: Geneve group

- phonon softening with doping: ok with LDA and TB theory
- phonon linewidth: strong increase at NP: why??

E_u (A) mode?



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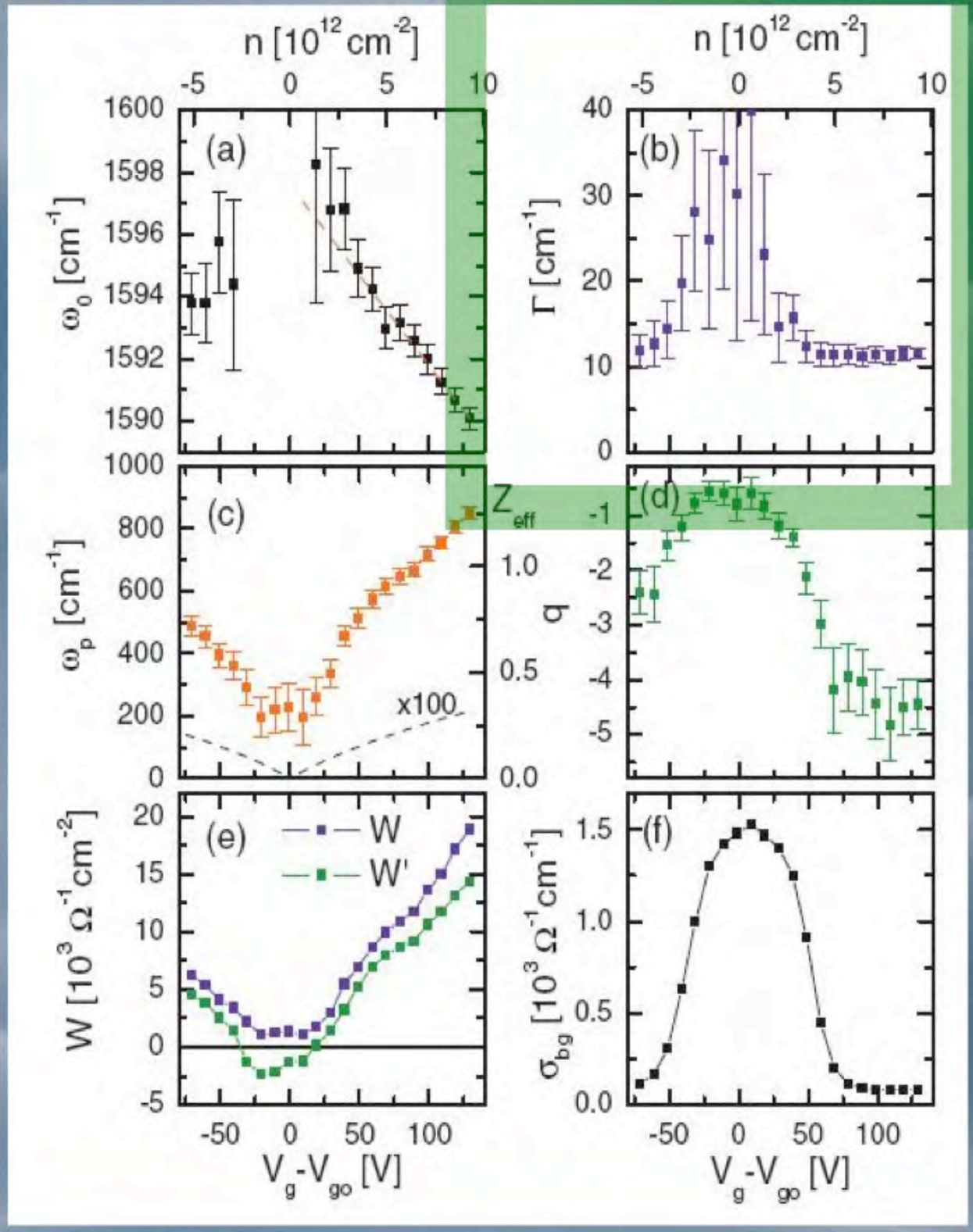
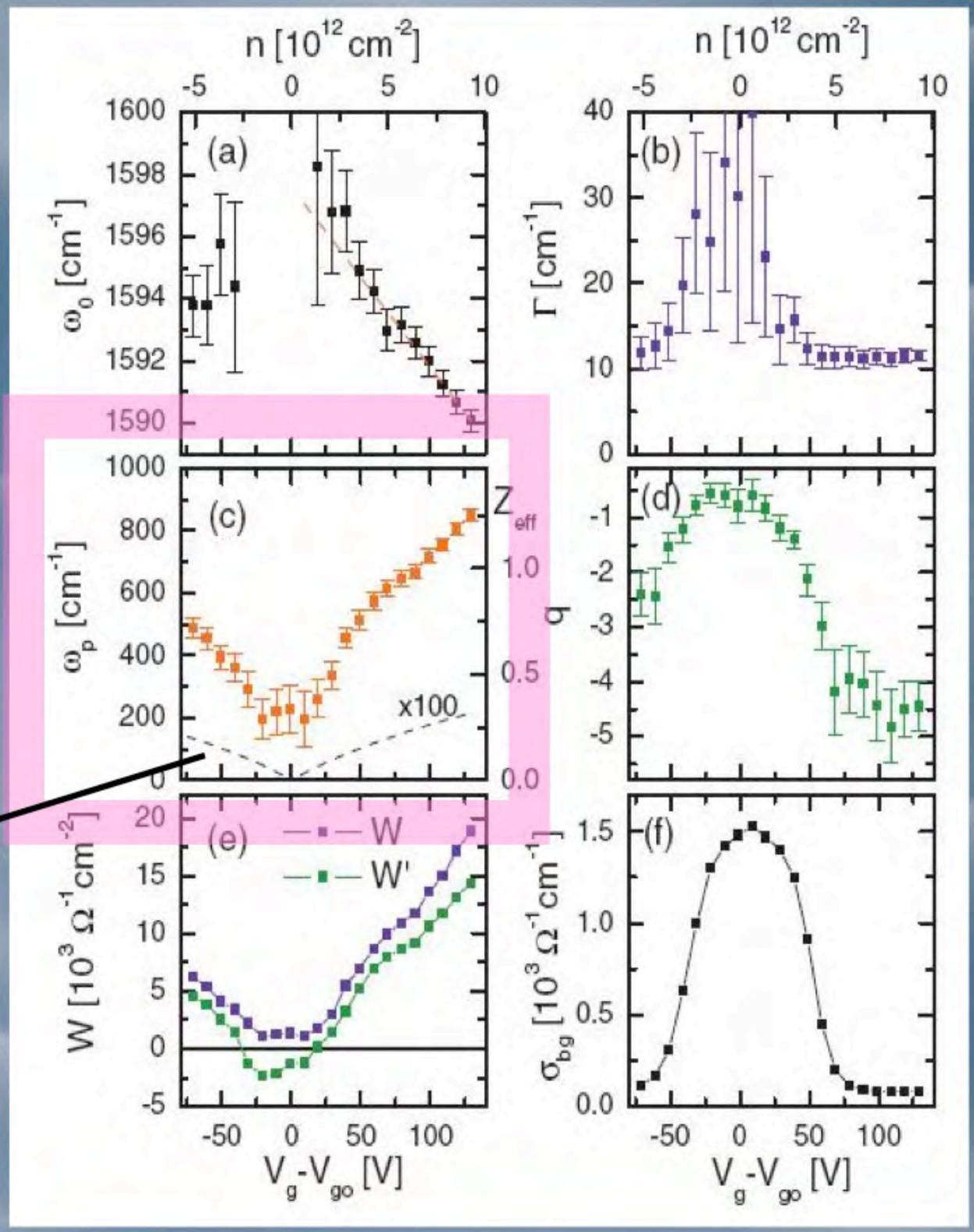


