東北大学
TOHOKU UNIVERSITY

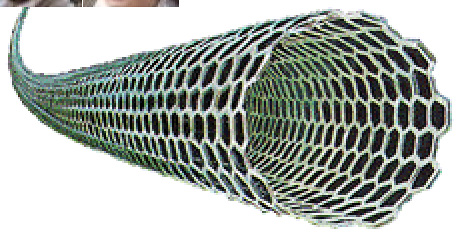
2nd Workshop on Nanoscience: Carbon-Related Systems and Nanomaterials,
National Cheng Kung University
July 4-7th, 2012

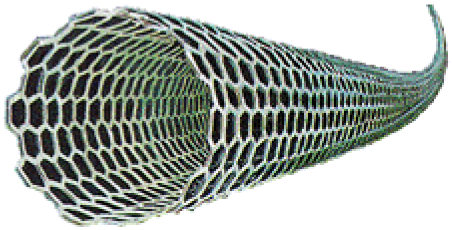
Optical characterization of nanotube and graphene

Riichiro Saito

**A. R. T. Nugraha, K. Sato,
L. C. Yin, K. Sasaki, C. Conxiao, Y. Ting,
G. Dresselhaus and M. S. Dresselhaus**

**Tohoku University, Sendai, Japan
Nanyang Technological University , Singapole
Massachussetts Institute of Technology, MA, USA**



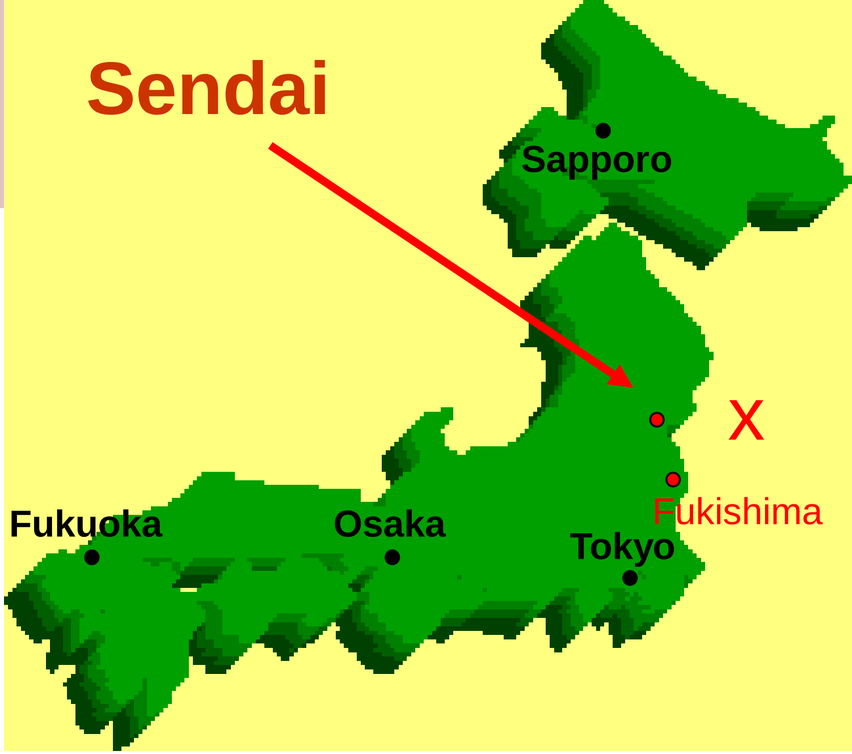


東北大学

Tohoku University

Sendai city 350km from Tokyo

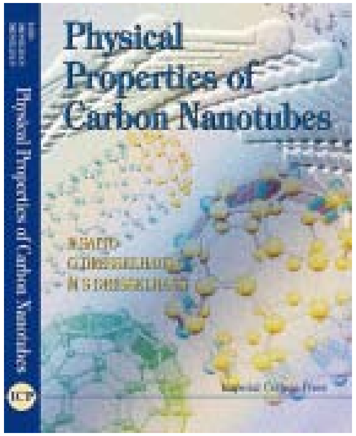
Sendai Pageant of Starlight   Sushi

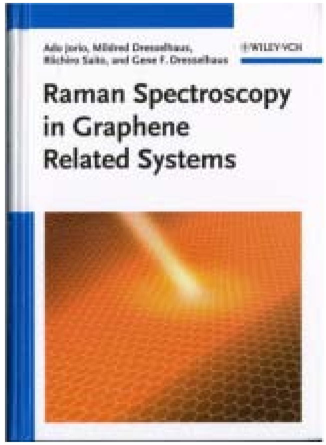


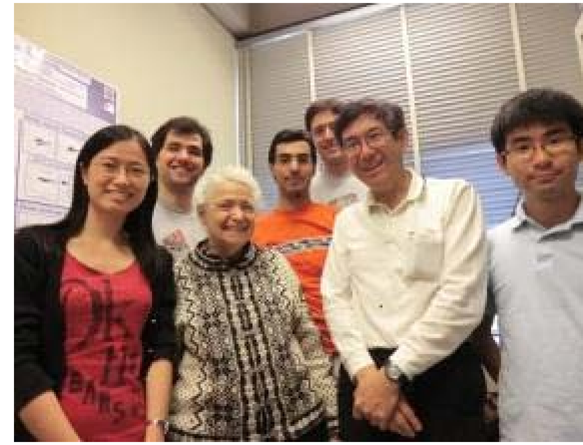
Outline of this 1 hour talk

1. Introduction of Nano Carbon

2. Optical (Raman) characterization
   - Carbon nanotubes
   - Graphene

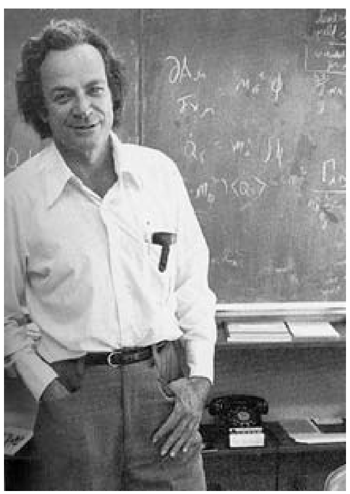


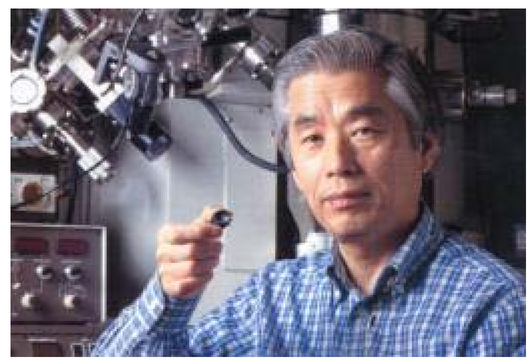




Introduction of Nano Carbon

Carbon material with 1-10nm size



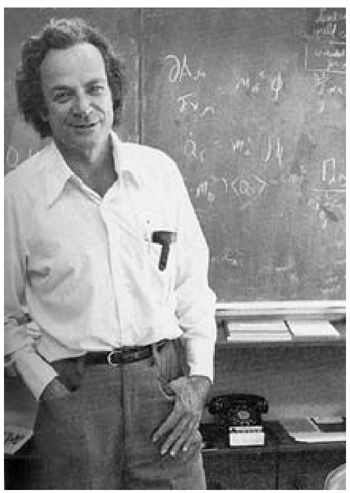


The size of human made objects

（From the American DOE report）

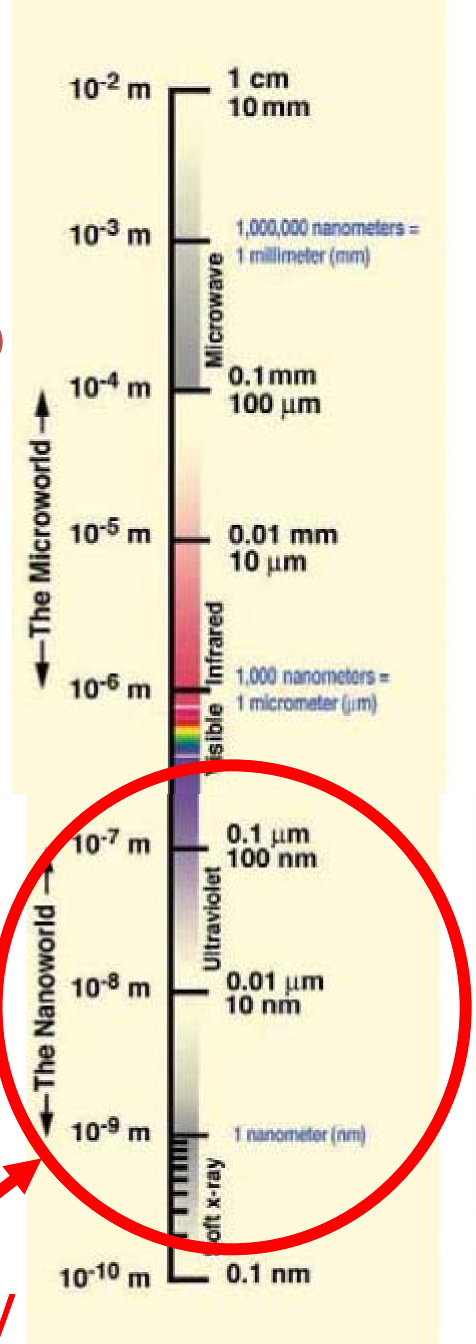
Lower limit of size optical microscope

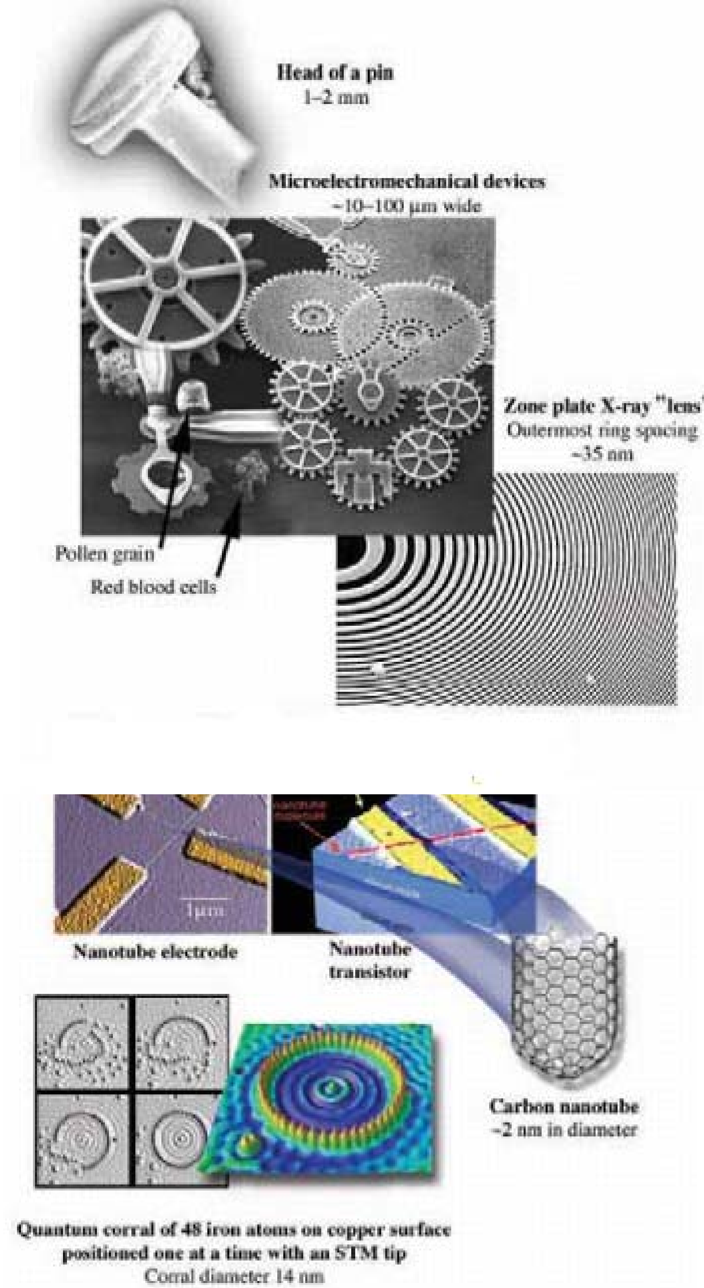
1 Micron = 1 μm



Richard Feynman

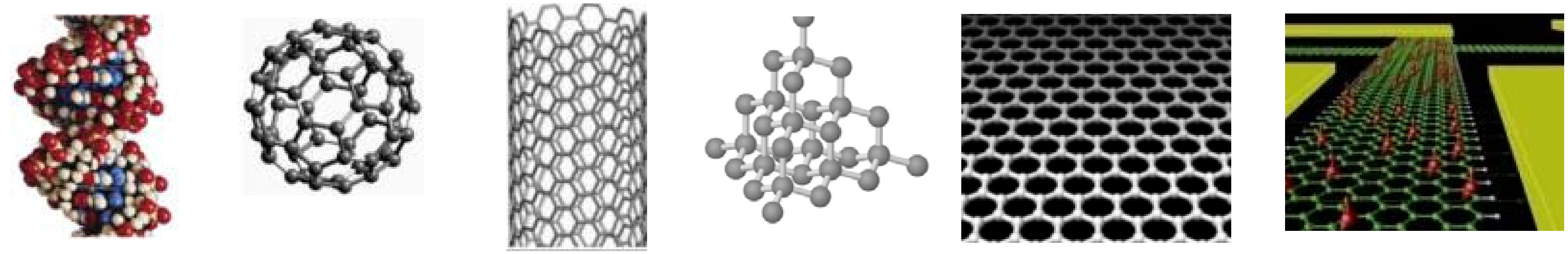
Undeveloped Territory in 1950’s

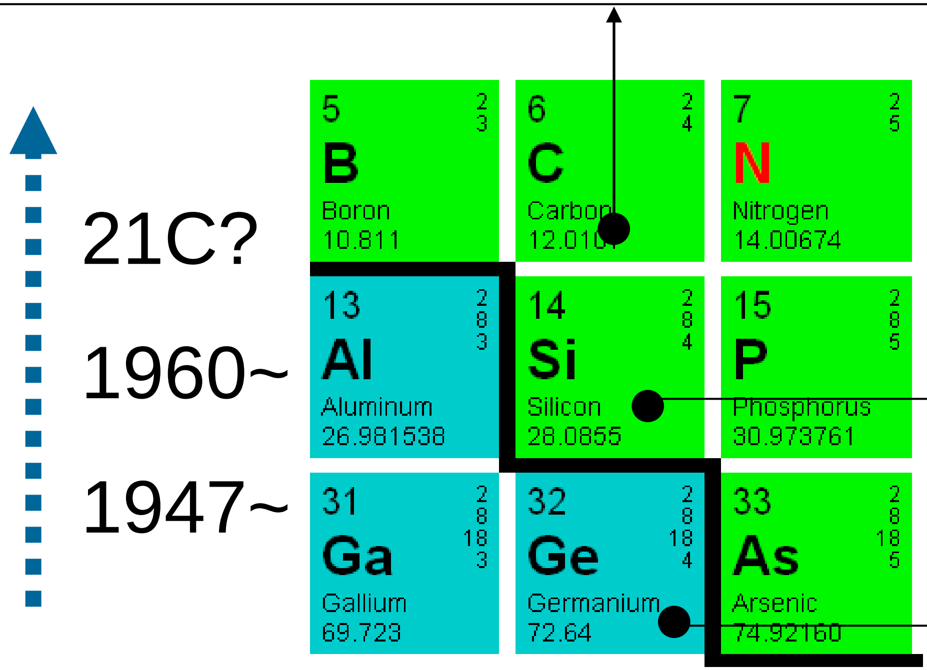


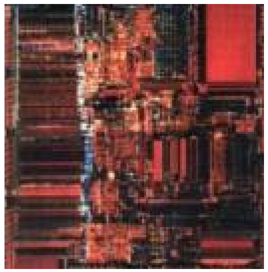


Courtesy Office of Basic Energy Sciences,
Office of Science, U.S. Department of Energy

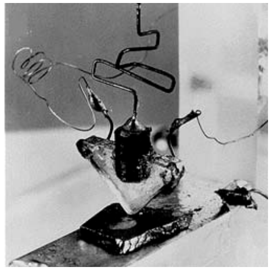
Why nano carbon?







Intel CPU

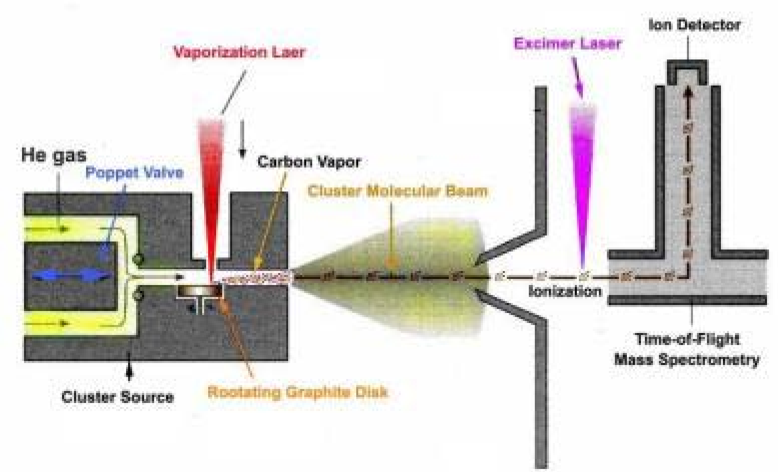


The first transistor

Semiconductor, small size, mobility, melting T

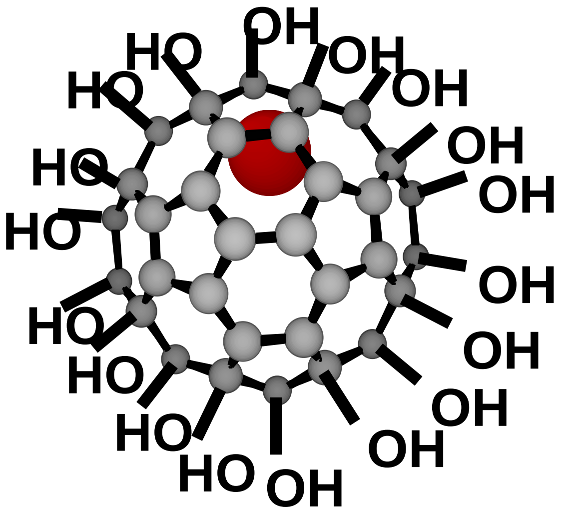
This slides is inspired by T. Ohta at LBNL and Fritz-Haber-Institut.

C_{60} molecule (1985 Sept. 12th)

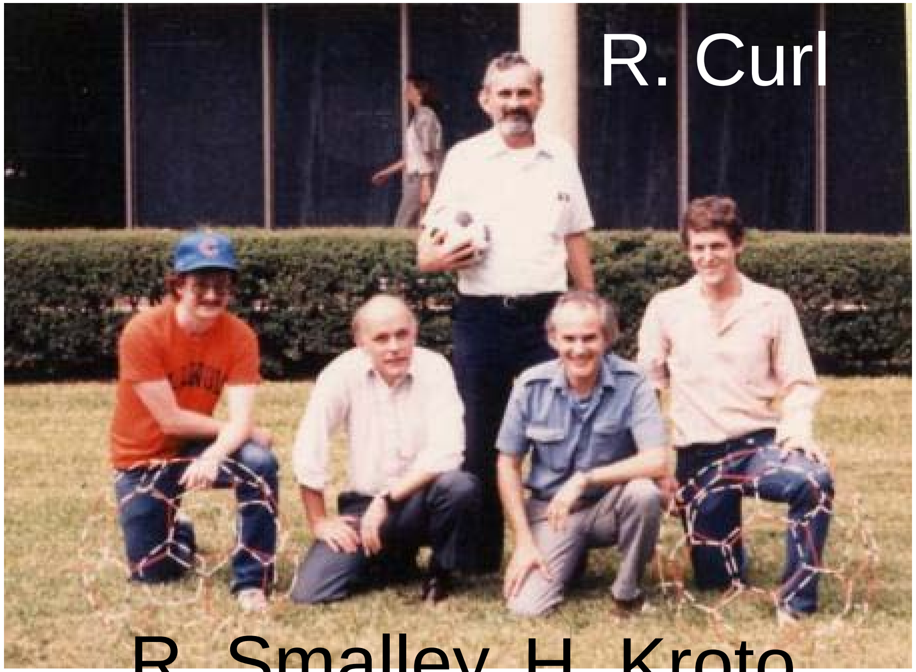


Laser Ablation

C_{60}



$Gd@C_{82}(OH)_n$

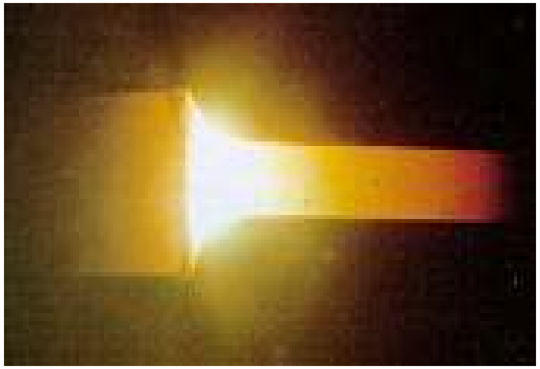


R. Curl

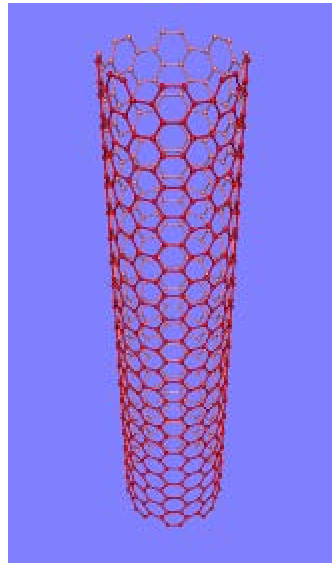
R. Smalley H. Kroto

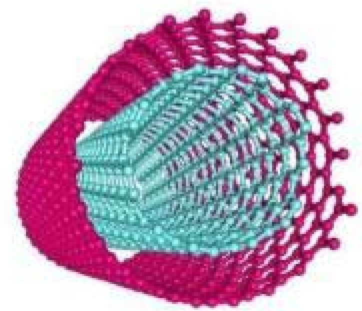
MRI applications

Carbon Nanotubes (1991)

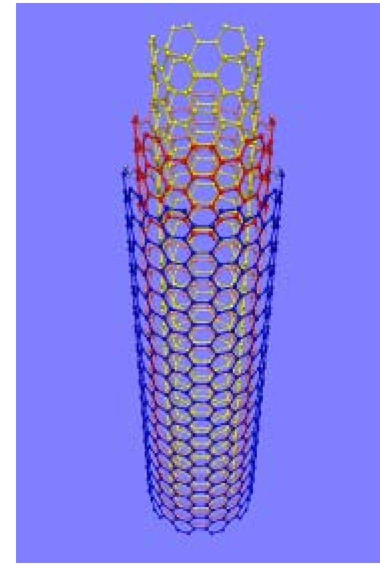


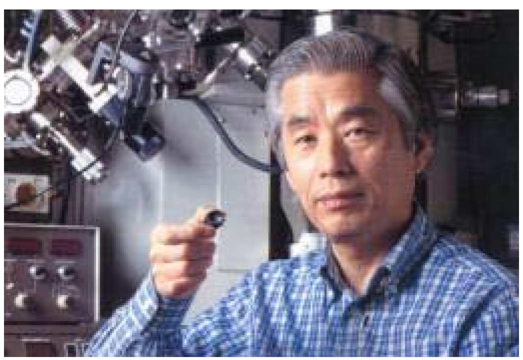
Arc Discharge





Double-wall nanotube

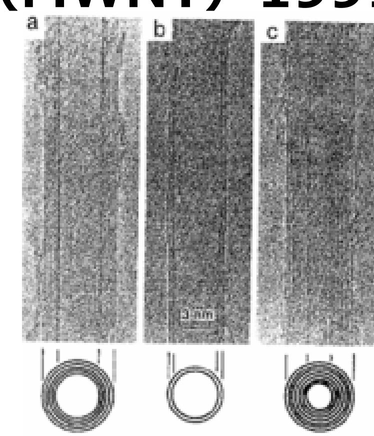




S. Iijima

Single-wall nanotube (SWNT) 1993

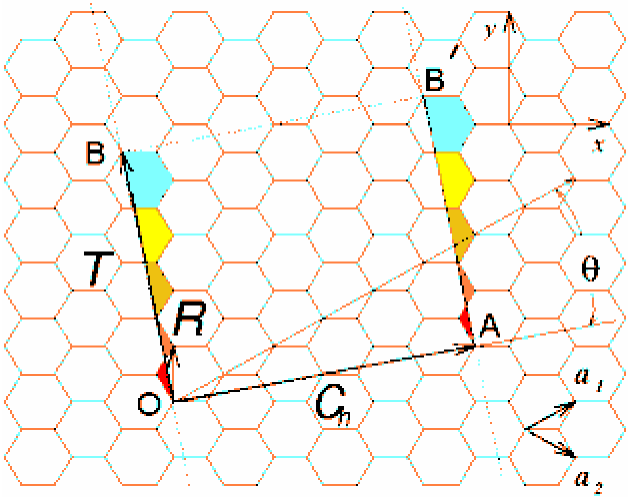
Multi-wall nanotube (MWNT) 1991



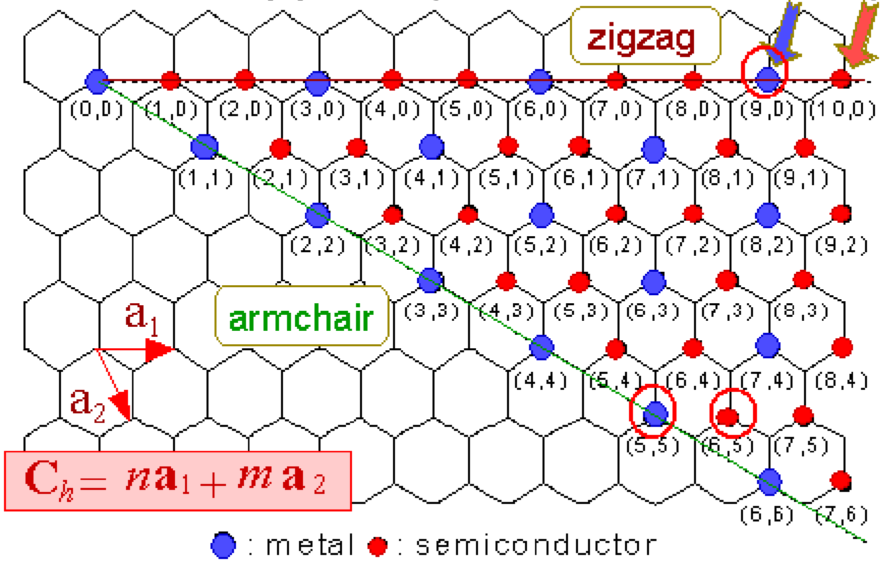
Chirality of Nanotubes (1991)

$C_h = na_1 + ma_2 \equiv (n, m)$

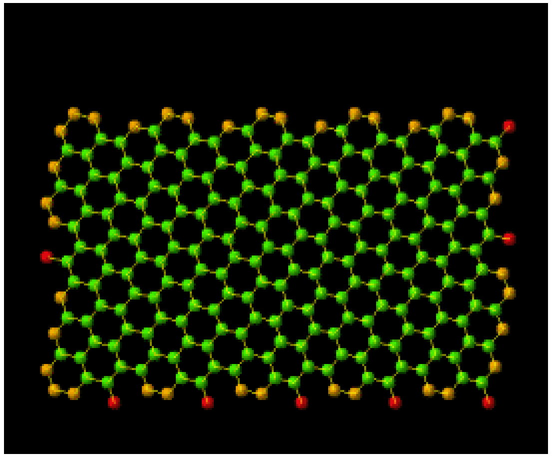
R. Saito *et al., Appl. Phys. Lett.* **60**, 2204 (1992)



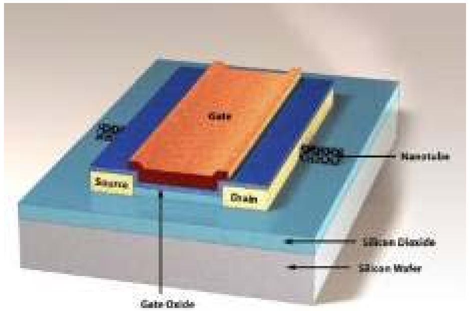
definition of chirailty



metallic or semiconducting

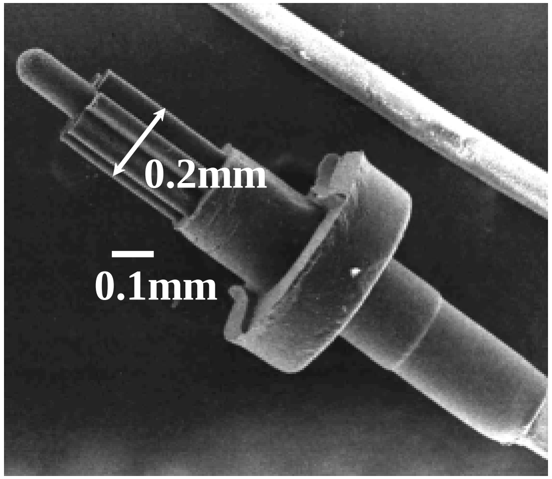


(10,5) nanotube



nanotube FET

Application of fiber-nanotube : Composite Endo



Tiny gear

M. Endo

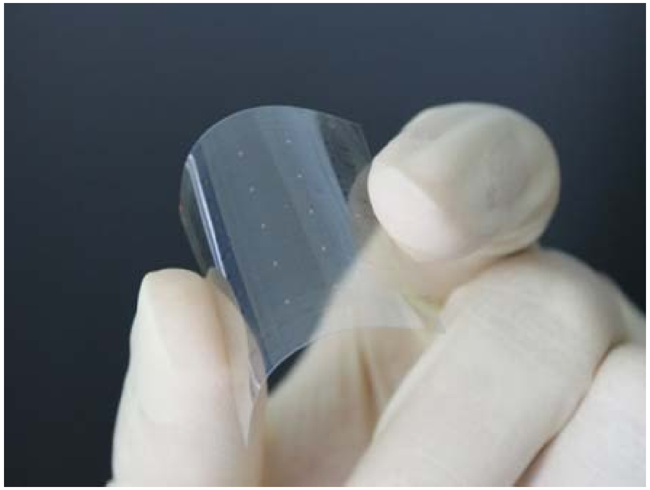
Hybrid bus
Pb buttery

Recent progress of nanotube

Artificial joint

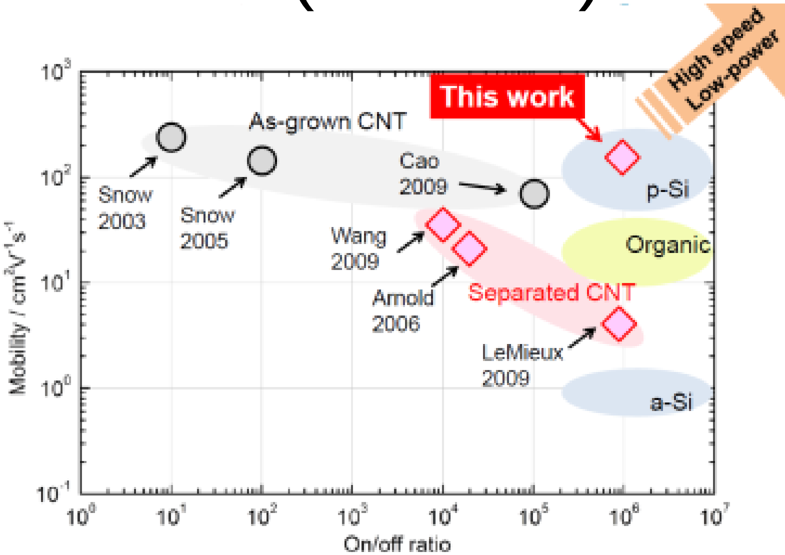
Less friction
Long life

Chirality separation
(H. Kataura)



Nanotube FET
(Y. Ohno)

High mobility
Low power
High T



Fullerene factory

Capacity = 40 tons fullerenes/year (as of May 2008)

Frontier Carbon Corporation http://www.f-carbon.com/

Exfoliated Graphene

- Breakthrough

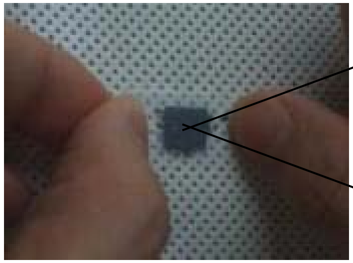
Micromechanical cleavage of graphite via adhesive tapes !

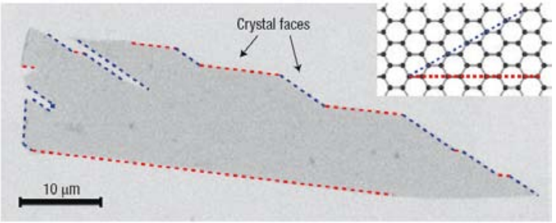
Novoselov *et al*, Science **306**, 666 (2004)

Optical microscope can count layer number

+

=

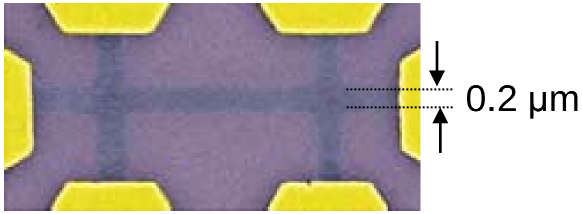




Scotch tape makes one atomic layer

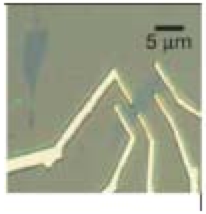
A. K. Geim Group @ Menchester

K. S. Novoselov *et al*, Nature **438**, 197 (2005)



P. Kim Group @ Columbia

Y. Zhang *et al*, Nature **438**, 201 (2005)

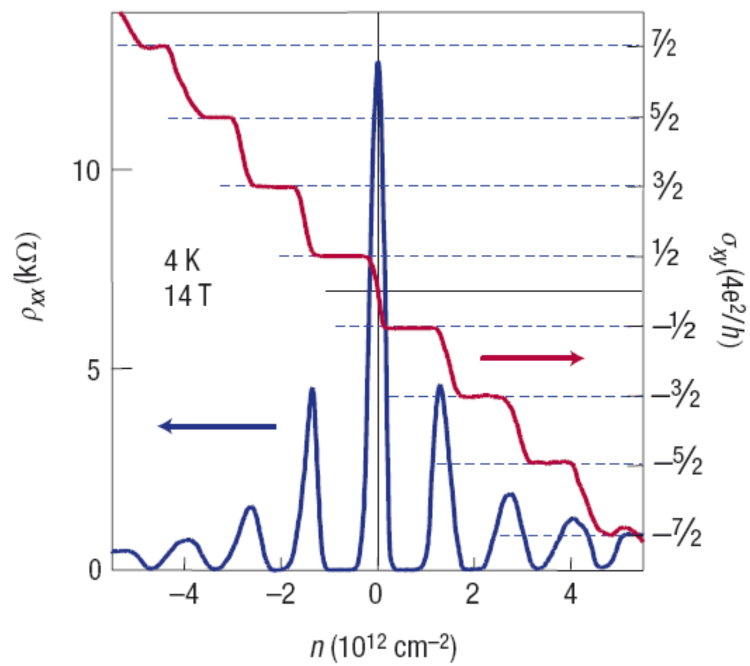


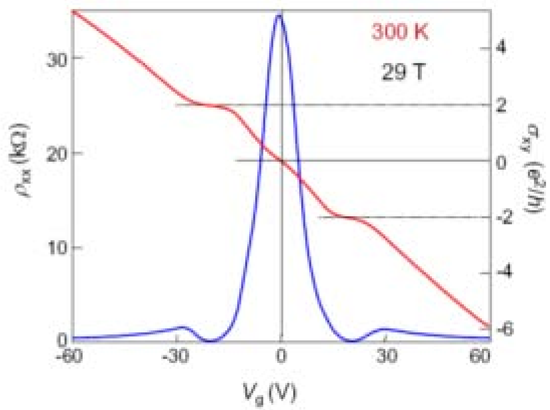
Electronic structure of graphene
- Consequences of chiral massless Dirac fermions

Half-integer Quantum Hall Effect (Room T) !

