Optical Spectroscopy of Nanostructures

Y. Ron Shen
Physics Department
University of California at Berkeley

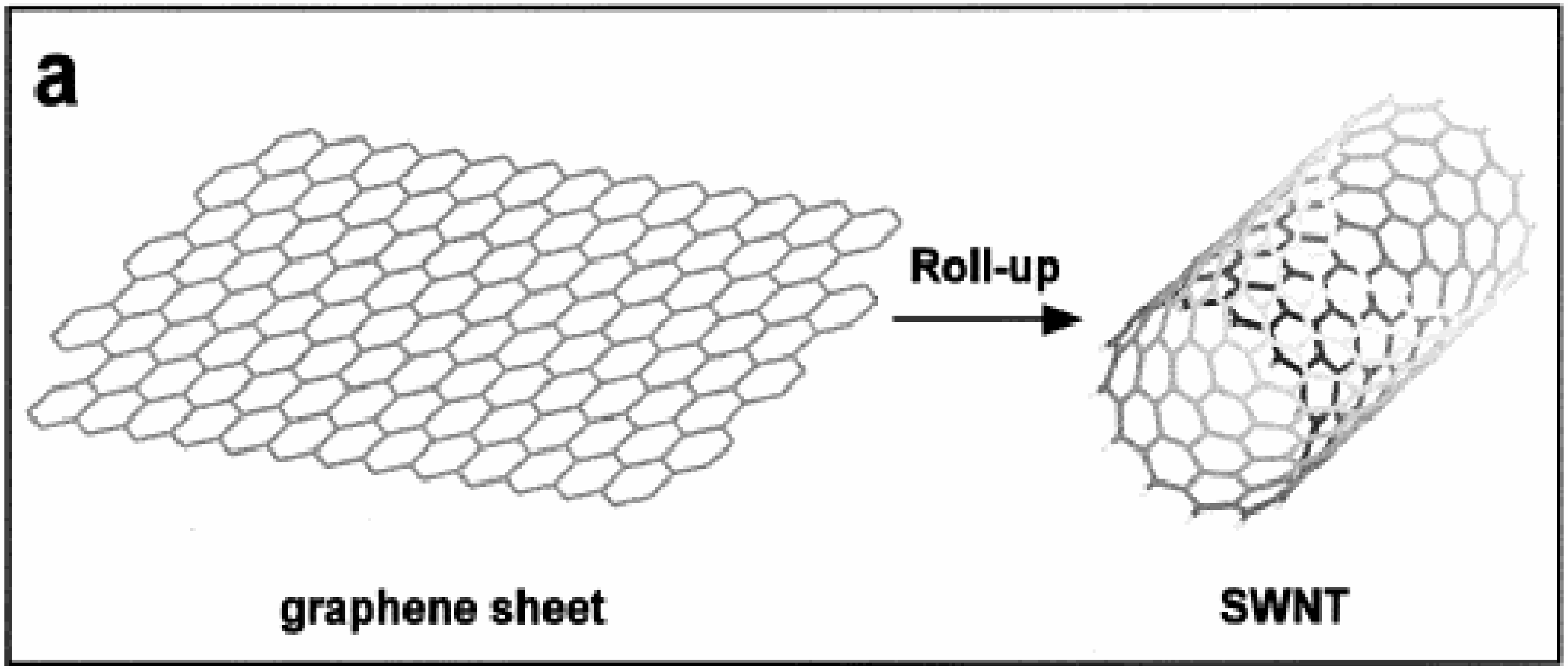
Nanophotonics

- Optical characterization of nanostructures:
  nanoparticles, nanorods, nanotubes, etc.
  Carbon nanotubes, graphenes, metamaterials
- Applications of Nanostructures to optics:
  nano-lasers, nano-lithography, metamaterials, etc.

Optical Characterization of Individual Carbon Nanotubes

Feng Wang

Single-Wall Nanotube (SWNT): A Quasi-1D System



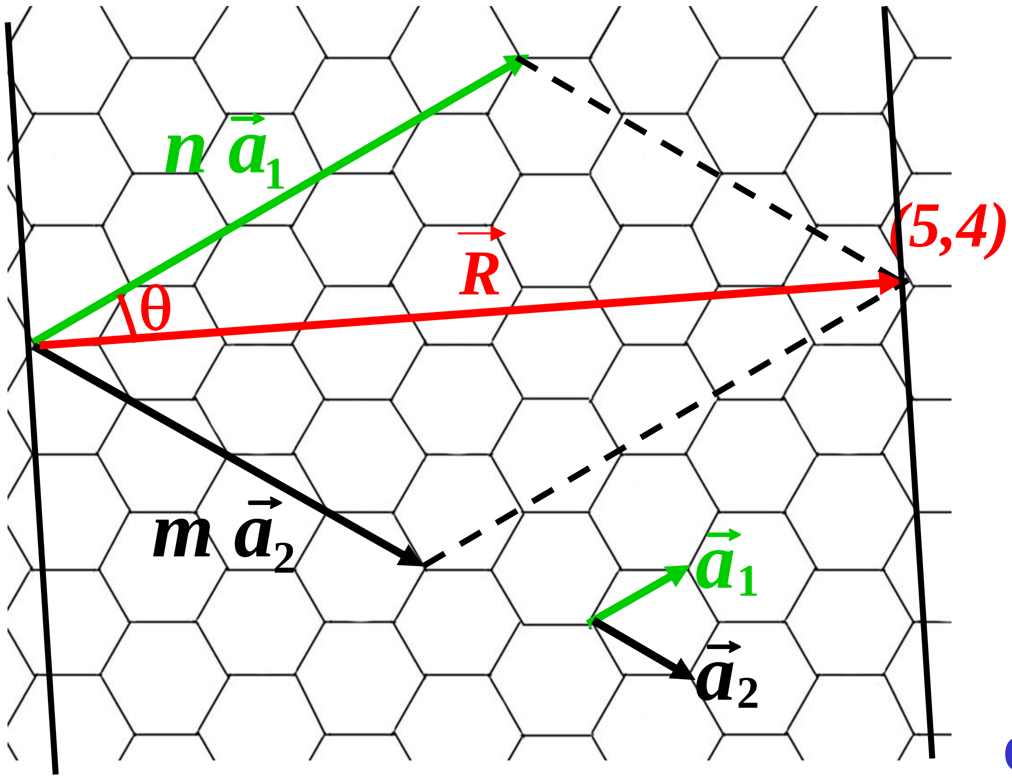
Hundreds of species depend on how it is folded.

Characteristics of Carbon Nanotubes

- Nearly ideal 1D systems
- High mechanical strength
- High thermal conductivity
- High current-carrying capacity
- Existence of both metals and semiconductors

A Family of Structures

Graphene:



$$\vec{R} = n \cdot \vec{a}_1 + m \cdot \vec{a}_2$$

$$|R| = a\sqrt{n^2 + m^2 + nm}$$

$$a^2 = a_1^2 = a_2^2 = 2\vec{a}_1 \cdot \vec{a}_2$$

(n,m): Chiral indices
d = R/π (tube diameter)
θ (chiral angle)

Over hundred species with diameters less than 2 nanometer

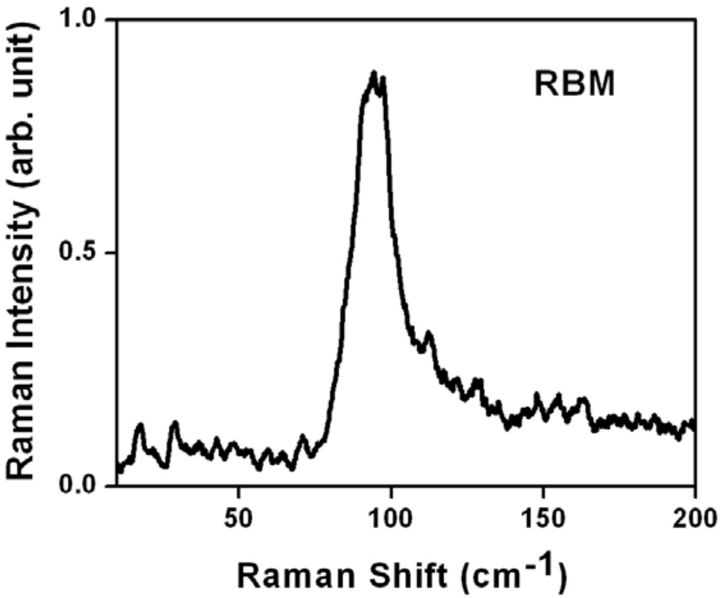
Optical Characterization of Single SWNTs

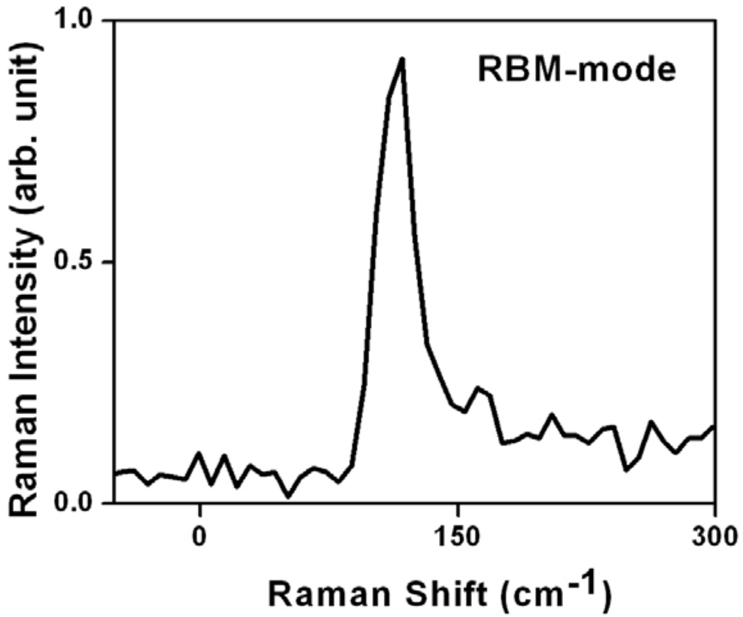
Avoiding complications from a bundle of nanotubes

Determination of Tube Diameter

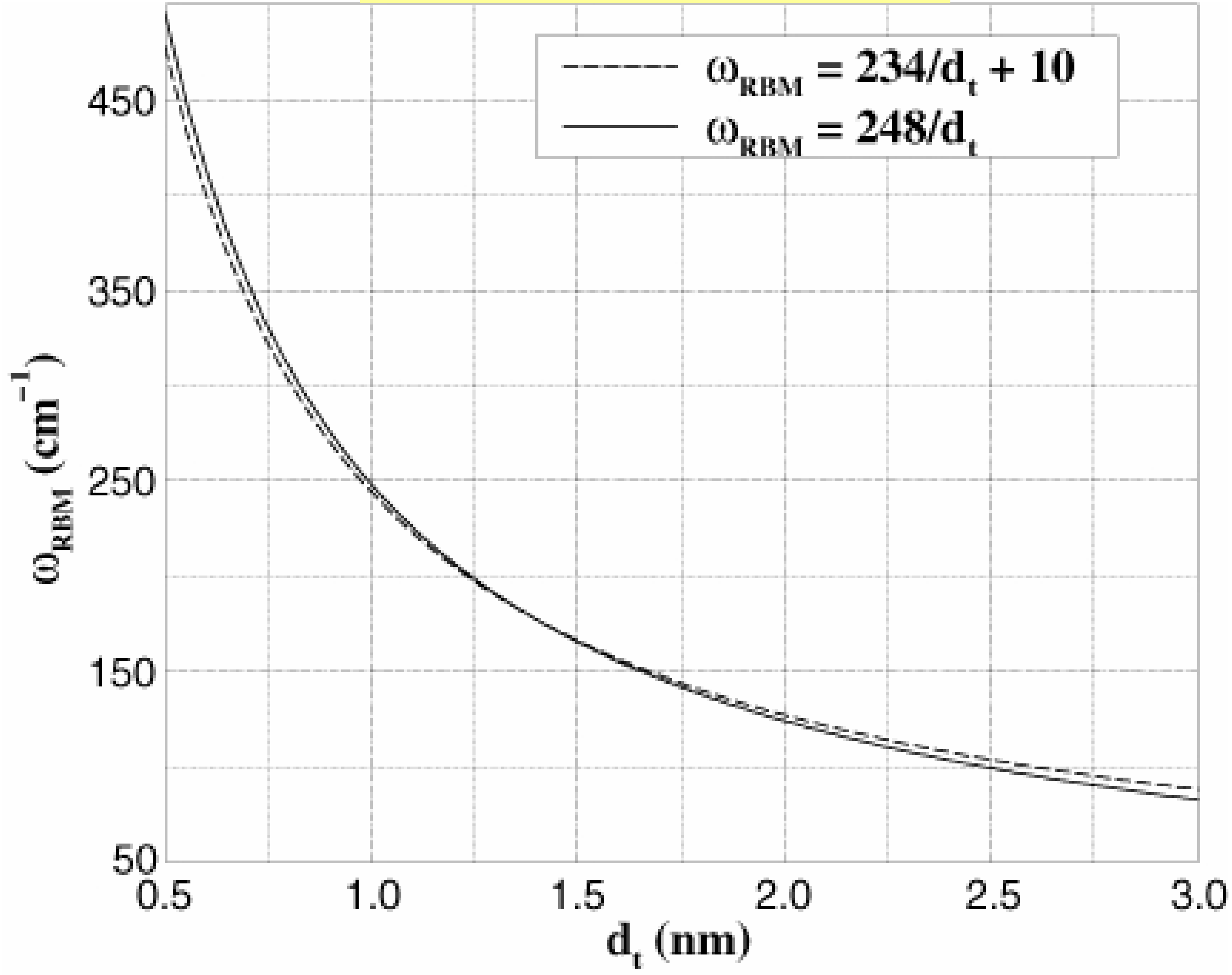
Raman spectrum of radial breathing mode (RBM)

(A. Jorio et al, New J. Physics 5, 139 (2003))





$$\omega_{RBM} = A/d_t + B$$



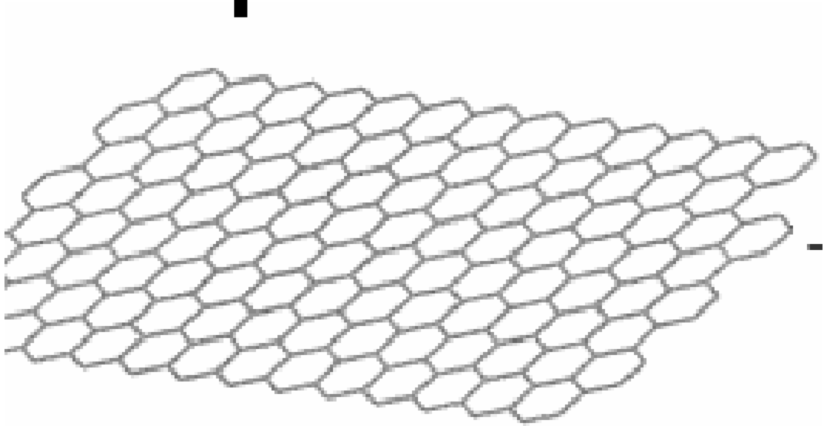
Determination of Chiral Indices

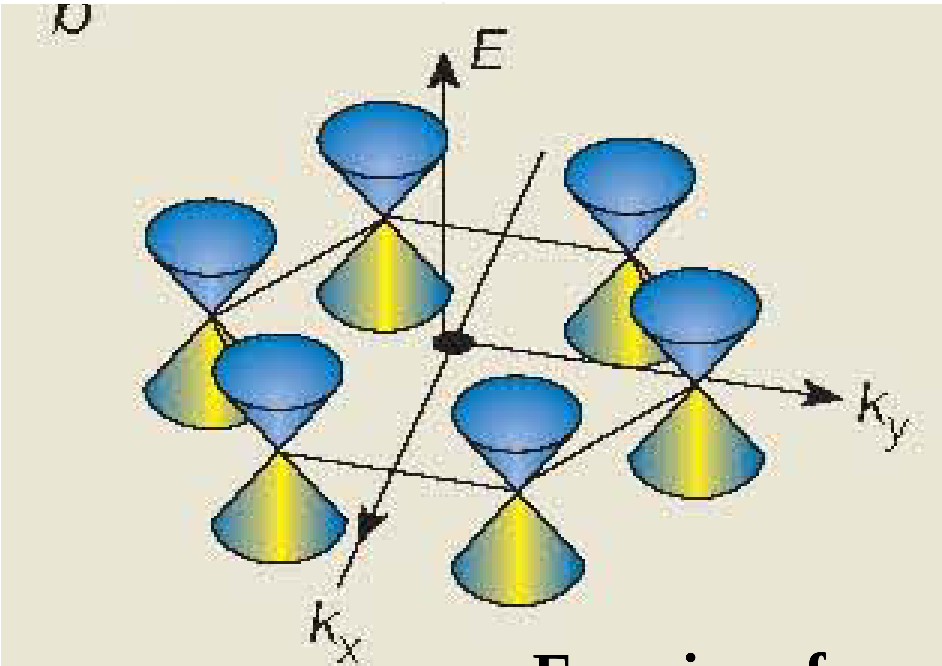
Tube can have same diameter but different chiral indices

