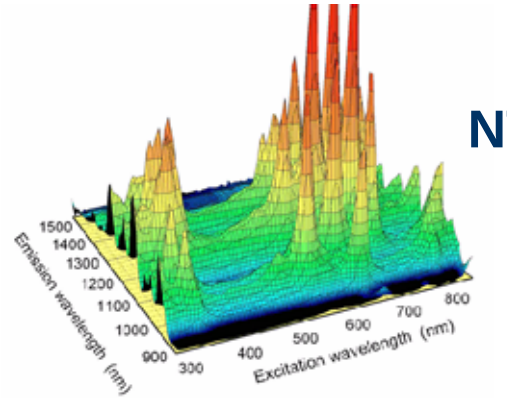
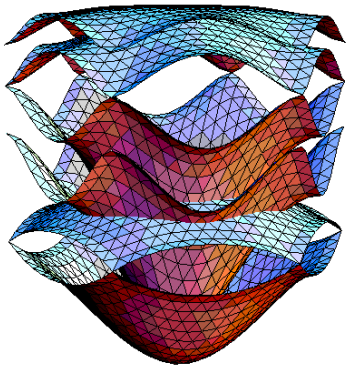


NT06: 7th International Conference on the Science and Application of Nanotubes, June 18-23, 2006 Nagano, JAPAN



Chirality and energy dependence of first and second order resonance Raman intensity



R. Saito (Tohoku Univ. CREST JST)
J. Jiang, K. Sato, Y. Oyama, J.S. Park, G. S. Chou, G. Samsonidze,
A. Jorio, M. A. Pimenta, A. G. Souza-Filho,
G. Dresselhaus, M.S. Dresselhaus



Dept. Physics, Tohoku Universityand CREST JST
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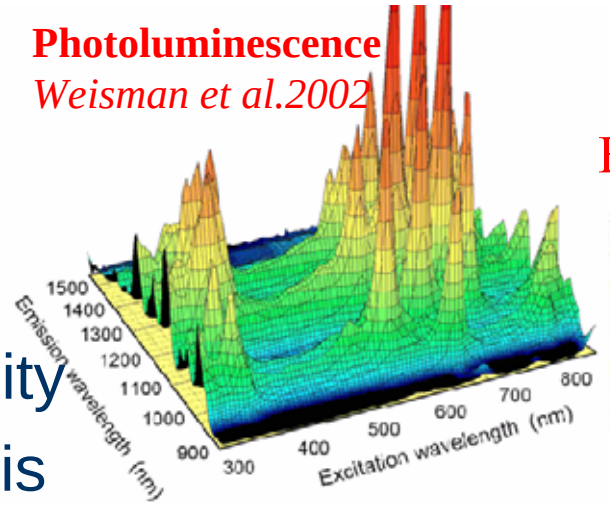
東北大学
TOHOKU UNIVERSITY
JST 科学技術振興機構 Japan Science and Technology Agency

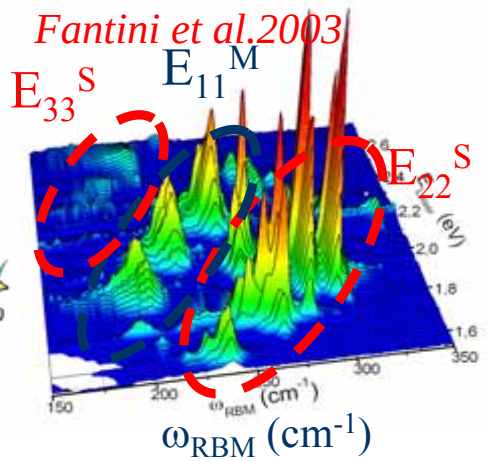
Intensity calculation of PL and Raman spectra
-- *Not all SWNTs are bright.* --

- Relative Raman intensity
  - (n,m) dependence
  - RBM,G, D, G'-band
- Photoluminescence Intensity
  - (n,m) population analysis
  - phonon associated relaxation process
  - Exciton based phenomena

Photoluminescence
Weisman et al.2002

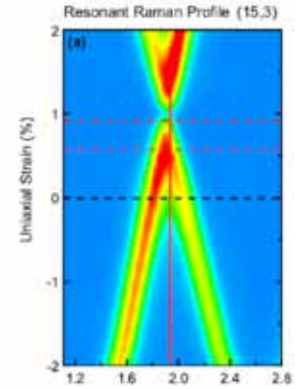


Resonance Raman
Fantini et al.2003

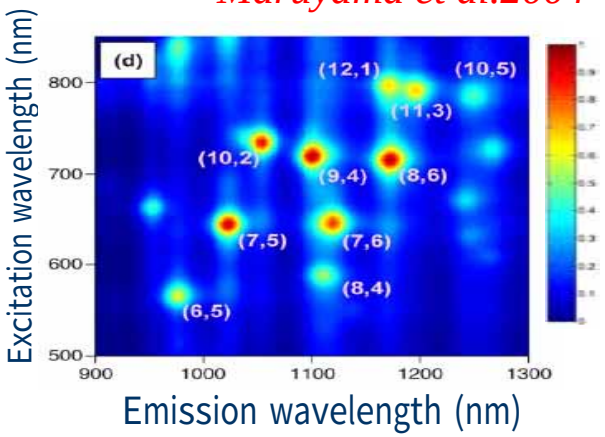


ω_{RBM} (cm^{-1})

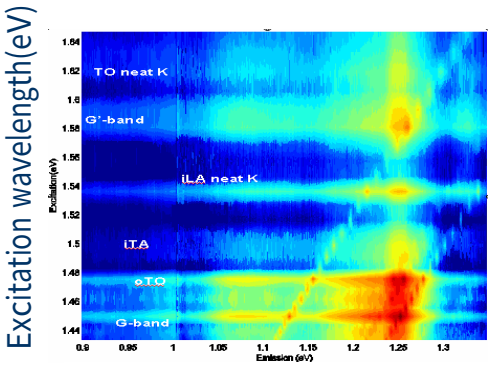
Pressure dependent Raman
A. Souza-Filho et al.2006



Type dependent PL
Maruyama et al.2004



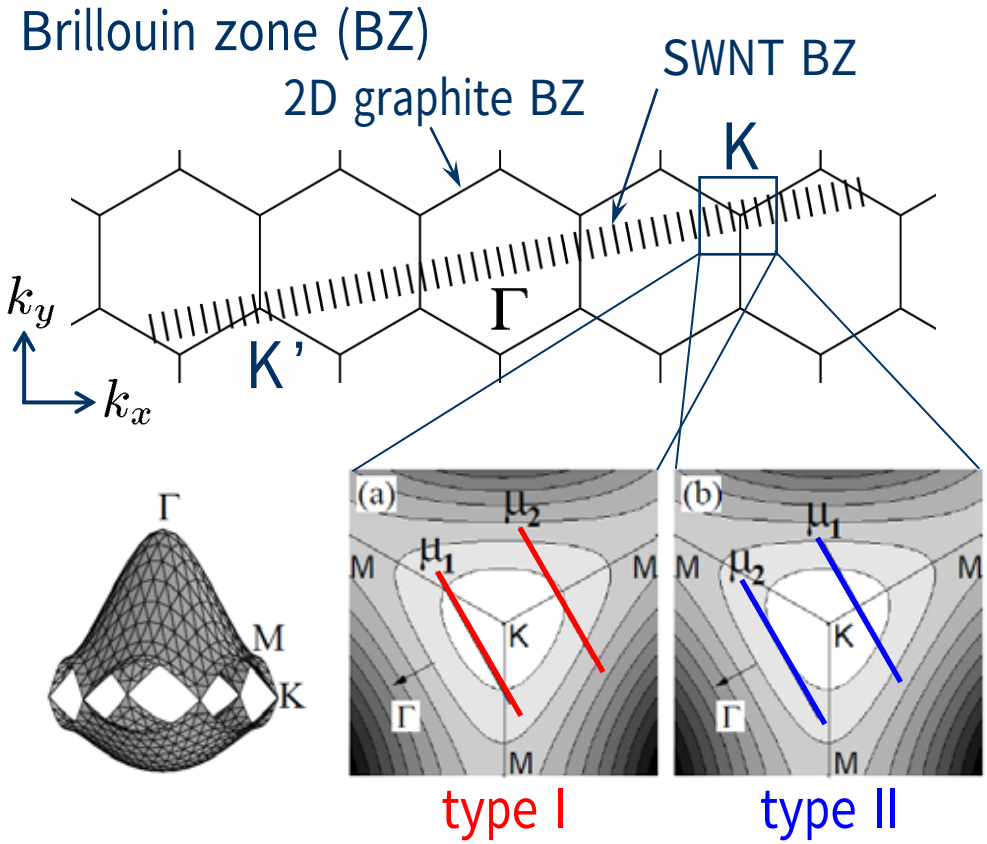
Phonon associated PL
S. G. Chou et al.2005

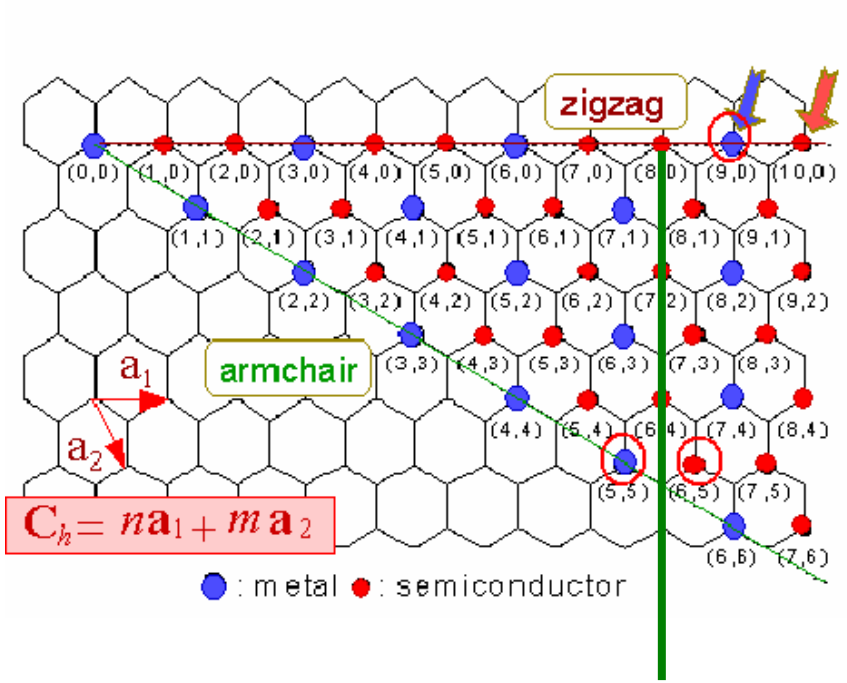


Emission wavelength (eV)

2n+m family in SWNT

R. Saito *et al.*, *Phys. Rev.* B, 72, 153413 (2005)





2n+m = const family

type I – type II separation

Family

mod (2n+m, 3) =
- 0 : metal
- 1 : type I SC
- 2 : type II SC

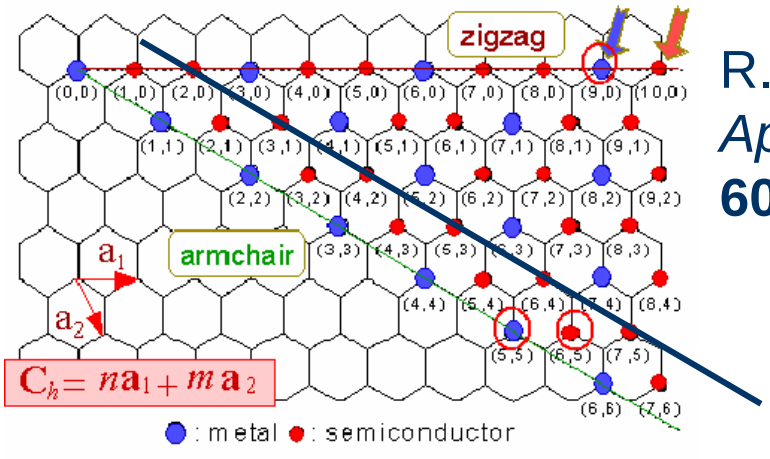
(example)

(8,0), (7,2), (6,4)

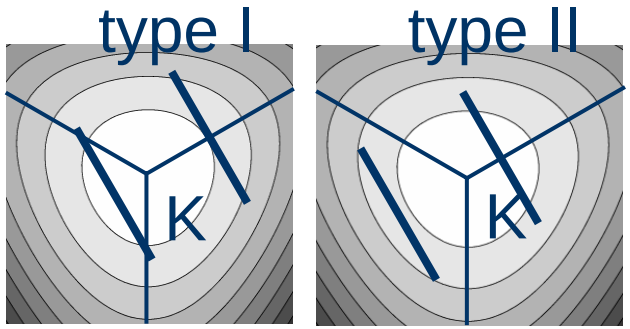
→ 2n+m = 16 type I family

2n+m and *n-m* family in SWNT

n - m = 2

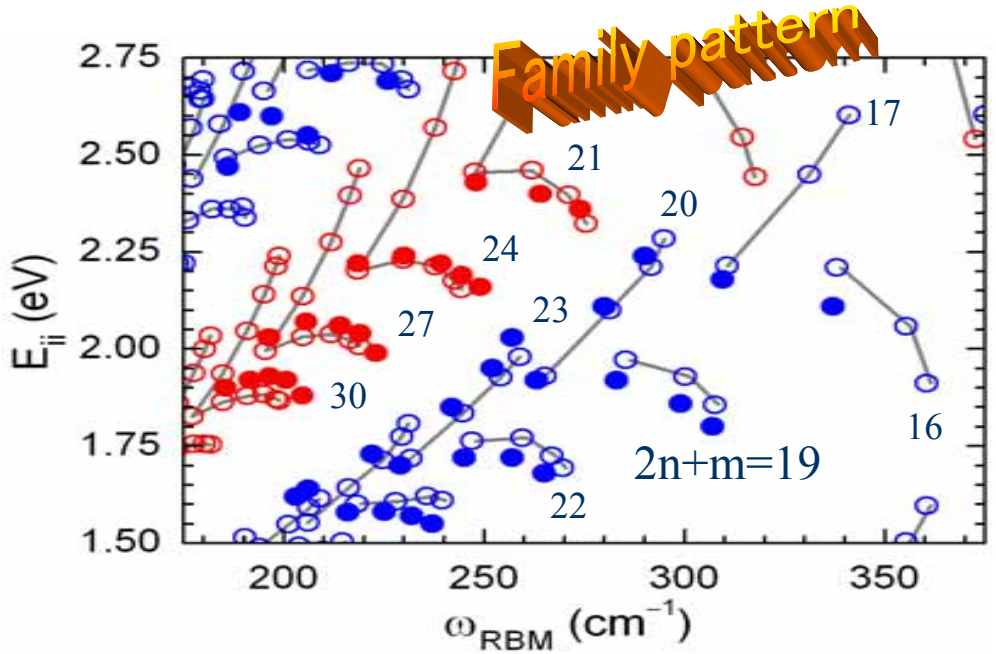


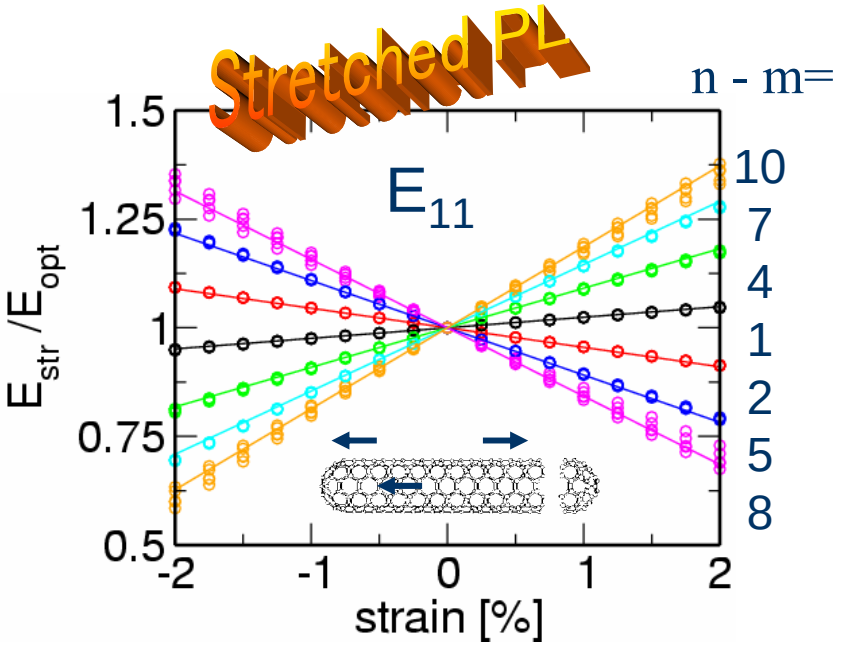
R. Saito *et al.*, *Appl. Phys. Lett.* **60**, 2204 (1992)



$$\mathrm{mod}(2n+m,3) = 1 \qquad 2$$

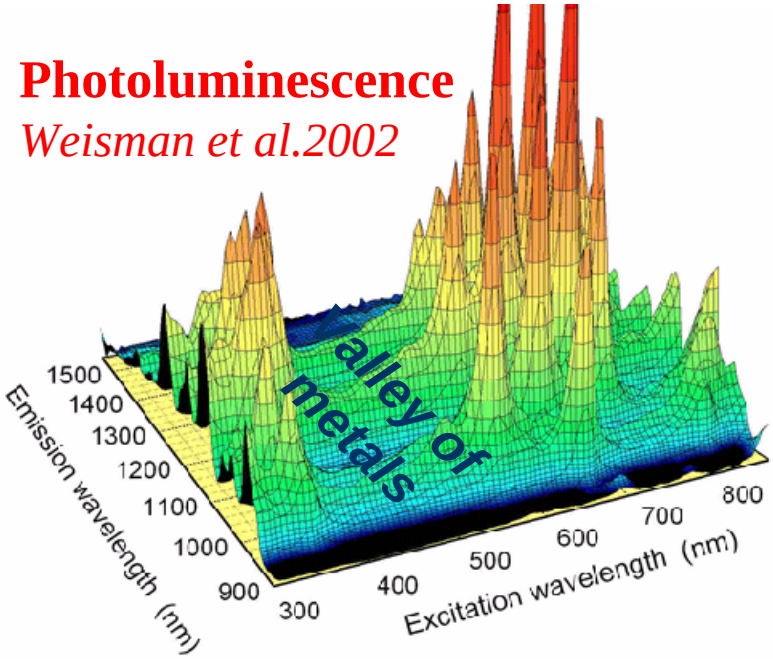
$$\mathrm{mod}(n-m,3) = 2 \qquad 1$$



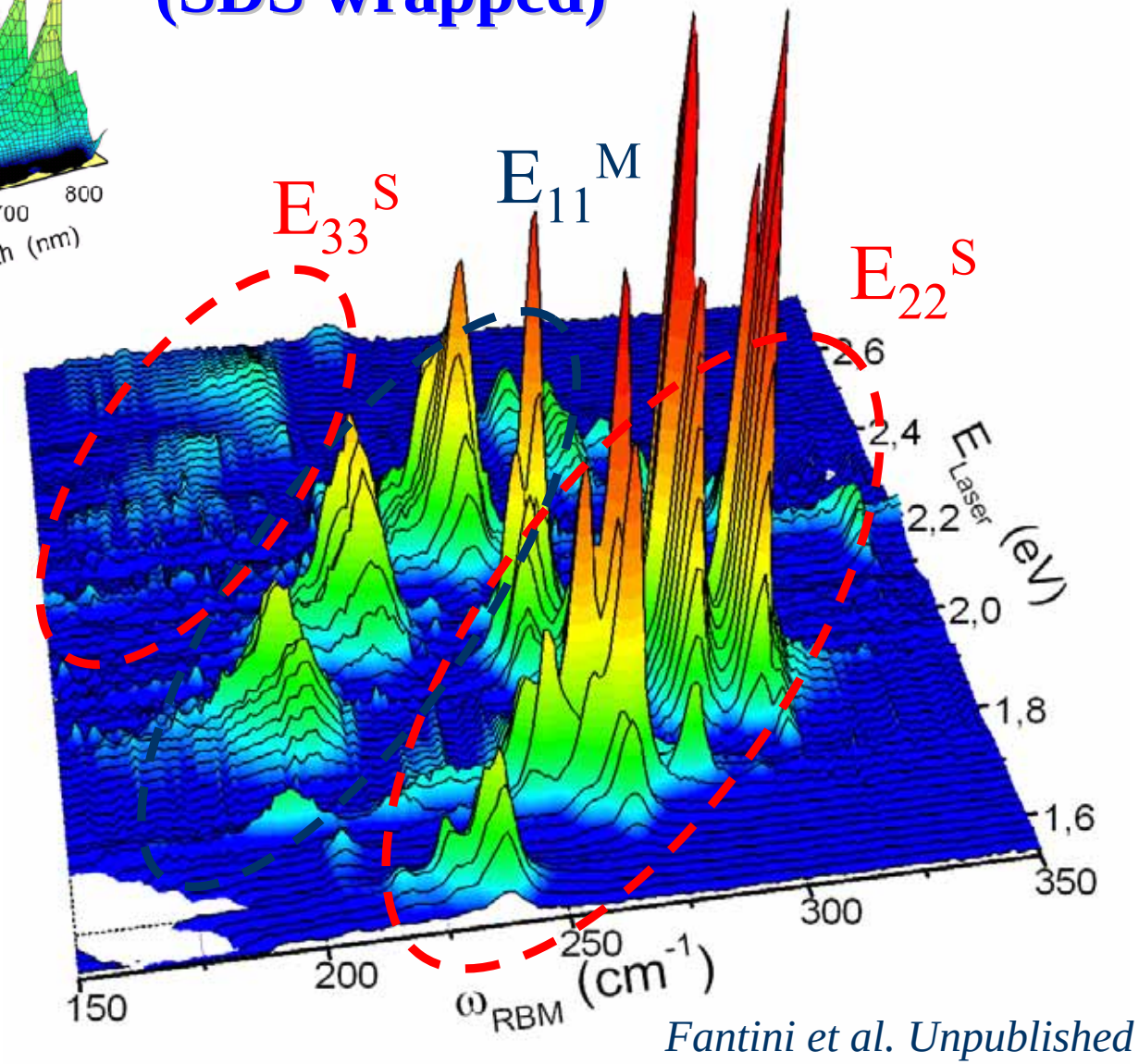


Photoluminescence

Weisman et al.2002



Spectroscopic measurements on HiPco Nanotubes in Solution (SDS wrapped)