(Manifestation of Berry's phase of pseudospin)

Half integer QHE at room T





$$R_{xy}^{-1} = \pm g_s \cdot \left(\nu + \frac{1}{2}\right) \cdot \frac{e^2}{h}$$

$$\nu = 1, 2, 3, \cdots$$

$$g_s = 2 \times 2 \text{ (spin \& sublattice)}$$

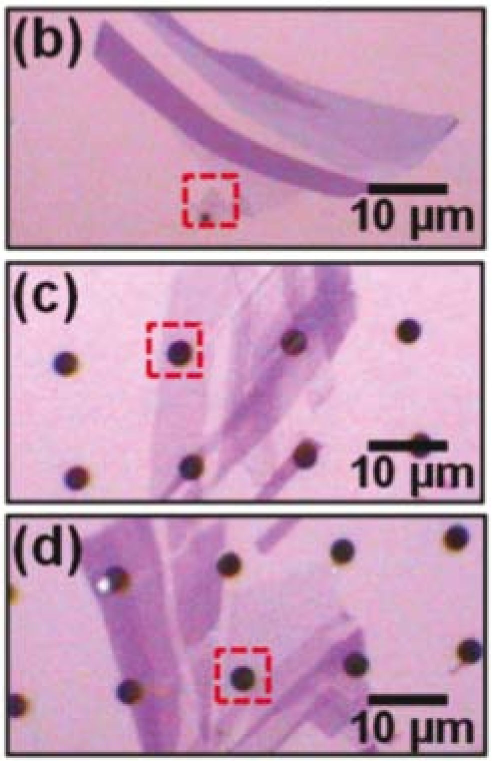
Zhang *et al* (05), Novoselov *et al* (05)

Kim & Geim *et al* (07)

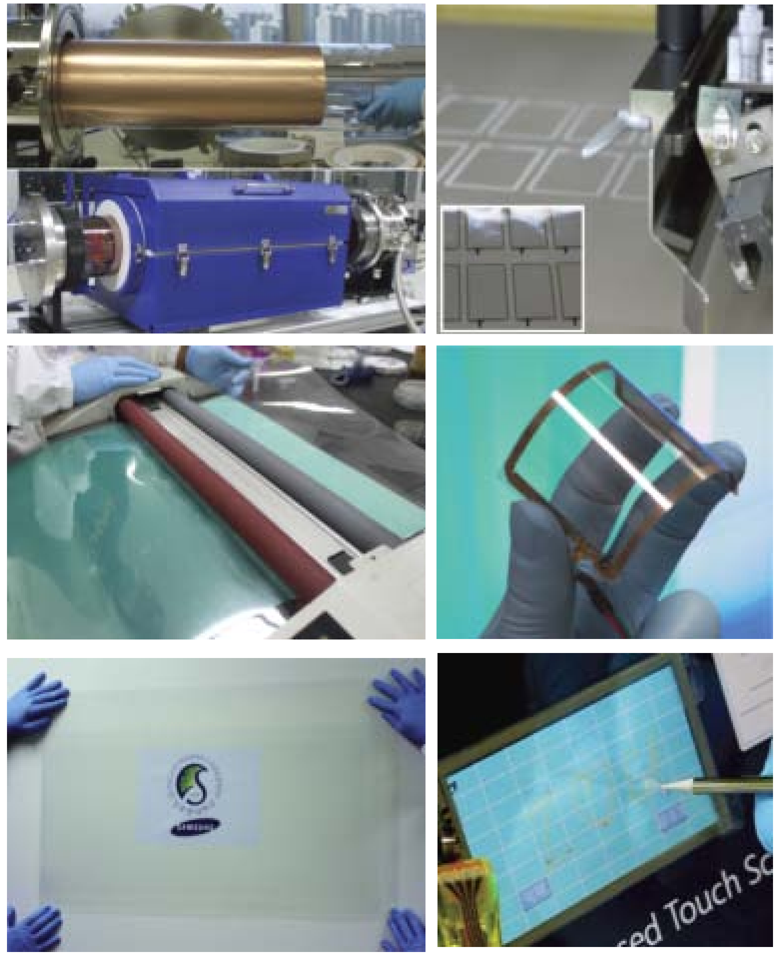
Haldane (88), T. Ando (02)

Touch screen application

Single and bi-layer graphene



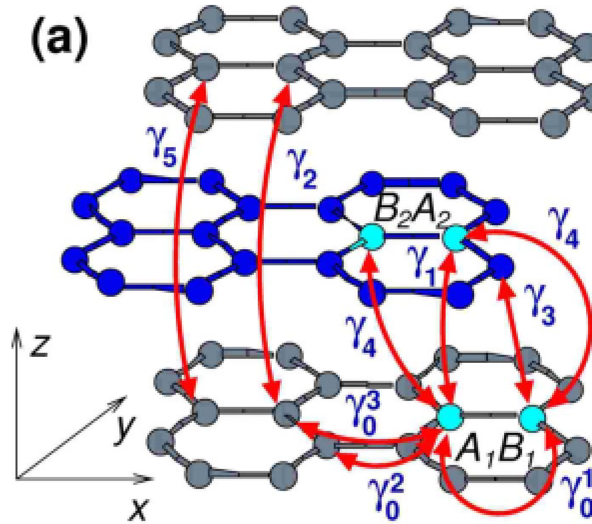
C. Cong et al., ACS Nano 5, 1600 (2011).



S. Bae et al., Nature Nanotechnology 5, 574 (2010).

CVD (Cu foil, gas mixture of CH_4 and H_2)

AB stacking graphene

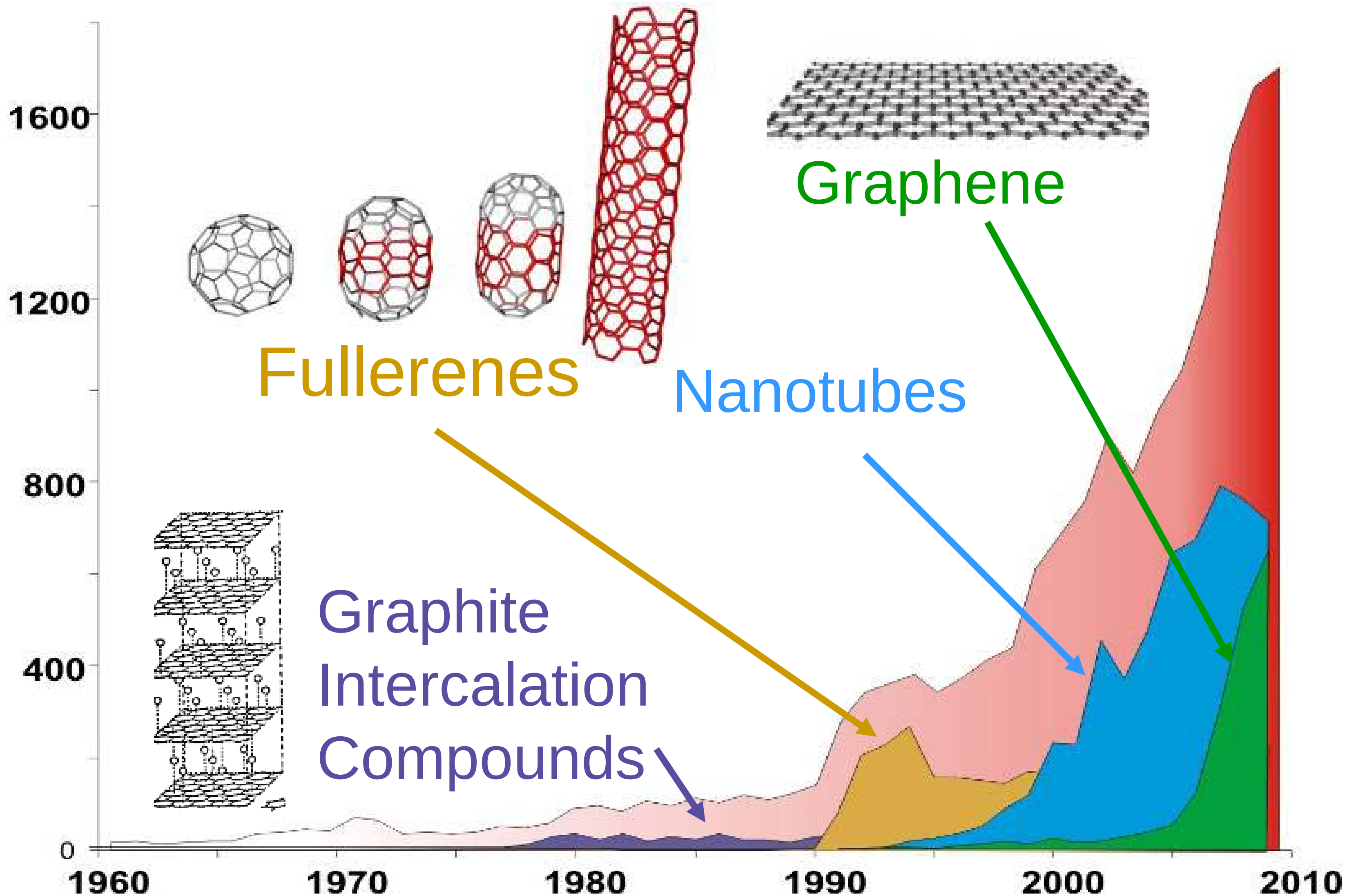


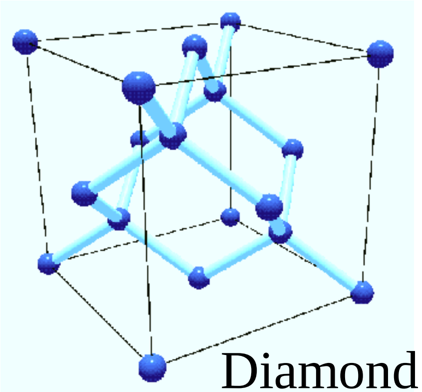
A. Gruneis et al., Phys. Rev. B 78, 205425 (2008).

Stacking order

Development of the field of nano-carbon research

Number of physics-related publications on Carbon

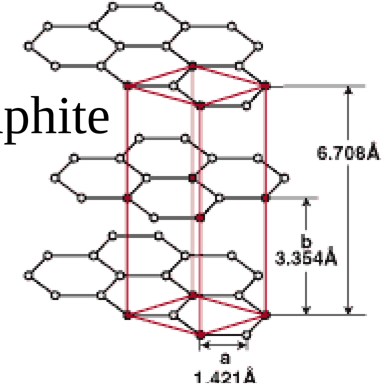



Diamond

Family of nano-carbon

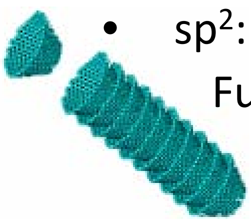
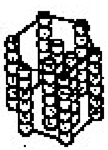
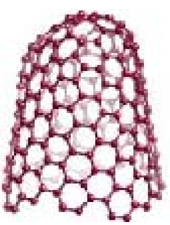
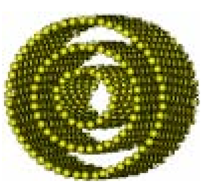
hybridization and geometry

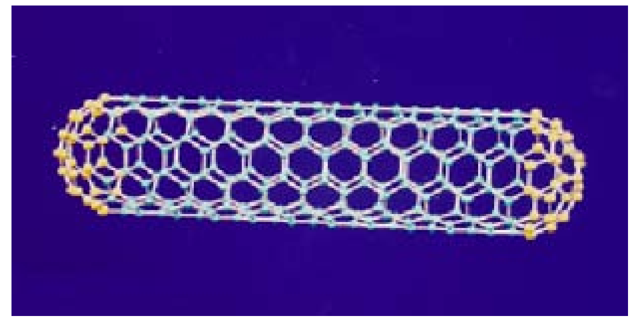
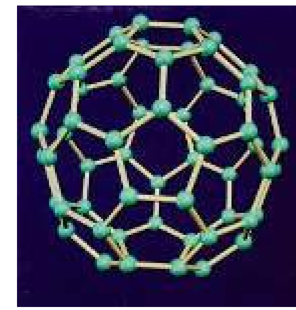
R. Saito, *in "Carbon Alloy" Elsevier (2003)*

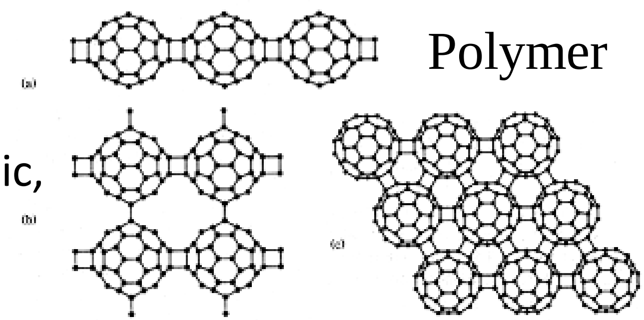
Graphite


- sp^3: Diamond (3D)
- sp^2: Graphene Graphite (2D)
  - Fullerene (0D)
    - Fullerene Polymer(1-3D)
    - Nanotube (1D)
    - Peapod (0D+1D)
- sp: Carbyne (1D)

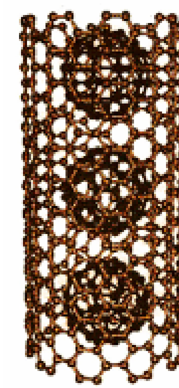
Not crystal: HOPG, VGCF, glassy, whisker, fiber, nanohorn, turbostratic, nanographite

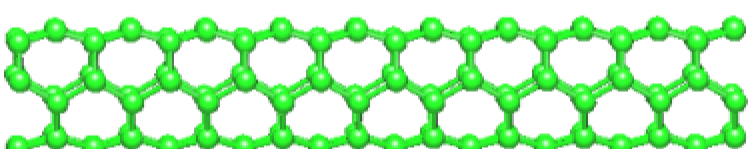





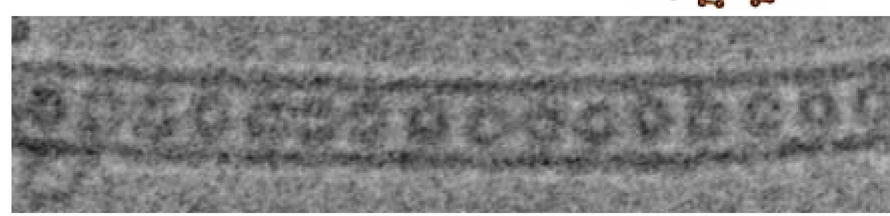
Fullerene





Polymer




nanographite

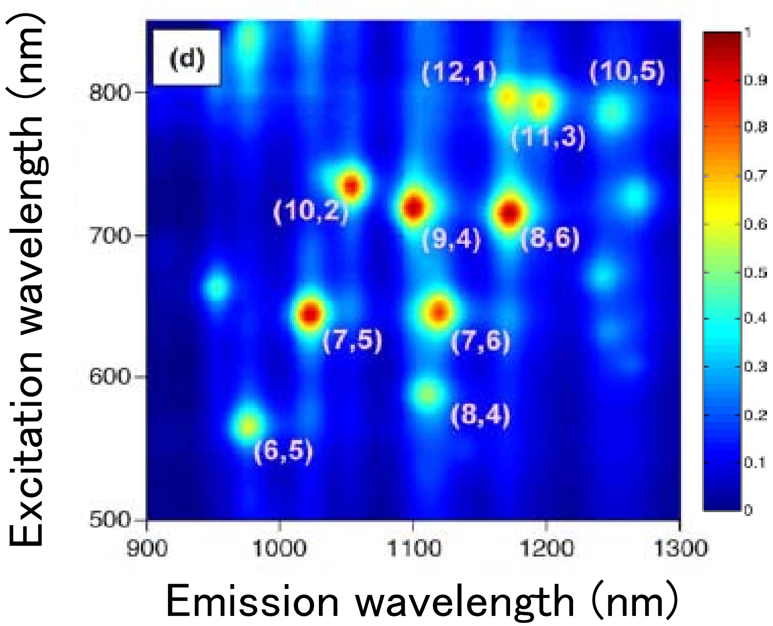

Peapod & Nanobud

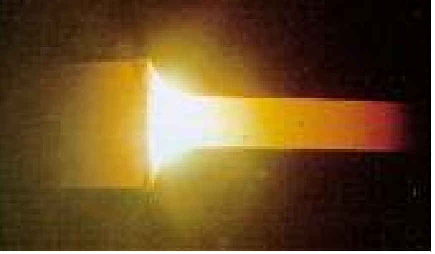
Competition between nanotube and graphene

B787

Requirement from society
Synthesis technique
Quality of material
Quantity and price
Physical properties

Optical properties of nanotubes



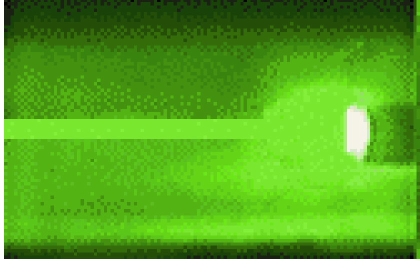


Arc Method:(by Y. Saito)

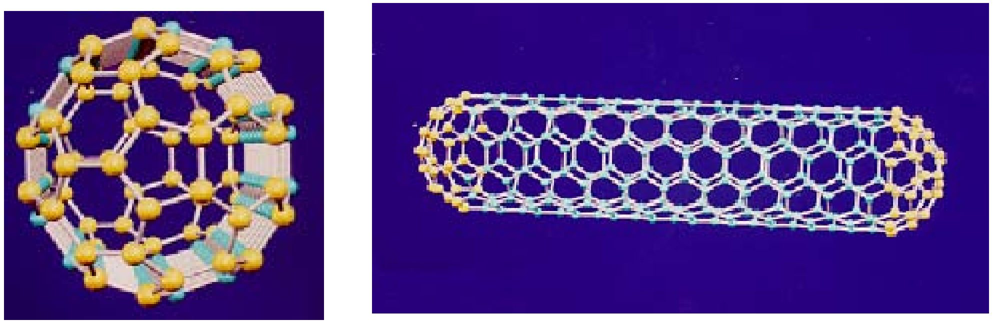
Nanotubes Structure

S. Iijima, (1991), M. S. Dresselhaus *et al.* (1991)

J. Mintmire *et al.*, R. Saito *et al.*, N. Hamada *et al*, K. Tanaka *et al*,

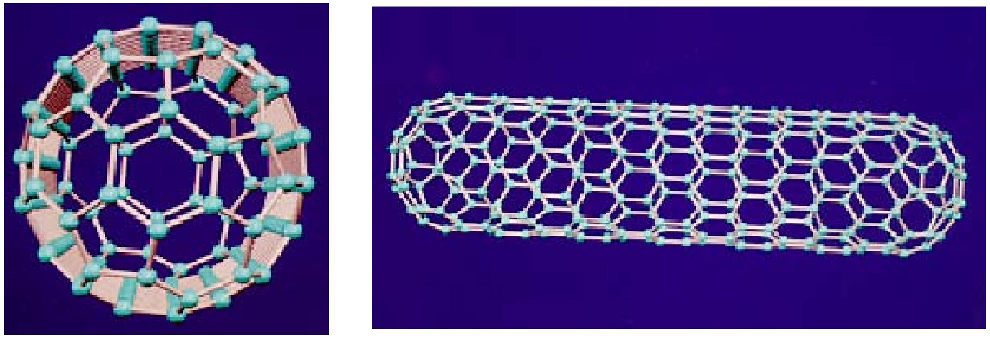


Laser Ablation:(by H. Kataura)



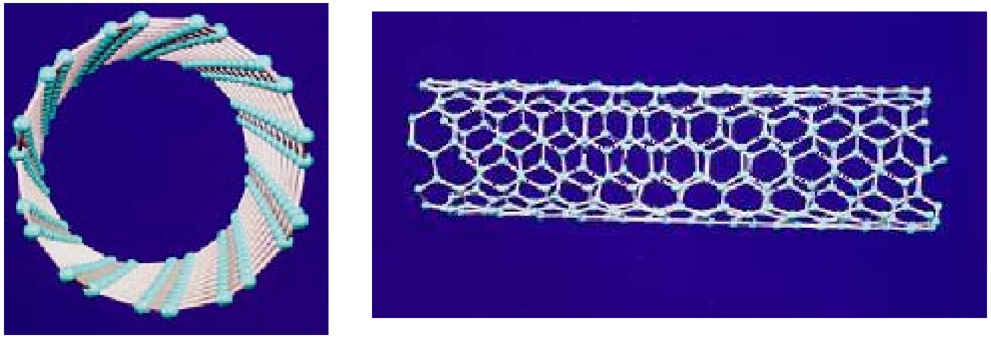
(5, 5)

Armchair



(9, 0)

Zigzag

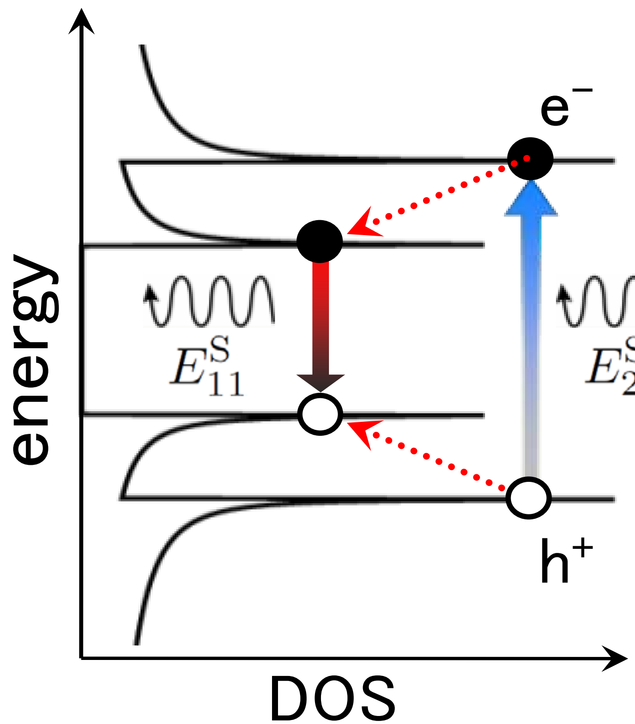


(6, 5)

Chiral

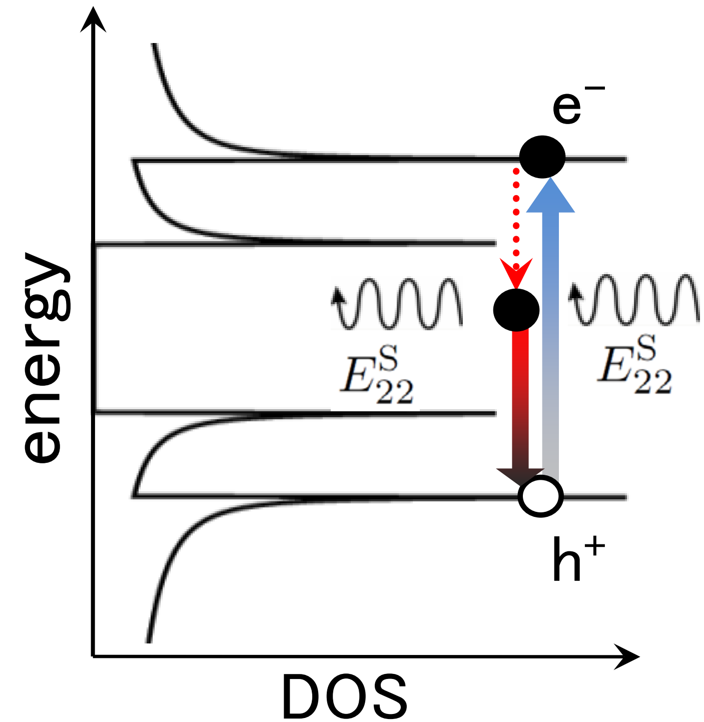
Photoluminescence and Raman

Photoluminescence

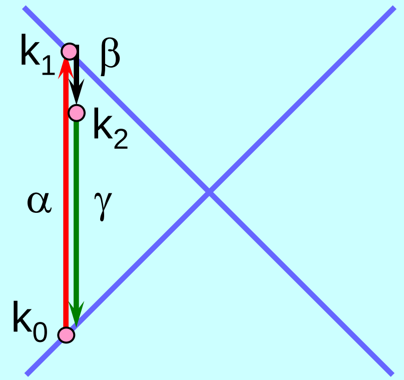


Spontaneous emission of light 1ns

Resonance Raman



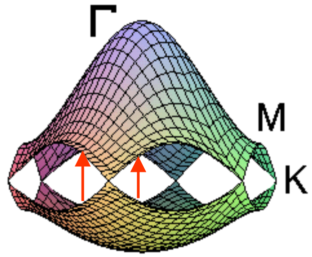
Inelastic scattering of light 1ps

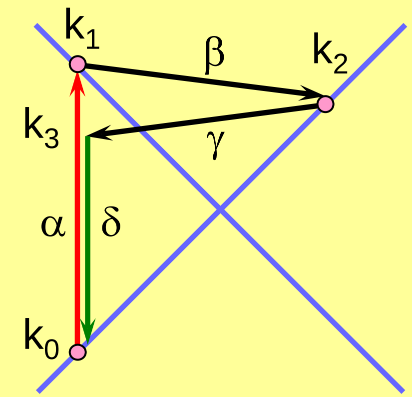


1st order Raman

1st and 2nd order resonance Raman processes

M. S. Dresselhaus et al. Phys. Rep. 409, 47 (2005).





2nd order Raman double resonance

Electron phonon interaction

- Raman intensity formula(1st)

$$M = \sum_{a,b,c} \frac{M_{op}^{ab} M_{el-p}^{bc} M_{op}^{ca}}{(E_{las} - E_{ab} + i\gamma)(E_{las} - E_{phon} - E_{ac} + i\gamma)}$$

Light emission

$E_{22}^{S} - h\omega_q$

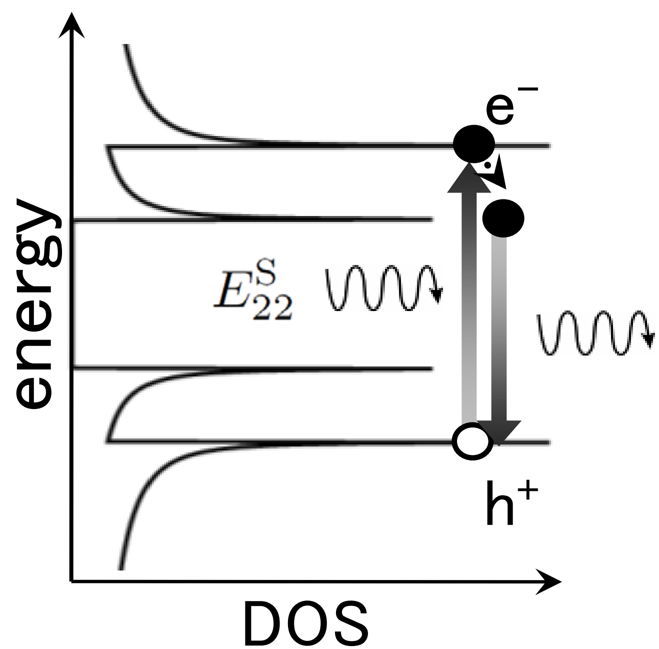
Light absorption

Intensity is enhanced

When optical absoption

occues.

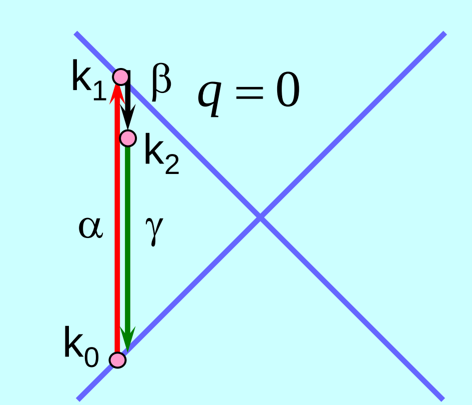
Resonant Raman effect



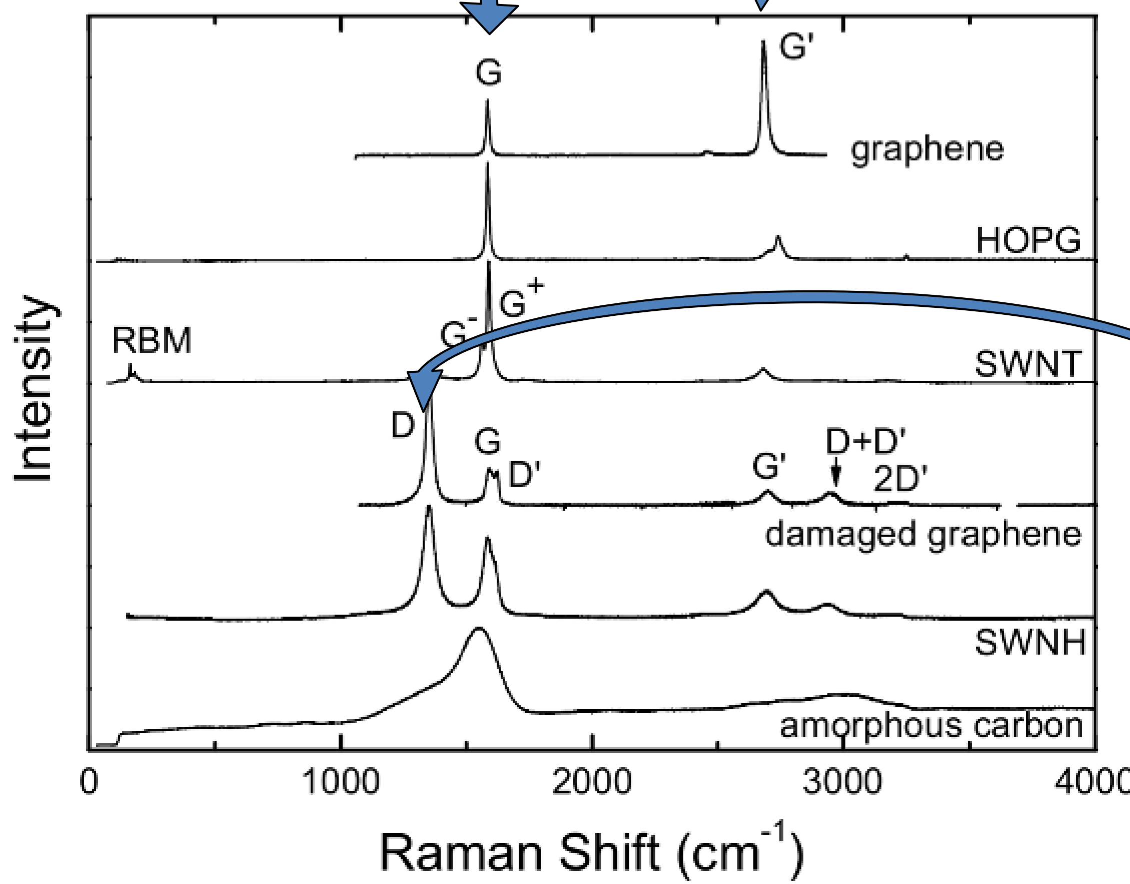
$h\omega_q$ Raman shift

Raman spectral of nano carbon

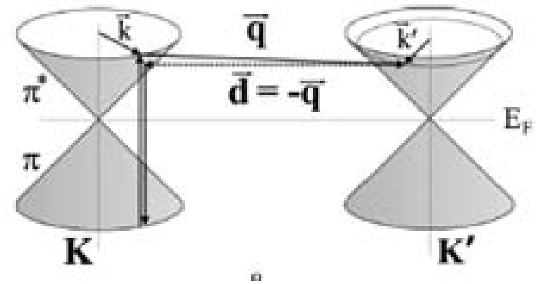
Spectral shape, Relative intensity,
Defect oriented Raman signals



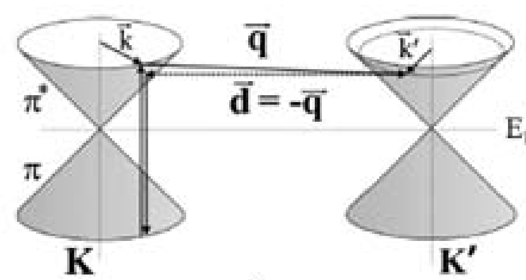
1st order Raman G, RBM
One phonon intra-valley



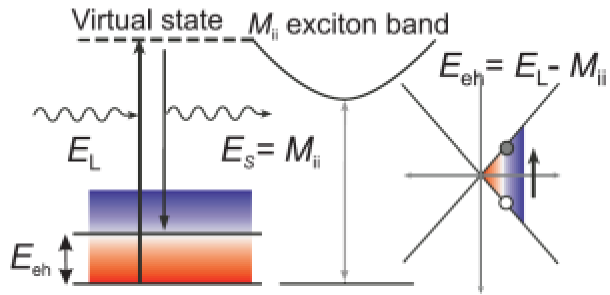
G' : inter-valley DR
Two phonon scattering



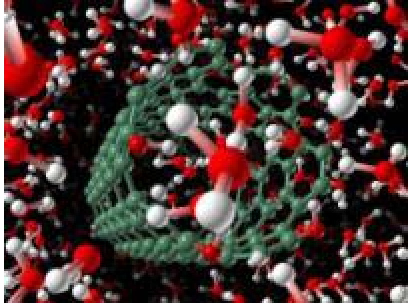
D: inter-valley DR
one phonon scattering
one elastic scattring



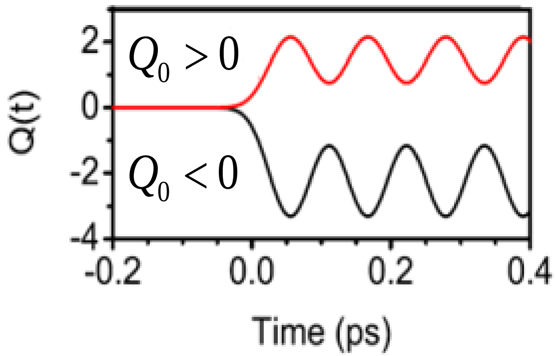
Defect is needed



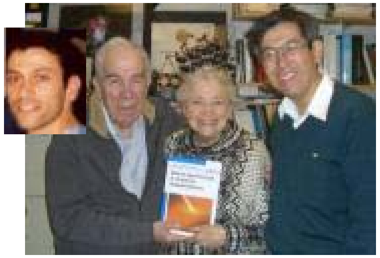
Recent our works

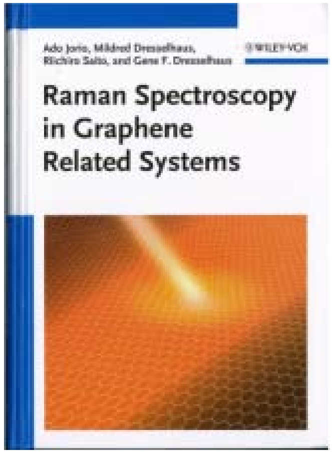


- Nanotube Raman spectroscopy
  - Exciton Environmental Effect
  - Electronic Raman spectra
  - Coherent phonon spectra



- Graphene Raman spectroscopy
  - ABA stacking order
  - Kohn anomaly effect





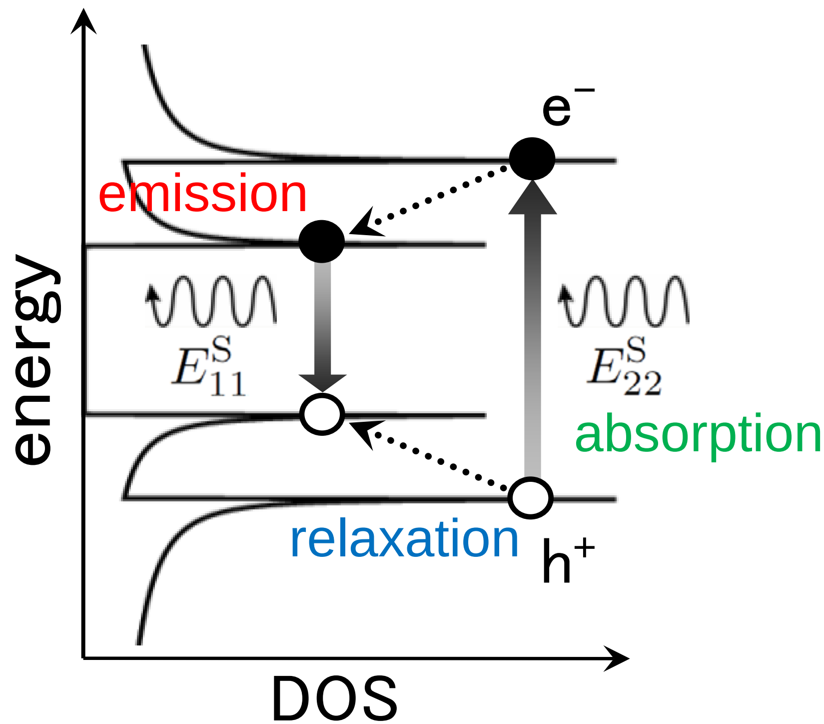
A. Jorio, R. Saito, G. Dresselhaus, M. S. Dresselhaus
“Raman Spectroscopy of graphene related systems” Wiley-VCH (2011),

Exciton Kataura Plots

How to assign (n,m) for different surrounding materials?

