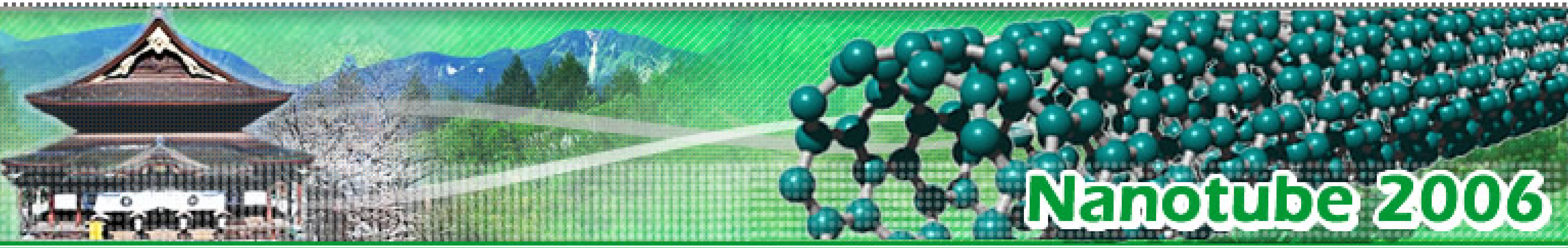


June 18 - 23, 2006

Nature of Optical Transitions in Carbon Nanotubes and Population Analysis

A.Jorio, M. A. Pimenta and P. T. Araujo

Physics Department, UFMG, Belo Horizonte, Brazil.

S. K. Doorn

Chemistry Division, Los Alamos National Laboratory, USA

S. Maruyama

Dept. of Mechanical Engineering, University of Tokyo, Tokyo, JAPAN

M. S. Dresselhaus (MIT)

Y. Oyama, J. Jiang, R. Saito (Tohoku)

NT06

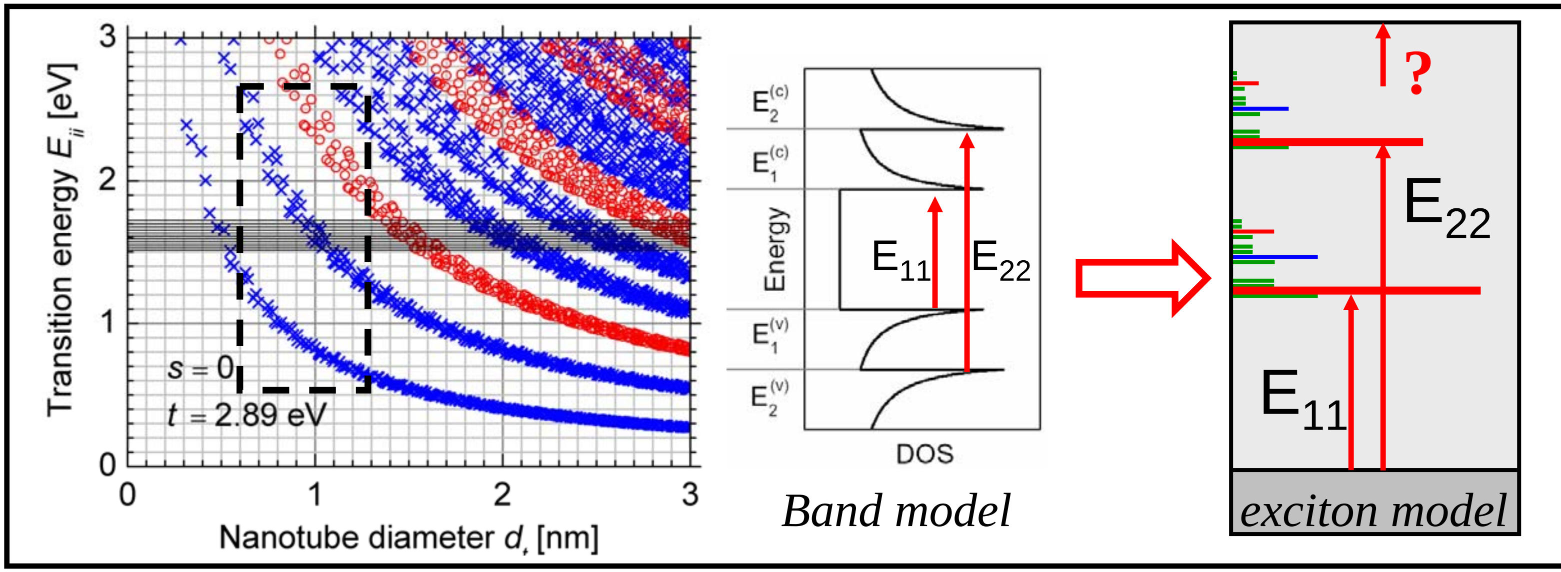
June 18-23, 2006, Nagano, Japan

NT07

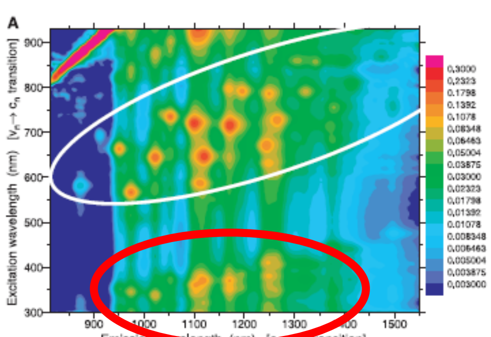
Outline

Introduction – Resonance Raman Scattering maps

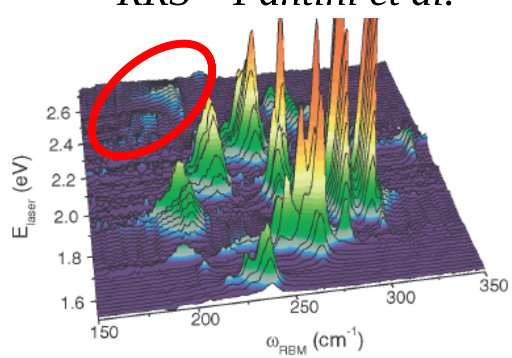
The exciton *and* the band-to-band pictures in carbon nanotubes



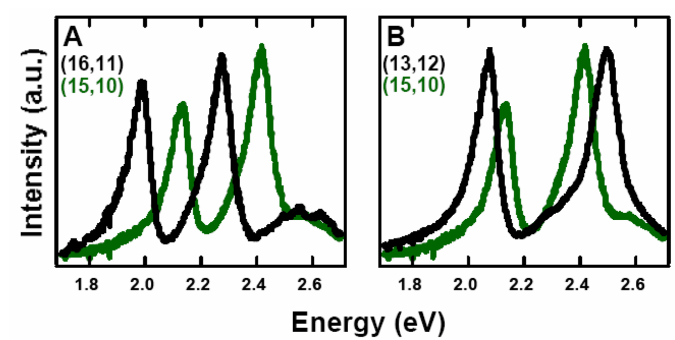
PLE – Bachilo et al.



RRS – Fantini et al.

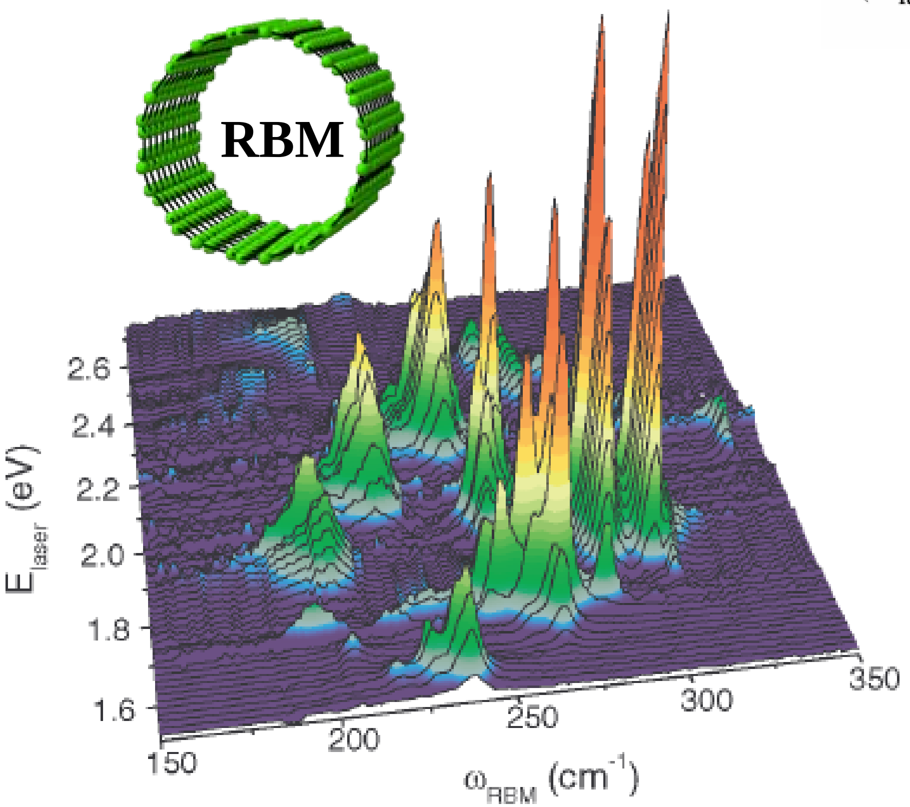


Rayleigh – Sfeir et al.



The Resonance Raman Scattering (RRS) Maps

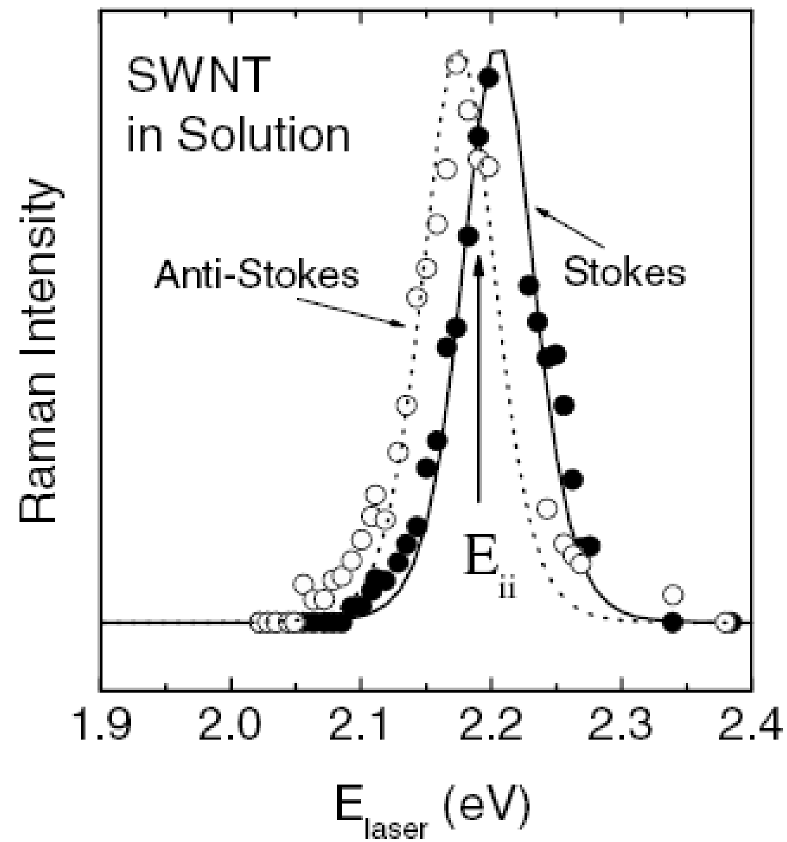
Radia Breathing Mode



$$\omega_{\mathrm{RBM}} = \frac{219}{d_t} + 15$$

Fantini et al. PRL (2004)

