Ústav fyzikální chemie J. Heyrovského, v.v.i.
Akademie věd České republiky

J. Heyrovský 1959

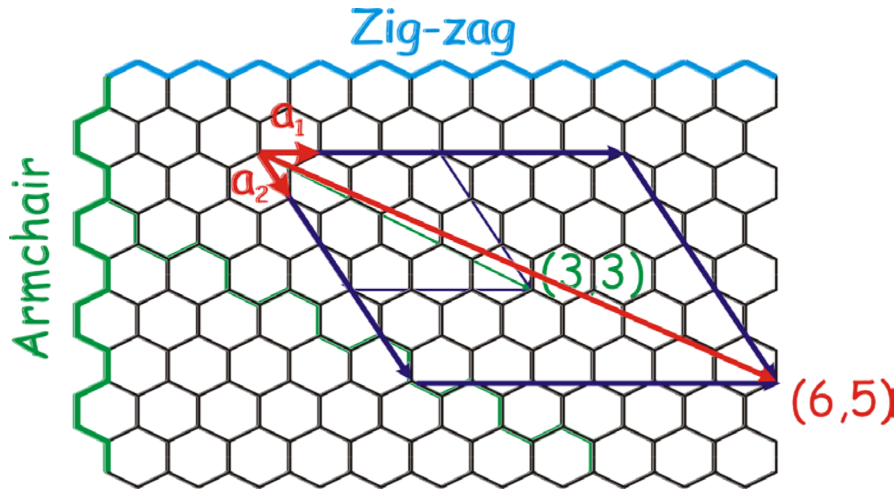
Uhlíkové nanostruktury z pohledu spektroelektrochemie

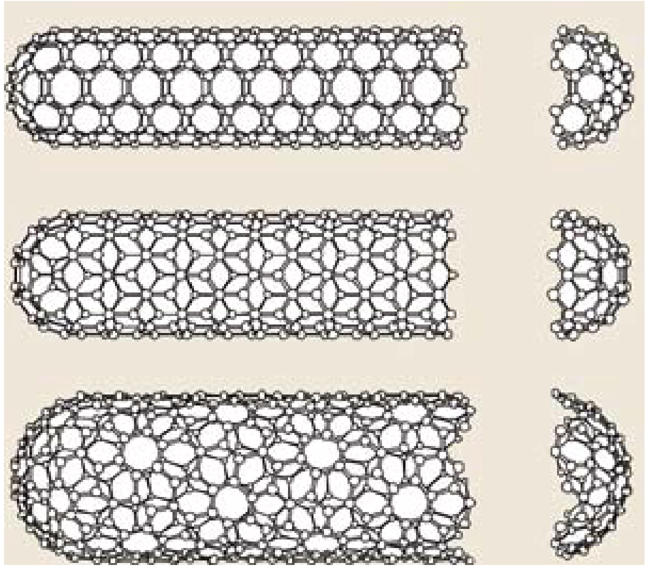
Ladislav Kavan

Chirality: (*n*, *m*)

chiral vector $C_h = na_1 + ma_2$
a_1 , a_2 …. unit vectors of the hexagonal structure

→ nanotube definition (n,m)





Armchair nT
(*n*=*m*) metal

Zig-zag nT
(*n*-*m*) = 3*i* metal
(*n*-*m*) ≠ 3*i* semi.

Chiral nT
(*n*-*m*) = 3*i* metal
(*n*-*m*) ≠ 3*i* semi.

nanotube diameter d_0

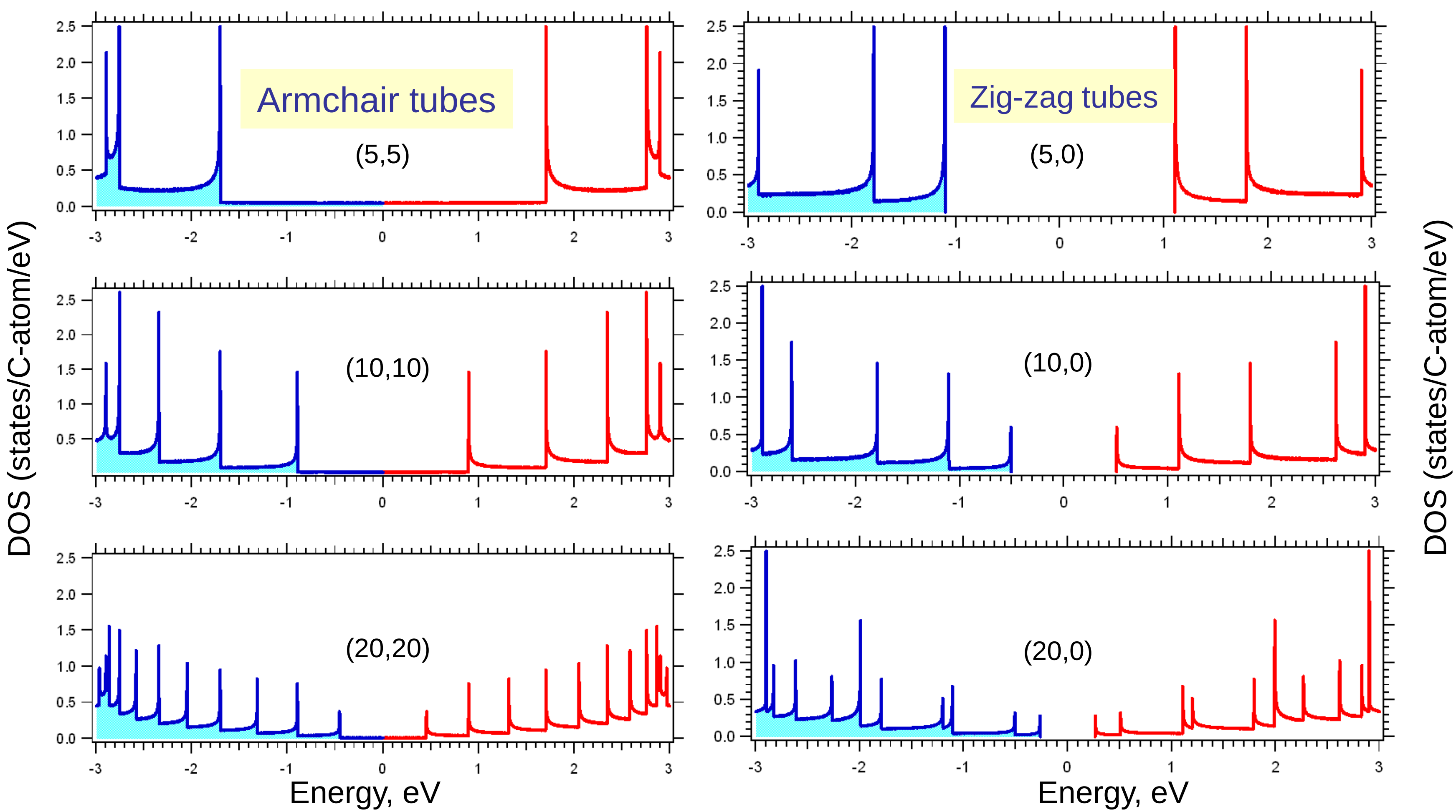
$$d_0 = \frac{a_{c-c}\sqrt{3}}{\pi}\sqrt{N}$$

$a_{C\text{-}C} = 1.42$ Å

$N = n^2 + nm + m^2$

Density of states (DOS) in SWCNT
→*Van Hove singularities*

$$DOS(E) = \left(\frac{L}{2\pi}\right)^d \int \frac{dk^d \delta(k(E)-k)}{|\nabla_k(E)|}; \nabla_k \to 0$$

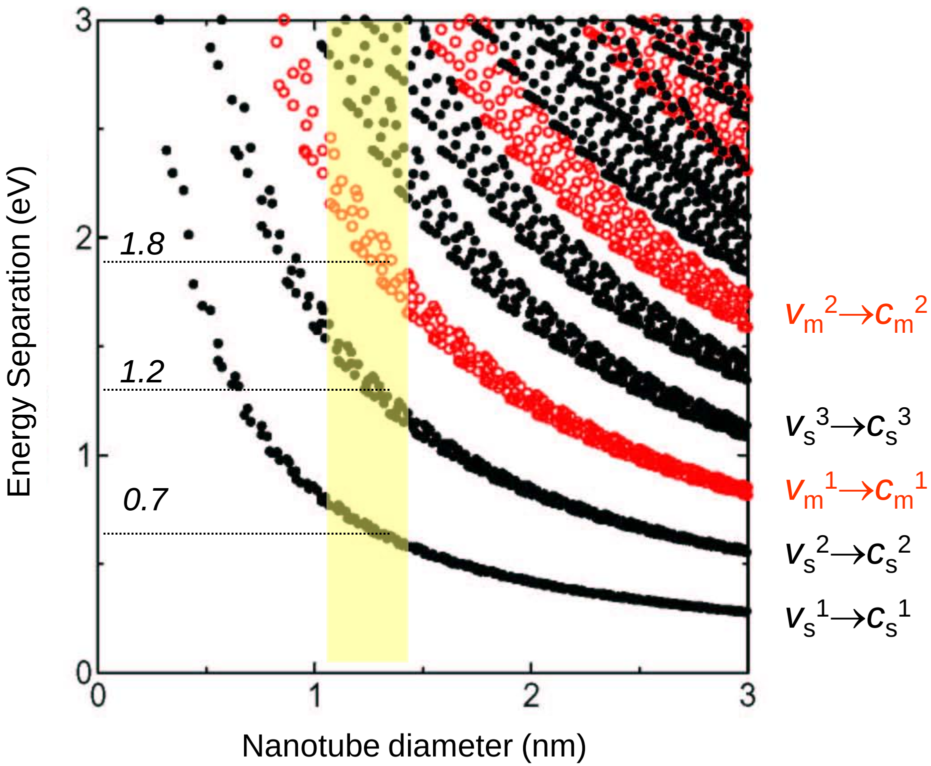


ΔE of singularities *vs.* diameter of SWCNT ("Kataura graph")

$$\Delta E_{ii} = \frac{2i\chi_0 a_{C-C}}{d} + \delta E$$

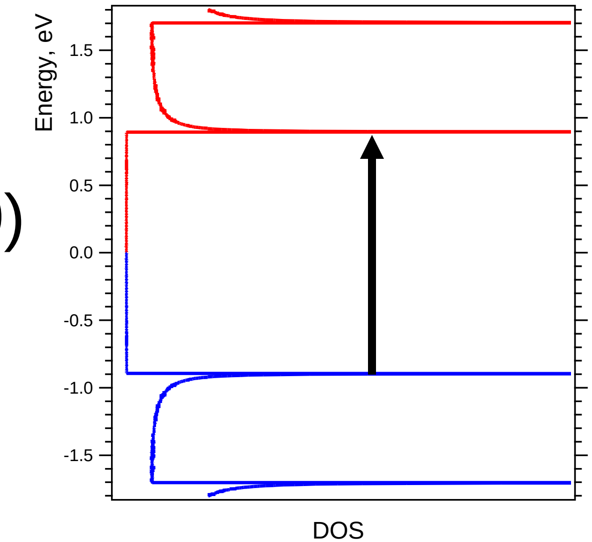
$\chi_0 \cong 2.4 - 2.9$ eV (overlap integral)
$a_{C\text{-}C} \cong 0.142$ nm

SWCNT $d \approx 1.1$-1.4 nm

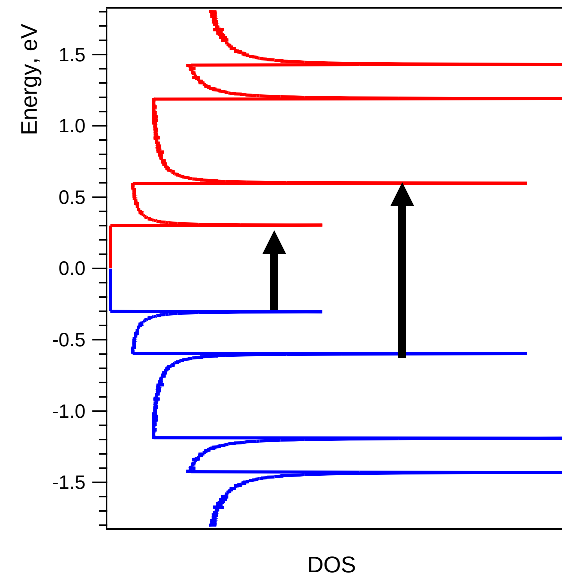


(n, m) to (40,40)

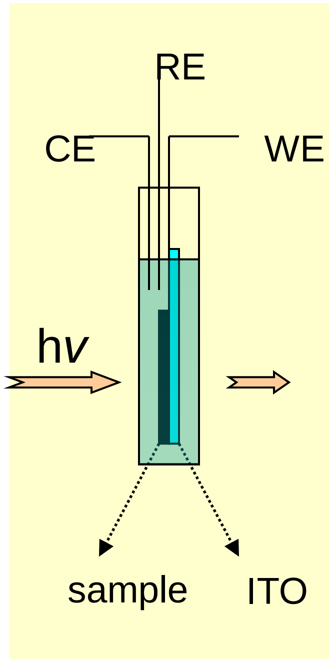
(10,10)