AB Kuzmenko et al, PRL 103, 116804 (2009)

Exp. results: Geneve group

- phonon softening with doping: ok with LDA and TB theory
- phonon linewidth: not clear, but poor exp. resolution
- linear dependence of bare intensity with doping: where from? why so huge Z?

NB: tight-binding calculations



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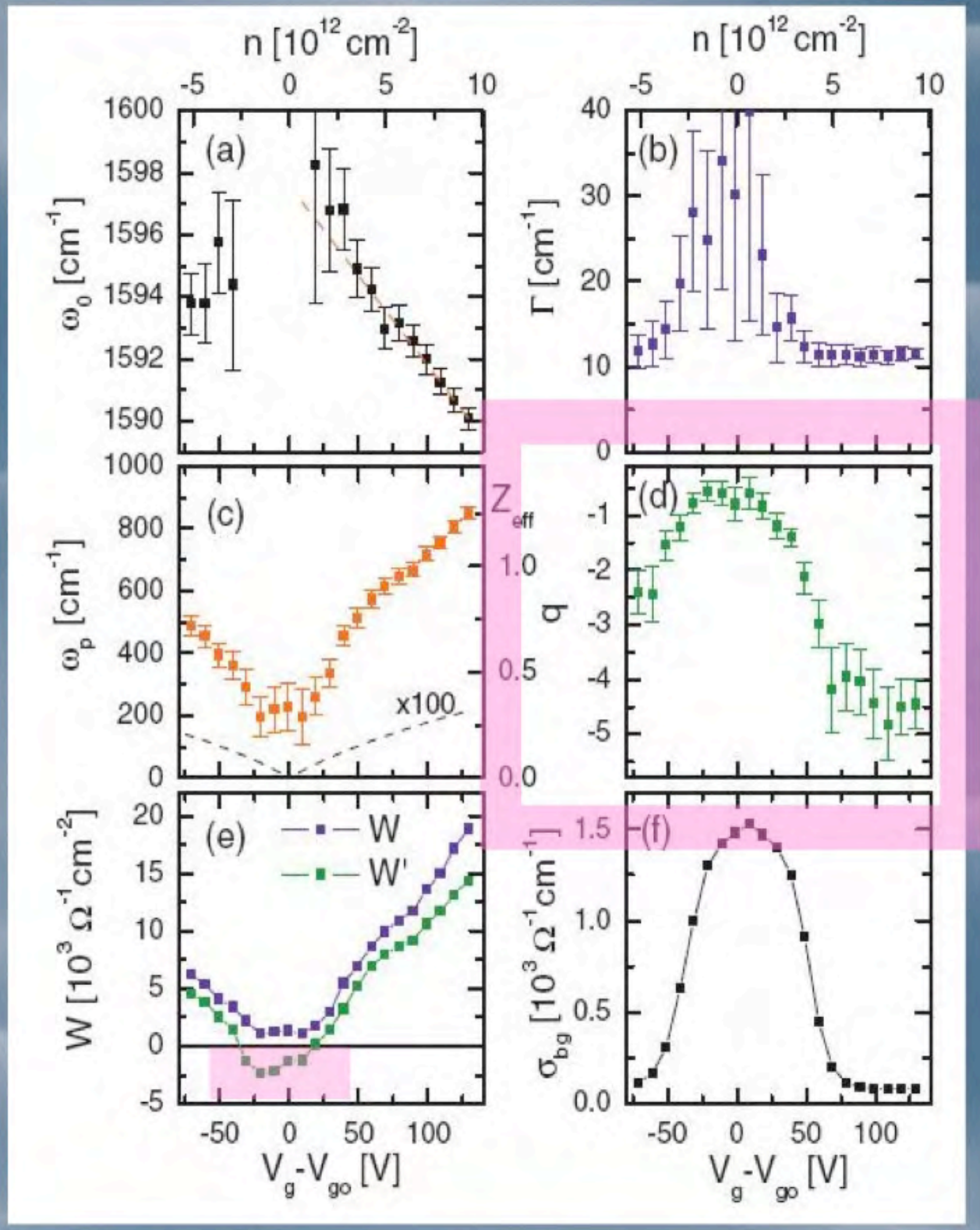
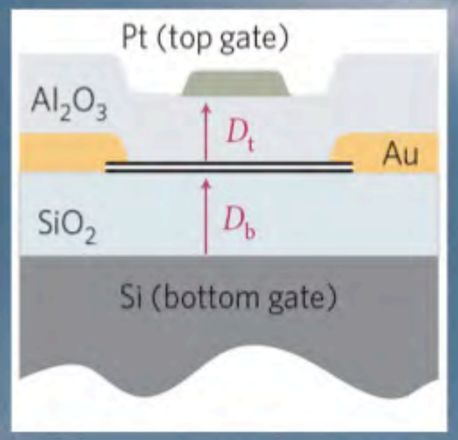
Exp. results: Geneve group