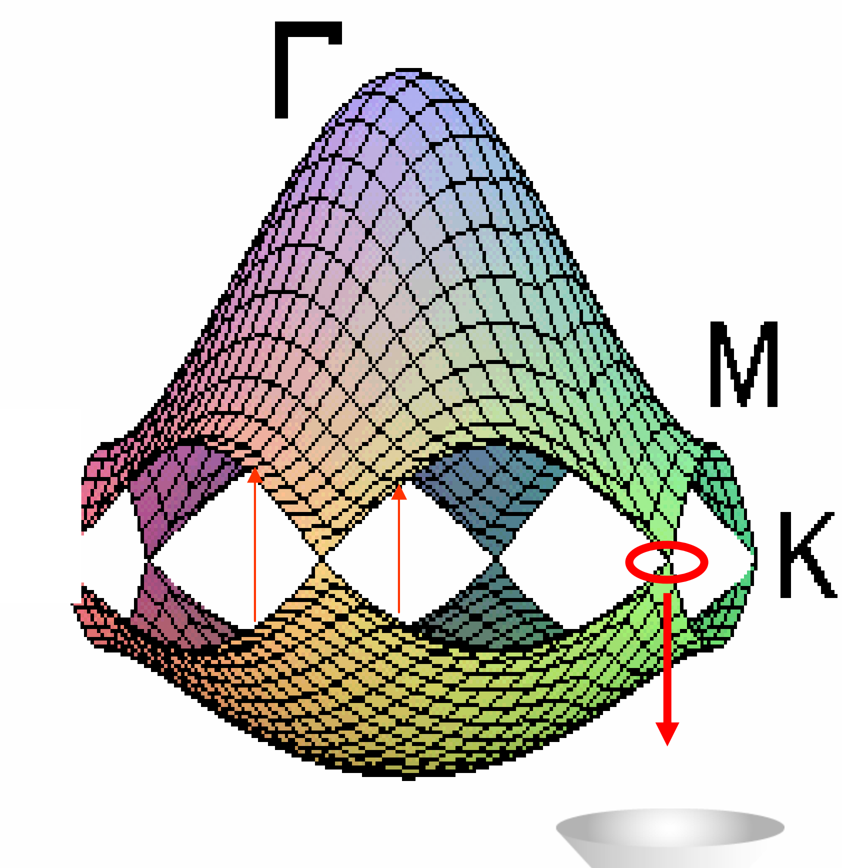
Optical Transitions $\Longleftrightarrow$ Chiral Indices

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

Graphene Electronic Structure



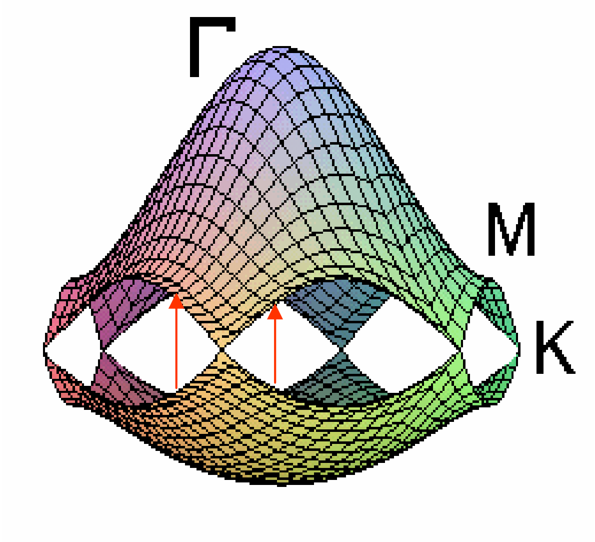




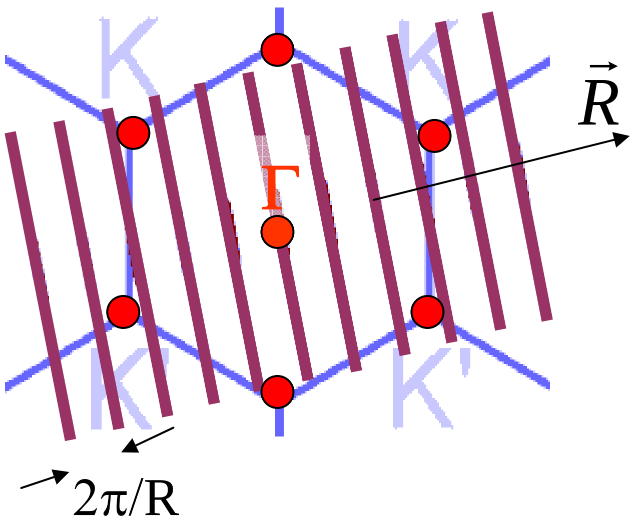
Fermi surface: K and K' points

(Zero-gap semiconductor)

Metallic and Semiconducting Nanotubes



Brillouin zone



For SWNT, cyclic or periodic boundary condition in the rolling direction ⇒⇒ only states on the red lines in the 2D BZ can exist. ***(k=2Nπ/R)***

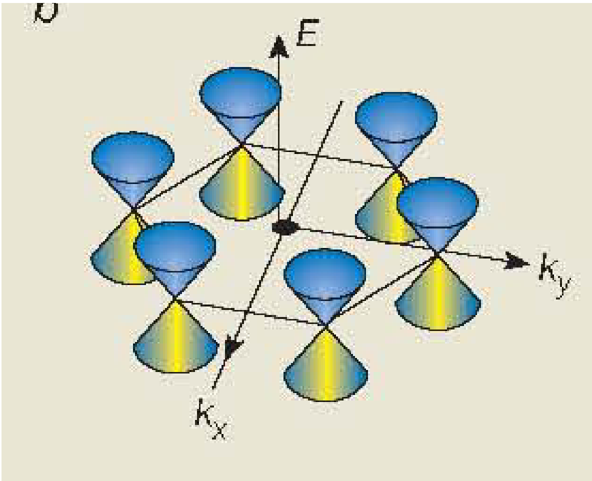
If K points are on the lines,

mod(n-m)≡n-m-3(interger)=0,
no energy gap
⇒⇒ metallic nanotubes

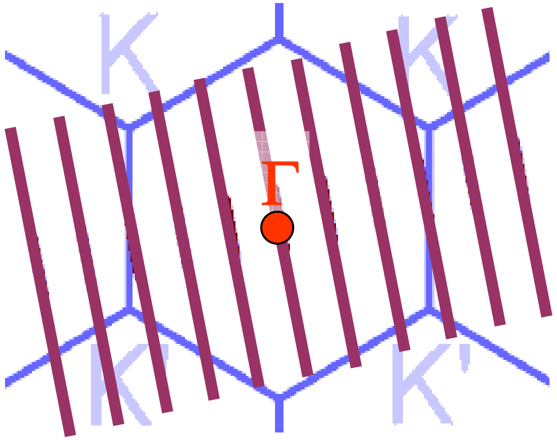
If K points are not on the lines,

mod(n-m)=1 or 2
energy gap appears
⇒⇒ semiconducting nanotubes

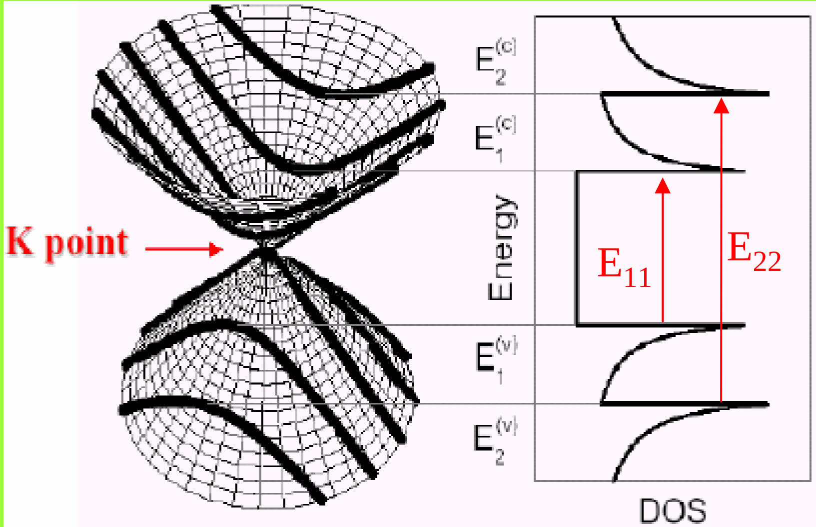
SWNT Electronic Structure



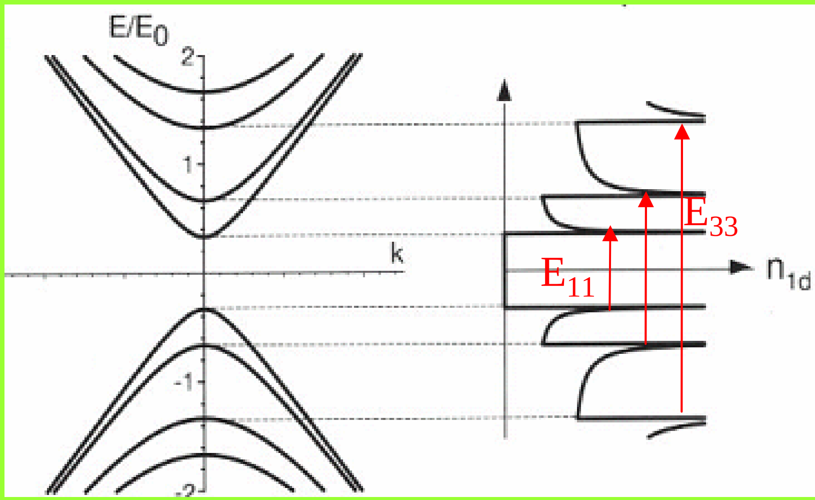
Brillouin zone



Metallic:



Semiconducting:



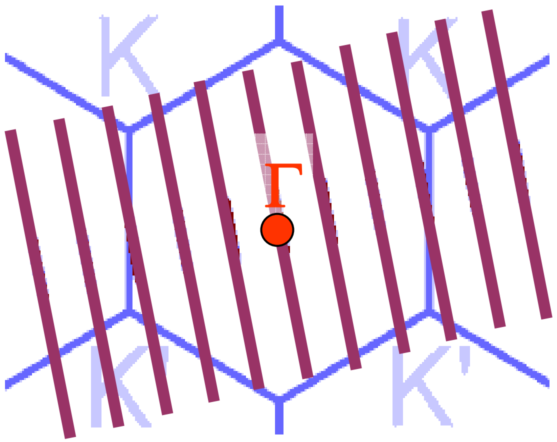
Categorization of SWNTs

Bandgap: d

Metallic or semiconducting: n-m (chiral angle θ)

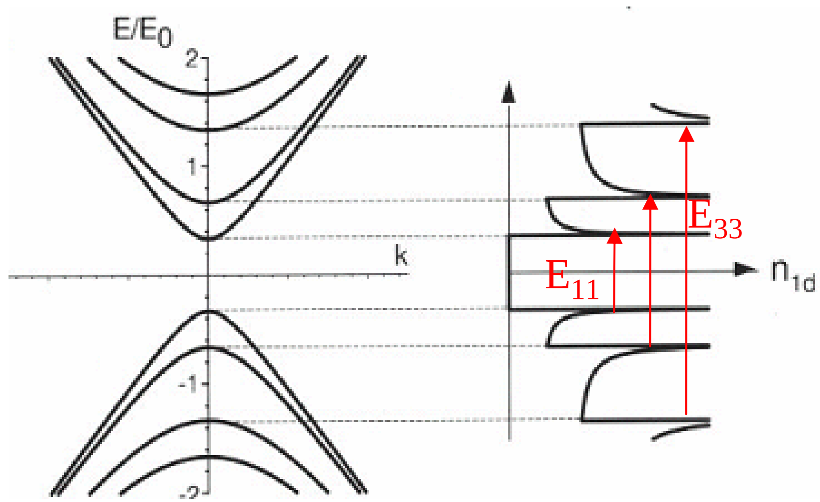
Metallic	***Semiconducting***	***Semiconducting***
mod(n-m,3)=0	***mod(n-m,3)=1***	***mod(n-m,3)=2***
e.g. (15,15), (18, 15)	**(16,15)**	**(17,15)**

SWNT Electronic Structure



Brillouin zone

Semiconducting:



- Lower-energy transitions can appear in the visible if the tube diameter is sufficiently small.
- Transitions would be characterized by 1D van Hove singularities unless exciton formation dominates.

Optical Spectroscopy of Single Nanotubes

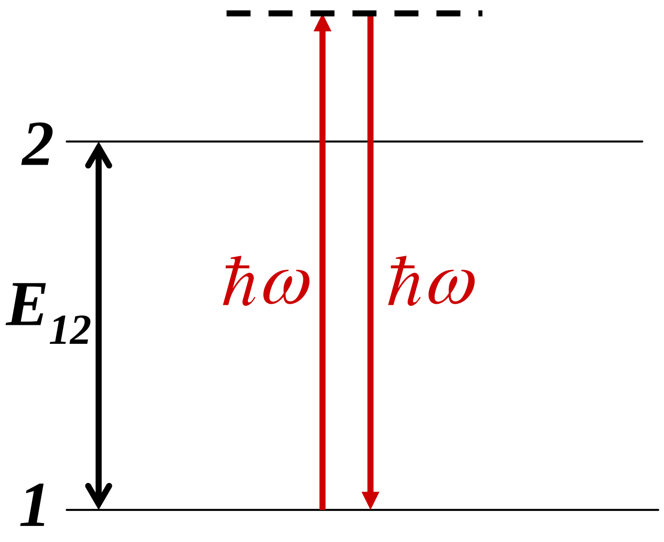
Resonance Raman spectroscopy: Intrinsically weak.

Fluorescence: Only possible for semiconducting tubes.

Elastic (Rayleigh) light scattering

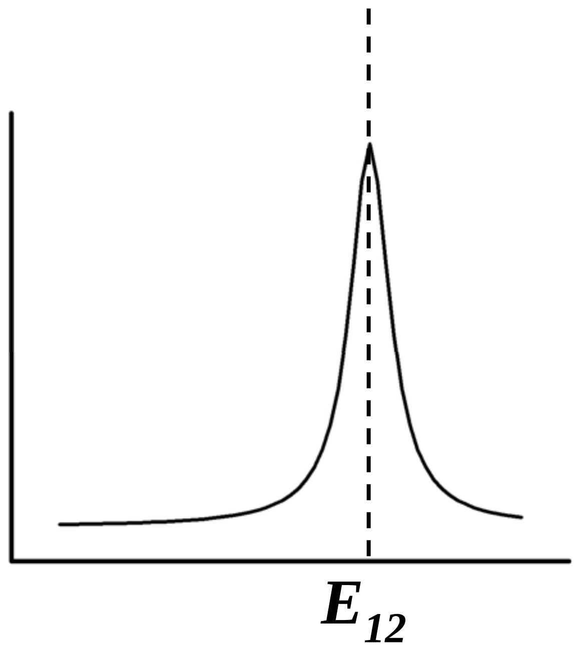
Absorption spectroscopy

Elastic Scattering Spectroscopy



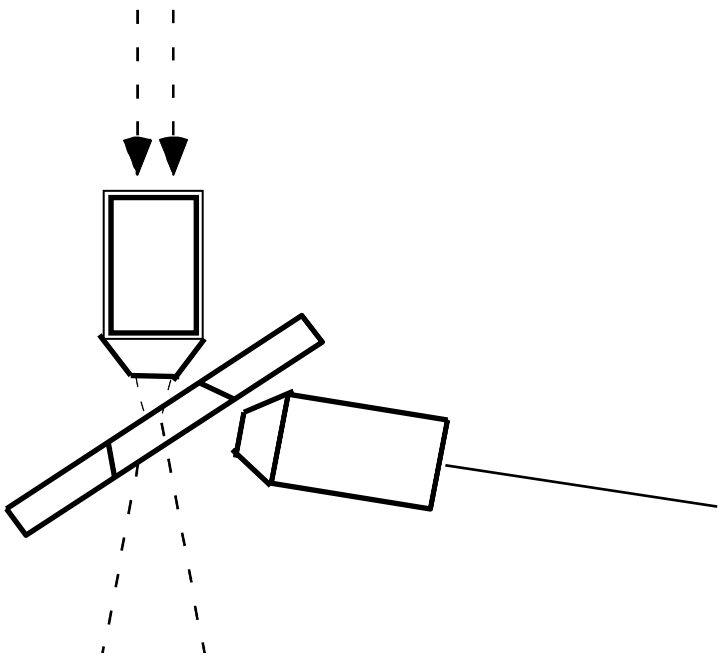
Elastic Scattering:

$$\sigma \propto |\varepsilon - 1|^2$$



Resonances correspond to electronic transitions.

