Quantum Transport and Dynamics in Nanostructures

The 4th Windsor Summer School on Condensed Matter Theory

6-18 August 2007, Great Park Windsor (UK)

Physics of Nanotubes, Graphite and Graphene

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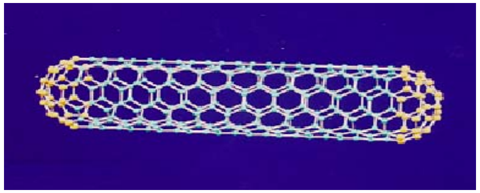
Physics of Nanotubes, Graphite and Graphene

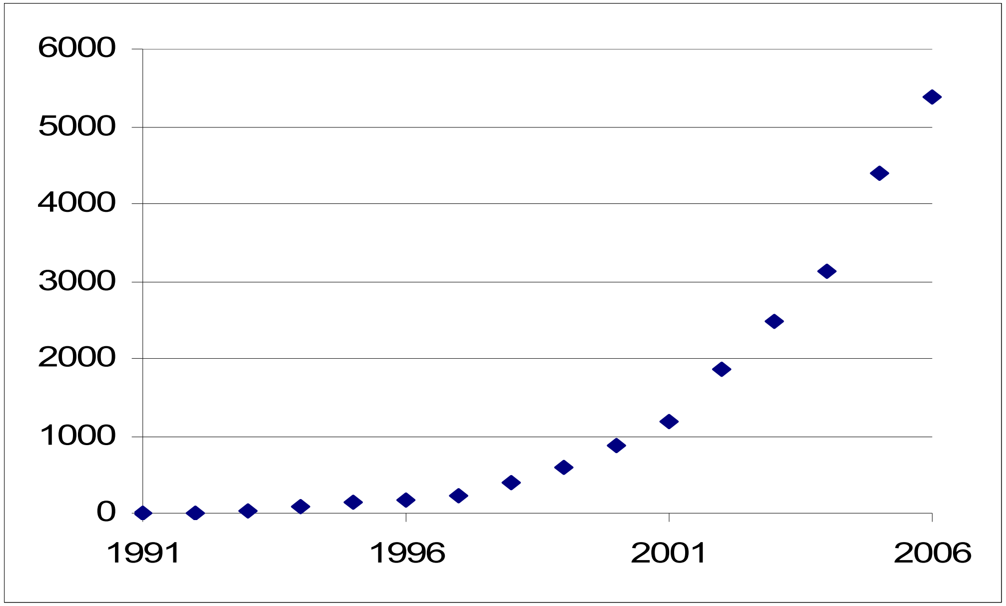
Outline of Lecture 1 - Nanotubes

- **Brief overview of carbon nanotubes**
- **Review of Photophysics of Nanotubes**
- **Phonon assisted Photoluminescence**
- **Double wall carbon nanotubes**
- **Nano-Metrology**

Carbon Nanotube research-
still a growing field

- ***1991 nanotube observation by Sumio Iijima (NEC) opening field***
- ***number of publications is still growing exponentially***

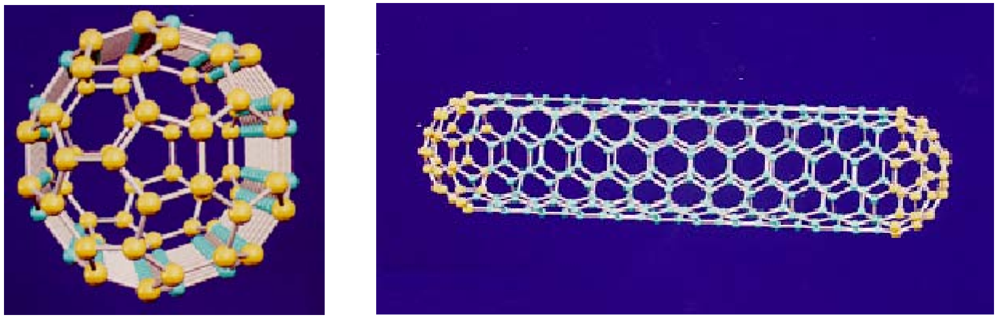




number of publications containing “Carbon Nanotube” vs. time

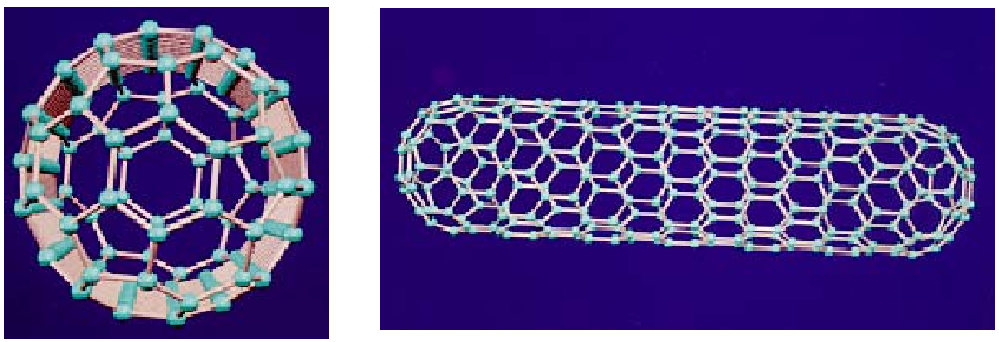
Iijima, S., *Helical Microtubules of Graphitic Carbon.* Nature, 1991. **354**(6348): p. 56-58.

Carbon Nanotubes



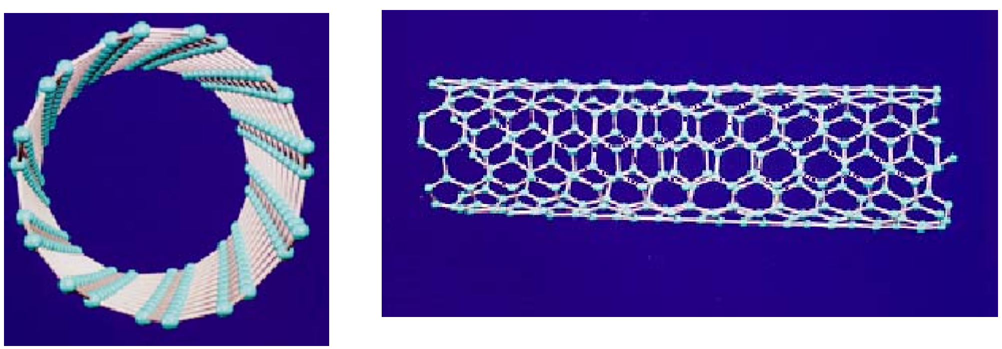
(5,5)

Armchair Nanotube



(9,0)

Zigzag Nanotube



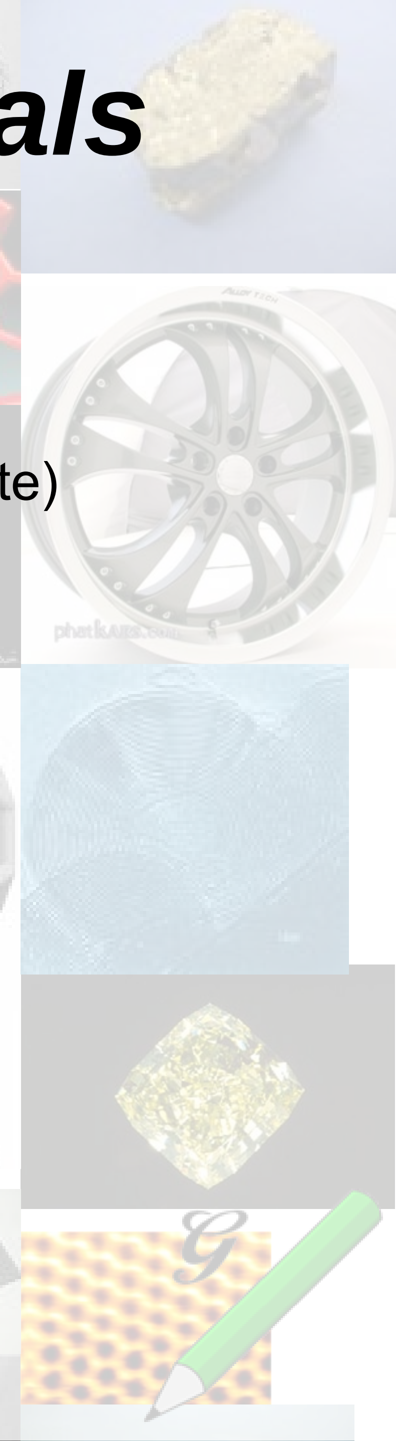
(6,5)

Chiral Nanotube

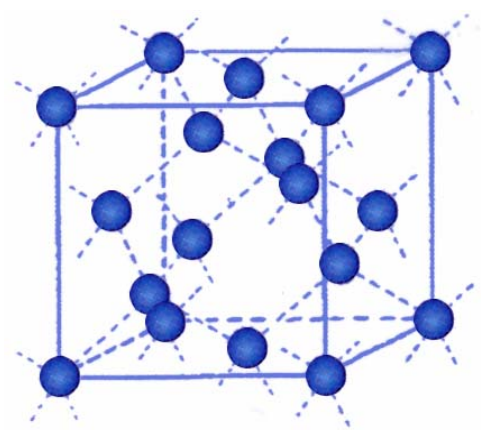
(*n*,*m*) notation focuses on symmetry of cylinder edge

Carbon materials

- Diamond
- Graphite (hexagonal, rhombohedral)
- HOPG (highly oriented pyrolytic graphite)
- Pyrolytic graphite
- Turbostratic graphite
- Kish graphite
- Liquid carbon
- Amorphous carbon
- Carbon and graphitic foams
- Carbon fibers
- Fullerenes
- Nanotubes
- Nanohorns
- Graphene fibers and scrolls
- Graphene
- Graphene ribbons

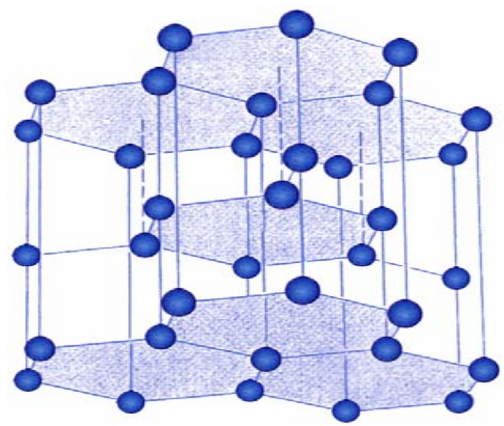


3D, 2D, 1D Carbon Materials



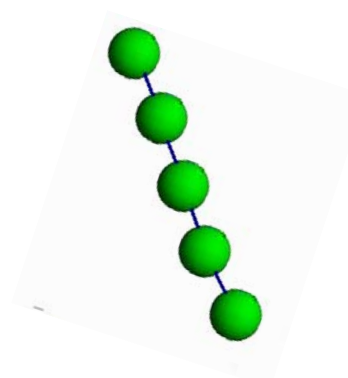
Diamond

sp^3 **(3D) 1332 cm**$^{-1}$



Graphite

sp^2 **(2D) 1582 cm**$^{-1}$

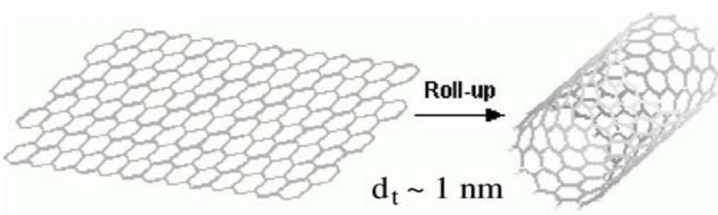


Chain

sp^1 **(1D) 1855 cm**$^{-1}$

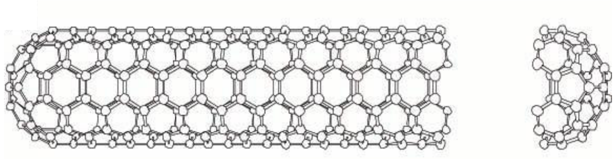
All are Raman active with characteristic frequencies

Unique Properties of Carbon Nanotubes within the Nanoworld

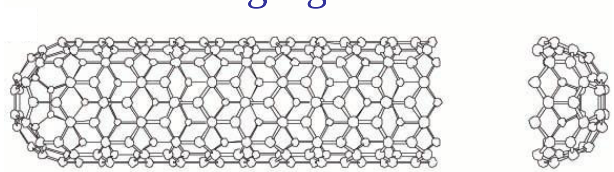


graphene sheet SWNT

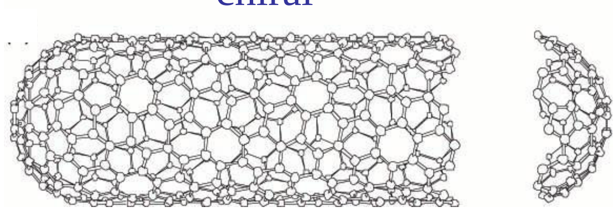
armchair



zigzag



chiral



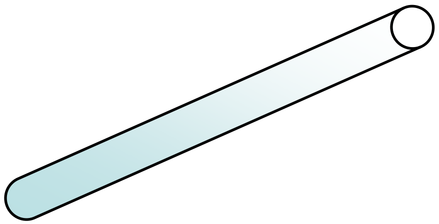
- Size: Nanostructures with dimensions of ~1 nm diameter (~10 atoms around the cylinder)

- Electronic Properties: Can be either metallic or semiconducting depending on diameter and orientation of the hexagons

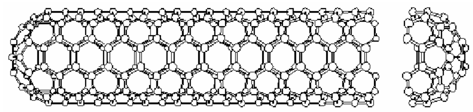
- Mechanical: Very high strength, modulus, and resiliency. Good properties on both compression and extension.

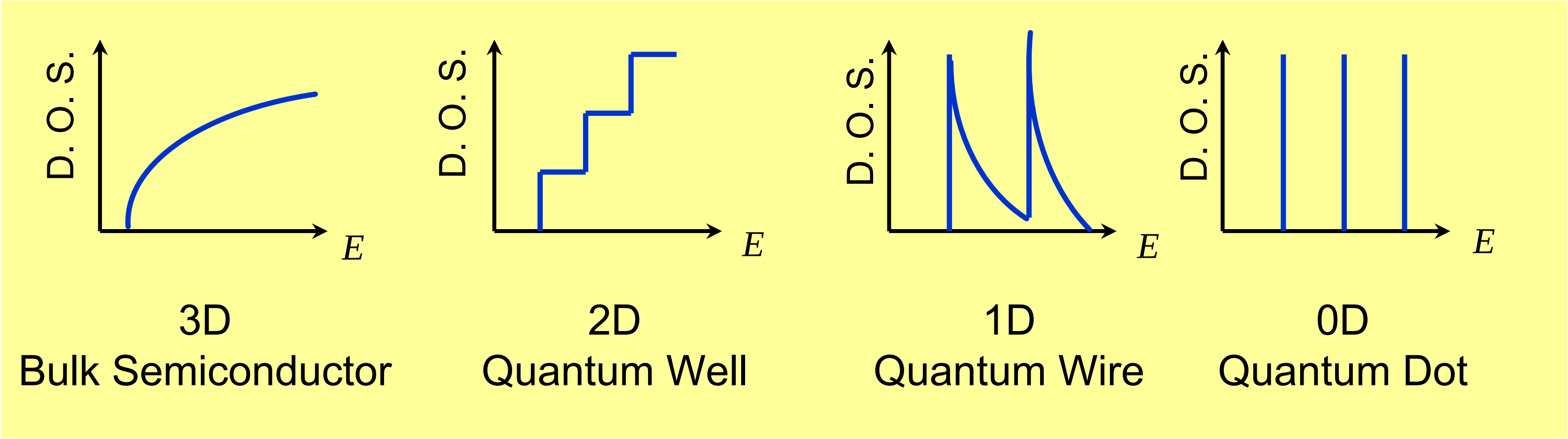
- Physics: 1D density of electronic states
- Single molecule Raman spectroscopy and luminescence.
- Single molecule transport properties.
- Heat pipe, electromagnetic waveguide.

One Dimensional Systems:

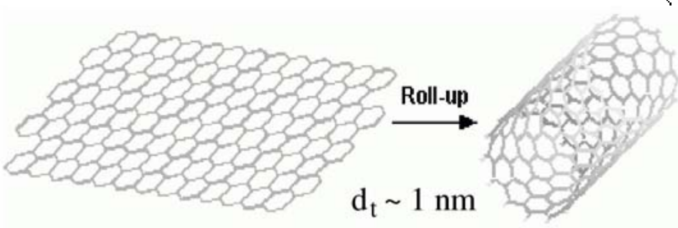


- **High aspect ratio**
- **Enhanced density of states**
- **Single wall carbon nanotubes SWNT: Chirality and diameter-dependent properties**



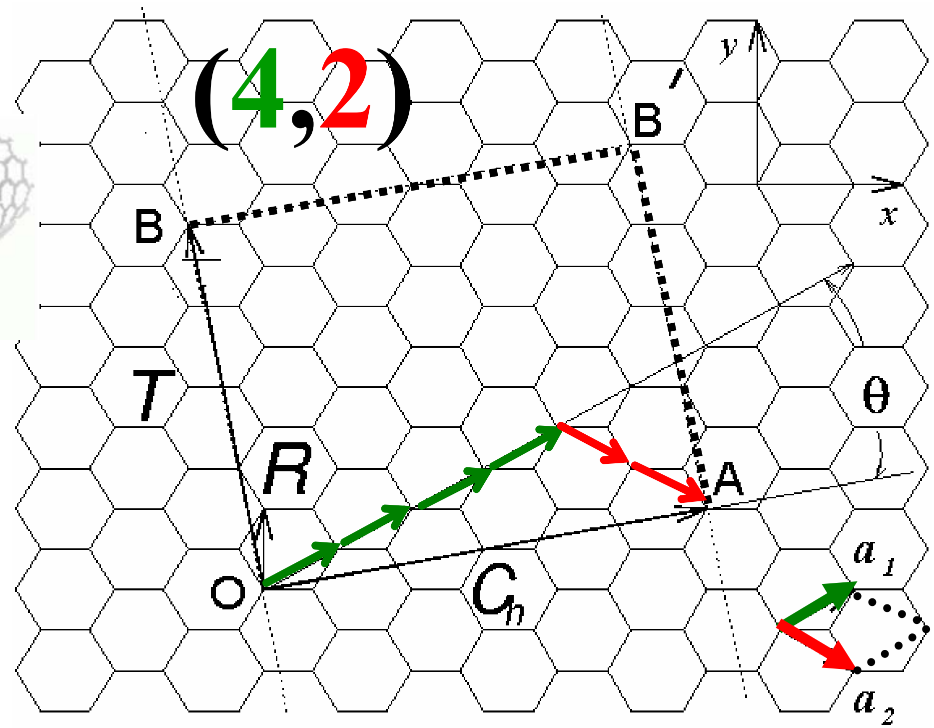


Nanotube Structure in a Nutshell



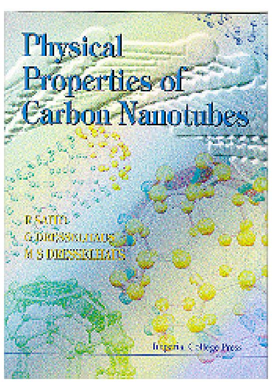
Graphene Sheet **SWNT**

Rolled-up graphene layer
Large unit cell.



$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n,m)$$

$$\begin{cases} d_t = \dfrac{L}{\pi} = \dfrac{a}{\pi}\sqrt{n^2 + nm + m^2} \\ \theta = \tan^{-1}\dfrac{\sqrt{3}m}{2n+m} \end{cases}$$

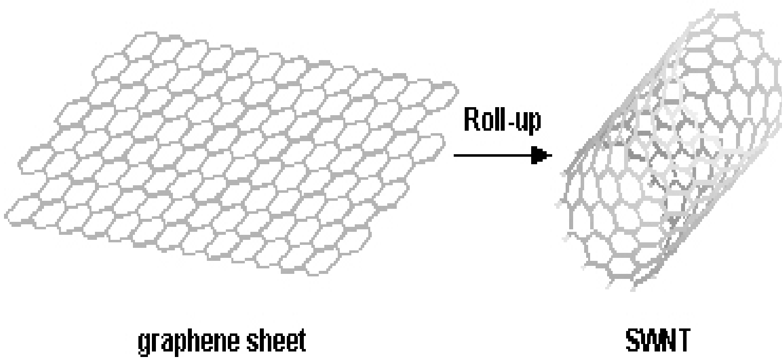


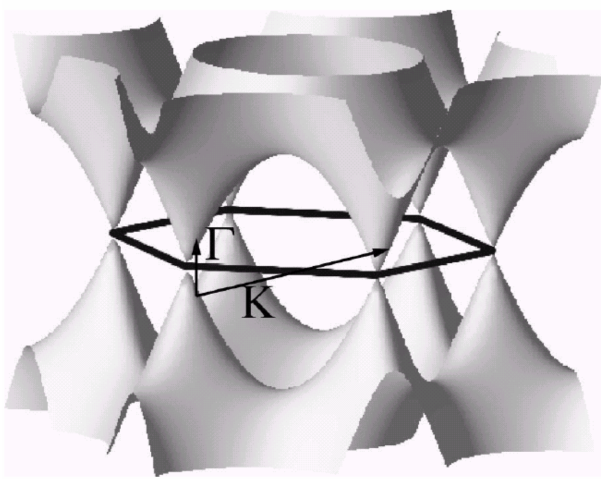
Each (*n*,*m*) nanotube is a unique molecule

R.Saito et al, Imperial College Press, 1998

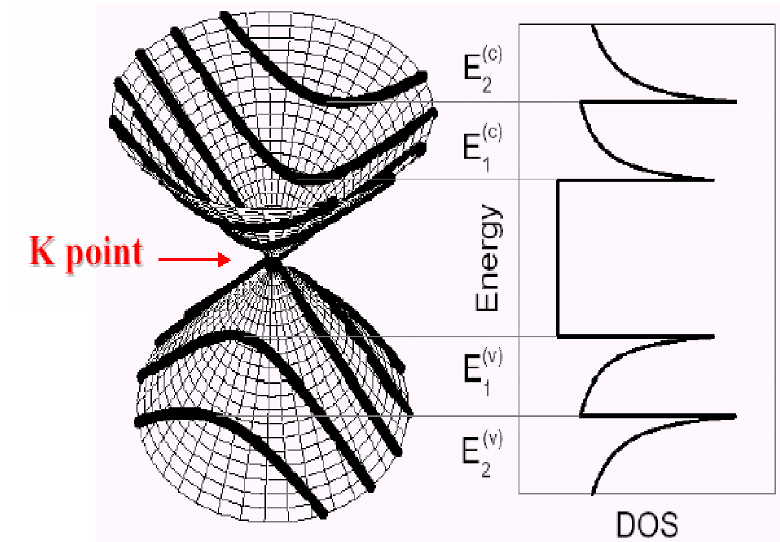
Electronic structure of a carbon nanotube

Rolling up 2D graphene sheet





Confinement of 1D electronic states



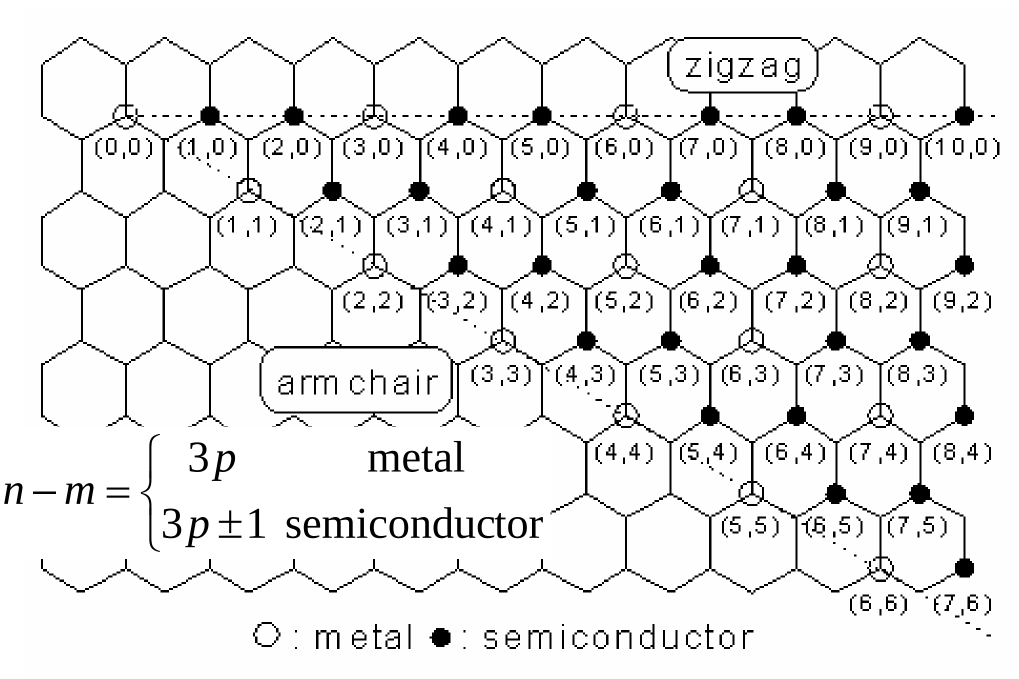
1D van Hove singularities - high density of electronic states (DOS) at well defined energies

Graphene ribbons resemble nanotubes in some ways

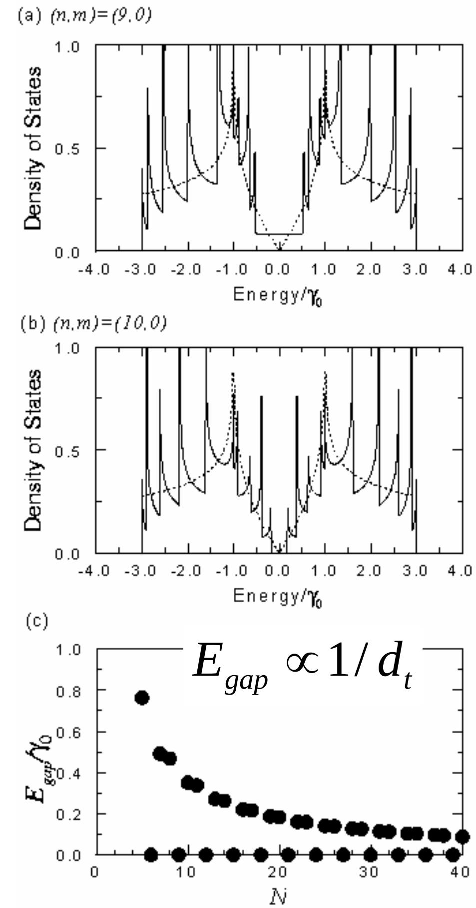
Metal or *Semiconductor* ?

