Crystal lattice dynamics

Graphene Seminar

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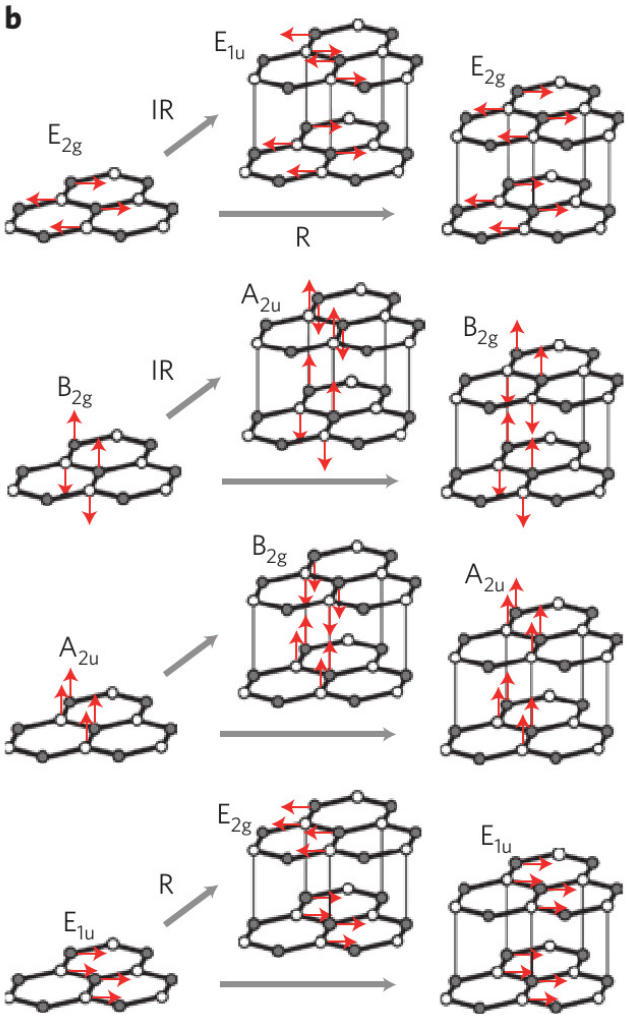
A general description of the phonon spectra in crystals



Nature Nanotechnology, **8**, 235 (2013).

Three dimensional space

Optical modes:

$$\omega_\xi^2((\vec{q} \to 0)) \to \textit{finite}$$

$\xi = 3(v-1).$ $\Rightarrow$ Fixed inertia centres

$$\sum_j M_j \vec{u}_j(\vec{q}=0) = 0$$

Acoustic modes:

$$\omega_\xi^2((\vec{q} \to 0)) \to 0$$

$\xi = 1, 2, 3.$

$\Rightarrow$ Displacements by the same vector

A general description of the phonon spectra in crystals

Let us assume a perfect crystal with periodic boundary conditions. The coordinates of the nuclei be $\vec{R}_{nj} = \vec{R}^{(0)}_{nj} + \vec{u}_{nj}$, n sites of the corresponding Bravais lattices, $j = 1, 2, \ldots, v$ atoms in elementary lattice, $\vec{u}_{nj}$ displacements.
For three dimensional Taylor's theorem

$$f(\vec{r} + \vec{a}) = f(\vec{r}) + \vec{a} \cdot \nabla f(\vec{r}) + \frac{1}{2}(\vec{a} \cdot \nabla)^2 f(\vec{r}) + \ldots$$

Potential energy

$$V(\vec{R}_{nj}) = V(\vec{R}_{nj}) + \frac{1}{2} \sum_{nn'ij\alpha\beta} A^{\alpha\beta}_{ni,n'j} u^{\alpha}_{ni} u^{\beta}_{n'j}$$

where the force-constant matrix $A^{\alpha\beta}_{ni,n'j} = (\frac{\partial^2 V}{\partial u^{\alpha}_{ni} \partial u^{\beta}_{n'j}})_{\vec{u}=0}$. The linear term vanishes for no net force on any atom in equilibrium.

