Freie Universität Berlin

Vibrational Properties and Raman Spectroscopy- Radial Breathing and High Energy Phonon Modes of Nanotubes and Graphene

Presented for the selected topics in physics seminar by Pierce Munnelly
09/05/11
Supervised by Sebastian Heeg and Benjamin Hatting

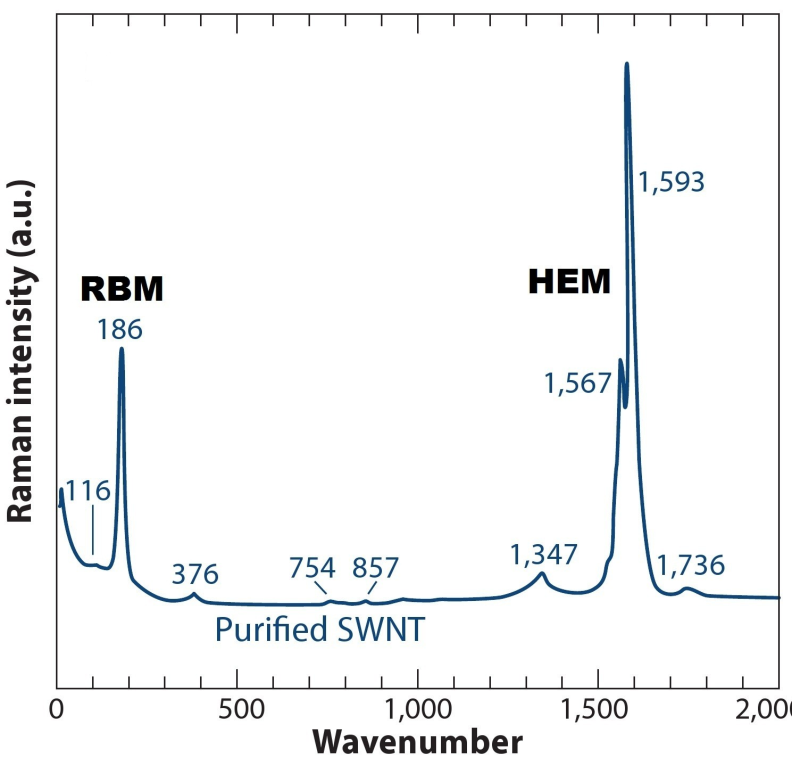
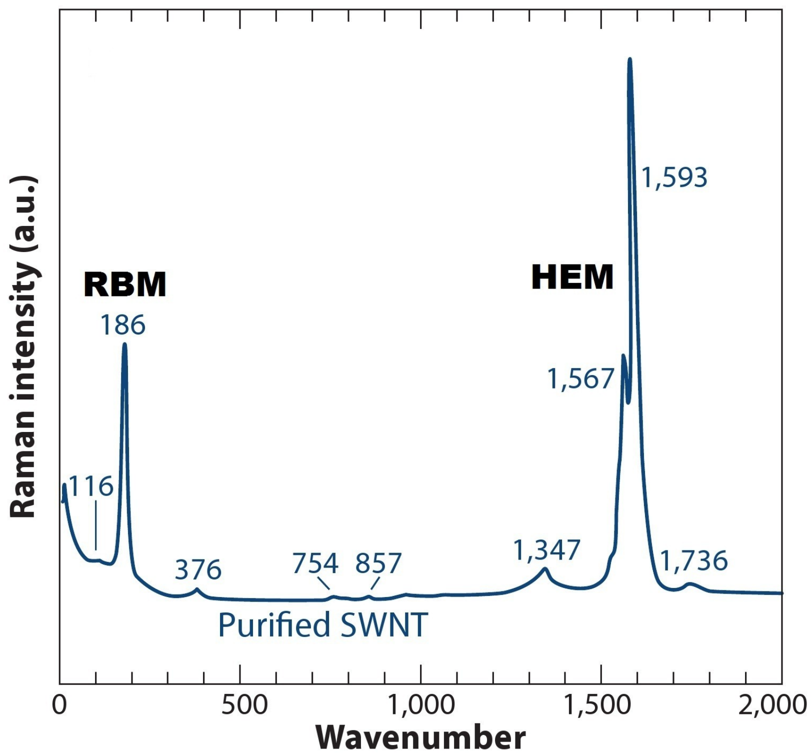


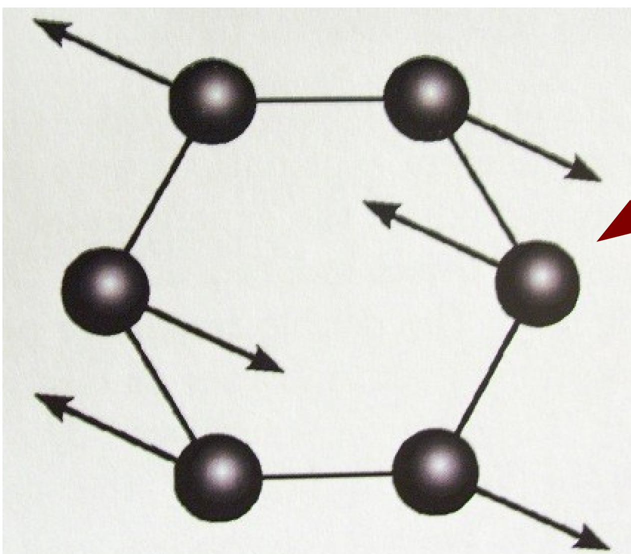
Image adapted by Benjamin Hatting from M.S. Dresselhaus et al., "Characterizing Graphite, Graphene and Carbon Nanotubes by Raman Spectroscopy"

