The Photophysics of Nano Carbons

Kavli Institute, UC Santa Barbara

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M. S. Dresselhaus, MIT

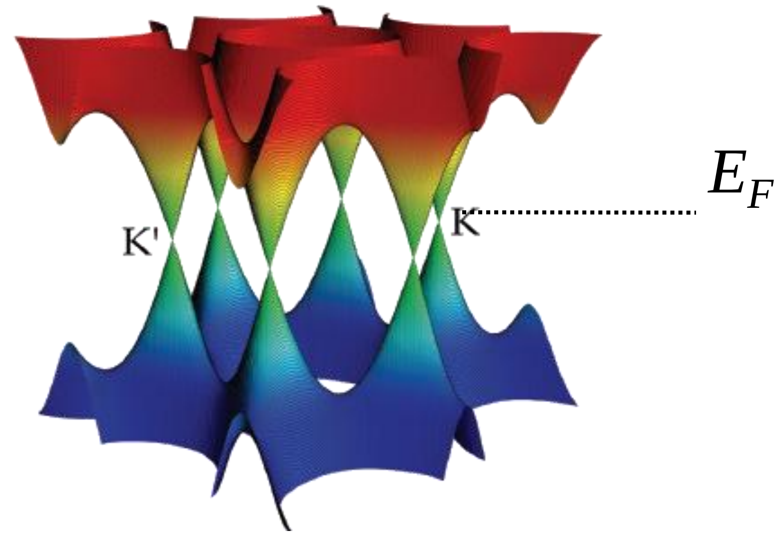
The Electronic Structure of Graphene

Near the K point

$E^{\pm}(\kappa) = \pm\hbar v_F \,|\,\kappa\,|$ linear κ relation

where $v_F = \dfrac{\sqrt{3}\gamma_0 a}{2\hbar}$

and $a = \sqrt{3} \cdot a_{c-c}$



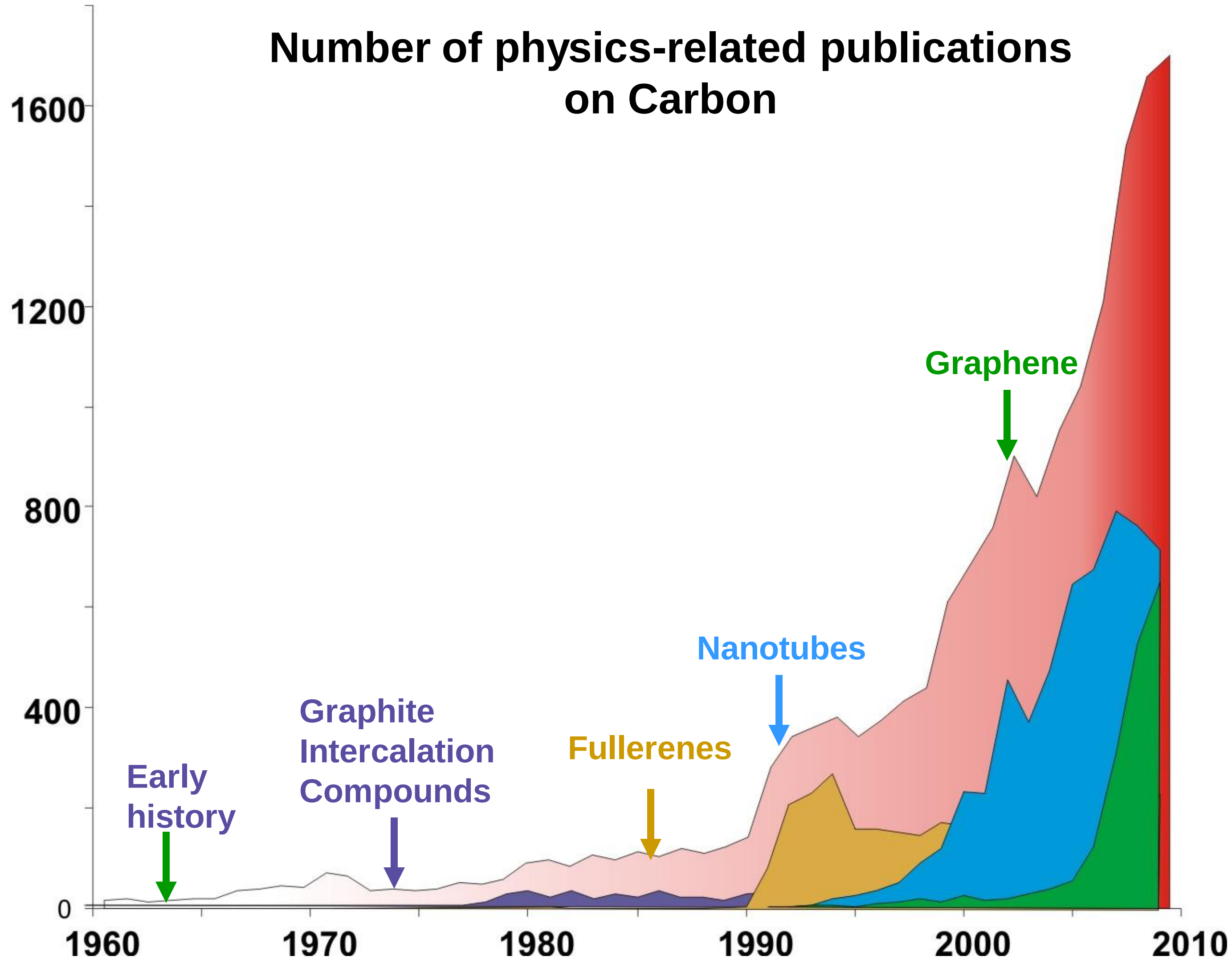
P.R. Wallace, Phys. Rev. **71**, 622 (1947)

and γ_0 is the overlap integral between nearest neighbor π-orbitals (γ_0 values are from 2.9 to 3.1eV).

In 1957-1960 McClure extended the 2D graphene electronic structure to 3D graphite and included the magnetic field dependence

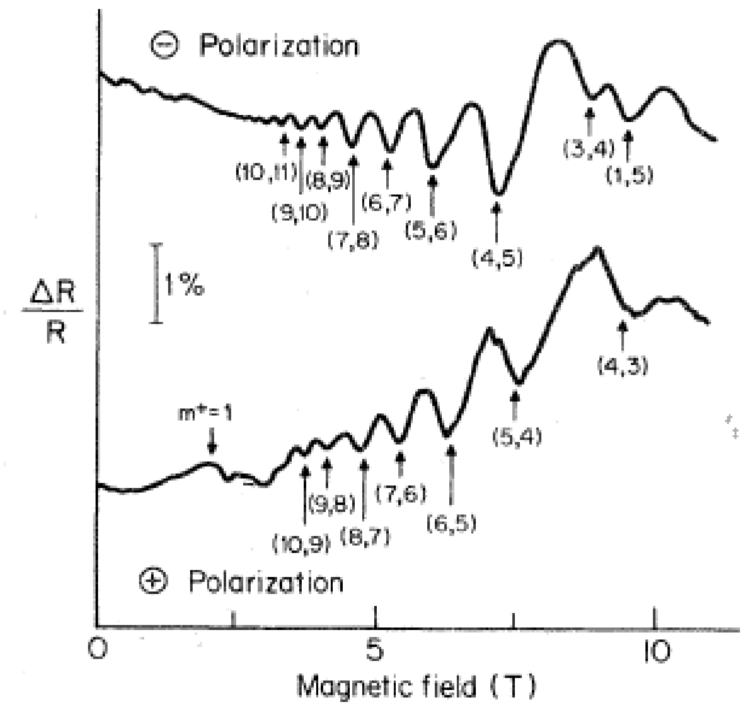
J.W. McClure, *Phys. Rev.*, **108**:612 (1957); **119**:606 (1960)

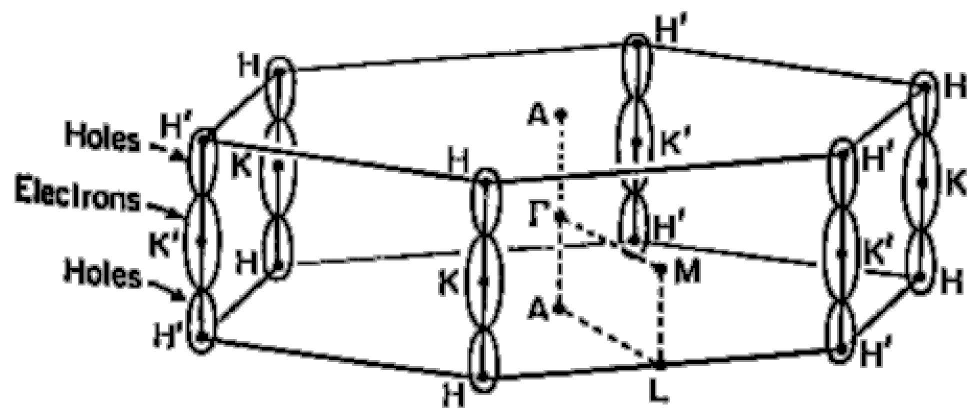
Graphene and the field of carbon research



Identification of Electrons and Holes in Graphite

Using circularly polarized radiation in the first magneto-optical experiment to use a laser, the locations of electrons and holes in the Brillouin zone for graphite were identified





P.R. Schroeder, M.S. Dresselhaus and A .Javan, *Phys. Rev. Lett.* 20:1292 (1968)

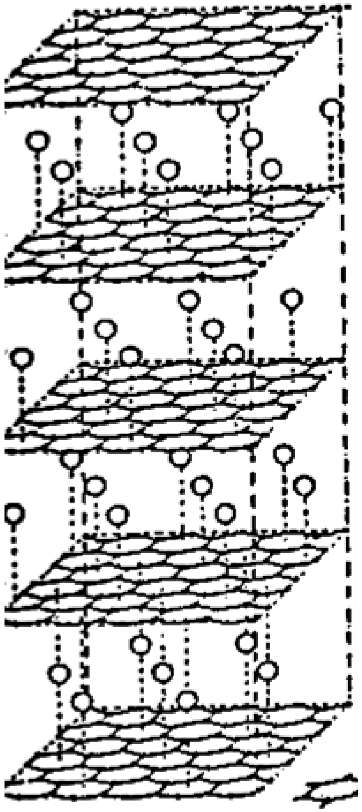
The implied selection rules established the location for electrons and holes in graphite that we use today

My entry into the Nanoworld (1973)

- Observation of superconductivity in stage 1 graphite intercalation compounds (C_8K)

  Hannay et al, *Phys. Rev. Lett.* 14:225 (1965)

  aroused much interest in nanocarbons since neither potassium nor carbon is superconducting
- Intercalation compounds allowed early studies to be made of individual or few graphene layers in the environment of the intercalant species.
- Many properties were studied 1973-1990.