Karssemeijer and Fasolino 2011

A general description of the phonon spectra in crystals

Average displacements are much smaller than the interatomic distance d: $\langle \vec{u}_{nj} \rangle \ll d$. High orders are omitted for the harmonic approximation. In order to obtain the equations of motion we define the Lagrange function for our problem $L = T - V$ and recall the Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\vec{u}}} - \frac{\partial L}{\partial \vec{u}} = 0$$

The kinetic energy is

$$T = \sum_{ni\alpha} \frac{M_i}{2} \left(\frac{d\vec{u}^{\alpha}_{ni}}{dt}\right)$$

and we get

$$M_i \frac{d^2 \vec{u}^{\alpha}_{ni}}{dt^2} = -\sum_{n'j\beta} A^{\alpha\beta}_{ni,n'j} \vec{u}^{\beta}_{n'j}$$

A general description of the phonon spectra in crystals

With the ansatz $\vec{u}_{ni}^{\alpha} = \frac{1}{\sqrt{M_i}}\psi_{ni}^{\alpha}e^{-i\omega t}$, $\psi_{ni}^{\alpha} = c_i^{\alpha}e^{i\vec{q}\vec{r}_n}$
($\vec{q}$ is the wave vector inside the first Brillouin zone) and translational symmetry, we obtain

$$\omega^2 c_i^{\alpha} = \sum_{\beta,j} D_{ij}^{\alpha\beta}(\vec{q})c_j^{\beta}$$

where
$D_{ij}^{\alpha\beta}(\vec{q}) = \sum_n \frac{A_{0i,nj}^{\alpha\beta}}{\sqrt{M_i M_j}} exp(i\vec{q}\vec{r}_n)$
is the dynamical matrix.

Phonon branches of graphene

- If every nuclei is given the same displacement from the equilibrium, simply be displaced.

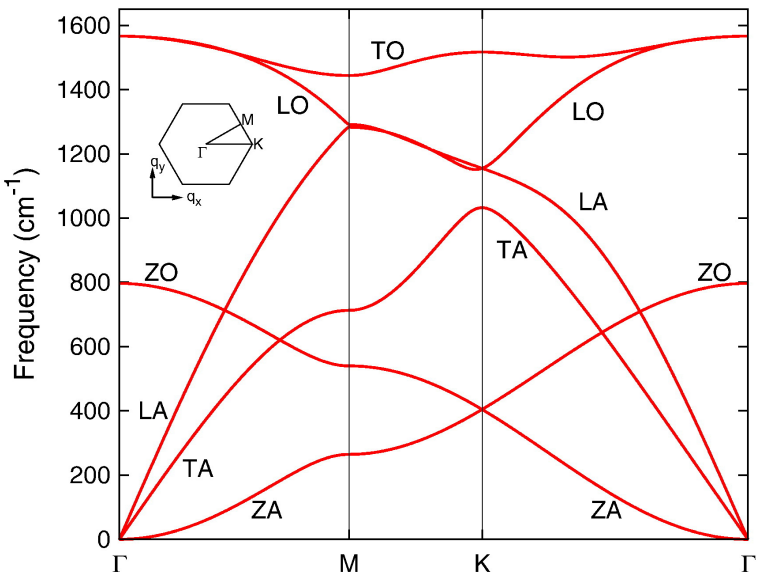
$$\sum_{nj} A^{\alpha\beta}_{0i,nj} = 0$$

- Owing to mirror symmetry
  $\hat{A}^{xz} = \hat{A}^{yz} = 0$,
  $M_i \frac{d^2 \vec{u}^{\alpha}_{ni}}{dt^2} = -\sum_{n'j\beta} A^{\alpha\beta}_{ni,n'j} \vec{u}^{\beta}_{n'j}$
  $M_i \frac{d^2 \vec{u}^{x}_{ni}}{dt^2} = -\sum_{n'j} A^{xz}_{ni,n'j} \vec{u}^{z}_{n'j} - \sum_{n'j} A^{xy}_{ni,n'j} \vec{u}^{y}_{n'j} - \sum_{n'j} A^{xx}_{ni,n'j} \vec{u}^{x}_{n'j}$
  modes of z-direction are rigorously separated from that of xy-plane.
- For sublattices A and B are equivalent, $D^{\alpha\beta}_{11} = D^{\alpha\beta}_{22}$
- Due to $D^{\alpha\beta}_{ij}(\vec{q}) = \sum_n \frac{A^{\alpha\beta}_{0i,nj}}{\sqrt{M_i M_j}} exp(i\vec{q}\vec{r}_n)$ and $\sum_{nj} A^{\alpha\beta}_{0i,nj} = 0$, one can get