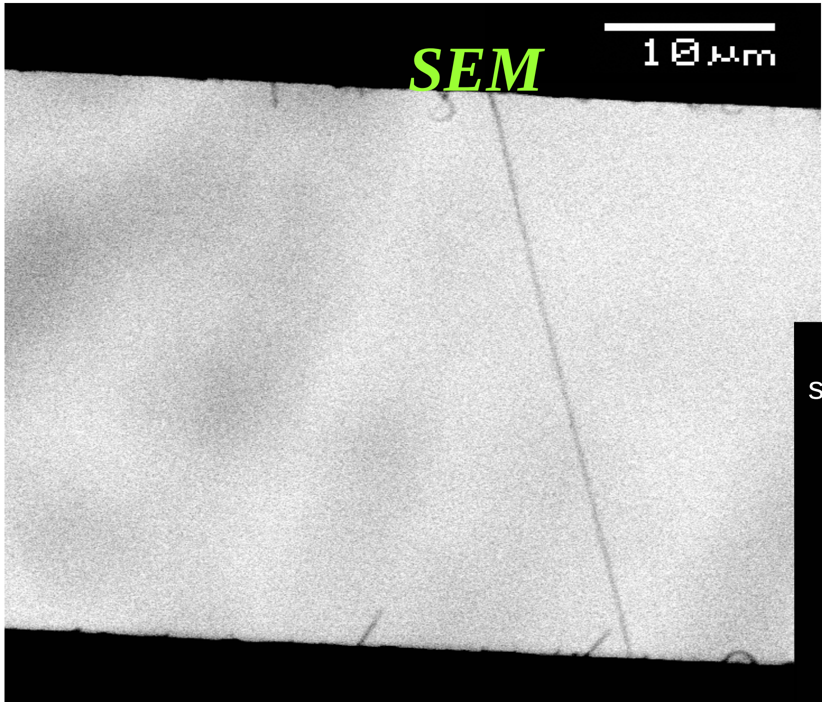
Experiment Arrangement

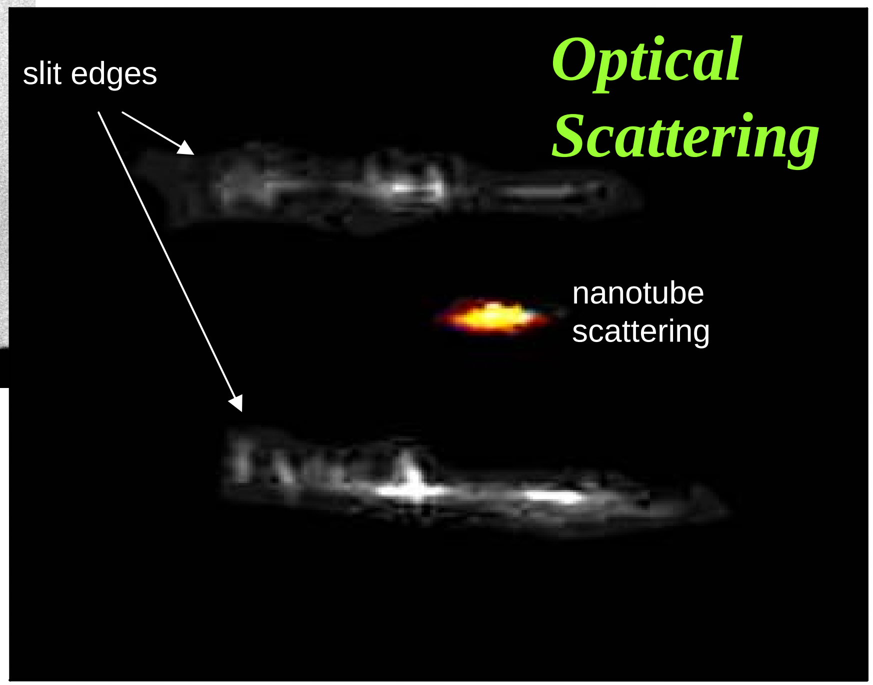


dark field imaging

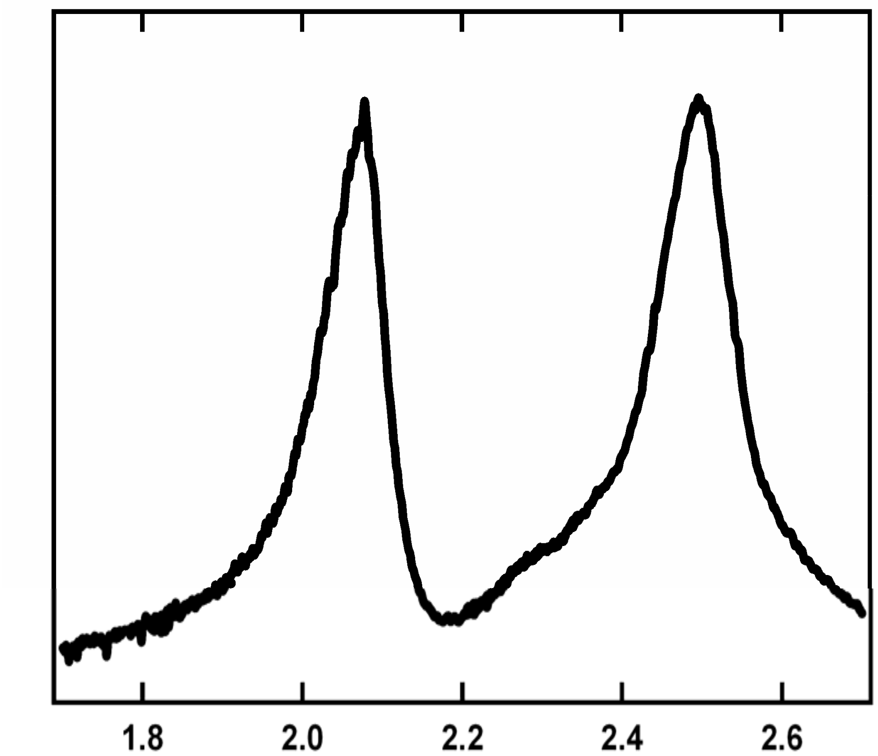
Suspended Carbon Nanotubes

- Reduced background ⟶ ***Suspended nanotube across slit***





Rayleigh Spectrum

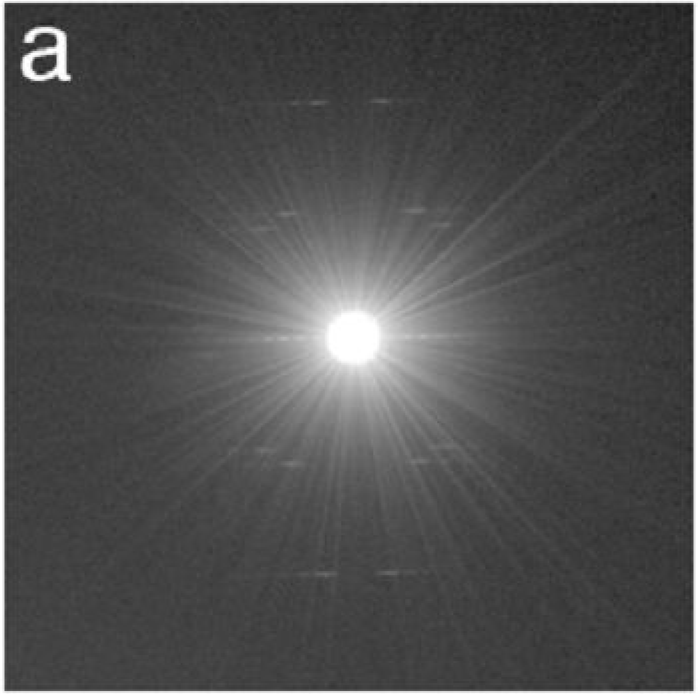


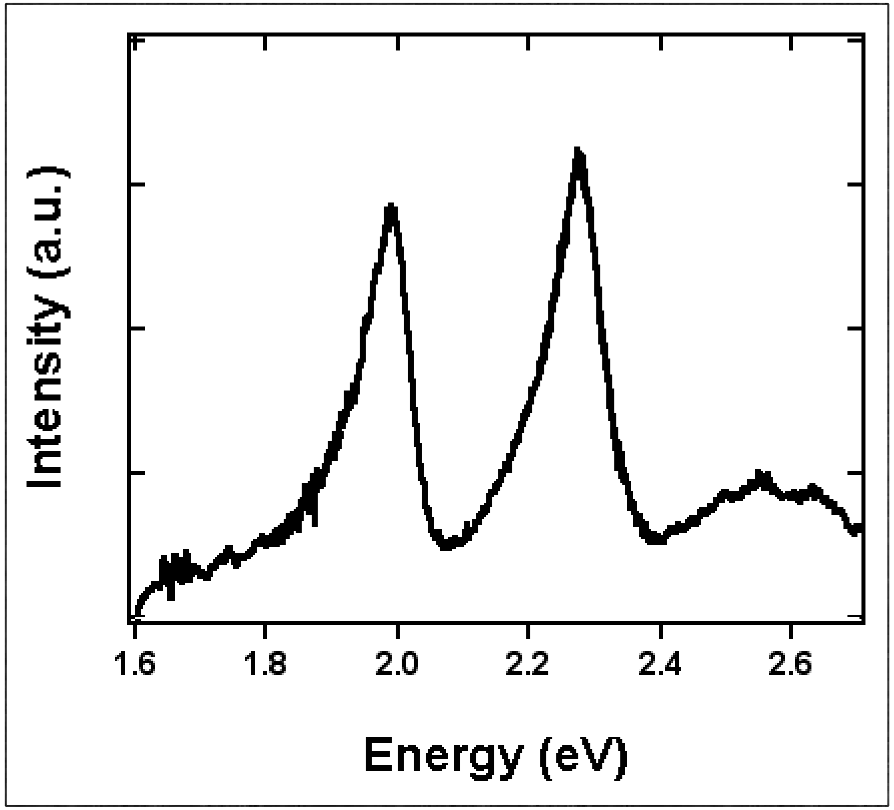
Energy (eV)

(13,12): d = 1.70 nm
mod(n-m,3)=1

M. Sfeir*, F. Wang* et al. Science, 306, 1540 (2004)

Correlation with Electron Diffraction

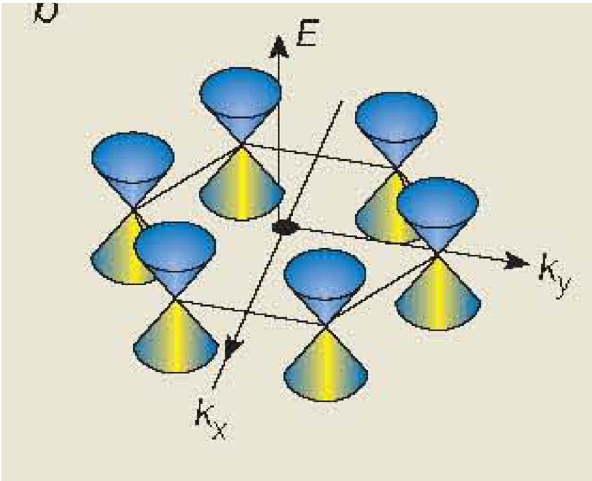




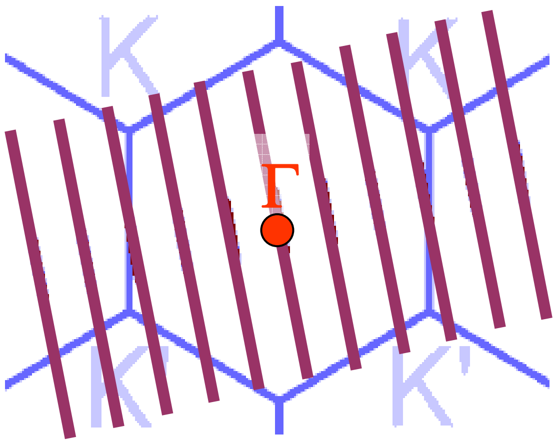
(16, 11) tube

M. Sfeir, T. Beetz, F. Wang et al. Science, 312, 554 (2006)

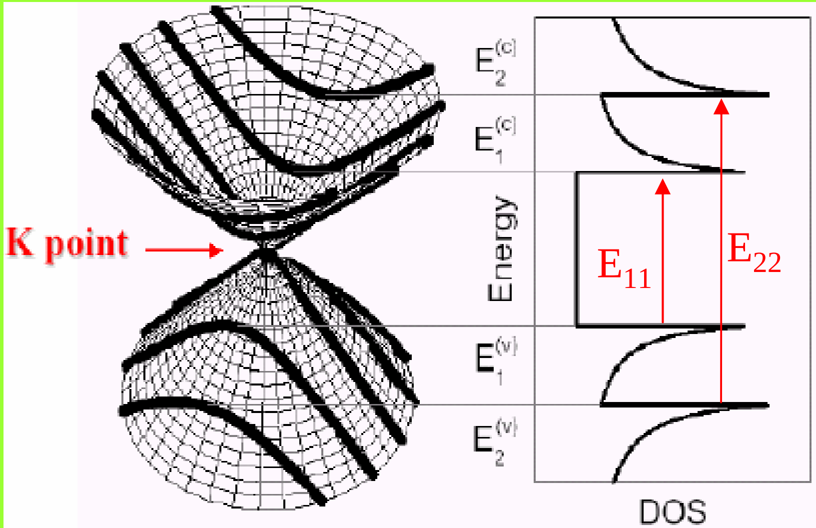
SWNT Electronic Structure



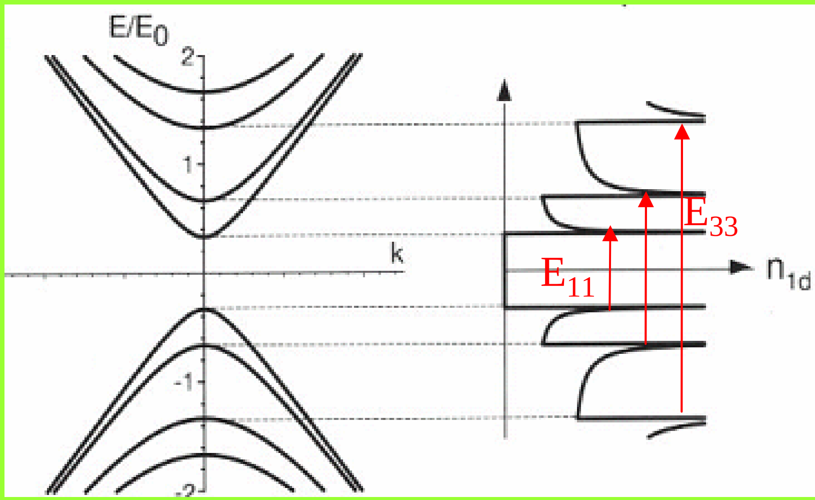
Brillouin zone



Metallic:

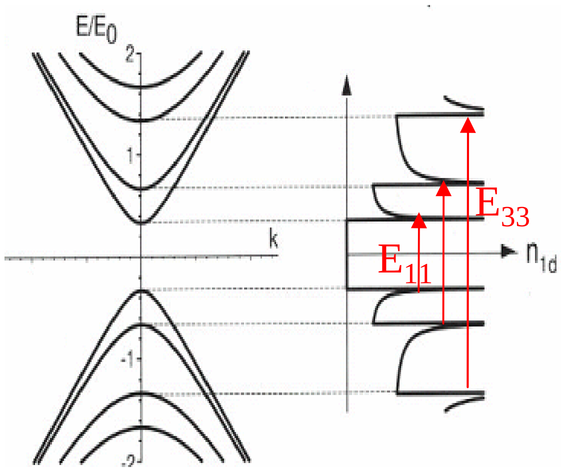


Semiconducting:



Family Trend

A set of qualitative rules:



1. **Diameter dependence:**

   Smaller diamter, larger E_{ii}.