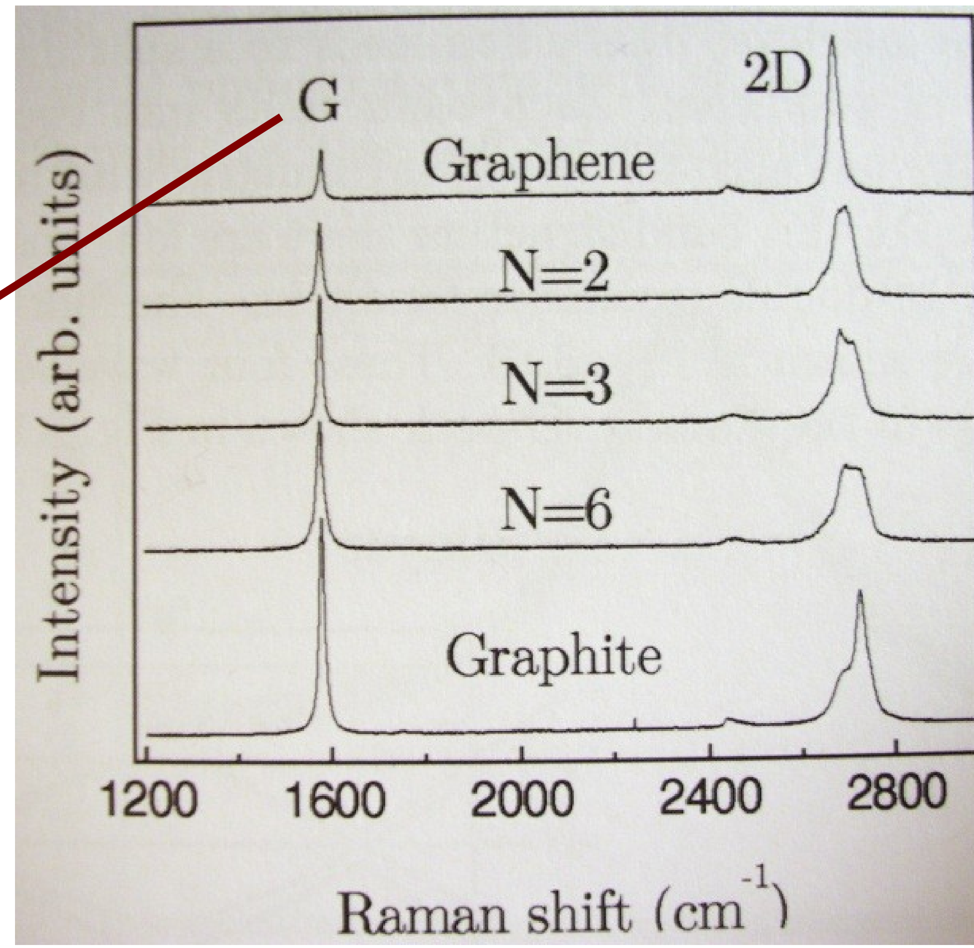
Outline

- Graphite/graphene phonons and zone-folding
- Anisotropic polarizability and selection rules
- Low energy mode (RBM)
- High energy modes (TO and LO)
- Raman Spectroscopy and Resonance
- Example Kataura plot
- Summary



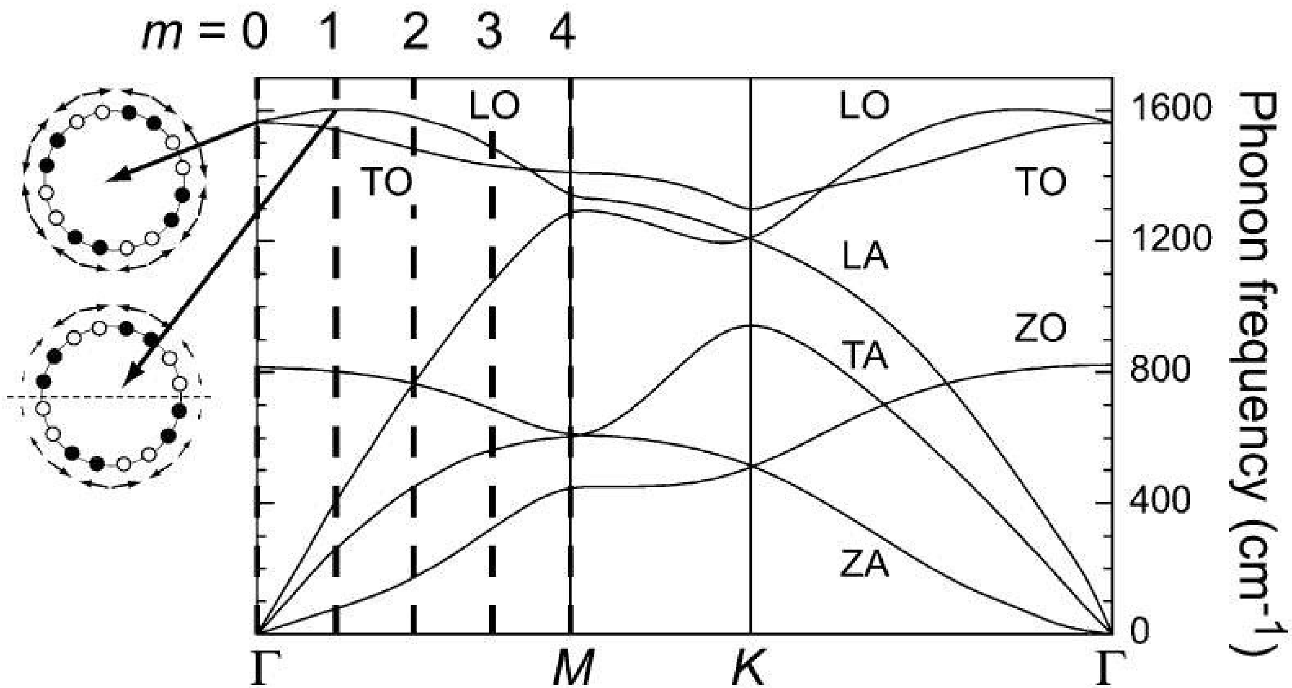
Raman Spectrum of Graphite

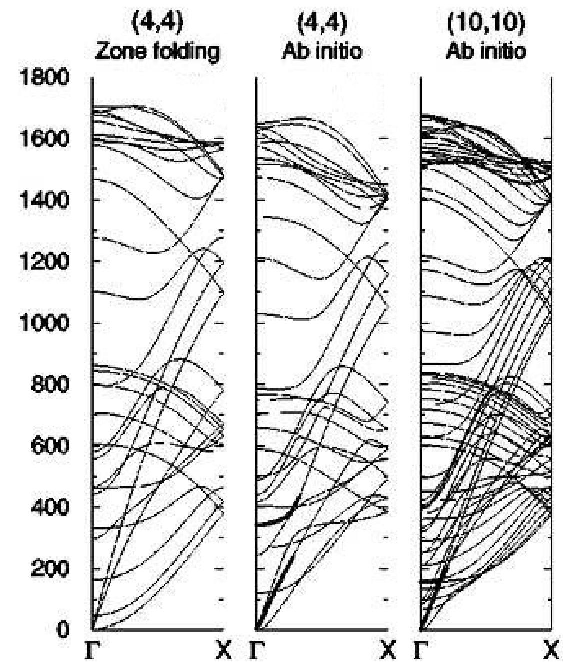




Images from Robert Panknin's diploma thesis, "Raman Spectroscopy on Folded Graphene" (2009)