C_8K

M.S. Dresselhaus and G. Dresselhaus, *Advances in Physics* 30:139-326 (1981)

PHYSICAL REVIEW B VOLUME 16, NUMBER 8 15 OCTOBER 1977

Raman scattering from in-plane lattice modes in low-stage graphite–alkali-metal compounds*

Systematic work on Donor GICs

RB:

Stage 1

Stage 2

Stage 3

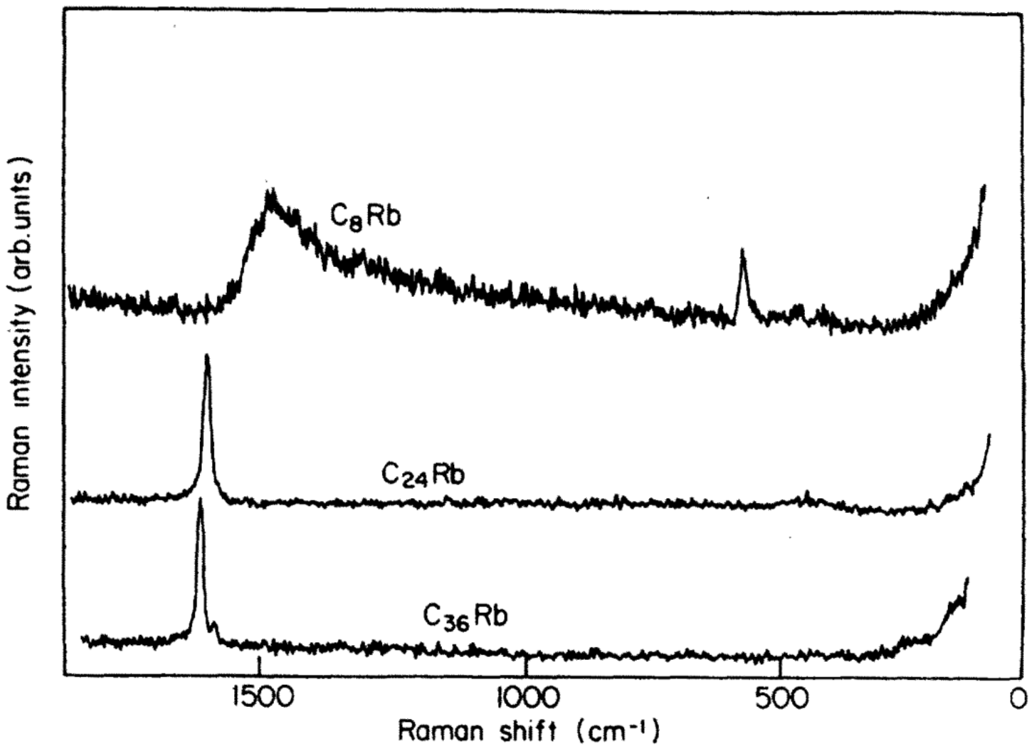
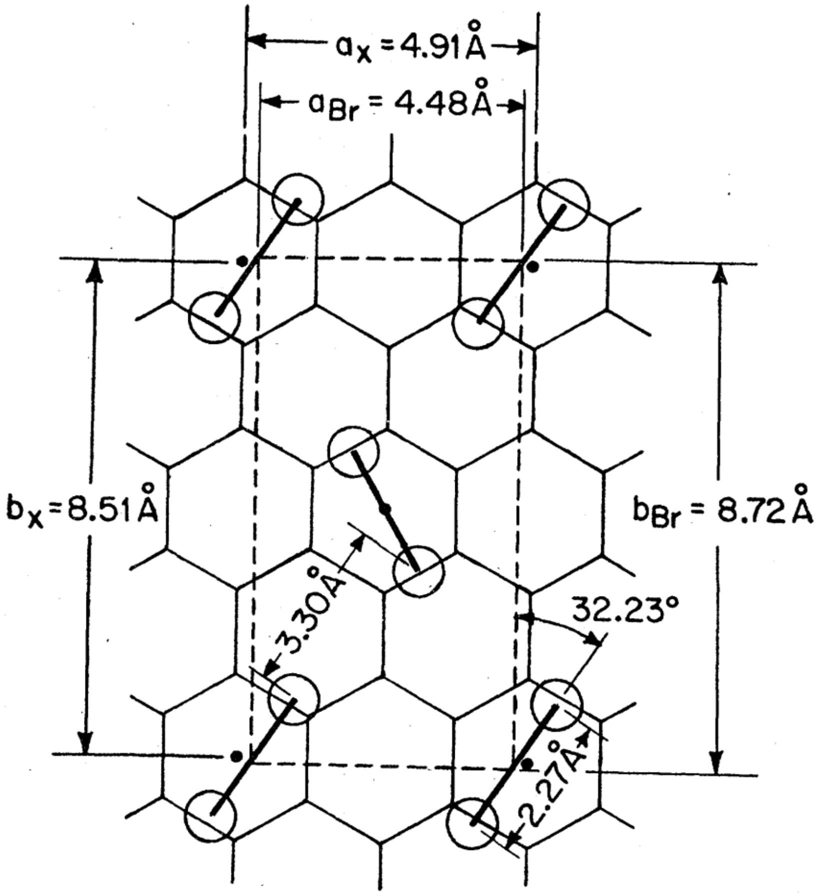


FIG. 1. Raman spectra of C_8Rb (stage 1), $C_{24}Rb$ (stage 2), and $C_{36}Rb$ (stage 3). The data were taken in the Brewster-angle backscattering geometry at 77 K. The line-shape parameters are given in Table I.

PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

In-plane intercalate lattice modes in graphite-bromine using Raman spectroscopy



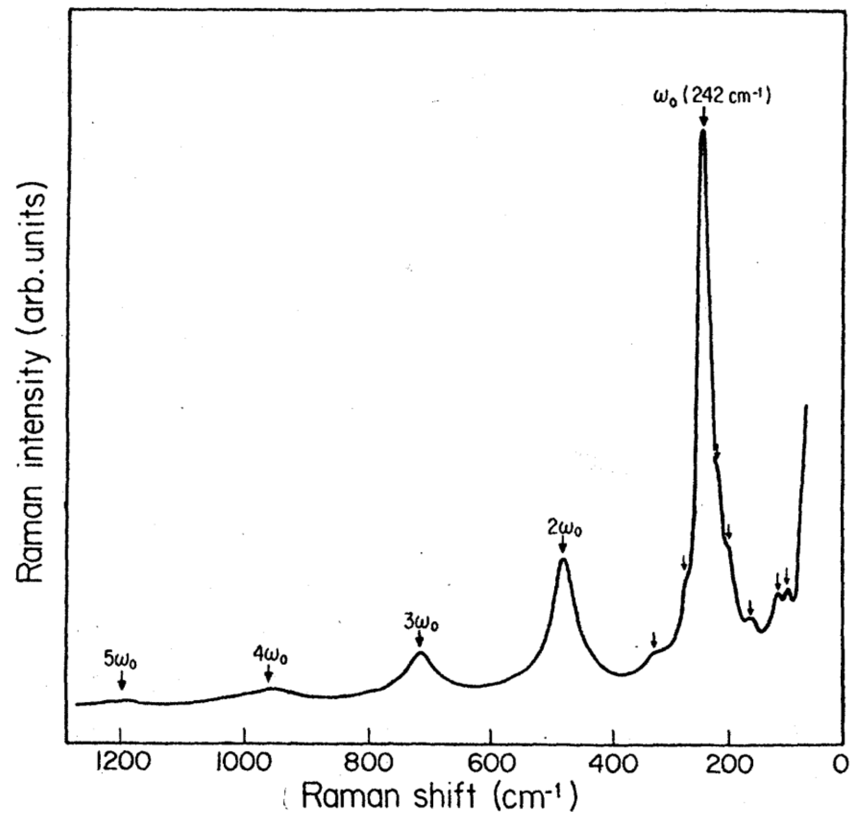
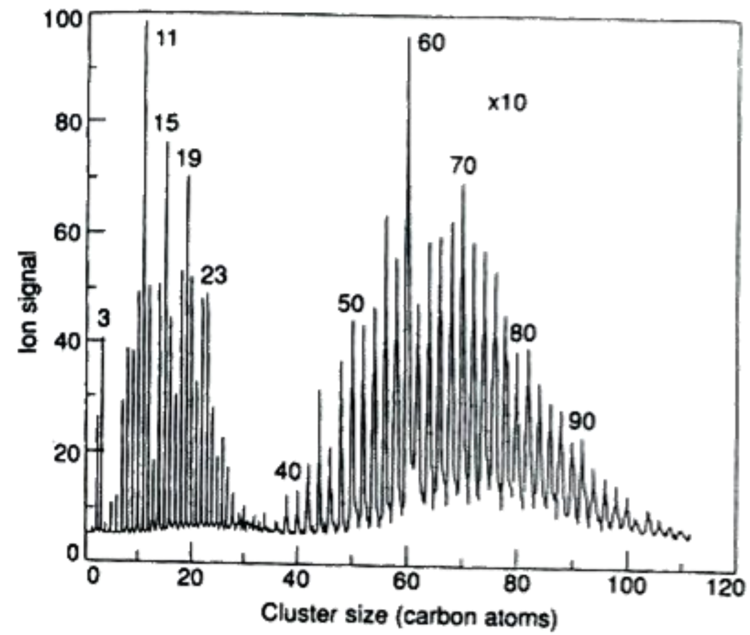


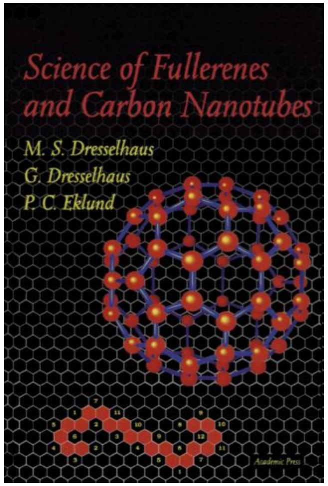
FIG. 4. Raman spectrum for a graphite-bromine compound with 2.7-mole% Br_2 at $T = 77$ K and laser energy 2.54 eV in the frequency region where the intercalate modes are dominant. The structure identified with the Br_2 stretching mode in the intercalation compound is denoted by ω_0, and its harmonics by $n\omega_0$. Fine structure in the vicinity of ω_0 is indicated by arrows.

Acceptor GIC with bromine

Discovery of Fullerenes

- The Laser ablation process used to make liquid carbon caused the emission of large carbon clusters (like C_{100}) rather than C_2 and C_3 with relatively low laser energy input
- A trip was made to Exxon Research Lab to discuss results.
- Soon (1984) Exxon published the famous result for the mass spectra. In 1985 fullerenes were discovered by Kroto, Smalley, and Curl

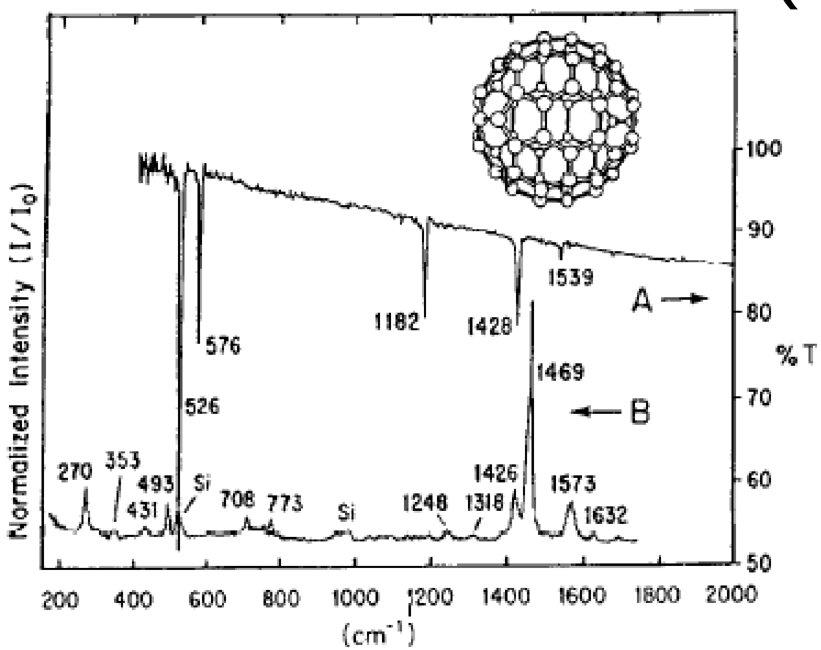




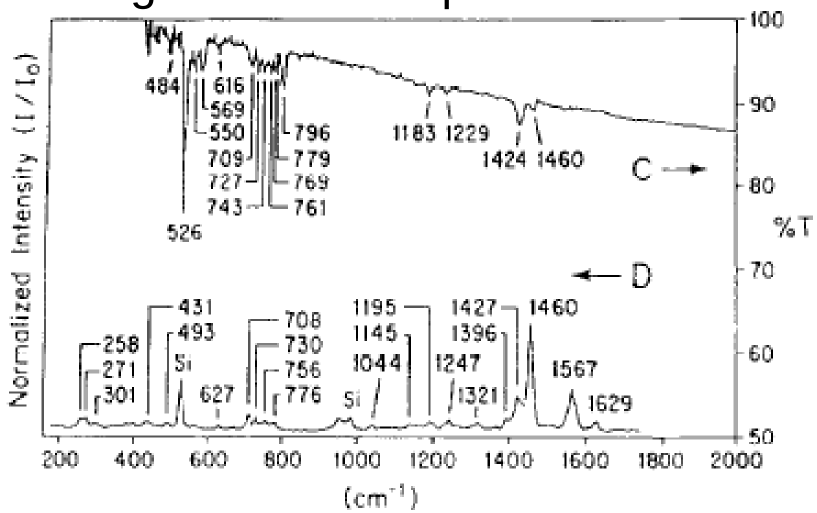
E.A. Rohlfing, D.M. Cox, and A.Kaldor. *J. Chem. Phys.*, **81**:332 (1984)

