Carbon Nanotube and Graphene Chemical Sensors

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NT '06 , Nagano

Outline

- SWNT and Nanowire Chemical Sensors
  - Where are we?
  - Thermoelectric Sensing of Gases with SWNT Mats
    - Physisorption (e.g., C_6H_{2n} ring molecules)
    - Gas Collisions (inert gases)
- On to Graphene
  - n-graphene layer films (nGLs)
  - Phonon properties of nGLs
  - Sensor properties—not yet!
- Summary and Conclusions

J|A|C|S
COMMUNICATIONS

Published on Web 08/19/2005

Complementary Detection of Prostate-Specific Antigen Using In_2O_3 Nanowires and Carbon Nanotubes

Chao Li,† Marco Curreli,‡ Henry Lin,§ Bo Lei,† F. N. Ishikawa,† Ram Datar,§ Richard J. Cote,§ Mark E. Thompson,‡ and Chongwu Zhou*,†,‡

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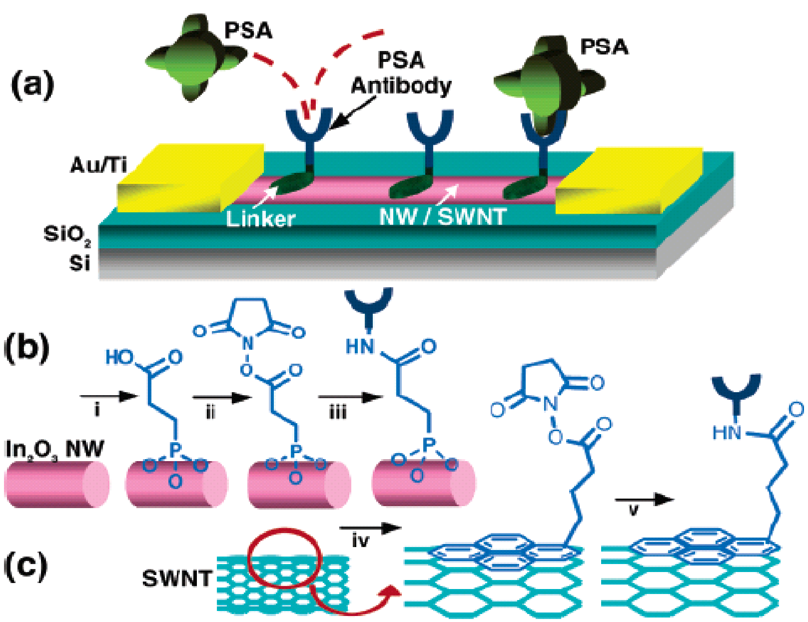
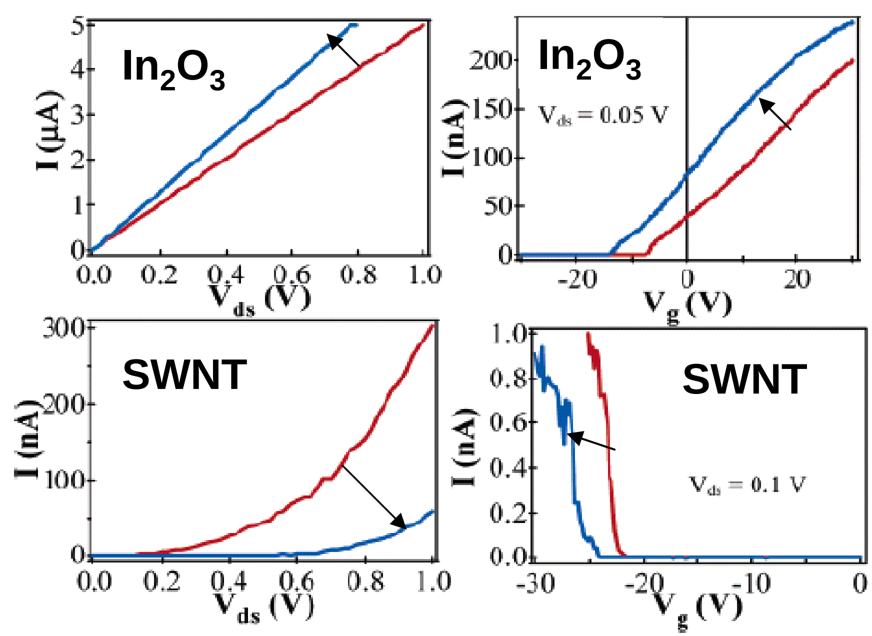


Red (before) Blue (after) PSA



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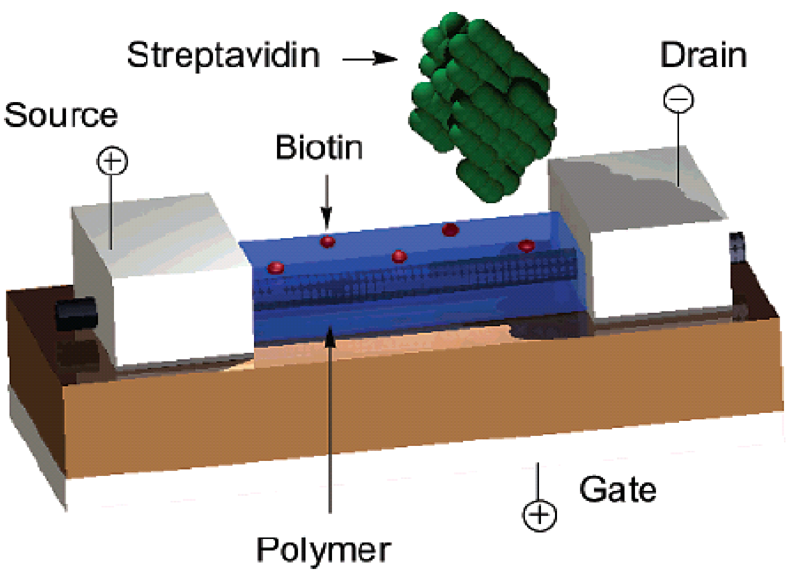
Electronic Detection of Specific Protein Binding Using Nanotube FET Devices

