# *Electron and phonon in carbon nanostructures: a local study with scanning tunneling spectroscopy*


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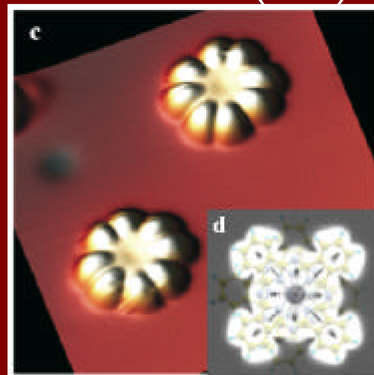
# Spectroscopy on atomic scale

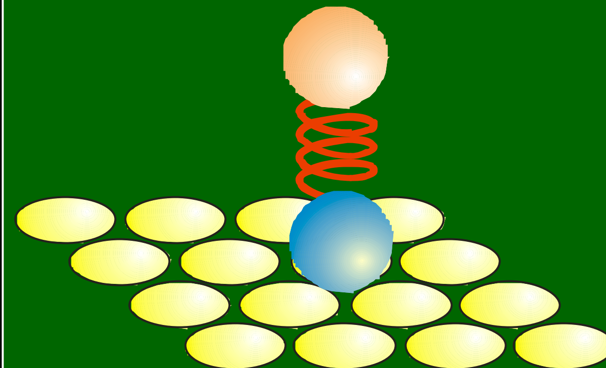
## Scanning Tunneling Spectroscopy:

Co and H-Co on Cu(111)

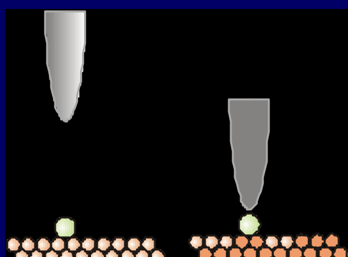
TbPc2 on Cu(111)

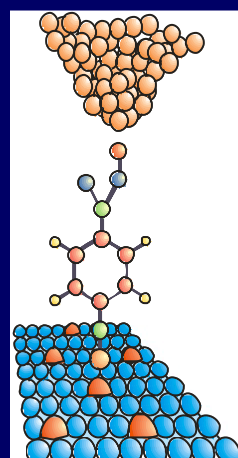


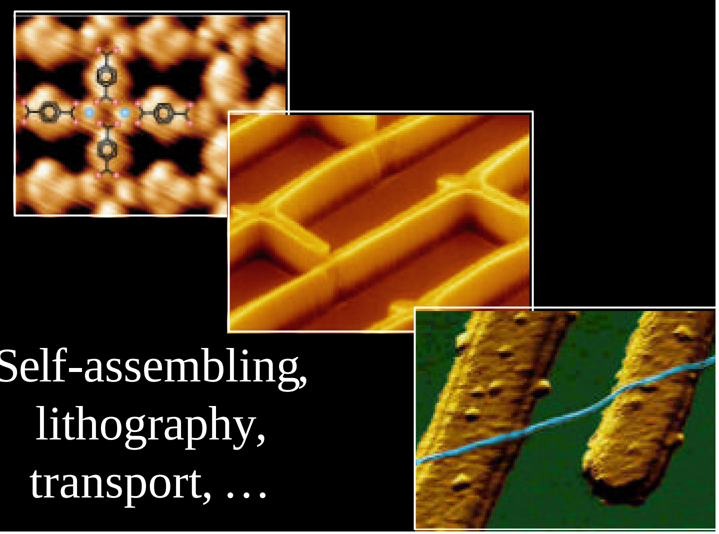

## Inelastic electron tunneling spectroscopy:



## Point contact spectroscopy:



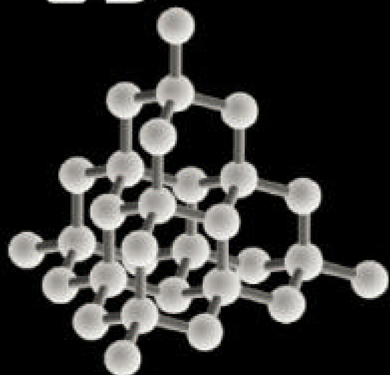




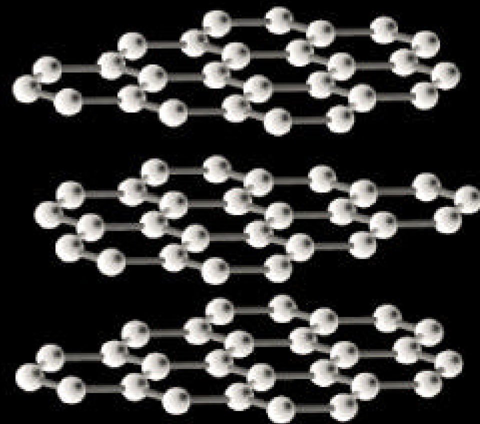
Self-assembling, lithography, transport, …

# Carbon allotropes

3D

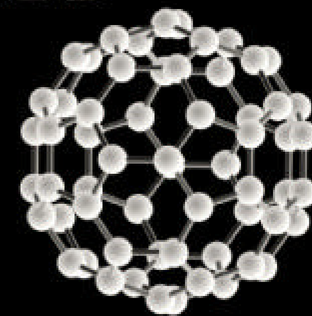


diamond (3D)



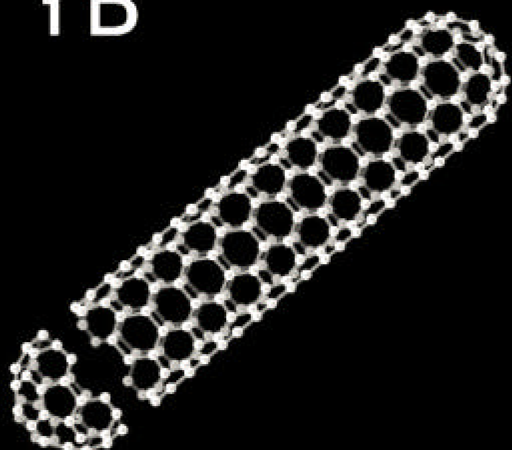
planar graphite

0D



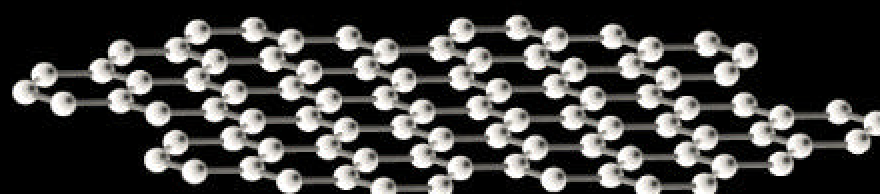
$C_{60}$ (0D)
1985

1D



single-walled carbon nanotube (1D)
1991

2D

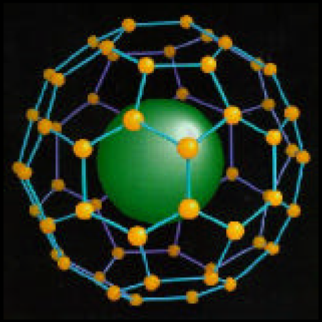


Graphene
2004

# Novel fascinations on Carbon

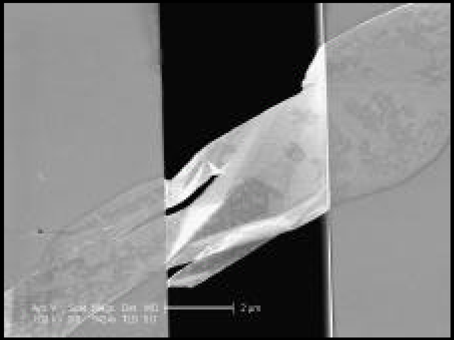
Fullerenes

Metallic, superconducting, isolating transition (doping level), Endohedral fullerenes (Metal or N): Magnetism and superconductivity



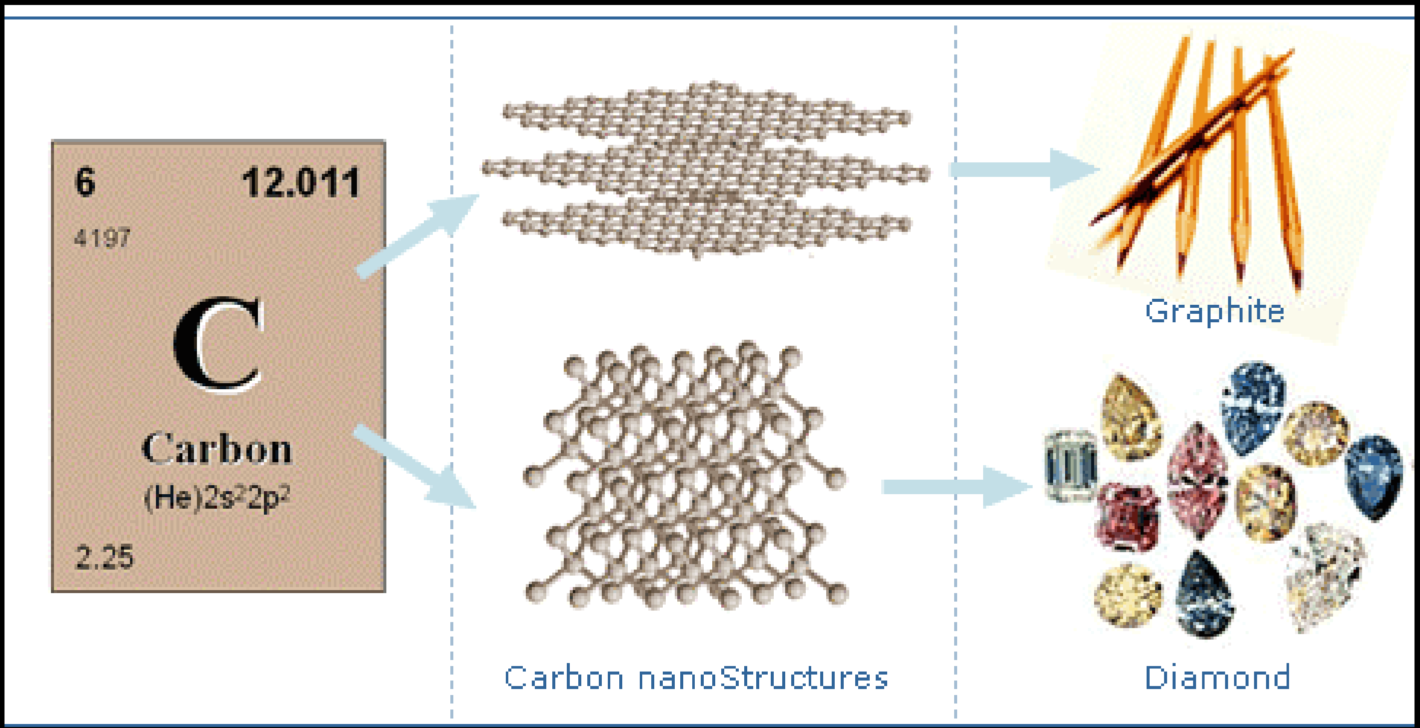
CNT

Electronic, mechanical and electrical new properties: Quasi 1D (model system for physicists!) , metallic or semiconductor, supports large current flux, high carrier mobility, electron field emitters, CNT-FET, Single electron transistors
high young modulus, high tensile strength, gas sensors, gas storage, …,

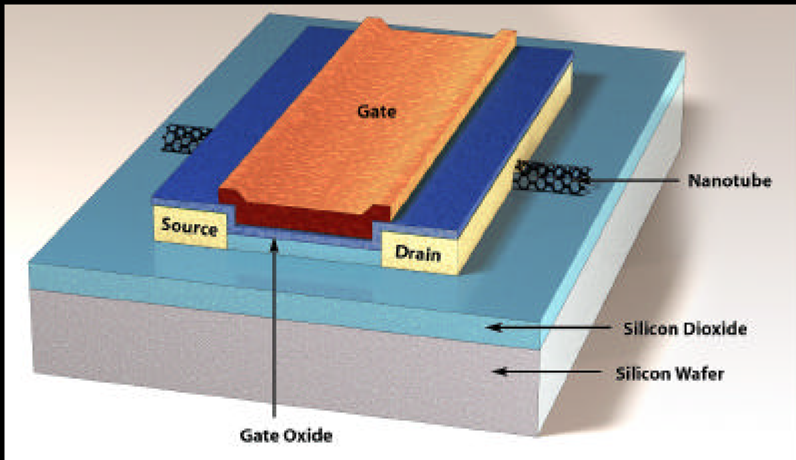


Graphene

2D conductor, linear electron band, electron velocity independent on energy, high carrier mobility, QHE at RT, gas sensor, …,

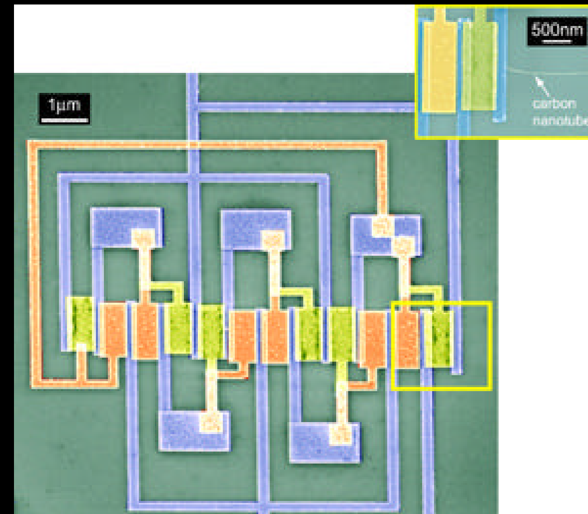

6
12.011
4197
C
Carbon
(He)2s22p2
2.25
Graphite
Carbon nanoStructures
Diamond

## Semiconducting SWCNTs as components of FETs



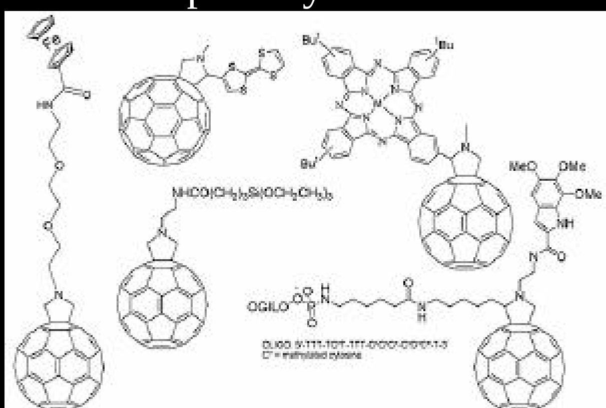

* S.J. Wind, J. Appenzeller, R. Martel, V. Derycke & Ph. Avouris; Appl. Phys. Lett. 80 (2002), 3817.