2. **n-m (chiral angle) dependence:**

   Semiconducting:

   $E_{ii}^{mod(n-m,3)=1} < E_{ii}^{mod(n-m,3)=2}$, ***i = odd integer.***

   $E_{ii}^{mod(n-m,3)=1} > E_{ii}^{mod(n-m,3)=2}$, ***i = even integer.***

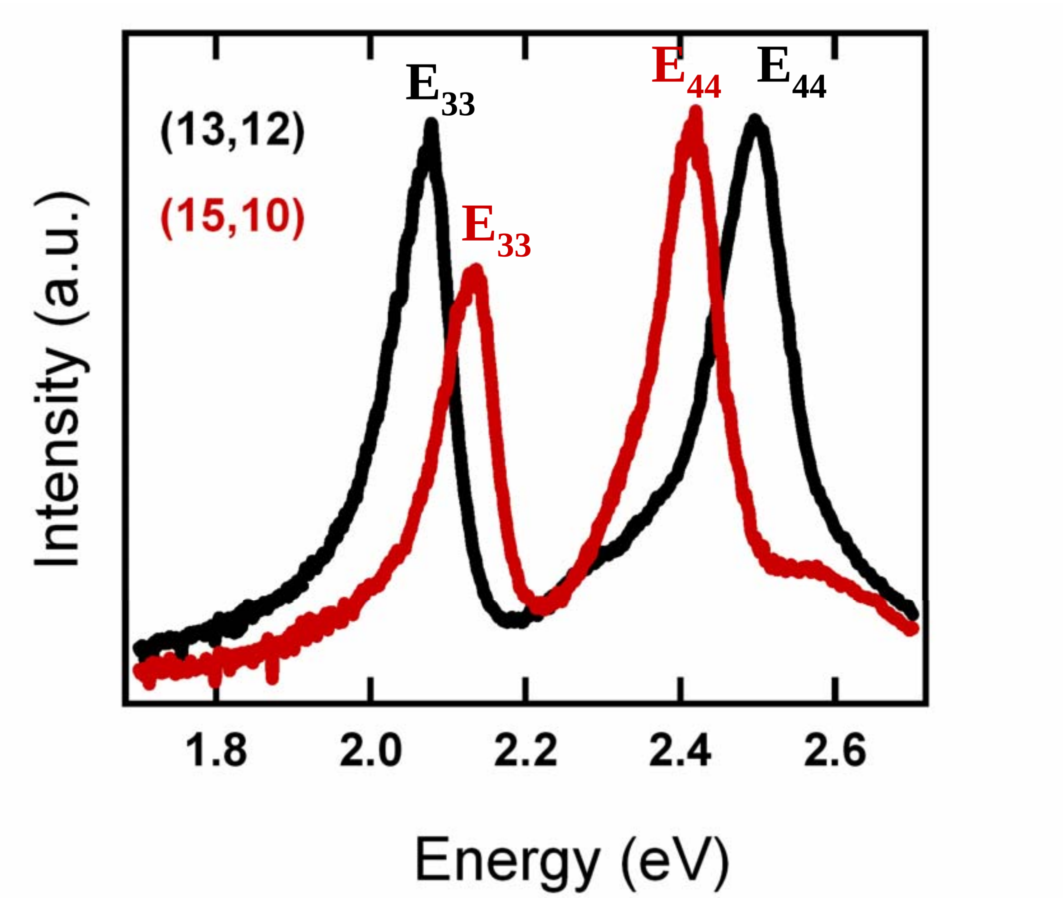
   Differences increase with n-m value.

   Metallic:

   Degeneracy with n-m=0. Peak splitting increases with n-m.

(Derived from tight binding calculation. Dresselhaus, Kataura, Weisman and others)

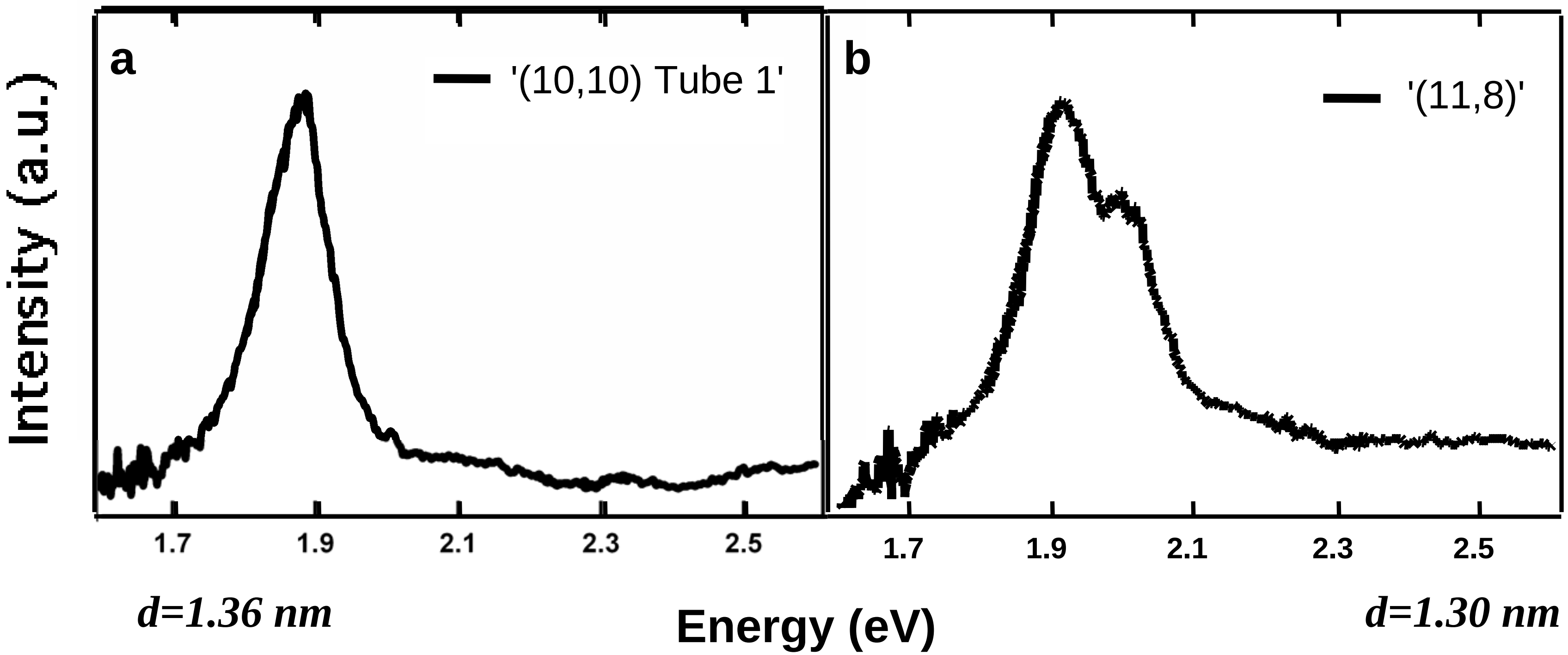
n-m Dependence: Semiconducting Nanotubes



(13,12): d = 1.70 nm
mod(n-m,3)=1

(15,10): d = 1.71 nm
mod(n-m,3)=2

n-m Dependence: Metallic Nanotubes

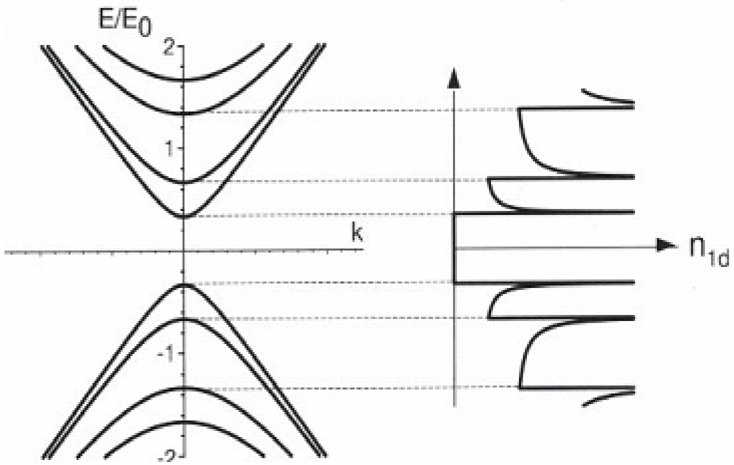


Degenerate transitions for (n-m)=0,

Degeneracy lifted for (n-m)≠0

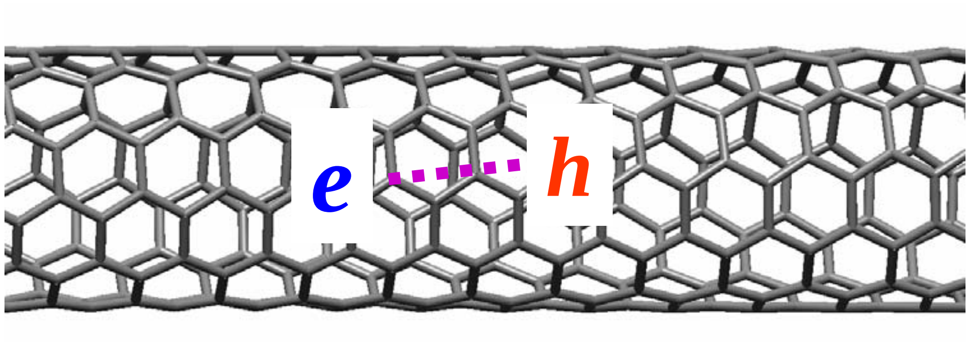
Nature of Optical Transitions

van Hove Singularities ?



Prevailing experimental interpretation

Strong e-h interaction ⇒⇒Excitons?

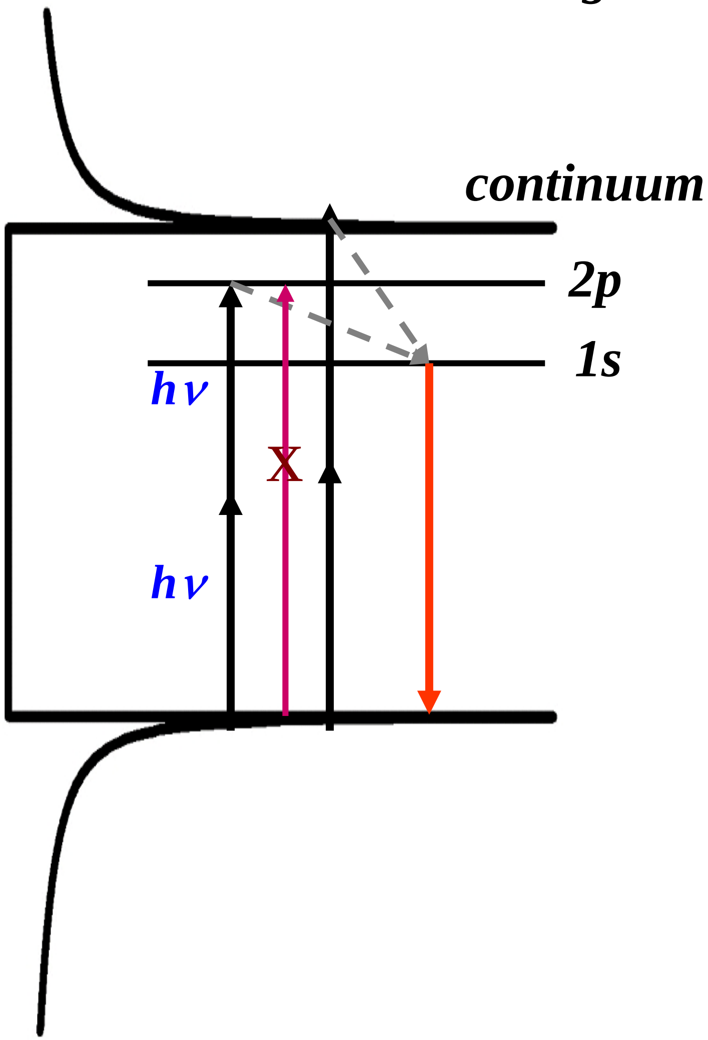


Theoretical prediction

(Avouris, Louie and others)

Confirmation of Existence of Excitons in Semiconducting Nanotubes

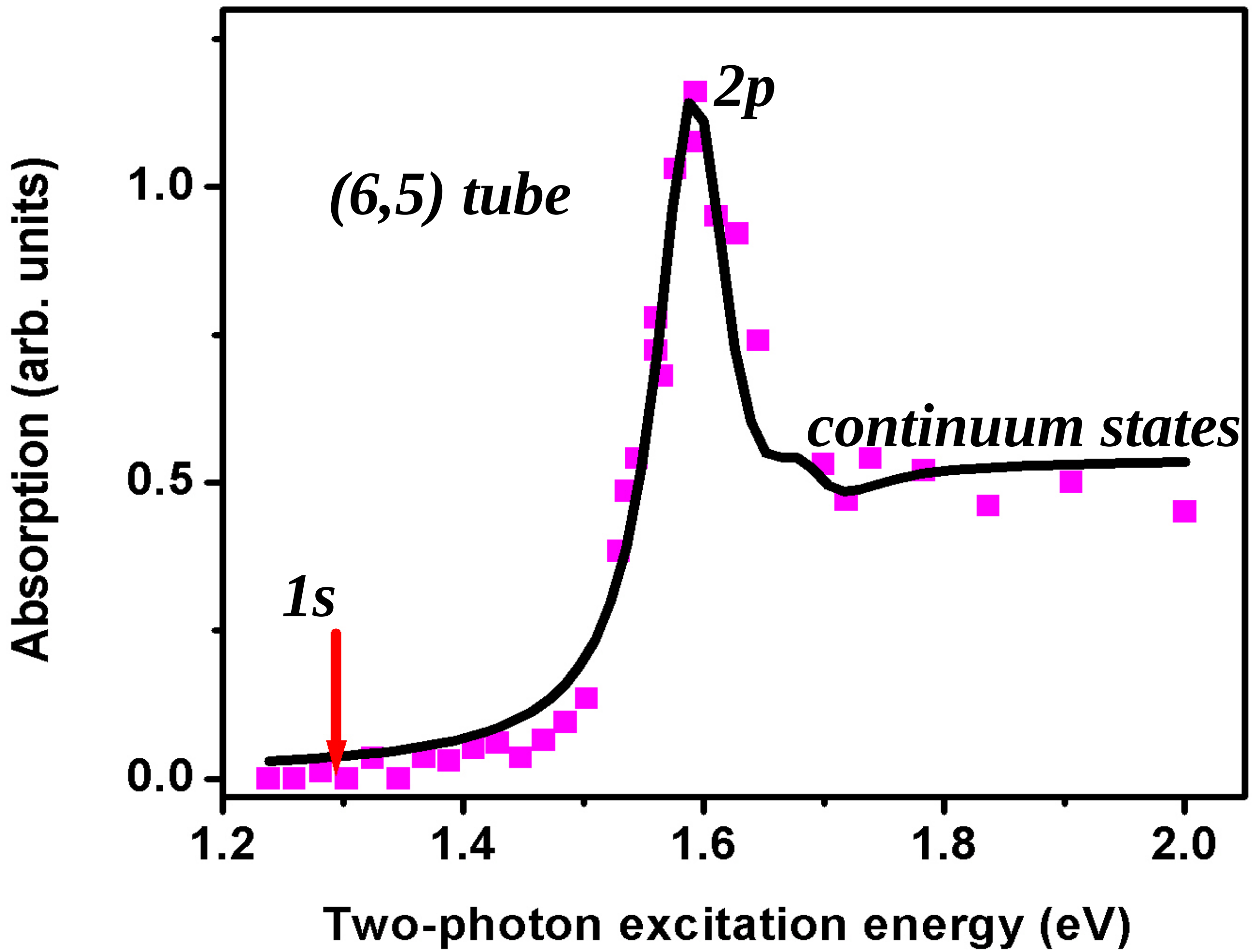
F. Wang et al. Science, 308, 838 (2005)



Allowed two-photon excitation to 2p exciton state relaxes to 1s and results in fluorescence from 1s.