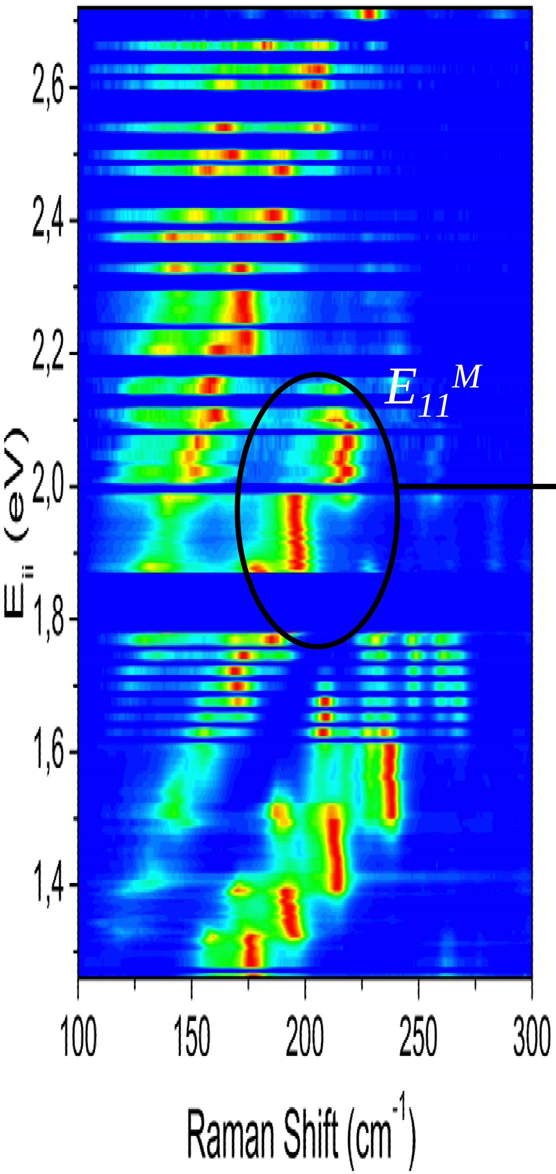
$$I(E_{\mathrm{laser}}) \propto \left| \frac{1}{(E_{\mathrm{laser}} - E_{ii} - i\Gamma)(E_{\mathrm{laser}} \pm E_{\mathrm{ph}} - E_{ii} - i\Gamma)} \right|^2$$



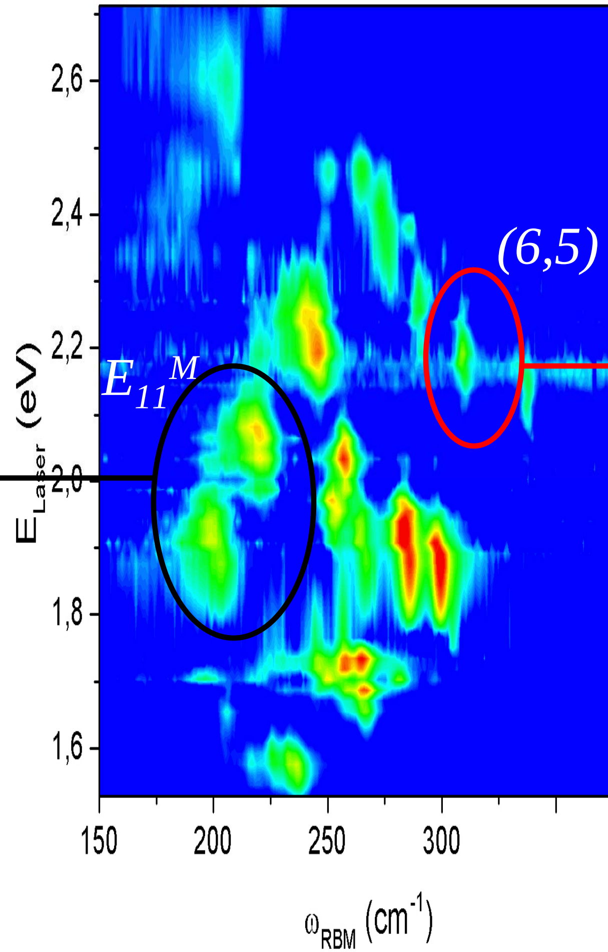
$(E_{ii}, \omega_{RBM}) \rightarrow (n,m)$

The Resonance Raman Scattering (RRS) Maps

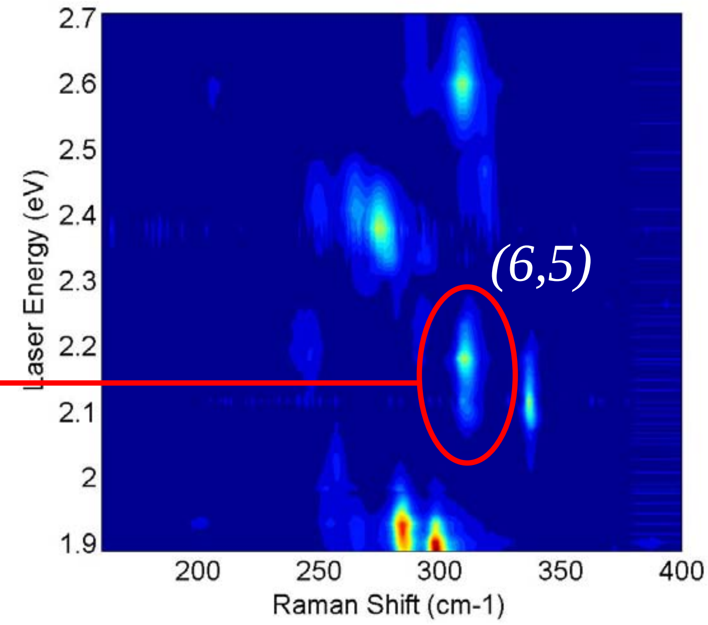
As grown Alcohol SWNTs



HiPco SWNTs + SDS



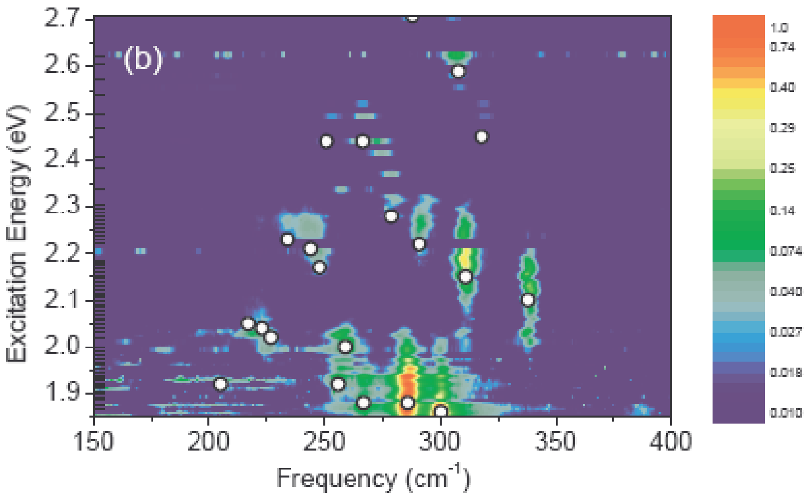
CoMoCAT SWNTs + SDS

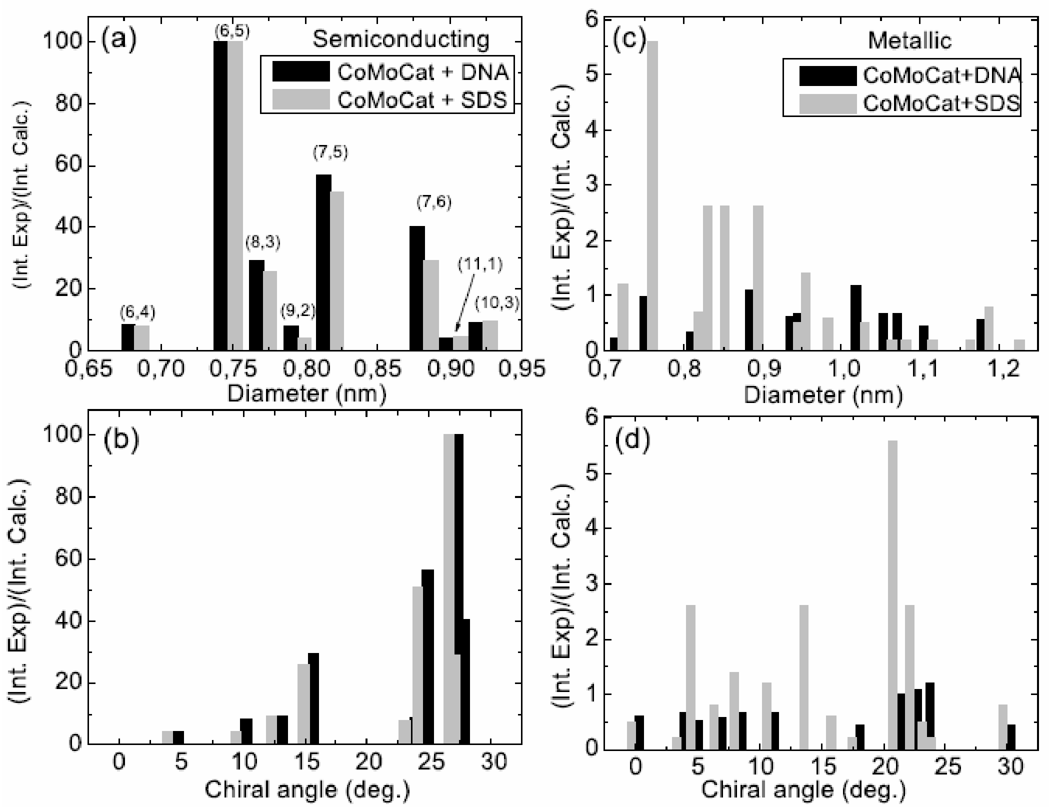


Characterizing sample growth and...