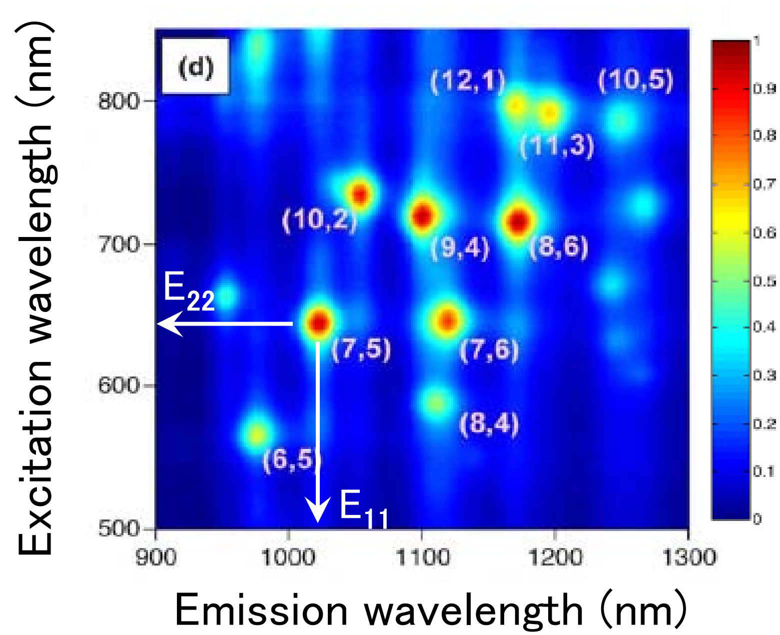
(n,m) assignment from Photo-Luminescence (PL)

Optical Process of PL



2D PL map of SWNTs

M. J. O' Connel *et al.*, Science **297**, 593 (2002)
S. M. Bachilo *et al.*, Science **298**, 2361 (2002)
Y. Miyauchi *et al.*, Chem. Phys. Lett. **387**, 198 (2004)



+ Intensity information
(type dependence, chiral angle dependence)
Y. Oyma et al. Carbon 44, 873-879 (2006).

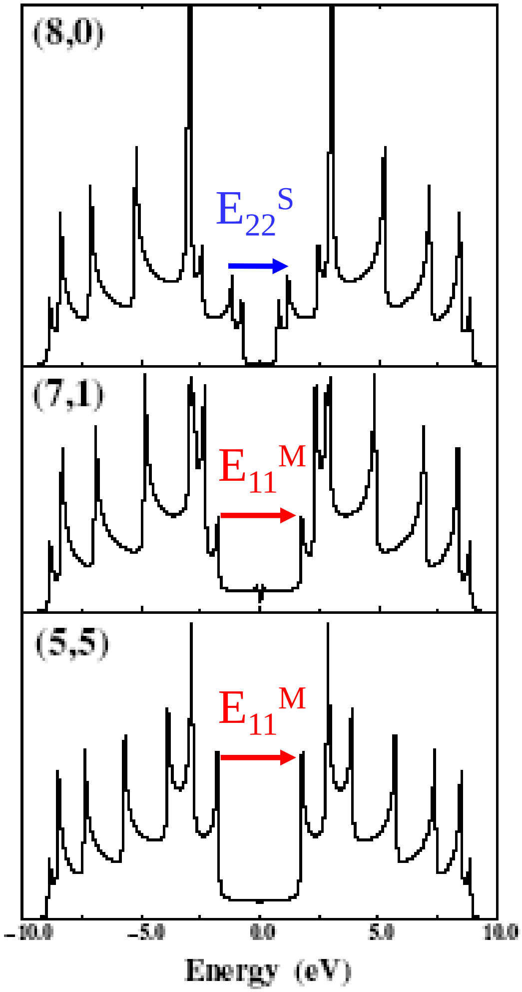
$$(E_{22}, E_{11}) \rightarrow (n,m)$$

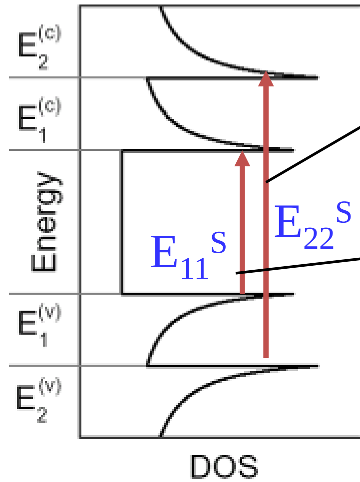
Raman Spectroscopy: the Kataura plot

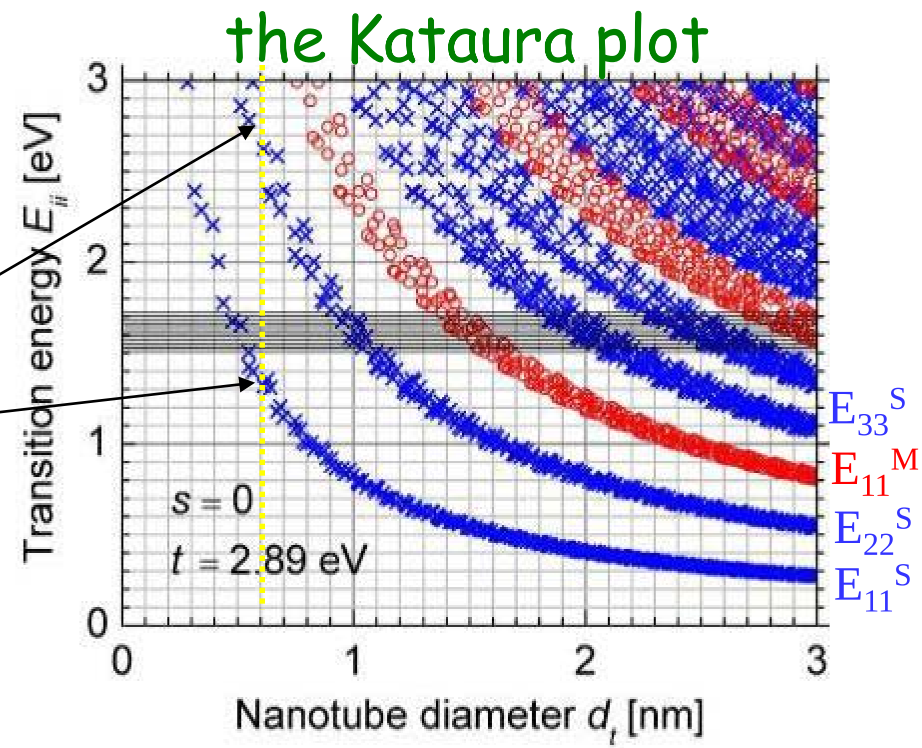
R. Saito et al., Phys. Rev. B 61, 2981 (2000)

vHS in the density of states (DOS)

Responsible for strong optical effects!







Raman Spectroscopy:

Excitation profile → E_{ii}

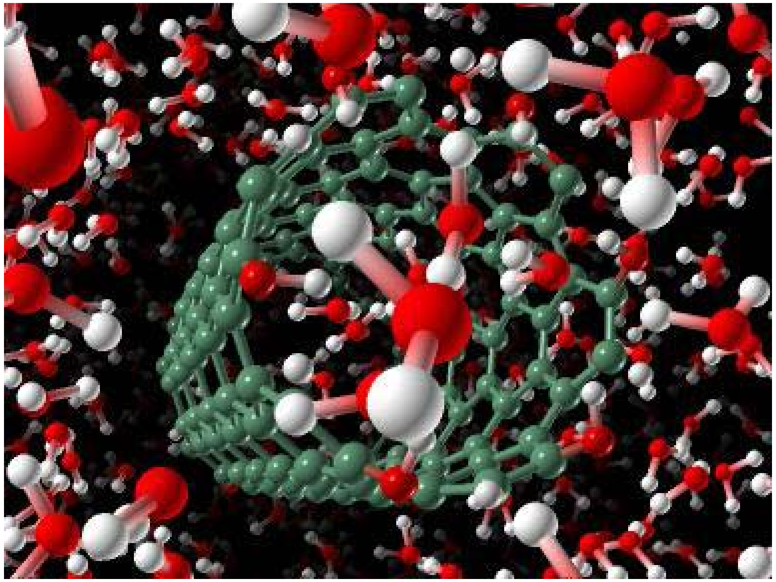
RBM frequencies → d_t, θ

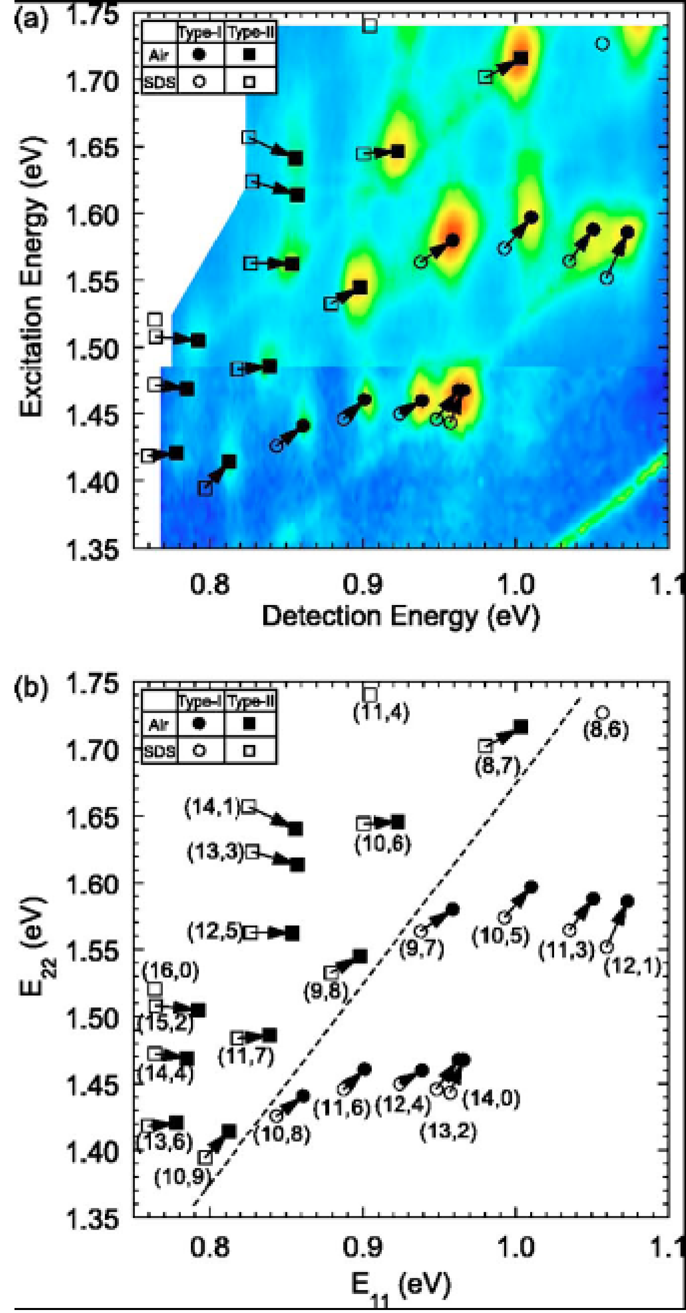
(E_{ii}, ω_{ph}, Int.) → (*n,m*)

P. B. C. Pesce *et al.* Appl. Phys. Lett. 96, 051910, (2010).

Environmental Effect of SWNTs

ΔE_{ii} (0-80meV) depending on surrounding materials





Dielectric screening of exciton.

Chirality dependent, type dependent

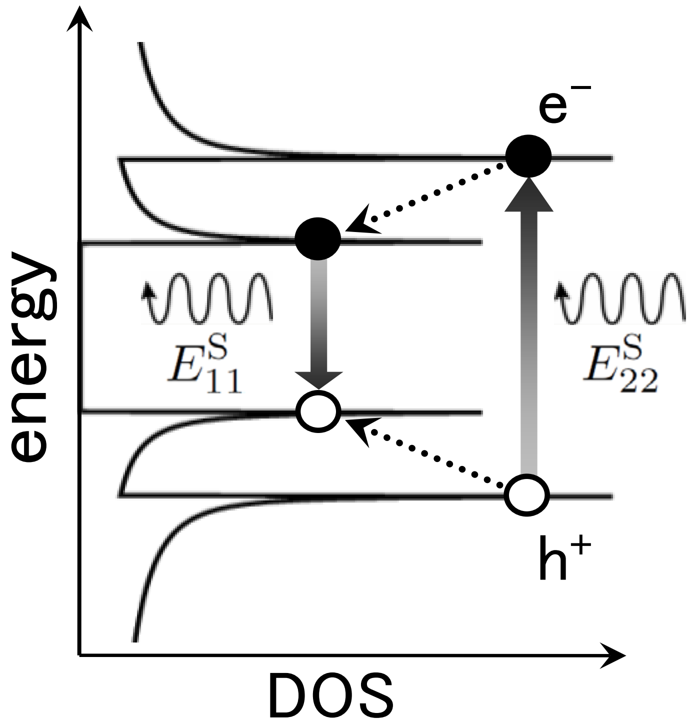
Effective mass

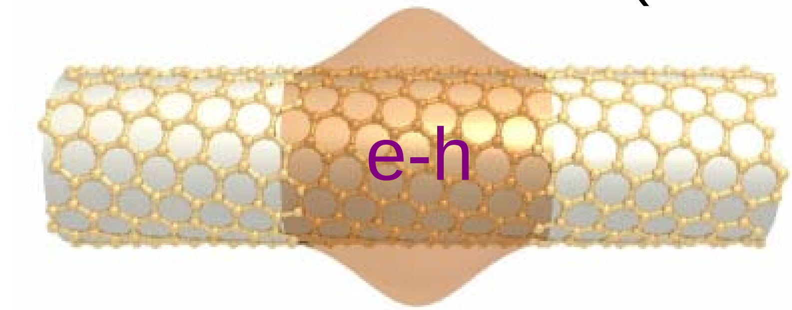
Y. Ohno et al., Phys. Rev. B 73, 235427 (2006)

Dielectric screening of the Coulomb interaction

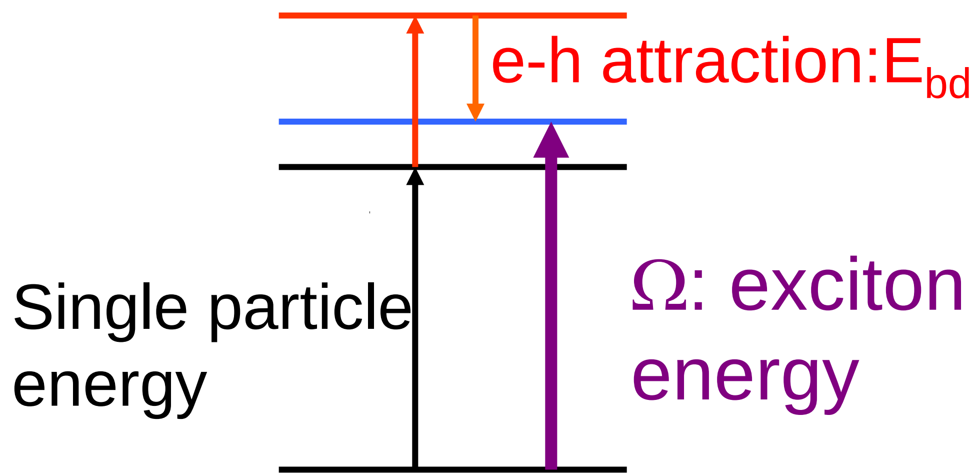
J. Jiang et al. *Phys. Rev.* B75 035405 and 035407(2007)

Many body term is modified.





e-e repulsion (self energy)



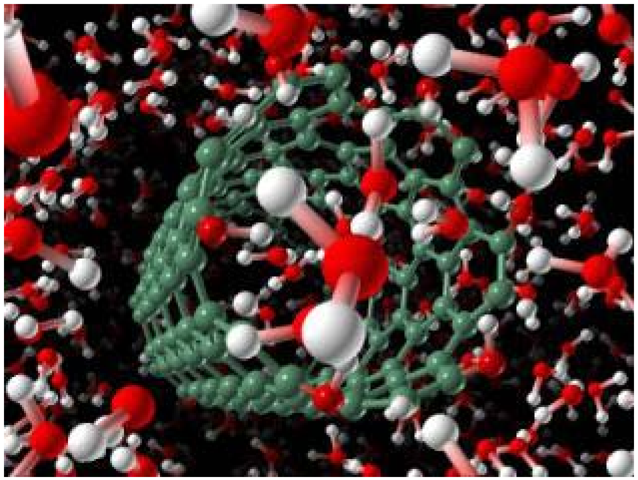
Ω decreases with increasing κ

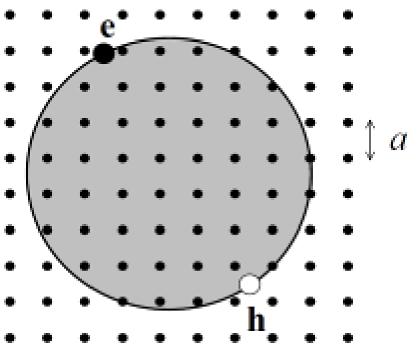
κ: dielectric constant

T. Ando, JPSJ 66, 1066 (97), (04), (05)
S. D. Spataru et al. PRL **92**, 077402(04).
V. Perebeinos, et al. PRL. **92**, 257402(04)
J. Maultzsch et al. PRB 72 2414026(05)

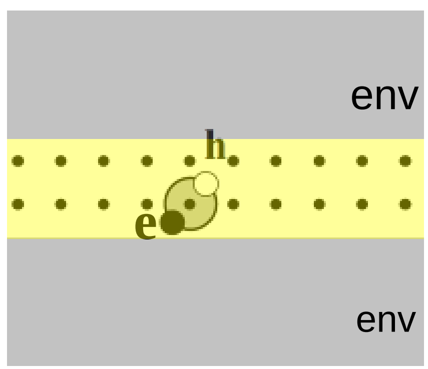
Environmental effect of excitons in SWNTs

Y. Miyauchi et al. ,*Chem. Phys. Lett* 442, 394 (2007)

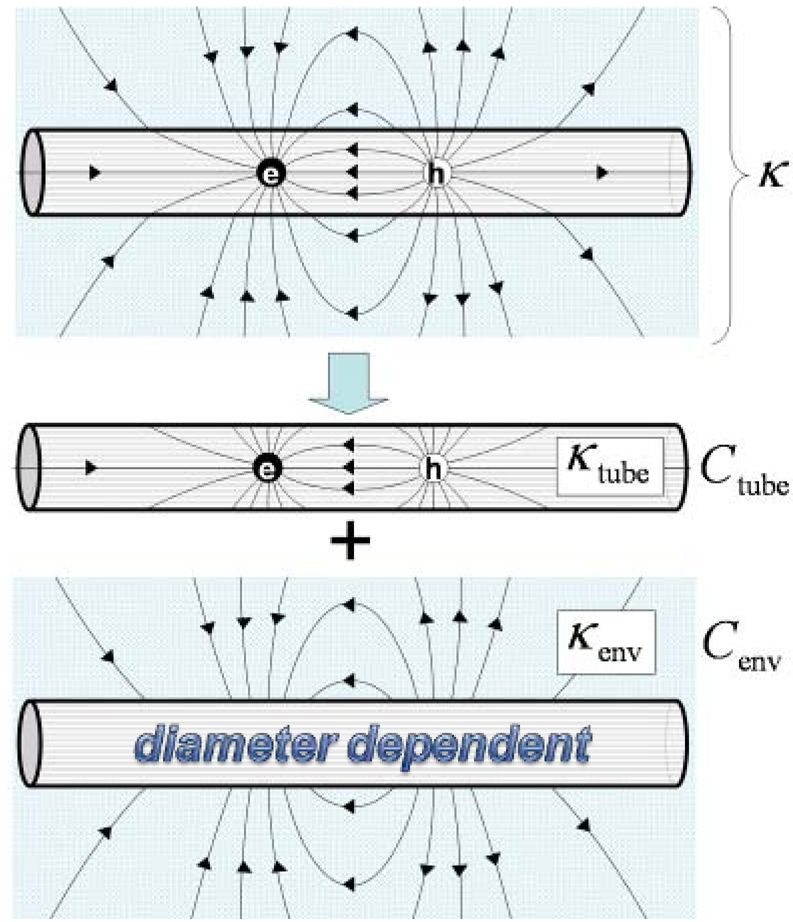




2D(3D) exciton



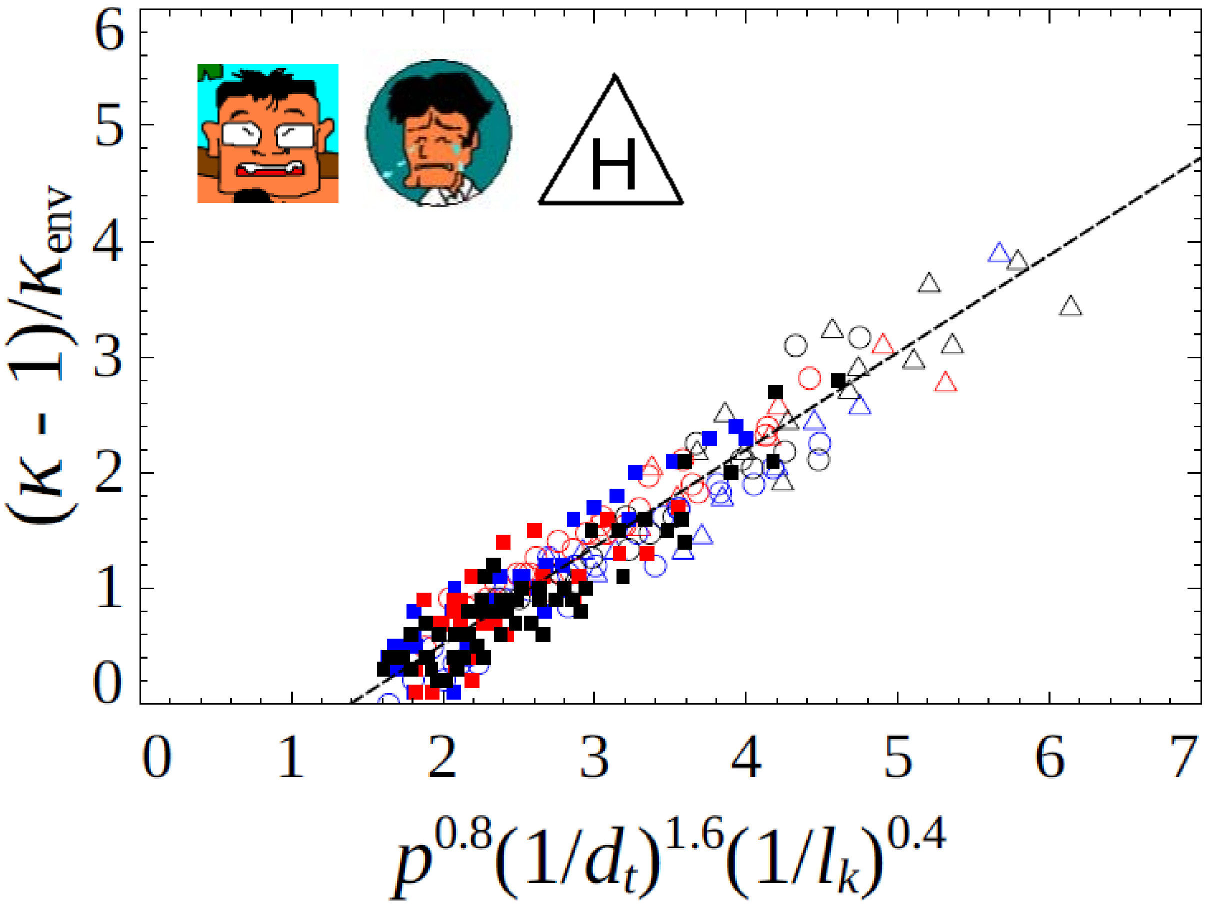
1D exciton

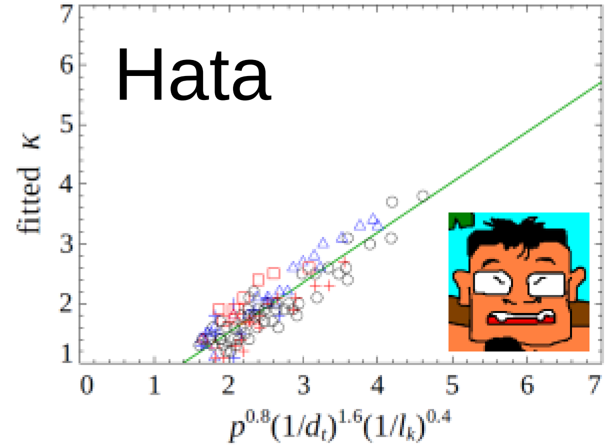


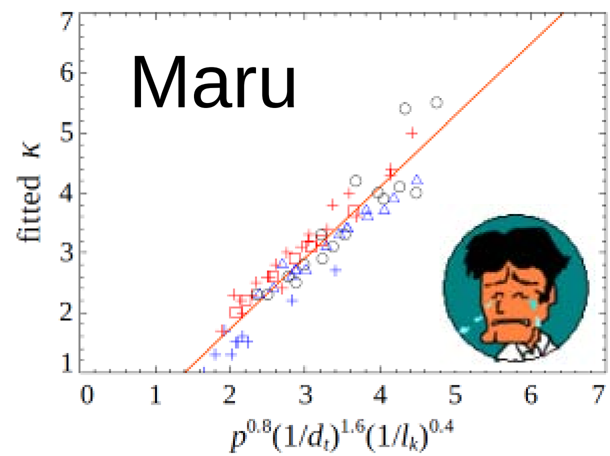
$$\frac{1}{\kappa} = \frac{C_{\mathrm{tube}}}{\kappa_{\mathrm{tube}}} + \frac{C_{\mathrm{env}}}{\kappa_{\mathrm{env}}}$$

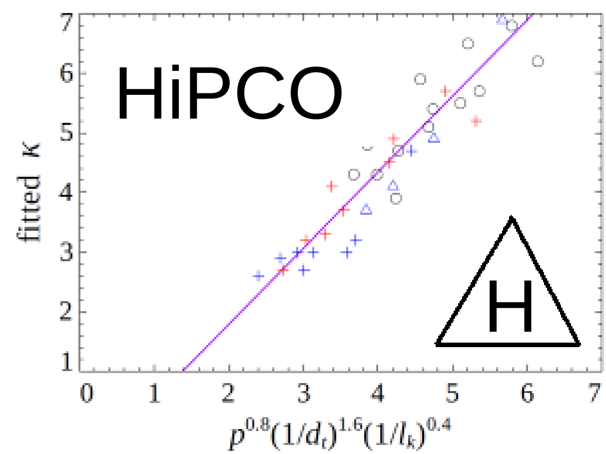
Exciton scaling function

A. R. T. Nugraha et al, APL 97, 091905, (2010)









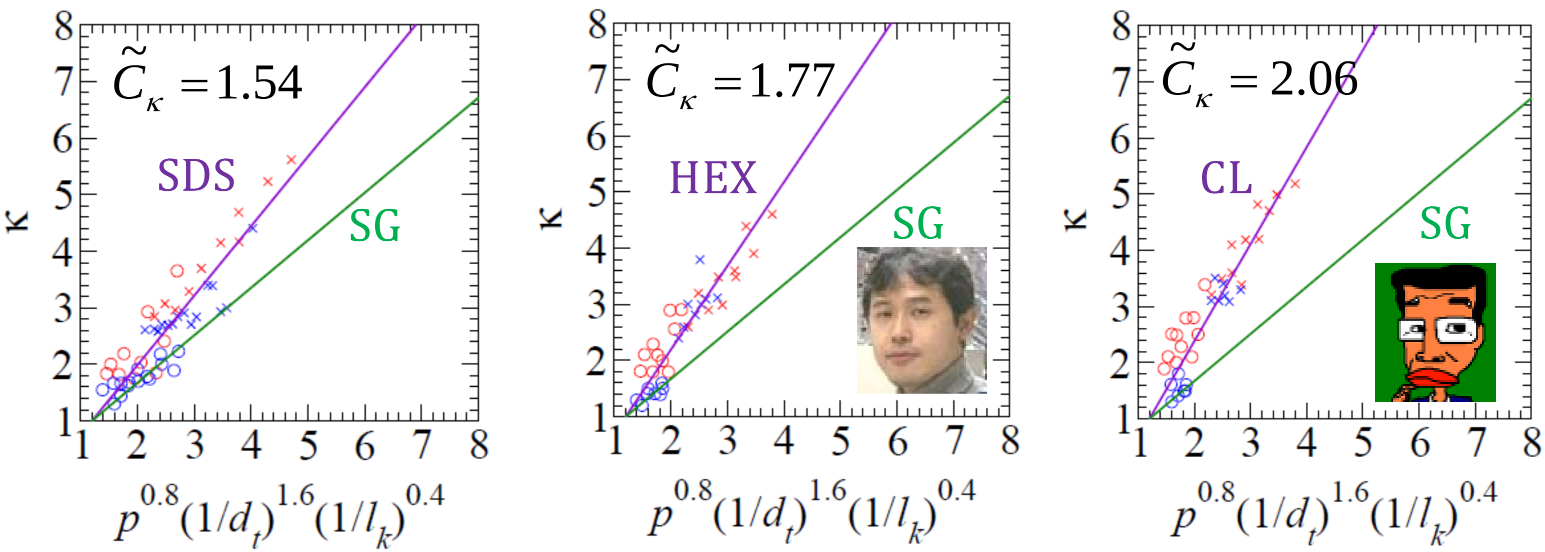
$$\kappa_{env}^{SG} : \kappa_{env}^{alc.ass} : \kappa_{env}^{HiPco} = 1.00 : 1.42 : 1.52$$

Only slope is different!

Web Pages of Exciton Kataura Plot

http://flex.phys.tohoku.ac.jp/eii/

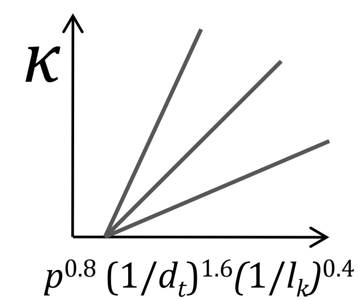
□ Data from photoluminescence spectroscopy



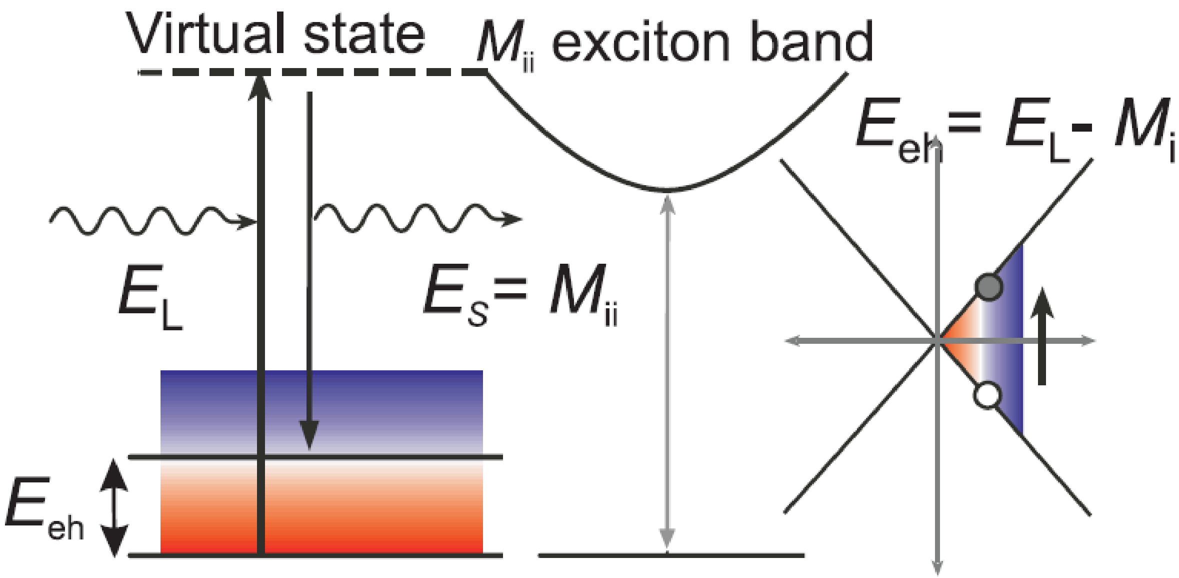
E_{11} (○)
E_{22} (X)

Red : SI
Blue : SII

Measurement	RRS			PL		
Synthesis method (Environment)	SG (as-grown)	ACCVD (as-grown)	HiPco (SDS)	HiPco (SDS)	ACCVD (HEX)	ACCVD (CL)
$\tilde{C}_\kappa$	1.00 ± 0.08	1.42 ± 0.03	1.52 ± 0.05	1.54 ± 0.05	1.77 ± 0.04	2.06 ± 0.06

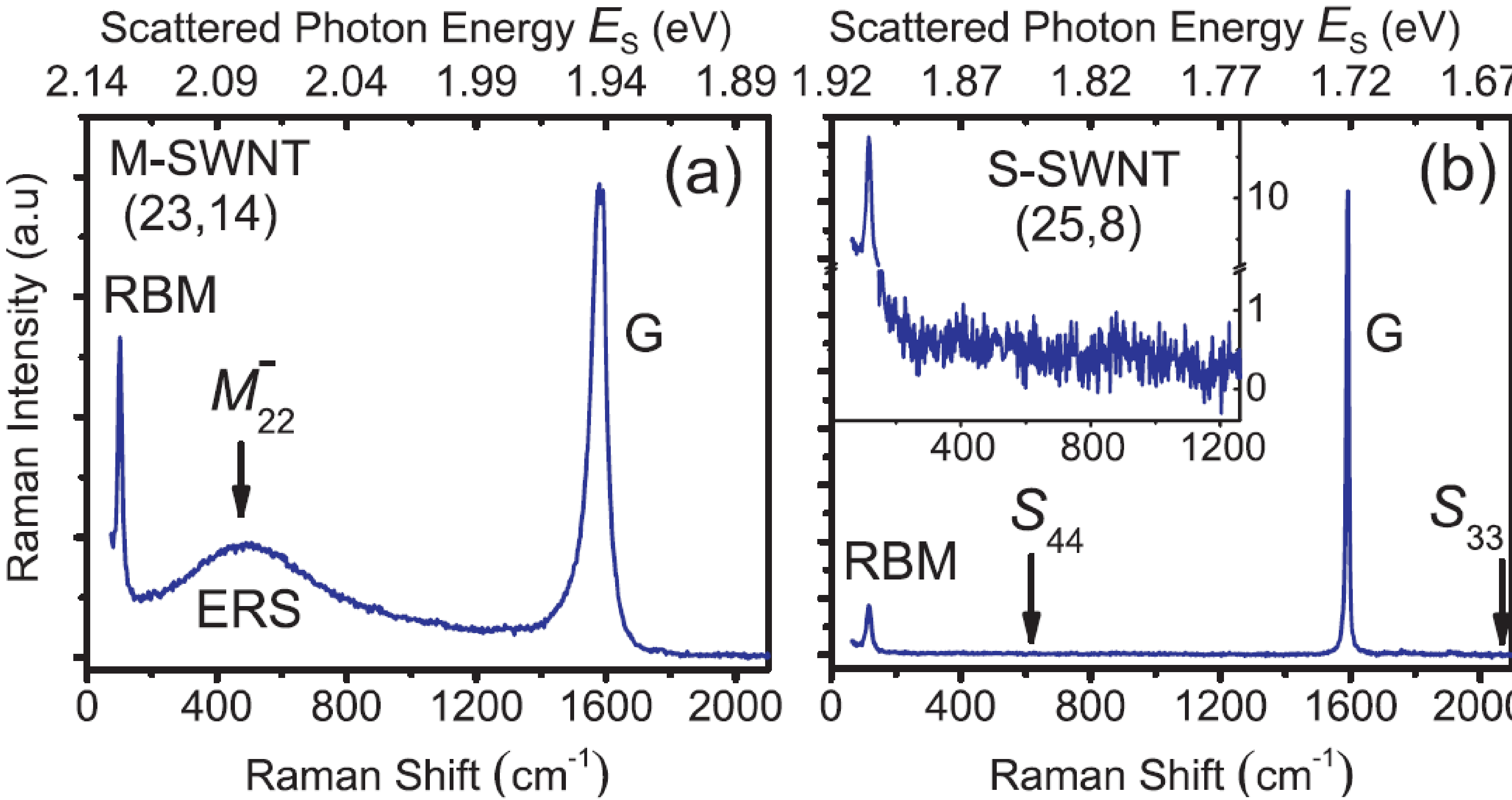


Elctronic Raman
How to characterize metallic SWNTs?



