Nature of Optical Transitions in Carbon Nanotubes and Population Analysis

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Outline

Introduction – Resonance Raman Scattering maps
The exciton and the band-to-band pictures in carbon nanotubes

Band model exciton model

PLE – Bachilo et al.
RRS – Fantini et al.
Rayleigh – Sfeir et al.
The Resonance Raman Scattering (RRS) Maps

Raman Intensity

Raman Intensity

Radia Breathing Mode

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

\[ \omega_{\text{RBM}} = \frac{219}{d_t} + 15 \]

\[ (E_{ii}, \omega_{\text{RBM}}) \rightarrow (n,m) \]

Fantini et al. PRL (2004)
The Resonance Raman Scattering (RRS) Maps

As grown Alcohol SWNTs

HiPco SWNTs + SDS (6,5)

CoMoCAT SWNTs + SDS (6,5)

Characterizing sample growth and...
...sample processing

CoMoCAT (Resasco)
SDS vs. DNA wrapping ...
by Fantini et al.

![Graphs and charts related to sample processing and CoMoCAT technology.](image-url)
The Kataura plot

The optical transition energies \( E_{ii} \) as a function of carbon nanotube diameter \( d_t \)

*Proposed by H. Kataura in 1999, considering first neighbour \( \pi \)-only TB model*
The deviations from a simple graphene zone folding picture

TB with curvature effect and $\sigma$-$\pi$ hybridization + many-body effects

Simple tight binding

$\sigma$-$\pi$ hybridization

Lattice distortion

As shown by the ratio problem...
The ratio problem for $E_{22}^S$ and $E_{11}^S$

$E_{22}^S / E_{11}^S$ smaller than 2!


For a linear dispersion
$E_{22}^S / E_{11}^S = 2$

Why do we have the ratio problem?
Why do we have the ration problem?

Optics without many-body effects

Optics with many-body effects

e-e attraction plus e-h repulsion gives rise to a net blueshift

How is the big picture?
The big picture: $E_{ii}$s obey 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 $p/d_t$

$$
\Delta E_{ii} = \gamma_0 a_{c-c} \frac{g}{4} \frac{2p}{3d_t} \log \frac{2\Lambda}{\frac{2p}{3d_t}}
$$

$PRL\ 2004$

$p = 1, 3, 3', 1' \ldots \ E_{11}^{II}, E_{22}^{II}, E_{11}^{III}, E_{22}^{III}, E_{11}^{IV}, E_{22}^{IV} \ldots$
All the physics is for $0.7 < d_t < 1.3 \text{nm}$ and $0.6 < E_{ii} < 2.7 \text{eV}$

What about $d_t > 1.3 \text{ nm}$?
What about higher $E_{ii}$?
The RRS of alcohol SWNTs
RRS on alcohol CVD SWNTs

Measurements over a broad energy (1.26 to 2.71 eV) and diameter (0.7 to 2.3 nm) range

Now we have to analyse the $E_{ii}$ and $\omega_{RBM}$!
Good agreement with published $E_{22}^S$, $E_{33}^S$ and $E_{44}^S$

Rayleigh by Sfeir et al.

<table>
<thead>
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<th>$(n,m)$</th>
<th>mod$(n-m, 3)$</th>
<th>$d_s$ (nm)</th>
<th>$\theta$ (°)</th>
<th>Transition</th>
<th>$E_S$ (eV)</th>
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<td>1.83</td>
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<td>24.2</td>
<td>$M_{22(1)}$</td>
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</table>

The anomalous scaling law for the higher optical transitions

\[ p = l^l \tilde{5}^3 \tilde{4}^2 \cdots \{01, E_2^{II}, E_2^{III}, E_2^{IV}, E_3^{III}, E_3^{IV}, \cdots \} \]
The difference between the scaling laws

The two photons experiment...

Maultzsch et al. PRB72, 24402(R) (2005)
Ma et al. JPCB109, 15671 (2005)
Band-to-band vs excitons?

Exciton binding energy: $E_b = -0.305/d_t$ (eV)

$E_{11}^S$ and $E_{22}^S$ Excitons

$E_{33}^S$ and $E_{44}^S$ free e-h pairs?

Kane and Mele

$$\Delta E_{ii} = \gamma_0 a_c c^g \frac{2p}{43d_t} \log \frac{2\Lambda}{3d_t}$$
Measuring the $E_b$ energy

Excitonic binding energy:

$E_{b11} = -0.318/d_t \, (eV)$

$E_{b22} = -0.298/d_t \, (eV)$
Chirality dependence of $E_{ii}$

Similar to prediction by the extended tight binding (ETB) within experimental accuracy ($\sim \pm 30\text{meV}$)
Summary

1 – Optics is a well established tool to characterize single wall carbon nanotube samples.

2 – $E_{11}^S$ and $E_{22}^S \rightarrow$ excitons

3 – $E_{33}^S$ and $E_{44}^S \rightarrow$ band-to-band?

4 – Exciton binding energy: 
$$E_b = -0.305/d_t$$
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