

Columbia University in the City of New York



Recent Faculty Hires:

Condensed Matter physics

Boris Altshuler
Igor Aleiner

Horst Stormer
Aron Pinczuk
Tony Heinz
Andy Millis
Phillip Kim
Mark Hybertsen

Chemistry and Materials

Jack Norton
Jim Leighton
Colin Nuckolls
Virginia Cornish
David Adams
Dalibor Sames
Brian Gibney

David Reichman
Laura Kaufman
Mike Steigerwald
Stephen O'Brien
Ruben Gonzalez

The Scale of Things – Nanometers and More

Things Natural

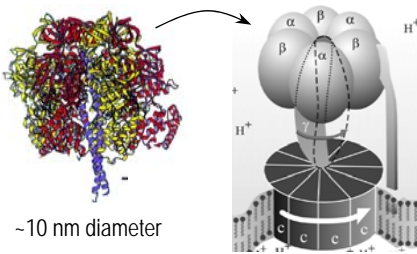


Dust mite
200 μm



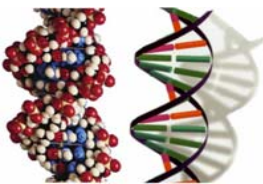
Human hair
~ 60-120 μm wide

Red blood cells
(~7-8 μm)

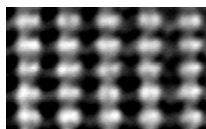


~10 nm diameter

ATP synthase



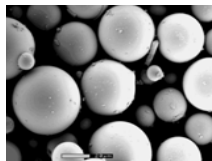
DNA
~2-1/2 nm diameter



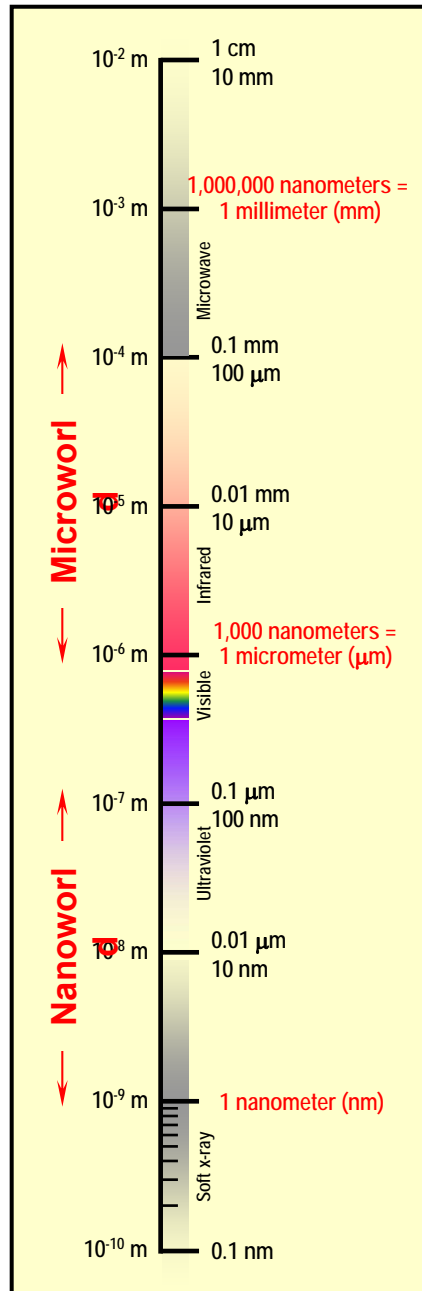
Atoms of silicon
spacing 0.078 nm



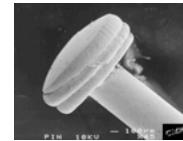
Ant
~ 5 mm



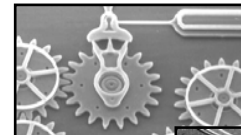
Fly ash
~ 10-20 μm



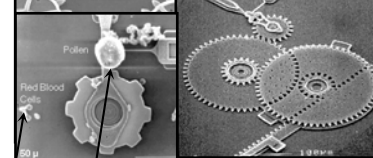
Things Manmade



Head of a pin
1-2 mm

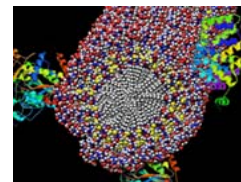


MicroElectroMechanical (MEMS) devices
10 -100 μm wide

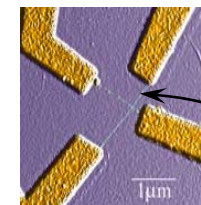


Pollen grain
Red blood cells

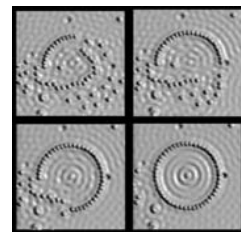
Zone plate x-ray "lens"
Outer ring spacing ~35 nm



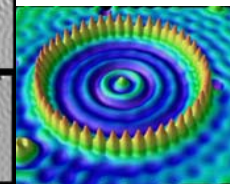
Self-assembled,
Nature-inspired structure
Many 10s of nm



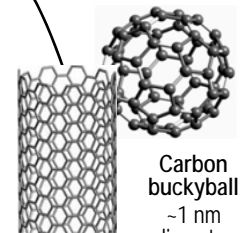
Nanotube electrode



Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm

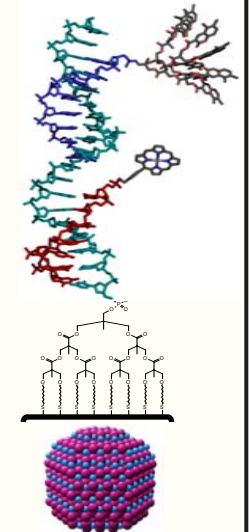


Carbon nanotube
~1.3 nm diameter



Carbon buckyball
~1 nm diameter

The Challenge



Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

Excited Electronic States of Carbon Nanotubes

Louis Brus

Chemistry Dept, Columbia University, New York, NY

NSF Nanocenter Collaboration: among Heinz, O'Brien, Hone, Turro, Friesner, and Brus groups at Columbia, and Zhu TEM group at Brookhaven.

1. Band Structure and Electron-Hole Binding – Excitons

Students F. Wang, G. Dukovic

2. Resonant Rayleigh and Raman Scattering from individual tubes and

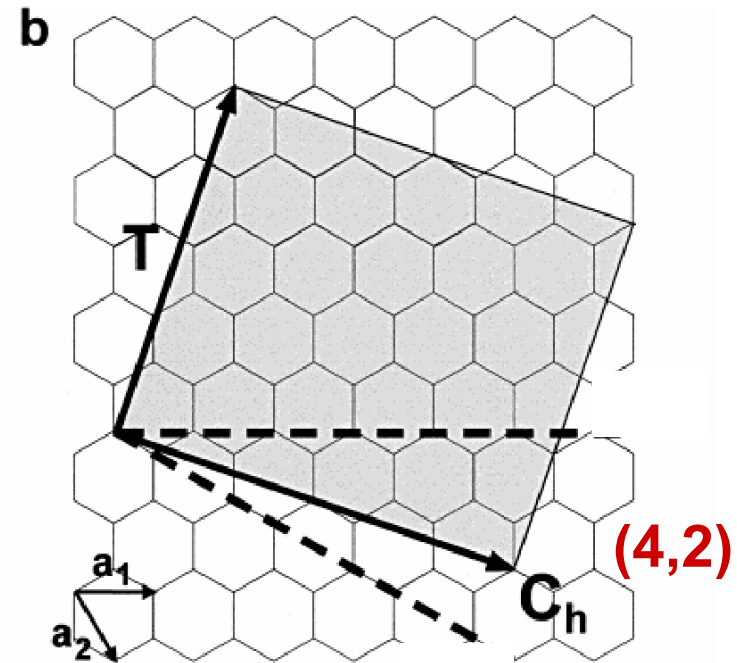
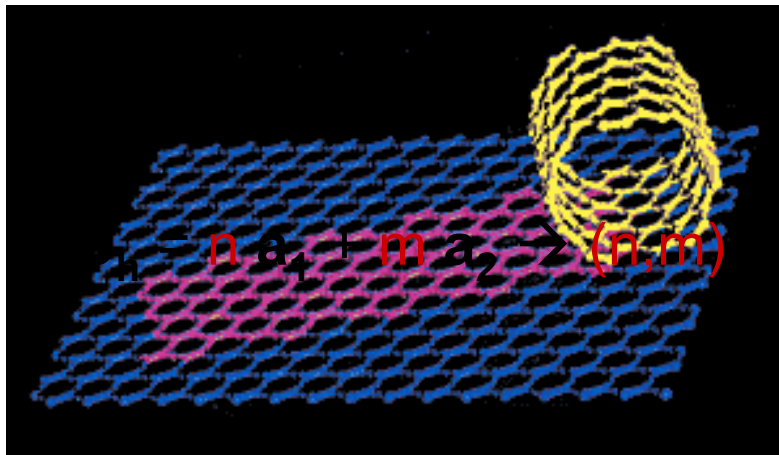
Spectral Assignment M. Sfeir, F. Wang, L. Huang,

C. Chuang T. Beetz (Brookhaven),

3 Growth, Short Tubes, and the Diffuse Interstellar Bands

Z. Zhou, L. Zhang

SWNTs – a family of long molecules

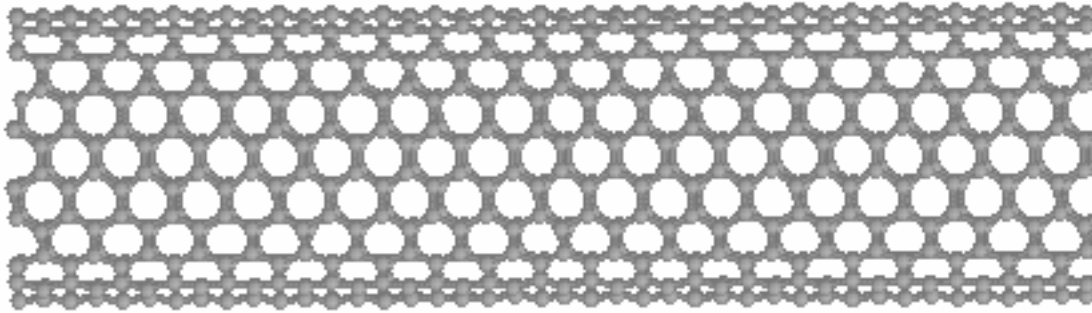


>100 distinct SWNT structures defined by indices (n, m)

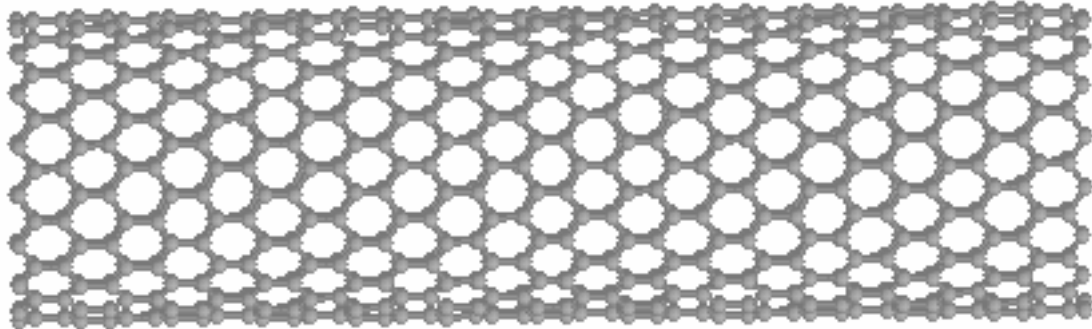
Defining structural features: diameter and chirality

Each physical structure has a unique electronic structure

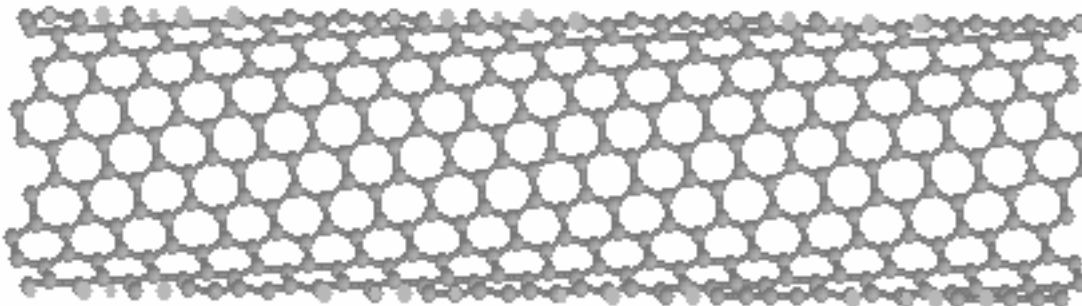
Molecular Tubes– some Chiral



*(10,10) Arm-chair
Metallic Wire*



*(18,0) Zig-zag
Small gap
Semimetallic Wire*



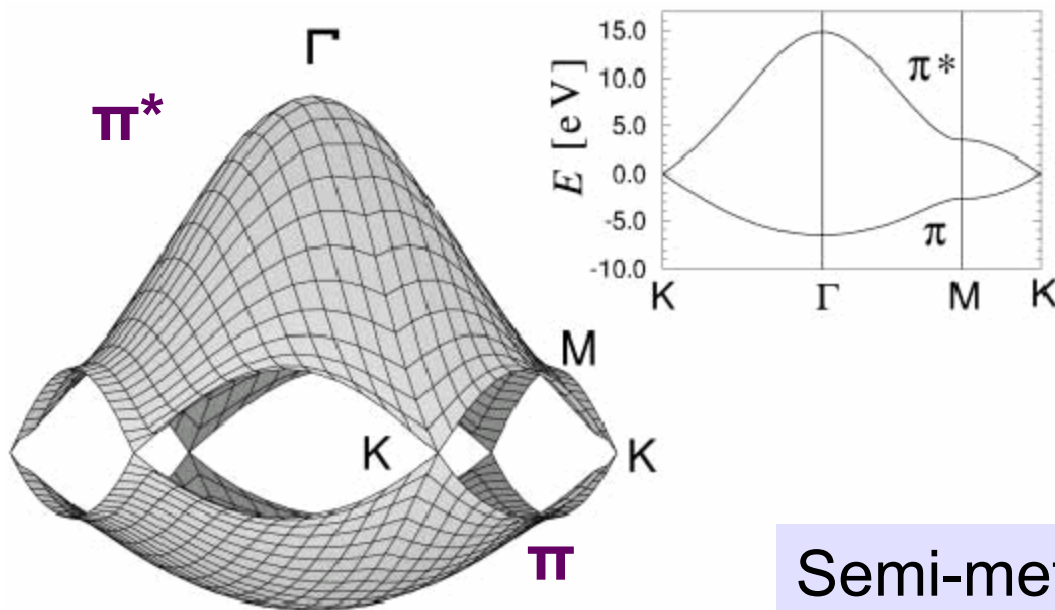
*(7,12)
Chiral
Semiconductor*

Images from Hongjie Dai

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

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

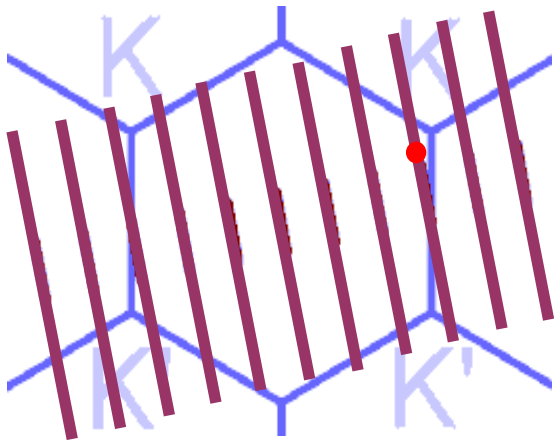
Electron momentum k is continuous for infinite plane of graphite



$\alpha = 0$
 $\gamma_0 = 3.033$ eV
(fitted to reproduce
ab initio results)

Semi-metallic behavior at K-points

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

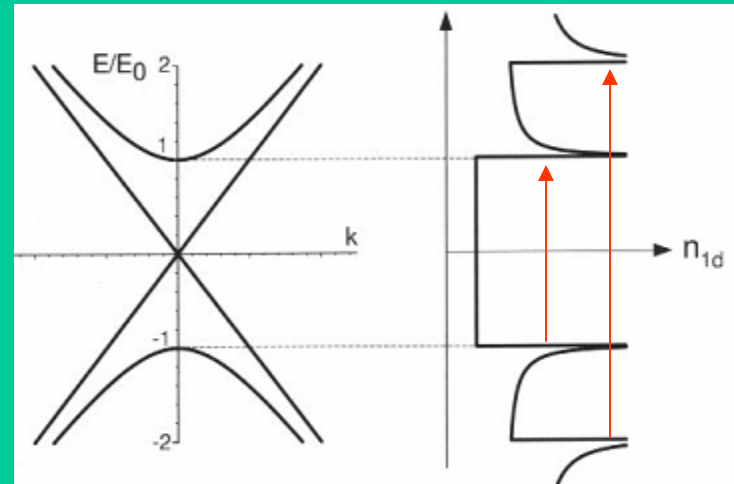


Nanotube:

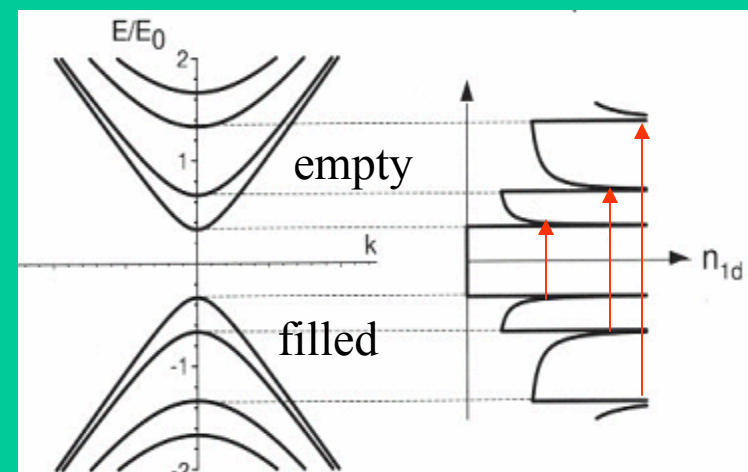
Electron momentum k quantized around circumference.

