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Carbon Nanotubes and Graphene

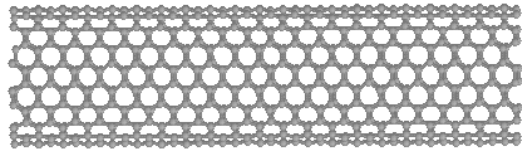
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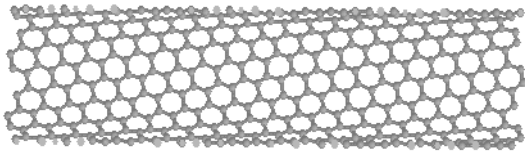
NSF Nanocenter Collaboration: among [Heinz](#), O'Brien, Hone, Kim, Nuckolls, Turro, Flynn and Brus groups at Columbia, and Zhu TEM group at Brookhaven.

1. Excited Electronic States of Carbon Nanotubes
2. Optical Characterization of Individual Carbon Nanotubes
3. Basal Plane Photochemical Reactions on Graphene

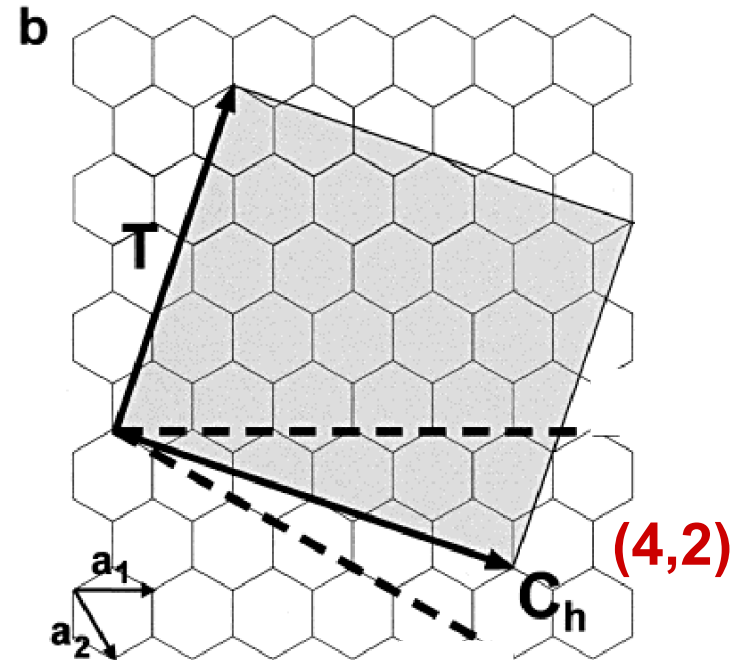
Single Wall Carbon Nanotubes (SWNTs) – a family of long molecules



(10,10) Arm-chair Metallic Tube



(7,12) Chiral Semiconducting Tube



~100 distinct SWNT structures defined by indices (n,m)

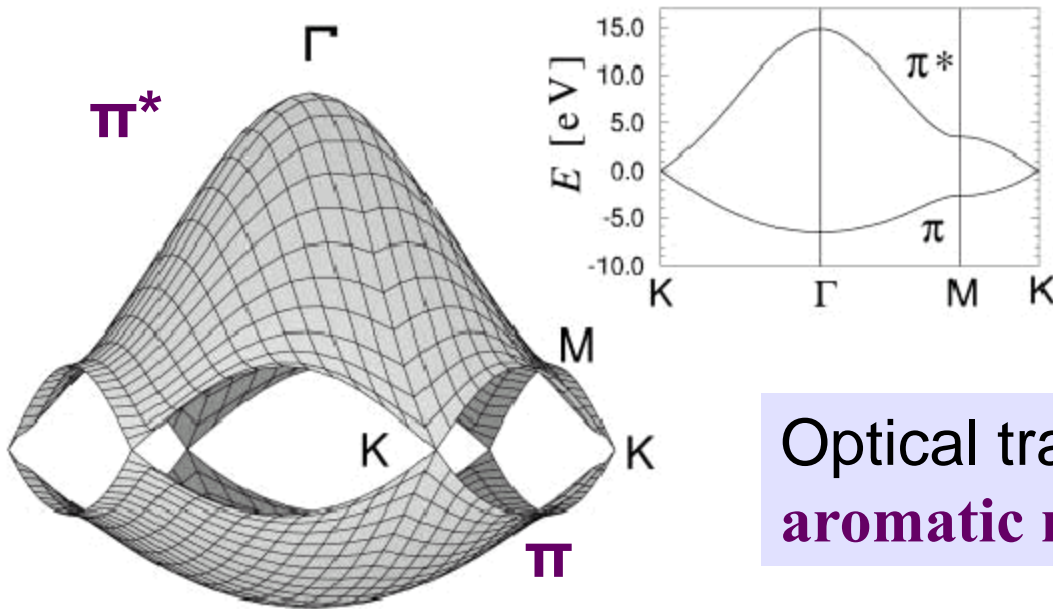
Some metallic and some semiconducting

Each physical structure has a unique electronic structure

Huckel π and π^* MOs (Band structure) of graphene

MO Energies are a function of electron momentum $k(x,y)$ in the plane of graphene

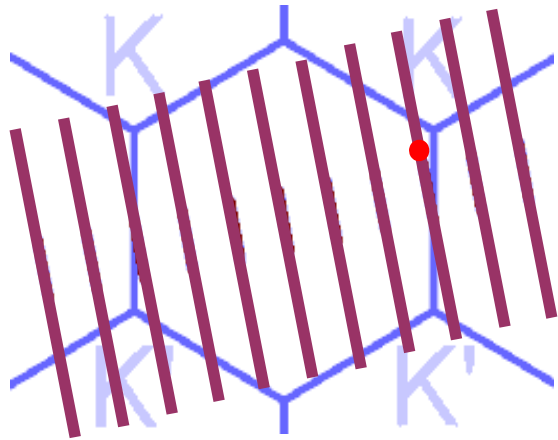
Electron momentum k is continuous for infinite plane of graphene



$\beta = 3.033 \text{ eV}$
Resonance integral

Optical transitions: π to π^* just as in aromatic molecules

Independent Electron Model: for one (n,m) tube, only a series of momentum stripes from graphene are allowed

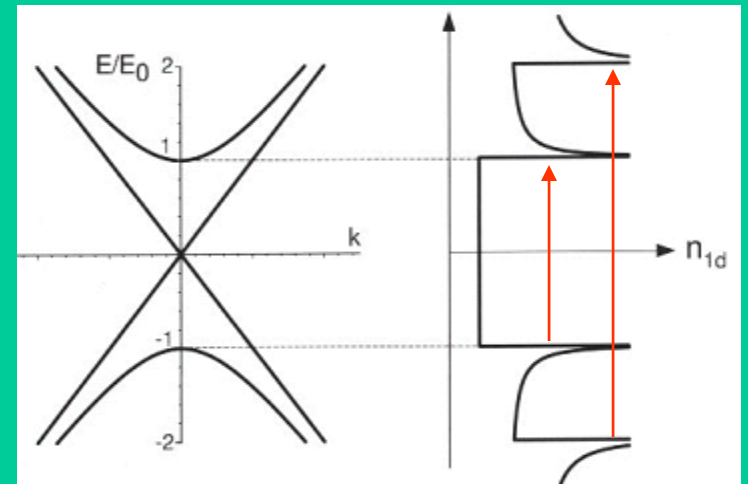


Nanotube:

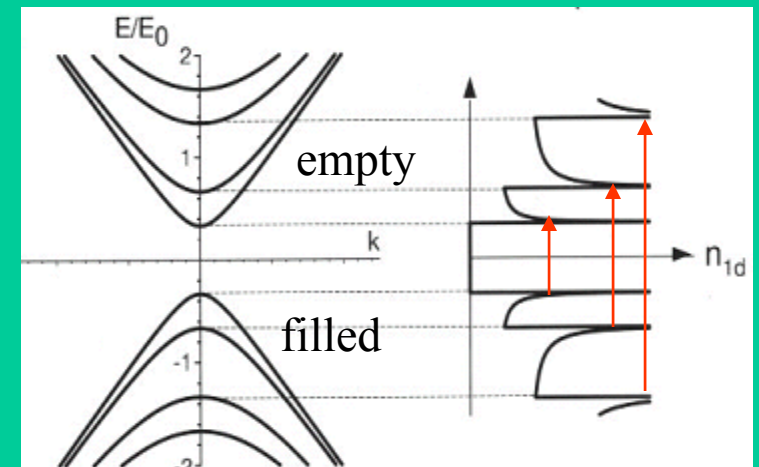
Electron momentum k quantized around circumference.

Electron momentum remains continuous along length

Metallic:

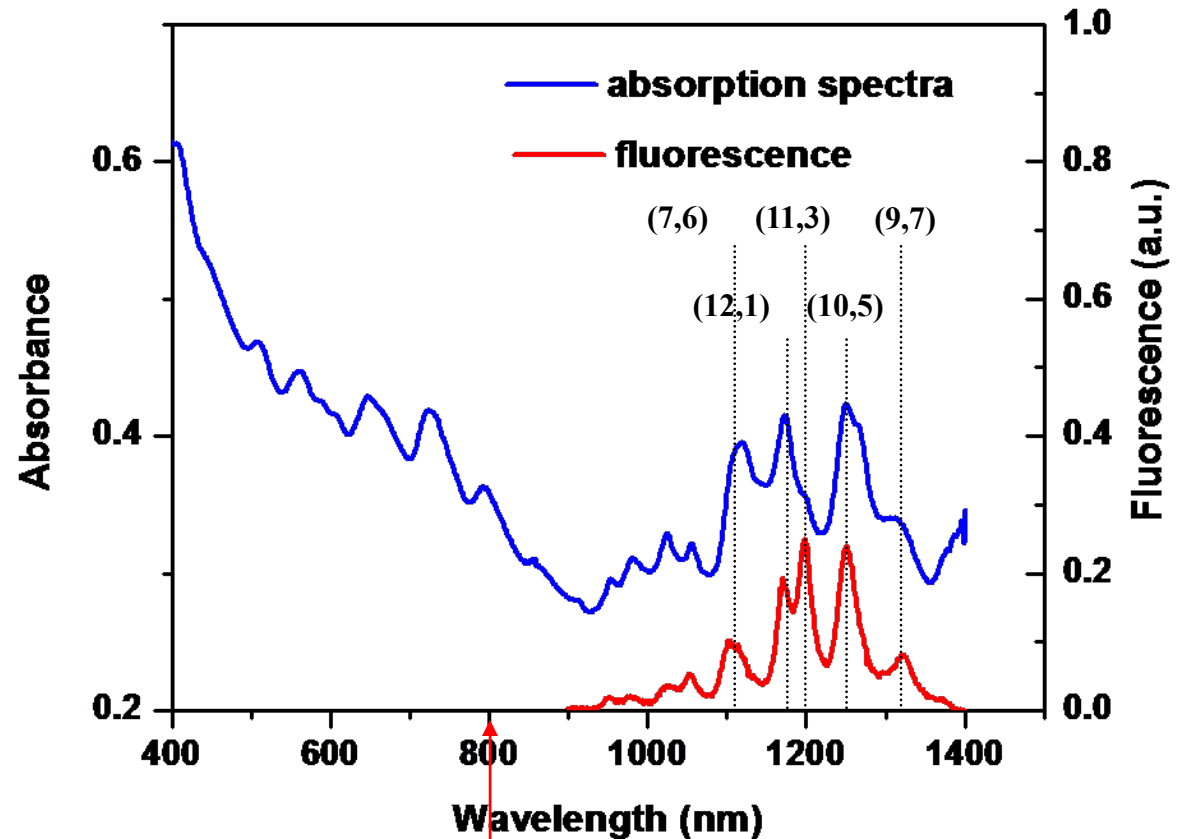
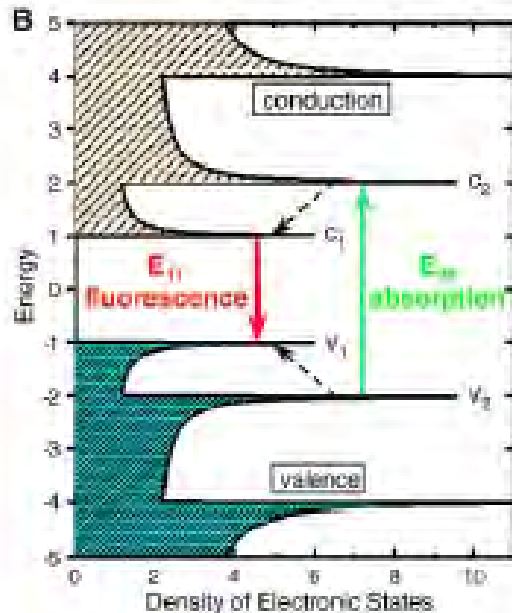


Semiconducting:



Experimental Optical Spectra of Mixture of Semiconductor SWNTs

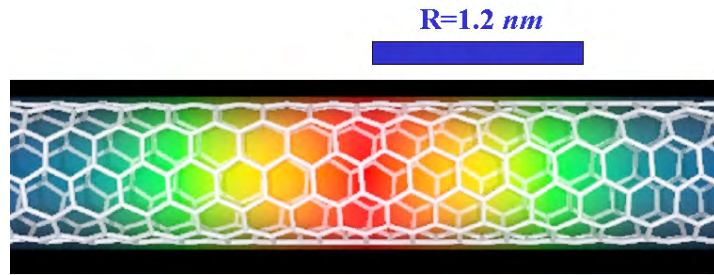
What are these electronic transitions –delocalized HOMO to LUMO, or localized Bound Excitons?