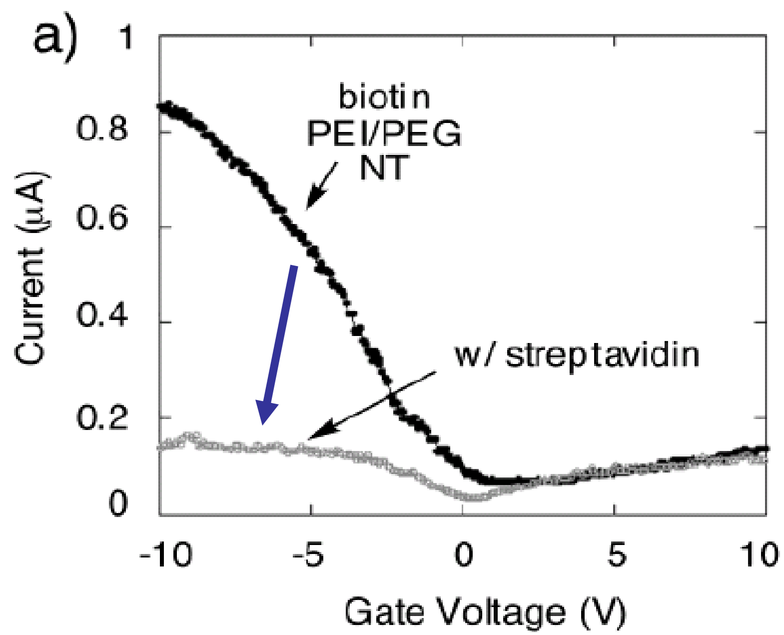
NANO LETTERS
2003
Vol. 3, No. 4
459−463

Alexander Star,* Jean-Christophe P. Gabriel, Keith Bradley, and George Grüner†

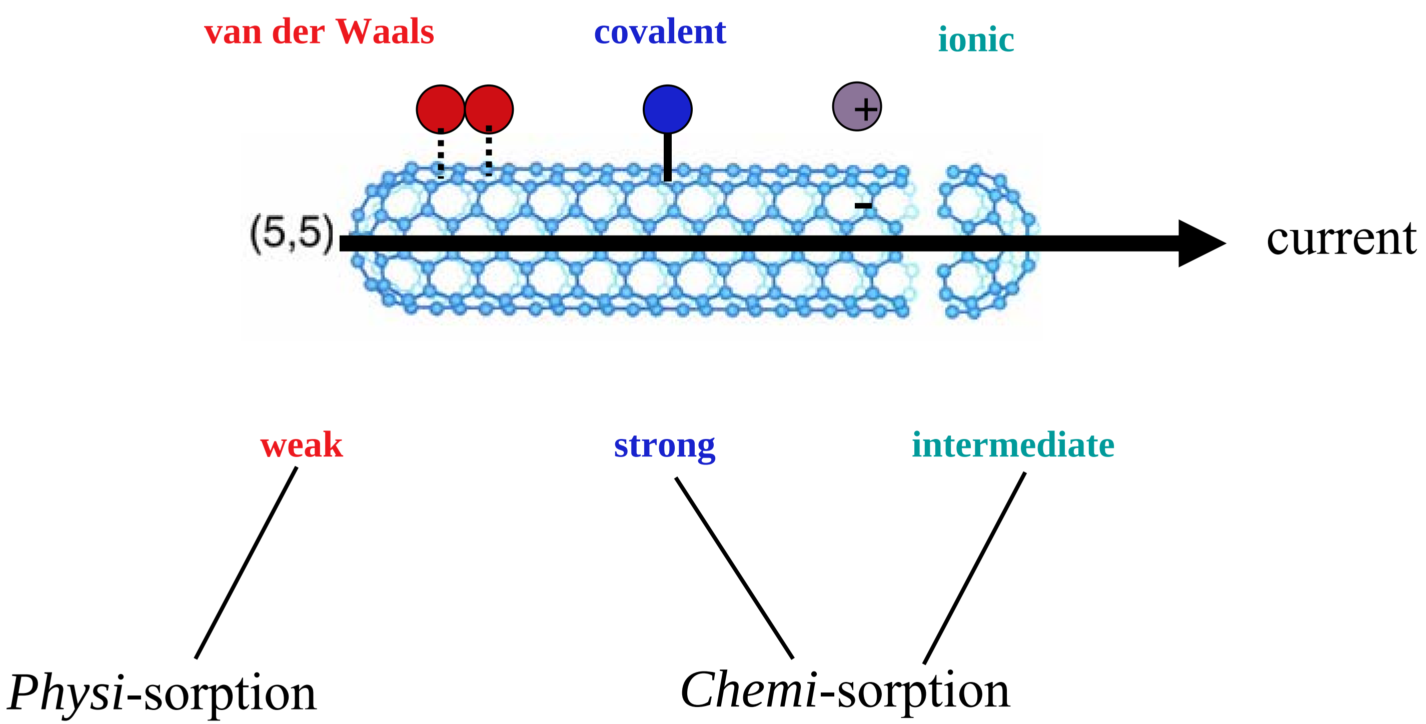
Nanomix Inc., Emeryville, California 94608

Received January 10, 2003; Revised Manuscript Received February 13, 2003



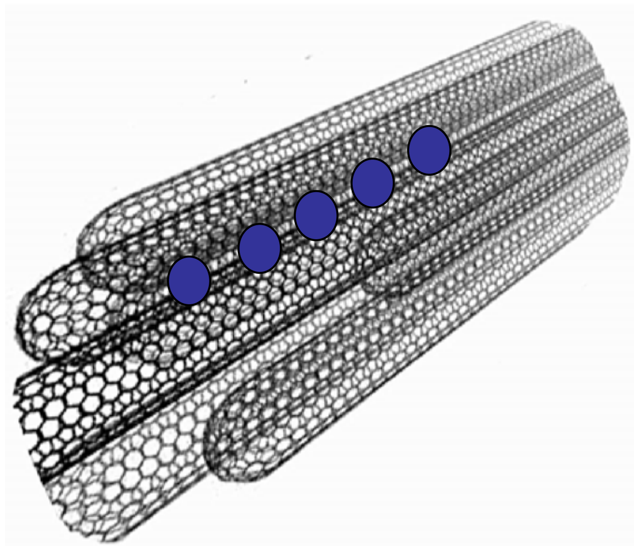


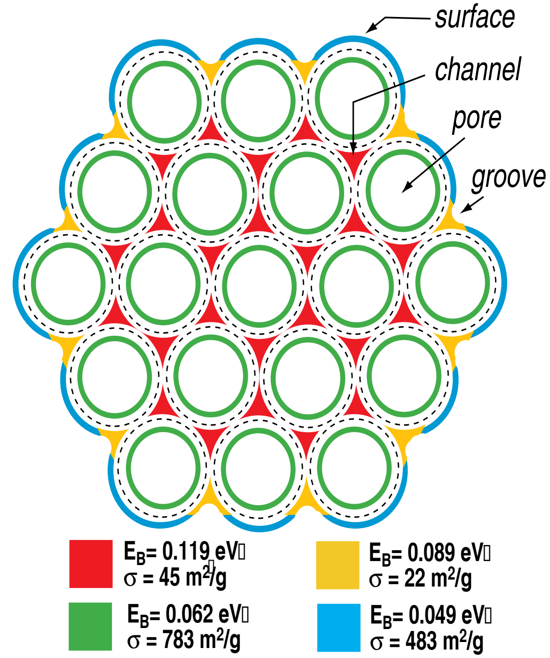
Static Gas-SWNT Interactions



One might presume that *only* the chemisorbed atoms/molecules will significantly effect the transport of electrons in the tube wall….

