Gas adsorption characterization of SWNT and other nanomaterials: beyond BET

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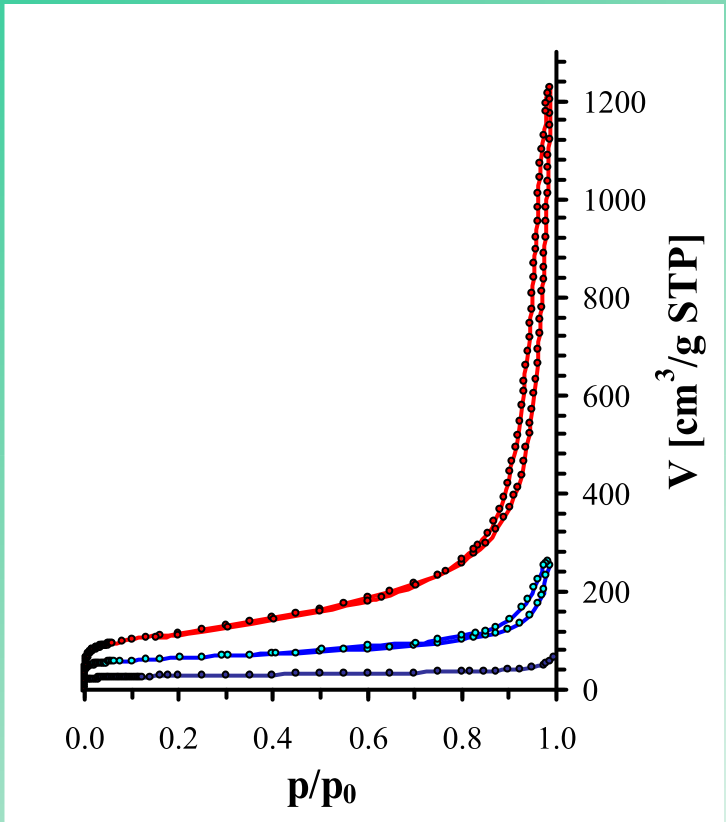
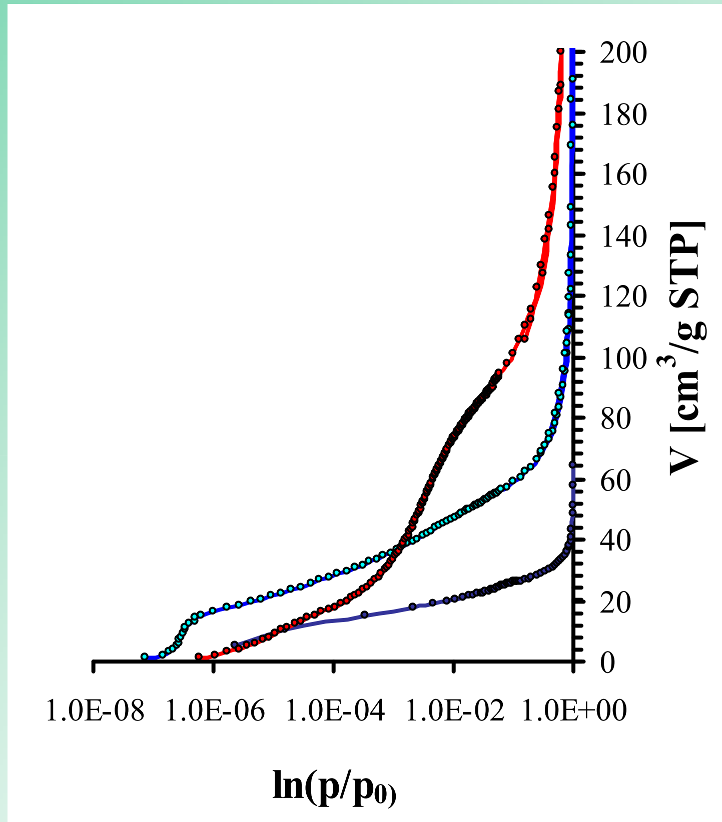
ISO 9277

Determination of the specific surface area of solids by gas adsorption using the BET method.

- implemented in 1995
- applicable to:
  - disperse, nonporous or macroporous solids
  - mesoporous solids (pore size 2–50 nm)

SWNT isotherms – Ar at 77K





HiPCO

NRC (laser-grown, open and closed)

BET

» **Brunauer, Emmett, Teller (1938)**

» **assumptions:**

- » multiple noninteracting layers
- » second and higher layers do not interact with adsorber
- » Langmuir theory applies

$$V = f\left(\frac{p}{p_0}\right) \Rightarrow \frac{1}{V\left[\frac{p_0}{p} - 1\right]} = \alpha\frac{p_0}{p} + \beta$$

gas adsorption on SWNT

- **reference sample – close-ended SWNT**
  - as-grown material
  - outgassing for 48 hrs at 295 K to <10^{-6} torr
- **processed sample – open-ended SWNT**
  - outgassing for 12 hrs at 295 K and for 30 minutes at 435 K
  - heating in dry air at 470 K for 2 hrs
  - outgassing at 385 K for 12 hrs
  - *between series of isotherm measurements:* ougassing for 4 hrs at 475 K
- **isotherms acquisition**
  - ASAP 2010 porosimeter (Micromeritics)
  - 1 and 0.1 torr capacitance manometers (Baratron)
  - liquid Ar and liquid N_2 temperature stabilization
  - 0.08 – 0.5 cm^3/g STP dosing (high resolution, $p < 3$ mtorr)
  - several full and partial Ar and Kr isotherms for each sample

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SWNT bundles - adsorption sites

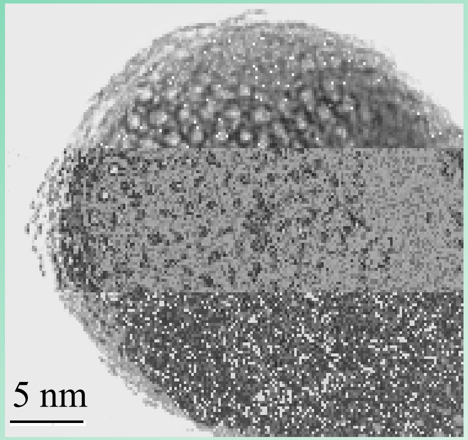
SIMS nanotubes

» typical bundles (~90 NT)

