Raman spectroscopy of individual freestanding single-walled carbon nanotubes of defined atomic structure

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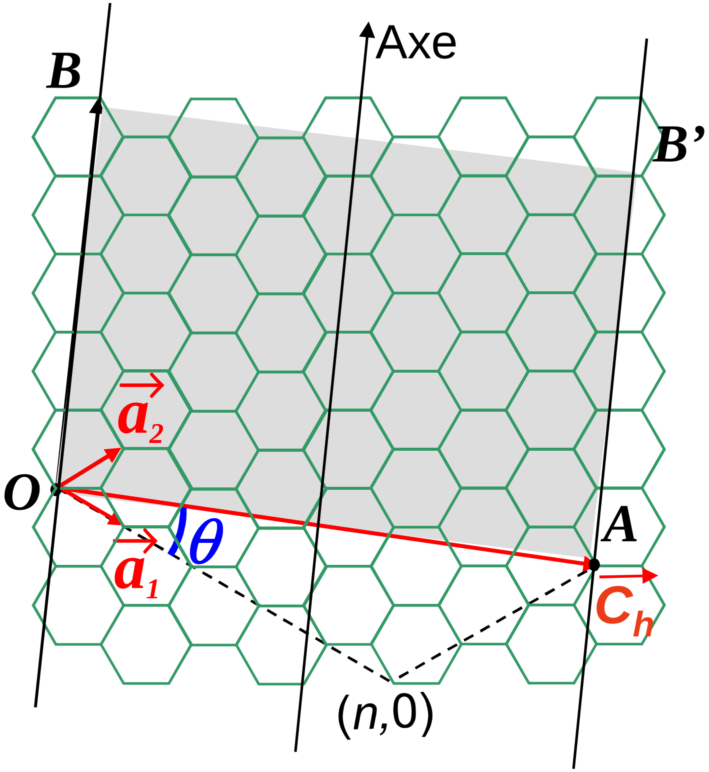
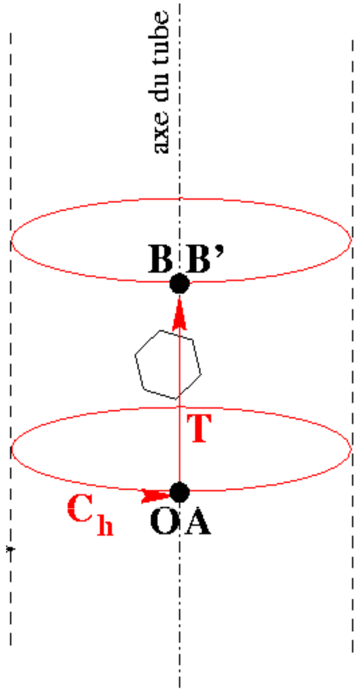
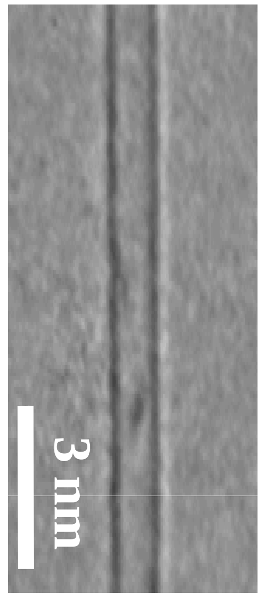
SWNT structure







$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \Rightarrow \textbf{(n,m)}$$

Diameter $d = \dfrac{|\vec{C}_h|}{\pi}$

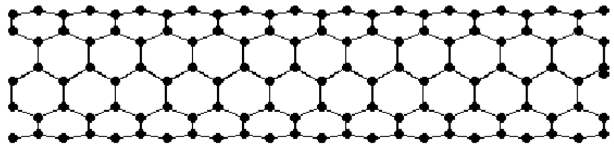
Chiral angle $\theta = \mathrm{Arc}\tan\left(\dfrac{m\sqrt{3}}{2n+m}\right)$

(n-m) mod 3 $\Rightarrow$ Metallic

(n-m) mod 3 = 1,2 $\Rightarrow$ Semiconductor

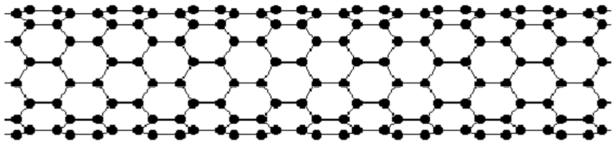
Tube (n,m)

n=m *armchair*



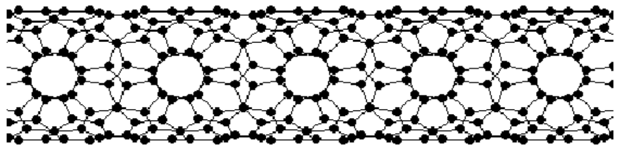
$\theta = 30°$

m=0 *zigzag*



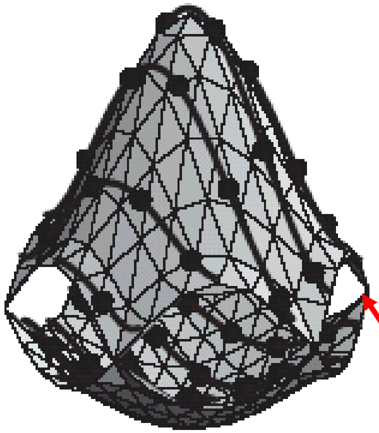
$\theta = 0°$

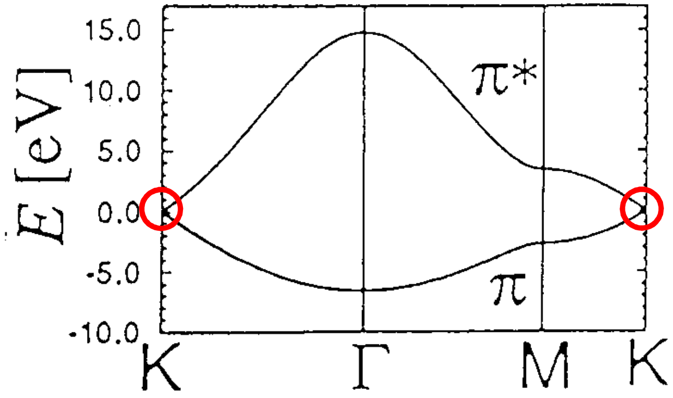
n,m *chiral*



$0° \leq \theta \leq 30°$

Electronic properties





Point K

$$E_g(\vec{k}) = \pm\gamma_0\left\{3 + 2\cos(\vec{k}\vec{a}_1) + 2\cos(\vec{k}\vec{a}_2) + 2\cos[\vec{k}(\vec{a}_1 - a_2)]\right\}^{1/2}$$

$$\vec{K}_{Ch}\,\vec{C}_h = 2\pi\mu$$

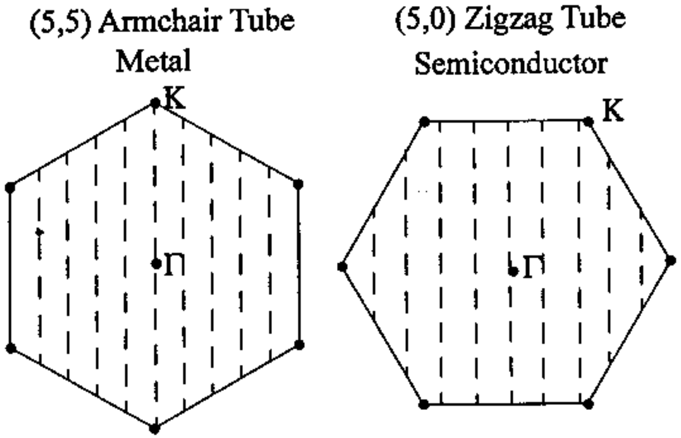
$$\mu = 0, \cdots, N-1$$

« Cutting lines »