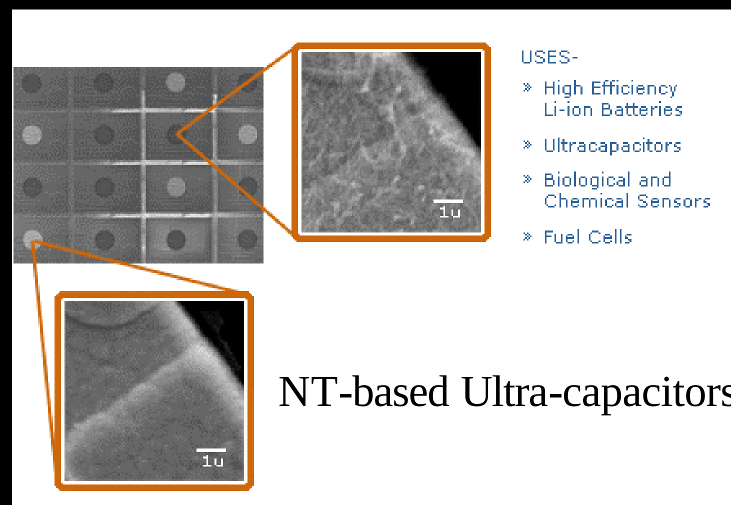
## Integrated Logic Circuit Assembled on a Single Carbon Nanotube



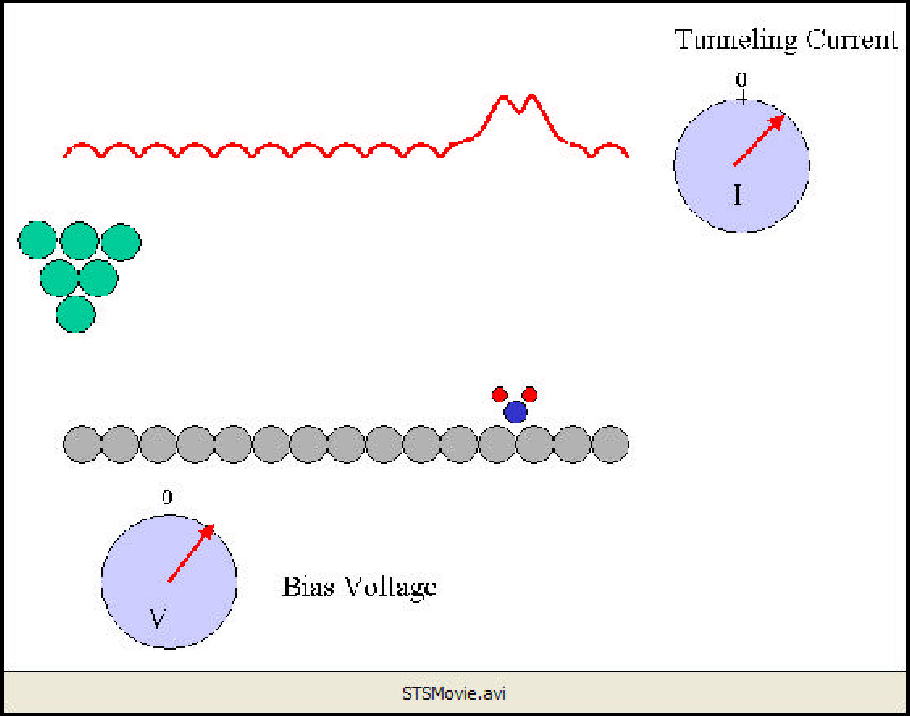

Z. Chen et al., Science 5768, 1735 (2006)

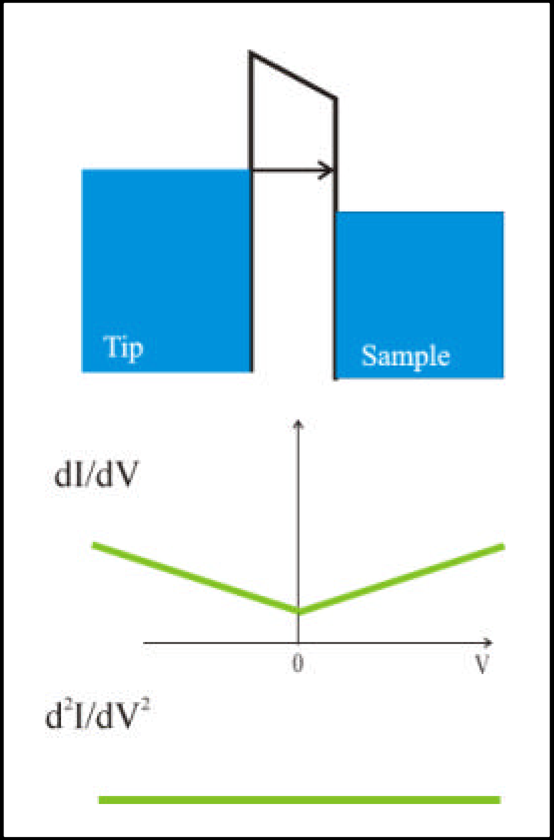
## donor-acceptor hybrids: natural photosynthesis





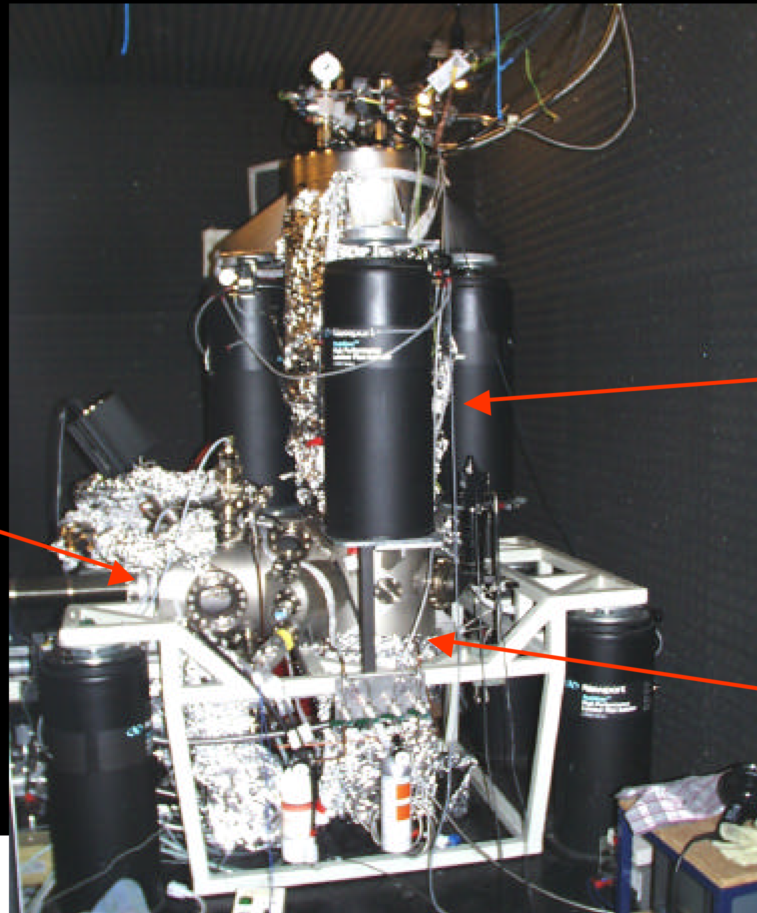
# Scanning Tunneling Microscopy & Spectroscopy