Structural Considerations



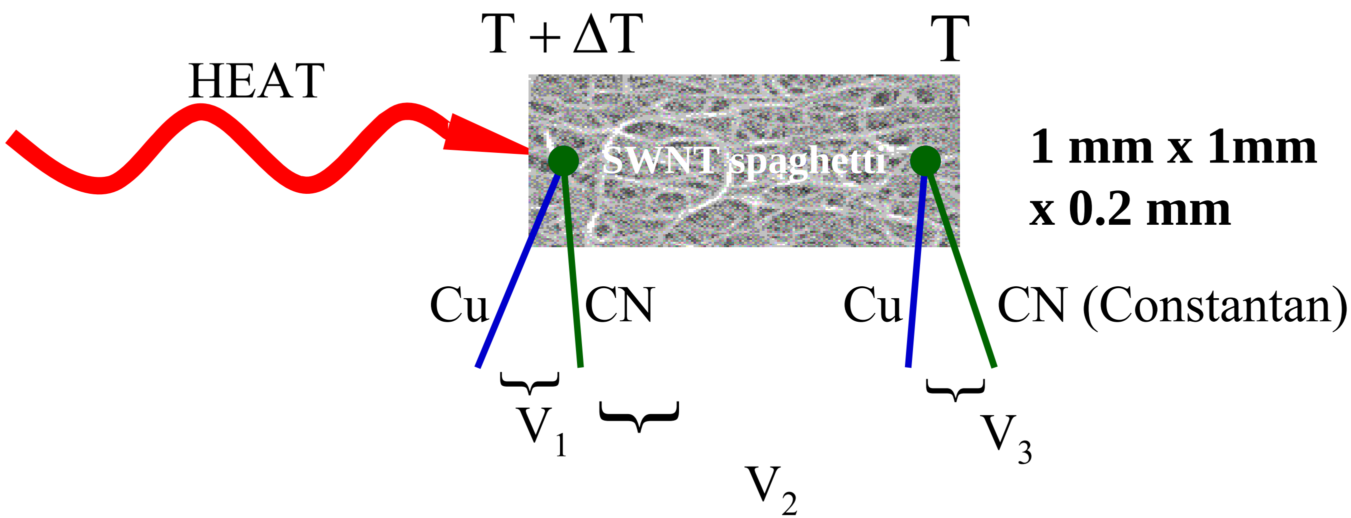


•Molecular adsorption at interstitial, groove and pore sites.

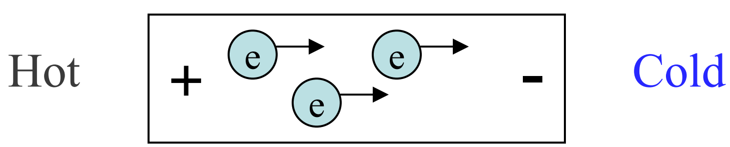
•No "bulk atoms"…only surface atoms…electrical transport should be sensitive to gas:SWNT interactions

•It takes time for atoms and molecules to saturate the surface via diffusion and to gain access to internal pores and channels

Thermoelectric Power (TEP)

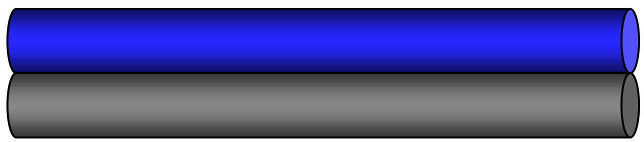


S = Seebeck Coefficient = $V_2/\Delta T$; V_2 = Open Circuit Voltage



c.f., H. Romero, G. U. Sumansekera, G.D. Mahan and P. C. Eklund, Phys. Rev. B., 65 (2002)

TEP(S) and Conductivity(σ) of a SWNT Bundle



Two tubes in parallel (e.g., metallic and semiconducting)

$$S = (1/\sigma)[S_1\sigma_1 + S_2\sigma_2] \sim S_1 \quad \text{and} \quad \sigma = [\sigma_1 + \sigma_2] \sim \sigma_1$$

Metallic tube (σ_1) dominates: i.e., $\sigma_1 >> \sigma_2$

=> Metallic tubes dominate the bundle transport

$$S = \frac{-\pi^2 k_B{}^2}{3e} T \left(\frac{d \ln \sigma(E)}{dE} \right)_{E_F}$$

Mott relation for a Metal

Effect of additional impurity scattering channel

$$S = \frac{-\pi^2 k_B{}^2}{3e} T \left(\frac{d \ln \sigma(E)}{dE} \right)_{E_F}$$

Mott relation for a Metal

$$\sigma(E) = e^2 v(E)^2 D(E) \tau(E)$$

σ = conductivity

v- free carrier velocity, D-density of states, τ-carrier lifetime

Matheissen's rule $\Rightarrow$ $\rho = \rho_0 + \rho_I$

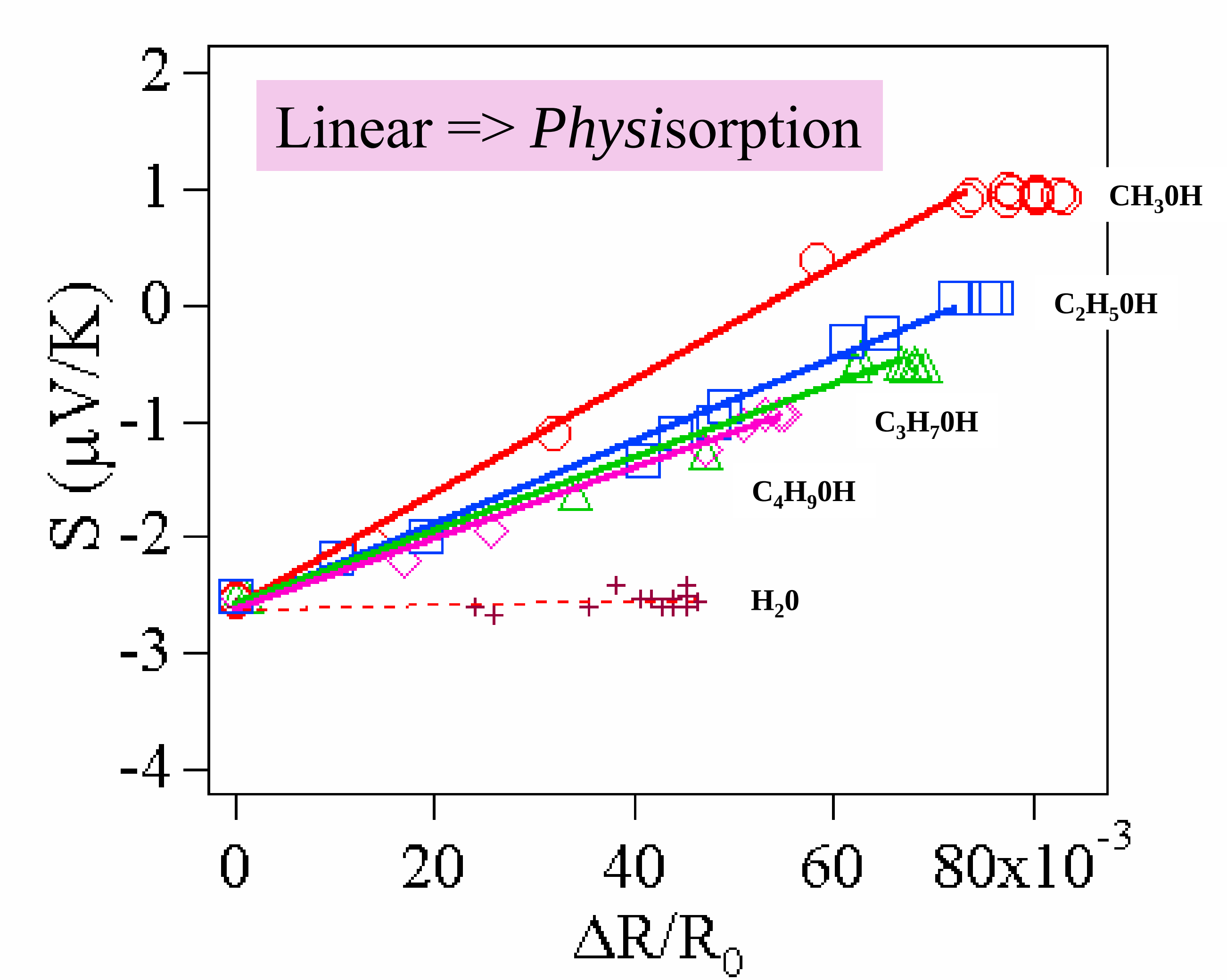
ρ_I due to gas

$$\Rightarrow \quad S = S_O + \frac{\pi^2 k_B{}^2 T}{3e} \left(\frac{\rho_I}{\rho_0} \right) \left(\frac{1}{\tau_I} \frac{d\tau_I}{dE} - \frac{1}{\tau_O} \frac{d\tau_O}{dE} \right)_{E_F}$$