Electron momentum remains continuous along length

Metallic:



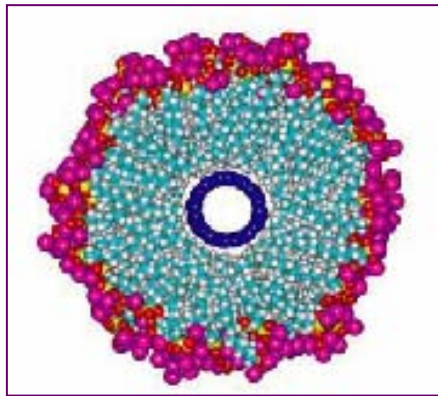
Semiconducting:



SWNTs in micellar solution

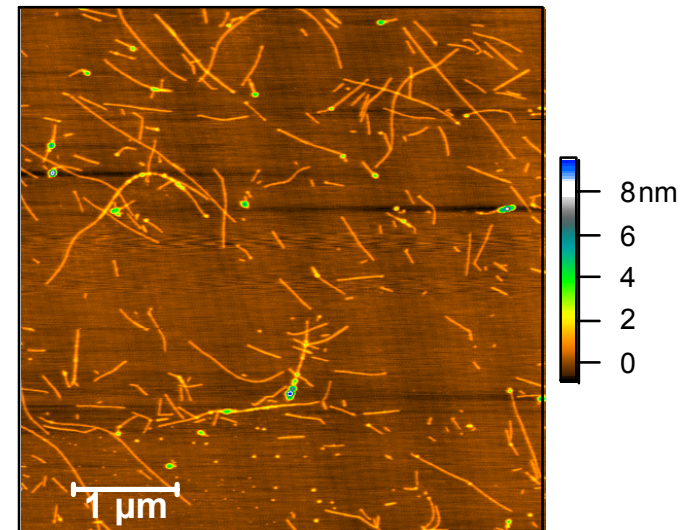
As-grown nanotubes: inter-tube interactions prevent solubilization

SWNT in SDS micelle



O'Connell, M. J. et al; *Science*
2002, 297, 593-596.

AFM image

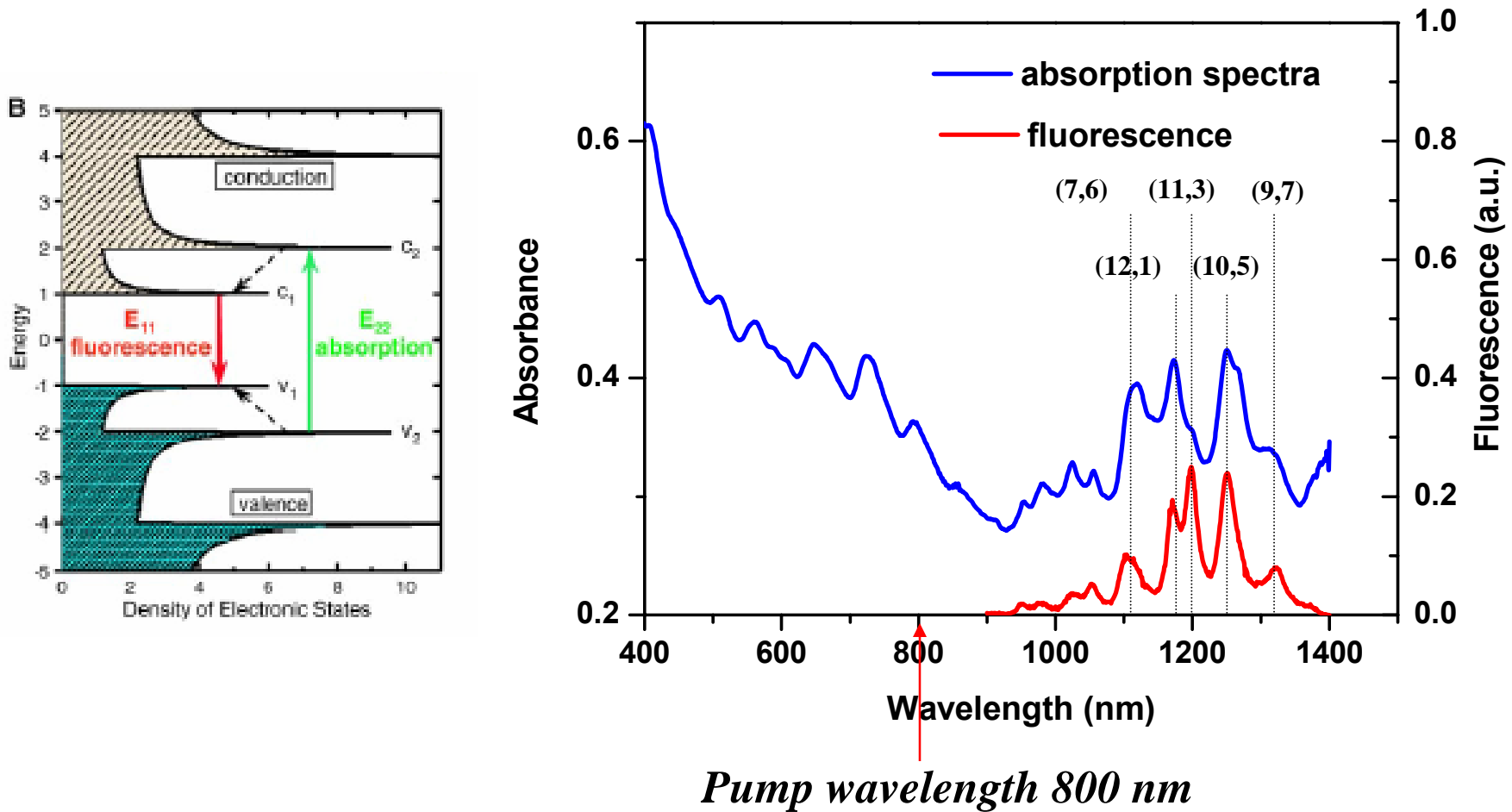


avg. length ~ 400 nm

Micellar solubilization allows measurement of
well-resolved optical spectra

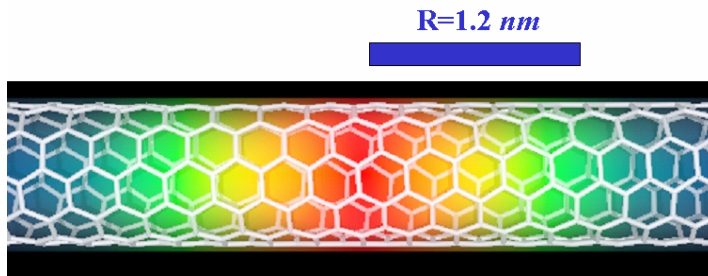
Experimental Micellar Optical Spectra of Semiconductor SWNTs :

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



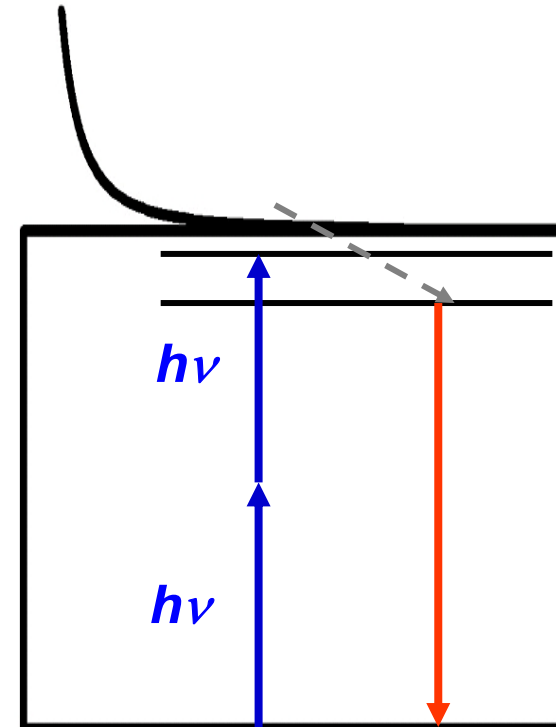
[(n,m) assignment according to S.M. Bachilo et al. Science **298**, 2361 (2002)]

Excitons Due to electron-hole attraction?



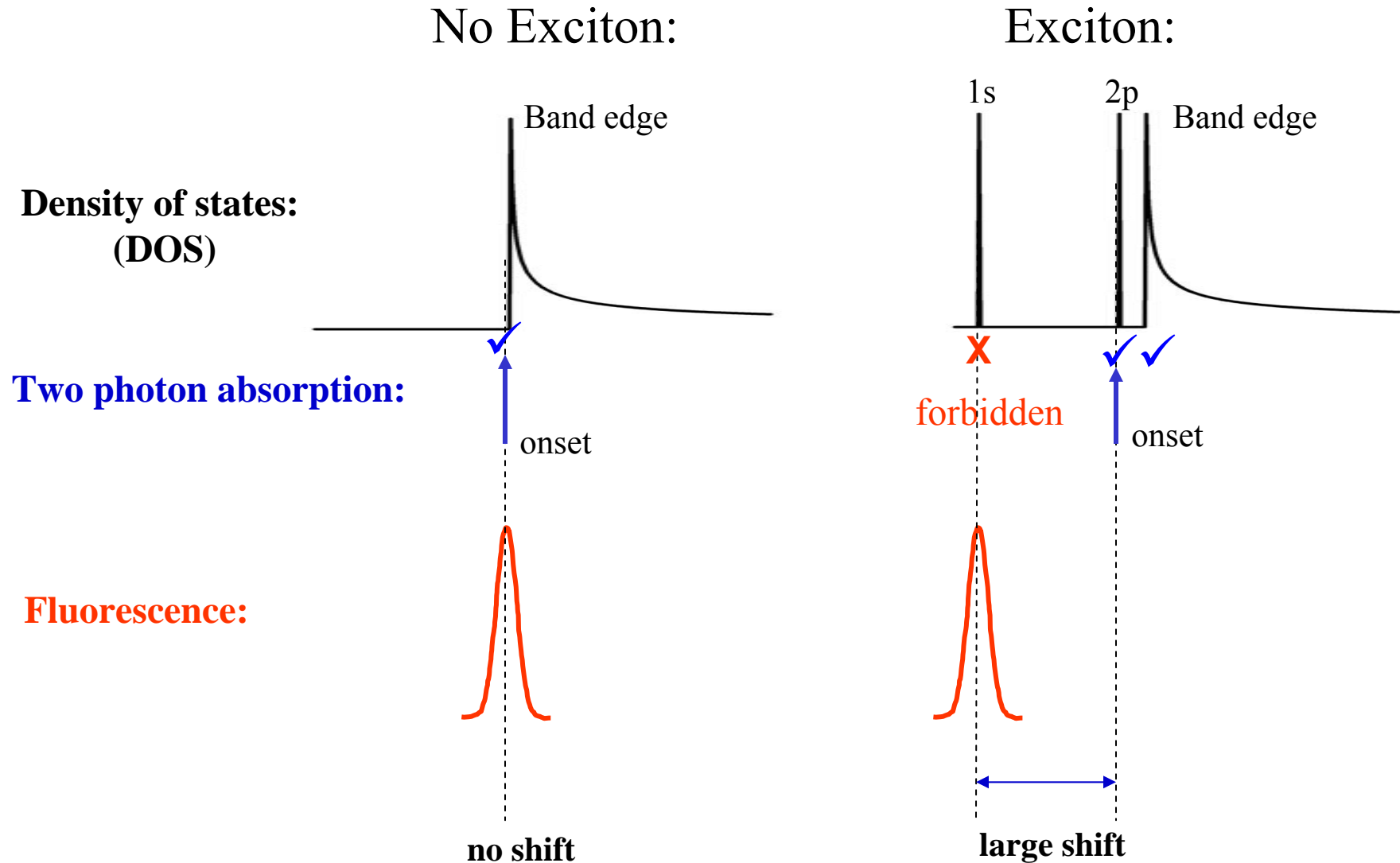
Exciton envelope wavefunction:

Neutral excited state moves as a unit along the SWNT?