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

- Density of States
- Depending on Chirality, Diameter



$$n - m = \begin{cases} 3p & \text{metal} \\ 3p \pm 1 & \text{semiconductor} \end{cases}$$



Each (n,m) nanotube is a unique molecule

Armchair graphene ribbons can be M or S

Physics of Nanotubes, Graphite and Graphene

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- **Double wall carbon nanotubes**
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Resonance Raman Spectroscopy (RRS)

A.M. Rao *et al.*, *Science* **275** (1997) 187

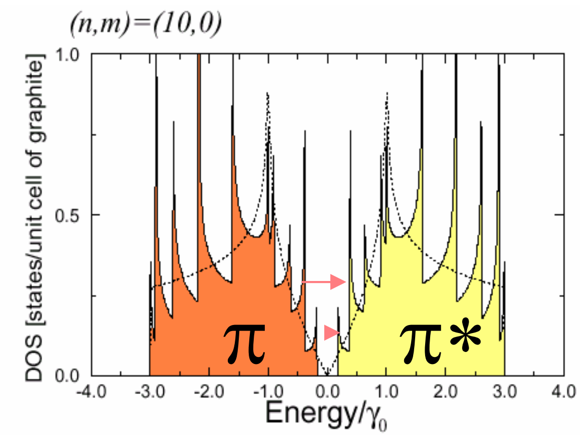
RRS: R.C.C. Leite & S.P.S. Porto, PRL **17**, 10-12 (1966)

Raman spectra from SWNT bundles

- Enhanced Signal

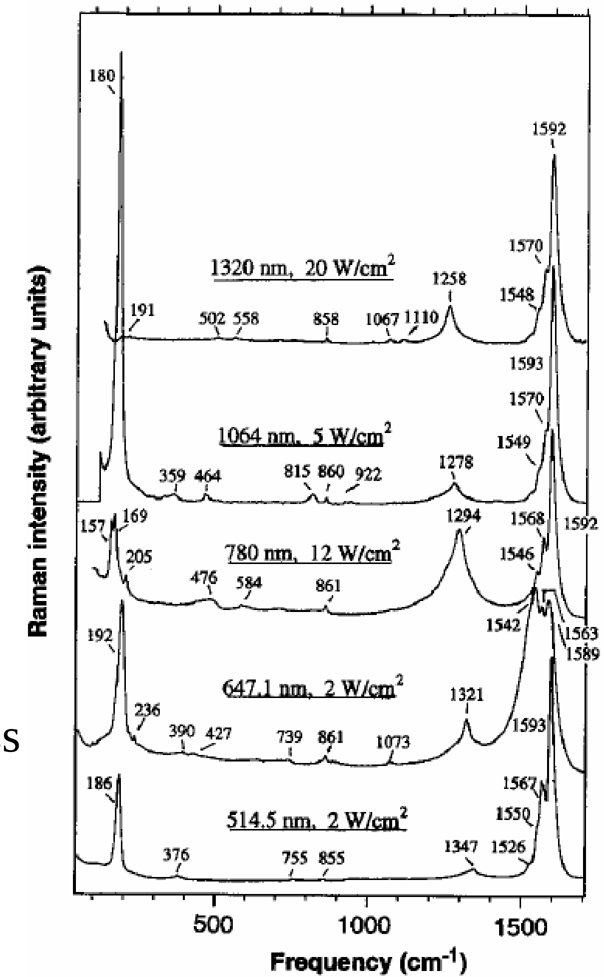
  ✓ Optical Absorption

  ✓ e-DOS peaks



diameter-selective resonance process

$$\omega_{RBM} = \alpha / d_t$$



E = 0.94eV

= 1.17eV

= 1.58eV

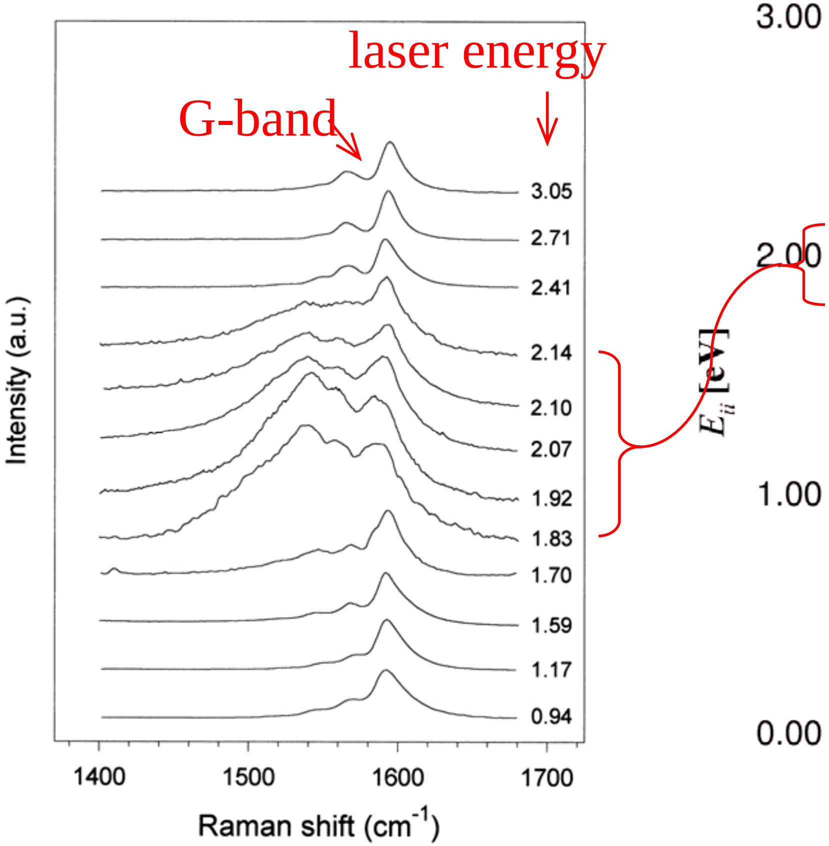
= 1.92eV

= 2.41eV

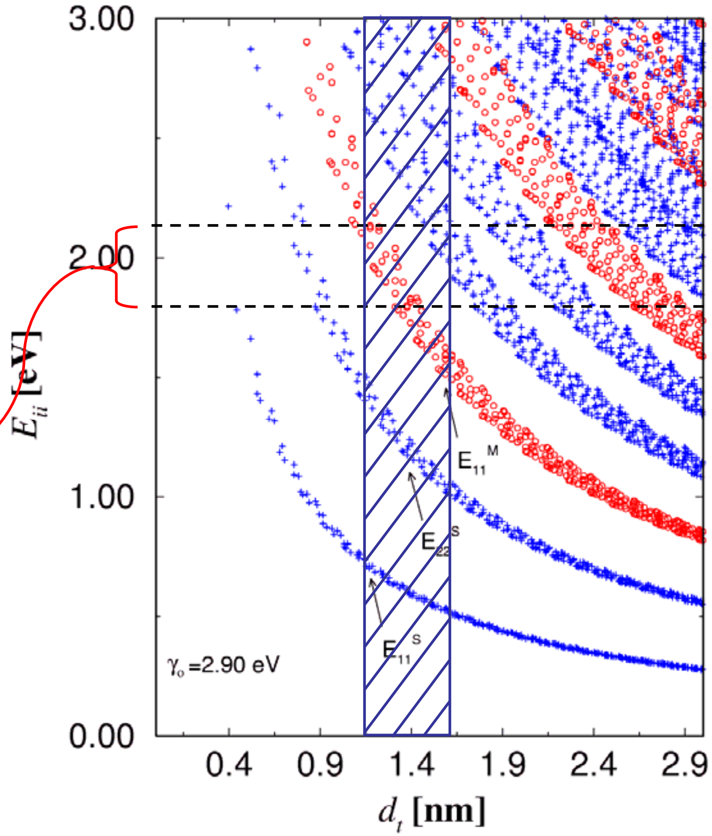
Resonant Raman Spectra of Carbon Nanotube Bundles

M. A. Pimenta (UFMG) *et al.*, *Phys. Rev.* B **58**, R16016 (1998)

G-band resonant Raman spectra



Diameter dependence of the Van-Hove singularities



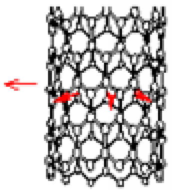
$d_t = 1.37 \pm 0.18$ nm

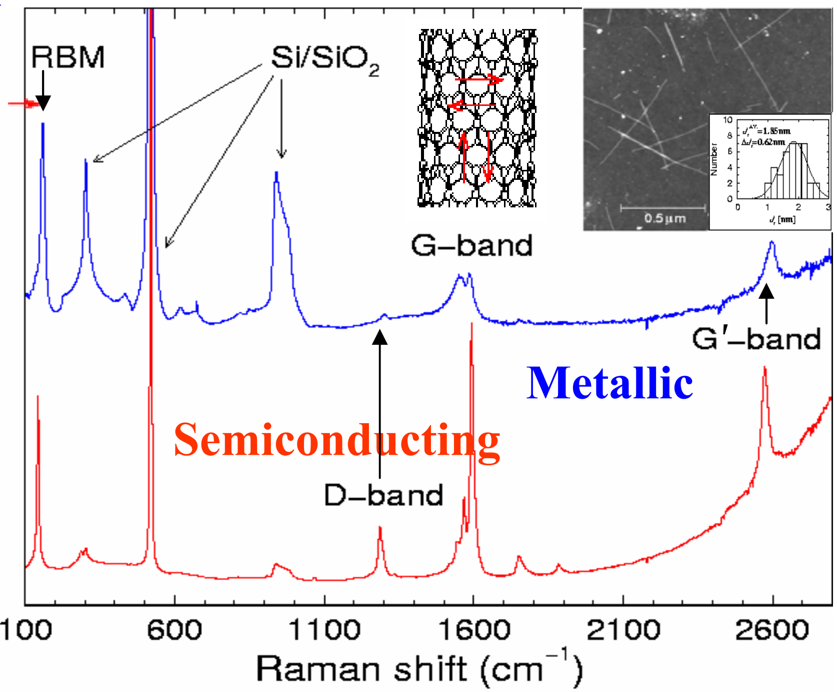
Single Nanotube Spectroscopy yields E_{ii}, (n,m)

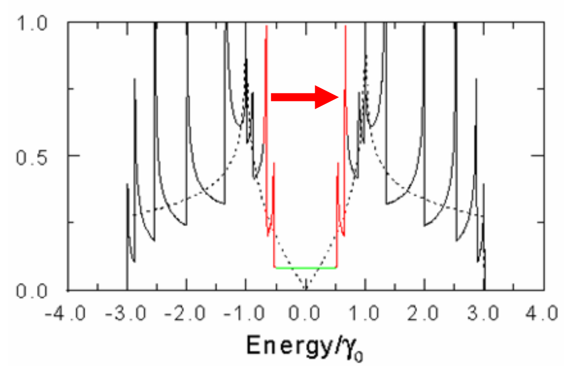
Resonant Raman spectra for isolated single-wall carbon nanotubes grown on Si/SiO_2 substrate by the CVD method

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

RBM







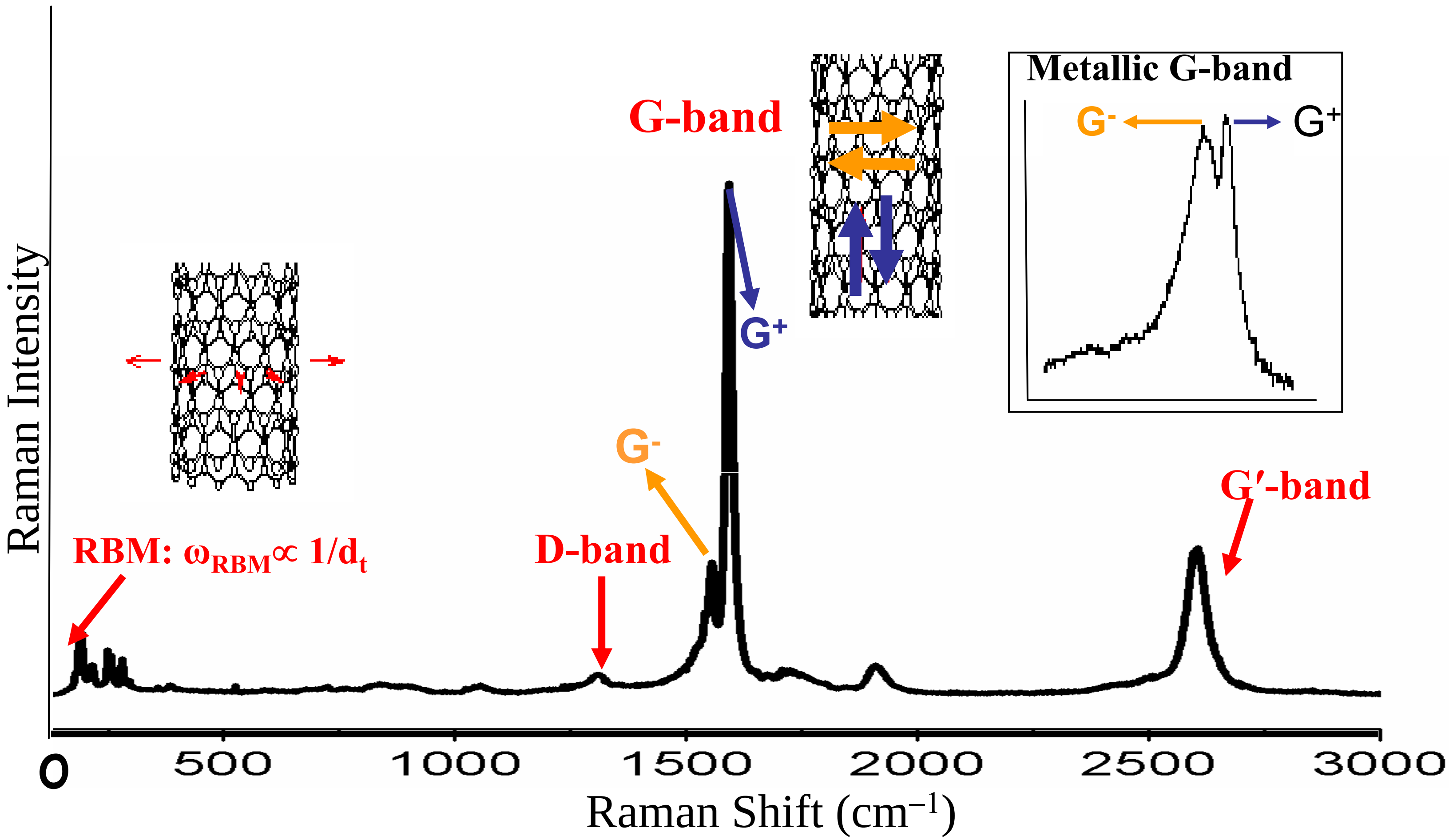
Each nanotube has a unique DOS because of trigonal warping effects

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

Raman signal from *one* SWNT indicates a strong resonance process

$(\omega_{RBM}, E_{ii}) \rightarrow (n,m)$

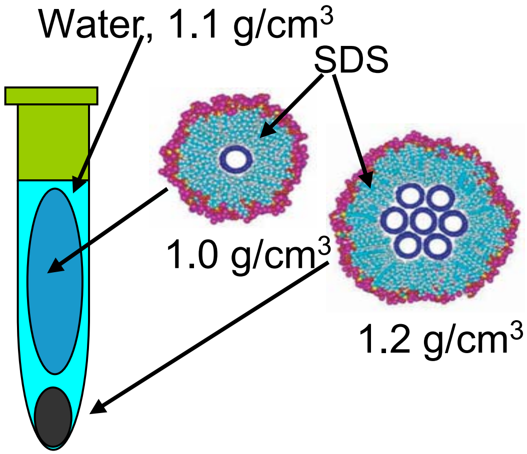
Raman Spectra of SWNT Bundles



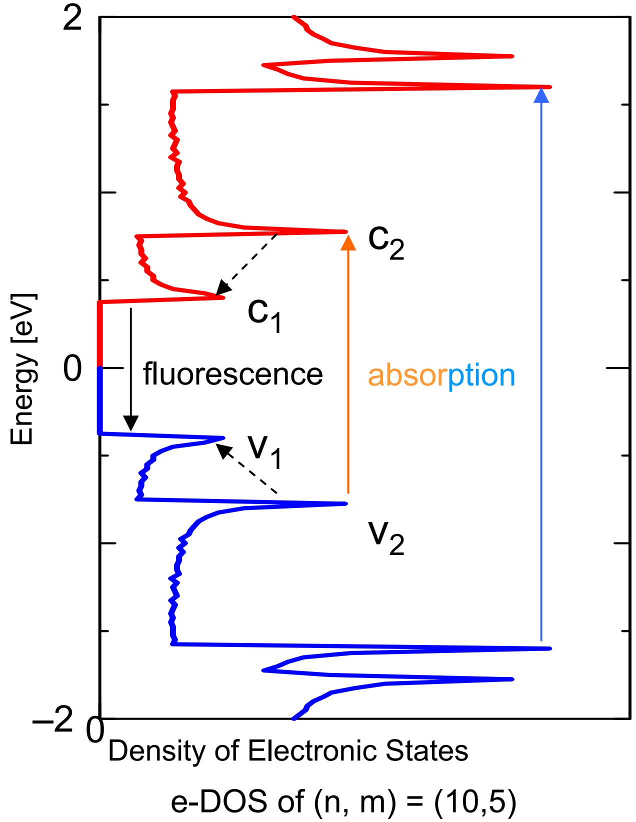
- RBM gives tube diameter and diameter distribution
- Raman D-band characterizes structural disorder
- G^- band distinguished M, S tubes and G^+ relates to charge transfer
- G’ band (2nd order of D-band) provides connection of phonon to its wave vector

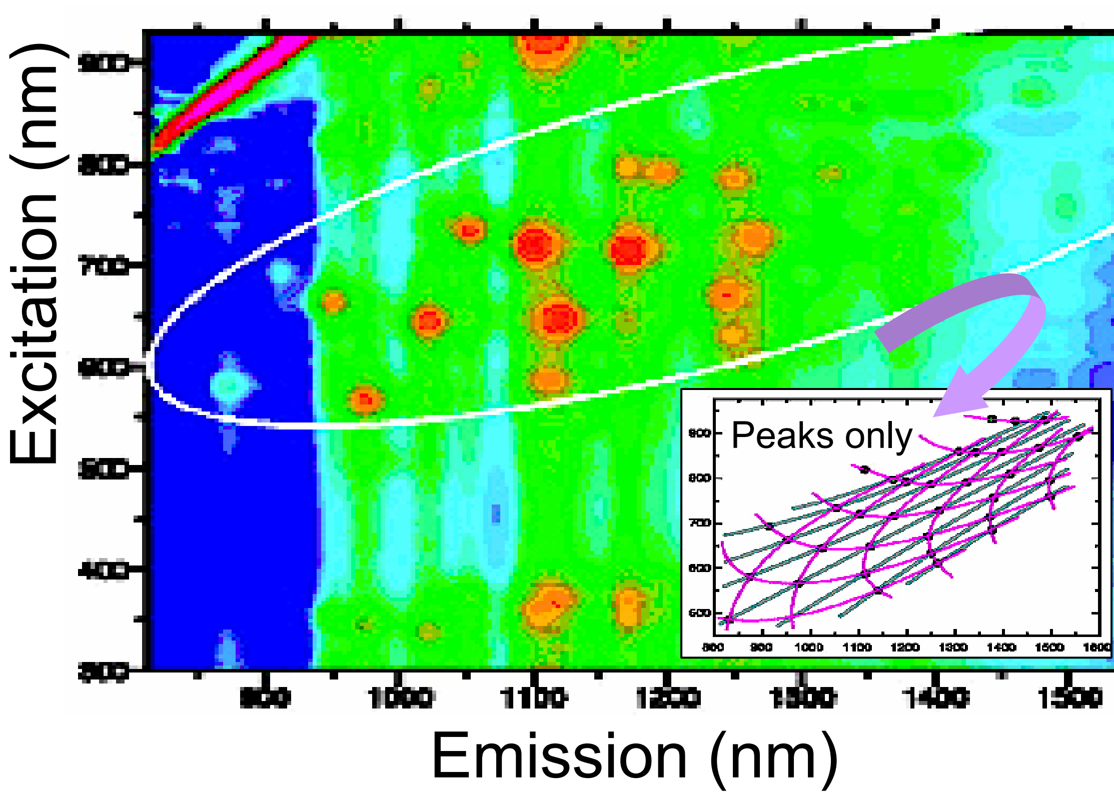
Band Gap Fluorescence

M. J. O'Connell *et al.*, Science 297 (2002) 593
S. M. Bachilo *et al.*, Science 298 (2002) 2361.



SDS=Sodium Dodecyl Sulfate



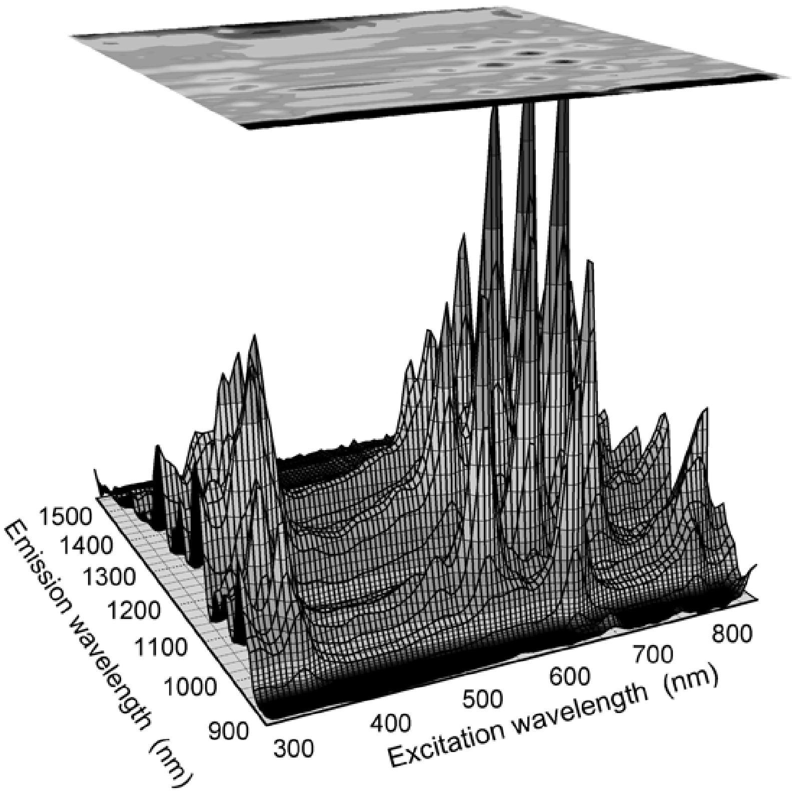


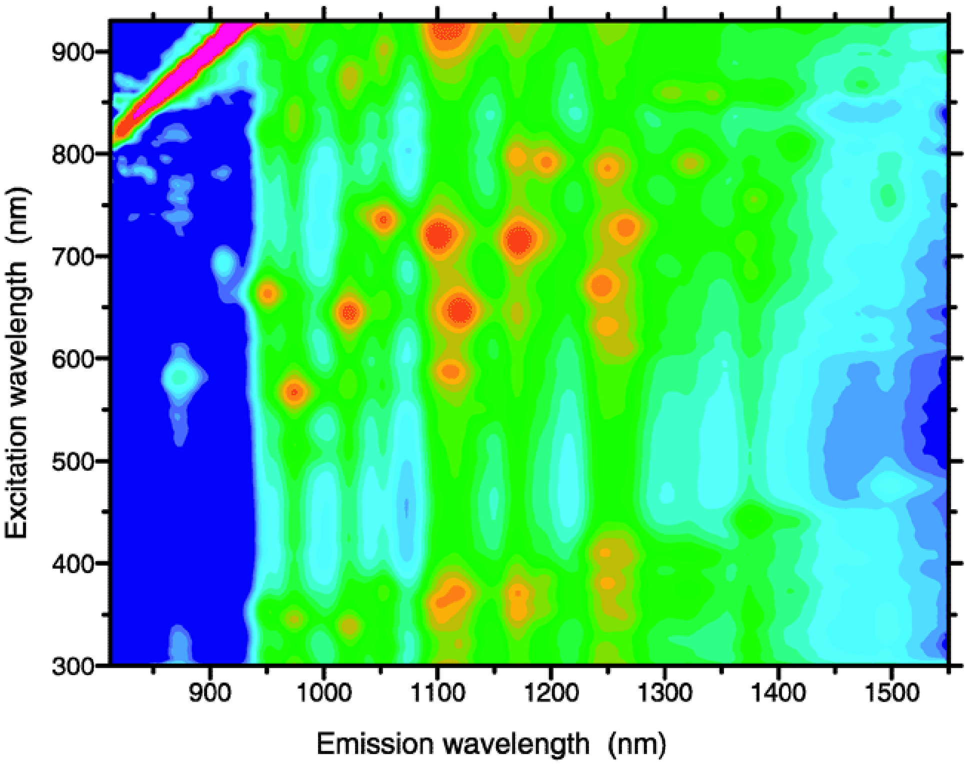
Initially (n,m) assignments were made by empirical excitation-emission pattern