Fullerenes took center stage (1991-1996)

Low resolution spectra



High resolution spectra



A and C – IR spectrum

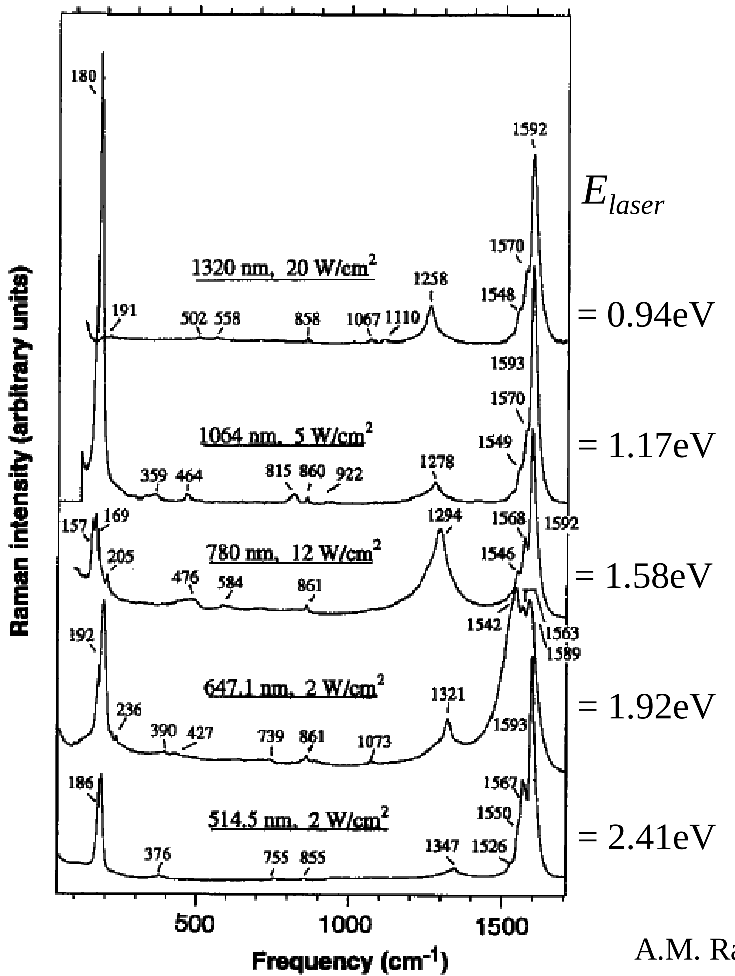
Films (d - 5000 A) for FTIR spectra were deposited on KBr substrates. The $4F_{1u}$ (IR-active) and 8Hg + 2Ag (Raman-active) lines in A are anticipated for a C60 molecule with I_h symmetry (inset).

B and D – Raman spectrum

The Raman spectra were taken at low laser power density (< 50 W / cm^2) with the 488 nm Ar ion line on films (d - 2000 A) deposited on Si(100) substrates.

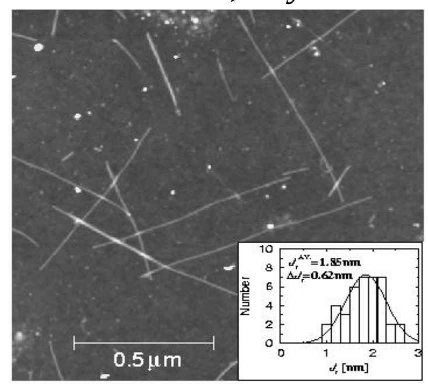
Resonance Raman Spectroscopy on single wall carbon nanotubes (SWNTs)

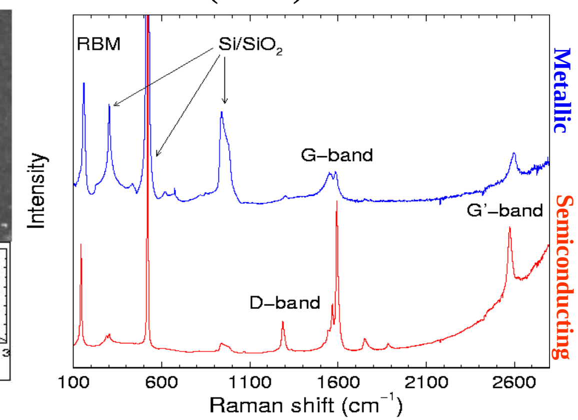
Resonance enhancement of Raman signal enabled detection of SWNTs in bundles



Single nanotube Raman spectroscopy was observed

A. Jorio et al., *Phys. Rev. Lett.* 86:1118 (2001)





From the spectrum of a nanotube its geometry and properties can be determined

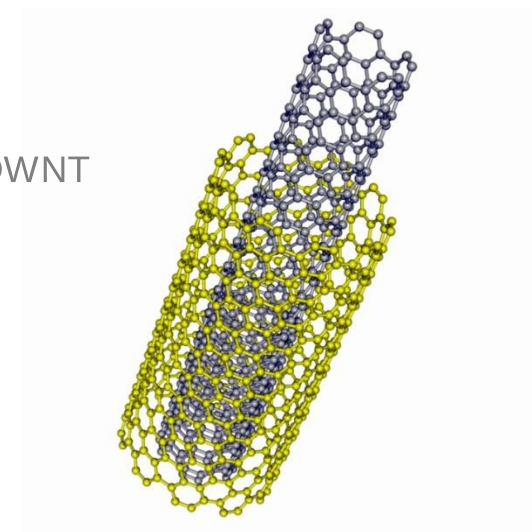
Single nanotube spectroscopy has since been demonstrated in photoluminescence and in Rayleigh scattering experiments.

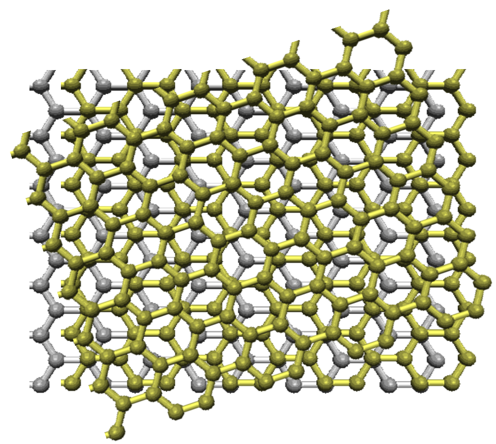
A.M. Rao, P.C. Eklund, R.E. Smalley, M.S. Dresselhaus, et al., *Science* **275**:187(1997)

Why Double Wall Carbon Nanotubes (DWNTs)?

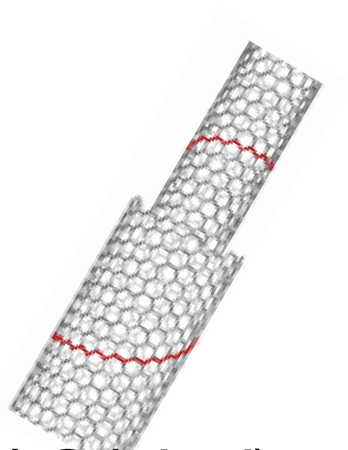
Simple system to study intertube and interlayer interactions