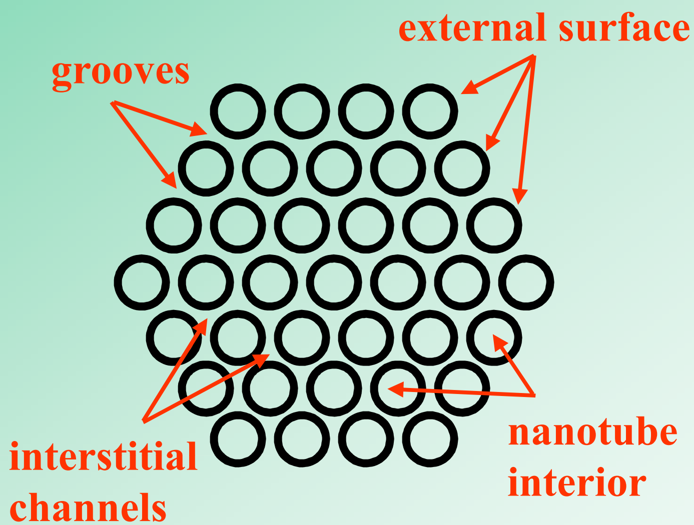
» SWNT diameter ~1.34(10) nm

» no open NT

» high purity >75% SWNT



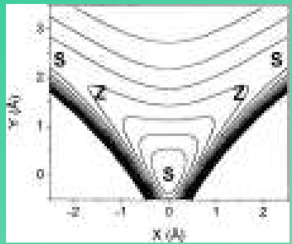
TEM image: very large bundle (169 nanotubes and 42 grooves)

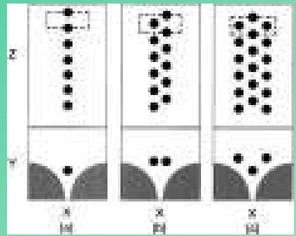


- **external surface and grooves**
  - » freely accessible
- **interstitial channel**
  - » possibly He, H_2
- **interior of nanotubes**
  - » molecule size limited
- **voids, cavities, imperfections**
  - » freely accessible mesopores

adsorption simulation – external sites

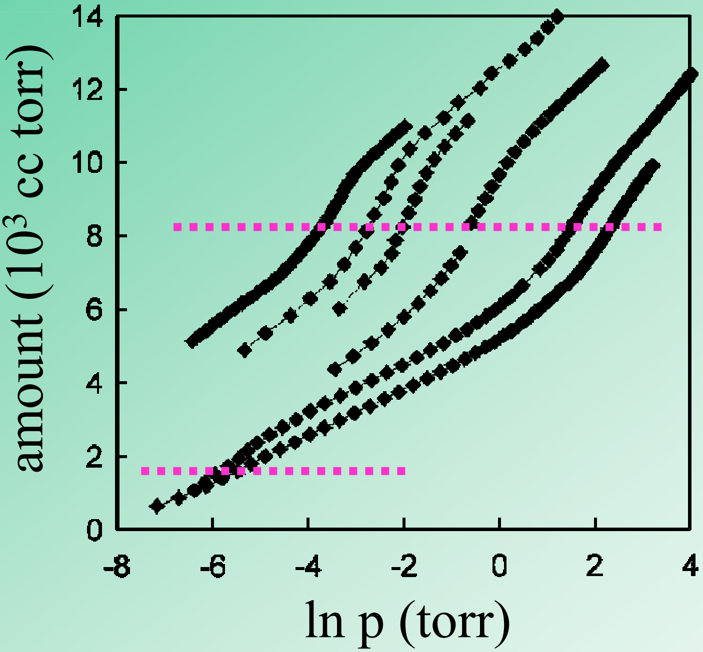
external potential and phases





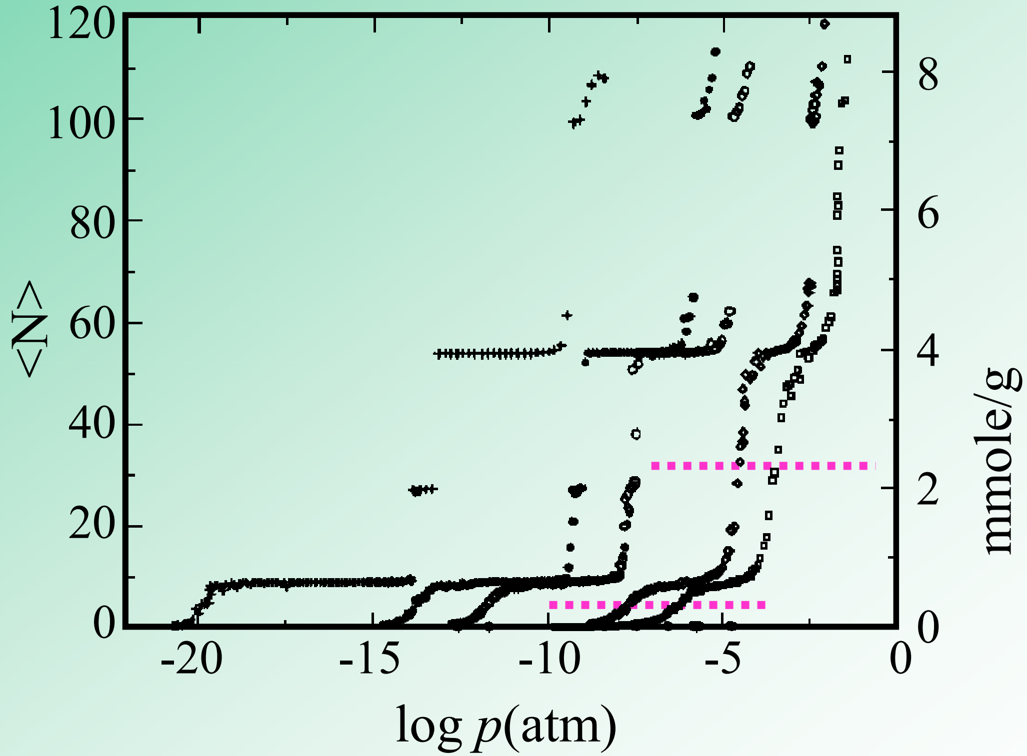
experimental isotherms

60, 63, 67, 72, 82, 87 K (→)



simulated isotherms

30, 40, 45, 60, 68 K (→)