Pump wavelength 800 nm

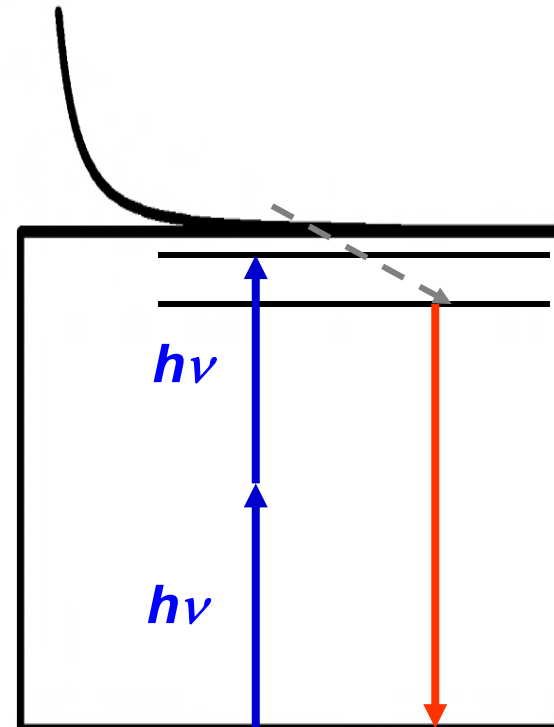
[(*n,m*) assignment according to S.M. Bachilo et al. Science **298**, 2361 (2002)]

Neutral Bound Excitons Due to electron-hole attraction?



Exciton envelope wavefunction:

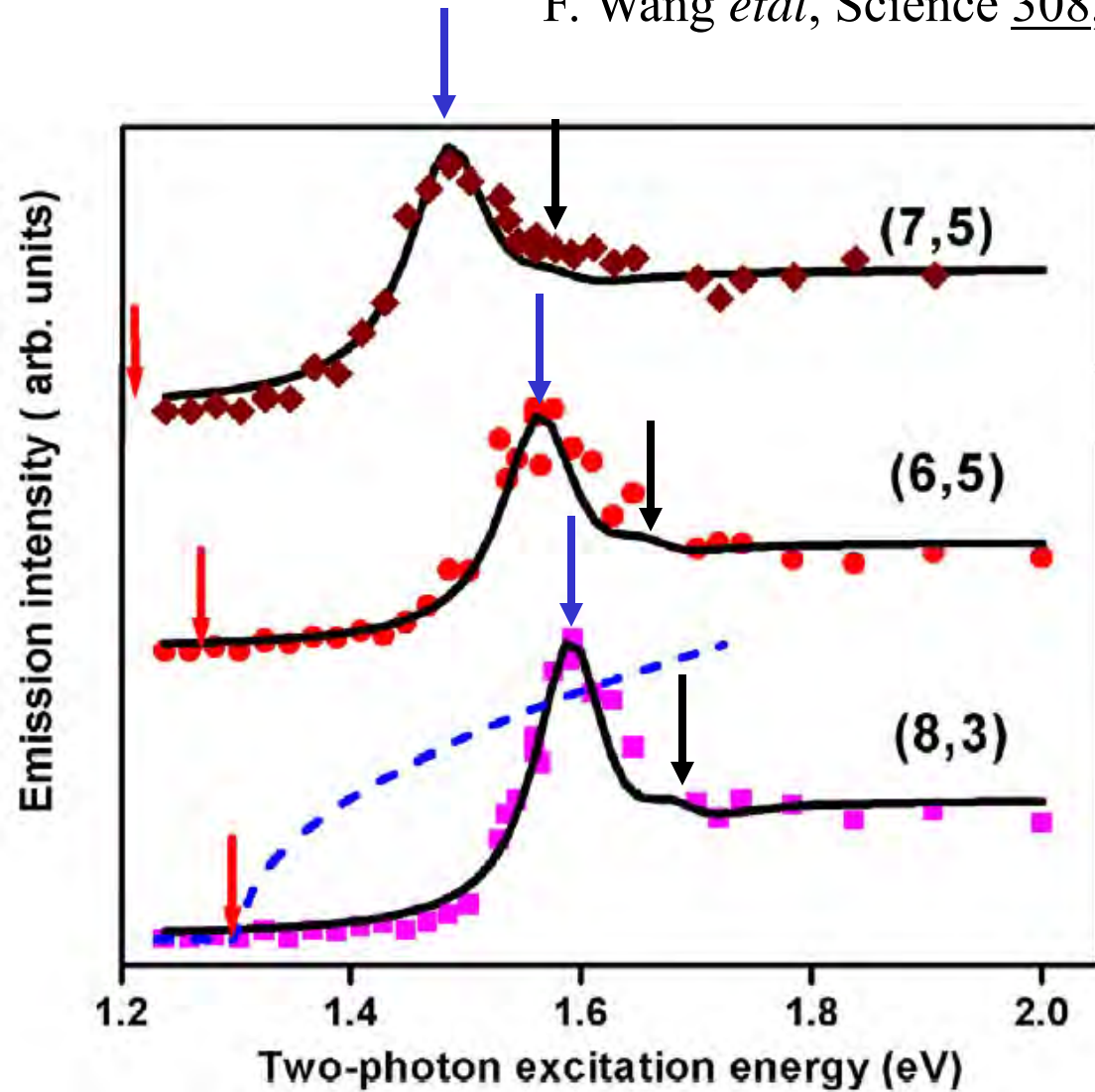
Neutral excited state moves as a unit along the SWNT?



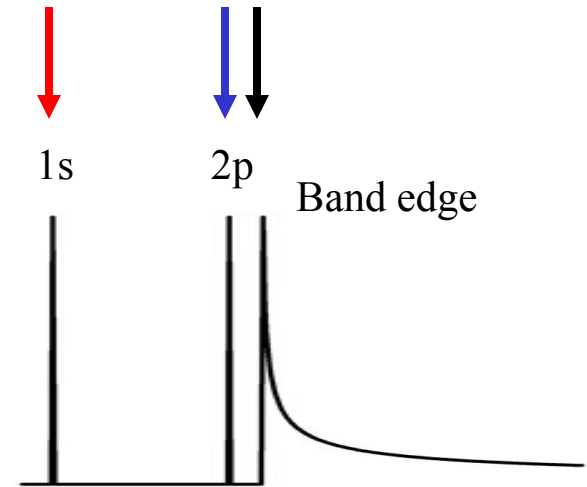
Exciton Bound states below the van Hove Band Edge

Two Photon Excitation spectra of individual fluorescence peaks

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

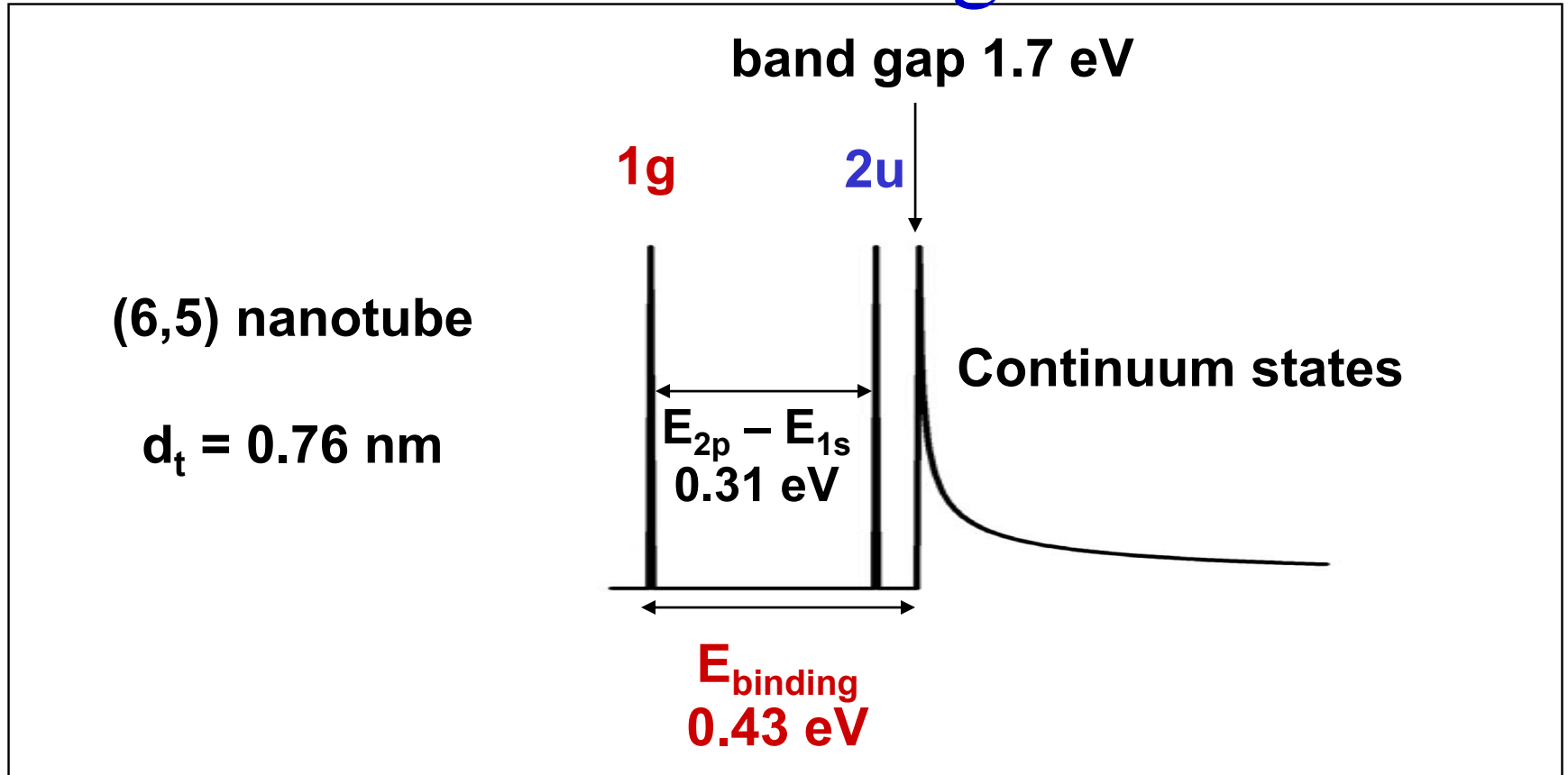


Energy levels of transitions observed directly from 2-photon excitation spectra and emission peak energy