Energy difference between 2p and 1s ⇒⇒ exciton binding energy

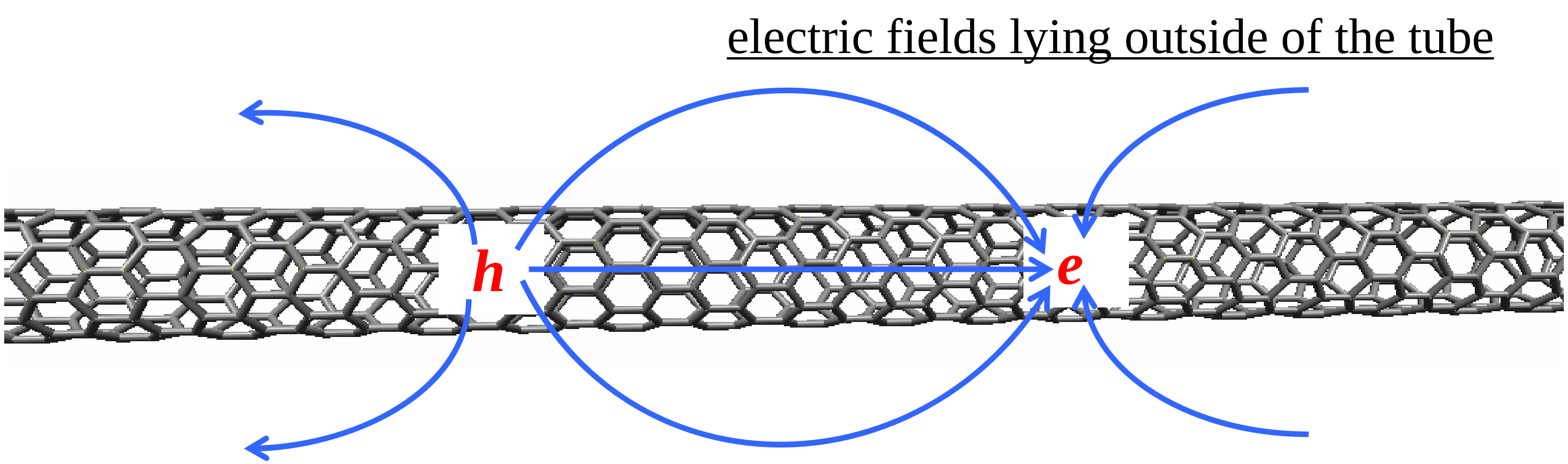
Two-photon Excitation Spectrum



1s-2p separation: ~ 300 meV, ***$E_{binding} \cong 420$ meV***

Strong e-h Interaction in 1D
⇒⇒ large exciton binding energy

electron and hole confined in 1D with ineffective screening



Exciton may even exist in metallic nanotoubes

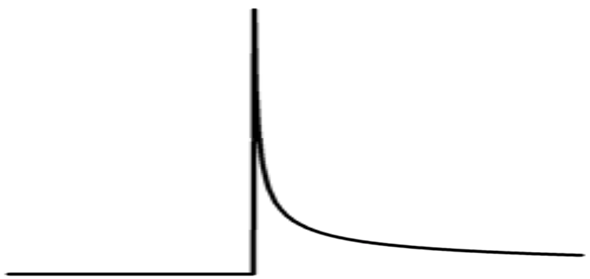
Identification of Excitons from Absorption Spectrum

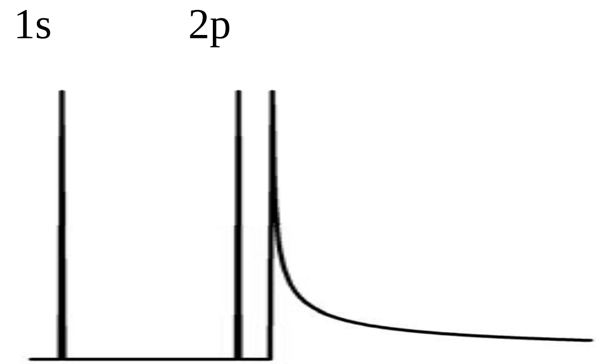
(possible even for metallic tubes)

Free carrier picture: van Hove singularity

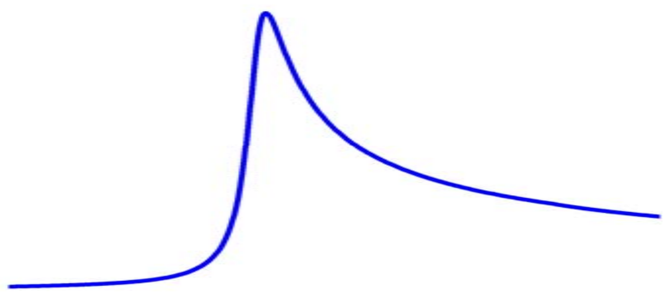
Exciton picture:

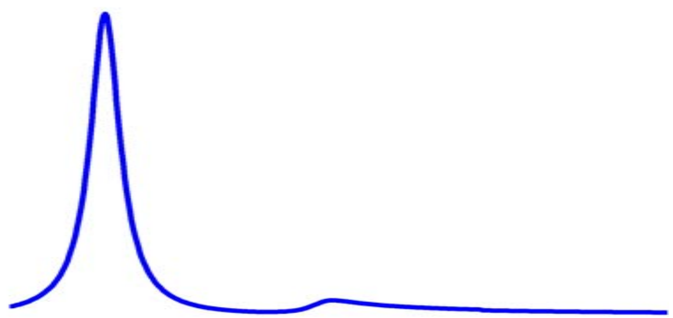
Density of states: (DOS)





Absorption spectrum:

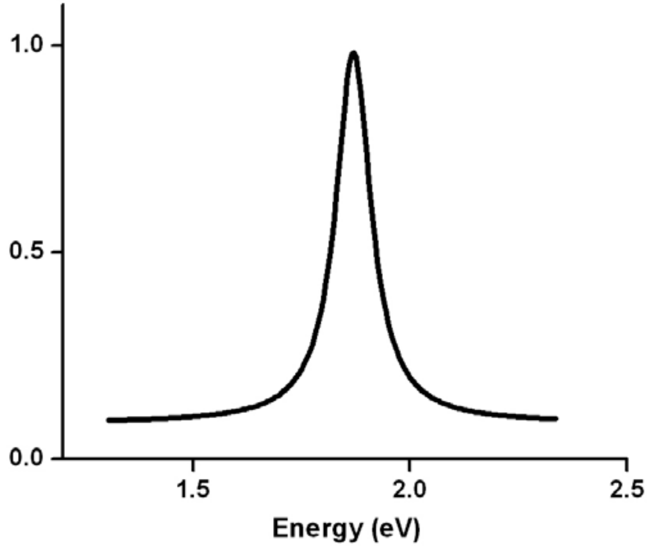




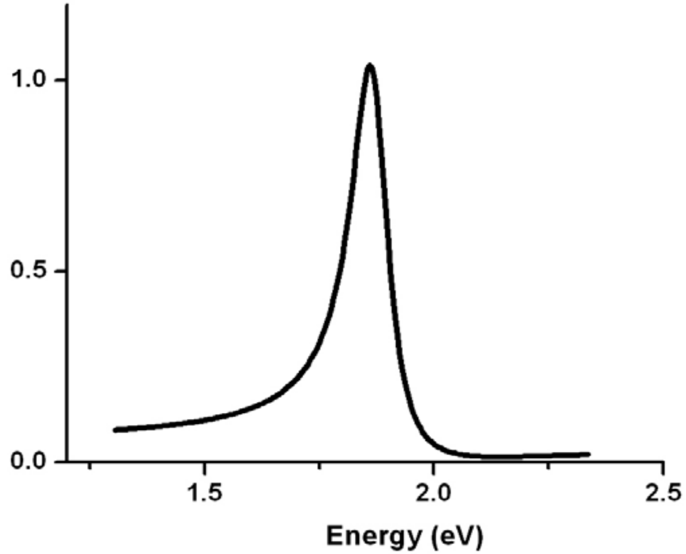
<u>Measure absorption spectrum of individual nanotubes.</u>

Absorption Spectroscopy vs. Elastic Scattering Spectroscopy

$$\sigma_{abs} \propto \mathrm{Im}(\varepsilon)$$



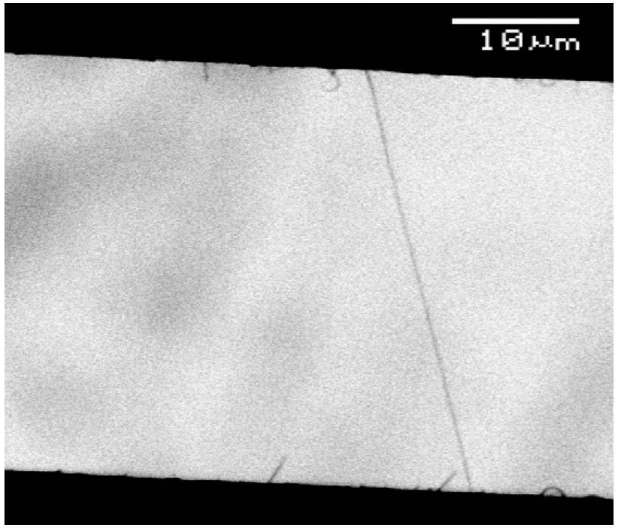
$$\sigma_{sca} \propto \left|\varepsilon - 1\right|^2$$



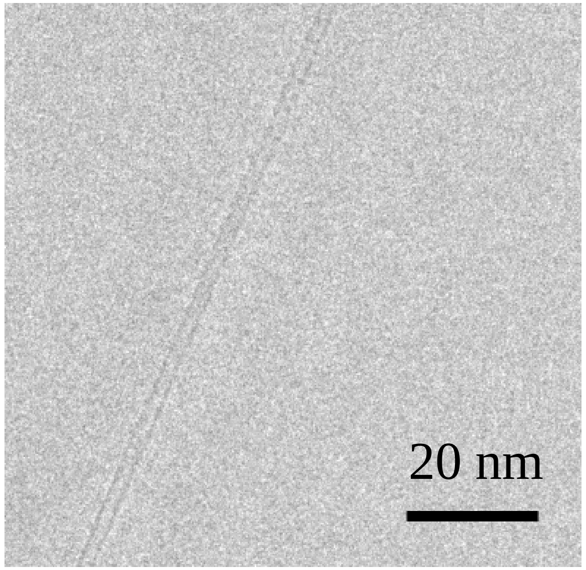
Interference between the real and imaginary part complicates the lineshape.

Example: A Lorentzian line with non-resonant background.

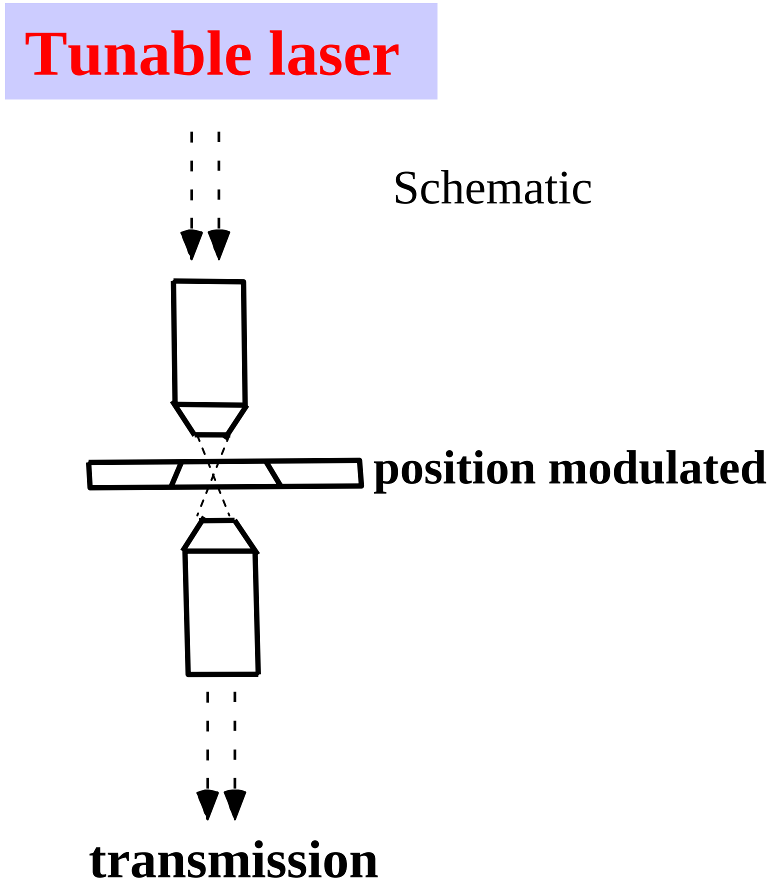
Experimental Setup



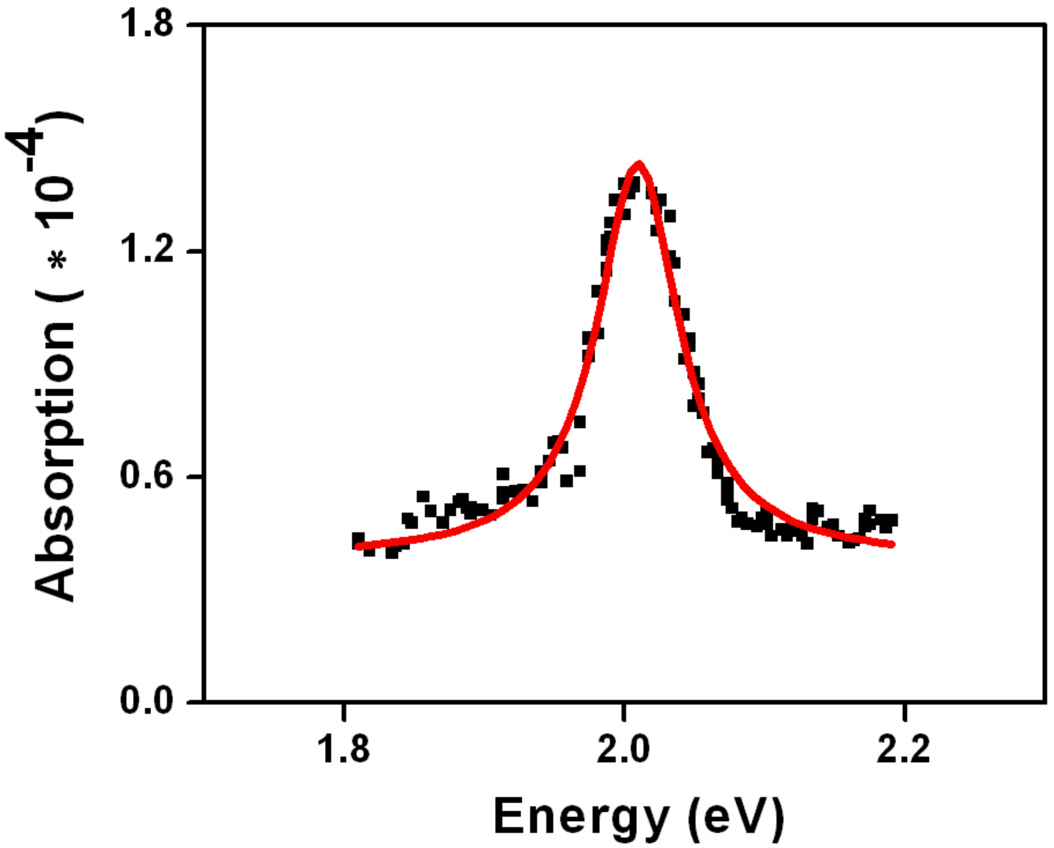
suspended nanotube across slit



Schematic



(16,15) Semiconducting SWNTs

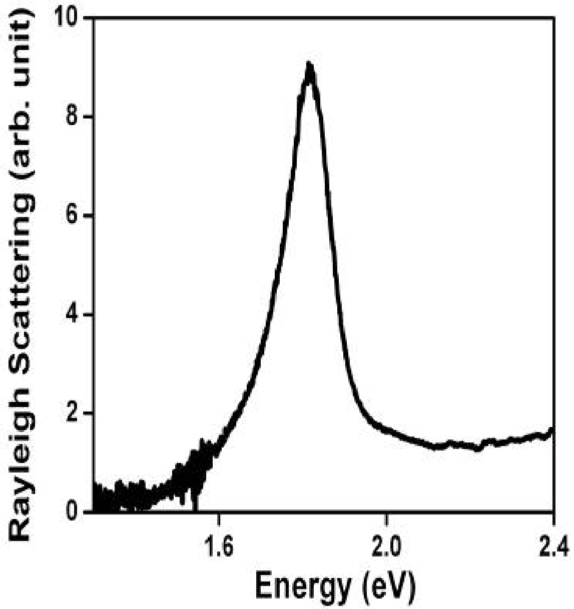


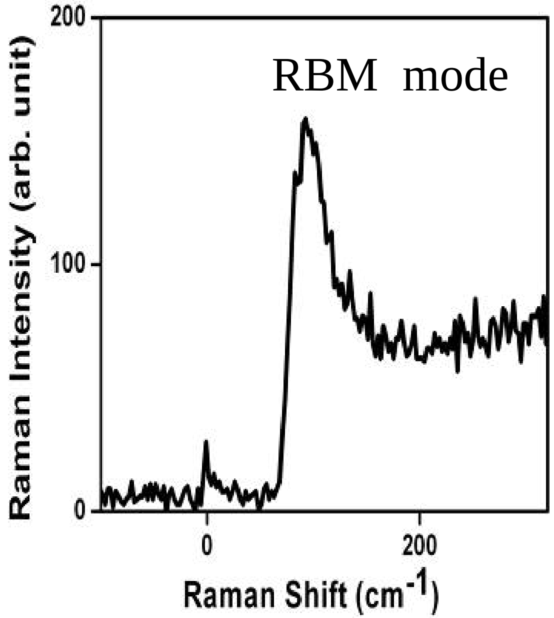
Absorption into continuum
Appears at much higher energy and weak