DWNT



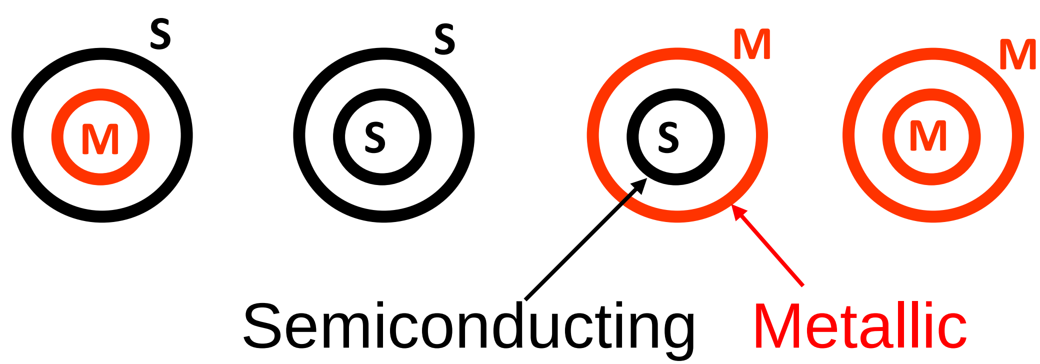


bilayer turbostratic graphene



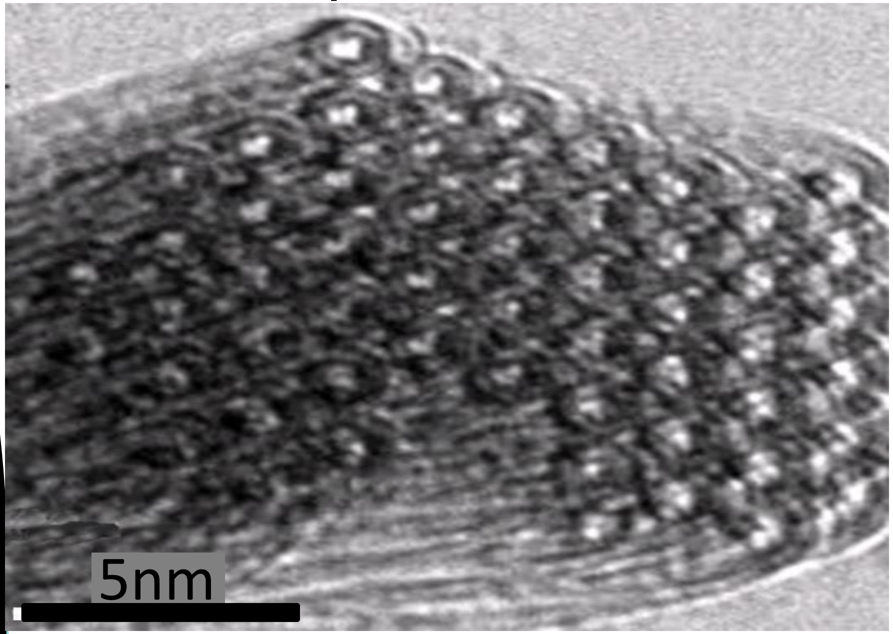
(n,m)@(n′,m′)
inner@outer

Four possible metallic/semiconducting configurations for DWNTs



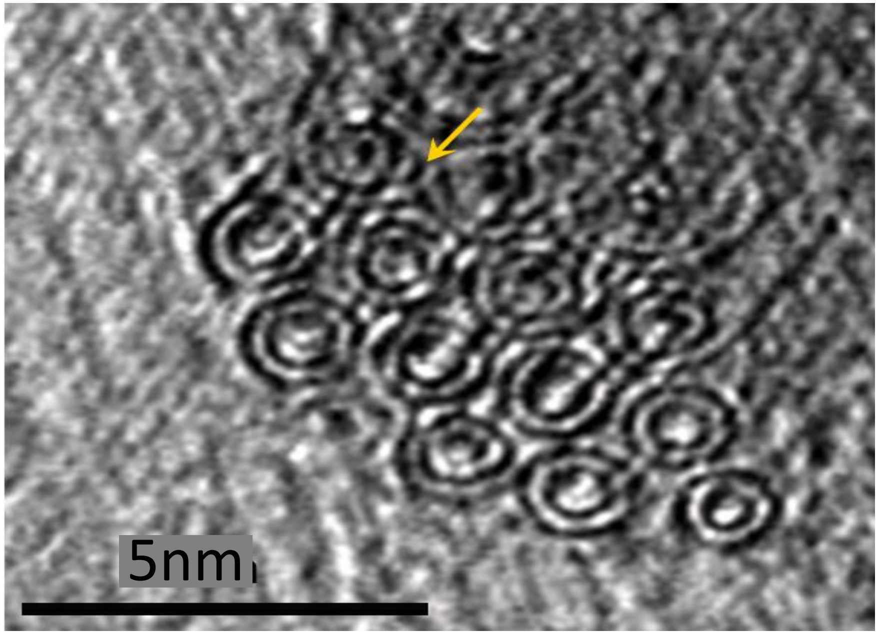
Pure DWNTs can withstand heat treatment

Undoped 1500°C



TEM courtesy of M. Endo

Undoped 2000°C

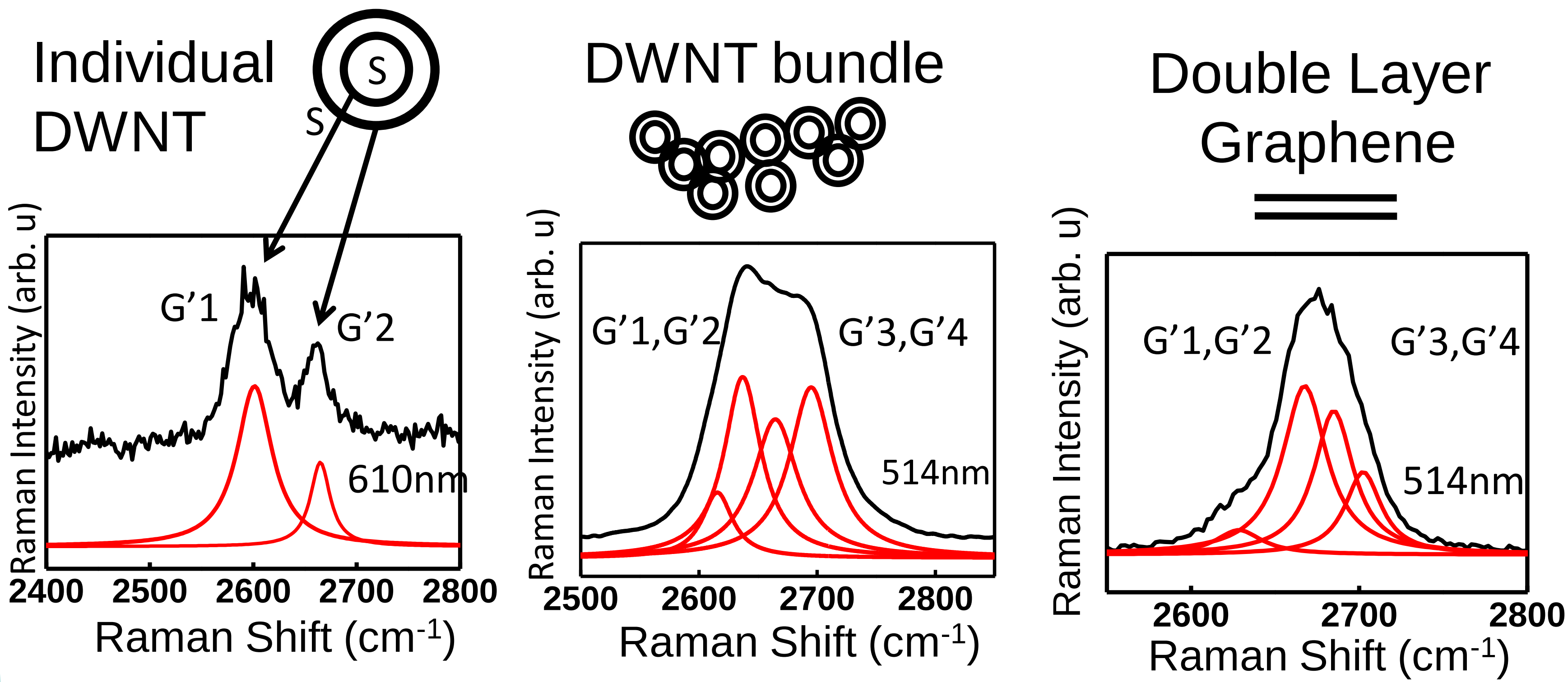


Structure is stable up to 2000°C

Low defect concentration

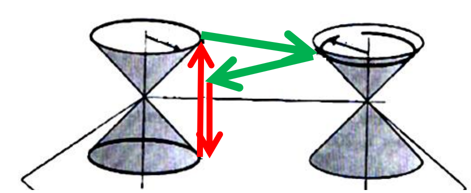
And we can study Raman spectra
for each inner and outer tube as a function of E_L

Weak interaction between layers within individual DWNTs gives new behavior for known Raman features



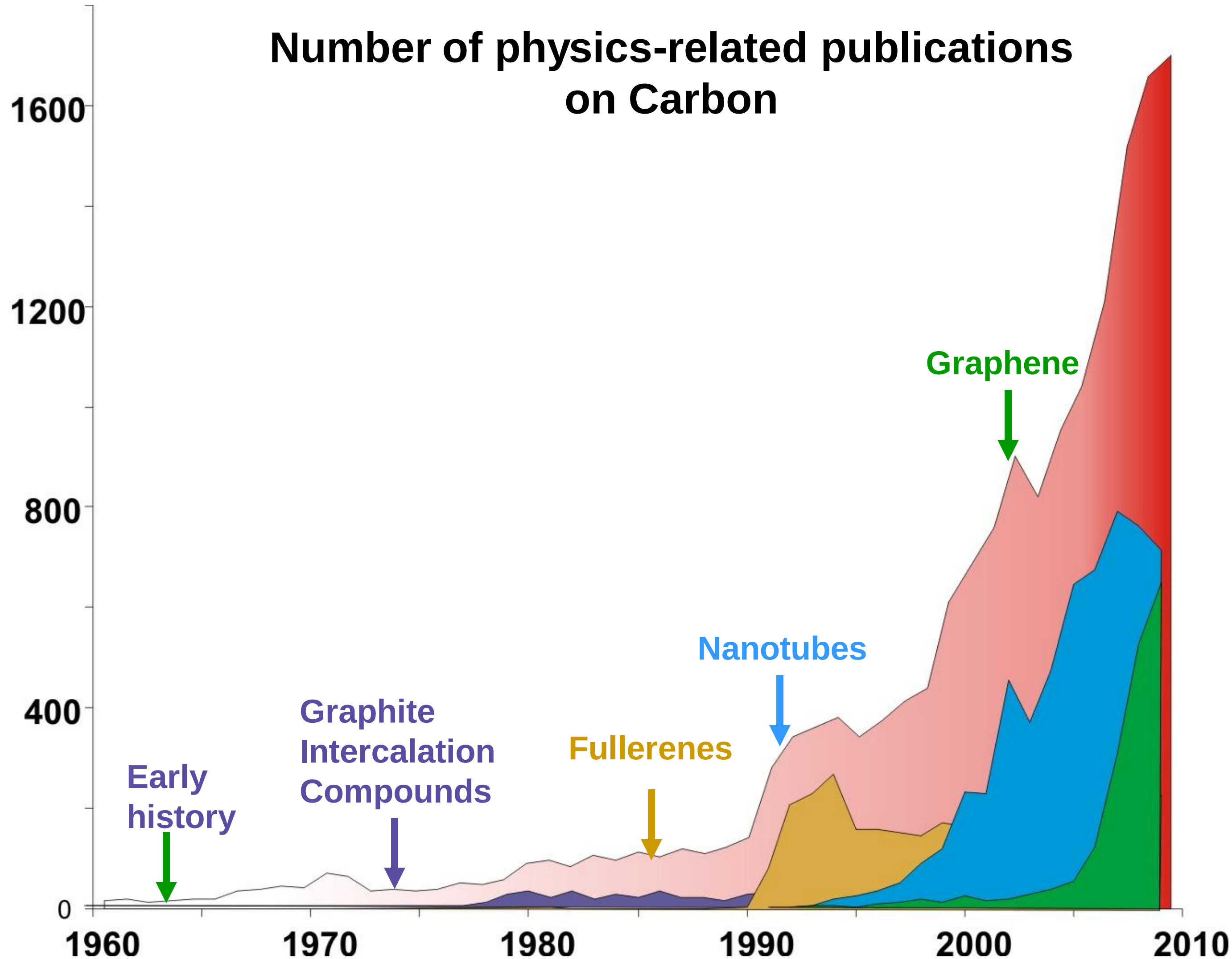
The nanotube curvature is responsible for phonon softening in double resonance processes

Origin of G' band



F. Villalpando-Paez et al. *Nano Letters*. 2008.

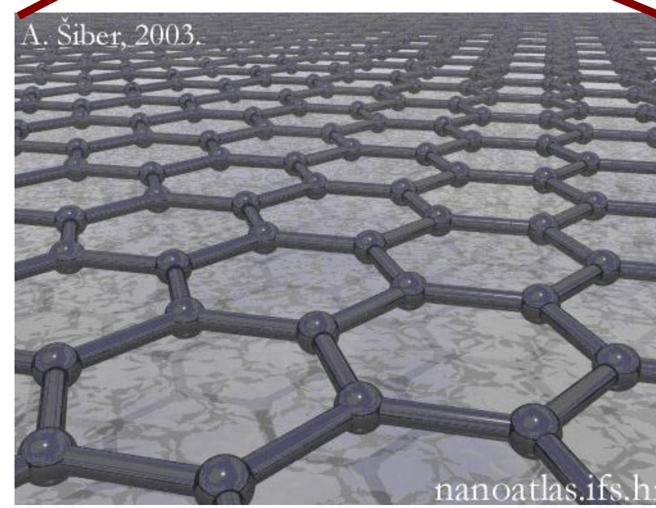
Graphene and the field of carbon research



Graphene: the amazing nanomaterial

✓ Thinnest material sheet imaginable…yet the strongest! (5 times stronger than steel and much lighter!)

✓ Graphene is a zero band gap semiconductor: it conducts as well as the best metals, yet its electrical properties can be modulated (it can be switched “ON” and “OFF”)



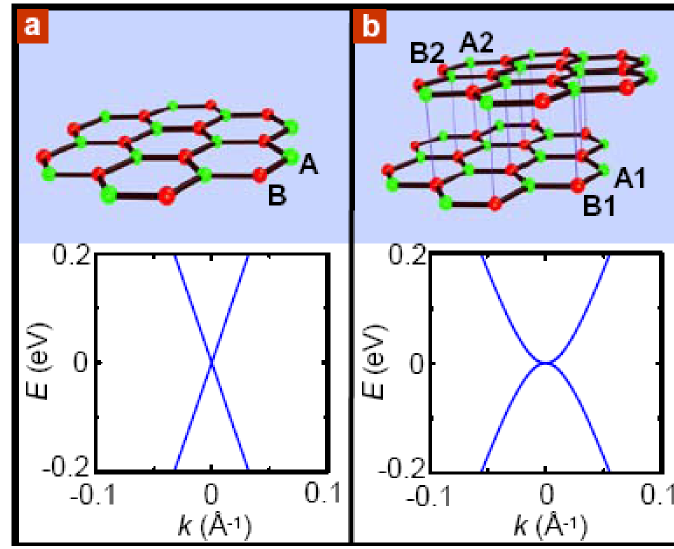
✓ High mobility ($\geq$100000 cm^2/Vs @RT) $\Rightarrow$ Ballistic conduction for hundreds of nm

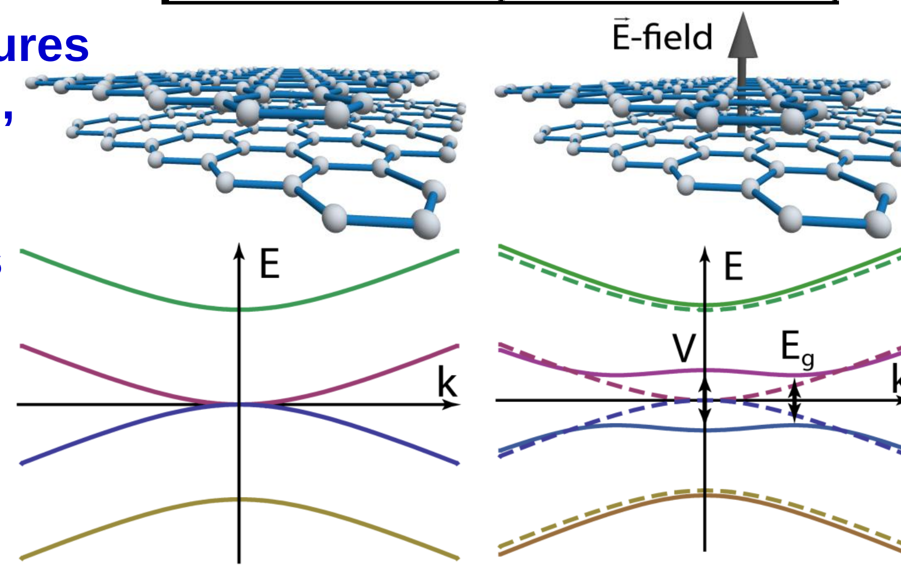
✓ Superb heat conductor (~$5 \cdot 10^3$ W/m·K)