1s – one photon allowed
2p – two photon allowed

Exciton energies

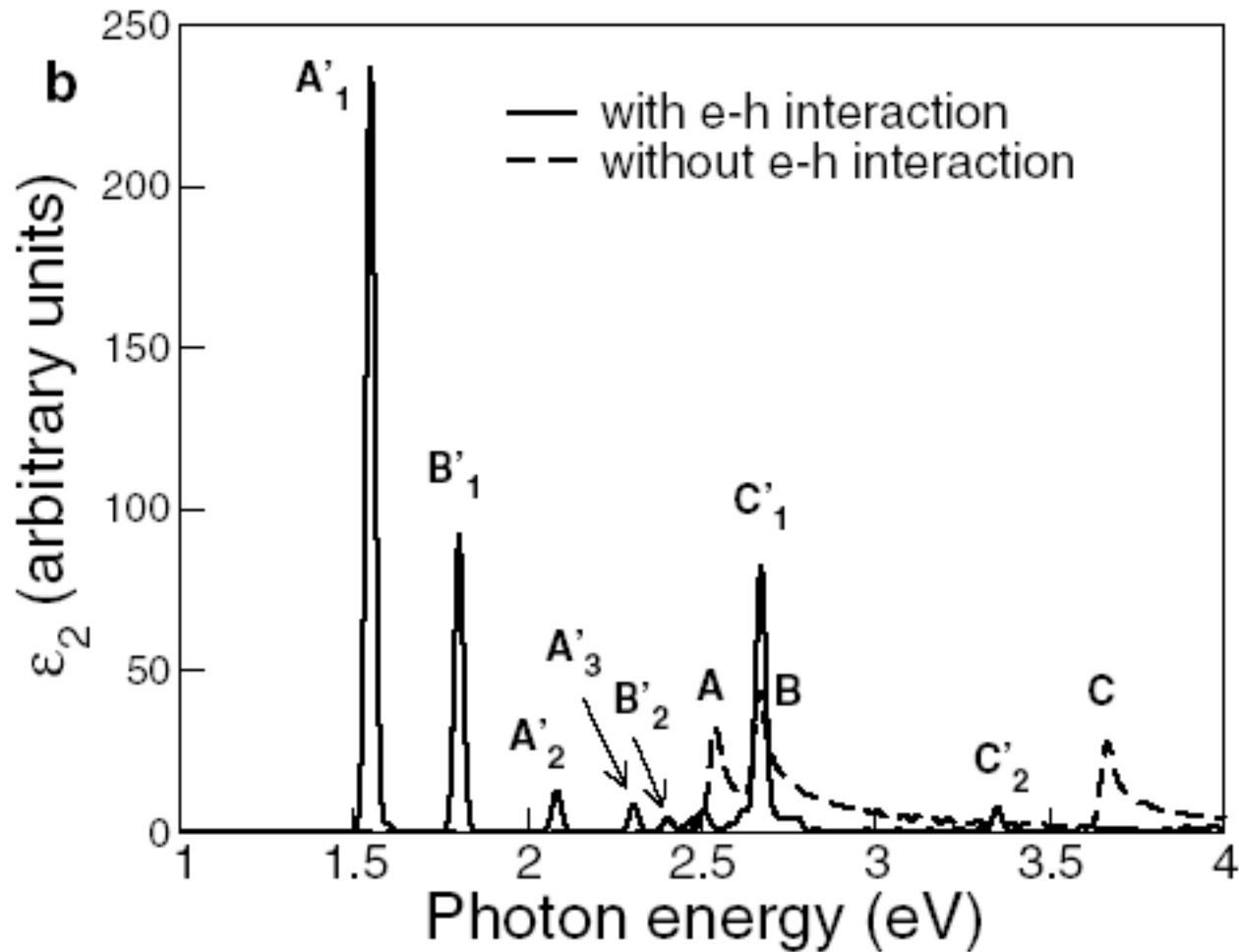


For comparison:

Poly(phenylene vinylene) $\sim 0.35 \text{ eV}$

Semiconductor nanowires \sim tens of meV

SWNT have a molecular spectrum with discrete transitions, rather than solid state continuous spectrum



Topic 2: Optical Spectroscopy of Single Nanotubes : Can we identify individual tubes?

Possible Techniques:

- Absorption Spectrum – too weak
- Resonance Raman – what excitation wavelength?
- Fluorescence Excitation -- not good for metallic tubes.

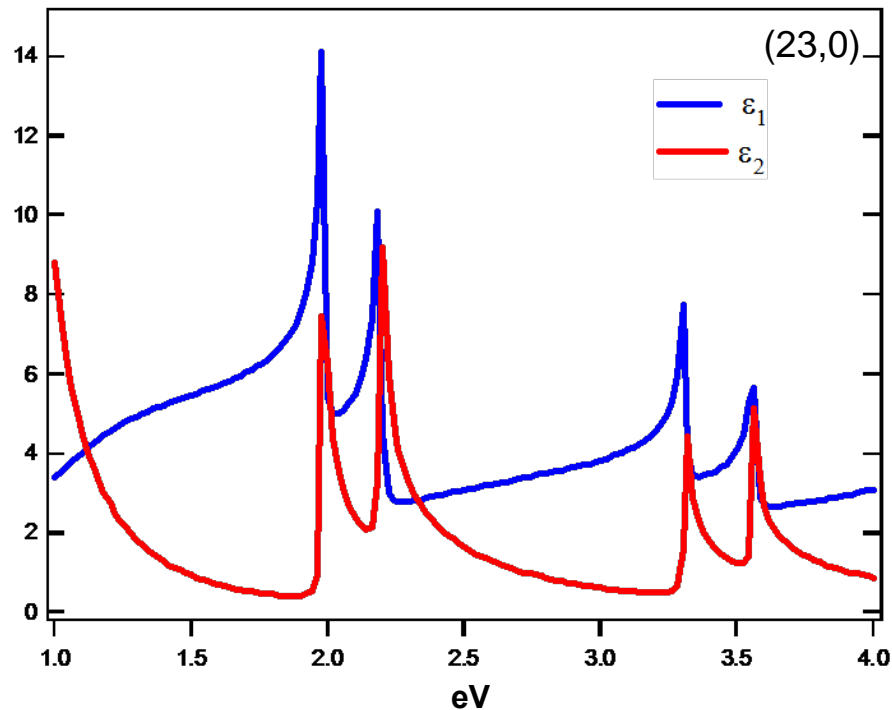
We perform white light *Resonant Rayleigh scattering*.

Advantages:

- Direct probe of electronic transitions, intrinsically stronger than Raman Scattering.
- Present for both semiconductor and metallic nanotubes.
- Data recorded in parallel – 1 minute signal averaging

Peaks in Resonant Rayleigh Scattering correspond to excited states in optical absorption

$$Q_{sca} \propto \frac{r^3 |\epsilon - 1|^2}{\lambda^3} \quad \epsilon = \epsilon_1 + i\epsilon_2$$

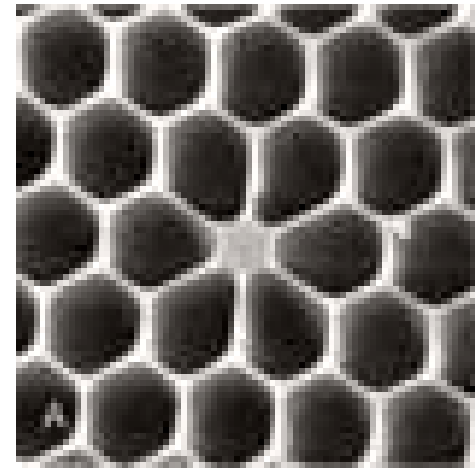
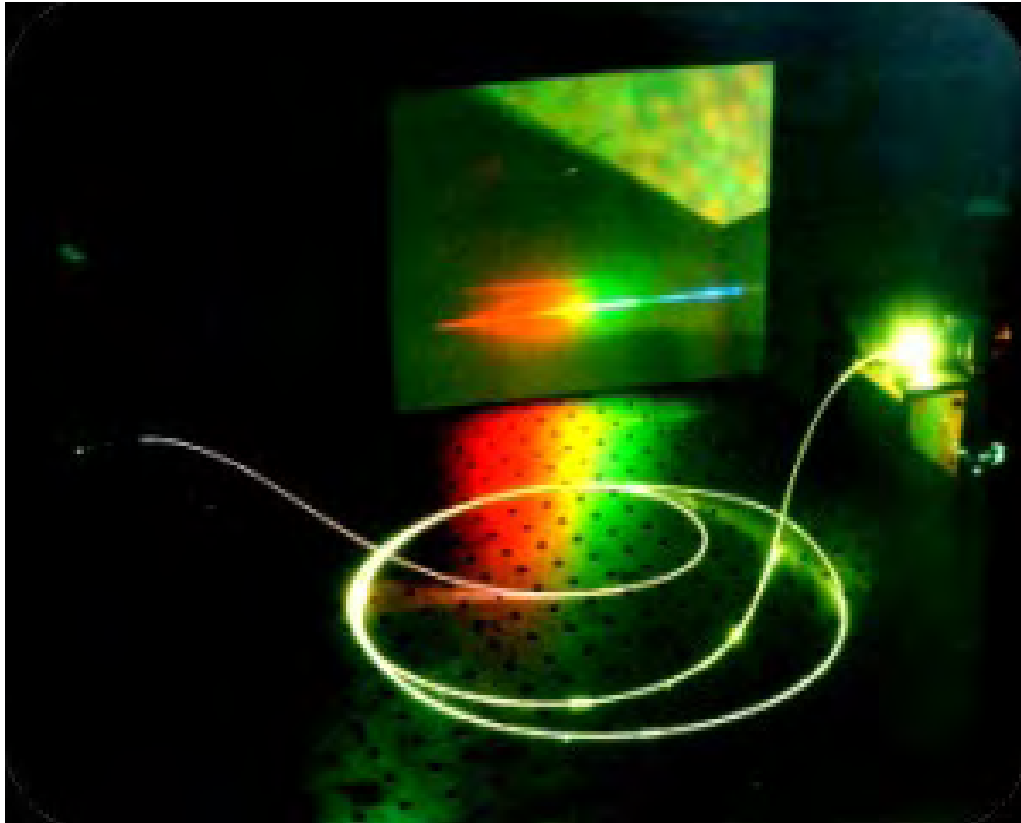


The scattering cross section for a single nanotube is $\sim 0.1\%$ of total extinction. The two become comparable at a diameter of around 40 nm.

Supercontinuum White Light Radiation generated in a microstructured core optical fiber

- High brightness – like laser
- Large spectrum bandwidth – like a light bulb

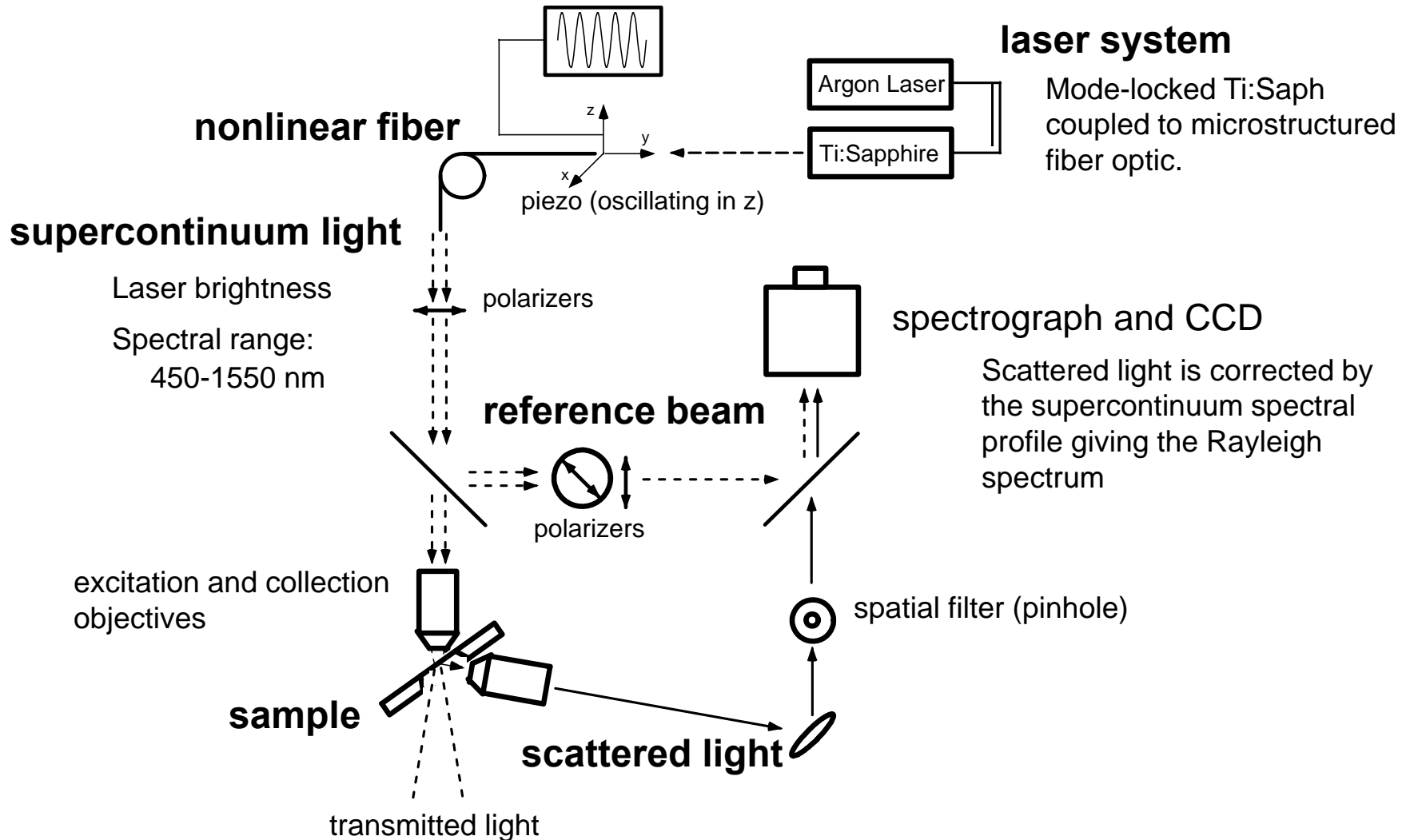
→ Spectral range:
450 - 1450 nm



Microstructured fiber: core ~ 2 μ m

White Light Rayleigh Scattering: Experimental Setup

Supercontinuum Generation



Growth and Imaging

CVD Growth Process

Si/SiO₂ substrates with slits patterned by optical lithography and wet etching.