Observation of Electronic Raman Scattering

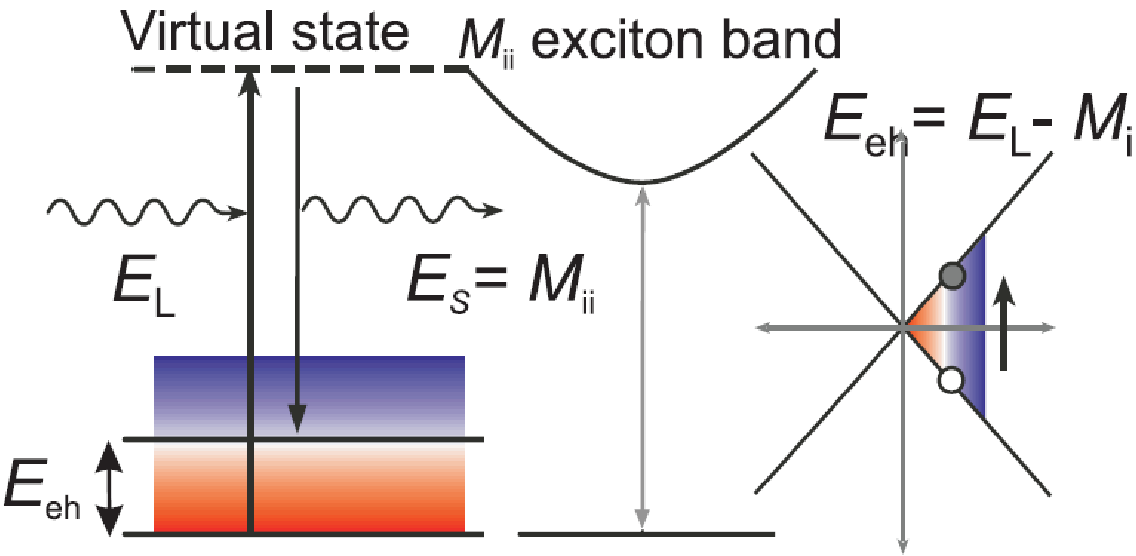
Farhat, et al. Phys. Rev. Lett. 107, 1547401 (2011)

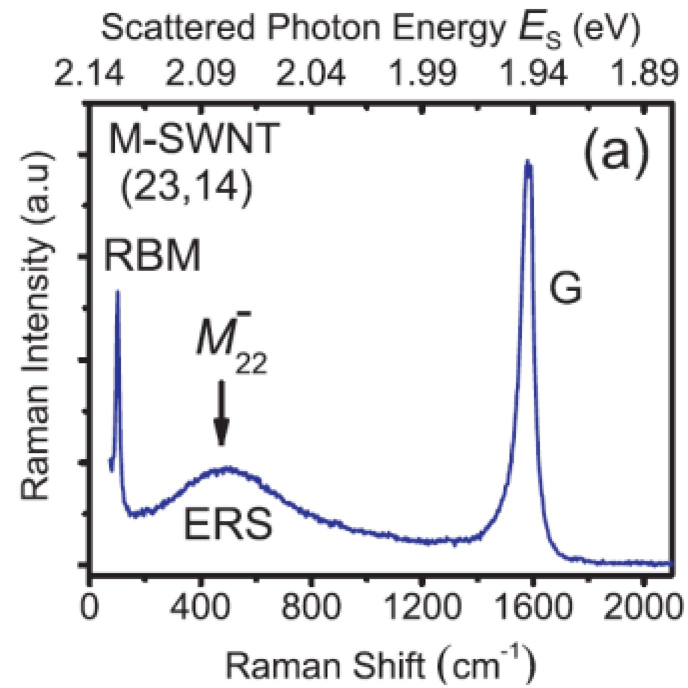


- ERS has no corresponding phonon mode
- ERS is observed only in MSWNT, with peak at M_{ii}

ERS mechanism

Farhat, et al. Phys. Rev. Lett. 107, 1547401 (2011)





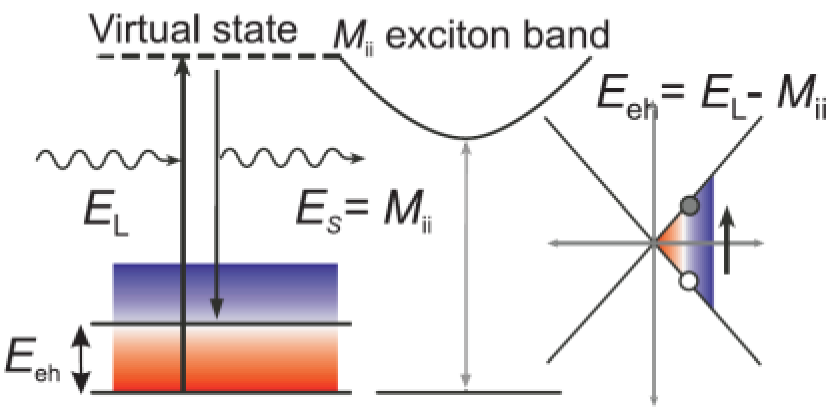
Electronic excitation around linear band by Coulomb interaction (broad spectra → fast process 10fs)

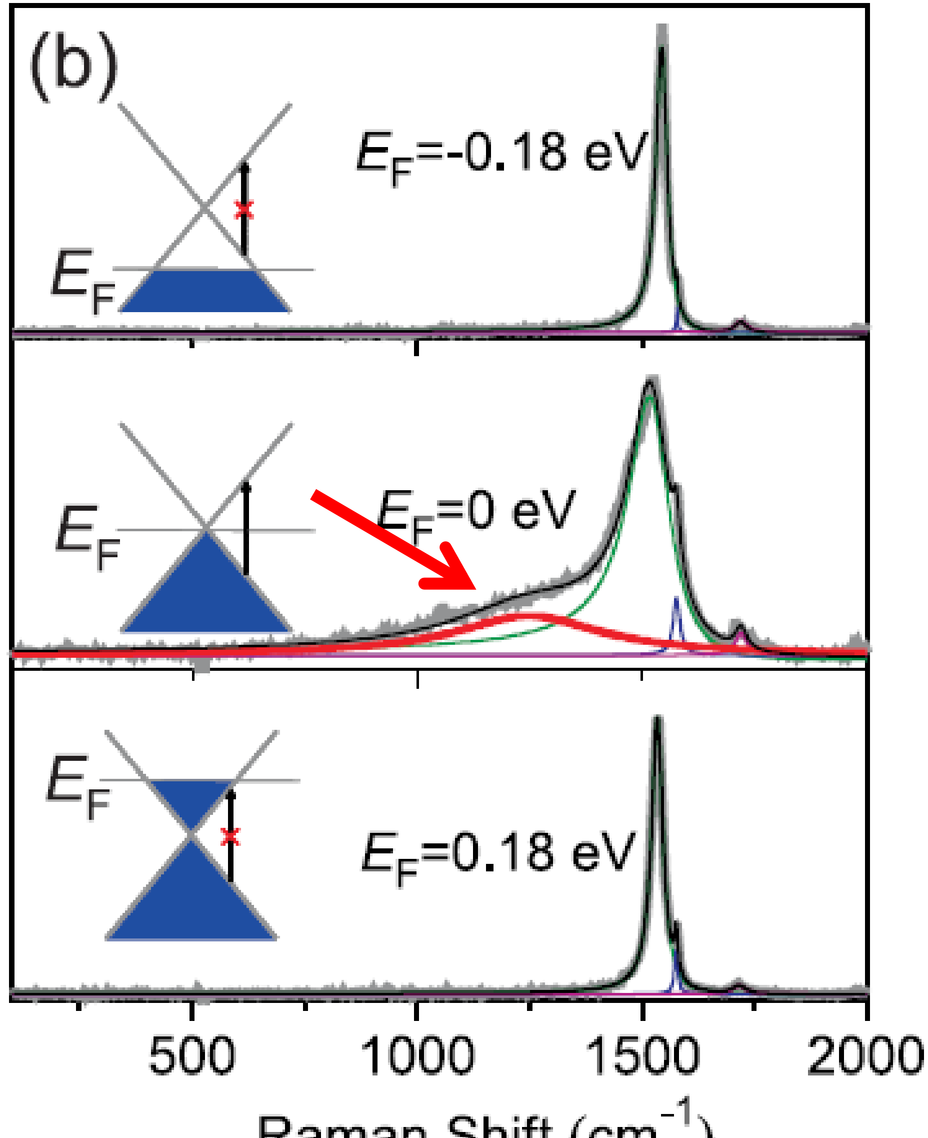
No M22 PL, opticall forbidden e-h excitation.

Gate dependence of ERS

Farhat, et al. Phys. Rev. Lett. 107, 1547401 (2011)

Changing E_F suppresses ERS
→ Evidence that e-h excitation is essential.

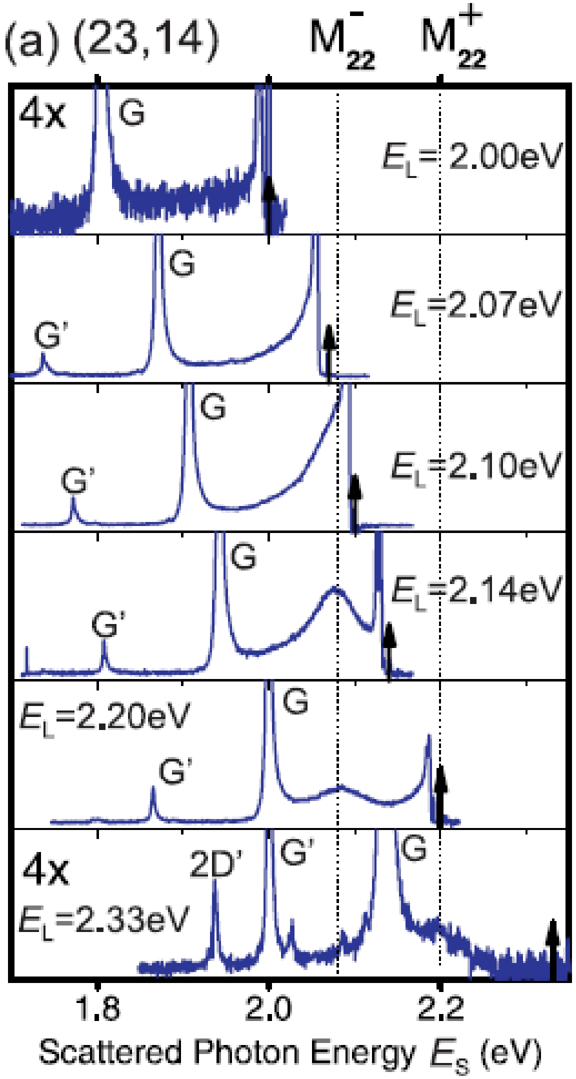




q=0 Coulomb interaction

The ERS peak modifies phonon G band

Farhat, et al. Phys. Rev. Lett. 107, 1547401 (2011)

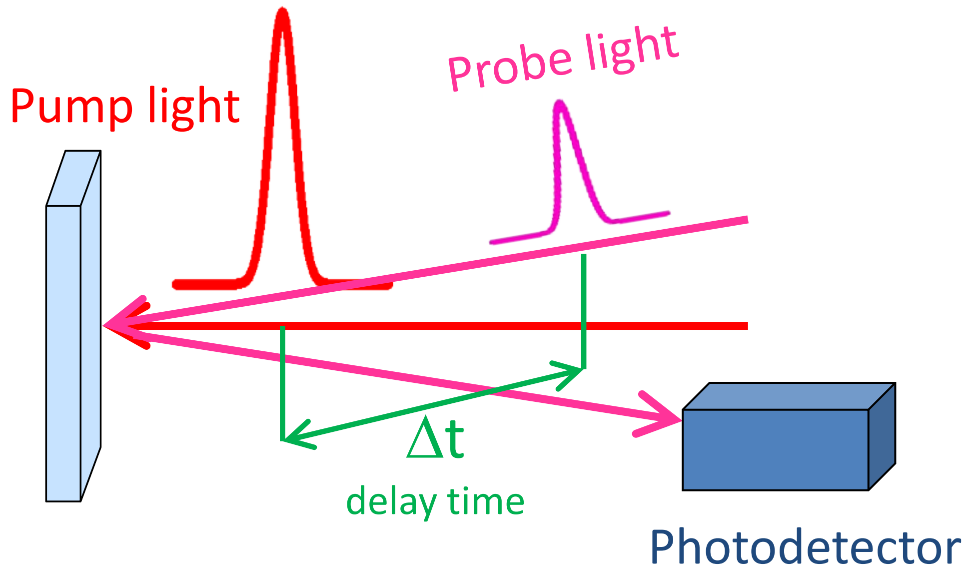


The farther laser energy from resonance, the broader ERS feature More asymmetric G band.

Origin of BWF lines (asymmetric broadening of G-band Raman)

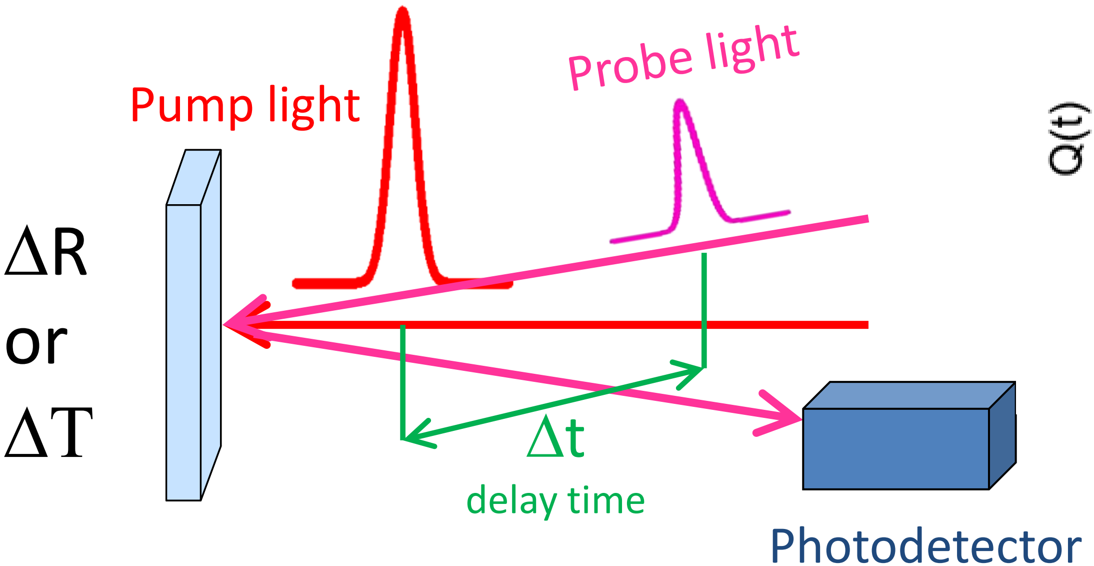
Coherent phonon

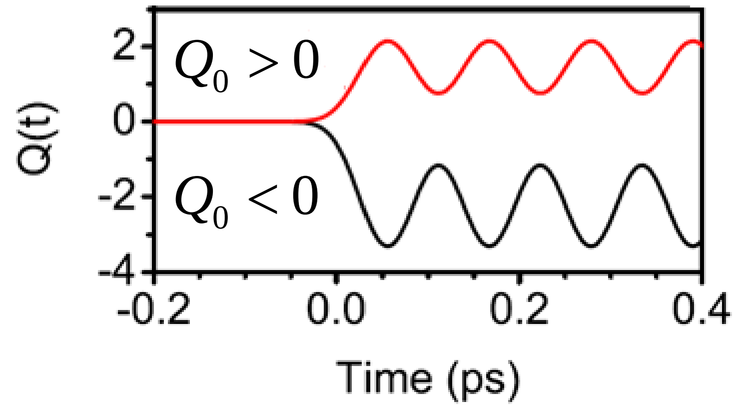
How to know the relaxation of photo-excited electron as a funtion of time?



Coherent phonon Spectroscopy of nanotube

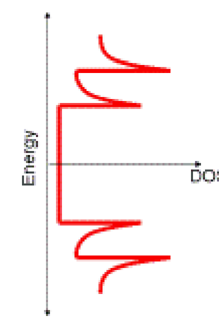
$\tau_{\text{pulse}} << T_{\text{phonon}}$



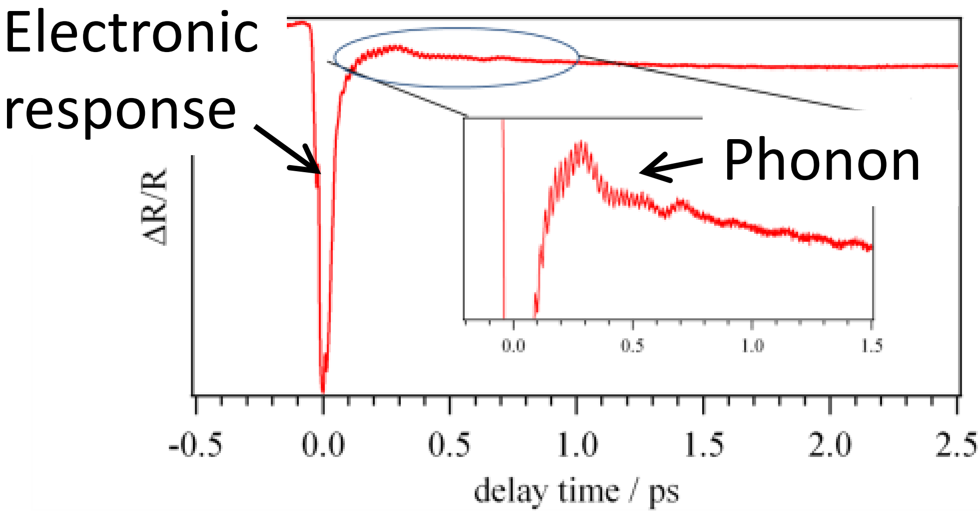


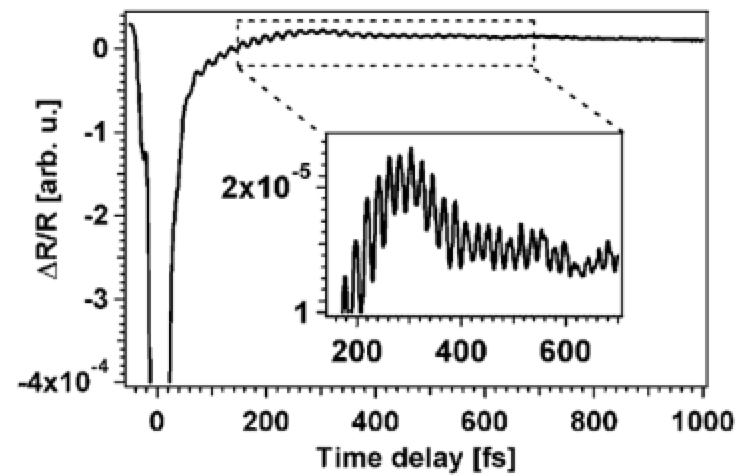
CP RBM amplitude

$$Q(t) = Q_0(1 - \cos(\omega_{\text{RBM}} t))$$

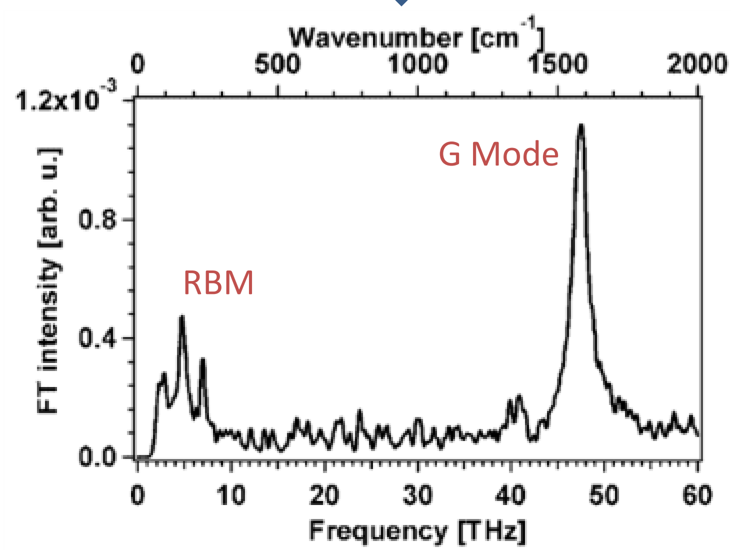


Coherent phonons (CP) in carbon nanotubes

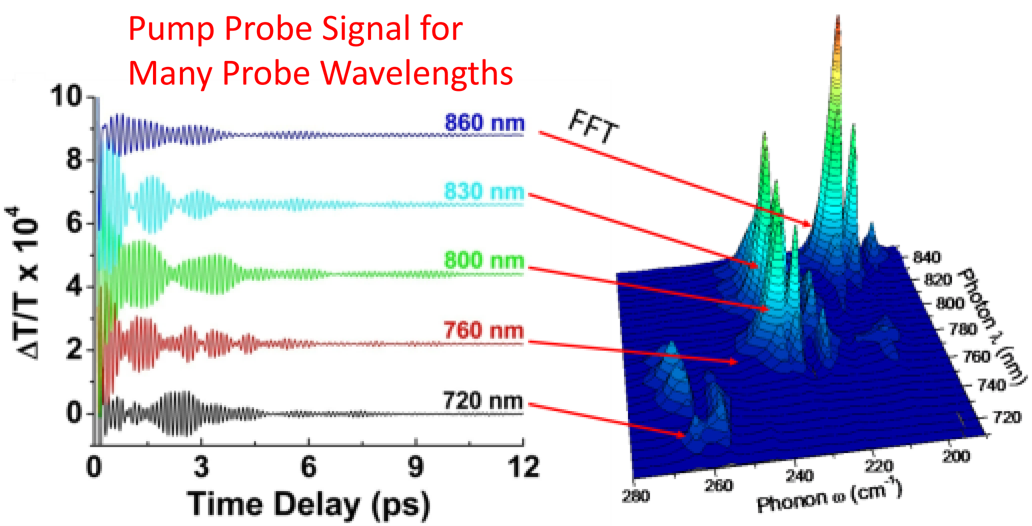




Fourier Transform



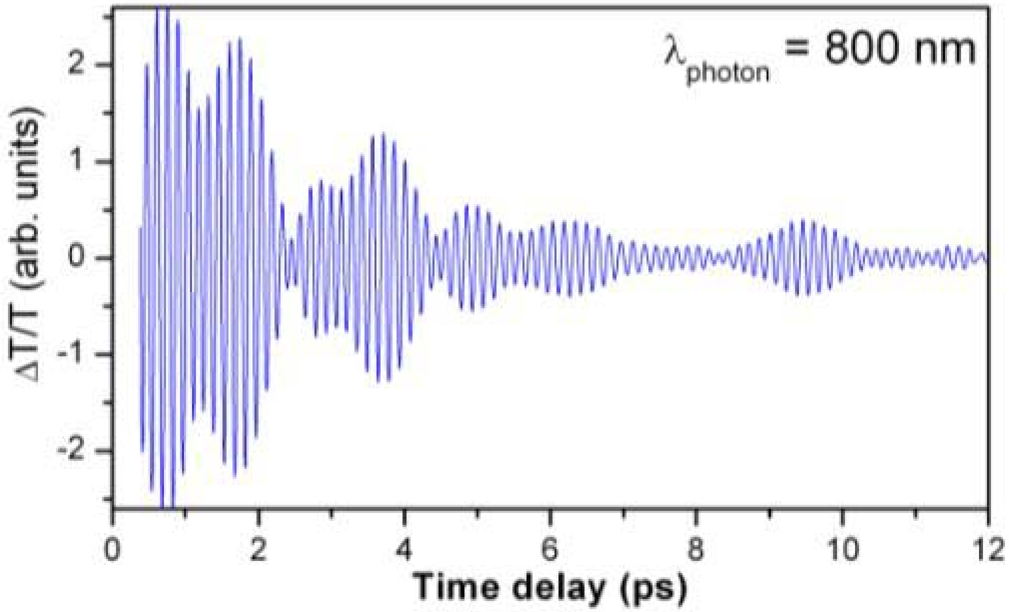
Pump Probe Signal for Many Probe Wavelengths

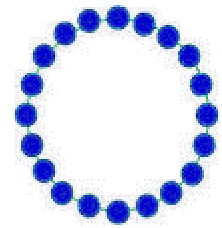


Y. S. Lim et al, Nano Lett. 6, 2696 (2006)

K. Kato et al, Nano Lett. 8, 3102(2008)

Chirality-dependent frequency

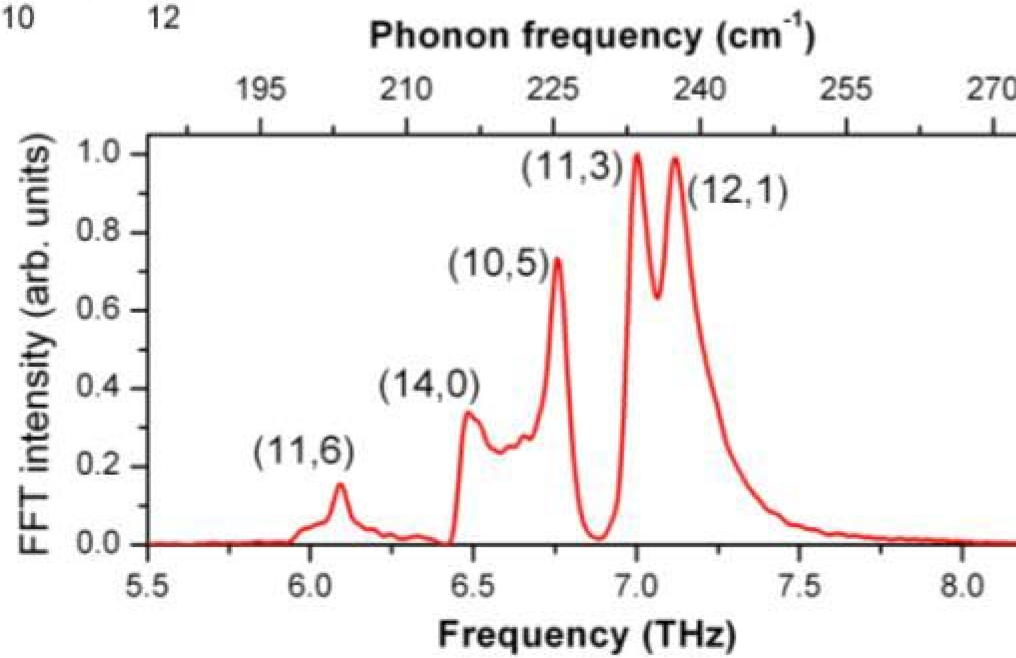




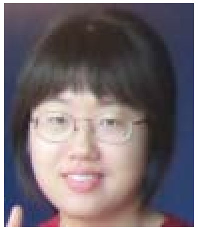
Radial Breathing Mode (RBM)

Kono group
(Rice University)

FFT



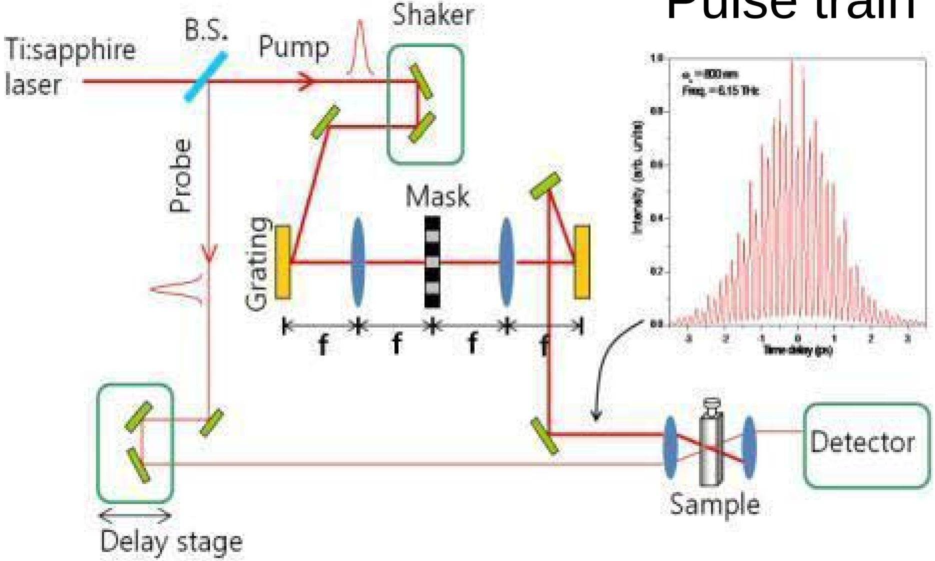
Nano Lett. 6, 2696 (2006)
Phys. Rev. Lett. 102, 037402 (2009)
Phys. Rev. B 79, 205434 (2009)
ACS Nano 4, 3222 (2010)



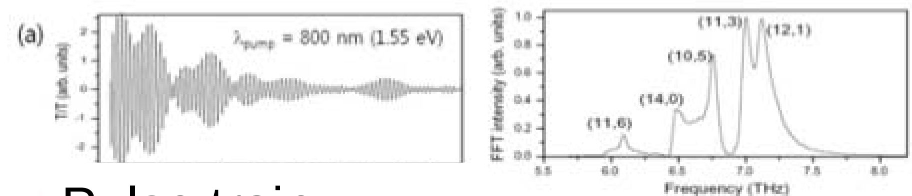

Pulse train excitation

J.-H. Kim et al., PRL 102, 037402 (2009)

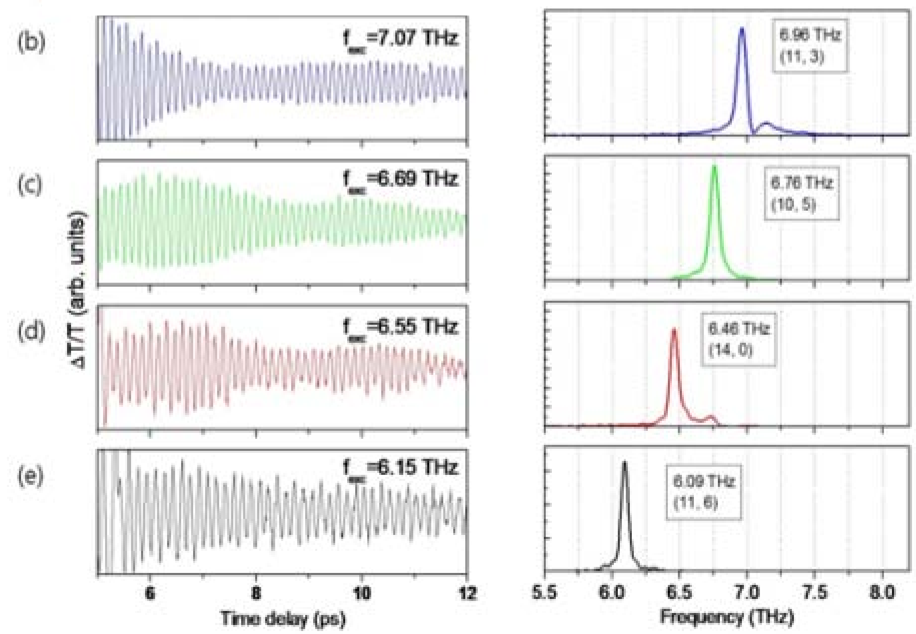
Pulse train



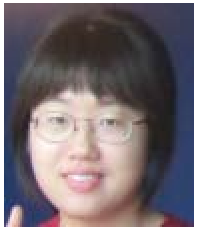
Single pulse



Pulse train



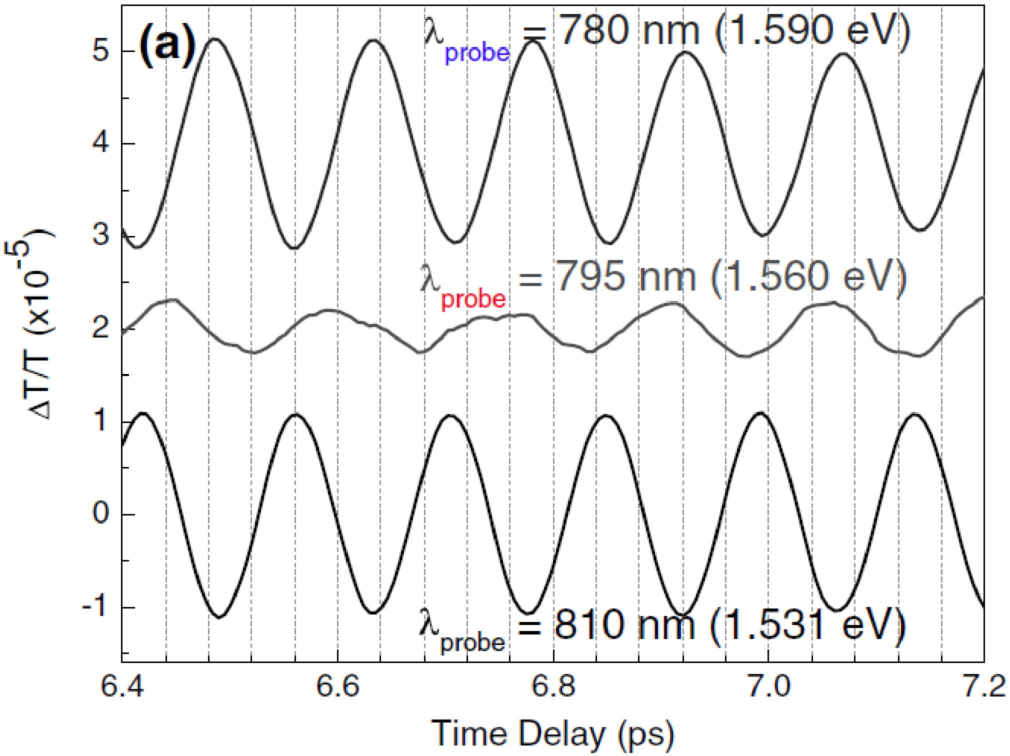
Pump pulses with frequency of ω_{RBM}

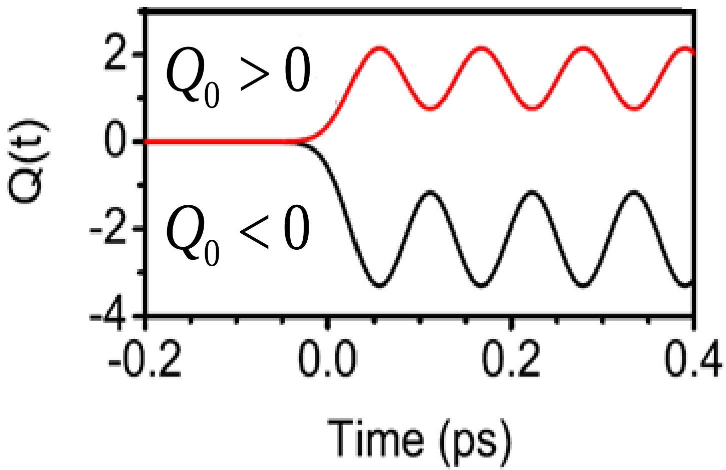


Wavelength dependent CP amplitude

J.-H. Kim et al., PRL 102, 037402 (2009)