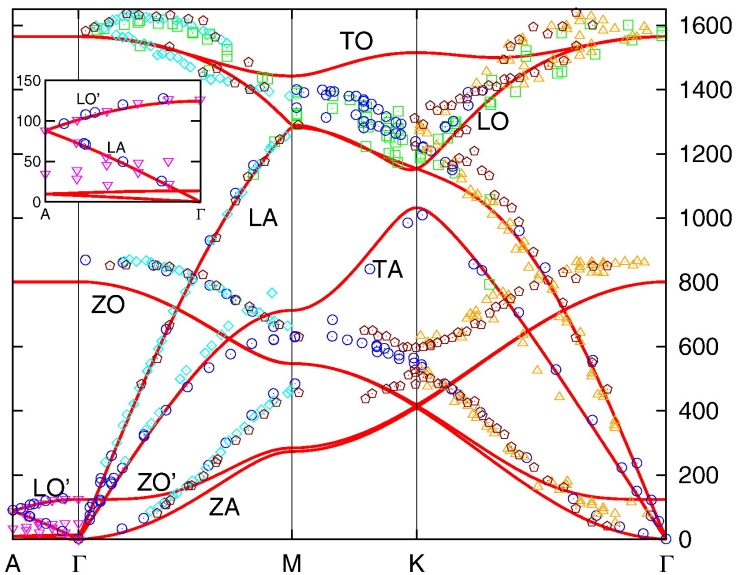
$$D^{\alpha\beta}_{12}(\vec{q} = 0) + D^{\alpha\beta}_{11}(\vec{q} = 0) = 0$$

Phonon branches of graphene

1. acoustic flexural mode ZA $\omega_{ZA}^2 = D_{12}^{zz}(\vec{q}) + D_{11}^{zz}(\vec{q})$
2. optical flexural mode OA $\omega_{ZO}^2 = D_{12}^{zz}(\vec{q}) - D_{11}^{zz}(\vec{q})$
3. two acoustic flexural mode in the plane $\alpha, \beta = x, y$ $D_{12}^{\alpha\beta}(\vec{q}) + D_{11}^{\alpha\beta}(\vec{q})$
4. two optical flexural mode in the plane $\alpha, \beta = x, y$ $D_{12}^{\alpha\beta}(\vec{q}) - D_{11}^{\alpha\beta}(\vec{q})$



Monolayer graphene

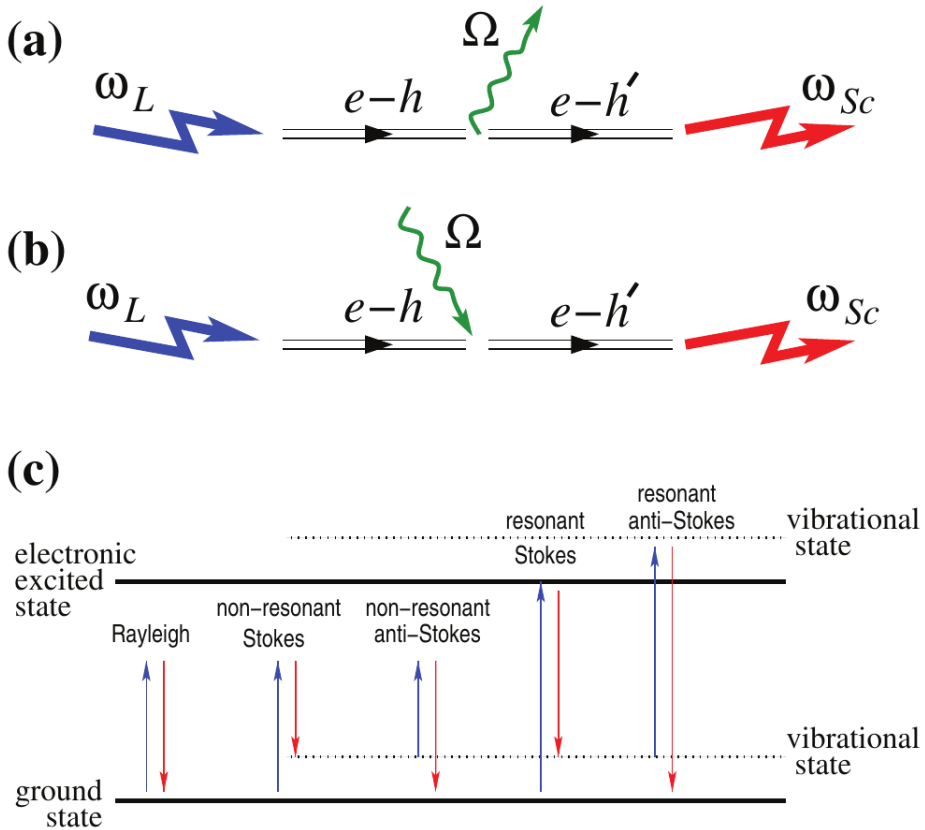


Calculation and measurement for graphite

Surface Science, **605**, 1611 (2011).