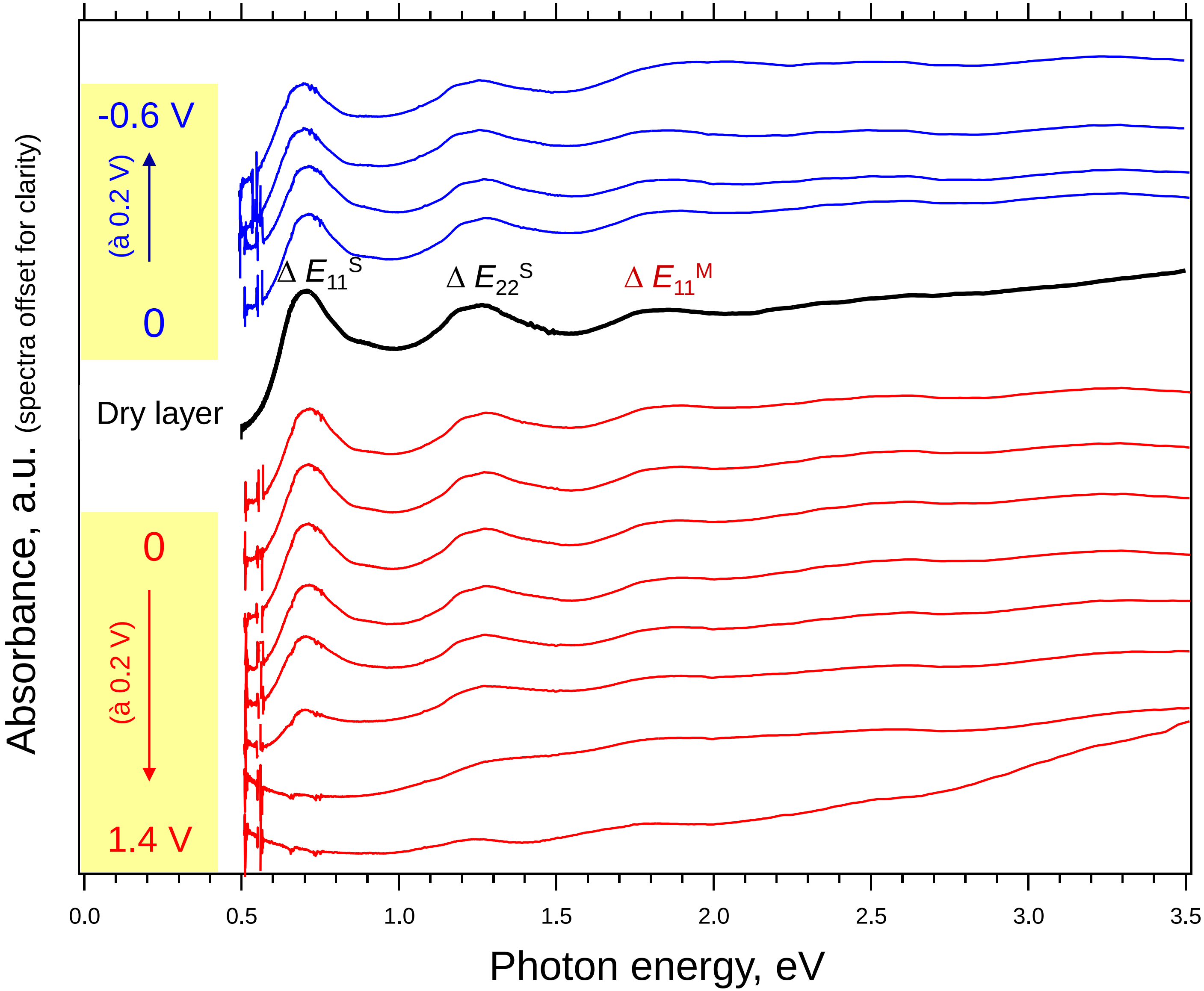


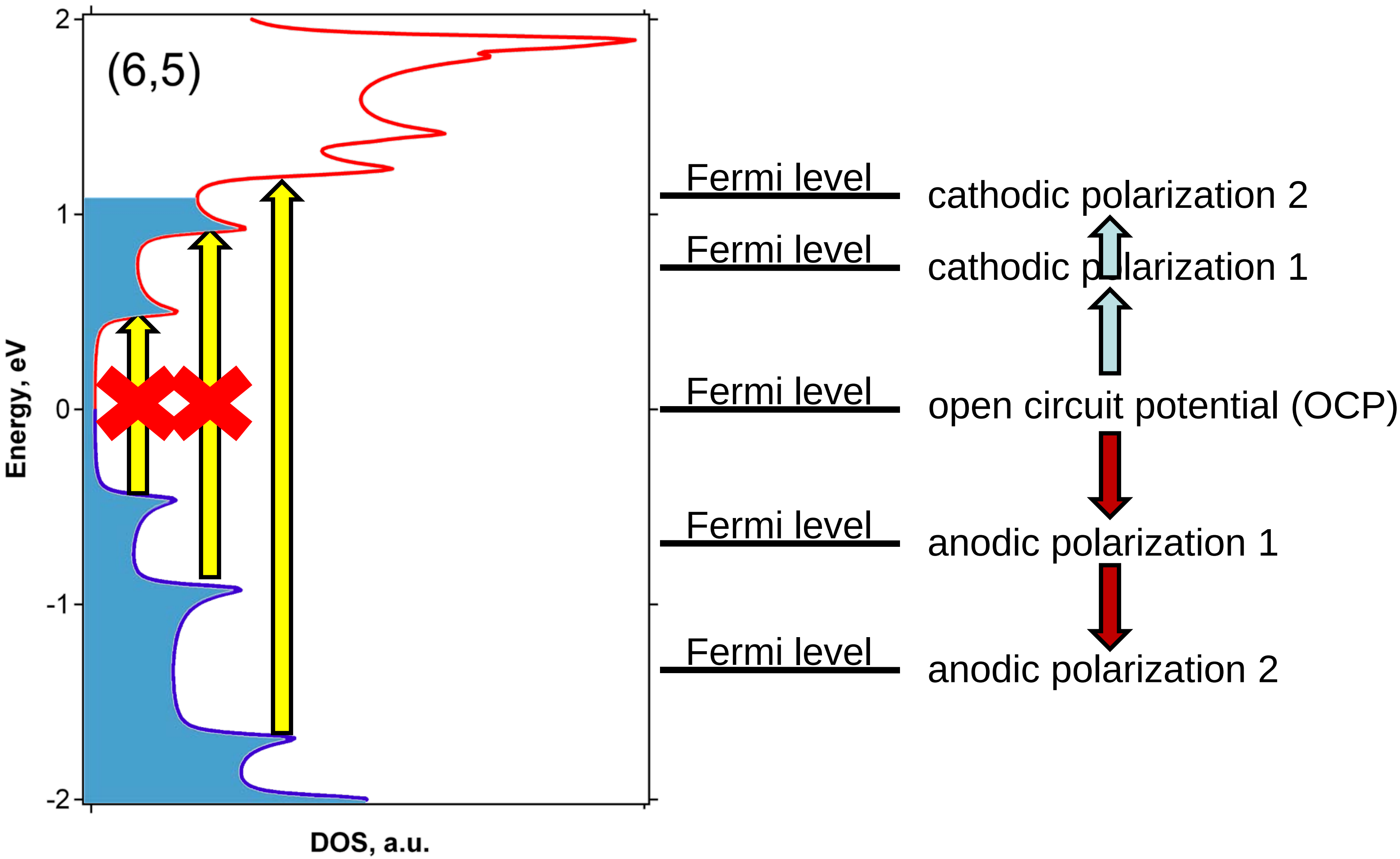
(11,9)



Vis-NIR spectra on ITO electrode - SWCNT *(0.2 M $LiClO_4$ + acetonitrile)*

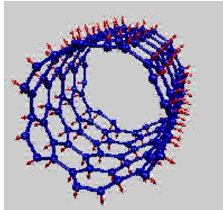




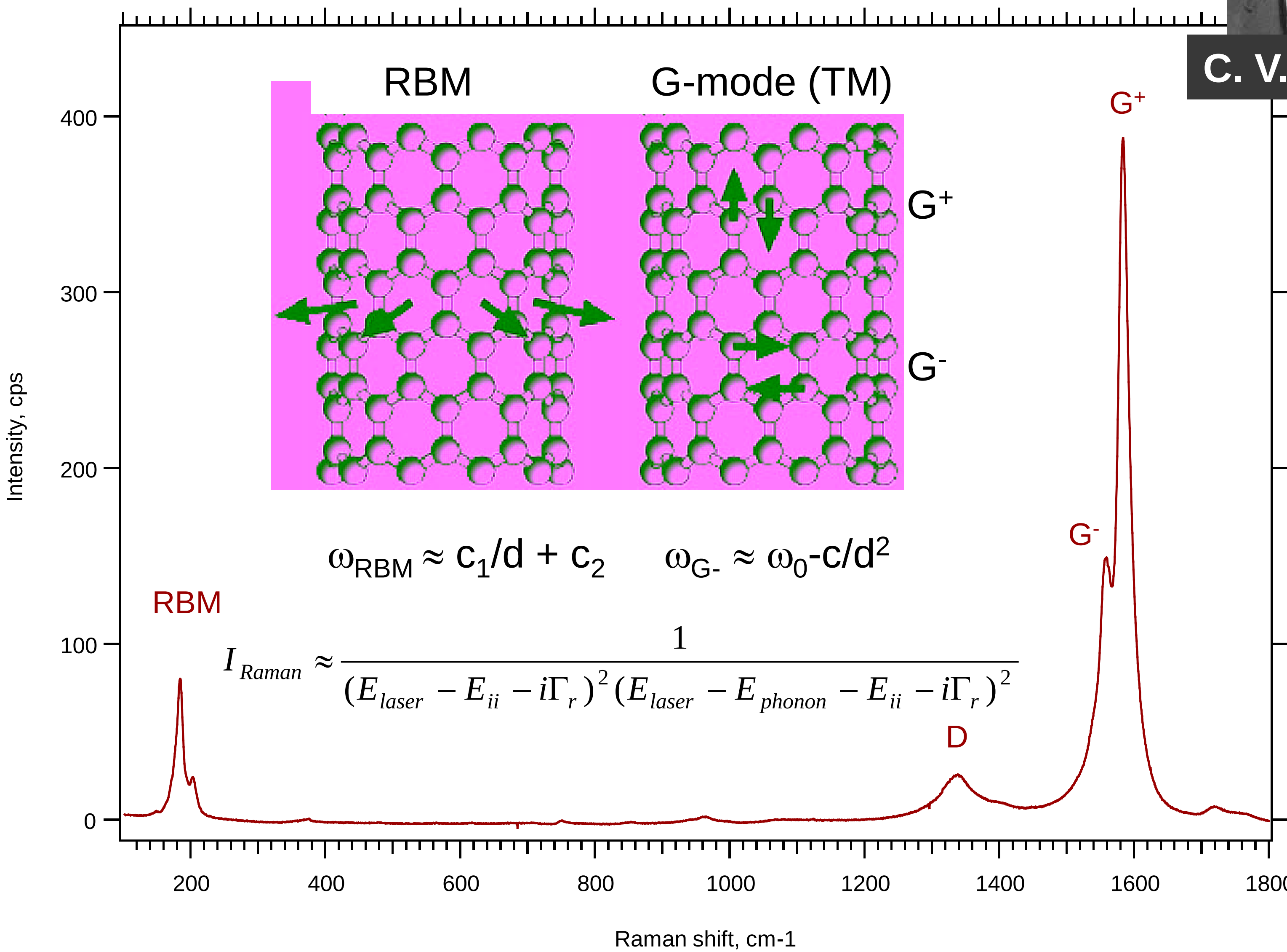


(6,5)
Energy, eV
2
1
0
-1
-2
DOS, a.u.
Fermi level
cathodic polarization 2
Fermi level
cathodic polarization 1
Fermi level
open circuit potential (OCP)
Fermi level
anodic polarization 1
Fermi level
anodic polarization 2

Raman spectrum of SWCNT



C. V. Raman

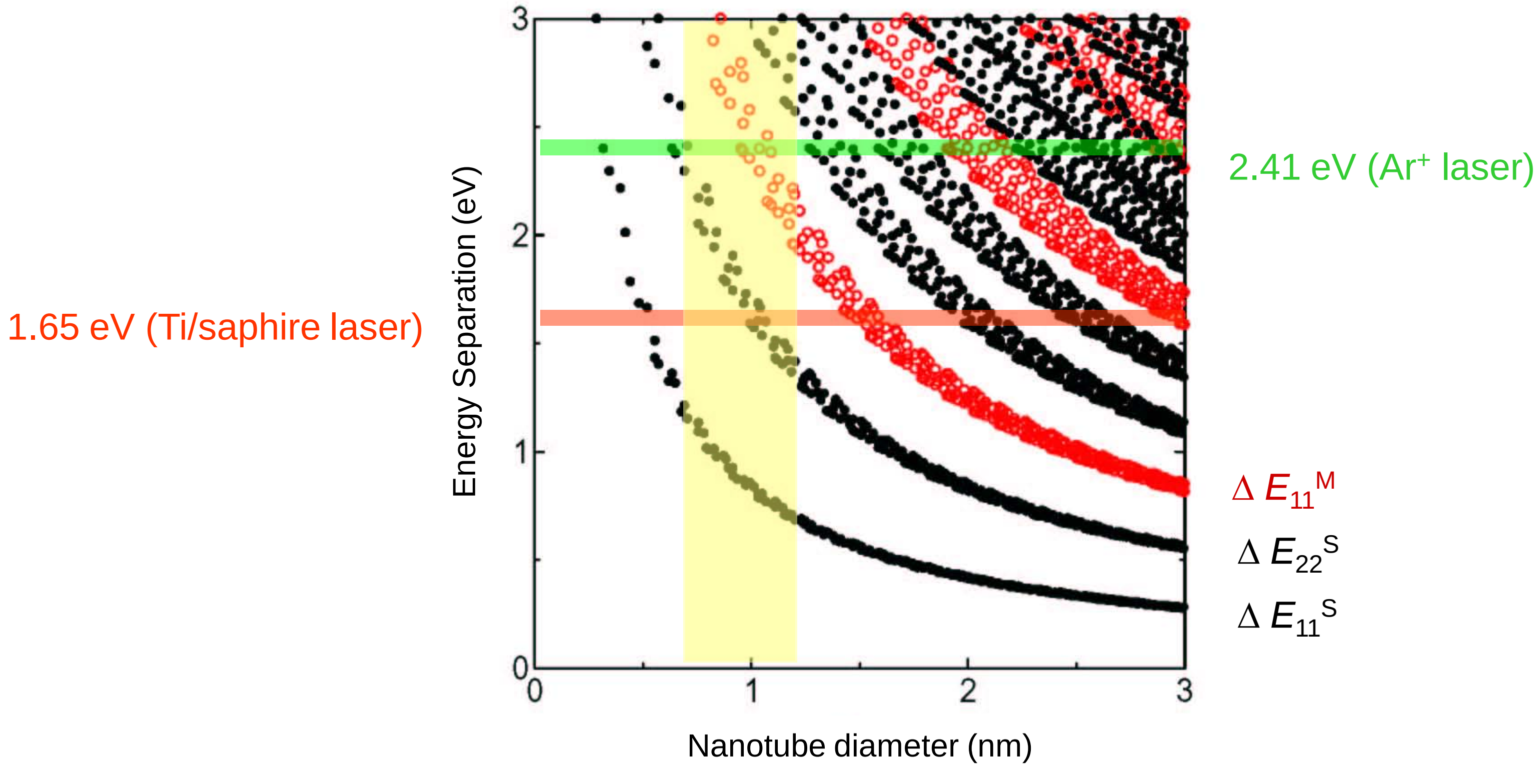


$$\omega_{RBM} \approx c_1/d + c_2 \qquad \omega_{G-} \approx \omega_0 - c/d^2$$

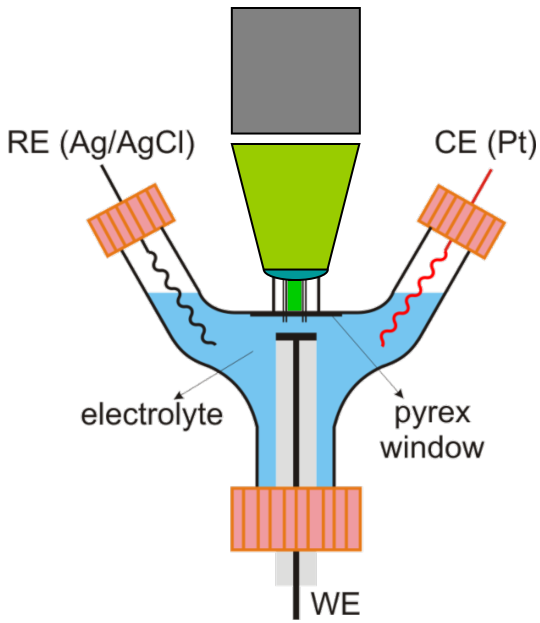
$$I_{Raman} \approx \frac{1}{(E_{laser} - E_{ii} - i\Gamma_r)^2 (E_{laser} - E_{phonon} - E_{ii} - i\Gamma_r)^2}$$