- phonon softening with doping: ok with LDA and tB theory
- phonon linewidth: not clear, but poor exp. resolution
- linear dependence of bare intensity with doping: where from? why so huge Z?
- Fano asymmetry: where from? related to el. optical background? points out finite intensity at n=0...!



AB Kuzmenko et al, PRL 103, 116804 (2009)

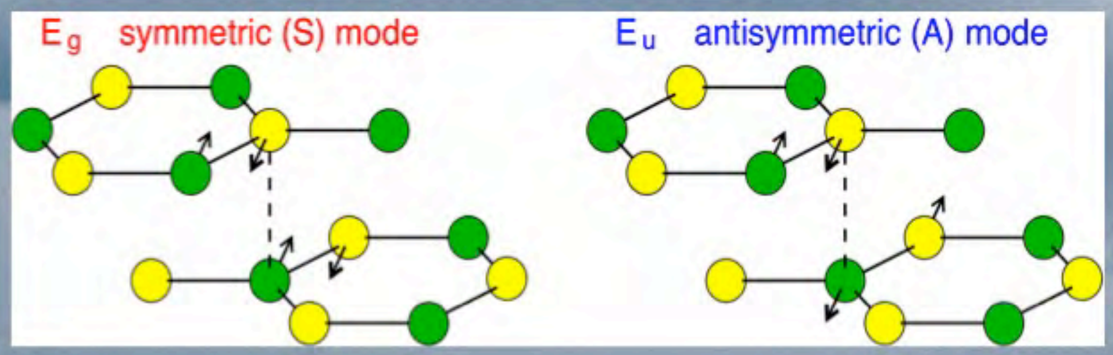
Exp. results: Berkeley group

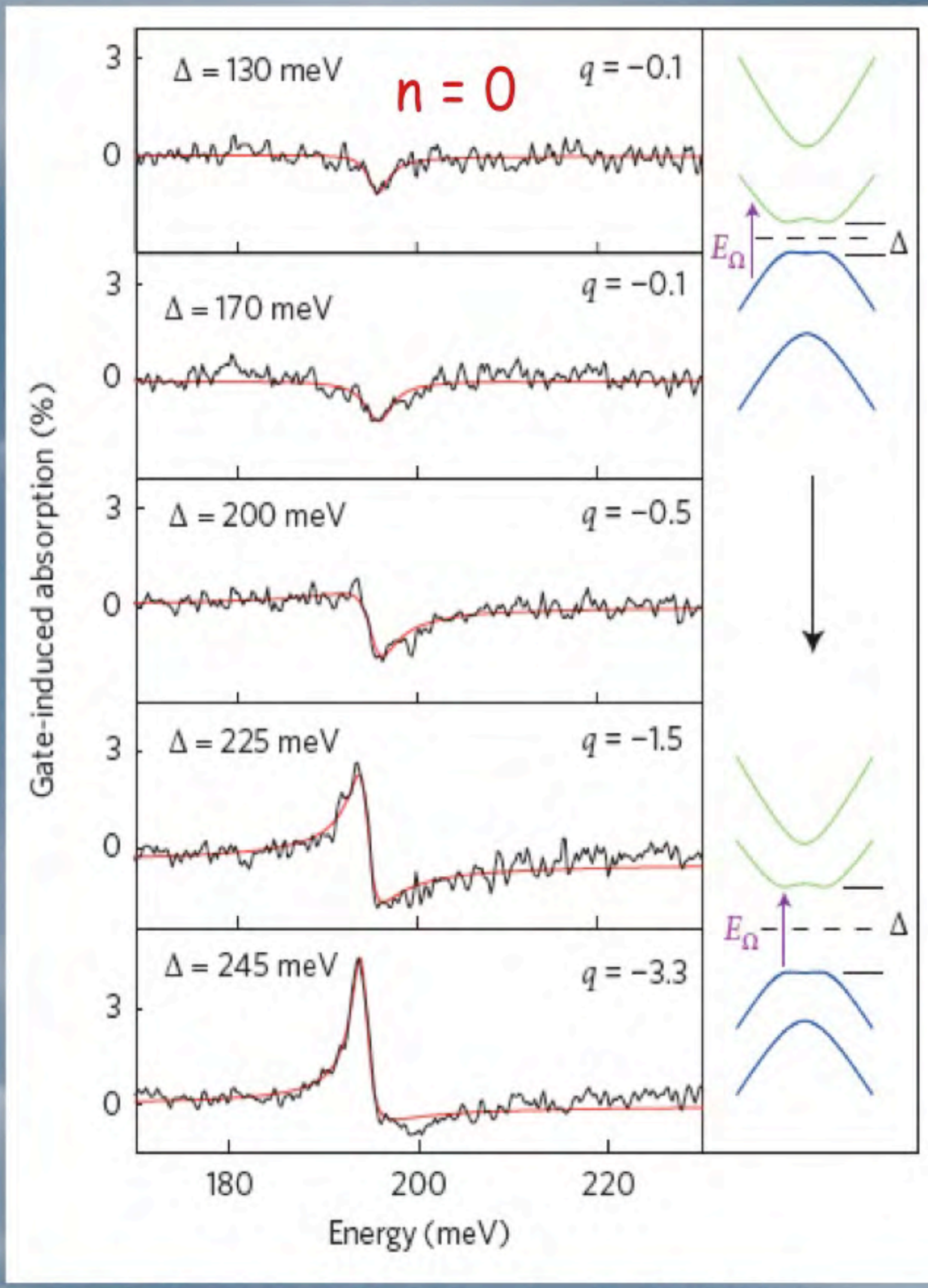


double-gated device
possible tuning doping and
Δ in independent way

- n = 0 and $\Delta \neq 0$: negative peak like us
- Fano effect as a function of Δ
- they attribute origin
  of negative peak at n = 0
  to E_g (S) (Raman-active) mode

