Tutorial on Physical Properties and Characterization of Carbon Nanotubes

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Outline on Characterization with a Focus on optical characterization

- What is in my sample?
- What we can learn from:
  - Photoluminescence?
  - Raman spectroscopy?
  - Fast Optics?
Sample characterization by SEM and TEM

Bundles of double wall carbon nanotubes produced at UFMG by the electric arc method and characterized by SEM and TEM
TEM for characterization of the purification process

**TEM**: characterizes the overall structure of nanotube samples showing catalyst particles and nanotube ropes.

Before purification: 30% of nanotubes

After purification: 90% of nanotubes
DWNT coalescence by heat treatment

High resolution TEM images of DWNTs doped with B (B.S. #6)

Heat treated at 1200°C

Heat treated at 1500°C

Coalescence of DWNTs outer shells are observed for 1500°C heat treatment

TEM images from M. Endo et al, Nano. Lett. (2005)
AFM image of SWNTs grown by Co nanoparticles with ethanol CVD. The area is 2.5 X 2.5um.

From J. Kong (unpublished)
SPM Tip produces rolling, sliding Motion

Effect of rolling and sliding motion of SWNT produced by scanning probe microscopy tip can be monitored by techniques such as Raman scattering

H. Son & J. Kong (unpublished)
Use of AFM to image a SWNT wrapped by DNA

STM/STS
Geometric structure (STM) and electronic density of states (STS)


(13,7) nanotube
Electronic structure of a carbon nanotube

Rolling up 2D graphene sheet

Confinement of 1D electronic states

1D van Hove singularities - high density of electronic states (DOS) at well defined energies
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Photoluminescence Measurements

- Nanotubes dispersed in aqueous solution using surfactants
- Only semiconducting tubes are seen

- Identified Ratio problem and family effect
Nanotube PL Spectroscopy

Most Measurements
- excitation at $E_{22}$, emission at $E_{11}$
- measured with Xe lamp
- Solution allows PL measurements on many SWNTs at once
- Allows excitation vs emission maps to be made
- $(2n+m)$ family patterns give $(n, m)$ identifications.

PL map of SDS- dispersed HiPco CNTs

Maruyama et al. NJP (2003)
PHOTOLUMINESCENCE

Data are shown as 2D and 3D maps

The observation of intensity and energy maps strongly influenced other photophysics characterization techniques for carbon nanotubes

Laser photoluminescence excitation spectroscopy (PLE)

- Can be done with laser excitations
- $\text{Ar}^+$ pumped Ti:Sapphire laser.
- $\text{Ar}^+$ pumped Dye laser
- Spex 750M monochromator.
- Low temp (350 – 1.5K).
- InGaAs diode array.
- LN$_2$ cooled CCD camera.

-For a special sample with a large concentration of (6,5) SWNTs allows study of phonon-assisted excitation and emission for specific phonons
Emission Identified with One and Two Phonon Processes:

- 2 iLO/iTO near $\Gamma$
- 2 iTO near $K$ (G' band)
- 2 iLO/iLA near $K$
- 2 oTO near $\Gamma$ (M-band)
- 1iLO/iTO near $\Gamma$ (G-band)

Two phonon process

One phonon process
Non-degenerate Pump-Probe

Frequency domain

Fast optics, Time domain

$E_{\text{pump}} = 1.57 \pm 0.01 \text{eV}, \sim E_{11}(6,5) + 2\hbar \omega_D$

$E_{\text{probe}} = \text{around } E_{11} \text{of (6,5) nanotube}$

(Instrument resolution ~250fs)


S. G. Chou et al. PRB 72 195415 (2005)
Exciton-phonon sidebands and Phonon-Assisted Processes

HiPco + SDS solution

$E_{22}^S - E_{11}^S$

Intensity

CoMoCAT+DNA – (6,5) enriched

$E_{11}^S - E_{11}^S$

Perebeinos et al, PRL 94, 027402 (2005)

Plentz et al. PRL 95, 247401 (2005)

Chou et al. PRL 94, 127402 (2005)
The ratio problem for $E_{22}^S$ and $E_{11}^S$

$$\frac{E_{22}^S}{E_{11}^S}$$ equals 1.75 instead of 2!