Raman scattering

Raman spectroscopy is an integral part of graphene research.
Raman scattering is the inelastic scattering of photons by phonons.



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Raman scattering

In general, Raman scattering can be described by pertubation theory. For an n-phonon process we have an $(n+2)$ order matrix element:

$$M = \sum_{s_0,\cdots,s_n} \frac{\langle f|\hat{H}^{em}|s_n\rangle\langle s_n|\hat{H}^{ph}|s_{(n-1)}\rangle\cdots\langle s_1|\hat{H}^{ph}|s_0\rangle\langle s_0|\hat{H}^{em}|i\rangle}{(\hbar\omega_L - E_n + i\Gamma_n/2)\cdots(\hbar\omega_L - E_1 + i\Gamma_1/2)(\hbar\omega_L - E_0 + i\Gamma_0/2)}$$

ω_L incident photon frequency
E_k, $\Gamma_k/\hbar$ energy and decay rates of these intermediate states
$\hat{H}^{em}$, $\hat{H}^{ph}$ interaction of electrons with the electromagnetic field and with phonons

Raman scattering

- For $\vec{k}_L$ incoming photon,$\vec{k}_{Sc}$ scattering photon, the lattice parameter a. one can get

$$\vec{k}_L = \vec{k}_{Sc} \pm \vec{q}$$

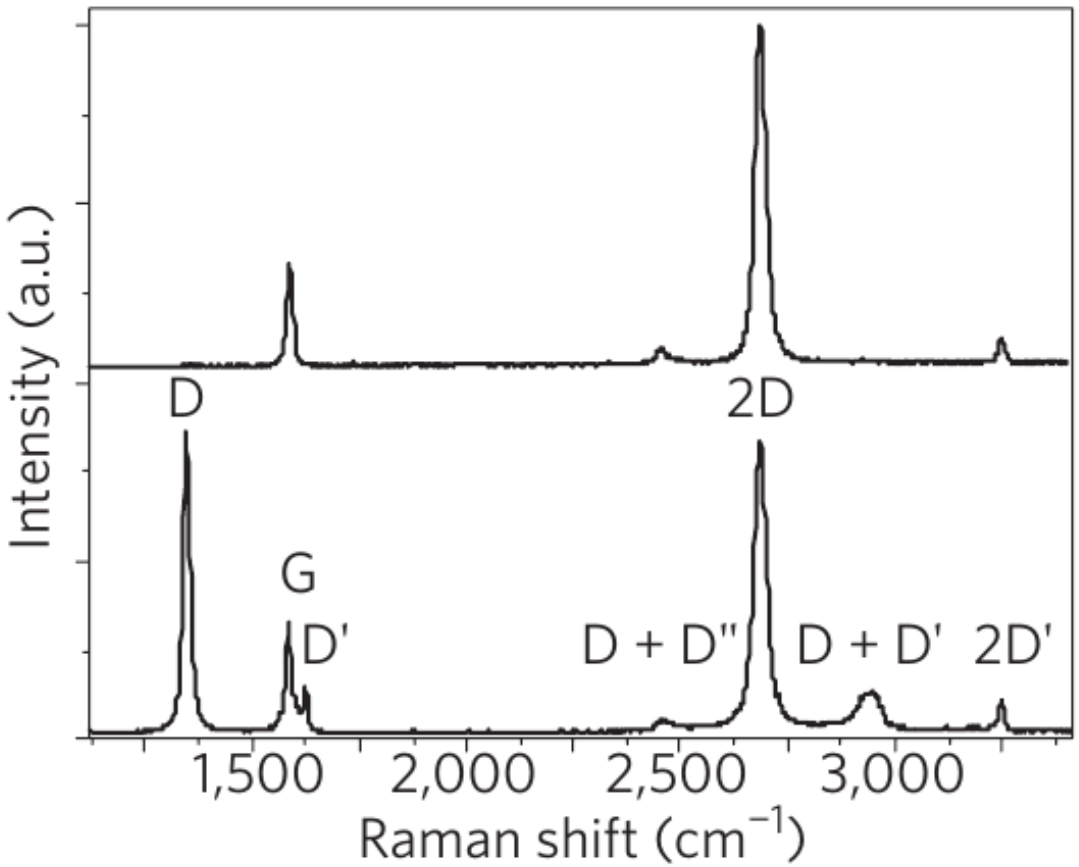
Because of the smallness of the lattice parameter $\vec{k}_L, \vec{k}_{Sc} \ll \pi/a$,

$$\vec{q} \ll \pi/a$$

the fundamental Raman selection rule. In the first order scattering, only one phonon near $\Gamma(\vec{q} \approx 0)$ can be measured.