(S allowed by symmetry in IR when $\Delta \neq 0$)





T-Ta Tang et al, Nat Nanotch 5, 32 (2010)

Towards an unifying theory

- what rules the IR phonon intensity of the A mode??
  (graphenes: monoatomic systems, no intrinsic dipole…)
- what rules the IR phonon intensity of the S mode??
- what the origin of the Fano lineshape of both modes and why their different Fano phenomenology??

- is it possible to find a common theoretical backrground explaining all these features?

- need of a quantitative theory to be predictable

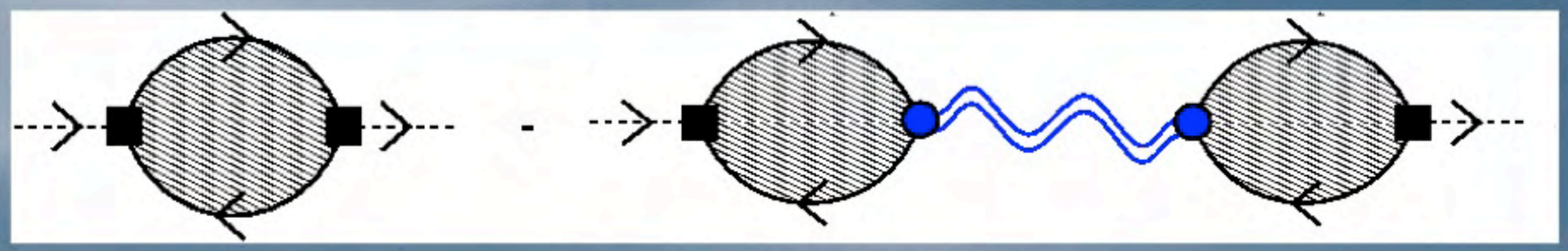
Rice (Michael) theory

applied to organic materials, fullerenes, molecular crystals...

electronic polarizability provides finite IR intensity to phonon modes allowed but otherwise not active

$\sigma_{el}(\omega) = -i\omega\chi(\omega)$ χ: el. polarizability (interband transitions)

χ: electronic background + el-ph interaction



$$\sigma_{tot}(\omega) = -i\omega\left[\chi(\omega) + \lambda_\nu x\chi(\omega)\chi(\omega)D_{ph}(\omega)\right]$$

Rice (Michael) theory

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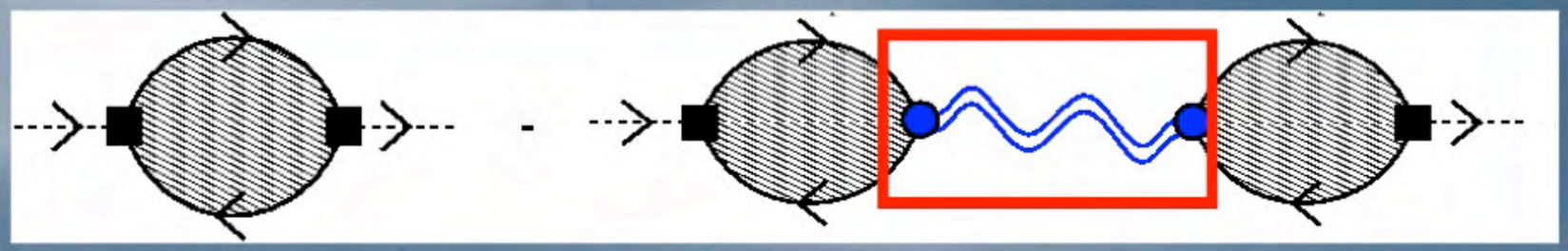

$$\sigma_{tot}(\omega) = -i\omega\left[\chi(\omega) + \lambda_v x\chi(\omega)\chi(\omega)D_{ph}(\omega)\right]$$

phonon resonance

Rice (Michael) theory

applied to organic materials, fullerenes, molecular crystals...

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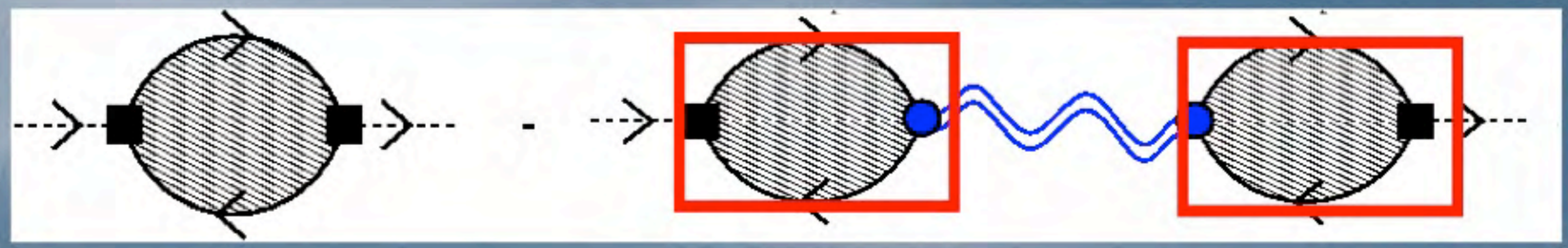