Phonon Band Structure of NTs





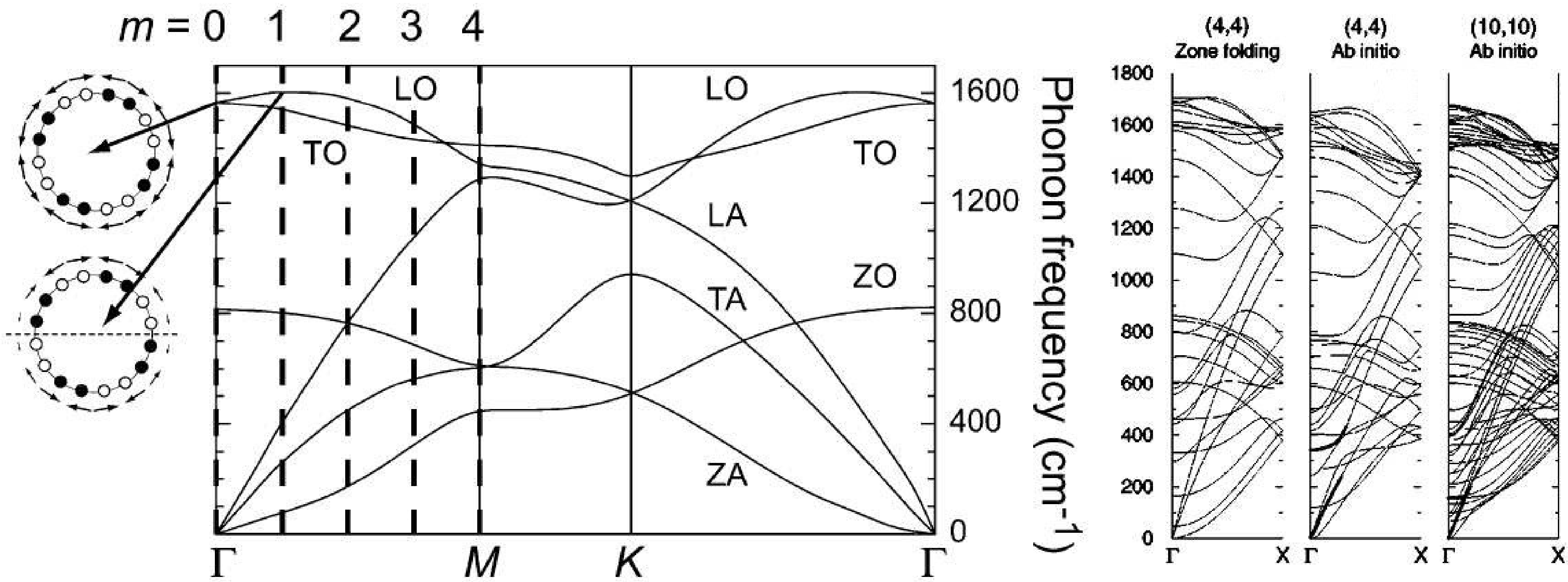
$$k_{\perp,\mathrm{m}} = 2\frac{m}{d}$$

$$\frac{-(n_{hex}-1)}{2} \leqslant m \leqslant \frac{n_{hex}}{2}$$

$6n_{hex}$ can be huge!

C. Thomsen and S. Reich, "Raman Scattering in Carbon Nanotubes" (2007) and D. Sanchez-Portal et al., "Ab Initio Structural, Elastic and Vibrational Properties of Carbon Nanotubes"

Phonon Band Structure of NTs

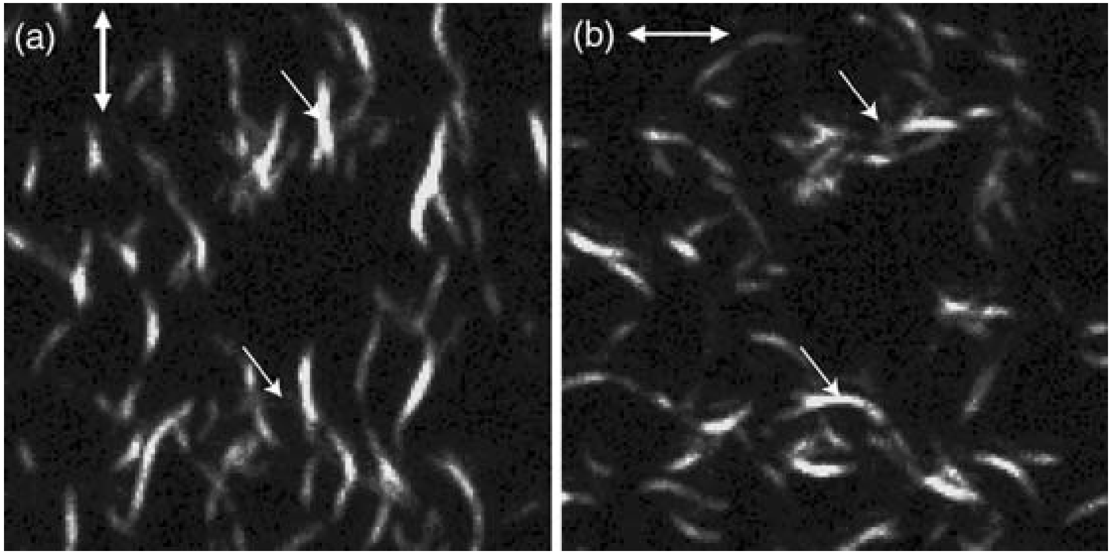


Dipole approximation: $$\Delta m_{el} = 0, \pm 1$$

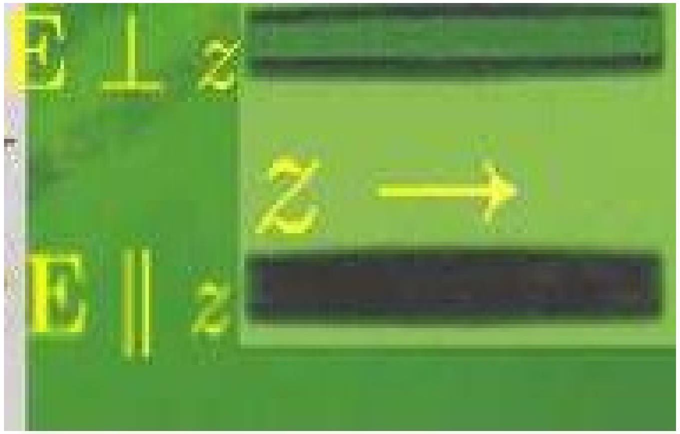
Conservation of angular momentum: $$m_{ph} = 0, 1, 2$$

C. Thomsen and S. Reich, "Raman Scattering in Carbon Nanotubes" (2007) and D. Sanchez-Portal et al., "Ab Initio Structural, Elastic and Vibrational Properties of Carbon Nanotubes"