Resonance Raman spectroscopy of SWNT

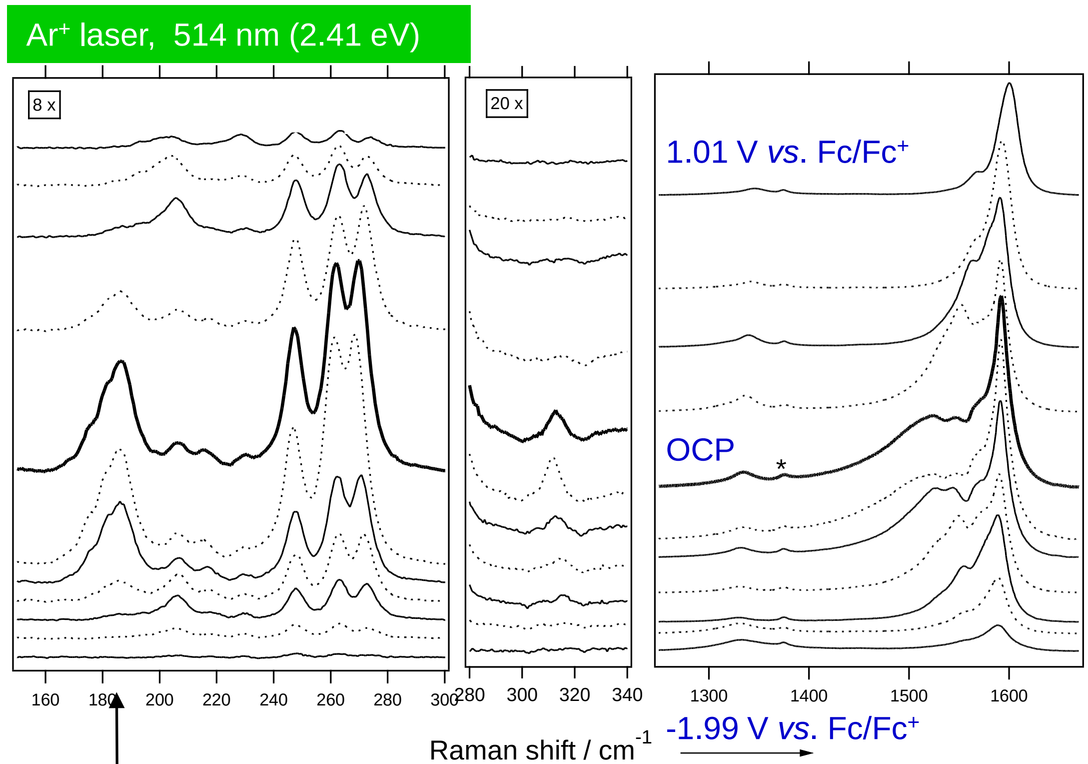
SWCNT ∅ ≈ (0.7 - 1.2) nm



In-situ Raman spectroelectrochemistry



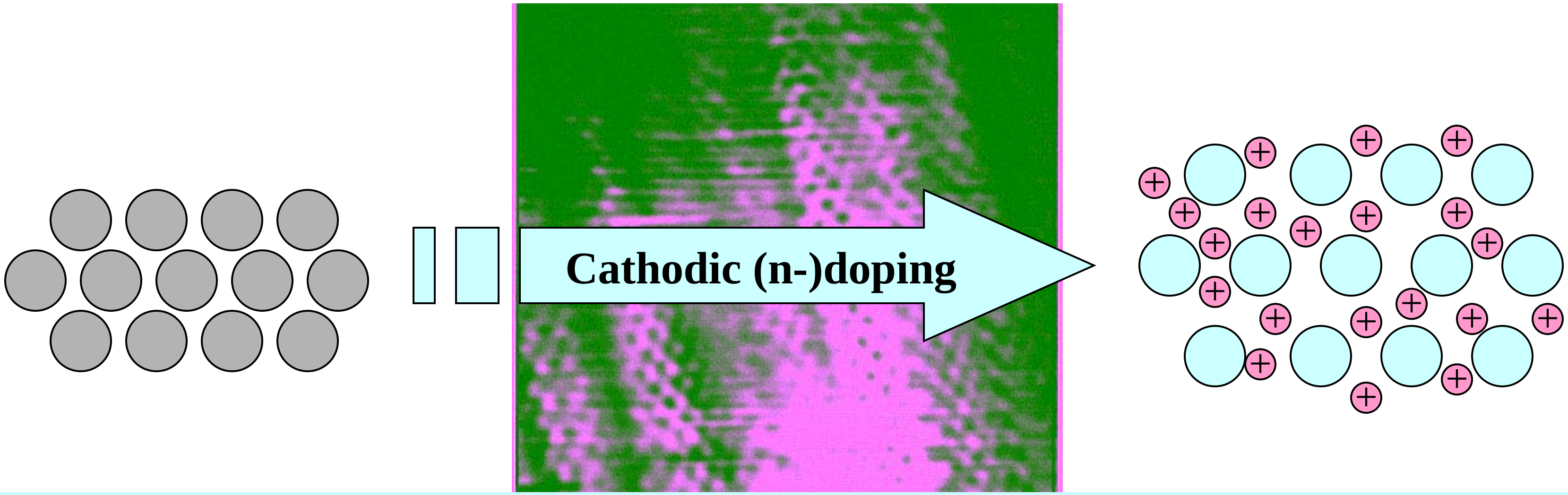
0.2 M $LiClO_4$ + acetonitrile



ΔE_{11}^{M} ; d ≅ 1.2 nm

ΔE_{22}^{S} ; d ≅ 0.8 nm

SWCNT bundles



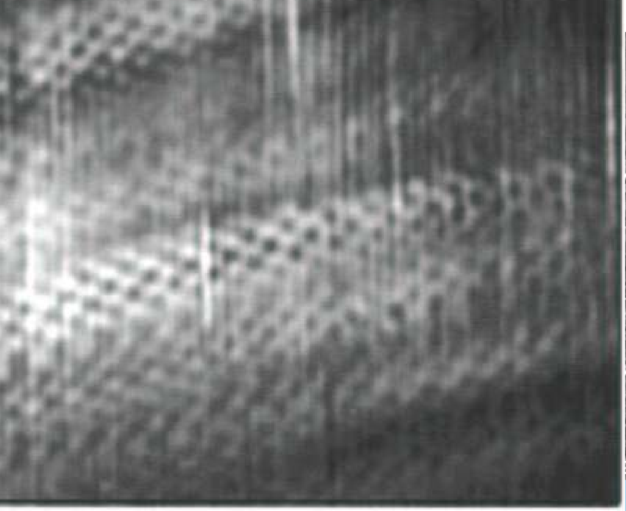
Energy storage: ⊕ = Li^+ (372 mAh/g ≈ $Li_{1.23}C_6$) - ***Li-ion battery***

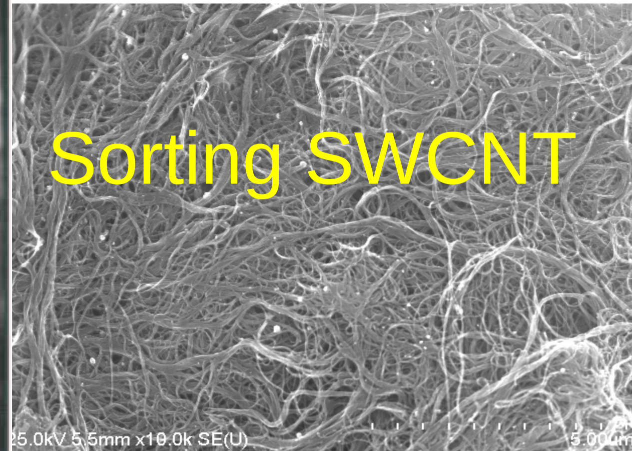
15-100 F/g – ***Supercapacitor***

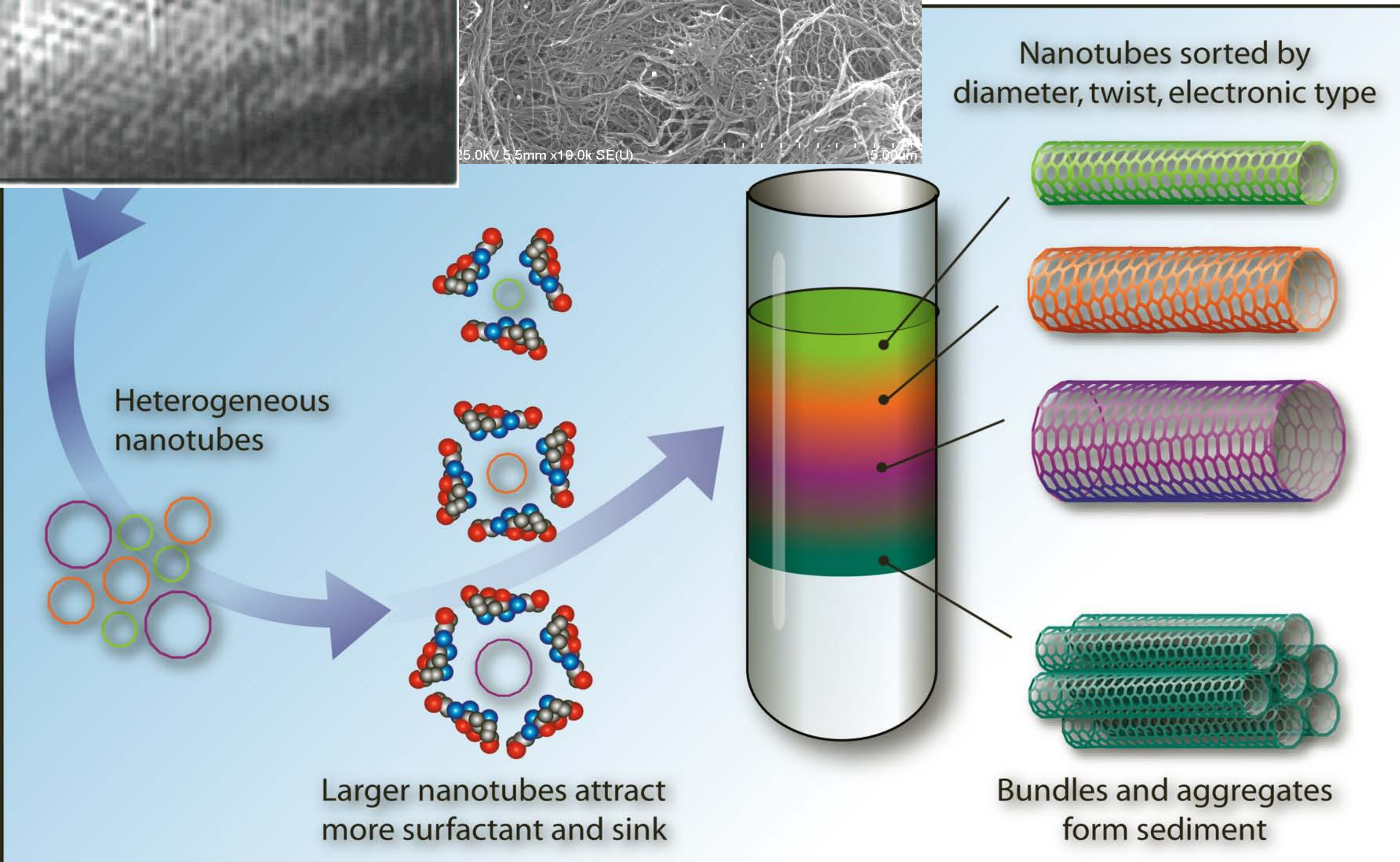
Elchem. H_2 storage: (110 mAh/g; 0.4 %)

Diameter-selective doping (Raman spectroelectrochemistry)