Exciton Bound states below the van Hove Band Edge

Selection Rules for two photon and one photon spectra

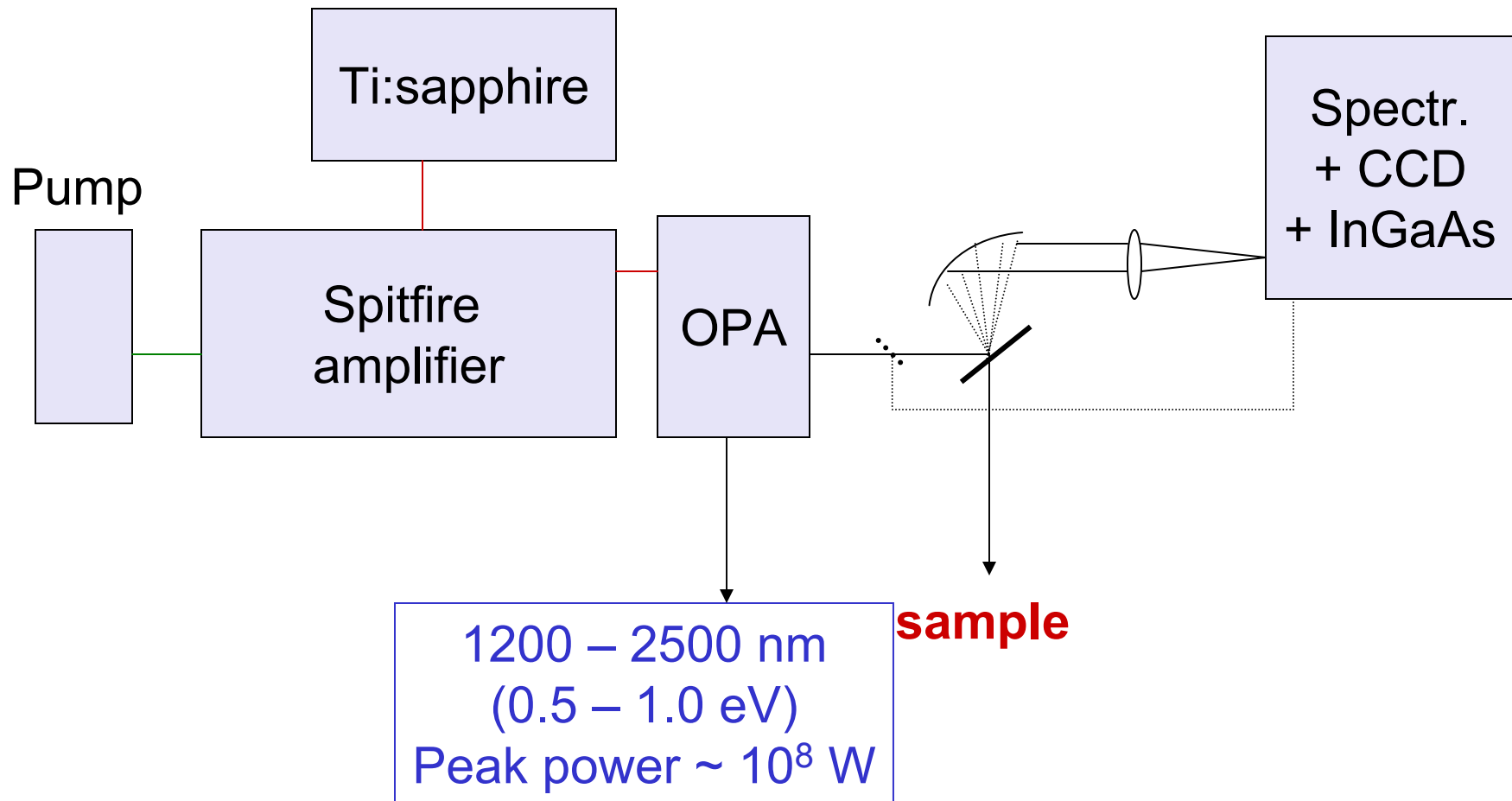


Experiment: Measure fluorescence intensity as a function of 2-photon excitation energy with tunable femtosec laser

Two-photon excitation spectroscopy

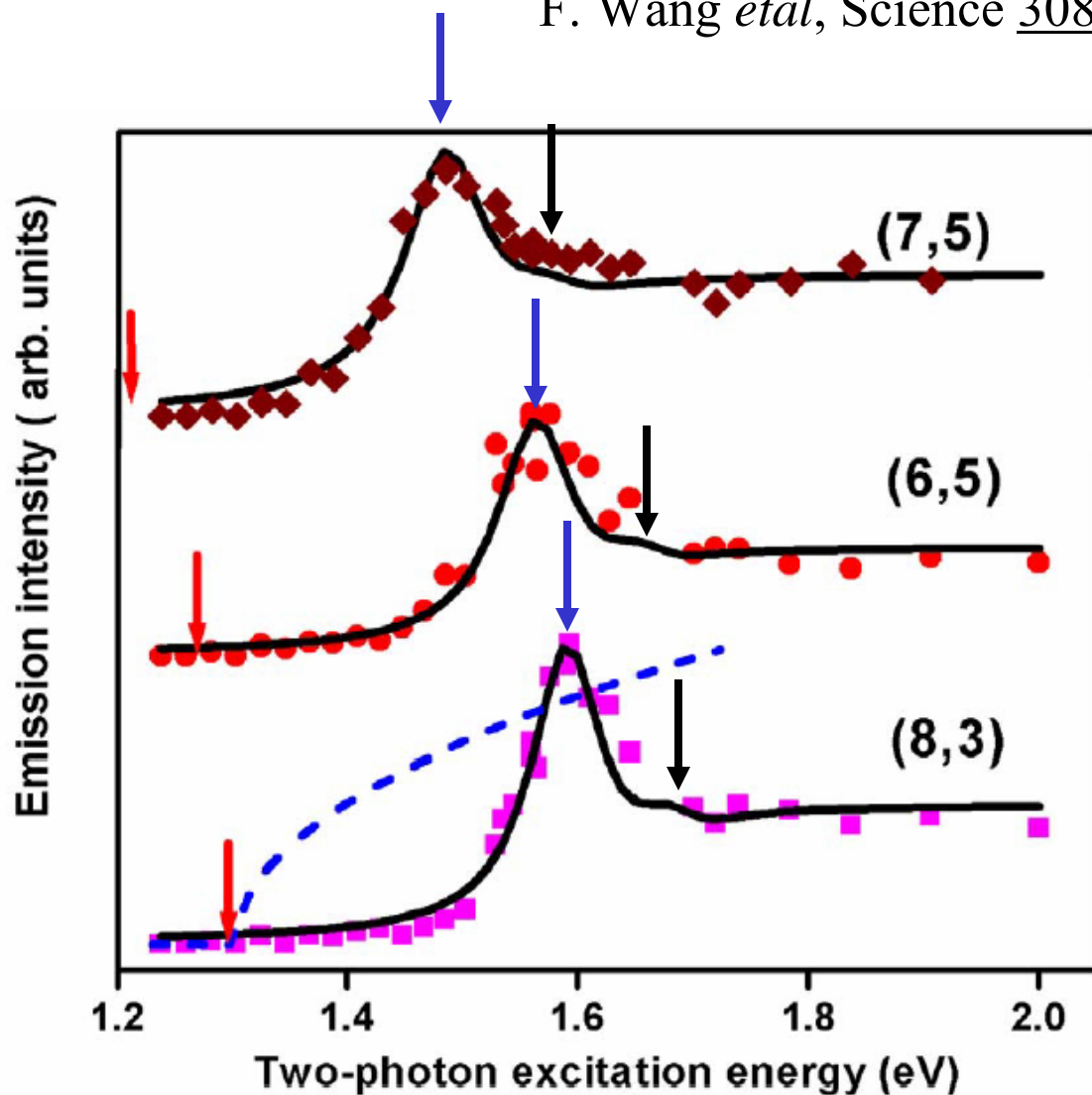
800 nm (1.55 eV)

130 fs

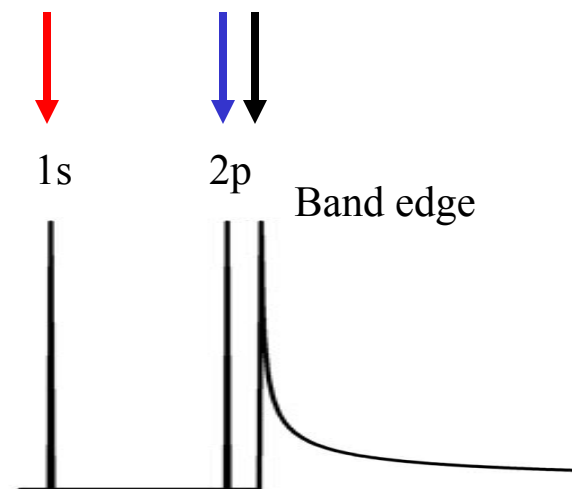


Two Photon Excitation spectra of individual fluorescence peaks

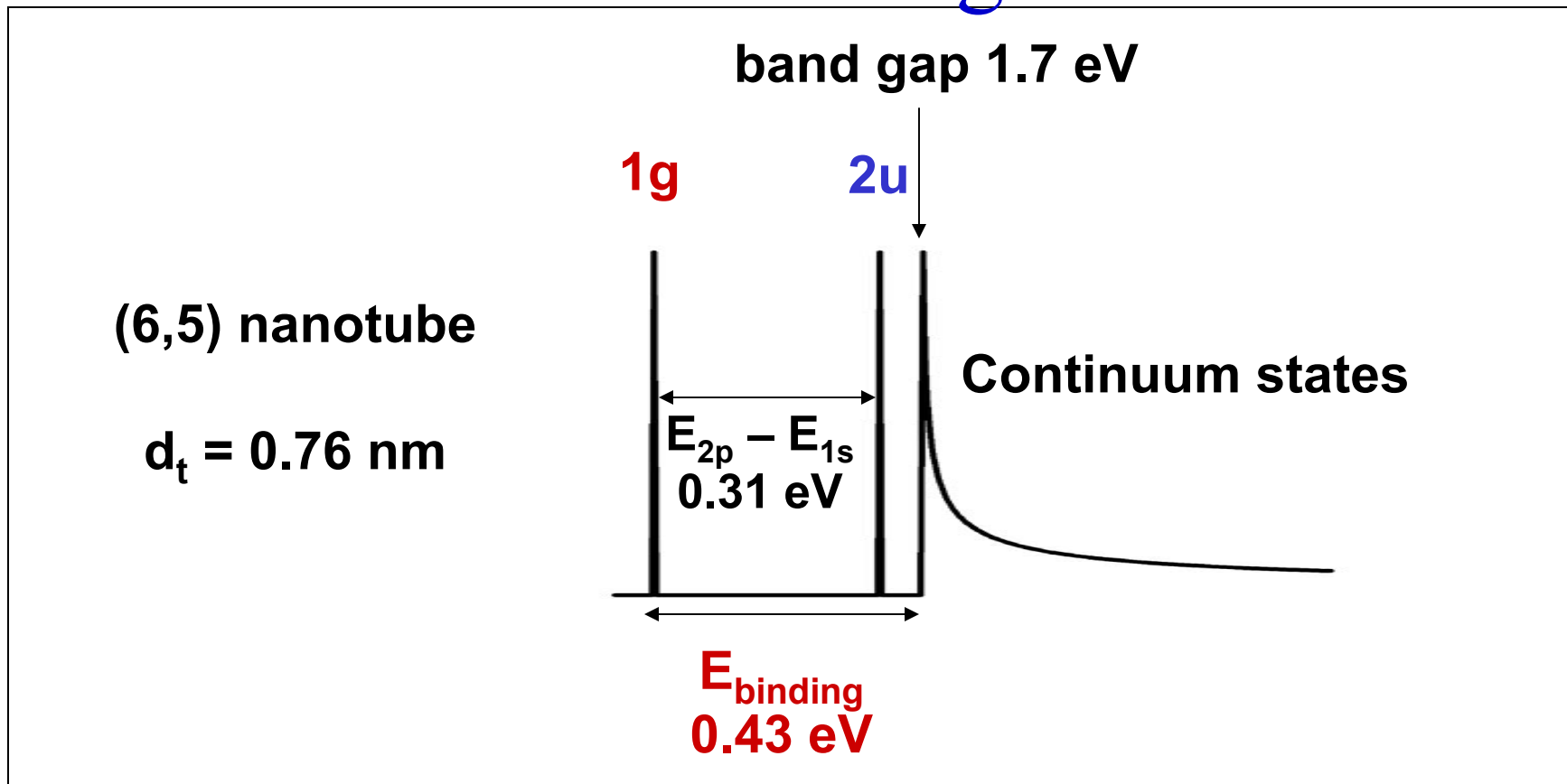
F. Wang *et al*, Science 308, 838(2005)



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



Exciton energies

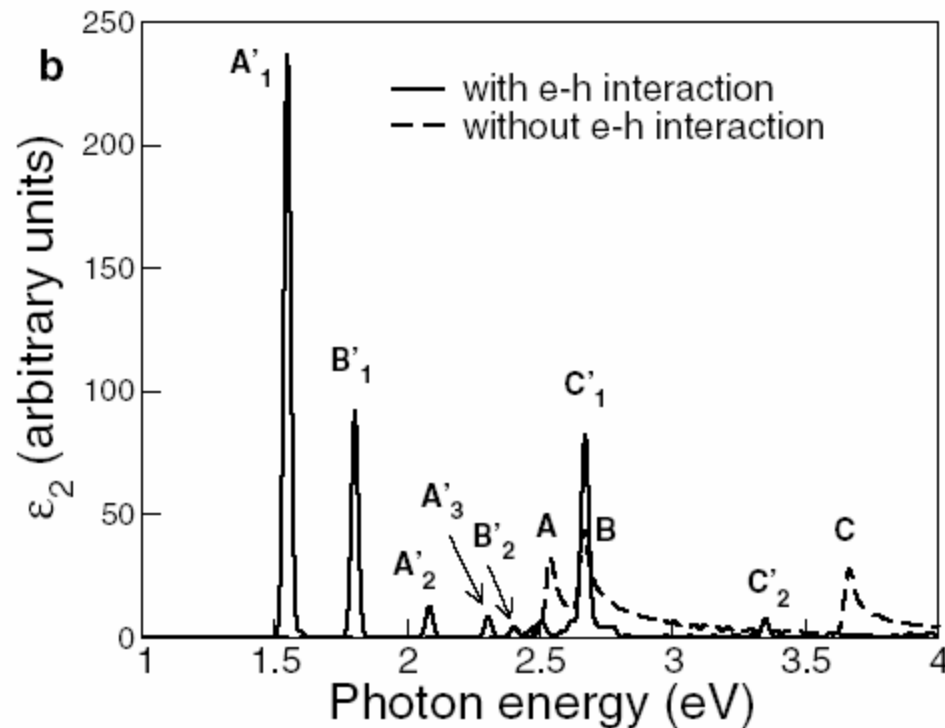


For comparison:

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

Semiconductor nanowires \sim tens of meV

Many-body effects in SWNTs

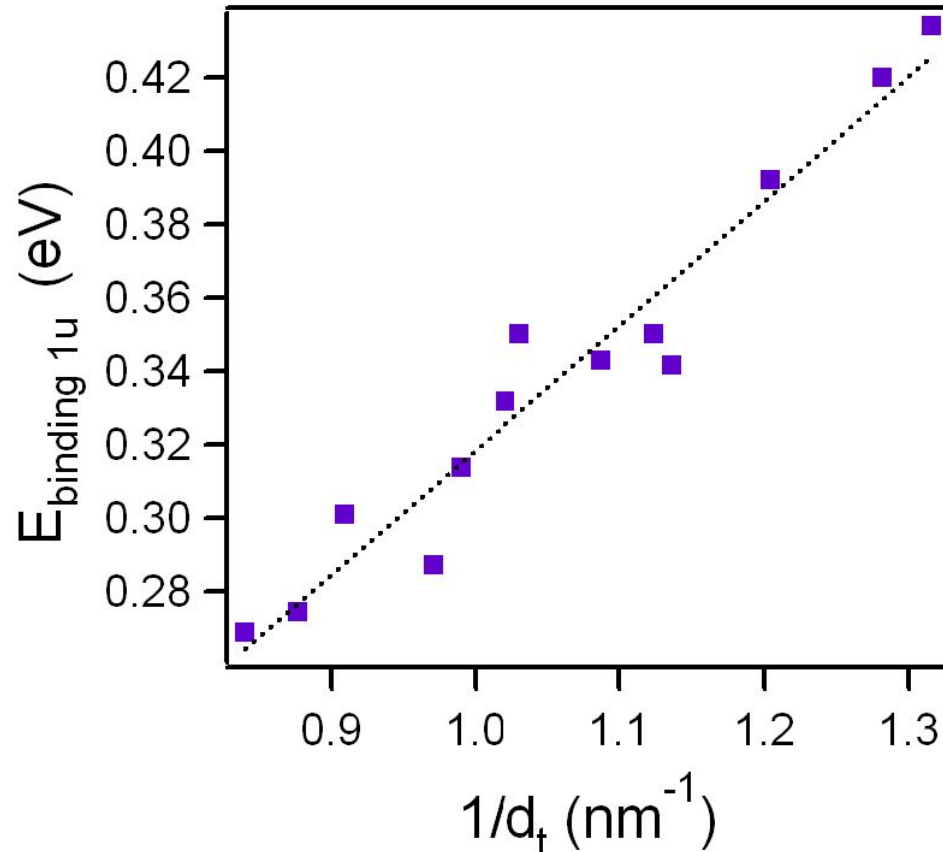


Spataru, C. D.; Ismail-Beigi, S.; Benedict, L. X.; Louie, S. G. *Phys. Rev. Lett.* **2004**, 92, 077402.