...sample processing

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



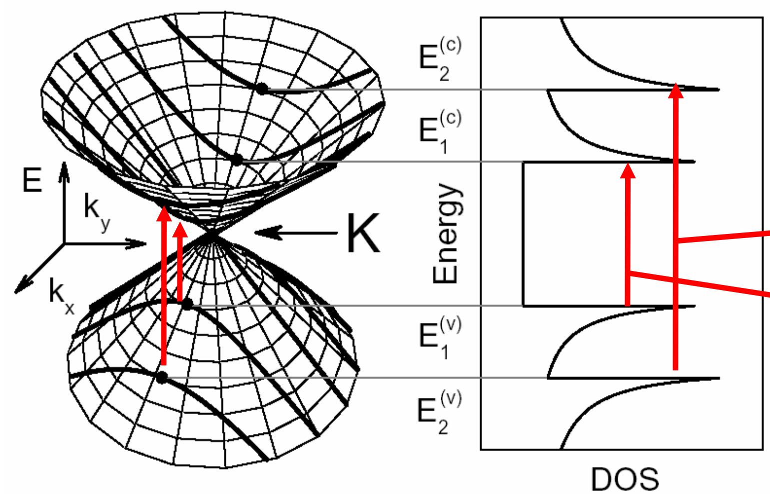


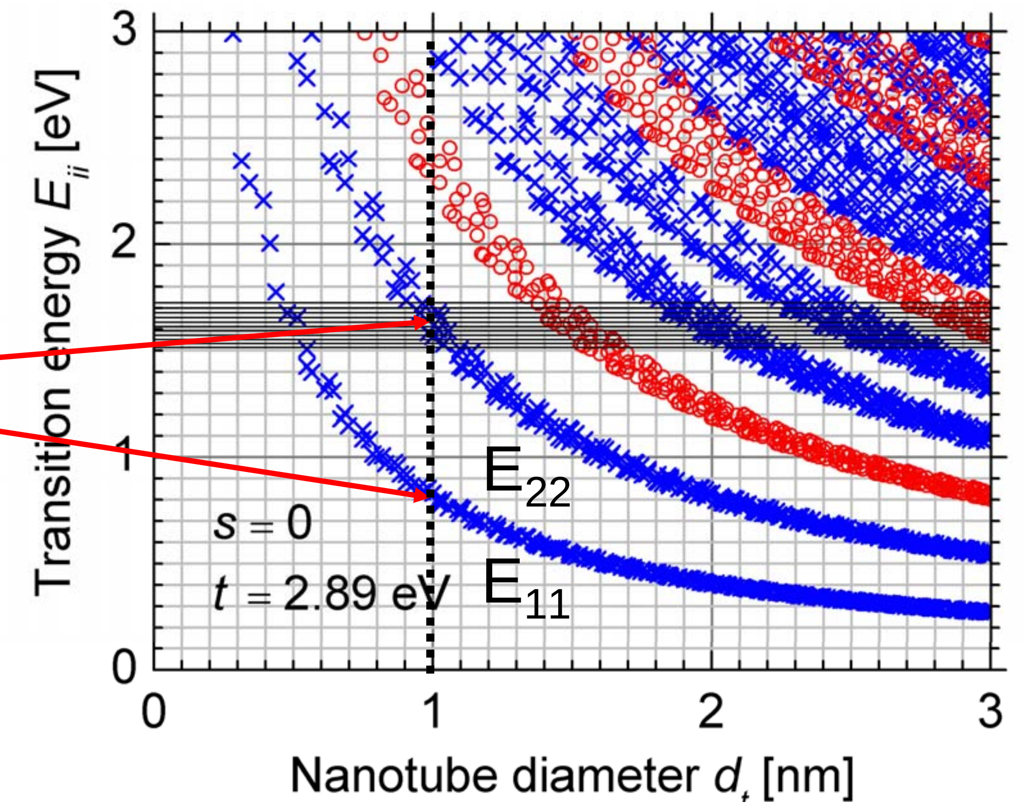
The Kataura plot

The optical transition energies E_{ii}

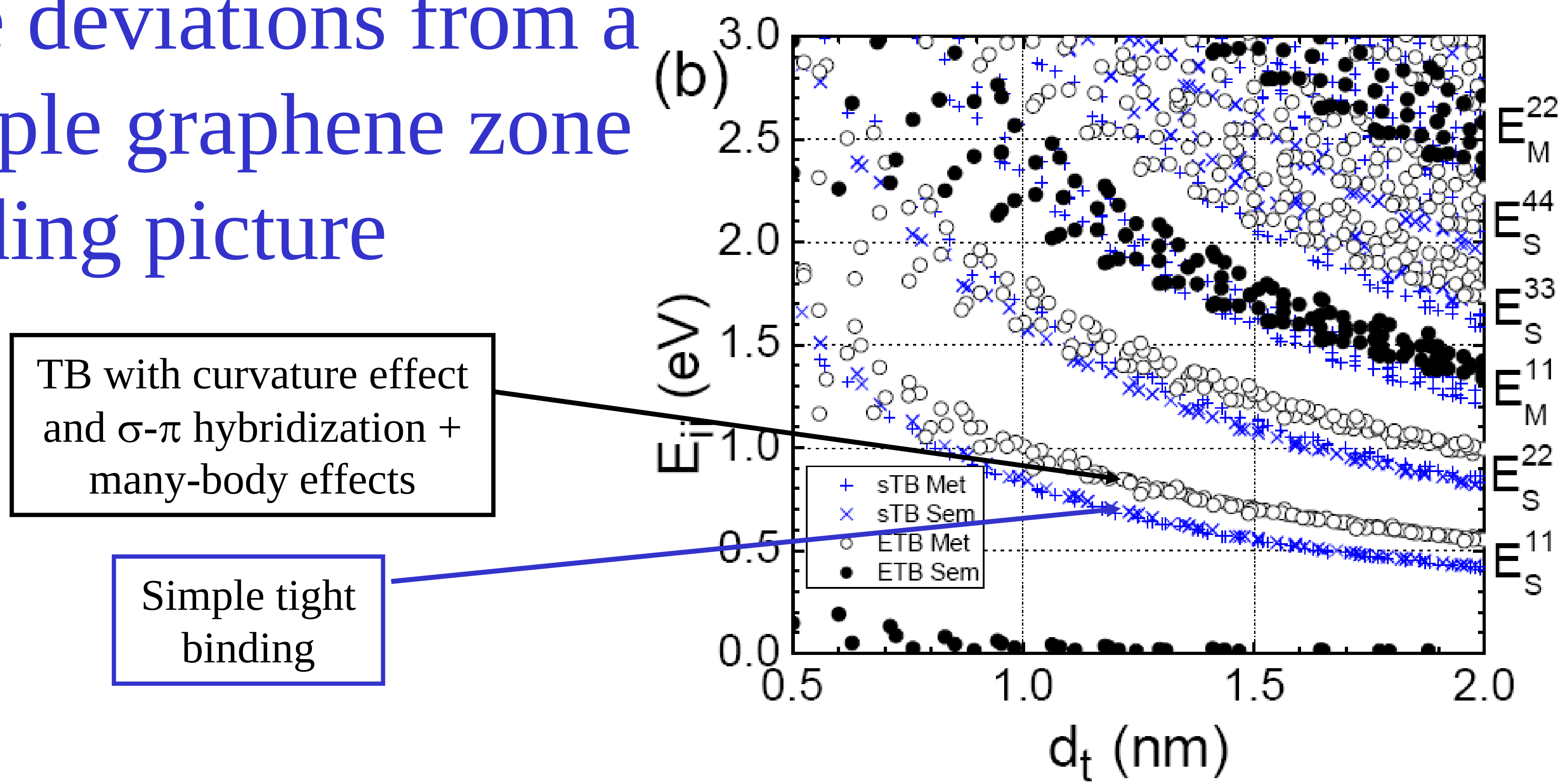
as a function of carbon nanotube diameter d_t

Proposed by H. Kataura in 1999, considering first neighbour π-only TB model

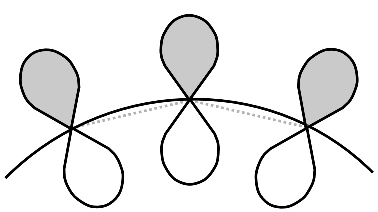




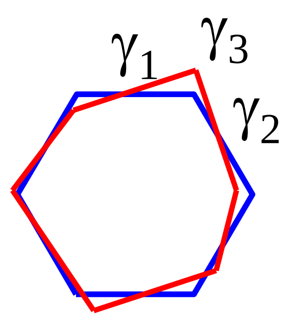
The deviations from a simple graphene zone folding picture



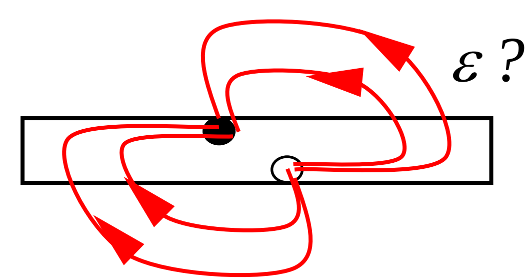
σ-π hybridization



Lattice distortion



e-e and e-h interaction



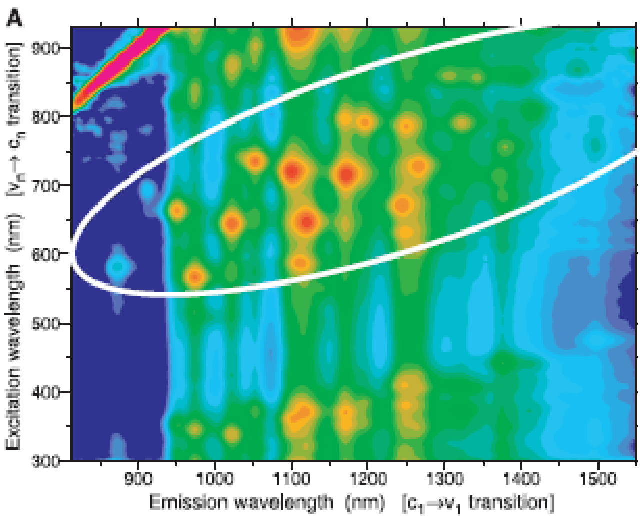
As shown by the ratio problem...

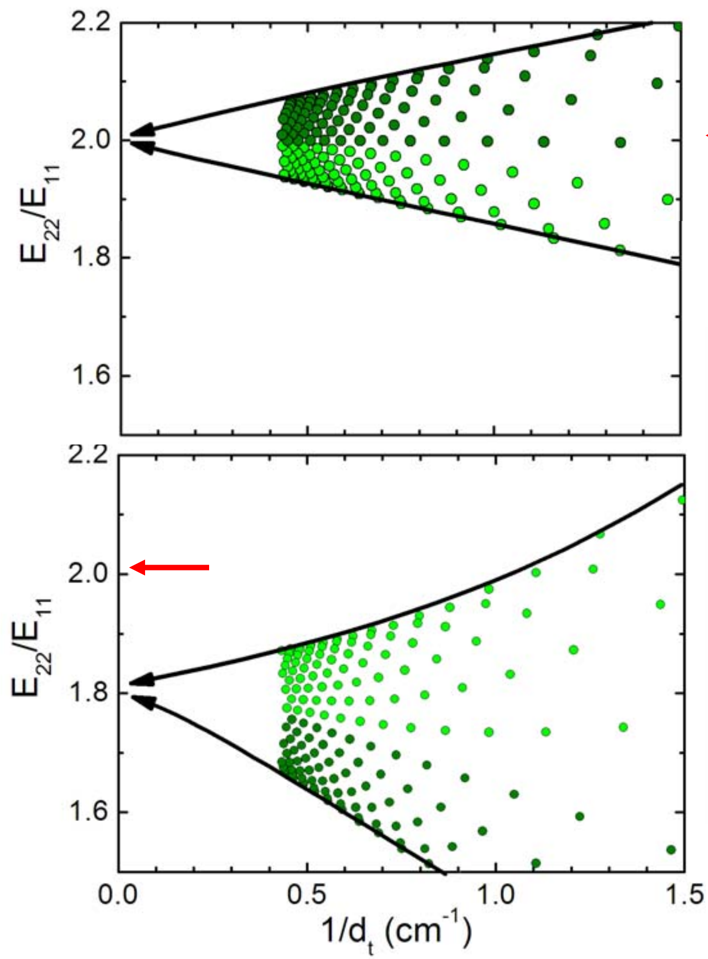
The ratio problem for E_{22}^{S} and E_{11}^{S}

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

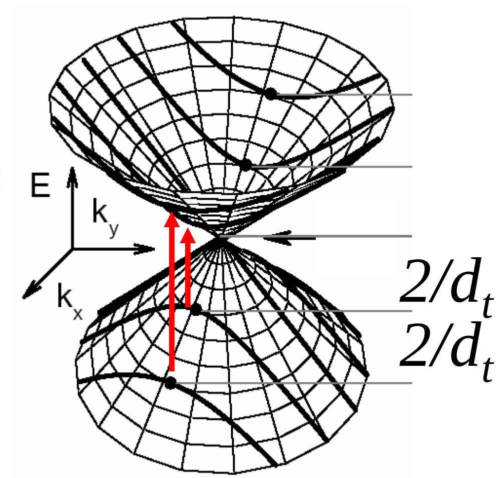
From EPL –

Bachilo et all. Science 298, 2361(2002)