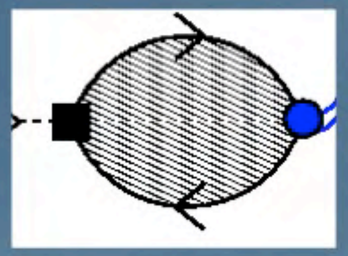
current/ electron-phonon response function

$$\sigma_{tot}(\omega) = -i\omega\left[\chi(\omega) + \lambda_\nu x \chi(\omega)\chi(\omega) D_{ph}(\omega)\right]$$

intensity ruled by the current/electron-phonon response function

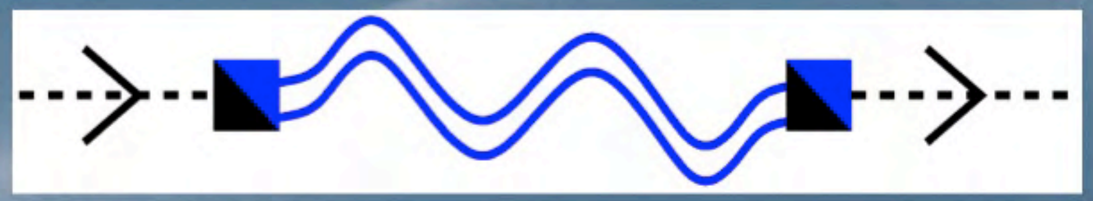
Rice theory in bilayer graphene

Rice theory: in its original application: semiconductors



χ: real function (α doping) tuning the phonon intensity

effective theory:



- interesting peculiarities of bilayer graphene:

zero gap semiconductor:
low energy interband transitions ➔ χ: complex quantity
➔ Fano asymmetry

tunable charged-phonon effects controlled by external voltage biases (doping and gap)

Fano-Rice theory in bilayer graphene

- interband transitions at low energy:

$$\chi_{jA} = \mathrm{Re}\chi_{jA} + i\mathrm{Im}\chi_{jA}$$

(gapped systems: $\mathrm{Im}\chi_{jA} = 0$)

$$D_{AA}(\omega) = \frac{1}{\omega - \omega_A + i\Gamma_A}$$

$$\sigma'_{ep}(\omega)\Big|_{\omega\approx\omega_A} = \frac{2\left[\chi'_{jA}(\omega_A)\right]^2}{\omega_A\Gamma_A}\,\frac{q_A^2 - 1 + 2zq_A}{q_A^2(1+z^2)} \qquad q_A = -\frac{\chi'_{jA}(\omega_A)}{\chi''_{jA}(\omega_A)}$$

Fano formula!

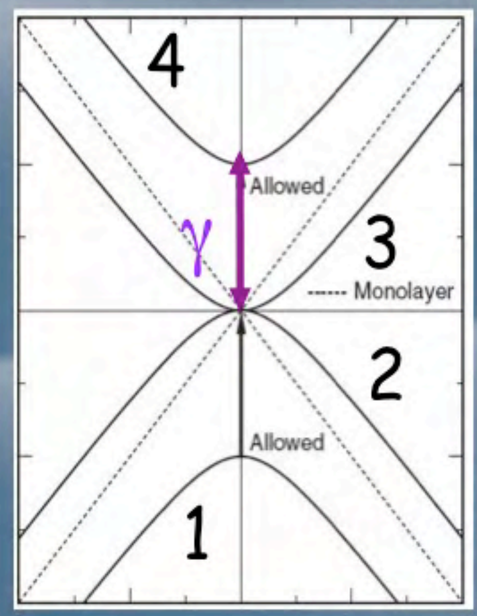
Fano and charged-phonon effects same origin!

it permits a microscopical identification

Phonon intensity in bilayer graphene

- Step by step analysis: gating induces doping but not E_z
  - in this case low-energy transitions between 2 and 3