(11,3) tube

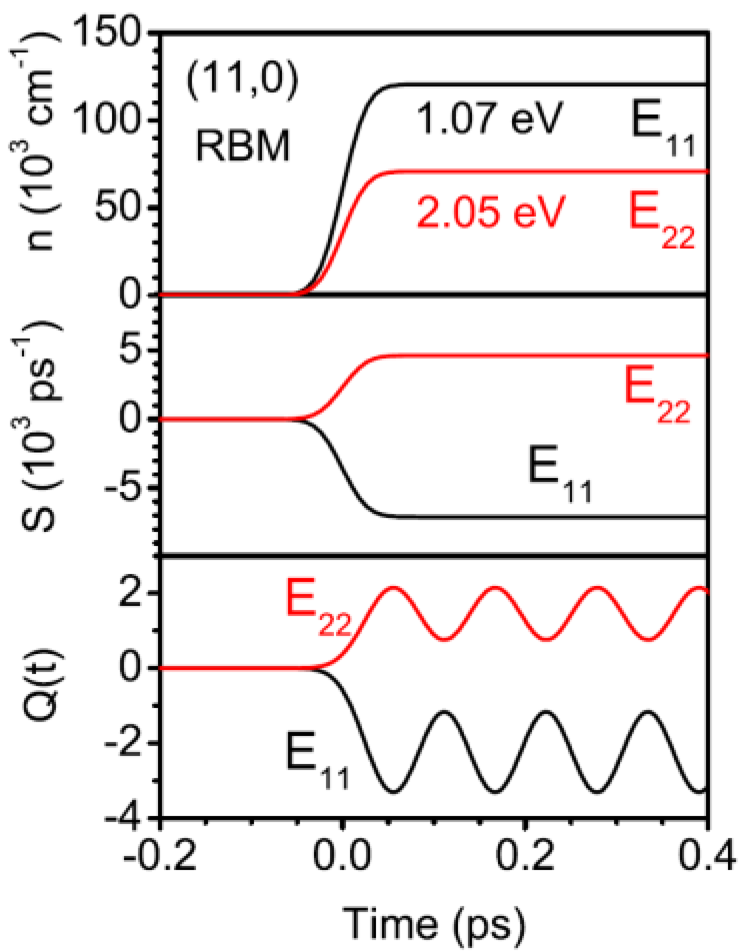




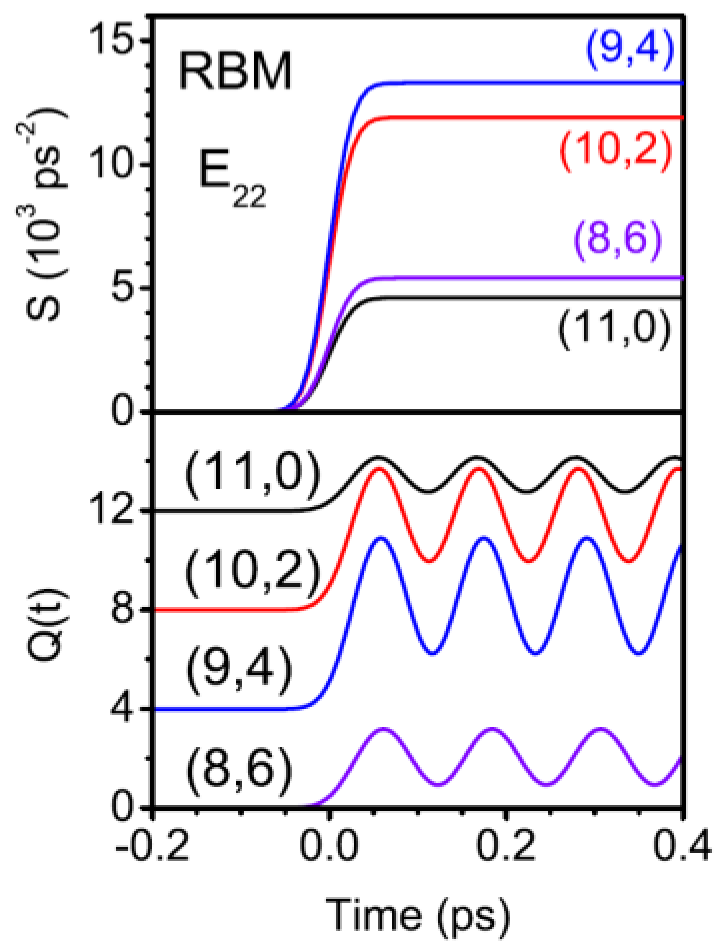
Family behavior of CP amplitude

G. Sanders et al, Phys. Rev. B 79, 205434 (2009)

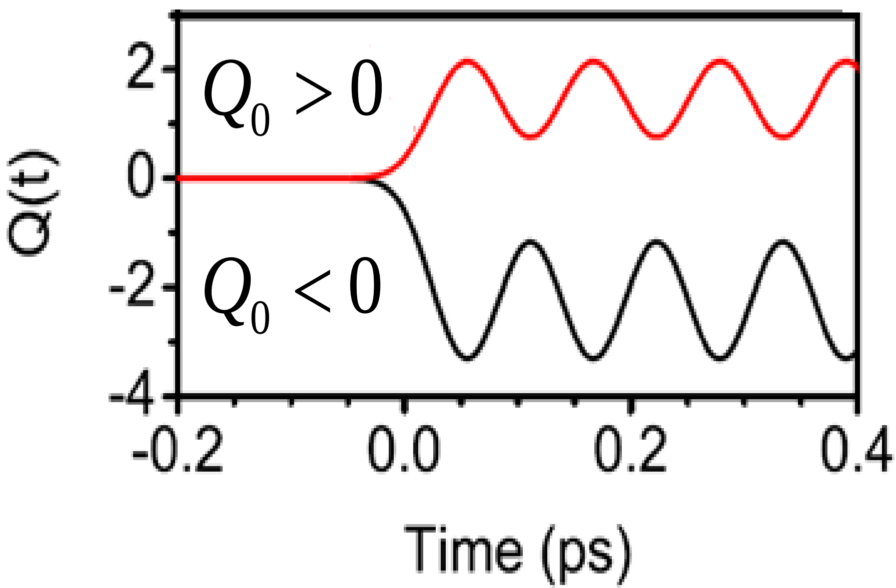
E11 and E22 for (11,0)



Family number $2n + m = 22$

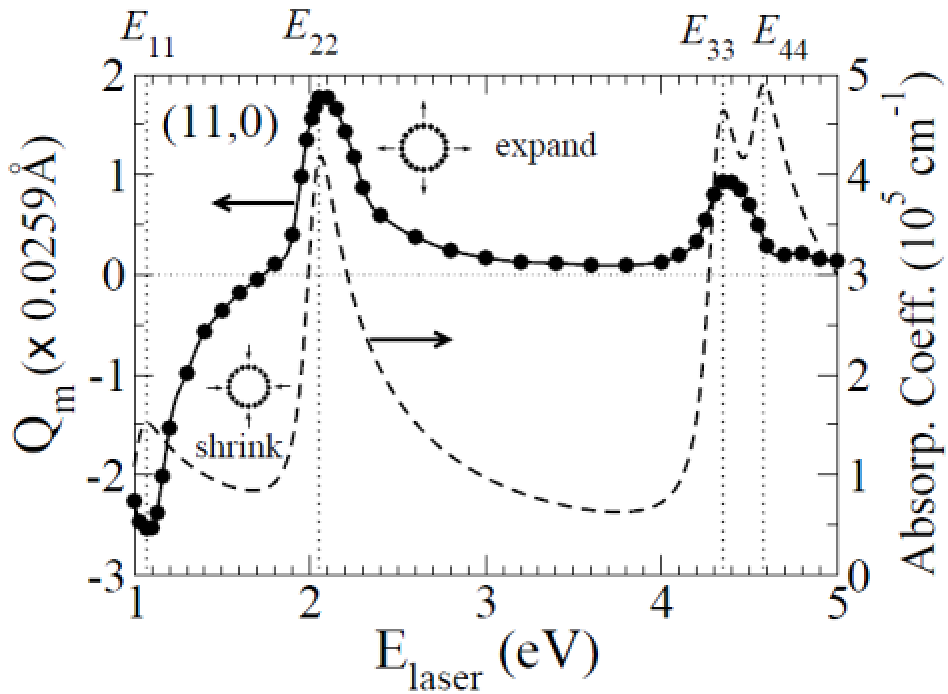


To expand or to shrink, that is the question.



Resonance behavior of CP amplitude

Nugraha et al, Phys. Rev. B 84, 174302 (2011).



$$\frac{\partial^2 Q_\beta(t)}{\partial t^2} + \omega_\beta^2 Q_\beta(t) = S_\beta(t)$$

$$S_\beta(t) = \sum_{\mu k} S_\mu^\beta(k)[f_{c\mu}(k) - f_{c\mu}^0(k)]$$

contains M_{op}

$$S_\mu^\beta(k) = -\frac{2\omega_\beta}{\hbar}[M_{c\mu}^\beta(k) - M_{v\mu}^\beta(k)]$$

Magnitude of oscillations

$$|Q| \propto |M_{el-ph}| \cdot |M_{op}|$$

Shrink or Expand? M_{el-ph}

sign (+/-) of el-ph matrix

Effective mass model for RBM el-ph interaction

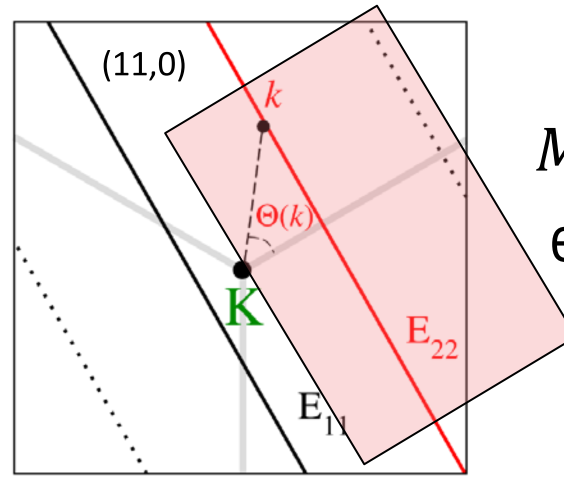
K. Sasaki et al, Phys. Rev. B 78, 235405 (2008)

For zigzag tubes:

$$M^{c}_{\text{el-ph}} = \langle c | H_{\text{el-ph}} | c \rangle = \frac{s_z}{d_t}\left(2g_{\text{on}} - g_{\text{off}} \cos\Theta(\mathbf{k})\right)$$

$$M^{v}_{\text{el-ph}} = \langle v | H_{\text{el-ph}} | v \rangle = \frac{s_z}{d_t}\left(2g_{\text{on}} + g_{\text{off}} \cos\Theta(\mathbf{k})\right)$$

$$M_{\text{el-ph}} = M^{c}_{\text{el-ph}} - M^{v}_{\text{el-ph}} = \boxed{\frac{s_z}{d_t}\left(-2g_{\text{off}} \cos\Theta(\mathbf{k})\right)}$$

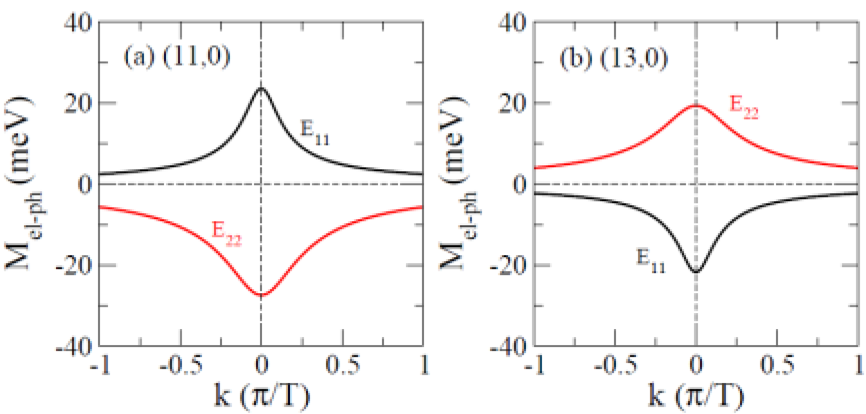


$M_{\text{el-ph}}<0$

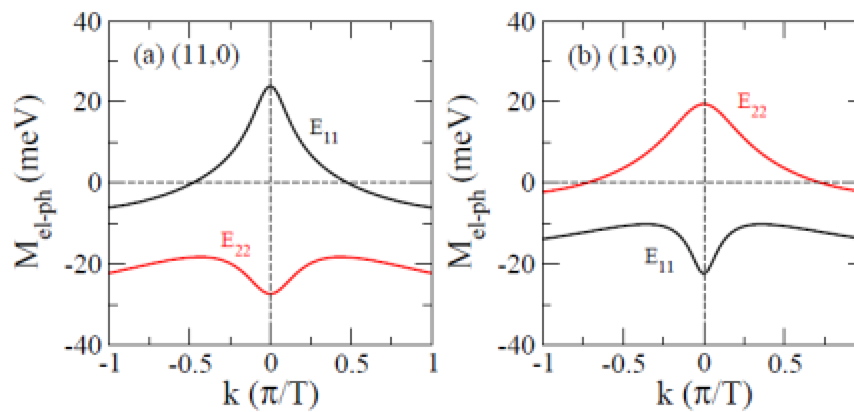
expanding

For chiral tubes:

$$M_{\text{el-ph}} = \frac{s_z}{d_t}\left(-2g_{\text{off}} \cos\left[\Theta(\mathbf{k}) + \theta\right]\right)$$



Eff. mass Model

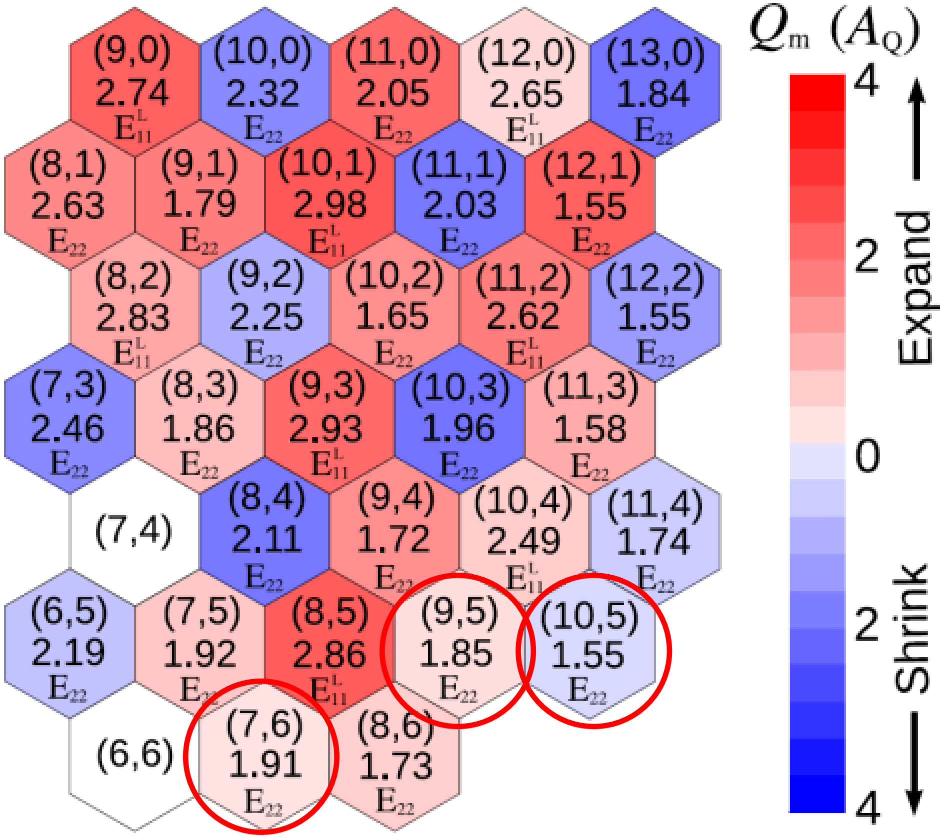


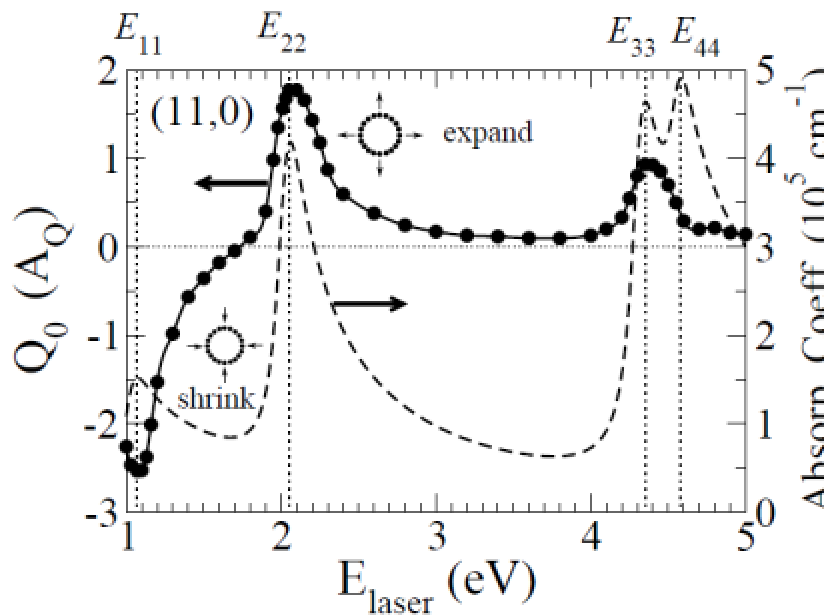
ETB Model

Map of coherent phonon amplitudes

Nugraha et al, Phys. Rev. B 84, 174302 (2011).

$$A_Q = \sqrt{\hbar / M\omega_{\mathrm{RBM}}}$$





□ Deviated results from basic rules: (7,6), (9,5), (10,5) etc. → near-armchair tubes

$$M_{\mathrm{el-ph}} = \frac{A_Q}{d_t}\left(-2g_{\mathrm{off}}\cos[\Theta(\mathbf{k})+3\theta]\right)$$

Phonon Softening

How do know the information of the Fermi energy?

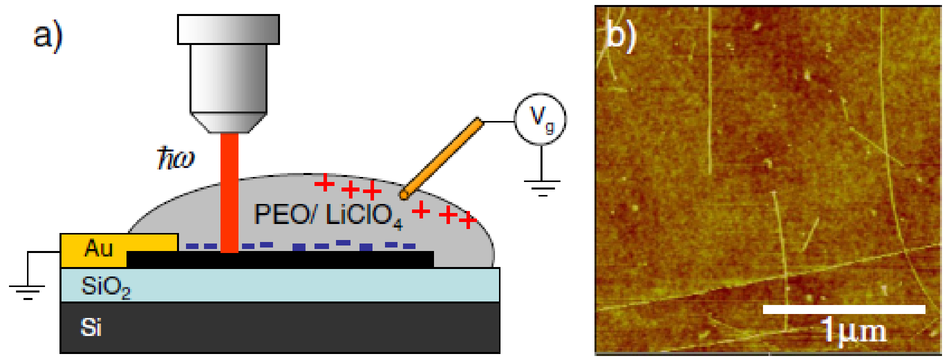
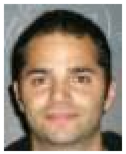


FIG. 1 (color online). (a) Schematic diagram of the experimental setup. The excitation laser shines through the PEO/$LiClO_4$ polymer electrolyte. (b) An AFM image indicating that the nanotubes are spaced out and are typically isolated from one another.

Electro-chemical doping and Raman spectrosocpy of single wall carbon nanotubes



H. Farhat *et al.*, *Phys. Rev. Lett.*, 99 145506(2007)

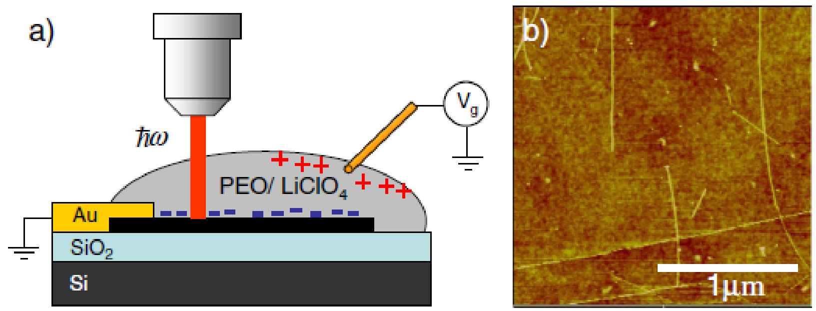
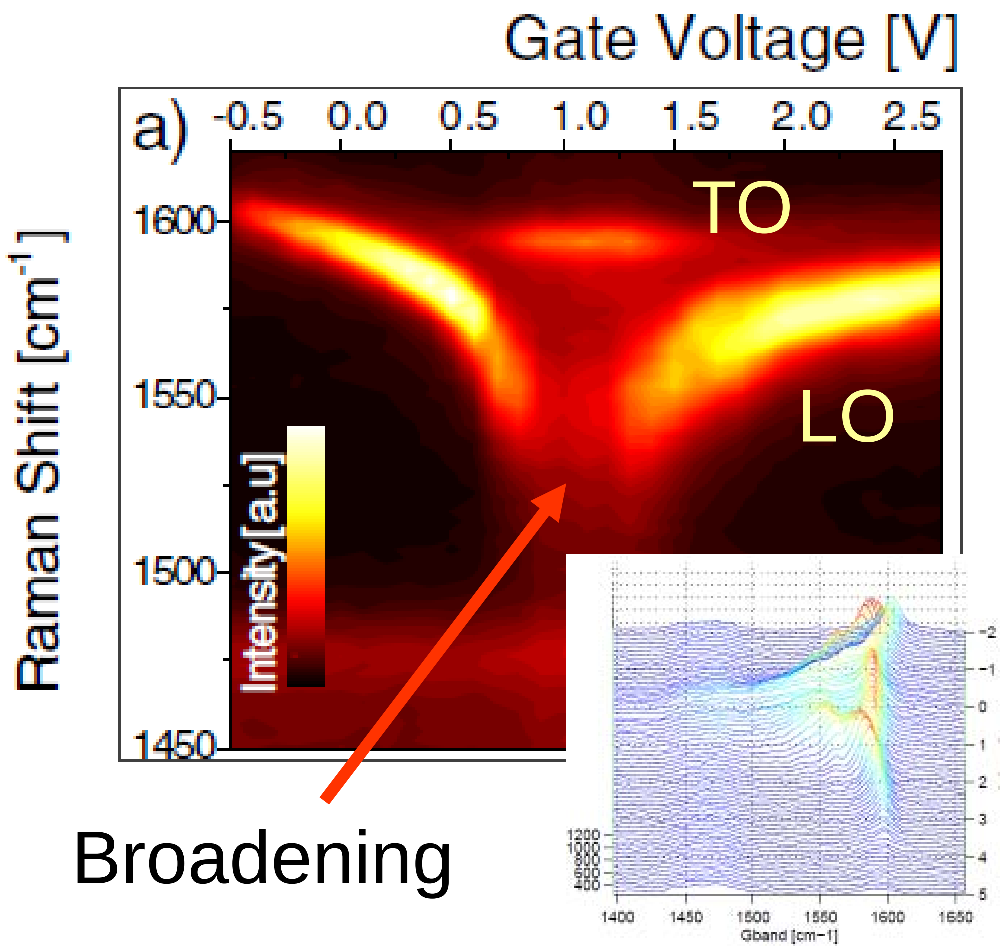


FIG. 1 (color online). (a) Schematic diagram of the experimental setup. The excitation laser shines through the PEO/$LiClO_4$ polymer electrolyte. (b) An AFM image indicating that the nanotubes are spaced out and are typically isolated from one another.

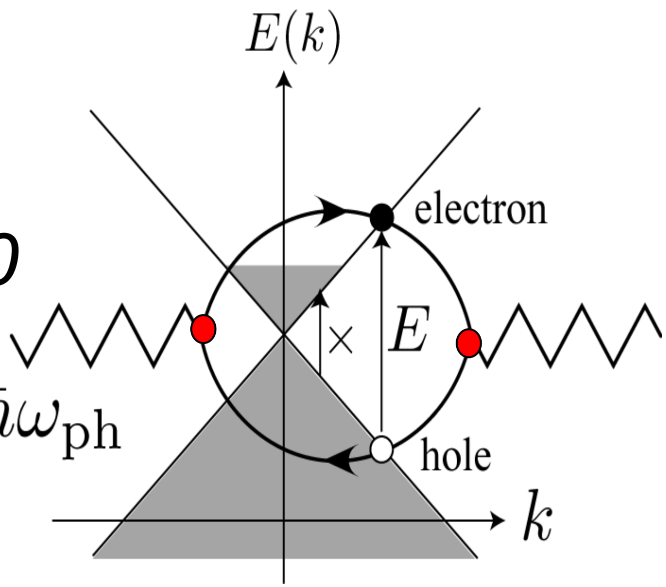
- isolated metallic SWNT
- E_F dependent
- upshift of TO?

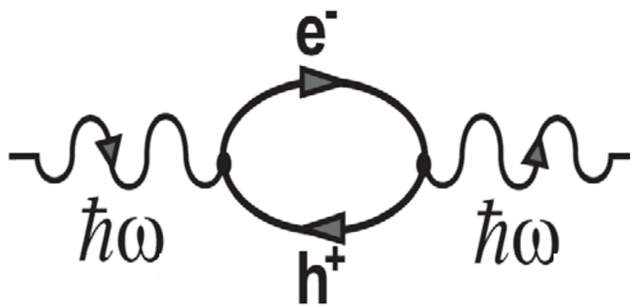


Electron-phonon interaction in Graphene

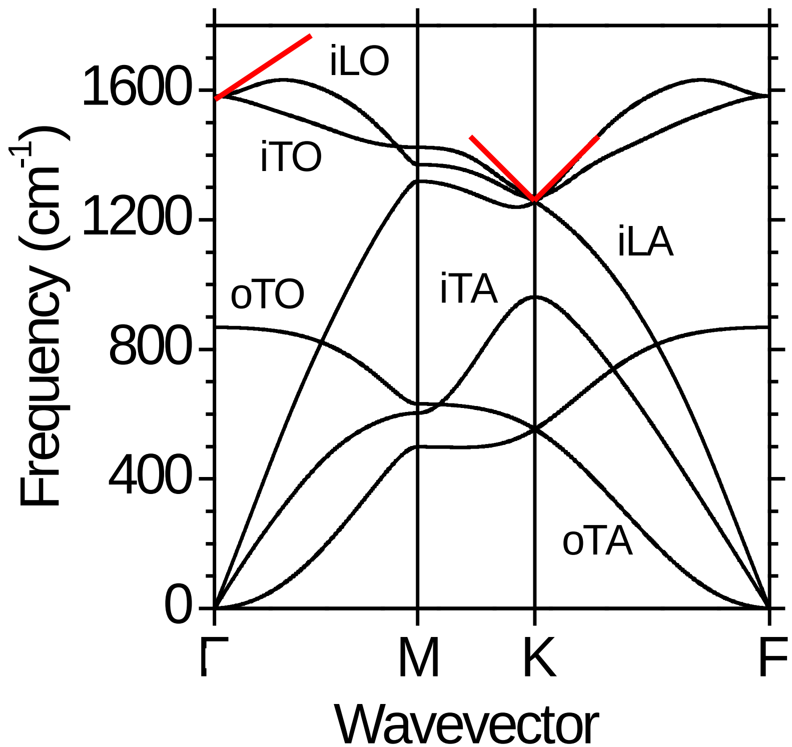
Renormalization of phonon energy (Kohn anomaly)

q=0





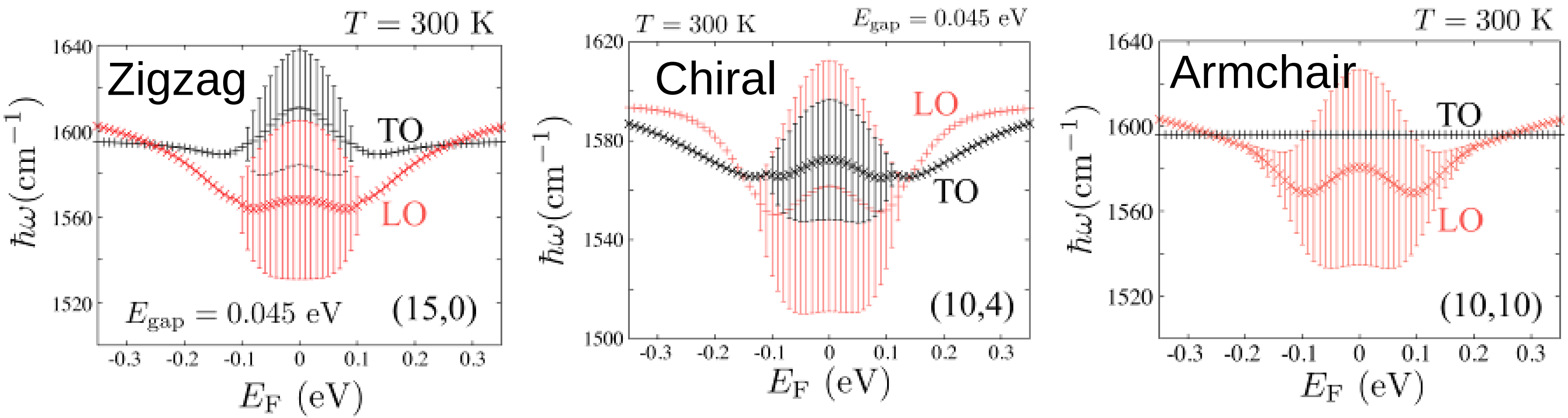
$$\hbar\omega = \hbar\omega^{(0)} + \hbar\omega^{(2)}$$



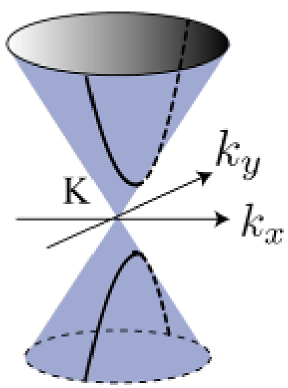
Piscanec et al. PRL (2004)
Ando et al, JPSJ (2006)
Sasaki et al. PR (2008)

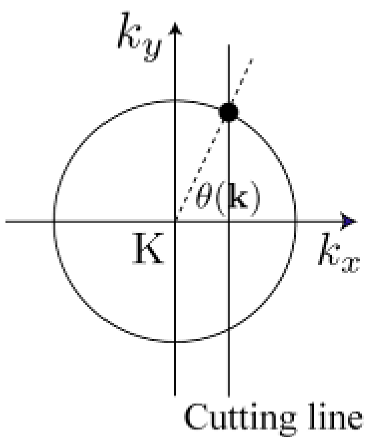
Chiral angle dependence of KA

K. Sasaki, R. Saito, et al. Phys. Rev. B, 77, 245441 (2008)



Why TO becomes hard for zigzag NT?





Θ dependent el-ph interaction

LO: $\langle {\rm eh}(\mathbf{k})|\mathcal{H}_{\rm ep}|\omega_l\rangle = -igu\sin\theta(\mathbf{k})$

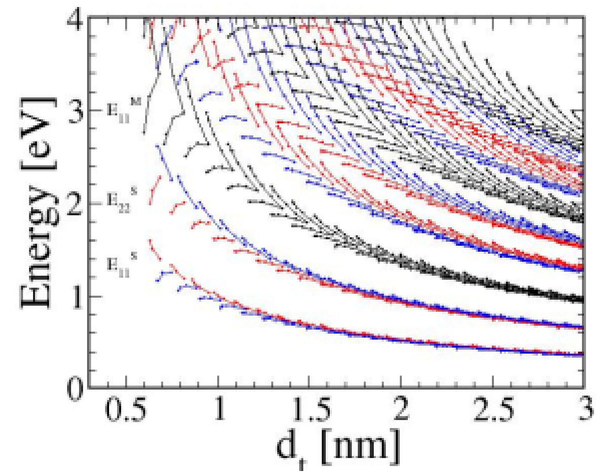
TO: $\langle {\rm eh}(\mathbf{k})|\mathcal{H}_{\rm ep}|\omega_t\rangle = -igu\cos\theta(\mathbf{k})$

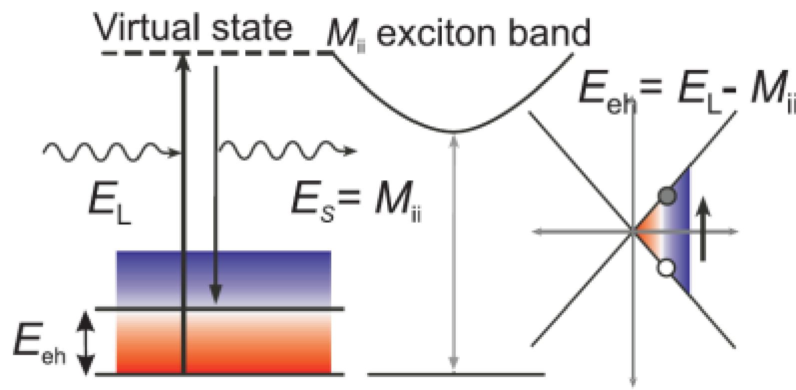
$$v_{\rm F}(A_x(\mathbf{r}), A_y(\mathbf{r})) = g(u_y(\mathbf{r}), -u_x(\mathbf{r}))$$

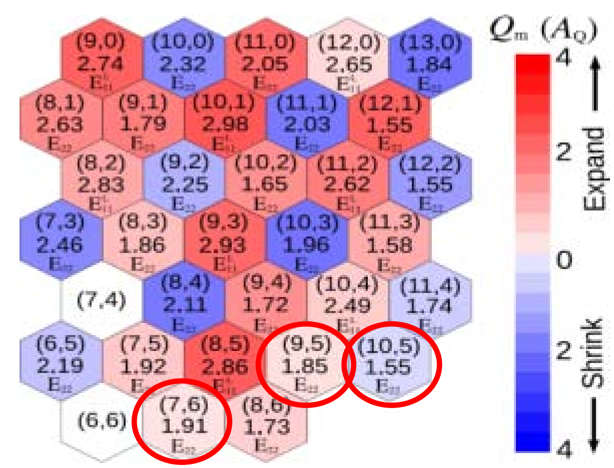
K. Ishikawa and T. Ando, J. Phys. Soc. Jpn. **75**, 84713 (2006).
T. Ando, J. Phys. Soc. Jpn. **77**, 14707 (2008).

Summary of NTs

- Exciton Kataura Plot
  - environment effect
- Electric Raman spectra
  - Coulomb interaction
- Coherent phonon
  - expand/shrink map
- Kohn anomaly
  - Chirality dependnt

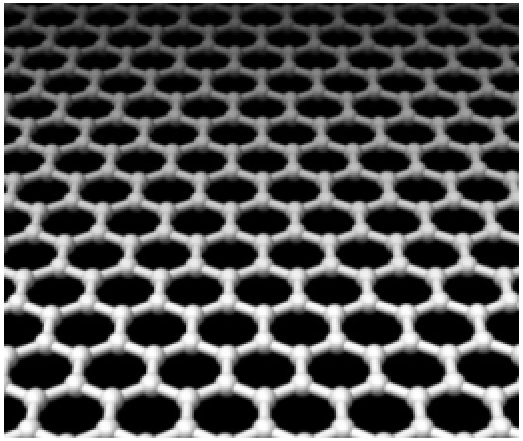




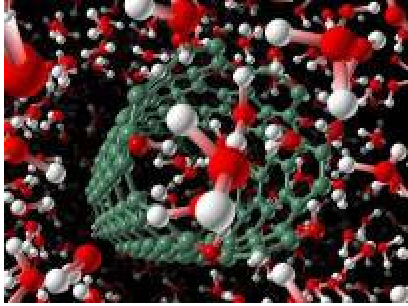


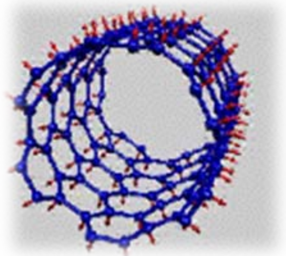
2011 MIT

Raman Spectroscopy of graphene

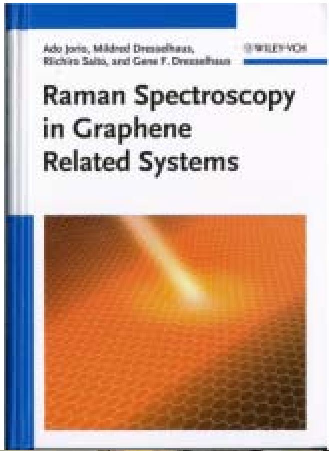


Outline





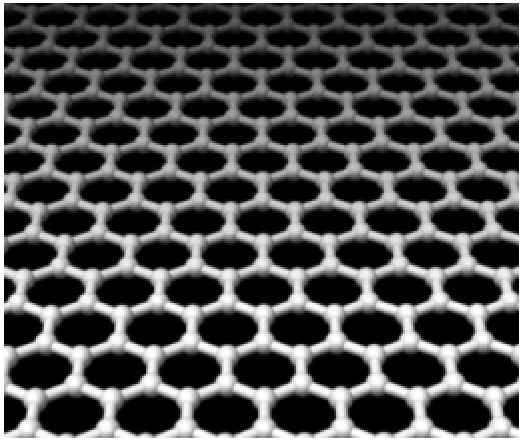
- Graphene Raman spectroscopy
  - Raman spectra of bilayer G (2LG)
  - ABA and ABC stacking order of 3LG
- Electro-Chemical doping
  - E_F dep. on double resonance Raman
  - origin of the 2450cm^{-1} peaks

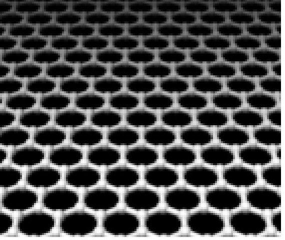


A. Jorio, R. Saito, G. Dresselhaus, M. S. Dresselhaus
"Raman Spectroscopy of graphene related systems"
Wiley-VCH, in press (2011)

Raman Spectroscopy of bilayer graphene

How to know the number of layers?