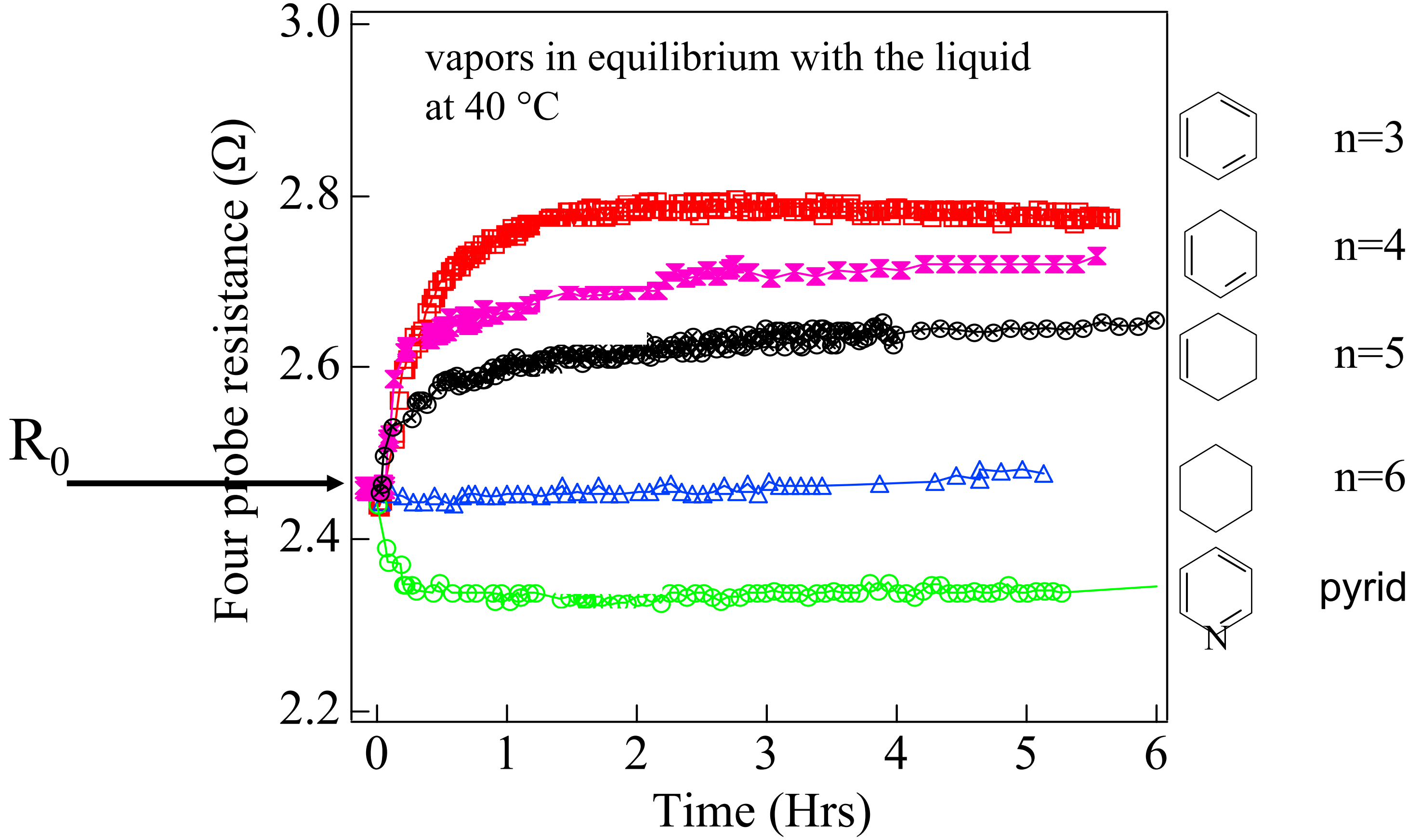
$\rho_I << \rho_0$

c.f., papers by: P.C. Eklund, H. Romero, et al.

(Linear) Thermopower vs. Extra Resistance (Physisorption)



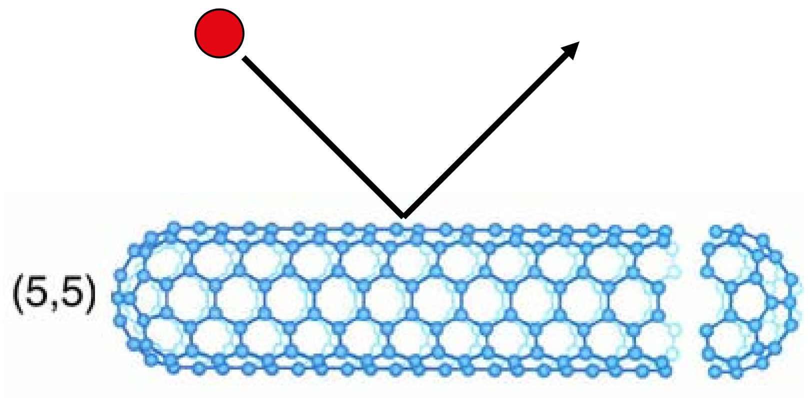
Resistive Response to C_6H_{2n} Adsorption



*Increase in R related to scattering via π-electron coupling.

*Pyridine decreases the resistivity via creation of additional carriers.