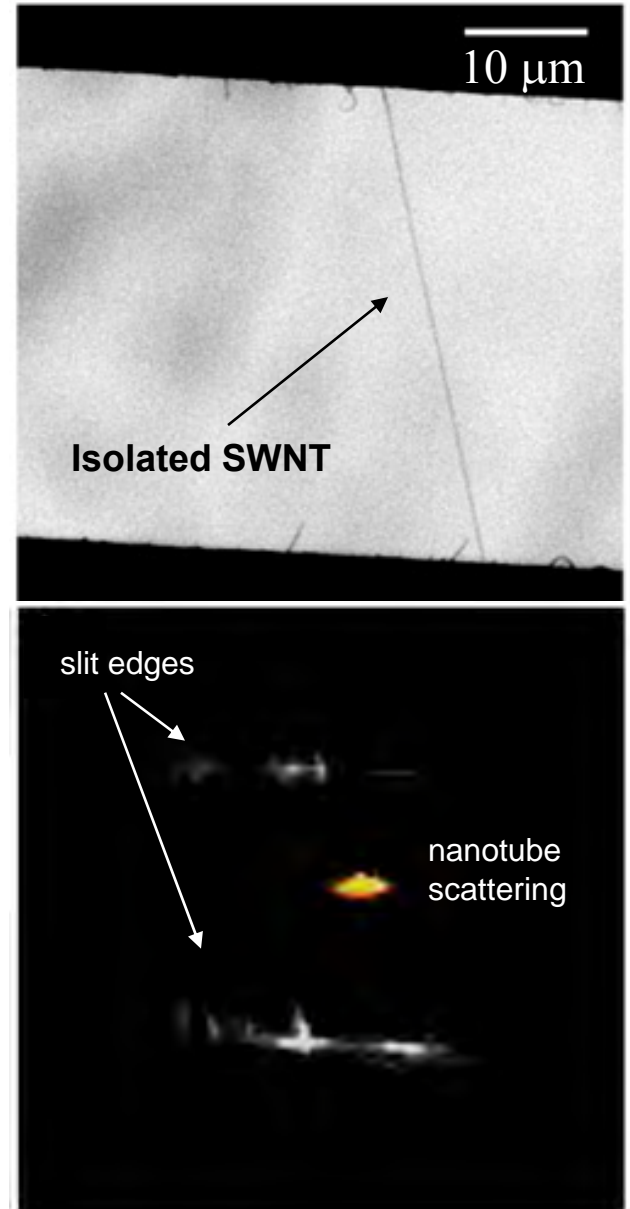
Directional growth determined by flow direction of feed gas, lengths > 100 microns:

- CO, methane, and ethanol gas
- Fe, FeMo, and CoMo catalysts

Imaging

Look at total integrated intensity on CCD to find tubes. Correlates to SEM images.

Single tubes scatter light much less than bundles. Distinguishable from the number of peaks in the spectra and width of features.

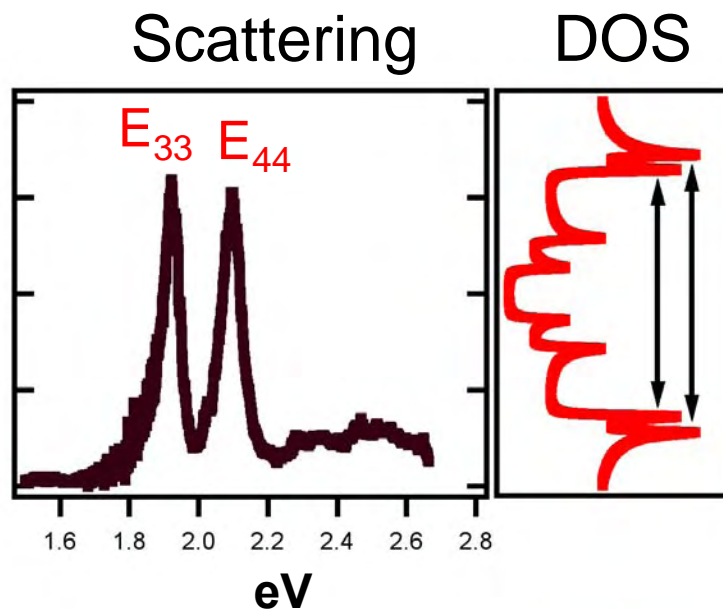


Experimental Single SWNT Resonance Rayleigh Spectra

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

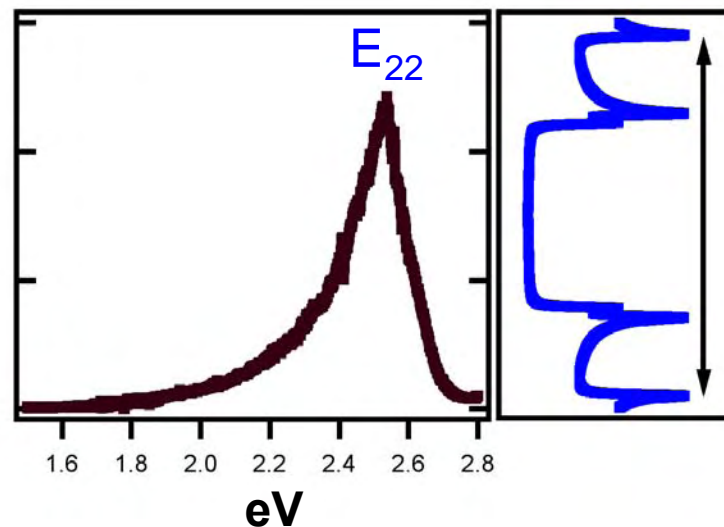
Semiconducting Carbon Nanotube

Two well separated E_{33} and E_{44} transitions for larger diameter tubes, E_{33} and E_{22} for smaller diameters.



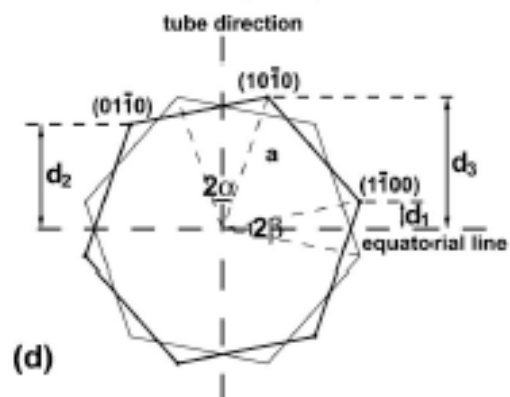
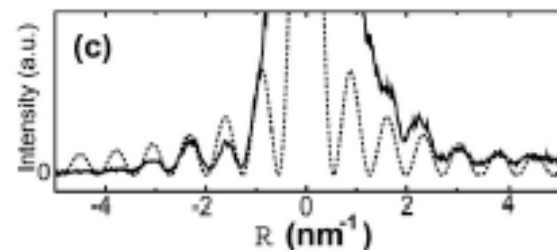
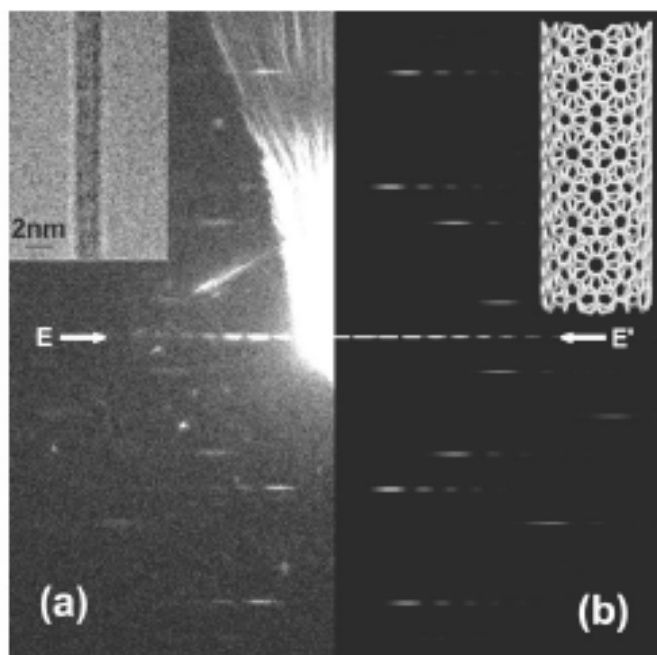
Metallic Carbon Nanotube

Single E_{22} transition observed in the visible – sometimes split into two very close peaks by trigonal warping effect



Determining Nanotube Structure by TEM Diffraction

Analyze electron scattering signal from ~ 50 nm collimated electron beam.

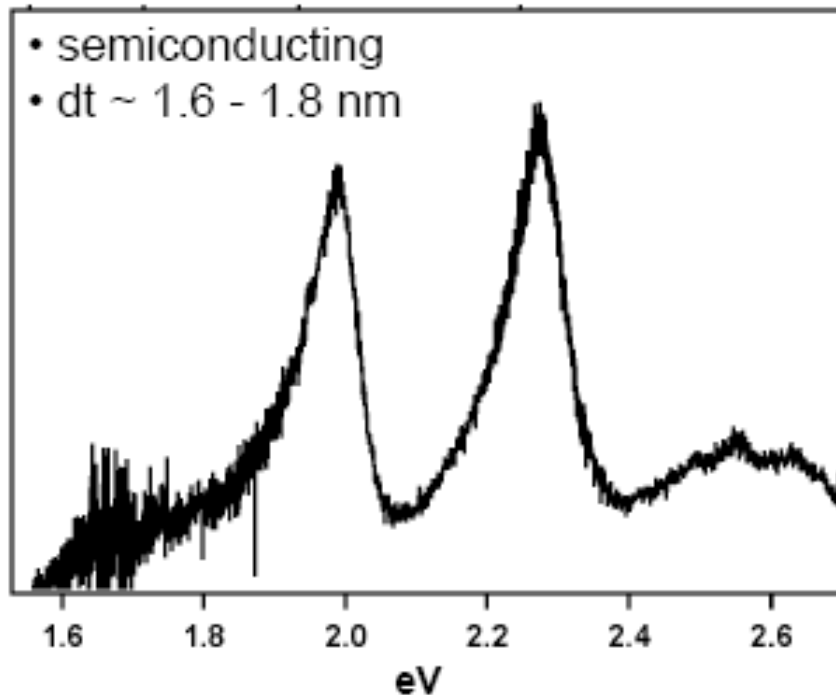


$$\text{Equatorial Oscillation} \propto J_0^2(\pi R D_0)$$

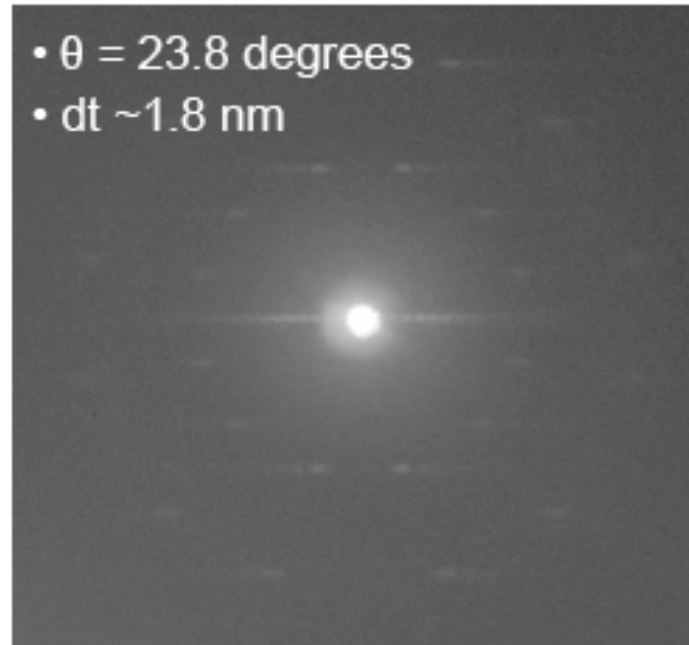
$$\alpha = \arctan\left(\frac{d_2 - d_1}{d_3}\right)$$

First Successful Structural Assignment of a Rayleigh Spectrum

Rayleigh Scattering (Columbia)



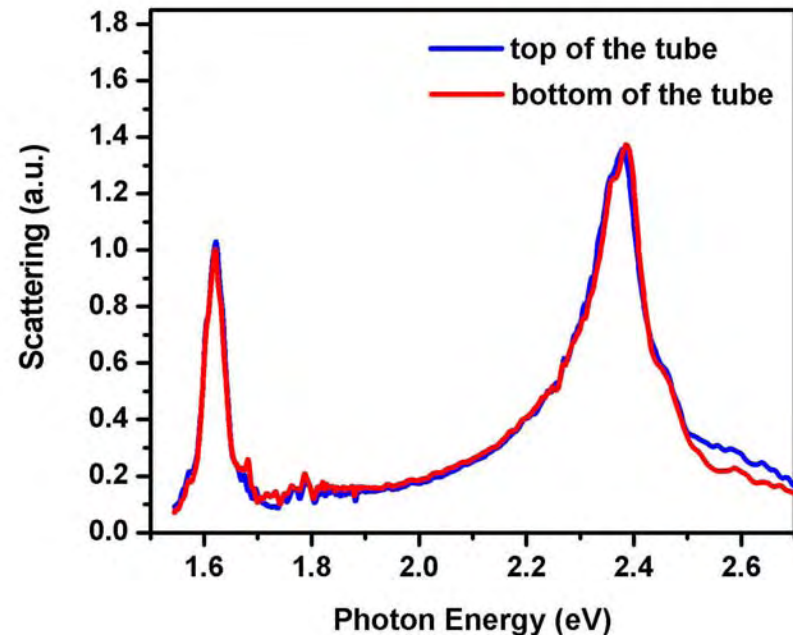
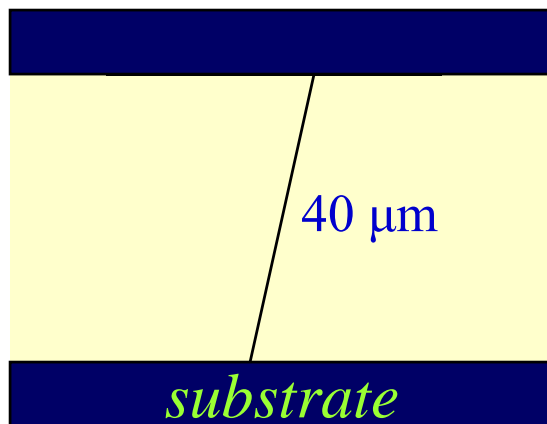
TEM Diffraction (BNL)



Through combination of TEM and Rayleigh scattering, transitions assigned to (16,11).