PHOTOLUMINESCENCE

SDS-wrapped HiPco nanotubes in solution

S. M. Bachilo et al., Science 298, 2361 (2002)

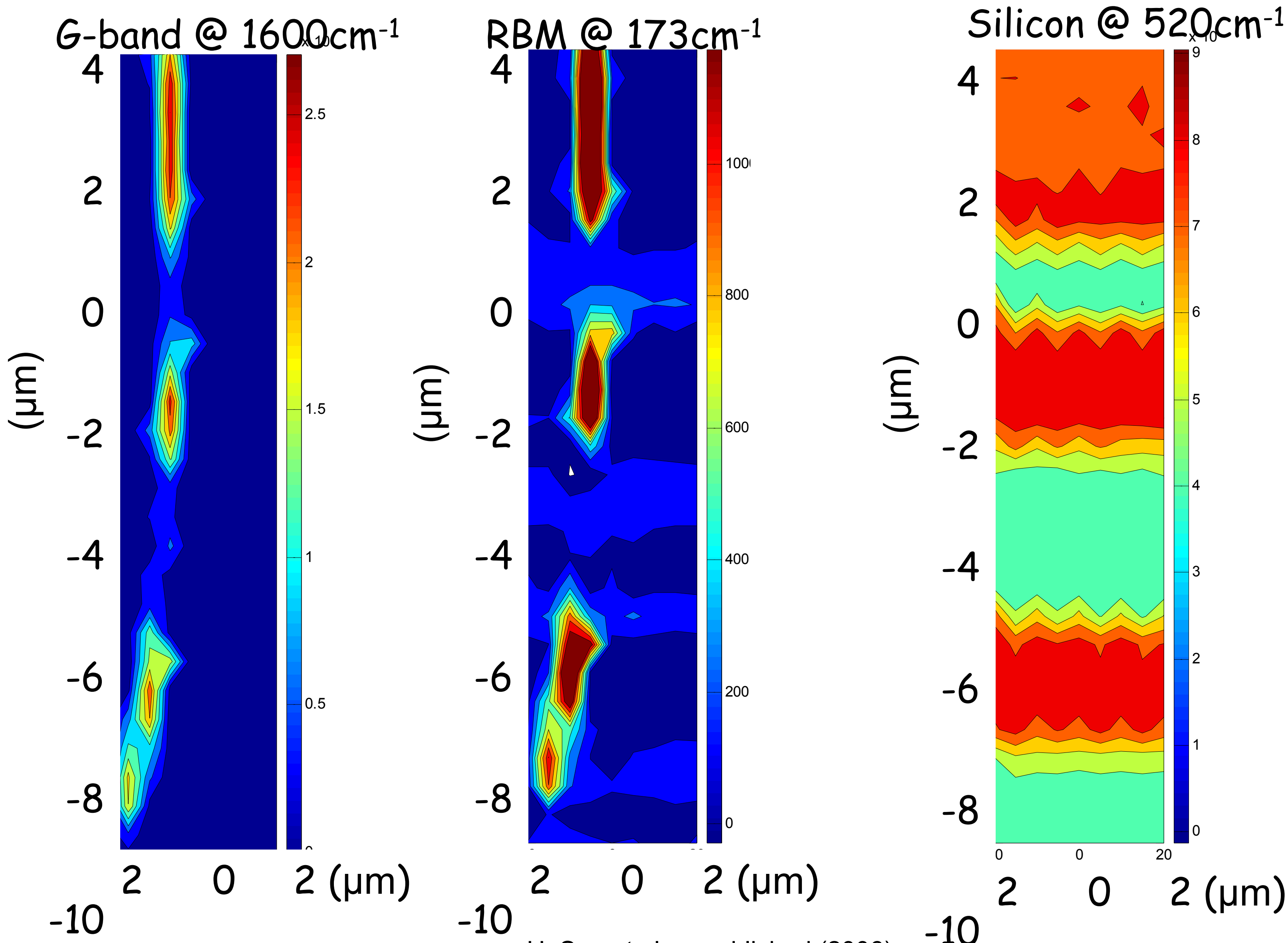




- ❖ $2n+m$=constant family patterns are observed in the PL excitation-emission spectra
- ❖ Identification of ratio problem
- ❖ Showed value of mapping optical transitions

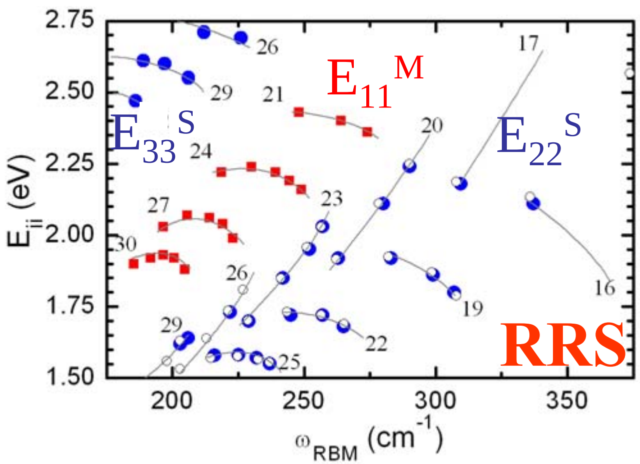
Perhaps this technique can be applied to study graphene ribbons

Raman Mapping of a Nanotube

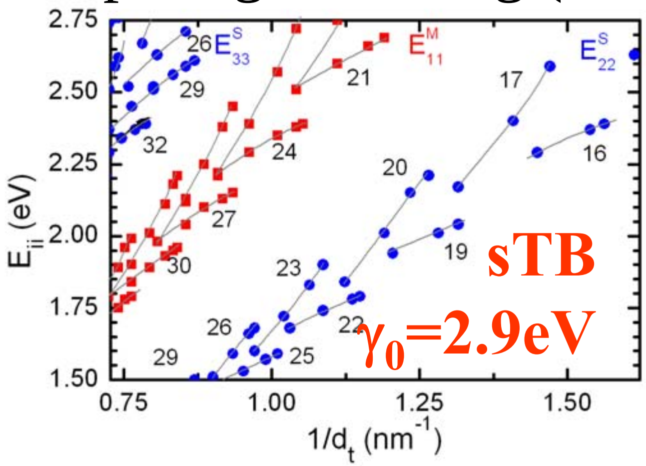


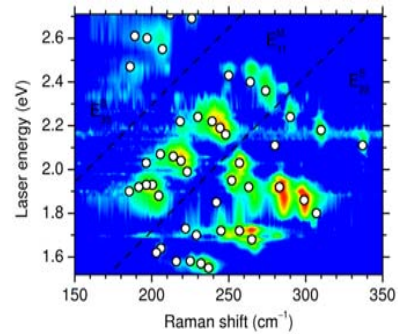
H. Son et al. unpublished (2006)

Resonance Raman Spectroscopy on the same sample used for PL



simple tight binding (**sTB**)

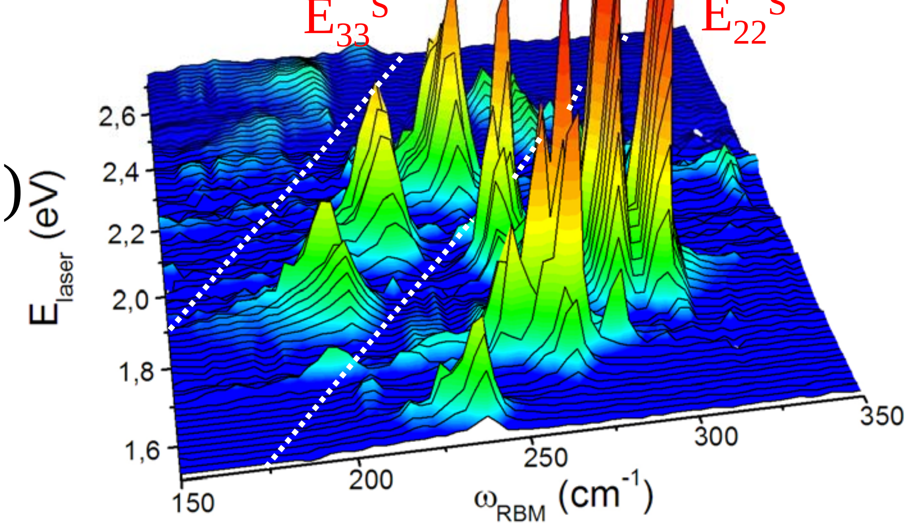




Fantini (UFMG) et al. PRL (2004) showed RRS and PL give the same E_{ii}

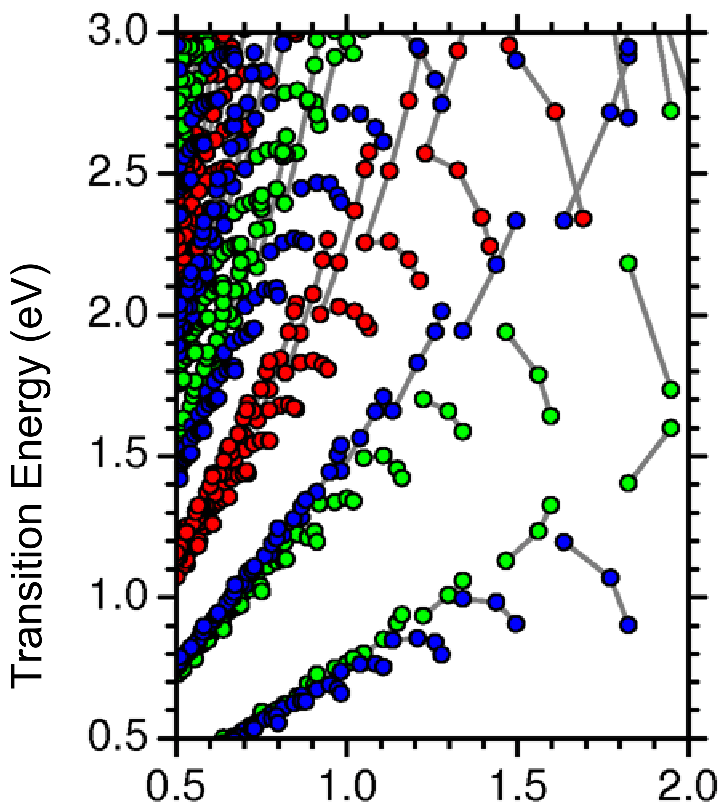
Family effects are mainly due to trigonal warping

2n+m = constant family behavior is observed



The **simple TB** does not describe E_{ii} correctly!

EXTENDED TIGHT BINDING MODEL



Inverse Diameter (1/nm)

M *2n+m=3p*

S1 *2n+m=3p+1*

S2 *2n+m=3p+2*

Kataura plot is calculated within the extended tight-binding approximation using Popov/Porezag approach:

- curvature effects (ssσ, spσ, ppσ, ppπ)
- long-range interactions (up to ~4Å)
- geometrical structure optimization

The extended tight-binding calculations show family behavior (differentiation between S1 & S2 and strong chirality dependence) similar to that of the PL empirical fit

Family behavior is strongly influenced by the trigonal warping effect

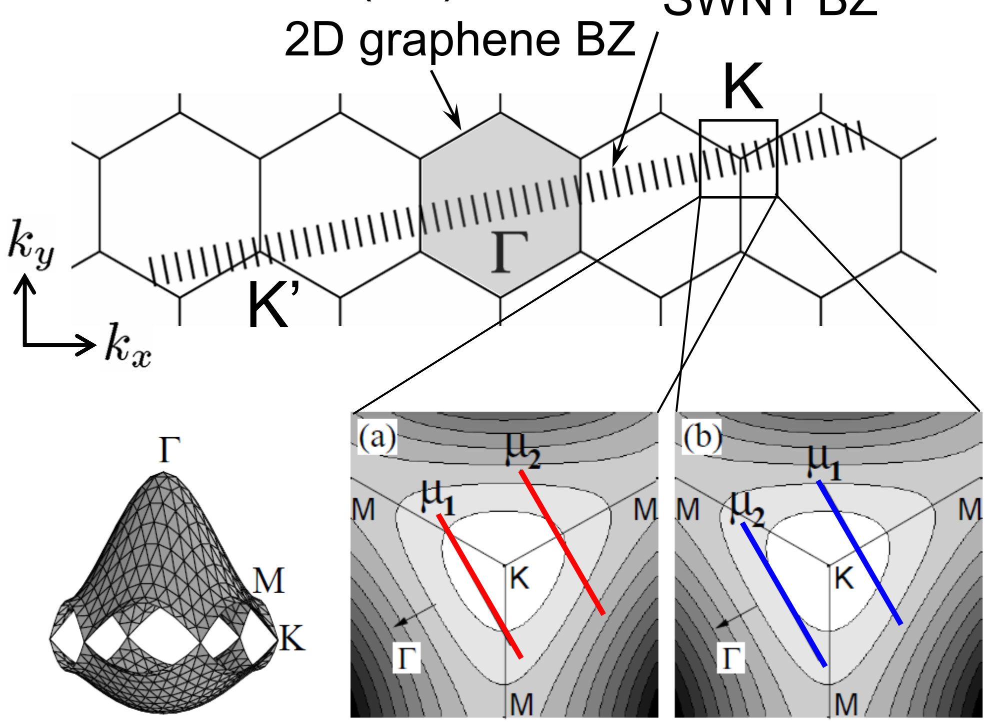
Ge.G. Samsonidze et al., APL 85, 5703 (2004)

N.V. Popov et al Nano Lett. 4, 1795 (2004) & New J. Phys. 6, 17 (2004)

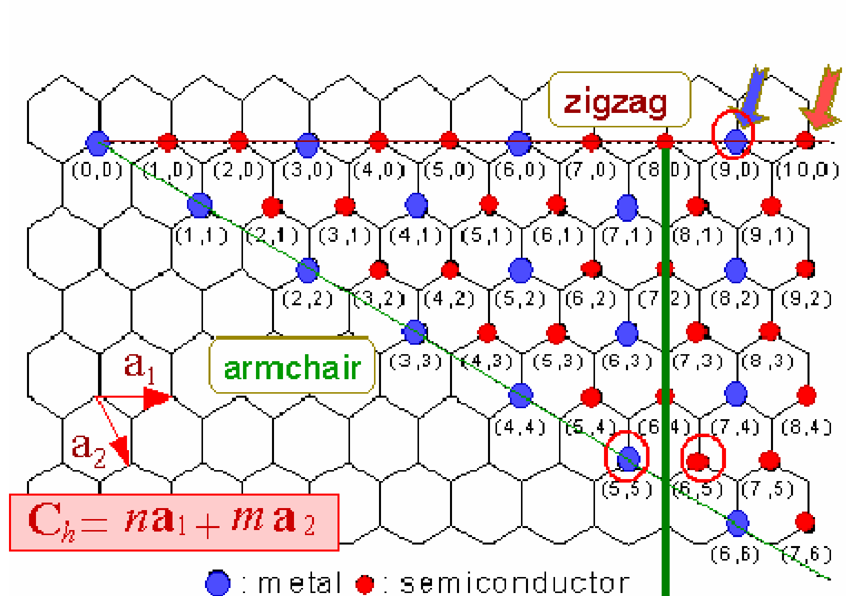
$2n+m$ families in SWNTs

R. Saito *et al.*, *Phys. Rev.* B, 72, 153413 (2005)

Brillouin zone (BZ)



type I type II



2n+m = const family
type I – type II separation

Family

mod (2n+m, 3) =
- 0 : metal
- 1 : type I SC
- 2 : type II SC

(example)

(8,0), (7,2), (6,4)

→ 2n+m = 16 type I family

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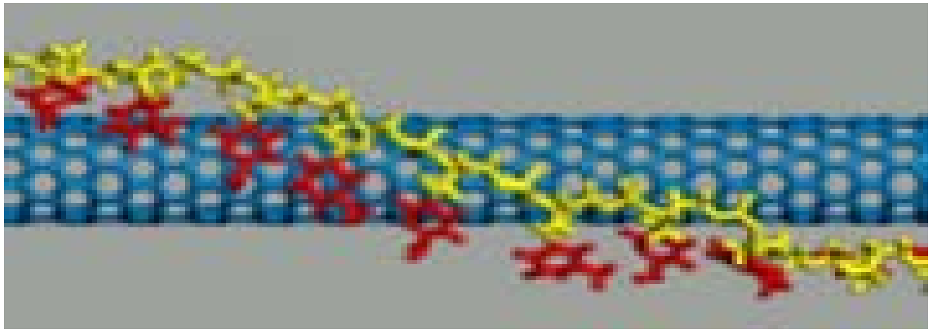
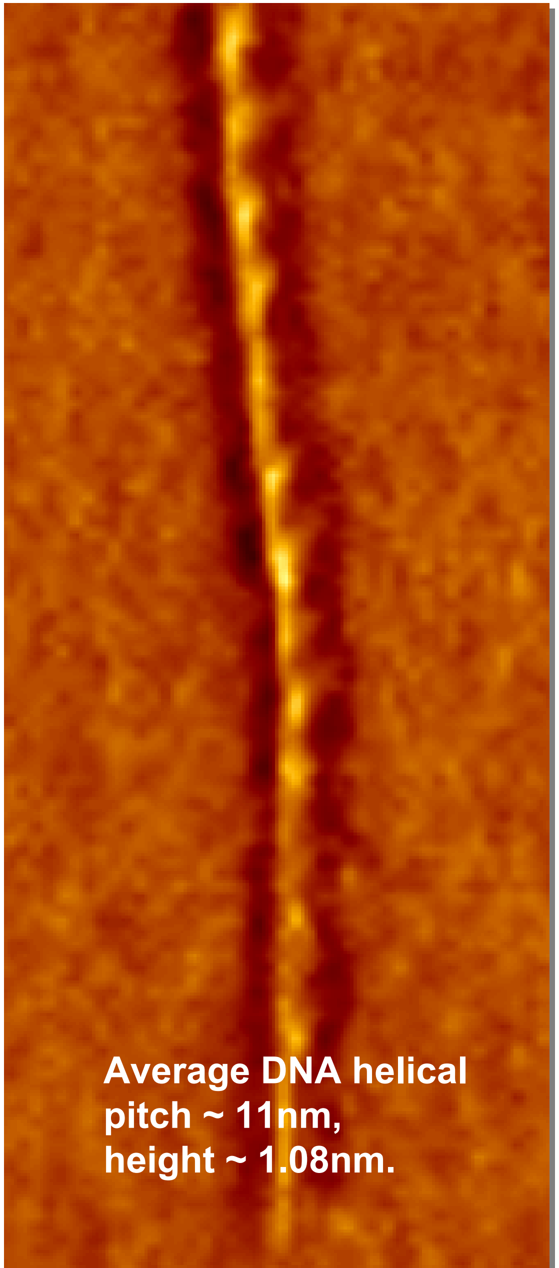
DNA wrapping of SWNTs

DNA Wrapping:
→ provides good separation of CoMoCAT SWNT sample

Subsequent fractionation:
→ results in sample strongly enriched in (6,5) species

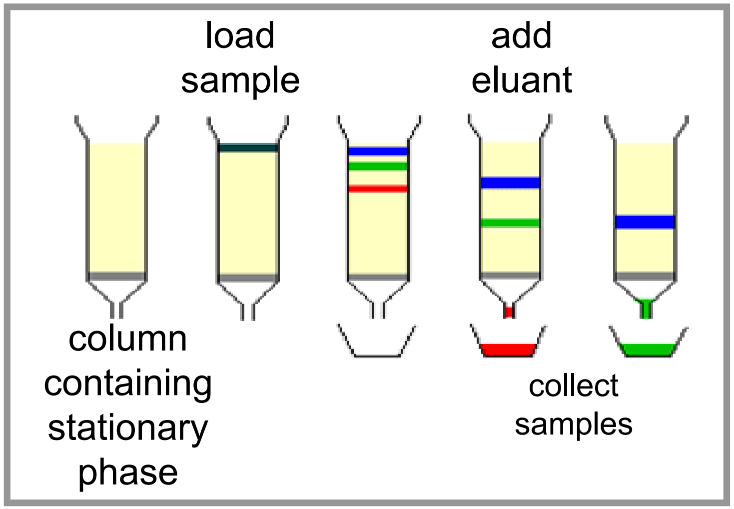


M. Zheng, *et al. Science 302, 1546 (2003)*



DNA-Assisted SEPARATION

M. Zheng *et al.*, *Science*, **302**,1546 (2003).

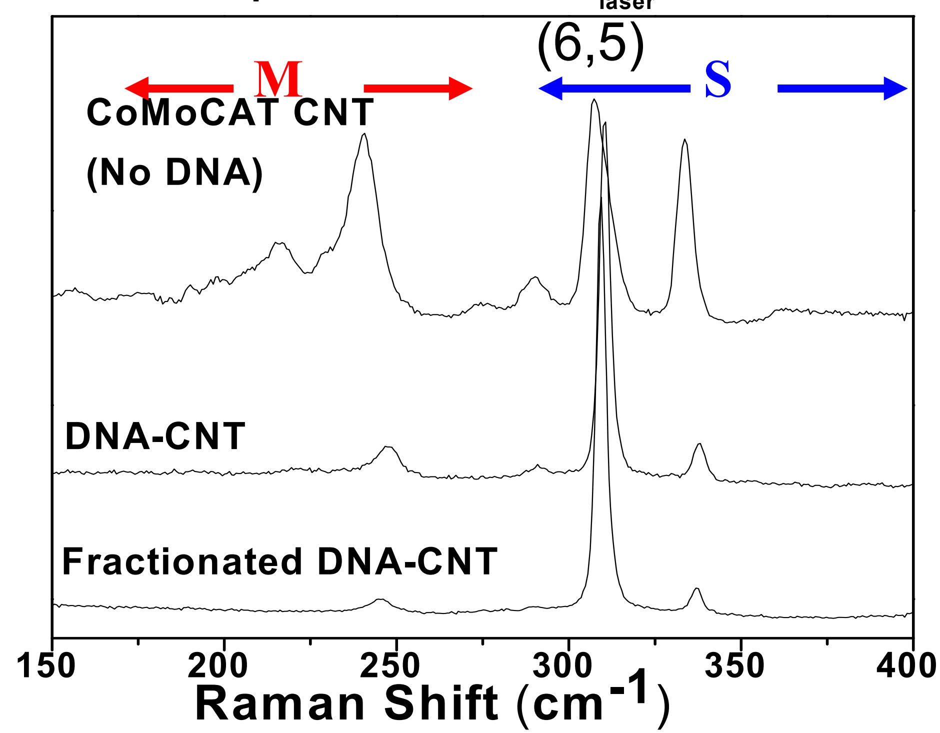


Ion-exchange chromatography (IEC)