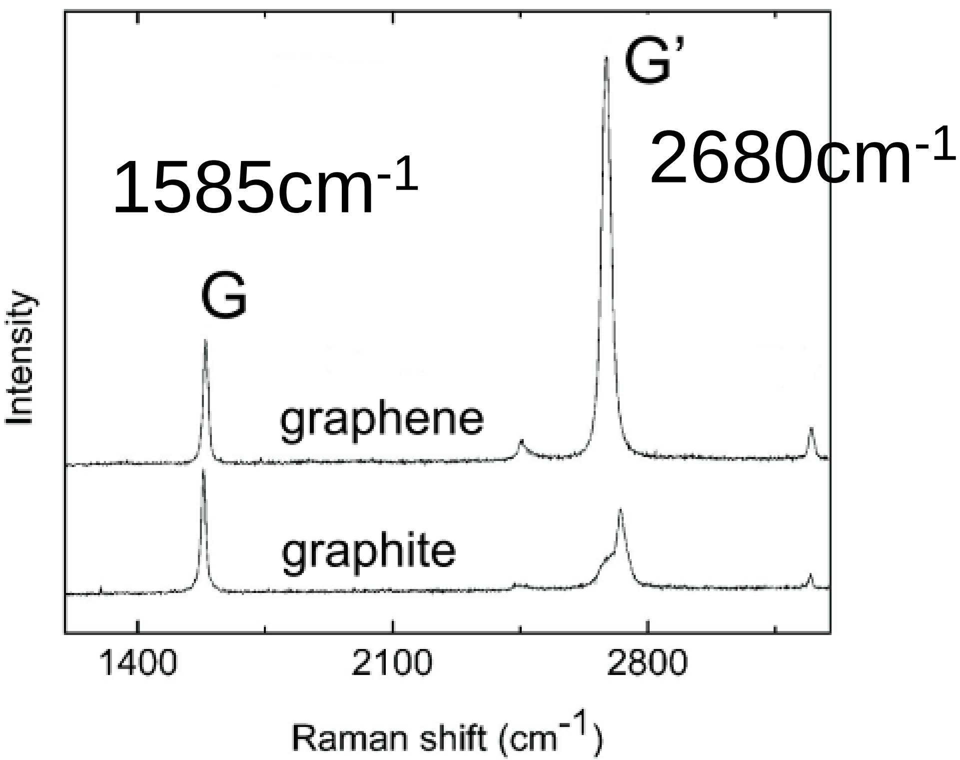


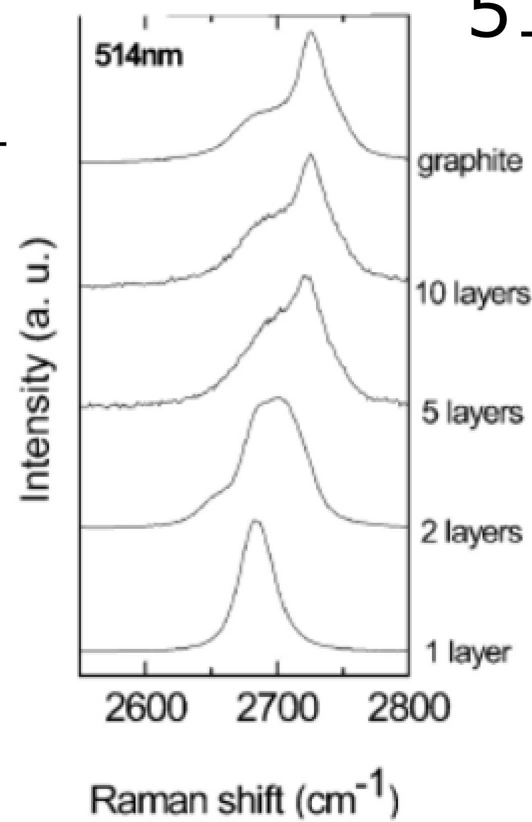
Raman spectra of graphne

A.C. Ferrari et al. PRL (2006)

- G’(2D) band is sharp and strong.
- number of graphene layer

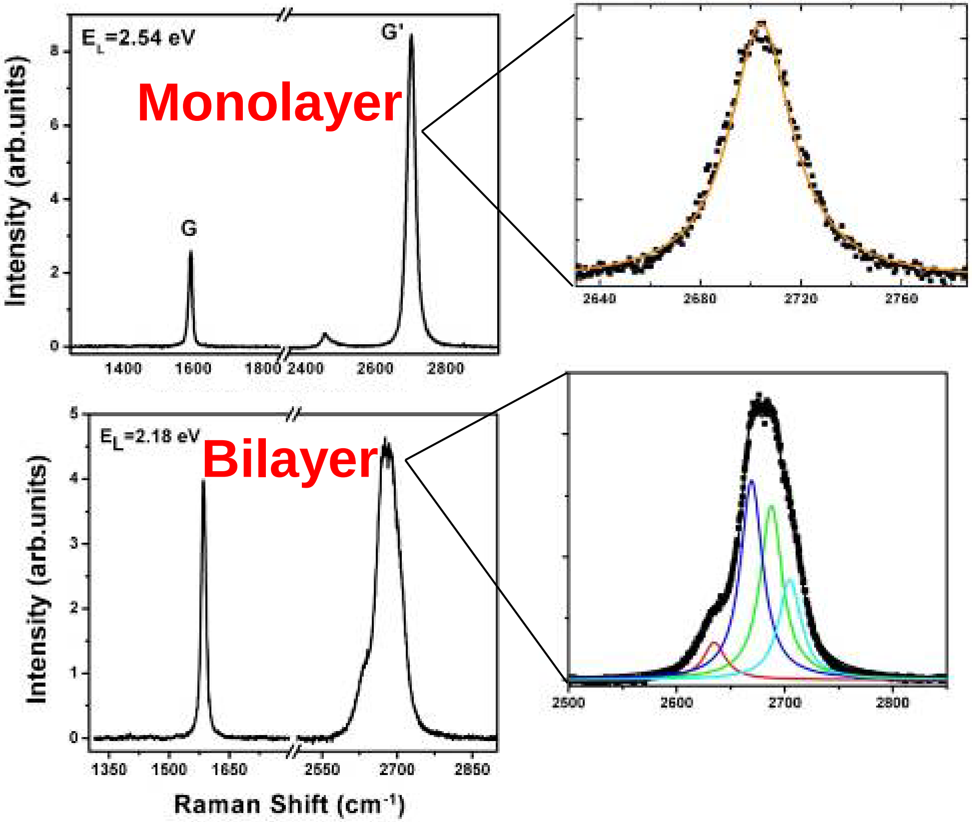
E=2.41eV
514nm



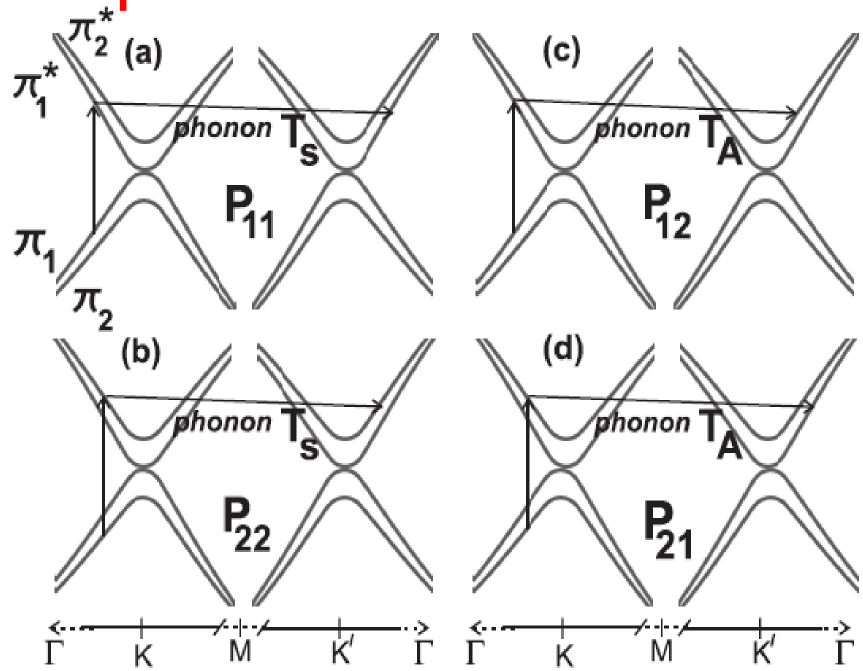


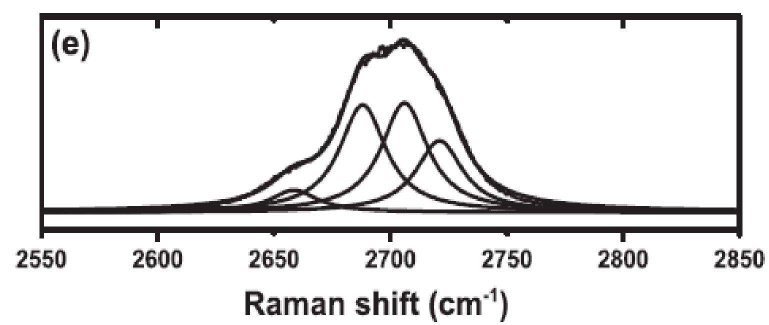
The G’ (2D) Raman band of bilayer graphene

J. S. Park et al. *Carbon* 47, 1303 (2009).



Double resonance processes in 2LG



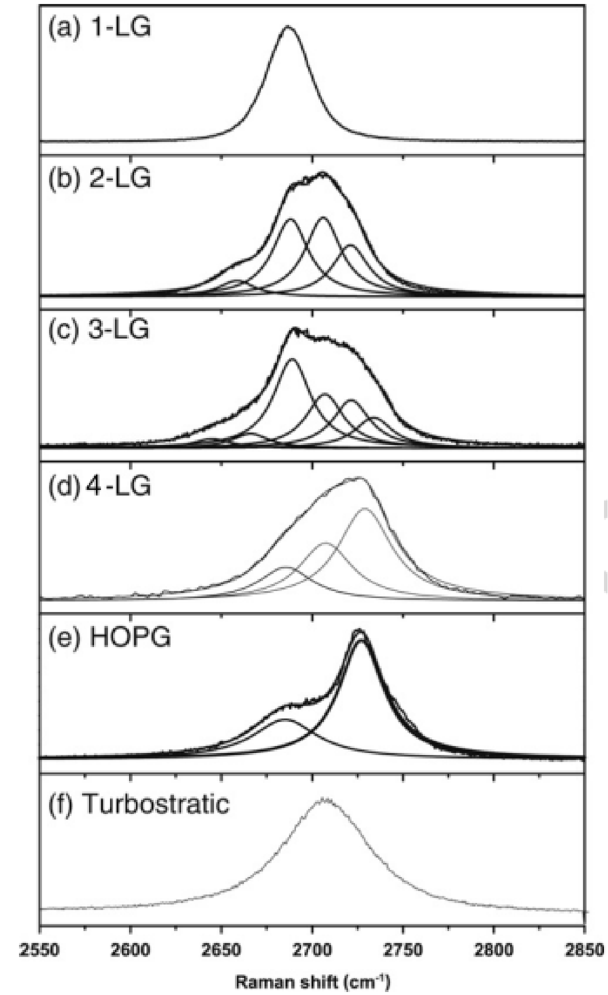


The G’ (2D) band of bilayer graphene consists of four peaks

A.C. Ferrari et al. PRL (2006)

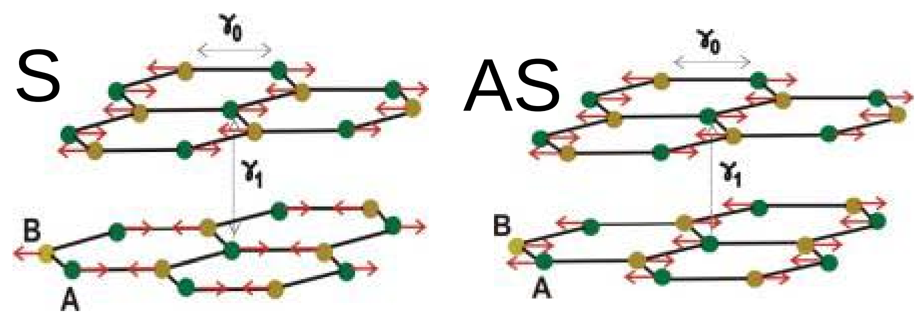
Number of graphene layer is available by

(1)G′ to G intensity ratio
(2)Spectral shape of G′
(3)Spectral width of G′
(4)Raman intensity of G



Stacking order of graphene

More analysis for
interlayer interaction of
2-LG.



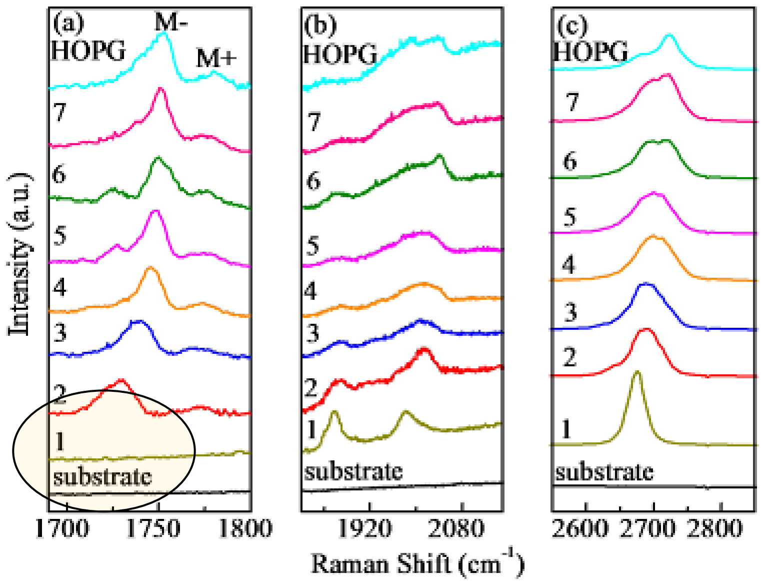
Malrad et al. Phys. Rev. Lett. 101, 257401, (2008)

New method for number of layers

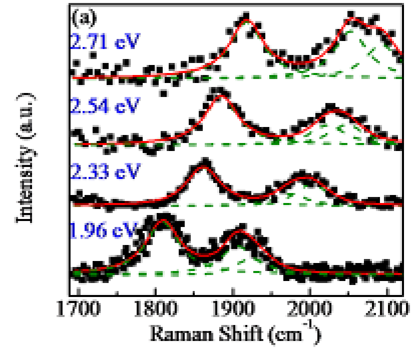
Y. Ting

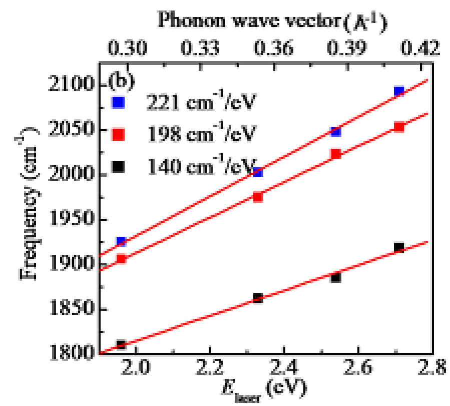
C. Cong et al. ACS Nano 5, 1600 (2011).

M iTOLA G' (2D)



dispersive!





iTOLA

M

M : oTA+LO

absent for 1L-G

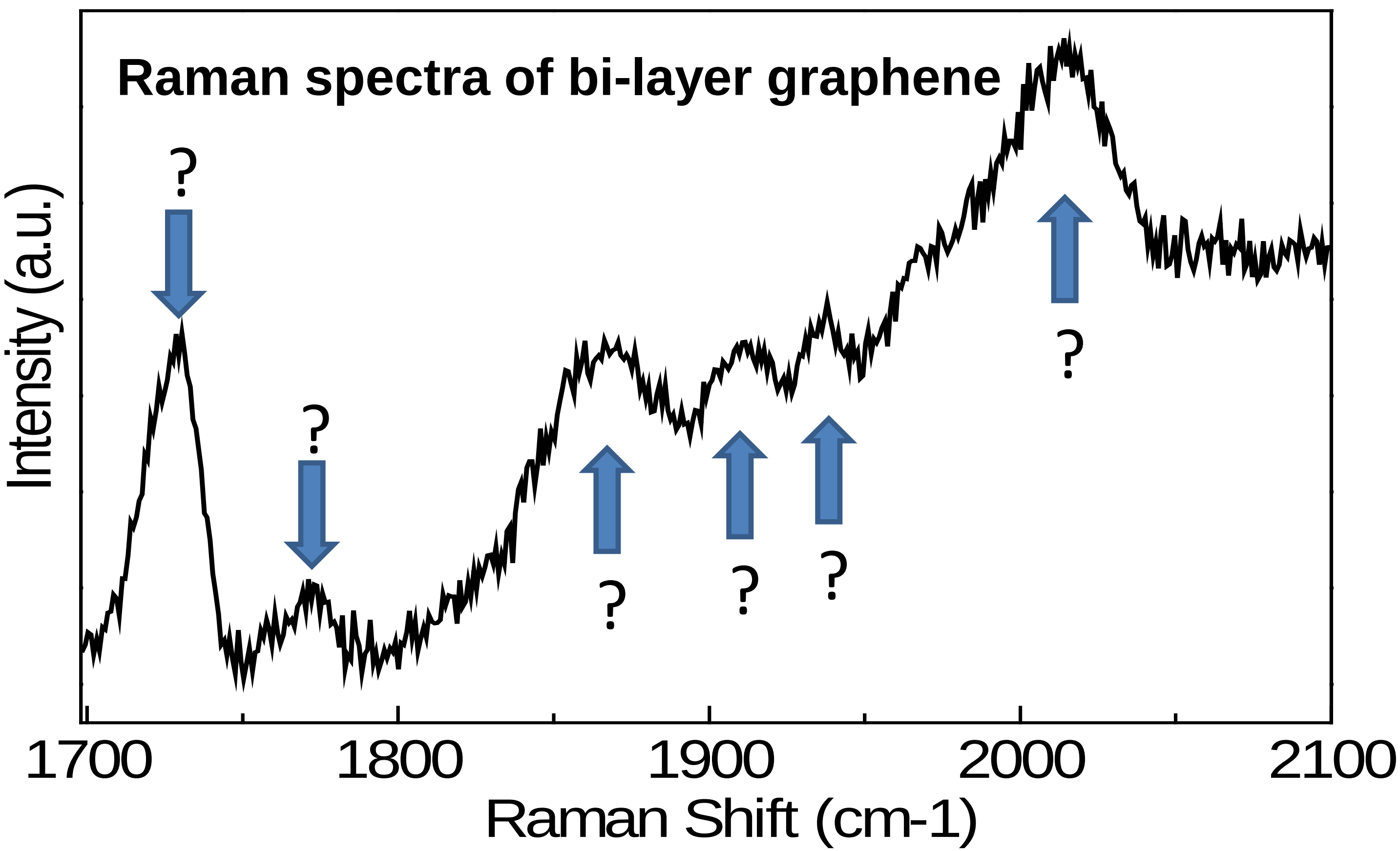
not affected by substrate

from $1700 cm^{-1}$ to $2000 cm^{-1}$

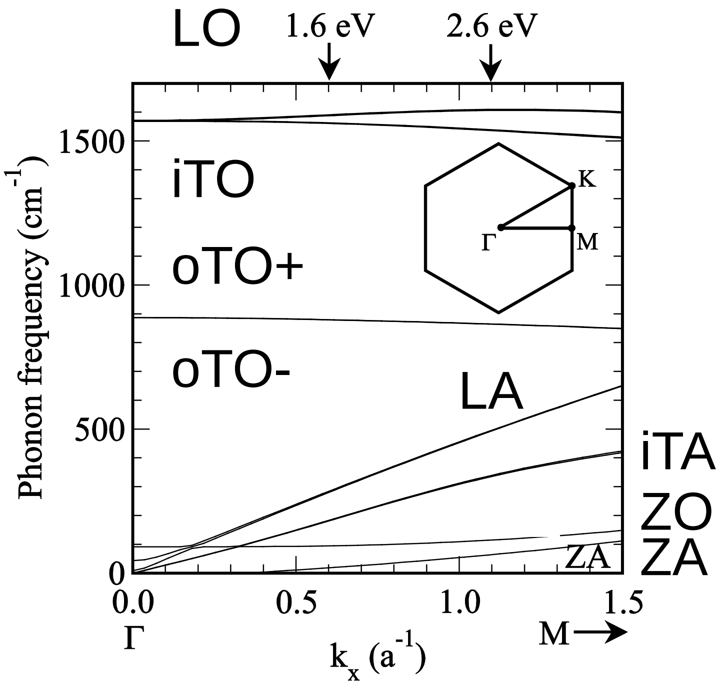
Calculation of Raman peaks

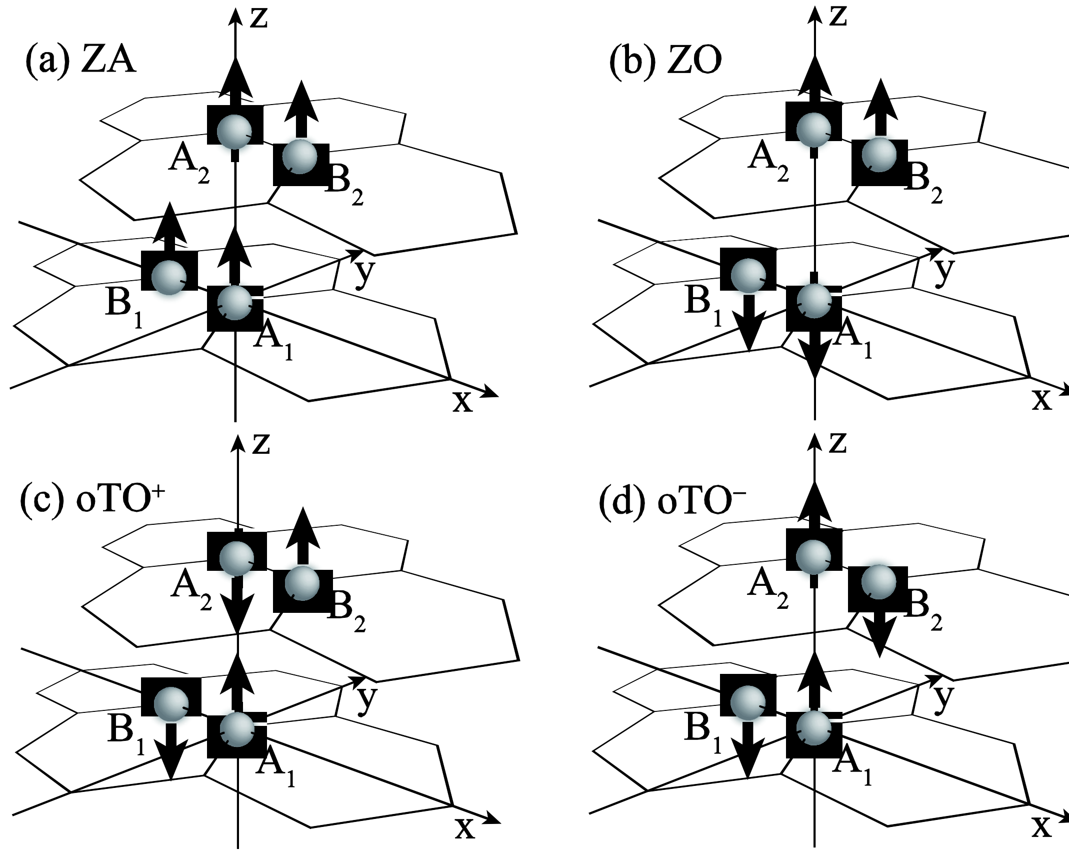
from 1700cm^{-1} to 2000cm^{-1}

K. Sato et al. Phys. Rev. B, 84, 035419 (2011)



Four different out-of-plane phonons of bi-layer graphene
K. Sato et al. Phys. Rev. B, 84, 035419 (2011)



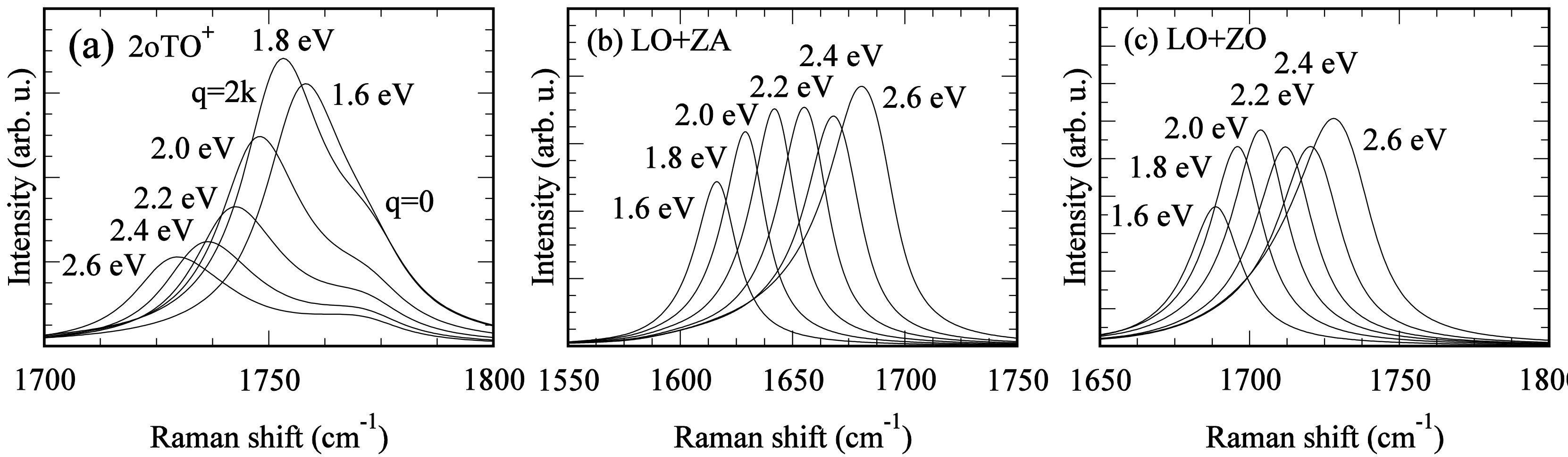


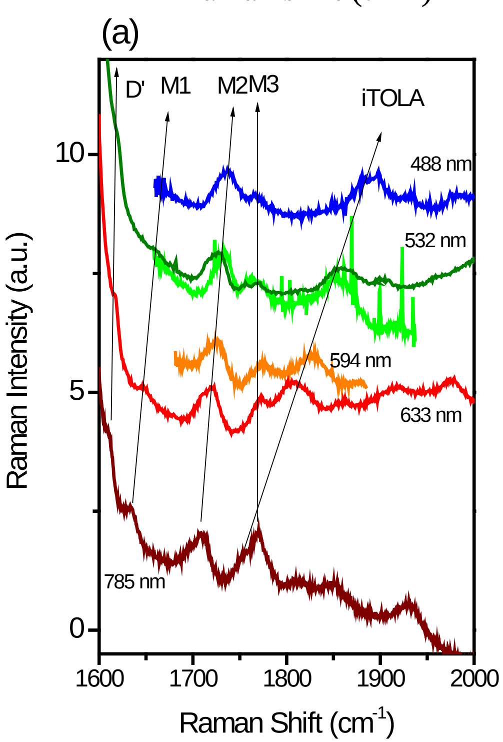
Force constant parameters

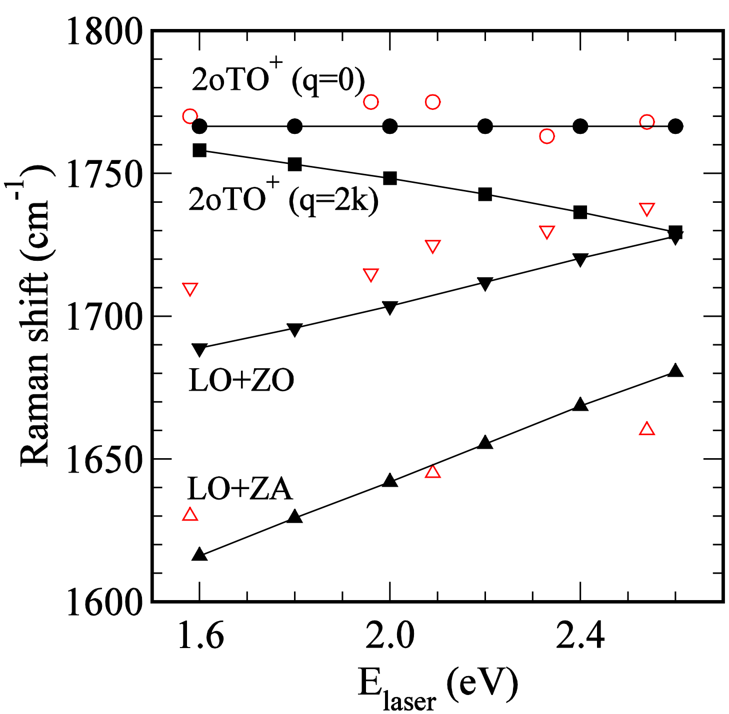
Out-of-plane : R. A. Jishi *et al*., Phys. Rev. B 26, 4514 (1982).

In-plane : M. Furukawa, Master thesis (2011).

2oTO, LO+ZO, LO+ZA modes appear from 1700cm^{-1} to 1800cm^{-1}



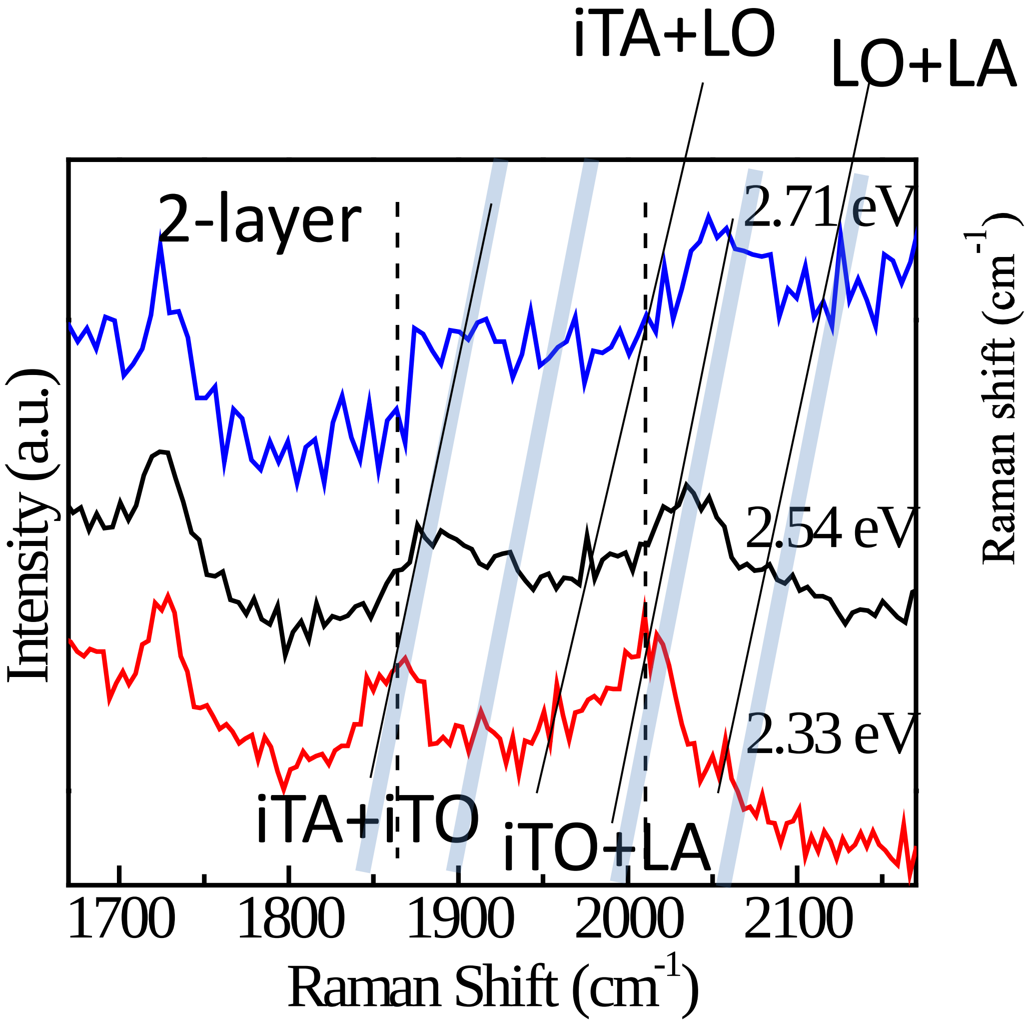


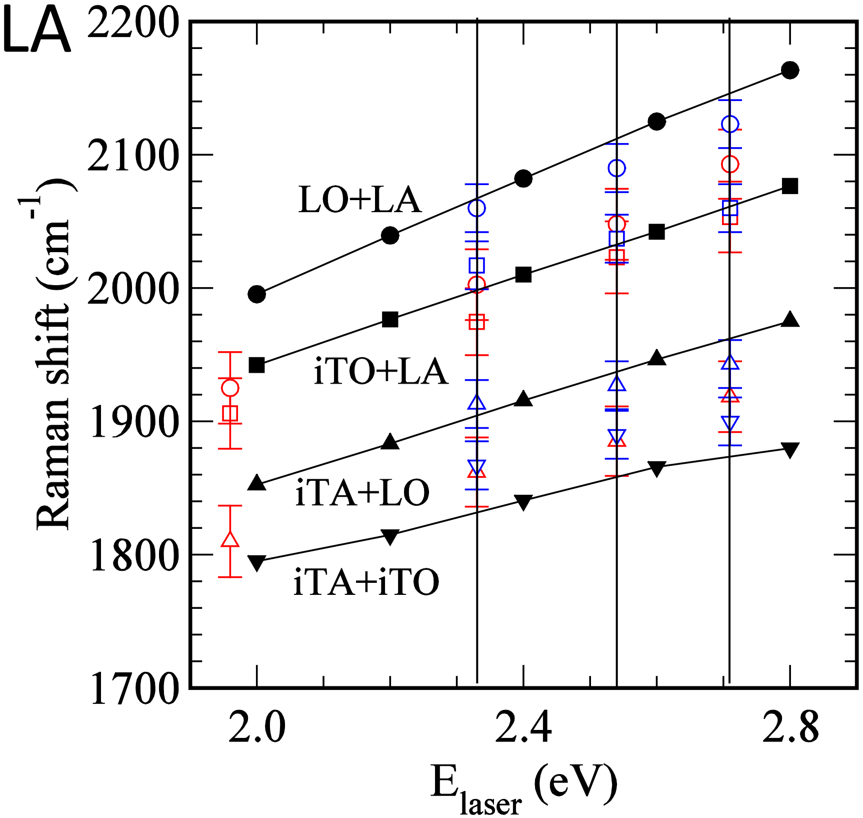


Black: Calculation

Red: BLG (experiment by Lui @ T. Heinz)

LO+LA, iTO+LA, iTA+LO and iTA+iTO modes appear from 1850 to 2100cm-1





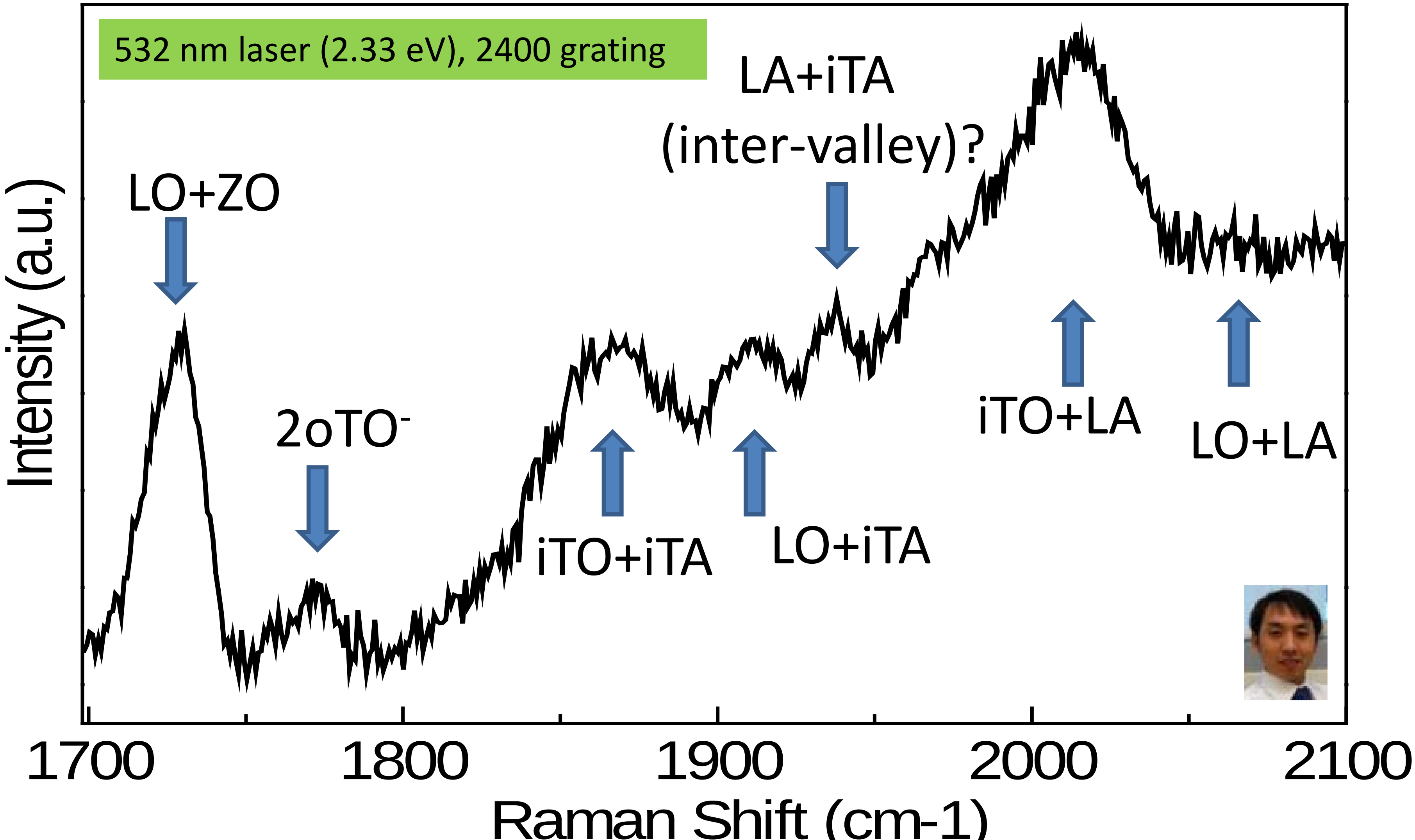
Black: Calculation

Red: SL graphene (exp.)