✓ Very high current densities (equivalent to ~10^9 A/cm^2)

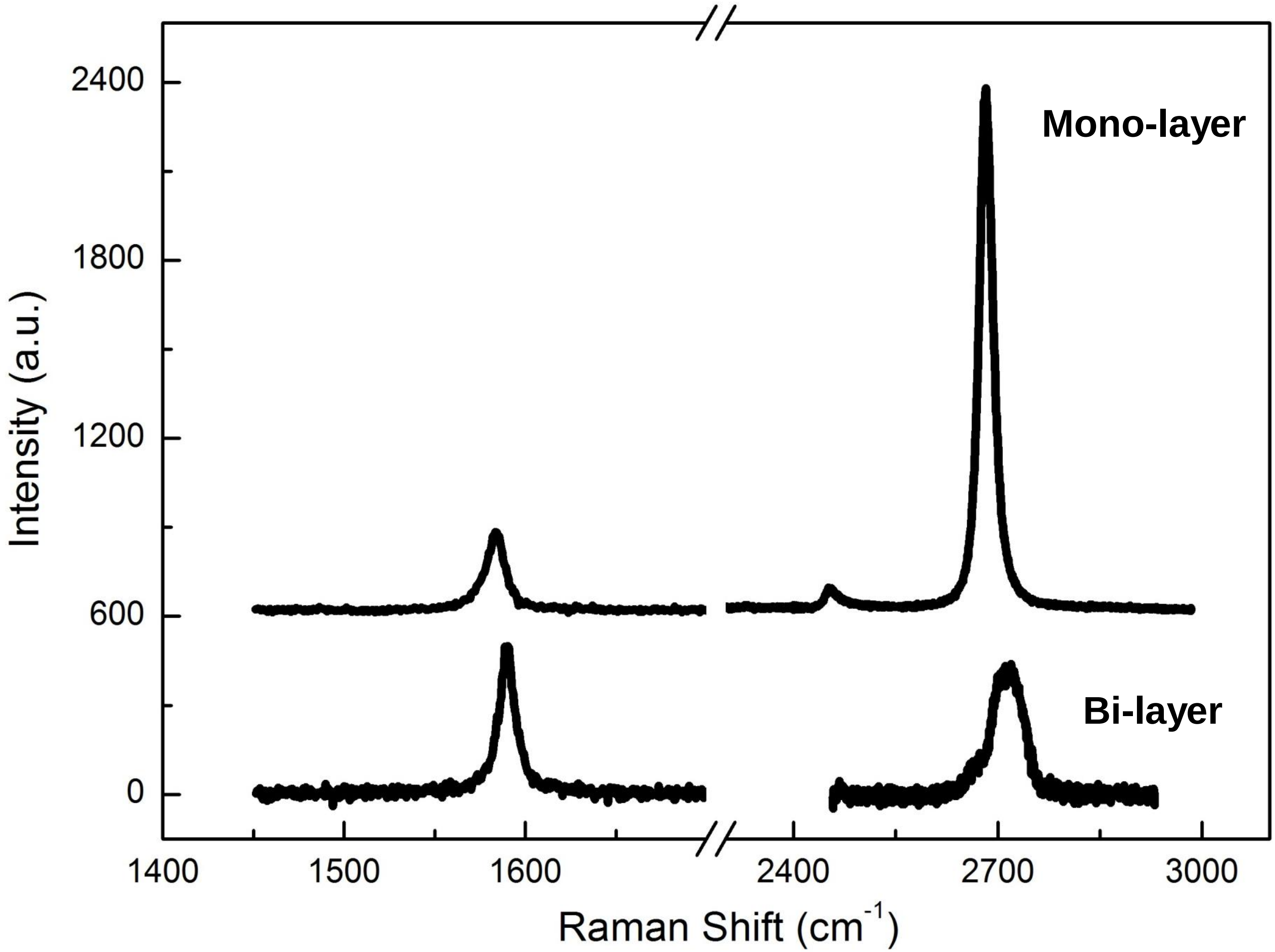
Graphene (mono-, bi- and tri-layer): QUALITATIVELY different materials

- ✓ **Bipolar materials (electrons and holes)**
- ✓ **Low energy behavior described by Dirac equation**
- ✓ **Truly 2D: pure surface with no bulk!**
- ✓ **Band structure can be modified by application of electromagnetic fields**
- ✓ **Band structure of graphene structures depends on geometry (stacking, size, and atomic structure)**
- ✓ **Interesting electron spin dynamics (weak spin orbit, nearly absent hyperfine interaction, etc…)**