- This work established family behavior and led to consideration of many body effects
The big picture: $E_{ii}$ obeys a scaling law

$E_{11}(d_t) = E_{22}(d_t/2)$

$E_{11}^S$ and $E_{22}^S$ follow a single scaling law when plotted as a function of $p/d_t$

$E_n(R) (eV)$

$\frac{\Delta E_{ii}}{\gamma_0 a_{C-C}} = \frac{2p}{4d_t} \log \left( \frac{2\Lambda}{3d_t} \right)$

PRL 2004

Kane & Mele, PRL 90, 207401 (2003)
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  - Raman spectroscopy?
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Resonant Raman scattering process

\[ |n_i, n_S; n_q; \psi_e \rangle \]

Raman intensity \( \rightarrow \) transition probability per unit time

\[
I(E_i) = C \sum_{a,b} \left| \frac{\langle f | H_{e-r} | b \rangle \langle b | H_{e-ph} | a \rangle \langle a | H_{e-r} | i \rangle}{(E_i - E_a - i\gamma)(E_i - E_b - i\gamma)} \right|^2
\]

\[
E_i - E_a = \hbar \omega_i - \Delta \varepsilon \quad \text{resonance with incident photon}
\]

\[
E_i - E_b = \hbar \omega_i \pm \hbar \omega_q - \Delta \varepsilon = \hbar \omega_s - \Delta \varepsilon \quad \text{resonance with scattered photon}
\]
Phonon Dispersion of 2D graphite

- $E_{2g2}$ Raman mode at 1580cm$^{-1}$

R. Saito, M.S. Dresselhaus and G. Dresselhaus
"Physical Properties of Carbon Nanotubes"
Imperial College Press (1998)
Phonon modes -- (10,10) Armchair


- $N=20$, $6N=120$ phonon modes
- 66 distinct, 4 acoustic
- 16 Raman (Group theory)
- $A_1$, $A_2$, $E_1$ symmetry modes are Raman active

7 Raman intensive modes:

- $E_{2g}$: $17 \text{ cm}^{-1}$
- $E_{1g}$: $118 \text{ cm}^{-1}$
- $A_{1g}$: $165 \text{ cm}^{-1}$
- $E_{2g}$: $368 \text{ cm}^{-1}$
- $E_{1g}$: $1585 \text{ cm}^{-1}$
- $A_{1g}$: $1587 \text{ cm}^{-1}$
- $E_{2g}$: $1591 \text{ cm}^{-1}$
The presence of the RBM and the special G-band doublet gives signature of small diameter (< 2 nm) carbon nanotubes in your sample.
Raman Spectra of SWNT Bundles

- RBM gives tube diameter and diameter distribution
- Raman D-band characterizes structural disorder
- G\textsuperscript{-} band distinguished M, S tubes and G\textsuperscript{+} relates to charge transfer
- G’ band (2\textsuperscript{nd} order of D-band) provides connection of phonon to its wave vector
Resonant Raman scattering in carbon nanotubes

- Resonance Raman process
- Raman lineshape can distinguish metallic and semiconducting nanotubes
- Kataura plots relate the $E_{ii}$ to (n,m) tubes


DNA-Assisted SEPARATION

Ion-exchange chromatography (IEC)
Hybrid DNA-SWNTs:
• M-SWNT different surface charge density, higher polarizability, elute before S-CNTs

Raman characterization shows that
• DNA wrapping removes metallic (M) SWNTs
• Chromatography further removes M SWNTs preferentially
Resonant Raman Spectroscopy Laboratory

- Triple monochromator with optical microscope
- Ar-Kr laser and Ar laser
- Tunable laser systems (Dye- and Ti:Sapphire)

1.5 – 2.7 eV
Single Nanotube Spectroscopy yields $E_{ii}, (n,m)$

Resonant Raman spectra for isolated single-wall carbon nanotubes grown on Si/SiO$_2$ substrate by the CVD method


Each nanotube has a unique DOS because of trigonal warping effects


Raman signal from *one* SWNT indicates a strong resonance process

$(\omega_{RBM}, E_{ii}) \rightarrow (n,m)$
G-band frequency dependence on tube diameter


\[ \omega_{G}^{+} \sim 1591 \text{ cm}^{-1} \]
\[ \omega_{G}^{-} = \omega_{G}^{+} - C/d_t^2 \]
\[ C_S = 47.7 \text{ cm}^{-1}\text{nm}^2 \]
\[ C_M = 79.5 \text{ cm}^{-1}\text{nm}^2 \]
Trigonal Warping Effect in Carbon Nanotubes

Splitting of the vHs in metallic SWNTs

R. Saito et al., PRB 61, 2981 (2000)


G' band spectra

For metallic tubes into $E_{11}^{M}$ and $E_{11}^{M}$

JDOS

Armchair zigzag
G’-band allows mapping of trigonal warping effect for phonons

2D Graphite — Double Resonance is selective of the wavevector magnitude
1D SWNTs — Double Resonance is selective of both magnitude and direction

magnitude – laser energy (2D&1D), direction – chirality (1D)