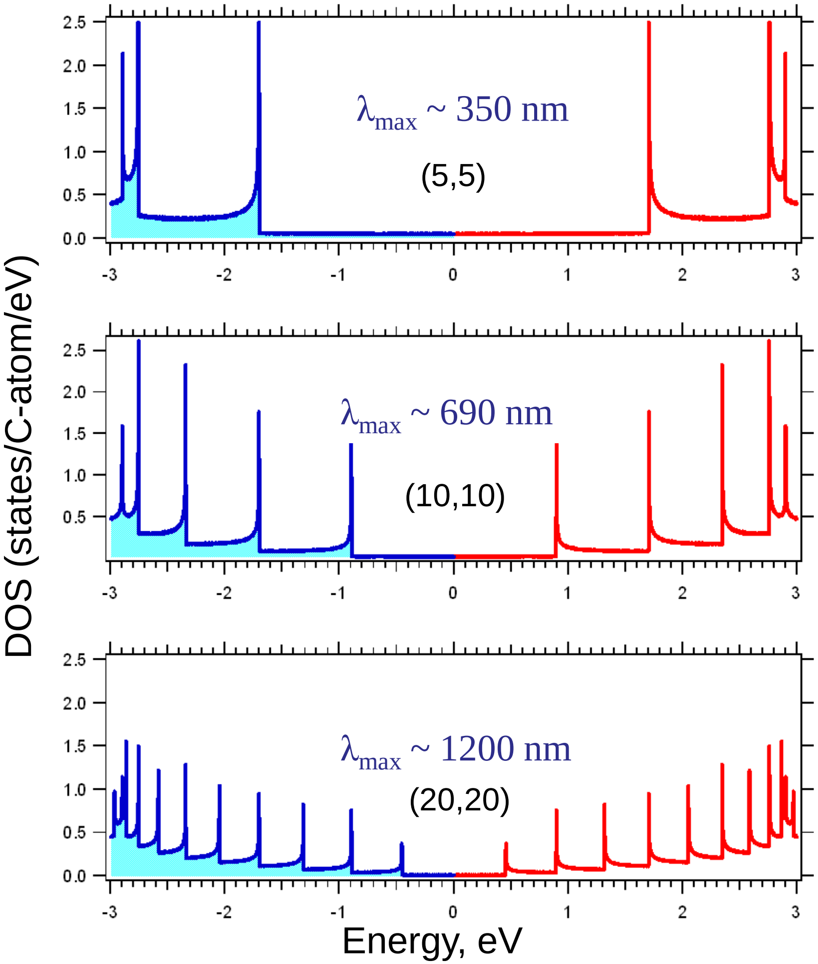
Sorting SWCNT

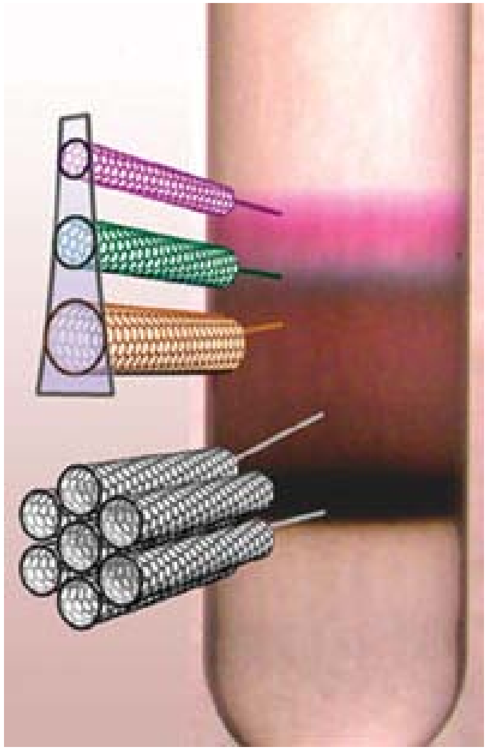






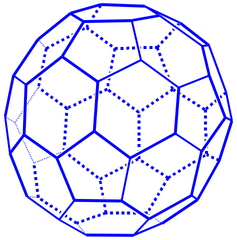
Armchair tubes



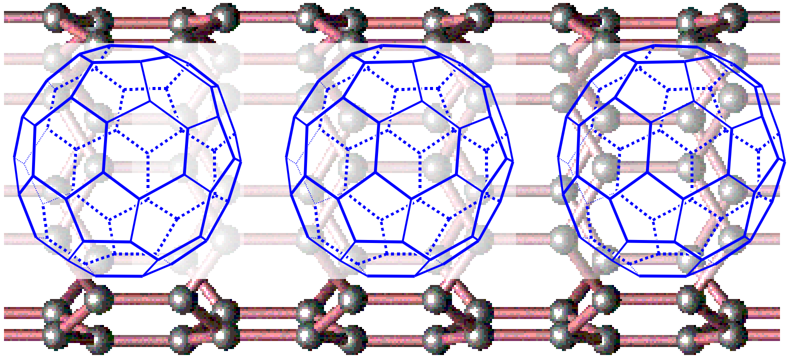


Green & Hersam, *Nature Nanotech*. **4**, 64, (2009)

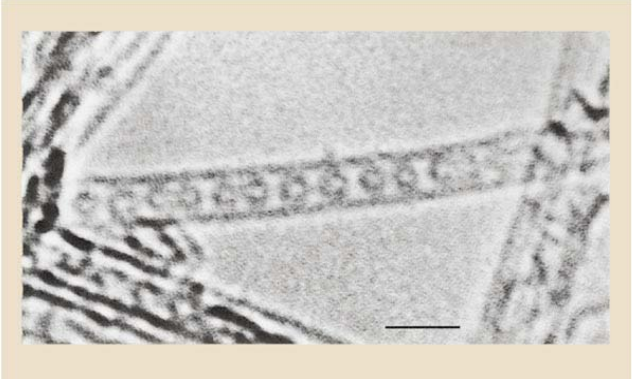
Formation of fullerene peapod (C_{60}@SWCNT)

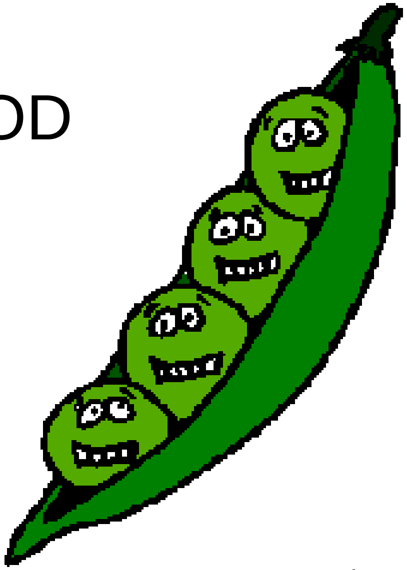


C_{60} (g)

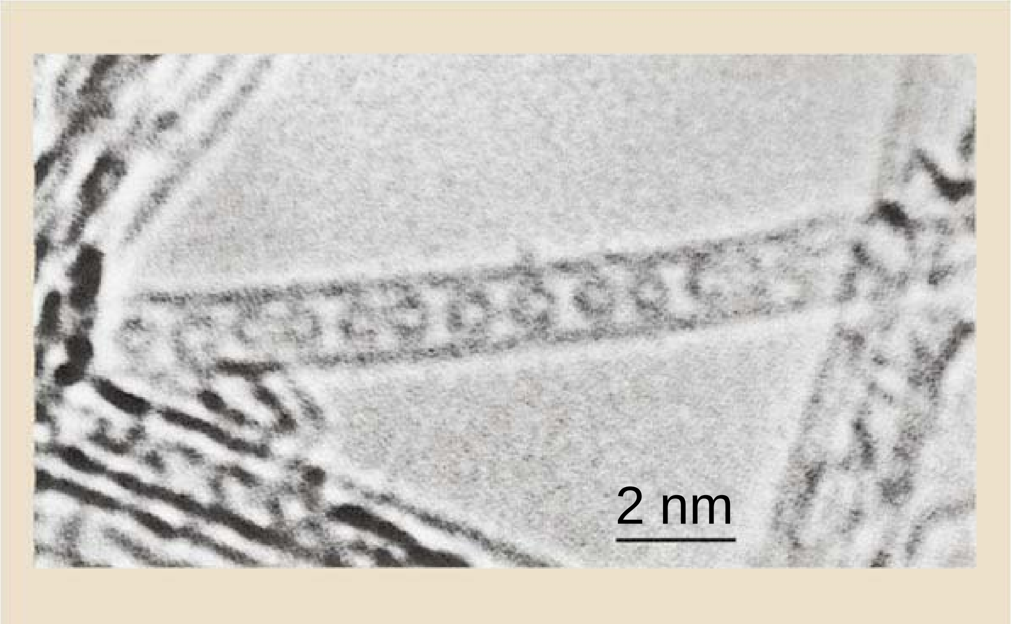


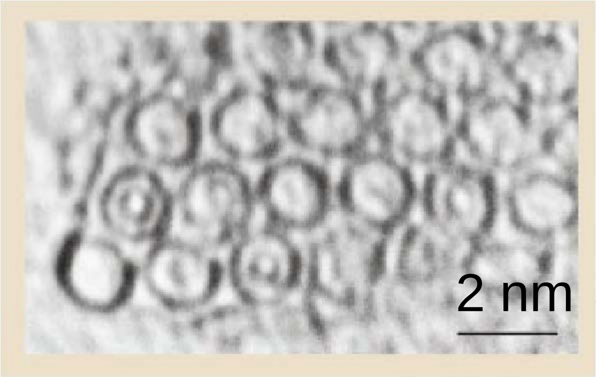
FULLERENE PEAPOD



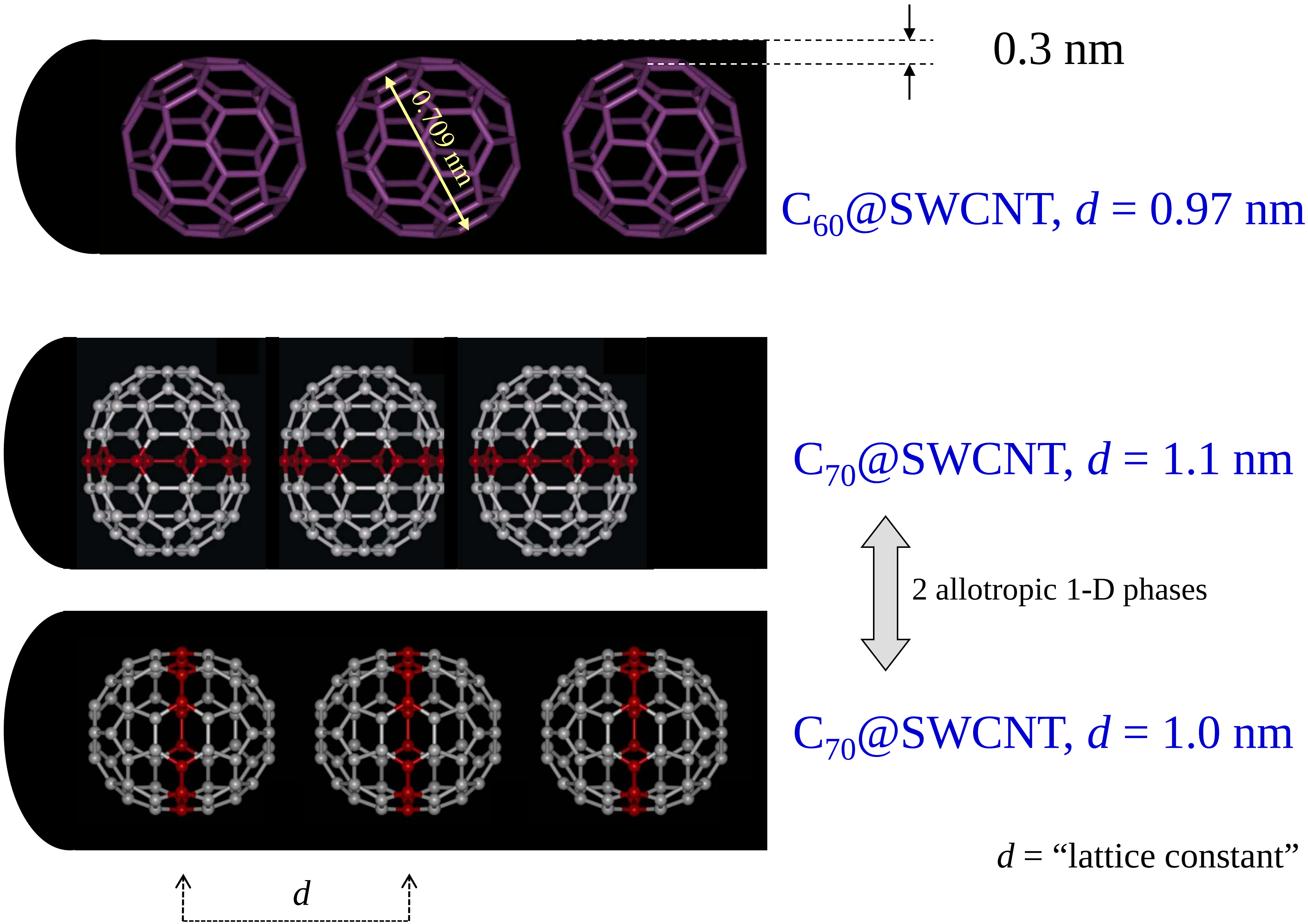


Fullerene peapod C_{60}@SWCNT



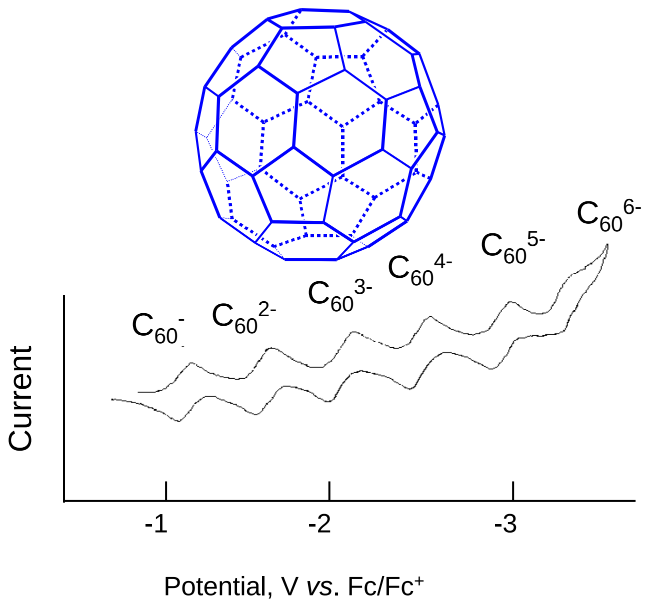


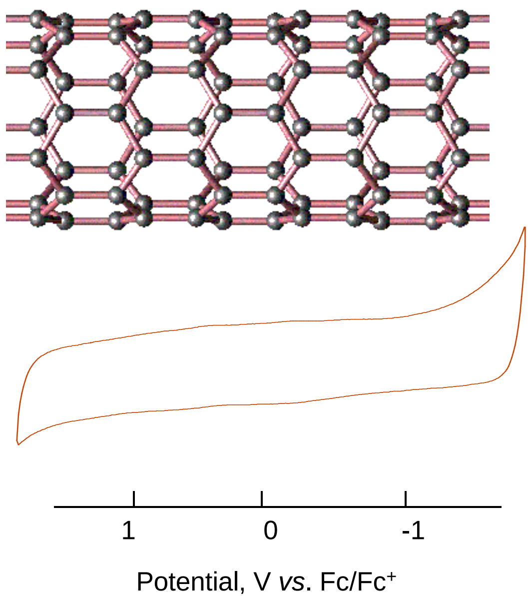
Smith,B.W.; Monthioux,M.; Luzzi,D.E., *Nature* **396**, 323 (1998)



0.3 nm
0.709 nm
C_{60}@SWCNT, d = 0.97 nm
C_{70}@SWCNT, d = 1.1 nm
2 allotropic 1-D phases
C_{70}@SWCNT, d = 1.0 nm
d = “lattice constant”
d