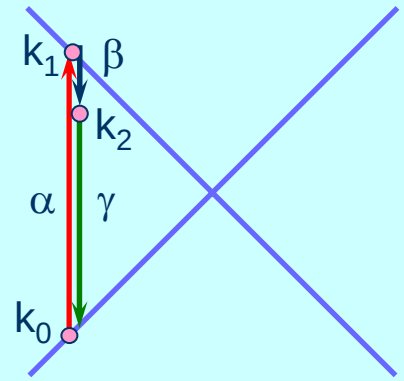


- Raman measurement 76 different laser lines (ArKr, HeNe, 3 different dyes, Ti:Sapphire).
- Dilor XY triplemonochromator
- Calibration: CCl_4 Raman spectra

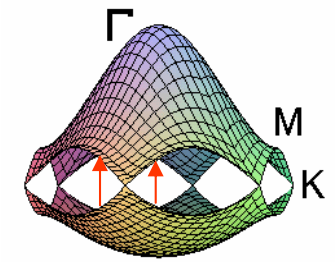
- Sample from M.Strano

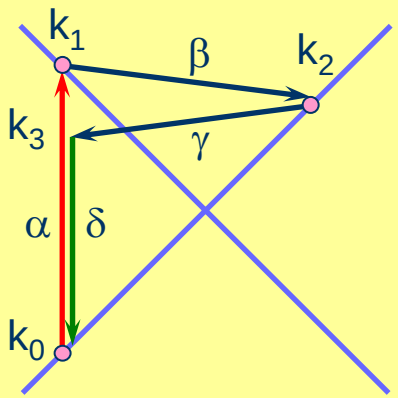
Fantini et al. Unpublished

Resonance Raman Intensity



1st order Raman





2nd order Raman

- 1st order Raman

$$M = \sum_{a,b,c} \frac{M_{op}^{ab} M_{el-p}^{bc} M_{op}^{ca}}{(E_{las} - E_{ab} + i\gamma)(E_{las} - E_{phon} - E_{ac} + i\gamma)}$$

Light emission — **Electron phonon interaction** — **Light absorption**

- 2nd order Raman

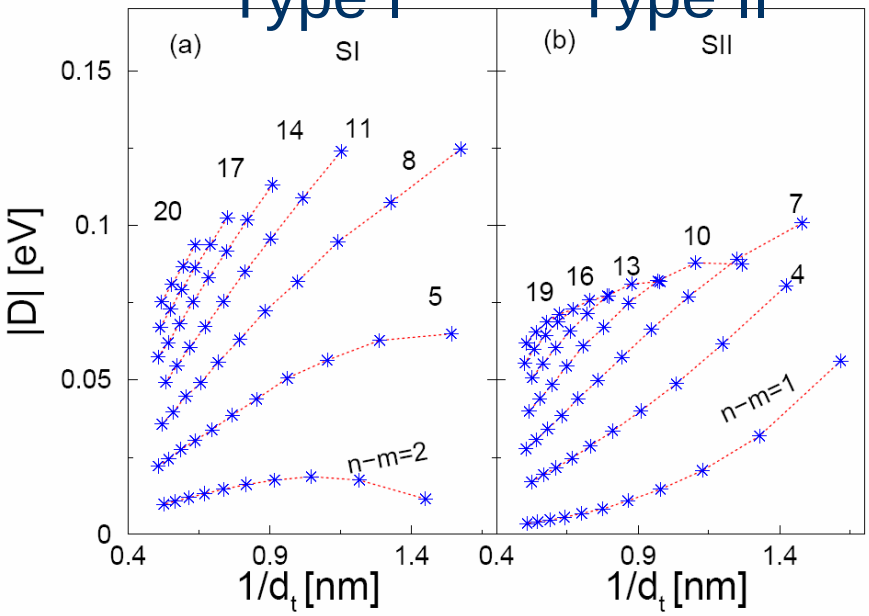
$$I(\mathrm{RS}) = \left| \sum_{0,1,2,3} \frac{M_\alpha M_\beta M_\gamma M_\delta}{\left[E_{laser} - \left(E_1^{el} - E_0^{el}\right) - i\Gamma_{el}\right]\left[\left(E_{laser} \pm E_1^{ph}\right) - \left(E_2^{el} - E_0^{el}\right) - i\Gamma_{el}\right]\left[\left(E_{laser} \pm E_1^{ph} \pm E_2^{ph}\right) - \left(E_3^{el} - E_0^{el}\right) - i\Gamma_{el}\right]} \right|^2$$

RBM: Family pattern of el-phonon matrix element

J. Jiang et al, Phys. Rev. B 72 235408 (2005)

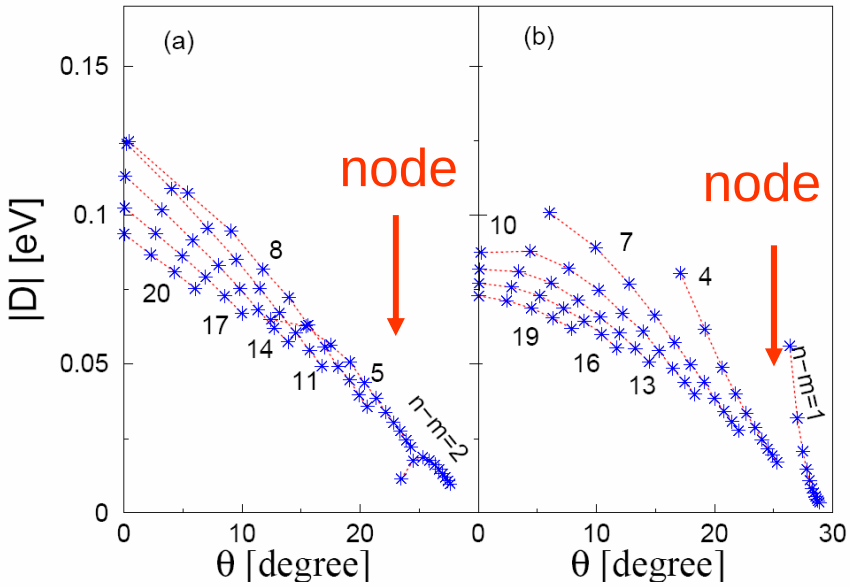
d_t dependence

Type I Type II



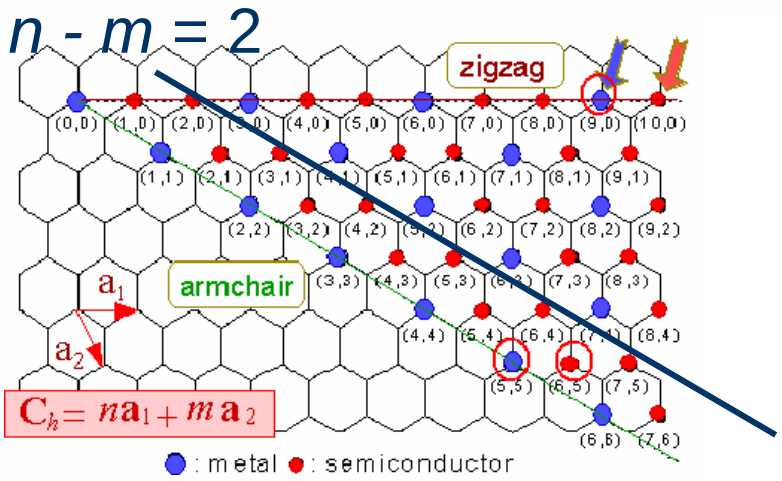
θ dependence

Type I Type II



- *n-m* family pattern, node
- *1/d_t dependence*
- *Type I > type II*

n - m = 2



Family pattern for G-band matrix element

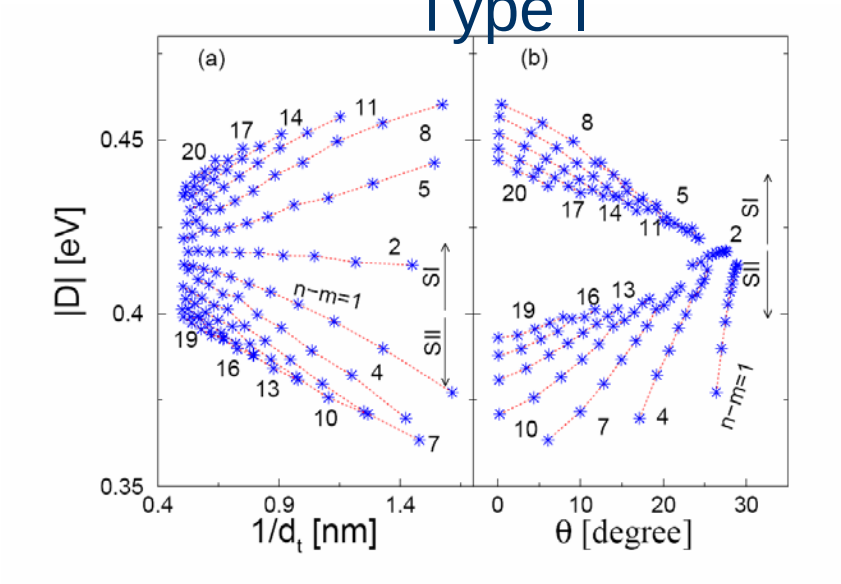
J. Jiang et al, Phys. Rev. B 72 235408 (2005)

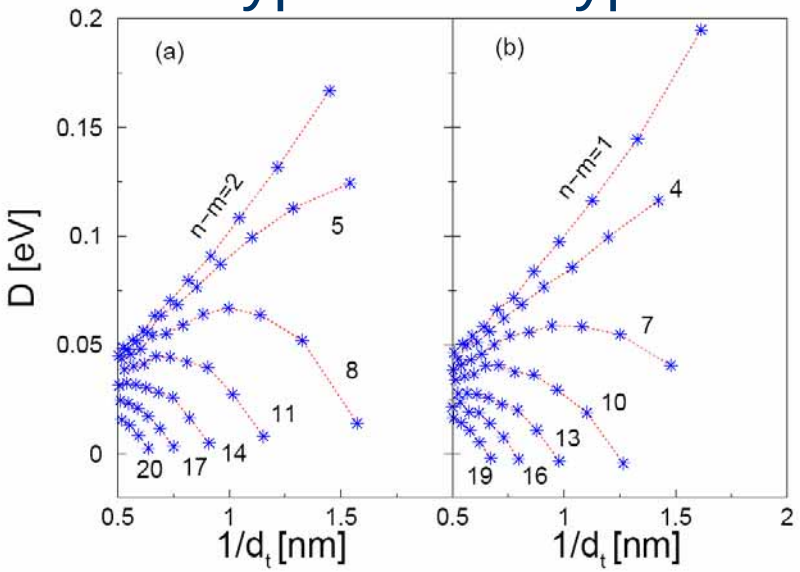
G+ (LO)

G-(TO)

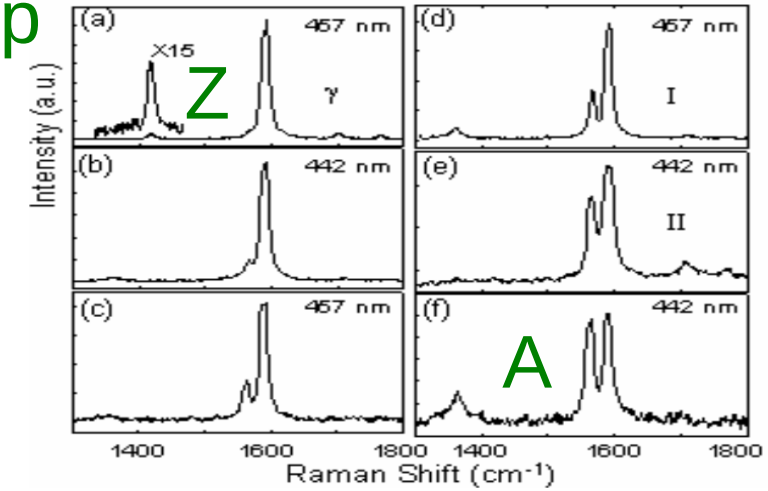
Type I

Type II





Exp



Z. Yu, L. E. Brus, *J. Phys. Chem. B* **105**, 6831 (2001)

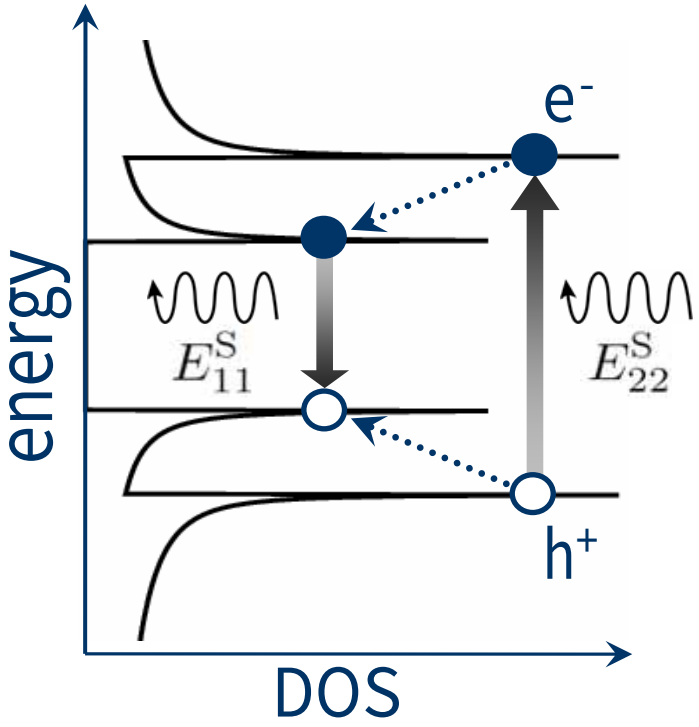
G+: not sensitive on diameter and θ

G-: sensitive both on diameter and θ

(G- near armchair)

Photo-Luminescence (PL)

Optical Process of PL



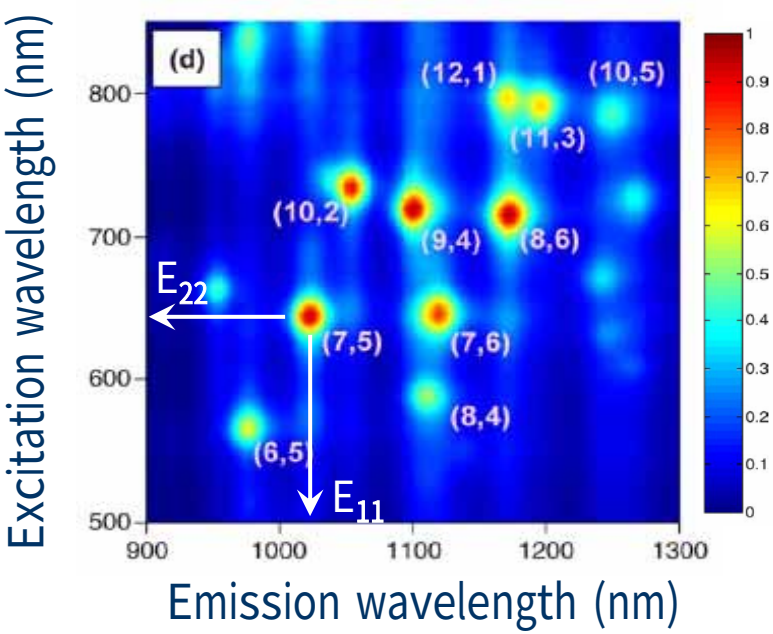
(1) photo absorption

(2) relaxation by phonon

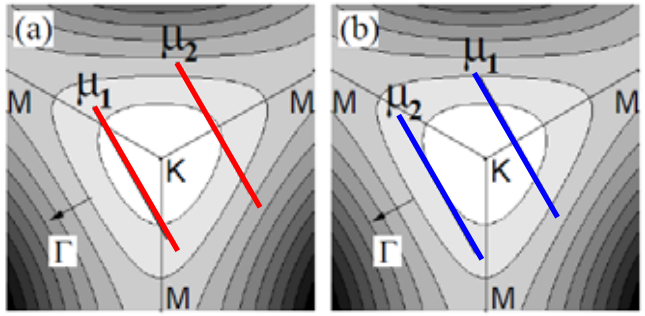
(3) photo emission

PL from diffrent (n,m)

M. J. O'Connel *et al.*, Science **297**, 593 (2002)
S. M. Bachilo *et al.*, Science **298**, 2361 (2002)
Y. Miyauchi *et al.*, Chem. Phys. Lett. **387**, 198 (2004)



PL Intensity chirality dep.
type I – type II dep.