*Gatica et al. JCP **114**, 3765 (2001)*

*Calbi et al. JCP **115**, 975 (2001)*

*Talapatra & Migone PRL **87**, 206106 (2001)*

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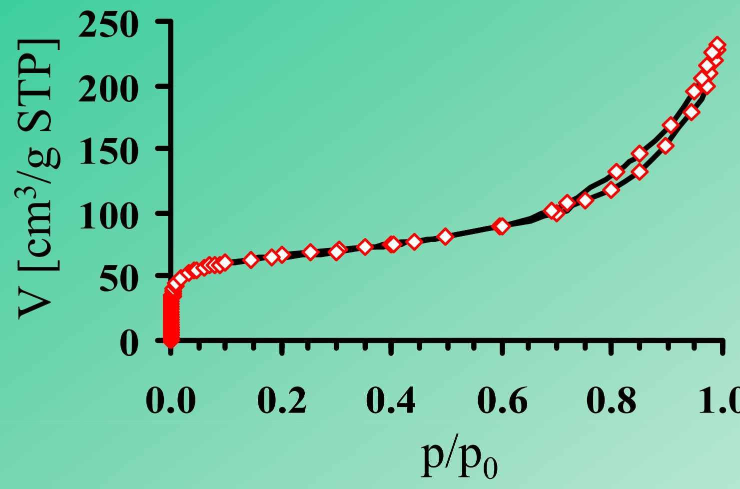
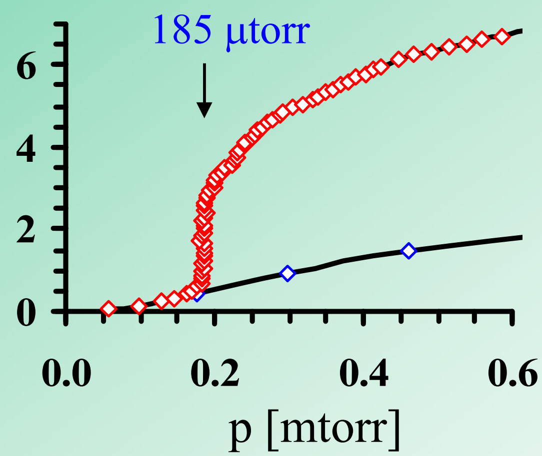
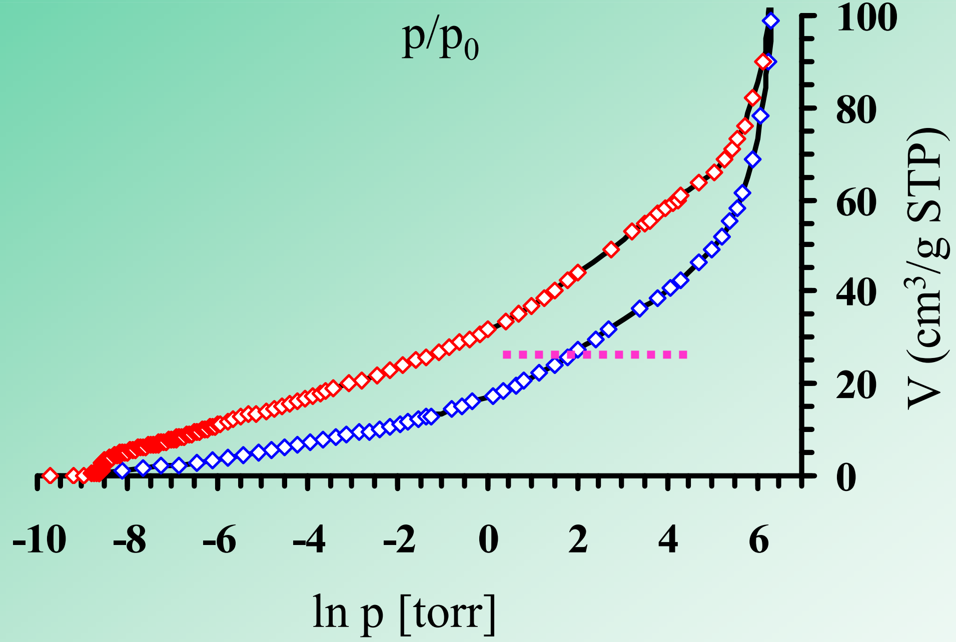
Ar adsorption on SWNT at 87 K

full isotherm – processed sample

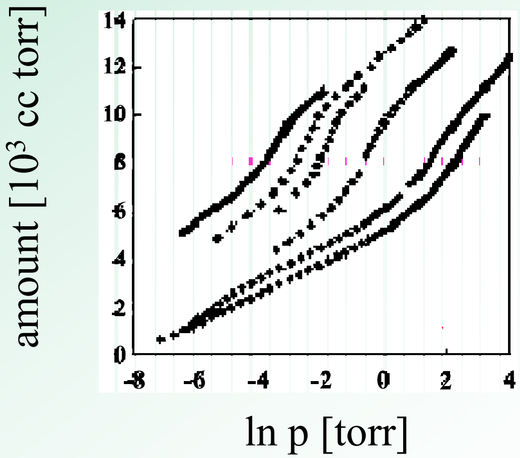






experimental isotherms

60, 63, 67, 72, 82, **87** K (→)



*Talapatra & Migone PRL **87**, 206106 (2001)*

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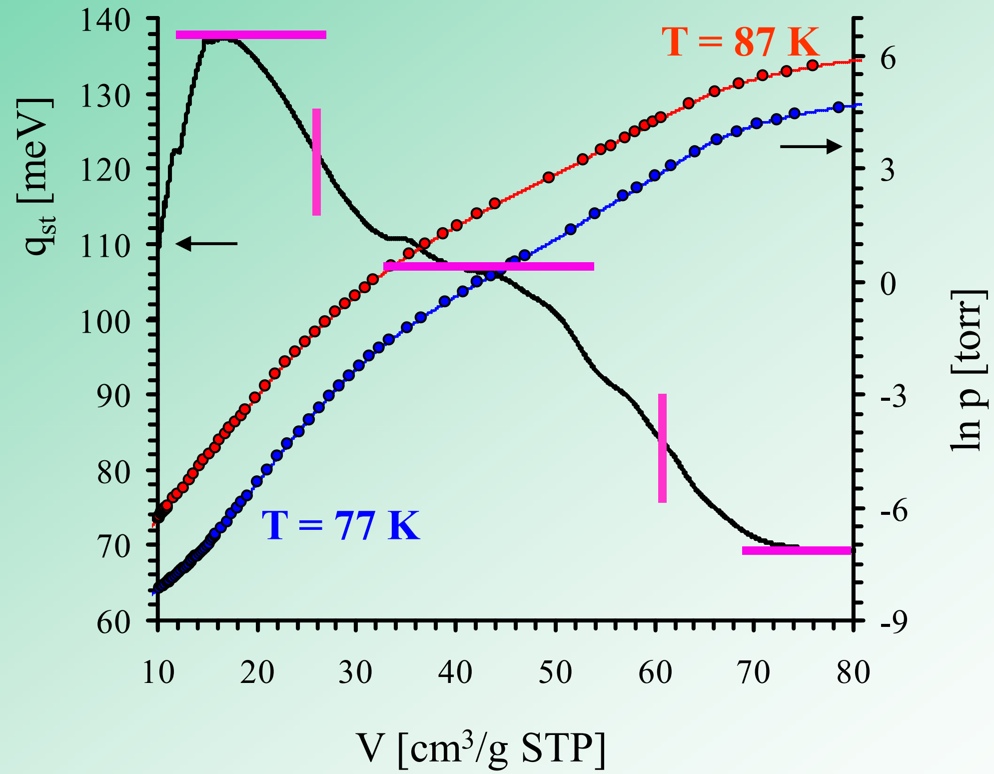
isosteric heat of adsorption