Electrochemistry of C_{60} and SWCNT

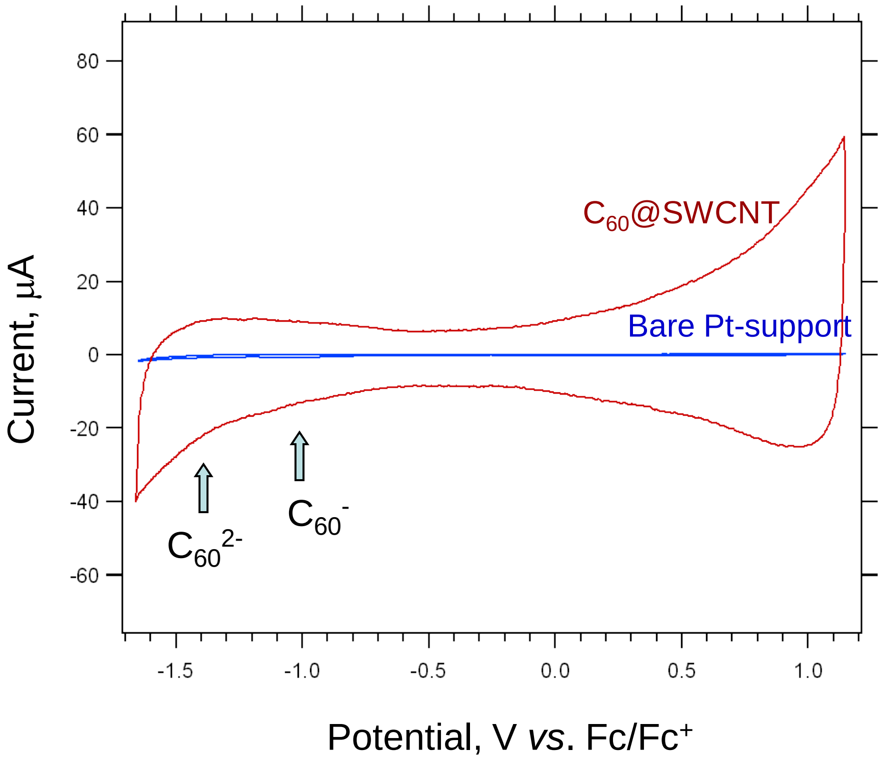




C_{60} (solution)……..CH_3CN/toluene + electrolyte solution (at-10^{o}C)

SWCNT (solid)...…..CH_3CN + electrolyte solution

Cyclic voltammetry of C_{60}@SWCNT



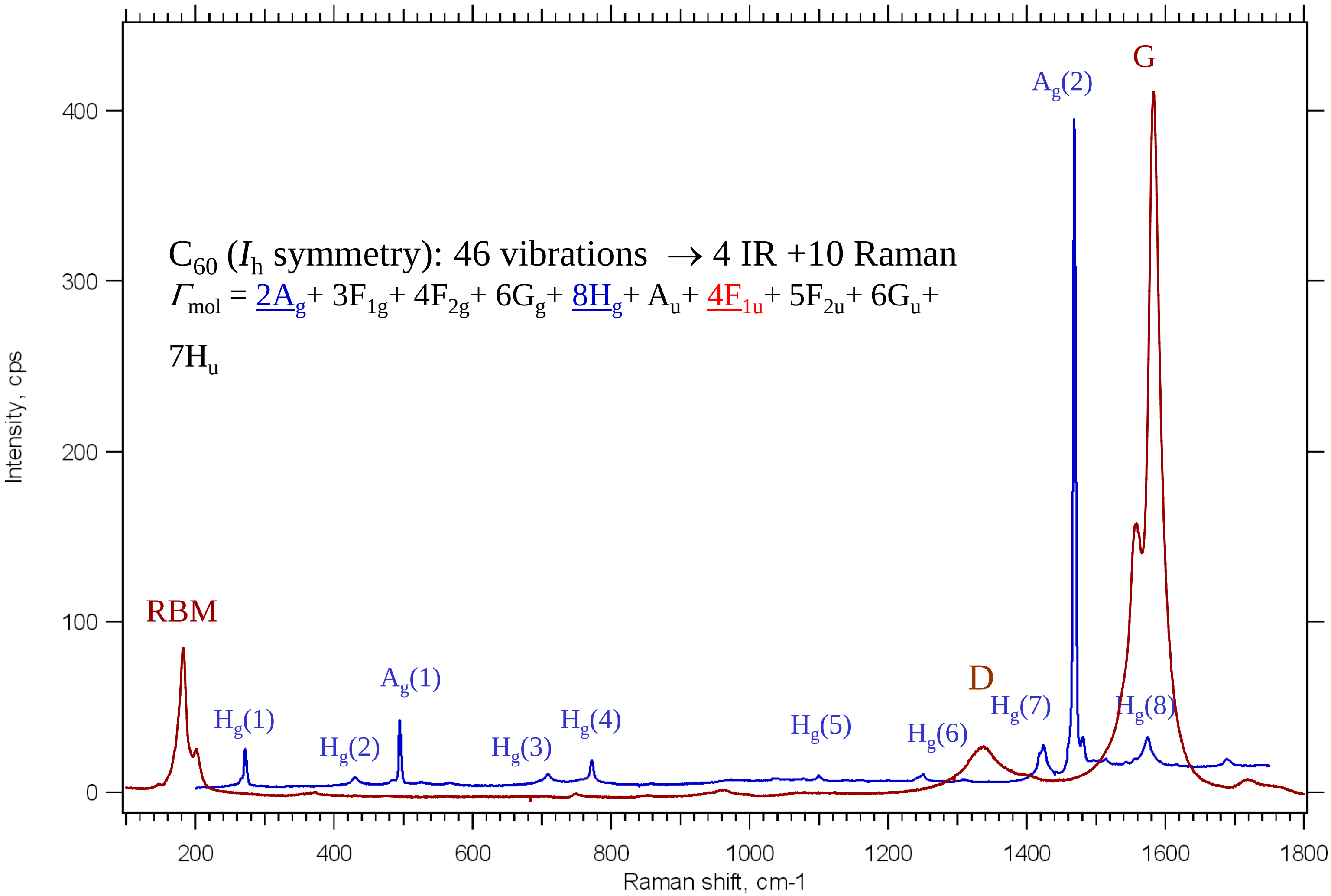
Δf… number of e^-/C-atom
C … capacitance ≈ 40 F/g

$$\Delta f = \frac{CM_C \Delta U}{F}$$

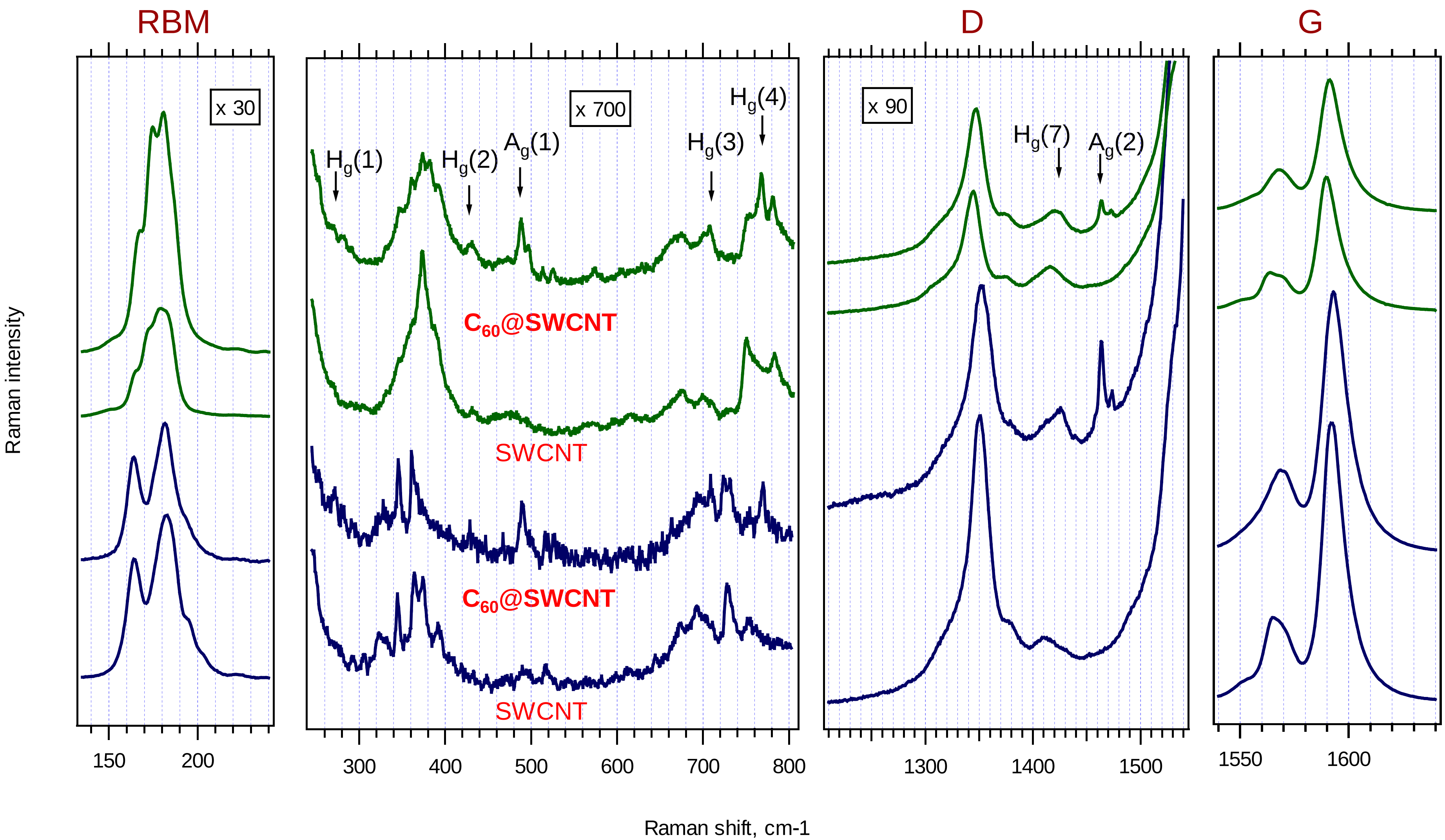
Δf = 0.005 e^-/C-at (found)
Δf = 0.017 e^-/C-at (assumed) for C_{60}/C_{60}^-

L. Kavan et al. *J. Phys. Chem*. **107**, 7666 (2003)

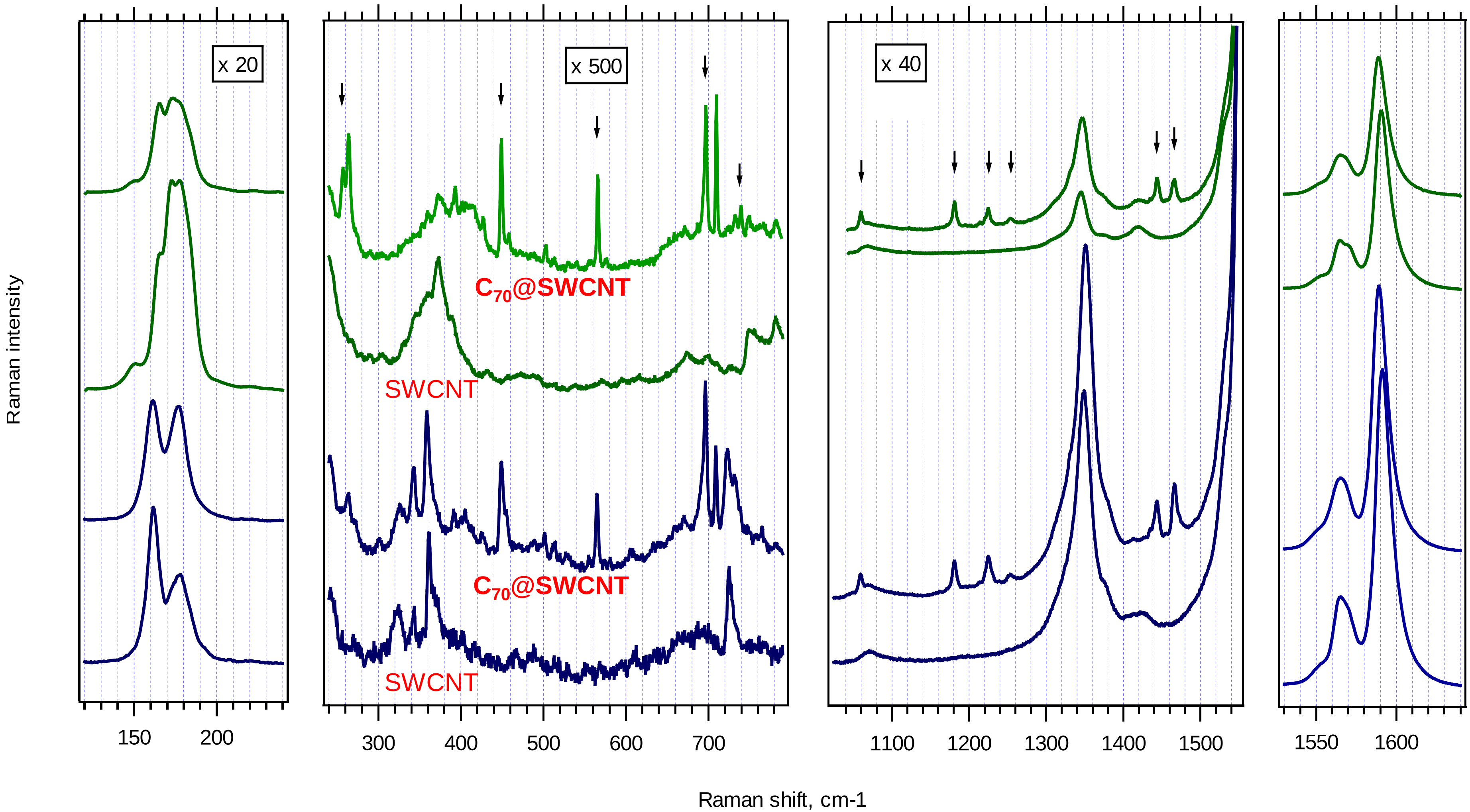
Raman spectra of C_{60} (single crystal) and SWCNT