Effects of Gas:SWNT Collisions

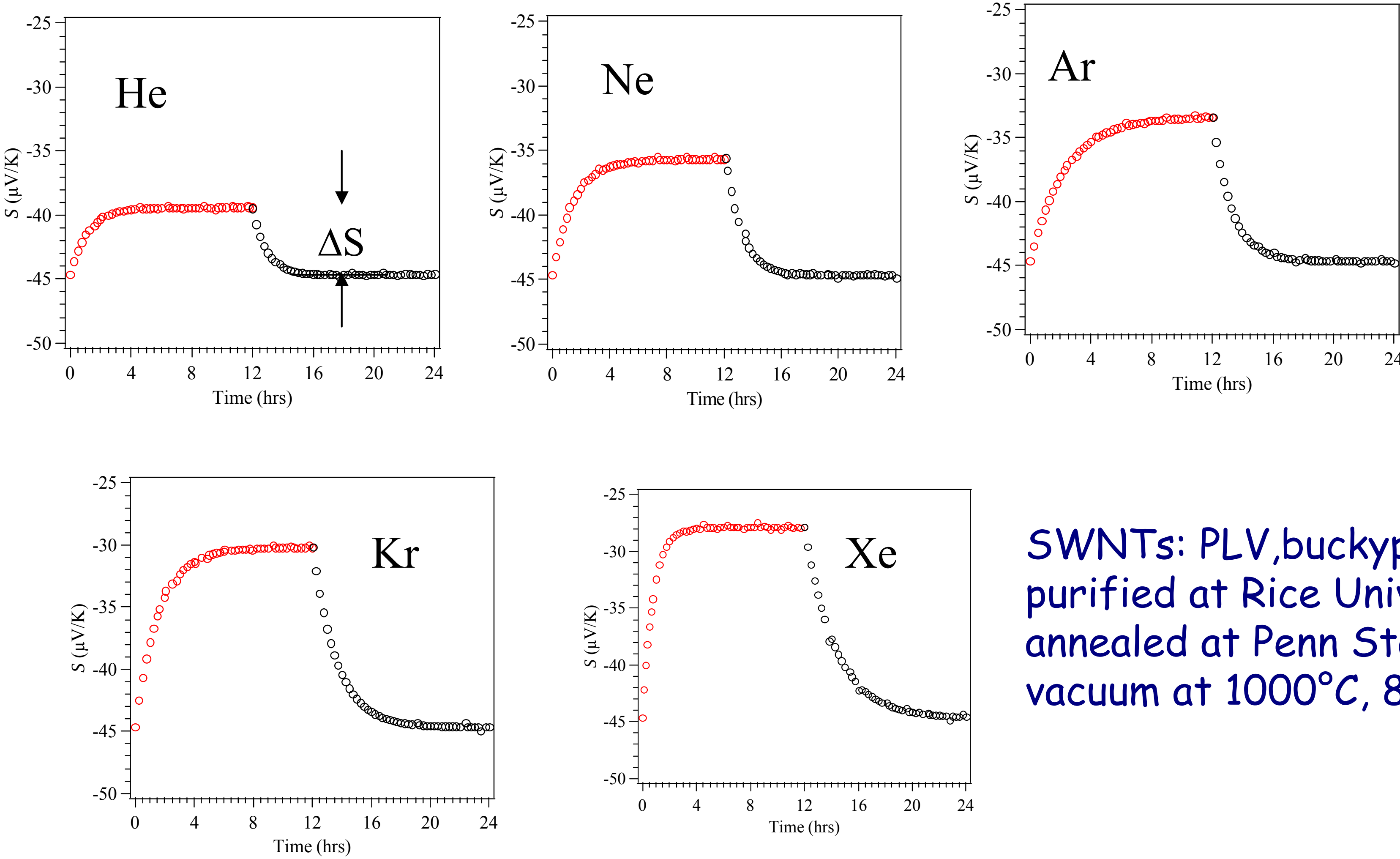


Gas molecule collisions with the tube wall should affect the electron mean free path:

- **?Direct scattering of electrons by atom collisions?**
- **?Generate a transient “dent”; non-thermal phonons then scatter electrons?**

TEP Response to Inert Gases

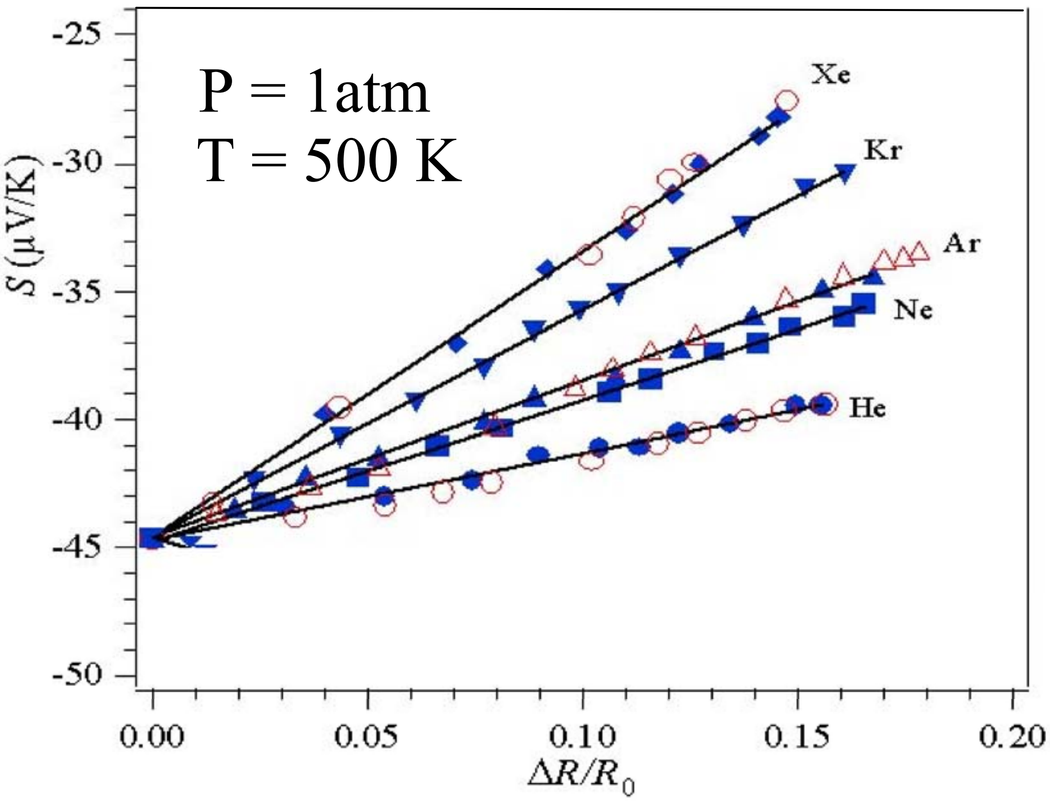
(Same sample: P=1atm and T=500 K)



SWNTs: PLV,buckypaper, purified at Rice Univ., annealed at Penn State in vacuum at 1000°C, 8hr

Inert Gas Collisions: TEP vs Resistivity

S vs $\Delta\rho$ is linear, in accord with the Mott Equation and a new scattering channel (gas collisons)



Same film sample; successive exposure to series of inert gases

Slope depends on the mass of the colliding atom

c.f., H. Romero, K. Bolton, A. Rosen and P. C. Eklund, *Science* (307) 2005

Computed Transient Power Spectrum (Local Vibrational Modes)