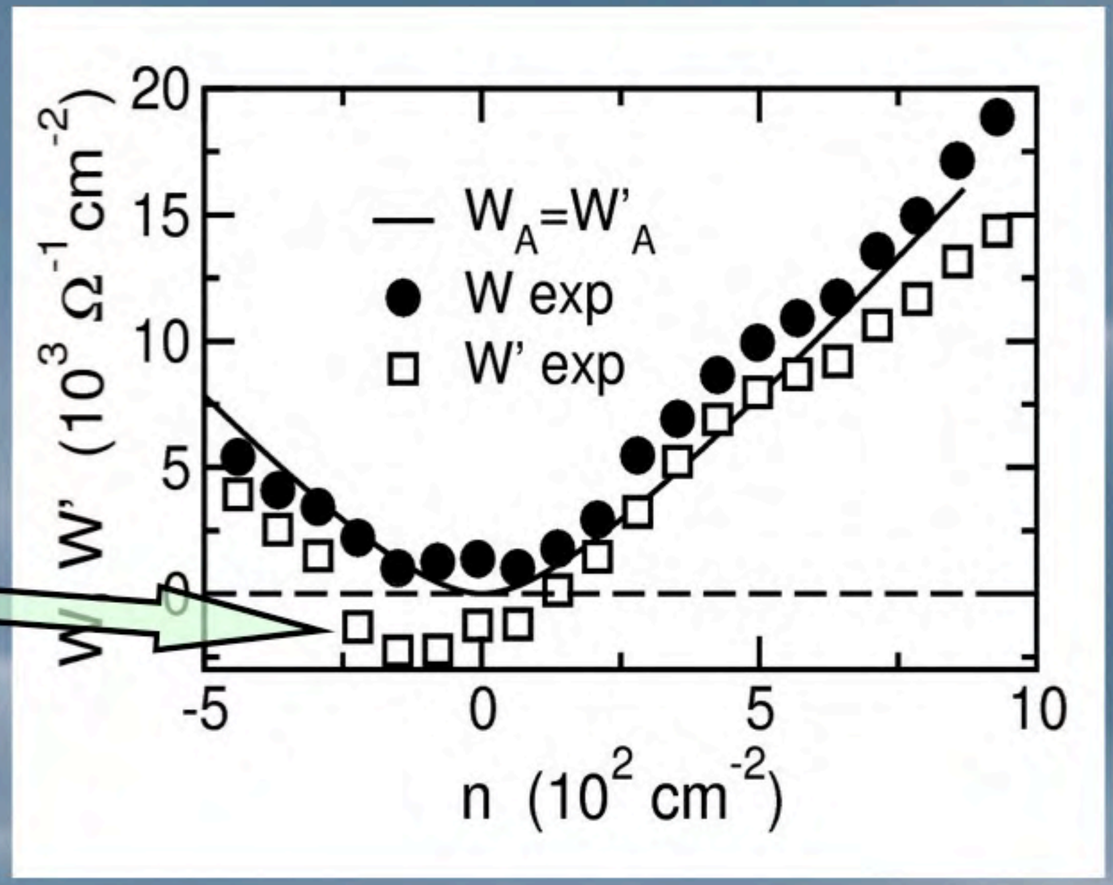
    system like a gapped semiconductor



$\mathrm{Im}\chi = 0$ ➔ *no* Fano effect

doping depedence of ω-integrated area W'
perfectly reproduced

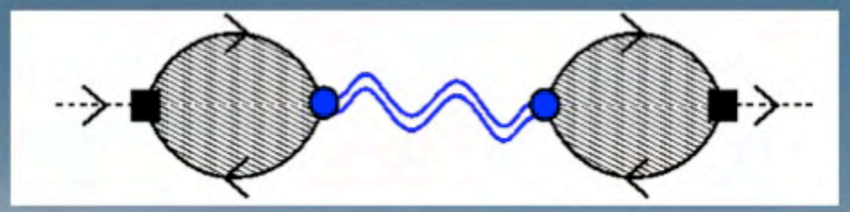
what about W_A?
negative area?

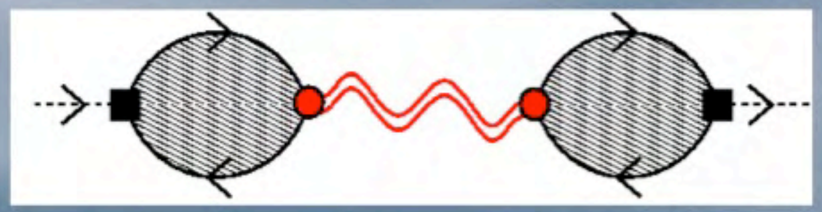


E Cappelluti et al, PRB 82, 041402 (2010)

Different phonon channels in optical conductivity

gating induces z-axis asymmetry E_z $\Delta > 0$ E_g (S) mode also IR active!

- two main IR channels present
  - 

    probes D_{AA} ph. propagator
  - 

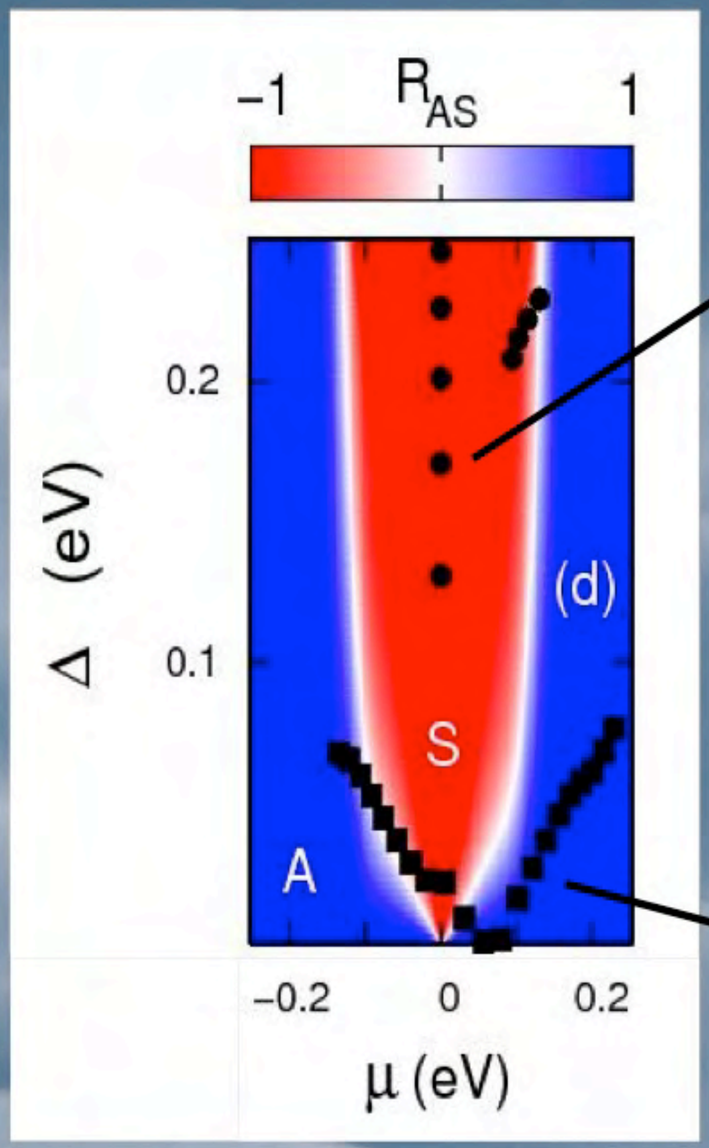
    probes D_{SS} ph. propagator

relative "intensity" ruled by p_A and p_S

total spectra dependent on the relative dominance of one channel vs. the other one