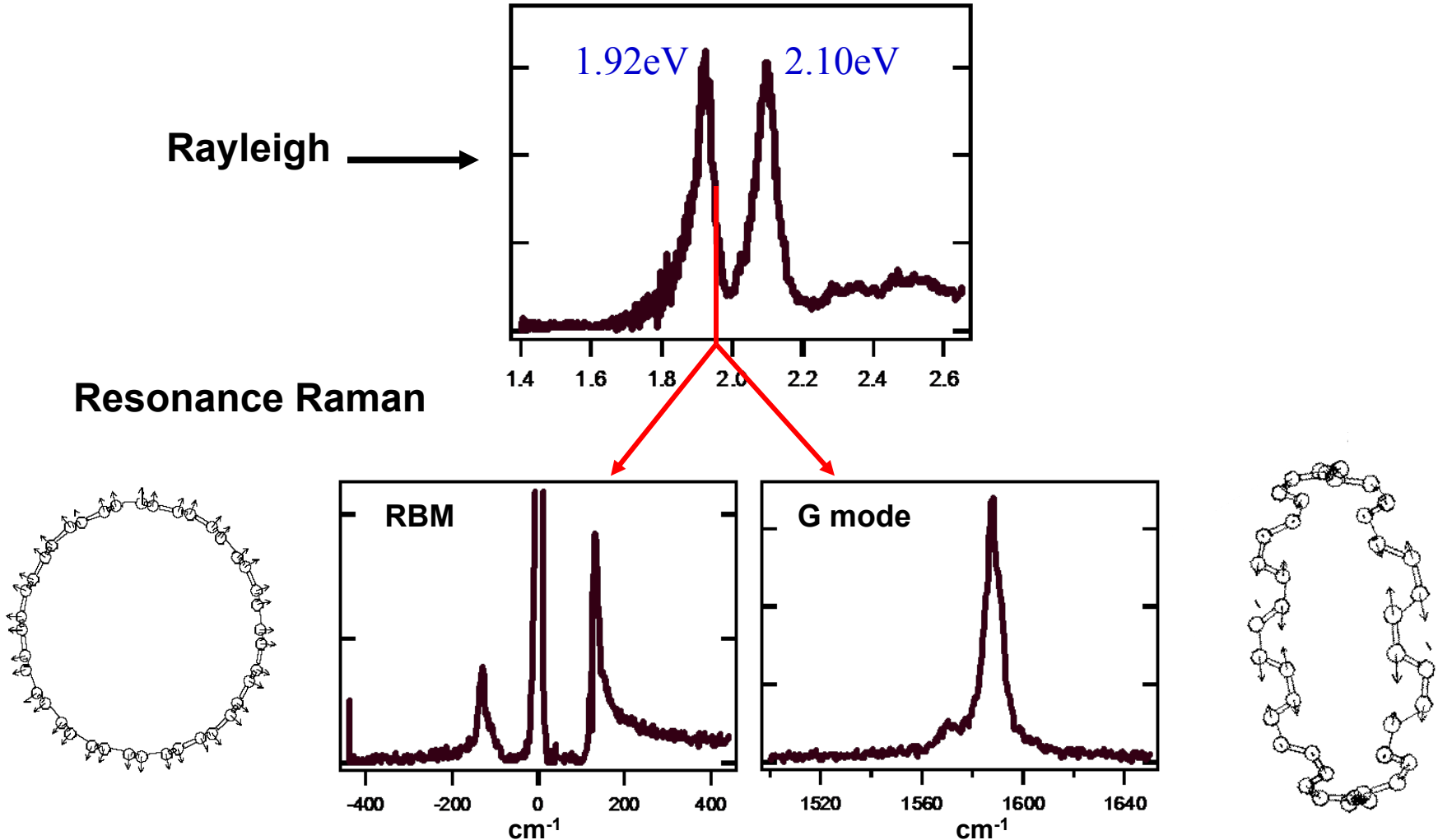
Scattering Spectra along the Nanotube: Single Tube

Does the nanotube keep the same chirality along the entire length?



Yes. At least up to $40\ \mu\text{m}$, a chain of several *millions* of carbon atoms.

Correlated Raman and Rayleigh Scattering from the Same Semiconductor Nanotube

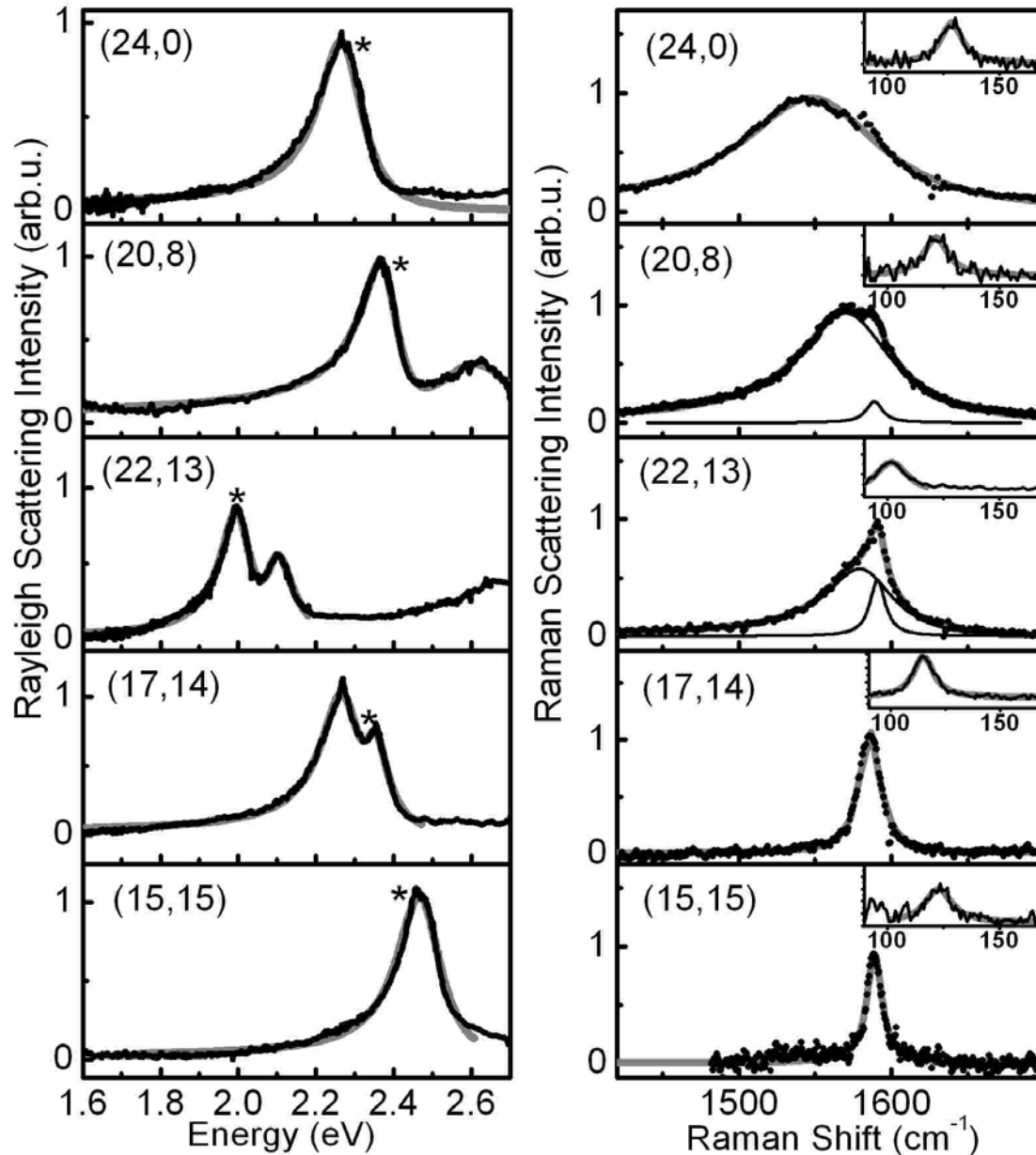


radial breathing mode → d=1.89nm

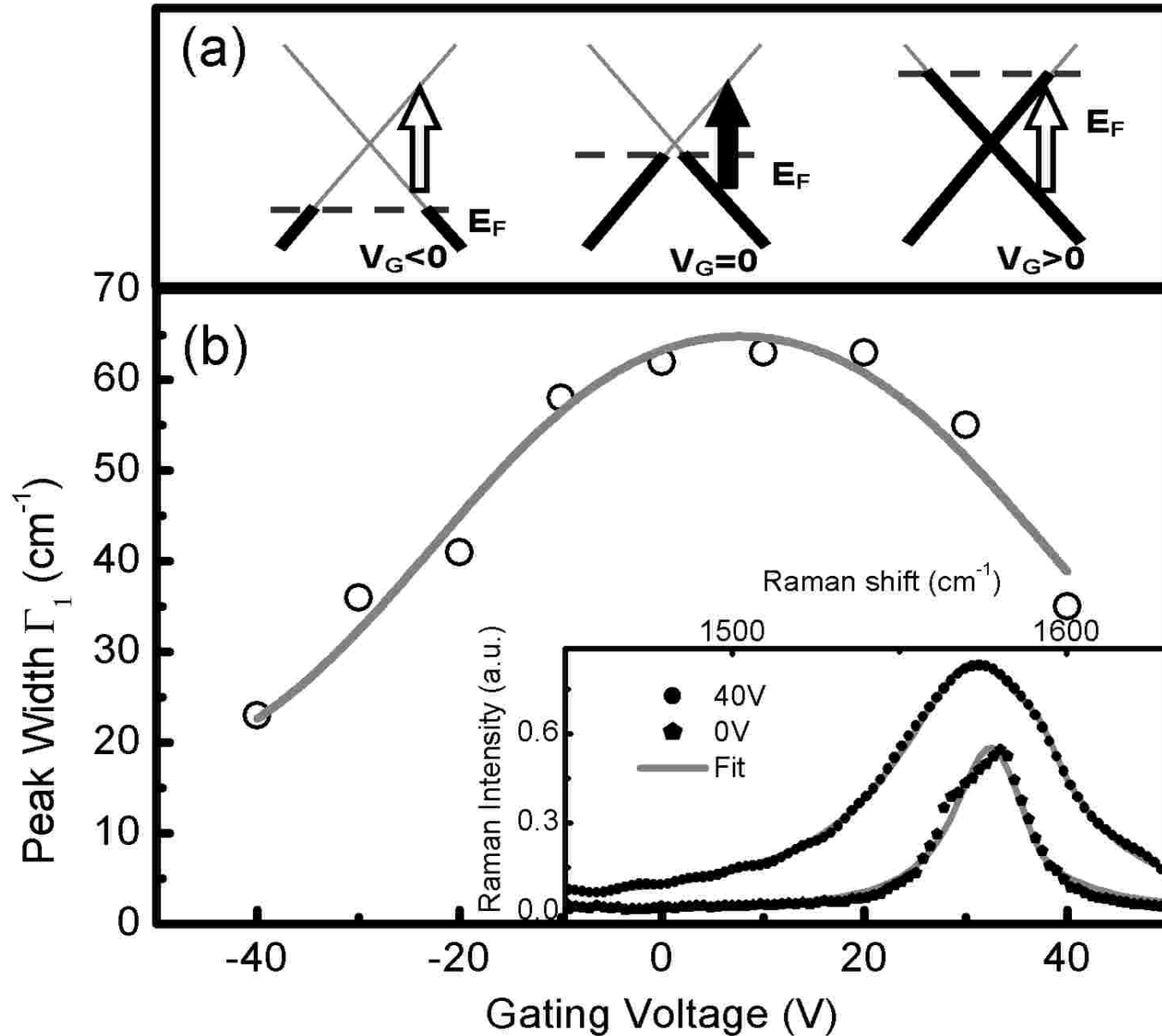
(21,4) nanotube: d=1.85nm. $E_{33}=1.87$, $E_{44}=2.10$ (tight binding model)