Predictions:

1. Optical transitions due to bound electron-hole pairs (excitons)
2. Increase in band-gap energy (band-gap renormalization)

Scaling of exciton binding energy



$$E_{\text{binding } 1u} \approx \frac{0.34 \text{ eV}}{d_t}$$

Consistent with theoretical predictions

(Perebeinos, V.; Tersoff, J.; Avouris, P. *PRL* **2004**, 92, 257402.)

Dukovic, G. et al; *Nano Letters* **2005**, 5, 2314.

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

Existing techniques:

- Resonance Raman spectroscopy.
- Fluorescence Excitation Spectroscopy.

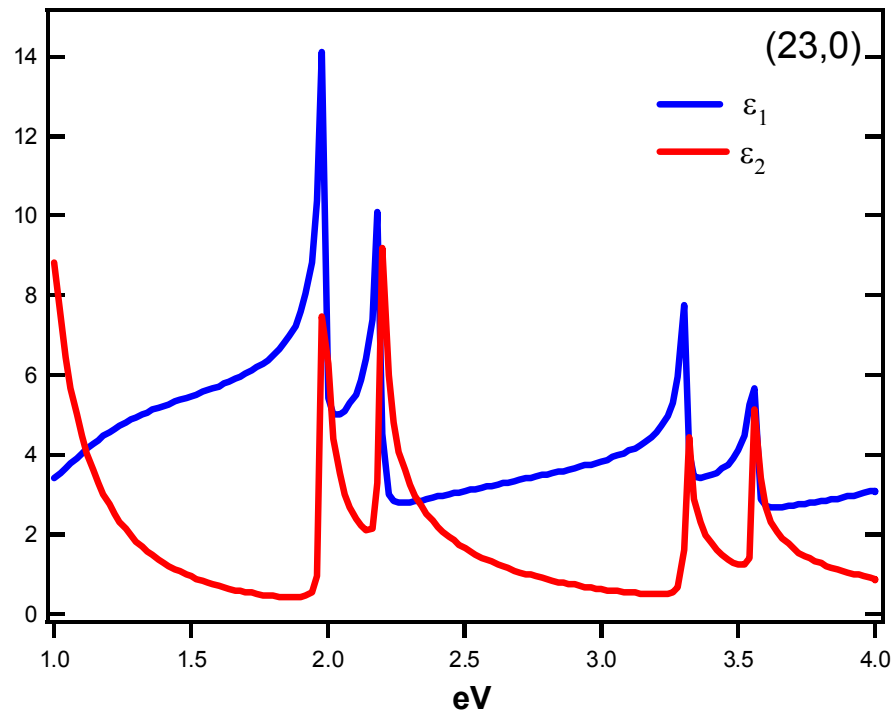
We perform white light *Rayleigh scattering spectroscopy*.

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

Theoretical Rayleigh Scattering from a Cylinder

$$Q_{sca} \propto \frac{r^3 |\varepsilon - 1|^2}{\lambda^3} \quad \varepsilon = \varepsilon_1 + i\varepsilon_2$$



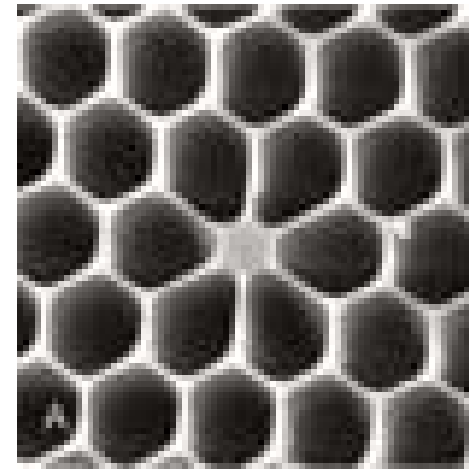
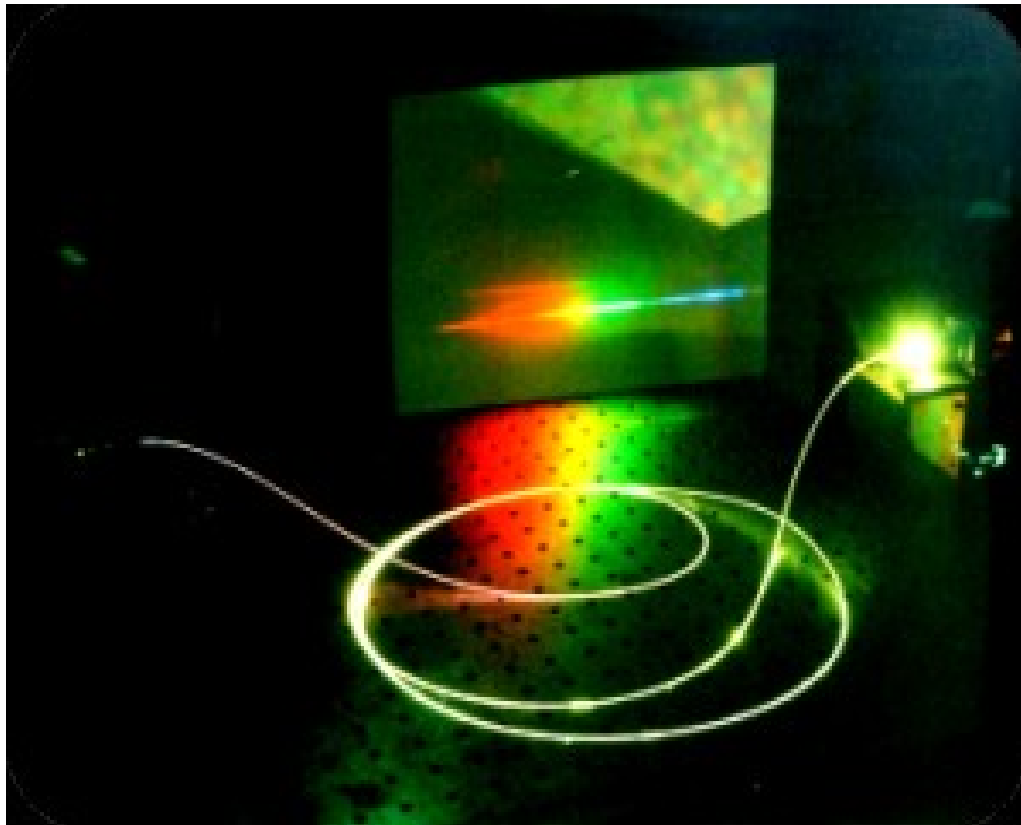
Peaks in the Rayleigh scattering spectrum are due to the peaked dielectric function, from interband transitions (above) or possibly excitons.

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

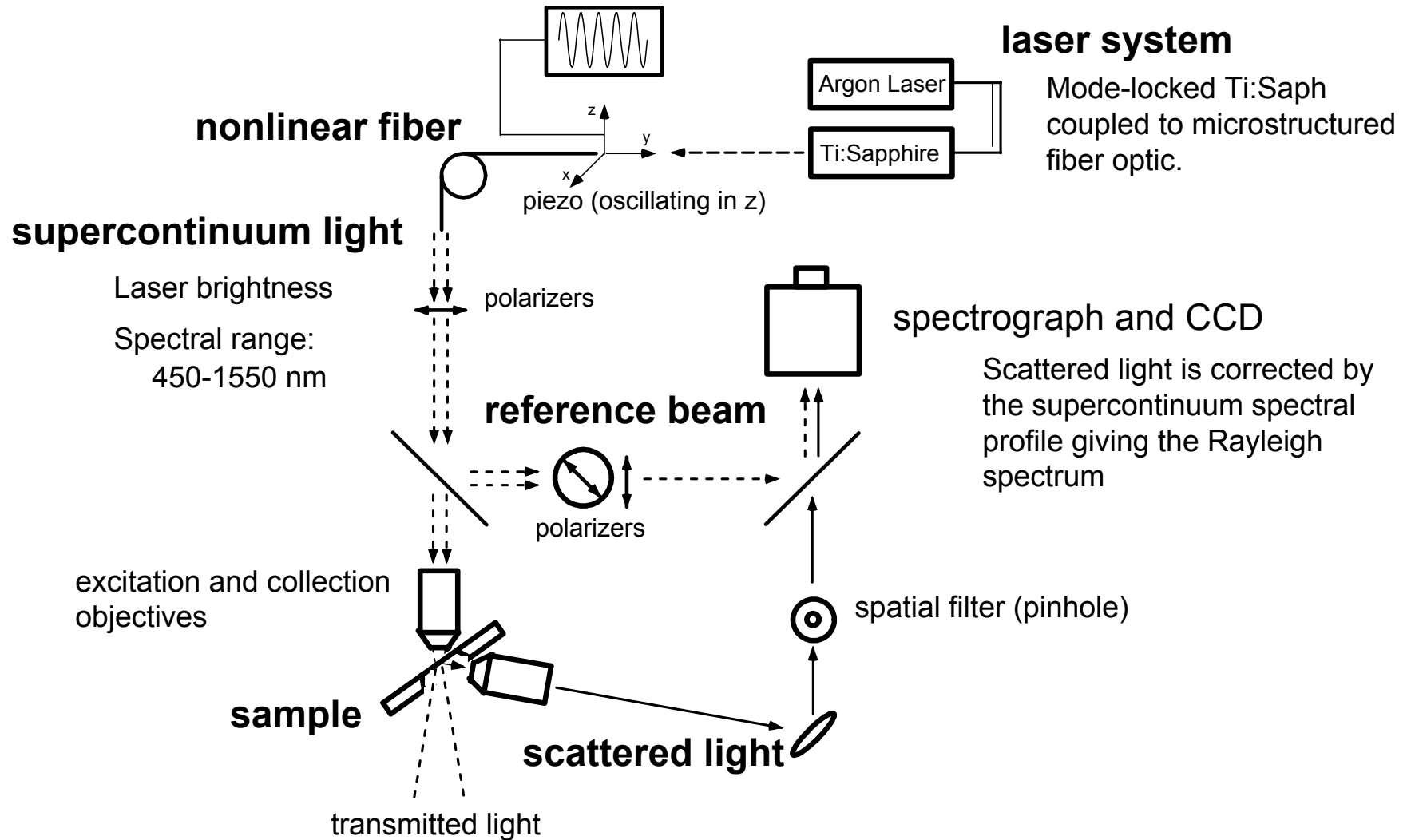
→ Spectral range:
450 - 1450 nm



Microstructured fiber: core $\sim 2 \text{ }\mu\text{m}$

Rayleigh Scattering: Experimental Setup

Supercontinuum Generation



Growth and Imaging

CVD Growth Process

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

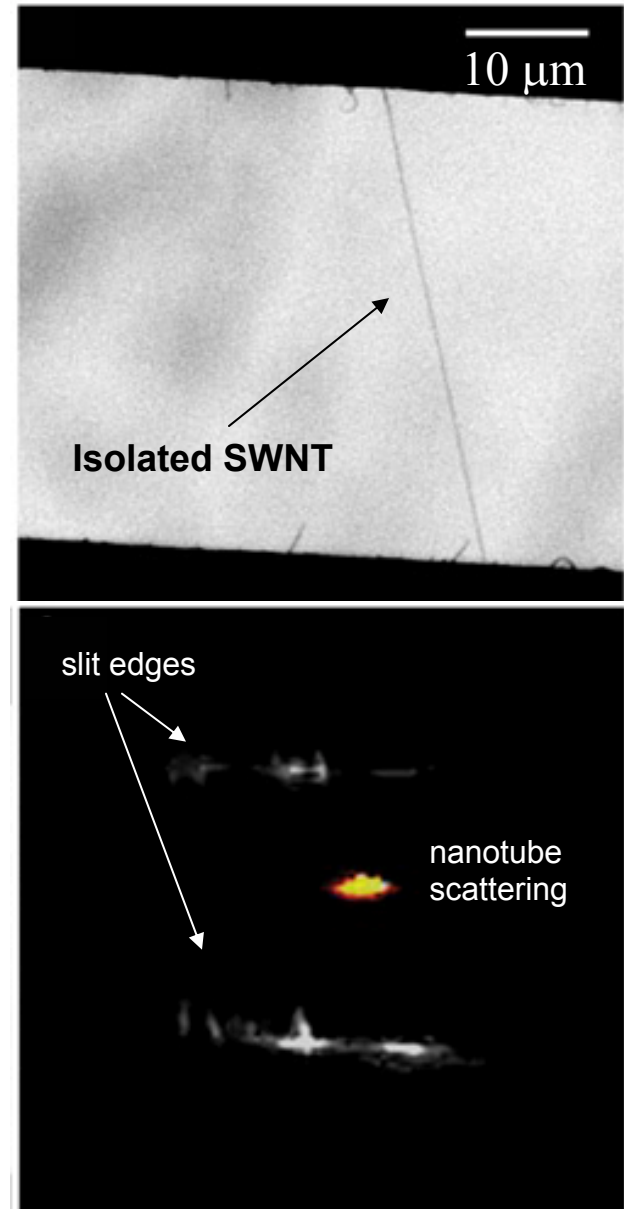
Directional growth determined by flow direction of feed gas, lengths > 100 microns:

- 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.