Hybrid DNA-SWNTs:

• M-SWNT different surface charge density, higher polarizability, elute before S-CNTs

RBM Spectra Taken at E_{laser} = 2.18eV



Raman characterization shows that

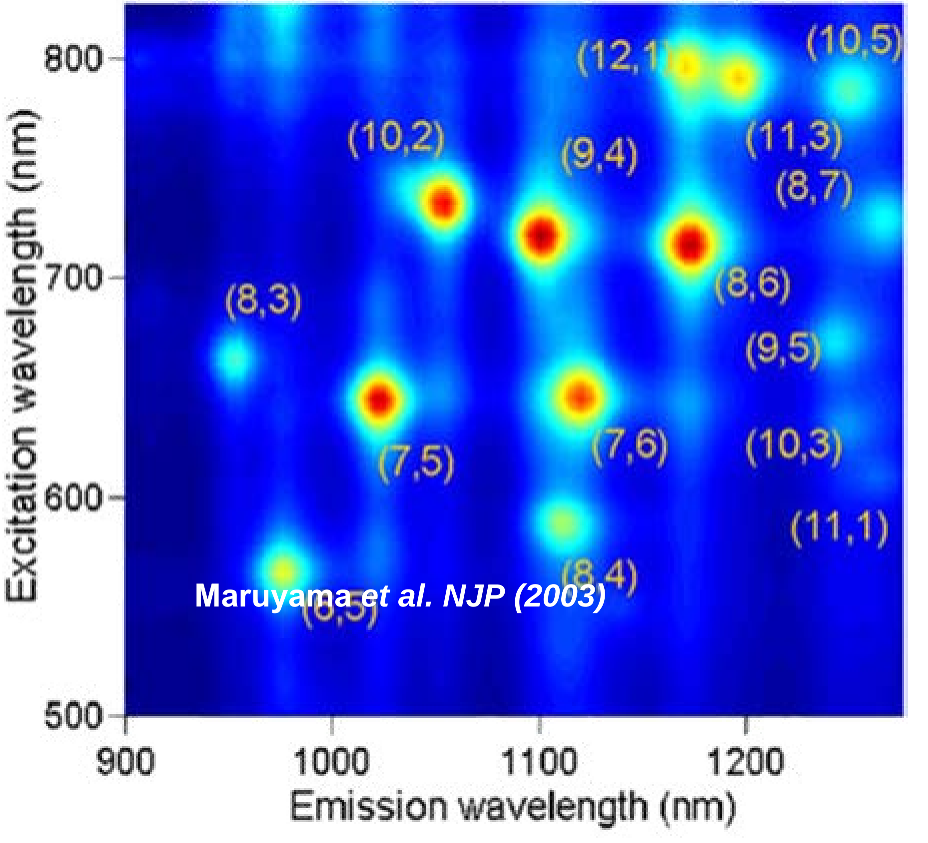
•DNA wrapping removes metallic (M) SWNTs

•Chromatography further removes M SWNTs preferentially

Nanotube PL Spectroscopy

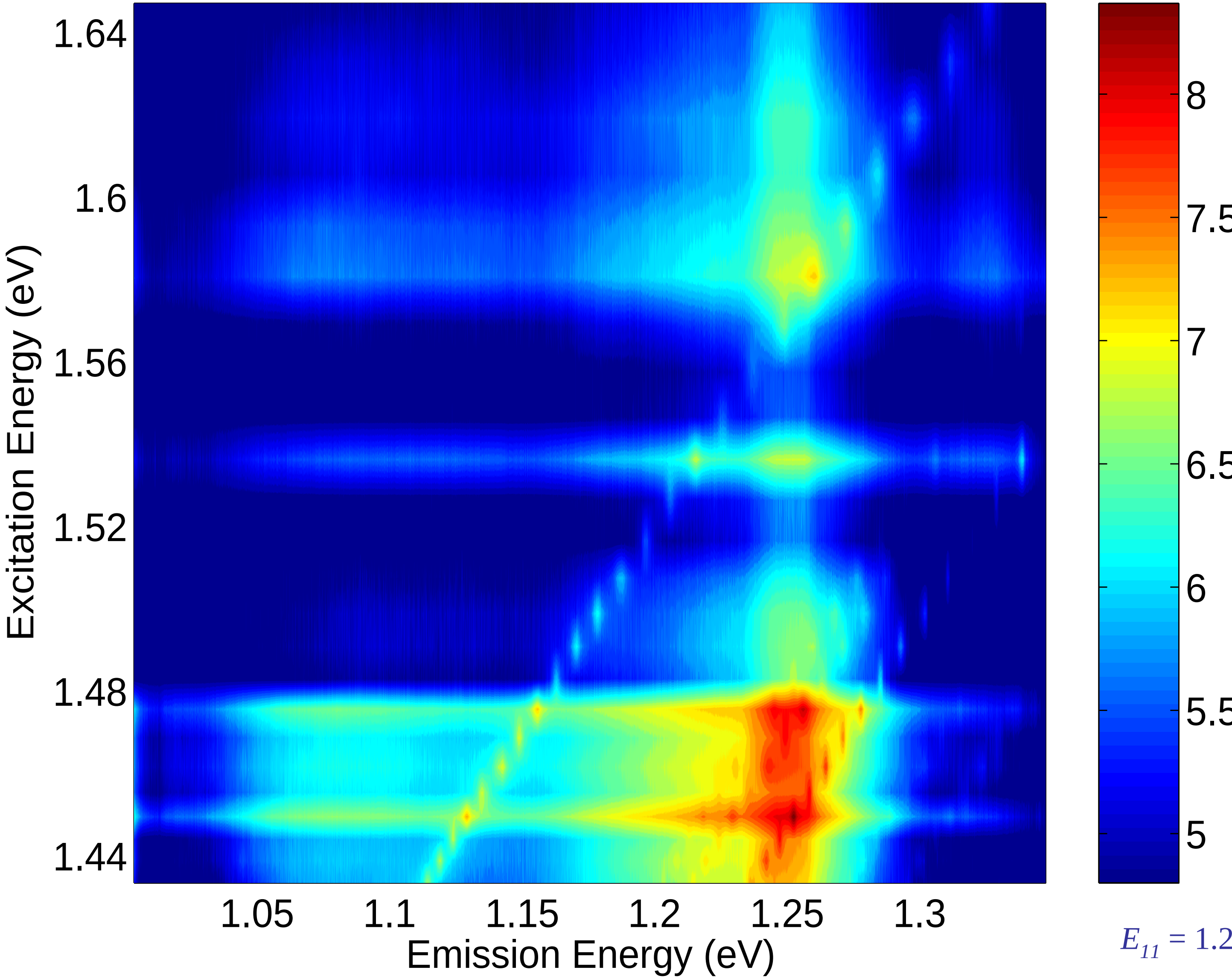
- **Most Measurements**
  - excitation at E_{22}, emission at E_{11}
  - measured with Xe lamp
  - (2n+m) family patterns provide (n, m) identifications.
- **Our Measurements**
  – (6,5) enriched sample
  – Intense light source (laser)
  – Allows observation of phonon assisted processes

PL map of SDS- dispersed HiPco CNTs



Maruyama's work suggests study of detailed phonon-assisted excitonic relaxation processes for different phonon branches.

PL Spectra of (6,5) Nanotubes



E_{11} = 1.26eV

E_{22} = 2.18eV

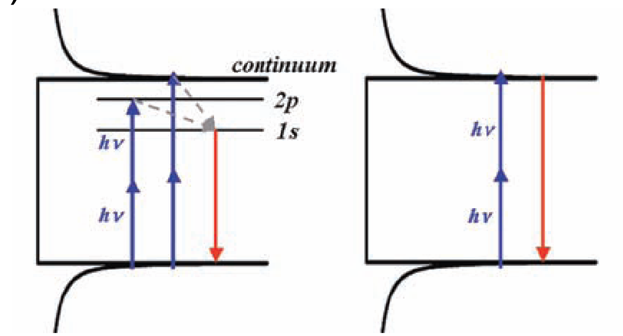
Phonon-assisted transitions on an expanded scale

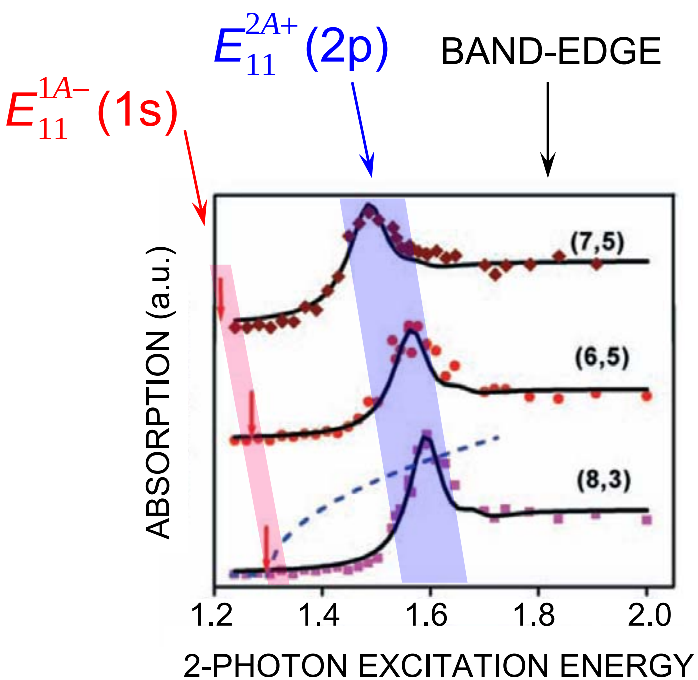
Chou, et al PRL **94**, 127402 (2005)

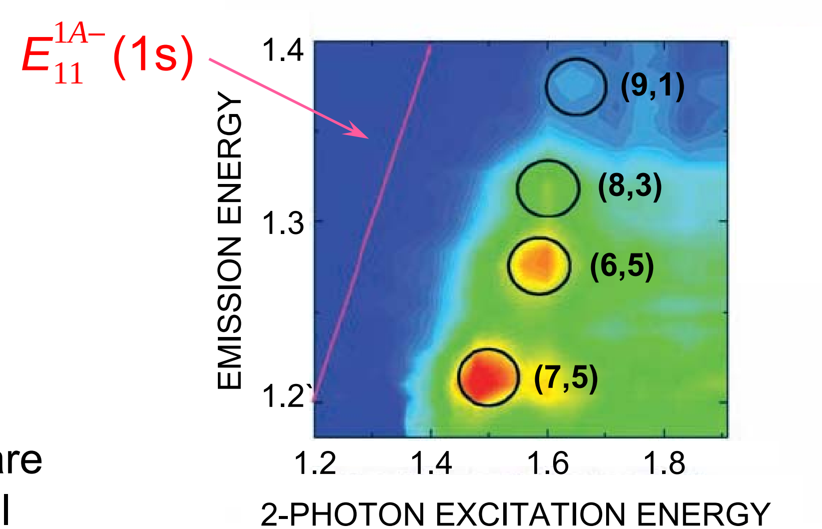
Excitons in Carbon Nanotubes

Experimental Justification for excitons

2-photon excitation to a $2A^{+}$ symmetry exciton (2p) and 1-photon emission from a $1A^{-}$ exciton (1s) cannot be explained by the free electron model







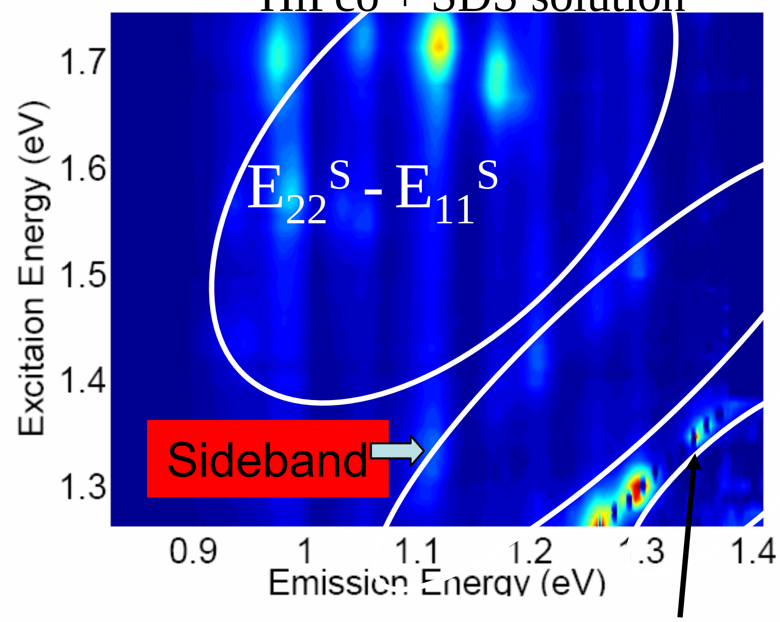
The observation that excitation and emission are at different frequencies supports exciton model

Wang et al. Science **308**, 838 (2005)

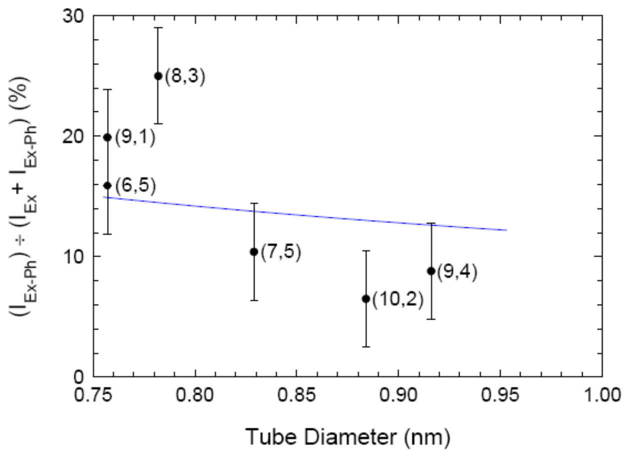
The exciton-phonon sidebands

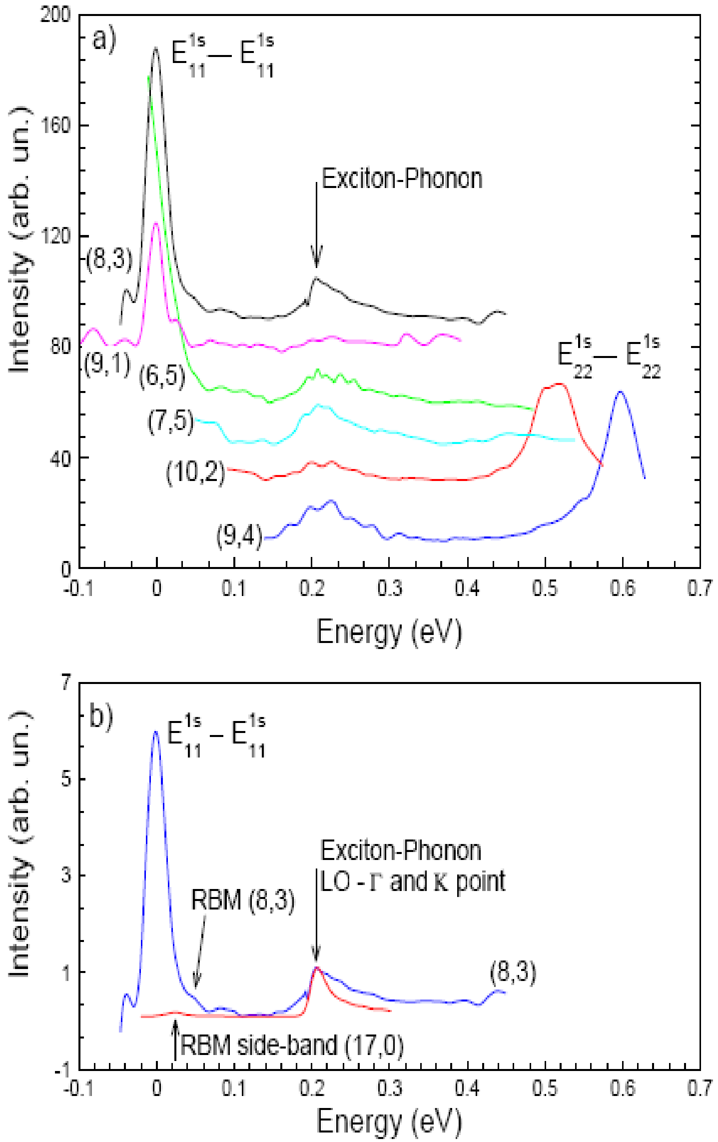
further support exciton model

HiPco + SDS solution



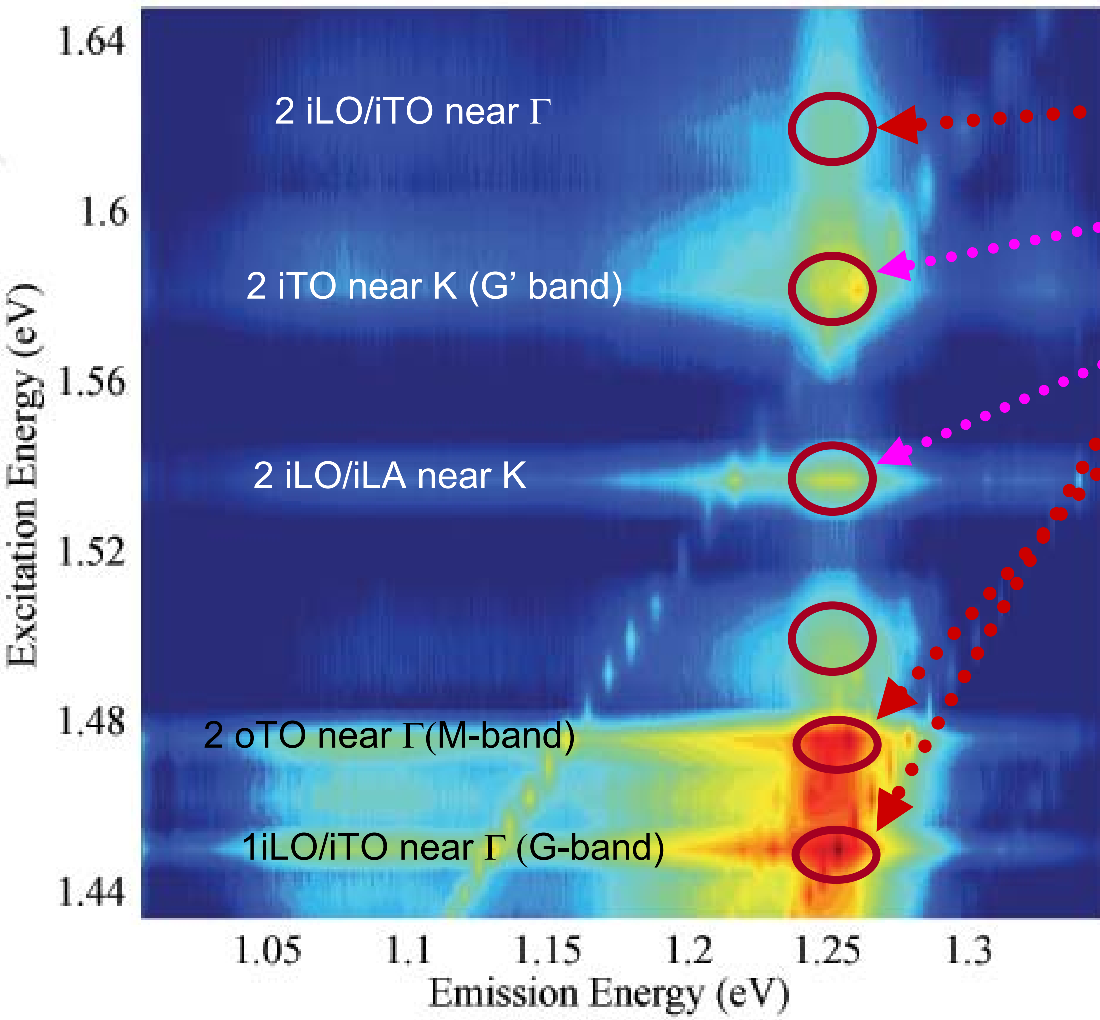
F. Plentz Filho (UFMG) *et al, PRL 95, 247401 (2005)*





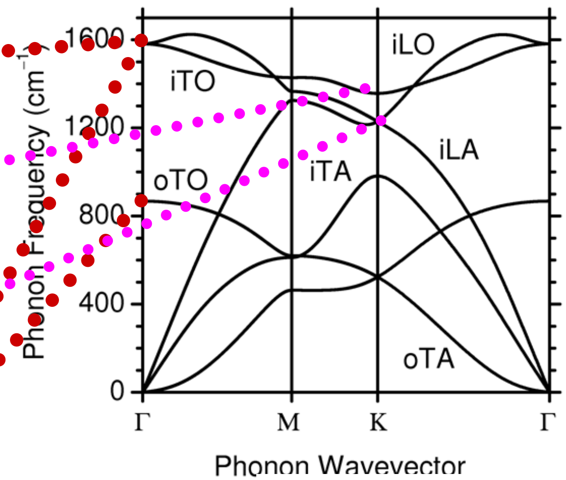
PRL 94, 027402 (2005)

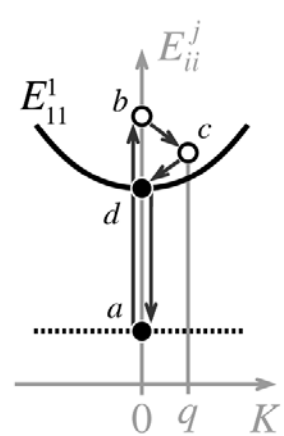
Emission Identified with One and Two Phonon Processes:



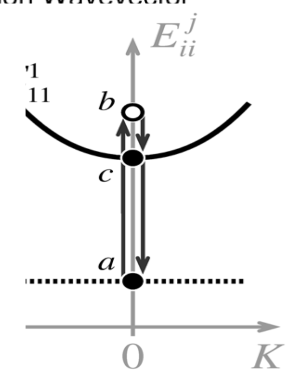
Chou et al., PRL **94**, 127402 (2005)