- For the emission of the two phonons with opposite wavevectors can always satisfy the fundamental selection rule.
Expected:A broad band

Raman scattering



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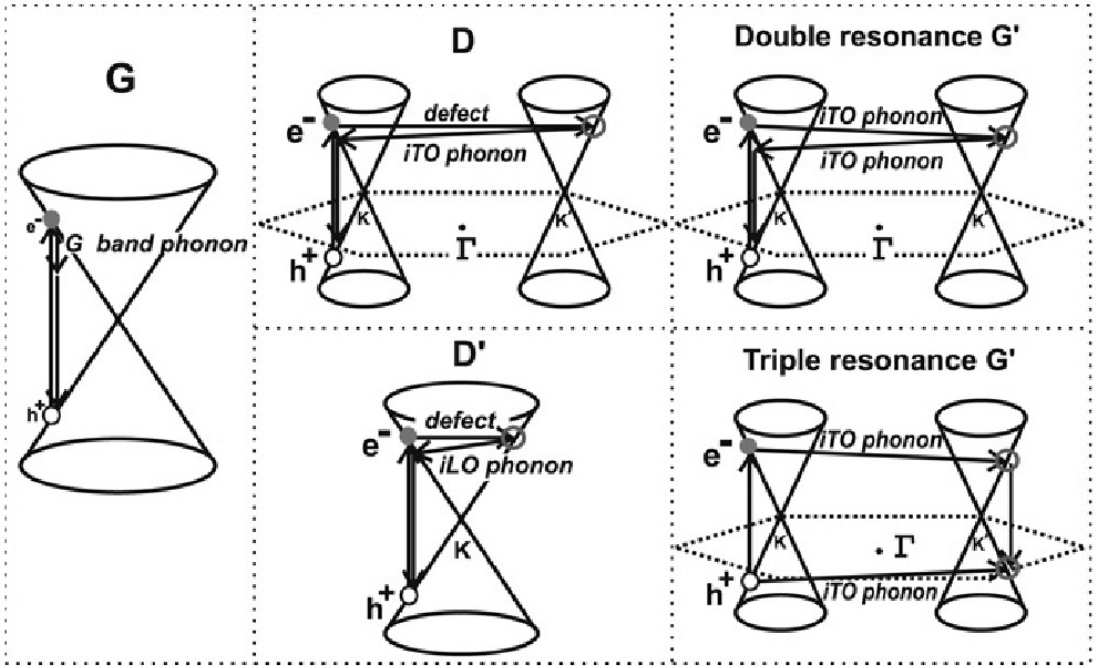
But not the main features, only a few features are seen.

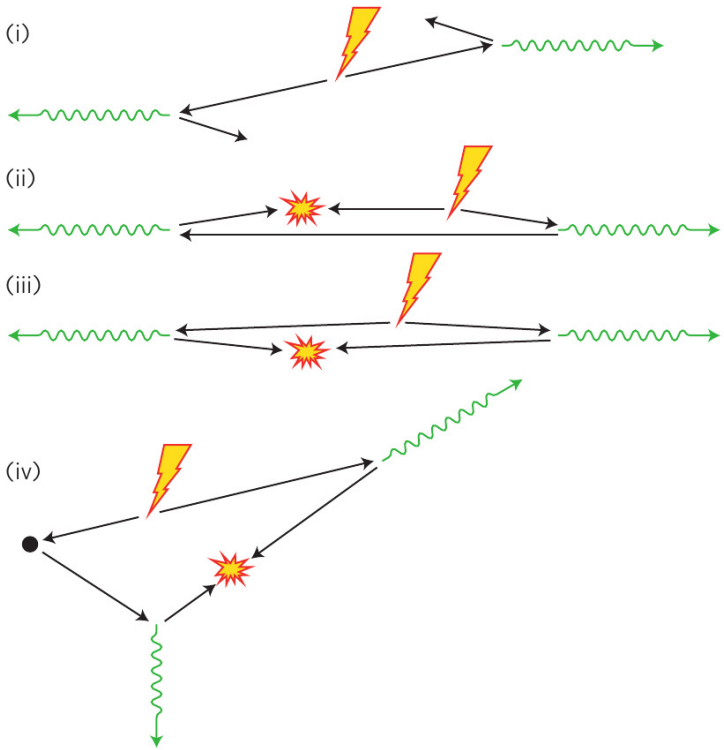
Raman scattering



Physics Reports, 473,51 (2009)

Resonance conditions favour a few phonon states with $\vec{q}$ coupling $\vec{k}_L$, $\vec{k}_{Sc}$ in the same valley ($\vec{q}$ near γ) or in different valleys ($\vec{q}$ near K). Due to the peculiar nature of the resonant process and the electron-phonon and electron-electron interaction.