Raman spectra of dry C_{60}@SWCNT $h\nu_{exc}$= 2.41 eV or 2.54 eV



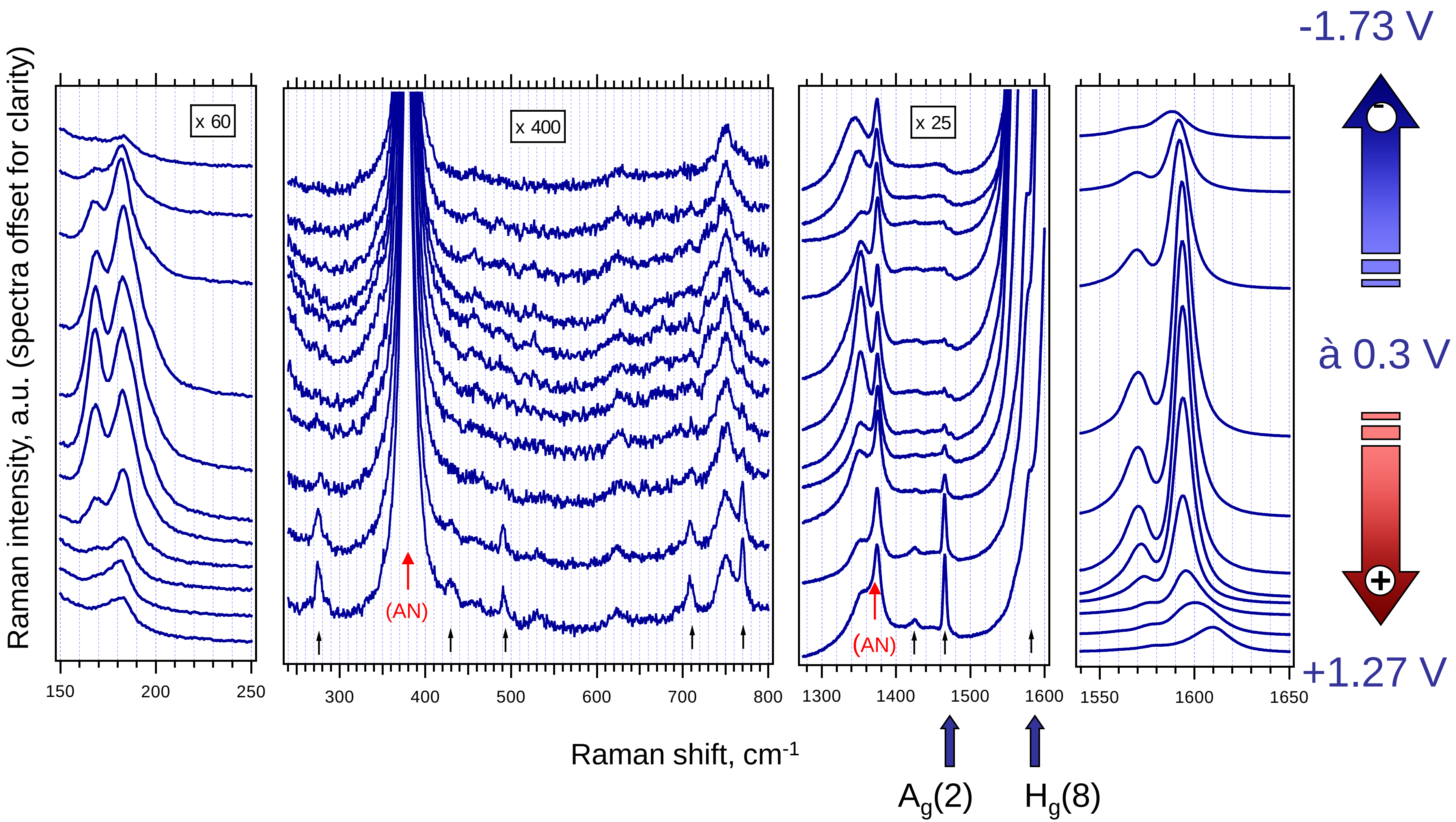
Raman spectra of C_{70}@SWCNT hν_{exc}= 2.41 eV or 2.54 eV



C_{70} (D_{5h} symmetry): 53 Raman active vibrations: $12A_1' + 22E_2' + 19E_1''$

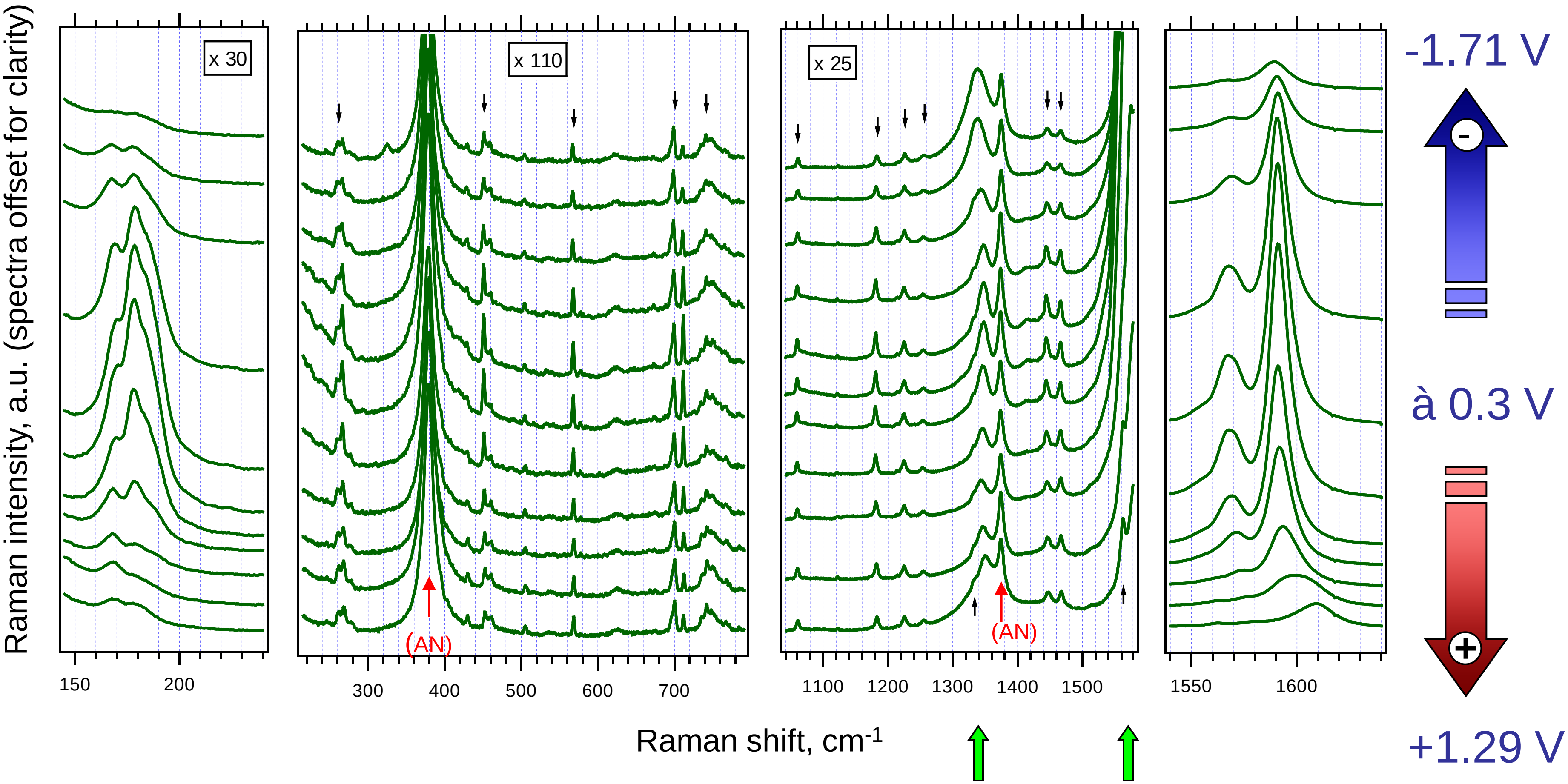
L. Kavan et al. *J. Phys. Chem*.B **107**, 7666 (2003)

Raman spectroelectrochemistry C_{60}@SWCNT ($h\nu_{exc}$= 2.54 eV)

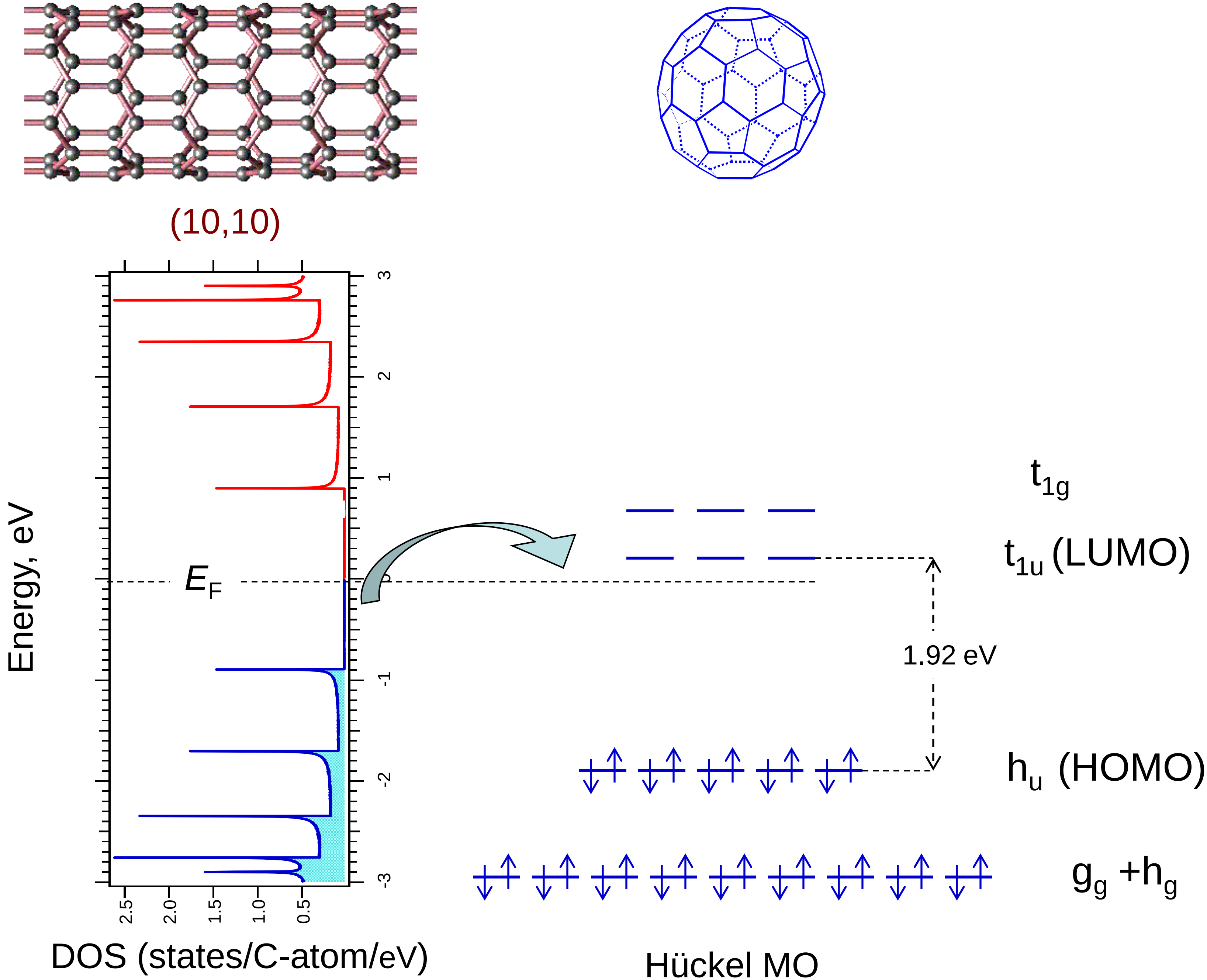


C_{60}@SWCNT film on Pt electrode in 0.2 M $LiClO_4$ + acetonitrile, potentials vs. Fc/Fc^+

Raman spectroelecrtochemistry: C_{70}@SWCNT ($h\nu_{exc}$= 2.41 eV)

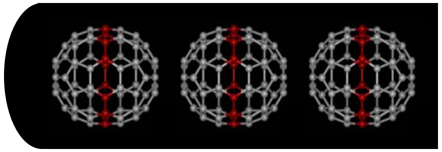


C_{70}@SWCNT film on Pt electrode in 0.2 M $LiClO_4$ + acetonitrile, potentials vs. Fc/Fc^+



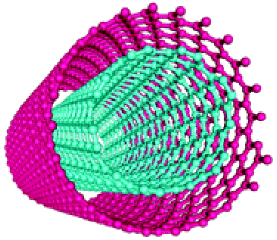
(10,10)
Energy, eV
E_F
3
2
1
-1
-2
-3
2.5
2.0
1.5
1.0
0.5
DOS (states/C-atom/eV)
t1g
t1u (LUMO)
1.92 eV
hu (HOMO)
gg +hg
Hückel MO