Antenna Effect



NT's in many orientations



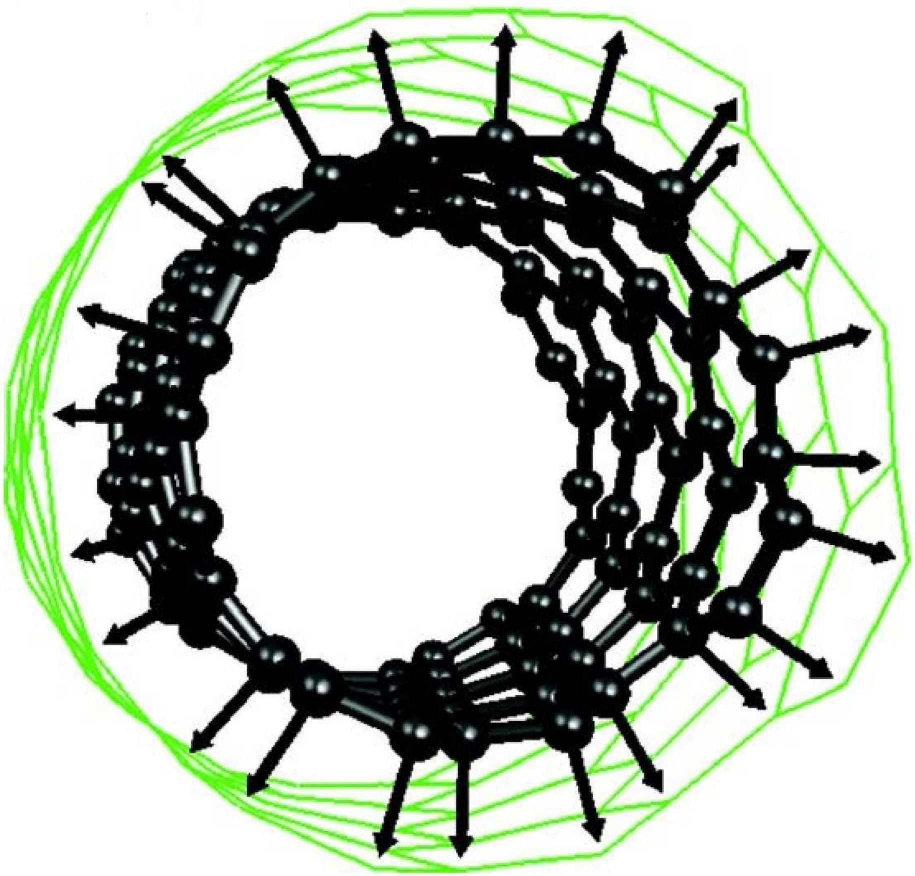
NT's in parallel: Darker area indicates absorption

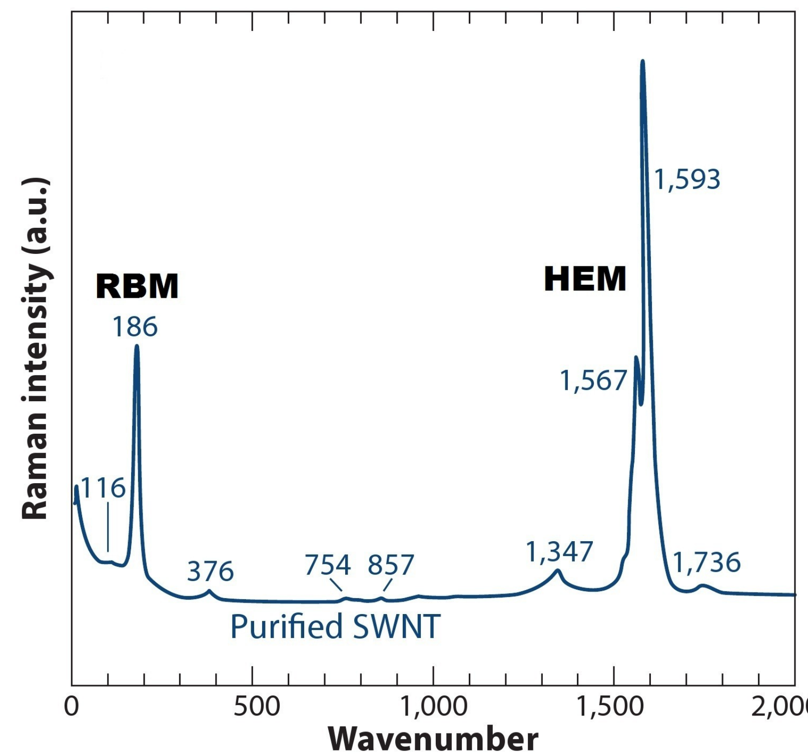
Further reduction of number of visible modes:

$$m_{ph} = 0$$

Right image adapted by Benjamin Hatting from N. Wang et al., "Single Walled 4 Angstrom Carbon Nanotube Arrays"(2000); left from C. Thomsen and S. Reich, "Raman Scattering..."