Quantum confinement — wavevector direction
Fit of the phonon dispersion around K

Anisotropy in phonon dispersion around K

Phonon Trigonal Warping Effect

Raman Spectra and Transport for One SWNT
New Research Directions for RRS

- AFM $d_t = 1$-$2$ nm $\Rightarrow$ single tube.
- No voltage applied to sample during Raman Spectroscopy.

\[ \omega_{RBM} = \frac{248}{d_t} \]
\[ \omega_{RBM} = 185 \text{ cm}^{-1} \Rightarrow d_t = 1.34 \text{ nm} \]

Resonance Raman Spectroscopy on the same sample used for PL

Family effect $2n+m=\text{constant}$

Mapping of RRS led to result that $E_{\text{ii}}$ is the same for RRS and PL

Fantini et al. PRL (2004) showed RRS and PL give the same $E_{\text{ii}}$
The Resonance Raman Scattering (RRS) Maps

\[ I(E_{\text{laser}}) \propto \frac{1}{(E_{\text{laser}} - E_{ii} - i\Gamma)(E_{\text{laser}} + E_{\text{ph}} - E_{ii} - i\Gamma)^2} \]

The Raman map for a given \( \omega_{\text{RBM}} \) allows determination of the resonance window for a given \((n,m)\) tube. Measurement of the Stokes and anti-Stokes profiles gives transition energy \( E_{ii} \).

\[ \omega_{\text{RBM}} \,(cm^{-1}) = \frac{219}{d_T \,(nm)} + 15 \]


\((E_{ii}, \omega_{\text{RBM}}) \rightarrow (n,m)\)
EXTENDED TIGHT BINDING (ETB)

Kataura plot is calculated within the extended tight-binding approximation using Popov/Porezag approach:

- curvature effects (ssσ, spσ, ppσ, ppπ)
- long-range interactions (up to ~4Å)
- geometrical structure optimization

The extended tight-binding calculations show family behavior (differentiation between S1 & S2 and strong chirality dependence) similar to that of PL empirical fit

ETB model is widely used for characterization of carbon nanotubes

Ge.G. Samsonidze et al., APL 85, 5703 (2004)
Br$_2$-doped double-wall nanotubes

Highly pure samples

M. Endo (Japan)

A. G. Souza Filho et al. (2006)

- Different configuration outer/inner tubes depending on laser energy,
- The Raman spectrum of the dopant and of the host
Semiconducting inner/Metallic outer configuration

RBM properties at $E_{\text{laser}}=2.33$ eV

- The effect of intercalation on individual inner (n,m) tubes can be studied.

- Spectrum from both the nanotubes and the dopant

Souza Filho et al PRB (2006)
Doping effects: changes in the Fermi level and electronic transitions $E_{ii}$ values

- Changes in the relative intensities indicate changes in $E_{ii}$ values
- Upshifts observed in the G band indicate charge transfer and changes in the $E_F$
- Br$_2$ is acting as an acceptor
- Intercalation of nanotubes is complementary to that of graphite but shows unique aspects

![Graph showing Raman intensity vs. frequency for pristine and Br$_2$-doped samples under different laser energies.](image)

- $E_{\text{laser}} = 1.58$ eV pristine
- $E_{\text{laser}} = 1.96$ eV Br$_2$-doped
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  - Fast Optics?
Pump-Probe Studies with Fast Optics

Pump-Probe Studies:
- Pump-Probe at the band edge

Transient Spectrum:
- Single or biexponential decay

Slow Component, $\tau_{\text{slow}}$:
- 10-180ps,
  - Radiative relaxation from band edge

Fast component, $\tau_{\text{fast}}$:
- 100-900fs, Intraband relaxation
- Rapid internal thermalization via electron-electron scattering.
  Gives reason for low PL intensity
Non-degenerate Pump-Probe

Frequency domain

Fast optics, Time domain

\[ E_{\text{pump}} = 1.57 \pm 0.01 \text{eV}, \sim E_{11}(6,5) + 2 \hbar \omega_D \]

\[ E_{\text{probe}} = \text{around} \ E_{11} \text{of (6,5) nanotube} \]

(Instrument resolution \(~250\text{fs}\))

Pump Probe Studies at Special $E_{\text{pump}}$

- $E_{\text{pump}} = 1.57\pm0.01\text{eV} \approx E_{11}^{1\text{A}}(6,5) + 2\hbar\omega_D$
- $E_{\text{probe}}$ is around $E_{11}^{1\text{A}}$ of $(6,5)$ nanotube