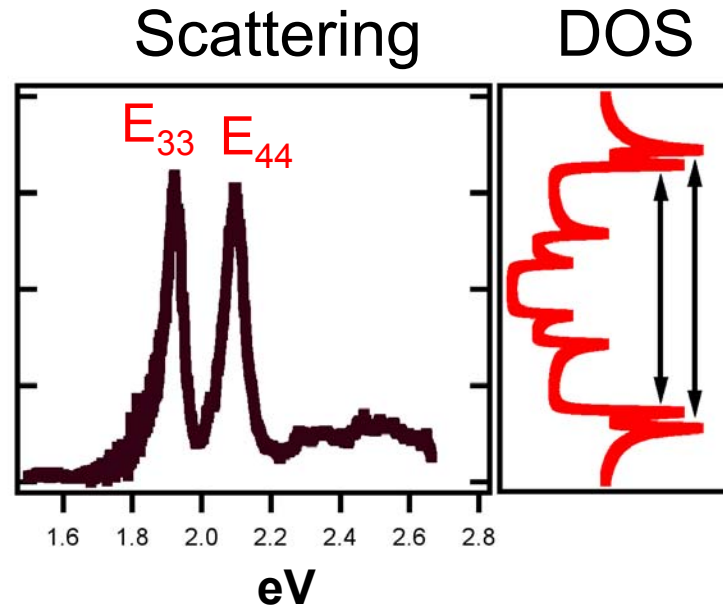


Experimental Single SWNT Resonance Rayleigh Spectra

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

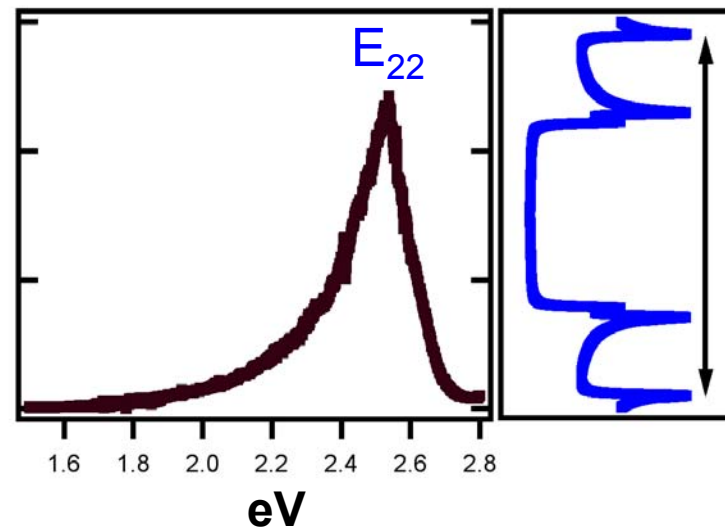
Semiconducting Carbon Nanotube

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



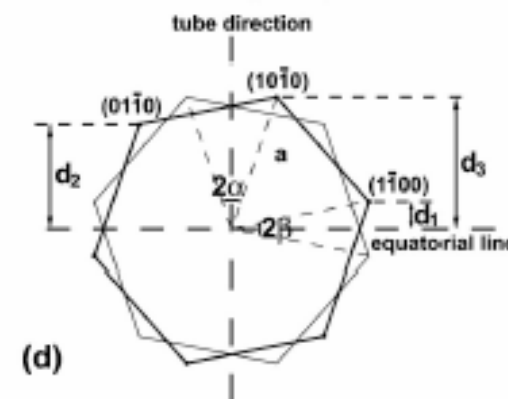
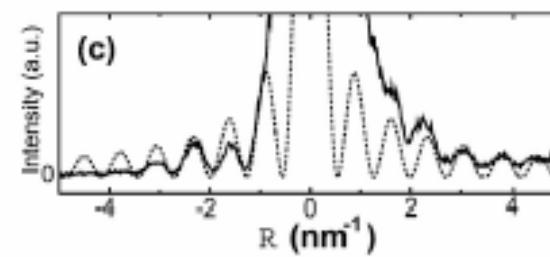
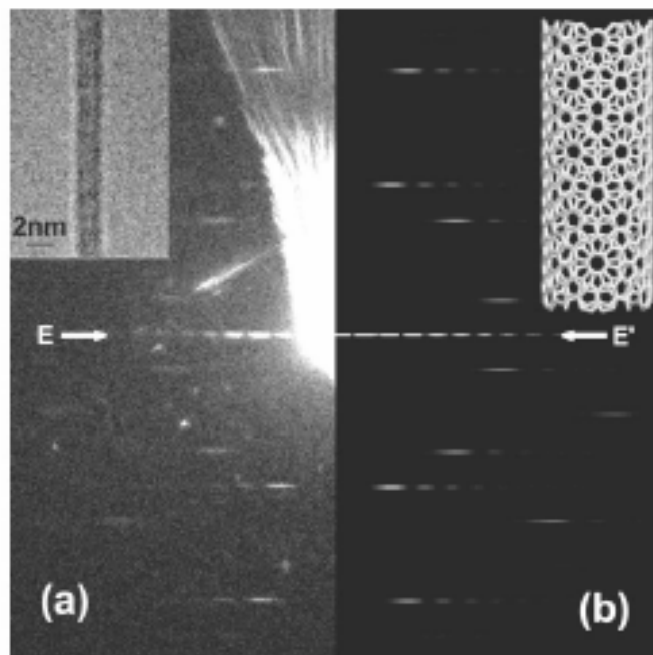
Metallic Carbon Nanotube

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.

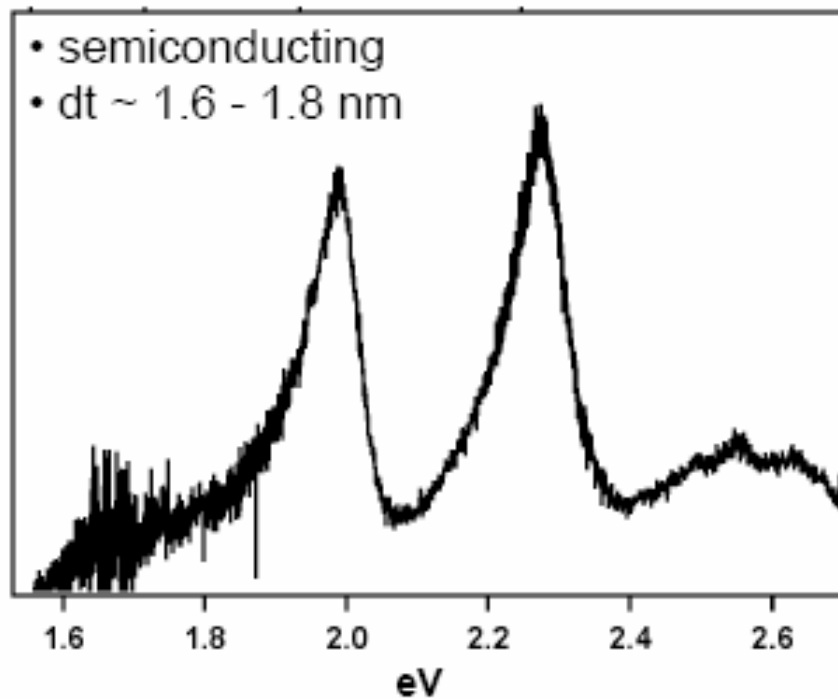


$$\text{Equatorial Oscillation} \propto J_0^2(\pi R D_0)$$

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

First Successful Structural Assignment of a Rayleigh Spectrum

Rayleigh Scattering (Columbia)



TEM Diffraction (BNL)

- $\theta = 23.8$ degrees
 - $dt \sim 1.8$ nm
-

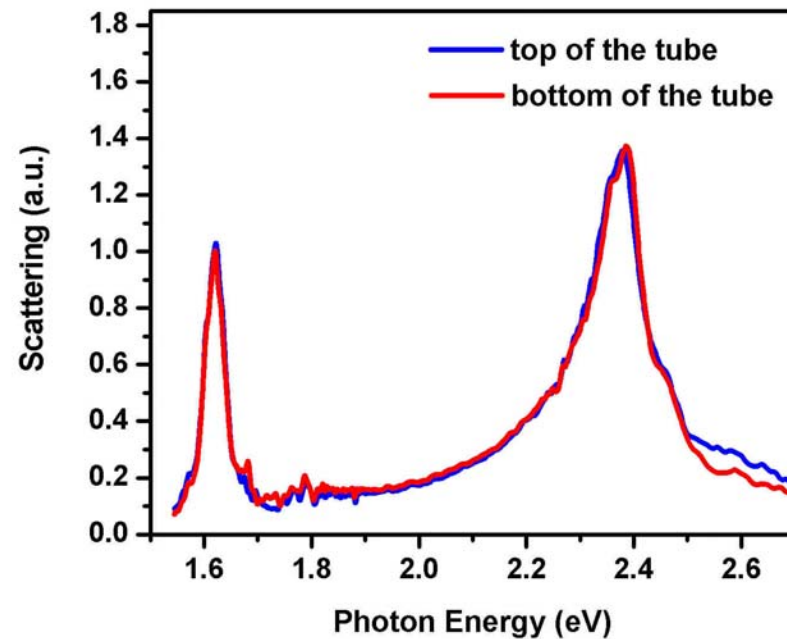
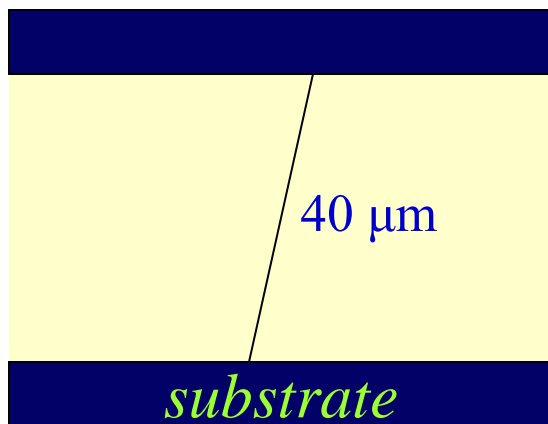
Through combination of TEM and Rayleigh scattering, transitions assigned to (16,11).

T. Beetz, Y. Zhu Brookhaven – M. Sfeir Columbia

Science 312, 554 (2006)

Scattering Spectra along the Nanotube: Single Tube

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



Yes. At least up to 40 μm, a chain of several *millions* of carbon atoms.

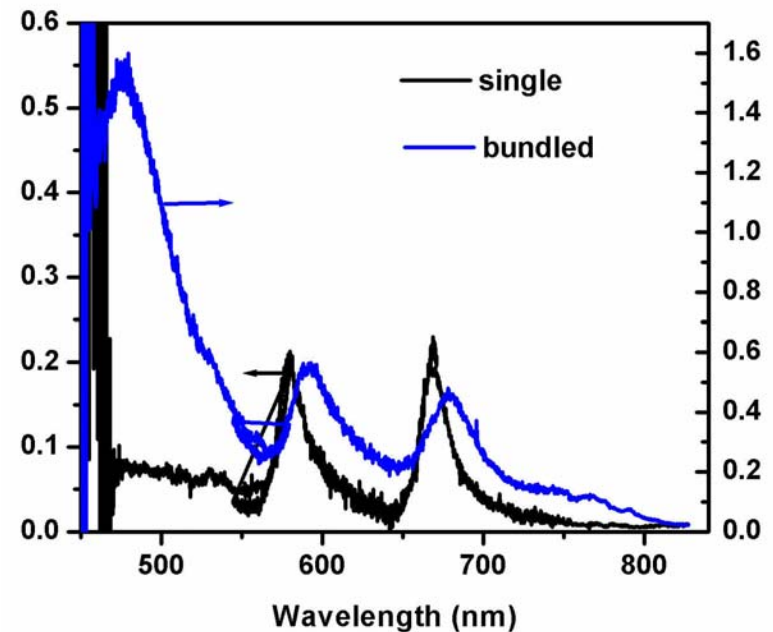
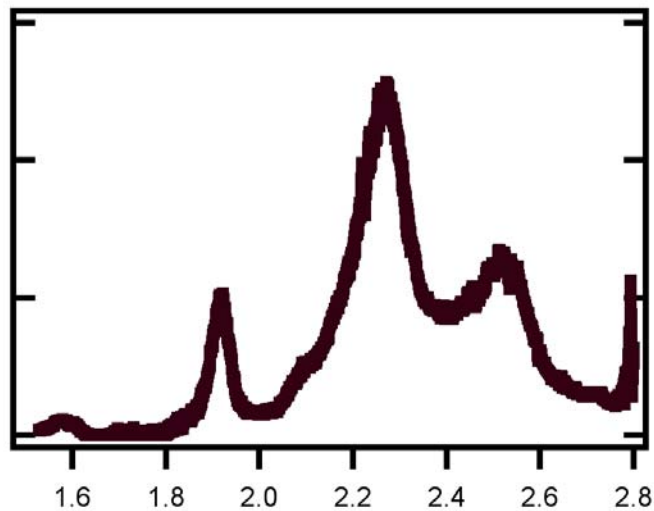
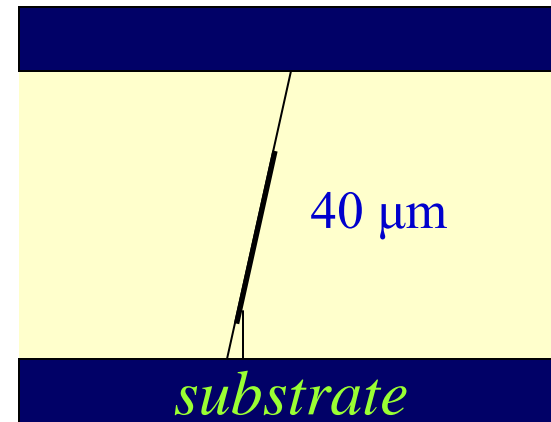
Scattering Spectra along the Nanotube: Single Tube to Small Bundle

Small Carbon Nanotube Bundle

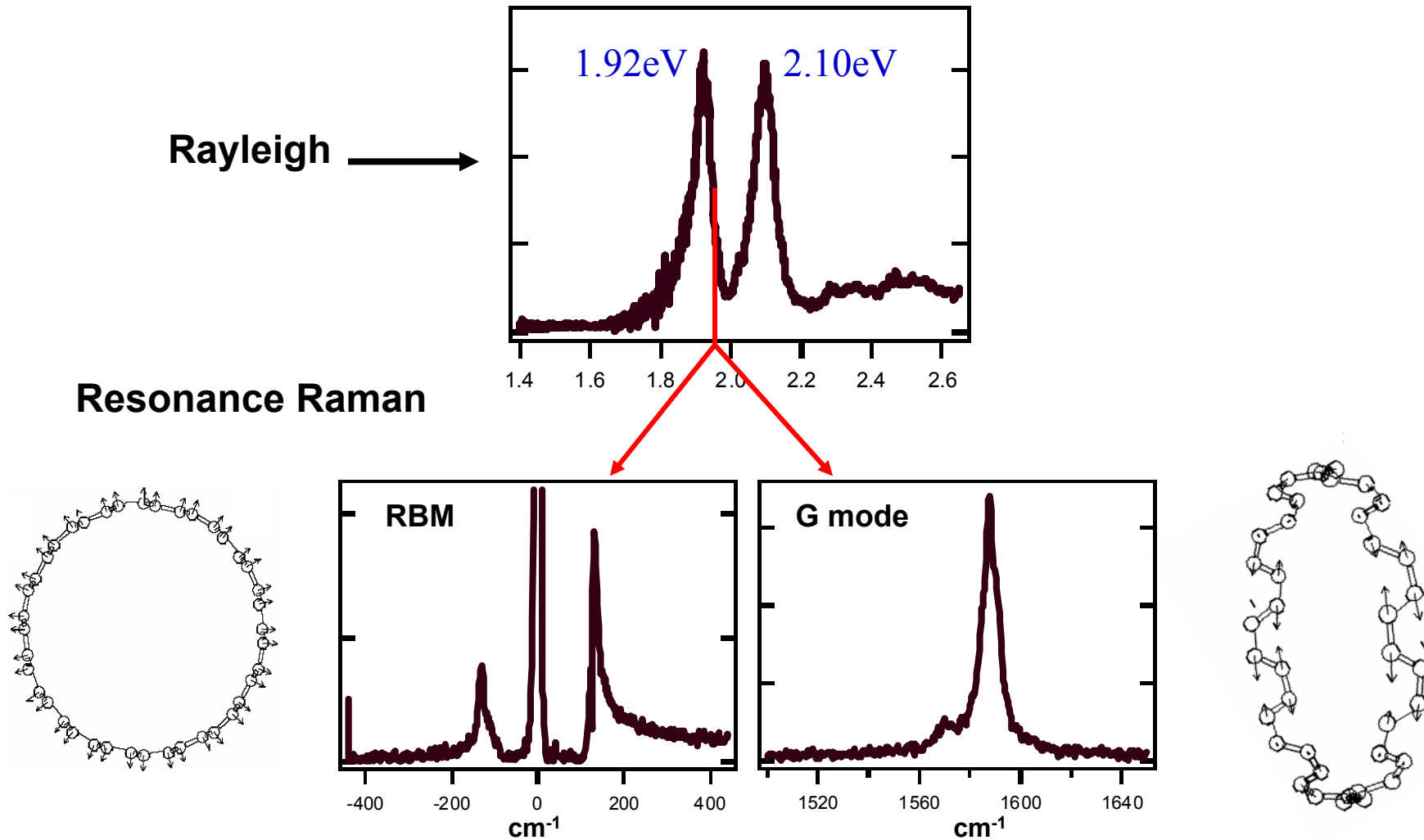
Four or more peaks, broadened compared to single nanotube spectra.

Bundling Effect, Tube Interactions

When in bundles, spectra broaden and red-shift by approximately 15 meV.



