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
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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

Phonon Band Structure of NTs

\[ k_{\perp,m} = 2 \frac{m}{d} \quad \frac{-(n_{\text{hex}} - 1)}{2} \leq m \leq \frac{n_{\text{hex}}}{2} \quad \text{can be huge!} \]

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

Further reduction of number of visible modes:

\[ m_{ph} = 0 \]

NT's in many orientations

NT's in parallel: Darker area indicates absorption

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

\[ \hbar \omega_1 = \hbar \omega_2 \pm \hbar \omega_{ph} \]
\[ k_1 = k_2 \pm q_{ph} \]
\[ m_1 = m_2 + m_{ph} \]
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

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

\[ d = a_0 \sqrt{n_1^2 + n_1 n_2 + n_2^2} / \pi \]

Image courtesy of Sebastian Heeg
HEM in metallic vs. semiconducting tubes

Broadening is a result of $e^-$/phonon coupling
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.