Blue: BL graphene (exp.)

Raman spectra of bi-layer graphene

K. Sato et al. Phys. Rev. B, 84, 035419 (2011).



Raman Spectroscopy of electro-chemical doping of single layer graphene

How to assign the combination modes of

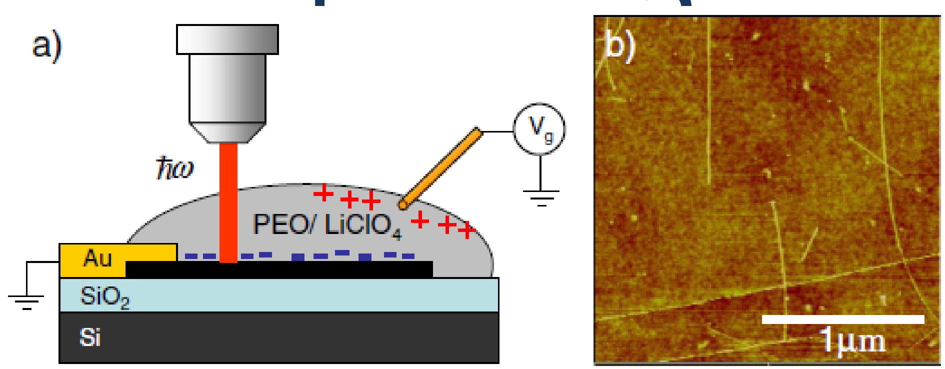
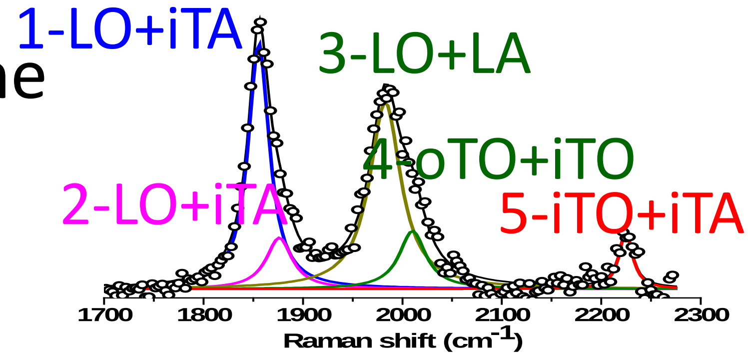
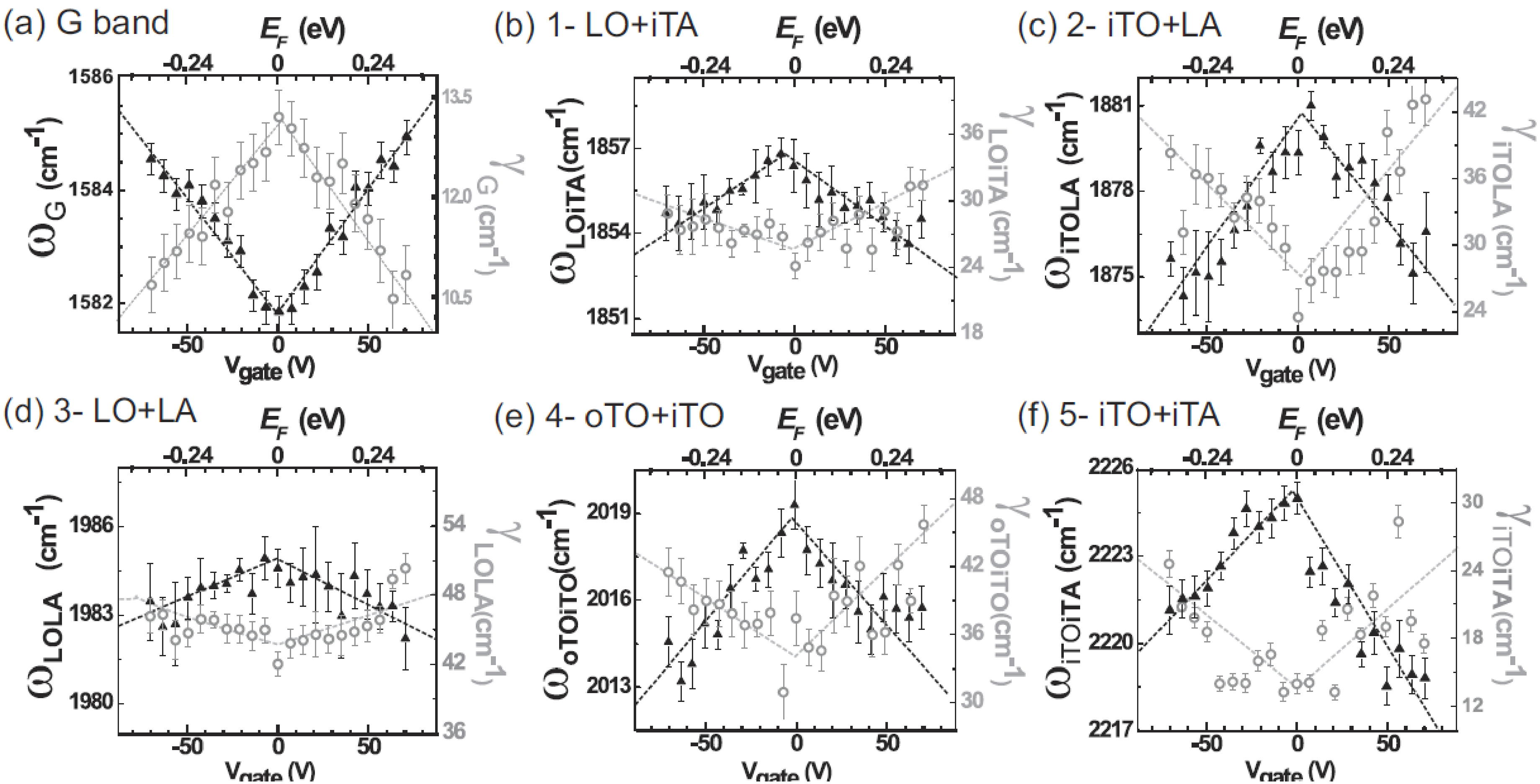


FIG. 1 (color online). (a) Schematic diagram of the experimental setup. The excitation laser shines through the PEO/$LiClO_4$ polymer electrolyte. (b) An AFM image indicating that the nanotubes are spaced out and are typically isolated from one another.

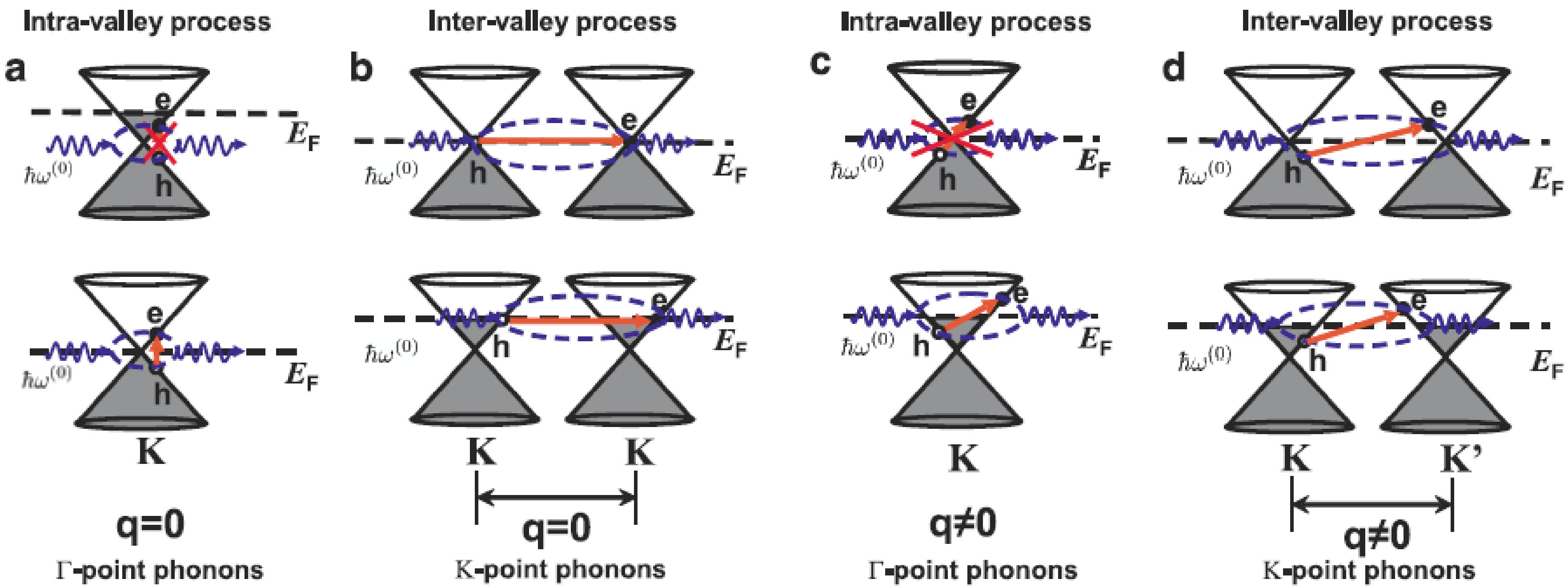
Gate voltage dependence of the M-bands of 1LG
D. L. Mafra et al., submitted

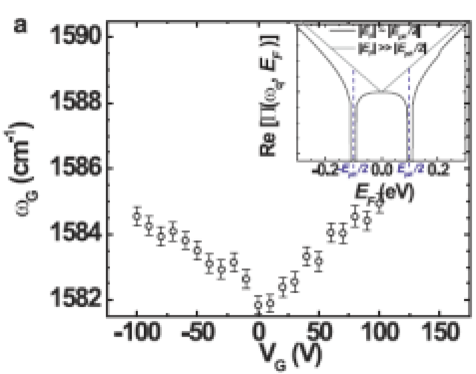


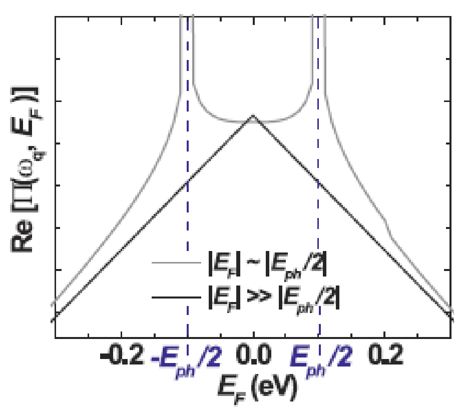


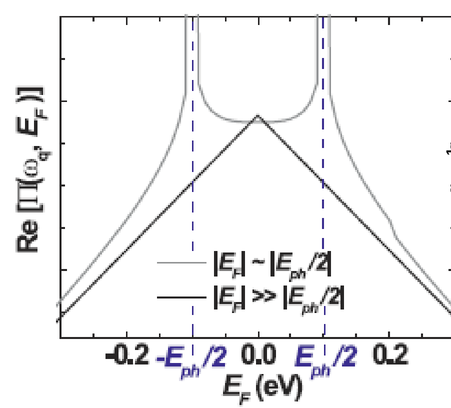
q=0 and q≠0 phonon gives different E_F dependence

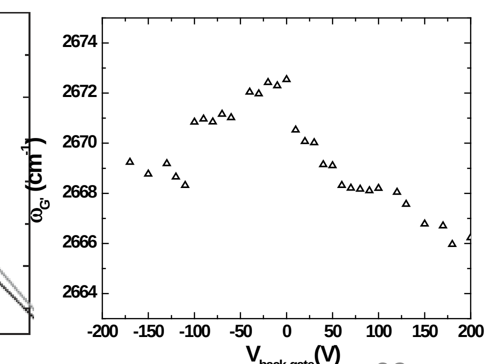
P. T. Aroujo et al, Phys. Rev. Lett. In press



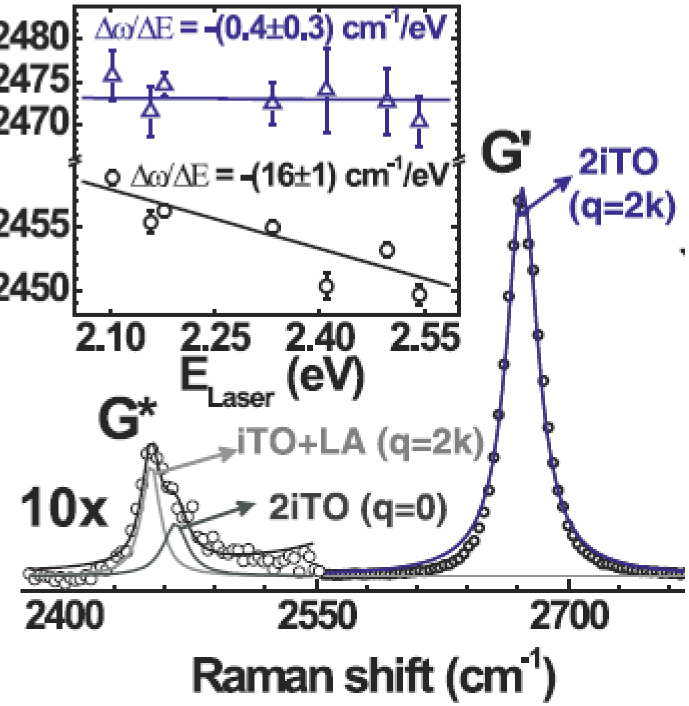


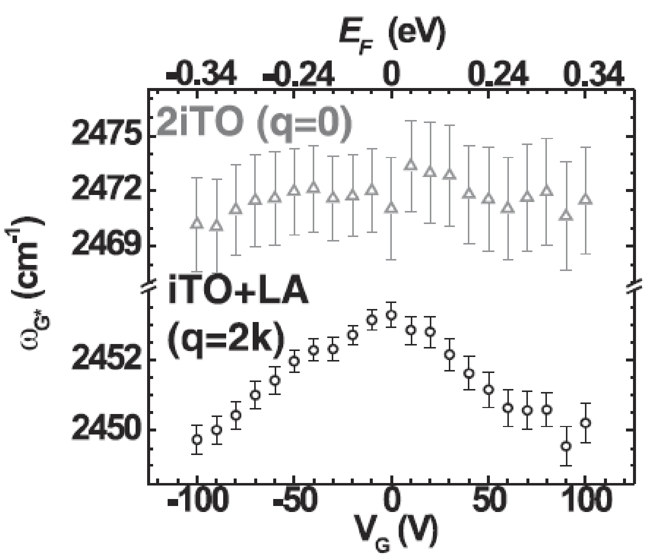






$2450cm^{-1}$ G* band problem





V_G mesurement !

R. Saito *et al., New J. Phys.*
5, 157 (2003).
both q=0 and q=2k exist in DR

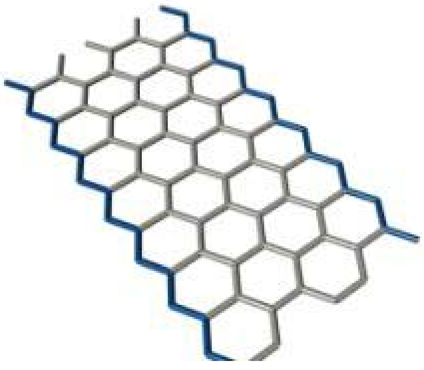
T. Shimada *et al., Carbon*
43, 1049 (2005).
q=0 DR 2iTO

D. L. Mafra *et al., Phys. Rev. B*
76, 233407 (2007).
q=2k DR iTO+LA

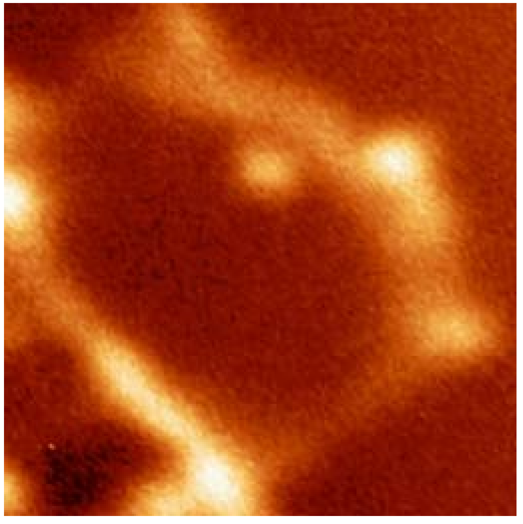
P. T. Araujo *et al., Phys. Rev. Lett.*
In press
both q=0 DR 2iTO
and q=2k DR iTO+LA

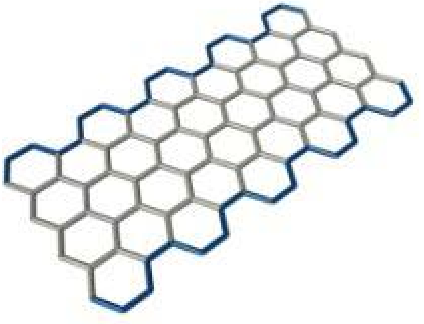
Raman imaging of graphene edge

How to know the edge structure?



zigzag edge



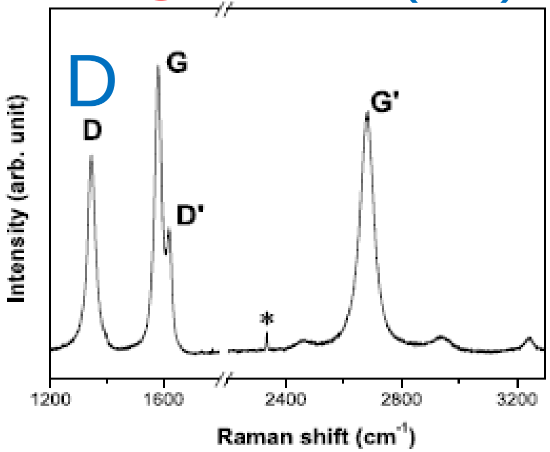


armchair edge

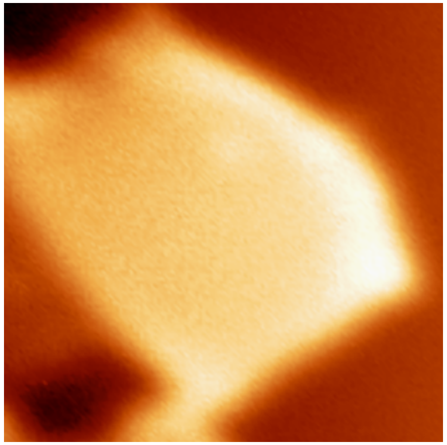
Raman imaging of graphene

M. A. Pimenta et al., Phys. Chem. Chem. Phys. 9, 1276 (2007)

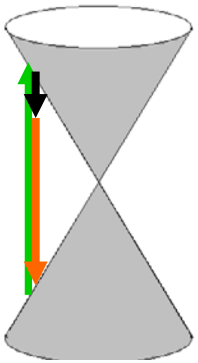
G G' (2D)

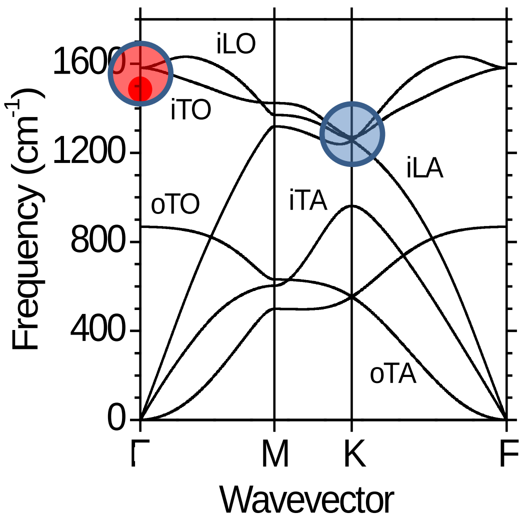


G-band image

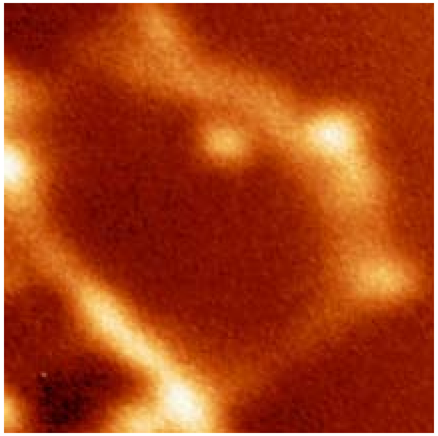


G band

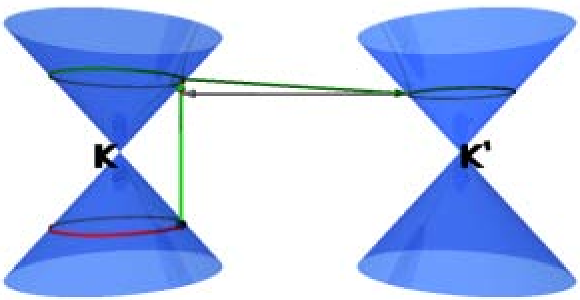




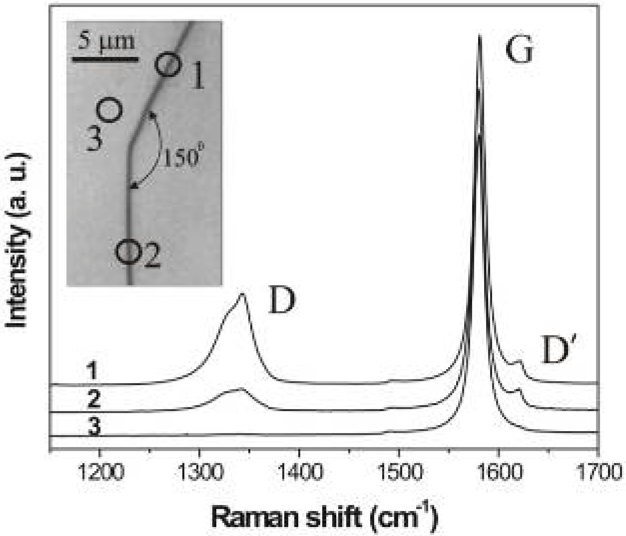
D-band image

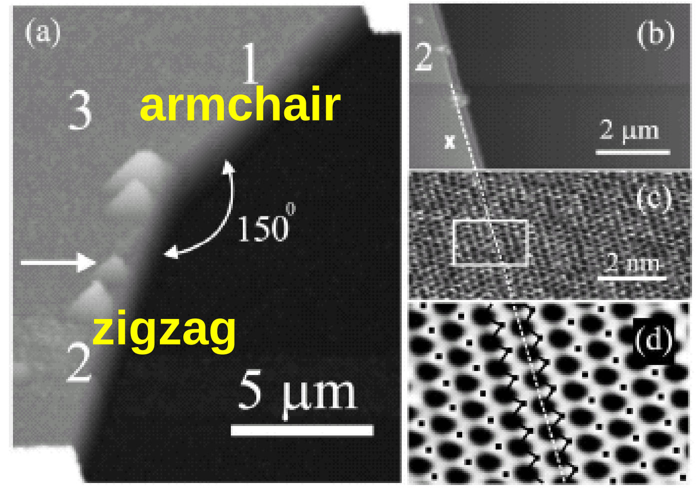


D band

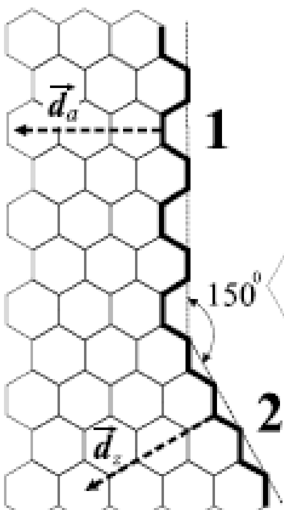


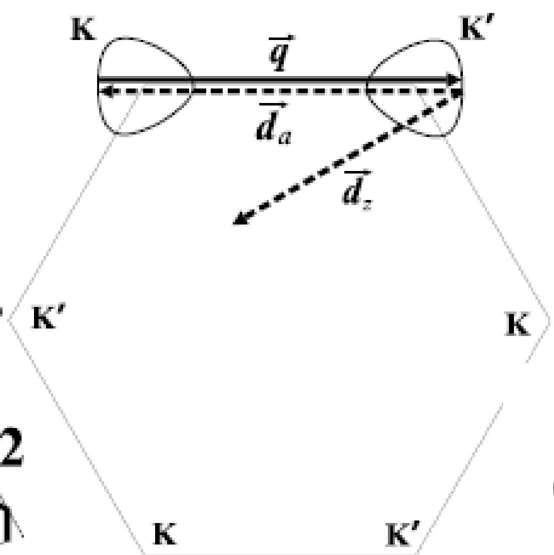
Raman scattering in graphites edges
L. G. Cançado et al. Phys. Rev. Lett., 93, 247401 (2004)





armchair edges



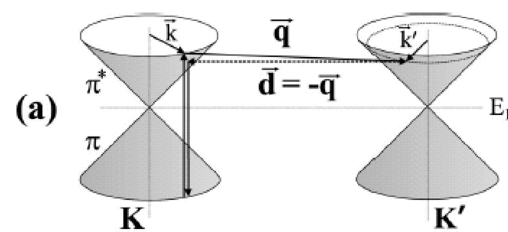


zigzag edges

armchair edges

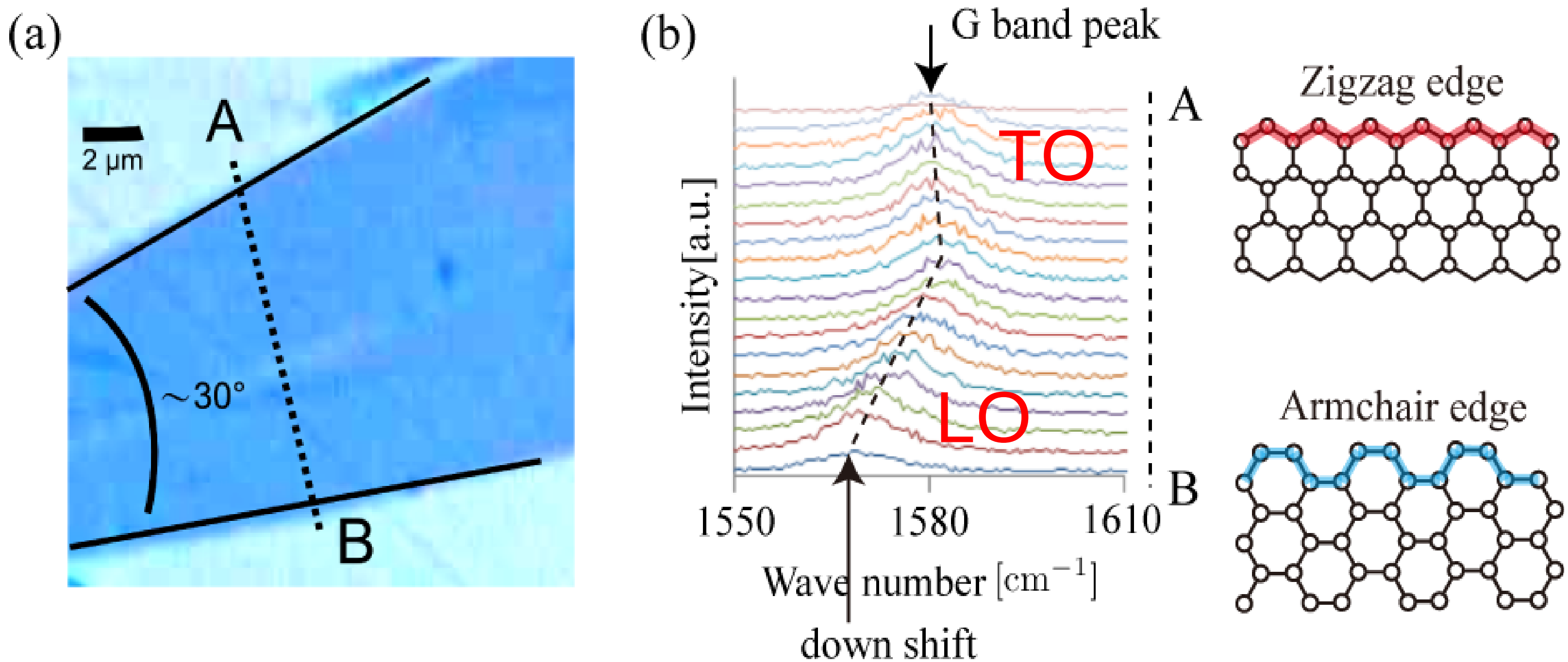
inter-valley scattring

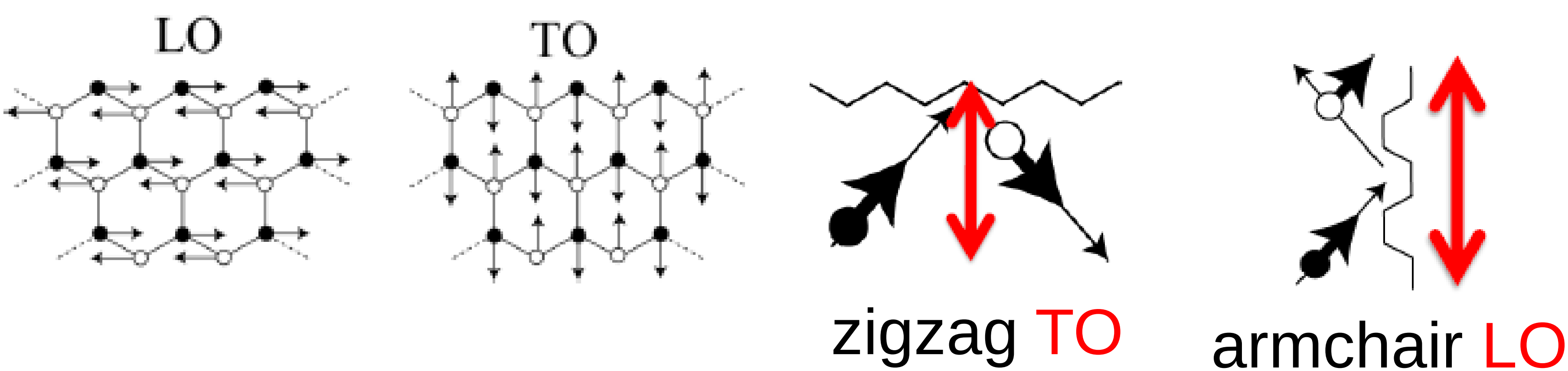
strong D signal



Edge dependent Kohn anomaly of G-band

K. Sasaki et al. Phys. Rev. B 80, 155450 (2009)

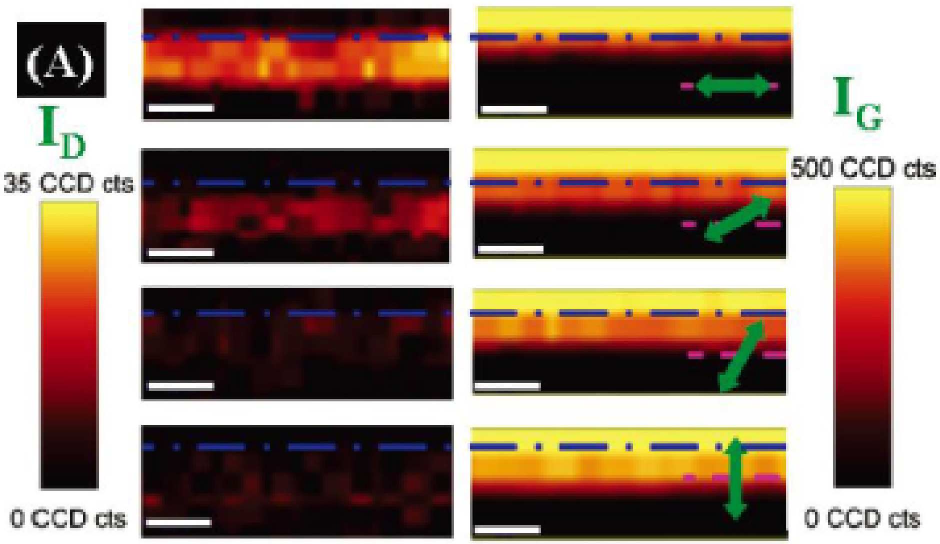


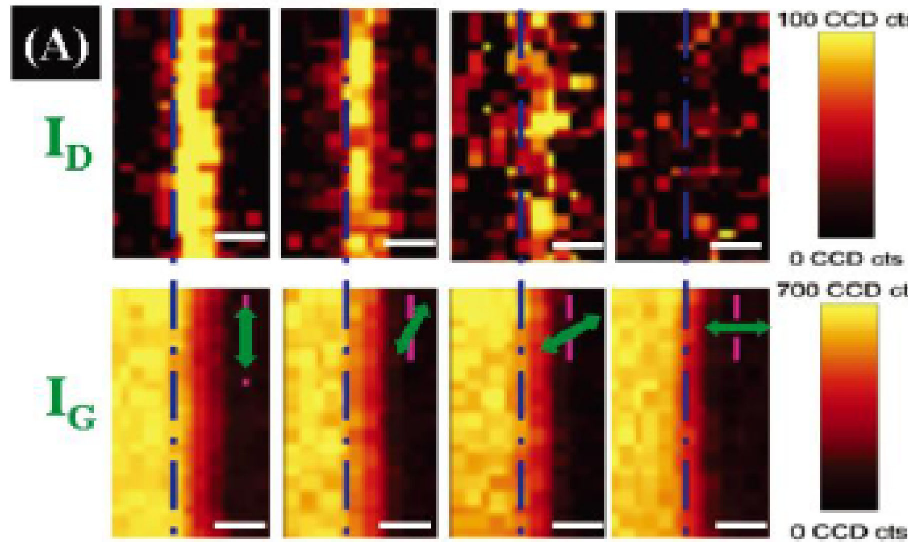


Polarization dependence of G

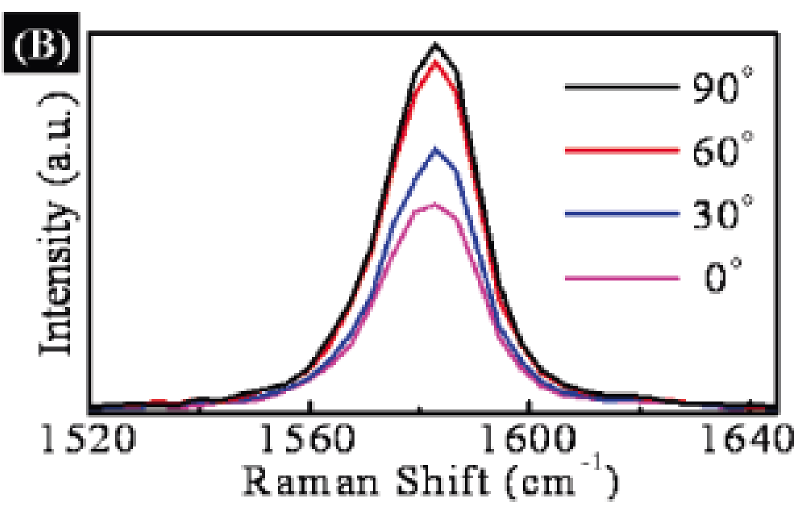
C. Cong, T. Yu and H. Wang
ACS Nano, 2010, **4**, pp 3175