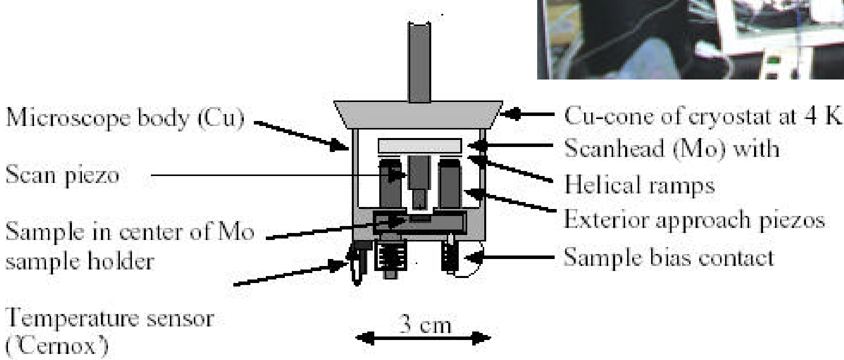




$dI/dV \sim \rho_{el}$

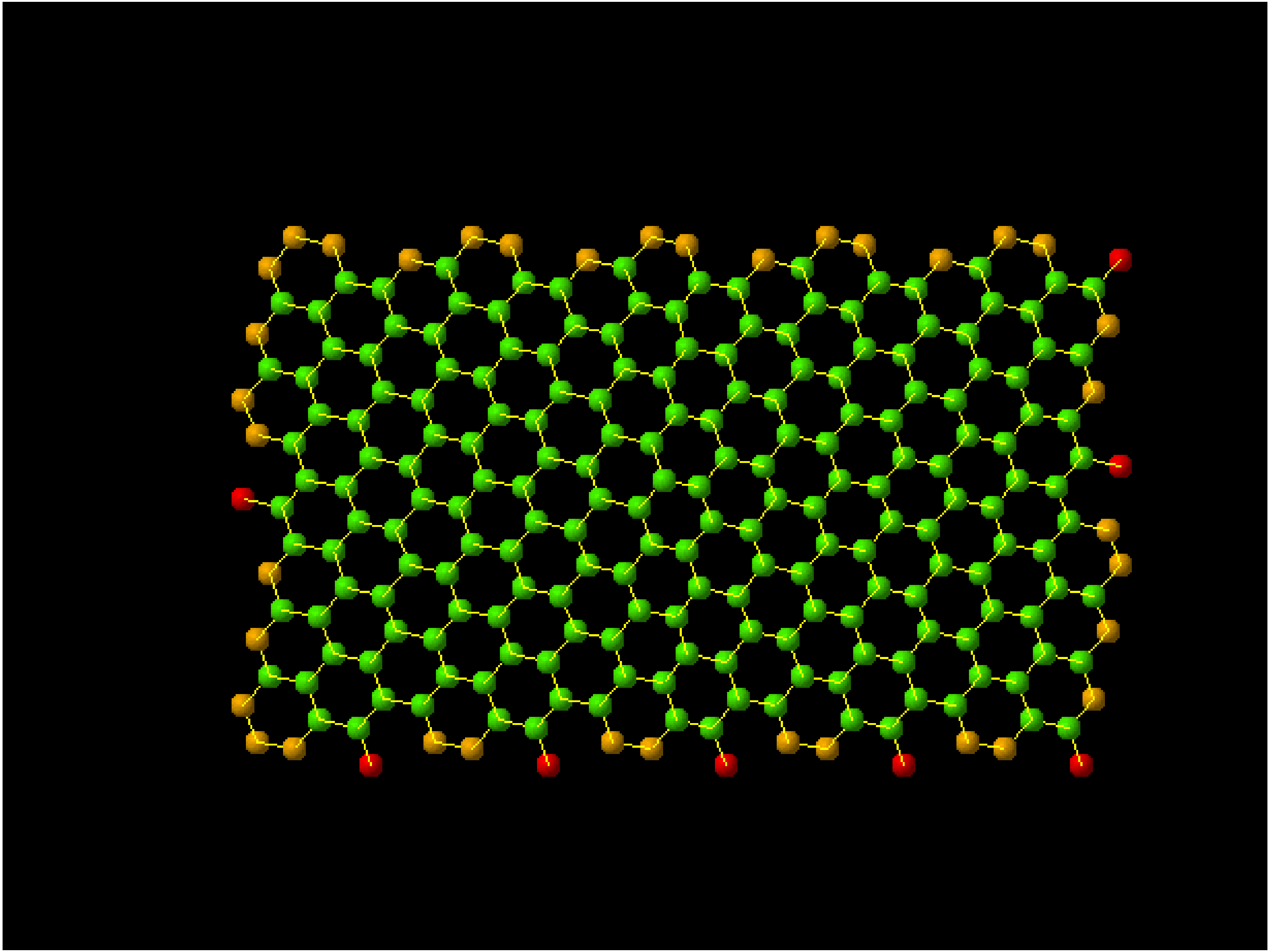
# 6K-STM



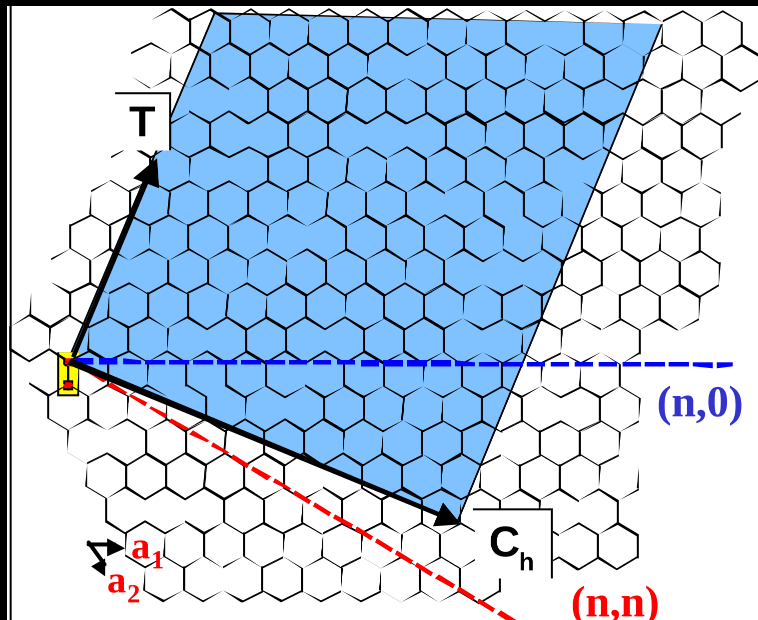
Preparation chamber
LHe-Cryostat
STM

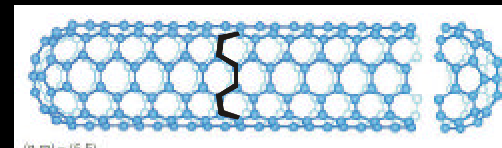



Microscope body (Cu)
Scan piezo
Sample in center of Mo sample holder
Temperature sensor ('Cernox')
Cu-cone of cryostat at 4 K
Scanhead (Mo) with
Helical ramps
Exterior approach piezos
Sample bias contact
3 cm

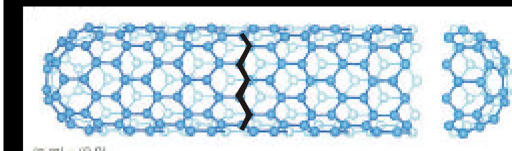


# Structure of single-wall carbon nanotubes (SWCNTs)

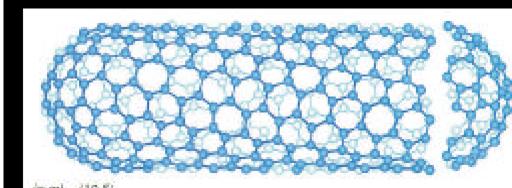


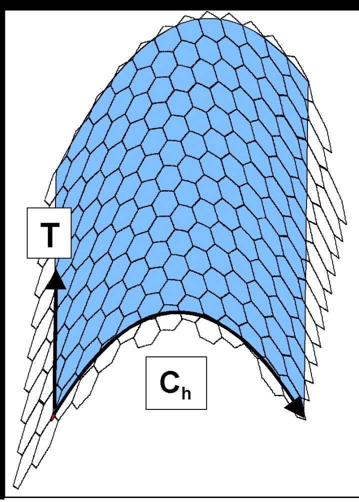
armchair (n,n)



zigzag (n,0)



chiral (n,m)



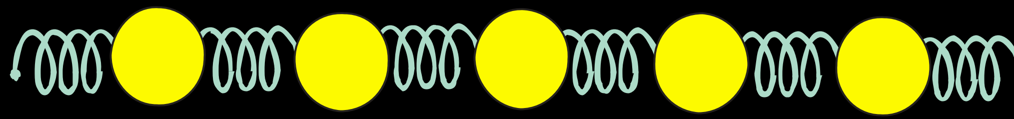

**roll-up vector:**

$\underline{C}_h = n\underline{a}_1 + m\underline{a}_2$ ° (n,m)

**metallic if (n-m) = 3q**

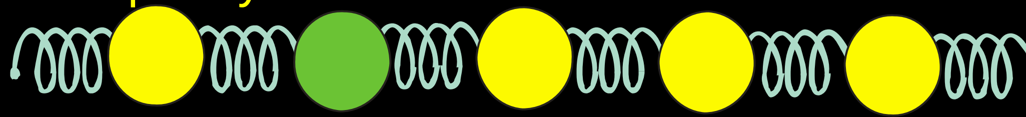
**q:integer**

**semiconducting if (n-m) ¹ 3q**

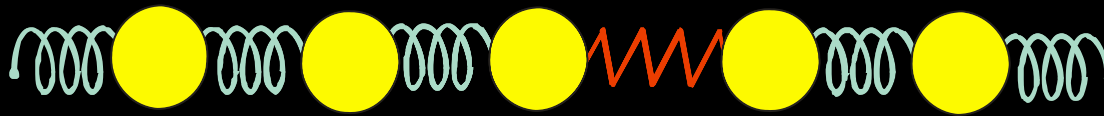


$$\omega(k) = 2\sqrt{\frac{K}{M}}\left|\sin \tfrac{1}{2}ka\right|$$

- Impurity atom

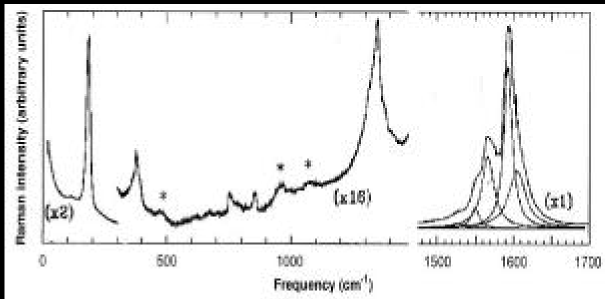


-Strain, different bond strength



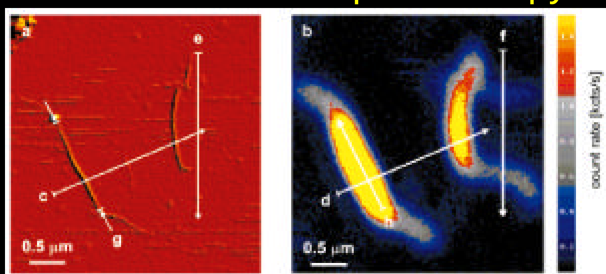
# Spatial resolution

## Raman Spectroscopy



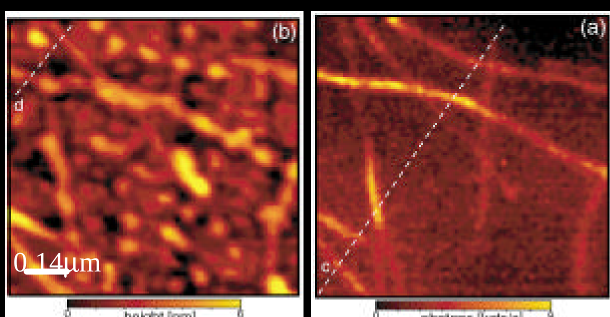

A.M.Rao et al. Science 275.187.1997

## Confocal Raman Spectroscopy

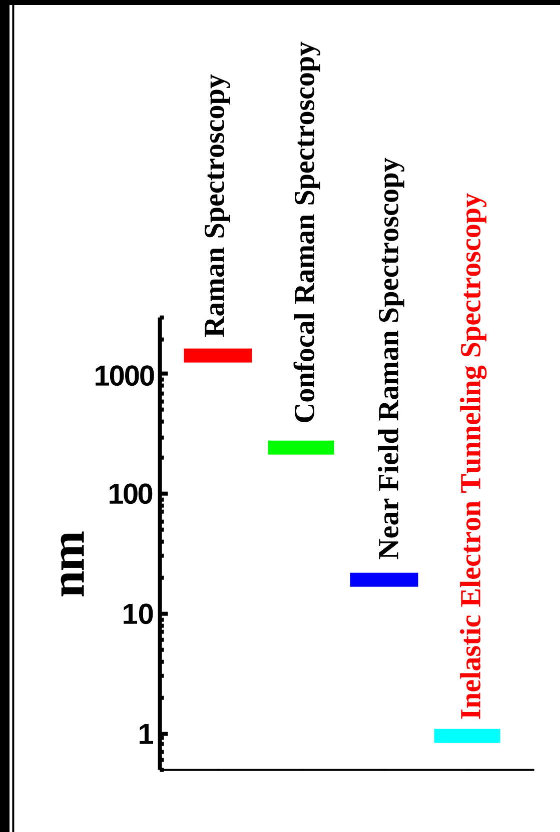


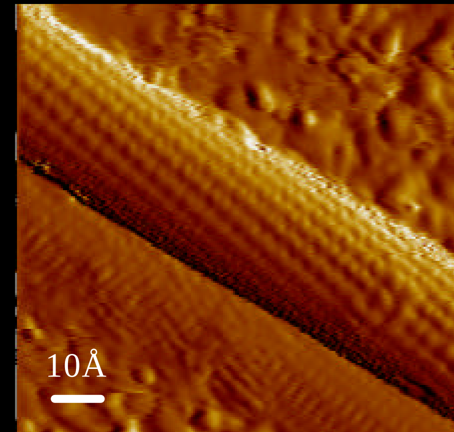

A.Mews et al. Adv.Mat.12.1210.2000

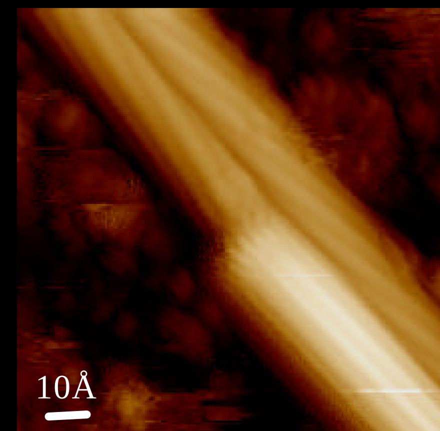
## Near-Field Raman Spectroscopy

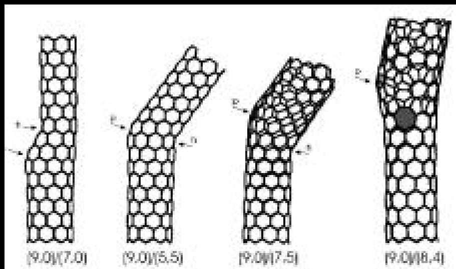



A.Hartschuh et al. PRL.90.095503.2003



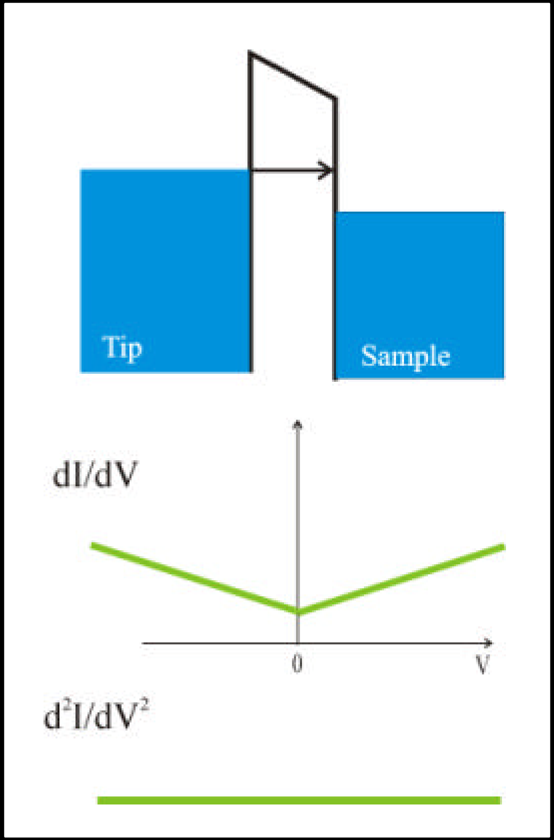
# Spectroscopy technique: Local probe of lattice dynamics (vDOS)