Optical channels and phonon switching in optical conductivity

- Δ-μ phase diagram



Berkeley

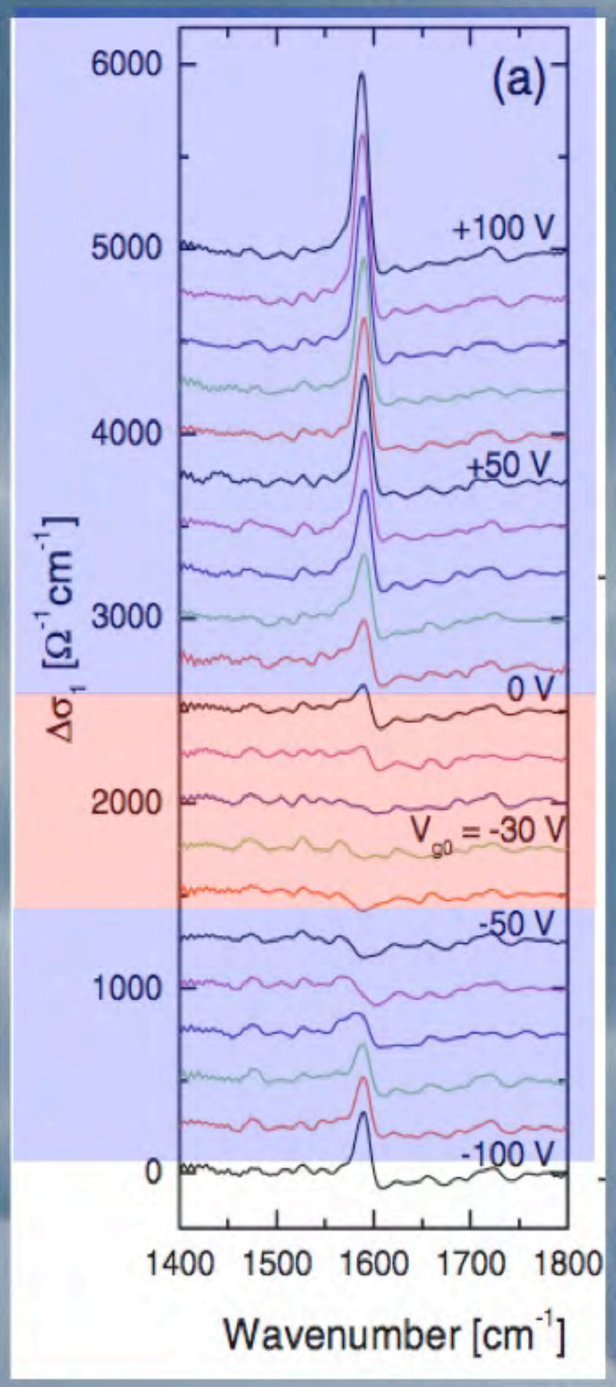
Geneve

E_u-*A* and E_g-S modes dominant in different regions of phase diagram: possible switching of intensity from one mode to other one

E Cappelluti et al, PRB 82, 041402 (2010)