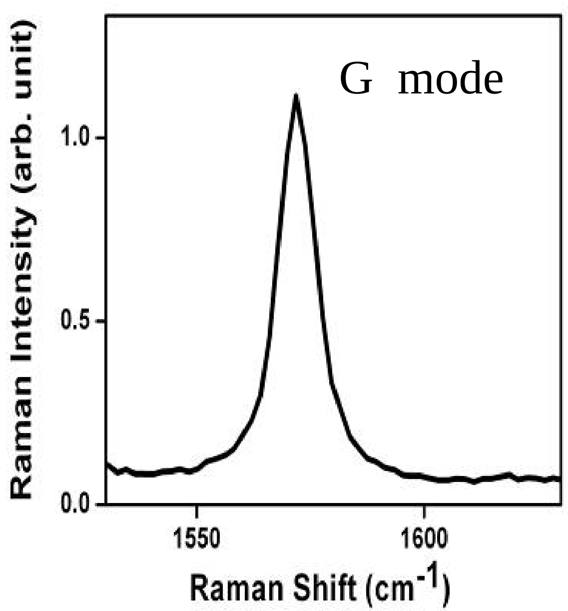
Optical Characterization of a Metallic SWNT

Rayleigh

Raman





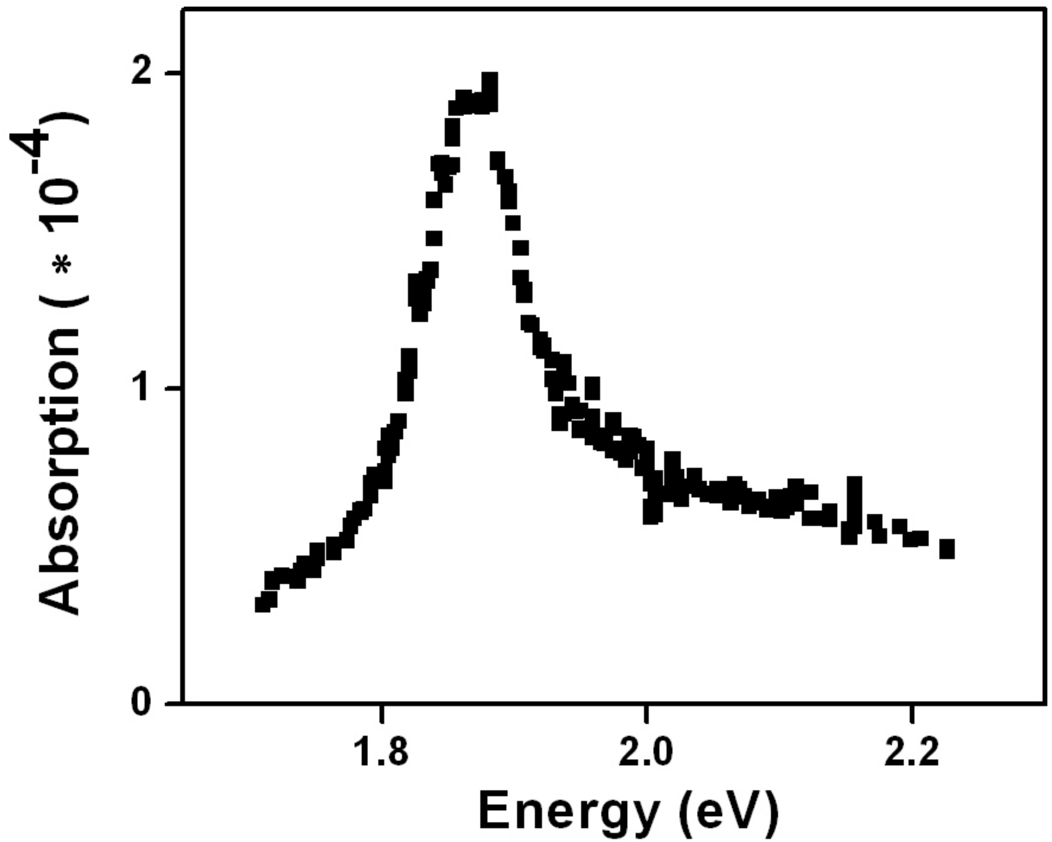


(21,21)

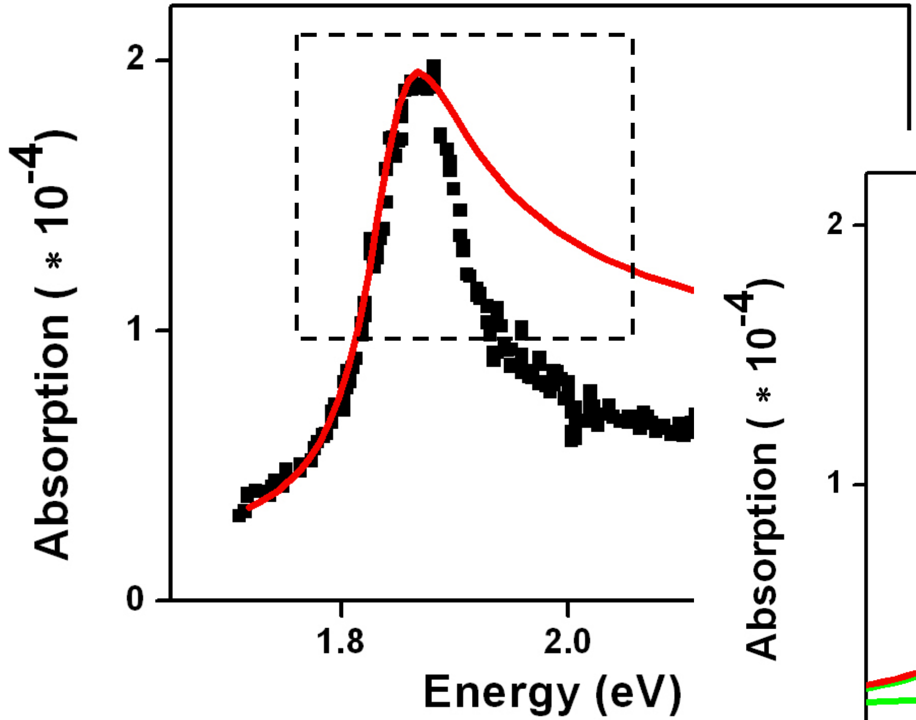
d = 2.9 nm

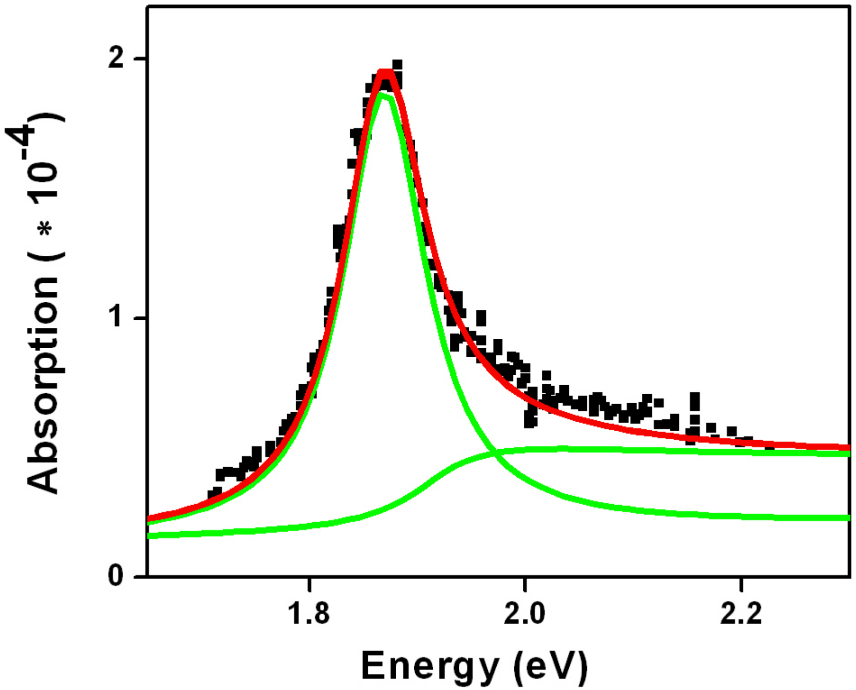
armchair

Absorption Spectrum of (21,21) Metallic SWNT



Lineshape Analysis

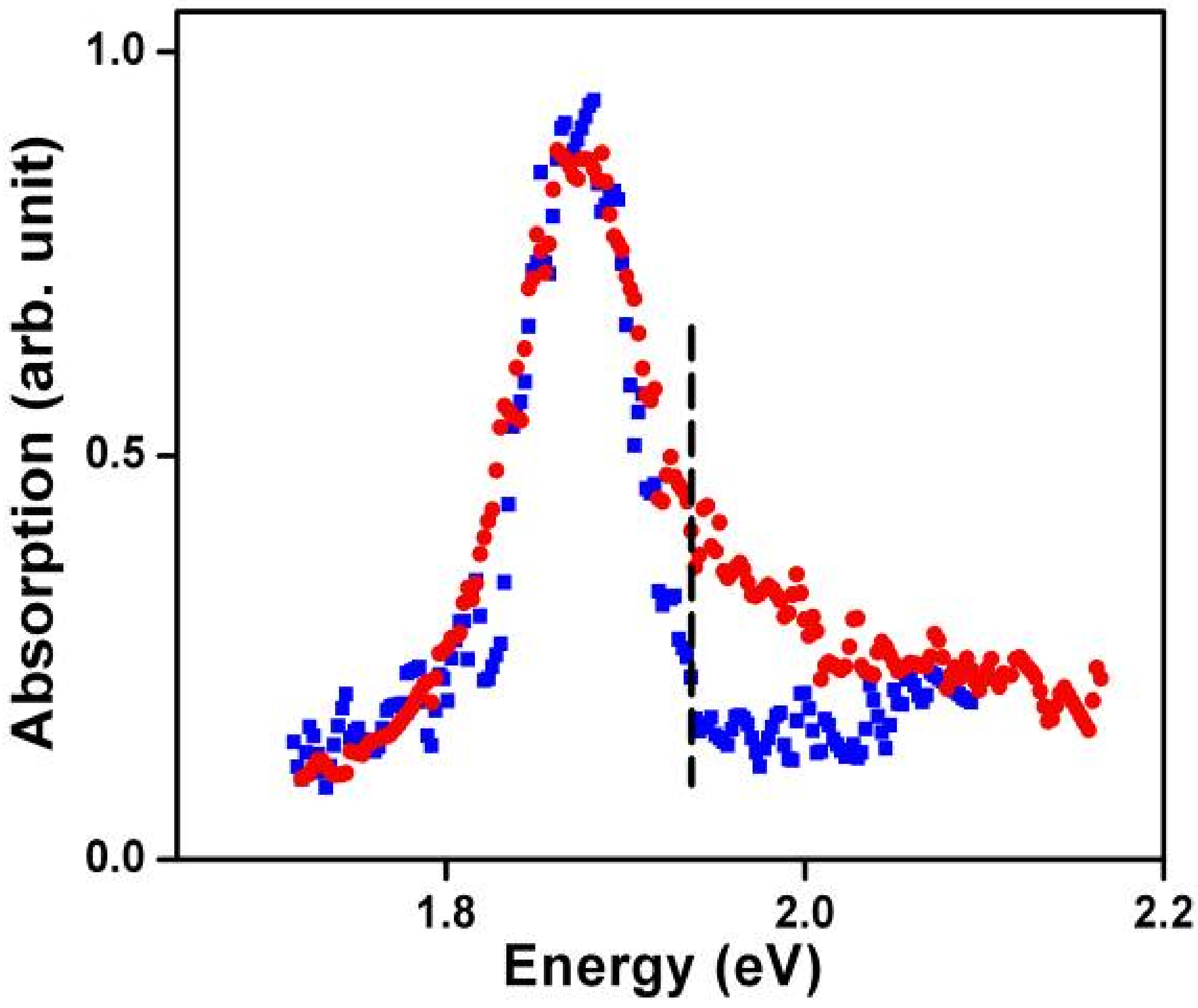




Signature of excitonic transition

$E_{binding}$ ~ 50 meV

Exciton Spectra of Semiconducting and Metallic SWNT

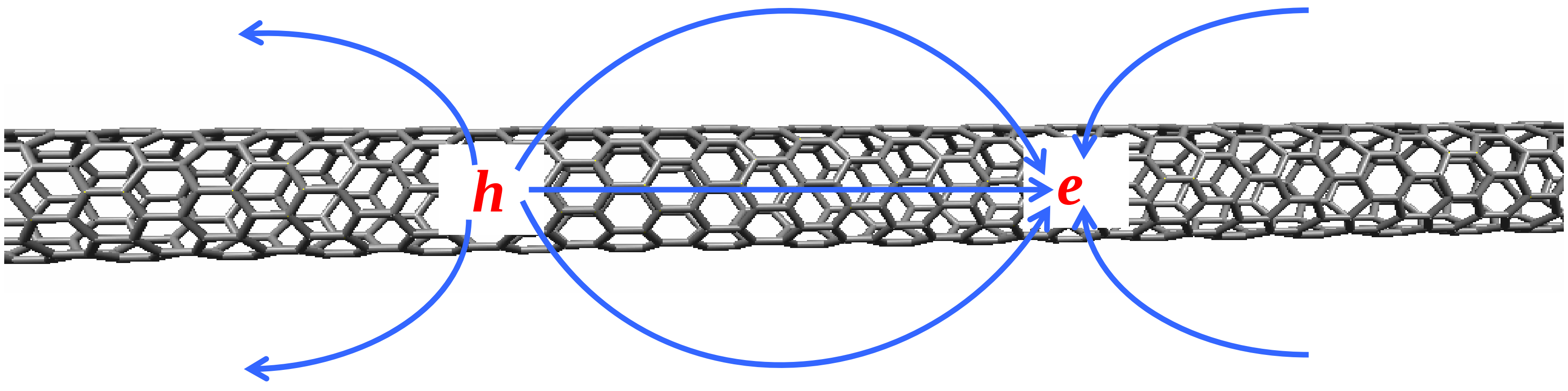


Reasons for Exciton Formation (*even in metallic nanotubes*): Strong e-h Interaction in 1D

Electron and hole are confined in 1D

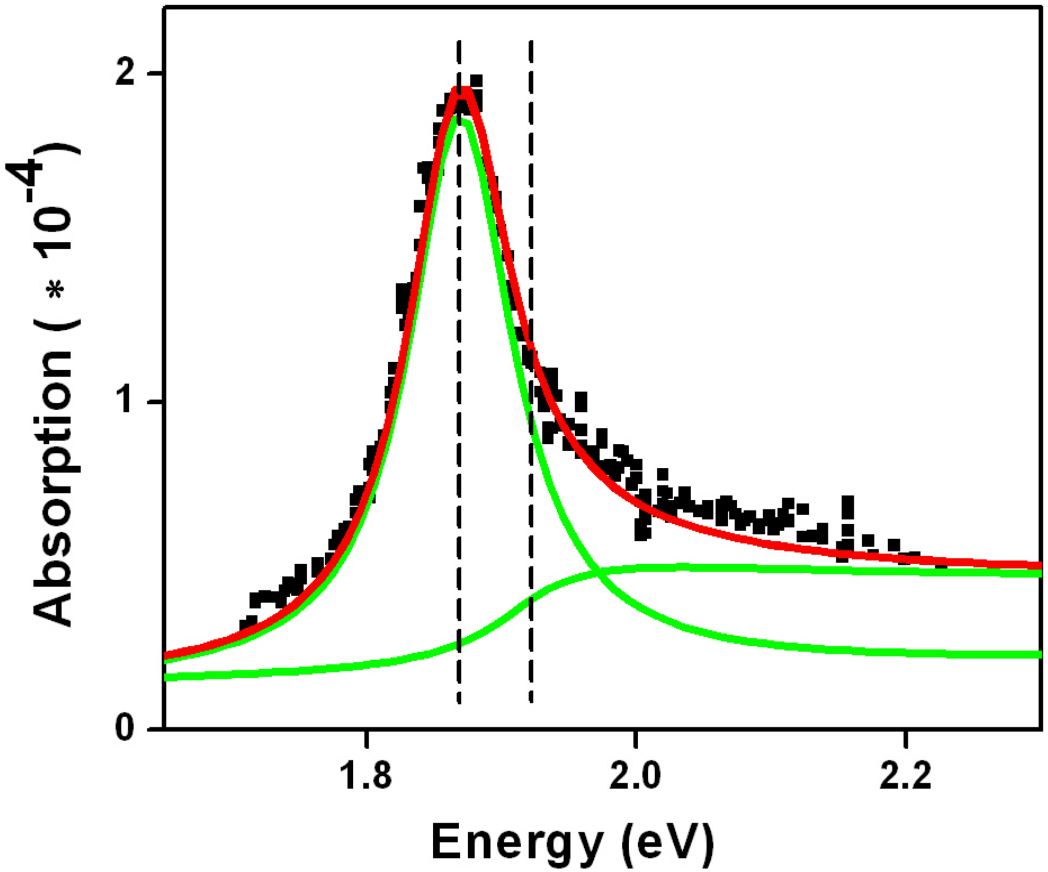
Ineffective dielectric screening

<u>electric fields lying outside of the tube</u>



Theoretical Model

Coulomb potential: $V(z) = \frac{1}{\varepsilon} \cdot \frac{e^2}{(|z| + 0.3\,d)}$



fitting: ε ***~10***

$E_{binding}$ = 50 meV

R_{ex} = 3.1 nm

Free Electron Screening in 1D

Thomas-Fermi Method: (q wavevector)