Inelastic Electron Tunneling Spectroscopy

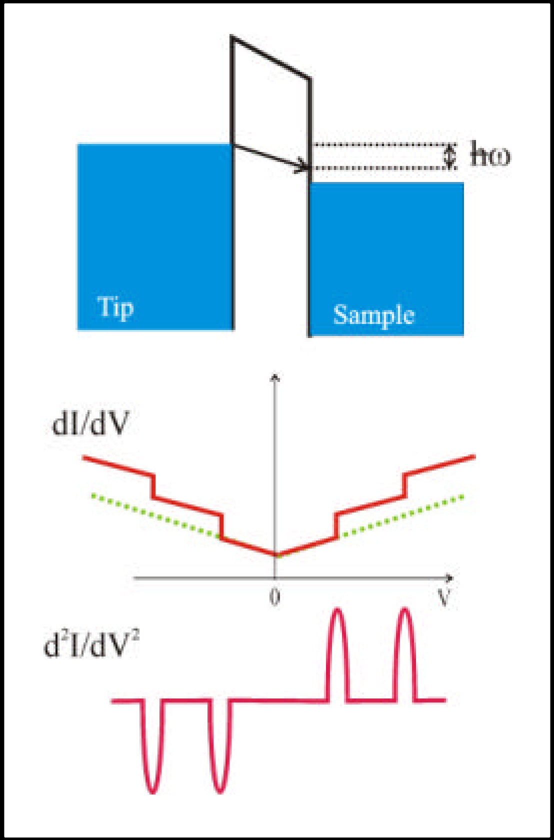
- Carbon nanotubes (SWCNT)

- Graphite (HOPG)

# Electron Tunneling Spectroscopy



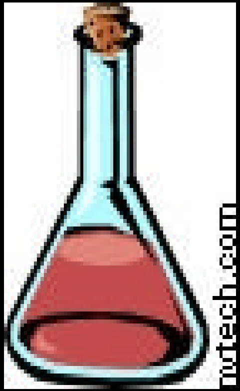

Elastic tunneling



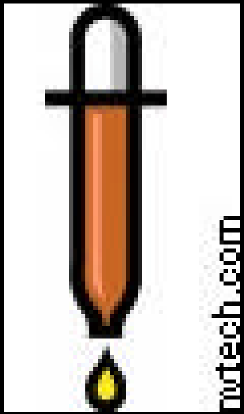

Inelastic tunneling

$$dI/dV \sim \rho_{el} + \rho_{in}$$

# SWCNT on Au/mica



+



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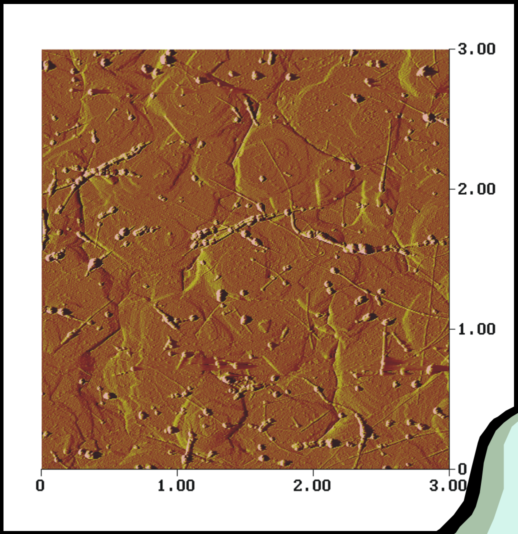
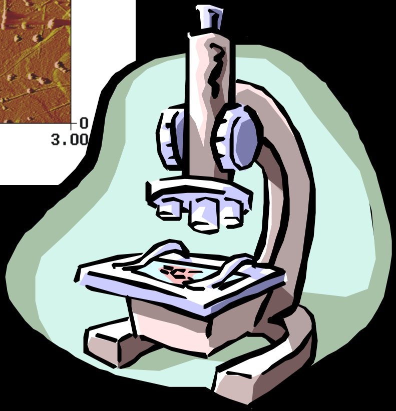
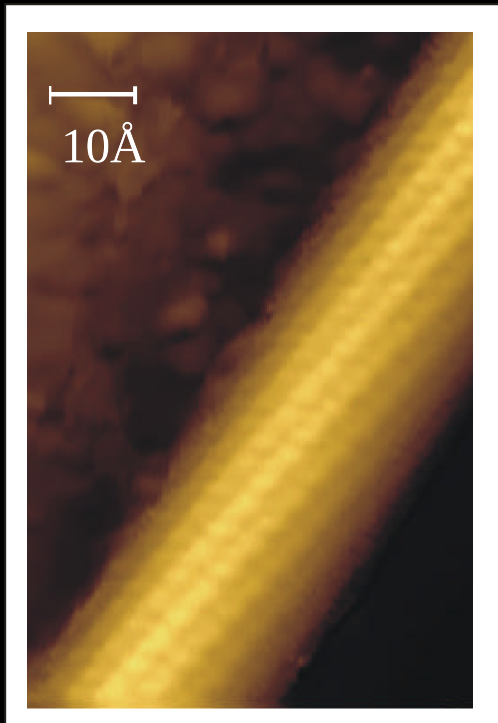


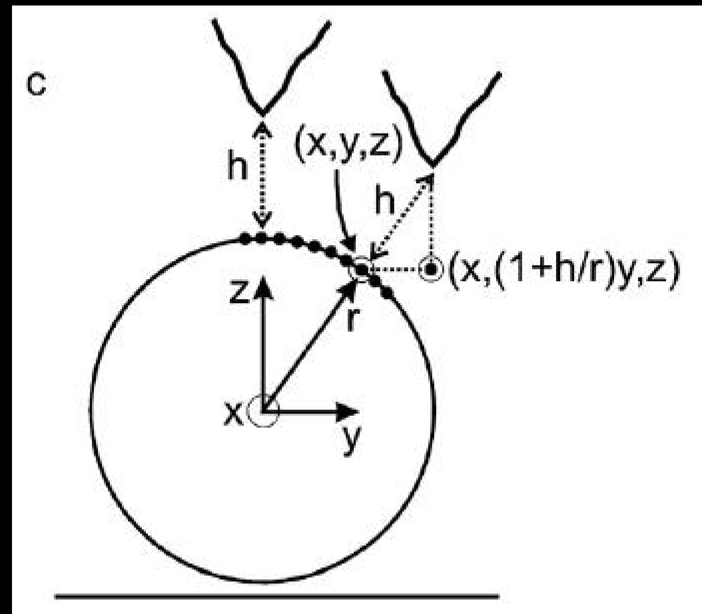



<u>Recipe:</u>
Disperse SWCNT in Dichlorethane,
Sonicate and centrifuge.
Deposit the solution on Au substrates

Acknowledgment:
* <u>M.Knez</u> , <u>Y.W.Fan</u> for the sample preparation

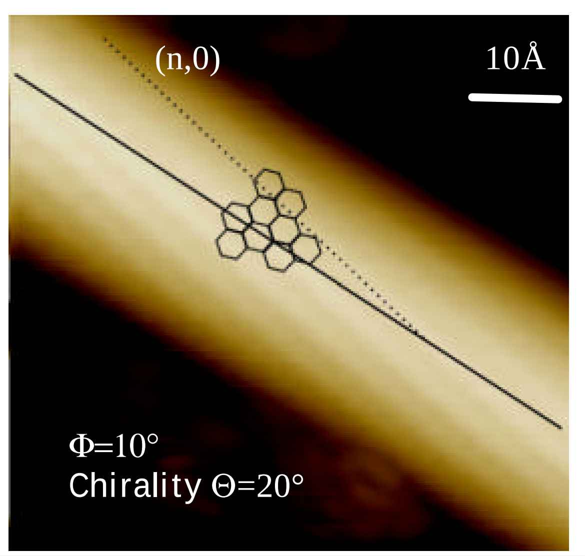
# From STM images....

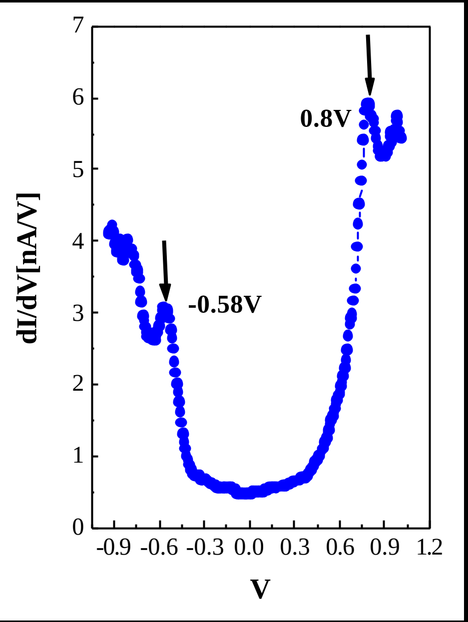


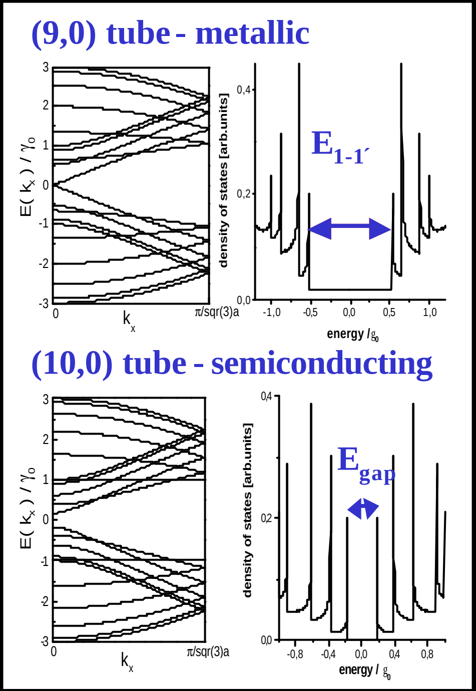



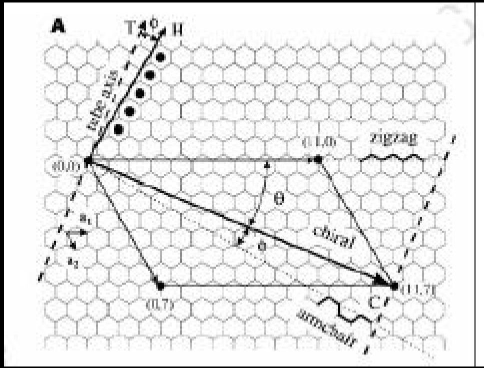

....to tube diameter ?

# Determination of (n,m)




Metallic tube

$\Delta E=6\gamma_0 a_{C-C}/d$

$\Delta E\sim1.38V$

Diameter ~15.4Å

Energy separation between the first vHs singulatities:

$\Delta E=2\gamma_0 a_{C-C}/d$ semiconducting

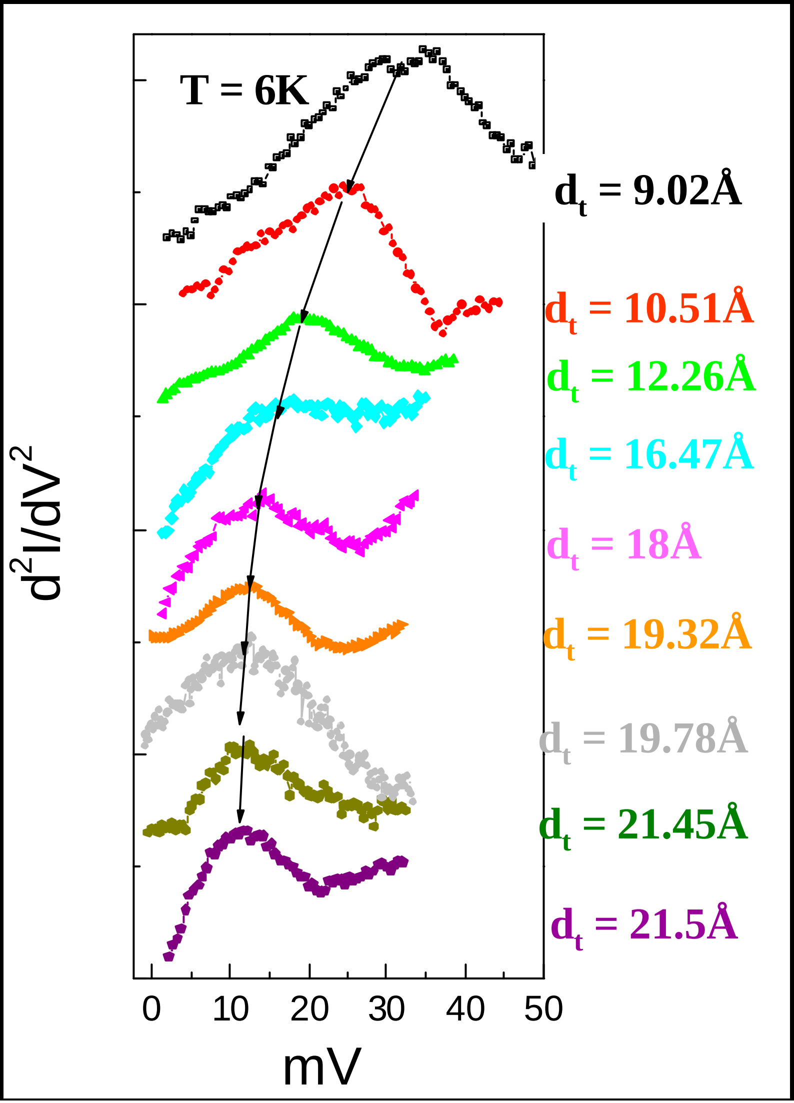
$\Delta E=6\gamma_0 a_{C-C}/d$ metallic

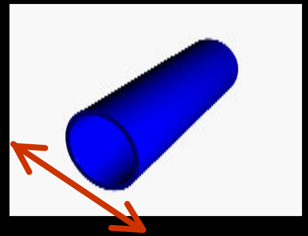
(14,8) tube

$\gamma_0$= 2.5 eV  tight-binding overlap energy

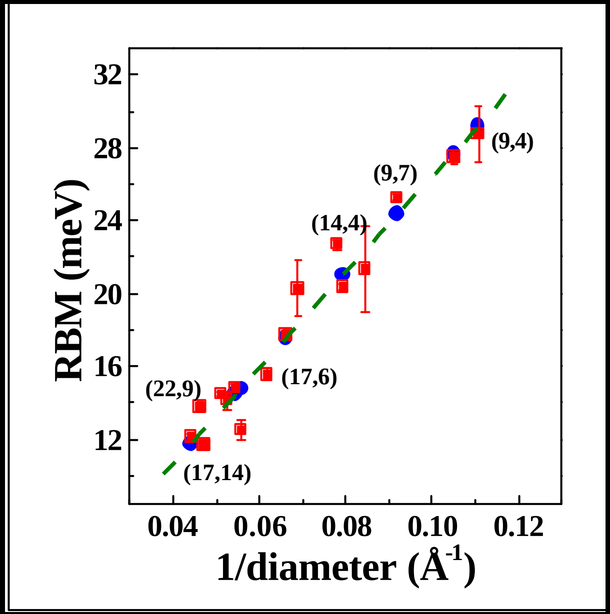
$a_{C-C}$=1.42Å lattice constant

# Dependence of the radial breathing mode on the SWCNT diameter



$$\omega_{RBM} = C/d$$




C=262meV*Å

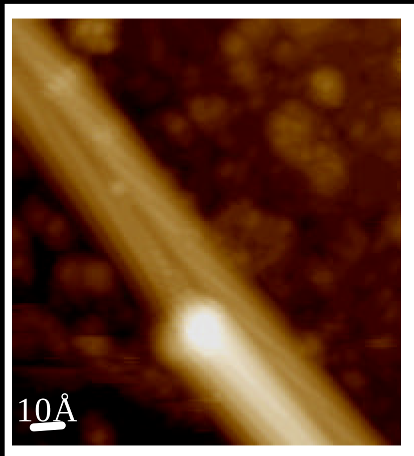
C~270-290meV*Å

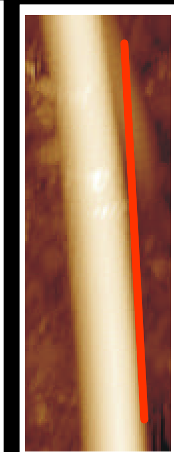
D.Sanchez-Portal et al PRB.59.12678.1999

J.Kurti et al. PRB.58.R8869.1998

# Local properties:

## Intramolecular-junction



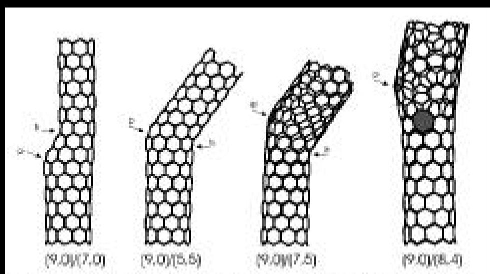
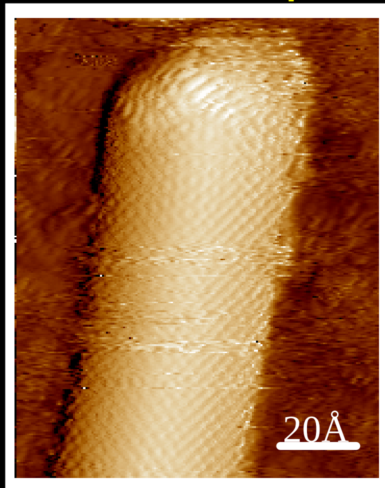
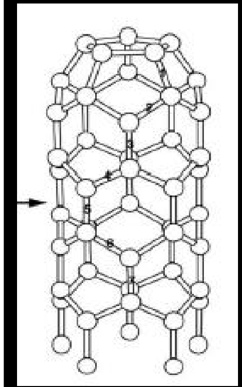



Fig. 2. A few examples of nanotube connections. From left to right: straight junction between two zig-zag nanotubes, a Dunlap knee formed by joining a zig-zag to an armchair nanotube, and (9,0) connected to two chiral nanotubes. The pentagons and heptagons are indicated by the p and h letters, respectively

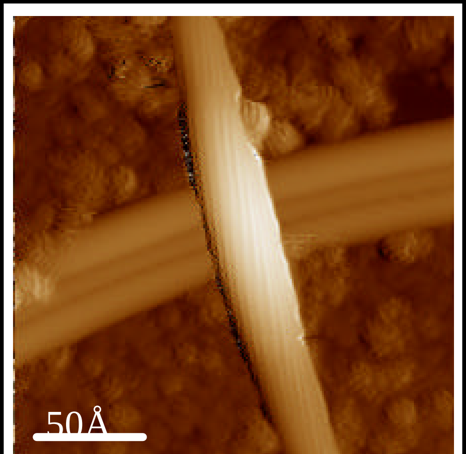
Ph.Lambin, V.Meunier, Appl.Phys.A 68.263.(1999)