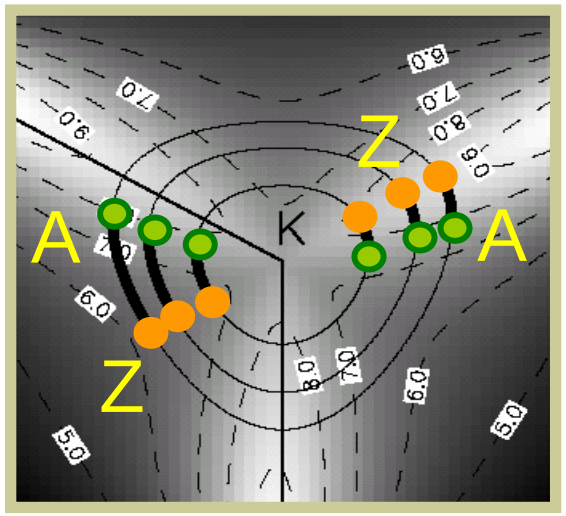


Chirality dependence of Photo-Luminescence

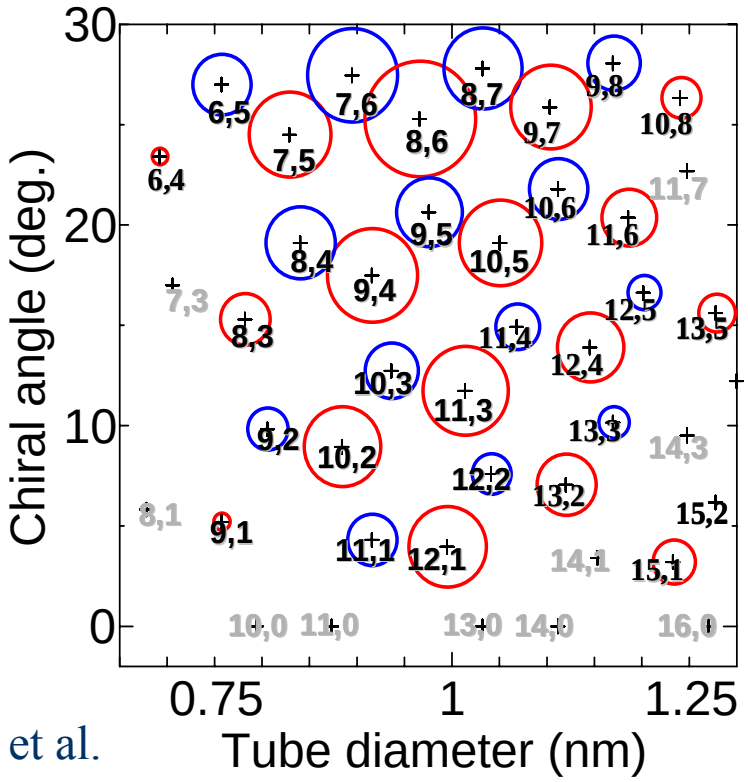
A. Gruneis *et al*, *Chem. Phys. Lett.* 387, 301 (2004)

S. Maruyama et al, nano-carbon (2004)

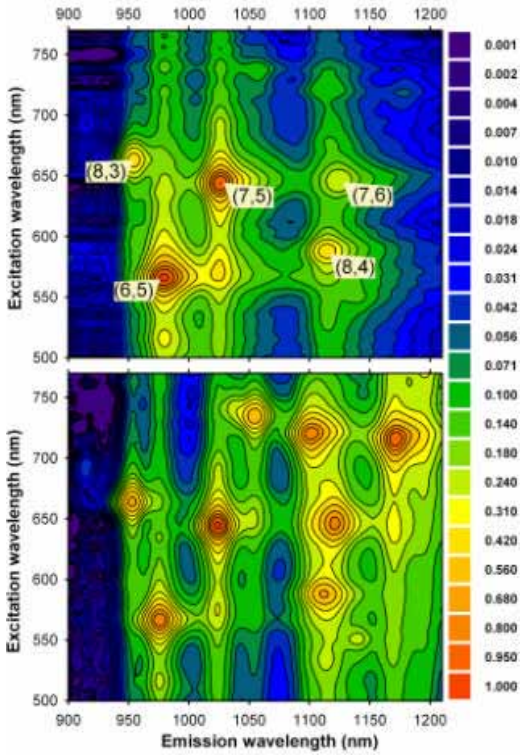
- PL is strong around Armchair.
- type I > type II (for E22 absorption)



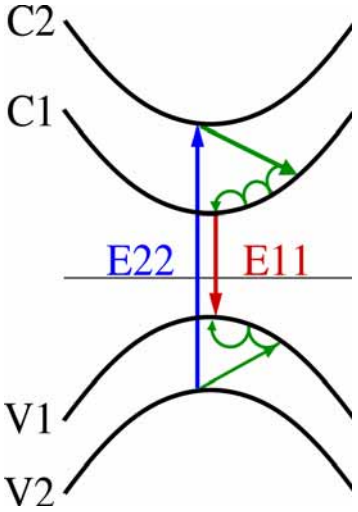
Theory A. Gruneis et al.



Exp. S. Maruyama et al.

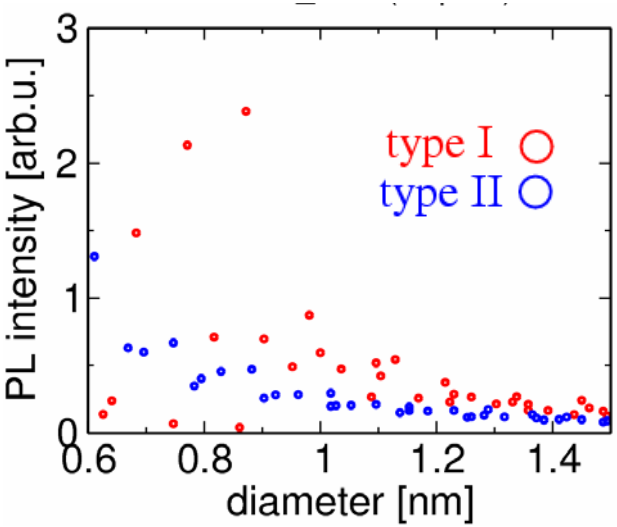


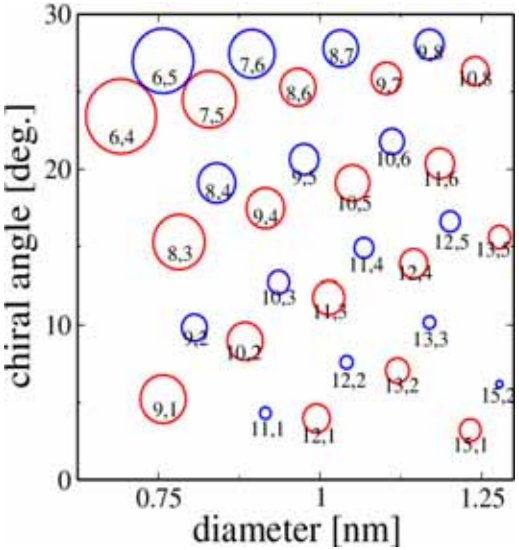
S. M. Bachilo et al., JACS, 125 (2003) 11186.



quantum efficiency = 3%

PL intensity at E11

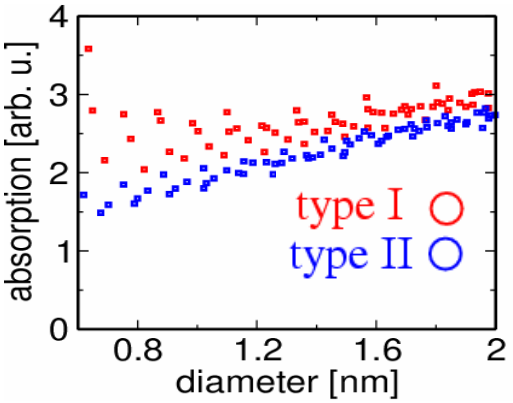




Evaluation of
(n,m) abundance

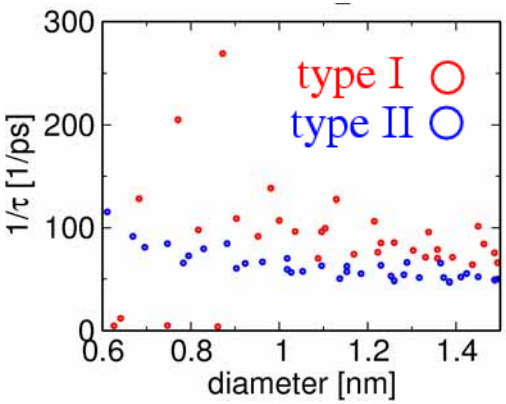
$$\text{Intensity} = \int_{E_{22}-\Delta E}^{E_{22}+\Delta E} W_{22}^{\text{ab}} \left|H_{\text{opt}}\right|^2 (JODS)\, dE$$

Induced absorption

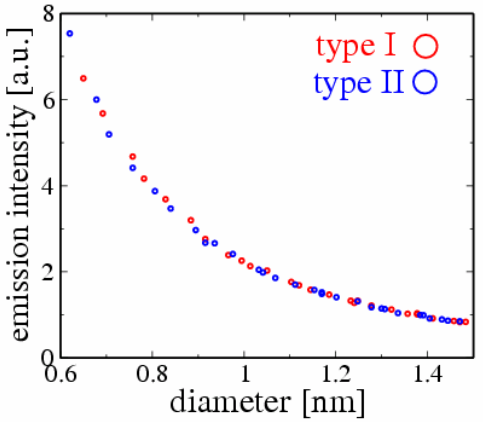


$$W_{22}^{\text{ab}} \propto \frac{I}{tE^2} \cdot \frac{\sin^2[(E_{22}-E)t/2\hbar]}{(E_{22}-E)^2}$$

phonon emission at E22



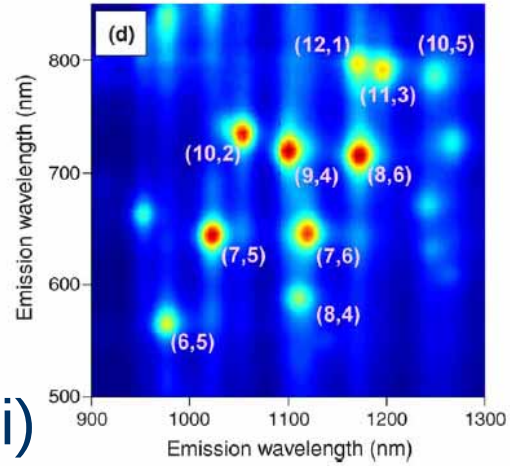
Spontaneous emission



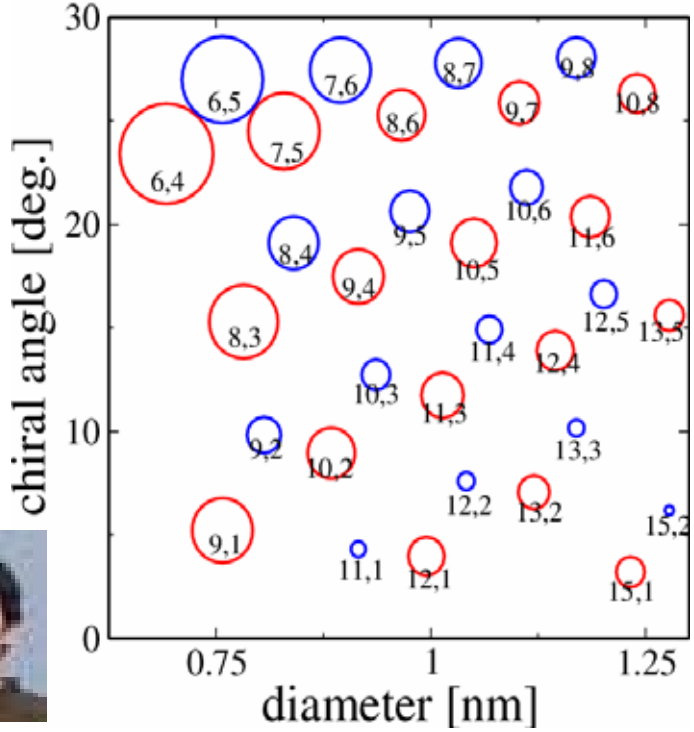
$$W_{11}^{\text{em}} \propto \frac{E}{t} \cdot \frac{\sin^2[(E_{11}-E)t/2\hbar]}{(E_{11}-E)^2}$$

Fluorescence spectroscopy

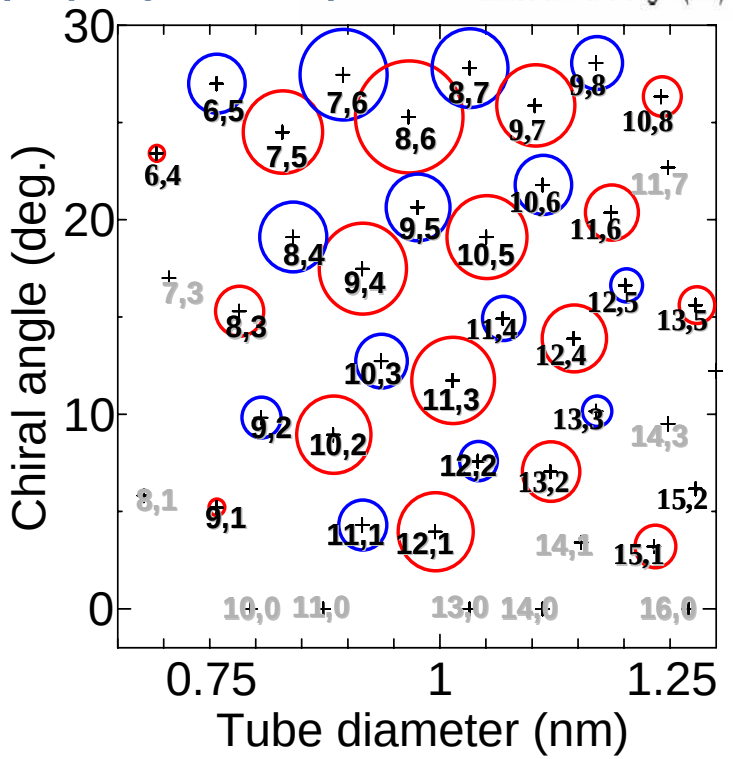
Y. Miyauchi *et al*. Chem. Phys. Lett. **387** 198 (2004)
Y. Oyama *et al, Carbon*, 44, 873 (2006)



Theory (Oyama)



Exp (Miyauchi)



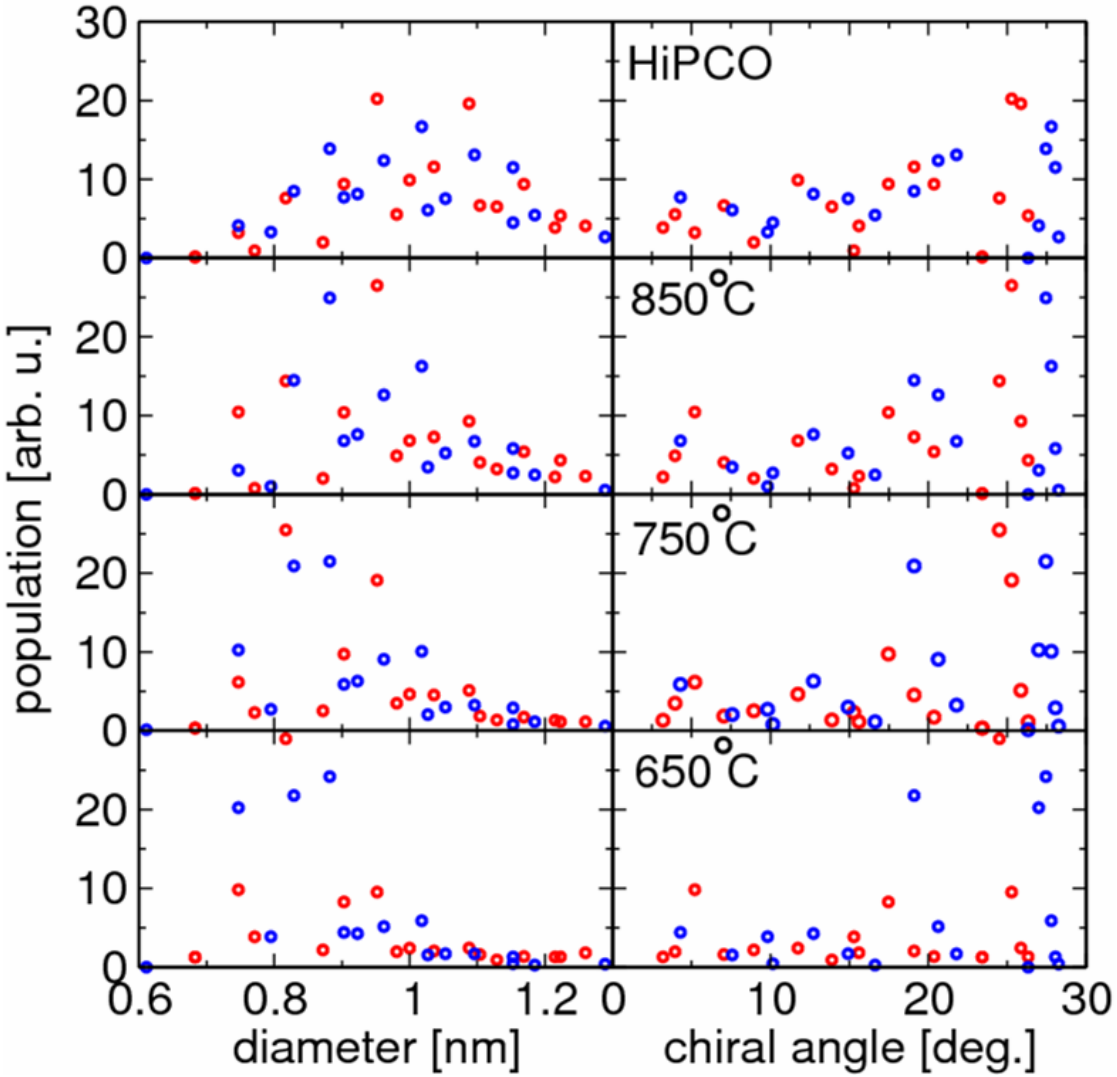
small diameter, near armchair
PL intensity large

polarization // tube axis

- HiPCO sample

Population of *(n,m)* by PL I_{exp}/I_{cal}

Y. Oyama *et al, Carbon*, 44, 873 (2006)



Population analysis:

1. PL I_{exp}/I_{cal}

   Y. Oyama et al, Carbon, 44, 873 (2006).

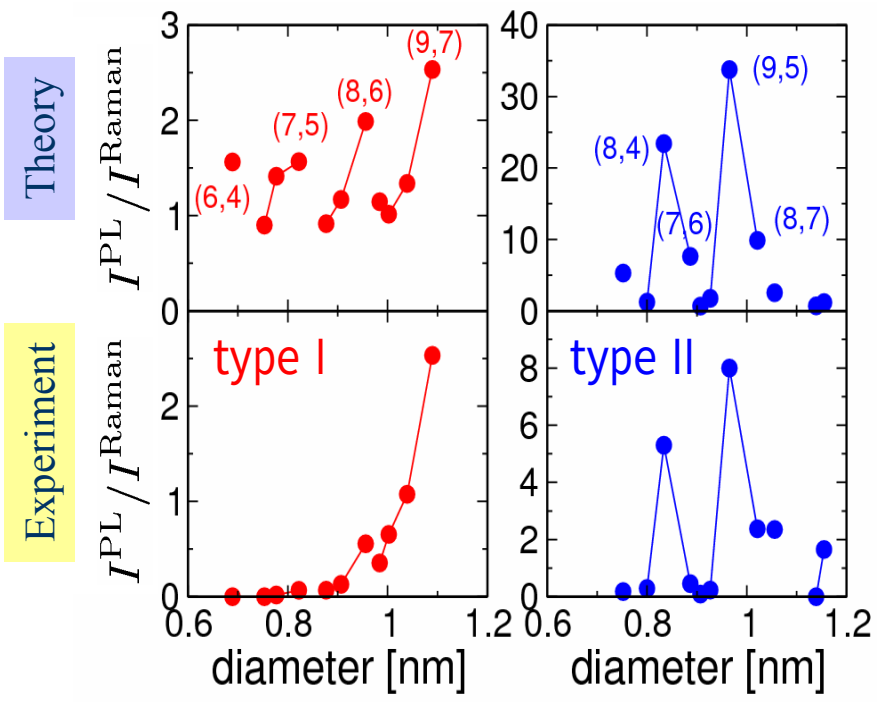
2. $I(\mathrm{PL})/I(\mathrm{Raman})$

   A. Jorio et al., APL, 88, 023109, (2006).

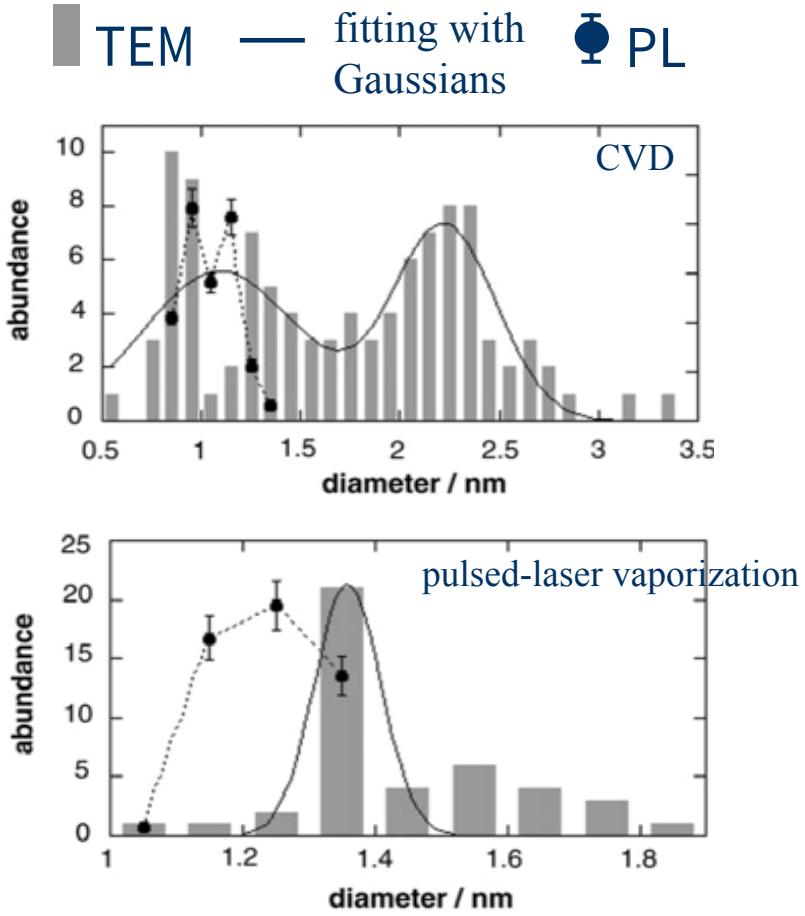
3. I_{exp}/I_{cal} and TEM

   T. Okazaki, CPL, 420 286 (2006)

population analysis



A. Jorio, *et al.*, Appl. Phys. Lett. **88**, 023109 (2006).



T. Okazaki, *et al.*, Chem. Phys. Lett. 420, 286 (2006).

Summary of PL and Raman intensity

- RBM intensity zigzag
- G+ intensity no chirality dep.
- G- intensity armchair
- PL intensity armchair

- Type I > Type II (optical absorption)
- (E22-E11) vs phonon energy
- resonance width (relaxation time)

Population analysis for Raman and PL is available.

Method: Our computational library for SWNTs
-- What do we need for intensity calculation? --

- Electron and phonon energy dispersion
  - extended tight binding (ETB, up 20 n.n. sites)
  - Porezag's interatomic potential
- Optical absorption and emission
  - dipole approximation
- Electro-phonon interaction
  - relaxation, ETB
- Raman intensity calculation
- PL intensity calculation
- Exciton calculation



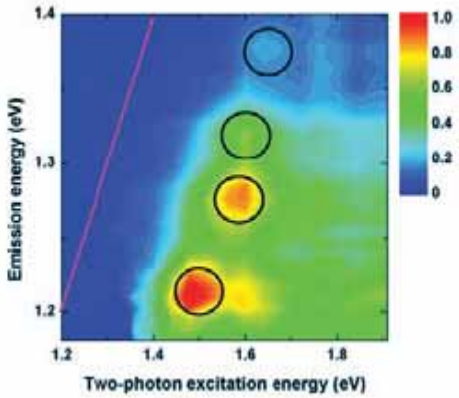




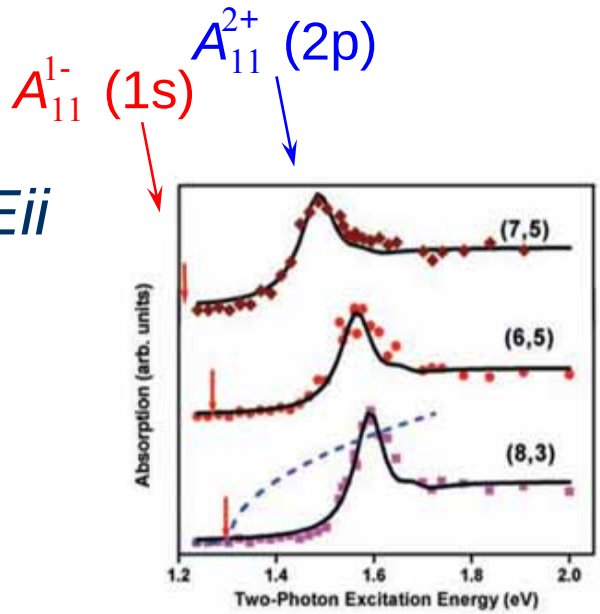



Exciton calculation

- Why?
  - Large binding energy (0.5eV)
    - even room temperature, exciton exists.
  - Exciton specific phenomena
    - dark exciton, two photon, environment
- What can we know or imagine?
  - Cancellation by self energy
    - ETB + many body effects reproduce *Eii*
  - Localized exciton wave function
    - enhancement of optical process
    - relatively short k dependence.



Wang et al. Science ***308****, 838 (2005)*



G028

ETB extension for Exciton

*T. Ando J. Phys. Soc. Japan, **66**, 1066 (1997), C. D. Spataru et al. PRL **92,** 077402 (2004)*

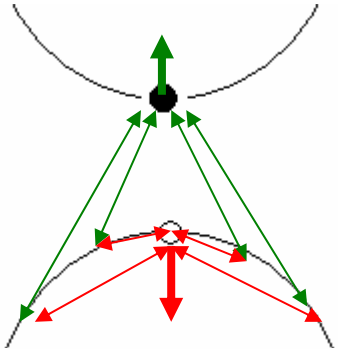
Bethe-Salpeter Equation

$$\left[(E_{k_c} - E_{k_v})\delta_{k_c k_{c'}}\delta_{k_v k_{v'}} + K_{k_c k_v, k_{c'} k_{v'}}\right]\Psi^n_{k_{c'} k_{v'}} = \Omega_n \Psi^n_{k_c k_v}$$

quasi-particle (QP) energy Coulomb interaction (C)

$$K_{k_c k_v, k_{c'} k_{v'}} = 2\delta_S K^x_{k_c k_v, k_{c'} k_{v'}} + K^d_{k_c k_v, k_{c'} k_{v'}}$$

exchange C direct C



Self-energy (Coulomb repulsion)

$v(\mathbf{r}, \mathbf{r}')$ Ohno's potential / κ :a static dielectric constant to consider polarization of environment

RPA approximation:

$$V(\mathbf{q}) = v(\mathbf{q})/\epsilon(\mathbf{q}) \qquad \epsilon(\mathbf{q}) = 1 + \frac{v(\mathbf{q})}{V}\Pi(\mathbf{q})$$

$$\Pi(\mathbf{q}) = -2\sum_{k,l,l'} \frac{f_{\mathbf{k}+\mathbf{q},l'} - f_{\mathbf{k},l}}{\epsilon_{\mathbf{k}+\mathbf{q},l'} - \epsilon_{\mathbf{k},l}} | < \mathbf{k}l|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}, l' > |^2$$

$$\mathrm{E}_{kv} = \sum_q \sum_{sus'u'} \frac{V_{sus'u'}}{\varepsilon(q)} e^{iq(Rus - Ru's')} C^*_{kv}(s) C_{k+q,v}(s) C^*_{k+q,v}(s) C_{kv}(s)$$