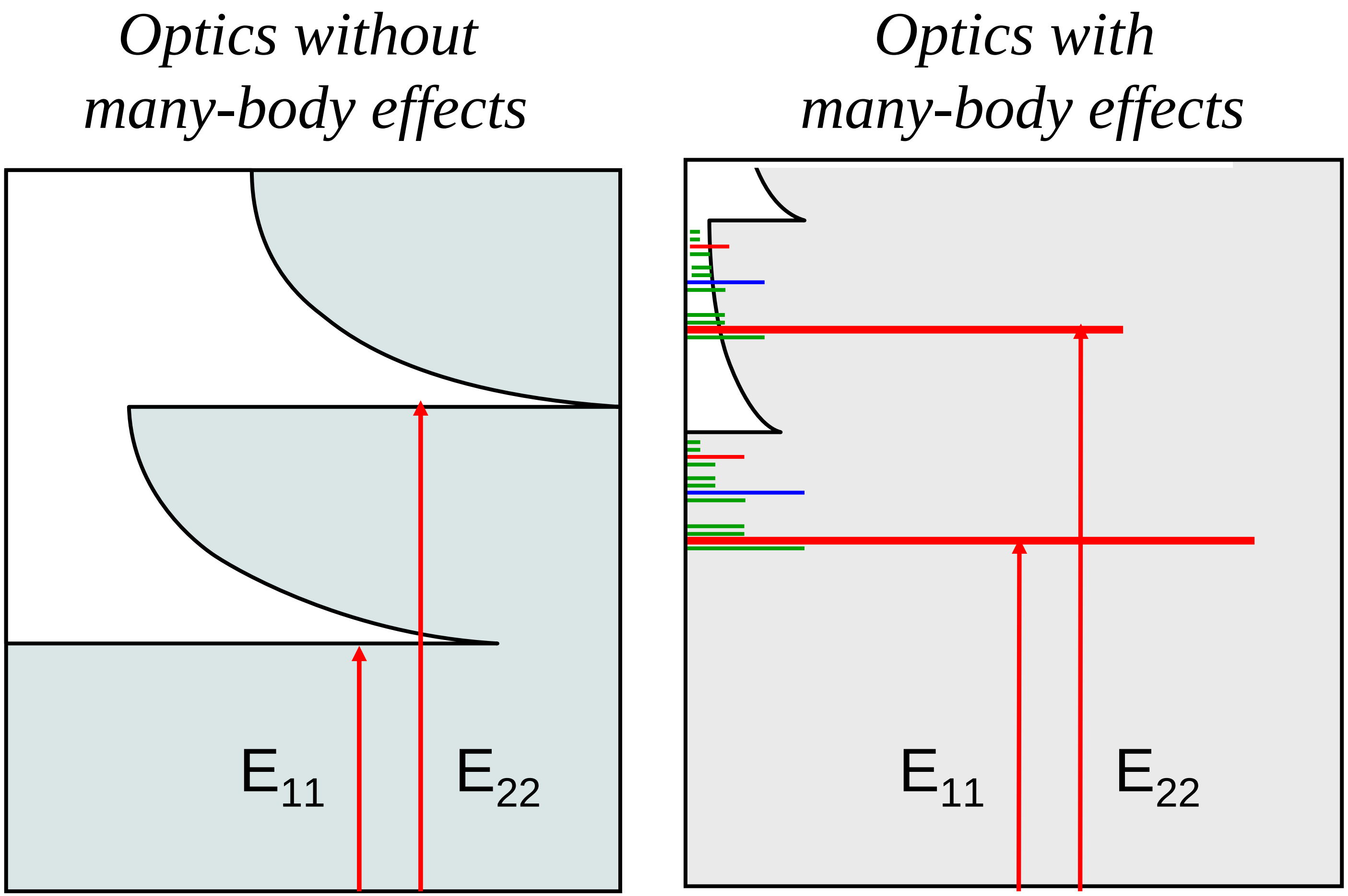


For a linear dispersion $E_{22}^{S} / E_{11}^{S} = 2$



Why do we have the ratio problem?

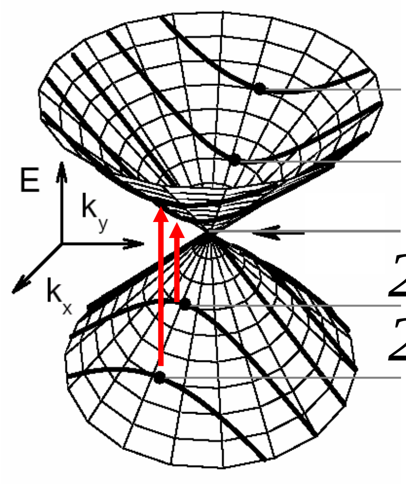
Why do we have the ration problem?



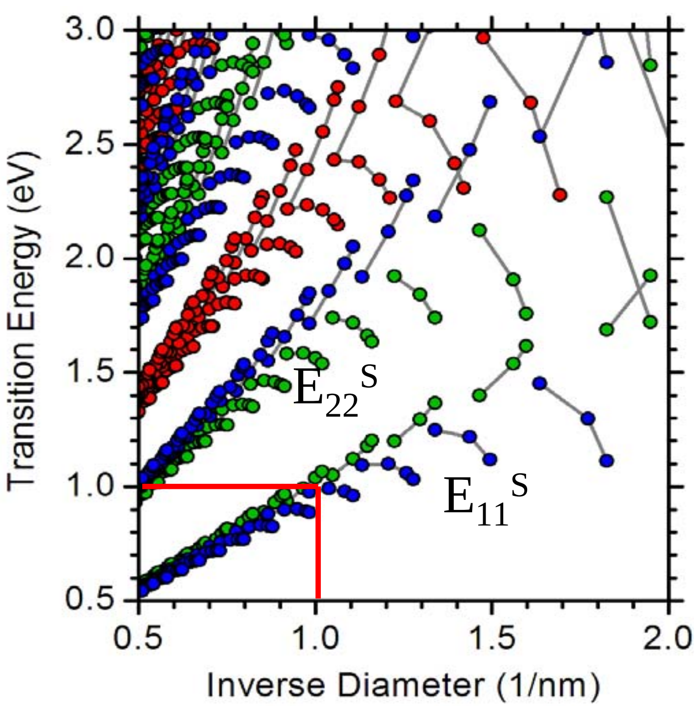
e-e attraction plus e-h repulsion gives rise to a net blueshift

How is the big picture?

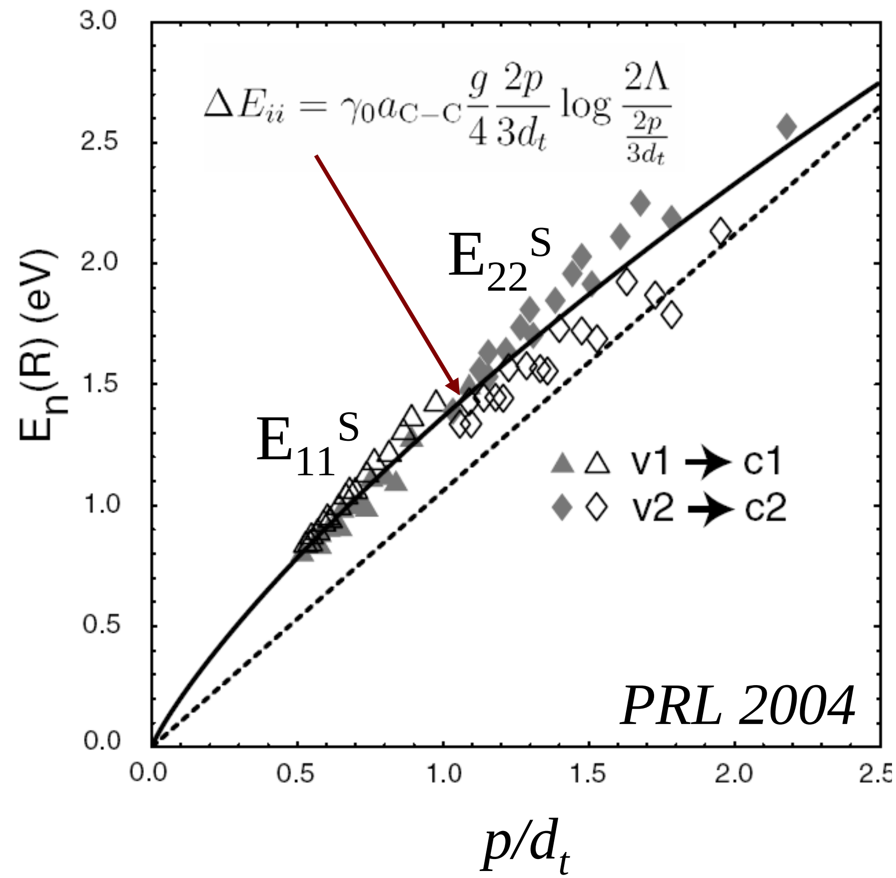
The big picture: E_{ii} s obey a scaling law



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

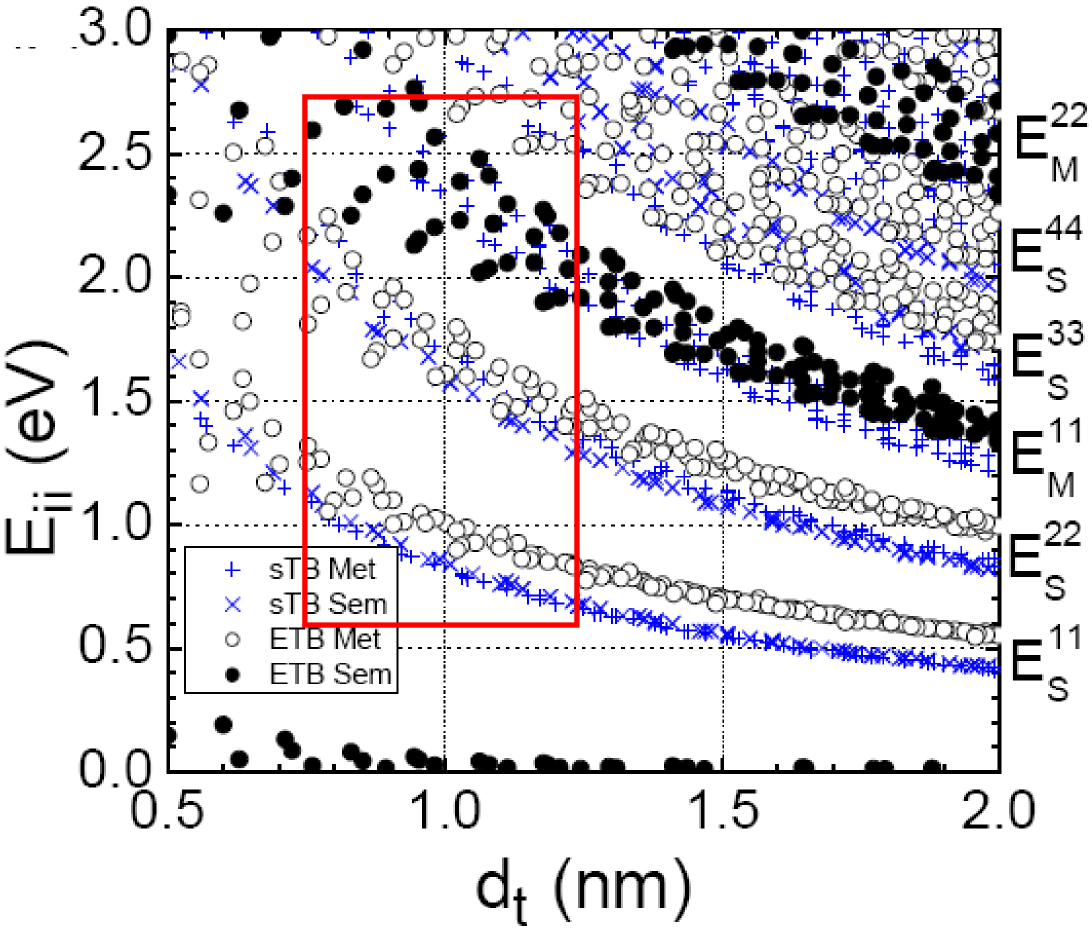


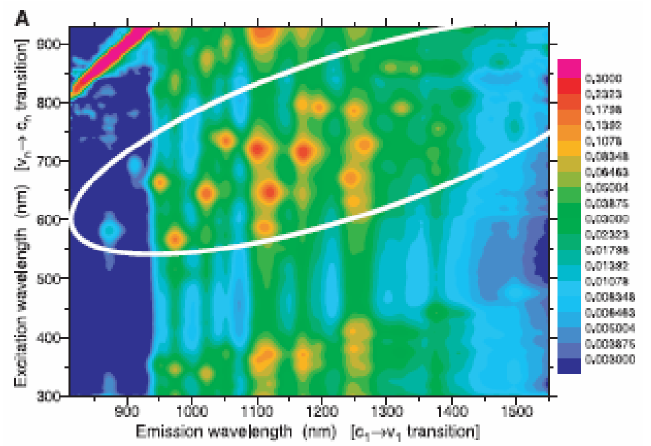
E_{11}^S and E_{22}^S follow a single scaling law when plotted as a function of p/d_t



p = 1, 2, 3, 4, 5… for E_{11}^S, E_{22}^S, E_{11}^M, E_{33}^S, E_{44}^S…

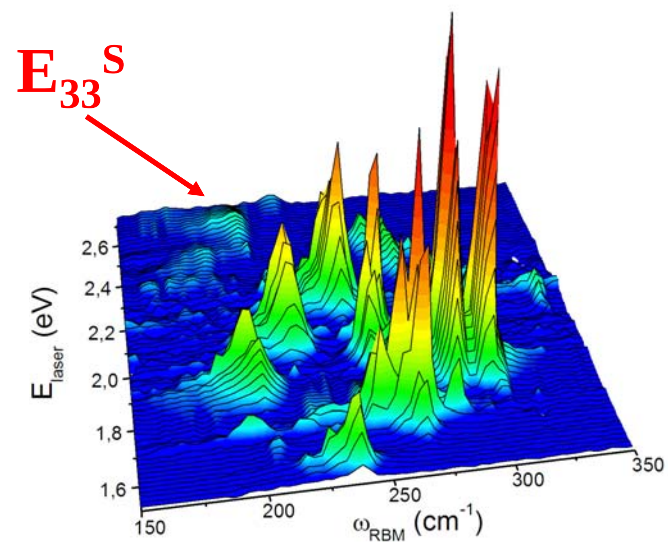
All the physics is for $0.7 < d_t < 1.3$nm and $0.6 < E_{ii} < 2.7$eV