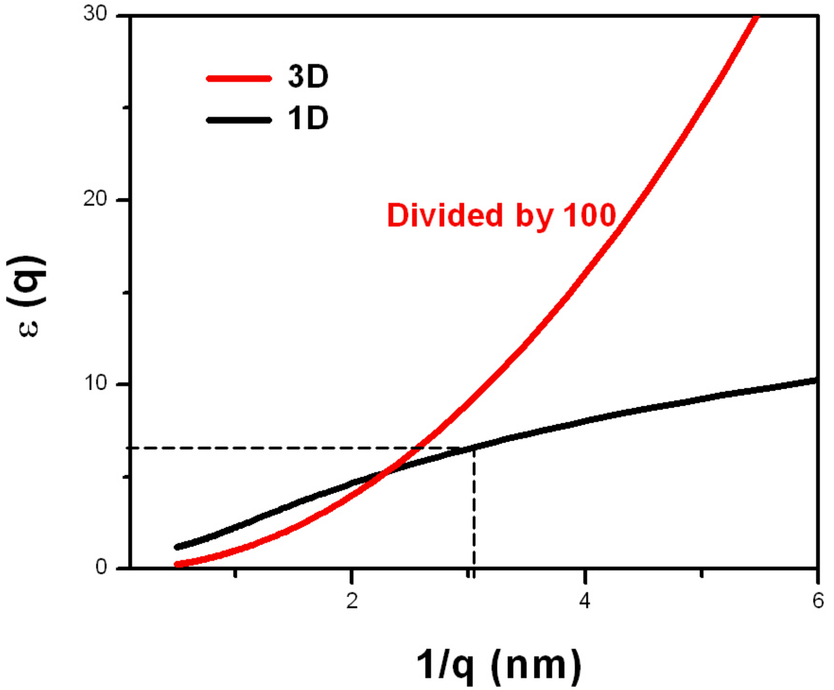
$$\phi(q,r) = \phi^{ext}(q,r) + \phi^{ind}(q,r)$$

$$\varepsilon(q) = \phi^{ext}(q,R)/\phi(q,R)$$

3D: $\varepsilon^{3D}(q) \sim (1/q)^2$

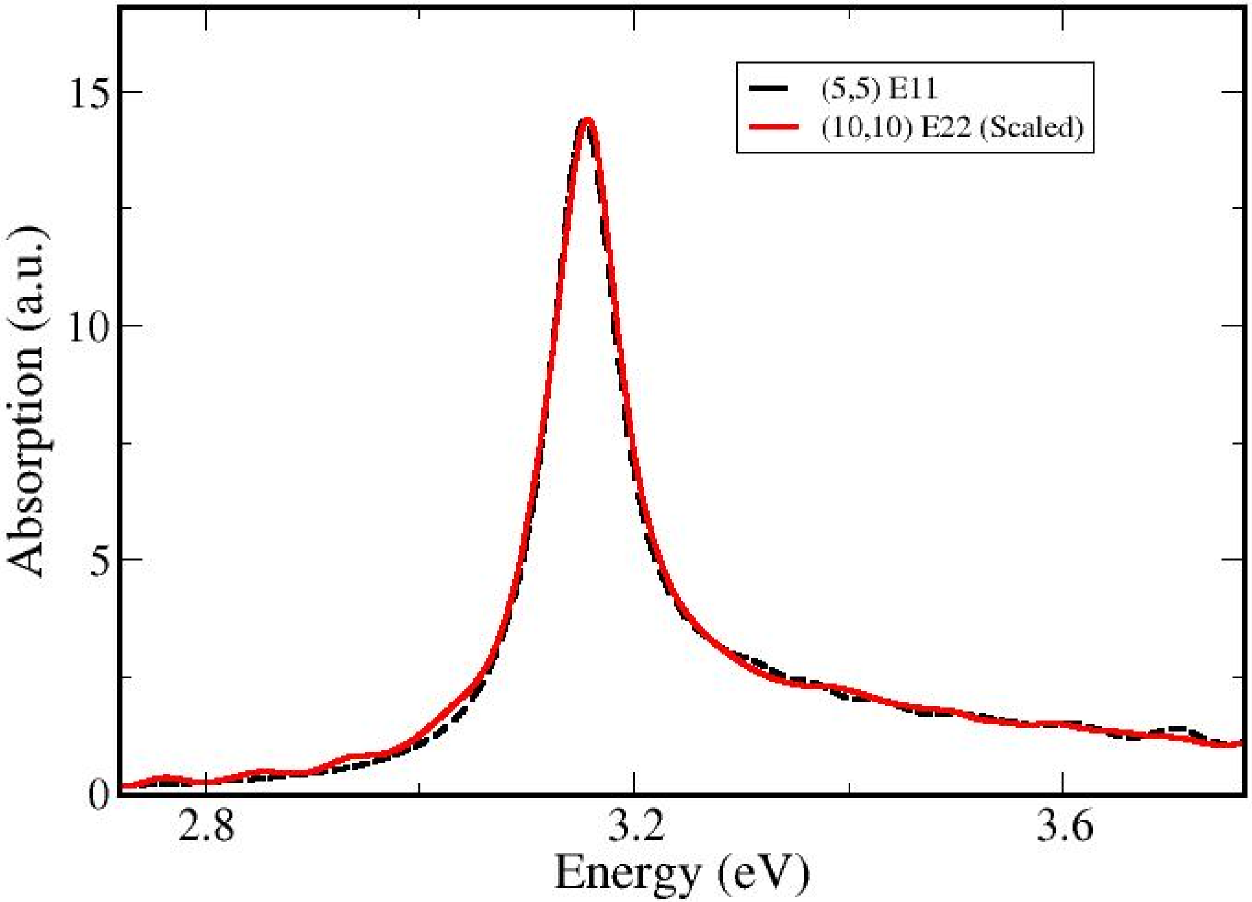
1D: $\varepsilon^{1D}(q) \sim \ln(1/q)$

For q ~ 1/ $R_{ex,}$ ε = 7



1D metal: free electron screening is far from perfect !

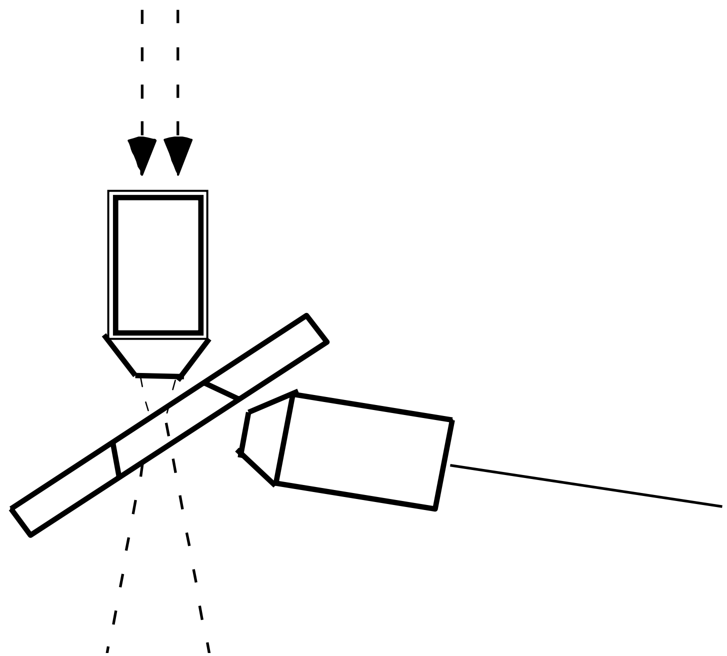
Theoretical Absorption Spectrum of Excitonic Transition in Metallic SWNT



Multi-Phonon Raman Scattering in Single SWNTs

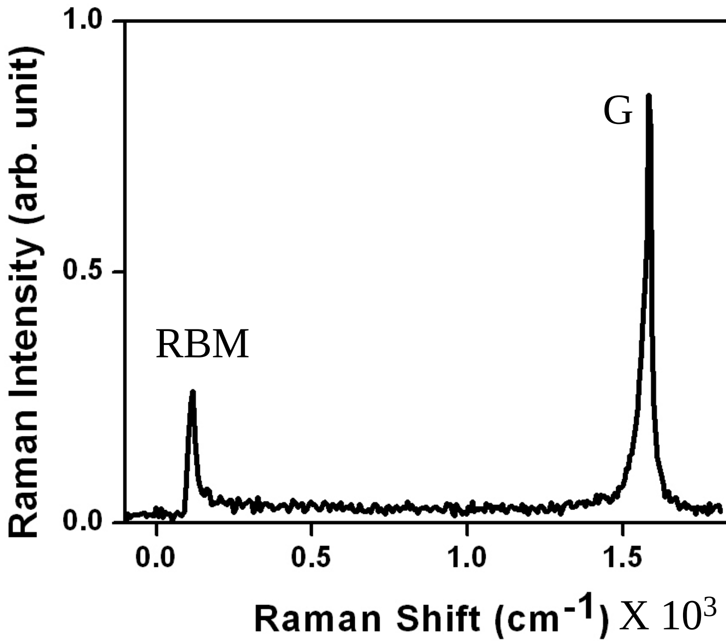
F. Wang et al. PRL 98, *047402* ***(2006)***

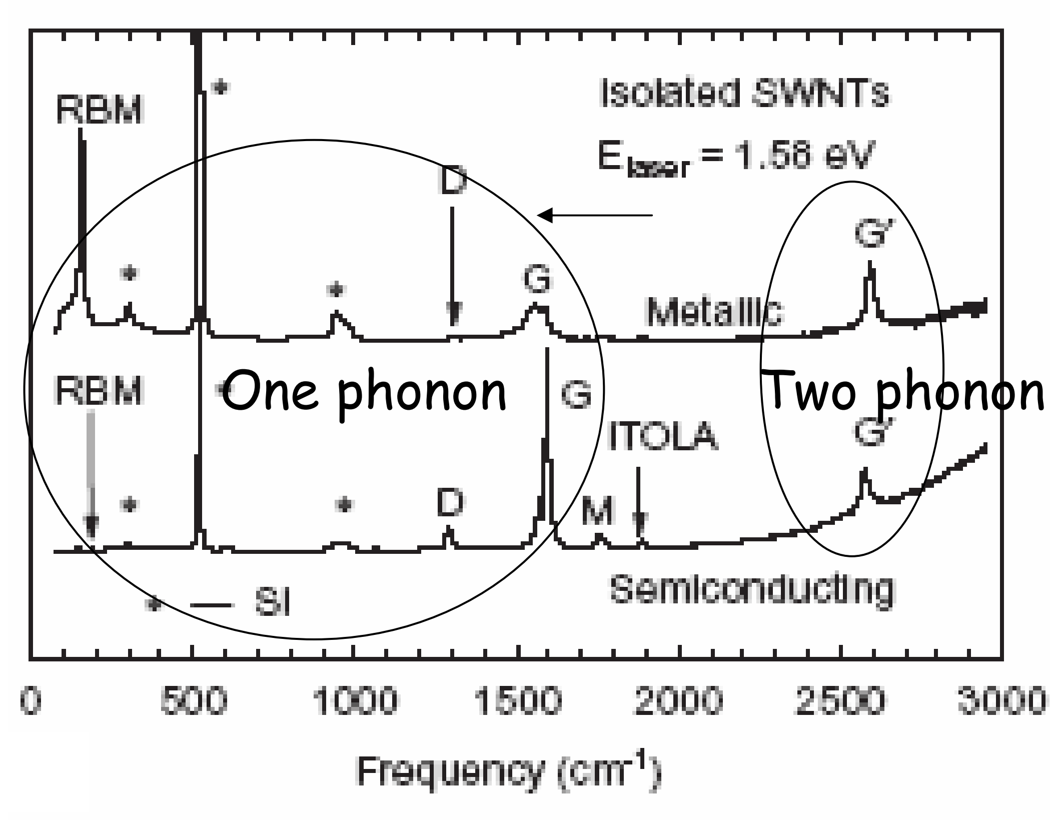
Experiment Arrangement



dark field imaging

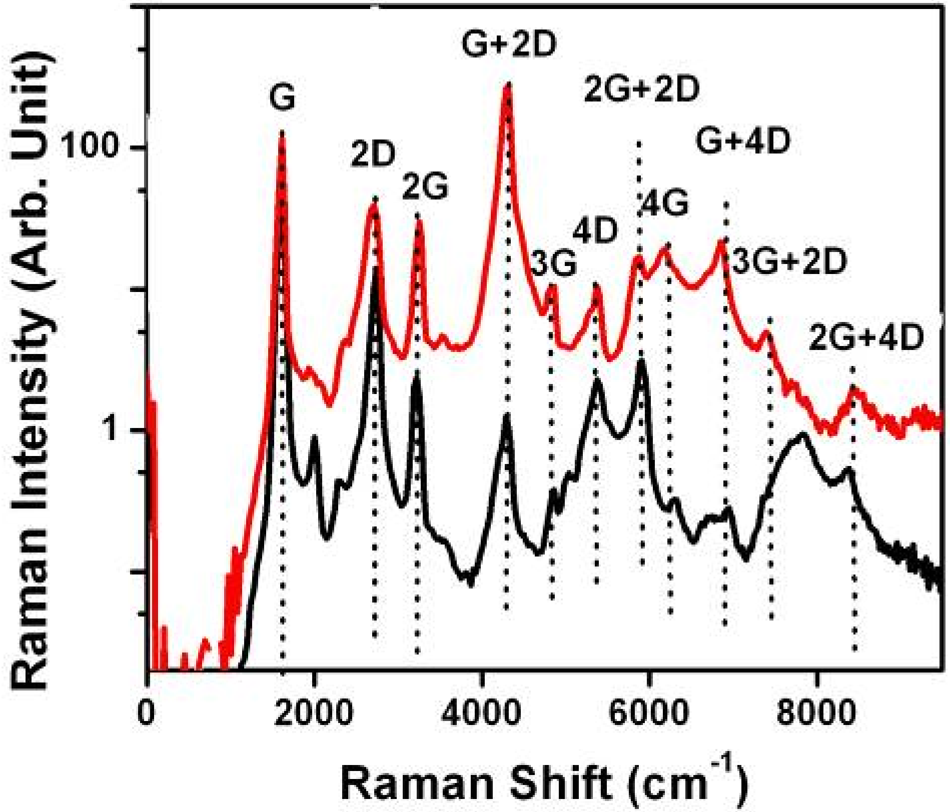
Raman Spectrum of SWNT

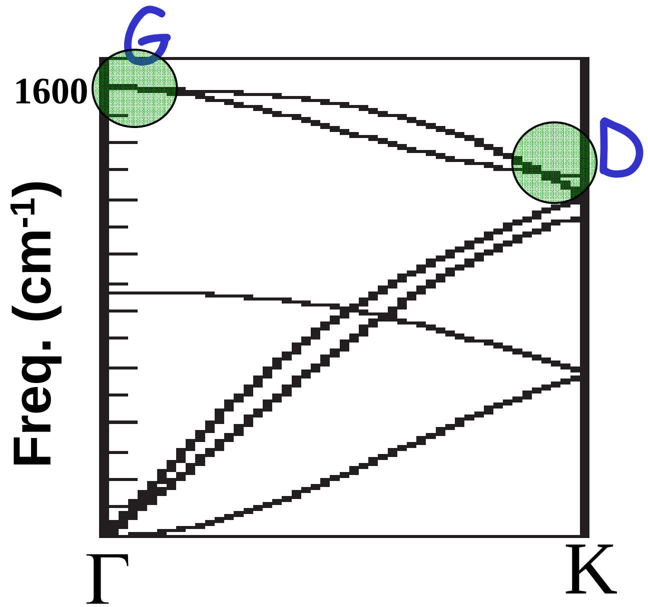




Brar et al. Phys. Rev. B 66, 155418 (2002)