n-m (2n+m) is a multiple of 3

n-m (2n+m) is not a multiple of 3

Metallic

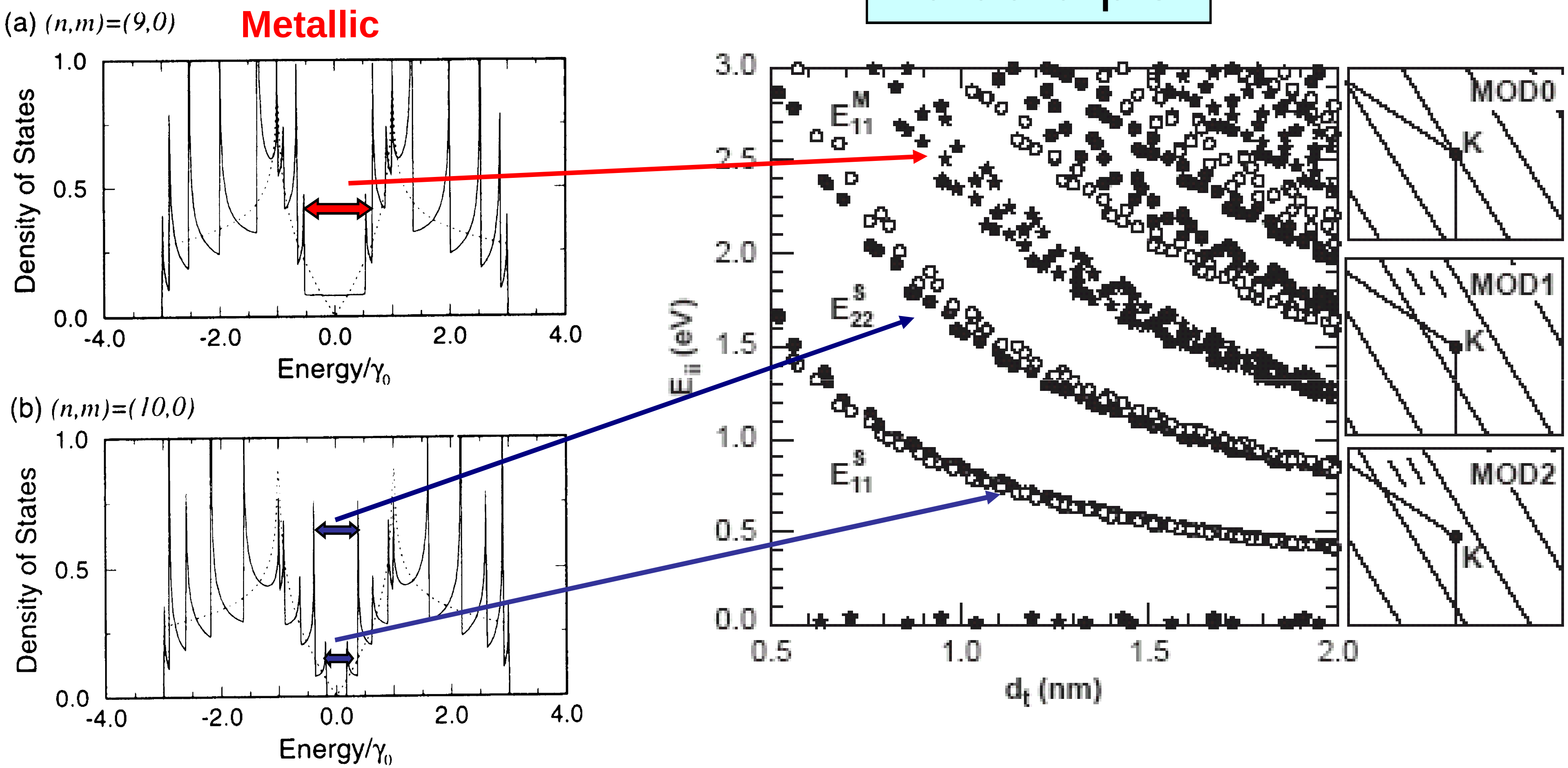


Semiconducting

Optical Transition Energies

n-m=3p Metallic

Kataura plot



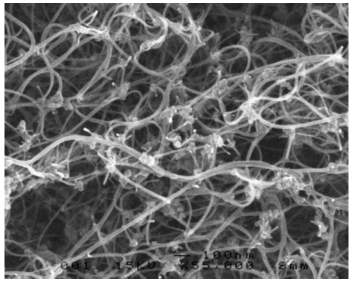
Semiconducting

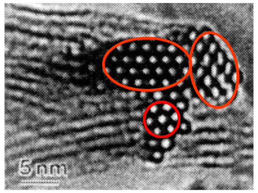
H. Kataura et al,Synth. Met., ***103*** *(1999) 2555*

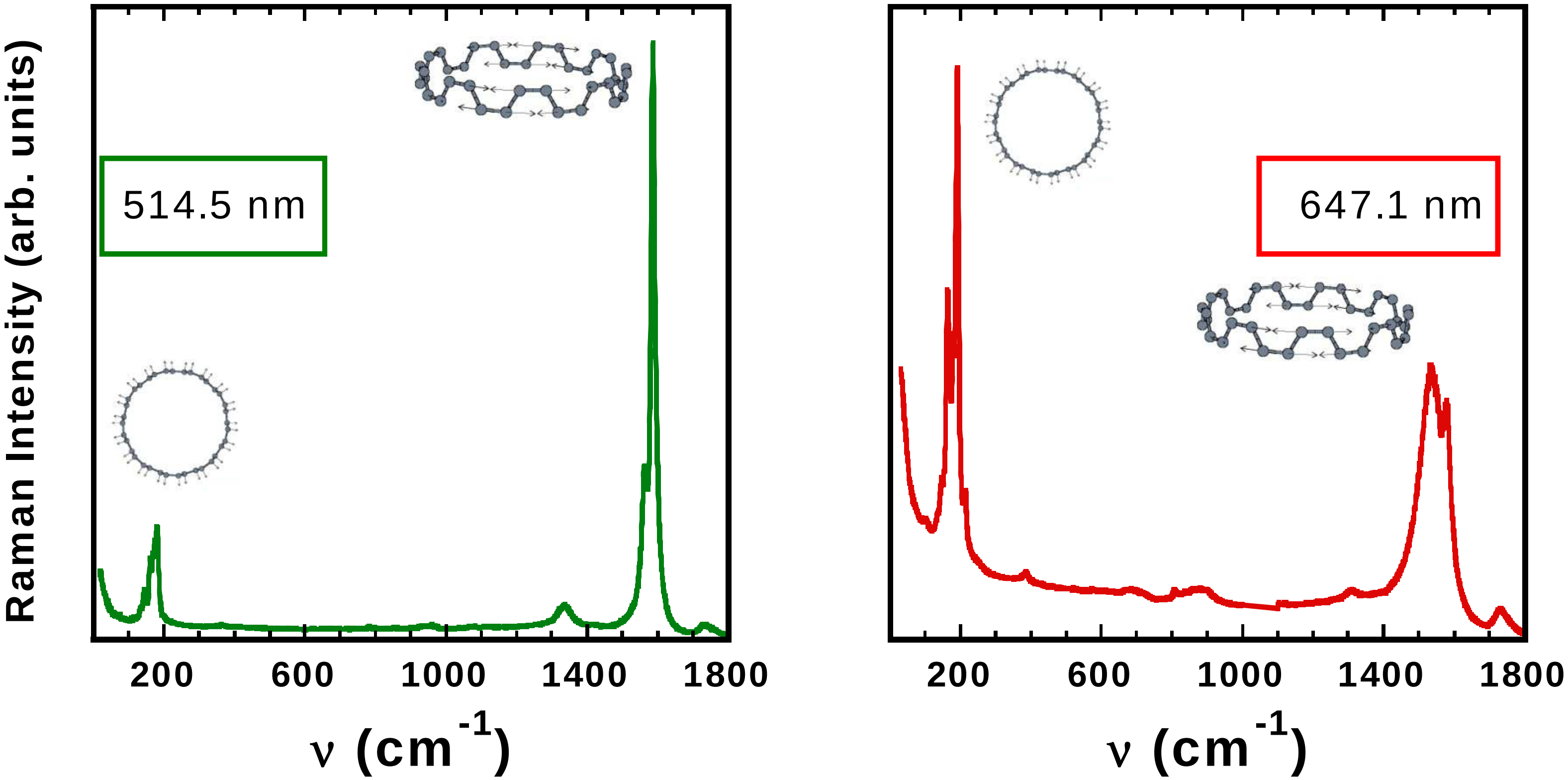
M. Dresselhaus et al, Phys. Reports, ***409*** *(2005) 47*

n-m≠3p Semiconducting

Raman spectroscopy of a nanotube bulk sample







Resonant process

Lattice structure and Raman spectrum of (n,m) individual, isolated and suspended single-walled carbon nanotubes

Electron Diffraction and Raman scattering
on the same individual SWNT

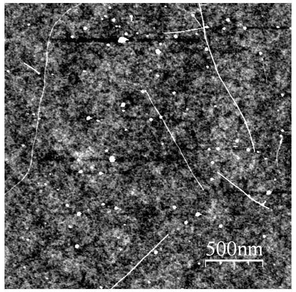
1- To prepare individual, isolated and freestanding SWNTs in such a way that acess by TEM is possible

2- To measure the same SWNT in the electron diffraction and Raman spectroscopy experiments