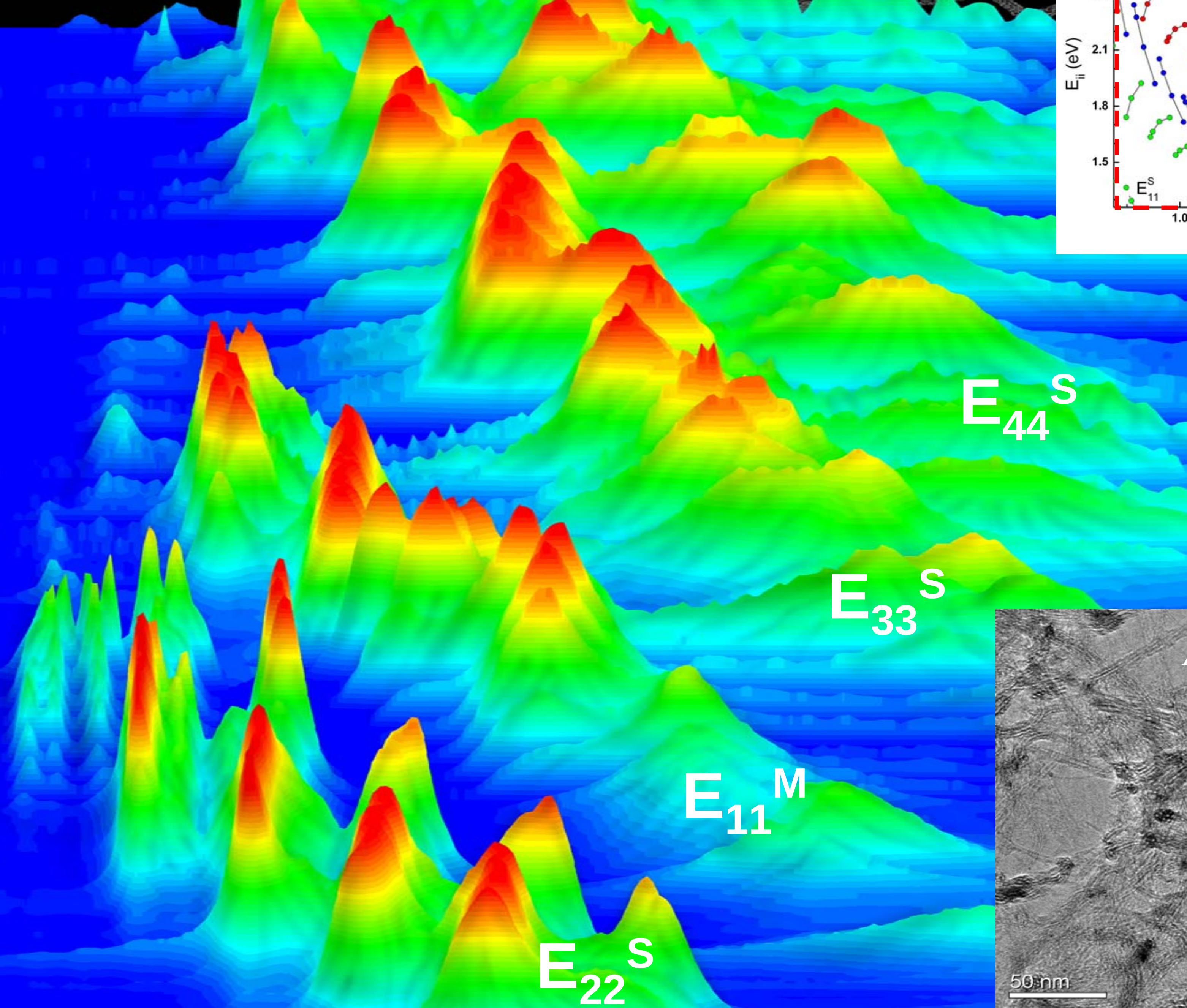
PL – Bachilo et al. Science **298**, 2361 (2002)

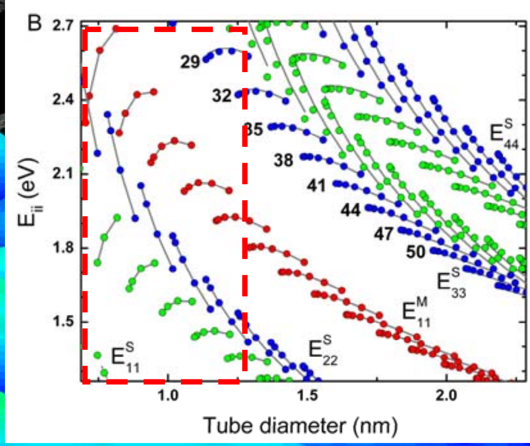
RRS – Fantini et al. PRL (2004)

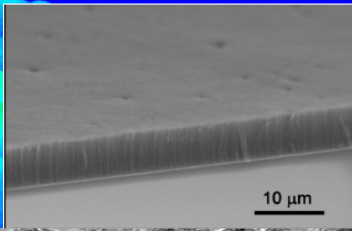


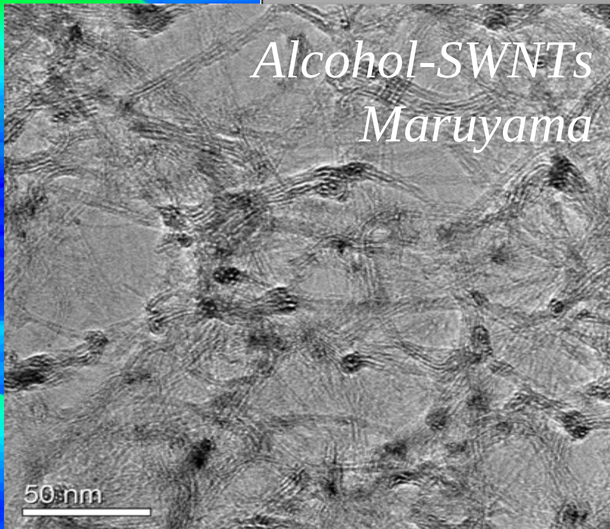
What about d_t > 1.3 nm ?
What about higher E_{ii} ?

The RRS of alcohol SWNTs

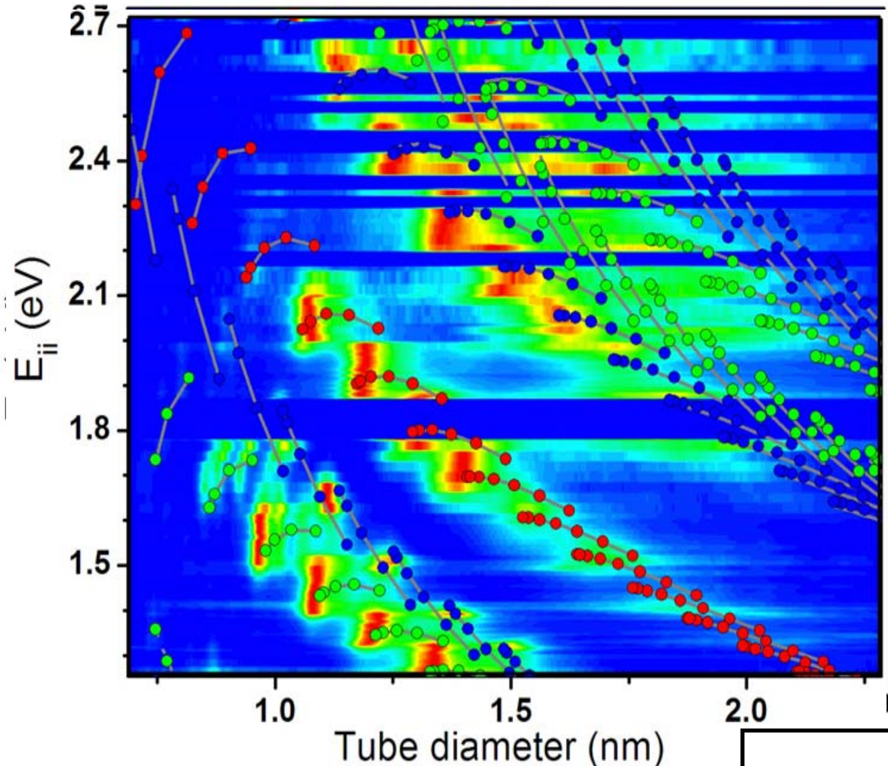


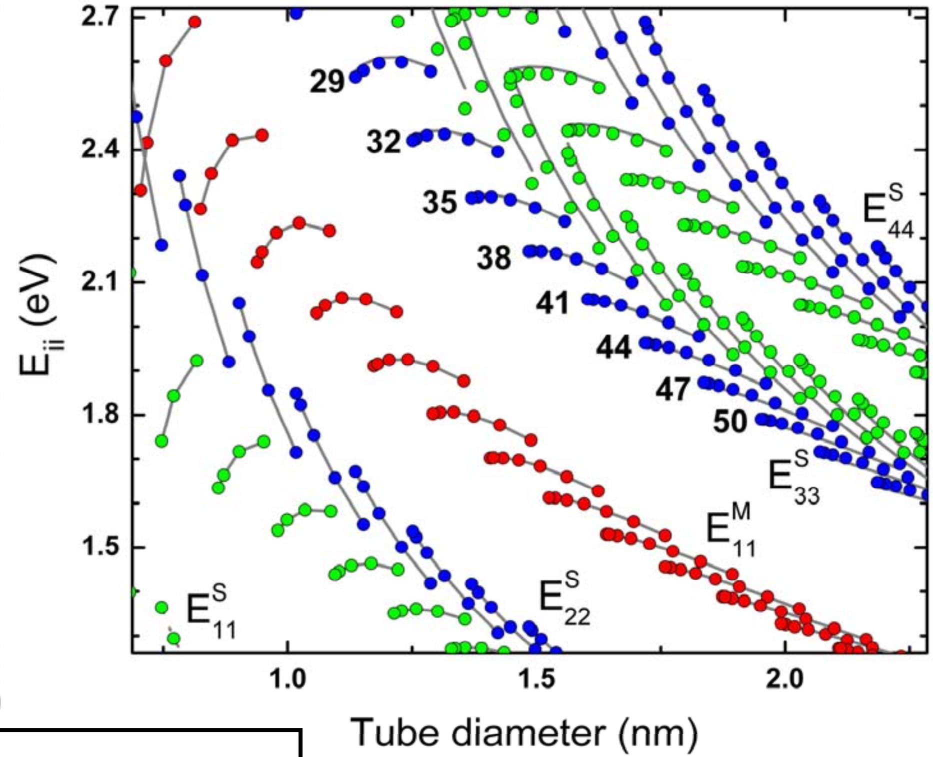






RRS on alcohol CVD SWNTs



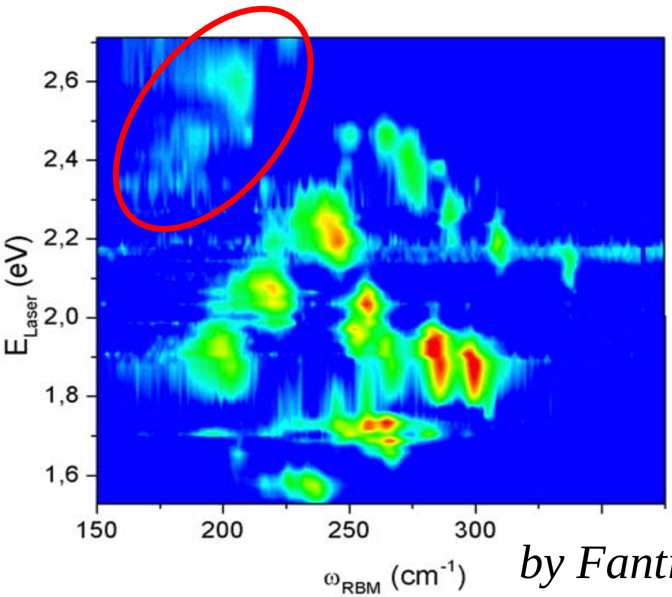


$$\omega_{\mathrm{RBM}} = \frac{219}{d_t} + 15$$

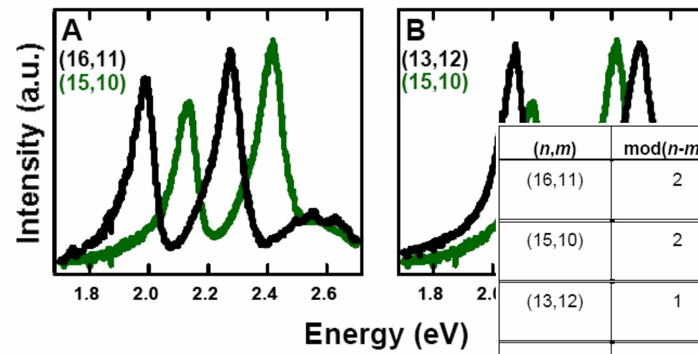
Measurements over a broad energy (1.26 to 2.71eV) and diameter (0.7 to 2.3nm) range

Now we have to analise the E_{ii} and ω_{RBM} !