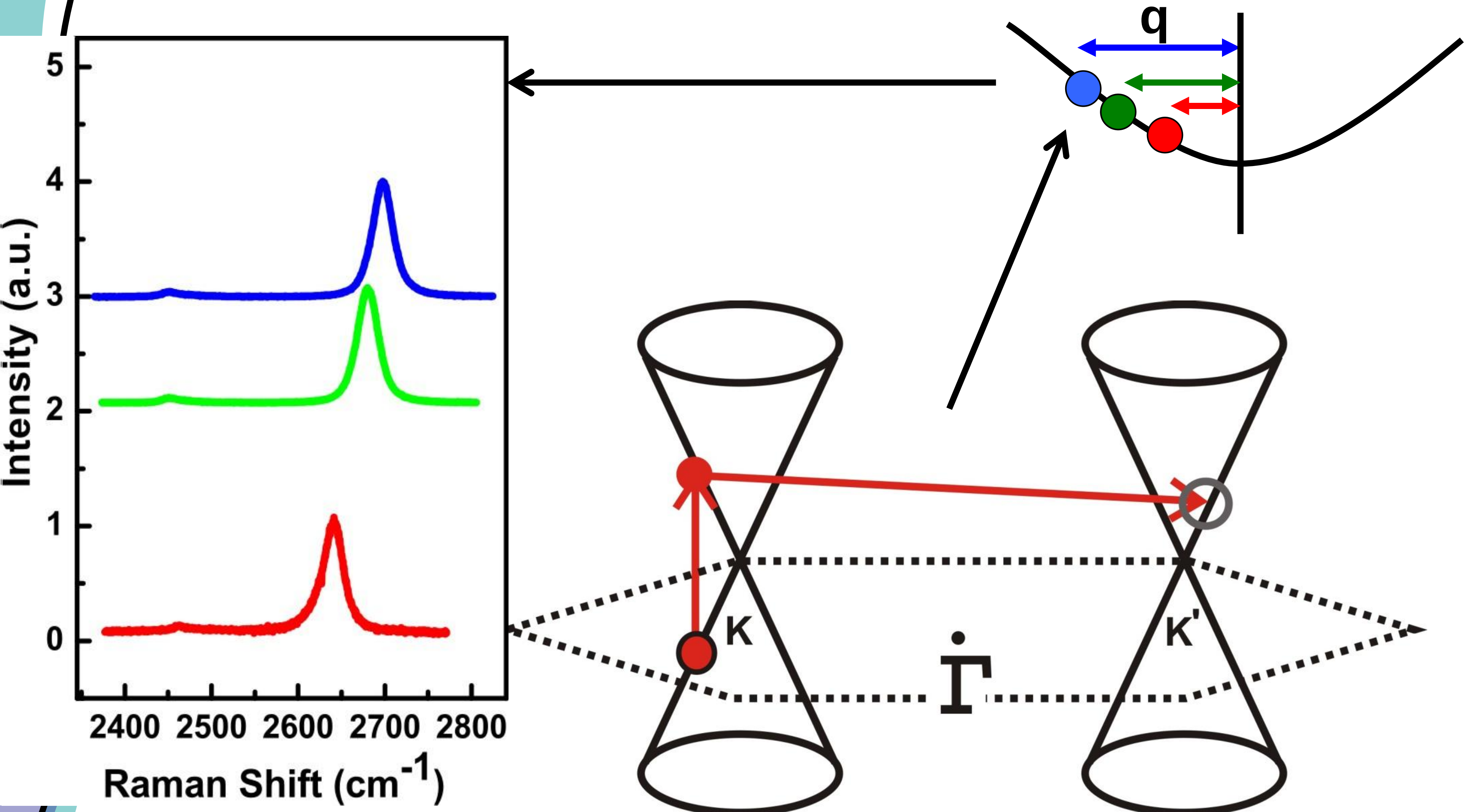
Raman Spectrum for Graphene



Ferrari et al., 2006

Dispersion of G′ band in nano-carbons

The double resonance Raman process + Resonant Raman

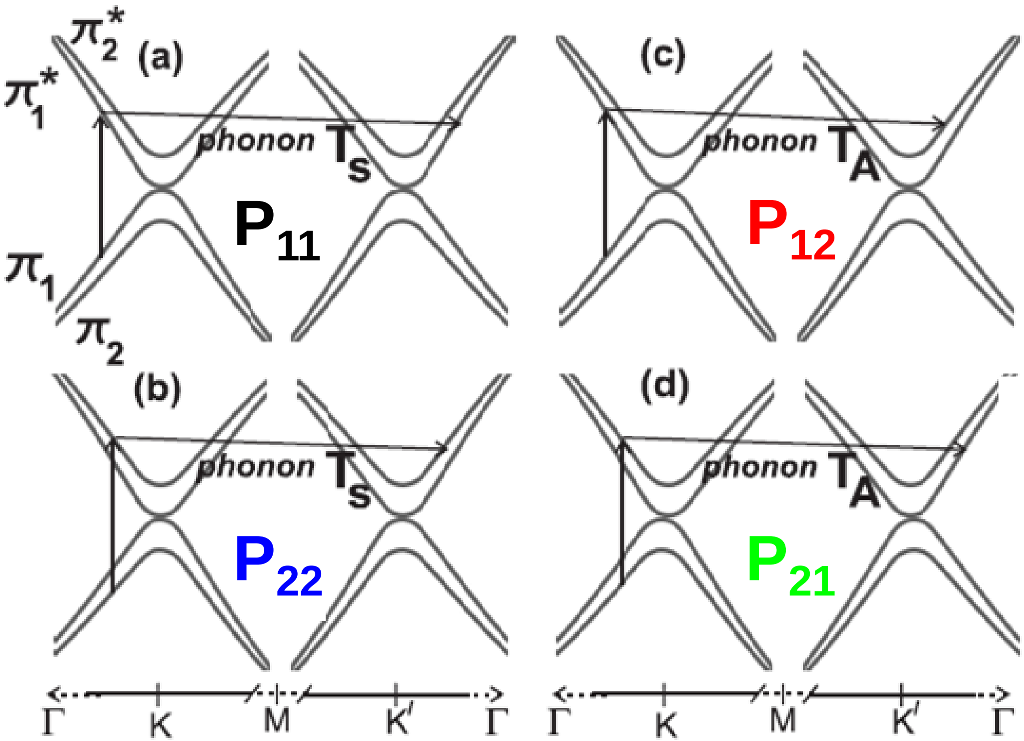


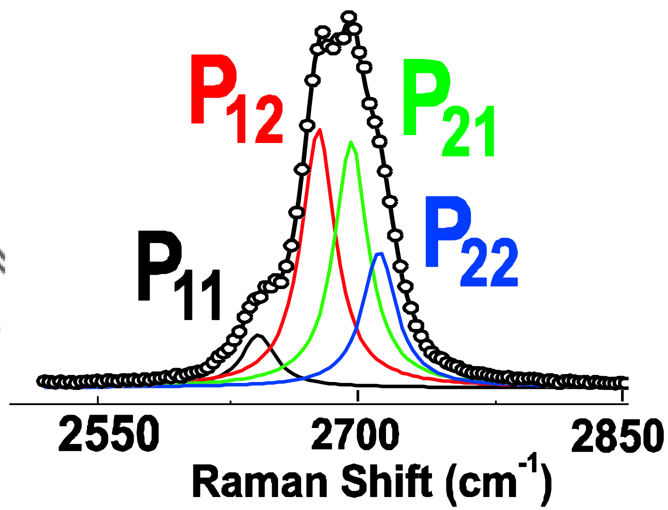
Reich and Thomsen, 2000

The four G’ peaks in bilayer graphene

Probing electrons in the visible range

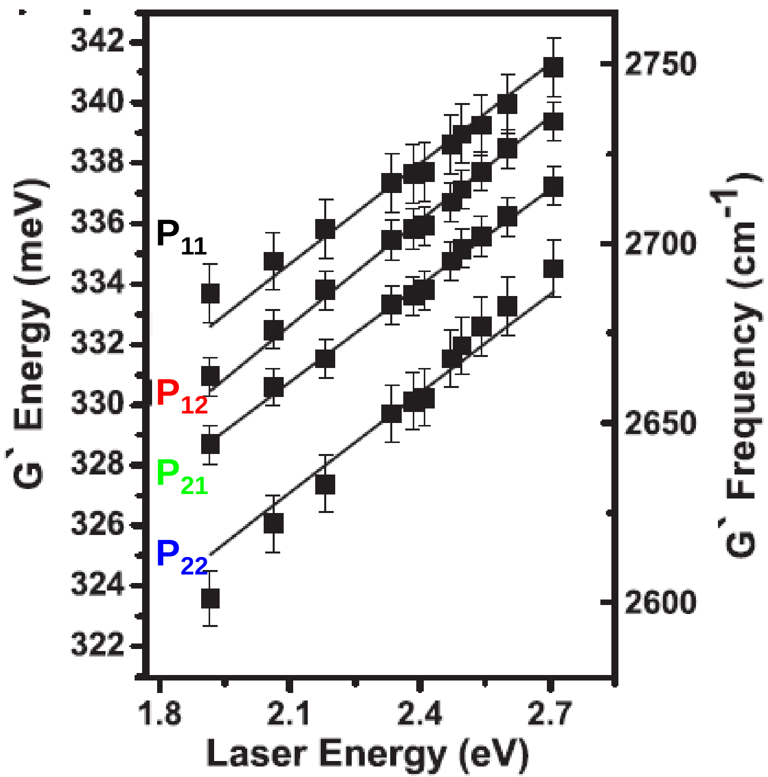
L. M. Malard et al., PRB *(2007).*

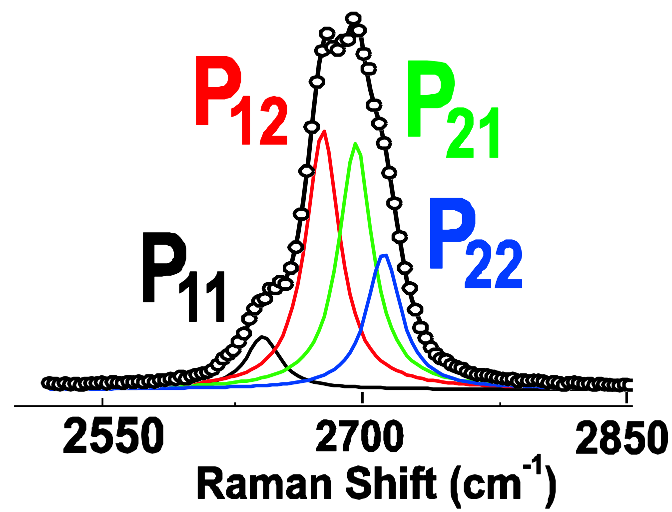




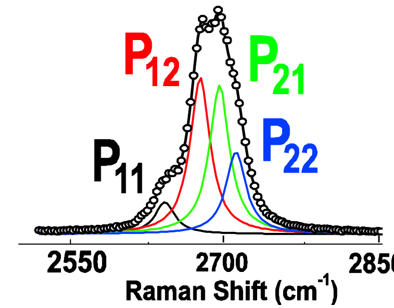
$q_{11}<q_{12}<q_{21}<q_{22}$

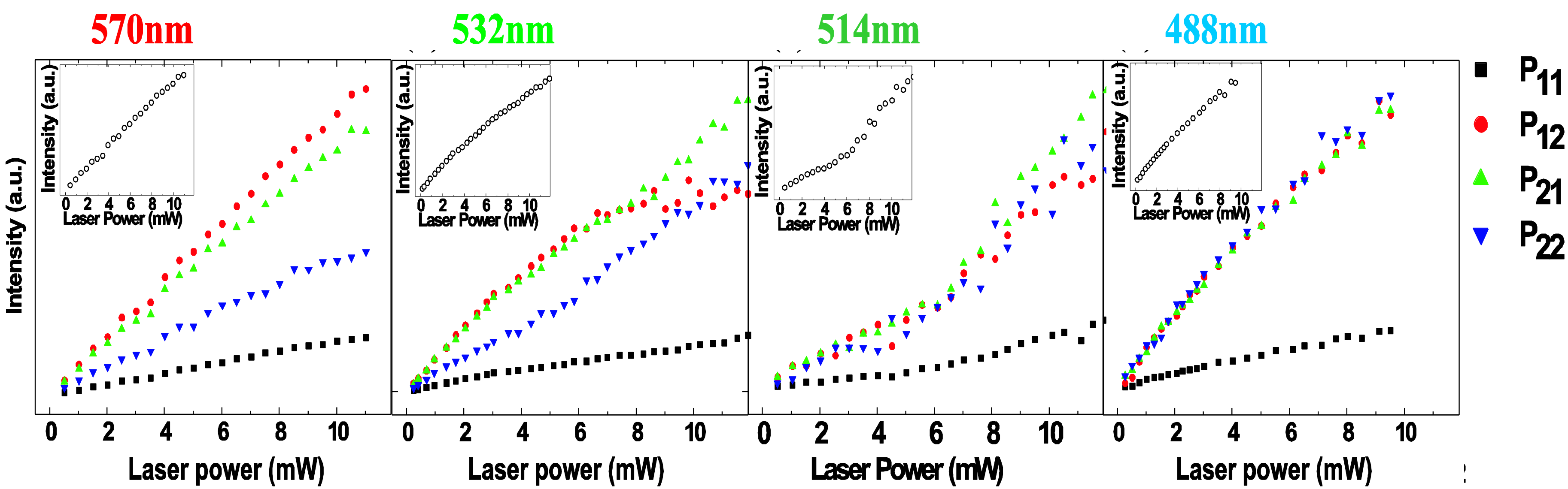
Dispersion of the four G′ peaks in bilayer graphene



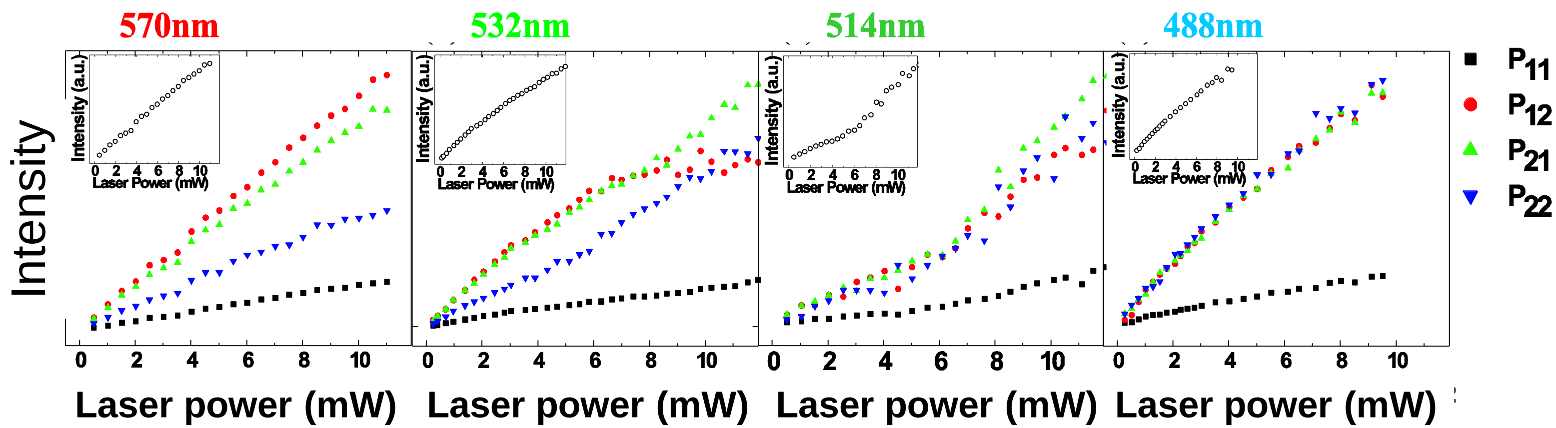


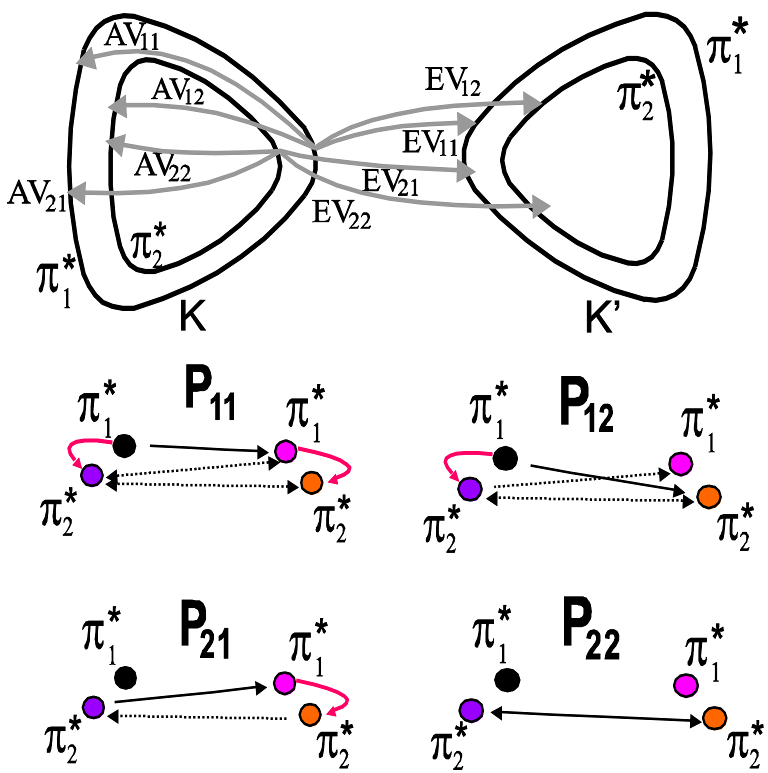
Phonon dynamics and thermalization between transitions: temperature and E_{laser} influences





Mafra *et al.* (2011)





- Relative intensity P_{12}~P_{21}>P_{22}>P_{11}
  - phonon relaxation time
    11 < 21 = 12 < 22
- Scattering from π_1* to π_2* by emitting phonon
- E_{laser} dependence
  - $E(\pi_2^*) – E(\pi_1^*)$ decreases as E_{laser} increases
  - Decay is faster for a higher E_{laser}

Mafra *et al.* (2011)

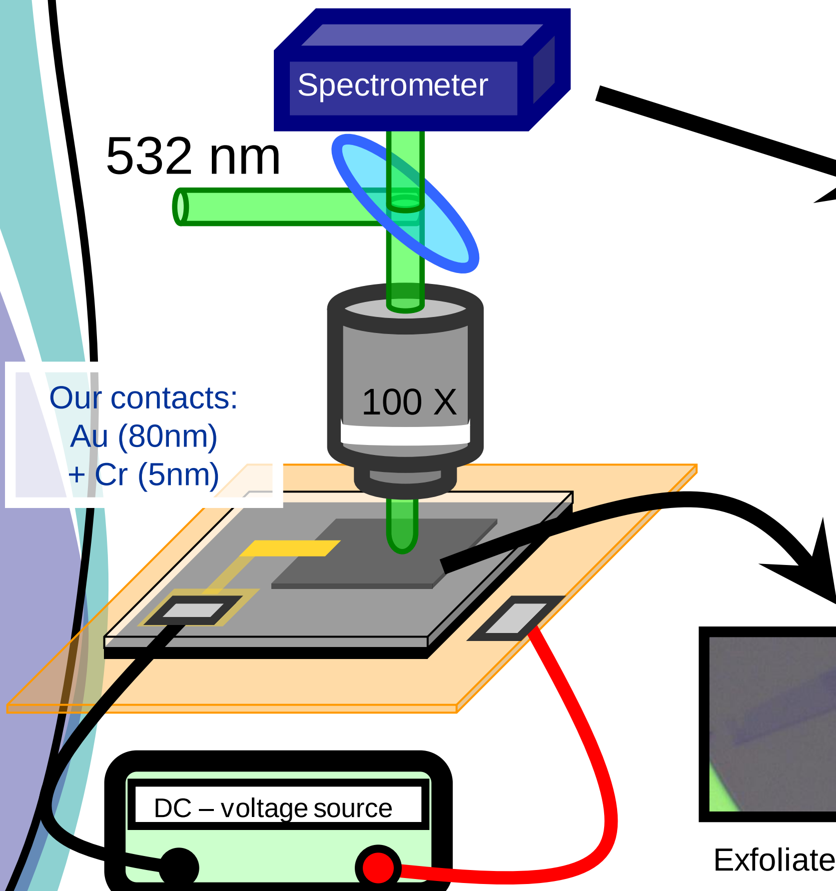
Phonon self-energy corrections to non-zero wavevector phonon modes in single-layer graphene