→ Perfect localization of the tubes on the samples

Experimental Procedure: Samples

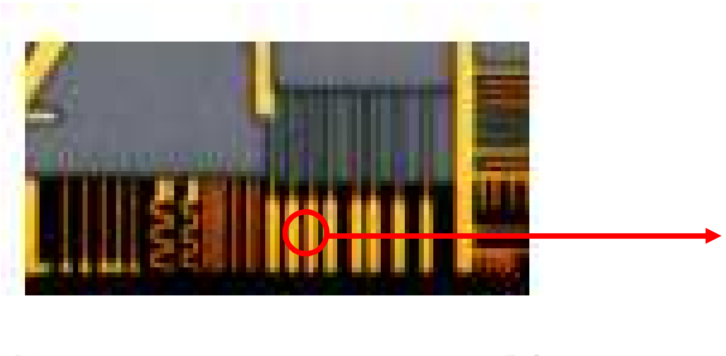
1- Individual SWNTs suspended between electrodes

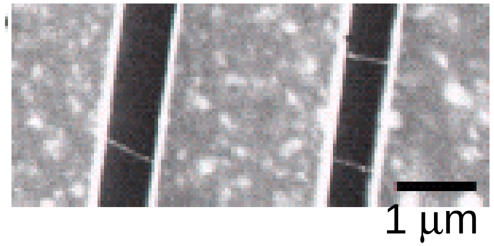


CVD synthesis of SWNTs on Si/SiO_2
CH_4 ou C_2H_4 as carbon feedstocks,

Low density of nanoparticles of catalyst Ni

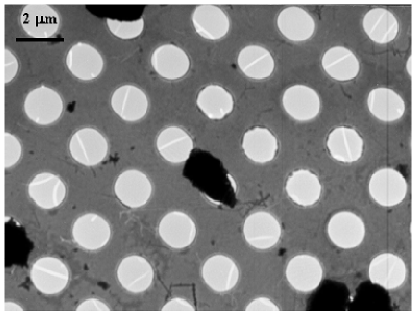
E-beam lithography and Etching





2- Individual SWNTs over holes

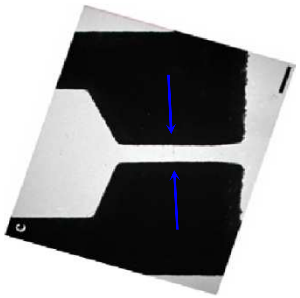
SiO_x membranes
CH_4 as carbon feedstocks



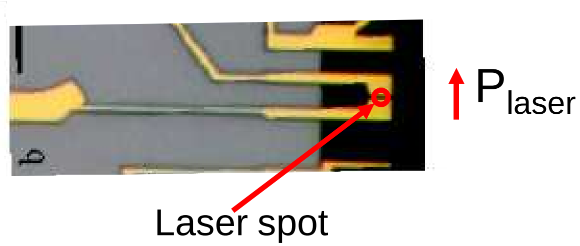
Experimental procedure

Before Raman

TEM image



Micro-Raman experiment

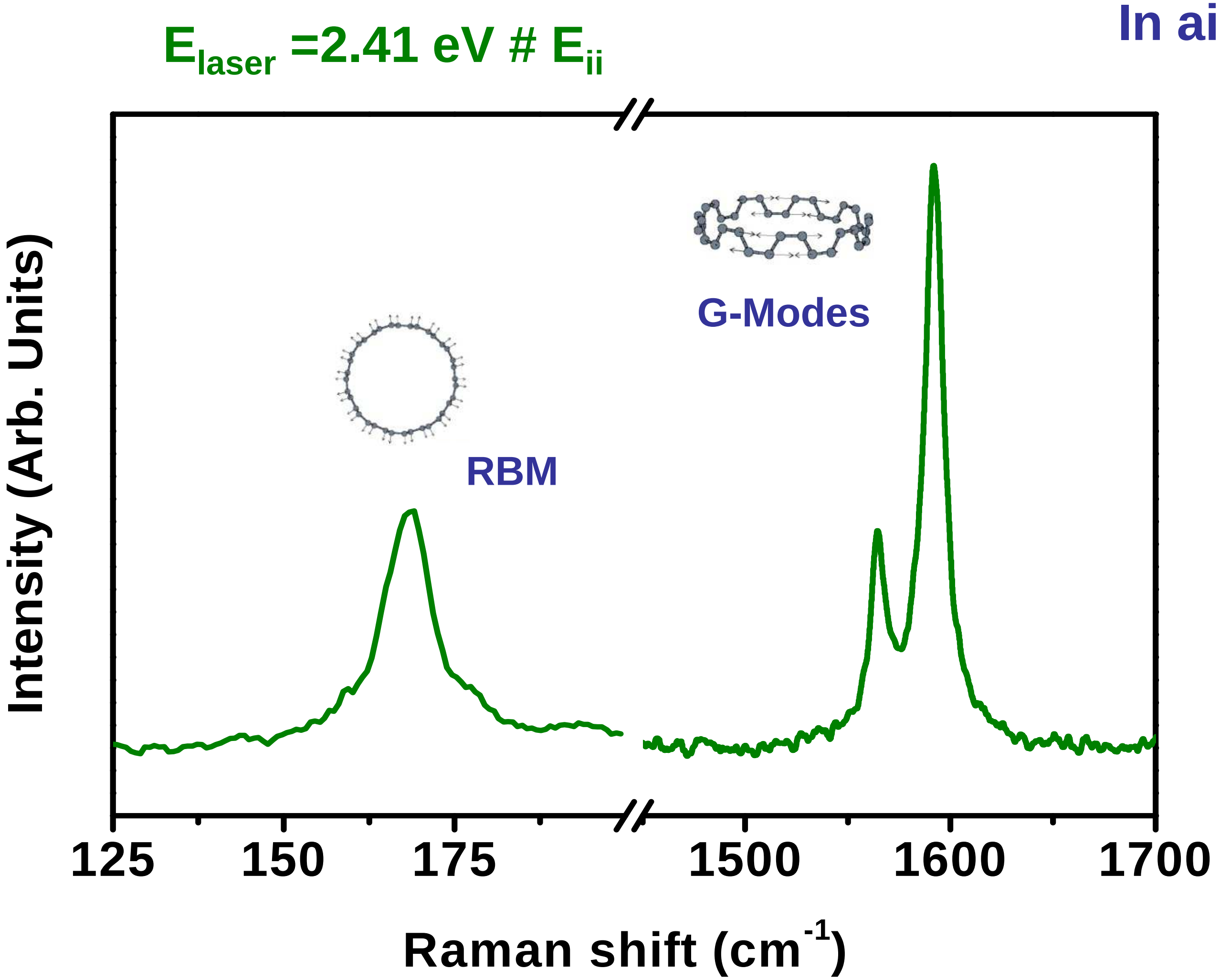


At a fixed excitation energy, E_{laser},
we try to detect a RBM signal using a short counting time (10 s)

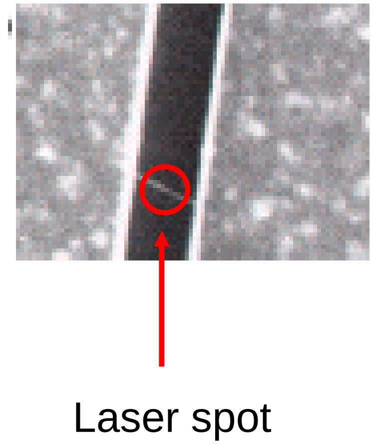
If a signal is detected → **E_{laser} # E_{ii}**

If no signal is detected, the excitation energy is changed, and we try again to obtain a signal by using a short counting time

Raman Spectrum of an individual, isolated freestanding SWNT



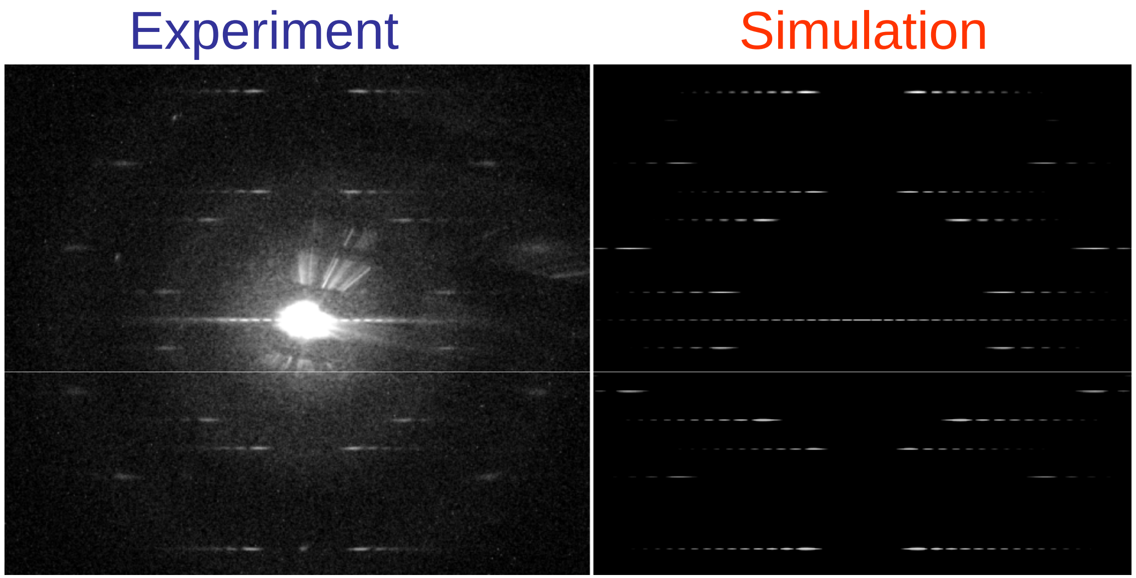
In air and room temperature



Intrinsic Raman features of the individual SWNT under investigation

After Raman experiments, Electron Diffraction experiments were performed on all the nanotubes that showed a Raman signal