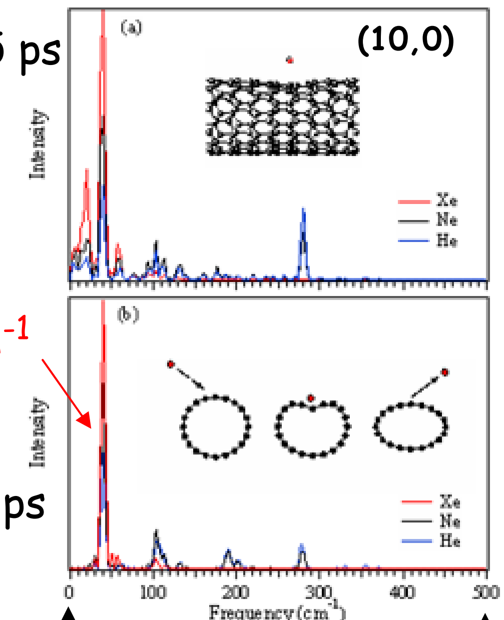
$\Theta_i = 45°$, KE =13kcal/mol

m=He,Ne,Xe

After 5 ps

40 cm^{-1}

After 10 ps



0 cm^{-1} 500 cm^{-1}

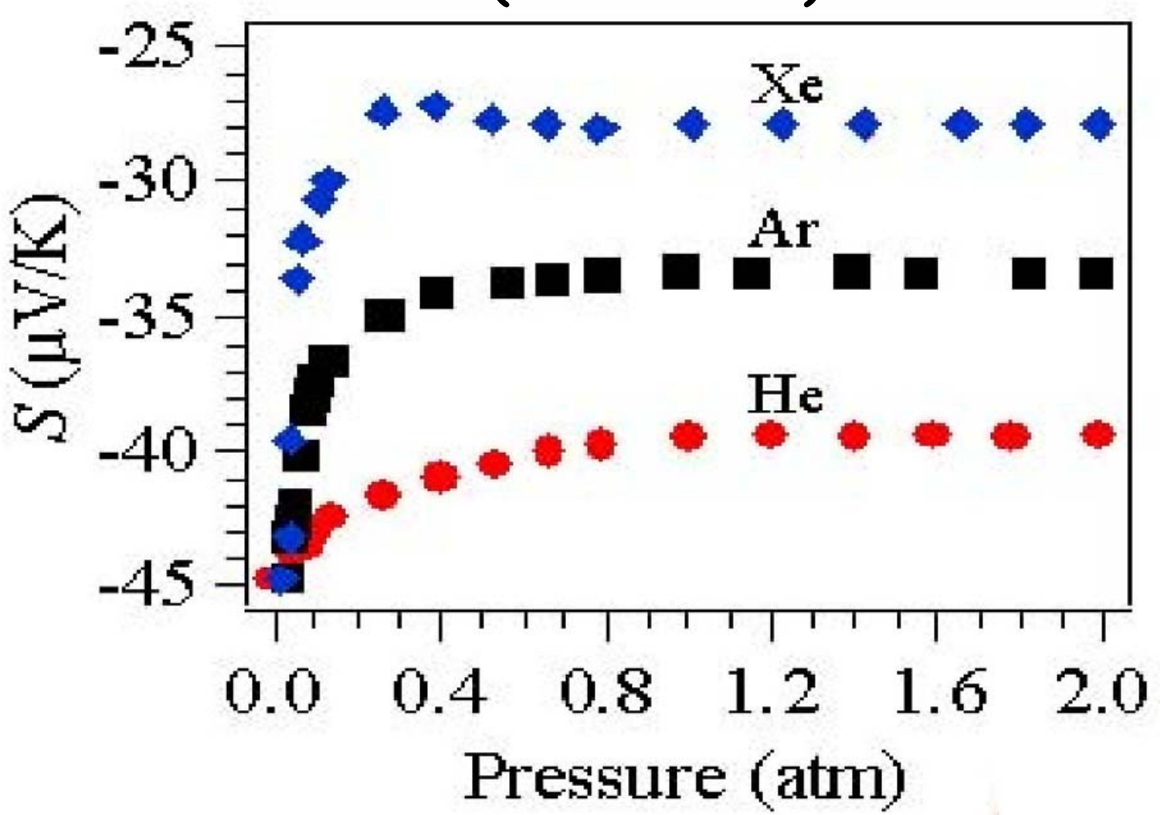
- Local energy spectrum; Derived from motion of C-atom nearest the collision (T_{tube}= 0 K).
- The amplitude of vibration, not the frequencies, are sensitive to the collider atom mass m
- Radial component of kinetic energy is key parameter
- The tube wall is dented, and then it rings in the low frequency "squash" mode
- Significant vibrational energy remains after 10 ps; 2-acoustic phonon decay

Simulations by K. Bolton and A. Rosen, Goteborg University/Chalmers Tech. Univ.

c.f., H. Romero, K. Bolton, A. Rosen and P. C. Eklund, *Science* (307) 2005

TEP (S) vs Pressure

(T = 500 K)



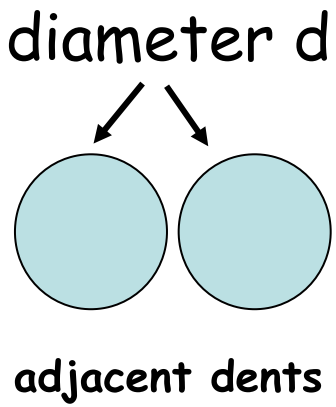
Saturation => Dent-Dent overlap at ~ 0.2 - 0.5 atm ??

Why do (S,ρ) saturate with pressure?

•Use Kinetic theory of Gases; Ask: What collision rate Q causes two dents with lifetime τ and diameter d to overlap?

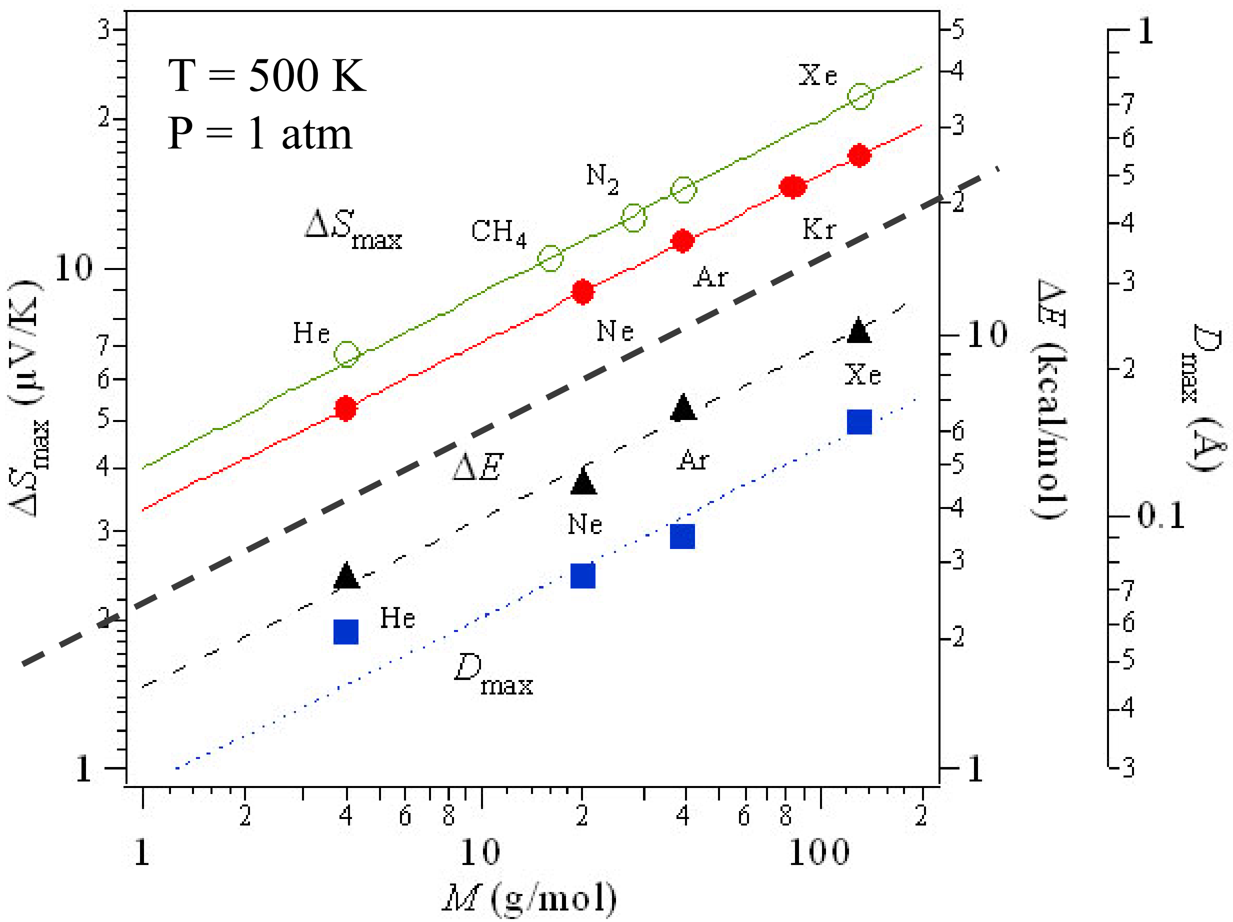
- $Q = P/(2\pi mkT)^{1/2}$ collisions/area.time, P = pressure
- Overlapping Dents ➡ $QA\tau = 1$ collision, Area $A \sim d^2$

