Raman of single and double walled nanotubes - pressure on nanoscale

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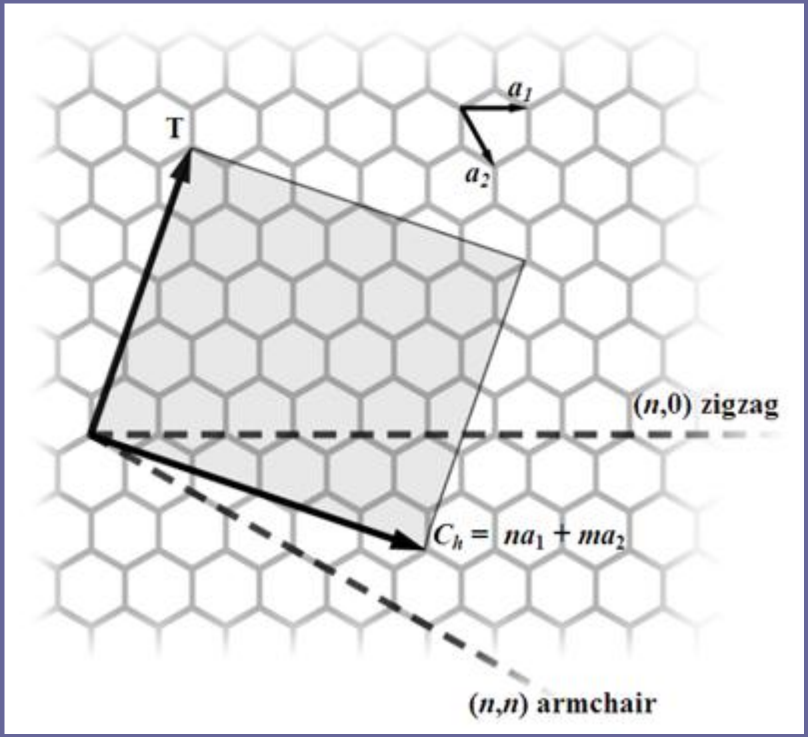
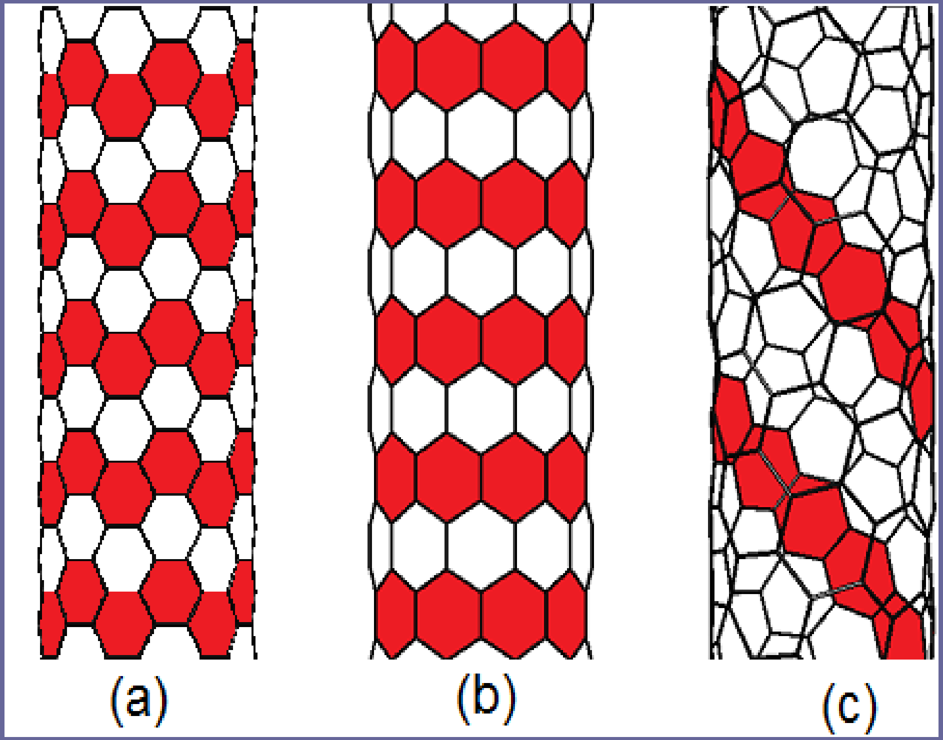
Carbon nanotubes - structure



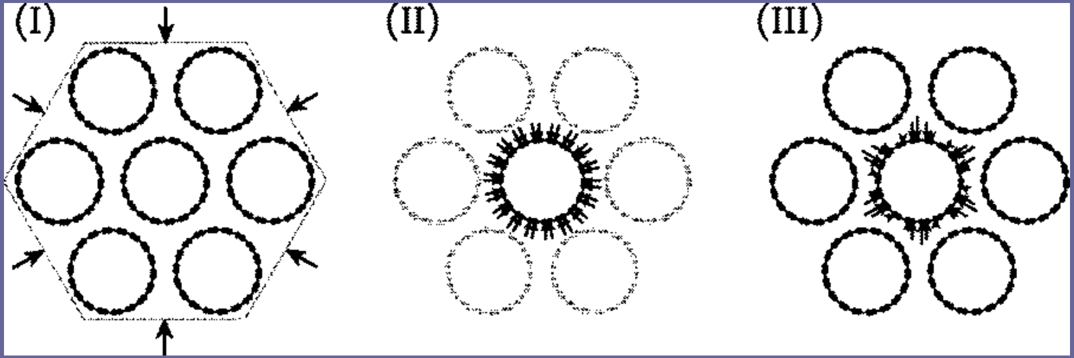


Armchair , when n=*m (n,n)* and $\theta = 30^0$ (a)
Zigzag, *m=0 (n,0)*, and $\theta = 0^0$ (b)
Chiral, *n≠m (n,m)* and $0^0 < \theta < 30^0$ (c)

The nanotube diameter d is related to m and n as $d = \frac{a}{\pi}\sqrt{(n^2 + nm + m^2)}.$