Radial Breathing Mode

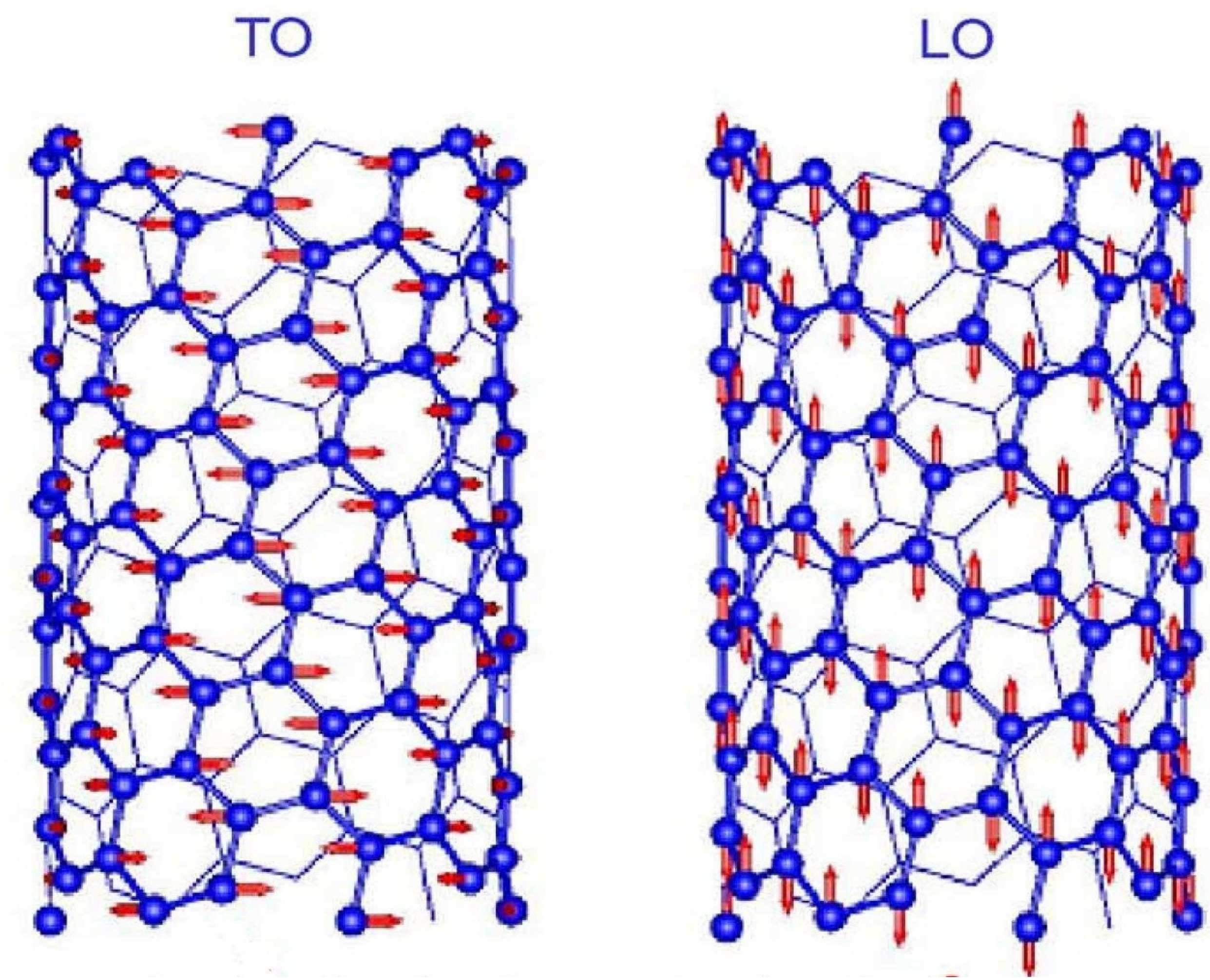


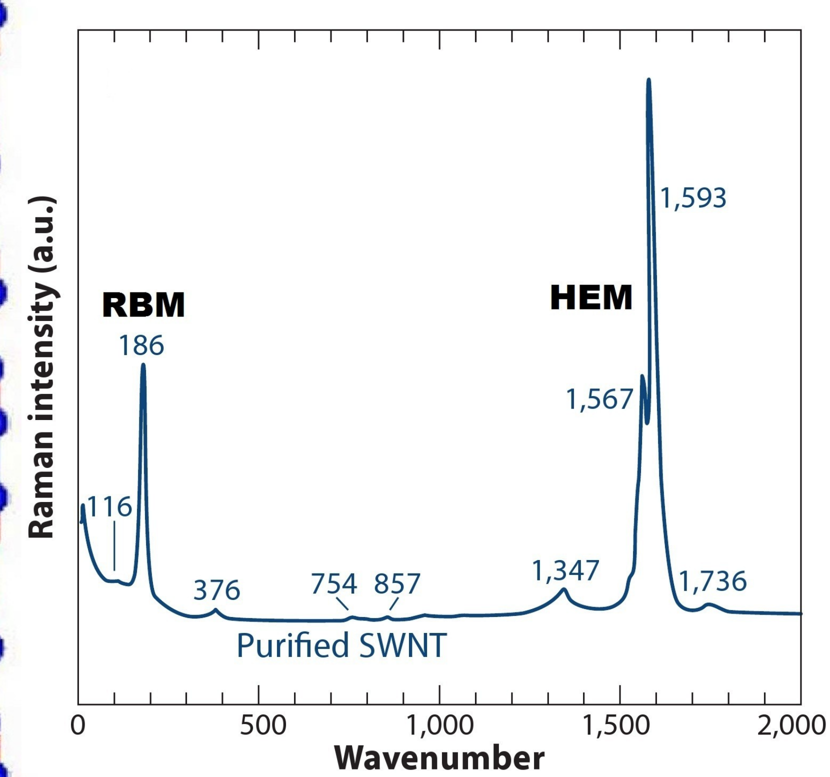


100-400 cm^{-1}

Images adapted by Benjamin Hatter from J. Maultzsch et al; "Radial Breathing Mode..." and S. Piscanec et al; "Optical Phonons in Carbon Nanotubes"

High Energy Modes





1100-1600 cm^{-1}

Images adapted by Benjamin Hatter from J. Maultzsch et al; "Radial Breathing Mode..." and S. Piscanec et al; "Optical Phonons in Carbon Nanotubes"

Raman Spectroscopy

- Excitation to a real or virtual state
- Inelastic scattering by phonon
- Relaxation by emission

- $\hbar\omega_1 = \hbar\omega_2 \pm \hbar\omega_{ph}$
- $\boldsymbol{k}_{\mathbf{1}} = \boldsymbol{k}_{\mathbf{2}} \pm \boldsymbol{q}_{\boldsymbol{ph}}$