J. Meyer
Max Planck Institut
Stuttgart



(24,11)

Electron diffraction states if the Raman spectra have been measured on an individual SWNT or on a small bundle

*J. C. Meyer et al., Ultramicroscopy **106** (2006) 176.*

The Radial Breathing Modes of (n,m) individual, isolated and suspended single-walled carbon nanotubes

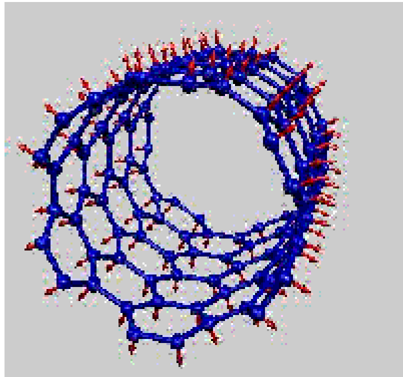
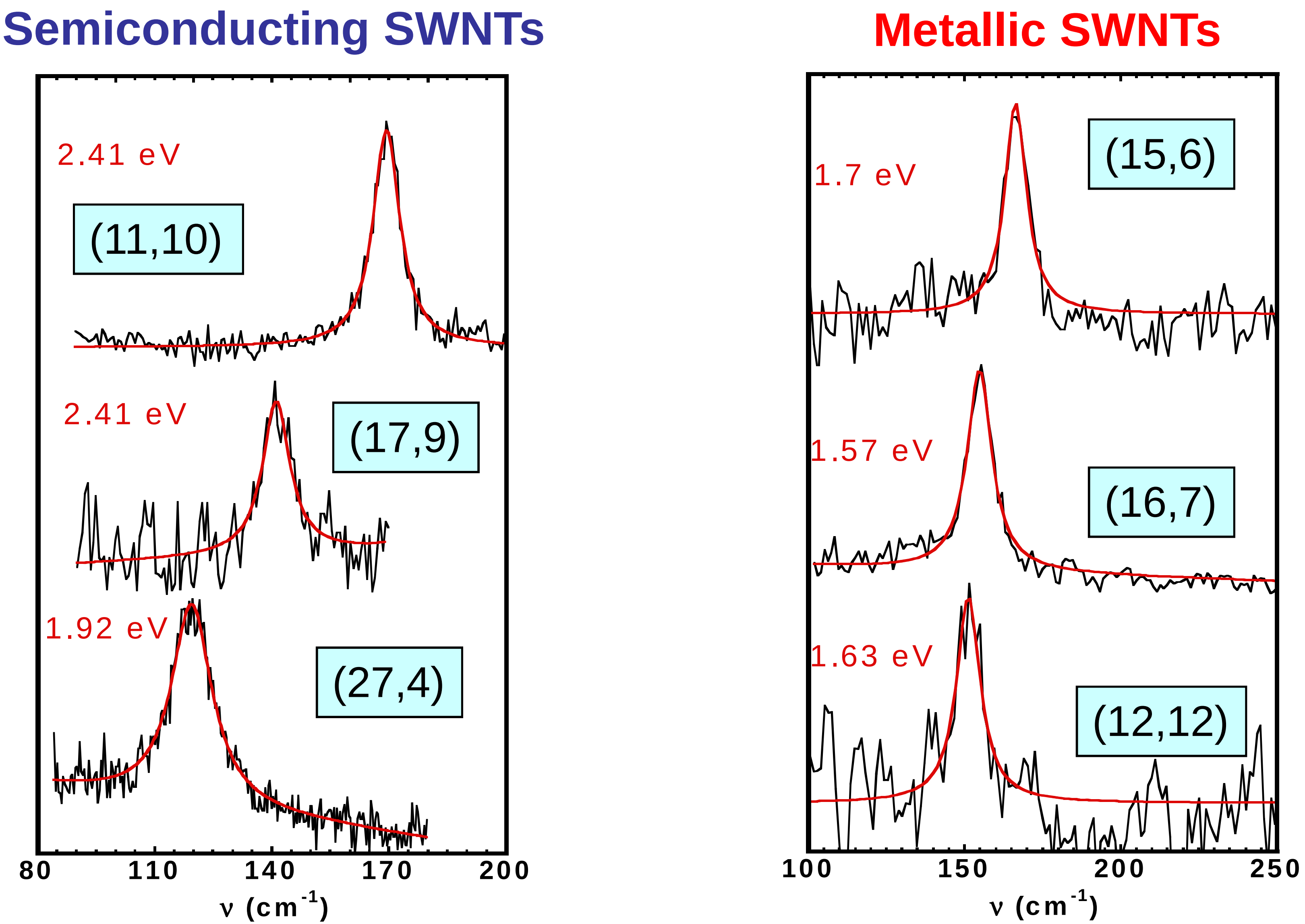


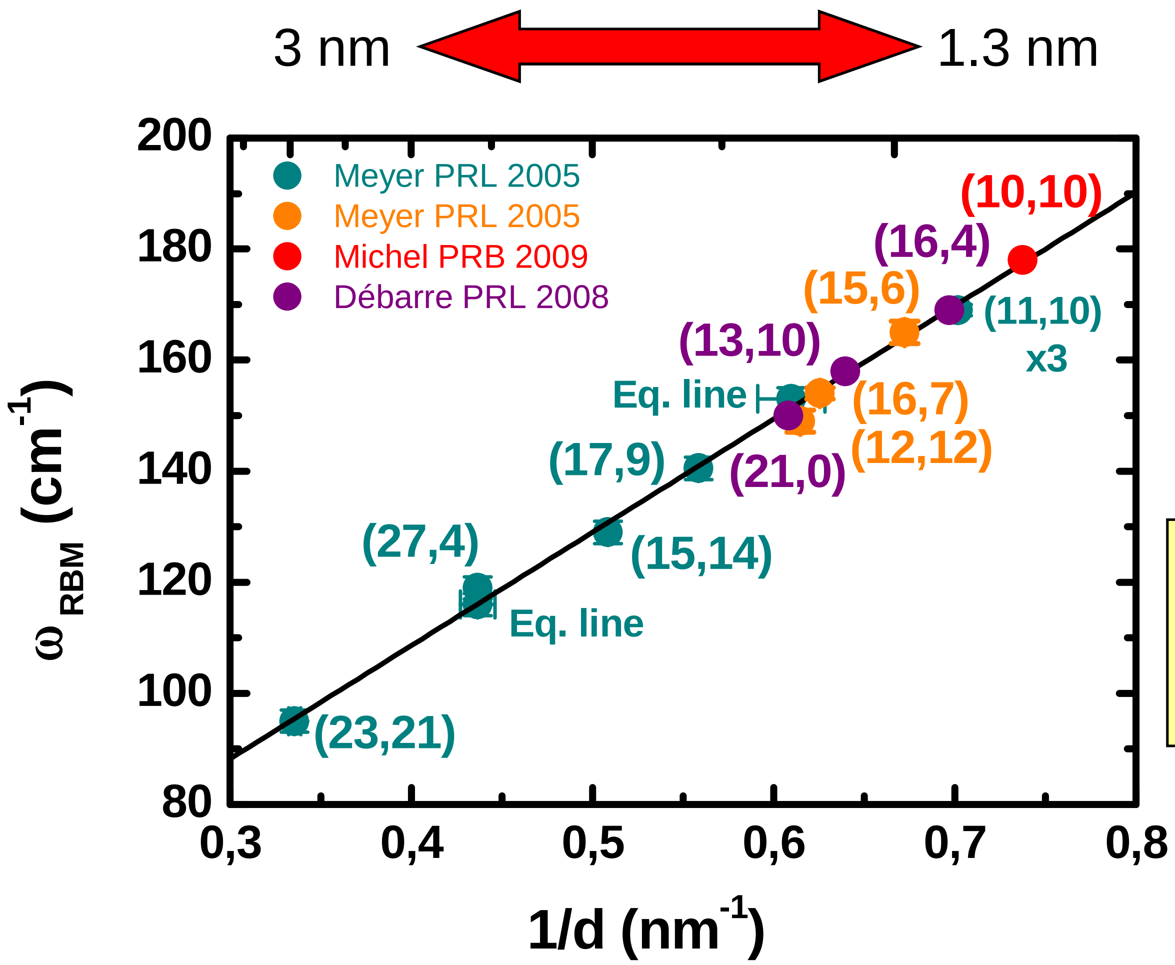
Image from: http://www-g.eng.cam.ac.uk/edm/research/ramanlab/raman_CNTs.html