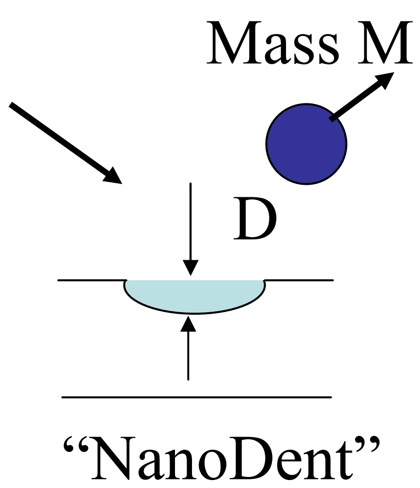
	He	Ar	Xe
dent lifetime (τ)	~100 psec	~100 psec	~100 psec
dent diameter (d)	1.5 nm	4.3 nm	6.4 nm
P_{sat}(calc)	0.97 atm	0.66 atm	0.54 atm
P_{sat}(expt)	0.79 atm	0.56 atm	0.53 atm



c.f., H. Romero, K. Bolton, A. Rosen and P. C. Eklund, *Science* (307) 2005

M^n Power Laws : Expt and Theory

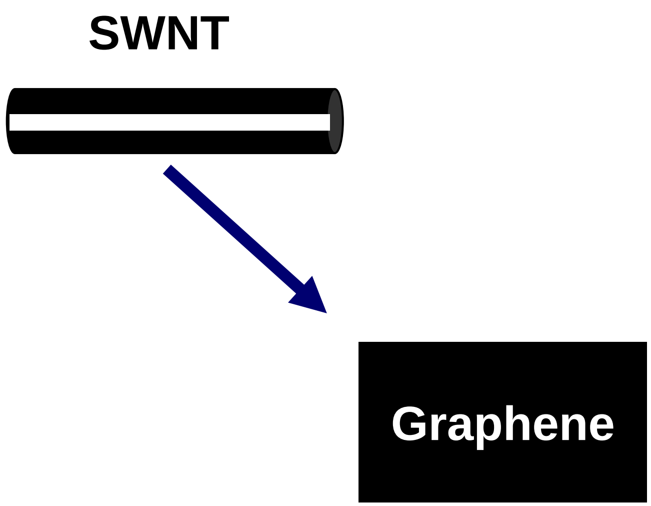


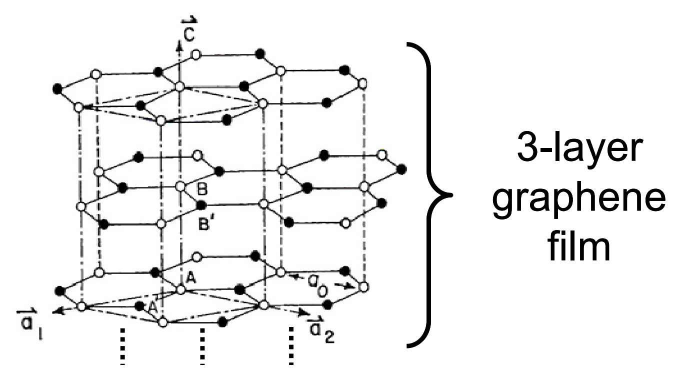


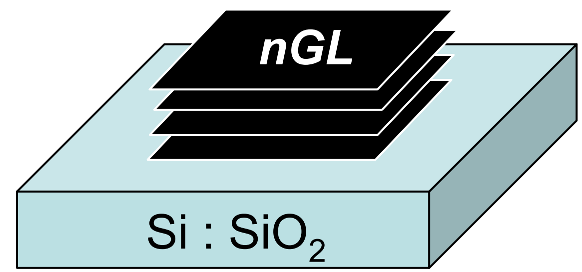
All slopes in the plot represent $M^{1/3}$ behavior

c.f., H. Romero, K. Bolton, A. Rosen and P. C. Eklund, *Science* (307) 2005

Phonon Properties of Ultrathin Graphitic Films





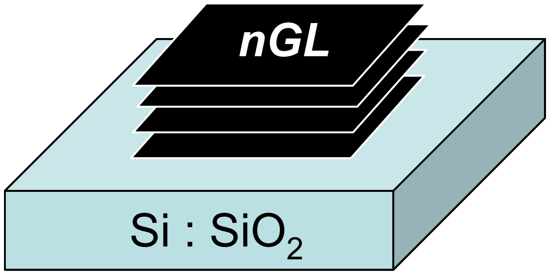


How are the phonon properties related???

***n*GL=n-layer graphene film**

Let's study the phonon properties vs n!