Rayleigh and Raman from Metallic Nanotubes

Wu et al, PRL **99**, 027402 (2007)



Electrostatic Gating varies width of C=C vibrational Raman
In metallic tubes -- broadening and Fano lineshapes



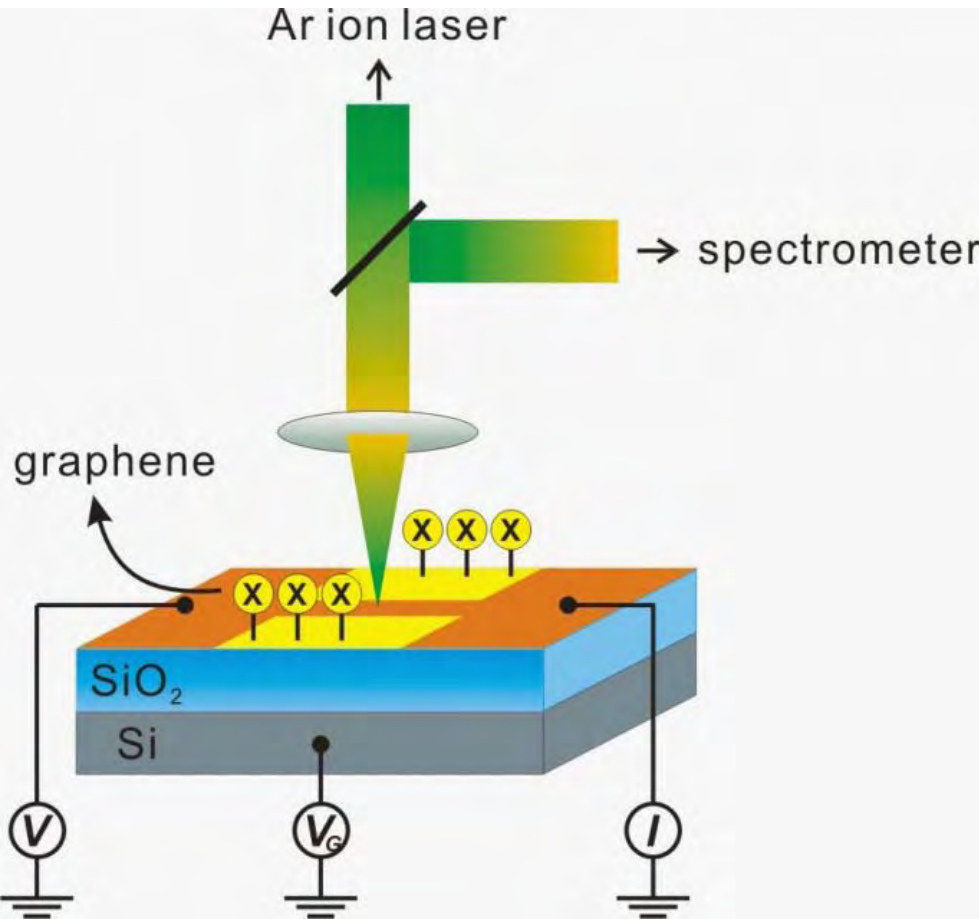
Summary

- Exciton binding energy about 0.4 eV -- SWNT optical transitions are molecular-like excitons.
- White Light Rayleigh scattering shows strong exciton optical transitions and distinguishes between metallic and semiconducting tubes.
- Phonons strongly coupled to electrons in metallic tube Raman -- broadening and Fano lineshapes.

Basal Plane Chemical Reactions and Intrinsic Physical Properties of Graphene

Postdocs Sunmin Ryu, Stephane Berciard, Li Liu

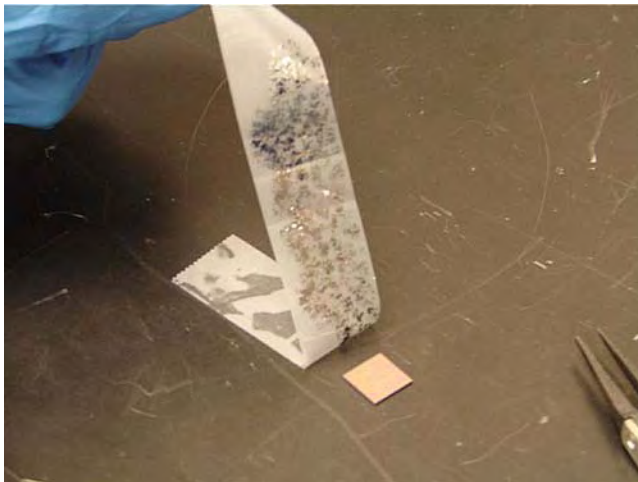
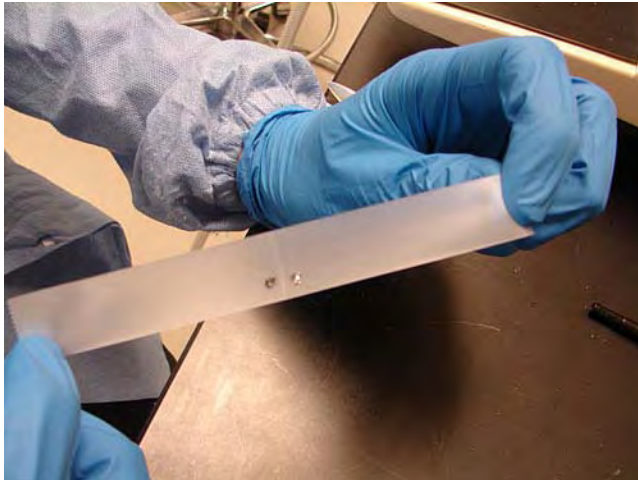
Kim, Heinz, Brus, Flynn groups
NSF Funded Columbia Nanocenter



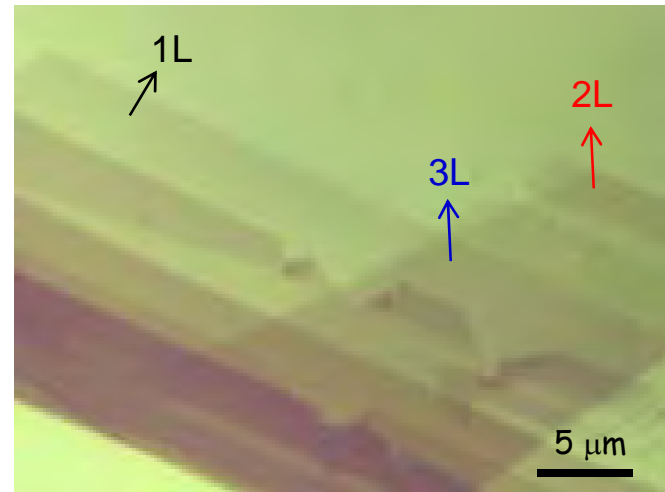
Outline:

- 1 Intrinsic Raman Spectra
- 2 Oxidation and H atom reactions on basal plane

Preparation of graphene



Micro-mechanical exfoliation
using “Scotch tape”



Kish graphite on 300 nm SiO₂/Si

-Scientific American
@ Columbia University

Remarkable Physical Properties

Andre Geim & Philip Kim

Quantum Hall Effect

One-atom-thick 2D crystal

Semi-metal with low density of states – easily doped

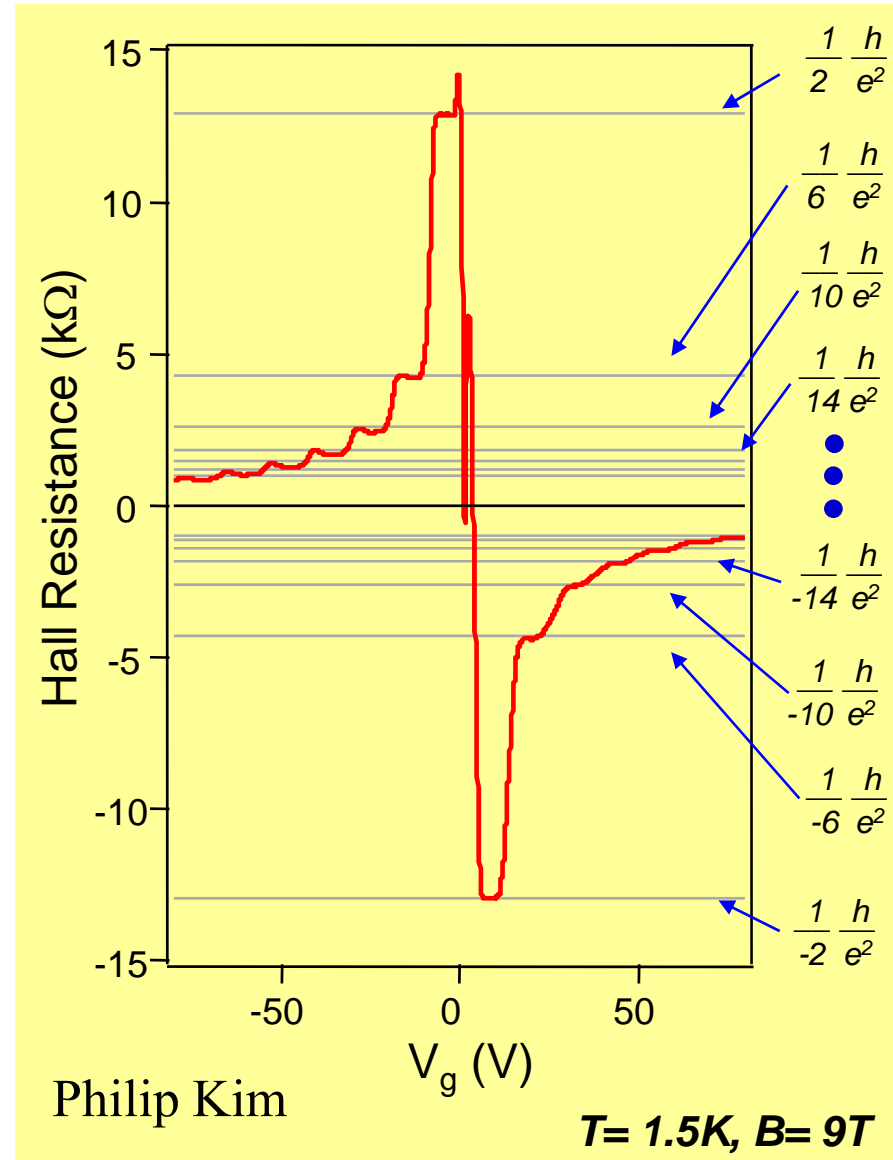
High electron mobility: $\sim 200,000 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$

High transparency: $1-T = 2.3\%/ \text{layer}$

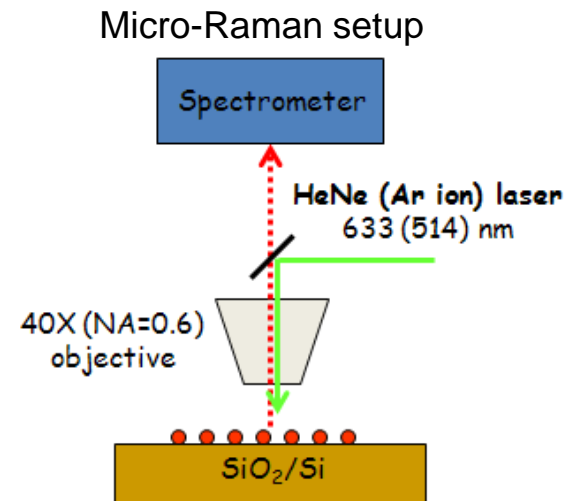
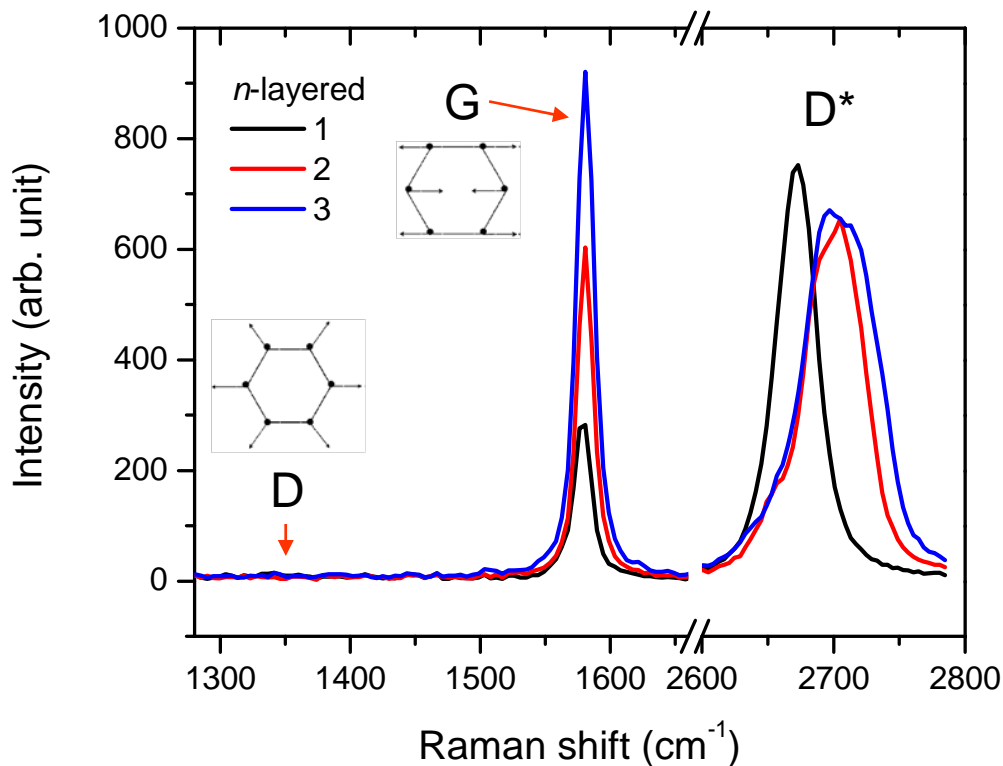
Excellent thermal conductivity $\sim 5,000 \text{ W/mK}$
(*copper $\sim 400 \text{ W/mK}$)