Good agreement with published E_{22}^S , E_{33}^S and E_{44}^S

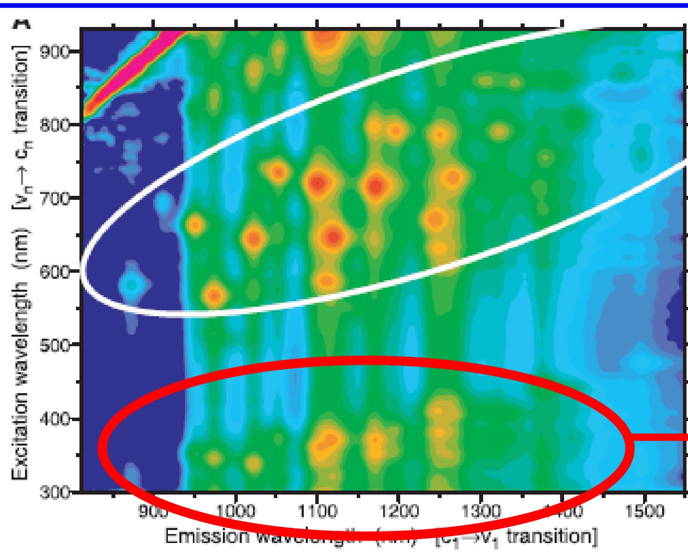


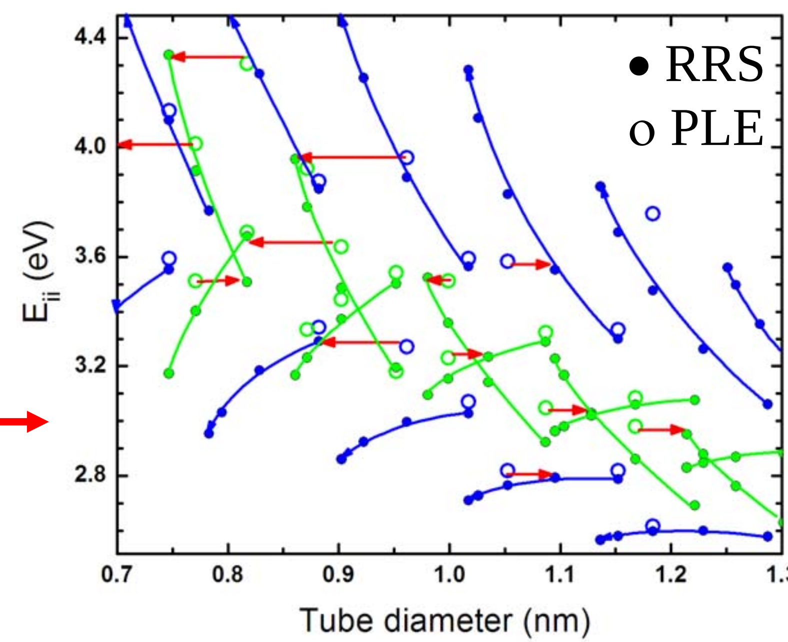
RRS
by Fantini et al.



Rayleigh by Sfeir et al.

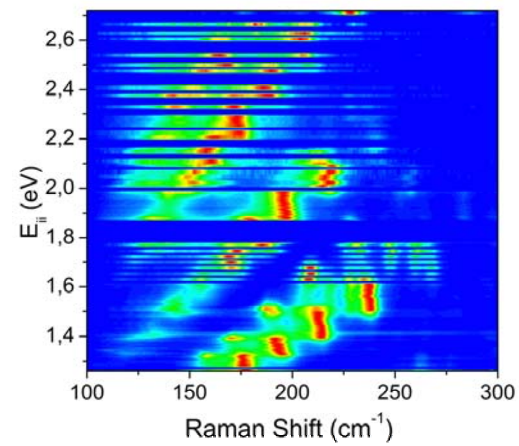
(n,m)	mod(n-m, 3)	d_t (nm)	θ (°)	Transition	E_{ii} (eV)
(16,11)	2	1.83	23.9	S_{33}	2.00
				S_{44}	2.30
(15,10)	2	1.71	23.4	S_{33}	2.15
				S_{44}	2.44
(13,12)	1	1.70	28.7	S_{33}	2.09
				S_{44}	2.52
(13,11)	2	1.63	27.2	S_{33}	2.19
				S_{44}	2.56
(10,10)	0	1.36	30	M_{11}	1.93
(11,8)	0	1.30	24.8	$M_{11(-)}$	1.93
				$M_{11(+)}$	2.02
(20,14)	0	2.35	24.2	$M_{22(-)}$	2.22
				$M_{22(+)}$	2.36

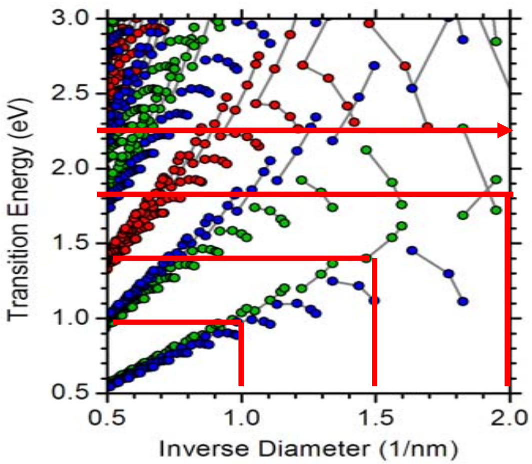


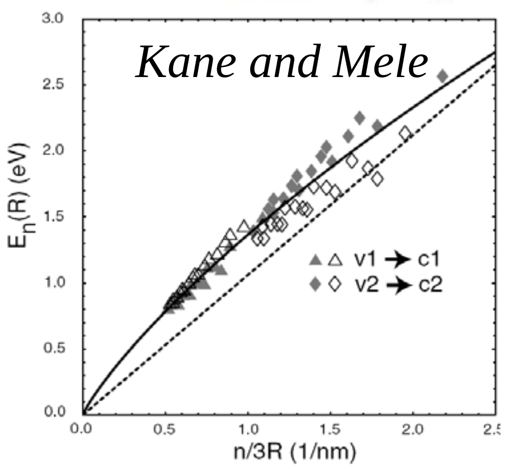


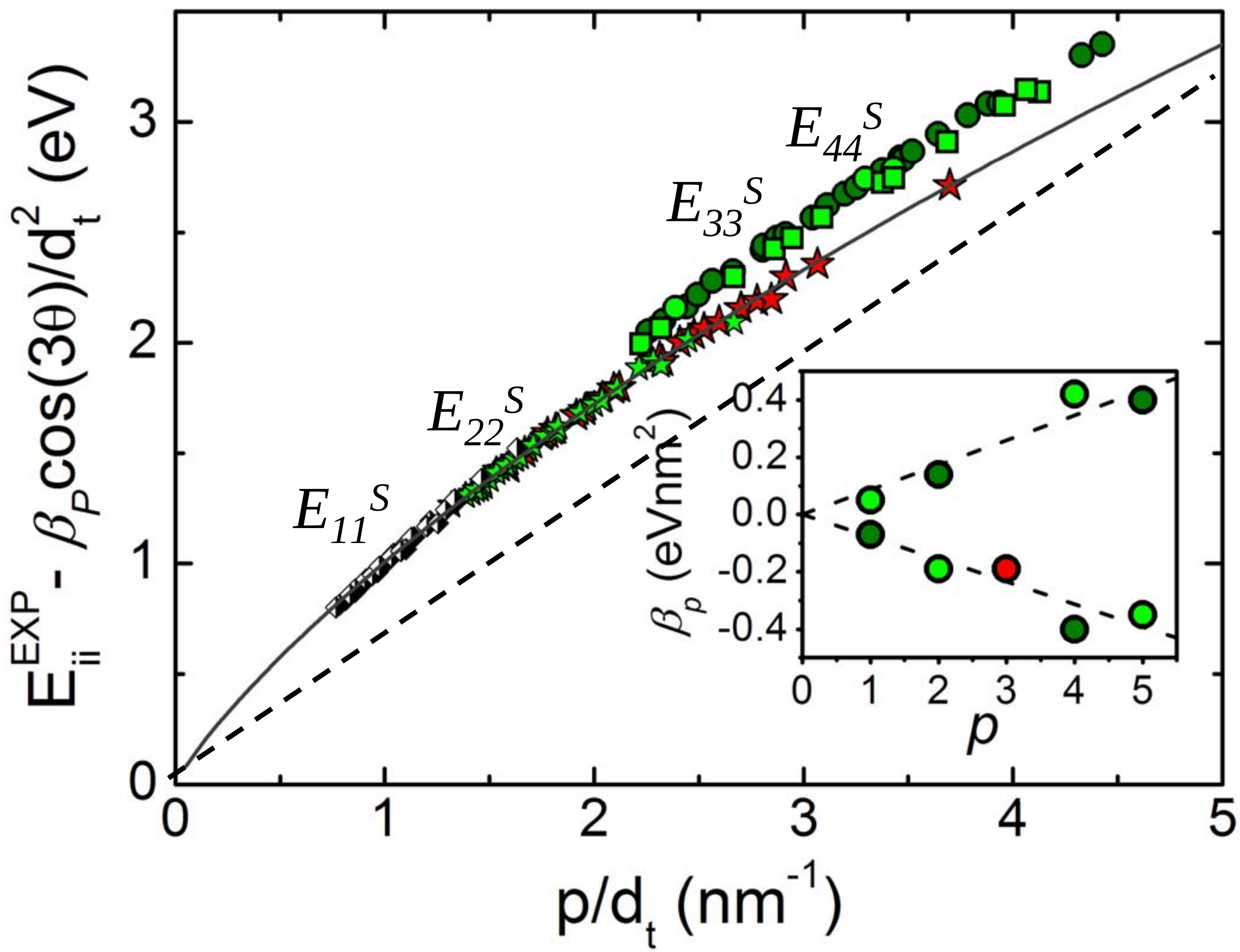
Bachilo et all. Science 298, 2361(2002)