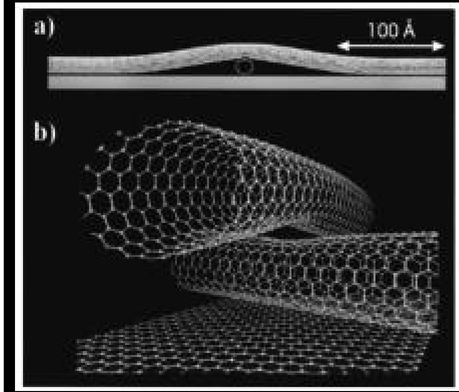
## Tube cap



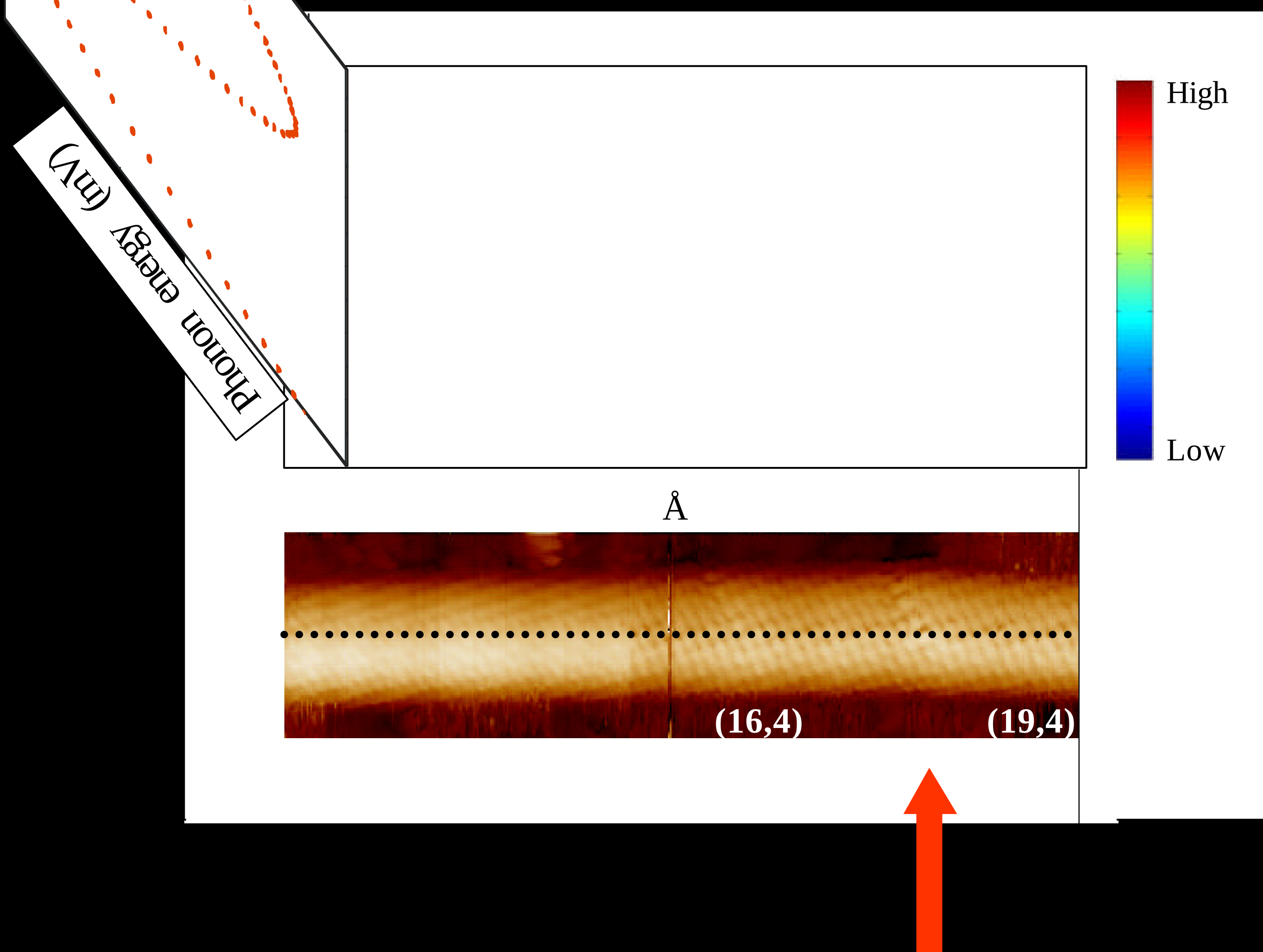



## Tube crossings

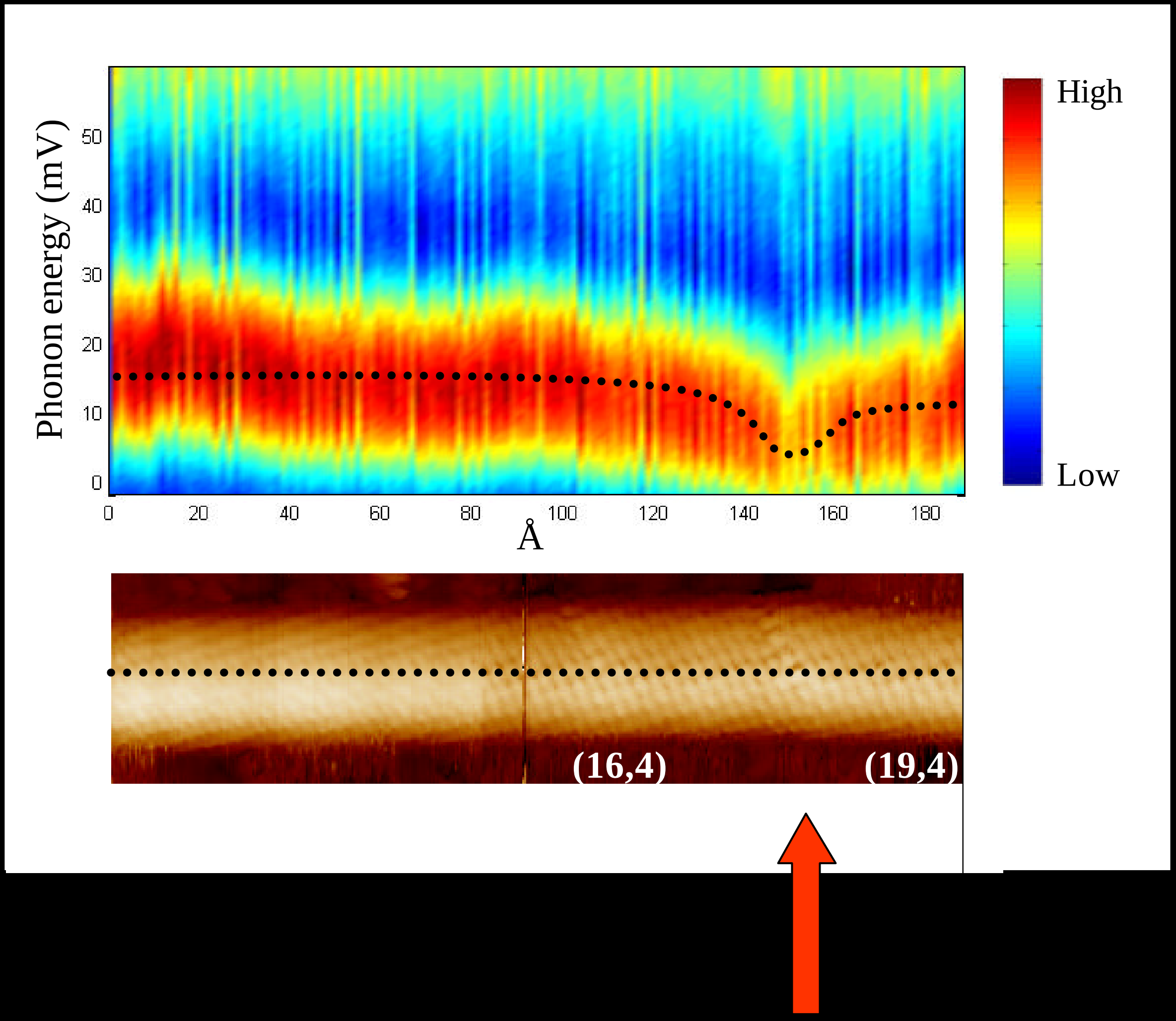


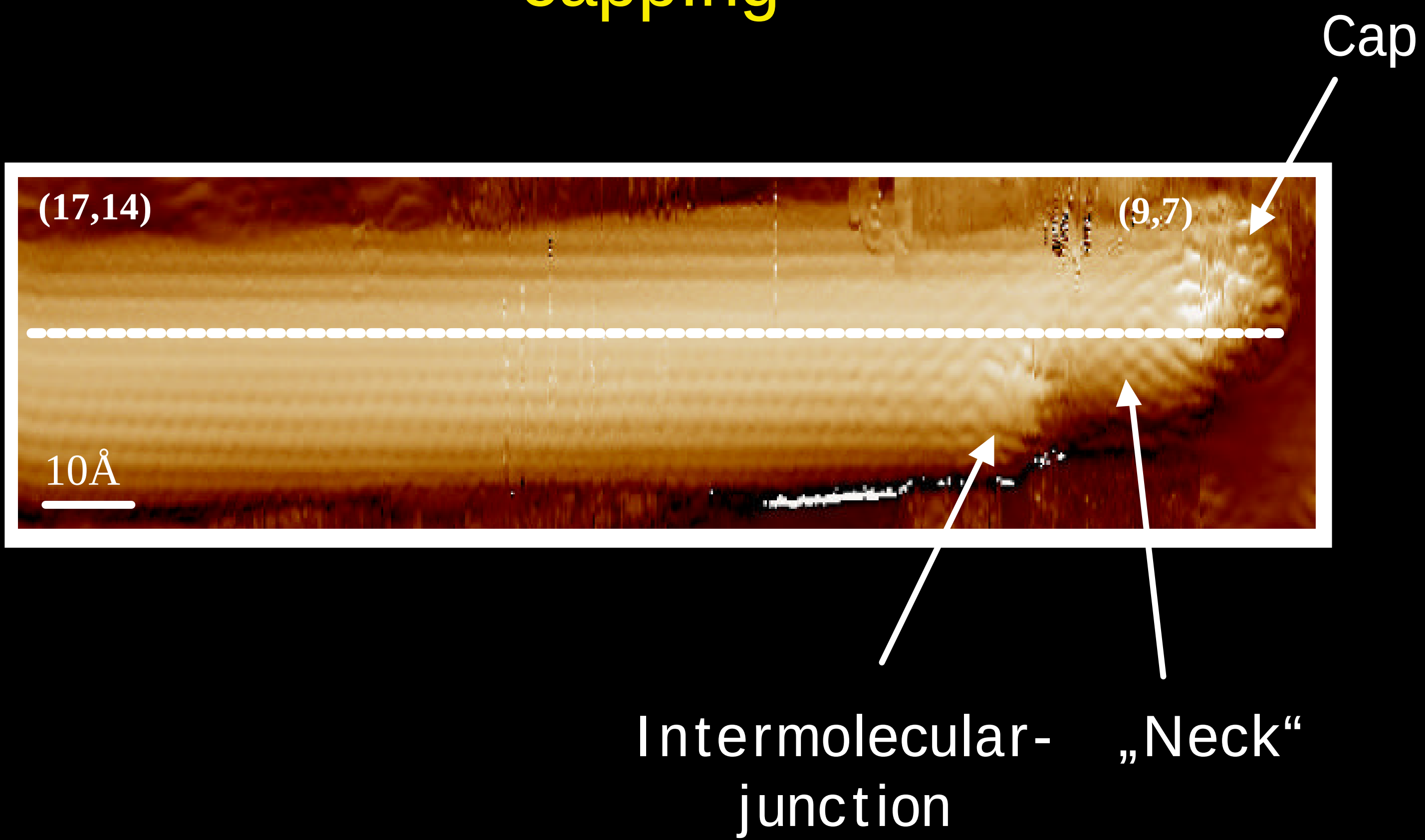
## cal probe: Intra-molecular junction or 5/7 pairs



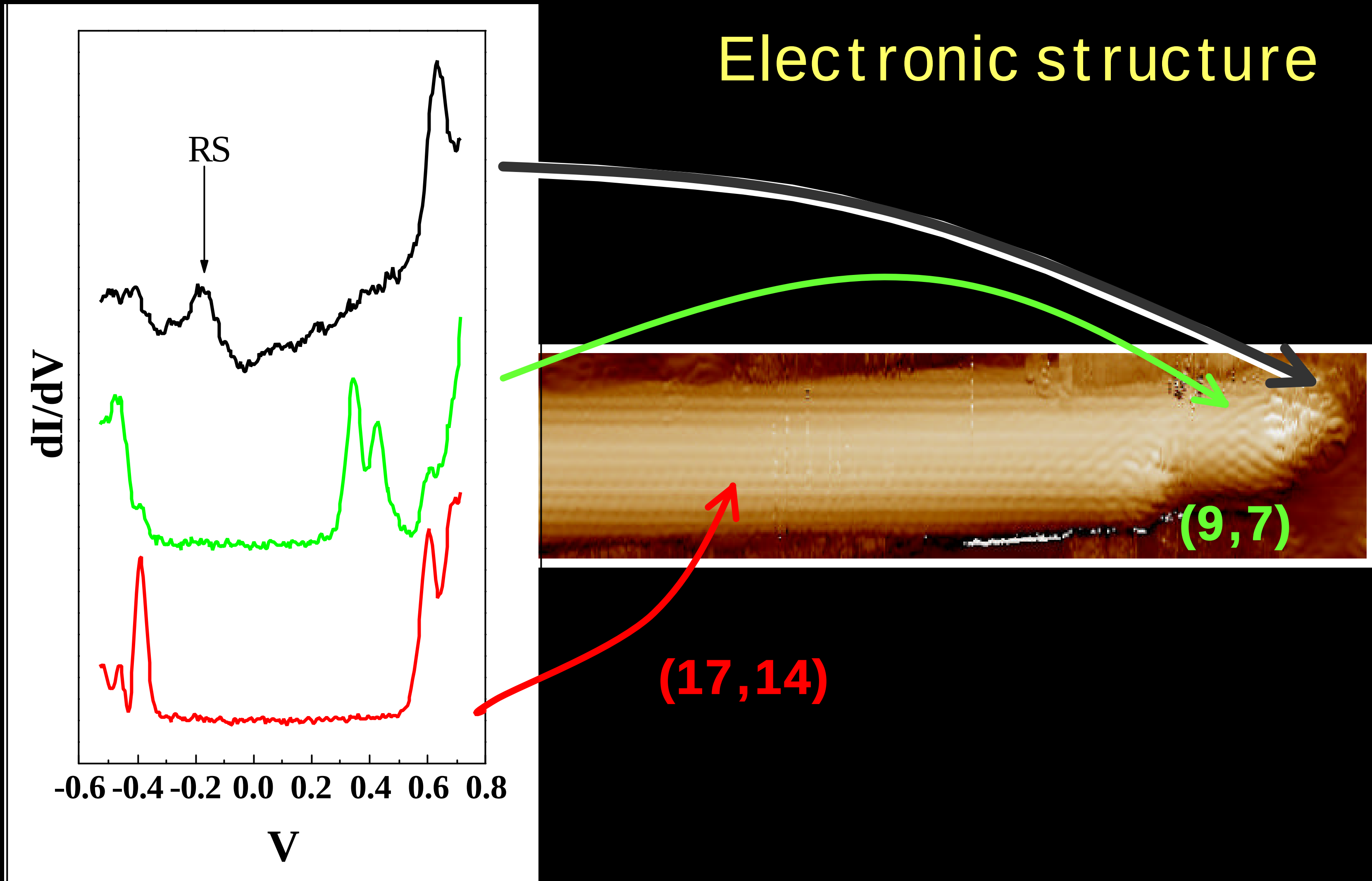
# Local probe: Intra-molecular junction or 5/7 pairs



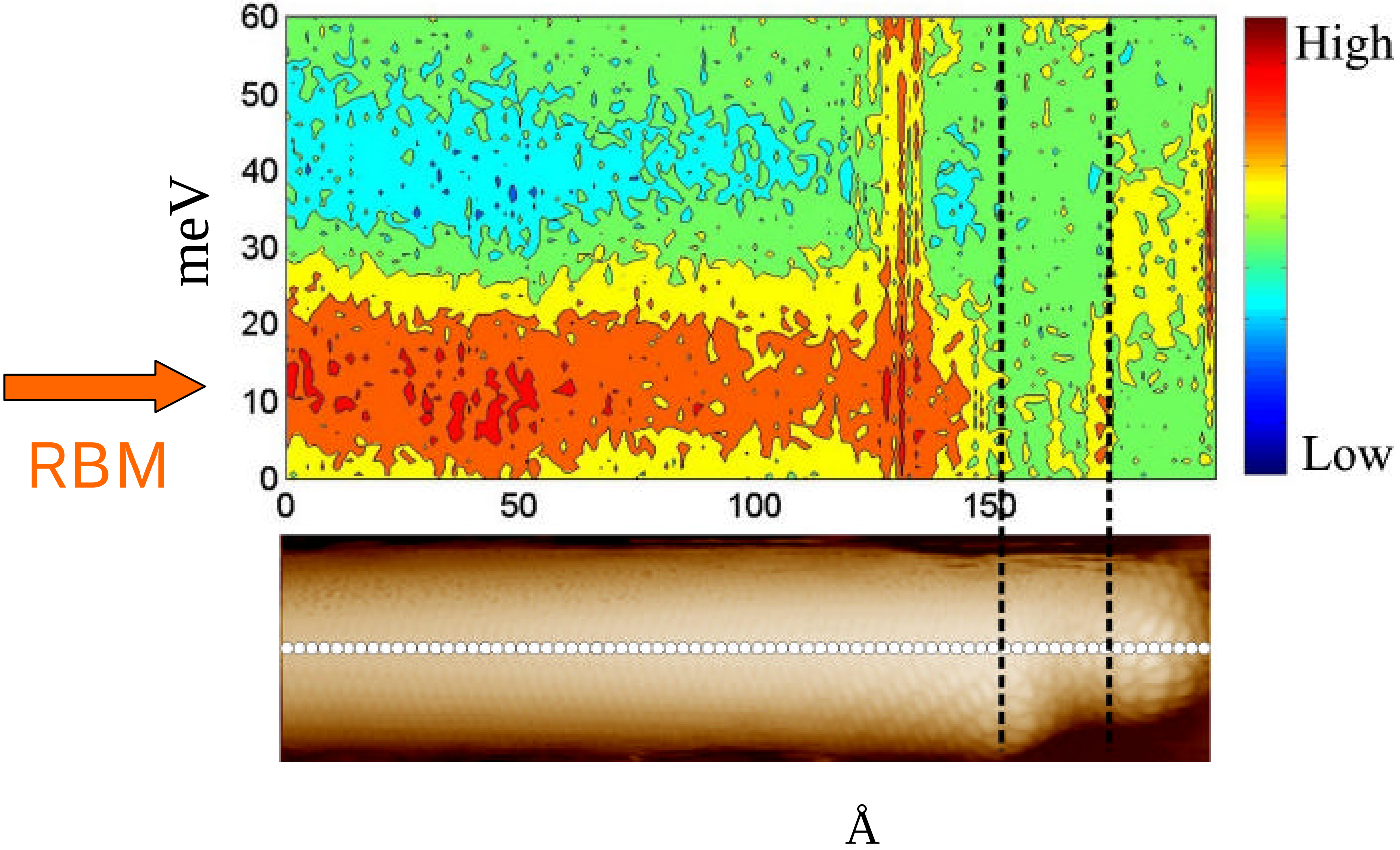
# Local probe: Nanotube capping



# Electronic structure



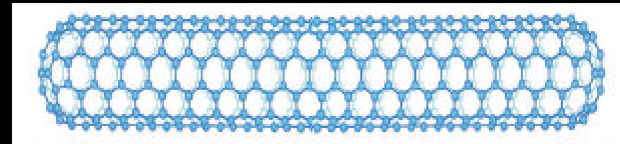
# Nanotube capping: $d^2I/dV^2$



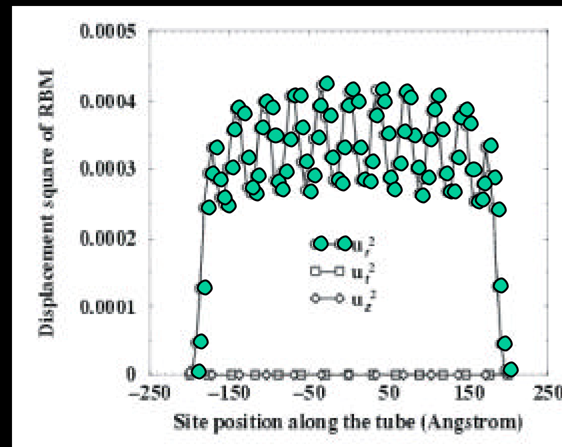

PRL.93.136103.2004

# Theory for RBM

(powered by C.S.Jayanthi et al)

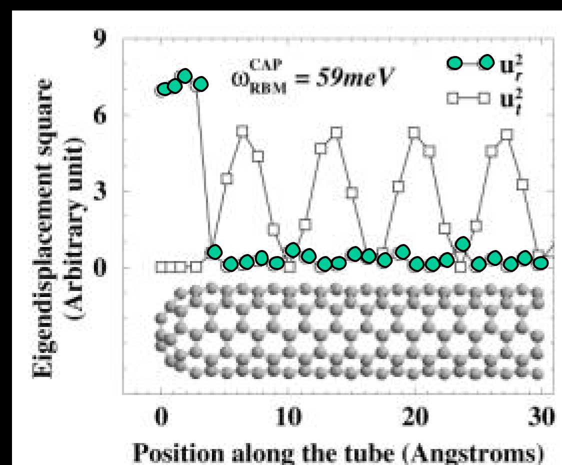


$(5,5)+C_{60}$




**-finite length:**

A tube can sustain an RBM only if its length exceeds 3.5nm.