Symmetry consideration

J. Jiang et al. unpublished

Centre of mass motion

$k_c - k_v = \overline{K}$:Good quantum number

Relative motion

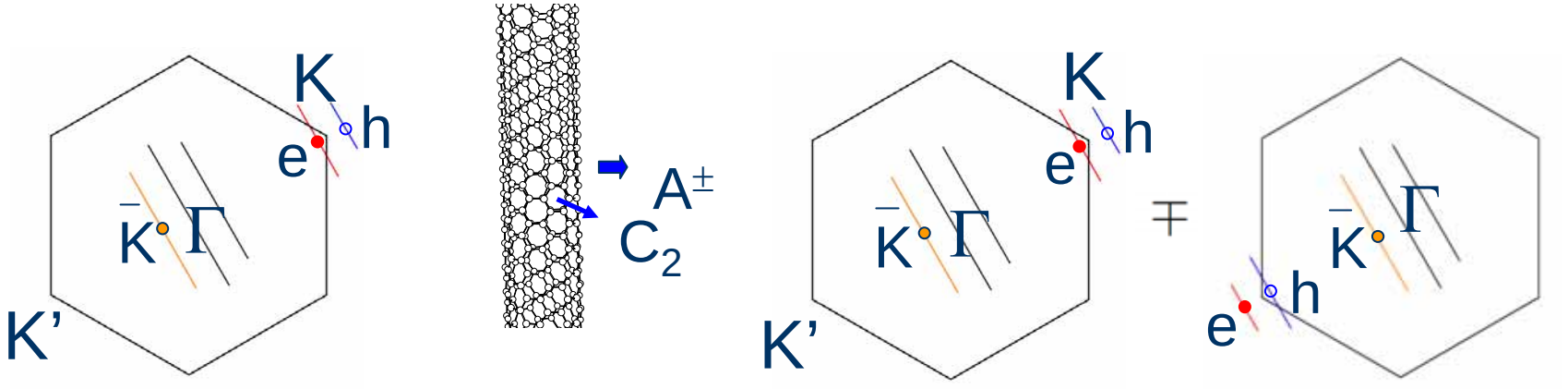
$(k_c + k_v)/2 = k$

Bright and dark exciton

A^- : bright exciton

A^+, E and E^*: dark excitons

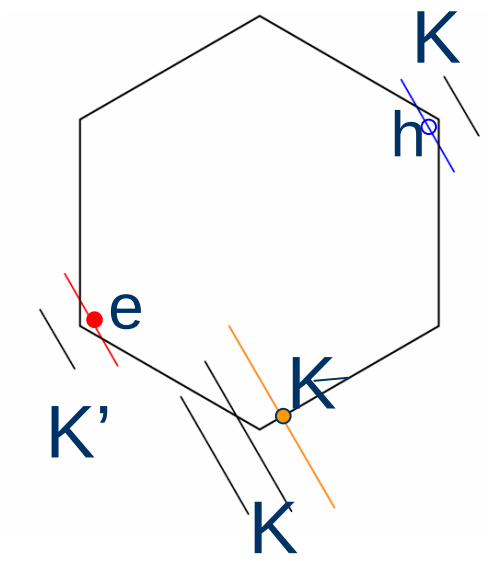
A symmetry exciton



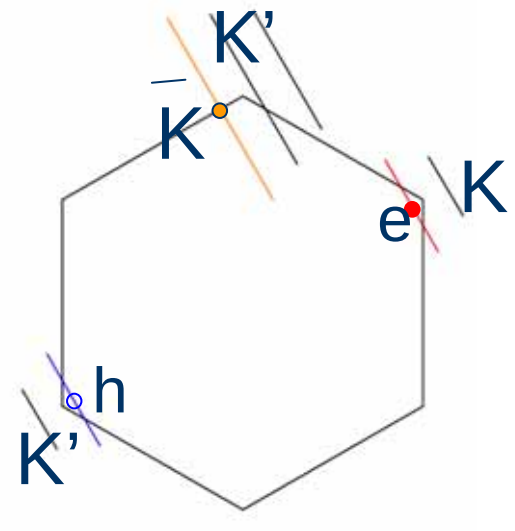
Exciton energy dispersion

J. Jiang et al. unpublished

E exciton



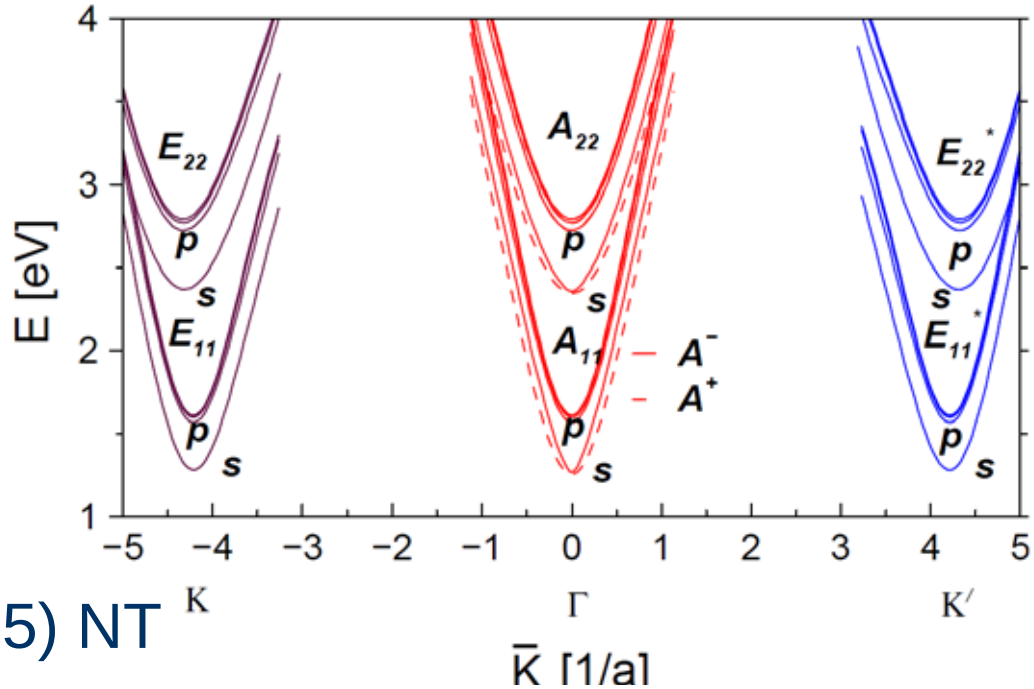
E * exciton



Bright and dark exciton

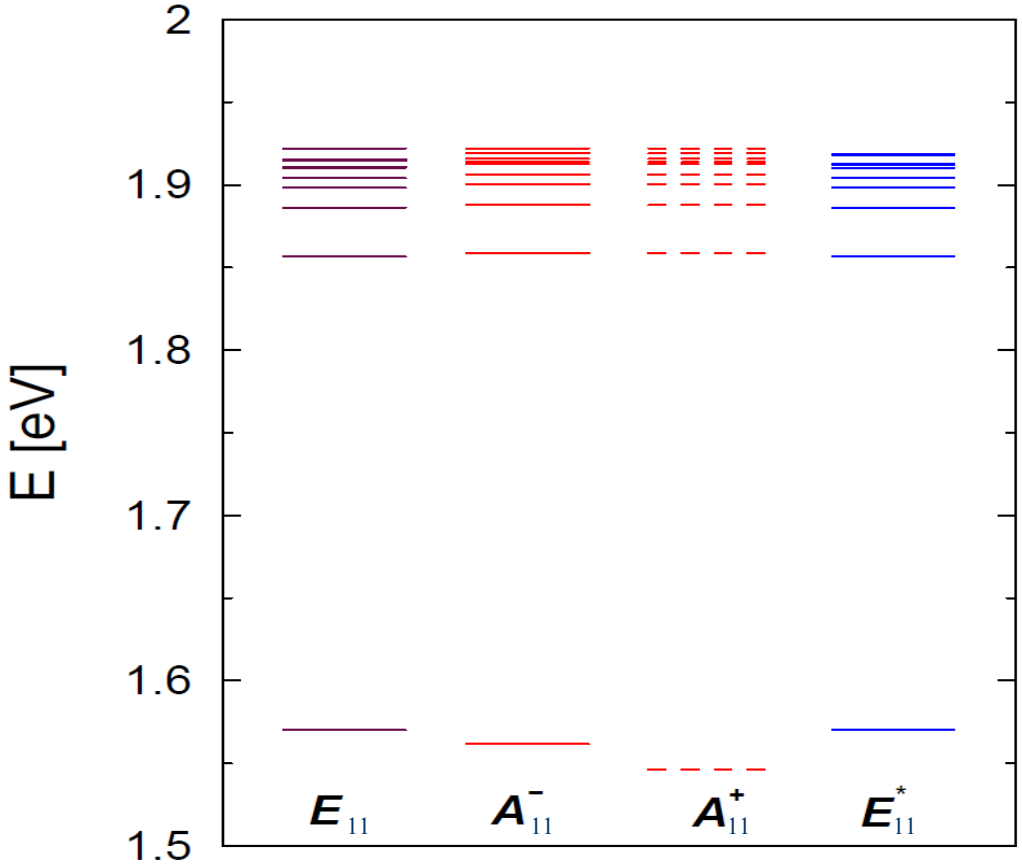
A^- : bright exciton

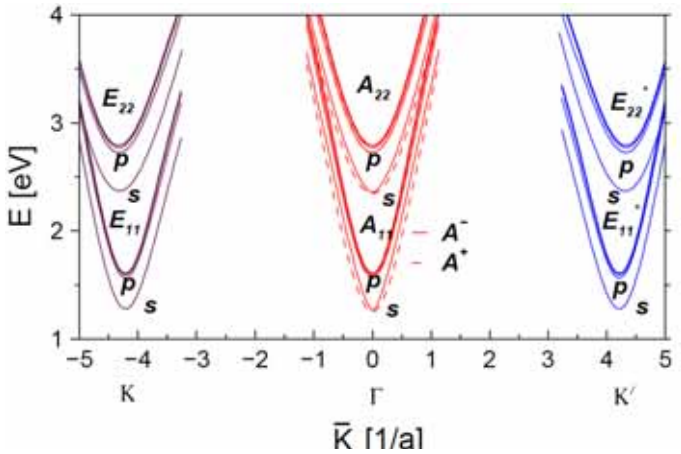
A^+, E, E^*: dark excitons



Dispersion for (6,5) NT

Dark state is the lowest



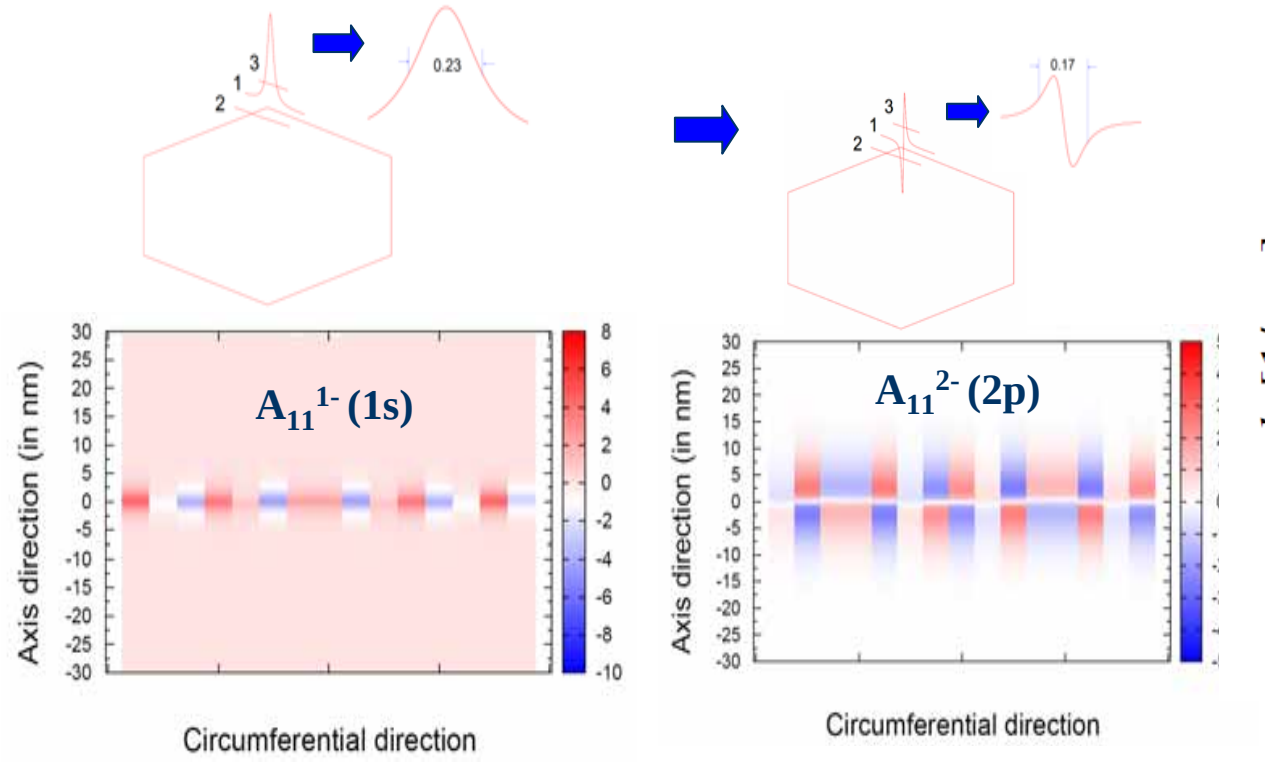


A^{-} : bright exciton

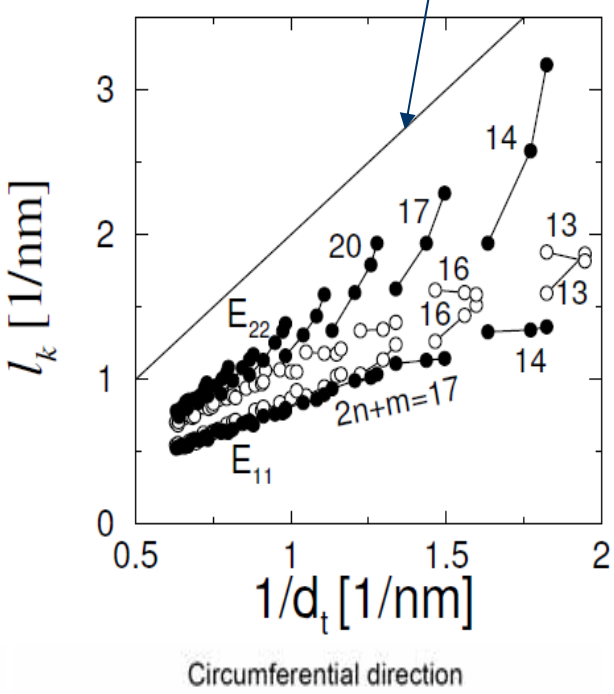
A^{+}, E and E^{*}: dark excitons

Exciton wavefunction for (8,0) NTs

J. Jiang et al. unpublished



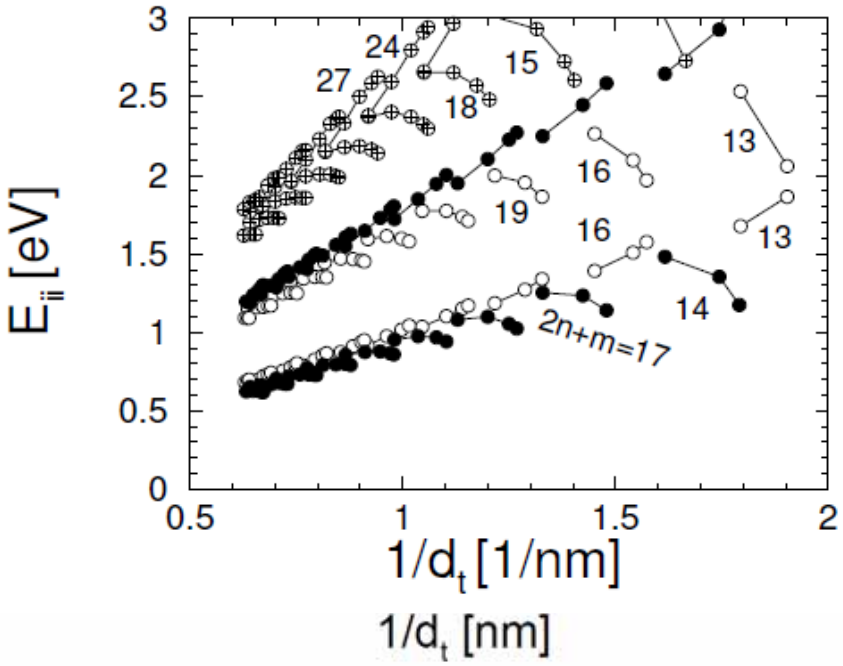
Cutting line spacing

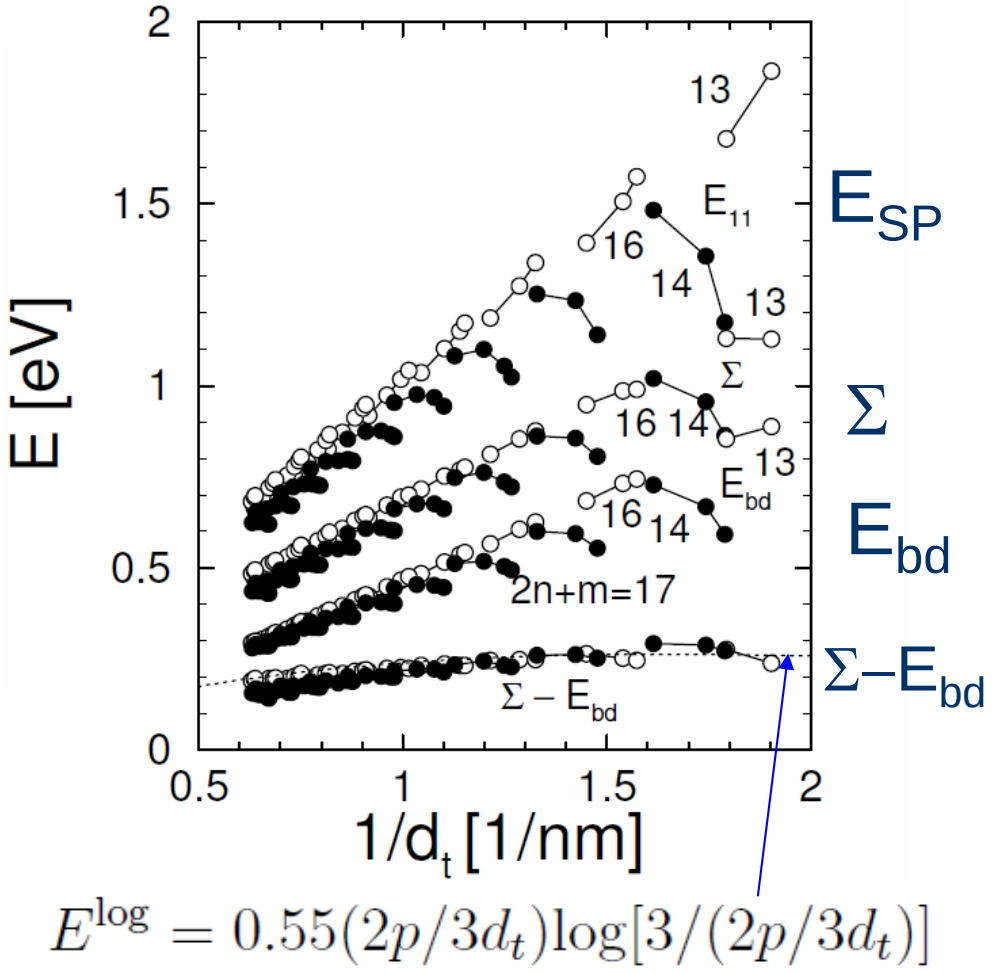


Distribute only one cutting line for any diameter.

Bright exciton Kataura plot

J. Jiang et al. unpublished





$$E^{\log} = 0.55(2p/3d_t)\log[3/(2p/3d_t)]$$

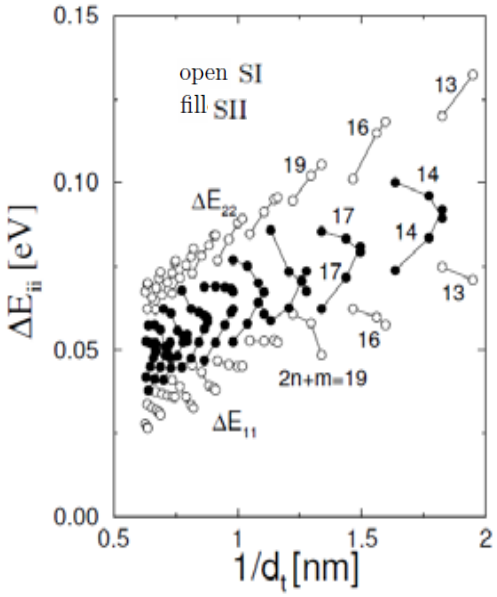
$\kappa=2$ is used for E22(S) and E11(M)

Justification of ETB+MB

The origin of the large family spread in Kataura plot - single particle part

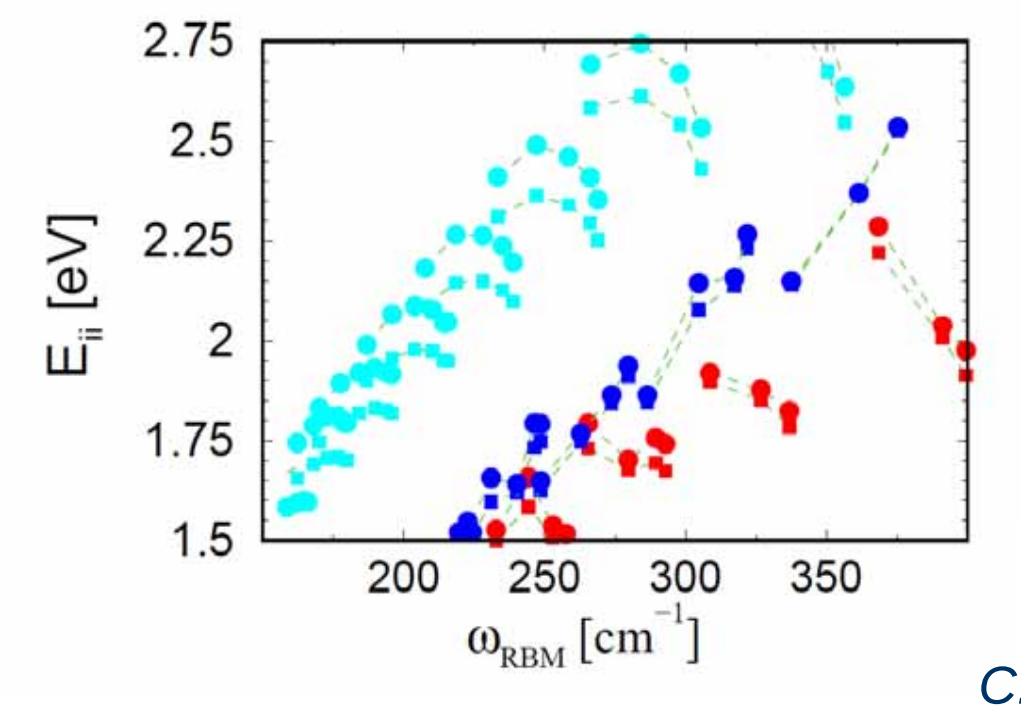
Environment effect

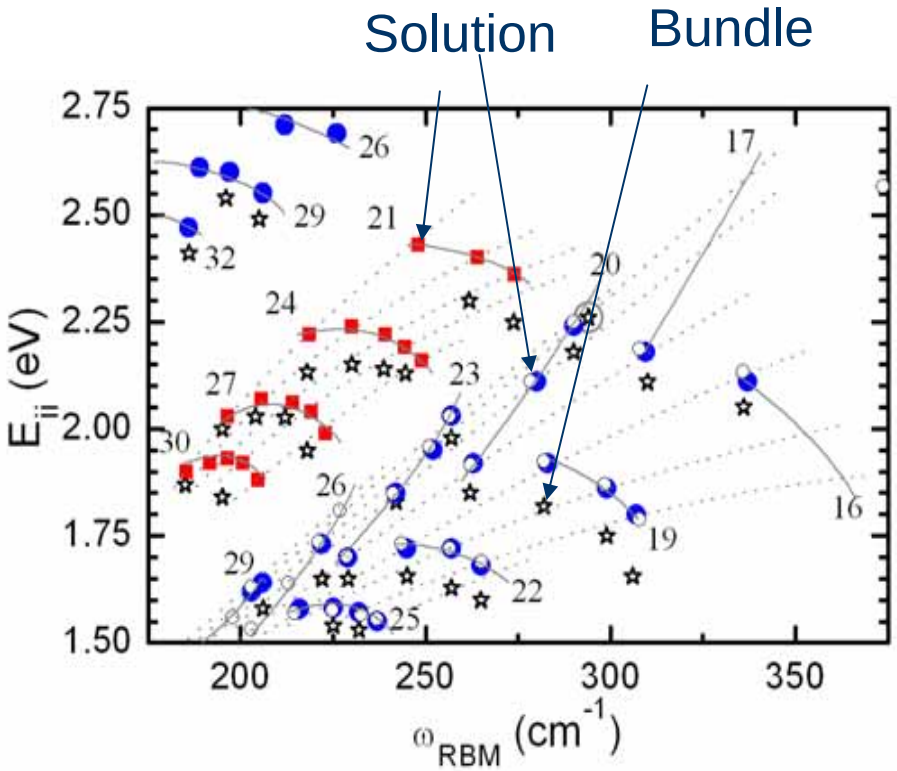
J. Jiang et al. *unpublished*



Circle: κ=1.75

Square: κ=3.5

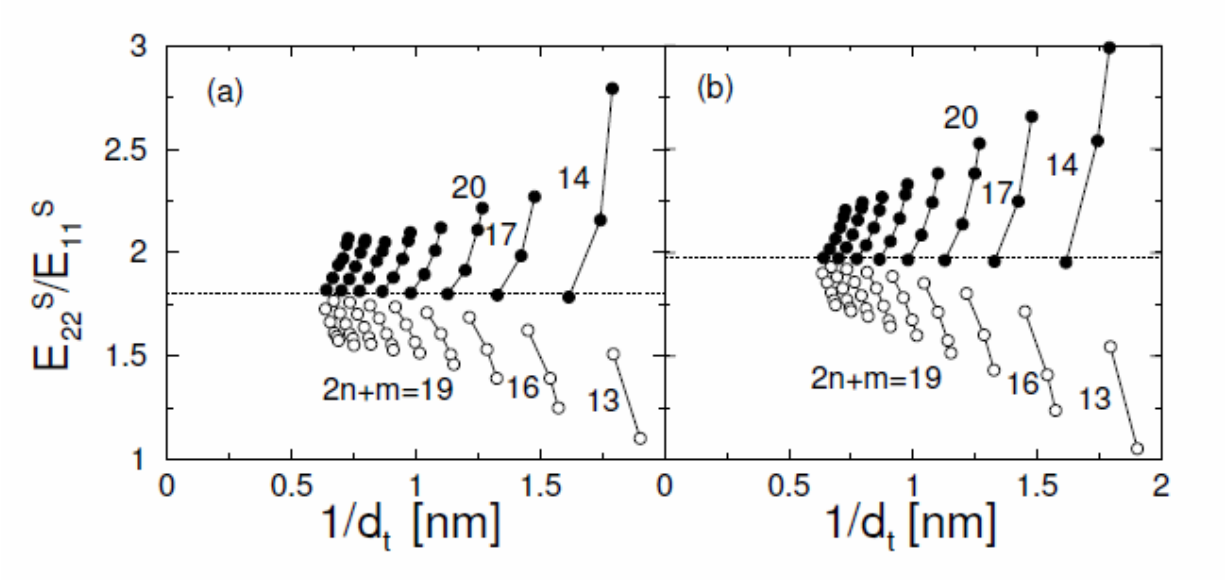




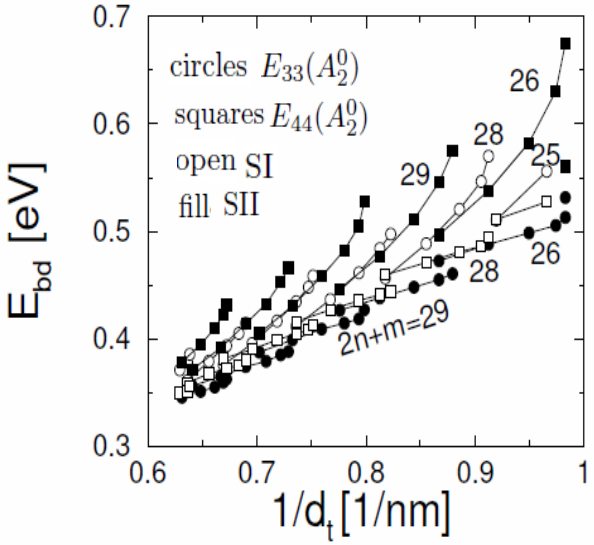
Experiment data

*C. Fanitini et al PRL **93**, 147406 (2004)*

Ratio problem



With MB Without MB

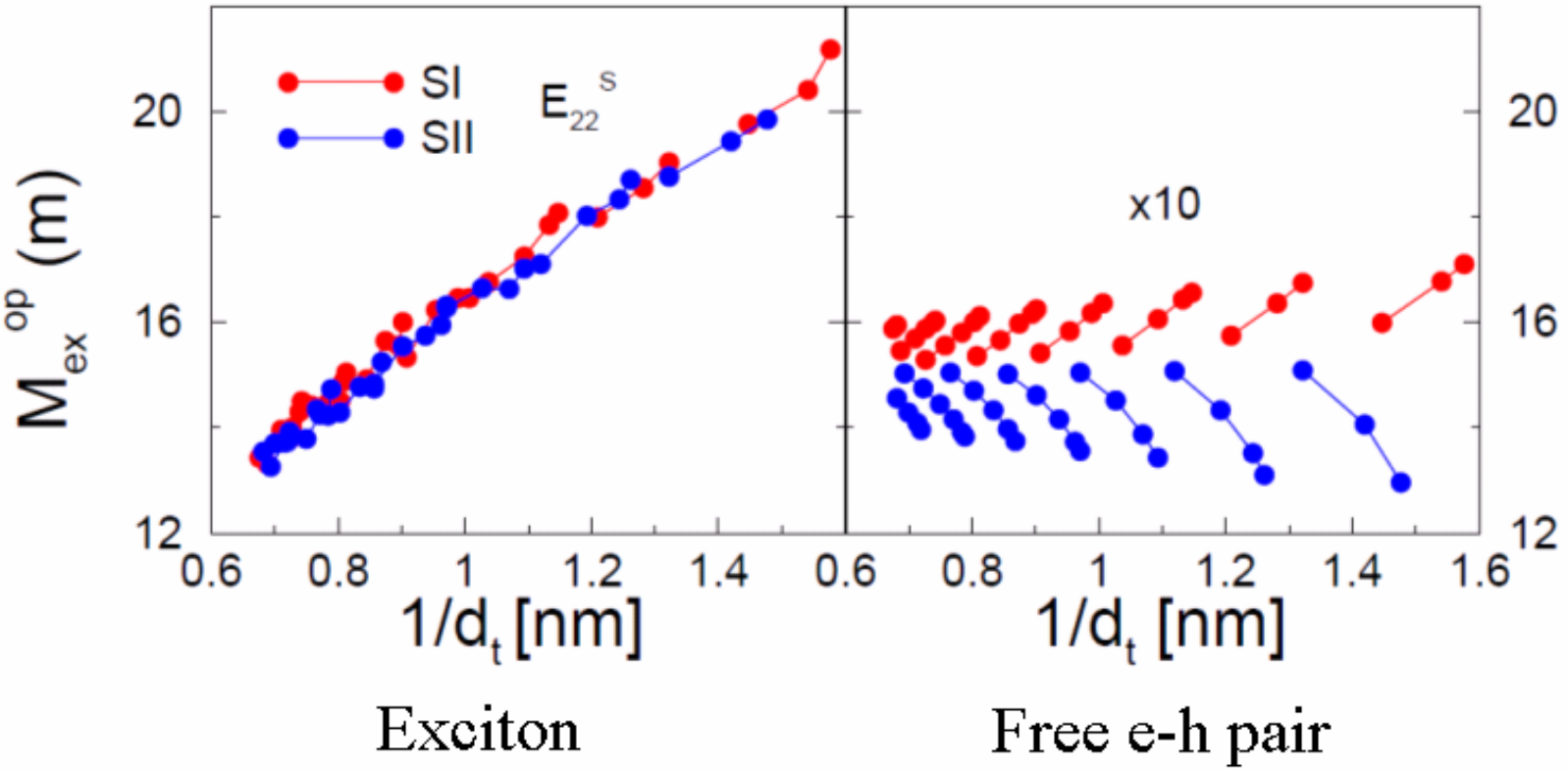


E33, E44 has similar

E_{bd} to E11 and E22.