Radial Breathing Modes



*J. Meyer, M. Paillet et al., PRL **95** (2005) 217401.*

Radial breathing modes frequency vs diameter



$$\omega_{RBM}\,(cm^{-1}) = \frac{204}{d\,(nm)} + 27\ cm^{-1}$$

This simple relation allows to derive the diameter of suspended individual nanotube in air from the mesurement of the RBM frequency

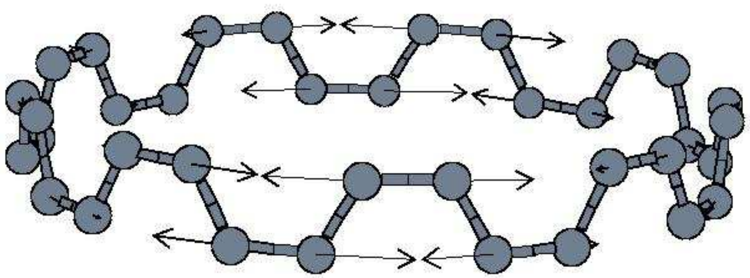
$$\omega_{RBM}(\mathbf{cm^{-1}}) = \frac{\mathbf{A}}{\mathbf{d(nm)}} + \mathbf{B}$$

B is associated to environmental effect

B= 0 with negligible environmental effect

J. C. Meyer *et al.* Phys. Rev. Lett. 95, 217401 (2005)
T. Michel *et al.* Phys. Rev. B in press (2009)
A. Débarre *et al.* Phys Rev. Lett. 101, 197403 (2008)

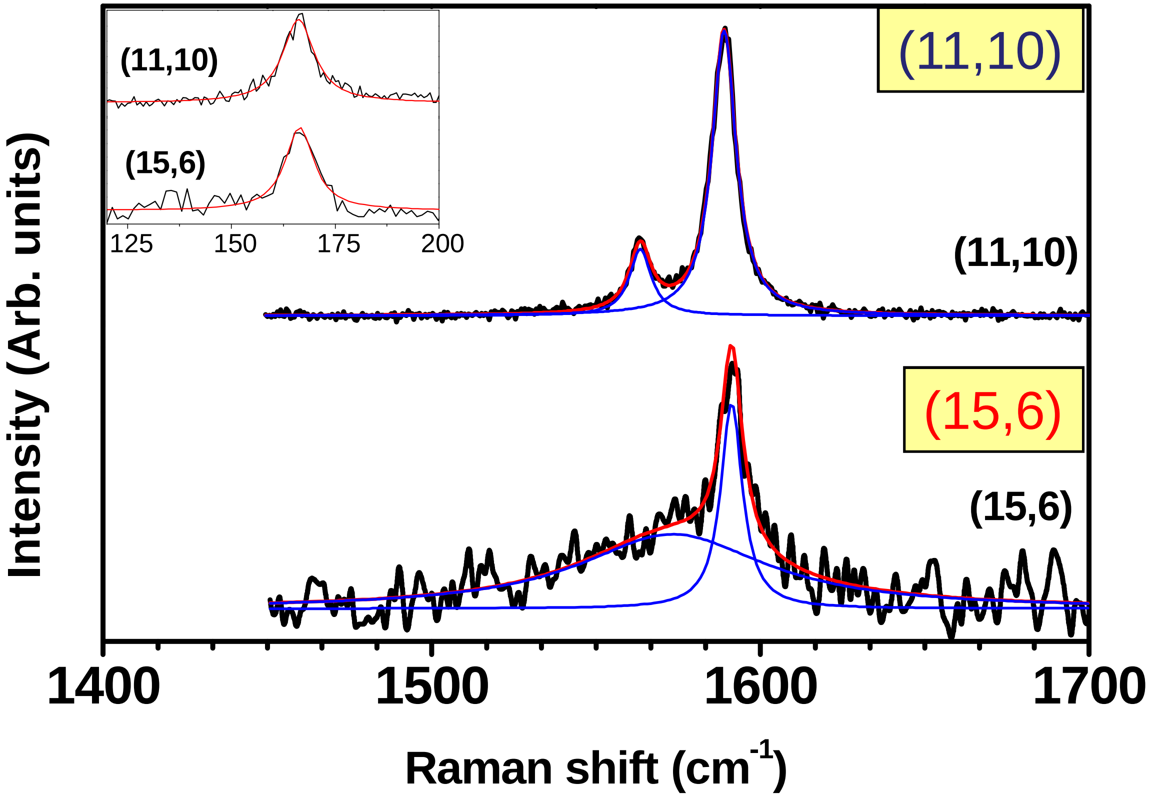
The G-modes of (n,m)-well identified SWNTs



G-modes of Chiral SWNTs

// // Polarization
Chiral SWNTs → 2 A_1 G-modes
as expected by calculations

Close diameters ≈1.45 nm



Semiconducting

2 narrow peaks

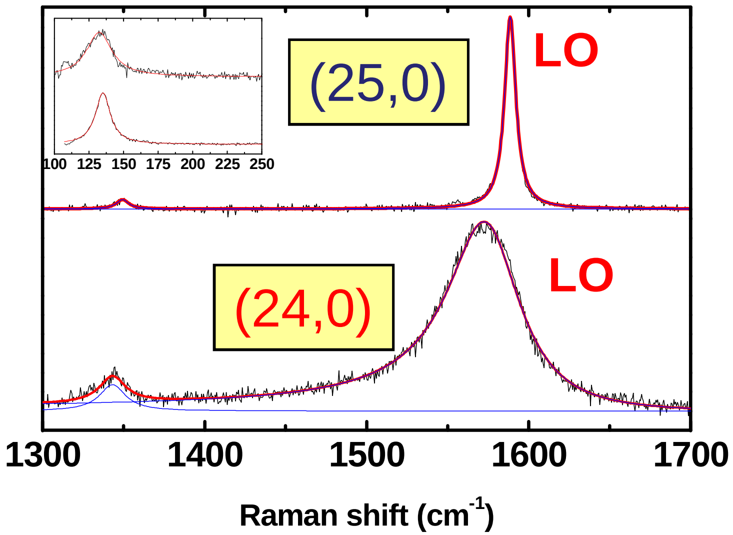
Metallic

1 narrow and 1 broad peak

T. Michel *et al.* Phys. Rev. B in press (2009)

G-modes of Achiral SWNTs

ZigZag (m = 0)



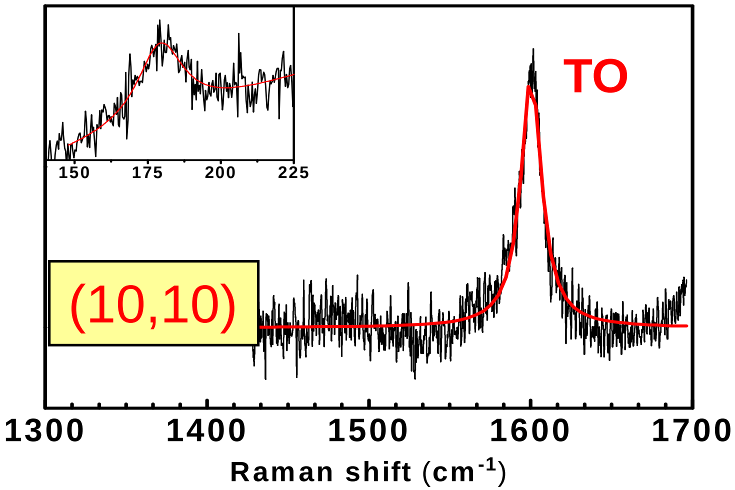
Semiconducting

1 narrow peak

Metallic

1 broad peak

Armchair (n = m)