The anomalous scaling law for the higher optical transitions



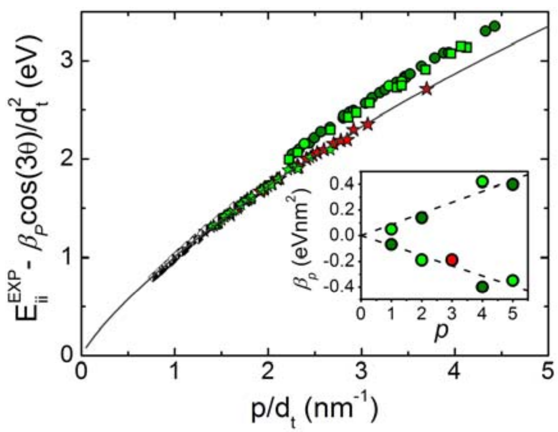


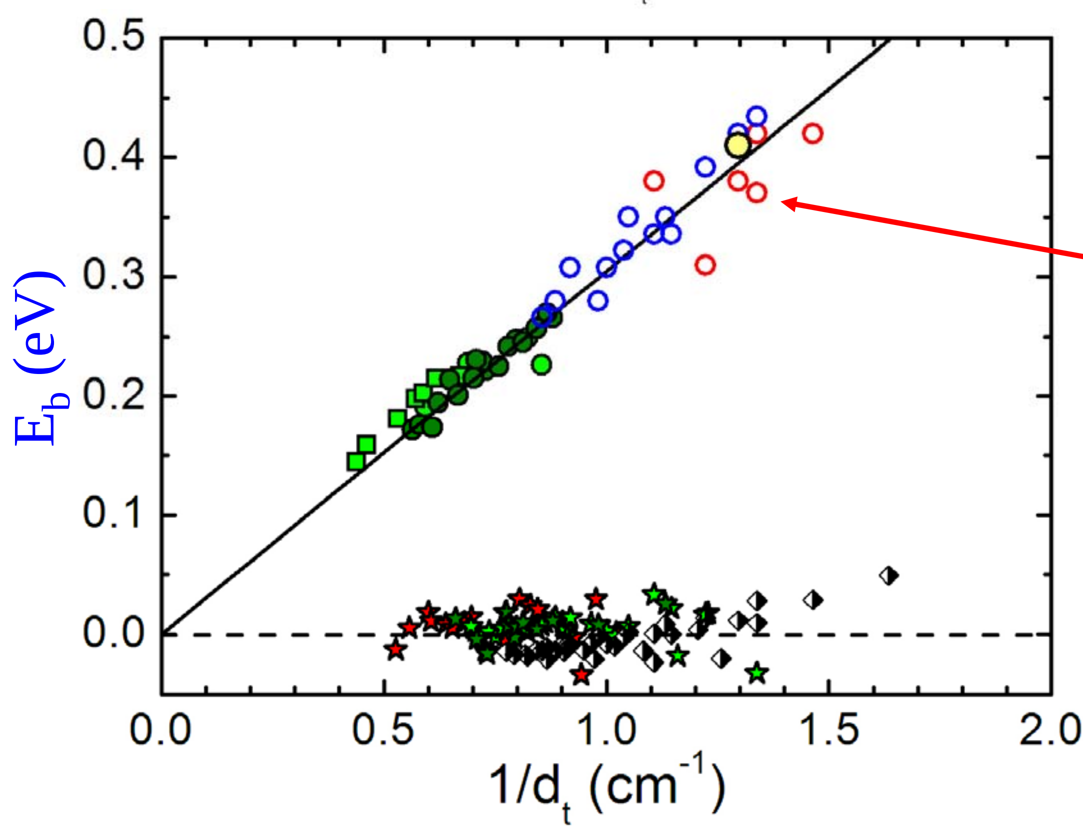




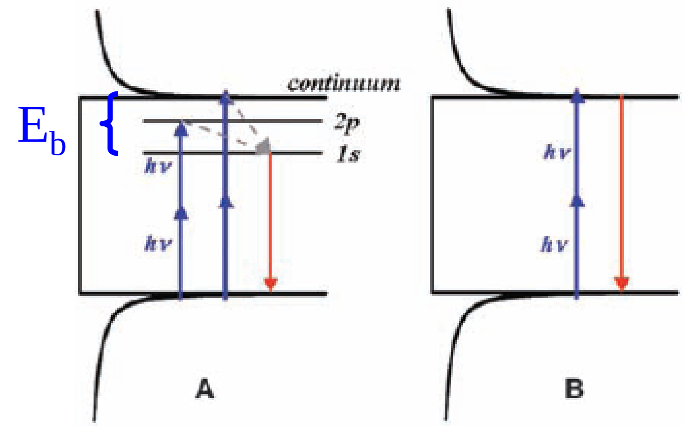
p = 1, 2, 3, 4, 5… for E^S_{11}, E^S_{22}, E^M_{11}, E^S_{33}, E^S_{44}…

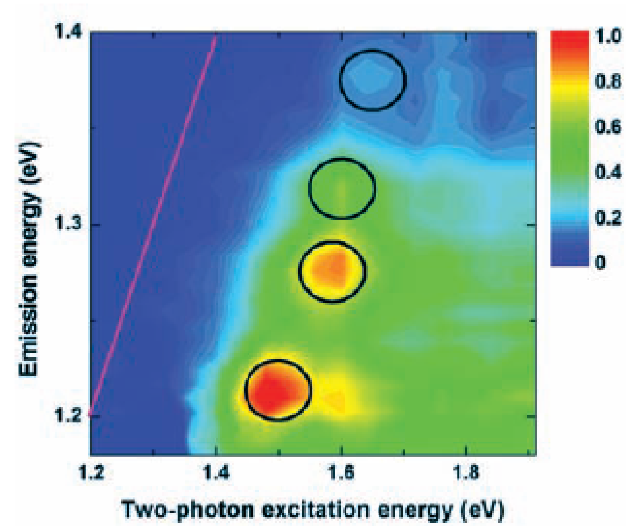
The difference between the scaling laws





The two photons experiment...





Wang et al. Science 308, 838 (2005)

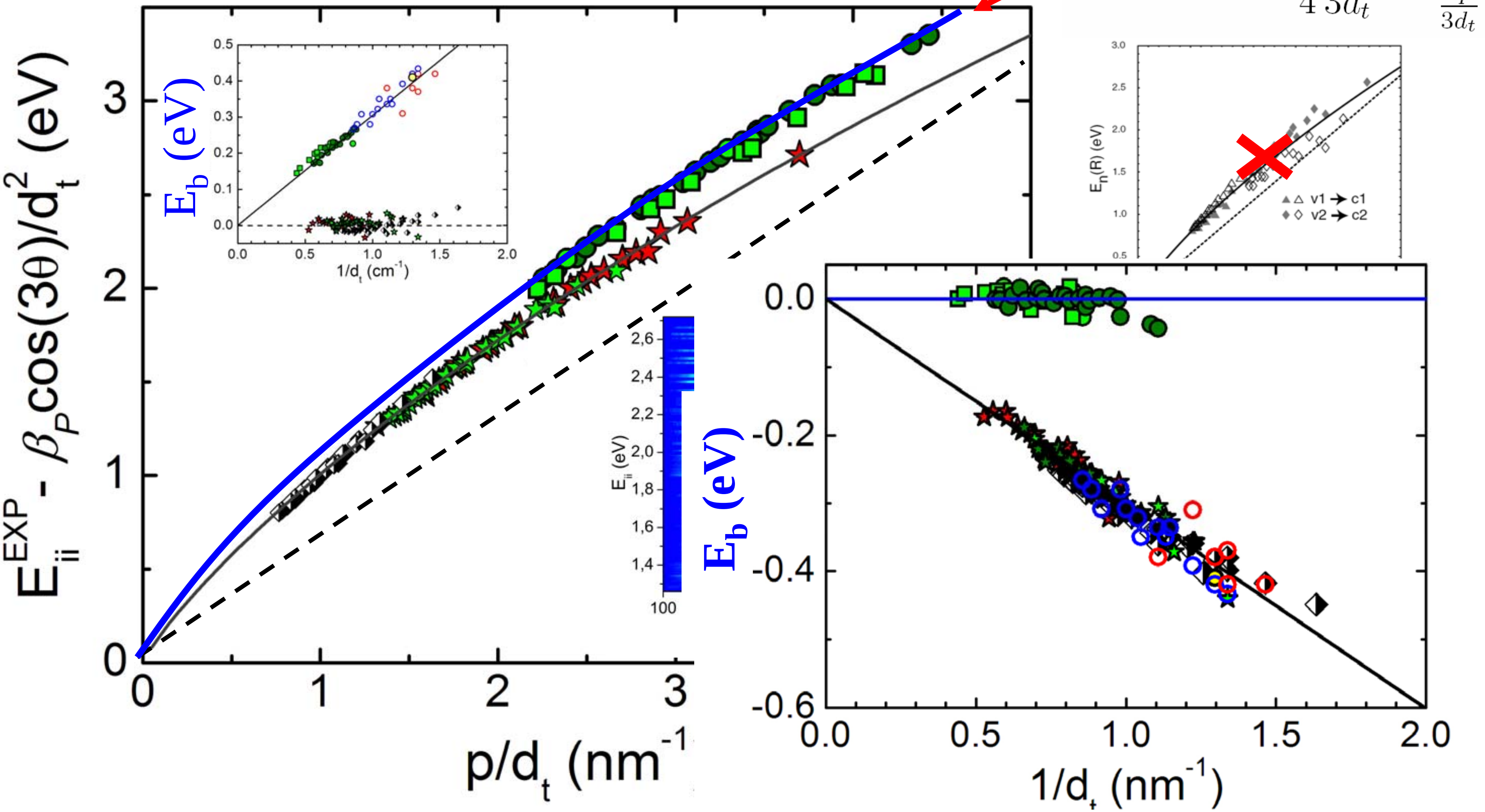
Maultzsch et al. PRB72, 24402(R) (2005)

● *Ma et al. JPCB109,15671 (2005)*

Band-to-band vs excitons?

Kane and Mele

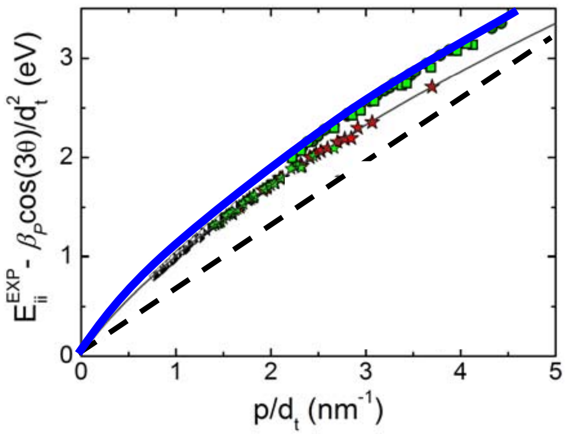
$$\Delta E_{ii} = \gamma_0 a_{\mathrm{C-C}} \frac{g}{4} \frac{2p}{3d_t} \log \frac{2\Lambda}{\frac{2p}{3d_t}}$$