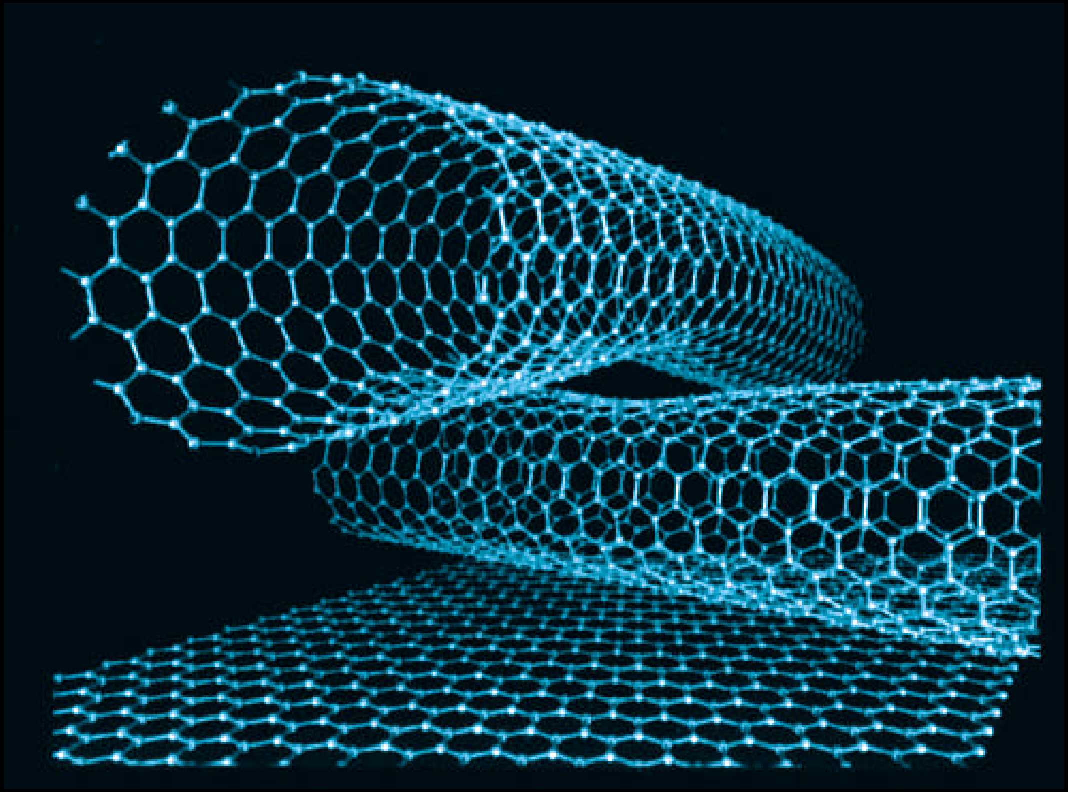



**-capped region:**

Transforms from radial to tangential character inside the tube

PRL.93.136103.2004

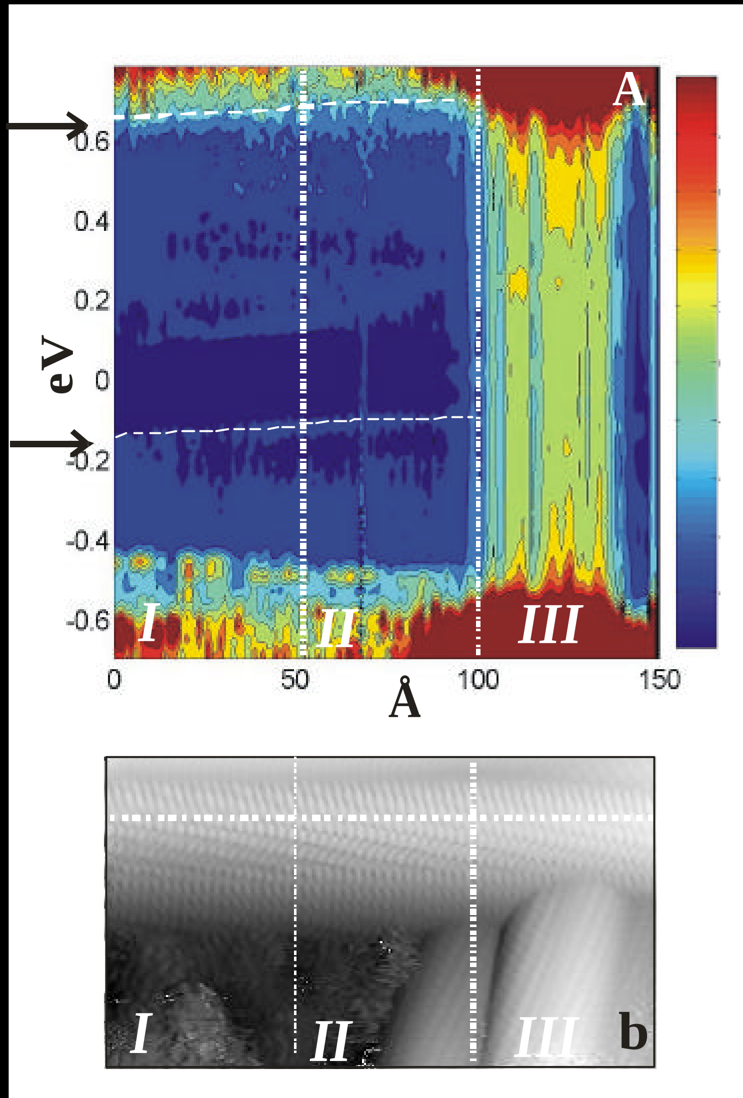
# Crossed Nanotube Junction
# pressure induced local metallization



Phys. Rev. Lett. 96, 086804 (2006)

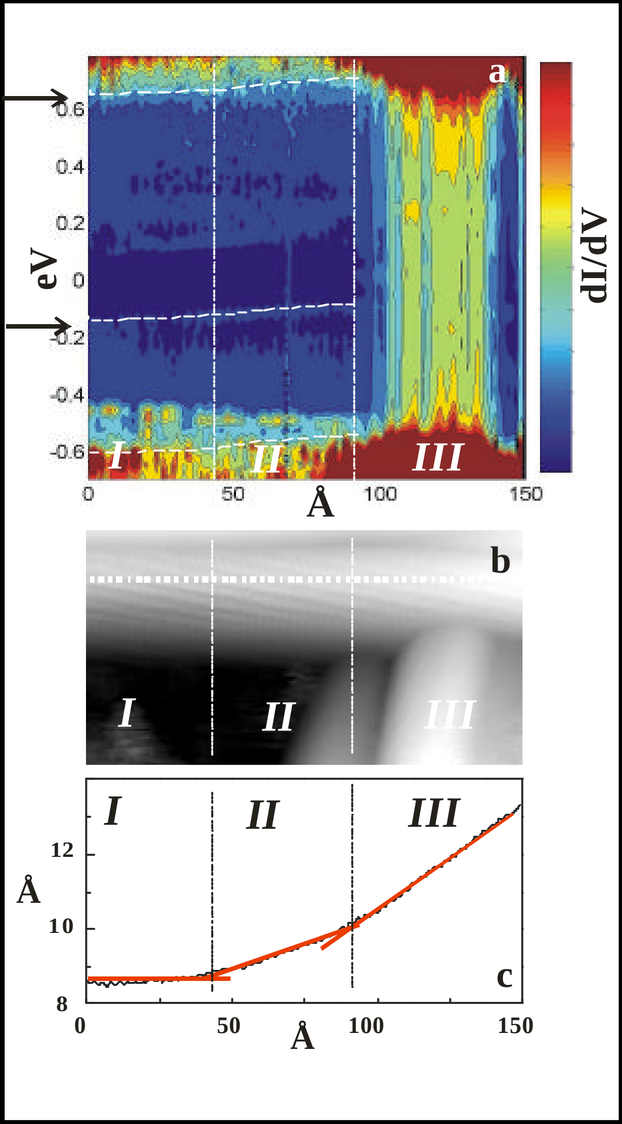
# If a (9,2) tube crosses a bundle...

1. DOS




PRL **96**, 086804 (2006)

# 1.1 DOS: Local pressure-induced metallization




d(9,2)=8.2Å
bundle~15Å

=

Tube compressed of ~35%
at the crossing junction

Pressure at crossing junction=15GPa
(Assuming Bulk modulus=35GPa)

PRL **96**, 086804 (2006)