Metallic

1 narrow peak

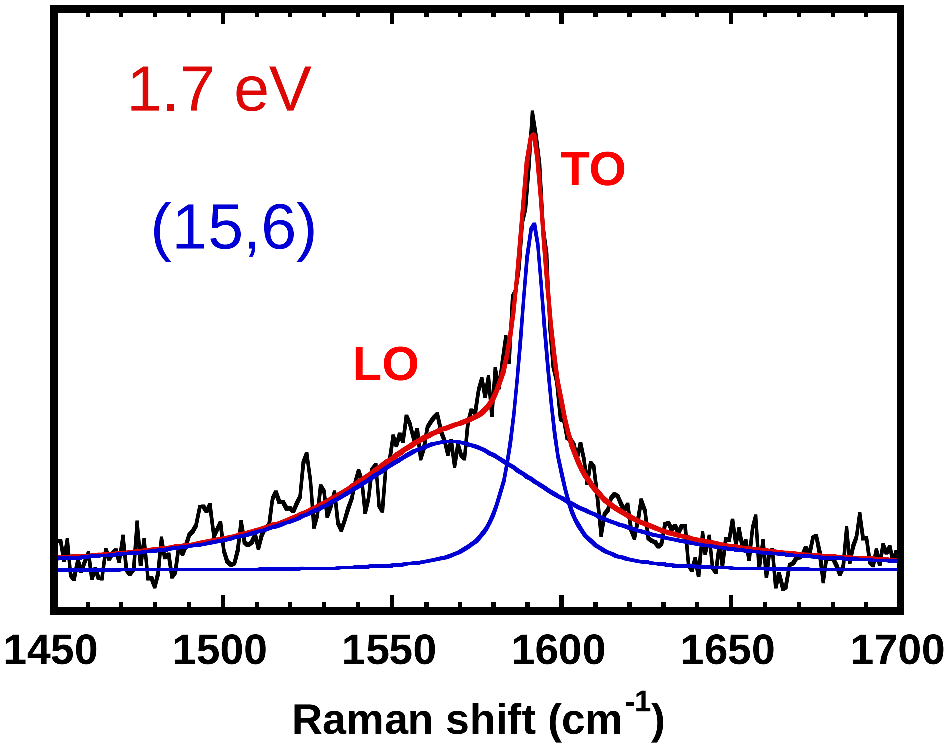
T. Michel *et al.* Phys. Rev. B in press (2009)

G-modes of Metallic SWNTs

(15,6) SWNT

Diameter =1.47 nm

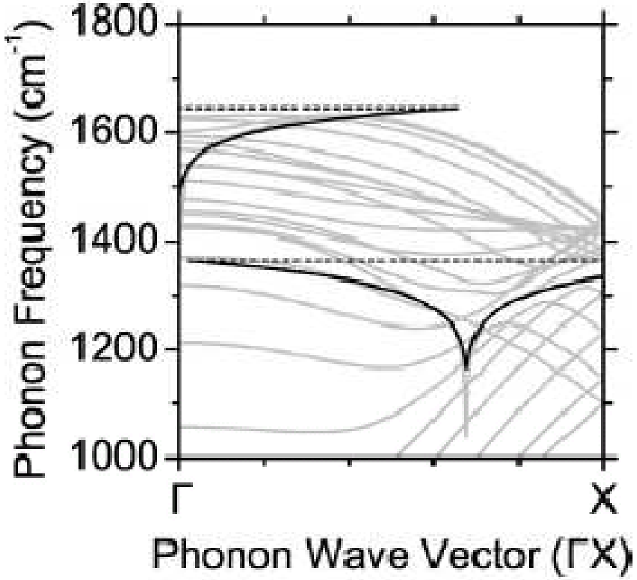
In resonance with the E^M_{11} transition



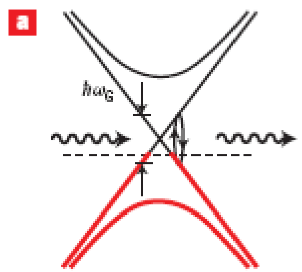
$$I(\omega) = I_1 \frac{[1+2(\omega-\omega_1)/q\Gamma_1]^2}{1+[2(\omega-\omega_1)/\Gamma_1]^2} + I_2 \frac{1}{1+[2(\omega-\omega_2)/\Gamma_2]^2}$$

Breit-Wigner-Fano (BWF)

Kohn anomaly



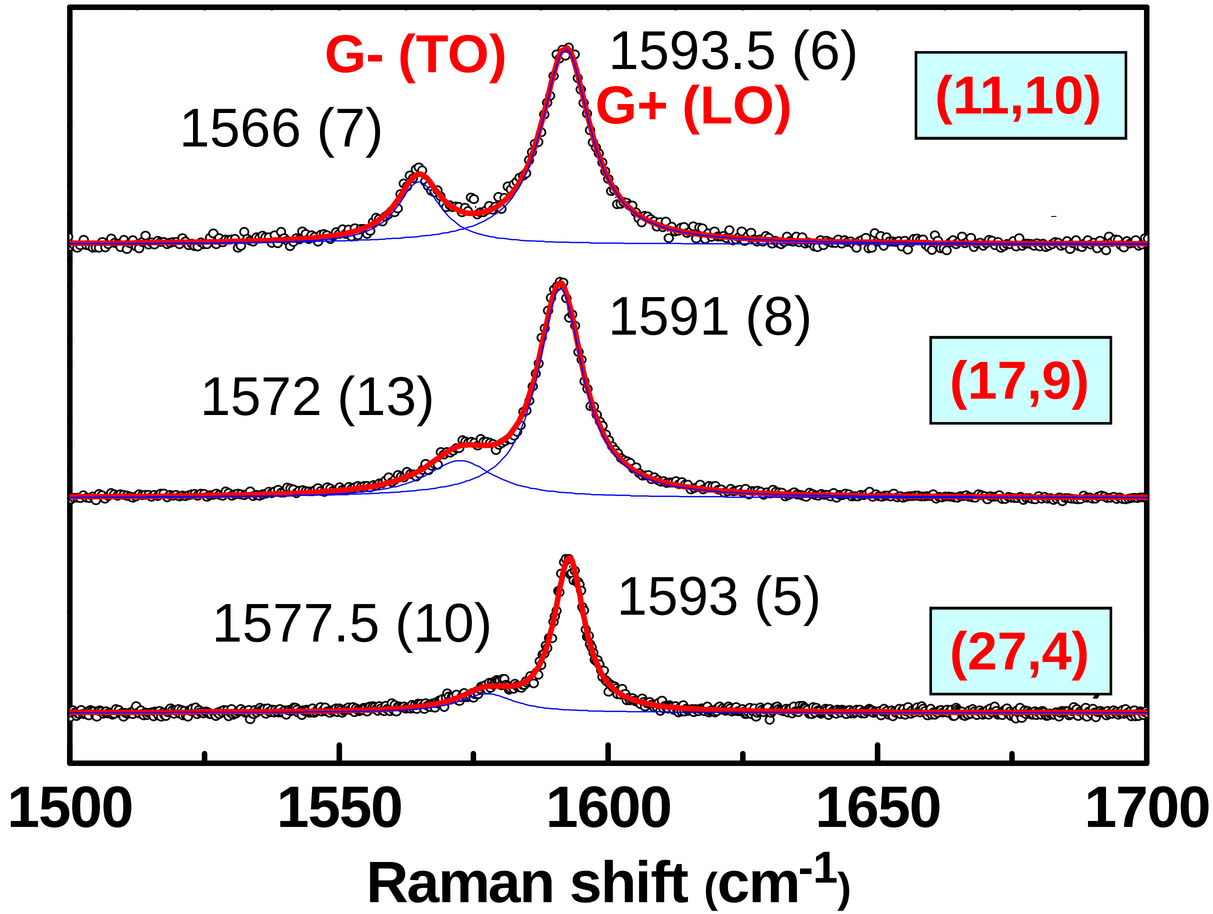
*G.G. Samsonidze et al, PRB **75** (2007) 155420*



$$\gamma^{EP}_{\Gamma-LO} = \frac{2\sqrt{3}\hbar a_0^2}{\pi M \omega_\Gamma \beta} \frac{\langle D^2_\Gamma \rangle_F}{d}; \quad \gamma^{EP}_{\Gamma-TO} = 0.$$