  $m_1 = m_2 + m_{ph}$

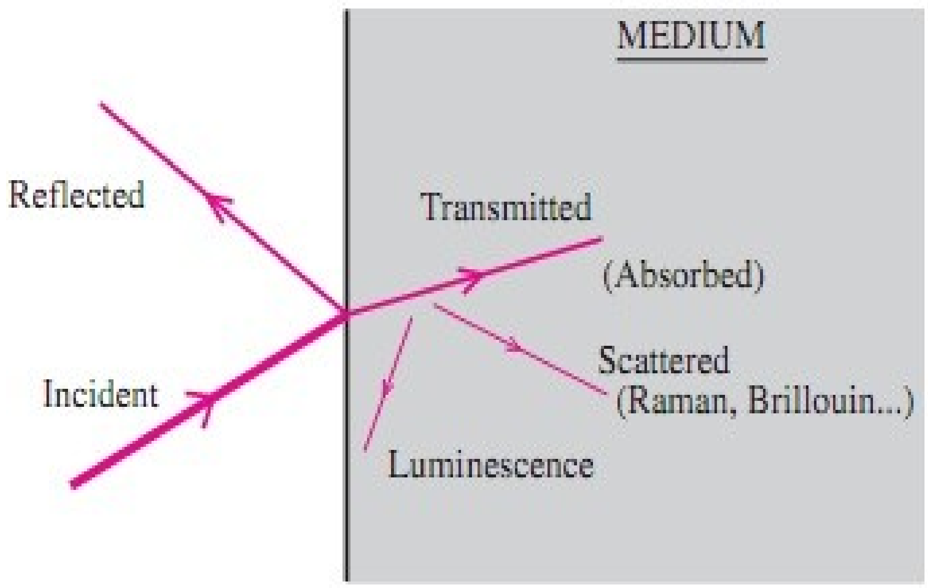
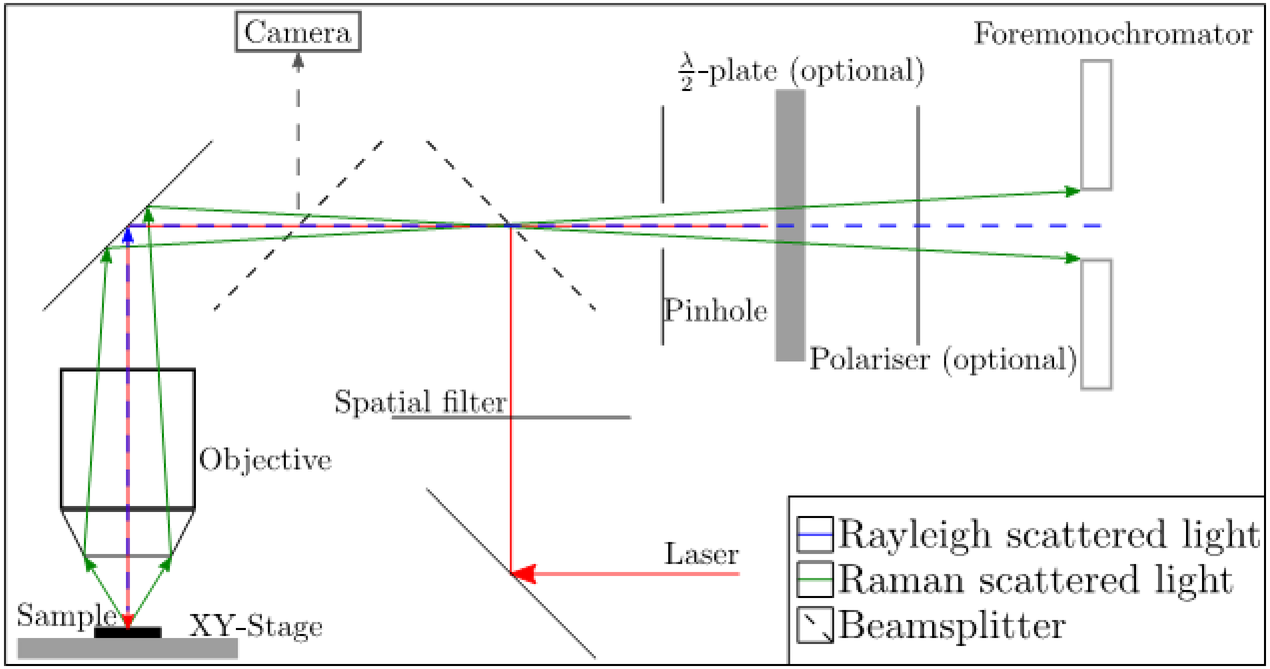


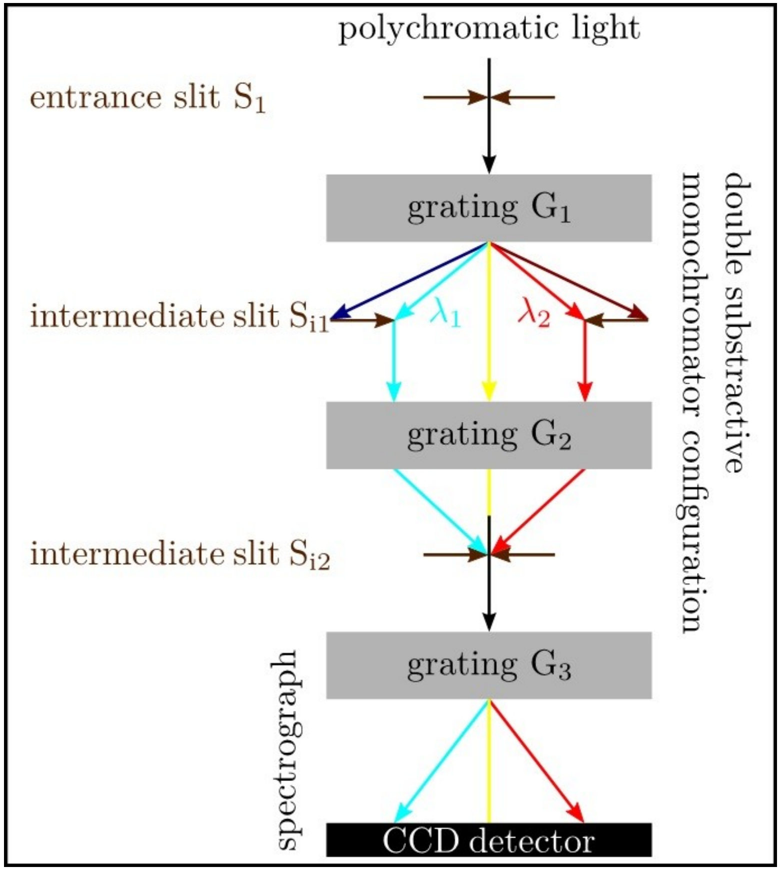
Image from Yu & Cardona, "Fundamentals of Semiconductors", 4th ed. Springer