Phonon dispersion relations of graphite





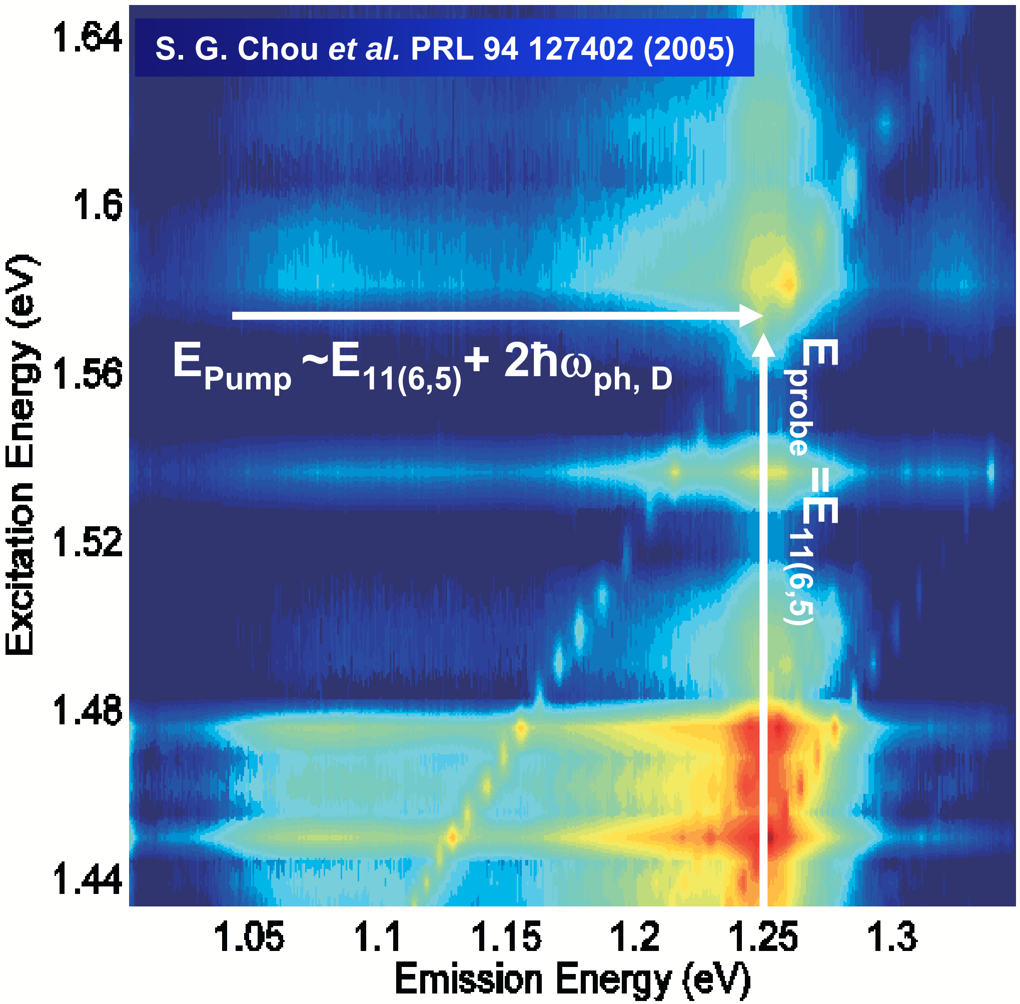
Two phonon process



One phonon process

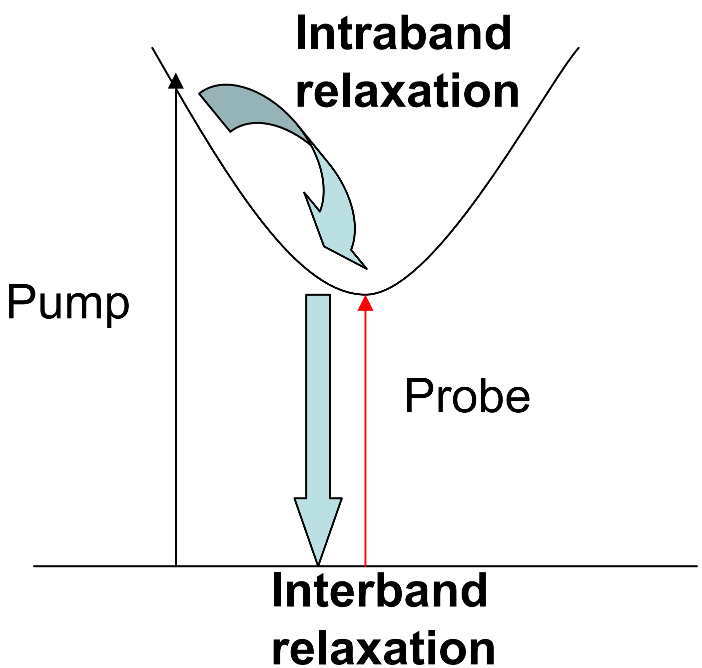
Non-degenerate Pump-probe

Frequency domain



Fast optics, Time domain

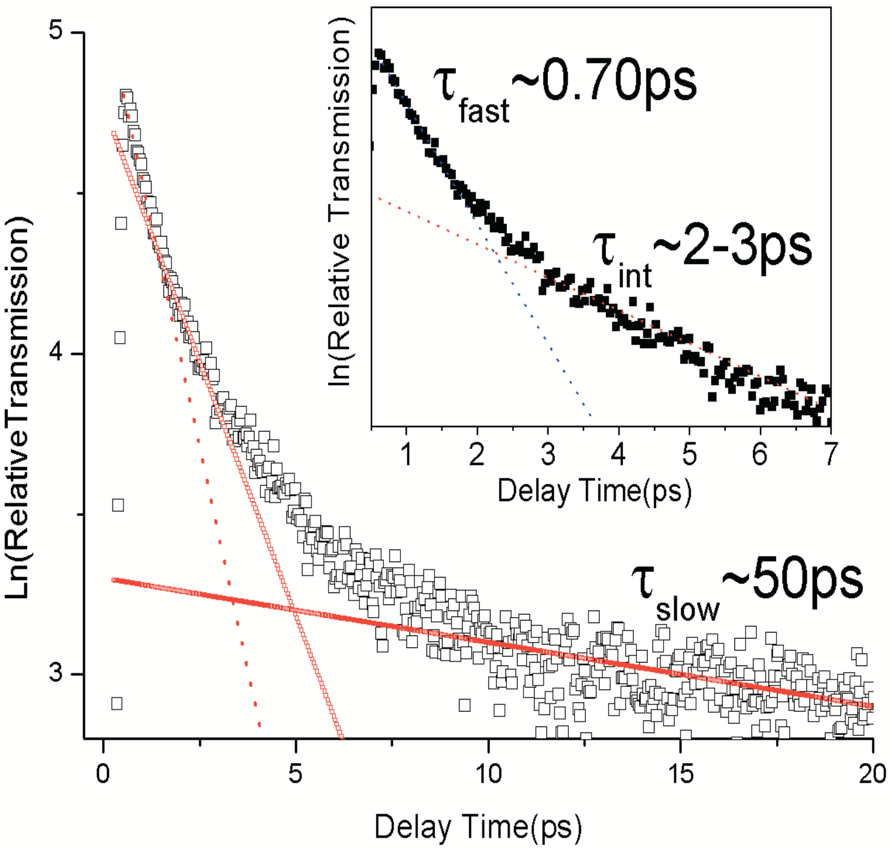
E_{pump} = 1.57±0.01eV, ~E_{11}(6,5)+2$\hbar\omega_D$
E_{probe} = around $E_{11}$of (6,5) nanotube
(Instrument resolution ~250fs)

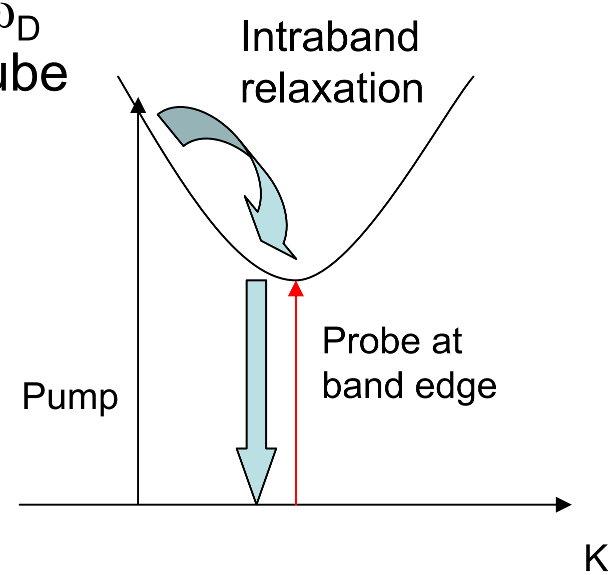


S. G. Chou *et al. Phys. Rev. B* (2005)

Pump Probe Studies at Special E_{pump}

- $E_{pump} = 1.57 \pm 0.01 eV \approx E_{11}^{1A-}{}_{(6,5)} + 2\hbar\omega_D$
- E_{probe} = around E_{11}^{1A-} of (6,5) nanotube

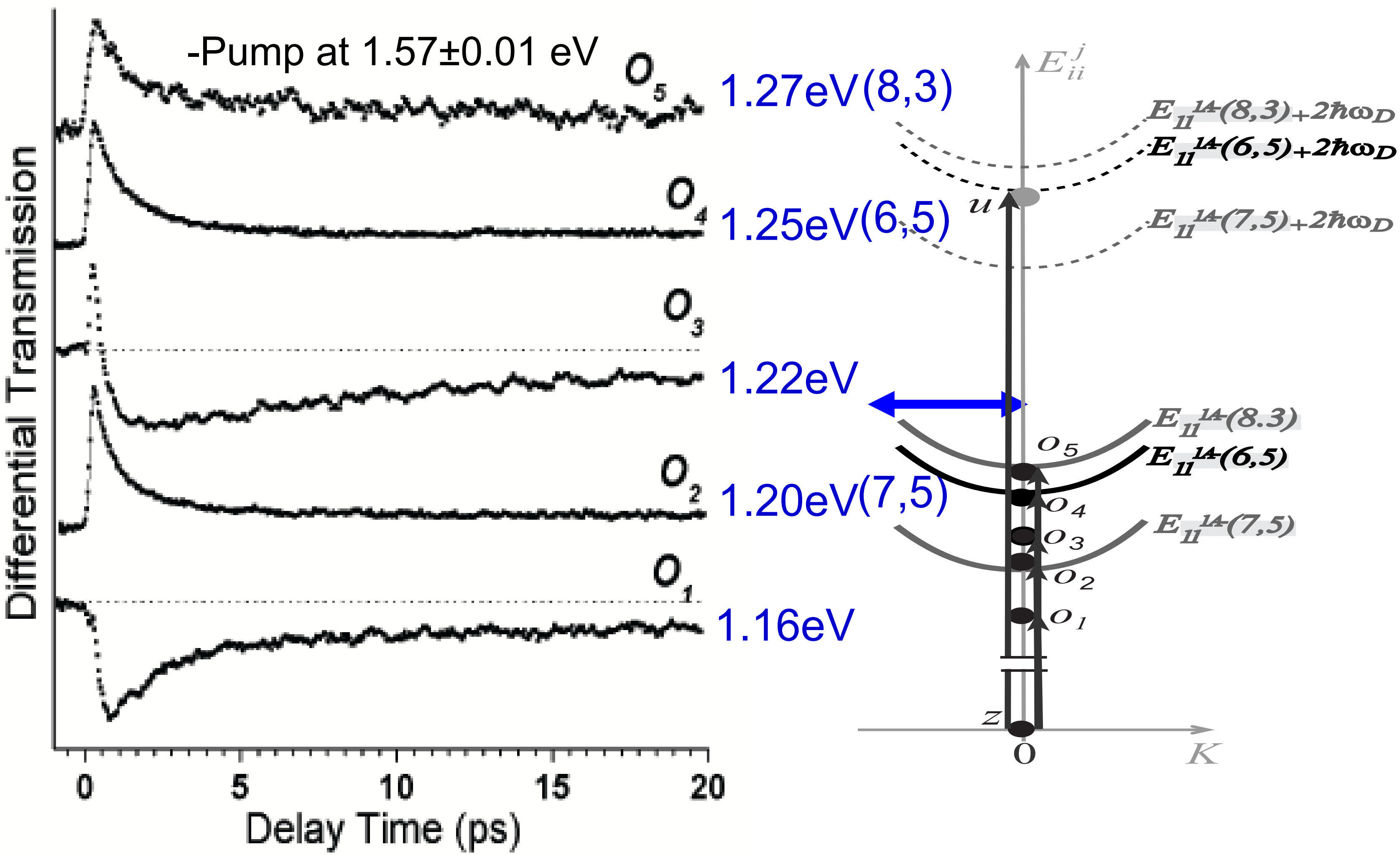




Exciton population at E_{11}^{1A-}(6,5):

- Quick rise (within 200fs)
- Three decay components:
  - τ_{fast}~680fs (dominant process)
  - τ_{int}~2-3ps (dominant process)
  - τ_{slow}~50ps (weak during first 20ps).

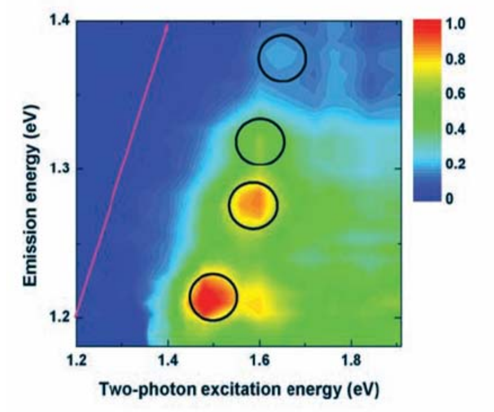
Probing at Different Energies:



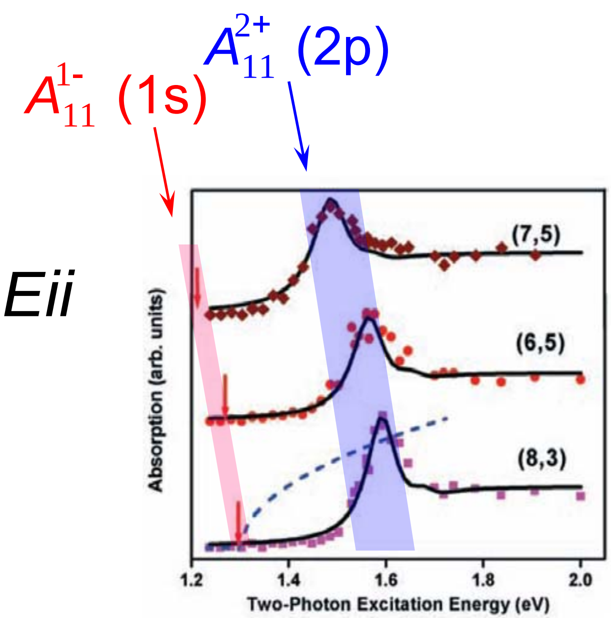
Exp.	(n,m)	E_{Probe}	FluenceJ/m^2	fast	%	Int	%	Slow	%
O_5	(8,3)	1.27eV	0.3	900fs	70	Several ps	Traces mixed	30ps	30
O_4	(6,5)	1.25eV	0.3	700fs	45	3ps	45	50ps	10
O_2	(7,5)	1.20eV	0.1	800fs	90	N/A	N/A	40ps	10

More on Excitons

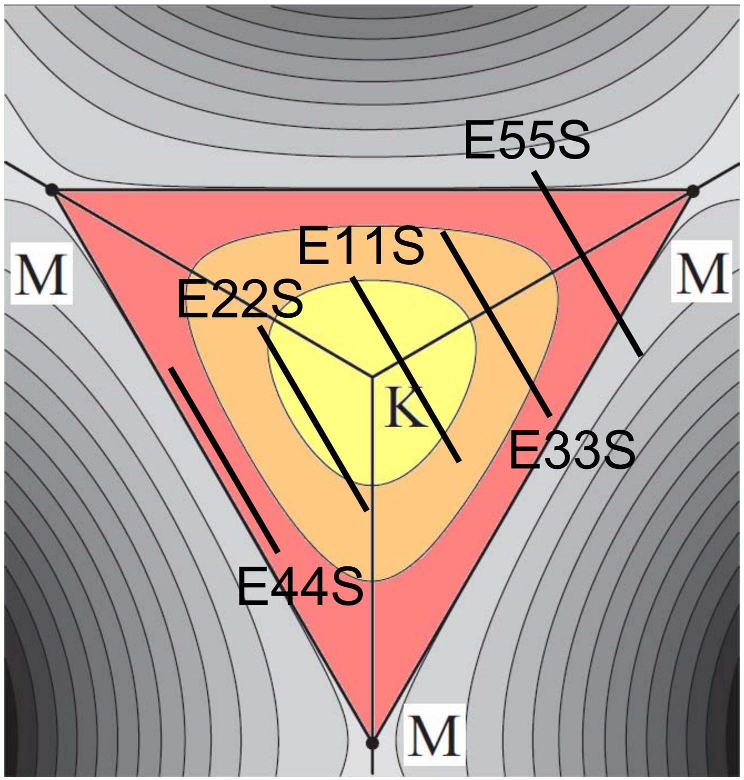
- Why?
  - Large binding energy (0.5eV)
    - Even at room temperature, excitons exist.
  - Exciton specific phenomena
    - dark excitons, two photon, environment
- What can we know or imagine?
  - Near cancellation by self energy
    - ETB + many body effects reproduce *Eii*
  - Localized exciton wave function
    - enhancement of optical process
    - Length dependence.

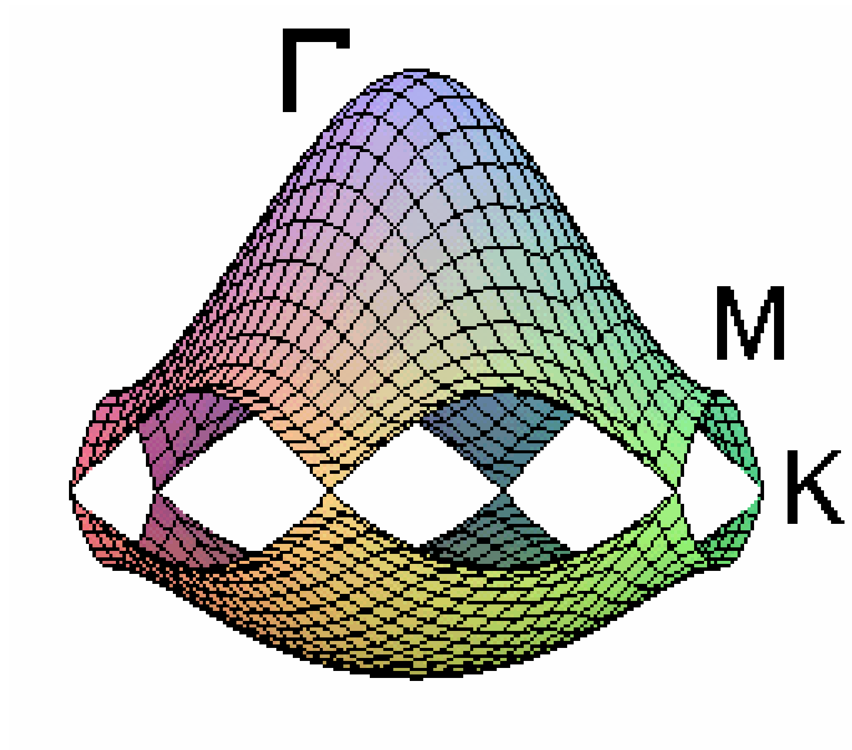


Wang et al. Science ***308****, 838 (2005)*



Exciton exists only in the 3M-triangle





Energy minima for the π* band exist only in 3MΔ.

Cutting lines occur around K-point.