Raman scattering



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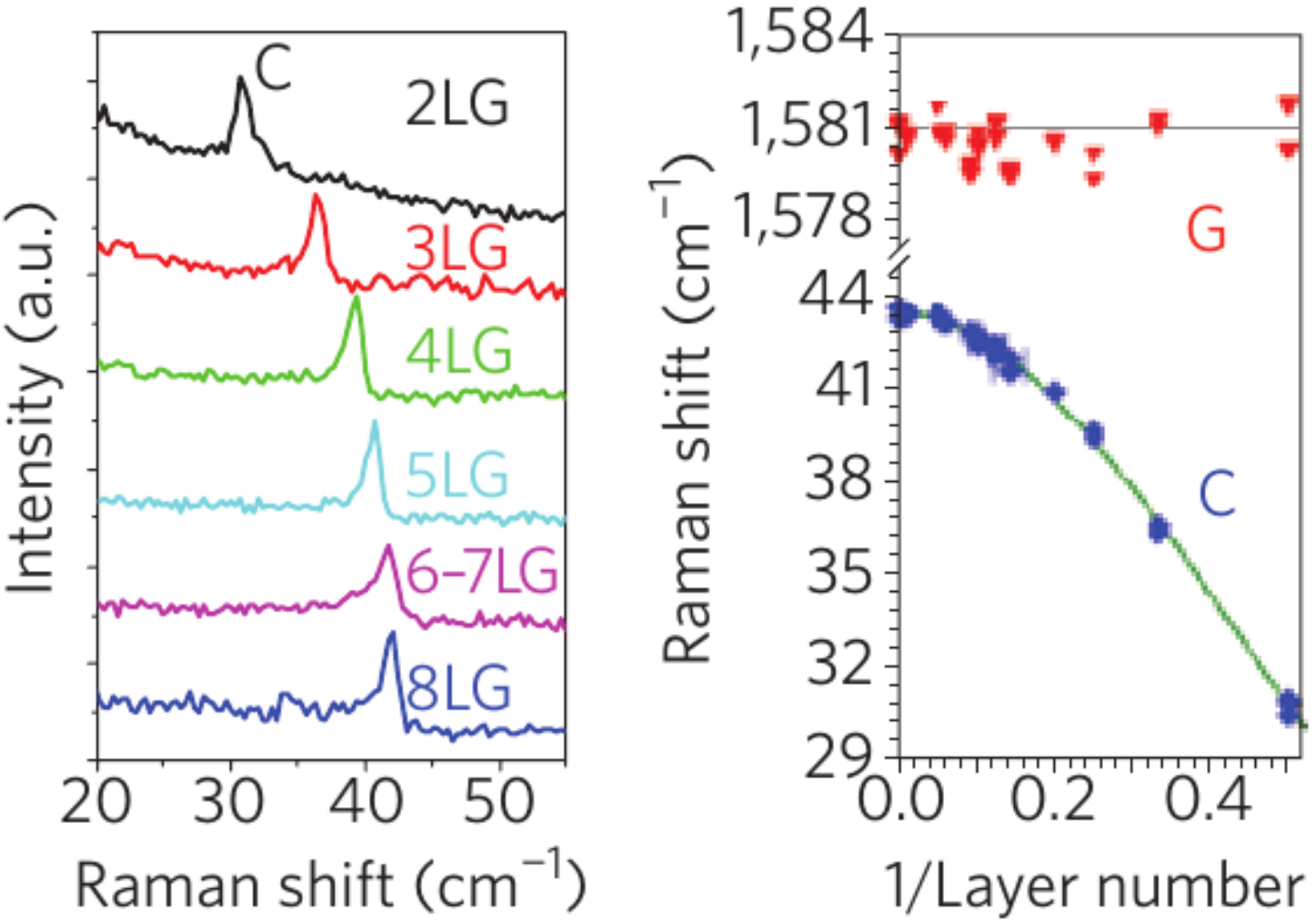
Real-space Raman processes.
Trajectories for two-phonon processes.
(i) Trajectory
for which radiative recombination
is impossible (ii) corresponding
to an ee process, incompatible with
the requirement that e and h travel for
the same amount of time. (iii) Trajectory
corresponding to $2D$, $2D'$. On phonon
emission, e and h must be back-scattered.
(iv)Trajectory corresponding to $D + D'$.