Raman Spectroscopy



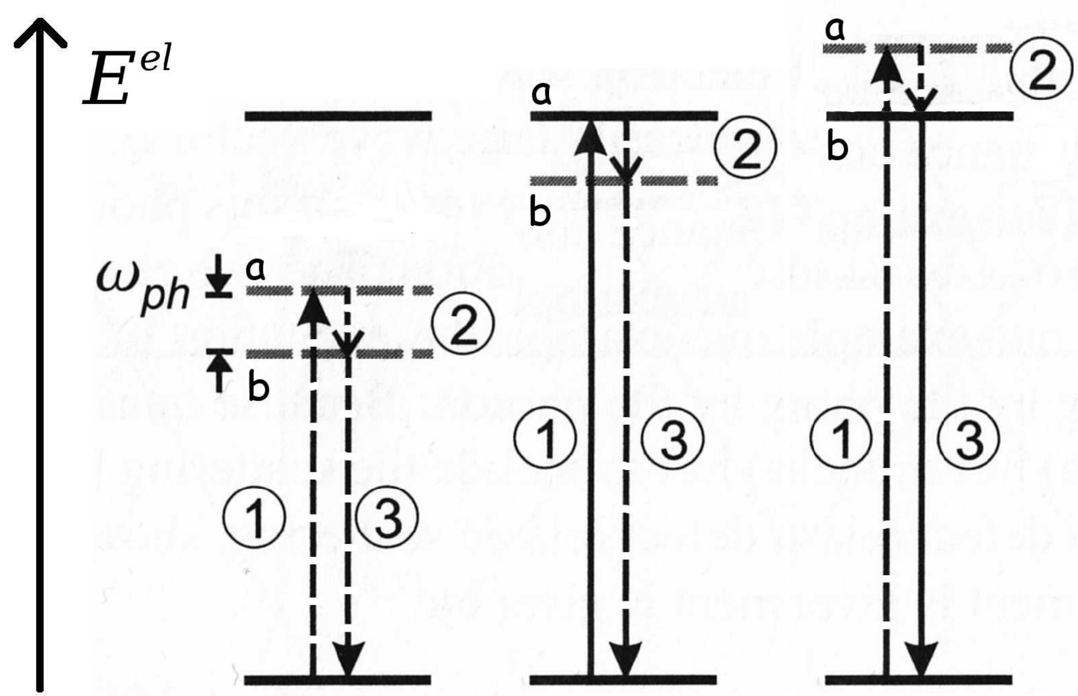
Schematic of lab setup

Spectrometer



Resonant Raman Scattering

- Optical transitions are vertical
- Resonant transitions separated by phonon energy
- Transition energies vary with chirality



1→ incident
2→ phonon scattering
3→ emission

Image adapted from S. Reich, C. Thomsen, J. Maultzsch; "Carbon Nanotubes: Basic Concepts and Physical Properties"

Raman Spectrum

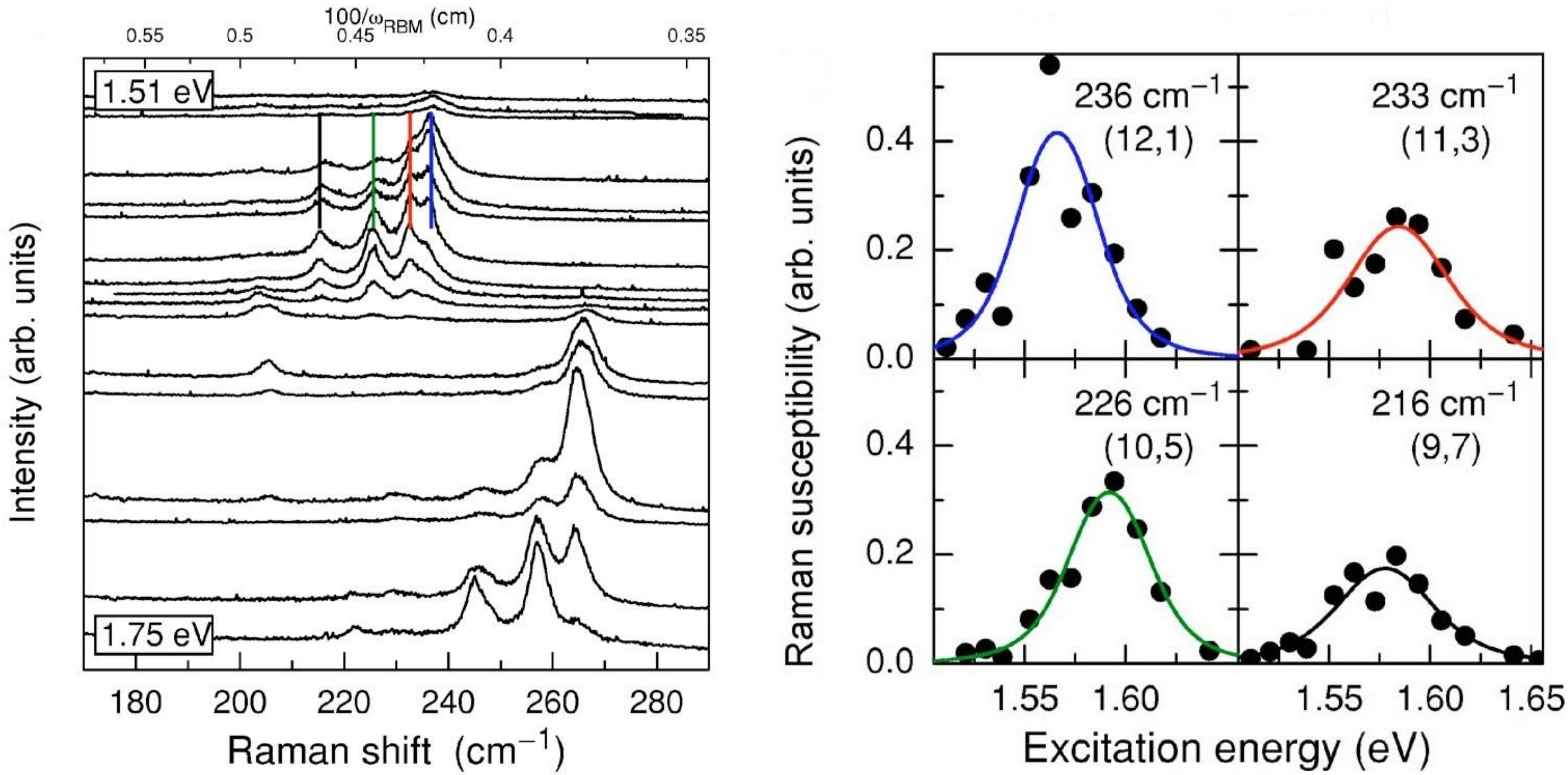
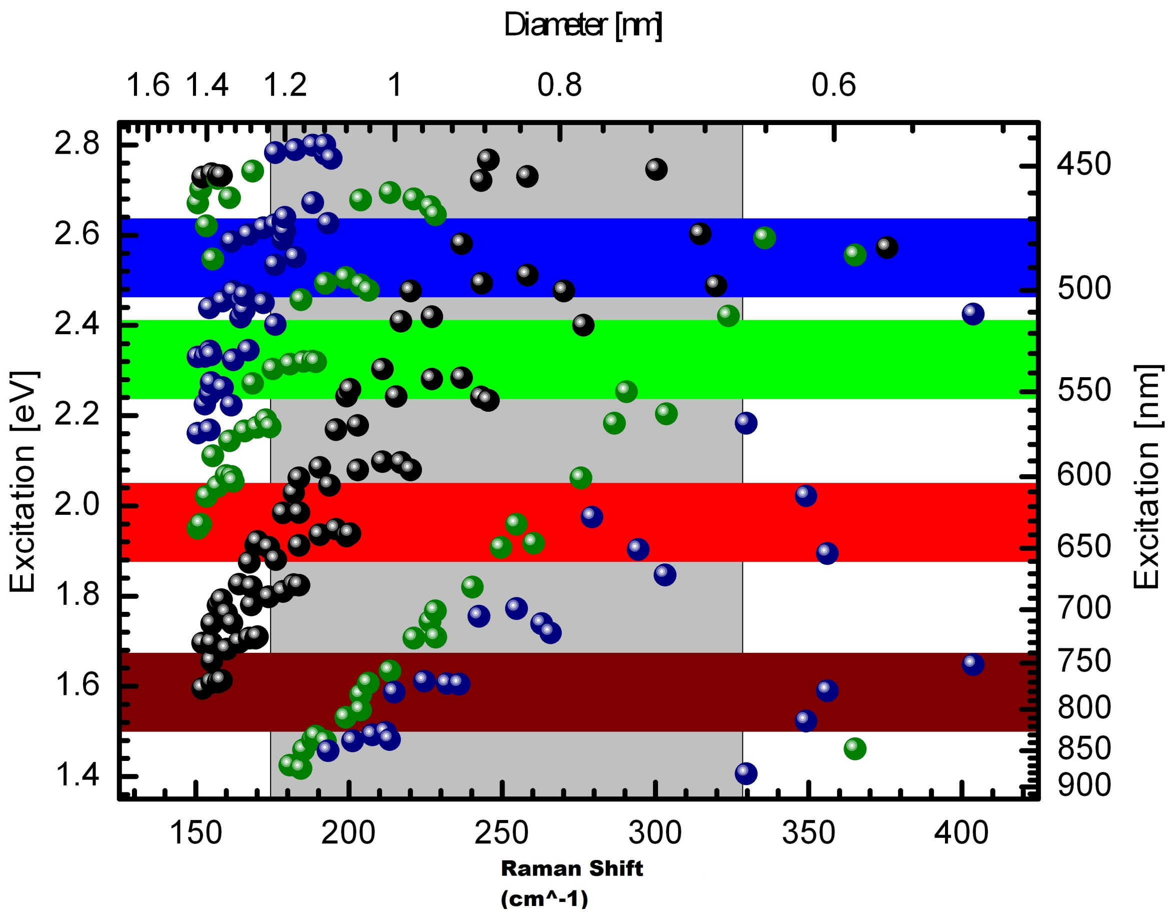