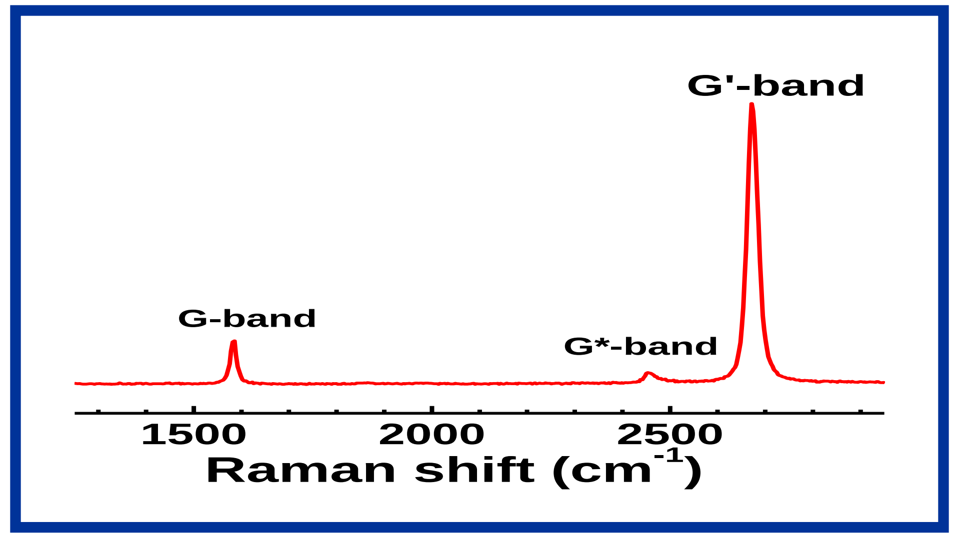
$$\Pi(\omega_{\mathbf{q}}, E_F) = 2\sum_{\mathbf{kk'}} \frac{|V_{\mathbf{kk'}}|^2}{\hbar\omega_{\mathbf{q}} - E^{eh}_{\mathbf{kk'}} + i\gamma_{\mathbf{q}}/2} \times (f_h - f_e)$$

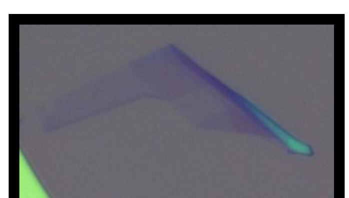
$$\hbar\omega_{\mathbf{q}} - \hbar\omega^0_{\mathbf{q}} = \mathrm{Re}[\Pi(\omega_{\mathbf{q}}, E_F)]$$

$\omega_{\mathbf{q}}$, $\gamma_{\mathbf{q}}$ (Self-consistently determined)

How do we obtain this information?





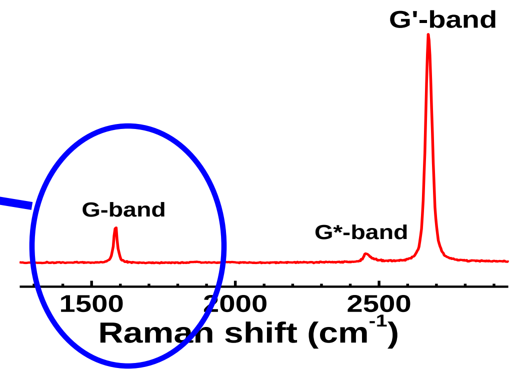


Exfoliated graphene

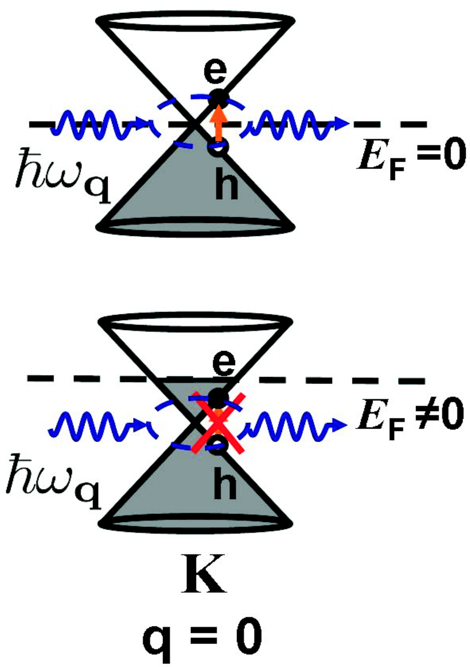
Experiment to vary Fermi level

What is known so far...

G-band results



Intra-valley process

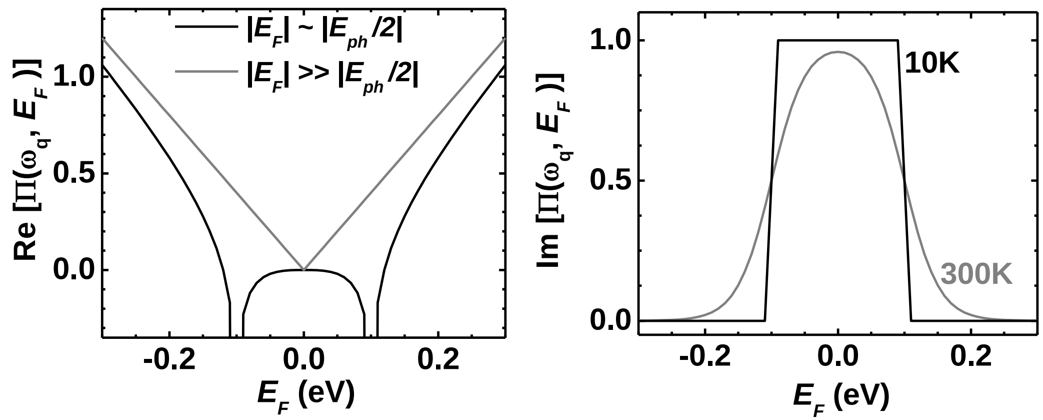


Γ-point phonons

Results for
G-band variation
with Fermi level

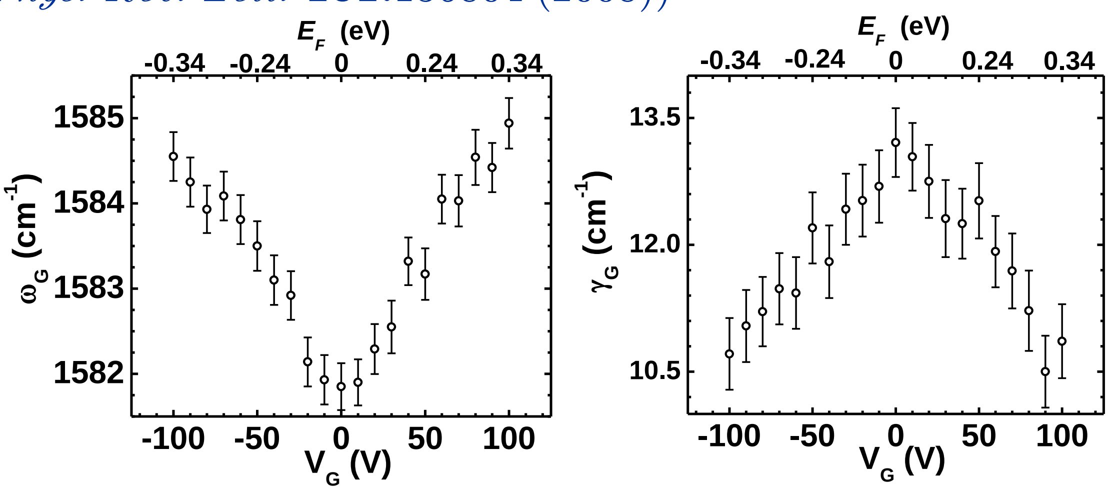
Theory:

(*Rev. Mod. Phys.* 81:109 (2009))



Experiment:

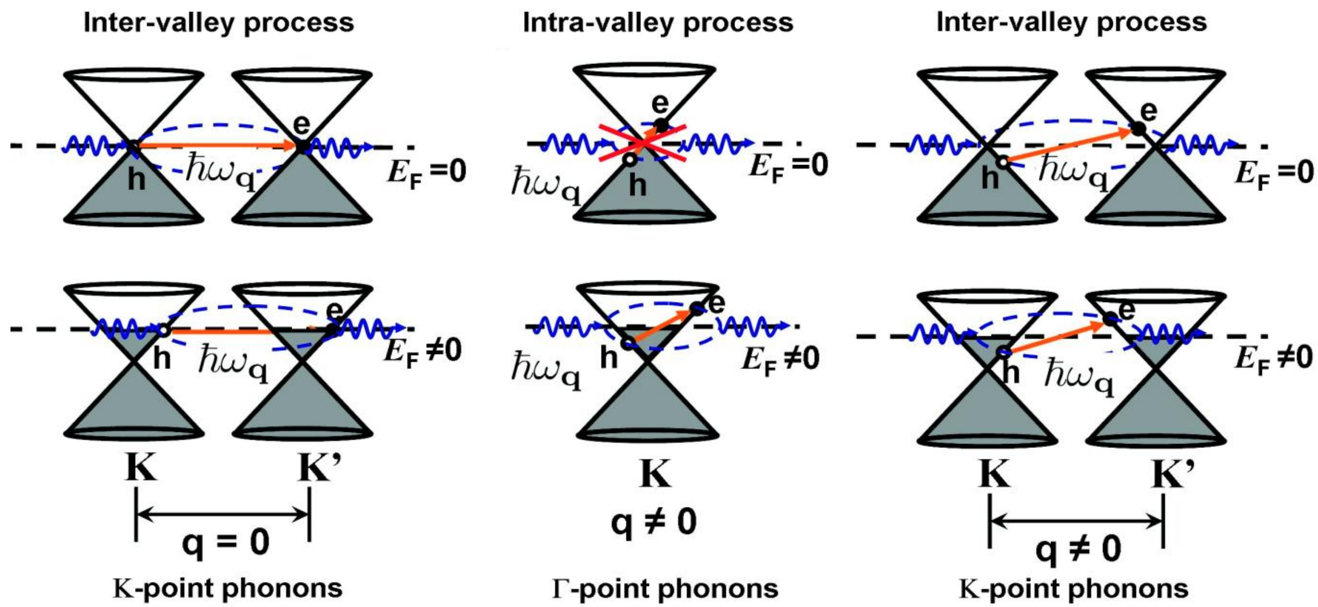
(*Phys. Rev. Lett.* **101:**136804 (2008))

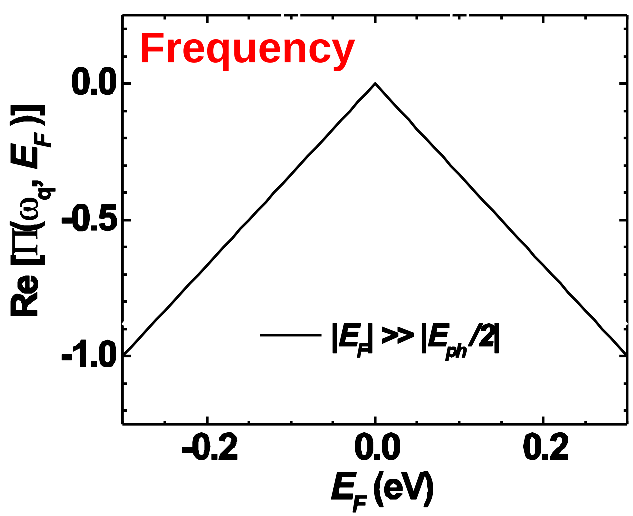


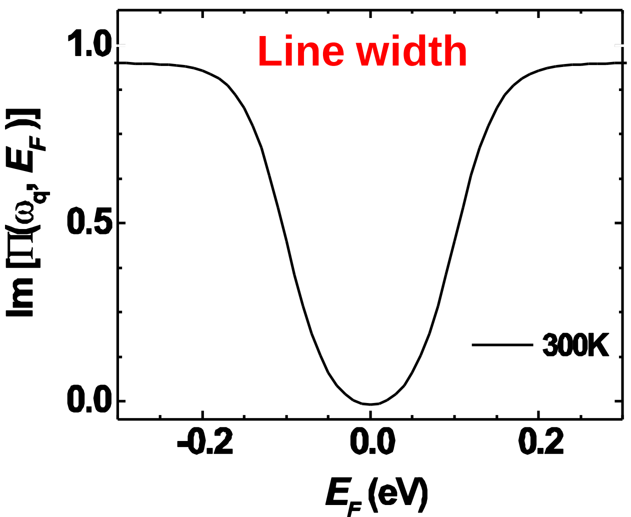
What is new? For combination and overtone modes...