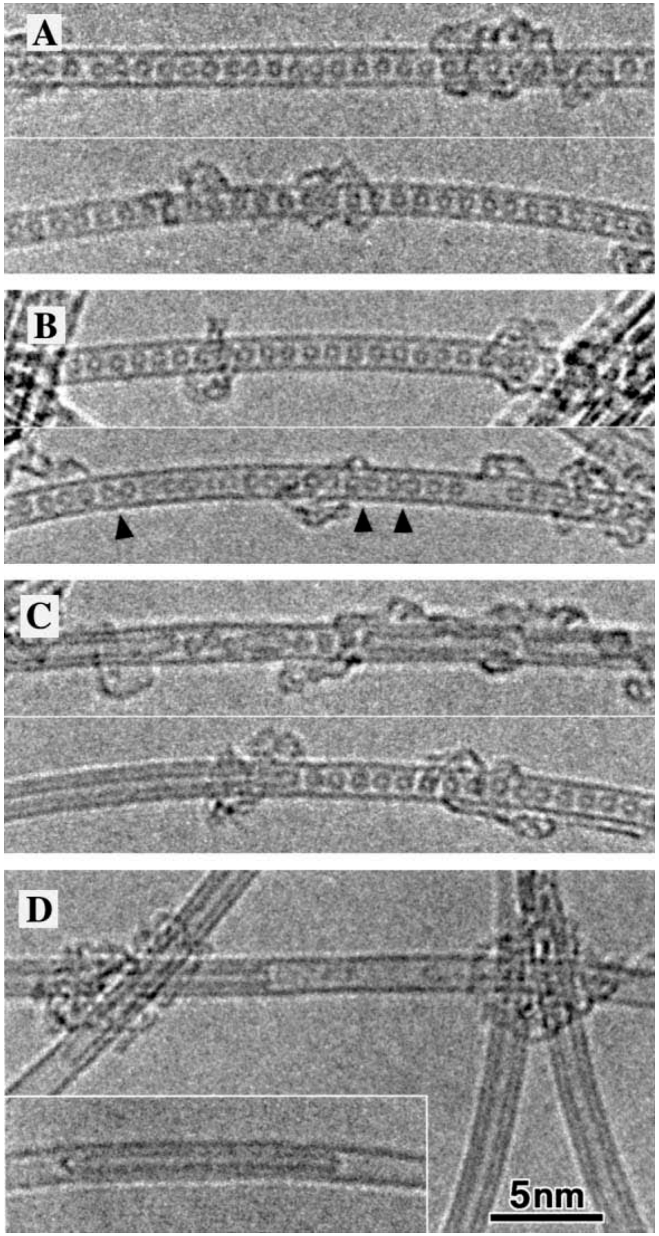
Double walled nanotubes



C_{60}@SWCNT

DWCNT





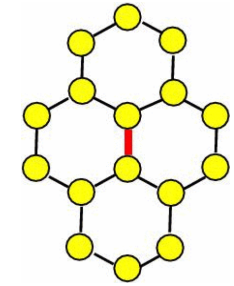
RT

800 ^{o}C

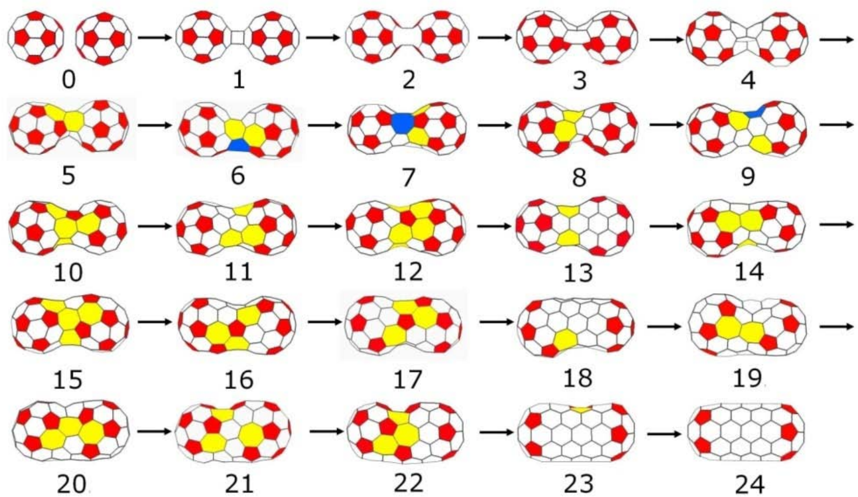
1000 ^{o}C

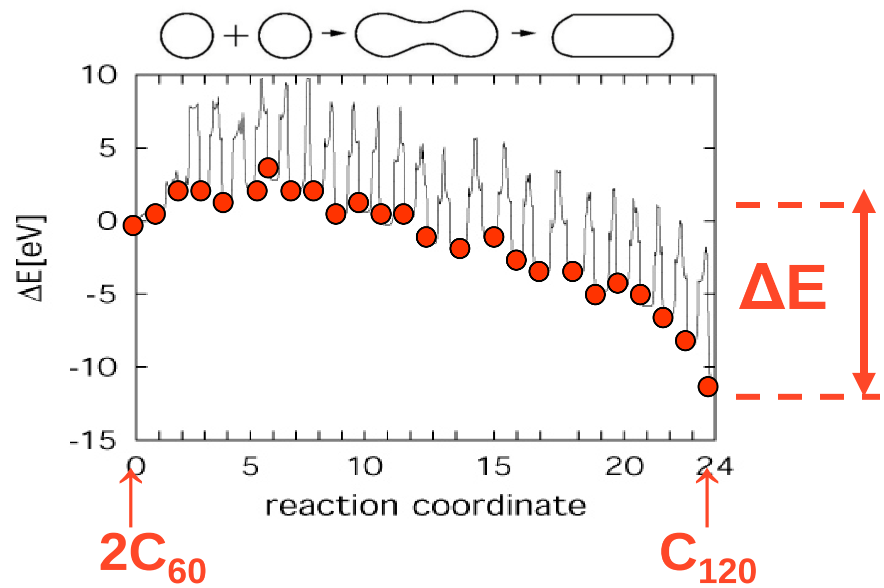
1200 ^{o}C

Stone-Wales rearrangement pathway for fusion of fullerenes

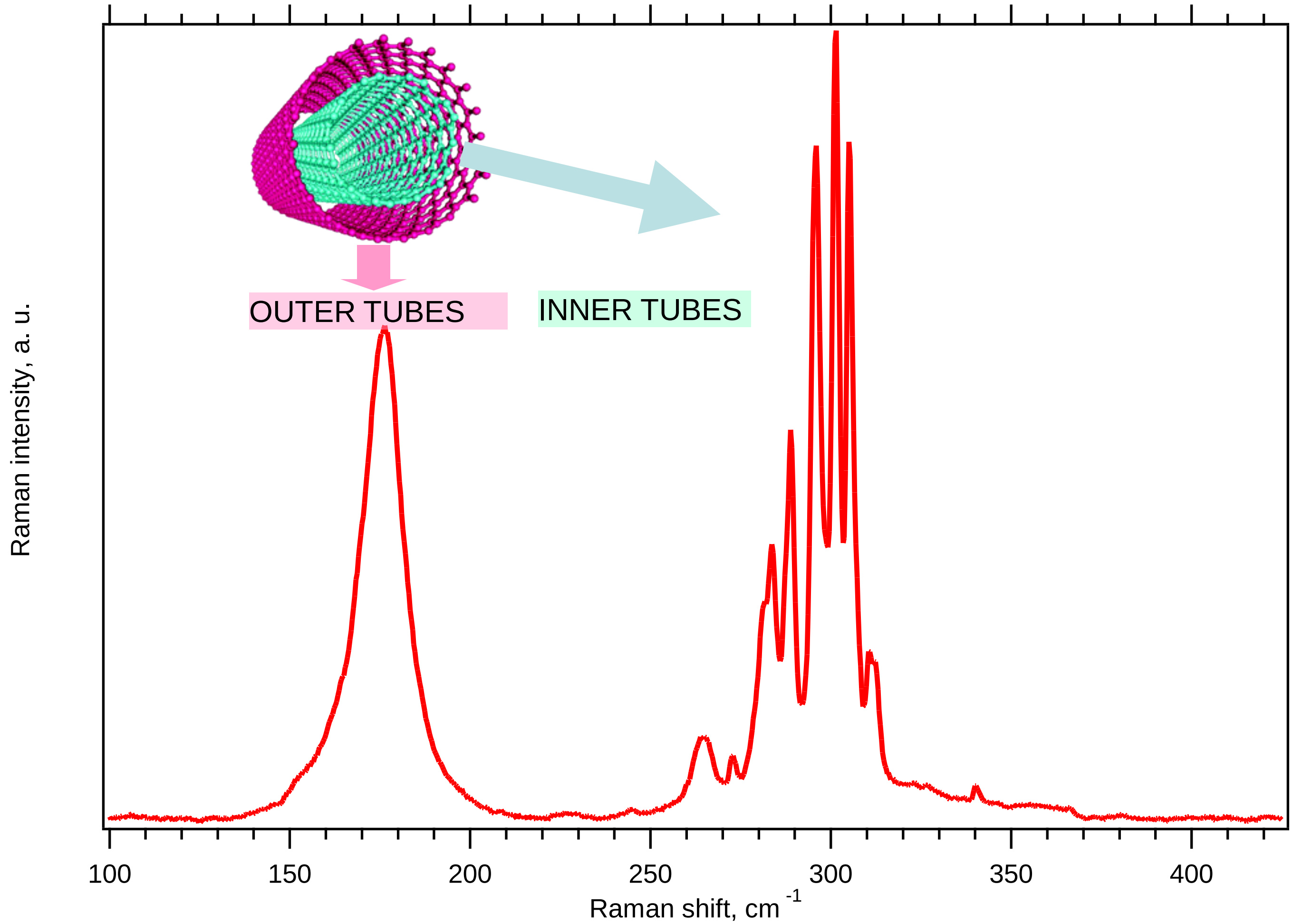


[Hiroshi Ueno, Shuichi Osawa, Eiji Osawa, and Kazuo Takeuchi, Fullerene Science And Technology **6**, 319-338 (1998)]

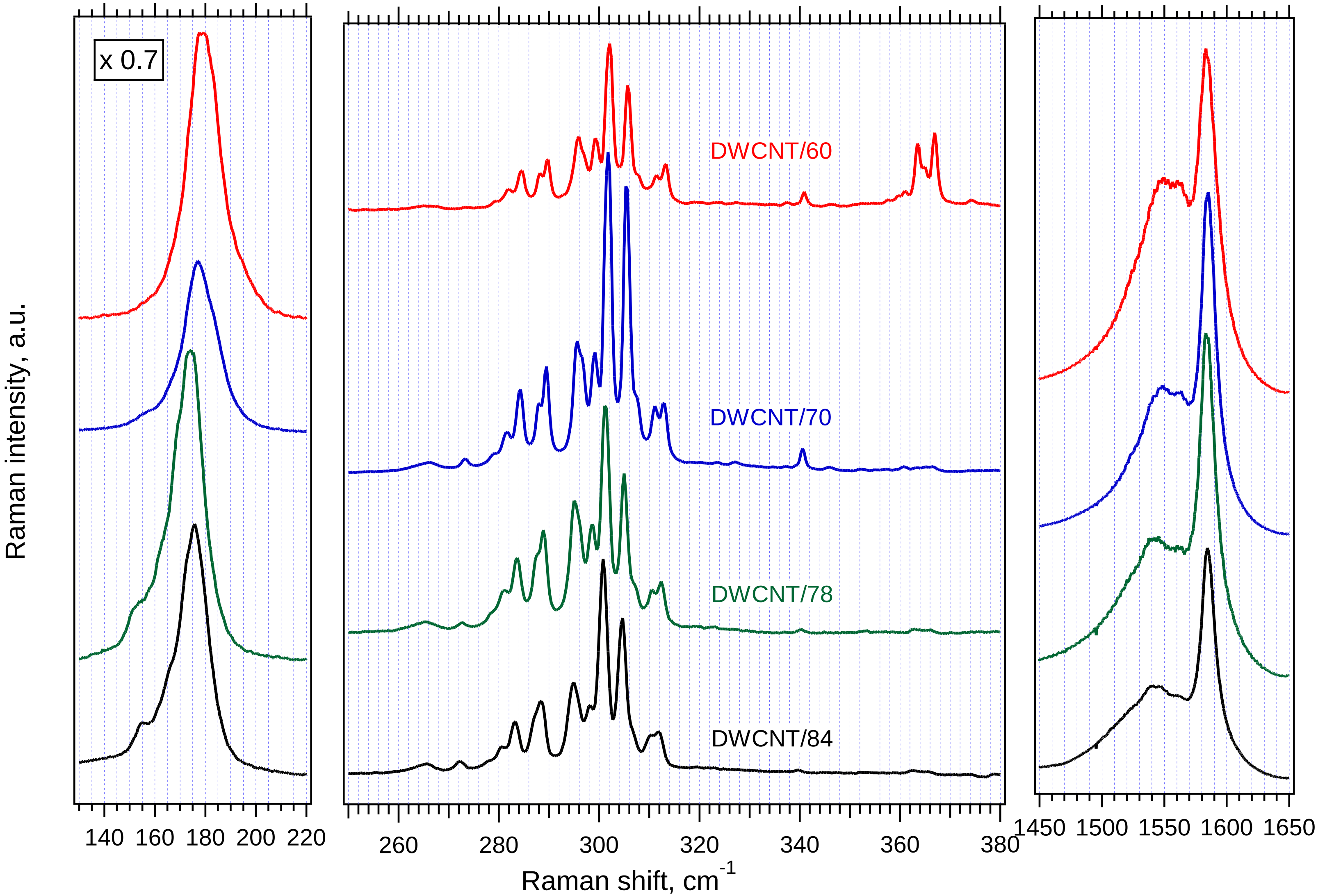




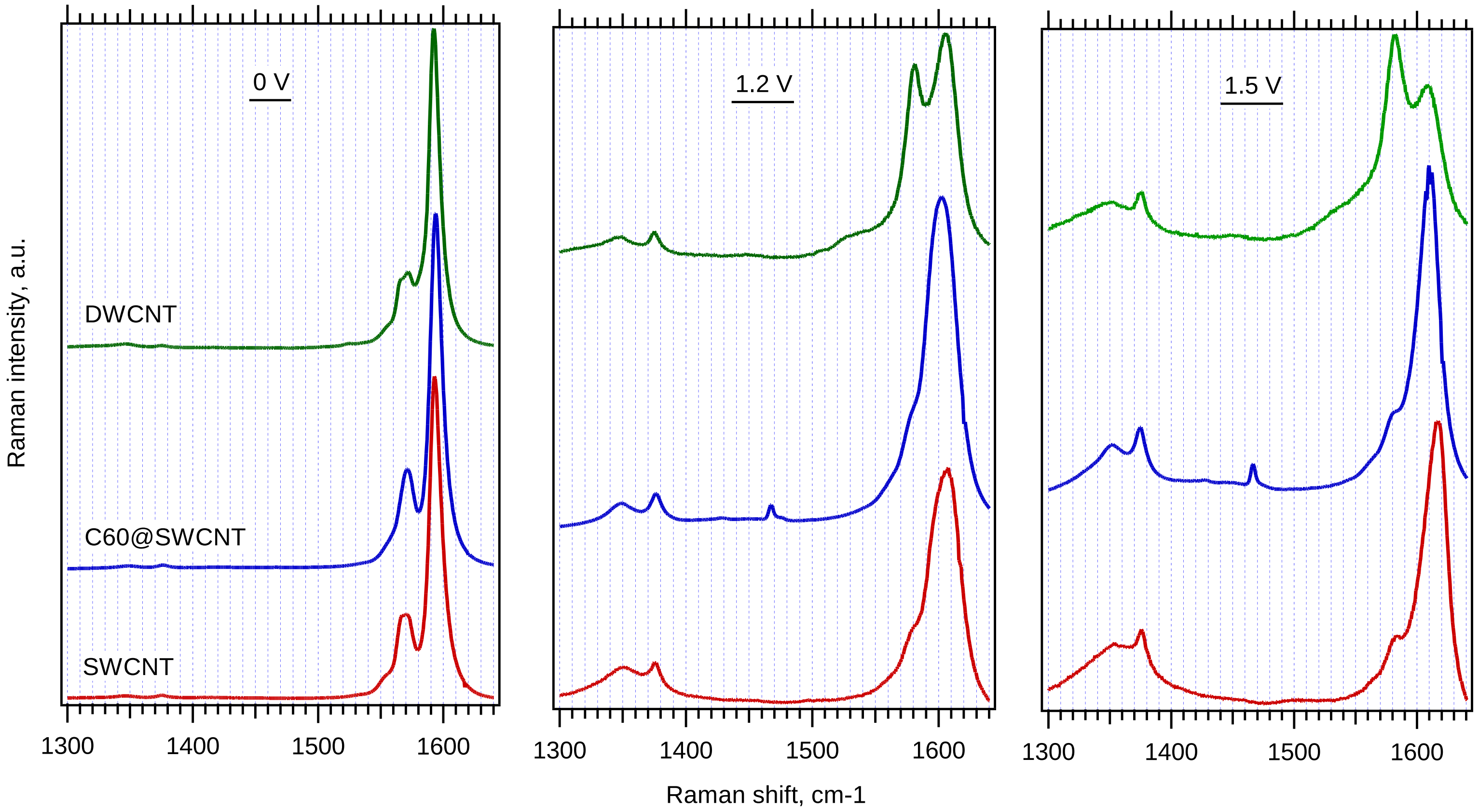
Raman spectra of DWCNT, hν_{exc}= 1.83 eV