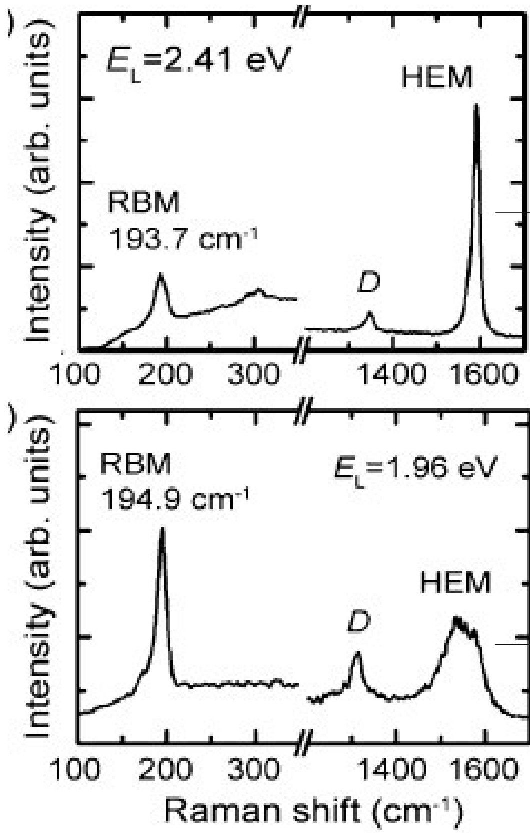
Image taken from J. Maultzsch et al.- "Radial Breathing..."

Kataura Plot



$$d = a_0 \frac{\sqrt{n_1^{\,2} + n_1 n_2 + n_2^{\,2}}}{\pi}$$

HEM in metallic vs. semiconducting tubes



Semiconducting

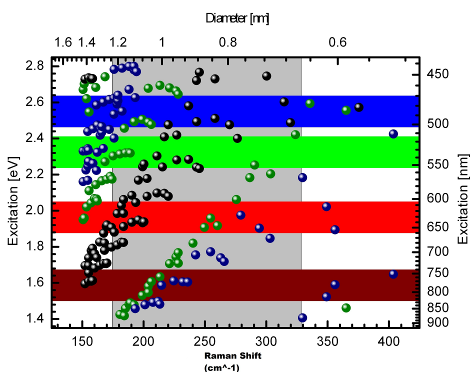
Metallic

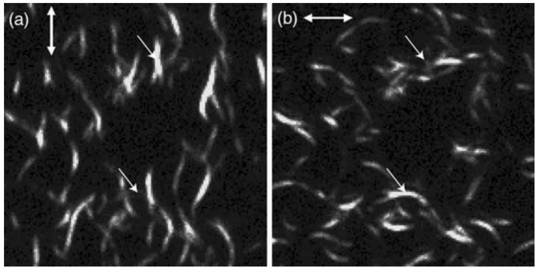
Broadening is a result of e^-/phonon coupling

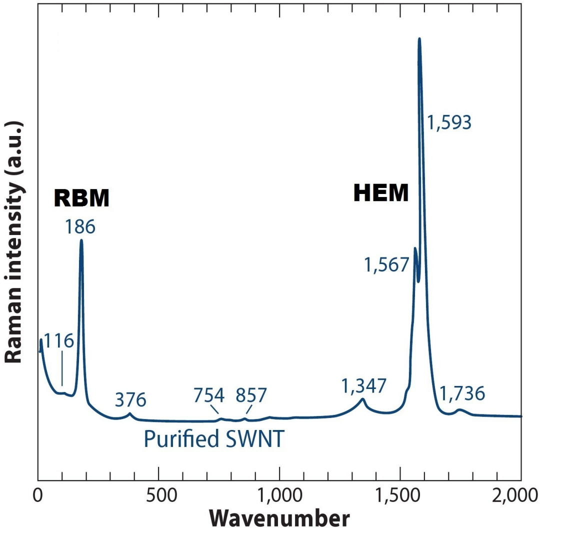
C. Thomsen and S. Reich, "Raman Scattering in Carbon Nanotubes" (2007)

Summary

- Zonefolding for graphite predicts many phonon branches in Nanotubes
- Raman active modes = a tiny fraction (3)
- Resonant Raman demonstrates RBM and HEM
- Useful for identification, orientation, doping and is non-destructive







Thanks to Sebastian Heeg, Benjamin Hatting and Professor Reich for their time.