Exciton-photon matrix element

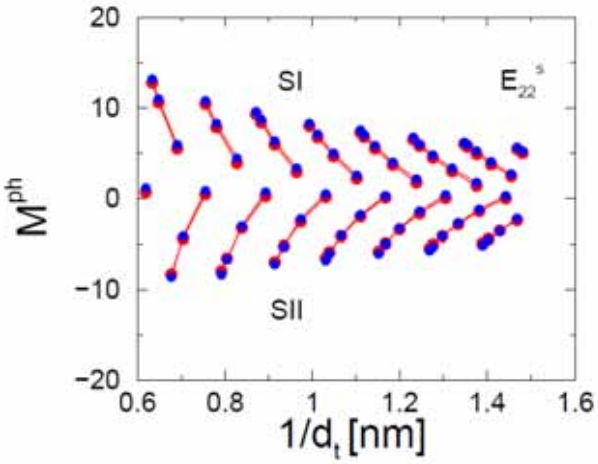
J. Jiang et al. unpublished.



No type dep, No family pattern but d_t dep.

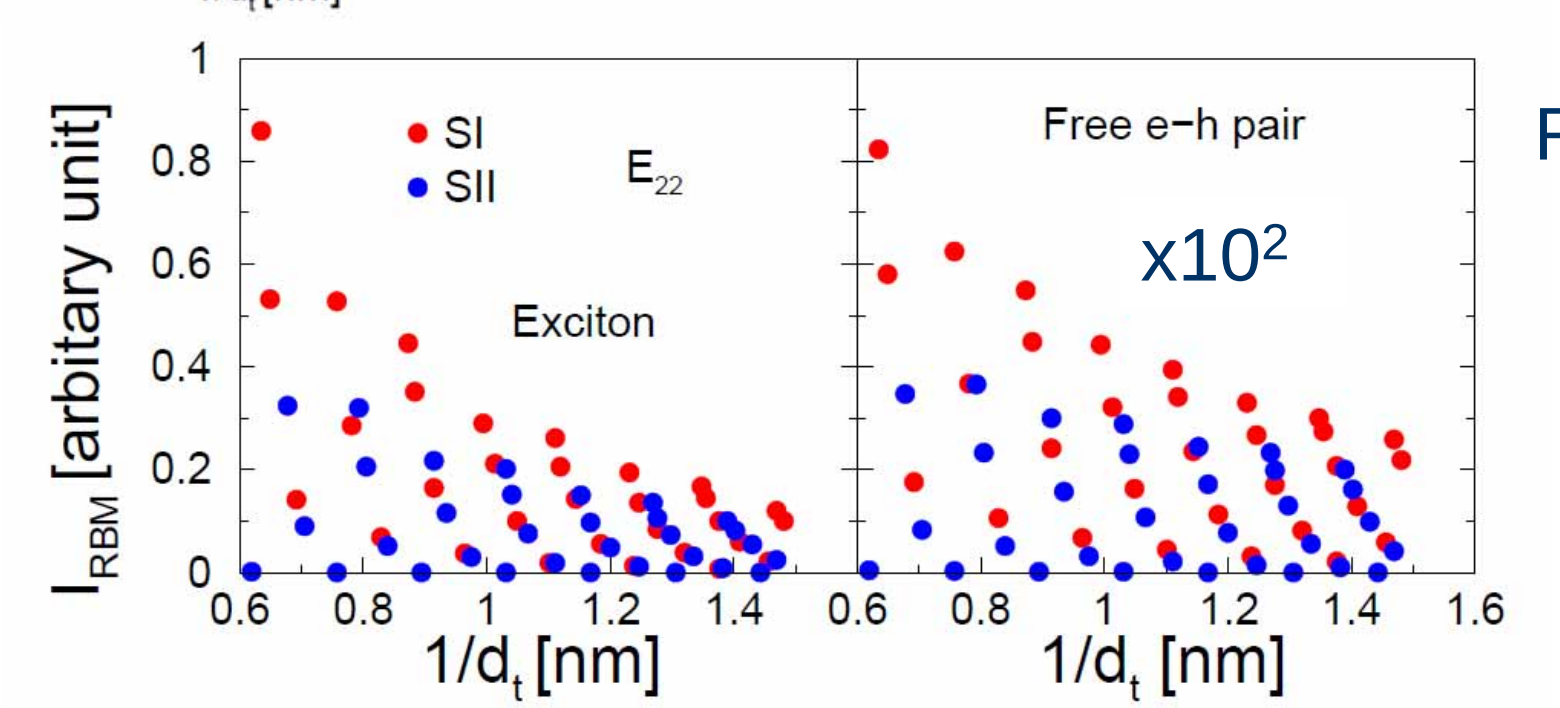
Exciton-phonon matrix element

J. Jiang et al. unpublished.

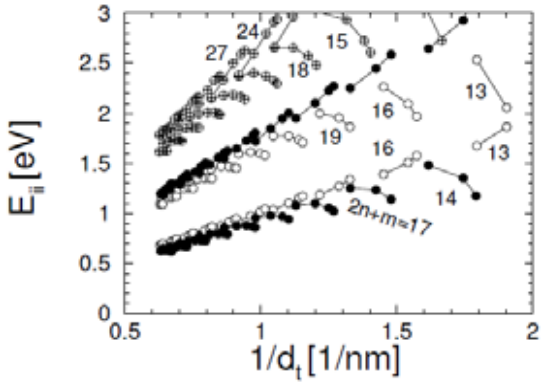


Matrix element, No difference!

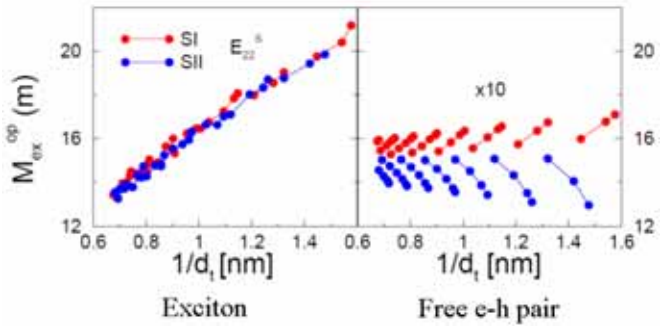
Intensity enhanced drastically



RBM

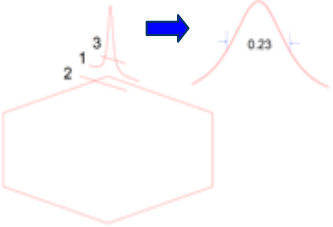


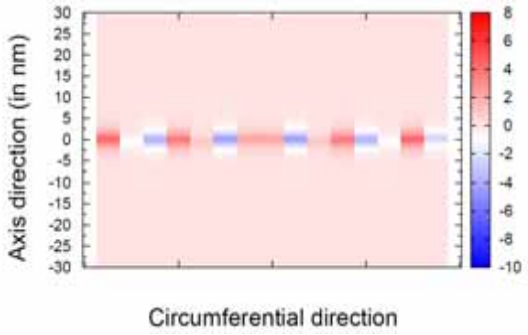
Summary

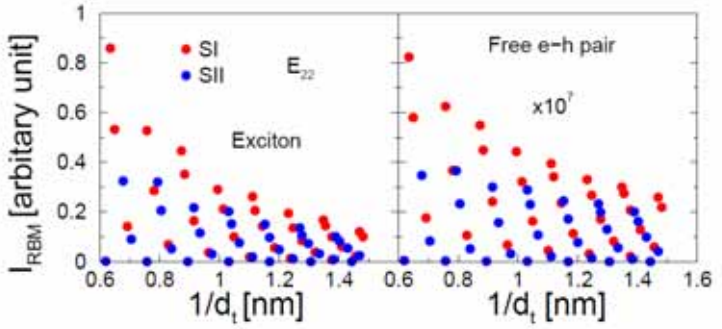


- Solution of BS equation
  - wavefunction on *one* cutting line
  - Exciton Kataura plot (family pattern)
  - similar E_b E_{22}, E_{33}, E_{44}
- exciton-phonon (no change)
- exciton-phonon (enhanced)
- Raman and PL intensity

  with exciton wavefunction (in pr







Electron-photon and electron-phonon matrix elements
-- *Dipole approximation and Deformation potential* --

A. Gruneis *et al*, *Chem. Phys. Lett.* 387, 301 (2004)

J. Jiang *et al*, *Chem. Phys. Lett.* 392, 383 (2004)

- electron-photon (P vector · dipole vector)

$$\mathbf{P}\cdot\left\langle \Psi^{C}(\mathbf{k})\middle|\nabla\middle|\Psi^{V}(\mathbf{k}')\right\rangle$$

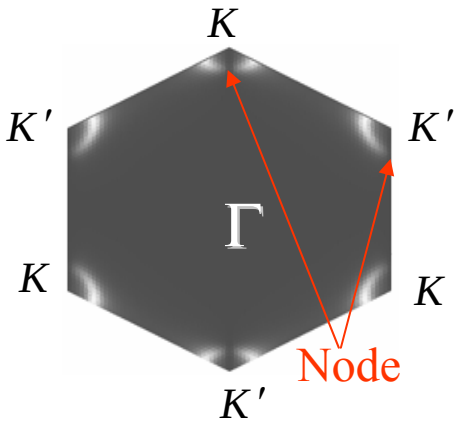
- electron-phonon (A-vib · V-deform)

$$-\frac{1}{2}A^{\nu}(\mathbf{q})\cdot\left\langle \Psi^{C}(\mathbf{r},\mathbf{k}',t)\middle|\delta V^{\nu}(\mathbf{r},\mathbf{q},t)\middle|\Psi^{C}(\mathbf{r},\mathbf{k},t)\right\rangle$$

Tight binding expansion:

anisotropic around K

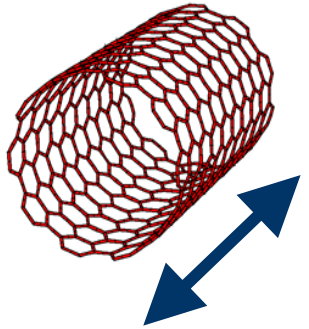
$$\Psi_l(\mathbf{r},\mathbf{k},t)=\frac{1}{\sqrt{N_u}}\sum_{l=1}^{N_u}\sum_{s=A,B}C_s(\mathbf{k})e^{i[\mathbf{k}\cdot(\mathbf{R}_l+\mathbf{r}_l)-\omega(\mathbf{k})t]}\,\phi(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_s)$$



Optical absorption in graphite

A. Grueneis et al. , PRB 67 165402 (2003)

R. Saito et al., Appl. Phys. A (2004)



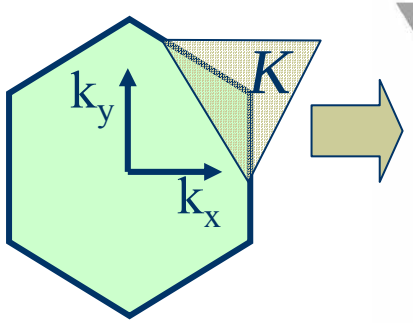
$$M_{v\to c} = i\frac{e\hbar}{m\omega}\sqrt{\frac{I}{\varepsilon c}}e^{i(\omega_f-\omega_i-\omega)t}\mathbf{P}\cdot\langle\Psi_c|\nabla|\Psi_v\rangle$$

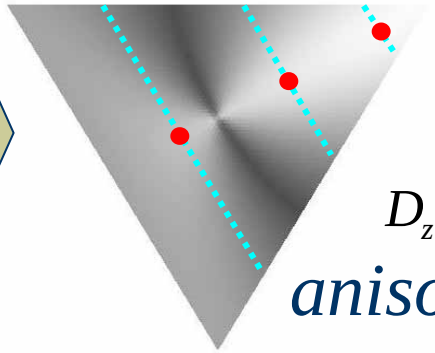
Polarization vector

Dipole vector **D**

SWNT (J. Jiang, 2003) $M_{v\to c}\propto \mathbf{P}\cdot\mathbf{D},\quad \mathbf{P}_{//}=(0,0,1),\quad M_{v\to c}\propto D_z$

$$D_z(\mathbf{k})=\frac{M\delta_{\mathbf{k},\mathbf{k}'}\delta_{\mu,\mu'}}{2w(\mathbf{k})}\left[\sin\left(\frac{\pi}{6}-\theta\right)\times\left\{\cos k_y a-\cos\frac{k_y a}{2}\cos\frac{\sqrt{3}k_x a}{2}\right\}+\sqrt{3}\cos\left(\frac{\pi}{6}-\theta\right)\sin\frac{\sqrt{3}k_x a}{2}\sin\frac{k_y a}{2}\right]$$

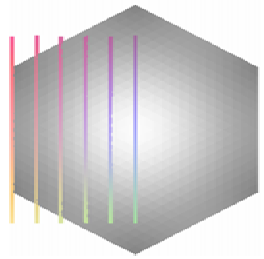




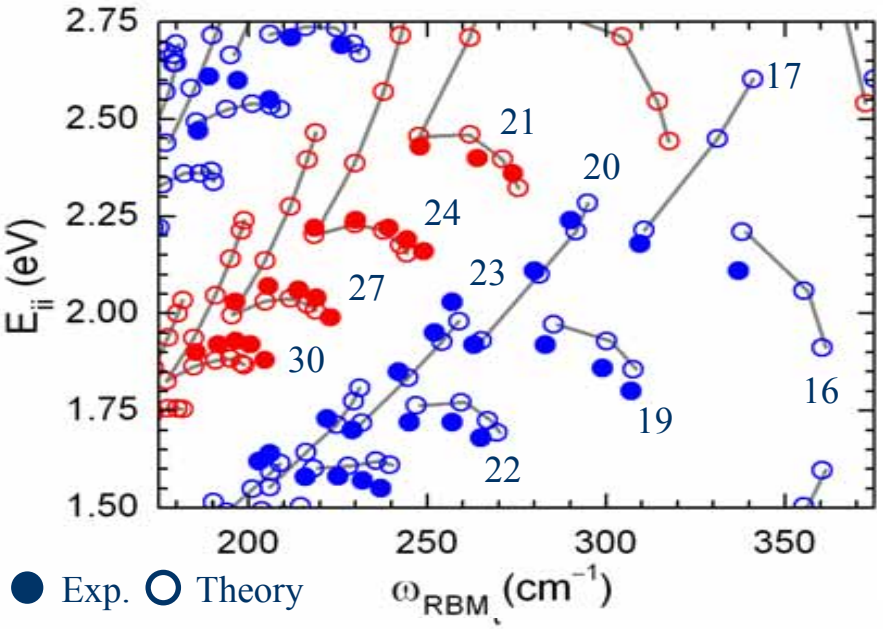
$D_z(\mathbf{k})$ *anisotropic*

$$\mathbf{k}=\mu\mathbf{K}_1+\frac{k}{\mathbf{K}_2}|\mathbf{K}_2|$$

$$(\mu=0,\cdots,N-1\quad -\frac{\pi}{T}<k<\frac{\pi}{T})$$

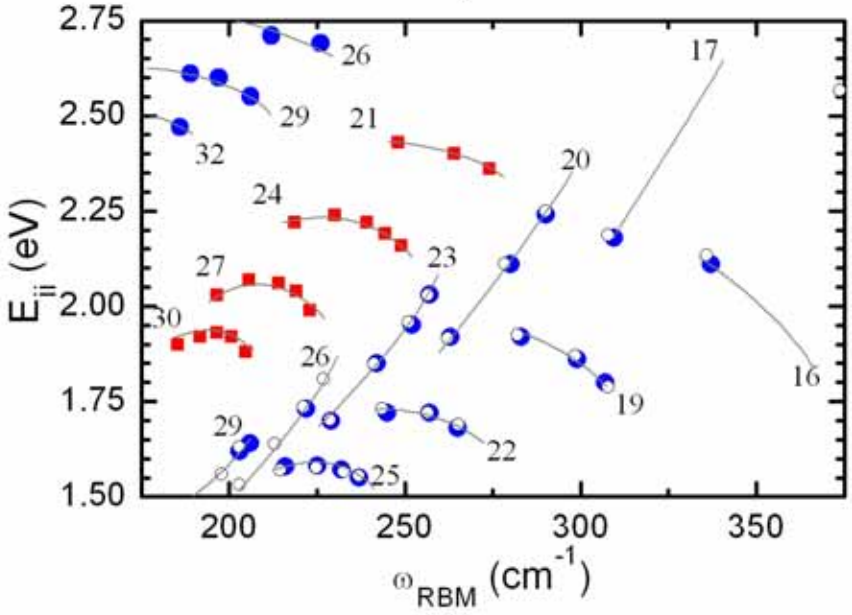


The Kataura plot for HiPco SWNTs - Result



Extended tight binding model

Ge.G.Samsonidze et al. Appl. Phys. Lett. 85, 5703 (2004) .