$$q_{st} = kT^2\left[\frac{\partial \ln(p)}{\partial T}\right]_V$$

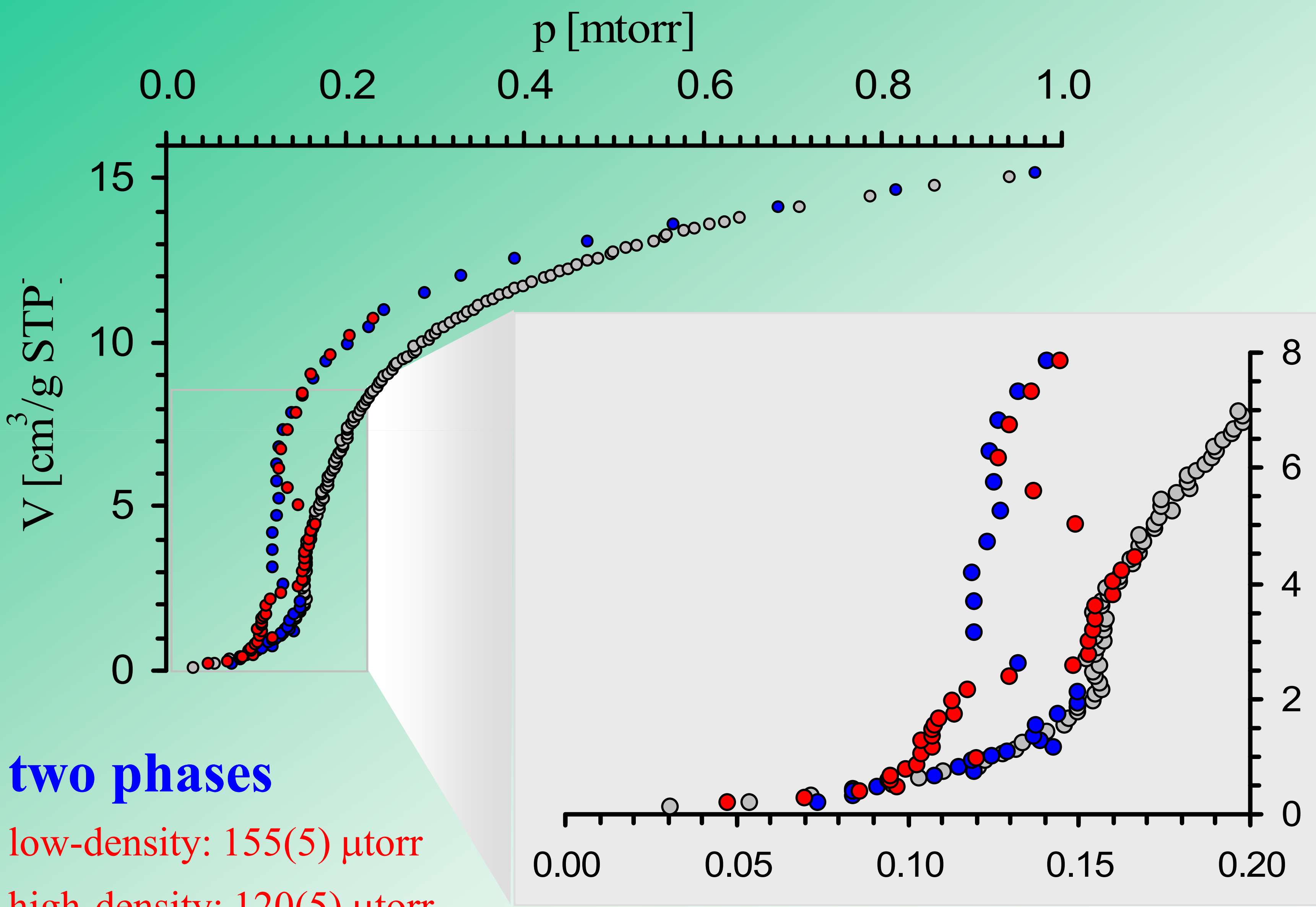
$$q_{st} = k\frac{(T_1+T_2)^2}{4}\frac{\ln(p_2)-\ln(p_1)}{T_2-T_1}$$

site	q_{st} /meV (a)	(b)	(c)	(d)
groove	137	137	160	195
1st layer	106	90		
2nd layer	70			



(a) this work – high coverage (77-87 K)
(b) Talapatra and Migone Phys. Rev. Lett. ***87****, 206106 (2001) – high coverage (60-87 K)*
(c) Wilson et al. J. Low Temp. Phys. ***126****, 403 (2002) – low coverage (~90 K)*
(d) Talapatra et al. J. Nanoscience Nanotech. ***2****, 467 (2002) – low coverage (110-160 K)*

Ar adsorption inside SWNT at 77 K



two phases

low-density: 155(5) µtorr

high-density: 120(5) µtorr

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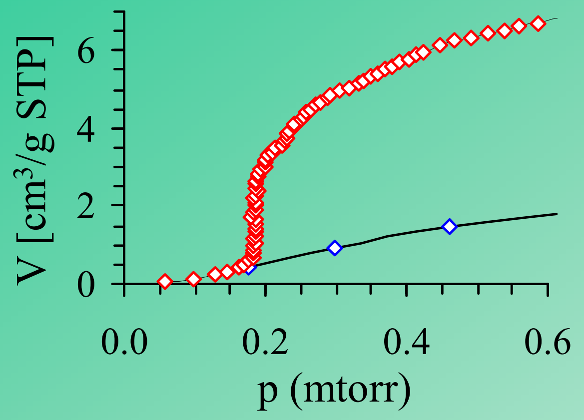
adsorption simulation – internal sites



step predicted at 77 K (p/p_0)

7×10^{-8} (1.02 nm SWNT)

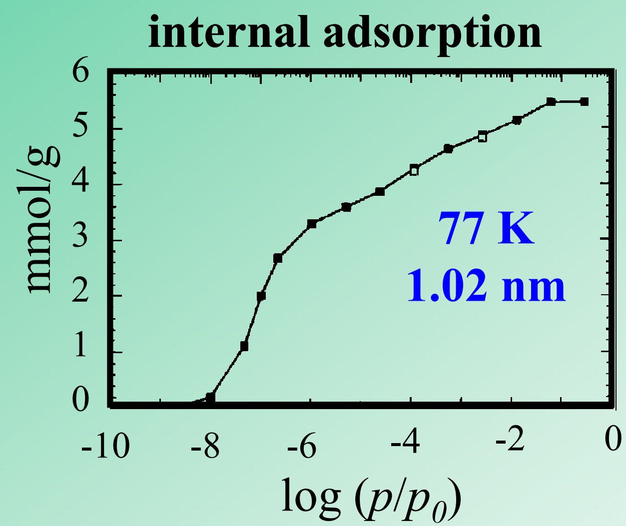
1.5×10^{-5} (4.78 nm DWNT)

step observed (p/p_0)