Correlated Raman and Rayleigh Scattering from the Same Semiconductor Nanotube

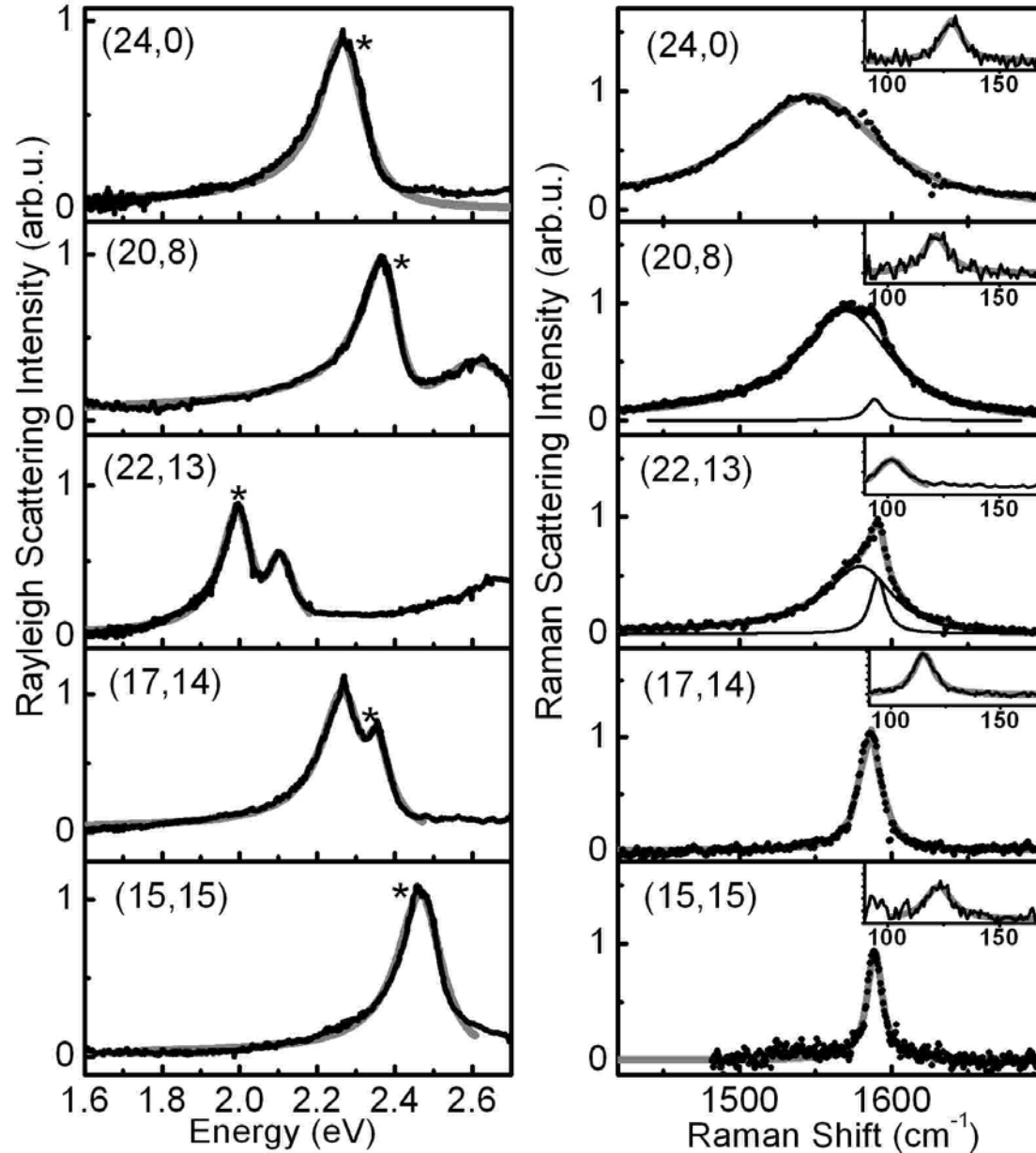


radial breathing mode → d=1.89nm

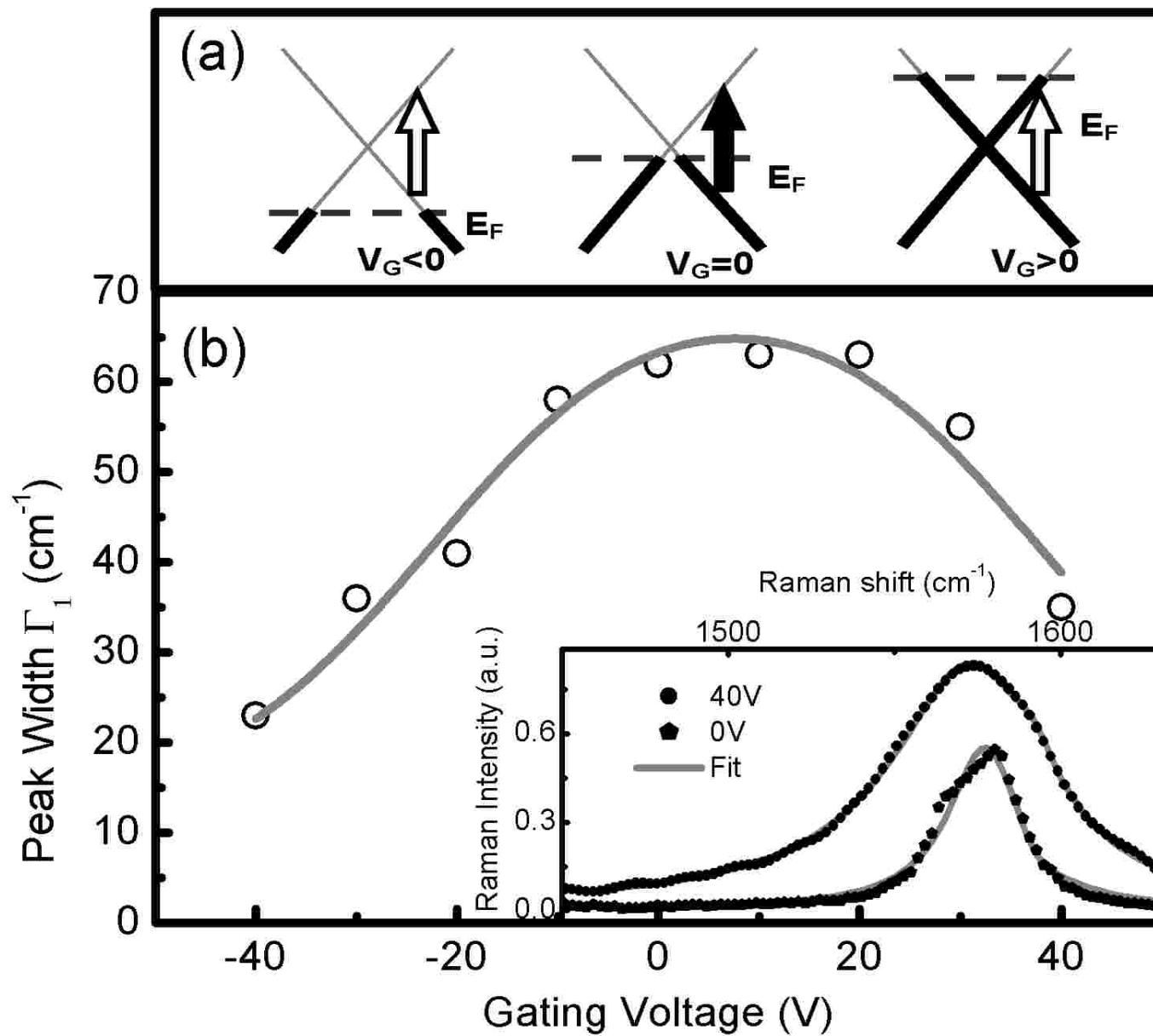
(21,4) nanotube: d=1.85nm. $E_{33}=1.87$, $E_{44}=2.10$ (tight binding model)

Rayleigh and Raman from Metallic Nanotubes

Wu, Maultzsch, Heinz etc to be published,

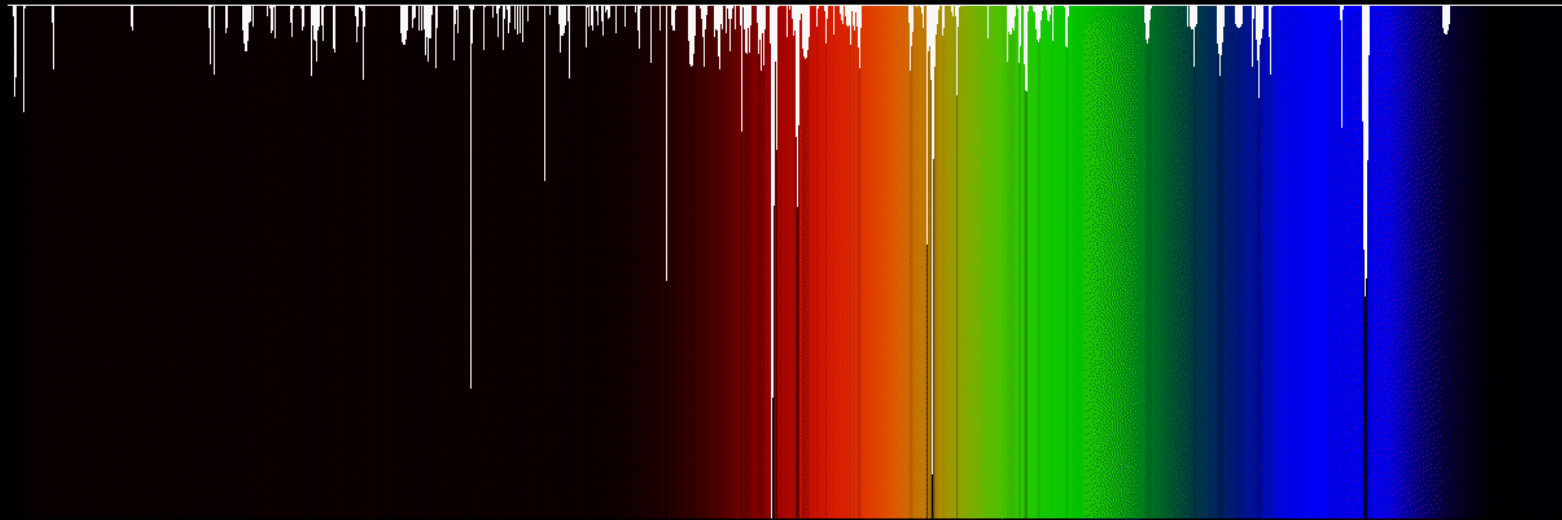


Electrostatic Gating varies width of phonon Raman



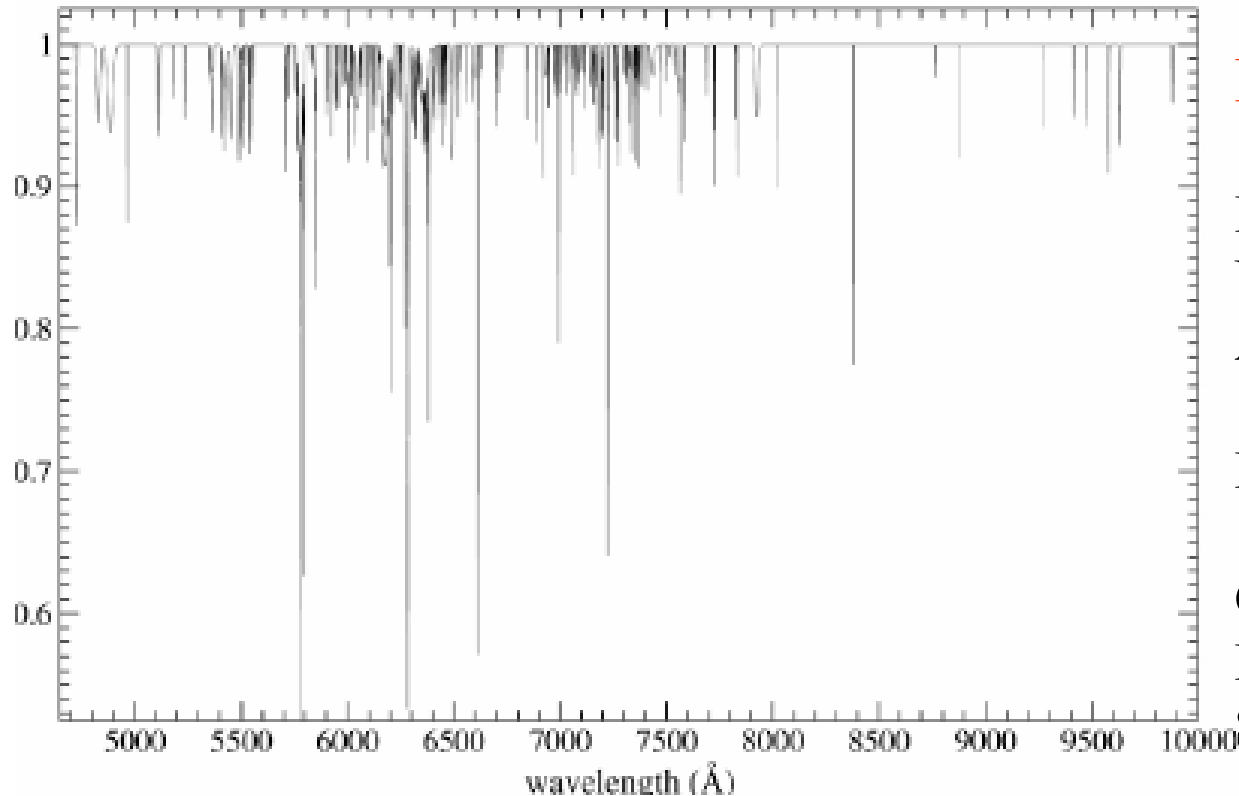
- Topic 3: SWNT Nucleation, Short Tubes, and the Diffuse Interstellar Bands

The Diffuse Interstellar Bands



Courtesy: P. Jenniskens, F.-X. Desert

synthetic DIB spectrum for 4U 1907+09



Diffuse Interstellar Bands

Electronic Transitions due to an Unidentified Family of Large Aromatic Molecules

Perhaps flat aromatic PAHS.

Could they be due to tubular PAHs , that is , short stubs of SWNTs?

Fig. 2. Entire synthetic DIB spectrum (4650 to 9950 Å) for 4U 1907+09 generated from the 180 identified DIBs and measured absorption features and their respective central wavelength positions (λ_{DIB}), equivalent widths (EW) and full width at half maximum ($FWHM$). This spectrum does not include stellar features nor atomic interstellar lines.

Linewidths a few Angstroms wide

Rotational contour? solid state
linewidth?

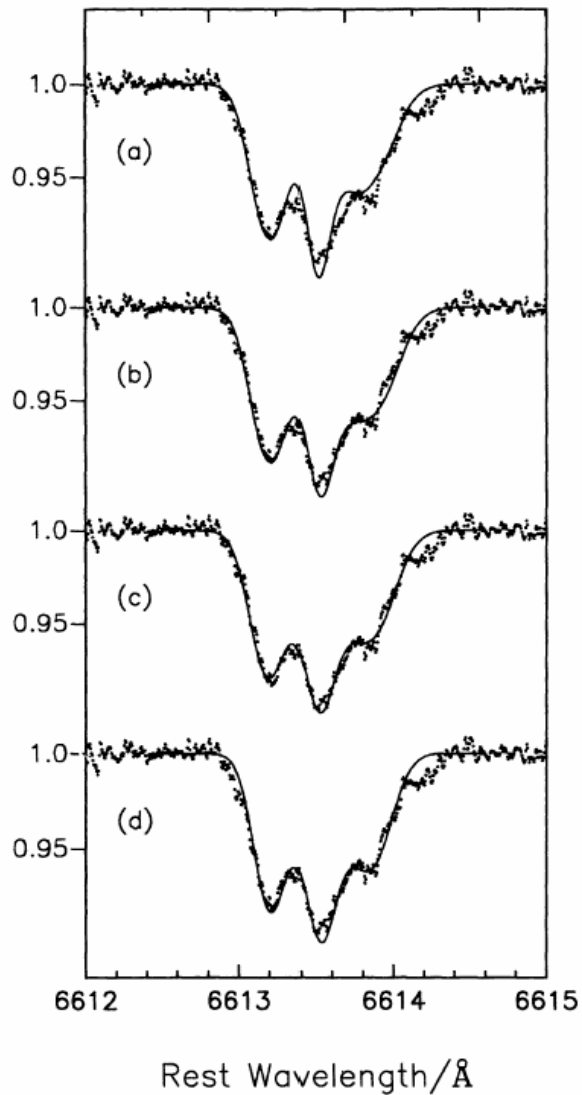
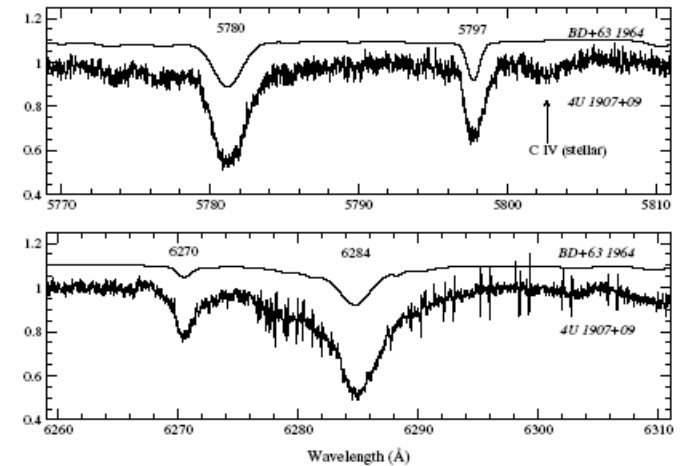


Fig. 6. Ultra-high resolution spectrum of the $\lambda 6614$ diffuse band showing fine structure. The solid lines in figures (a) to (d) are fits from different starting parameters corresponding to a range of molecular size/rotational temperature (~ 10 - 100 K) combinations. See [52] for details. Reproduced with permission from [52].