# 1.2 DOS: Image-charges

Contact potential

$\Delta = \Delta_{holes} - \Delta_{image}$

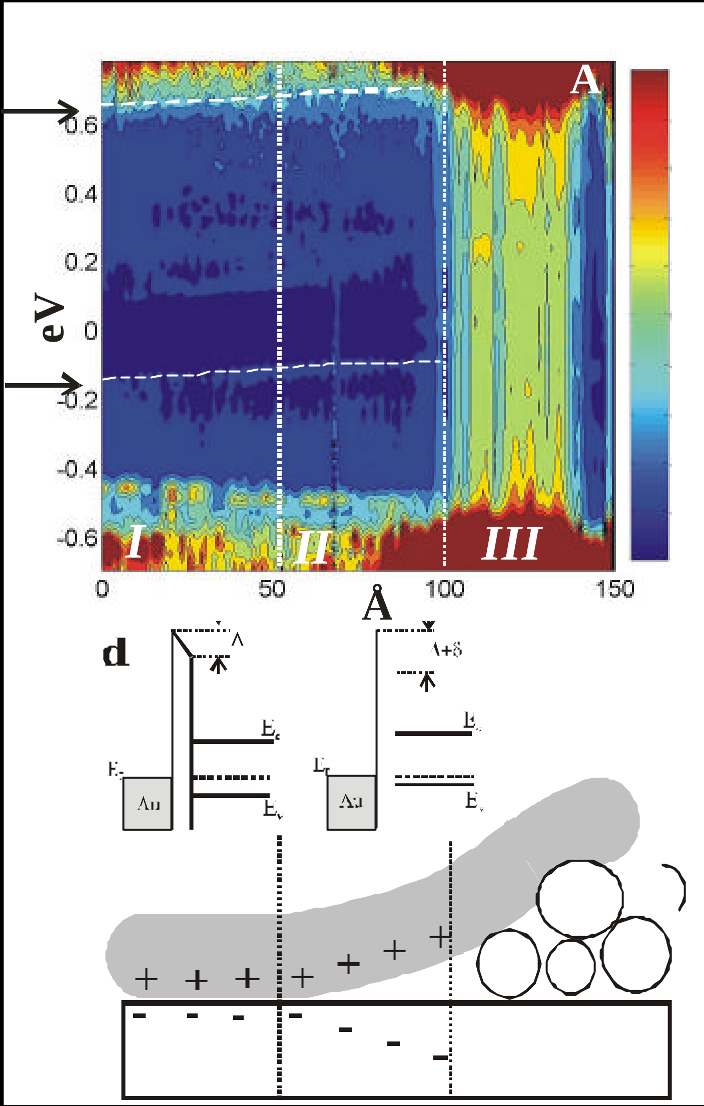
$\Delta V = \Delta Q / C_{TS}$

$\Delta V = 60\text{meV}$

$C_{TS} \sim 0.1\text{aF}$

$\Delta Q$= additional 0.025hole/nm

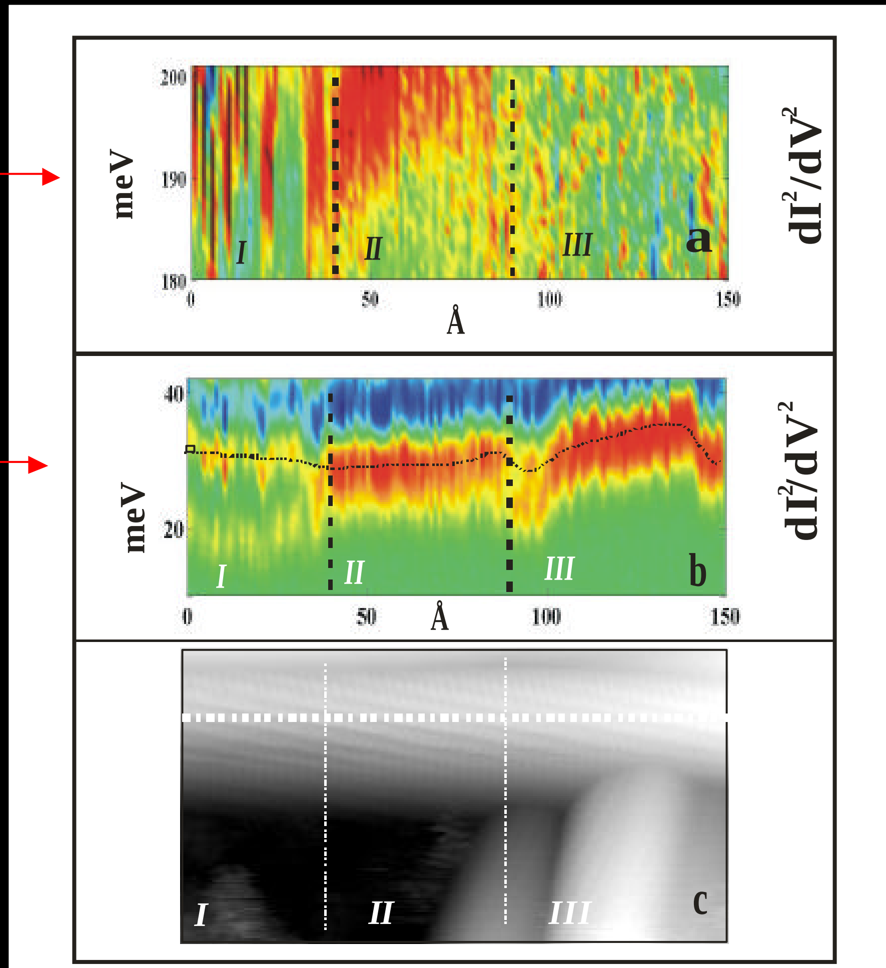
(= ~25% total charge transferred )



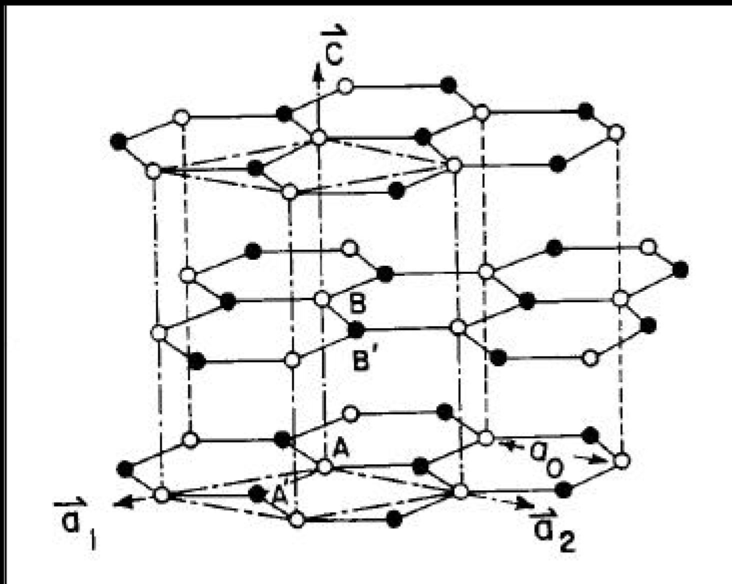
# 2. Vibrational density of states

G-band

RB-mode



# HOPG



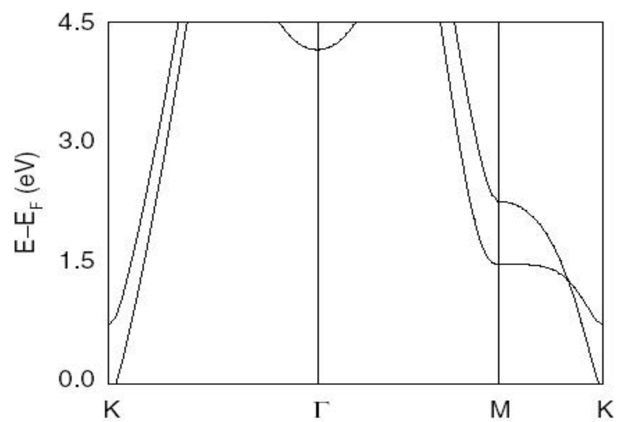
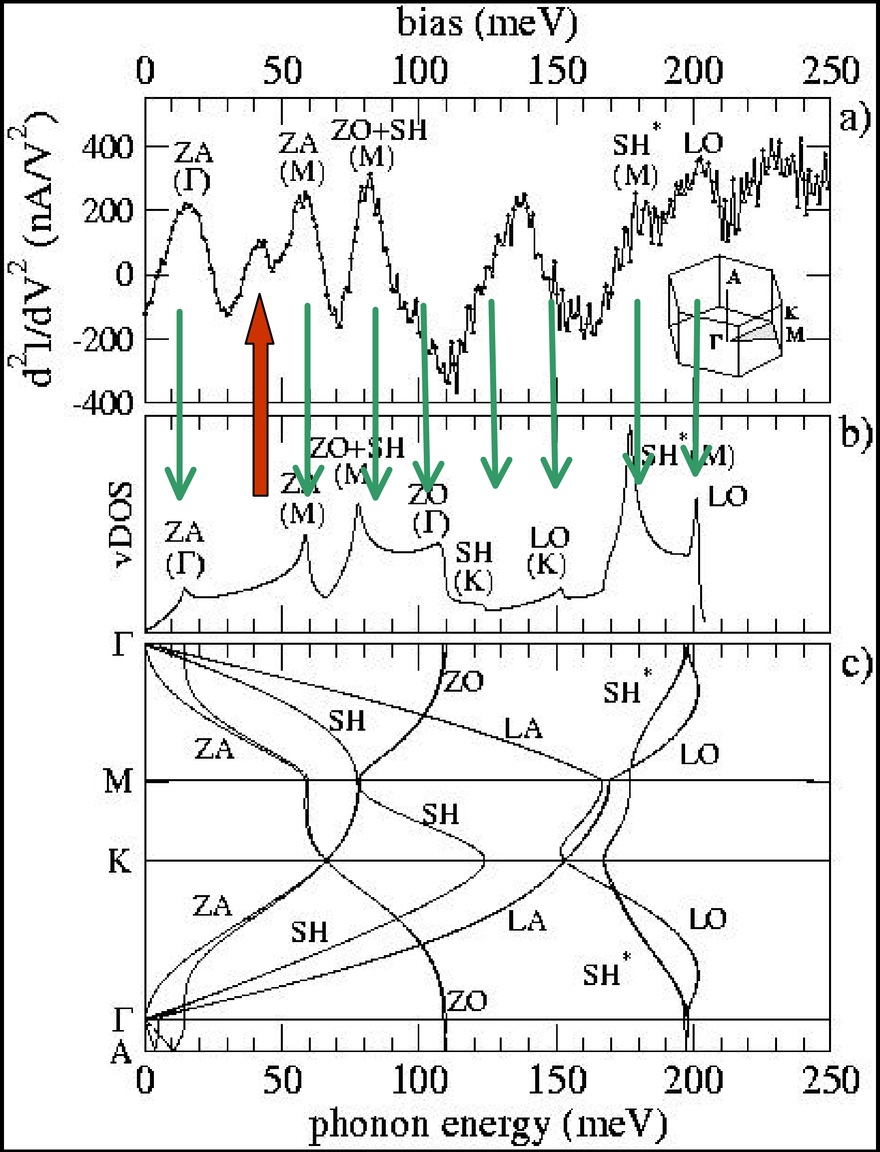




FIG. 1. Graphite $\pi$-band structure near some relevant points $M$, $\Gamma$, and $K$ in the energy range considered in this work.

# IETS of HOPG

Phonons
+
Plasmon



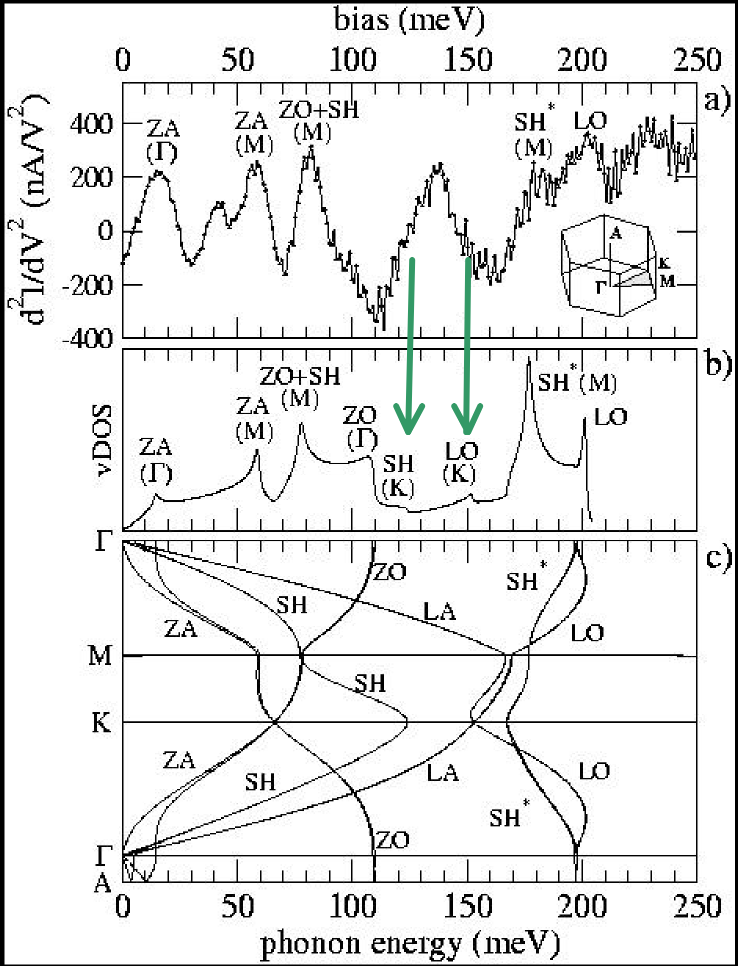

Experiment

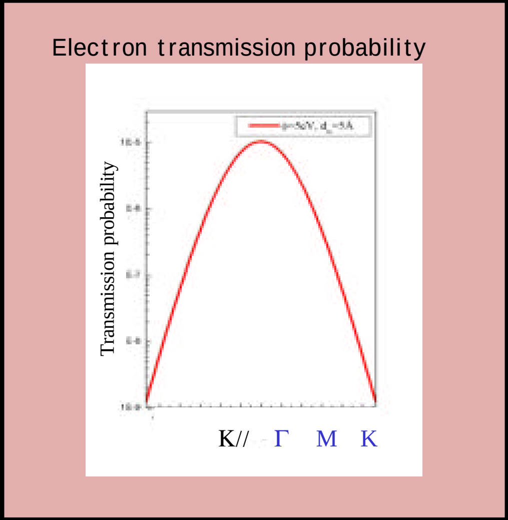
DFT
powered
by
L.Wirtz,
A.Rubio

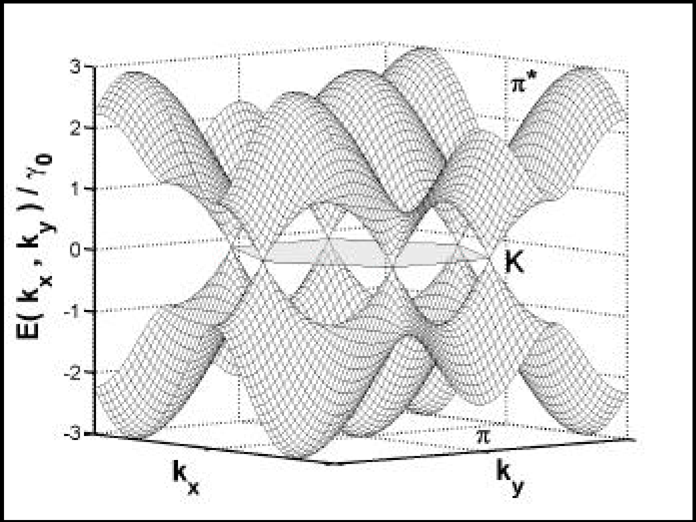
PRB **69**, R121414, (2004)

The total density of phonons can be detected with STM-IETS

# Phonon assisted tunneling process




-Enhancement of the phonon modes at K

## Take home message

- Inelastic Tunneling Spectroscopy as probe of lattice dynamics (vDOS)
  1. HOPG (phonon assisted tunneling process)
  2. SWCNT: RBM + G band

- Map of the vibration frequencies along the tube
  1. vibrational modes vs. tube structural changes (i.e. 5/7 pairs or tube deformations)
  2. charge transfer

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You for your attention!

[redacted]