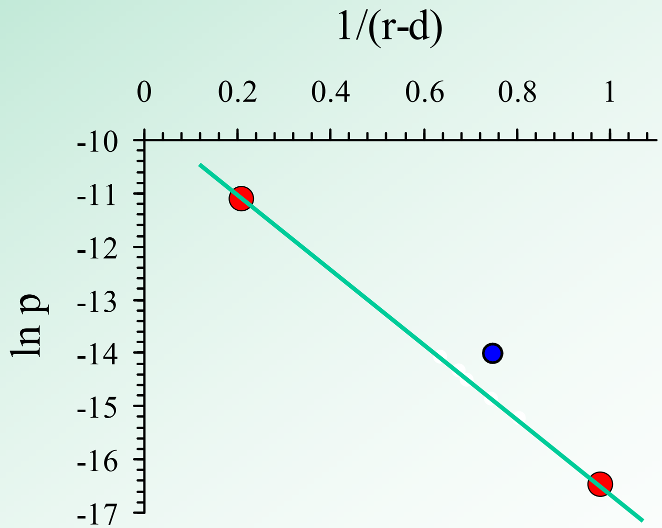
(1.34 nm SWNT)

6.8×10^{-7} (at 77 K)

2.5×10^{-7} (at 87 K)



Maddox and Gubbins Langmuir ***11****, 3988 (1995)*



ln p ~ 1/(r-d)

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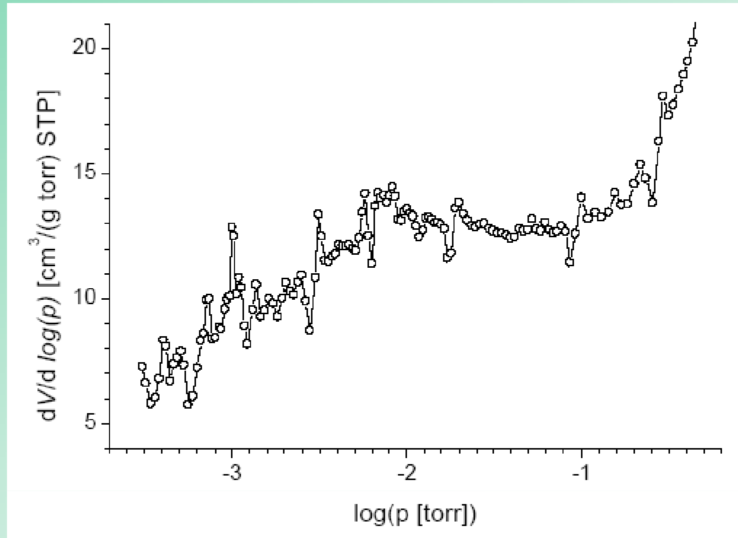
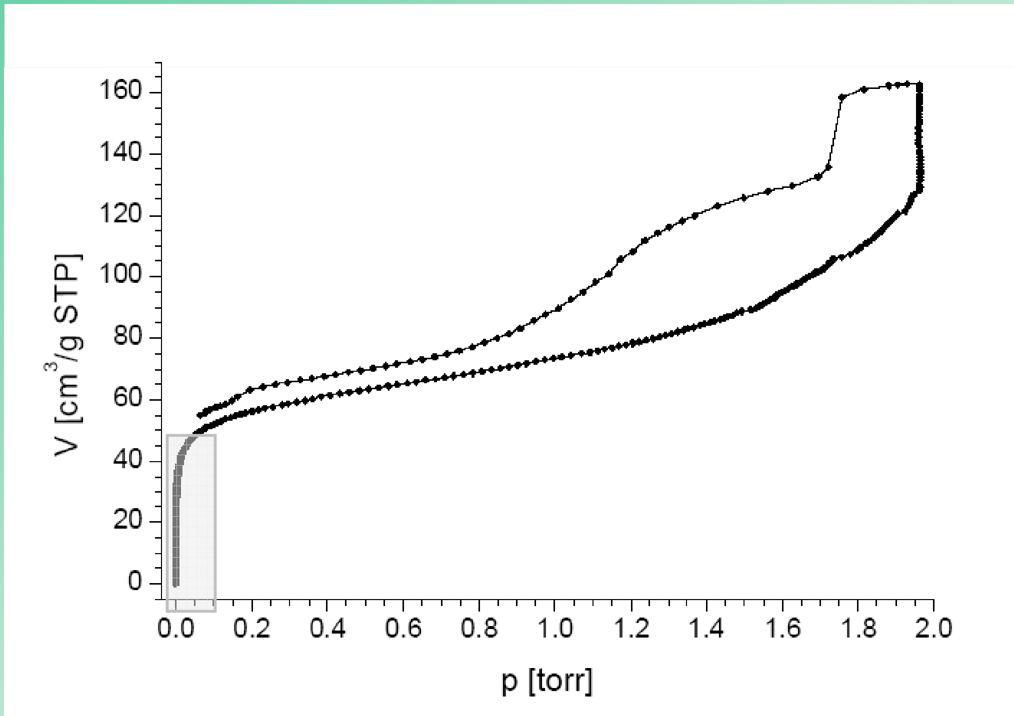
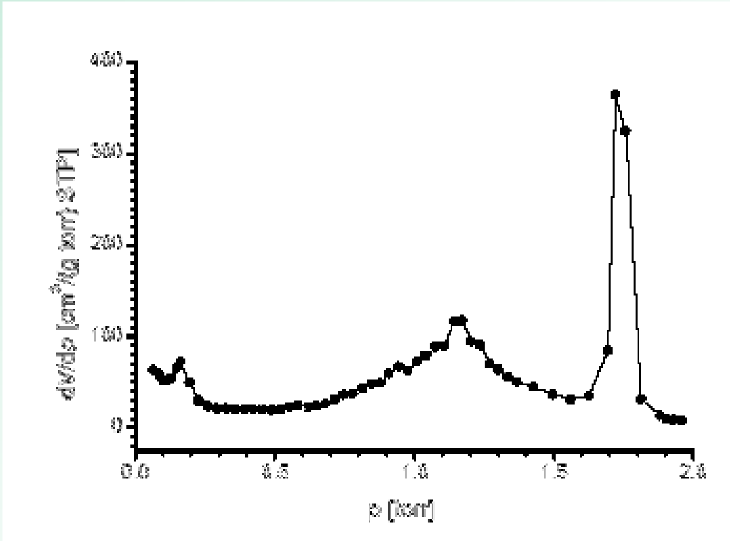
Kr adsorption and desorption at 77 K