Symmetry considerations

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

Centre of mass motion

$k_c - k_v = \overline{K}$:Good quantum number

Relative motion

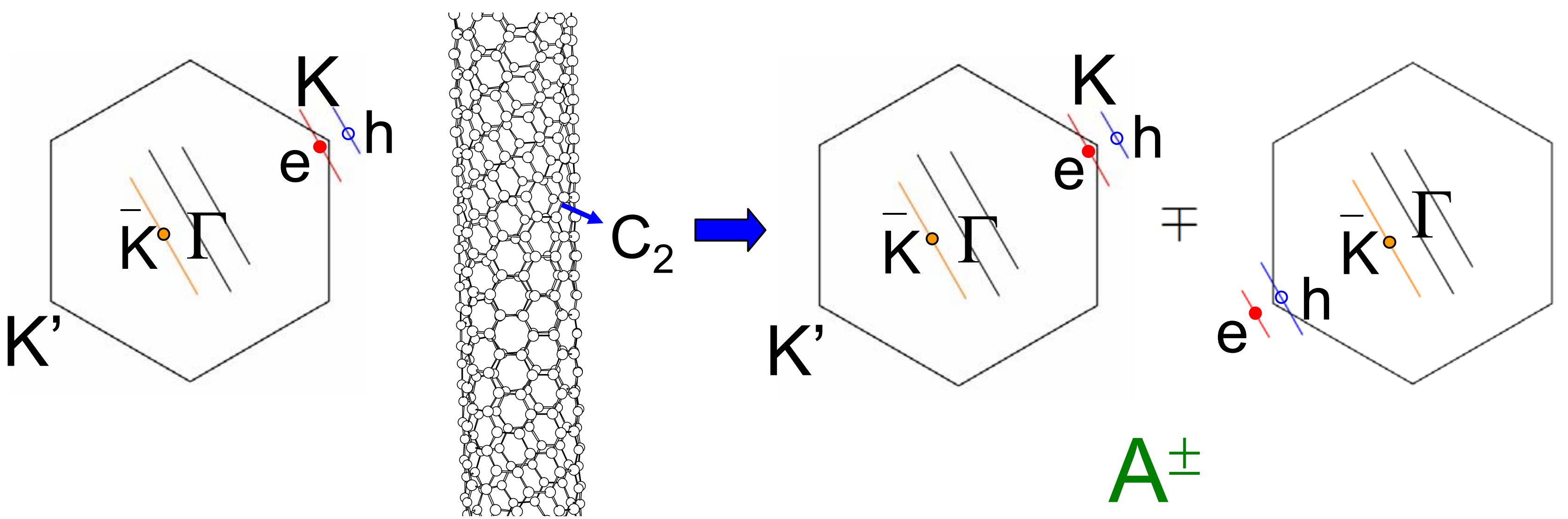
$(k_c + k_v)/2 = k$

Bright and dark excitons

A^-: bright exciton

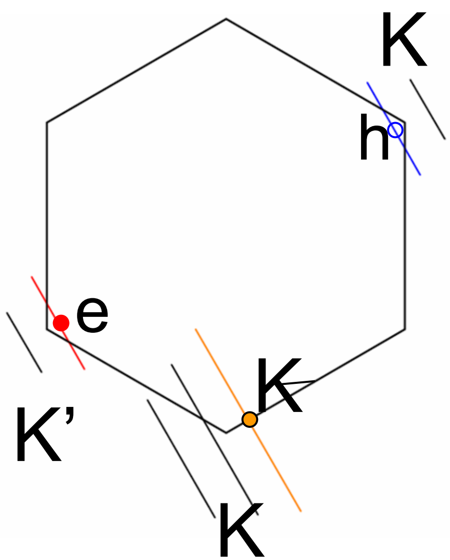
A^+, E and E^*: dark excitons

A symmetry excitons



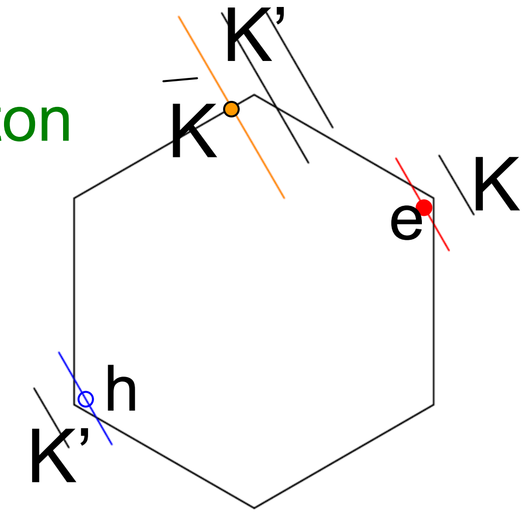
E symmetry exciton and its dispersion

E exciton



$$k_c - k_v = \overline{K}$$

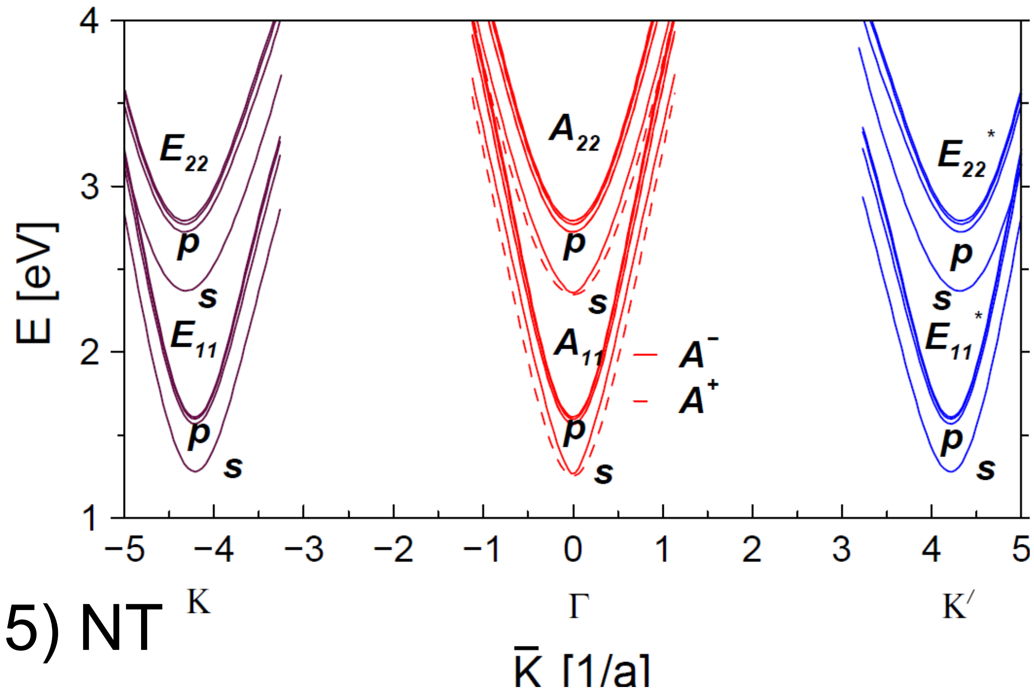
*E** exciton



Bright and dark excitons

A^- : bright exciton

A^+, E, E^*: dark excitons

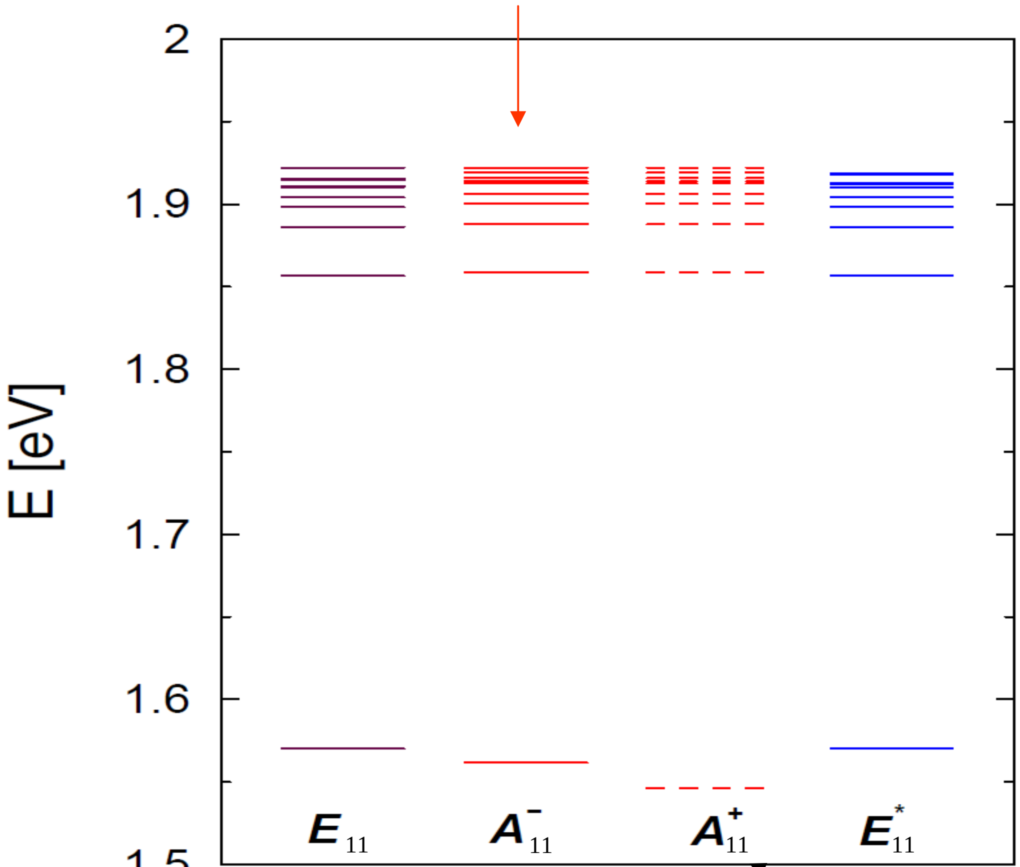


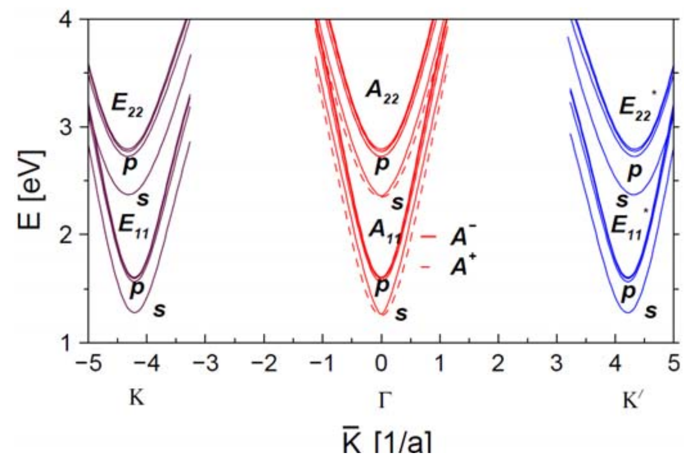
Dispersion for (6,5) NT

Dark state has the lowest energy

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

A^- : bright exciton





A^- : bright exciton

A^+, E and E^*: dark excitons

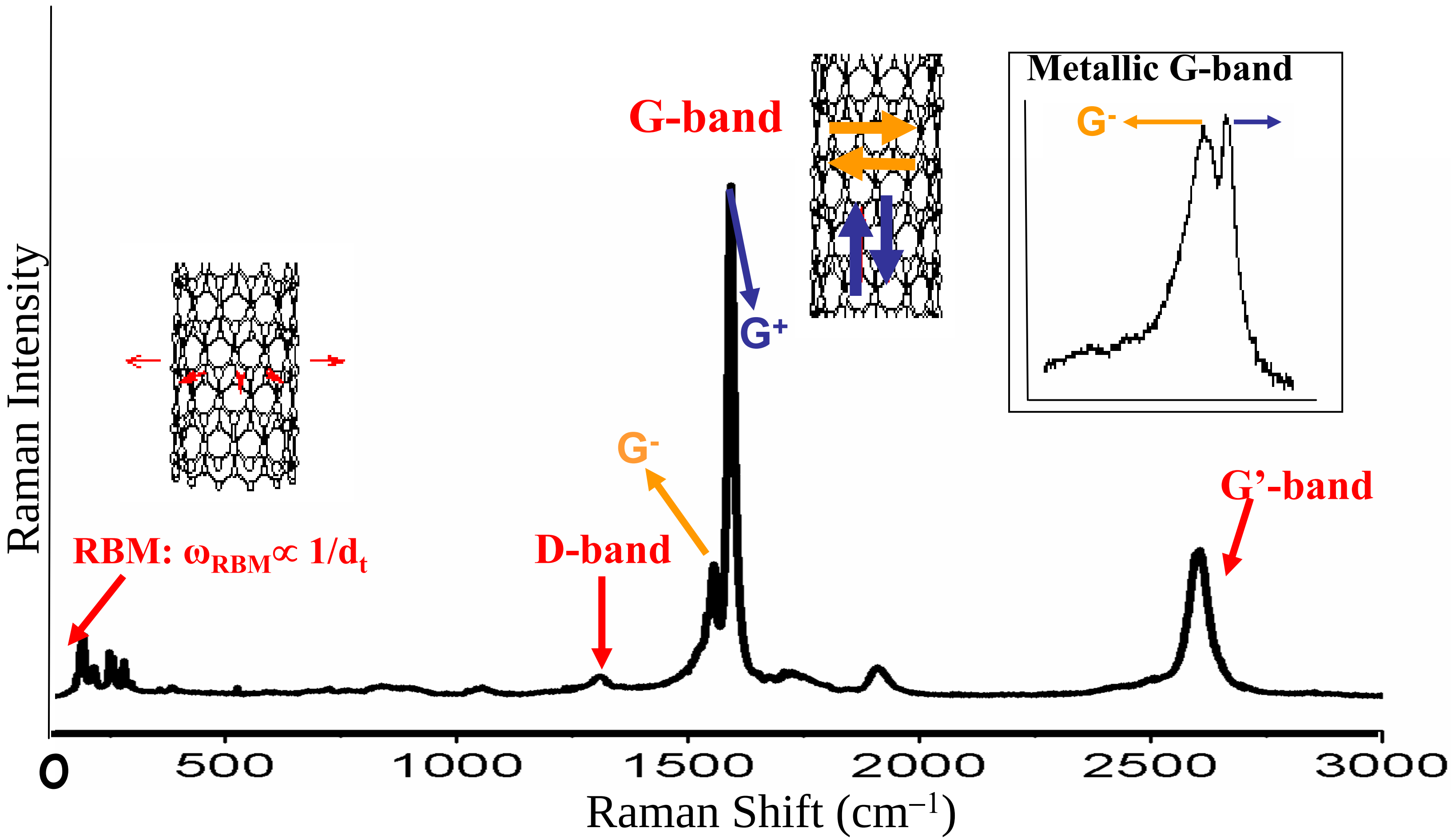
Lowest energy but not symmetry allowed

Physics of Nanotubes, Graphite and Graphene

Outline of Lecture 1 - Nanotubes

- **Brief overview of carbon nanotubes**
- **Review of Photophysics of Nanotubes**
- **Phonon assisted Photoluminescence**
- **Double wall carbon nanotubes**
- **Nano-Metrology**

Raman Spectra of SWNT Bundles



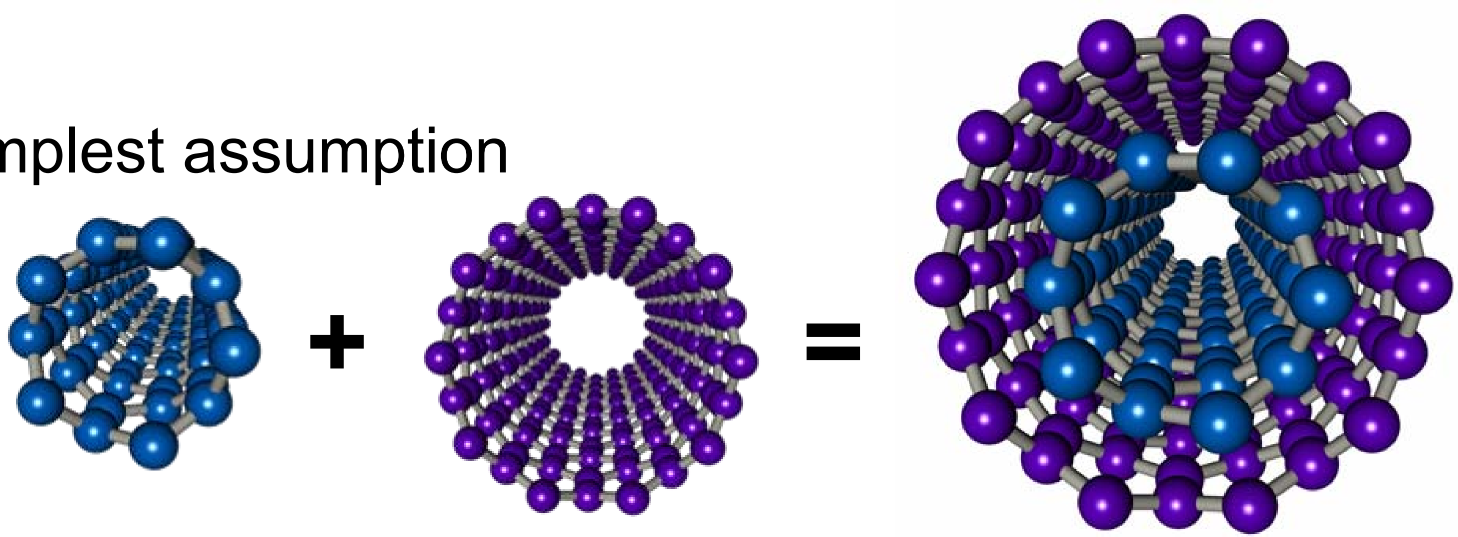
Photophysics of SWNTs is now at an advanced stage
Photophysics of MWNTs (DWNTs) is at an early stage

Motivation for studying DWNTs

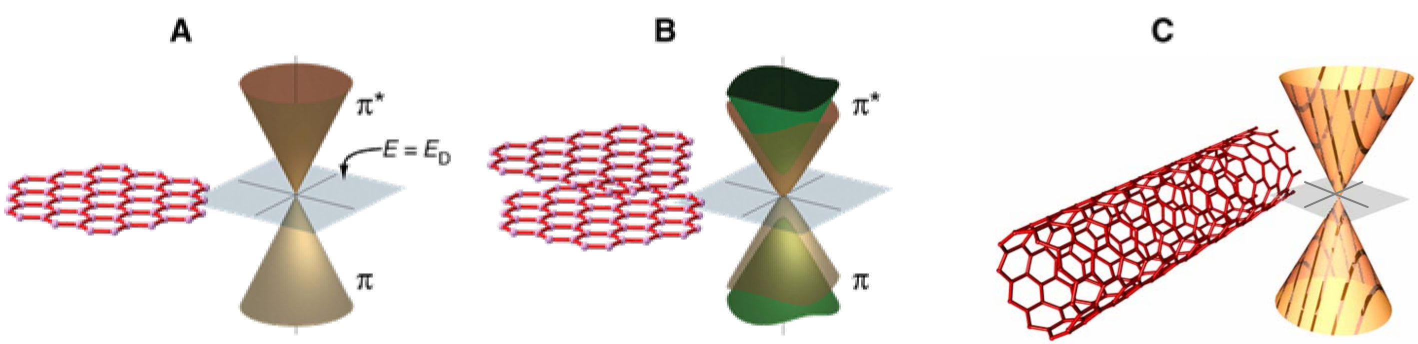
- **Applications**
  - **world shows much interest**
- **Synthesis**
  - **world has made major progress**
- **Promising for fundamental physics**
- **Study of the interface between DWNTs and bilayer graphene should enrich both areas**

Approaches to DWNTs

- simplest assumption



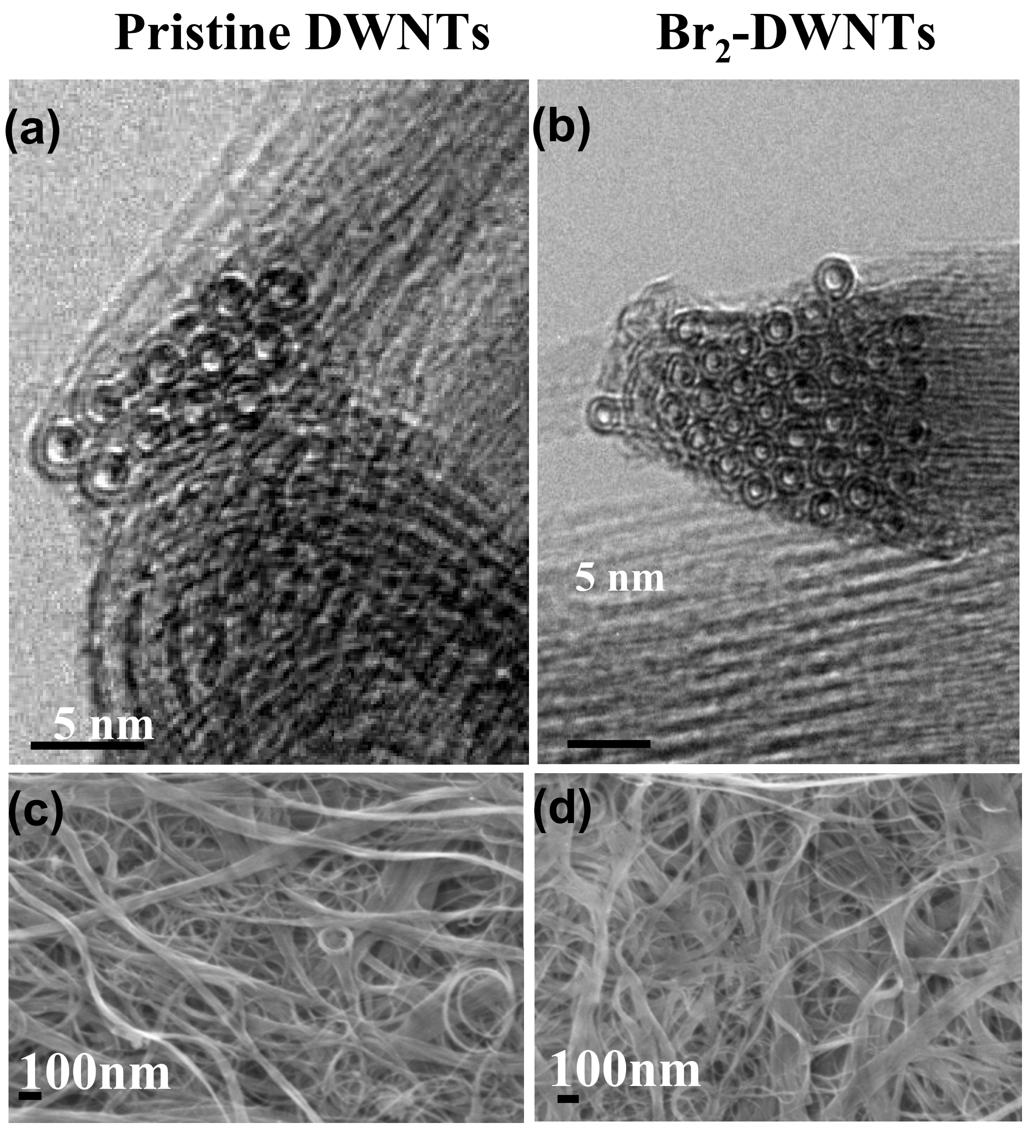
Suggests using Kataura plots for SWNTs as first approximation for DWNTs, but E(k) of monolayer and bilayer graphene say more detail is needed



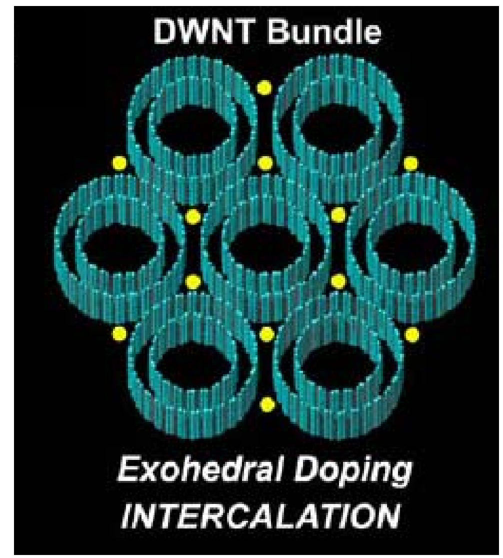
Br_2-doped double-wall nanotubes

TEM images

SEM images

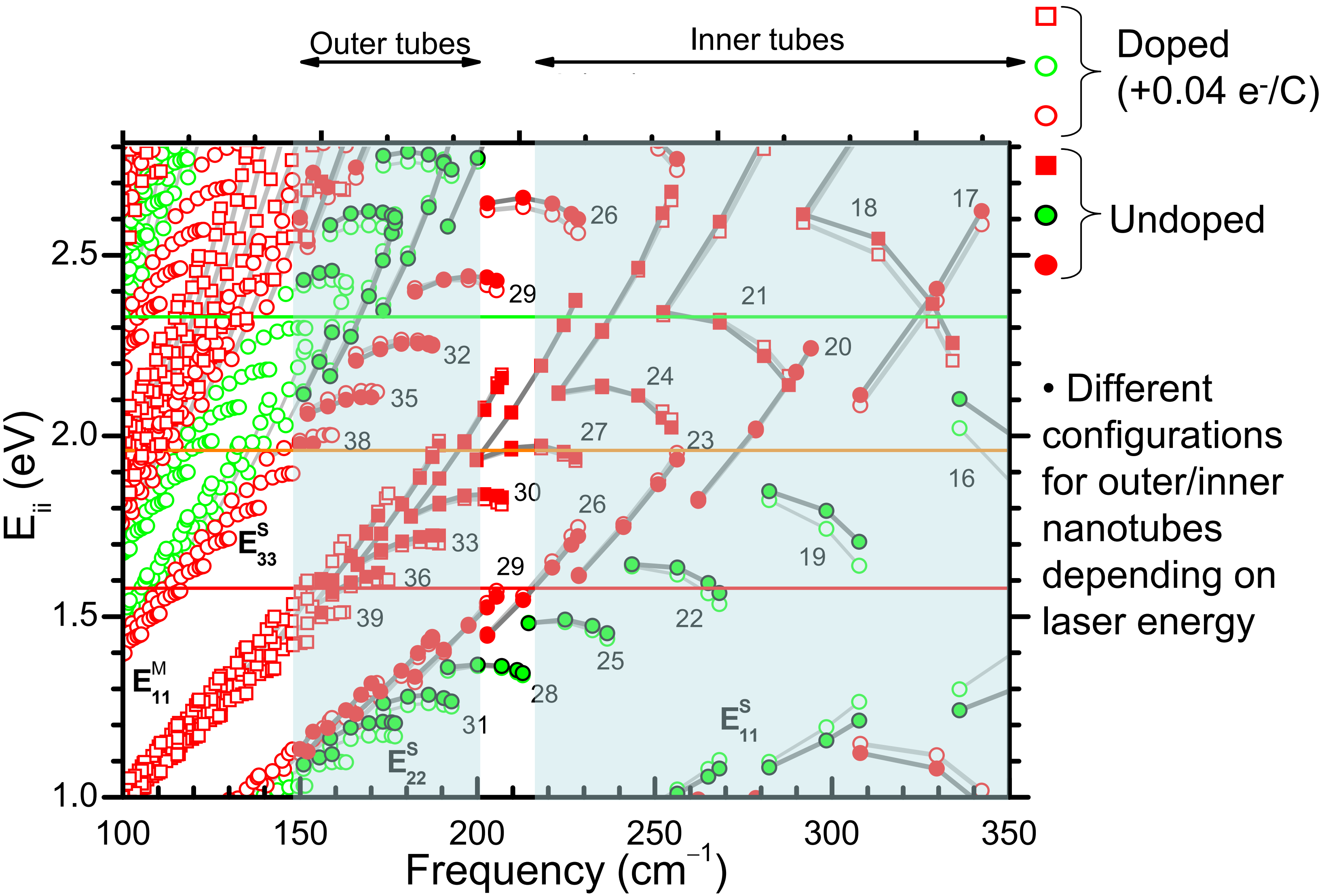


Highly pure samples (99% of DWNTs + 1% of SWNTs + catalysts particles)



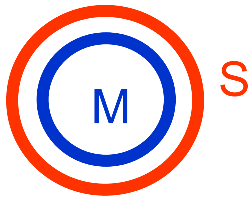
Endo et al. Nanolett. **4**,1451 (2004)

Kataura plot: undoped vs. doped SWNTs using Extended Tight Binding Model



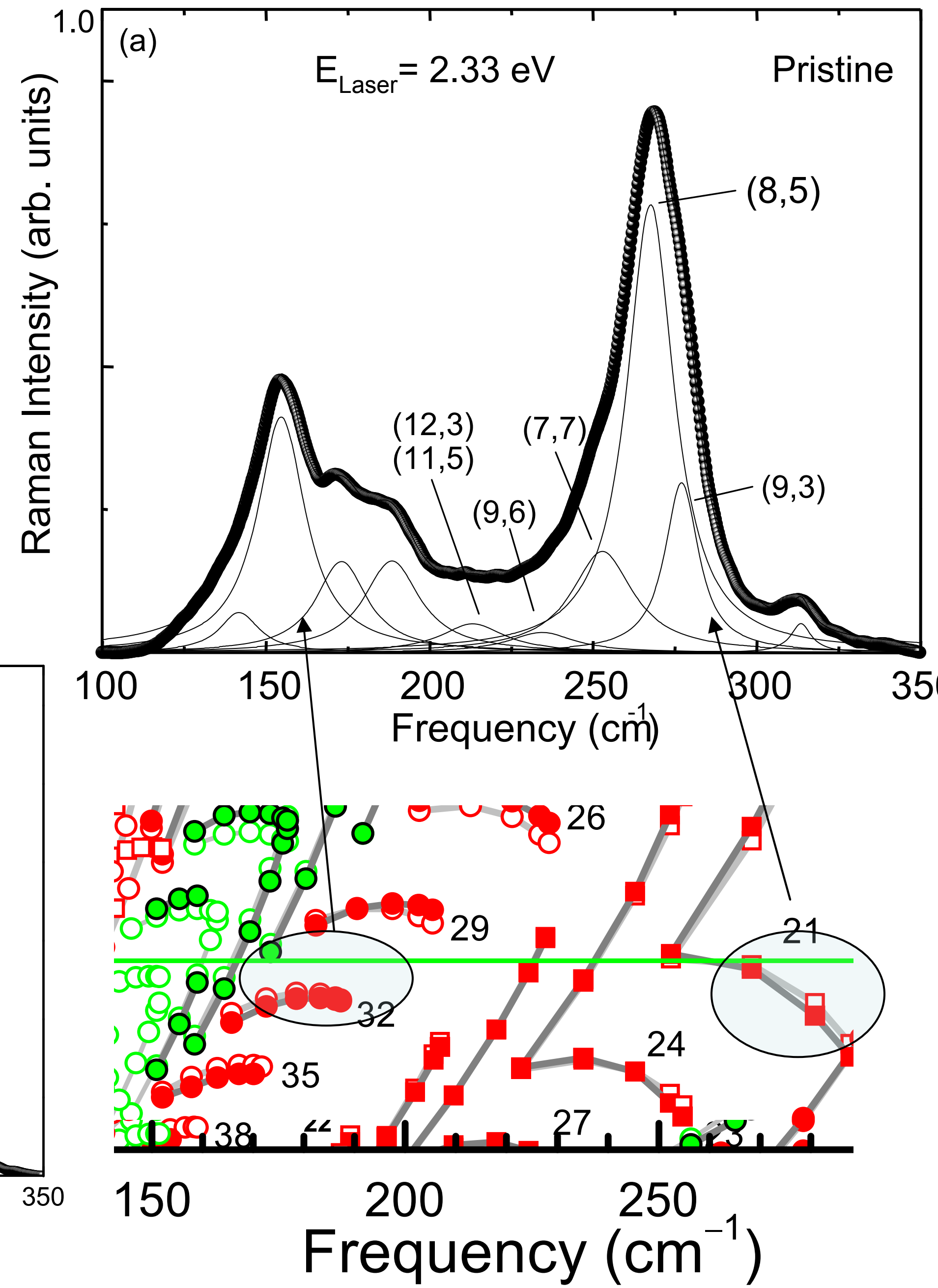
• Different configurations for outer/inner nanotubes depending on laser energy