Superior Young's modulus $\sim 1,000 \text{ GPa}$
(*steel $\sim 200 \text{ GPa}$)

Remarkable properties all result from strong aromatic pi chemical bonding



Strong Resonance Raman scattering



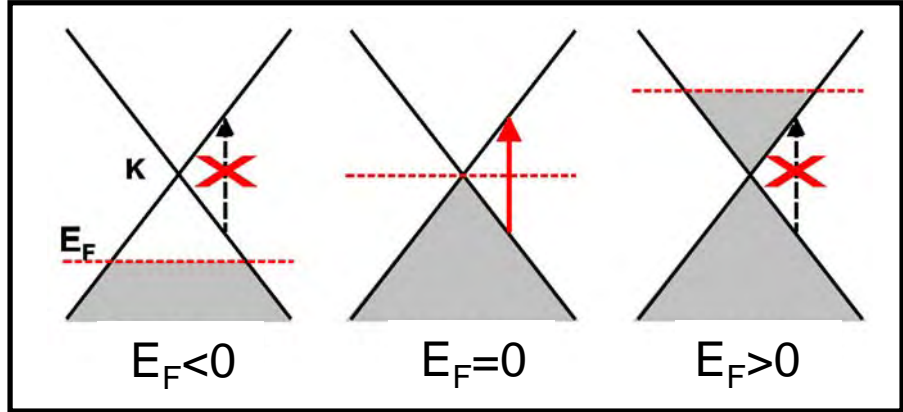
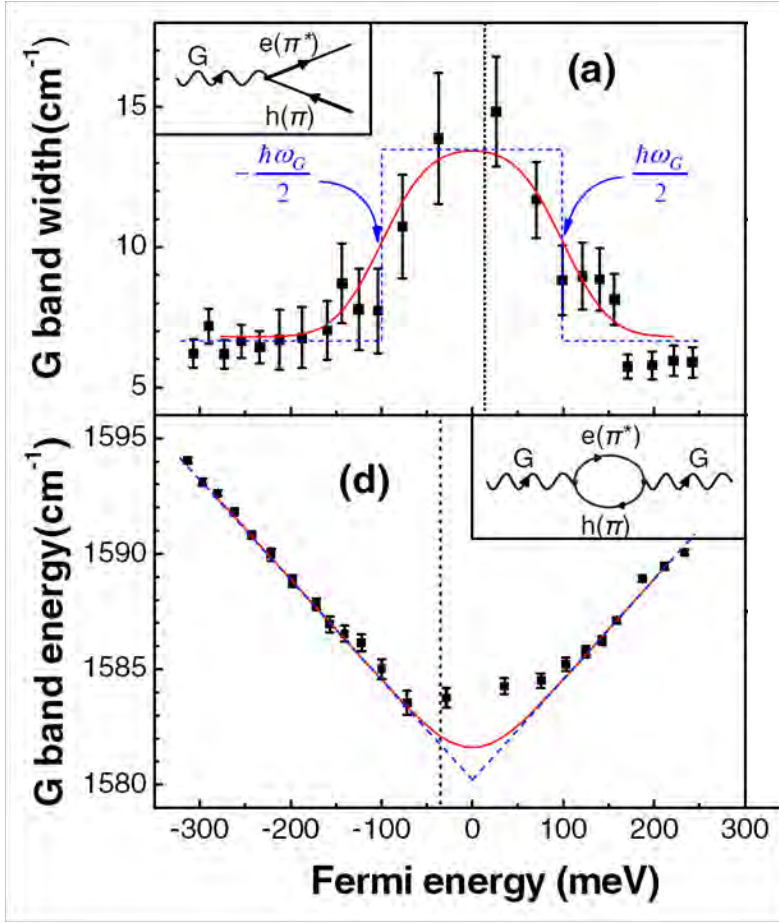
- A. Ferrari *et al.* PRL (2006)
- J. Yan *et al.* PRL (2007)
- ...

- G mode: C-C stretching ($\sim 1580 \text{ cm}^{-1}$)
 $\Delta\omega_G \propto n^{1/2} \propto \Delta|E_F|$; measures **charge density (n) - doping**
- D mode: ring-breathing ($\sim 1350 \text{ cm}^{-1}$)
 activated by **structural defects – sp² carbon to sp³ carbon**
- D* mode: overtone of D mode ($\sim 2700 \text{ cm}^{-1}$)
 indicates **thickness**

Carbon-Carbon stretch vibration (Raman G band) couples to metallic electrons

A Shift of the Fermi Energy induces:

- Phonon energy renormalization: $\omega_G \uparrow$ when $|E_F| \uparrow$
- Narrowing of the the G band width

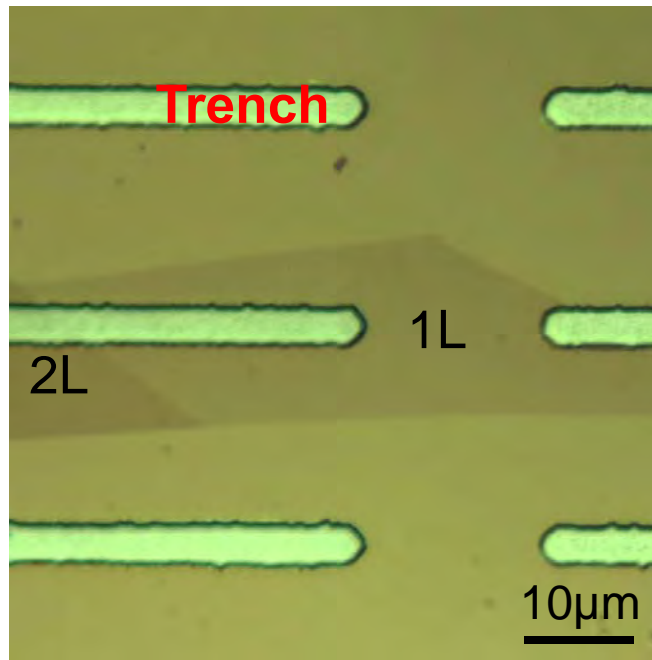


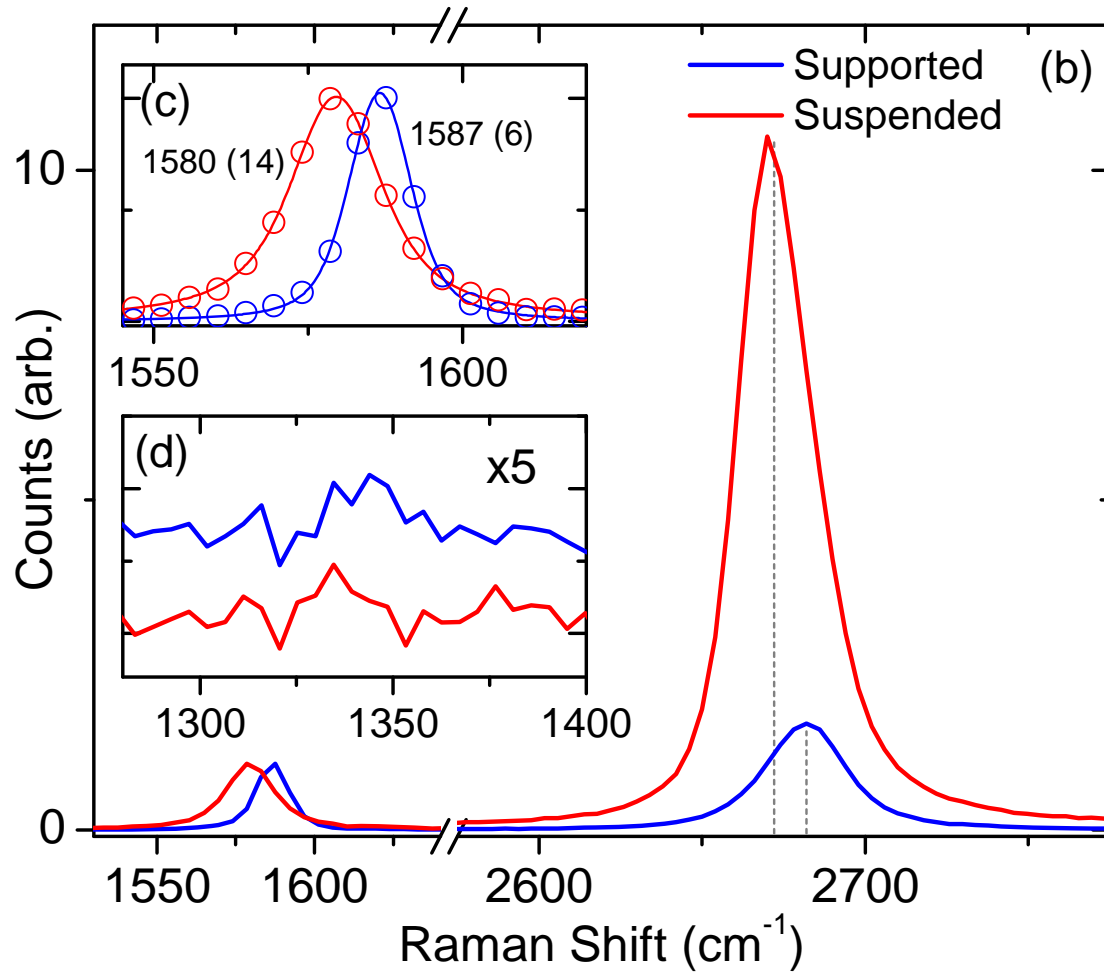
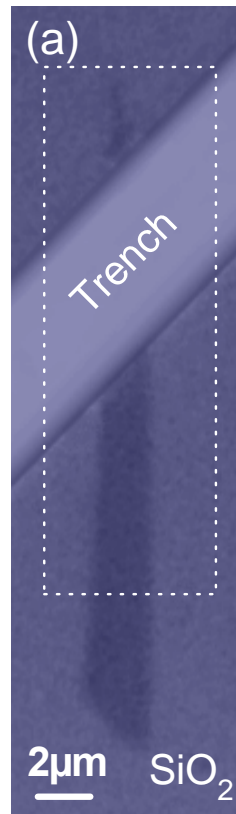
$\Gamma_G \downarrow$ when $|E_F| \uparrow$ (reduction of Landau Damping)

J. Yan et al. PRL **98**, 166802 (2007)
 Similar results by A. Geim, A. Ferrari *et al.*
 Nature Mater. 2007
 Nature Nano. 2008

Intrinsic Raman Properties – comparison of graphene suspended over a trench versus supported on Silicon dioxide