Experimental results

- From the Stokes and anti-Stokes Raman resonance windows

The (*n*,*m*) assignment is based on the family patterns observed in the (ω_{RBM} , E_{ii}) plot

Good agreement with experimental results obtained by PL for semiconducting SWNTs

Extended tight binding method, including curvature effect and many body interactions fit better the experimental results

Only the lower E_{11}^{M} branch is observed

Accuracy: E_{ii} ~ 10meV, ω_{RBM} ~ 0.5cm^{-1}

Atomic Deformation potential vector

$$\mathbf{m}_\sigma(\mathbf{R}_{l'}, \mathbf{r}_{s'}, \mathbf{R}_l, \mathbf{r}_s) = \int \phi(\mathbf{r} - \mathbf{R}_{l'} - \mathbf{r}_{s'} - \mathbf{r}_\sigma) \nabla v(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}_l - \mathbf{r}_s - \mathbf{r}_\sigma) d\mathbf{r}$$

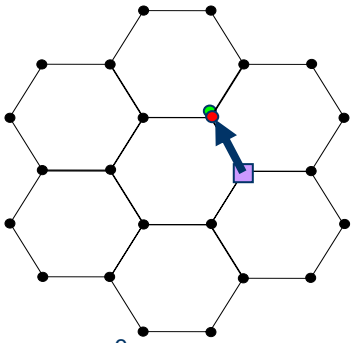
three center integral

- Graphite
  - → Deformation vector is *parallel* to the plane

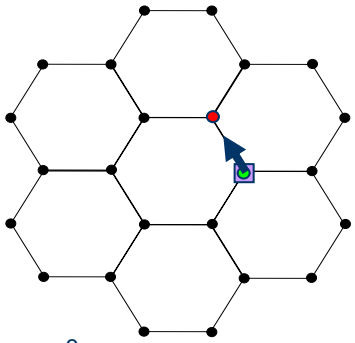
No Raman for out-of-plane phonon modes

- SWNT
  - → Deformation vector has *perpendicular components*

Strong Raman for RBM and out-of-plane phonon modes



6.7eV/A the largest (on site)



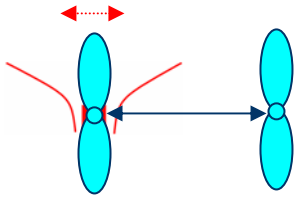
3.4eV/A the second largest (off site)

6.7eV/A: the largest **m**

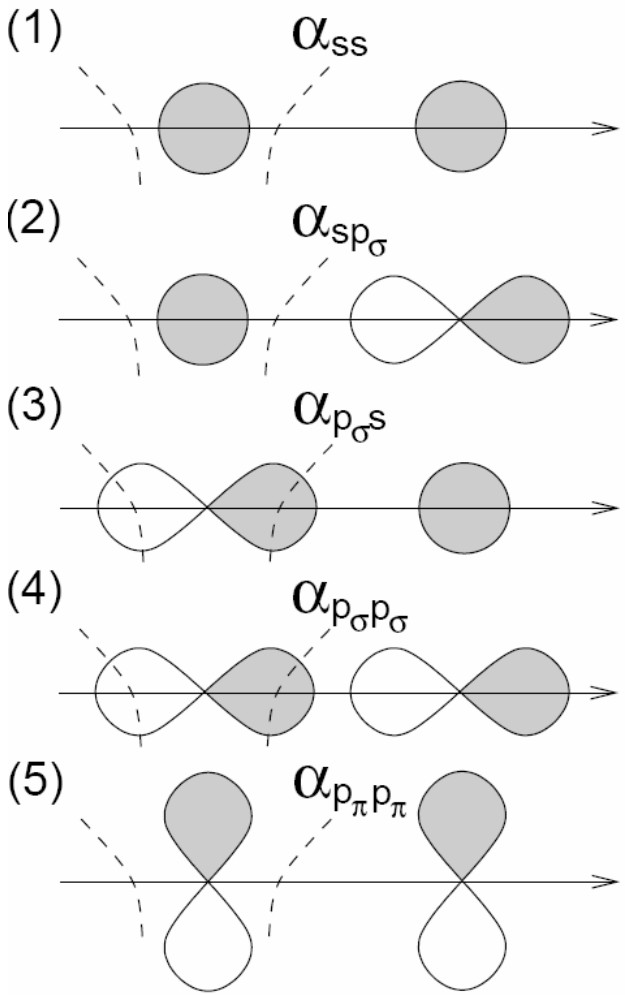
Curvature effect in electron-phonon interaction

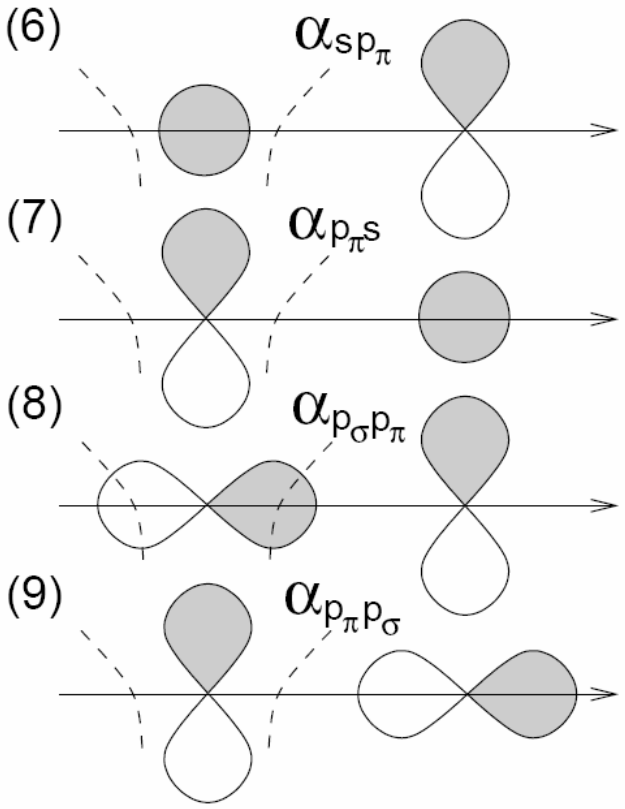
J. Jiang et al, Phys. Rev. B 72 235408 (2005)

α terms



Slater-Koster parameters for electron-phonon matrix element



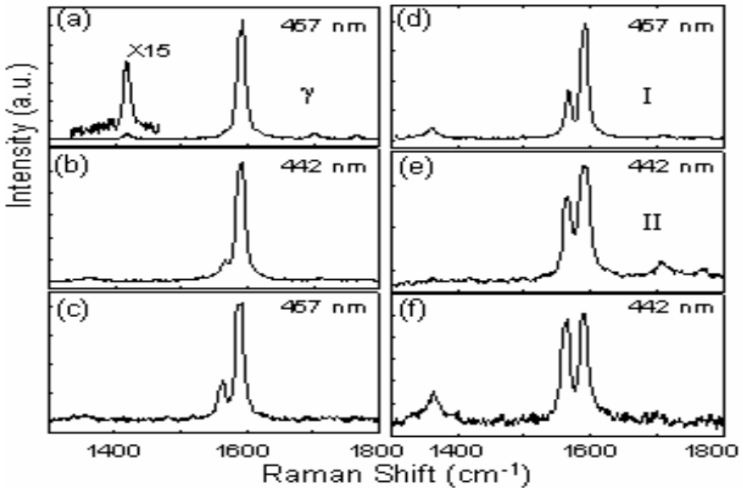


(1)-(5): along bond direction
(6)-(9): perpendicular to bond direction

Electron-phonon interaction for G-band

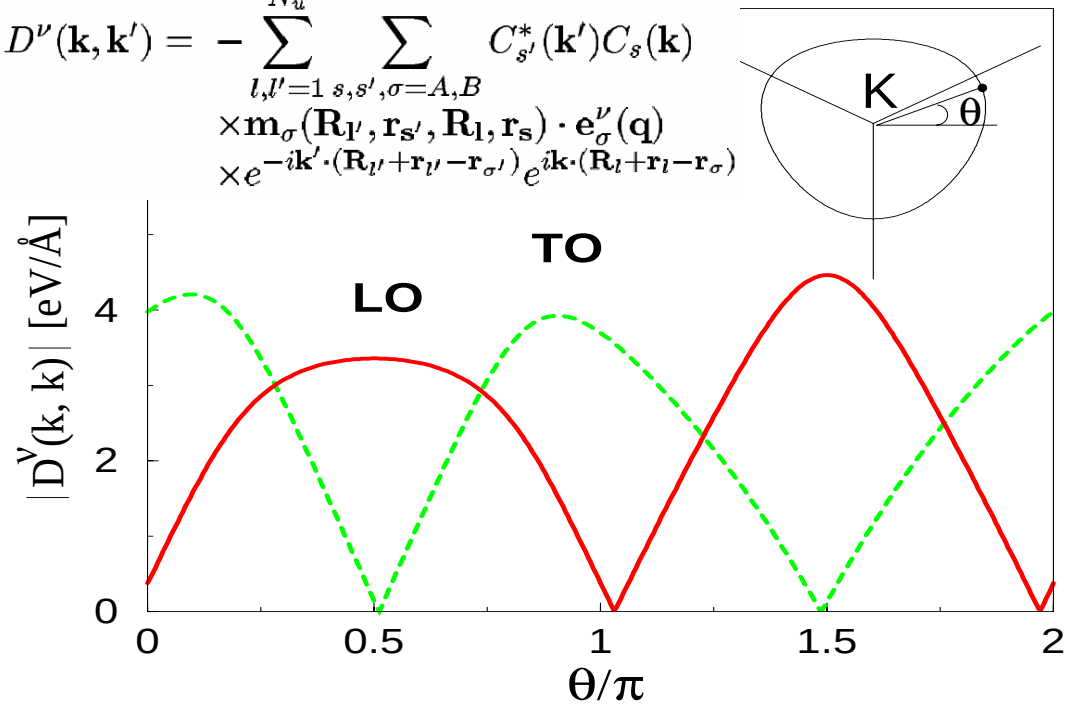
J. Jiang *et al. Chem. Phys. Lett.* 392, 383 (2004)

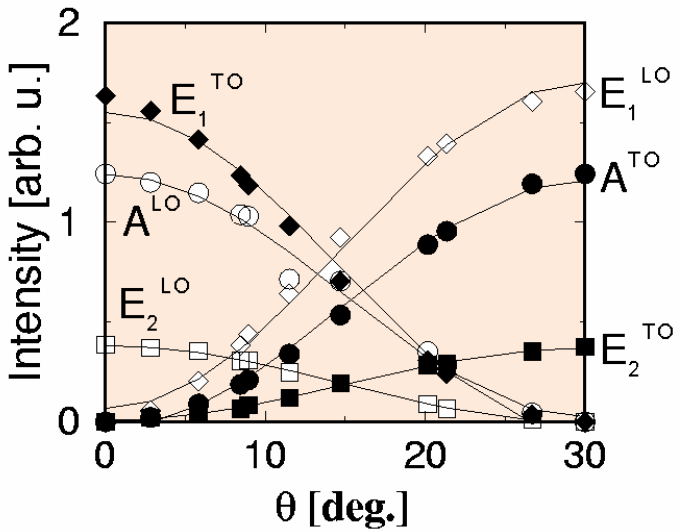
- ***q=0, D(k,k)*** → 1st order Raman
- chirality dependence of G-band



Z. Yu, L. E. Brus, *J. Phys. Chem. B* **105**, 6831 (2001)

$$D^{\nu}(\mathbf{k},\mathbf{k}') = -\sum_{l,l'=1}^{N_u}\sum_{s,s',\sigma=A,B} C^{*}_{s'}(\mathbf{k}')C_{s}(\mathbf{k}) \times \mathbf{m}_{\sigma}(\mathbf{R}_{l'},\mathbf{r}_{s'},\mathbf{R}_{l},\mathbf{r}_{s})\cdot\mathbf{e}^{\nu}_{\sigma}(\mathbf{q}) \times e^{-i\mathbf{k}'\cdot(\mathbf{R}_{l'}+\mathbf{r}_{l'}-\mathbf{r}_{\sigma'})}e^{i\mathbf{k}\cdot(\mathbf{R}_{l}+\mathbf{r}_{l}-\mathbf{r}_{\sigma})}$$



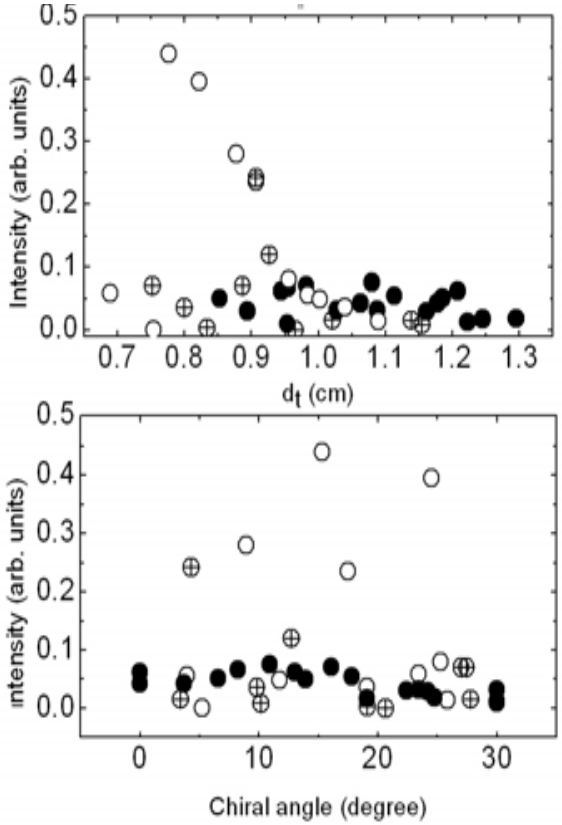


R. Saito *et al*, *Phys. Rev.* **B**63, 085312 (2001)

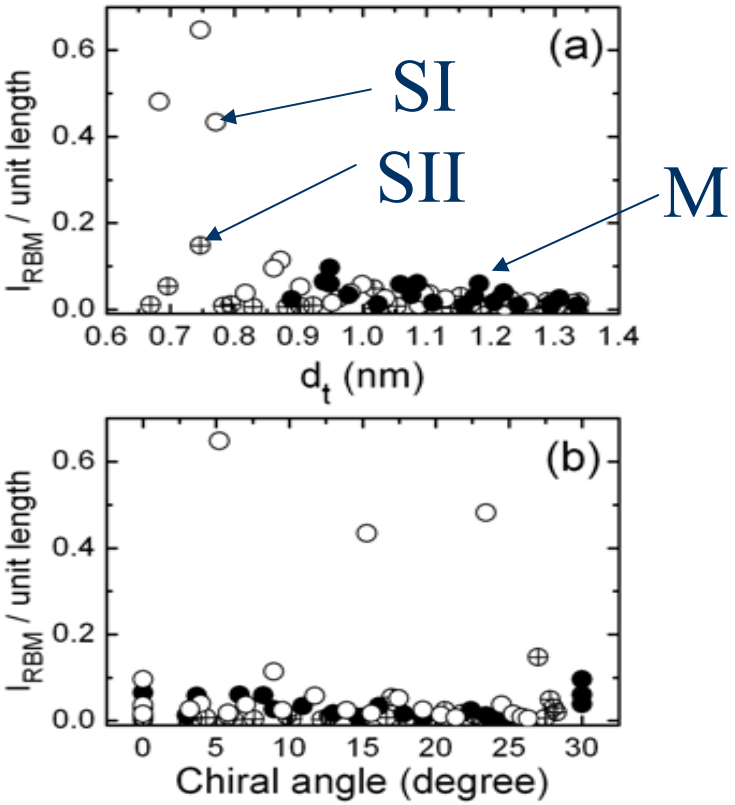
Analysis of RBM Raman intensities

A. Jorio *et al*, , *Phys. Rev.* B (2005)

Experiment



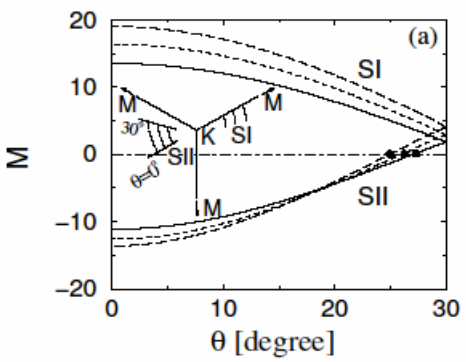
Calculations

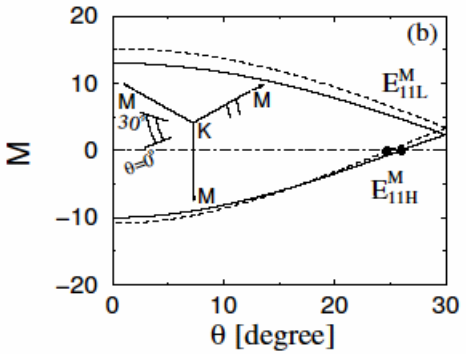


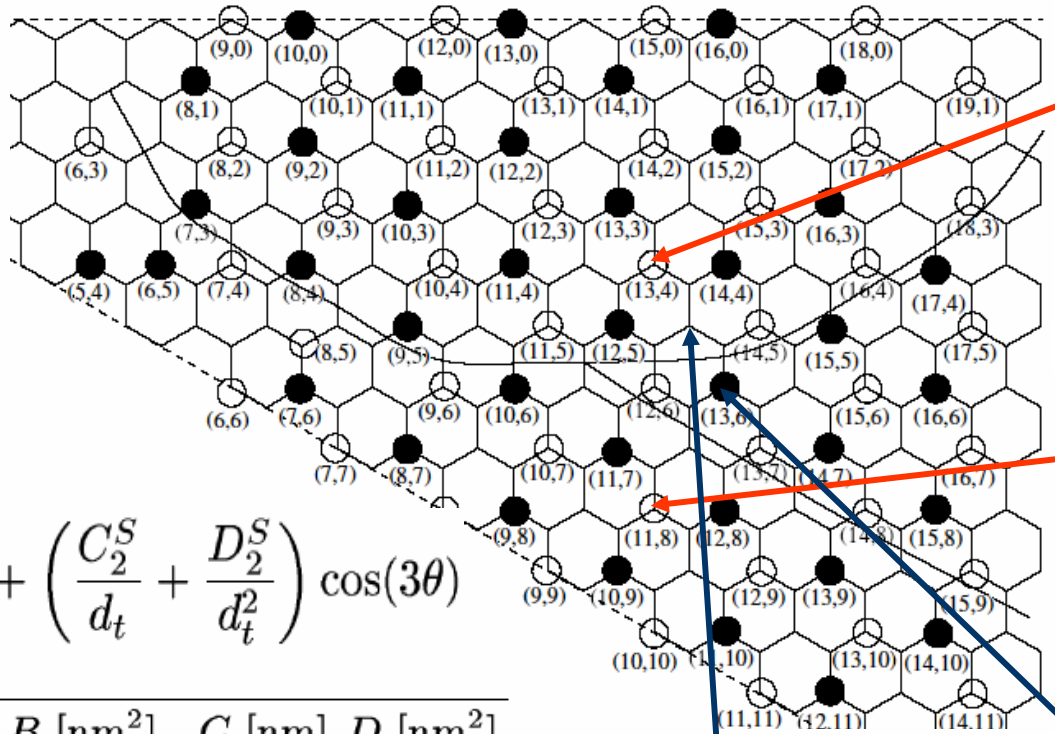
Diameter, chirality and type I vs. type II dependence is observed in good agreement with calculations of Raman intensity

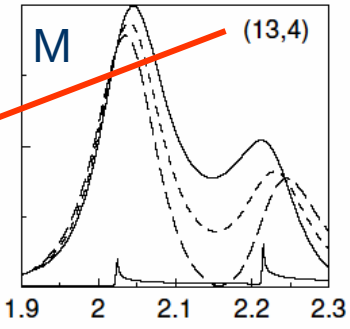
Quantum interference effect of RBM Raman intensity

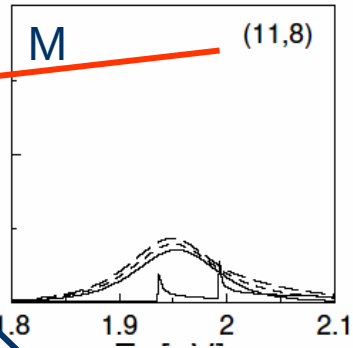
J. Jiang *et al*, Phys. Rev. 71, 205420 (2005)