several endohedral and exohedral phases

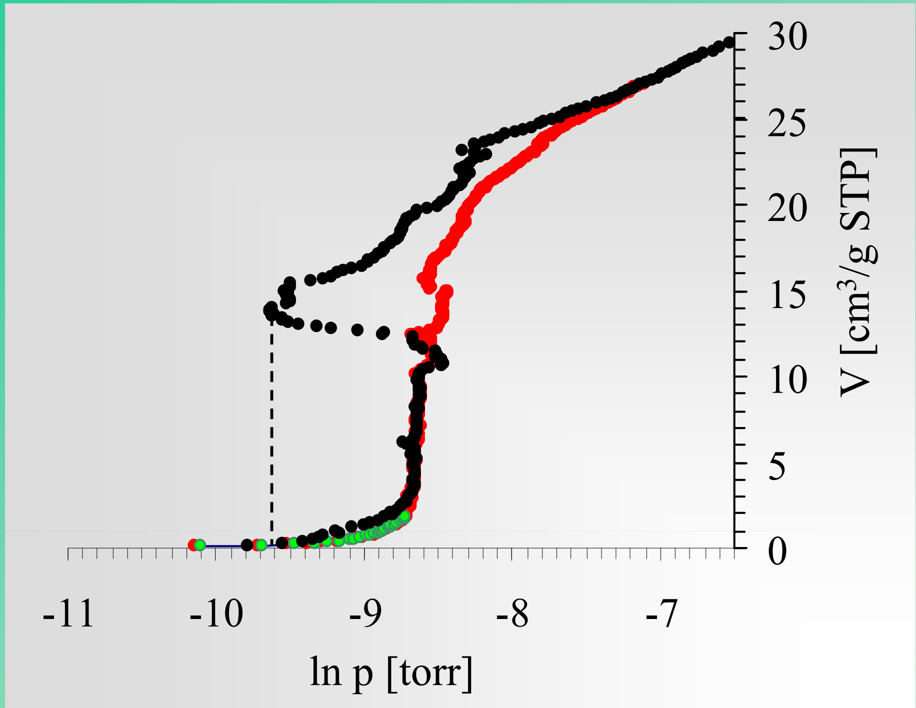
- first layer groove
- first monolayer
- second layer groove
- second monolayer

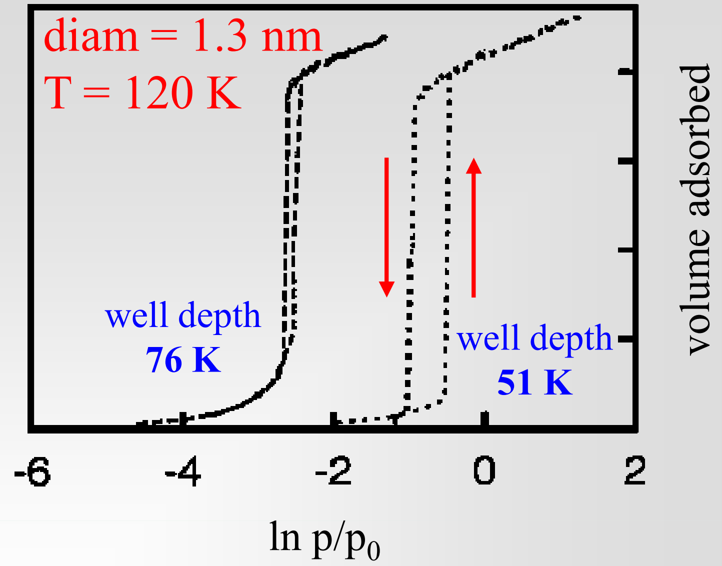




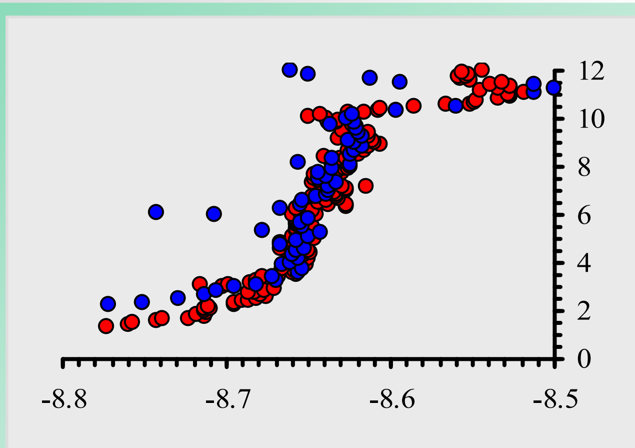


Kr adsorption inside SWNT at 77 K





Steele & Bojan Adv. Colloid Interface Sci. ***76-77**, 153 (1998)*



- **two branches - real effect**
- **condensation/evaporation hysteresis**
- **first-order phase transition**
- **improved experiment + modeling**

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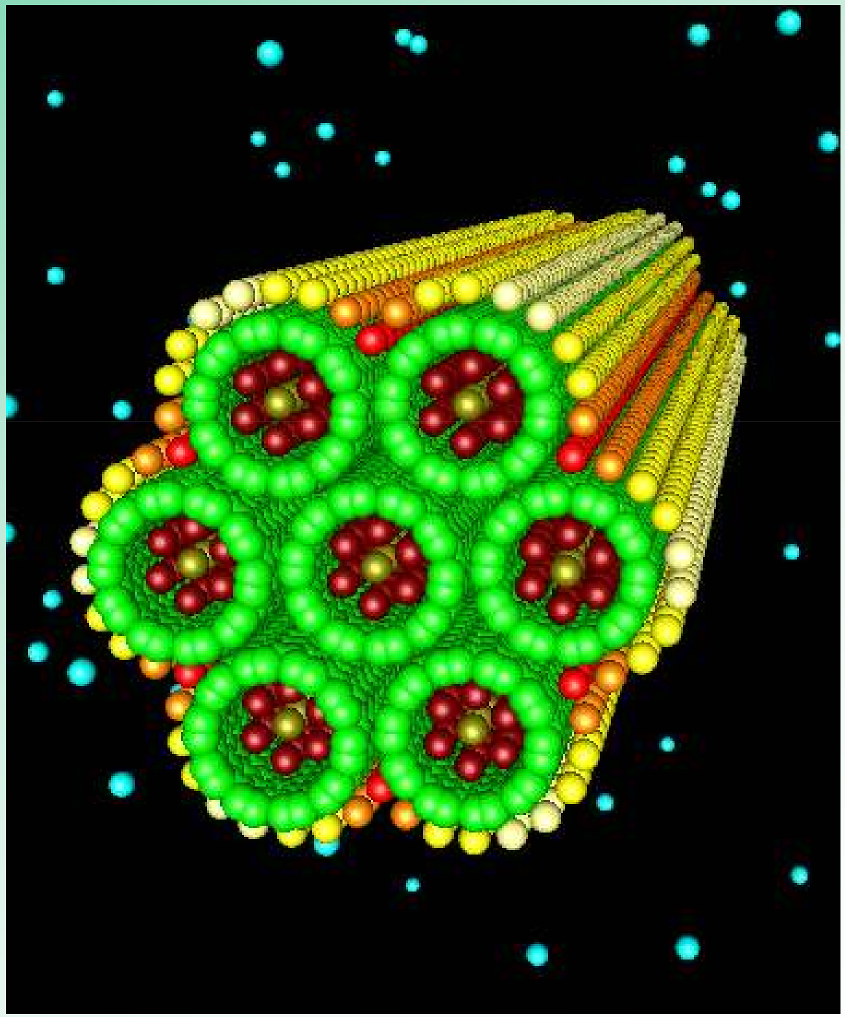
SWNT bundles – adsorption sites