Optical microscope image

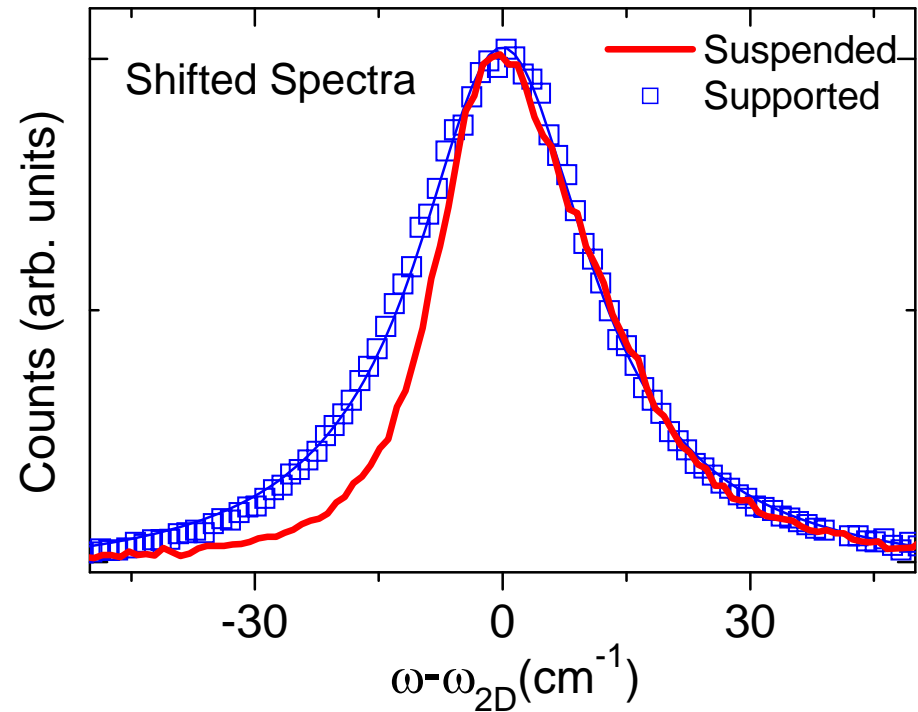




- Softer and Broader G mode
- No significant D band (D/G ratio < 1%)
- **Drastically reduced 2D/G intensity ratio**

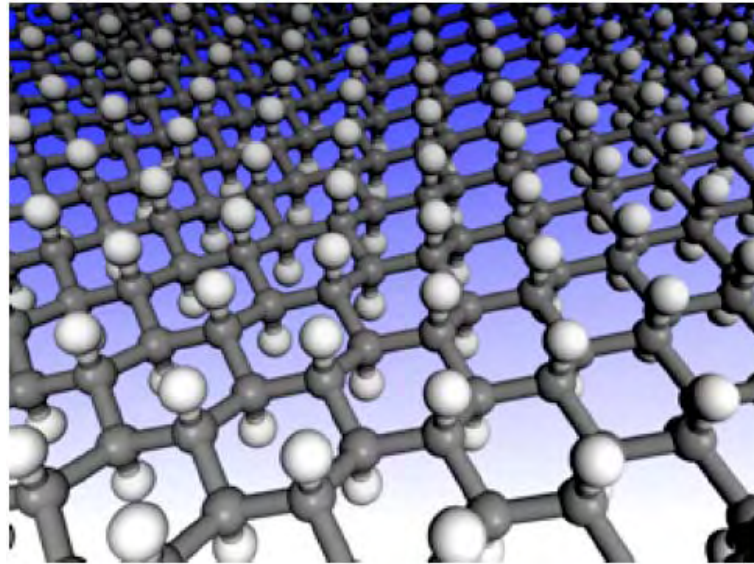
Asymmetric lineshape of the 2D Mode

Supp. graphene: Quasi-Lorentzian
Susp. graphene: Positively Skewed



- This lineshape does not stem from *Inhomogeneous heating or strain*
- No physical interpretation in terms of two distinct phonon modes
- This lineshape is **polarization independent**
- It **does not depend on excitation wavelength**

Reversible Hydrogenation of Graphene



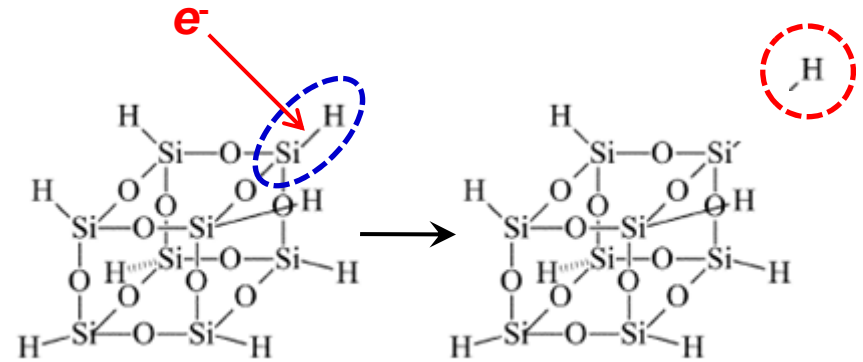
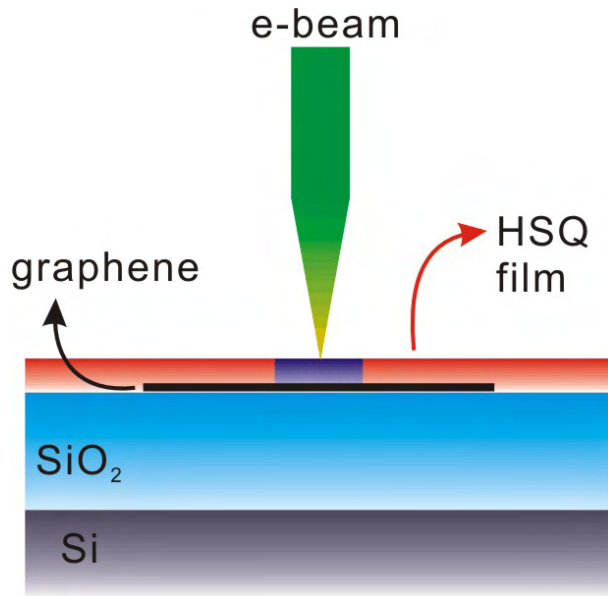
- *J. Sofo et al. PRB 75, 153401 (2007)*

Graphene: semimetal

Graphane: large band gap insulator

Background: H atoms bind weakly to bulk HOPG graphite in vacuum

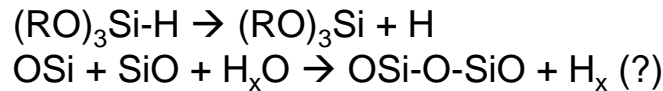
In situ generation of hydrogen atoms



Cage structure of HSQ
(hydrogen silsesquioxane)

C. Yang and W. Chen, *J. Mater. Chem.* (2002)

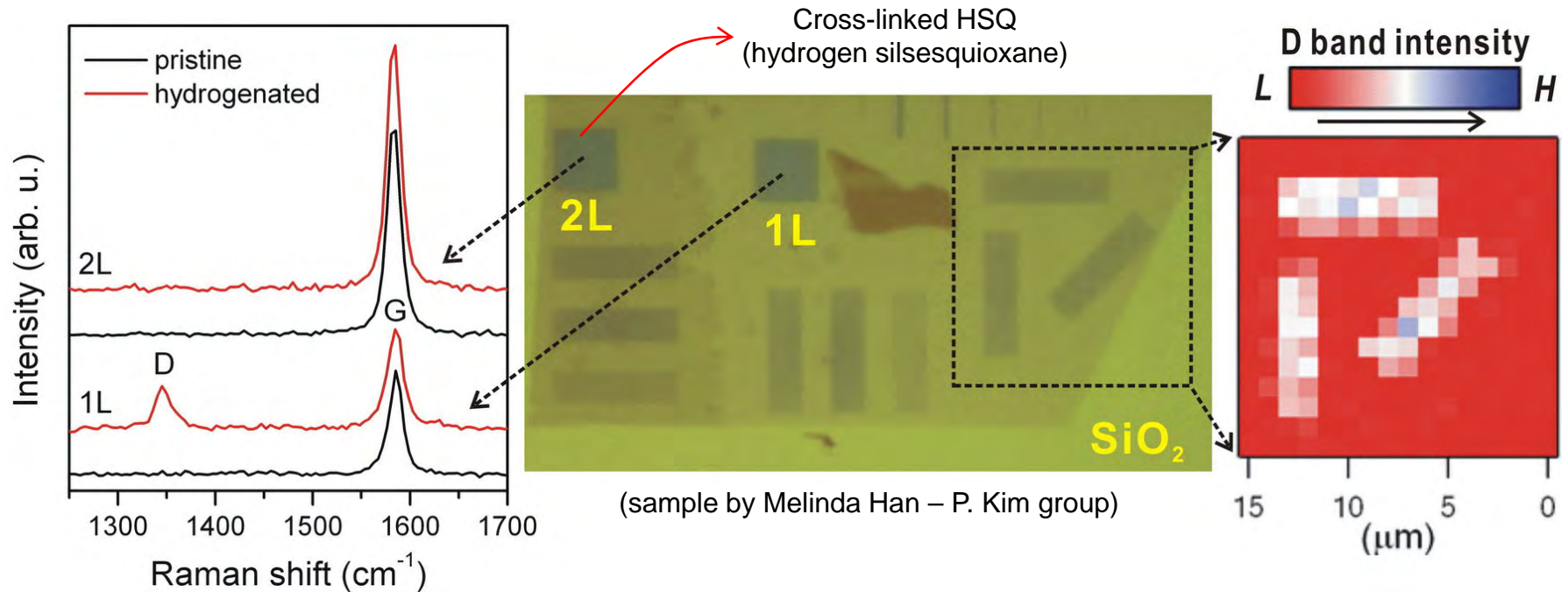
Electron beam induced cross-linking mechanisms



H. Namatsu et al., *JVST B* (1998)

- E-beam breaks Si-H bonds and generates hydrogen atoms
- E-beam allows high spatial resolution (limited by diffusion of H atoms)

Patterning graphene by hydrogenation

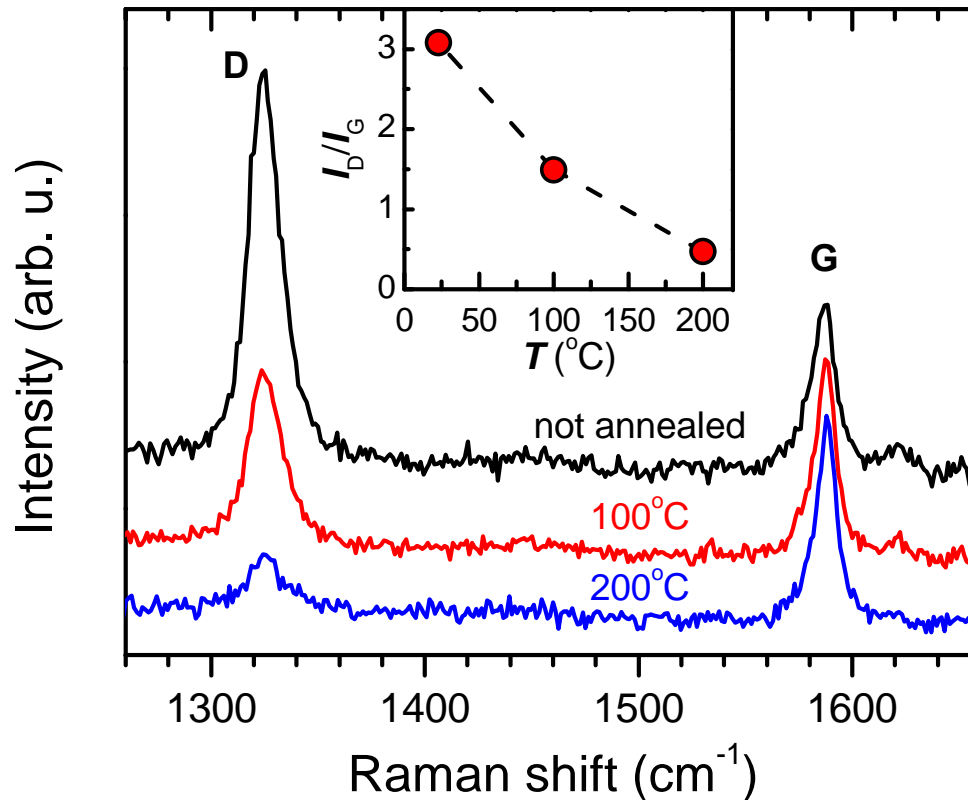


- Spatially localized hydrogenation can be achieved using focused e-beam (resolution ~ 15 nm)
- Hydrogenation is ~ 15 times faster for 1L than 2L graphene
- In situ generation of H atoms can be readily applied to graphene devices

S. Ryu et al., *Nano Lett.* **8**, 4597 (2008)

S. Ryu et al., International Patent filed (2007)

Reversible hydrogenation



- Hydrogenated graphene is stable in ambient condition
- Thermal annealing restores sp^2 crystalline structure
- Each H atom is estimated to donate $\sim 0.003e$ electron to graphene

S. Ryu et al., *Nano Lett.* **8**, 4597 (2008)

S. Ryu et al., International Patent filed (2007)

Summary:

1. Basal plane chemical reactions can be observed via the intensity of the D band. H atoms show **reversible** binding to graphene.
2. Single layer graphene more reactively chemically than bilayer or bulk HOPG.
2. G band shift and width is a measure of the doping. Fermi level can be shifted by almost a volt.
3. Extremely strong 2D band has an asymmetric line shape and is extraordinary sensitive to the environment. Not understood.