Theory:

For Γ(K)-point q≠0 and K-point q=0 phonons:



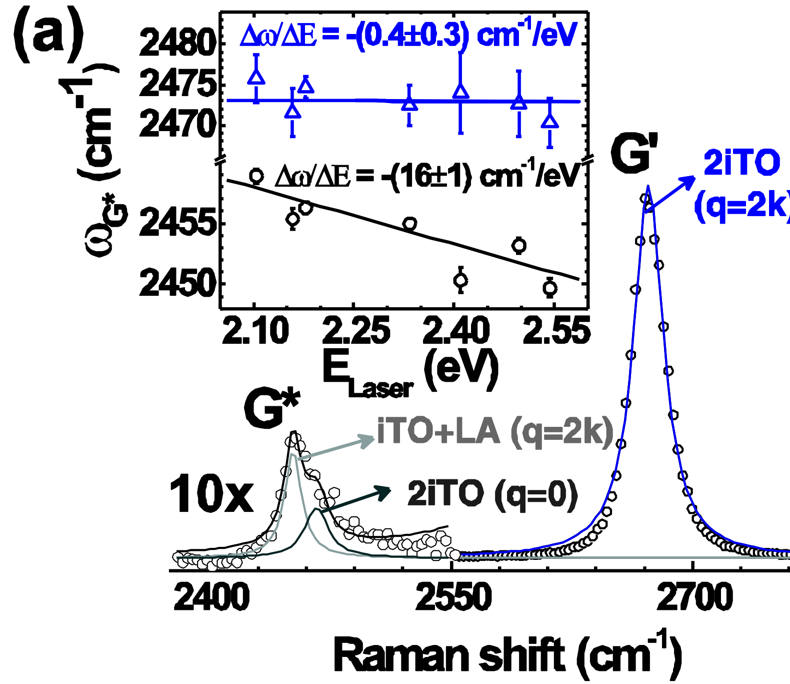




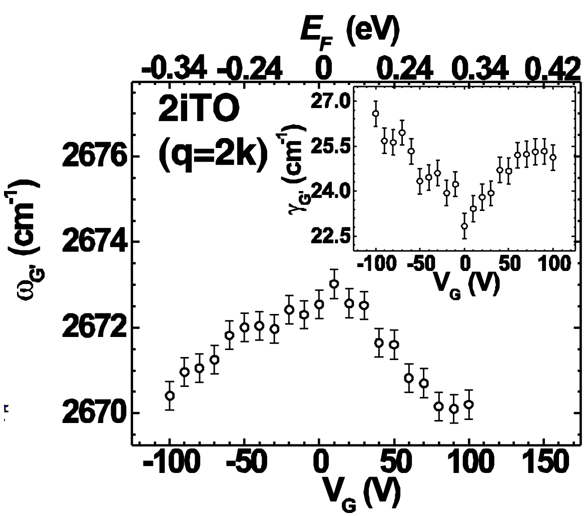
Araujo *et al.* 2011

Experiment:

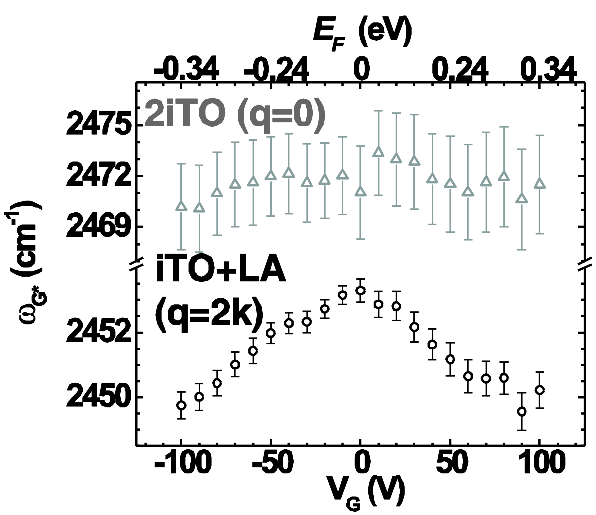
We applied these combined techniques to study the G* and G′ modes, which are the most prominent double resonance $q\neq0$ Raman features in the graphene spectrum. Our theoretical approach satisfactorily explains the experimental results and within this framework, we also showed that the G* mode is an asymmetric peak composed of both, the iTO+LA combination mode, which is an intervalley $q=2k$ process, and the 2iTO overtone mode, which is an intervalley $q=0$ process.

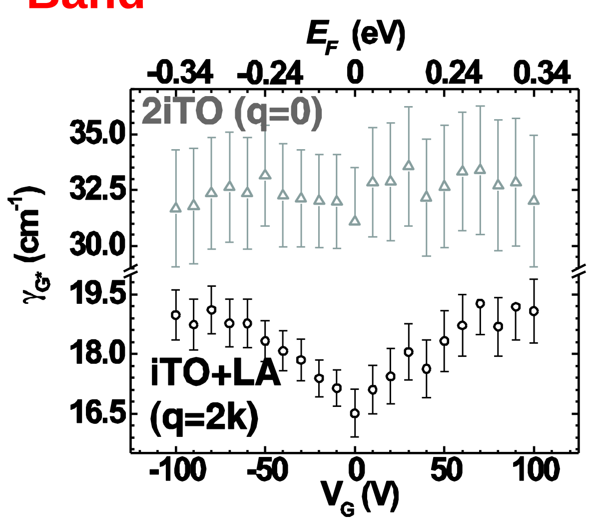


G'- Band

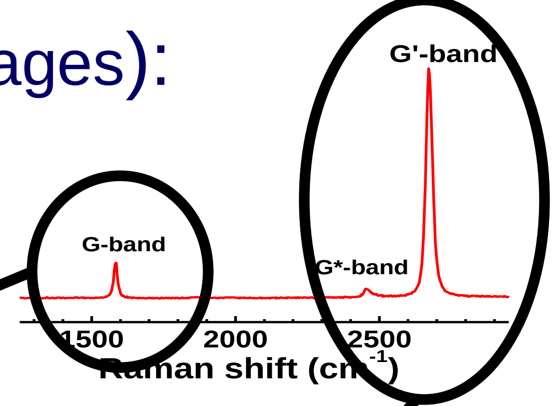


G*- Band

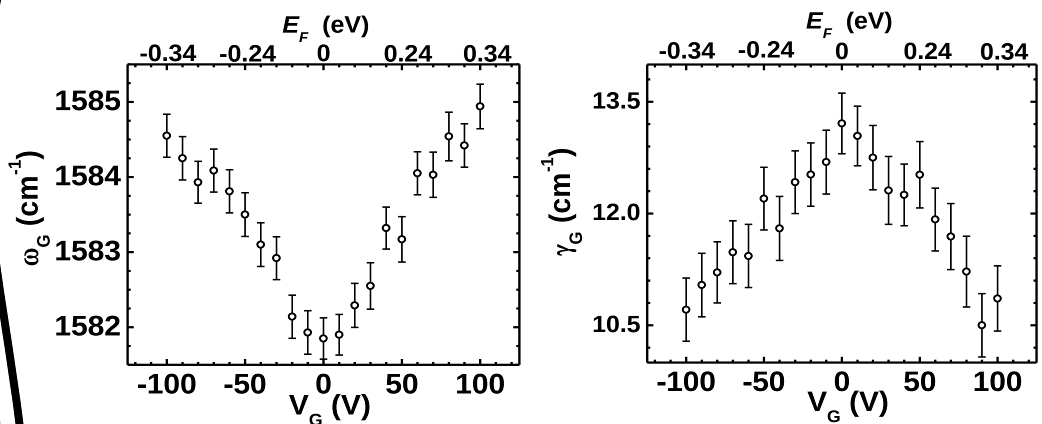


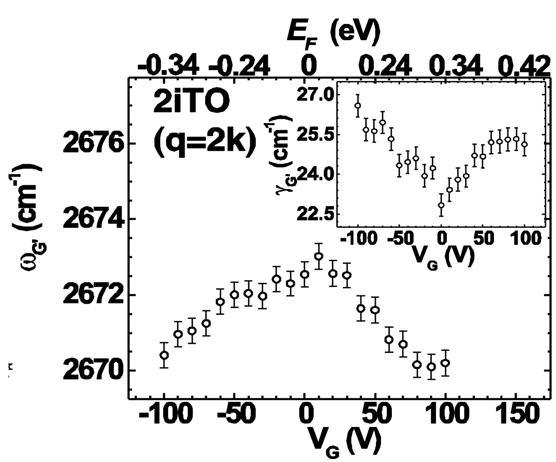


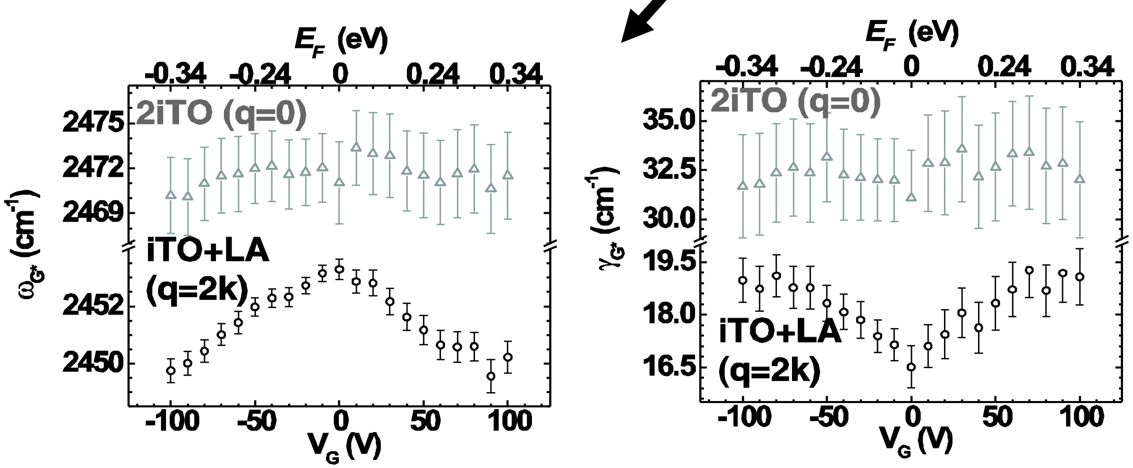
Conclusions (The take-home messages):



G – band







G′ – band

G* – band

Thank you

Collaborators:

G. Dresselhaus, MIT
H. Son, MIT
J. Kong, MIT
M. Hofmann, MIT
F. Villalpando, MIT
M.A. Pimenta, UFMG Brazil
A. Jorio, UFMG Brazil
A. Souza Filho, UFC Brazil
L.G. Cancado, UFMG Brazil
P. T. Araujo, MIT
D. L. Mafra, MIT/UFMG
G.G. Samsonidze, Bosch
M. Endo, Shinshu U
R. Saito, Tohoku U
K. Sasaki, Tohoku U
Y.A. Kim, Shinshu U
M. Terrones, IPICYT, Mexico

The End