Applications

It is used to determine the number and orientation of layers, the quality and types of edge, and the effects of perturbations, such as electric and magnetic fields[1], strain [2], doping [3], disorder [4] and so on.

[1] Kossacki, P. et al. Electronic excitations and electron-phonon coupling in bulk graphite through Raman scattering in high magnetic fields. Phys. Rev. B **84**, 235138, (2011).
[2] Yoon, D., Son, Y. W. Cheong, H. Strain-dependent splitting of double resonance Raman scattering band in graphene. Phys. Rev. Lett. **106**, 155502 (2011).
[3] The influence of strong electron and hole doping on the Raman intensity of chemical vapor-deposition graphene. ACS Nano **10**, 6055 (2010).
[4] Cançado, L. G. et al. Quantifying defects in graphene via Raman spectroscopy at different excitation energies. Nano Lett. **11**, 3190 (2011).

Different layers



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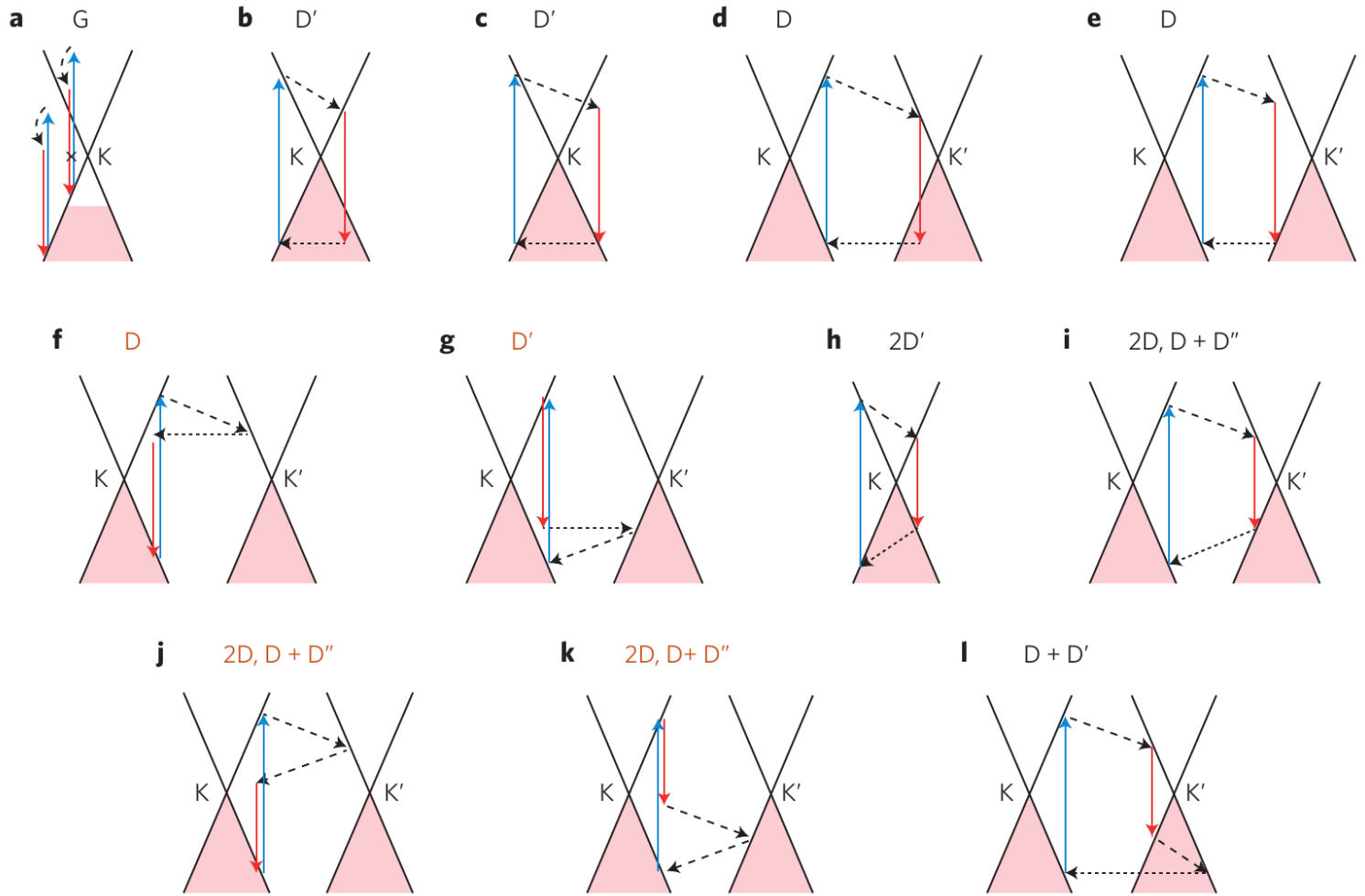
Effect of impurities