*M. Lazzeri et al., PRB **73** (2006) 155426*

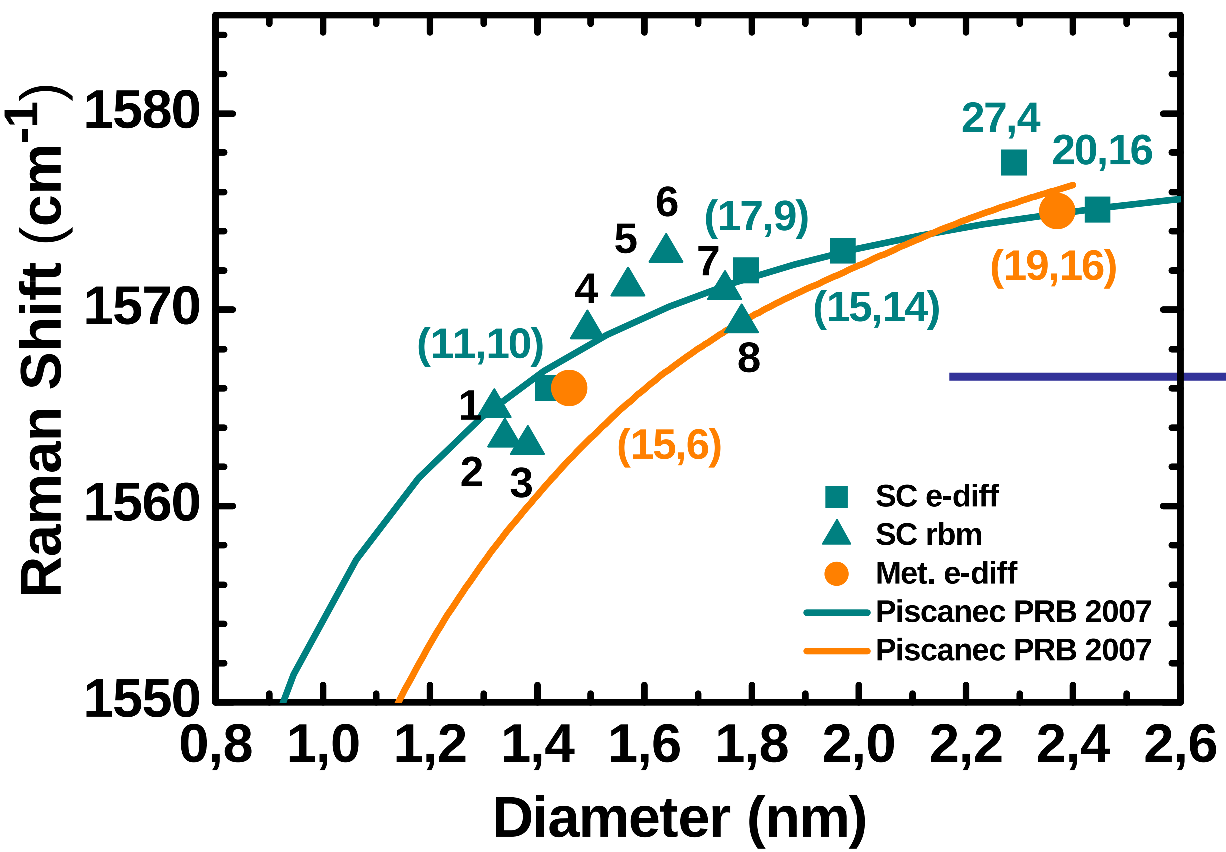
G-modes of Semiconducting SWNTs



G- frequency varies with diameter
G+/G- intensity ratio depend on both diameter and chiral angle

*M. Paillet et al., PRL **96** (2006) 257401*

Frequencies of G- modes



A tool to determine the diameter of a nanotube under investigation

// // Polarization

Achiral nanotubes : 1 G mode (A_{1g})

Chiral nanotubes : 2 G modes (A_1)

M. Paillet *et al.*, PRL **96** (2006) 257401
T. Michel *et al.*, Phys. Rev. B in press (2009)

Optical Transition Energies

At a fixed excitation energy, E_{laser},
If a RBM signal is detected by using a short counting time

$$E_{laser} \# E_{ii}$$

Energy Transitions of individual SWNTs

M. Paillet *et al.*, PRL **96** (2006) 257401
T. Michel *et al.*, *PRB* ***75*** *(2007) 155432*
T. Michel *et al.*, Phys. Rev. B in press (2009)

Experimental transitions energies

E_{laser} # E_{ii}

Semiconducting

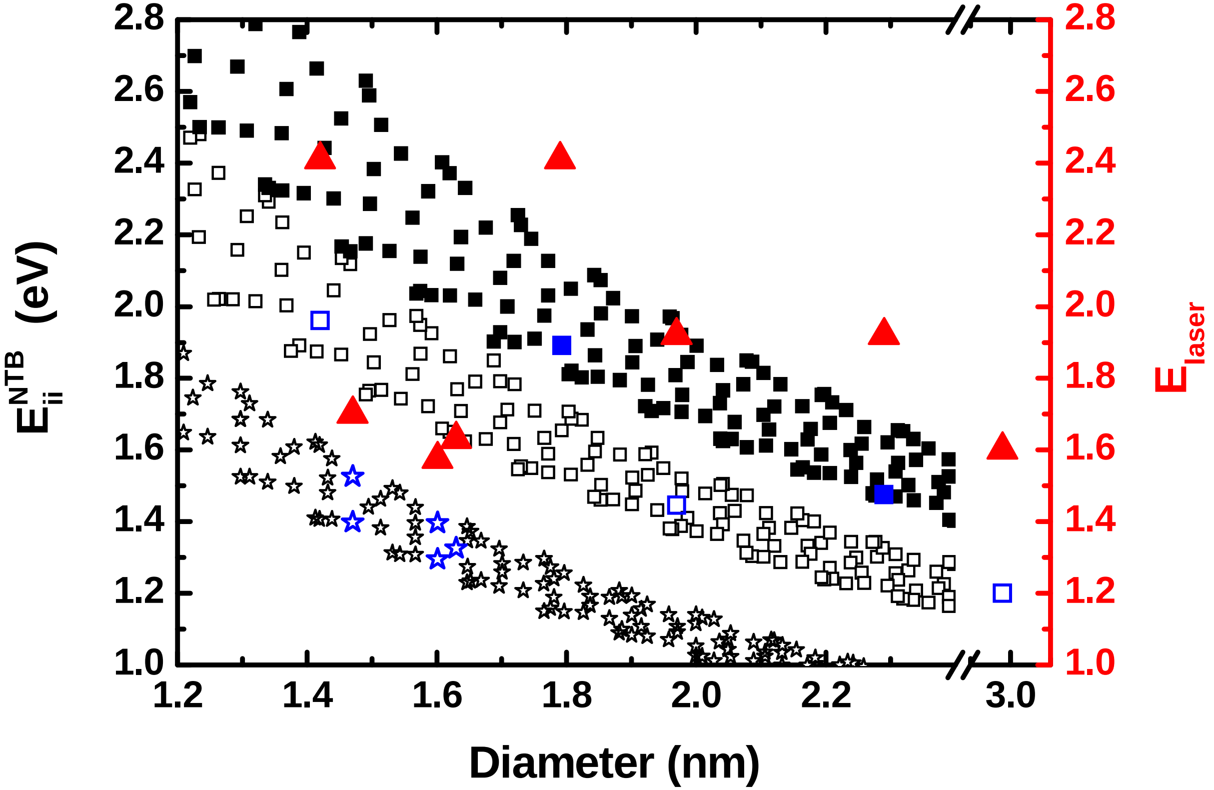
(11,10)	2.41 eV
(17,9)	2.41 eV
(15,14)	1.92 eV
(27,4)	1.92 eV
(23,21)	1.60 eV