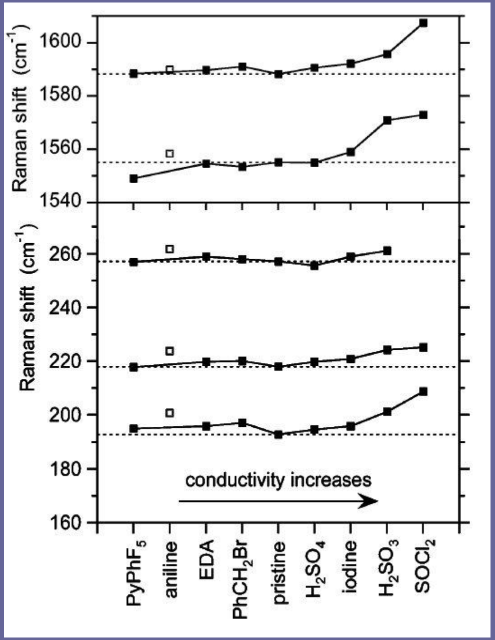
Motivation

Early experiments by U. D. Venkateswaran, et. al. PRB 1999: radial mode intensity disappears beyond 1.5 GPa, and the tangential mode intensity also drops considerably above this pressure



Sandler *et al.*PRB 2003:At first in the linear regime the tubes get smaller in diameter. At a critical higher pressure the tubes collapse and above this point the pressure coefficient are close to that of bulk graphite.

V. Skakalova *et al.J. Phys. Chem. B 2005*: Strong effects of chemical environment on CNT



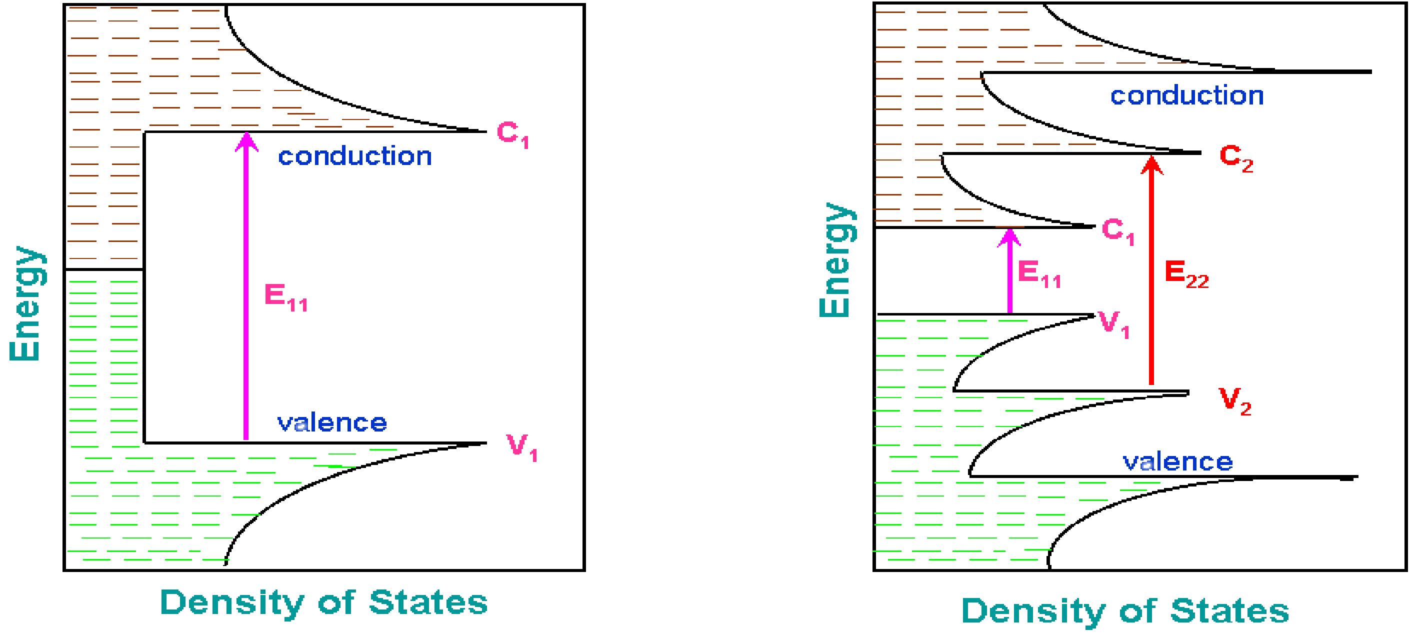
Motivation

Results of the HP studies of CNT from different laboratories show significant discrepancies in transition pressures:1.7 to 3.5 Gpa for SWCNT and 5-10 GPa for DWCNT

There have been no systematic studies of the effects of PTM on CNT behaviour

A range of unusual (plateaus, etc.) effects in HP behaviour of CNT is observed and these effects have not been adequately explained.