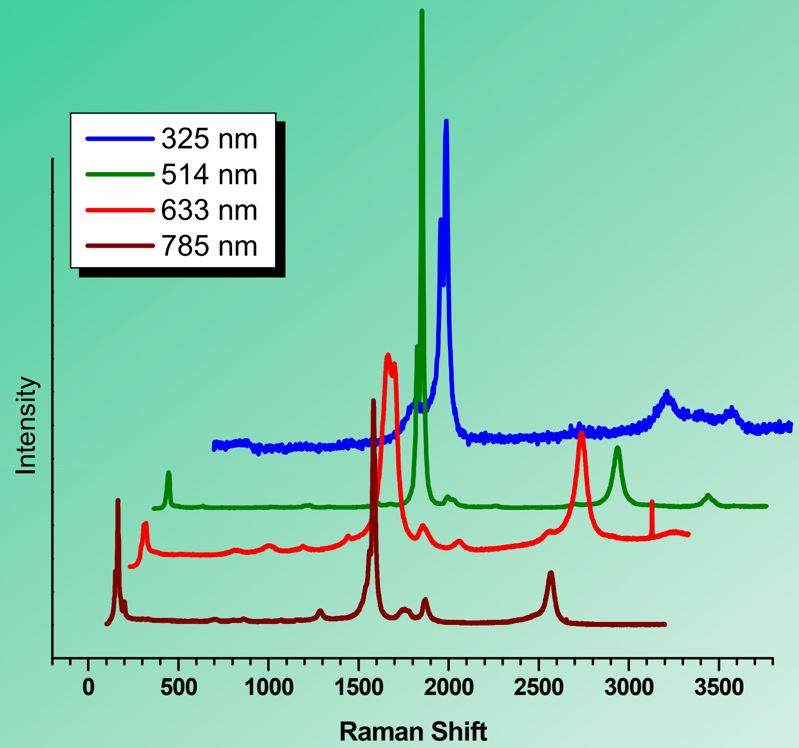
"corn on the cob"

Ar phases on bundles of open-ended SWNT - artist rendition

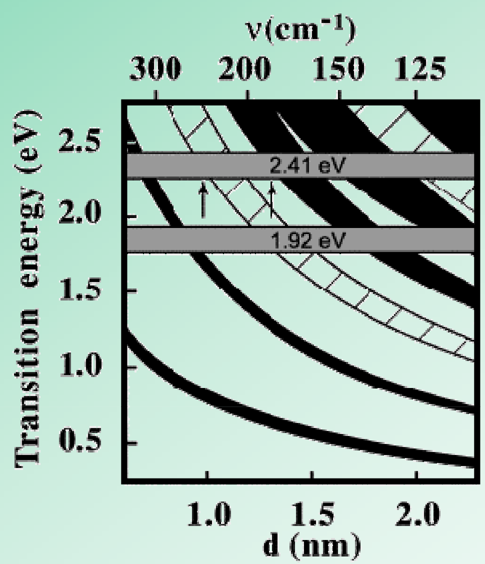
- carbon atoms
- internal monolayer
- axial adsorbate
- one-channel phase
- three-channel phase
- external monolayer
- gas phase Ar atoms



Raman spectroscopy of SWNT

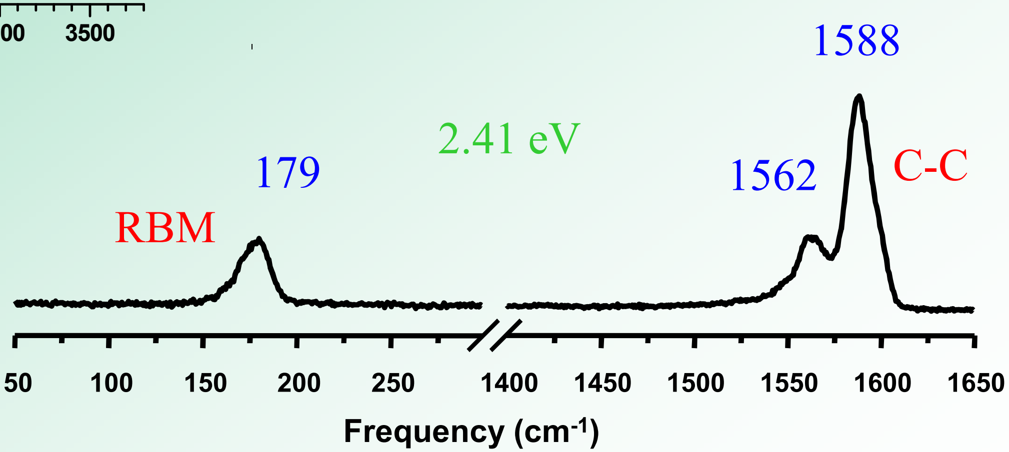


allowed optical transitions



RBM master equation

$$\nu\ (cm^{-1}) = 238/[d\ (nm)]^{0.93}$$



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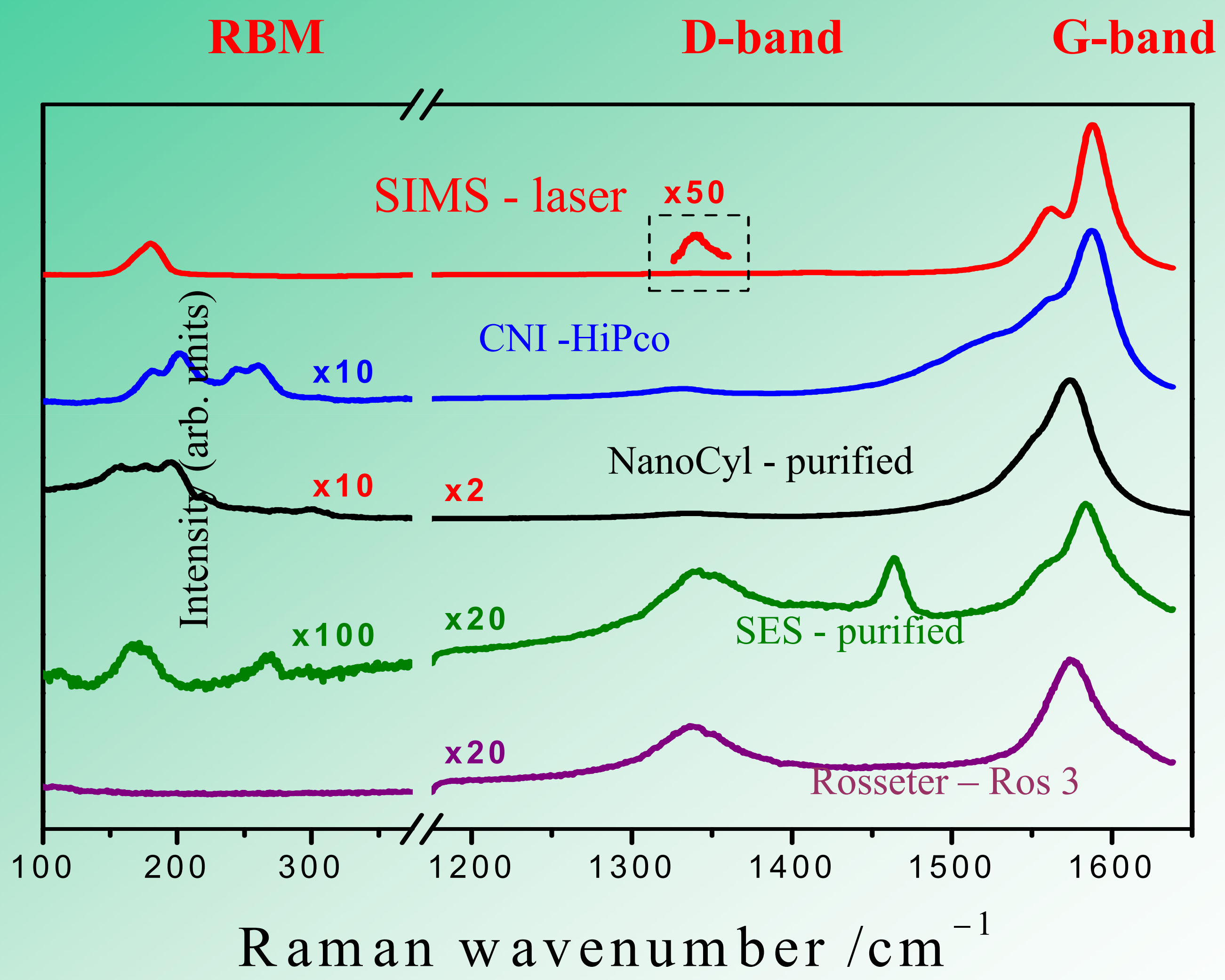
quality variation of SWNT materials