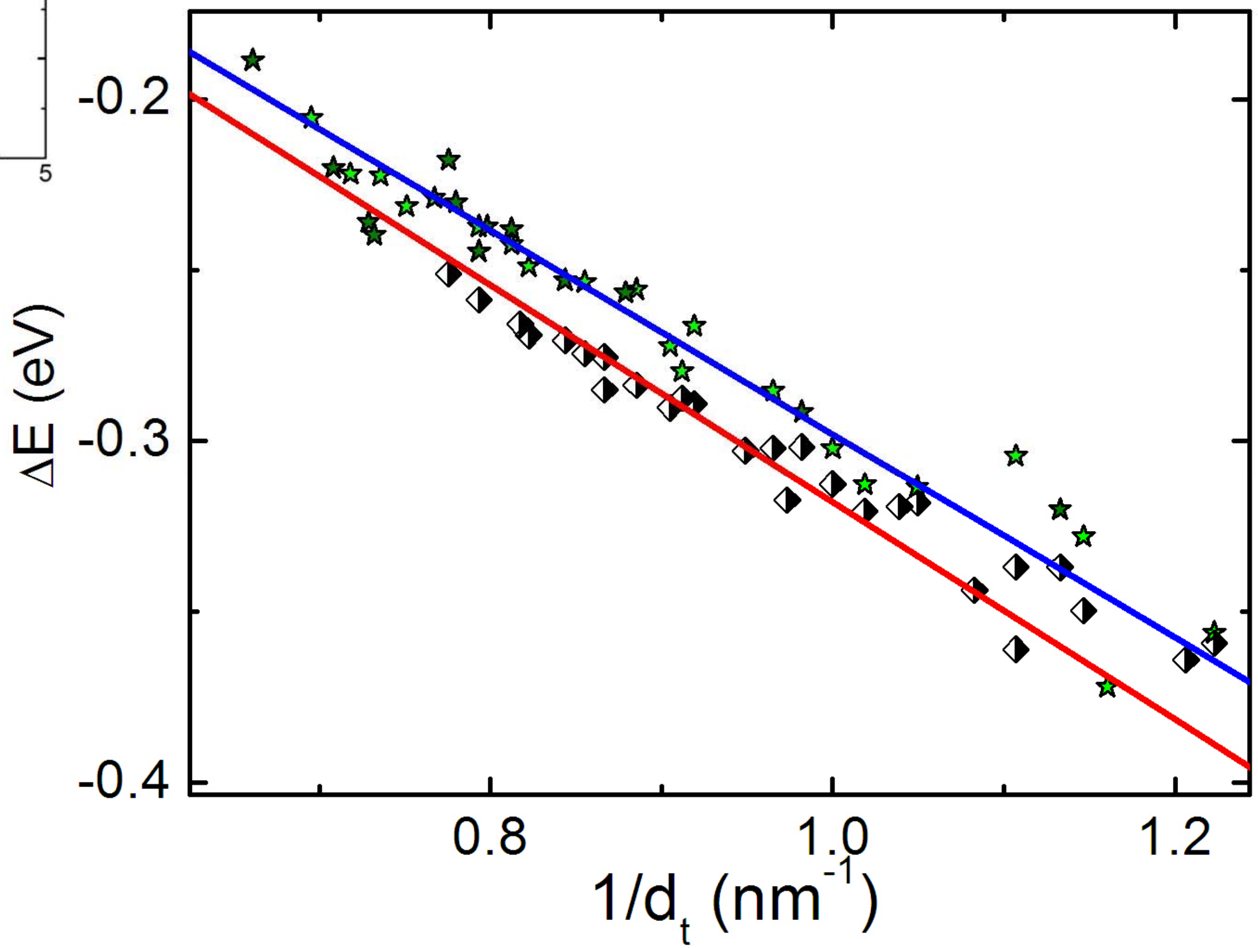


Exciton binding energy: E_b = -0.305/d_t (eV)

E_{11}^S and E_{22}^S Excitons **E_{33}^S and E_{44}^S free e-h pairs?**

Measuring the E_b energy

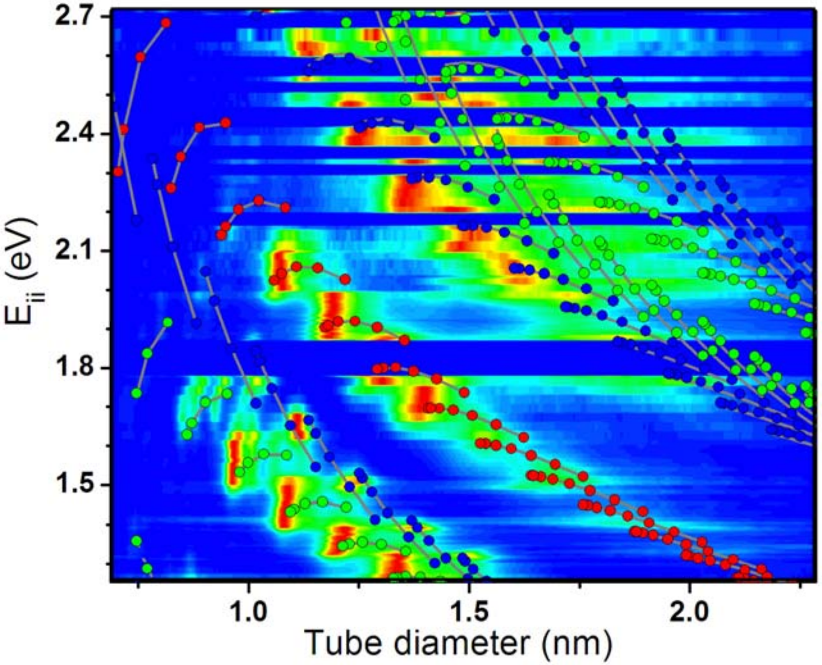


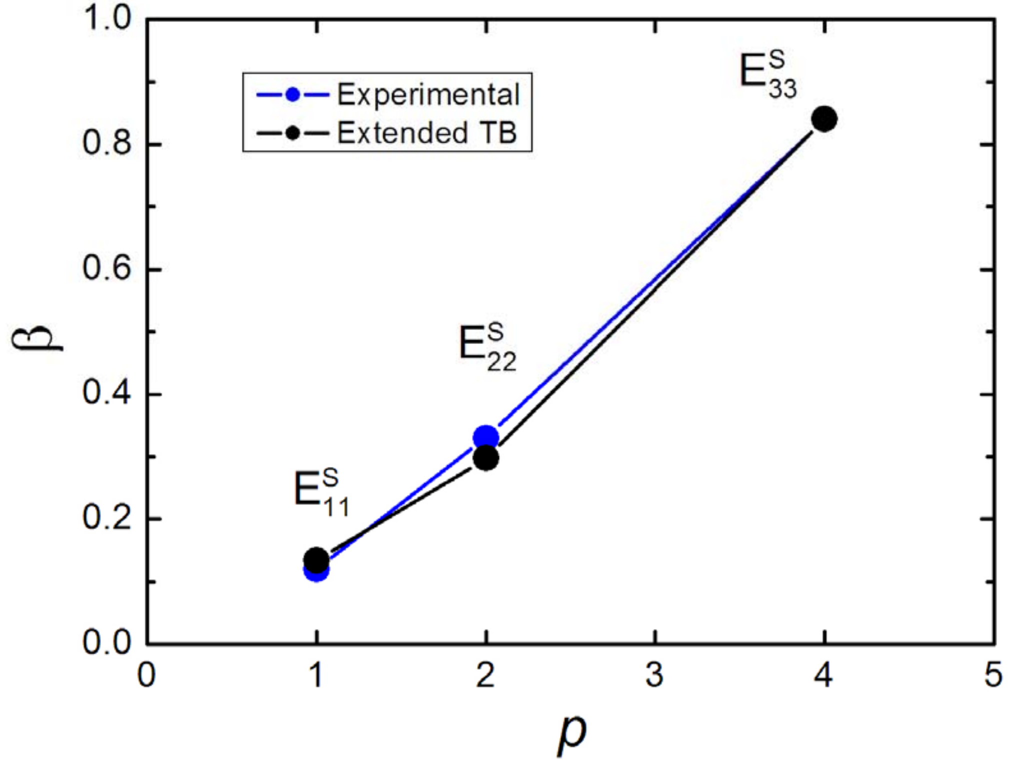


Exciton binding energy: E_{b11} = -0.318/d_t (eV)

E_{b22} = -0.298/d_t (eV)

Chirality dependence of E_{ii}



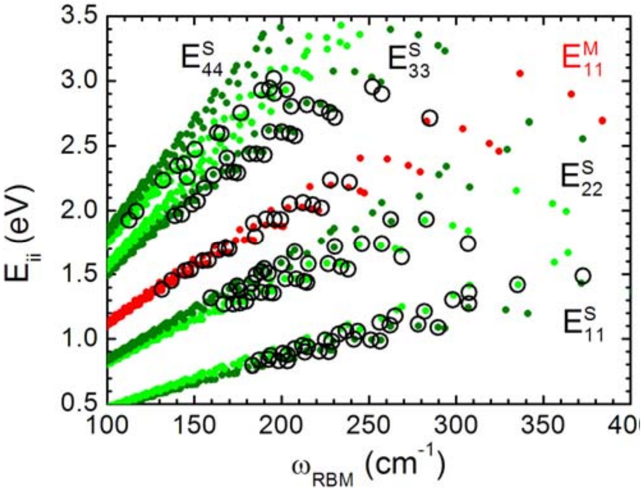


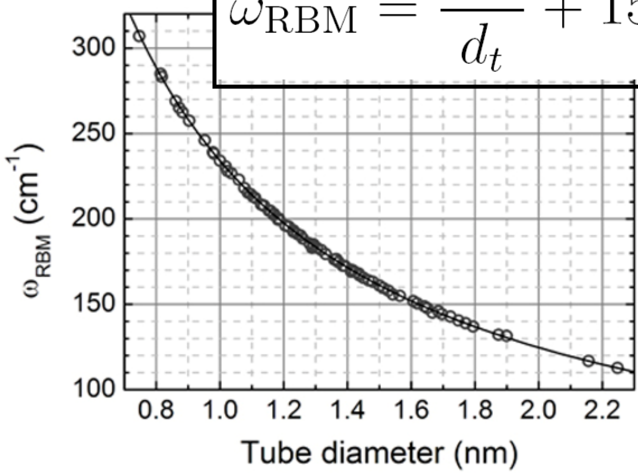
Similar to prediction by the extended tight binding (ETB) within experimental accuracy (~ ±30meV)

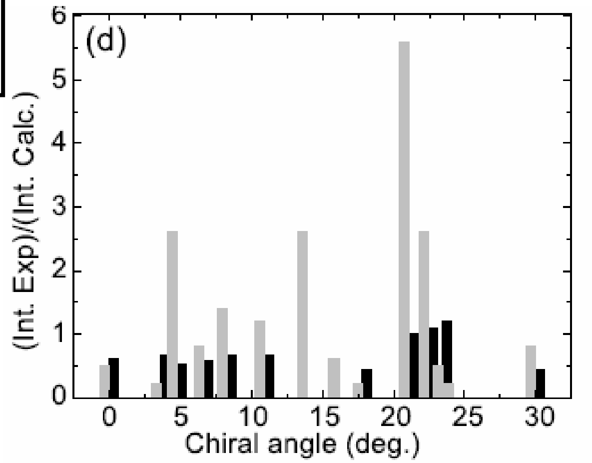
Summary

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

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





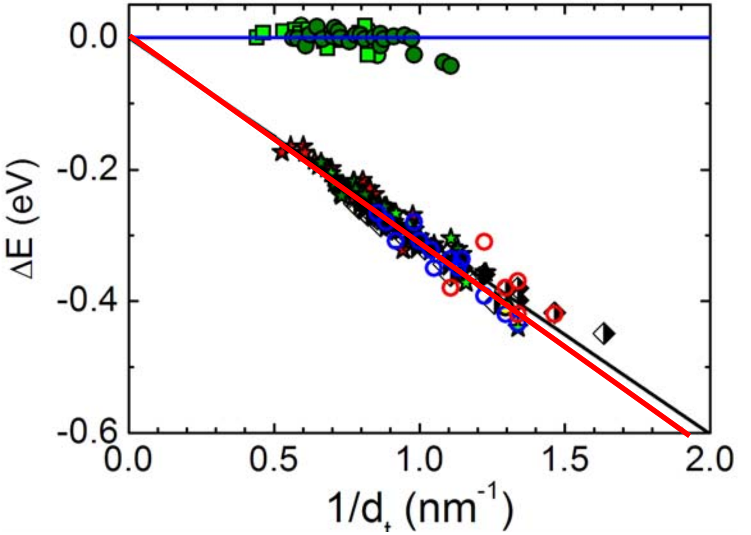


2 – E_{11}^{S} and E_{22}^{S} → excitons

3 – E_{33}^{S} and E_{44}^{S} → band-to-band?

4 – Exciton binding energy:

$$\mathbf{E_b = -0.305/d_t}$$



Acknowledgement

- **M.A.Pimenta, C.Fantini, P.T.Araujo, I.O.Maciel, L. G. Cancado (UFMG) –** RSS
- **H.B.Ribeiro and F.Plentz (UFMG) –** (PLE)
- **L.O.Ladeira, R. G. Lacerda, A. Ferlauto (UFMG) –** (Samples)
- **A. P. Santos and C. A. Furtado (CDTN) –** (Chemistry)
- **S. K. Doorn (LANL) –** (RRS)
- **M. S. Dresselhaus, G. Dresselhaus, S. G. Chou, Ge. G. Samsonidze (MIT) –** (exp and theory)
- **R. Saito**, **J. Jiang , A. Grueneis, N. Kobayashi, Y.Oyama (Tohoku) –** (theory)
- **H. Chacham (UFMG), R. B. Capaz (UFRJ), S. G. Louie (Berkeley) –** (Theory)
- **S. Maruyama (TU), M. Strano (UI), D. Resasco (UO). A.M.Rao –** (samples)