Carbon nanotubes – electronic and optical properties



Metallic SWNT

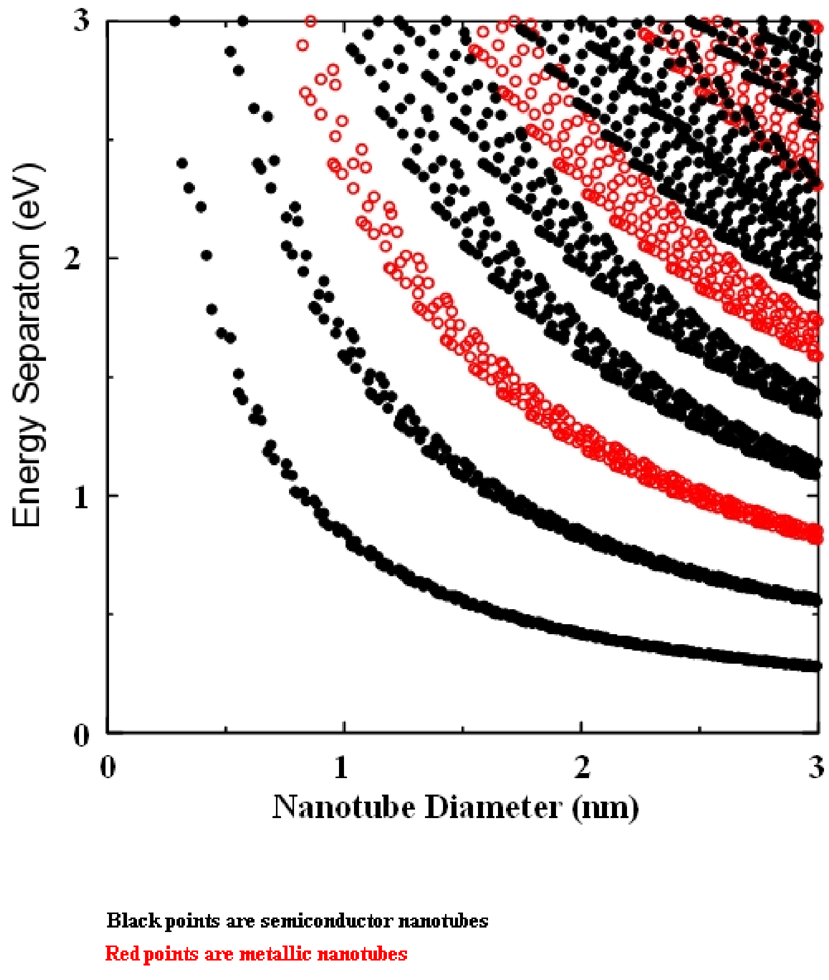
$v_1 \rightarrow c_1$ corresponds to the “first van Hove” optical transition

Semiconducting SWNT

$v_2 \rightarrow c_2$ corresponds to the “second van Hove” optical transition

Optical transitions are rather sharp (~10 meV) and strong. Consequently, it is relatively easy to selective excite nanotubes having certain (n, m) indexes, as well as to detect optical signals from individual nanotubes.

Kataura plot (Hiromichi Kataura, 1999)

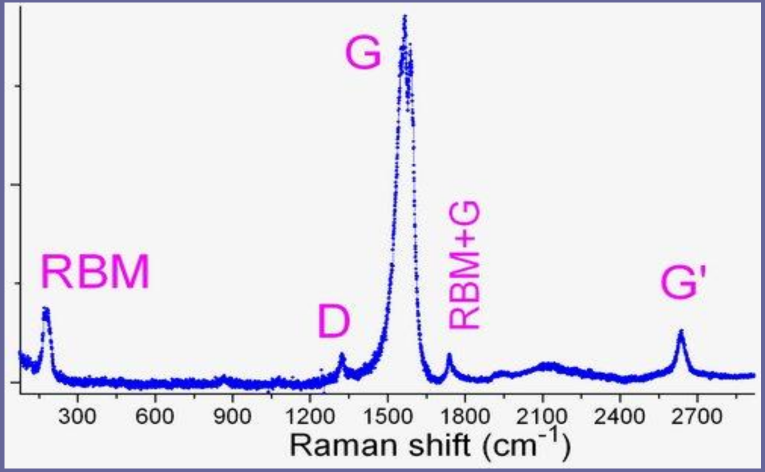


Black points are semiconductor nanotubes

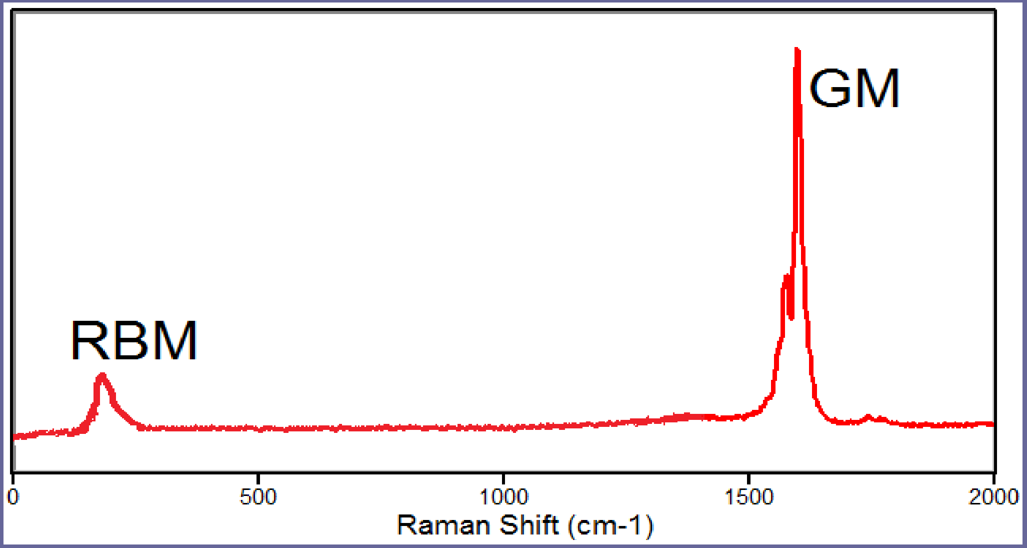
Red points are metallic nanotubes

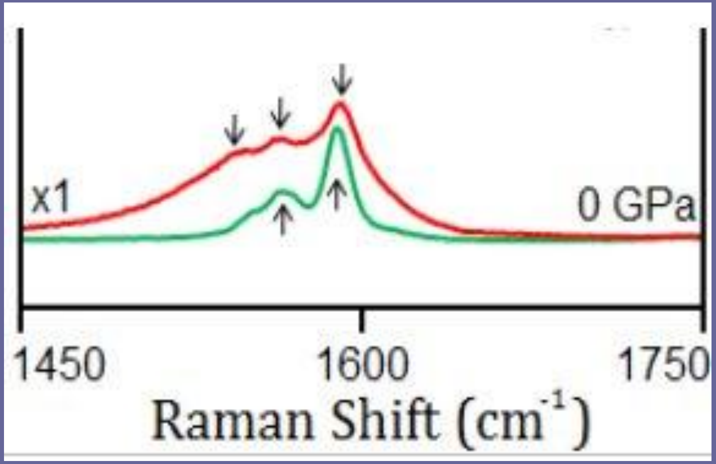
The oscillating shape of every branch of the Kataura plot reflects the intrinsic strong dependence of the SWCNT properties on the (n, m) index rather than on its diameter. For example, (10, 0) and (8, 3) tubes have almost the same diameter, but very different properties: the former is a metal, but the latter is semiconductor.