Metallic

(15,6)	1.70 eV
(16,7)	1.57 eV
(12,12)	1.64 eV

Calculated transition energies

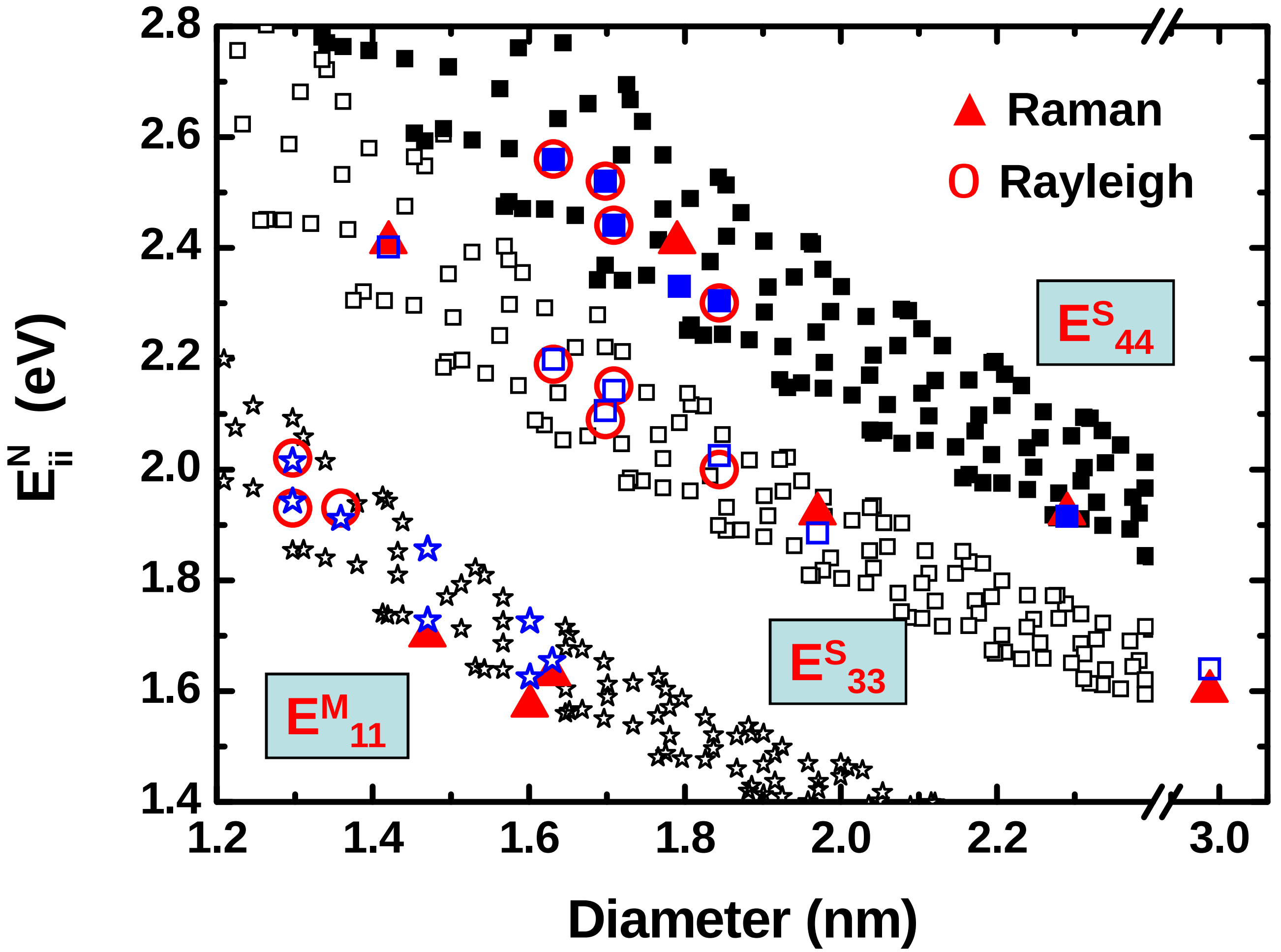
V. N. Popov, New J. Phys. ***6*** *(2004) 1-17*
V. N. Popov and L. Henrard, PRB ***70*** *(2004) 115407*



M. Paillet *et al.*, PRL **96** (2006) 257401

Combined Raman-Electron diffraction: T. Michel *et al.*, *PRB* ***75*** *(2007) 155432* → ▲

Combined Rayleigh –Electron diffraction: M. Y. Sfeir *et al.*, Science **312** (2006) 554 → **O**



Rigid shift of the calculated E_{ii}

E^S_{44} 0.44 eV

E^N_{ii}

E^S_{33} 0.43 eV

E^M_{11} 0.32 eV

The best estimation of the E^M_{11}, E^S_{33} and E^S_{44} optical transitions for individual nanotubes in the 1.2-3 nm diameter range

Identification of SWNT from Raman scattering

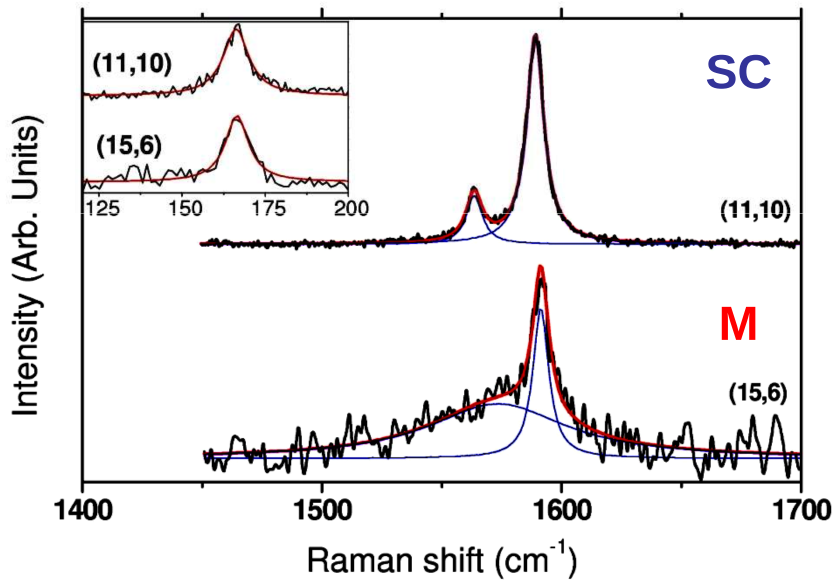
Raman criteria for the identification of SWNTs

RBM frequency → Diameter, d

Line shape of the G-modes → Chiral angle, M or SC character

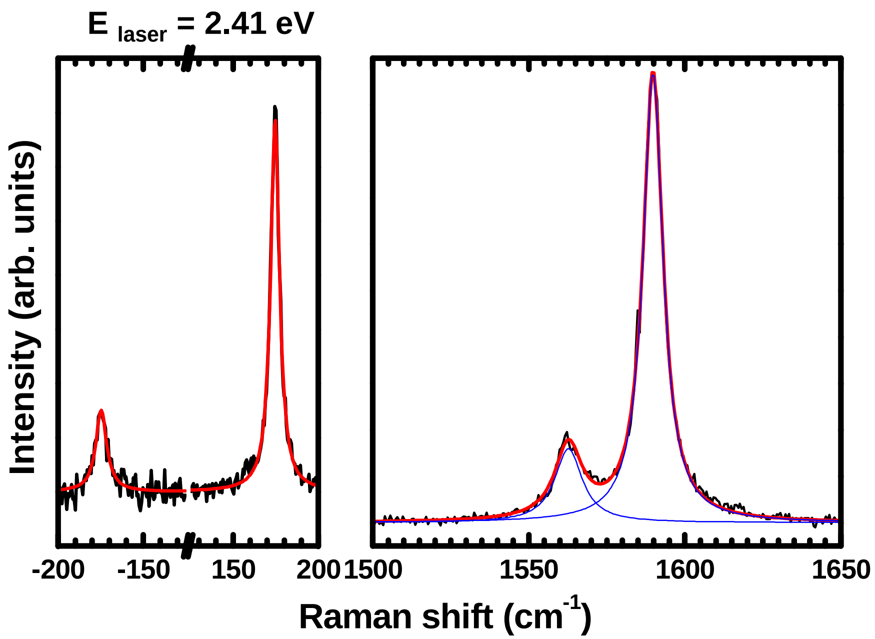
G- frequency → Diameter, d

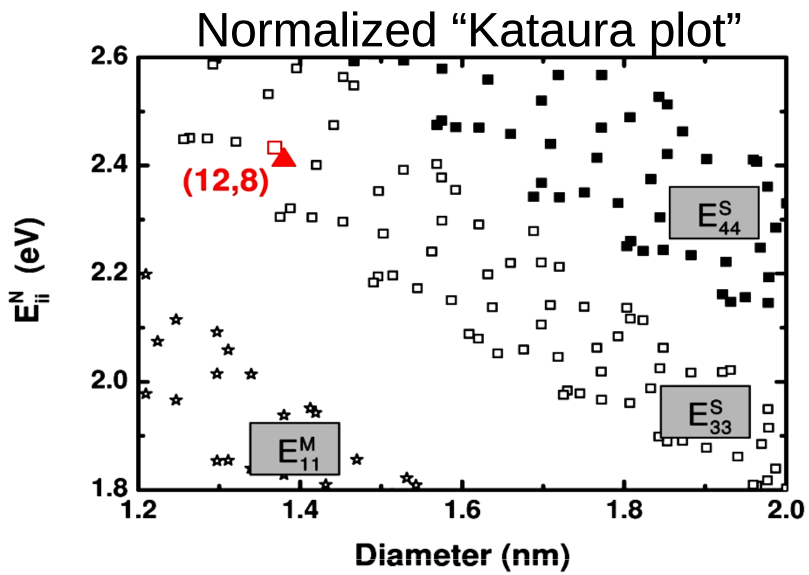
Resonance energy → E_{ii}



(d,E_{laser}) in normalized Kataura plot → (n,m) if the tube is individual

Identification of an individual SWNT





RBM @ 174.6 cm^{-1} ➡ d = 1.38 nm

G-mode profile ➡ semiconducting

TO @ 1563 cm^{-1} ➡ d ≈ 1.4 nm

High signal @ 2.41 eV ➡ $E_{33} \approx 2.41$ eV

➡ **(12,8)** d = 1.37 nm, E_{33} = 2.43 eV

Conclusions

Raman Spectroscopy / Electronic Diffraction

Structure / Properties

Criteria for nanotube identification by Raman only have been defined

Metologic Approach

***In-situ* identification of nanotubes**

During measurements of photoluminescence, transport, phototransport,…