Cox, Kayen, Foing,
Ehrenfreund A&A 438,
187 (2005)

Graphite dust and PAHs are present in the Interstellar Medium

PAHs emit vibrational luminescence following electronic excitation under collision free conditions

How are they formed?

B. T. Draine

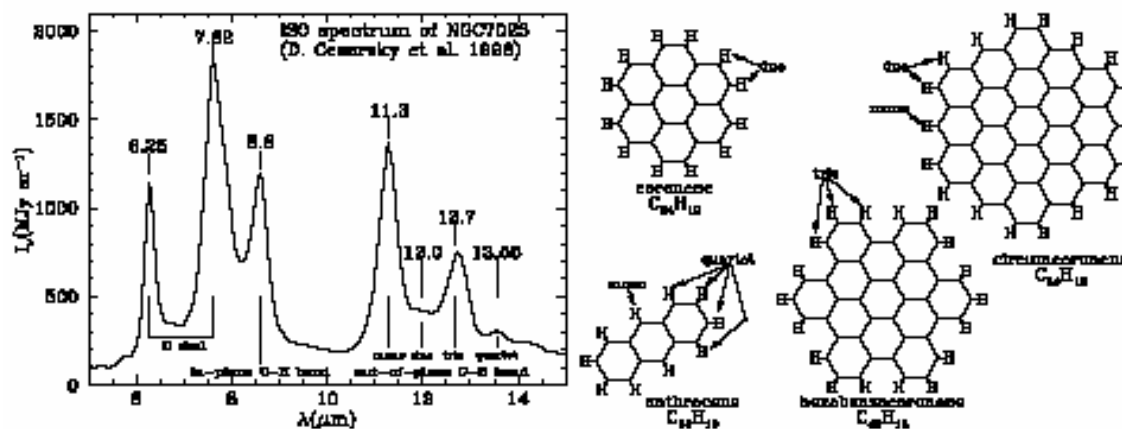


Fig. 1.3. PAH emission features in the 5-15 μm emission spectrum of the reflection nebula NGC 7023 (Cesarsky et al. 1996), and four PAH molecules, with examples of mono, duo, trio, and quartet H sites indicated.

*Carnegie Observatories Astrophysics Series, Vol. 4:
Origin and Evolution of the Elements
ed. A. McWilliam and M. Rauch (Cambridge: Cambridge Univ. Press)*

Interstellar Dust

B. T. DRAINE
Princeton University Observatory

Astrophysical Graphite Formation at High Temperature

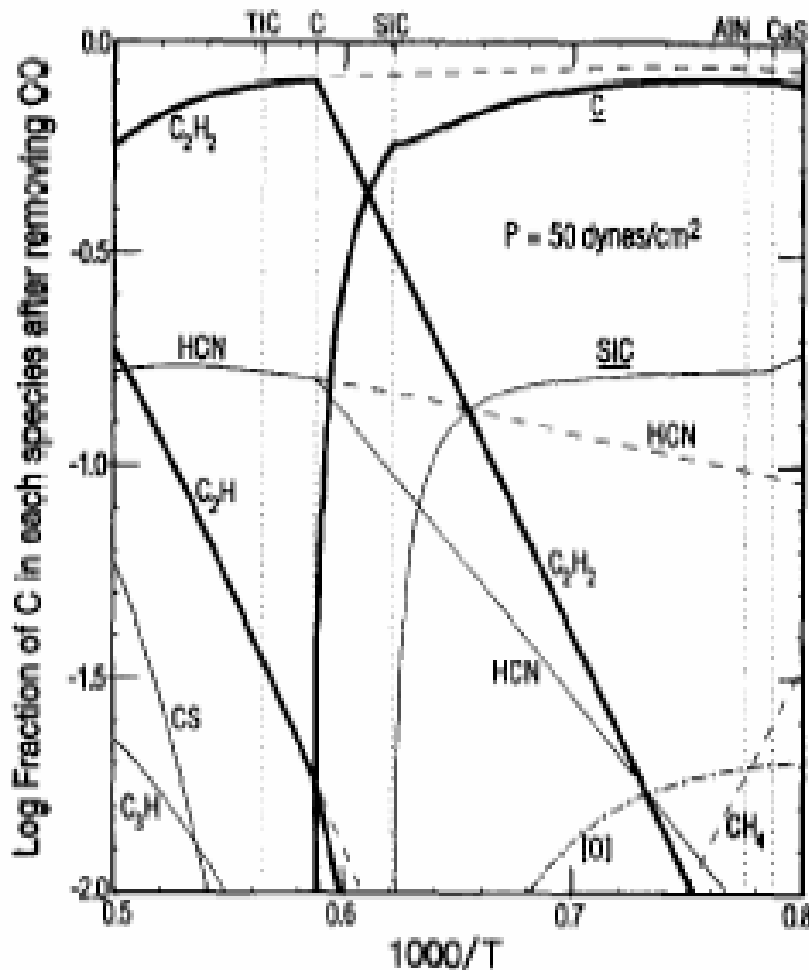


FIG. 3. The ratio C/O = 1.122 as in Fig. 2, but for $P = 50$ dyne/ m^2 . Now HCN is a significant component. Note that graphite now condenses after TiC, but before SiC. Also note the presence of additional condensates, AlN and CaS, at low temperatures. The dashed and dotted curve labeled [O] is the fraction of the total oxygen that is not in CO and can be read off of the same scale (i.e., at $1000/T = 0.8$, $[O] = 10^{-1.7}$).

Graphite and PAH formation in the outflows of Carbon Rich Stars:

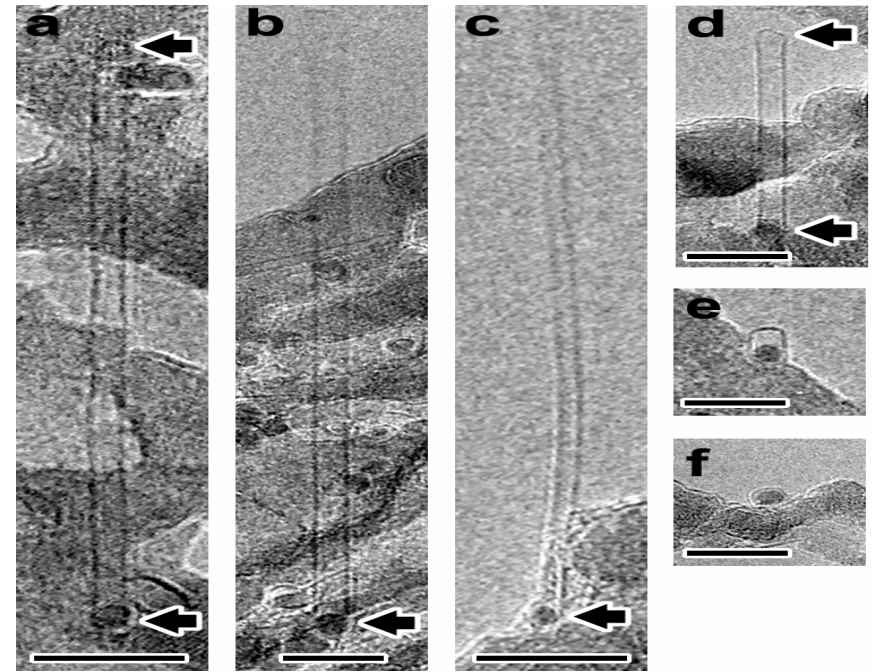
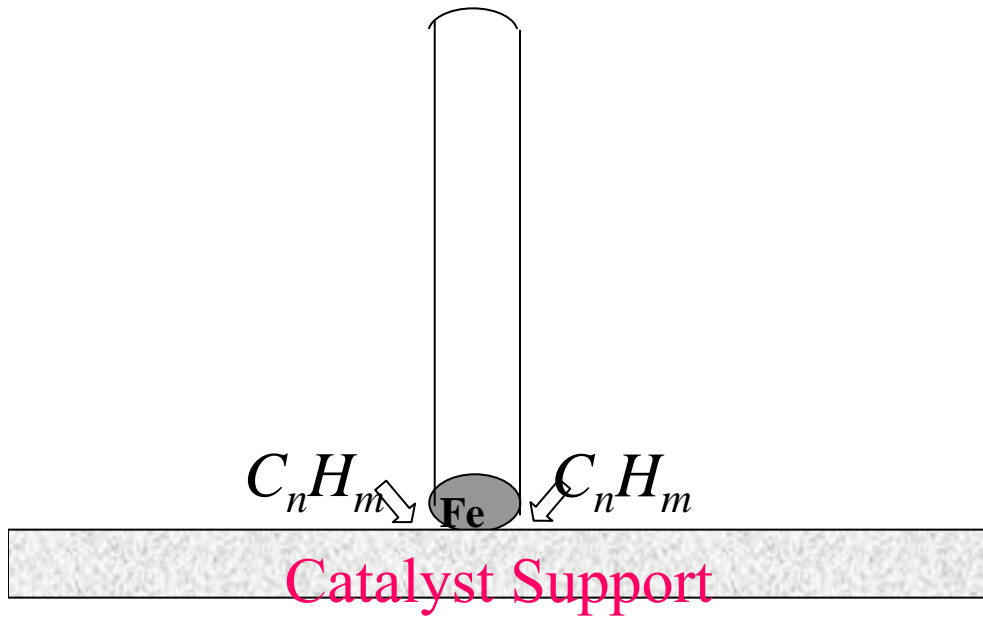
Graphite condenses from acetylene at about 1700 K in equilibrium thermodynamics -- probably supercools to about 1200 K.

Fe in about 10% abundance compared to carbon. Fe predicted to be present as neutral metallic clusters.

Perhaps short stubs of SWNT are formed on Fe clusters.

Sharp and Wasserburg, *Geochem. Cosmochem. Acta* 59, 1633 (1995)

How are SWNTs made? Chemical Vapor Deposition 800 C on a metallic Fe particle catalyst



Images from Hongjie Dai

Reduced metallic Fe present in outflow of stars

C/Fe ratio about 10/1

Thus, formation of tubular graphite near C rich stars??

Laboratory Nanotube growth at very low pressure

Lin et al Nanoletters 2006, 6, 449

TEM images acquired after growth and cooling

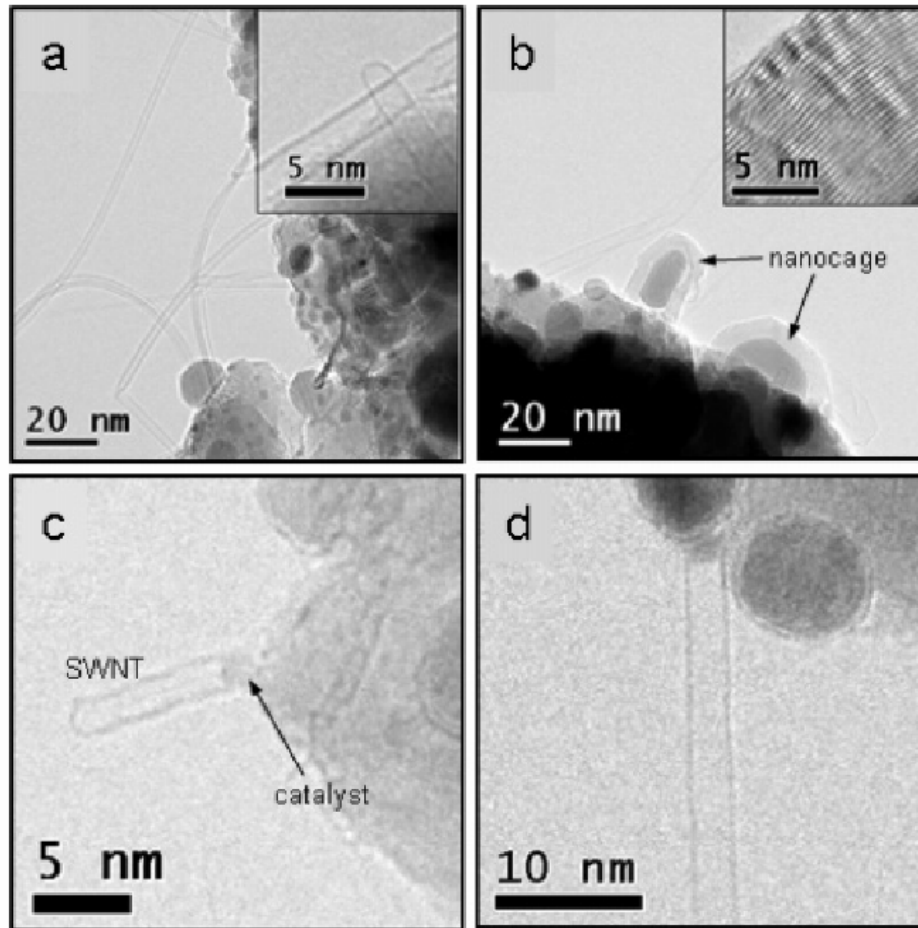


Figure 1. TEM images acquired after growth. (a) Bundled SWNTs; (b) nanocages; (c and d) base growth of SWNTs showing a direct relationship between Ni catalysts and diameters of SWNTs.