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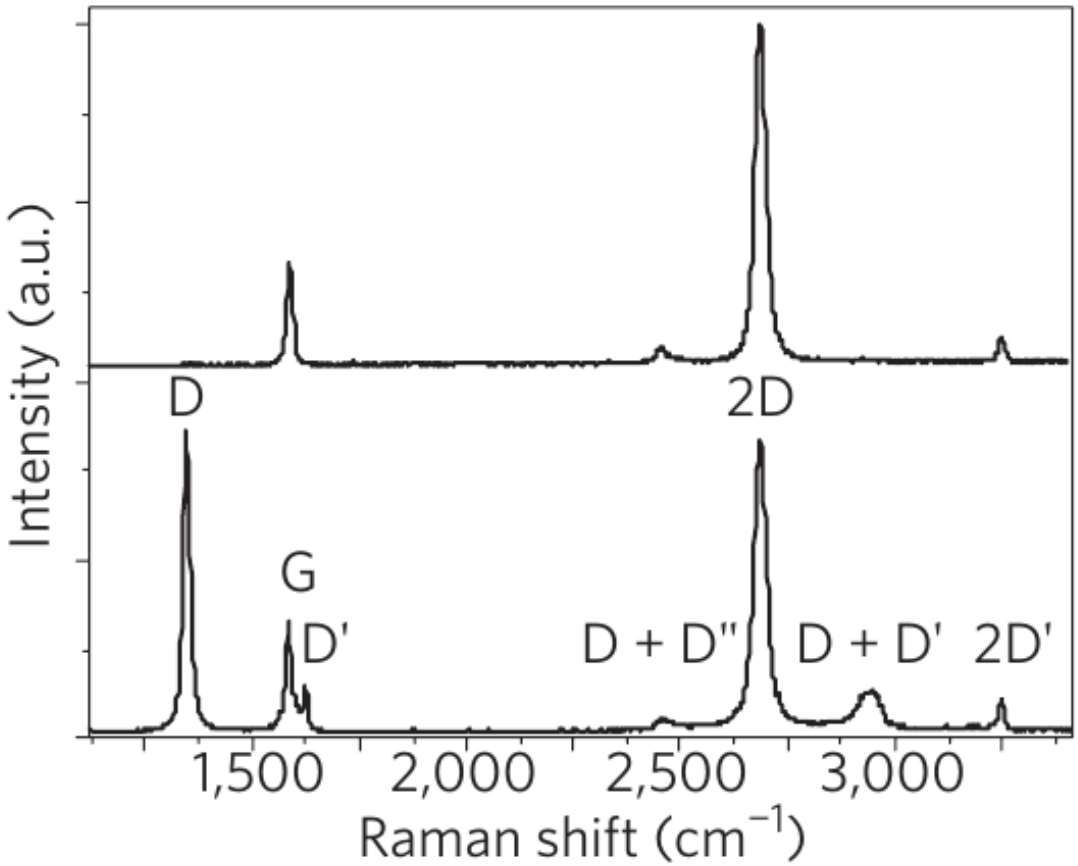
Effect of impurities



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Summary

1. Phonon spectra of graphene
   - A general description of the phonon spectra in crystals
   - Phonon branches of graphene
2. Raman spectra of graphene
   - What is Raman scattering
   - Applications of Raman spectroscopy of graphene

Thank You!

- Phonons of graphene and graphitic materials derived from the empirical potential LCBOPII, *L. J. Karssemeijer, Annalisa Fasolino*, Surface Science, **605**, 1611 (2011).
- Raman spectroscopy as a versatile tool for studying the properties of graphene, *Andrea C. Ferrari and Denis M. Basko*, Nature Nanotechnology, **8**, 235 (2013).
- Raman spectroscopy in graphene, *L. M. Malard, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus*, Physics Reports, 473,51 (2009).