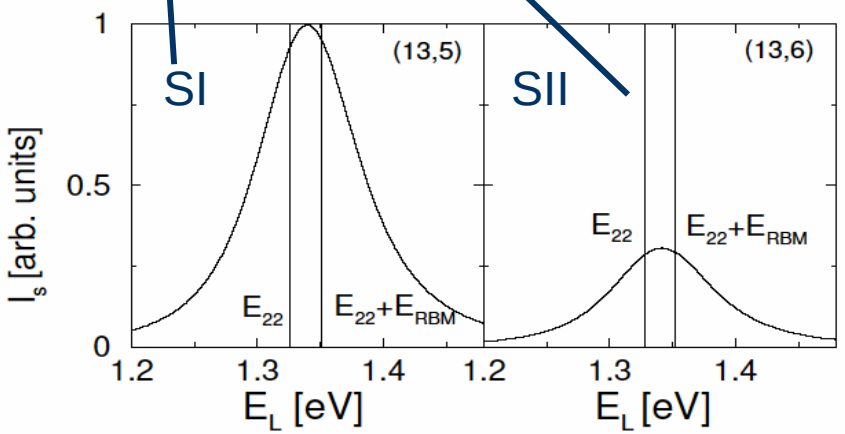






$$\frac{I_2^S(d_t,\theta)}{C} = \frac{A_2^S}{d_t} + \frac{B_2^S}{d_t^2} + \left(\frac{C_2^S}{d_t} + \frac{D_2^S}{d_t^2}\right)\cos(3\theta)$$

type	A [nm]	B [nm^2]	C [nm]	D [nm^2]
SI	-0.03187	-0.04106	0.07297	0.4163
SII ($\theta < 25°$)	0.09683	-0.2997	0.03431	0.4300
SII ($\theta \geq 25°$)	-0.0005478	0.03230	-0.26691	0.01084
M	-0.05525	-0.06549	0.05871	0.7578
Arm	-0.2634	0.4302	0	0

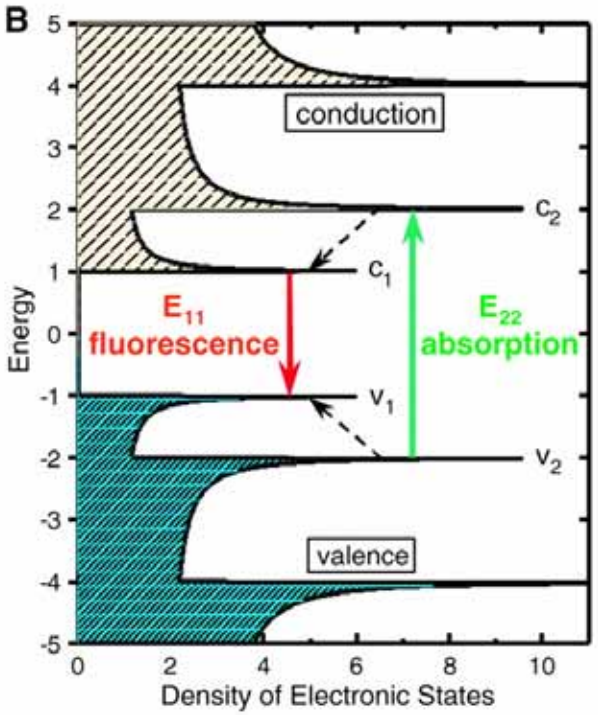


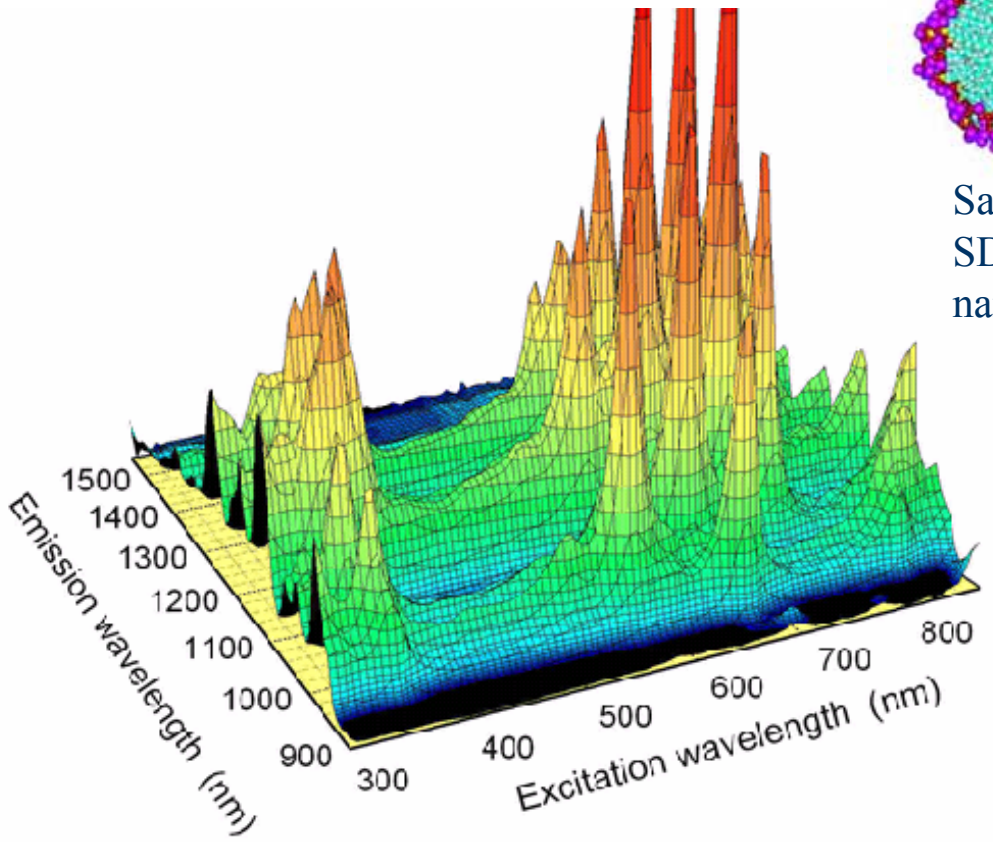
Fluorescence from SDS-wrapped nanotubes

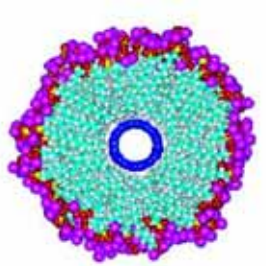
Structure-Assigned Optical Spectra of Single-Walled Carbon Nanotubes

S. M. Bachilo *et al.*, Science 298, 2361 (2002)

Absorption and Emission

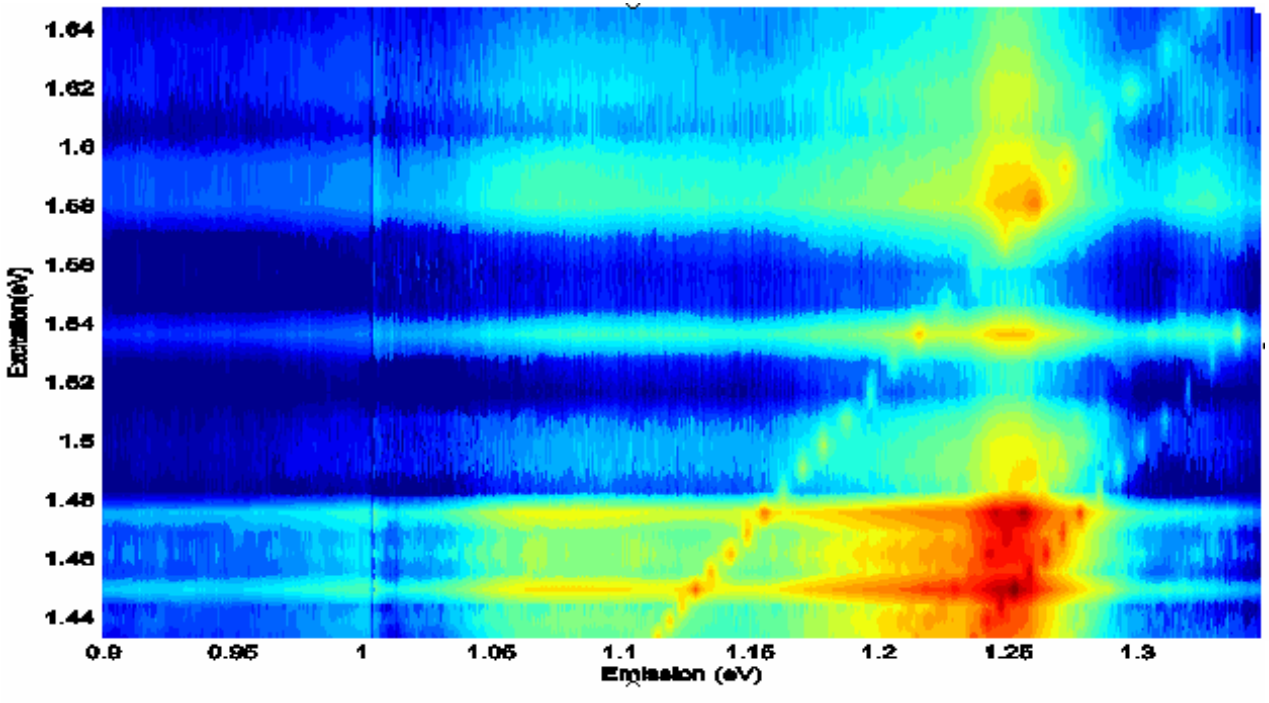


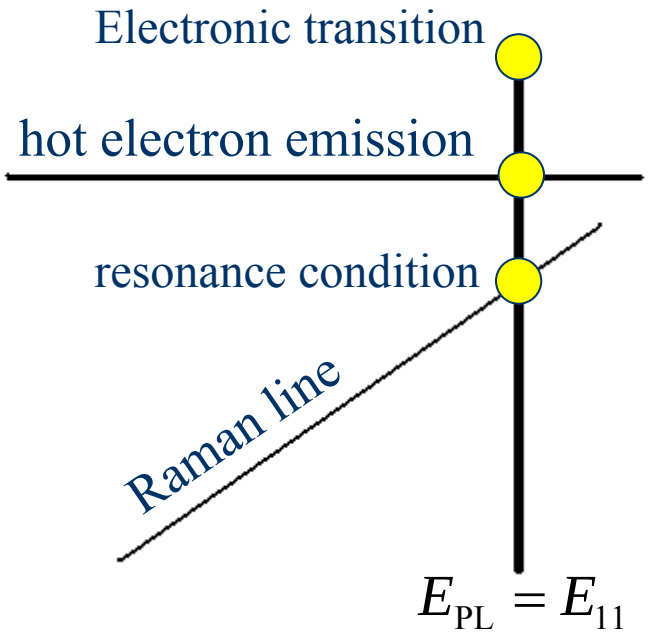




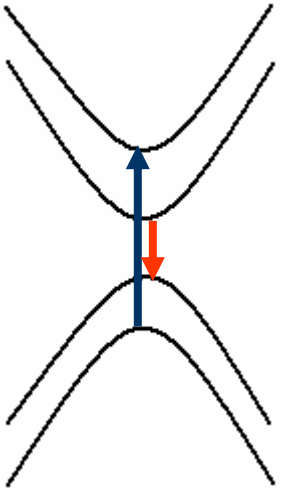
Sample: SDS-wrapped nanotubes

Each peak on the figure represents the observed E_{22} & E_{11} transitions for one SWNT.





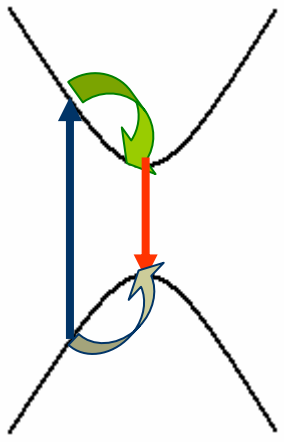
Electronic transition



$E_{ex} = E_{22}$

$E_{PL} = E_{11}$

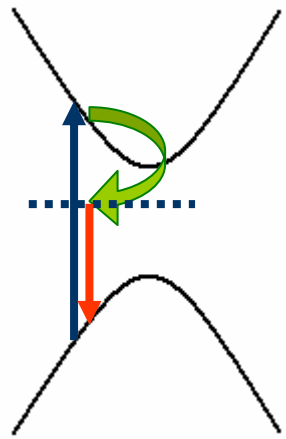
2-phonon jump



$E_{ex} = E_{11} - 2\hbar\omega$

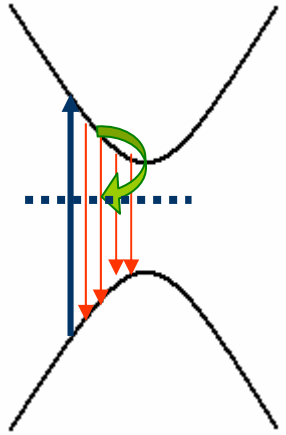
$E_{PL} = E_{11}$

Raman line



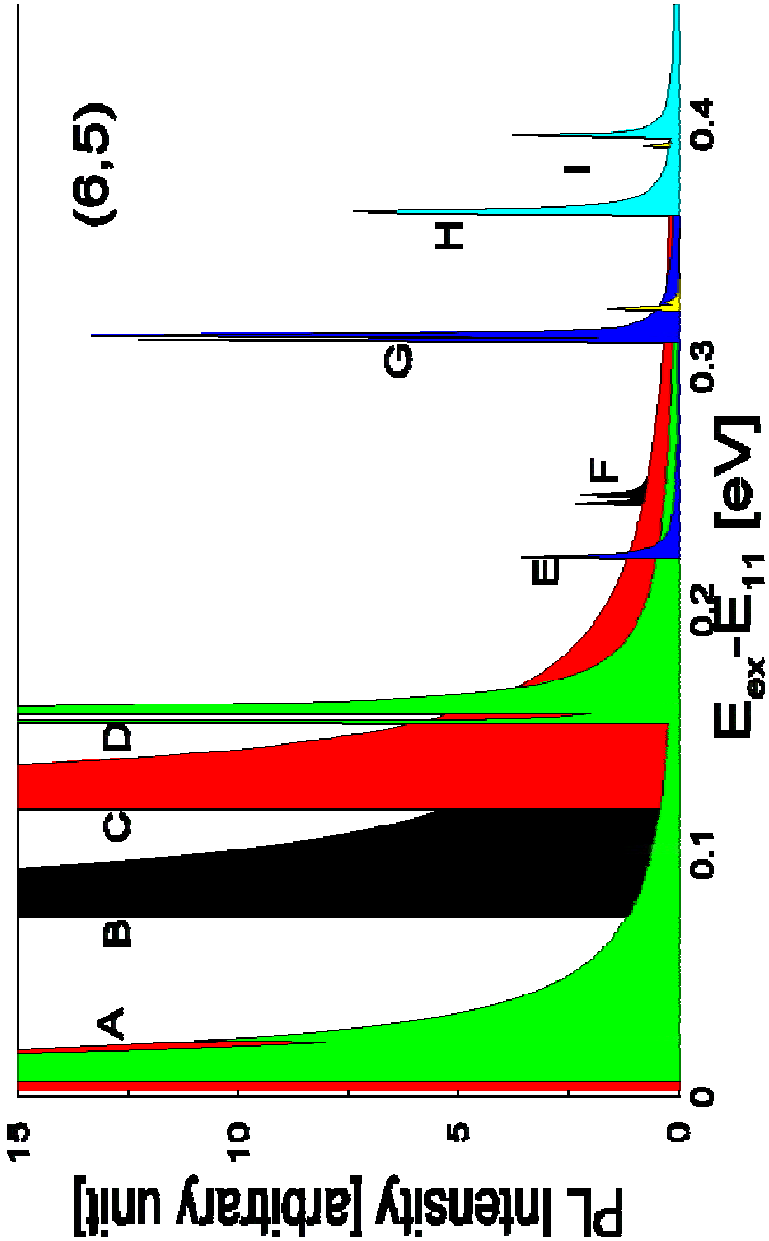
$E_{PL} = E_{ex} - \hbar\omega$

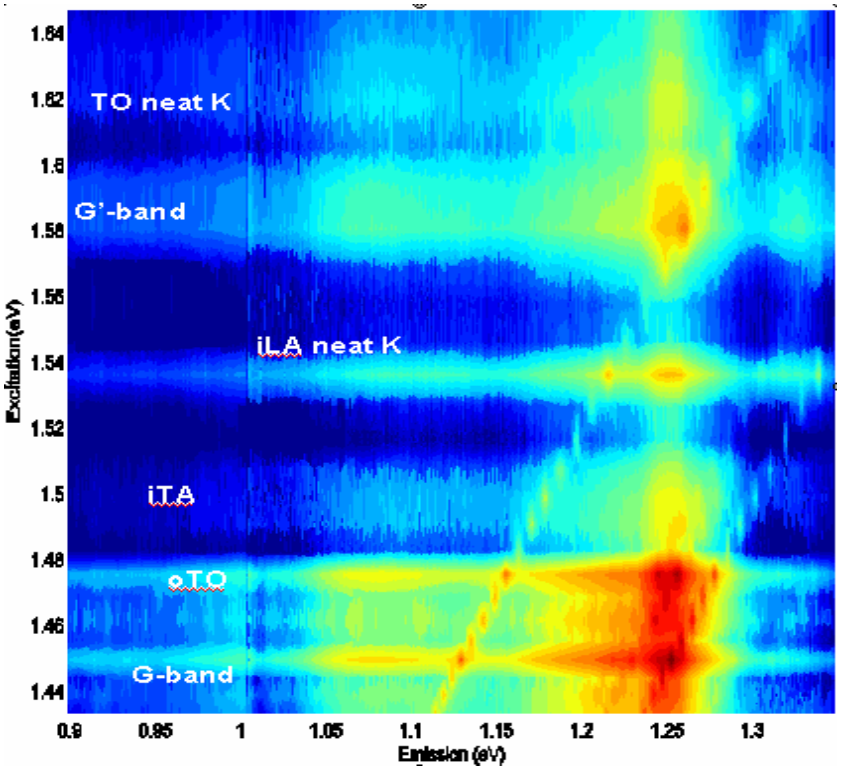
hot electron emission

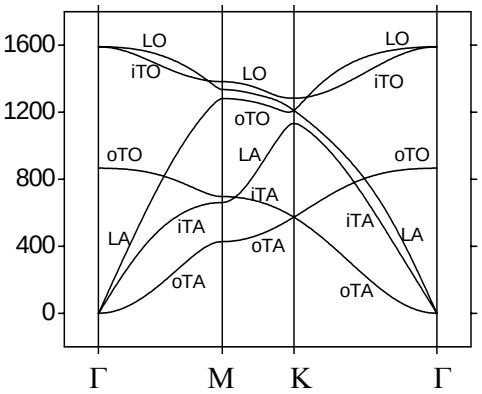


$E_{ex} = C$

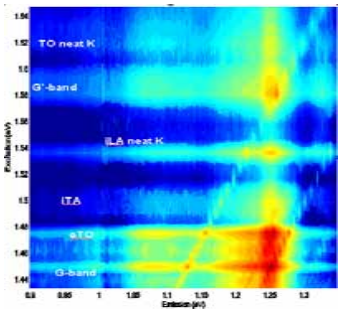
Phonon States of Nanotubes Observed in PL







A:LA,TW
B:RBM
C:oTA(near K)
D:oTO(near K)
E:oTO
F:iTA(near K)
G:iLA(near K)
H:TO(near K)
I: LO



Summary

- PL and Resonance Raman intensity
  - *Matrix element 1/d_t*
  - type I > type II, chirality dependence
  - RBM near zigzag
  - G+: not d_t chirality dependent
  - G-: near armchair
- Population analisys of SWNT is established.