Exciton population at $E_{11}^{1\text{A}}(6,5)$:
- Quick rise (within 200fs)
- Three decay components:
  - $\tau_{\text{fast}} \sim 680\text{fs}$ (dominant process)
  - $\tau_{\text{int}} \sim 2-3\text{ps}$ (dominant process)
  - $\tau_{\text{slow}} \sim 50\text{ps}$ (weak during first 20ps)
Probing at Different Energies:

-Pump at 1.57±0.01 eV

<table>
<thead>
<tr>
<th>Exp.</th>
<th>(n,m)</th>
<th>$E_{\text{Probe}}$</th>
<th>Fluence J/m²</th>
<th>fast</th>
<th>%</th>
<th>Int</th>
<th>%</th>
<th>Slow</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>O₅</td>
<td>(8,3)</td>
<td>1.27 eV</td>
<td>0.3</td>
<td>900 fs</td>
<td>70</td>
<td>Several ps</td>
<td>Traces mixed</td>
<td>30 ps</td>
<td>30</td>
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<tr>
<td>O₄</td>
<td>(6,5)</td>
<td>1.25 eV</td>
<td>0.3</td>
<td>700 fs</td>
<td>45</td>
<td>3 ps</td>
<td>45</td>
<td>50 ps</td>
<td>10</td>
</tr>
<tr>
<td>O₂</td>
<td>(7,5)</td>
<td>1.20 eV</td>
<td>0.1</td>
<td>800 fs</td>
<td>90</td>
<td>N/A</td>
<td>N/A</td>
<td>40 ps</td>
<td>10</td>
</tr>
</tbody>
</table>
Pump Fluence Dependence
- Probing at E_{11}^{1A-}(6,5):

- Clear pump fluence dependence for $\tau_{int}$ and $\tau_{slow}$
- % weight for $\tau_{int}$ increases with increasing pump fluence
- Observed fluence dependence can be explained by the proposed decay process for each time scale.
Transient Absorption ($O_3$ and $O_1$):

- $\Delta T < 0$ suggests the presence of transient absorption processes.
- Observed previously for probe energies slightly below $E_{11}$ (Yang et al. PCCP, 7, 512-517(2005))
- Timescale $\sim 10$ps
- Phonon absorption from a virtual state (anti-Stokes processes)

**Transient Absorption:**

- $E_{\text{Probe}} = 1.22\text{eV} (O_3)$
- $E_{\text{Probe}} = E_{11}^{1A^\circ}(6,5) = 1.26\text{eV}$

Graph:
- Relative Transmission vs. Delay Time (fs)
- $E_{\text{Probe}}$ values for $O_3$ and $O_1$}

**Diagram:**
- Pump
- $E_{11}$
-虚基态
- Transient Absorption at $E_{\text{Probe}}$
- $|0>$
Different Decay Processes

$\tau_{\text{fast}}$:
Decay via e-e interactions dominated by Auger process.

$\tau_{\text{slow}}$:
non-radiative recombination

$\tau_{\text{int}}$:
- Exciton population at $c$ can be depleted by absorbing a “hot” D-band phonon $\rightarrow b \leftrightarrow c$ process can establish detailed balance and keep exciton population at $c$ at an almost steady state.
- Excitons at $b$ can also leak into $d$ and never return to $c$. Thus, $\tau_{\text{int}}$ is really the timescale of such a phonon “leaking” process.
Evidence for excitons in two-photons optical spectroscopy

Maultzsch el al PRB 72, 241402 (2005)

Density of the 1s-exciton envelope wave function for a (6,5) SWNT
Symmetry of Excitons in Chiral Tubes

Exciton Symmetry Effective Mass Approximation

\[ \mathcal{D}(\psi^{EMA}) = \mathcal{D}(\phi_c) \otimes \mathcal{D}(\phi_\nu) \otimes \mathcal{D}(F_\nu), \]

Envelope function

\[ \mathcal{D}(F_\nu) = \begin{cases} A_1 - \nu \text{ even} \\ A_2 - \nu \text{ odd} \end{cases} \]

Symmetry of the Bloch Function for the exciton

\[ \mathcal{D}(\phi_c) \otimes \mathcal{D}(\phi_\nu) = A_1 + A_2 + E_{2\mu} + E_{-2\mu} \]

Both \( \nu \) even and odd envelope functions have exciton states active for 1-photon (\( A_2 \)) and 2-photon (\( A_1 \)) excitation. Therefore two photon absorption depends on magnitude of matrix elements.
Direct Measurement of Exciton Binding Energy by Fast Optics

Excitation to either $E_1$ or $E_2$ leads to occupation of $E_n$ by an Auger process which relaxes either to $E_1$ or $E_{eh}$ yielding an exciton binding energy of $(E_{eh}-E_{11}) = 0.41\text{eV}$ for the (8,3) SWNT.
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