Two different polarization-dependences

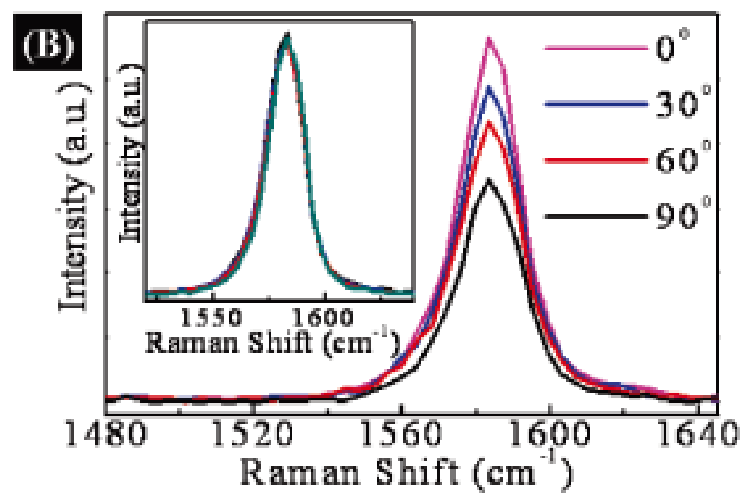




Scale bar 400 nm



60% Zigzag, 40% Armchair



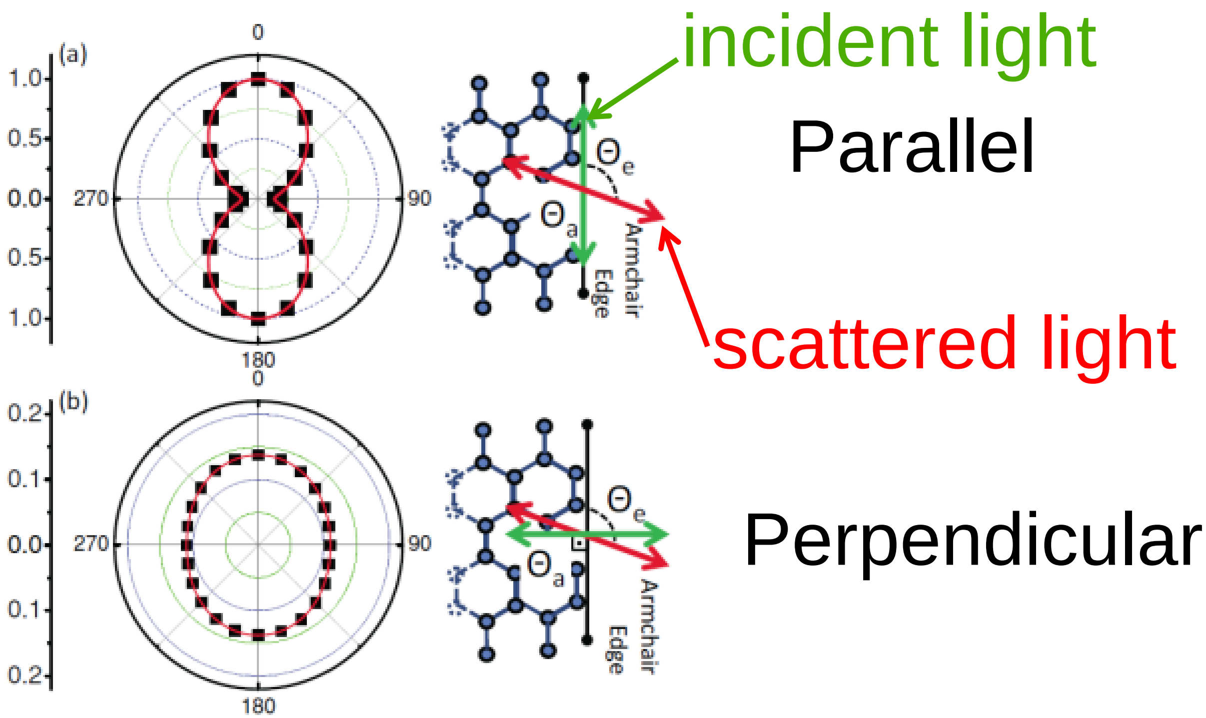
60% Armchair, 40% Zigzag

Polarization dependence of D at edges

K. Sasaki et al. Phys. Rev. B 82 205407 (2010)

E. Barros et al. Phys. Rev. B 83, 245435, (2011).

Armchair edge



electron-phonon ⇔ pseudo spin of graphene

experiment: Honjie Dai group (unpublished)

Edge of graphene layer

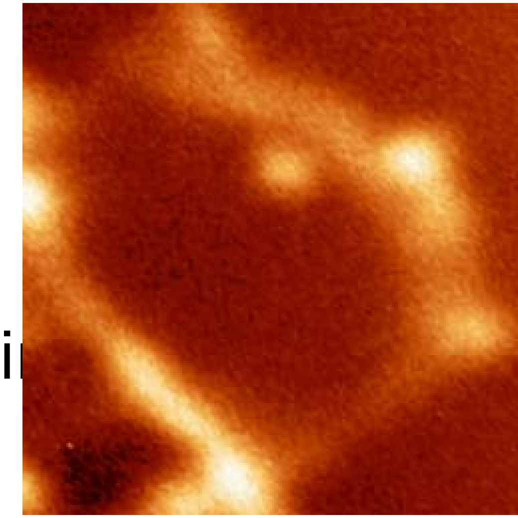
(1)Strong D-band (A)

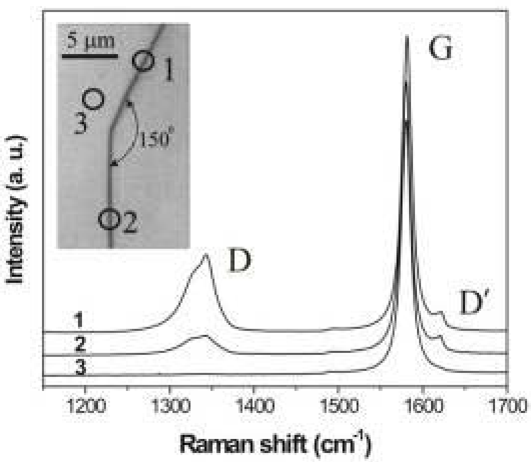
(2)kohn anomaly TO (Z) and LO (A, softeni

(3)Polarization dependence (G, D, G’)

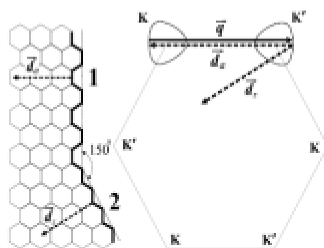
(4)1450cm^{-1} (Z) and 1530cm^{-1} (A)

D-band image





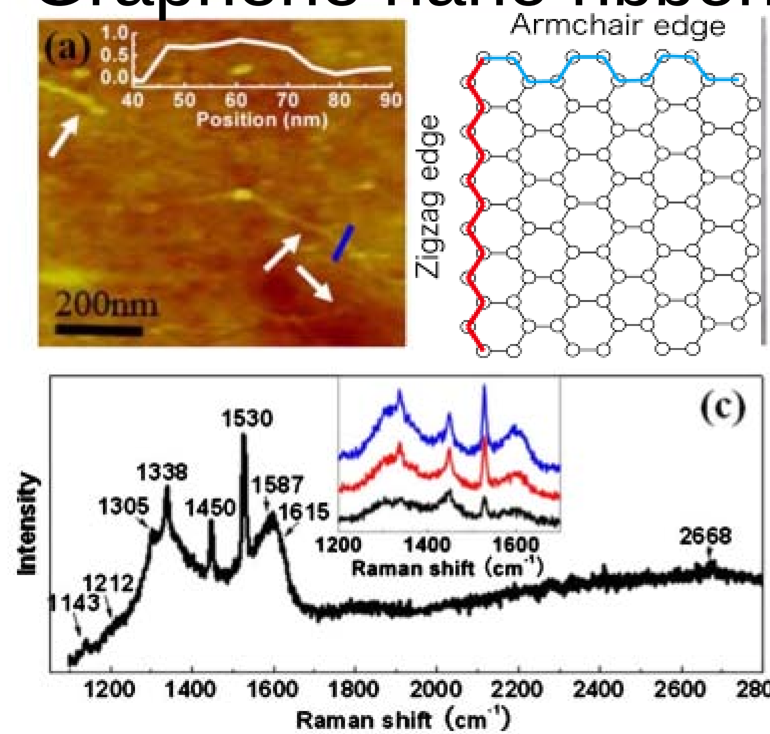
L. G. Cançado, et al. Phys. Rev. Letters, 93, 247401 (2004)



1450cm^{-1}(Z)
1530cm^{-1}(A)

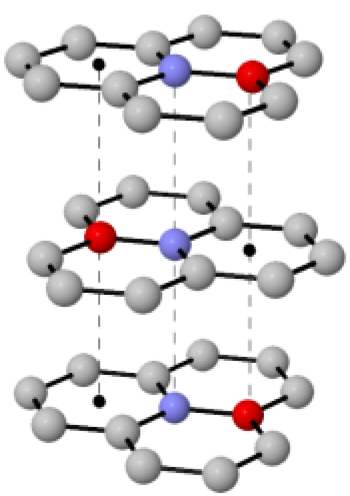
W. Ren et al., Phys. Rev. B 81, 035412 (2010)

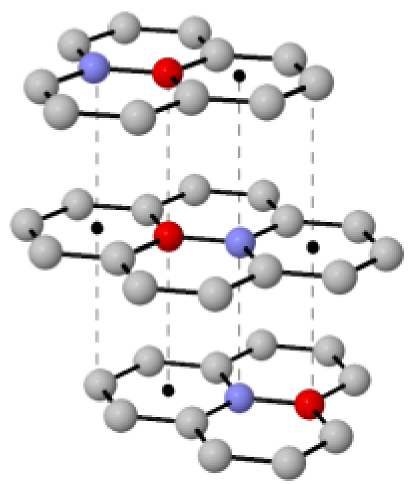
Graphene nano ribbon



Raman of 3L graphene

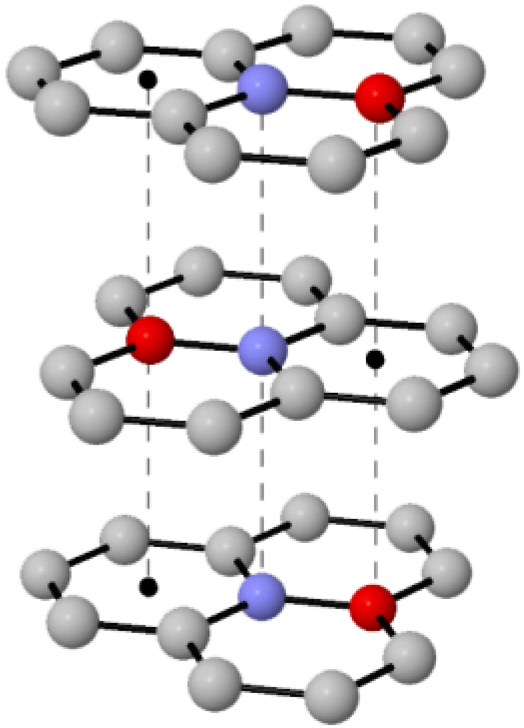
How to distinguish the stacking order?





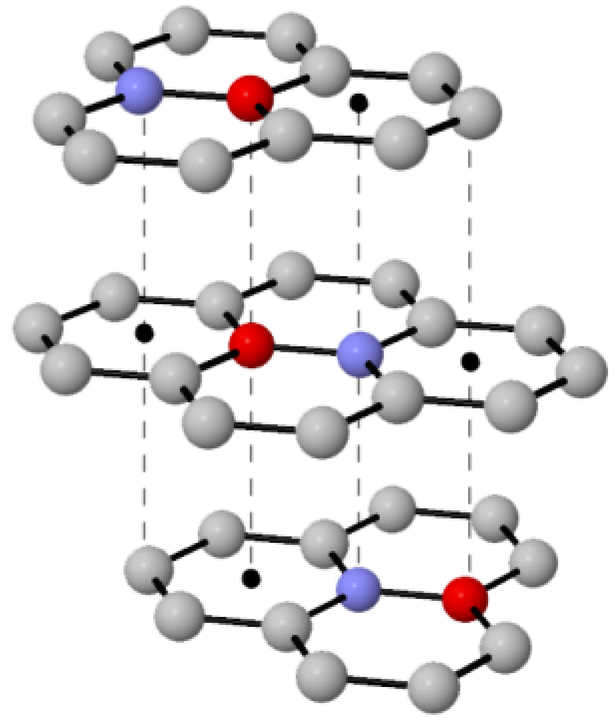
Stacking order of tri-layer graphene

ABA stacking



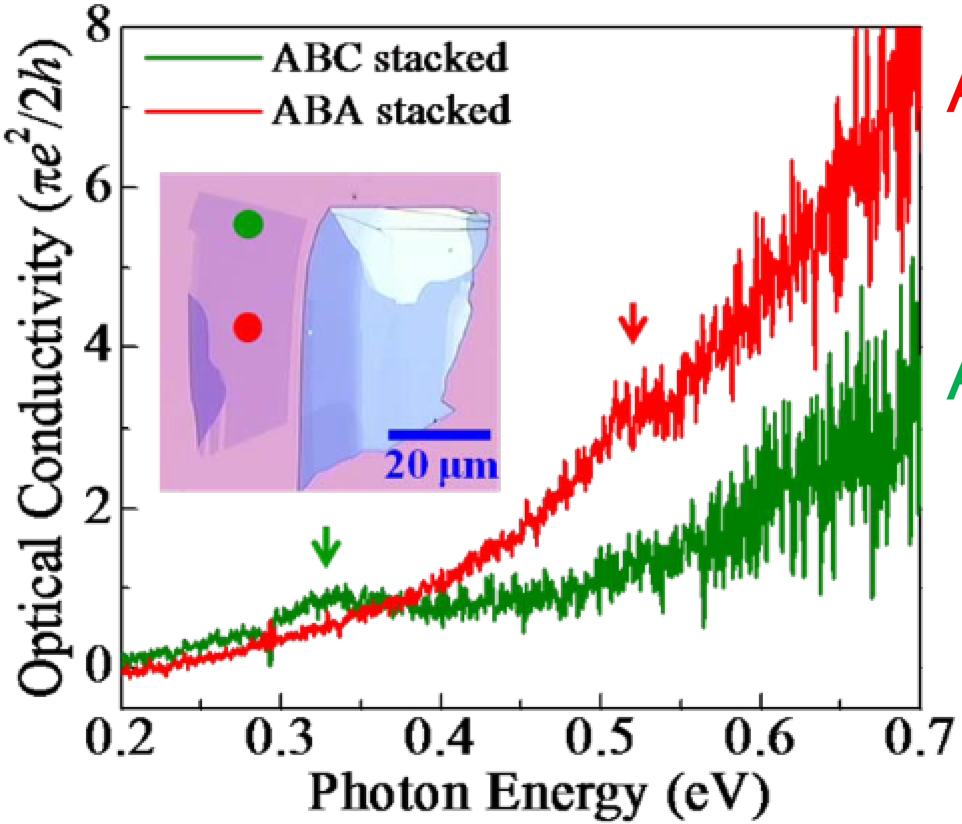
Bernal structure

ABC stacking



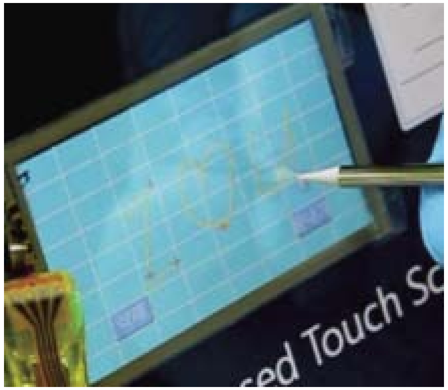
Rhombohedral structure

Optical conductivity is large for ABA stacking!
C. Cong et al., ACS Nano 5, 8760 (2011).



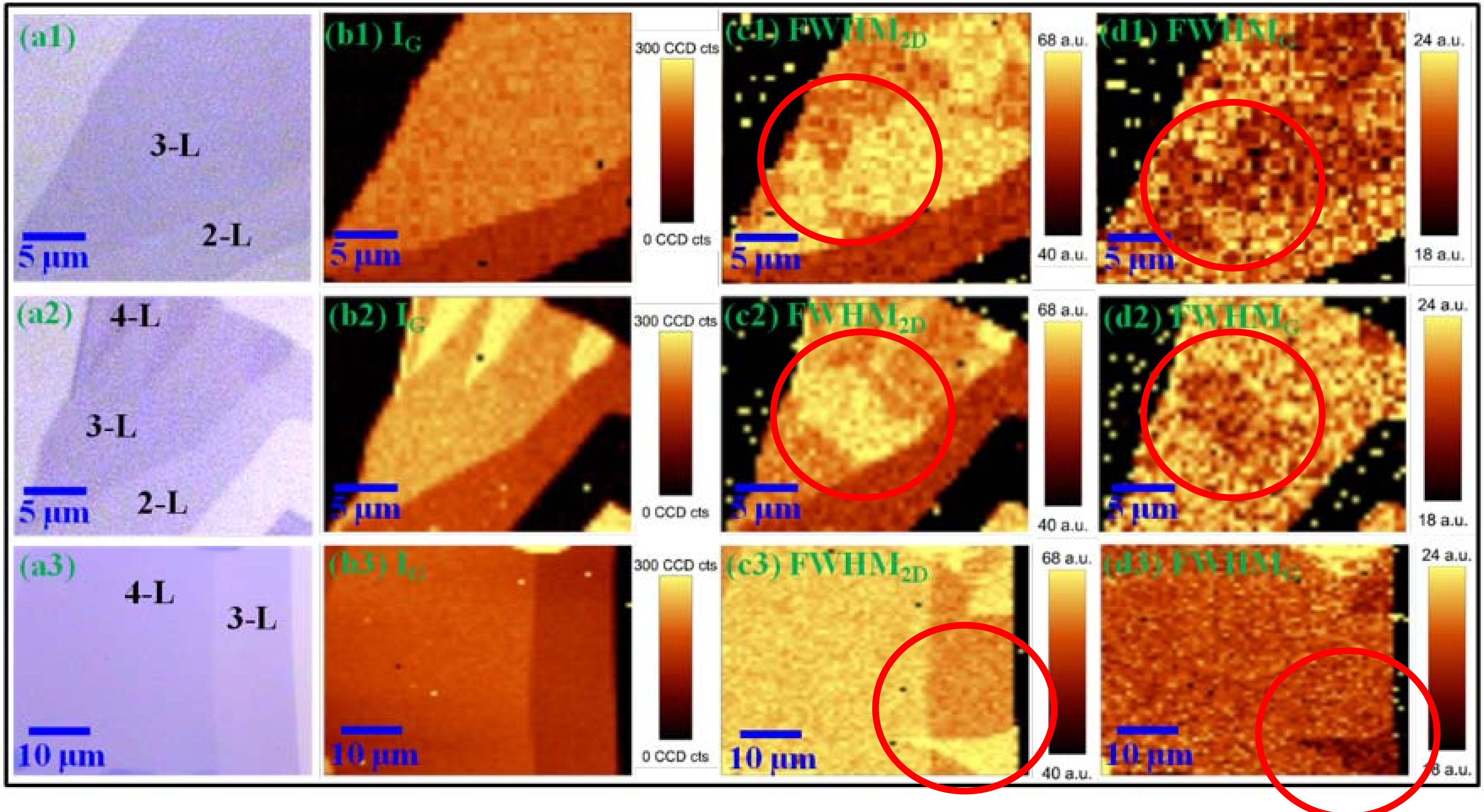
ABA

ABC



Optical and Raman images of 3L graphene

C. Cong et al., *in press*, ACS Nano (2011)



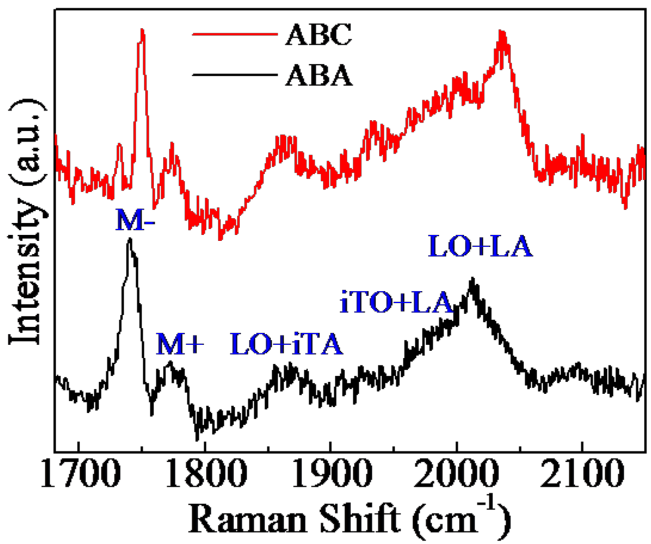
optical Intensity (G) FWHM (G') FWHM (G)

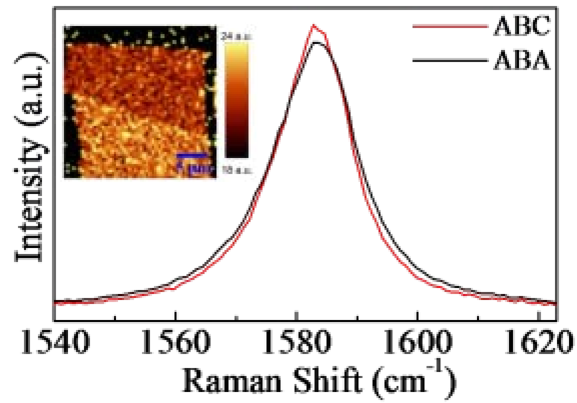
Distinguishable, however, sensitive to environment!!

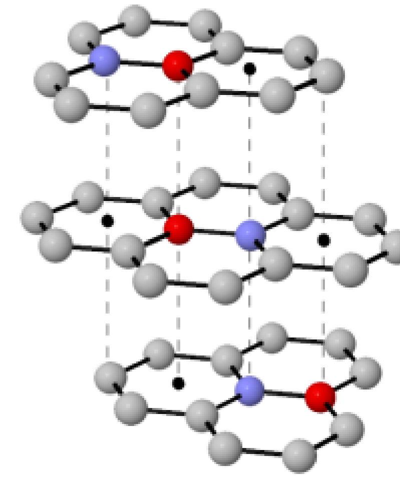
Spectral difference between ABA and ABC

C. Cong et al., ACS Nano 5, 8760 (2011)

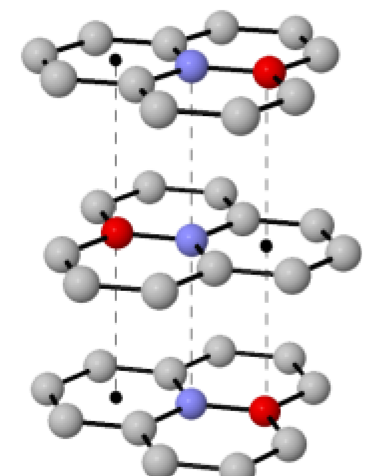
ABC







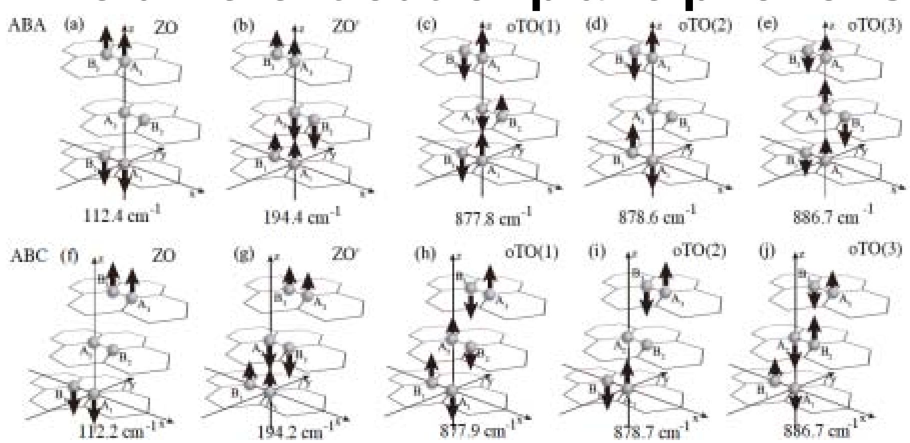
ABA



Five different out-of-plane phonons

ABA

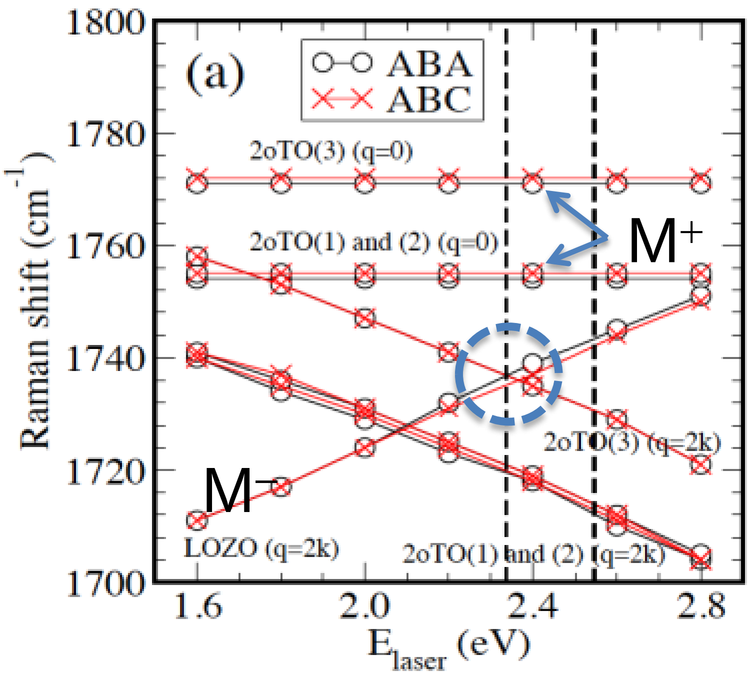
ABC



Phonon frequency is the same!

Spectral difference between ABA and ABC

C. Cong et al., ACS Nano 5, 8760 (2011).

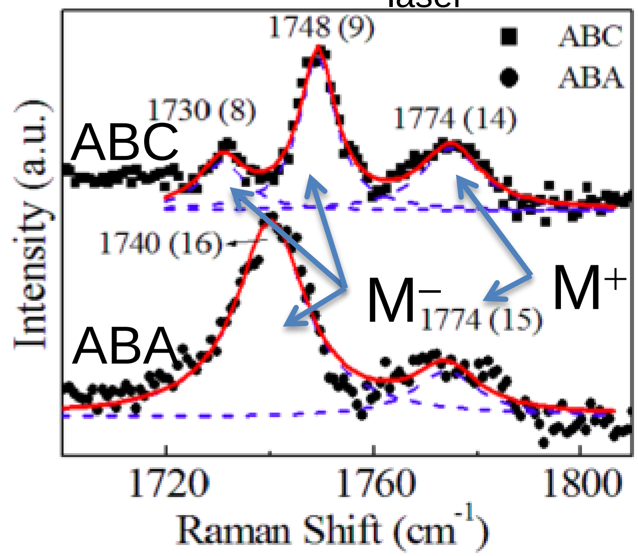


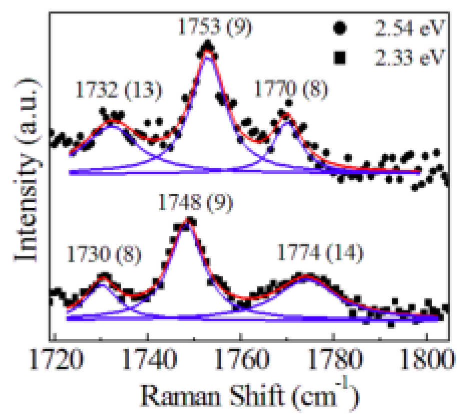
Raman spectra changes as E_{laser} changes

→ double resonance Raman

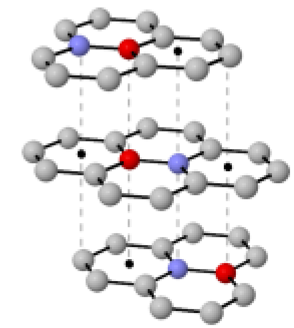
Around 1740cm^{-1}

E_{laser} = 2.33 eV

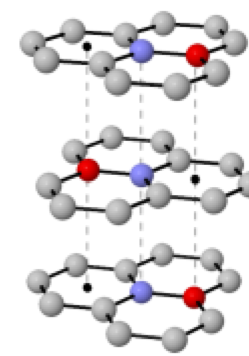


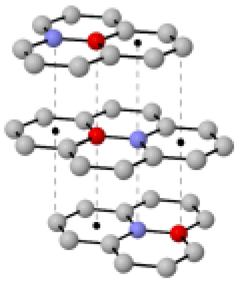


ABC

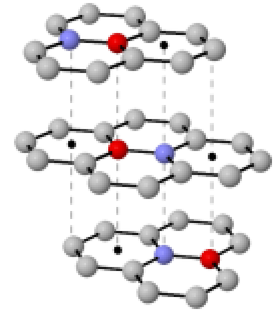


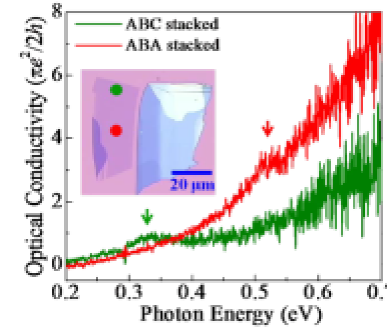
ABA



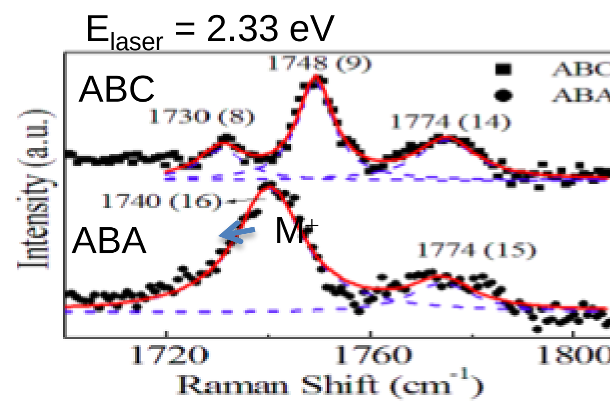


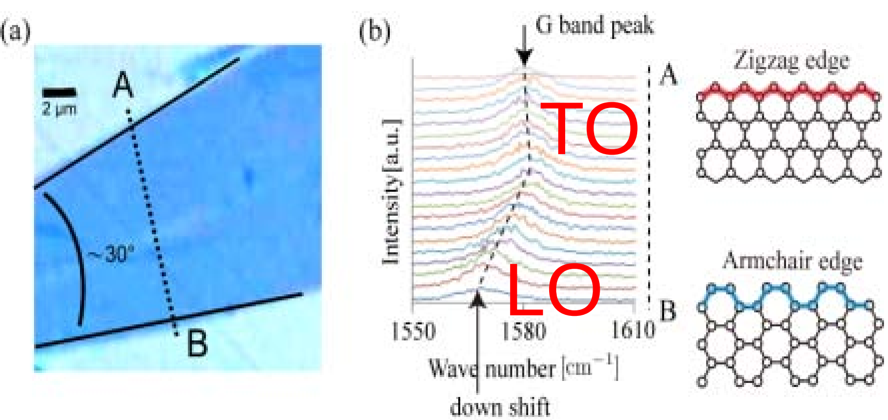
Summary of graphene

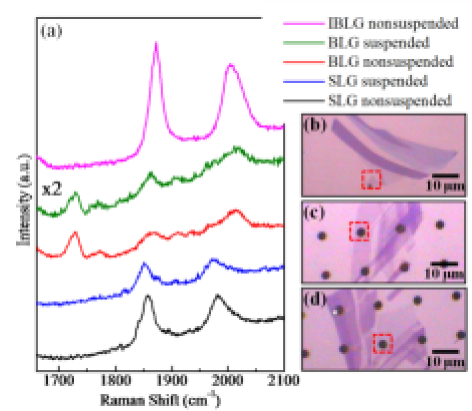


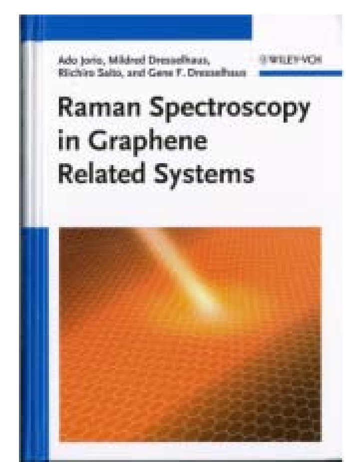


- *Stacking order of graphene*
  - *1800-2000cm^{-1} new modes*
  - *number of layers. edge shape*
  - *Graphene edge characterization*
  - *ABA and ABC stacking in 3L-G*
    - *Width of G and G' band*
    - *double resonance Raman 1740cm^{-1} peak*

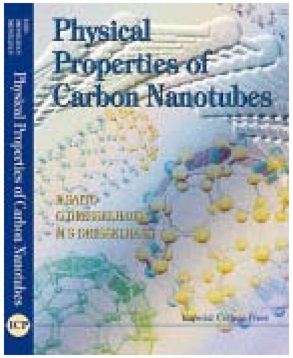




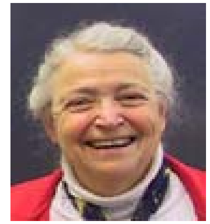




Books and review articles of groups

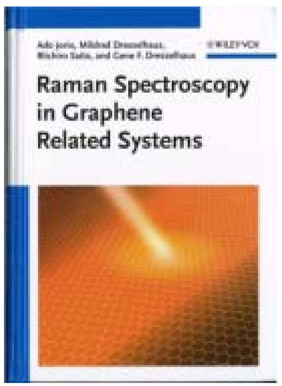


R. Saito et al. "Physical Properties of Carbon Nanotubes" Imperial College press (1998)



M. S. Dresselhaus et al.

Nano Lett. 10, 751 (2010)
Phys. Rep. 409, 47-99 (2005)
Matel. Sci. Eng. 23, 129 (2003)
Carbon 40 2043 (2002)
Carbon 33 883 (1995)



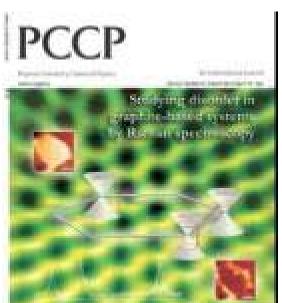
A. Jorio et al. "Raman Spectroscopy in Graphene Related Systems" Wiley VCH (2011)

R. Saito et al.

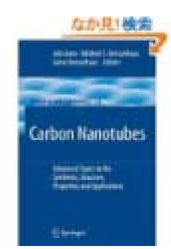
Adv. in Phys. 60, 413-550, (2011).
New. J. Phys. 5, 157.1.-15 (2003).

A. Jorio et al.

New. J. Phys. 5, 139.1-17 (2003)



M. A. Pimenta et al.
Phys. Chem. Chem. Phys. 9, 1276 (2007) for D-band



Thank you.