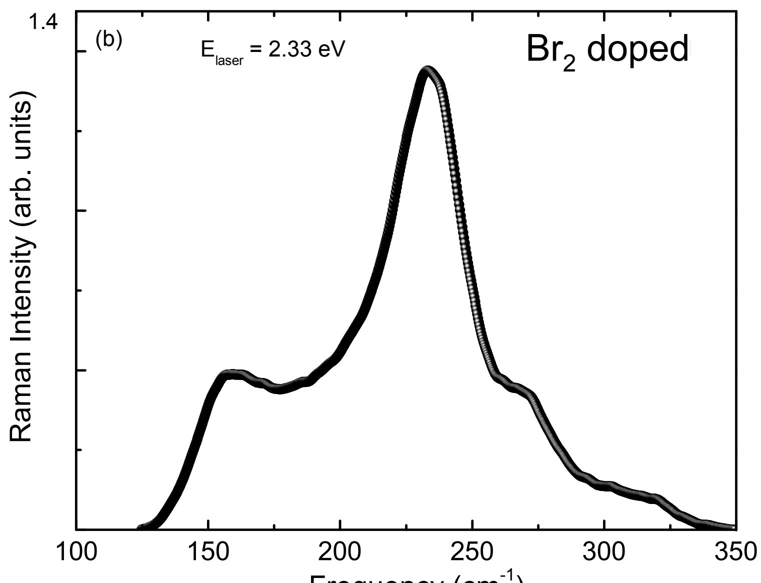
Semiconducting outer/Metallic inner configuration



RBM properties at E_{laser}=2.33 eV

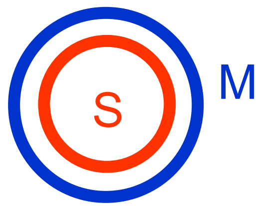
- **Breathing mode spectrum from the Br_2 dopant**
- **Resonance with Bromine electronic transitions**
- **Can identify individual (n,m) inner tubes from Kataura plot**





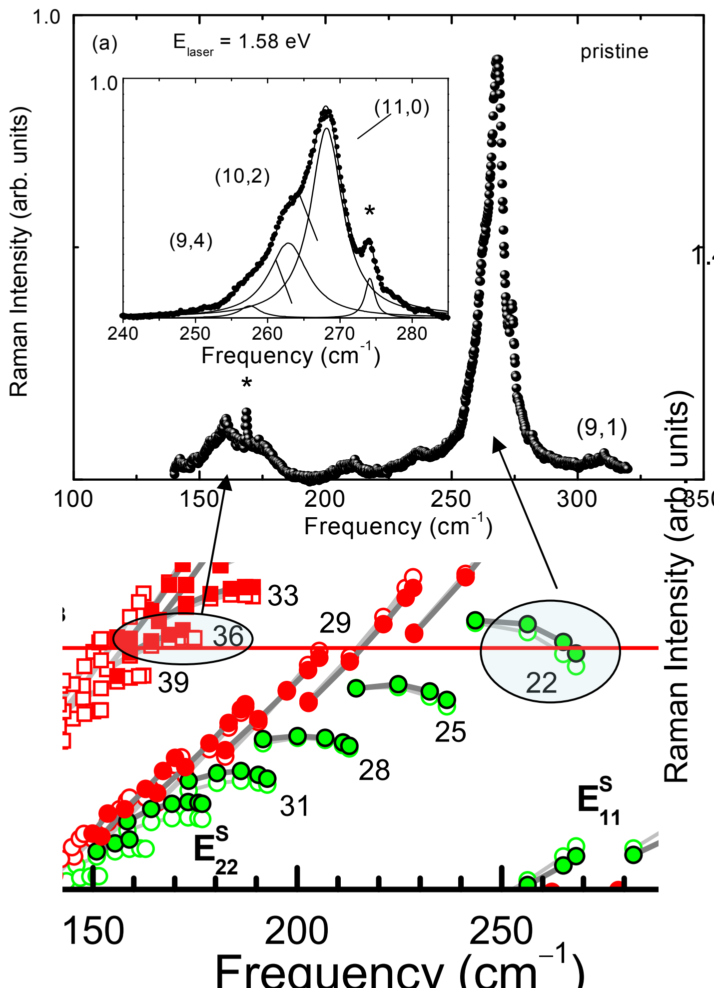
A.Souza-Filho. et al PRB (2006)

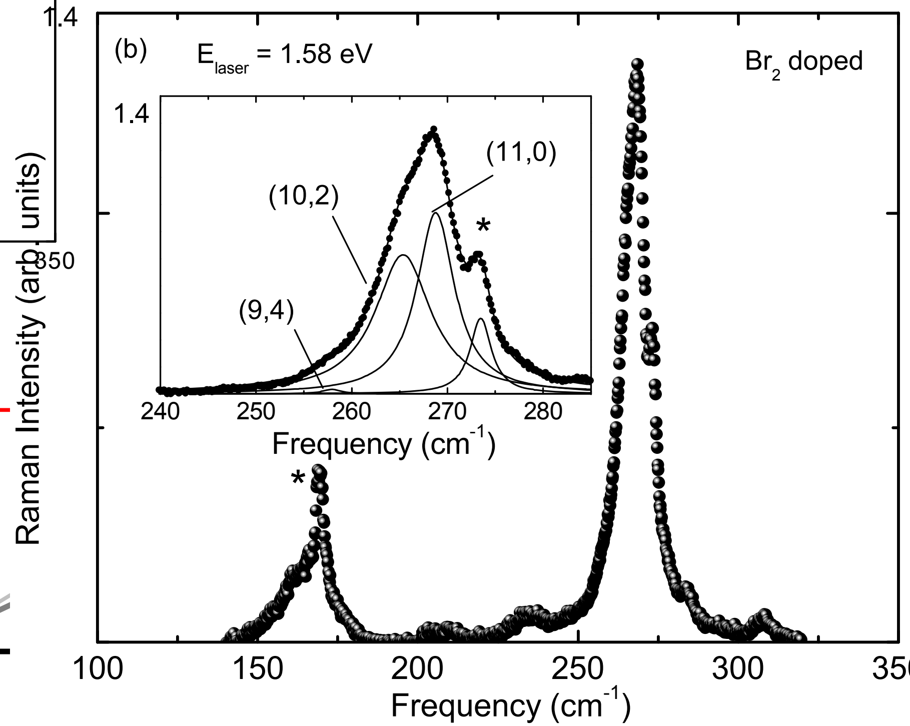
Metallic outer/Semiconducting inner configuration



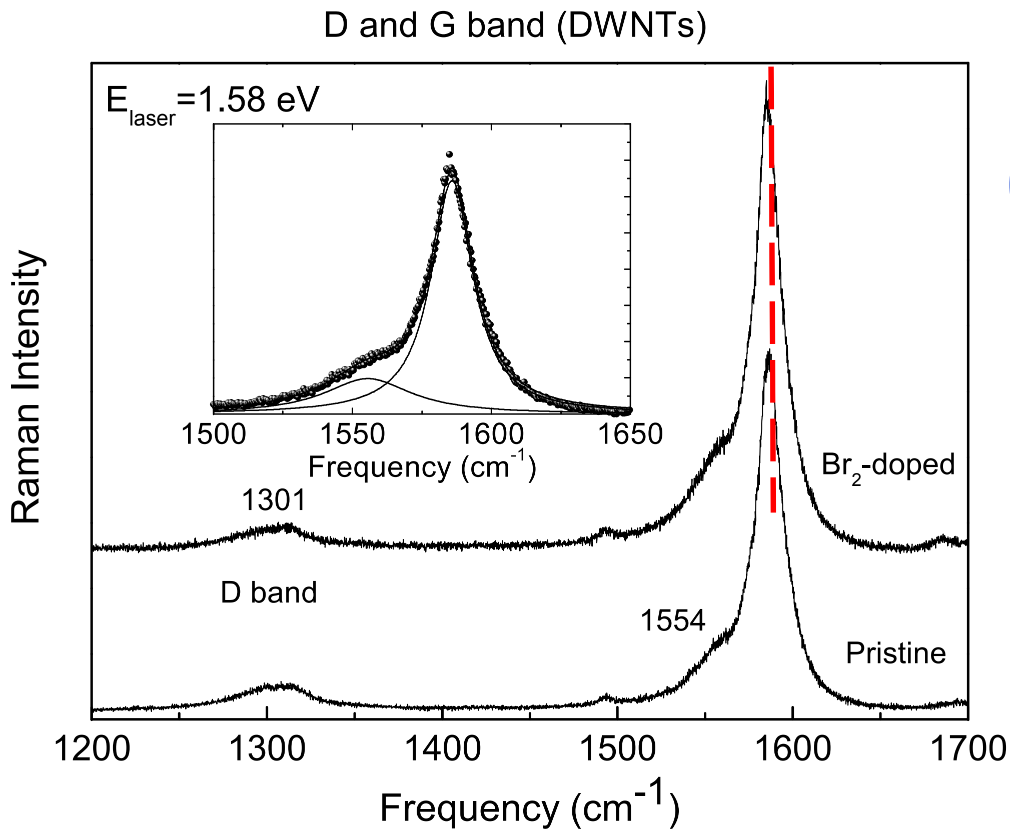
- Intensity enhancement after bromine doping
- Doping changing relative intensities of (n,m) tubes
- The Kataura plot for SWNTs gives identification for inner wall tubes and shows doping effect

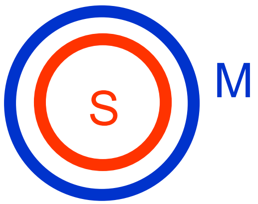
RBM properties at E_{laser}=1.58 eV





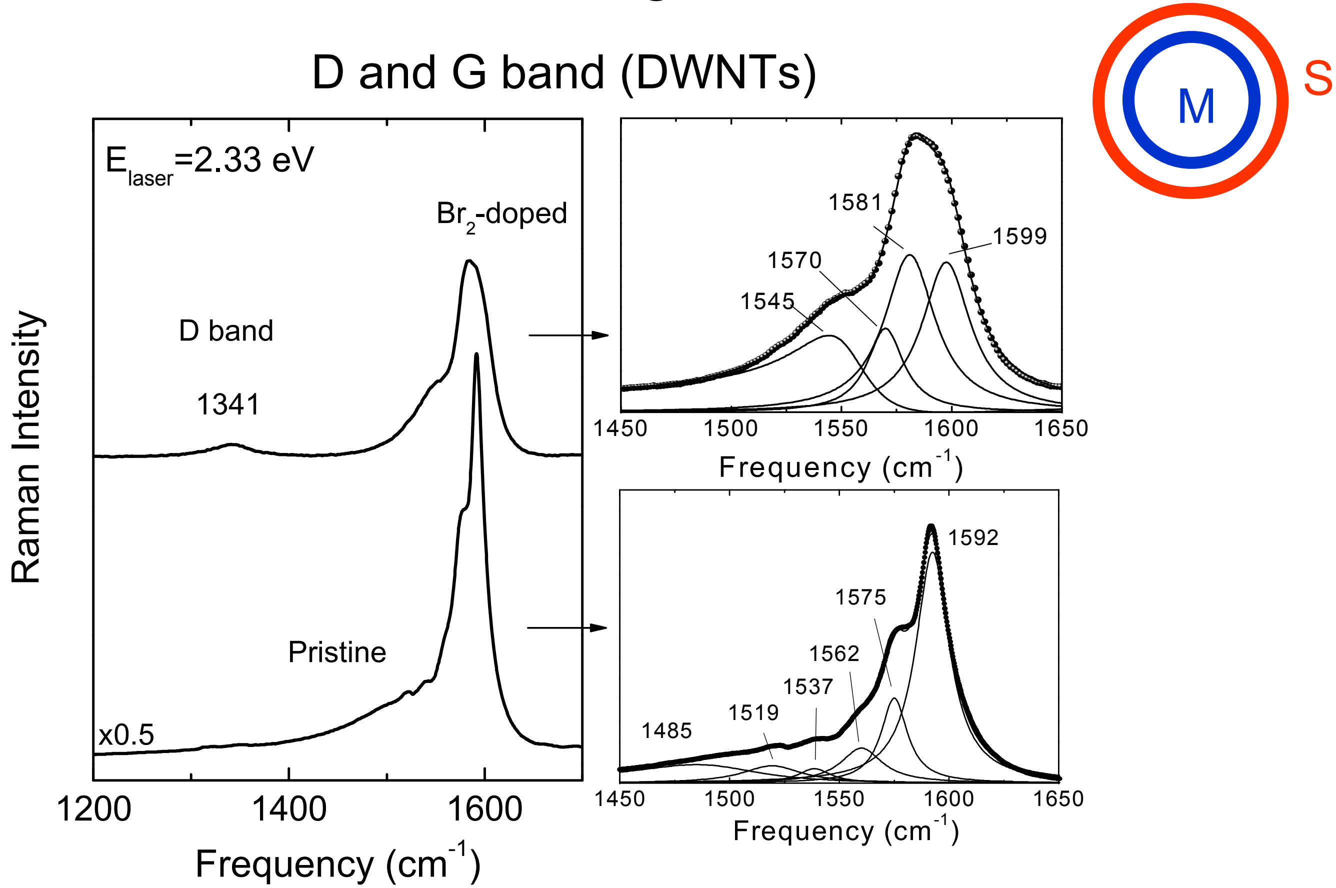
Metallic shielding effects
Metallic outer/semiconducting inner wall





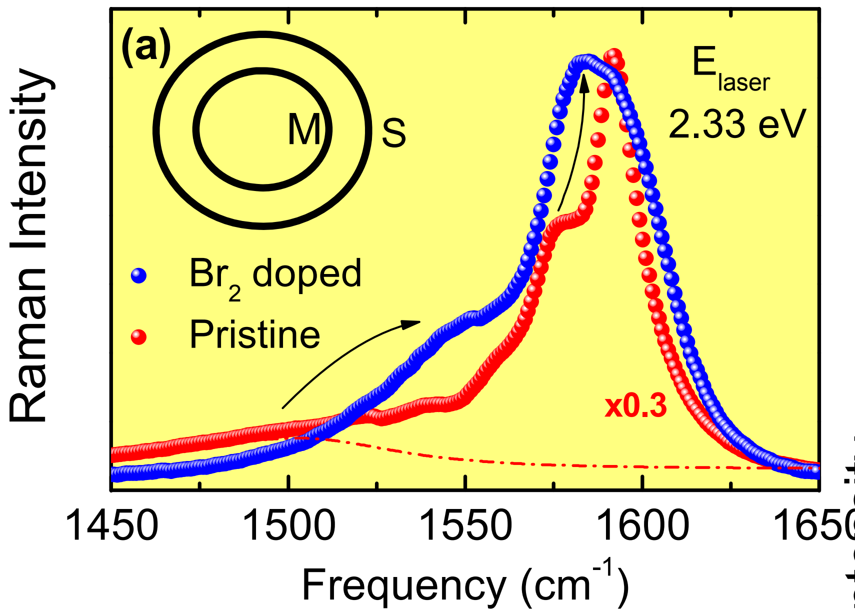
- The G-band is predominantly from semiconducting Nanotubes (based on diameter dependence)
- No shift in the G-band for semiconducting inner tubes
- The inner tubes are shielded by the metallic outer tubes

Charge transfer effects
Semiconducting outer/metallic inner

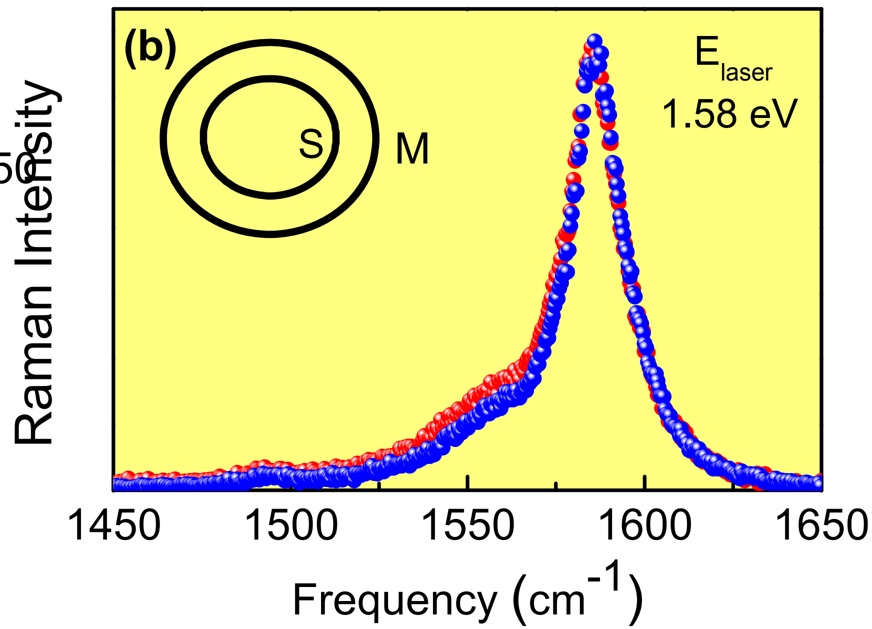


- The G-band profile is a mixing of semiconducting and metallic profiles;
- Shift in the G-band from semiconducting outer tubes indicates charge transfer to the Br_2 molecules
- The BWF (Breit Wigner Fano) decreases after doping.
- The decrease in the overall intensity indicates depletion of states

Charge transfer and screening effects



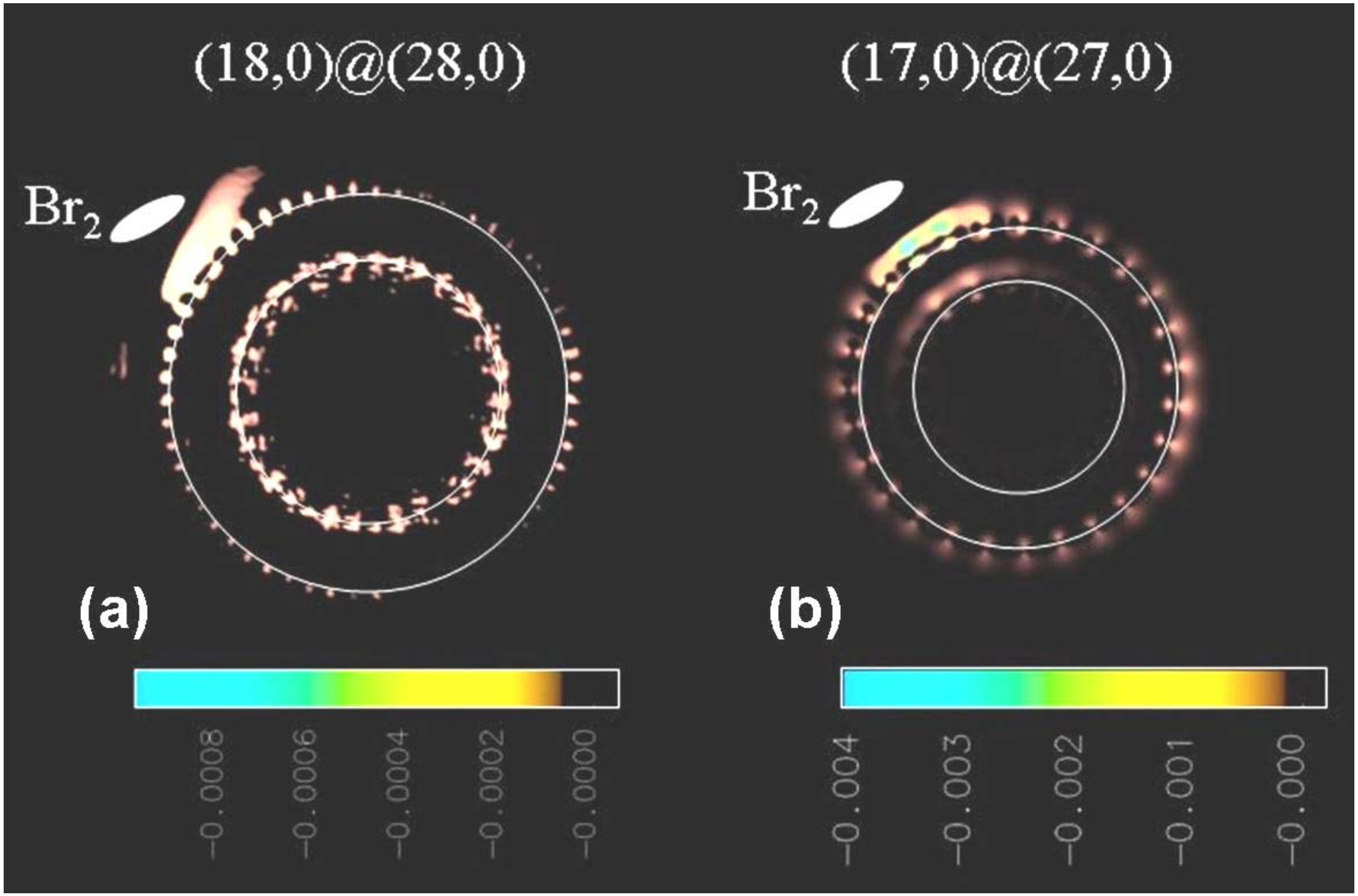
G band Raman spectra of Br_2 doped DWNTs.