Raman



RBM - Radial breathing mode (v_{RBM} = 223/d + 10)
DM - D or disorder mode
GM – G or graphitic mode

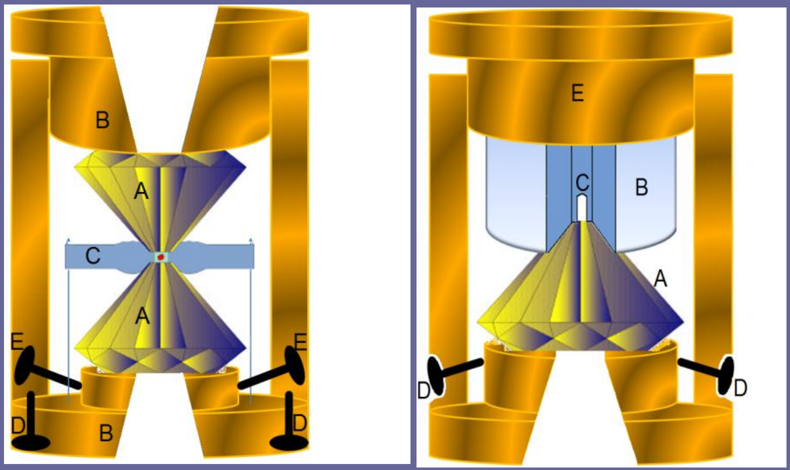


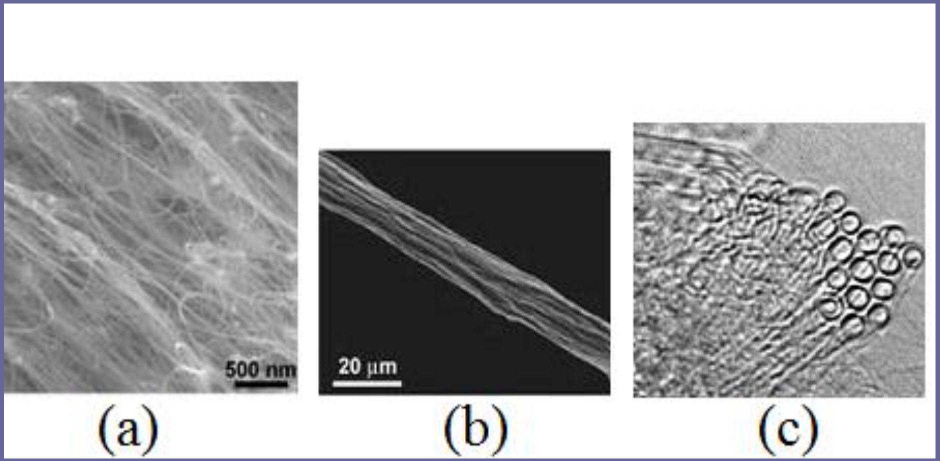


Experiment

Experimental Programme:

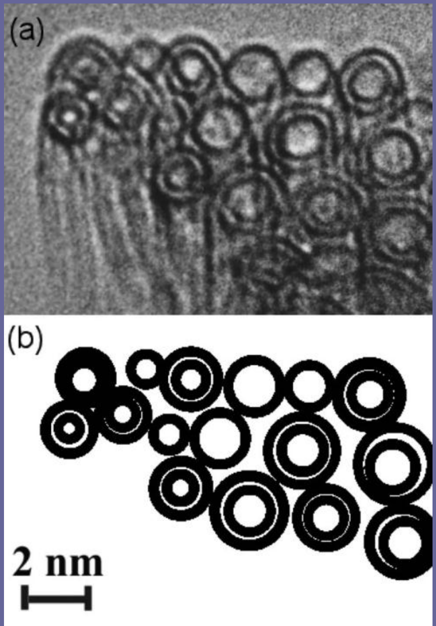
- CNTs in various PMT
- CNT under different excitation energies