related standards

» Particle size analysis -Photon correlation spectroscopy (ISO 13321)

» Particle size analysis - Laser diffraction methods - Part 1: General principles (ISO 13320-1)

» Determination of particle size distribution - Single-particle light interaction methods - Part 1: Light interaction considerations (ISO 13323-1)

» Determination of particle size distribution - Small angle X-ray scattering method (ISO/TS13762)

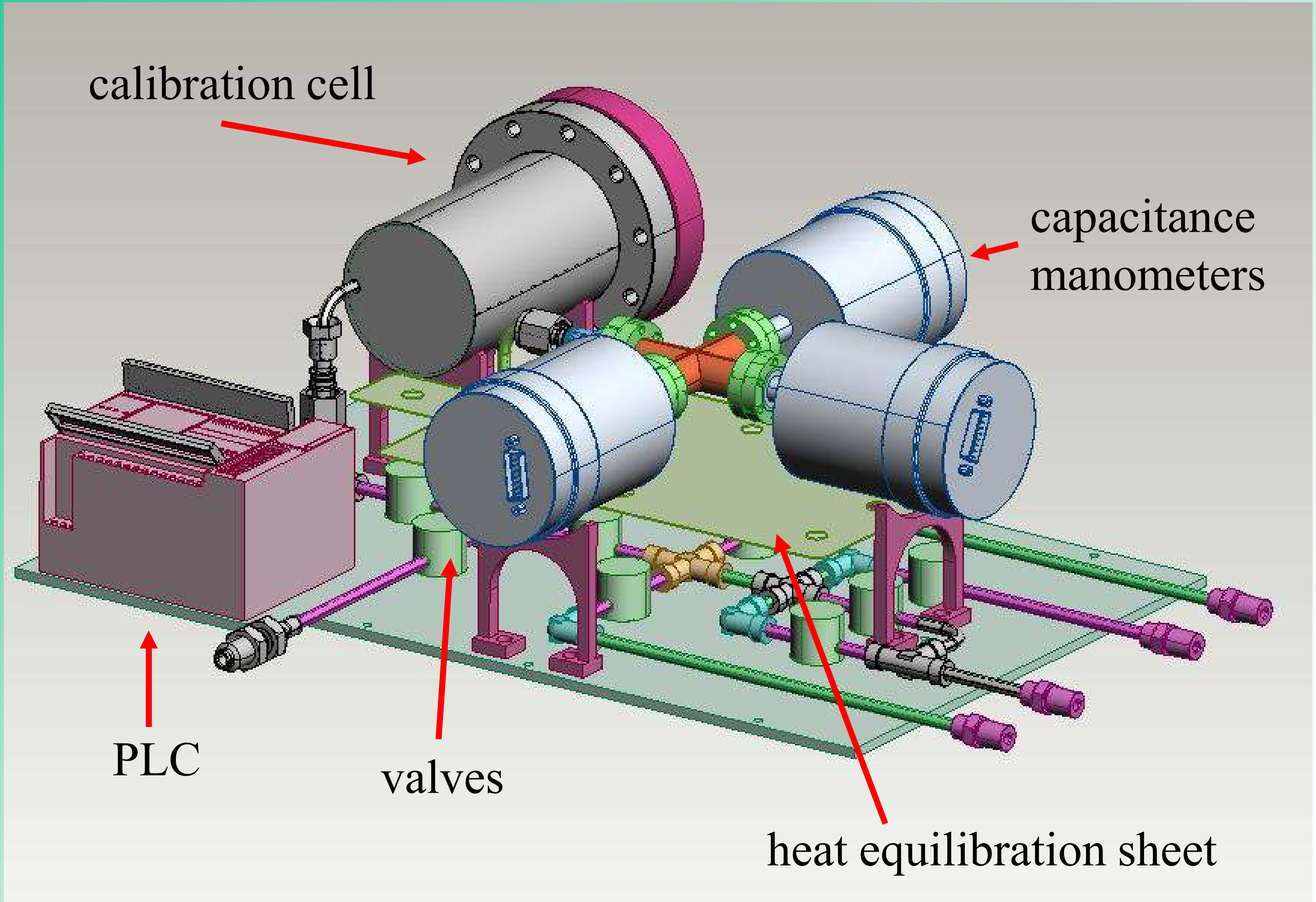
SWNT standards

» **TEM**	(TS10797)
» **SEM and EDX Analysis**	(TS10798)
» **UV-Vis-NIR absorption spectroscopy**	(TS10868)
» **NIR-PL spectroscopy**	(TS10867)
» **EGA-GCMS**	(TS11251)
» **TGA**	(TS11308)
» **Raman spectroscopy**	(TS10812)

single walled carbon nanotubes

- **seamless tube of rolled graphene**
  - 1-5 nm in diameter
  - 0.1-1 μm in length
  - endless bundles (10-200 NT)
  - metallic or semiconducting (~1 eV)
- **high electrical (ballistic) conductivity**
  - 10^9 - 10^{13} A/cm^2
- **high thermal conductivity**
  - 2× diamond
- **strongest material known**
  - Young modulus: ~10× steel
  - tensile strength: ~100× steel
- **high chemical stability**

gas handling and process control modules



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