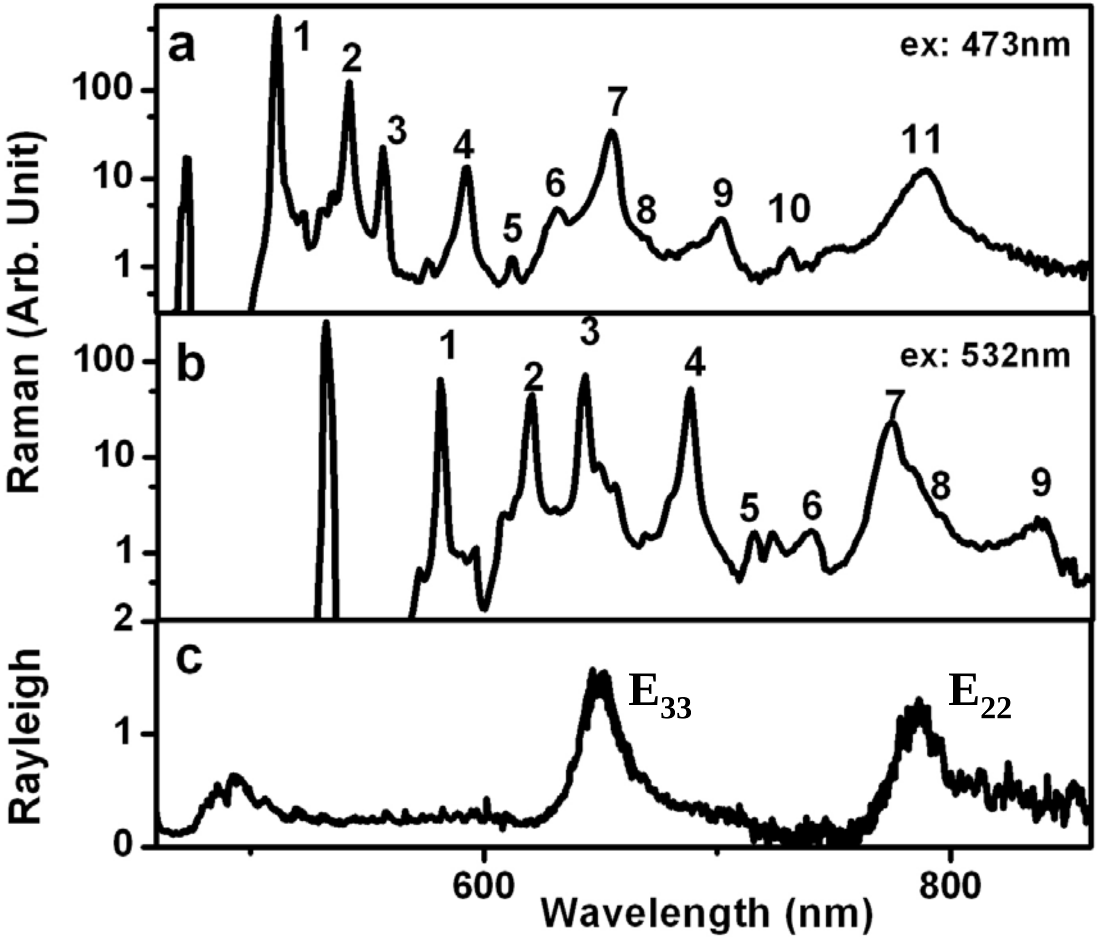
Multi-Phonon Raman Spectra of Single SWNTs





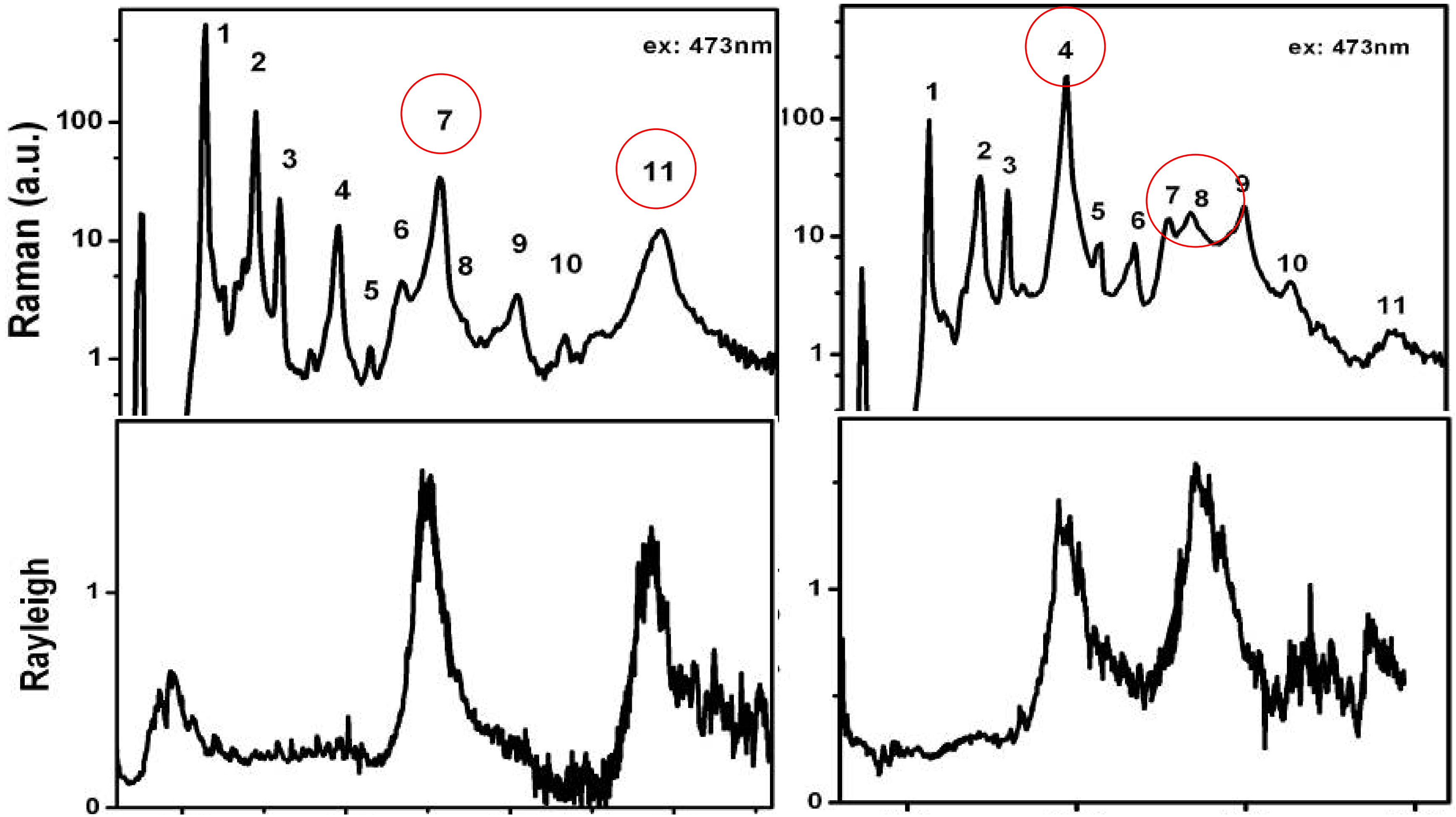
Excitation at 473 nm on two nanotubes with d ~ 2 nm

Raman Spectra with Different Excitation Wavelengths



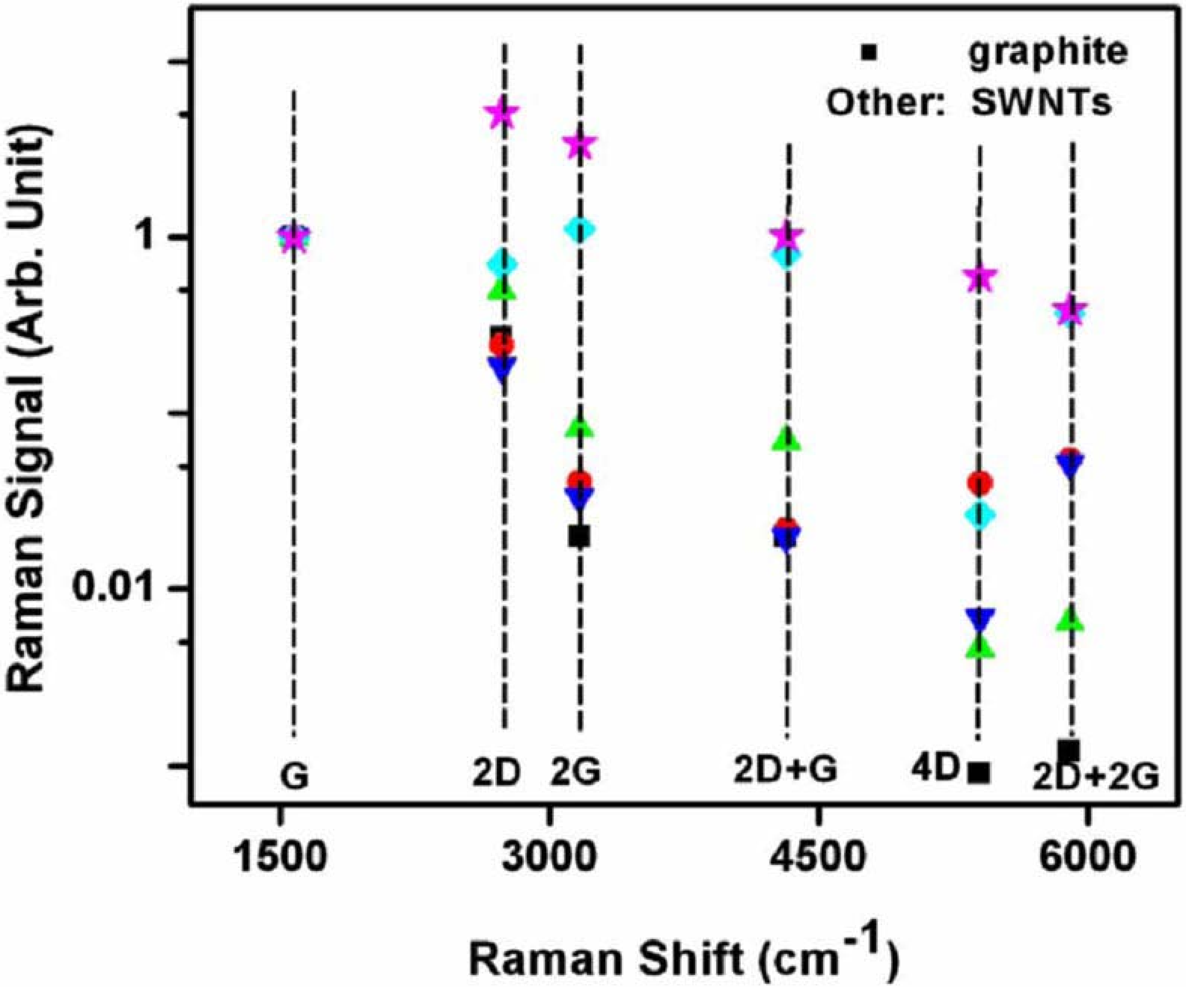
d ~ 2 nm

Individual Nanotube Characteristics



Resonance enhancement for outgoing photons

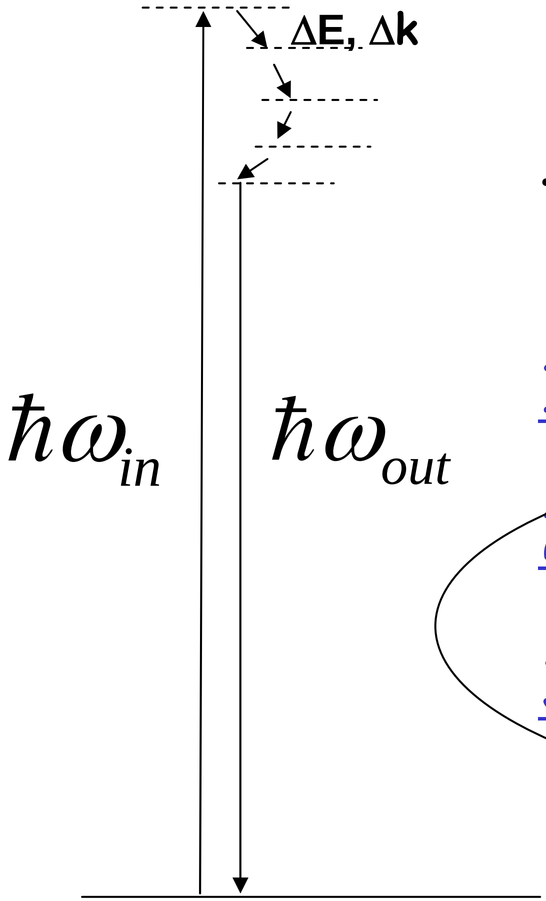
Comparison of Raman Strengths between SWNT and Graphite



Characteristics of Multi-Phonon Raman Spectra of SWNTs

- Combinations of zone-center and even number of zone-edge modes observed (result of momentum conservation)
- **Narrow** combination modes up to 6 phonons observed; mode strength decreasing slowly with increasing order (near intermediate resonances in multi-phonon scattering likely to be important)
- Mode strengths much stronger than those from graphite (stronger electron-phonon scattering in 1D systems)
- Relative mode strengths depend on tubes and excitation wavelength (resonant enhancement dominant)

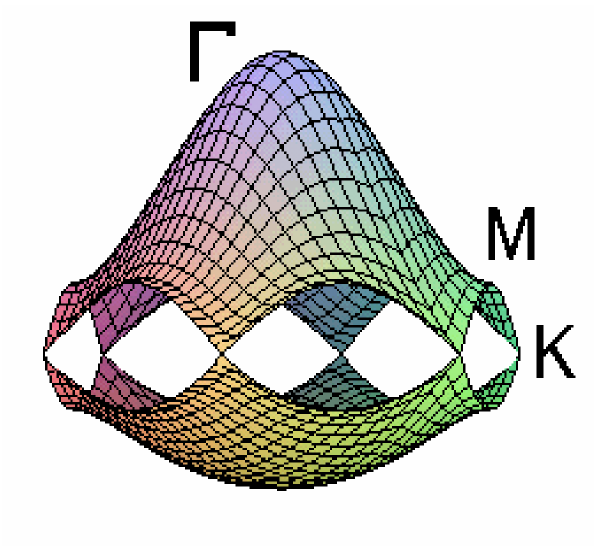
Multiphonon Raman Scattering

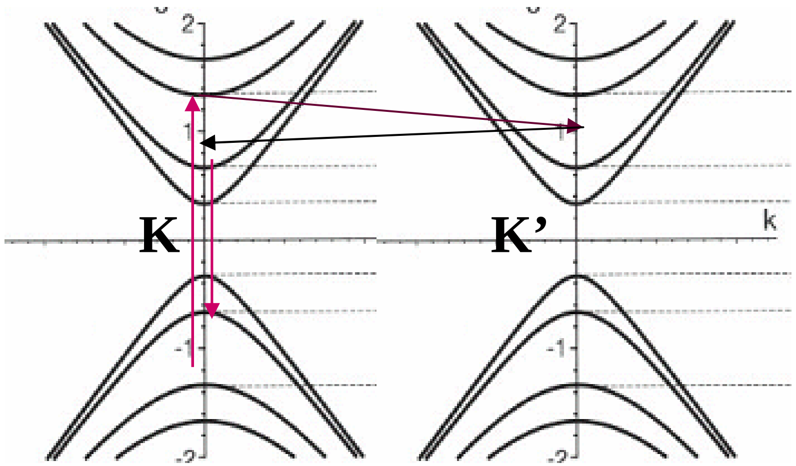


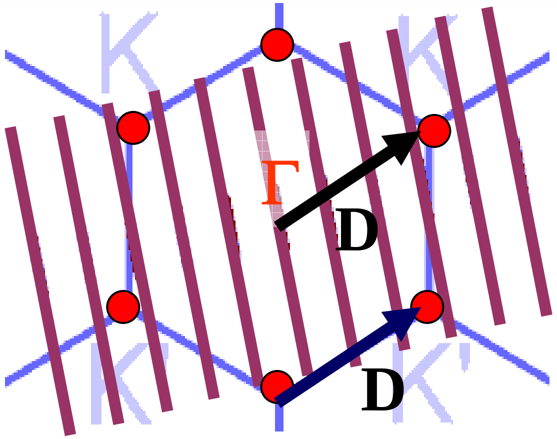
Three important factors:

1. Electron-phonon interactions
2. Resonance enhancement
3. Phonon density of states

Resonant Enhancement in Multi-phonon Raman Scattering







Initial and final transitions:
near K points

Intermediate resonances:
near K or K’

$$(\hbar\omega_{in} - m\hbar\omega_G - n\hbar\omega_D) \sim E_{ii}(K) \text{ or } E_{ii}(K')$$

Summary

- Optical spectroscopy can be used to characterize single SWNTs.
- Electronic properties of SWNT vary significantly depending on chiral indices.
- Excitons exists with high binding energy even in metallic tubes.
- Resonant enhancement leads to observation of multi-phonon Raman scattering.