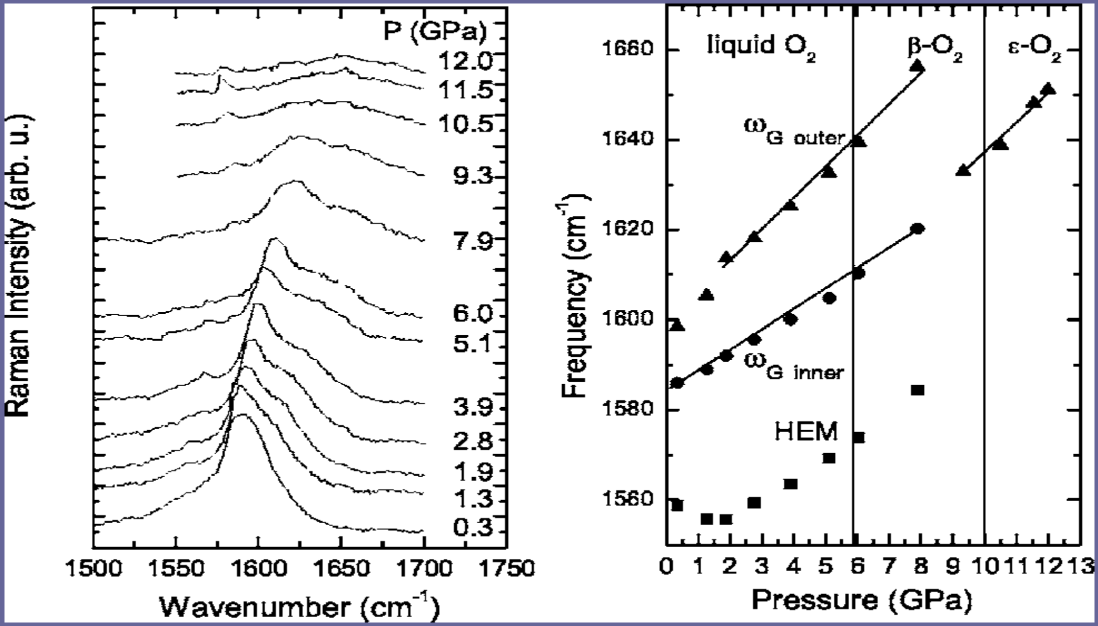


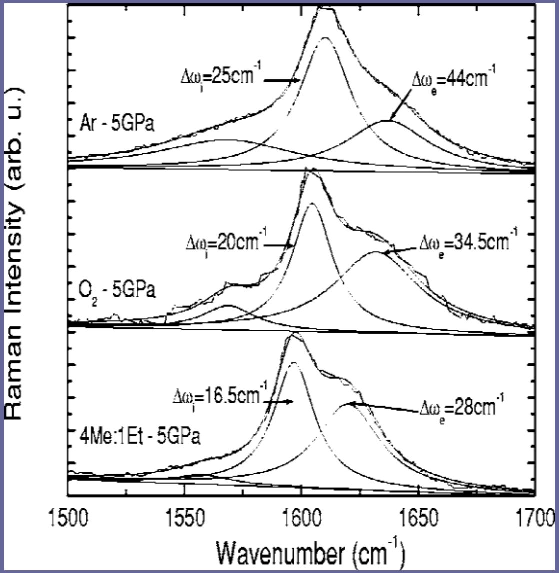


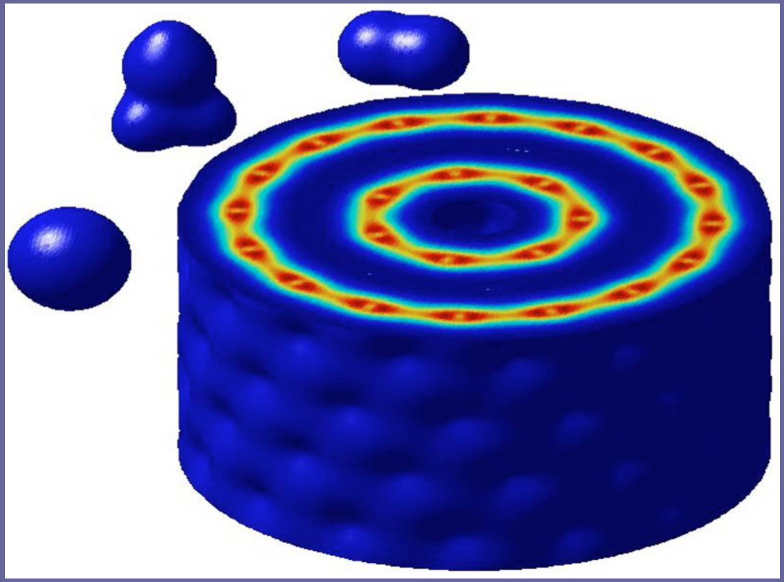
Standard and Zen DACs

Different media









Different media

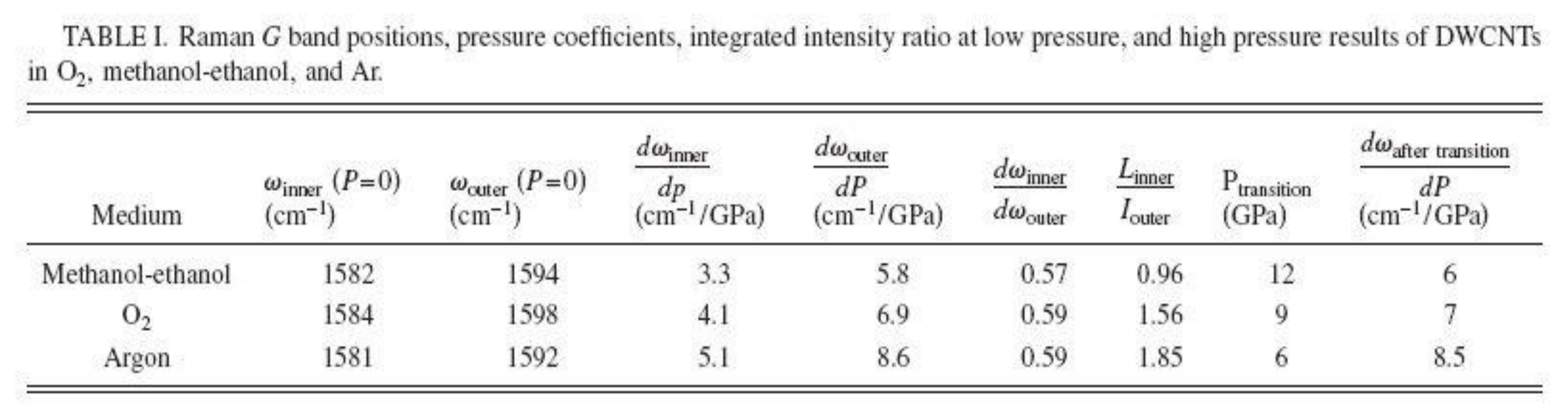
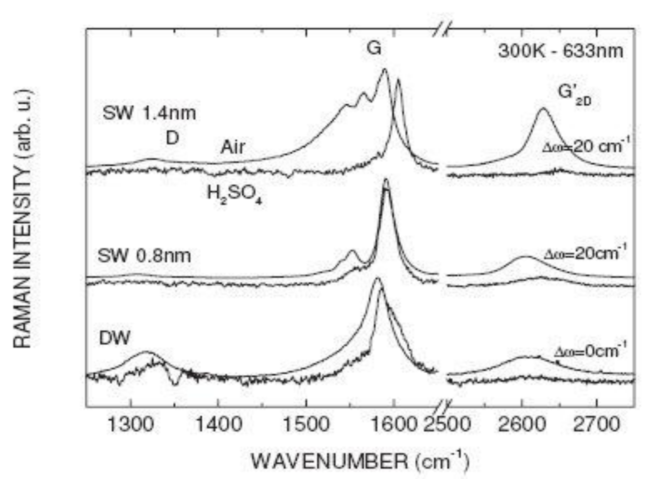