Es. Phonon switching in optical conductivity

Geneve group



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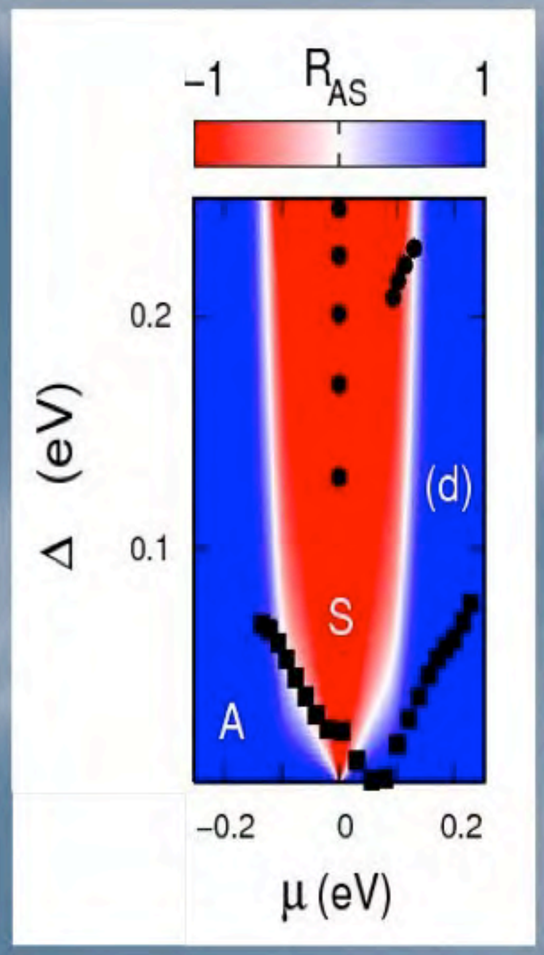
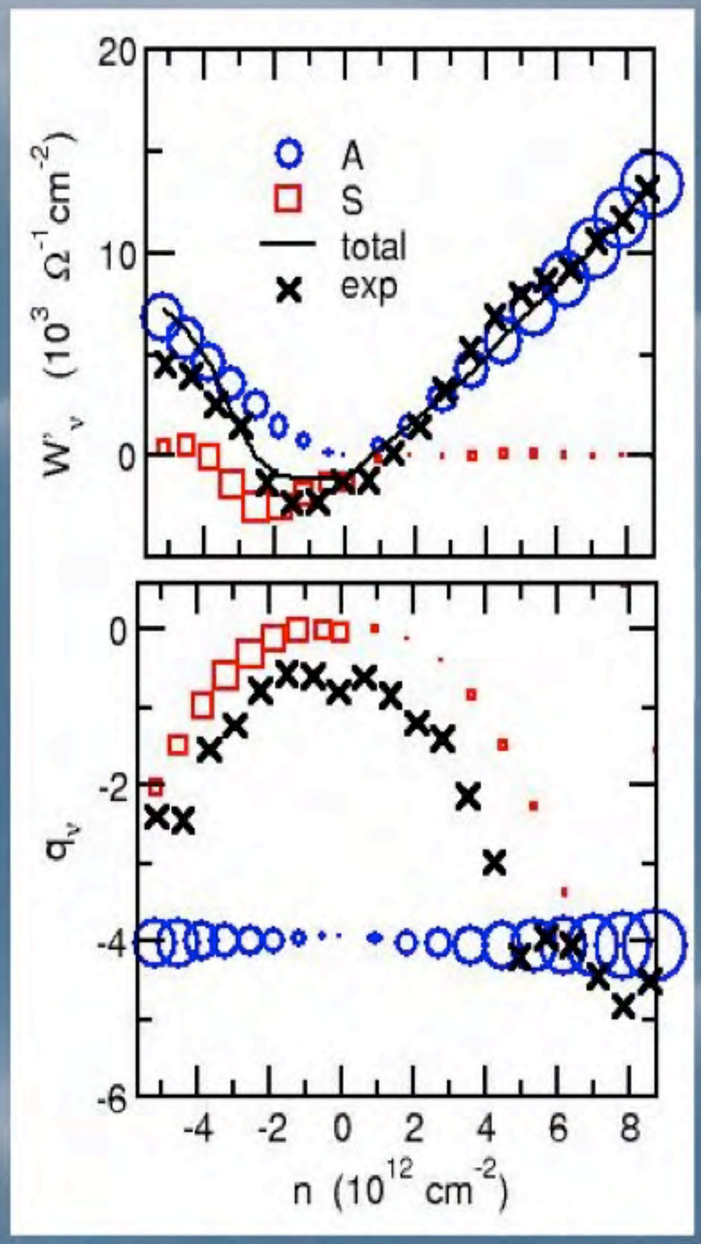
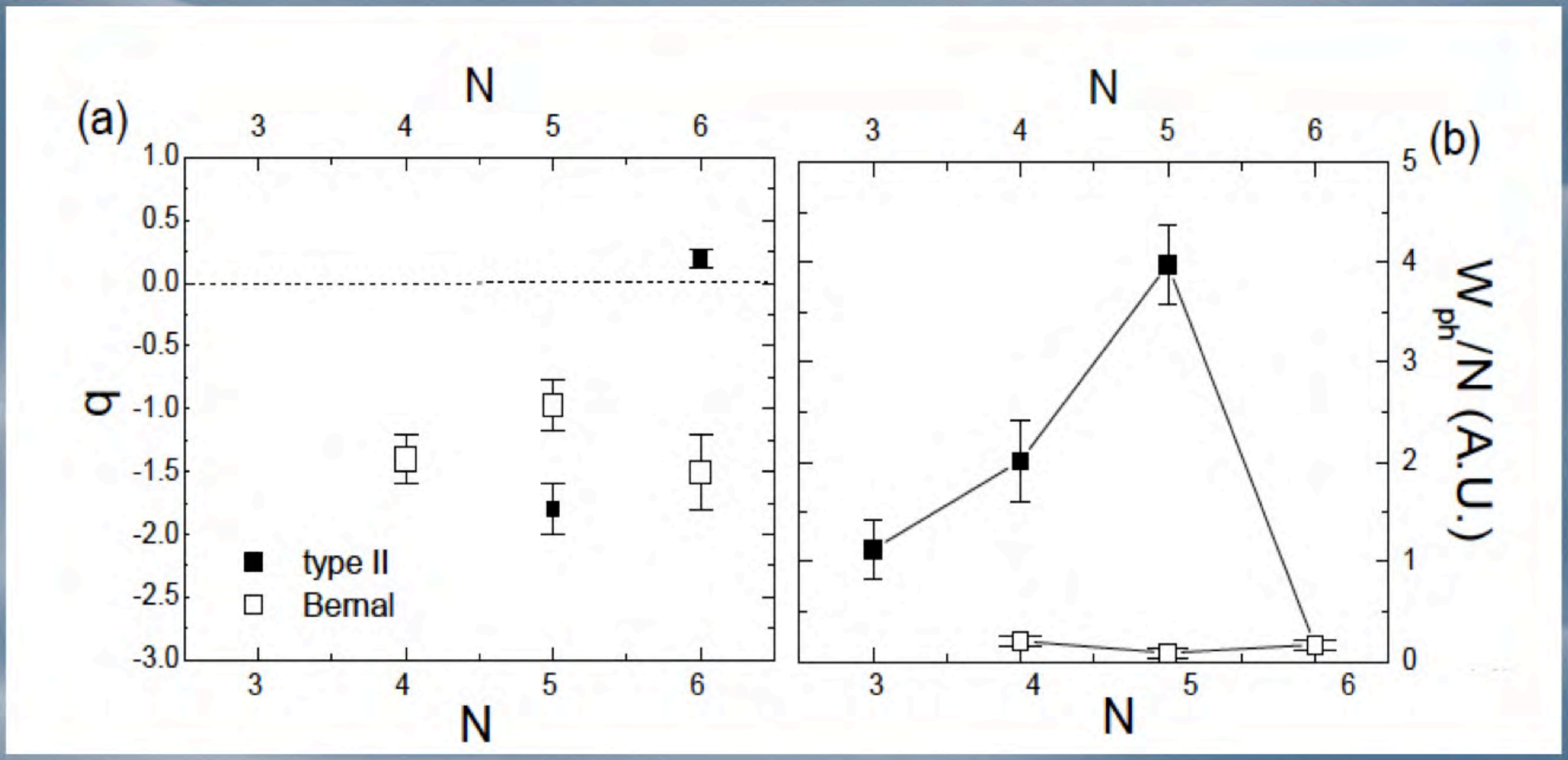




E Cappelluti et al, PRB 82, 041402 (2010)

experimental integrated area and Fano asymmetry interpolates and switches from A to S mode

Perspectives: multilayer graphene and stacking



ZQ Li et al., preprint (2011)

intensity and Fano asymmetry strong depending on N-layer and stacking order

Conclusions

- unified theory of IR intensity and Fano profile
- different phonon mode peak triggered by different channels
- complete phase diagram for charging and Fano properties
- phonon intensity switching observed in experimental data
- suitable tool to characterize graphene systems (Δ, n)

PRL 103, 116804 (2009) PHYSICAL REVIEW LETTERS week ending 11 SEPTEMBER 2009

Gate Tunable Infrared Phonon Anomalies in Bilayer Graphene

A. B. Kuzmenko,[1] L. Benfatto,[2,3,4] E. Cappelluti,[3,4] I. Crassee,[1] D. van der Marel,[1] P. Blake,[5] K. S. Novoselov,[5] and A. K. Geim[5]

RAPID COMMUNICATIONS

PHYSICAL REVIEW B 82, 041402(R) (2010)

Phonon switching and combined Fano-Rice effect in optical spectra of bilayer graphene

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