Catalyst:

Ni supported on MgO

C-source:

$C_2H_2 - 10^{-6}$ torr

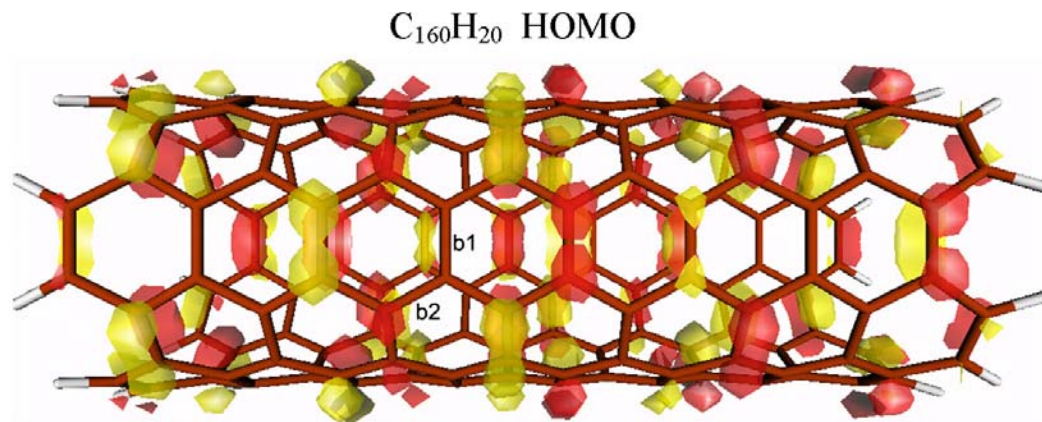
particle diameter < 6nm
→ SWNTs

Particle vs. nanotube
diameter = 2-1:1

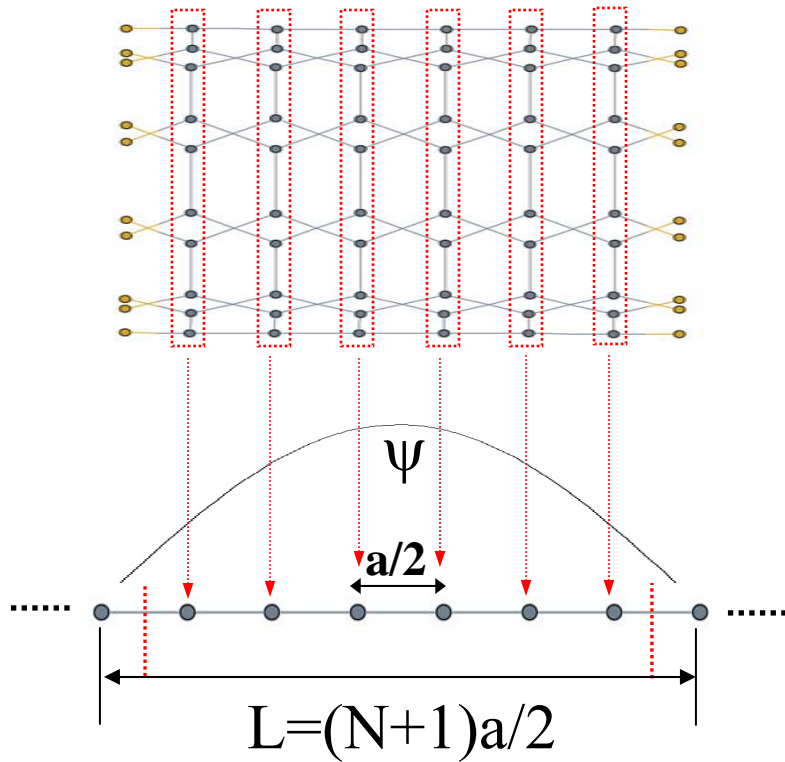
bigger particles →
nanocages

Fe clusters grow to perhaps 7-10 Angstroms diameter
– they then begin to catalyze growth of narrow diameter tubes

Finite pieces of the (5,5) metallic tube: Hybertsen, Steigerwald, Zhang,
Zhou



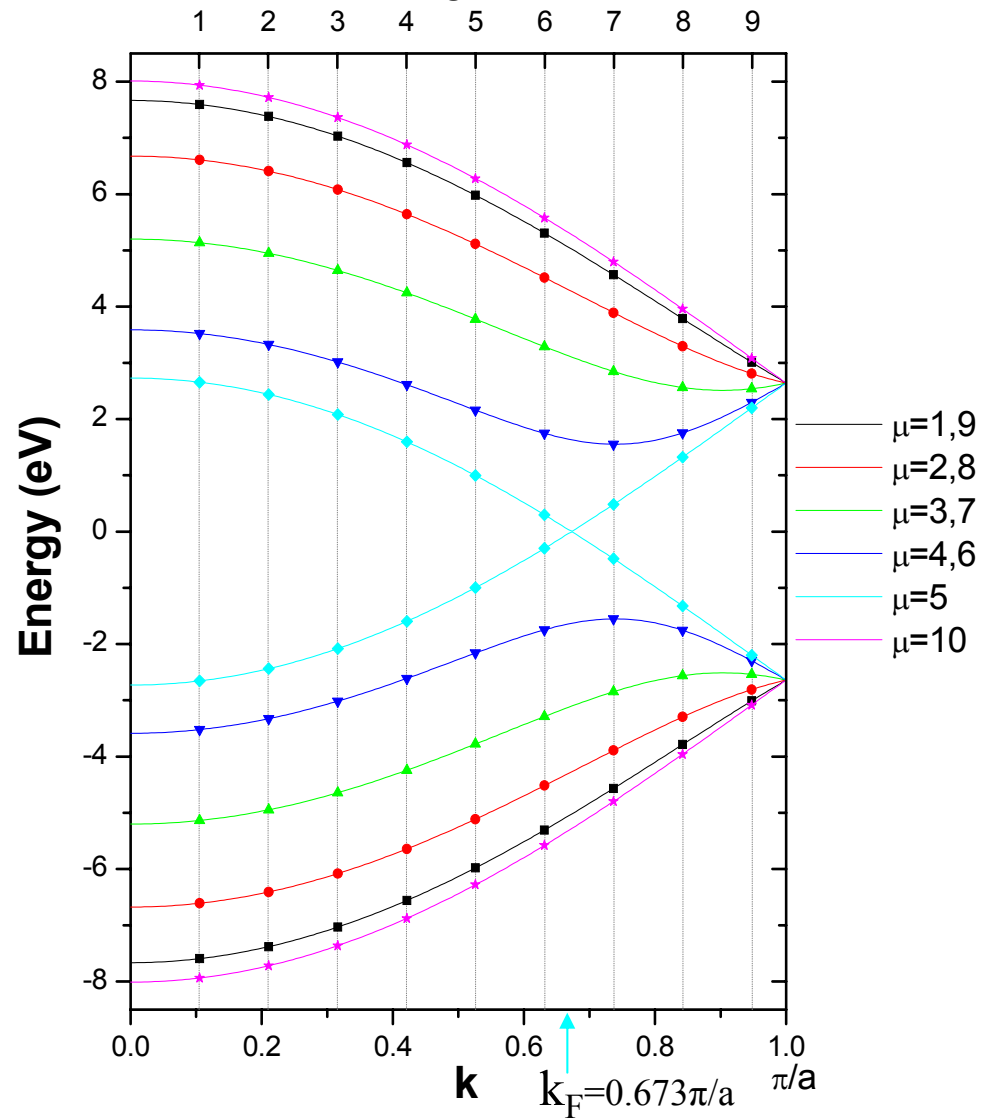
Length quantization



Quantum confinement:
 $\sin(k_J L) = 0$

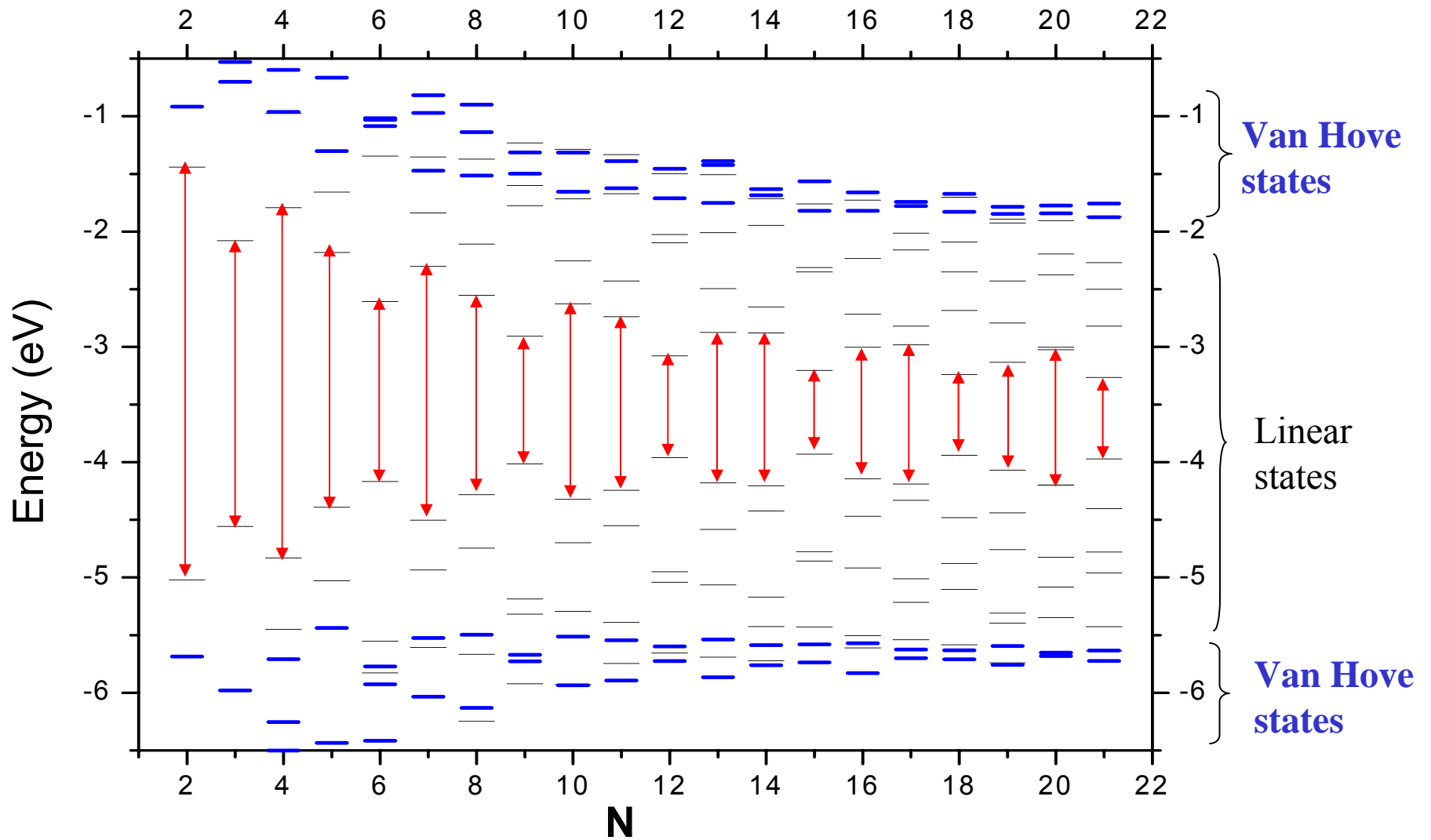
Allowed states:
 $k_J = 2J\pi / (N+1)a$

Energy bands of (5,5) CNT



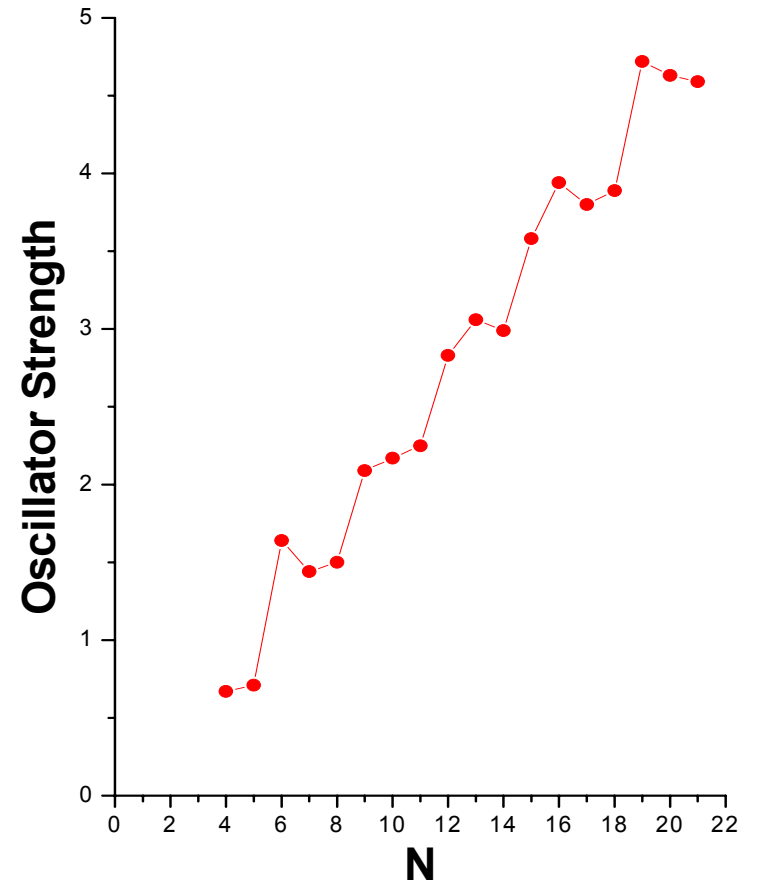
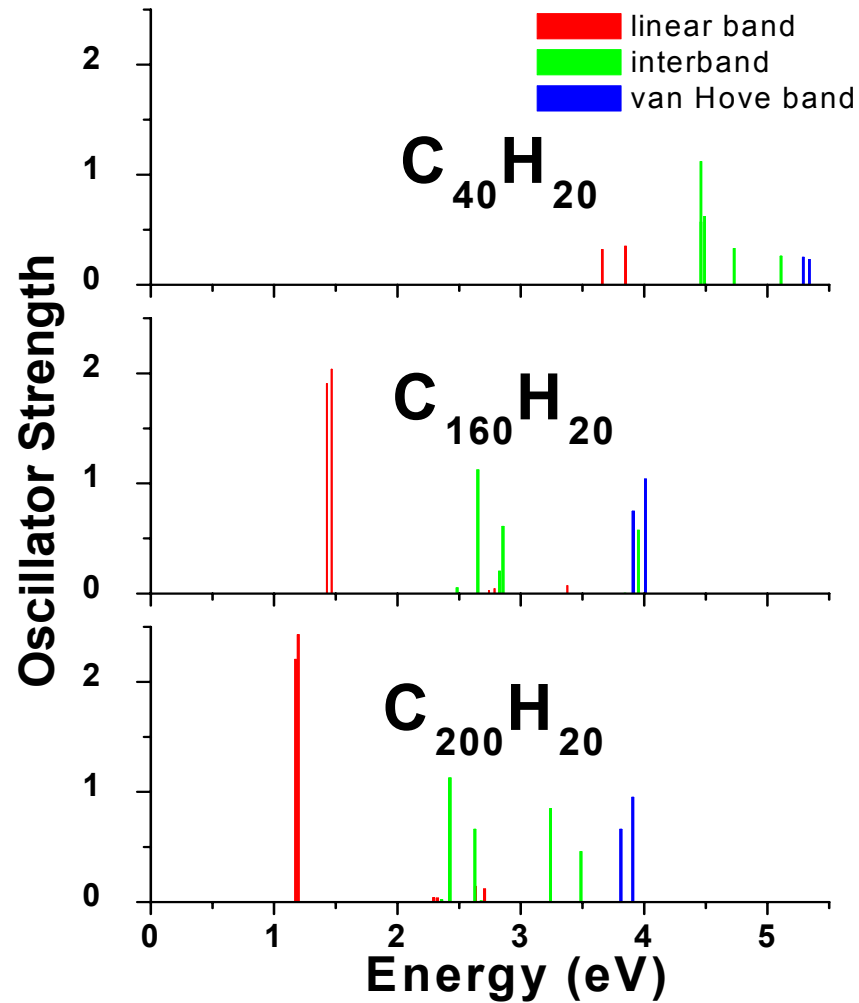
Ding, Yan, Cao *PRB* 2002

Size Dependence of MO States



Intense, charge transfer, end-to-end optical transition
 moves to lower energy as tube lengthens

Linear band transitions
 Strength vs. N



GRAPHITE, TUBULAR PAHs, AND THE DIFFUSE INTERSTELLAR BANDS

ZHIYONG ZHOU,¹ MATTHEW Y. SFEIR,¹ LEI ZHANG,¹ MARK S. HYBERTSEN,² MICHAEL STEIGERWALD,¹ AND LOUIS BRUS¹

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ABSTRACT

Planar polycyclic aromatic hydrocarbons (PAHs) are candidates for the diffuse interstellar band (DIB) carriers. Nanometer-size Fe metallic particles, expected to be present during astrophysical graphite growth, are catalytic for formation of a related species—large tubular PAH molecules. We propose that tubular PAH molecules are a component of the interstellar medium. Electronic structure calculations, on a specific family of tubular PAH molecules derived from elongated C₆₀, reveal intense electronic transitions in the visible and near-IR, which vary systematically with length. We analyze these molecules as DIB carriers within the known constraints.

Subject headings: astrochemistry — dust, extinction — ISM: molecules — stars: carbon

Perhaps short stubs of metallic carbon nanotubes are carriers of DIBs

Summary

- Exciton binding energy about 0.4 eV -- SWNT optical peaks are excitons.
- Exciton Auger recombination extremely fast.
- Rayleigh scattering shows strong exciton optical transitions and distinguishes between metallic and semiconducting tubes. Phonons strongly coupled to electrons in metallic tube Raman.
- Astrophysical nucleation of graphite and PAHs should be catalyzed by Fe clusters – short SWNTs may be carriers for Diffuse Interstellar Bands