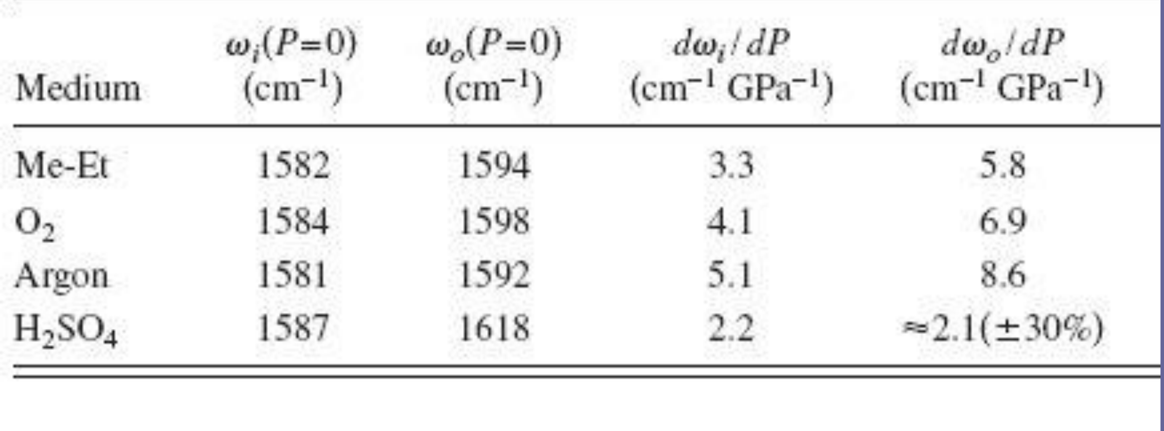
TABLE I. Raman *G* band positions, pressure coefficients, integrated intensity ratio at low pressure, and high pressure results of DWCNTs in O_2, methanol-ethanol, and Ar.

Medium	ω_{inner} $(P=0)$ (cm^{-1})	ω_{outer} $(P=0)$ (cm^{-1})	$\frac{d\omega_{\text{inner}}}{dp}$ $(\text{cm}^{-1}/\text{GPa})$	$\frac{d\omega_{\text{outer}}}{dP}$ $(\text{cm}^{-1}/\text{GPa})$	$\frac{d\omega_{\text{inner}}}{d\omega_{\text{outer}}}$	$\frac{L_{\text{inner}}}{I_{\text{outer}}}$	$P_{\text{transition}}$ (GPa)	$\frac{d\omega_{\text{after transition}}}{dP}$ $(\text{cm}^{-1}/\text{GPa})$
Methanol-ethanol	1582	1594	3.3	5.8	0.57	0.96	12	6
O_2	1584	1598	4.1	6.9	0.59	1.56	9	7
Argon	1581	1592	5.1	8.6	0.59	1.85	6	8.5

This results show that surface interaction effects at the nanometric scale can lead to a change of up to 50% in the stress transmission using DWCNTs. We observe differences in the pressure behavior of DWCNTs as a function of pressure transmitting medium.