Raman spectra of DWCNT (λ_{exc} = 676 nm) from peapods C_{60} – C_{84}

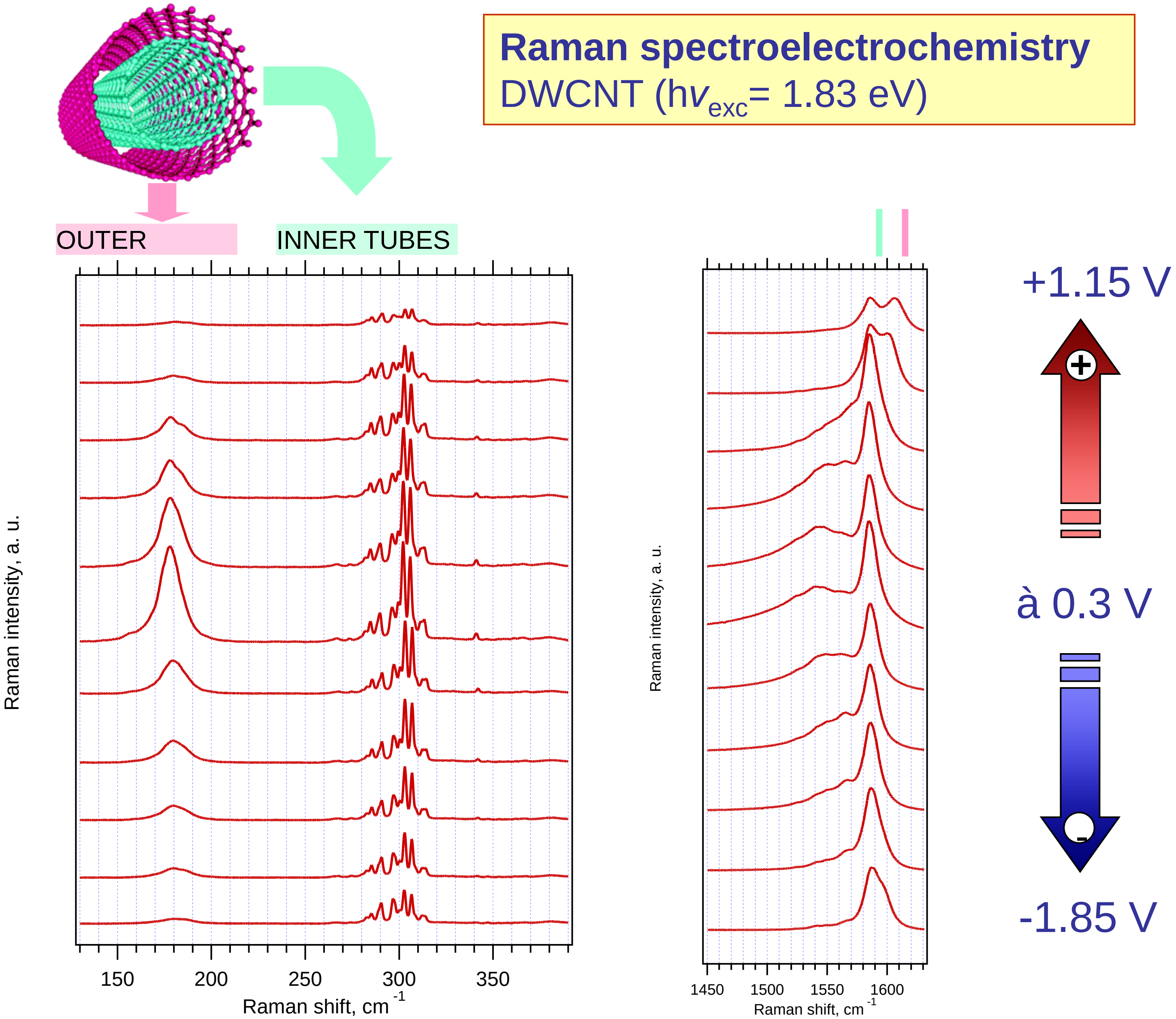


Raman spectroelectrochemistry (hν_{exc}= 2.41 eV)



DWCNT film on Pt electrode in 0.1 M $LiClO_4$ + AN

Raman spectroelectrochemistry
DWCNT ($h\nu_{exc}$= 1.83 eV)

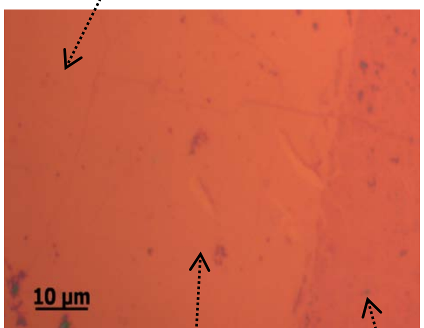


DWCNT film on Pt electrode in 0.1 M $LiClO_4$ + AN

^{13}C-labeled graphene and $^{13}C/^{12}C$ double layer graphene

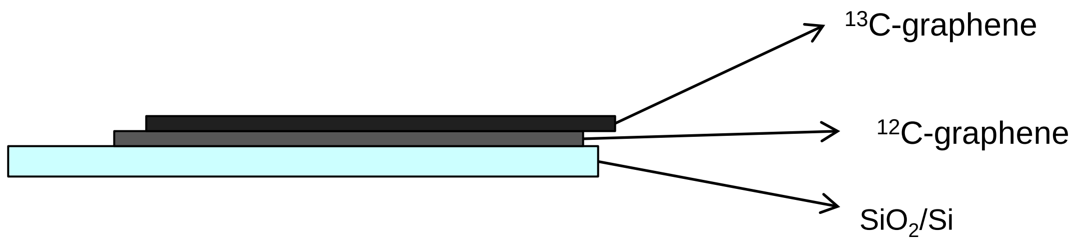
Synthesis by CVD: substrate Ni@SiO_2/Si
$CH_4 + H_2$; 1000°C, 5 min $^{13}CH_4$ (Aldrich)
PMMA transfer to clean SiO_2/Si

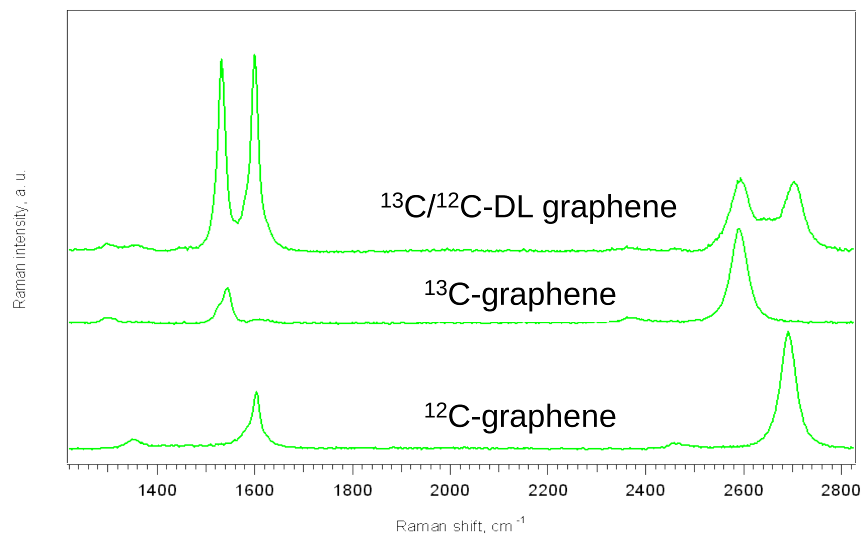
Free substrate



^{13}C@^{12}C-graphene

^{12}C-graphene





Raman spectra of the ^{12}C-graphene, ^{13}C graphene, and $^{13}C/^{12}C$ double-layer (^{13}C is on top, ^{12}C at bottom. Excitation: 2.33 eV laser (Nd-YAG).

continuum model:

$(\omega_0-\omega)/\omega_0 = 1- [(12 + c_0)/(12+c)]^{1/2}$

ω_0 .....frequency of ^{12}C mode(s)

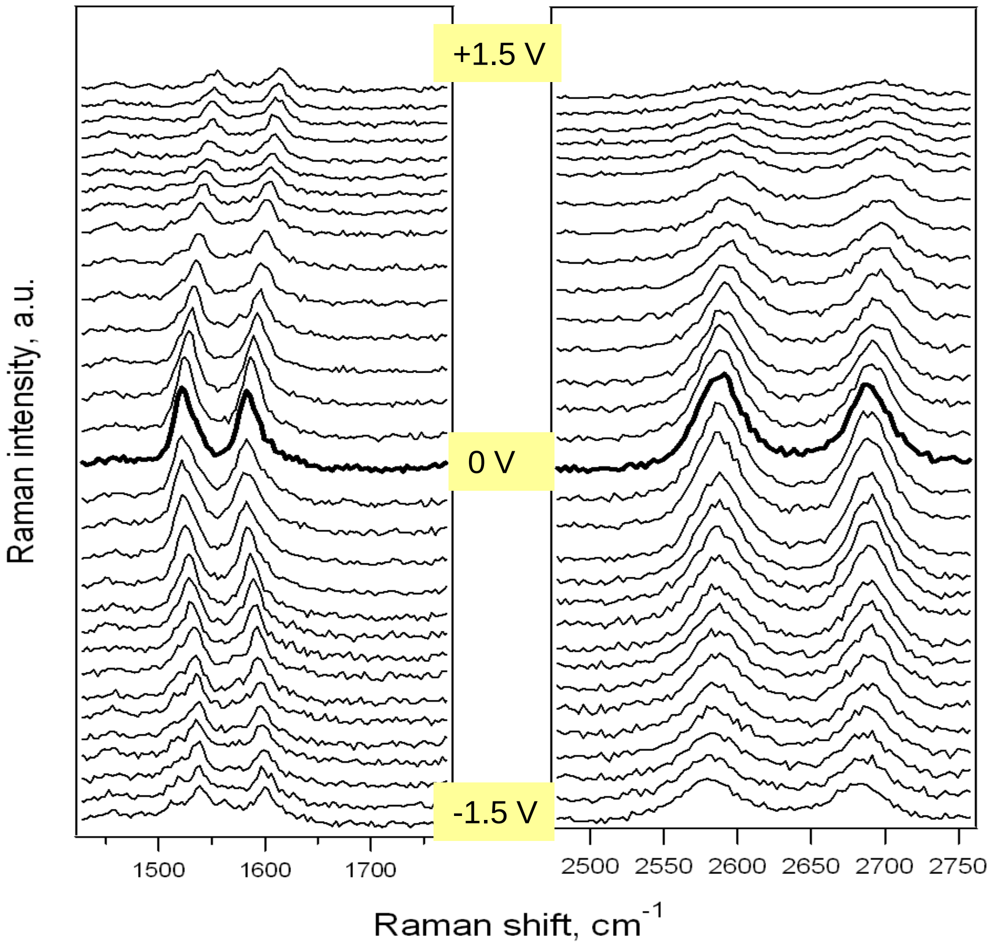
ω ......frequency of ^{13}C mode(s)

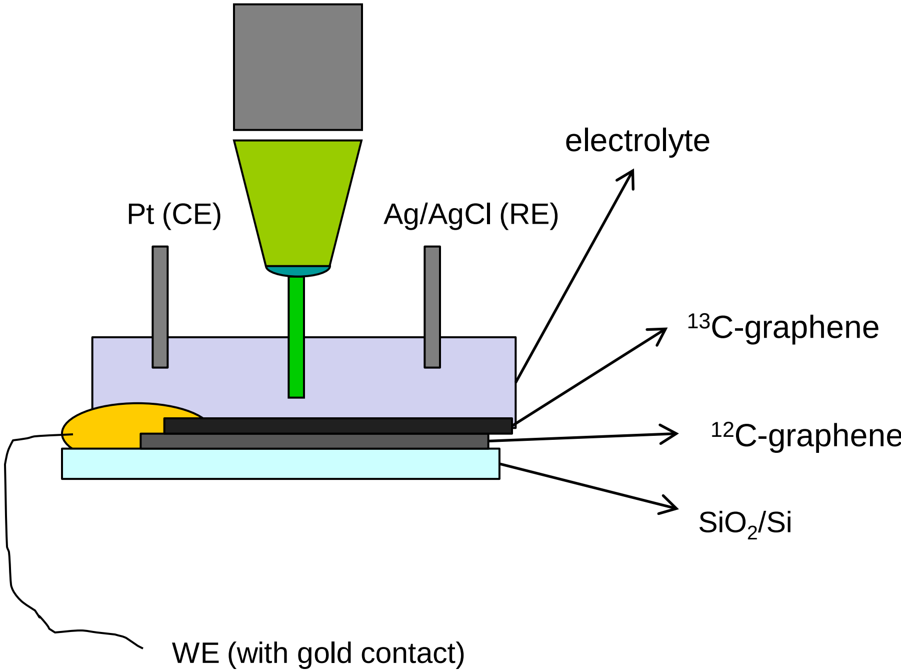
c_0= 0.0107 (natural abundance of ^{13}C)

c = 0.99 (concentration in ^{13}C enriched sample)

Kalbac, Frahat, Kong, Janda, Kavan, Dresselhaus,
Nano Lett. **9,** 2011, DOI: 10.1021/nl2001956

Spectroelectrochemistry of $^{13}C/^{12}C$ double layer graphene





Raman spectroelectrochemistry (2.33 eV laser excitation energy)
Electrolyte: 0.1 M $LiClO_4$ dissolved in dry propylenecarbonate/PMMA
Electrode potentials from -1.5 to 1.5 V vs. Ag/Ag^+ (from bottom to top).

Kalbac, Frahat, Kong, Janda, Kavan, Dresselhaus,
Nano Lett. **9,** 2011, DOI: 10.1021/nl2001956

Spectroelectrochemistry:

● L. Kavan, L. Dunsch, "Spectroelectrochemistry of carbon nanostructures" *ChemPhysChem* **8**, 974-998 (2007).

● L. Kavan, L. Dunsch, "Electrochemistry of Carbon Nanotubes" in (A. Jorio, G. Dresselhaus, M.S. Dresselhaus, Eds.) Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, Springer, Berlin, 2008, pp. 567-603.

● L. Kavan, L. Dunsch, "Spectroelectrochemistry of carbon nanotubes" *ChemPhysChem* **12,** 47-55 (2011).