Metallic inner tubes highly affected by doping

Semiconducting inner tubes is not affected when shielded by metallic tubes

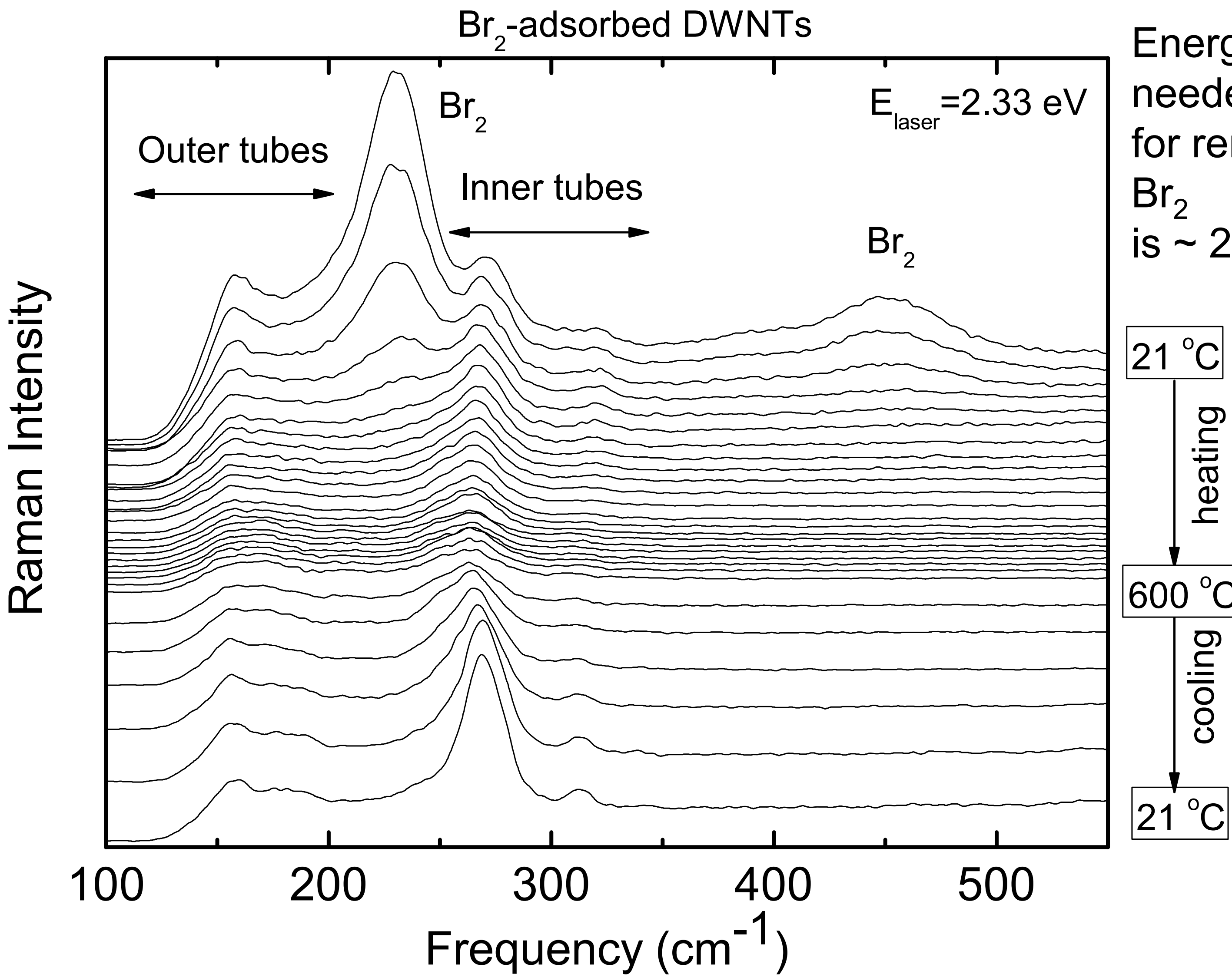
Calculated electronic charge density difference (ρ_{doped} - $\rho_{undoped}$) of DWNTs



Calculation supports experimental observations about charge transfer

A.G. Souza Filho et al Nano Letters (2007)

Undoping experiments on bromine doped DWNTs

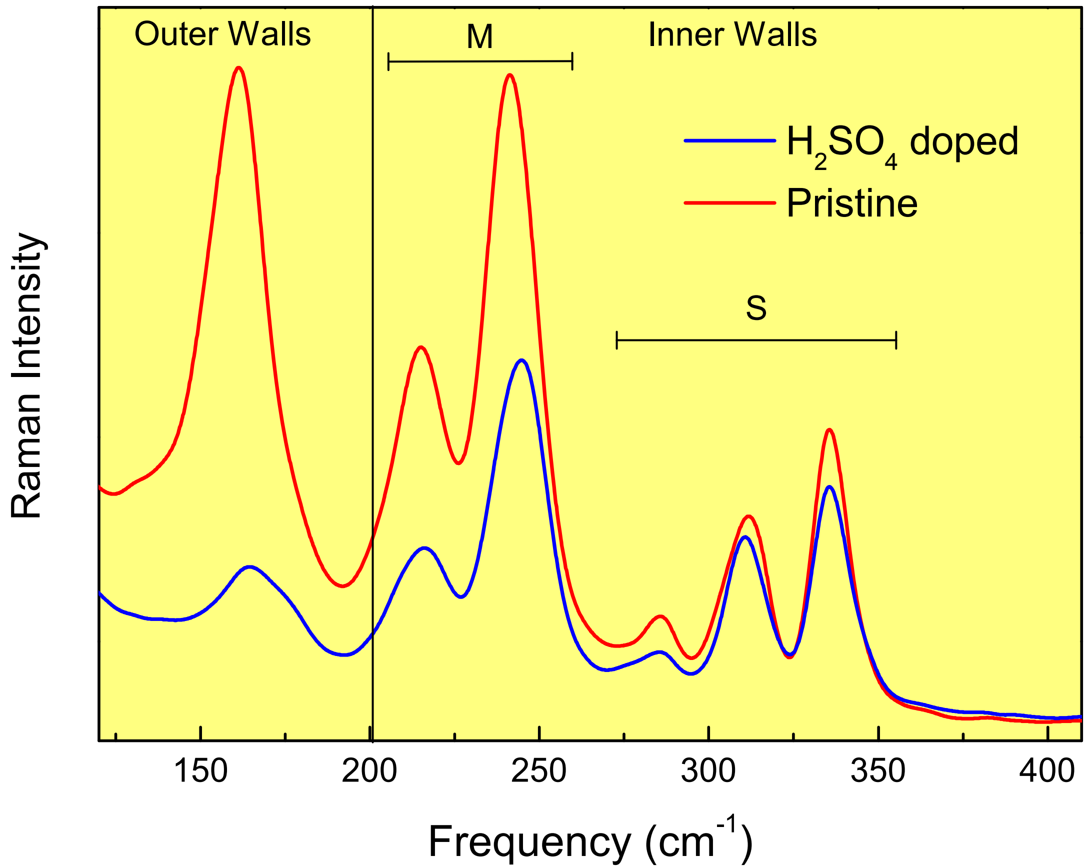


Energy needed for removing Br_2 is ~ 25 meV

- **The dopant is completely removed after heat treatment**

Souza Filho et al, PRB (2006)

Spectrum for RBM for pristine and H_2SO_4doped DWNTs



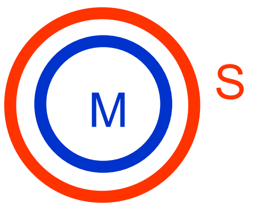
E_{laser}=2.052 eV

- Outer walls strongly affected by doping
- Inner semiconducting (S) tubes weakly interact with dopant
- Inner metallic (M) tubes more strongly interact with dopant

E. Barros et al, PRB (2007)

What we learned from intercalation studies of DWNTs

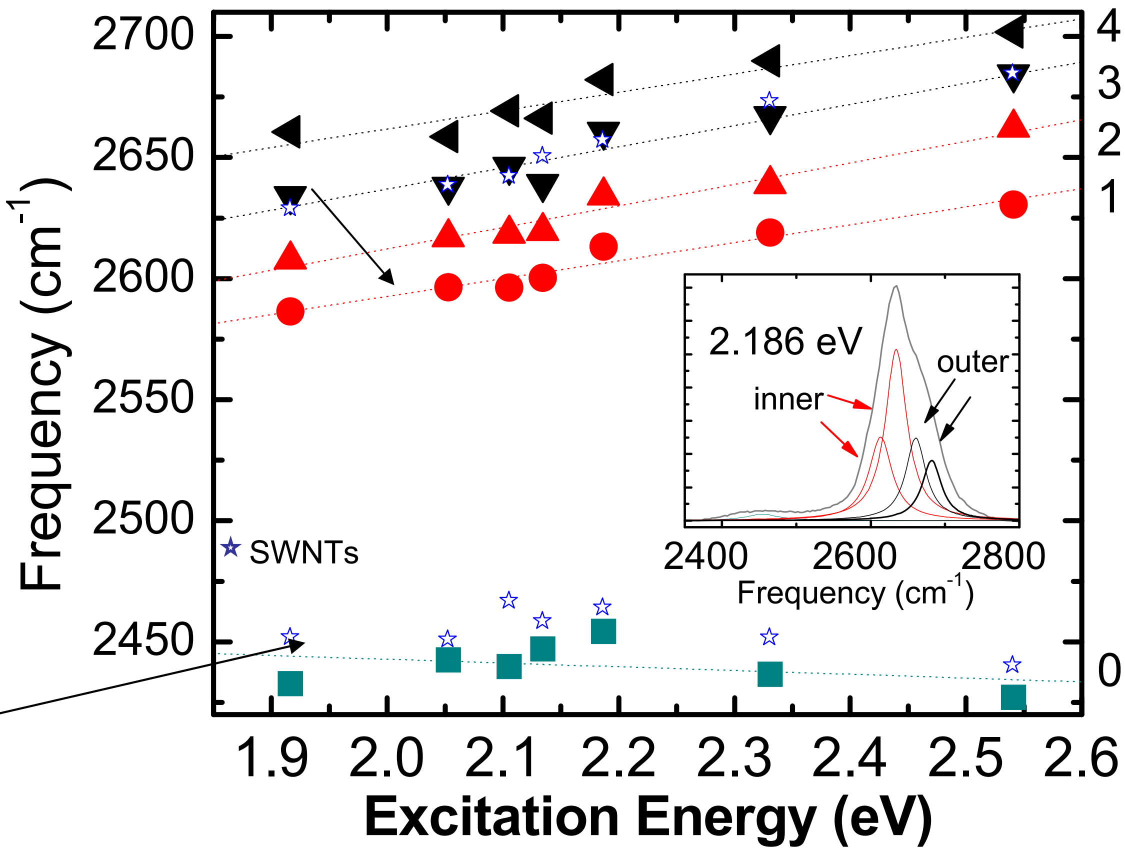
- The Kataura plot from SWNTs provides a semi-quantitive interpretation of frequencies for inner wall tubes for DWNTs


- The M/S configuration shields inner semiconducting tubes from the effect of the dopant
- The S/M configuration allows charge transfer to inner metallic tubes


This work potentially relates to bilayer graphene

Laser Energy Dependence of G′-band Spectra

The SWNT G’ band corresponds to peak 3 of DWNTs



The ~2450 cm^{-1} peak (TO+LA) in DWNTs is downshifted relative to the corresponding peak in SWNTs

Some resemblance to bilayer graphene

E. B. Barros et al., PRB in press (2007)

Physics of Nanotubes, Graphite and Graphene

Outline of Lecture 1 - Nanotubes

- **Brief overview of carbon nanotubes**
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- **Phonon assisted Photoluminescence**
- **Double wall carbon nanotubes**
- **Nano-Metrology**

The problem of Nano-metrology

Why do we need metrology for nanotechnology?

Why do we need reference standards?

What is new about metrology at the nano-scale?

What does nanoscience have to do with metrology?

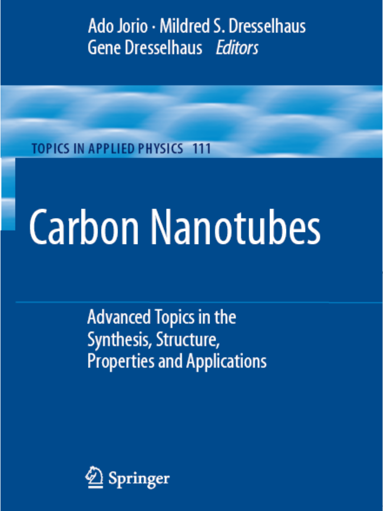
World wide production of Carbon Nanotubes

MWNTs 270 tons/yr (2.45 $\times$ 10^5 kg/year)

SWNTs 7 tons/yr (6.35 $\times$ 10^3 kg/year)

8K US$ / kg to 5.0 $\times$ 10^5 US$ / kg

(R. Blackmon, http://www.wtec.org/cnm/)



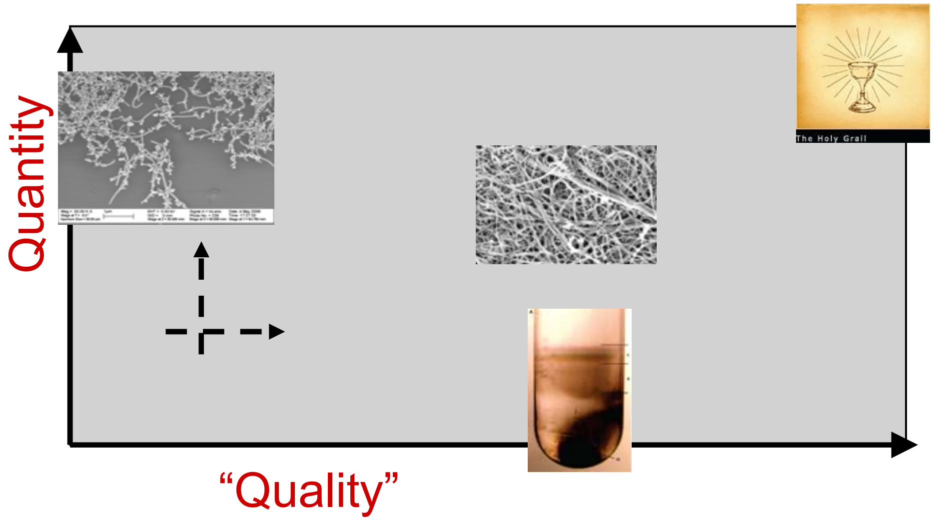
Metrology is guided by applications

Potential Applications of Carbon Nanotubes

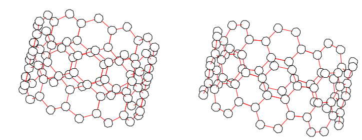
by M. Endo, M. S. Strano, P. M. Ajayan @ Springer TAP111

	Large Volume Applications	**Limited Volume Applications (Mostly based on Engineered Nanotube Structures)**
Present	- Battery Electrode Additives (MWNT) - Composites (sporting goods; MWNT) - Composites (ESD* applications; MWNT) *ESD – Electrical Shielding Device	- Scanning Probe Tips (MWNT) - Specialized Medical Appliances (catheters) (MWNT)
Near Term (less than ten years)	- Battery and Super-capacitor Electrodes - Multifunctional Composites - Fuel Cell Electrodes (catalyst support) - Transparent Conducting Films - Field Emission Displays / Lighting - CNT based Inks for Printing	- Single Tip Electron Guns - Multi-Tip Array X-ray Sources - Probe Array Test Systems - CNT Brush Contacts - CNT Sensor Devices - Electro-mechanical Memory Device - Thermal Management Systems
Long Term (beyond ten years)	- Power Transmission Cables - Structural Composites (aerospace and automobile etc.) - CNT in Photovoltaic Devices	- Nano-electronics (FET,Interconnects) - Flexible Electronics - CNT based bio-sensors - CNT Fitration/Separation Membranes - Drug-delivery Systems

What should we measure? At which scale?



vs.

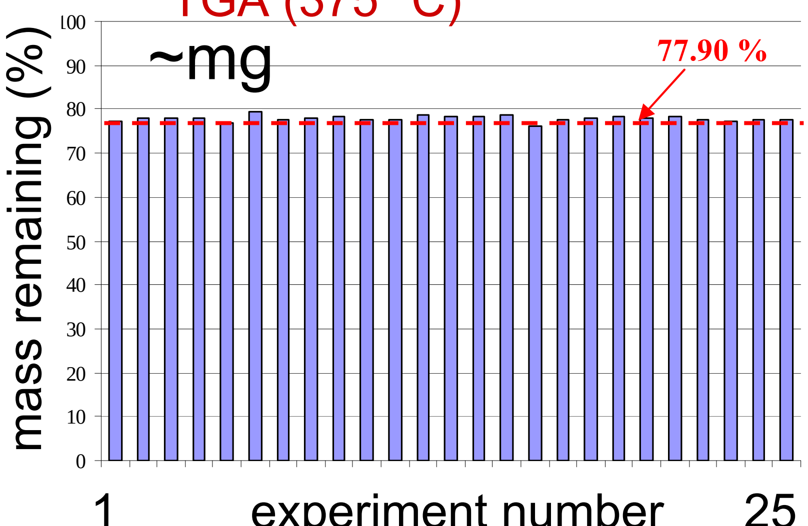


Statistical Comparison

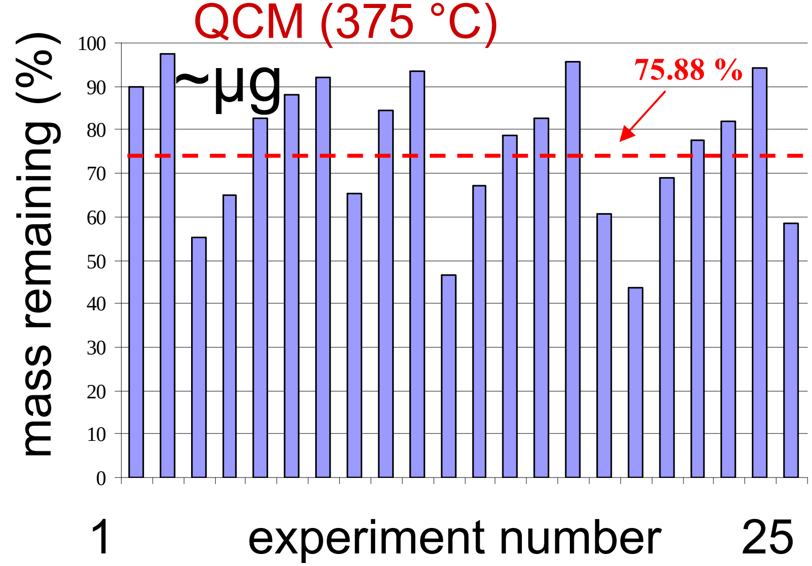
Thermogravimetric analysis (TGA)
Quartz cyrstal microbalance (QCM)

QCM shows SWNTs are *non-homogeneous already at the μg scale*

TGA (375 °C)



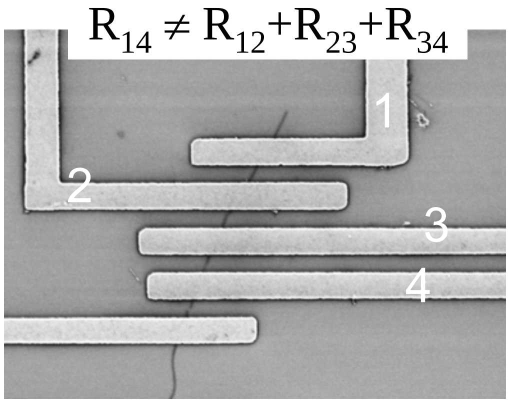
QCM (375 °C)



Can we trust the measurements?

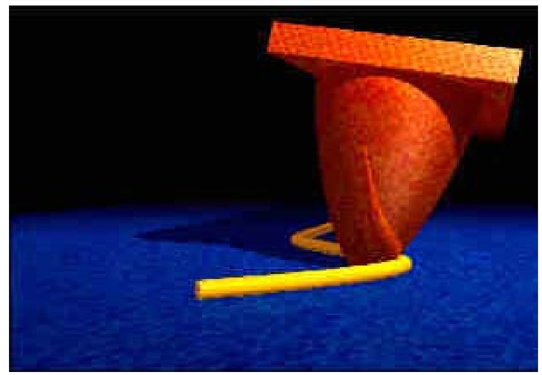
What do we use for measuring nanomaterials properties?

4-PROBES TRANSPORT



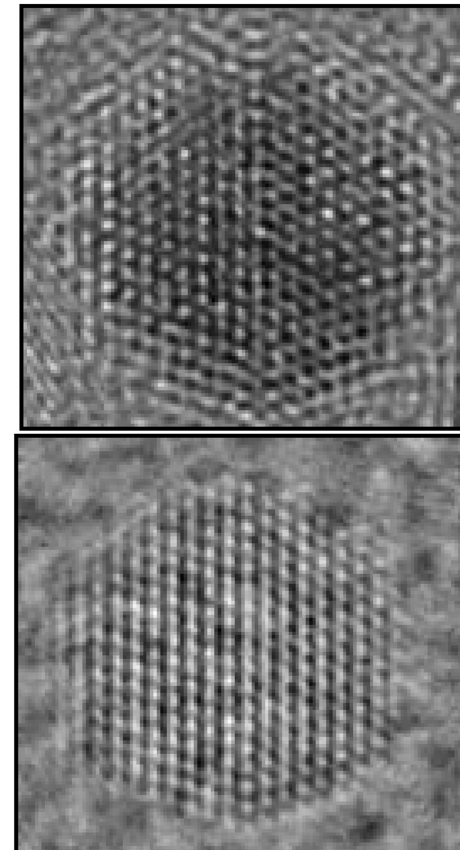
*Purewal et al.,PRL **98**,186808 (2007)*

SCANNING PROBES



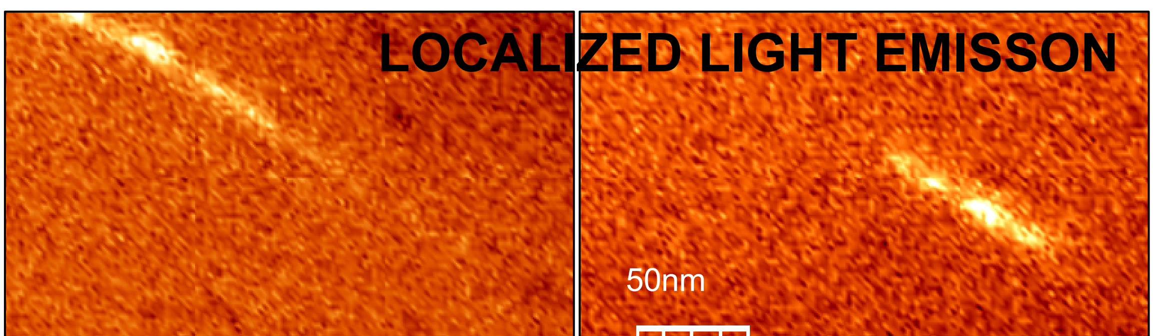
IBM Website

ELECTRON MICROSCOPY



From Hubert - FEI

LIGHT: Raman and photoluminescence

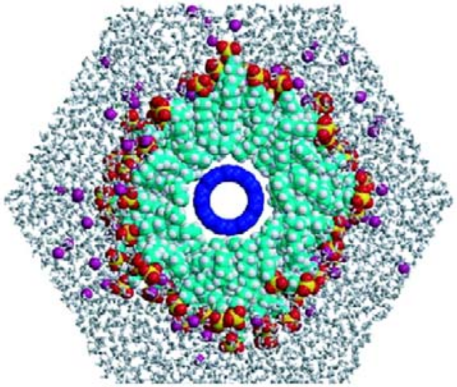


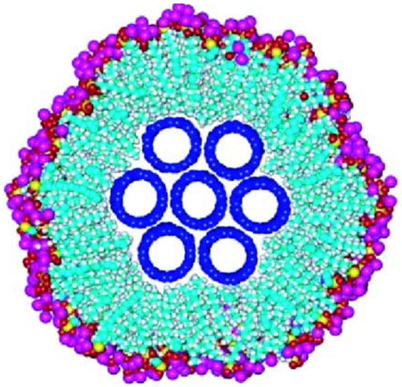
From Achim Hartschuh

Can we trust the measurements?

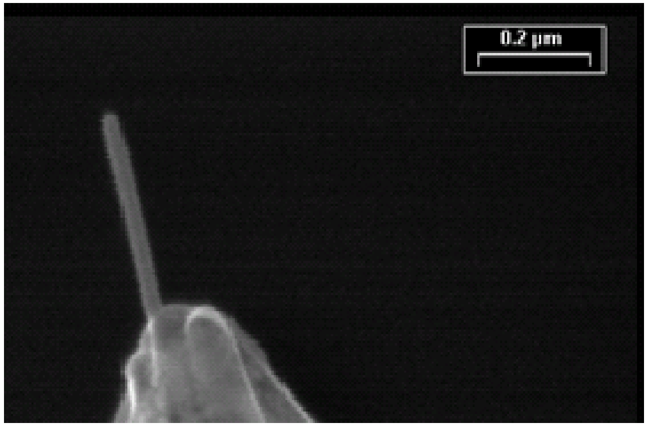
What is the ideal environment?

Encapsuled by micelles

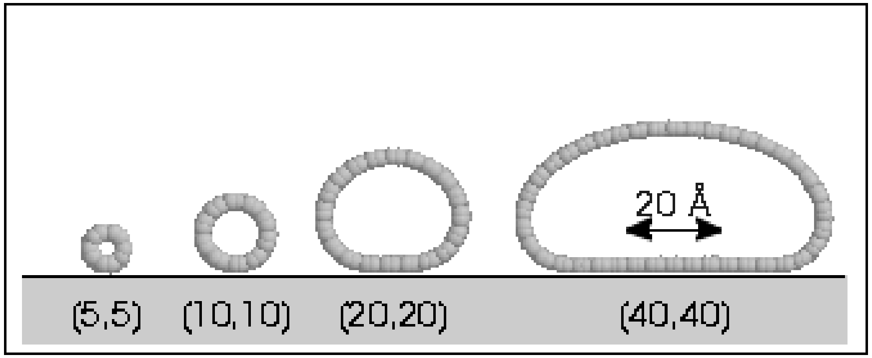




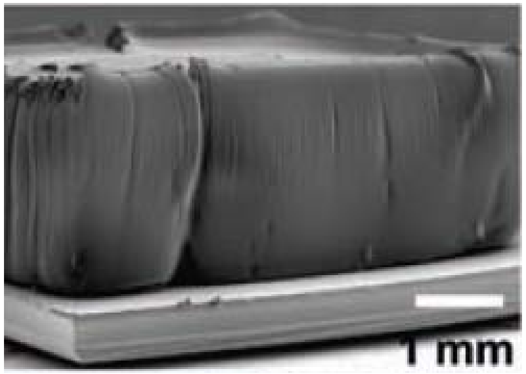
Suspended in air



Sitting on a substrate



Within a forest



Nano-metrology is a wide open area for development requiring collaboration between metrology and nanoscience experts