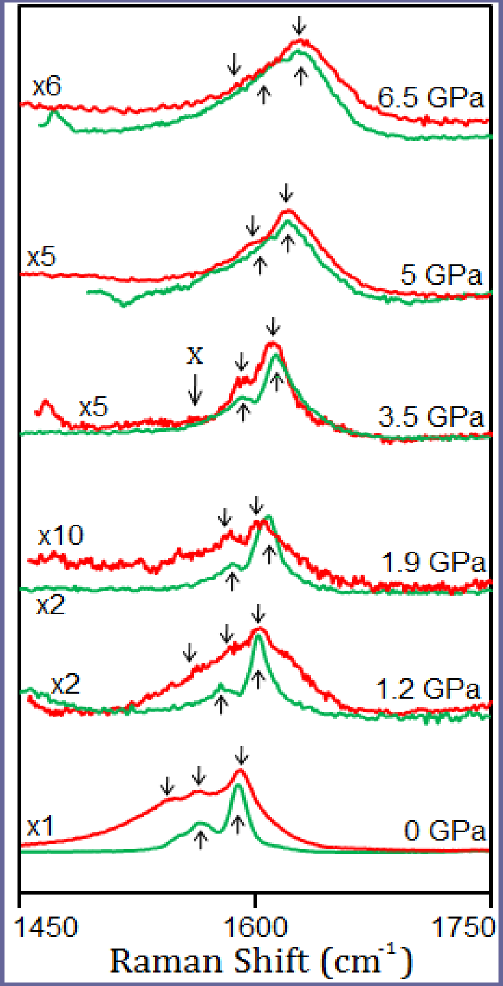
Different media

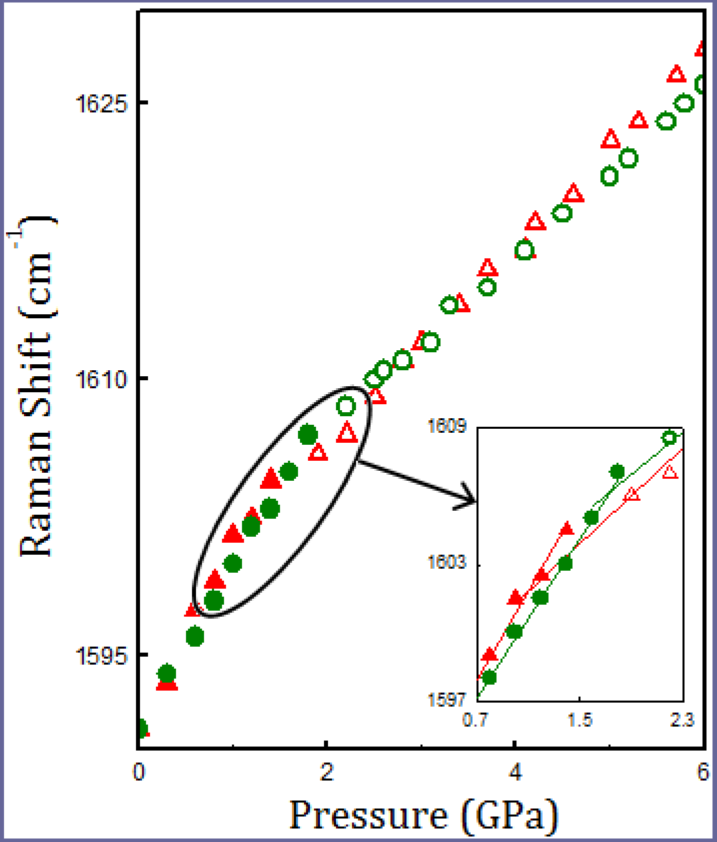


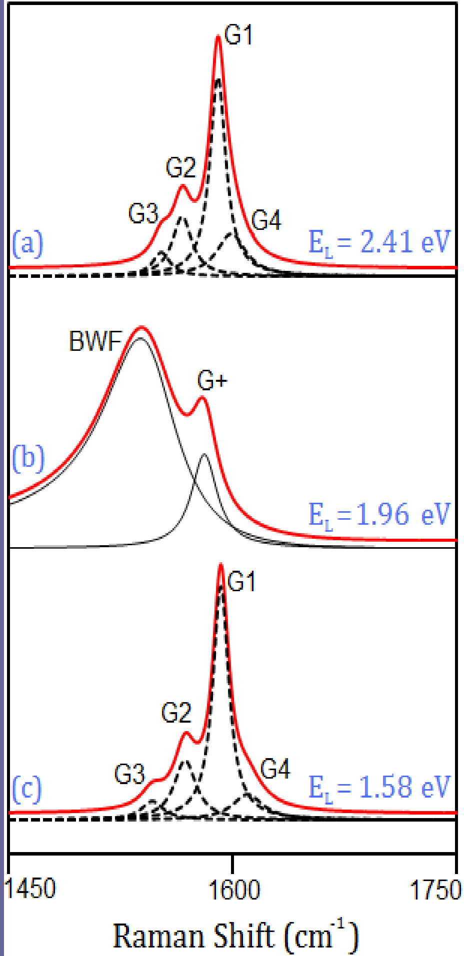


Medium	$\omega_i(P=0)$ (cm^{-1})	$\omega_o(P=0)$ (cm^{-1})	$d\omega_i/dP$ (cm^{-1} GPa^{-1})	$d\omega_o/dP$ (cm^{-1} GPa^{-1})
Me-Et	1582	1594	3.3	5.8
O_2	1584	1598	4.1	6.9
Argon	1581	1592	5.1	8.6
H_2SO_4	1587	1618	2.2	≈2.1(±30%)

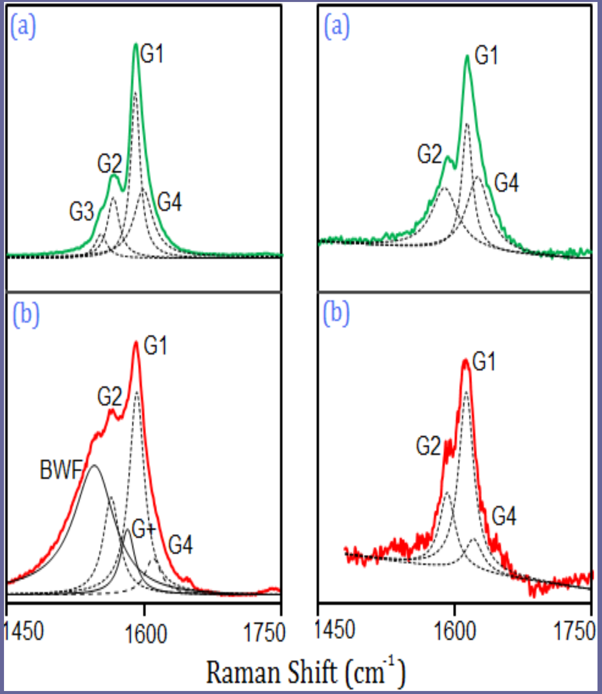
Different excitation wavelength



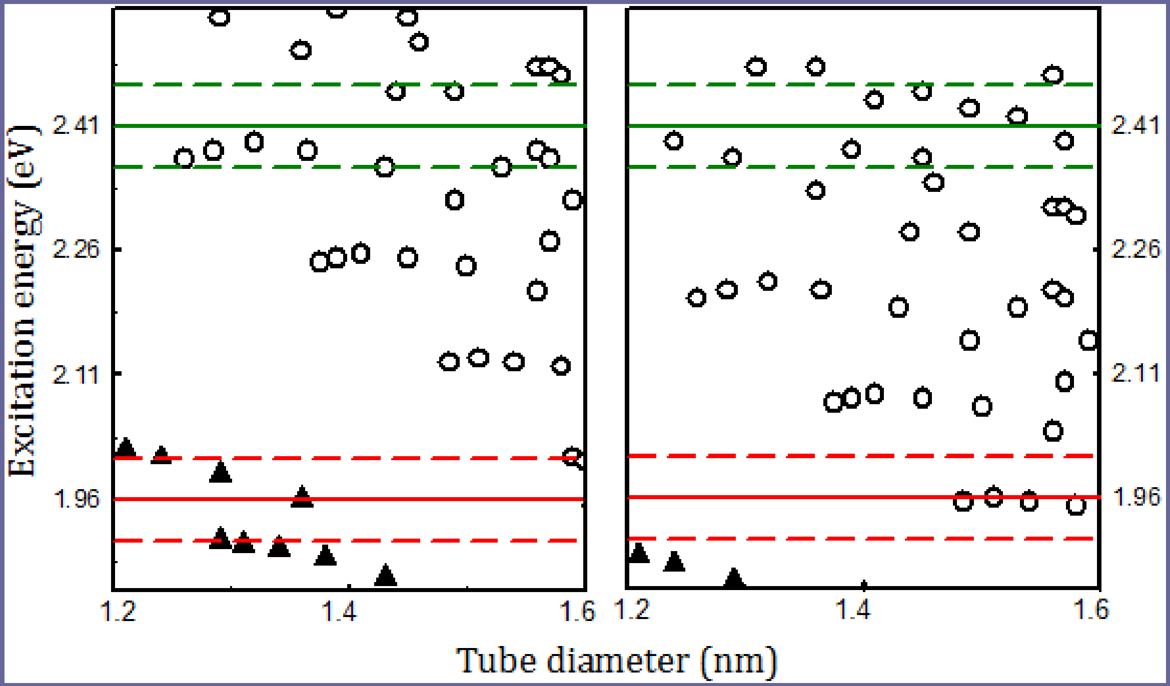




Different excitation wavelength

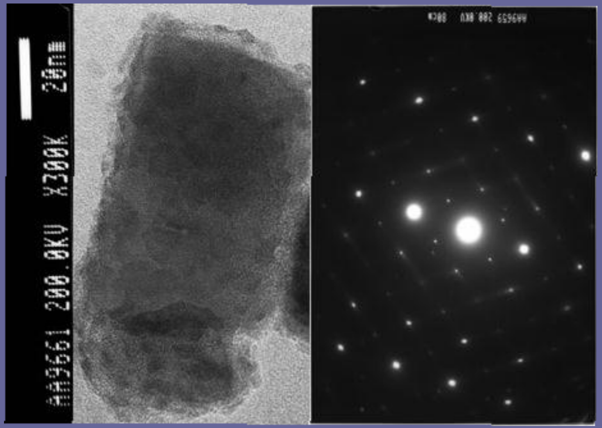


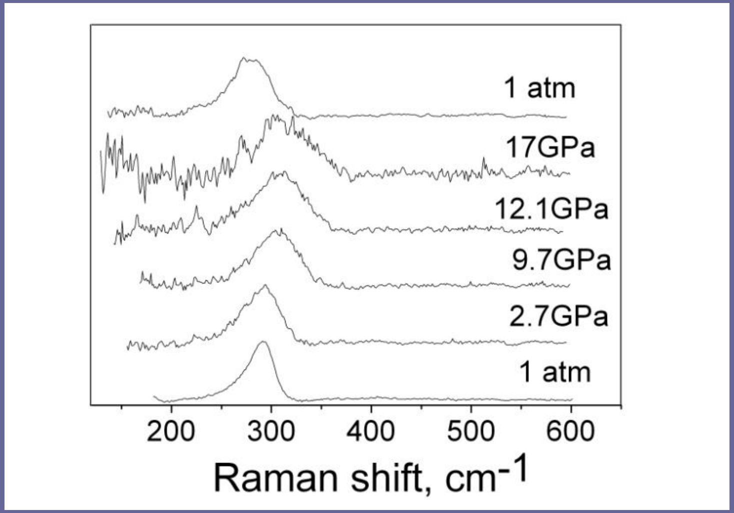
Ambient and HP (3.5 GPa) signals from SWCNT

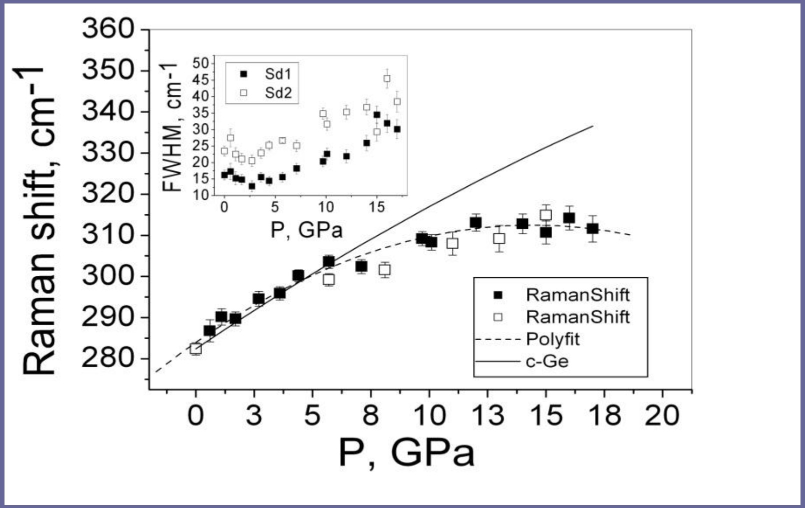


Kataura plot corresponding to SWCNT in our experiments

Beyond CNTs: nano Ge







Nanocrystalline Ge under pressure

Conclusions

PMT can have strong electronic effects on CNTs
PMT ordering effects play significant role in pressure transmission on nanoscale
Increase in GM frequency is correlated with decrease in transition pressure
(relevance of ruby line as a reference?)

$$\omega_T = \left(\frac{d\omega}{dP} \times P_T \right) + \omega_0$$

Transition pressure shows dependence on laser excitation wavelength and differences in P_{tr} and plateaus are explained as metallic and semiconducting tubes moving in and out of resonance with the excitation energy.

PMT effects and laser excitation effects may be important in HP Raman response of other nanoparticles

CNTs are one big mess!

Future work

- Tunable Raman under high pressure
- Combination of Raman and x-ray techniques (e.g. XRD, XAS)
- Extending the class of nanosized objects to peapods and other nanoparticles
- Looking closely into relevance of existing pressure references to nanoscale objects