Motivation

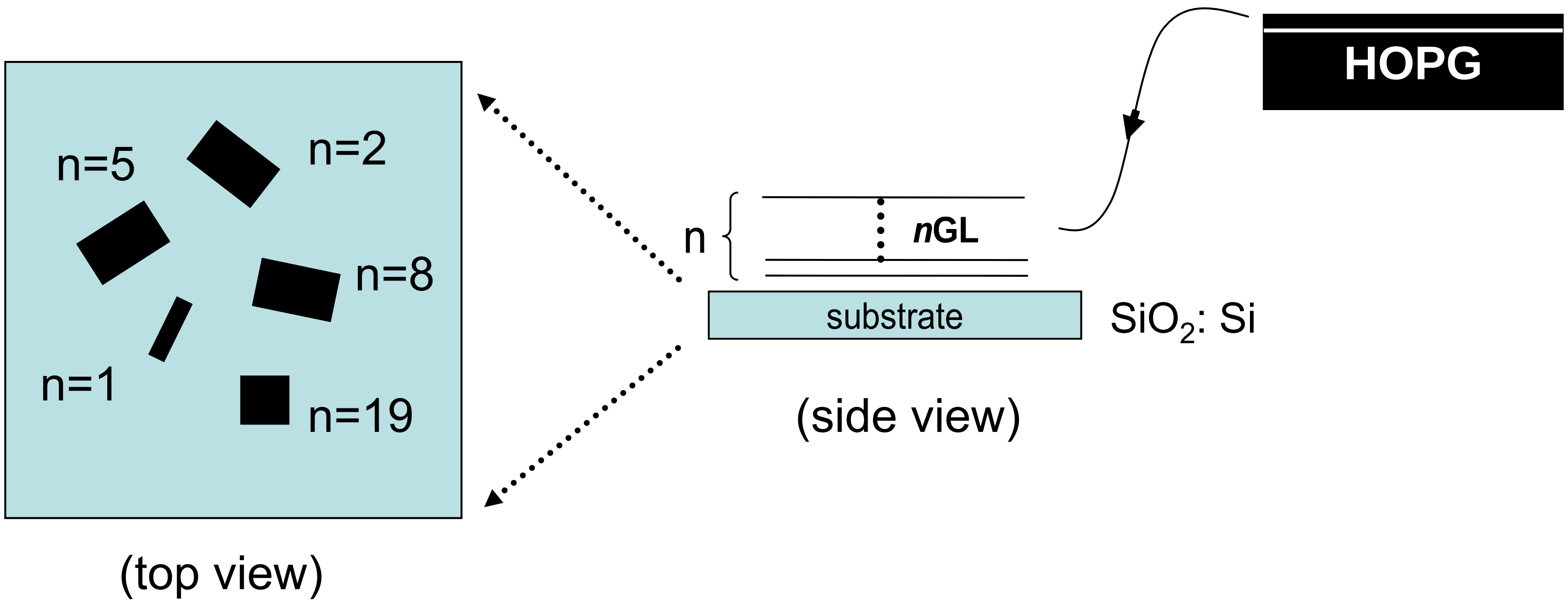


- Exciting transport results in ultrathin graphitic films containing a few atomic layers have been reported
  - `High carrier mobility; gate-controlled transport; Quantum Hall effect *(Kim et al; de Heer et al)*

- We call these carbon systems n-graphene layer films or ***n*GL's**

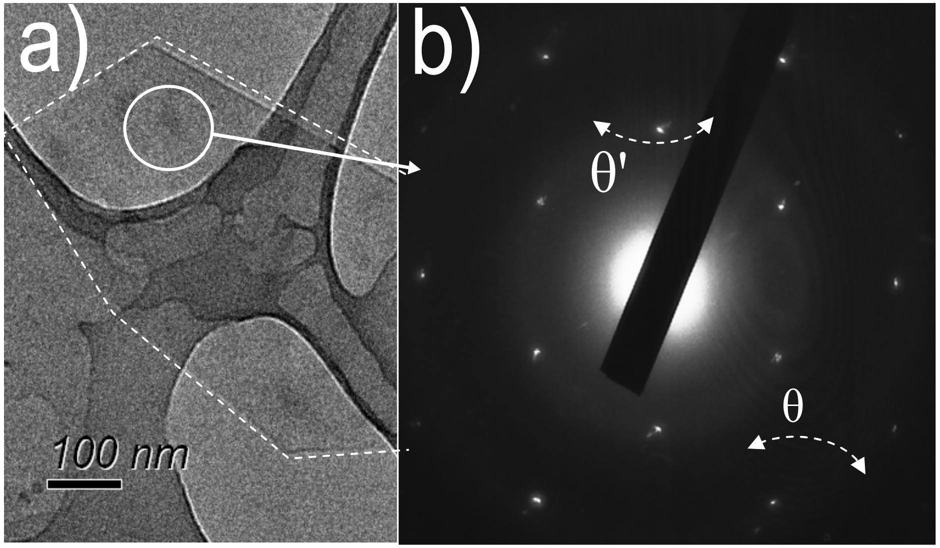
- Using phonons to probe the system vs number of layers (n)…..how will the system evolve?

*n*GL Film Preparation



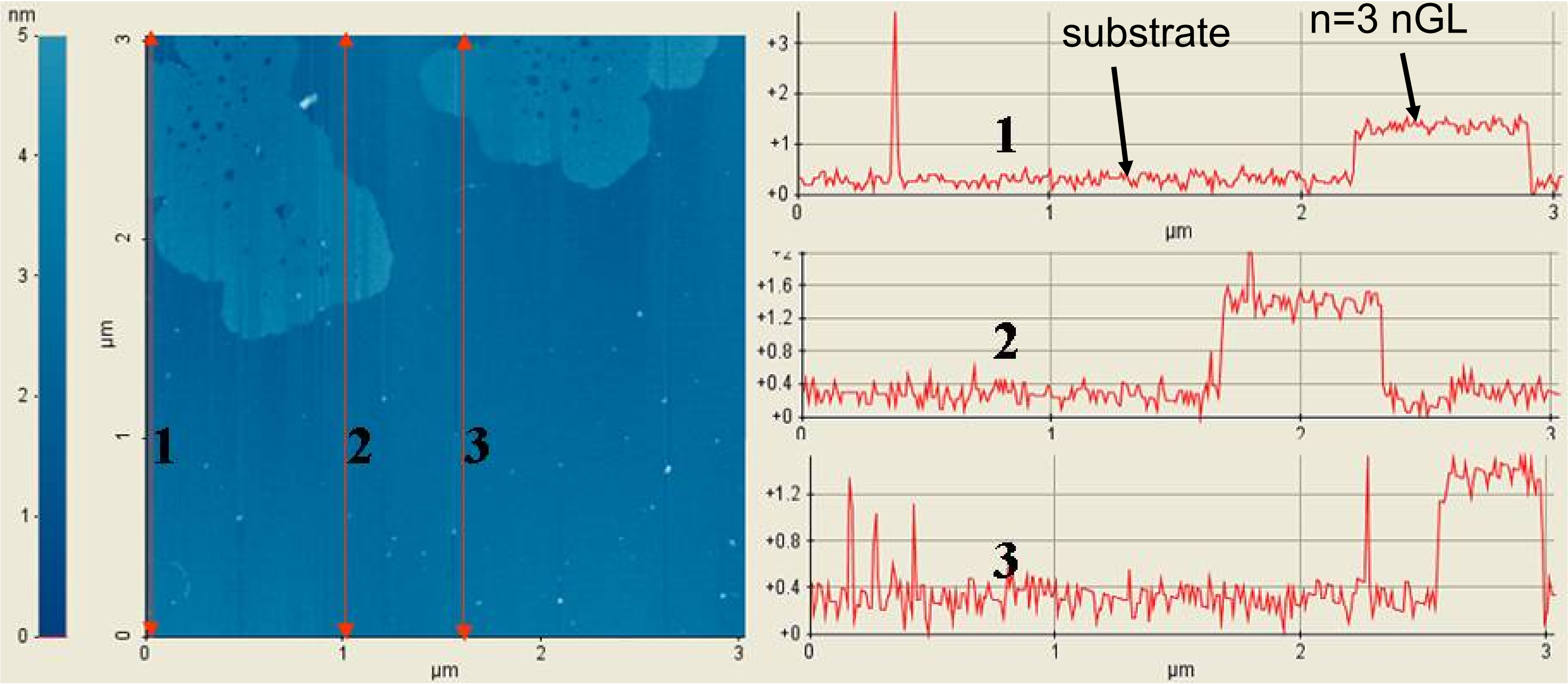
Film thickness measured by AFM z-scans

TEM image (a) and SAD (b) of nGL



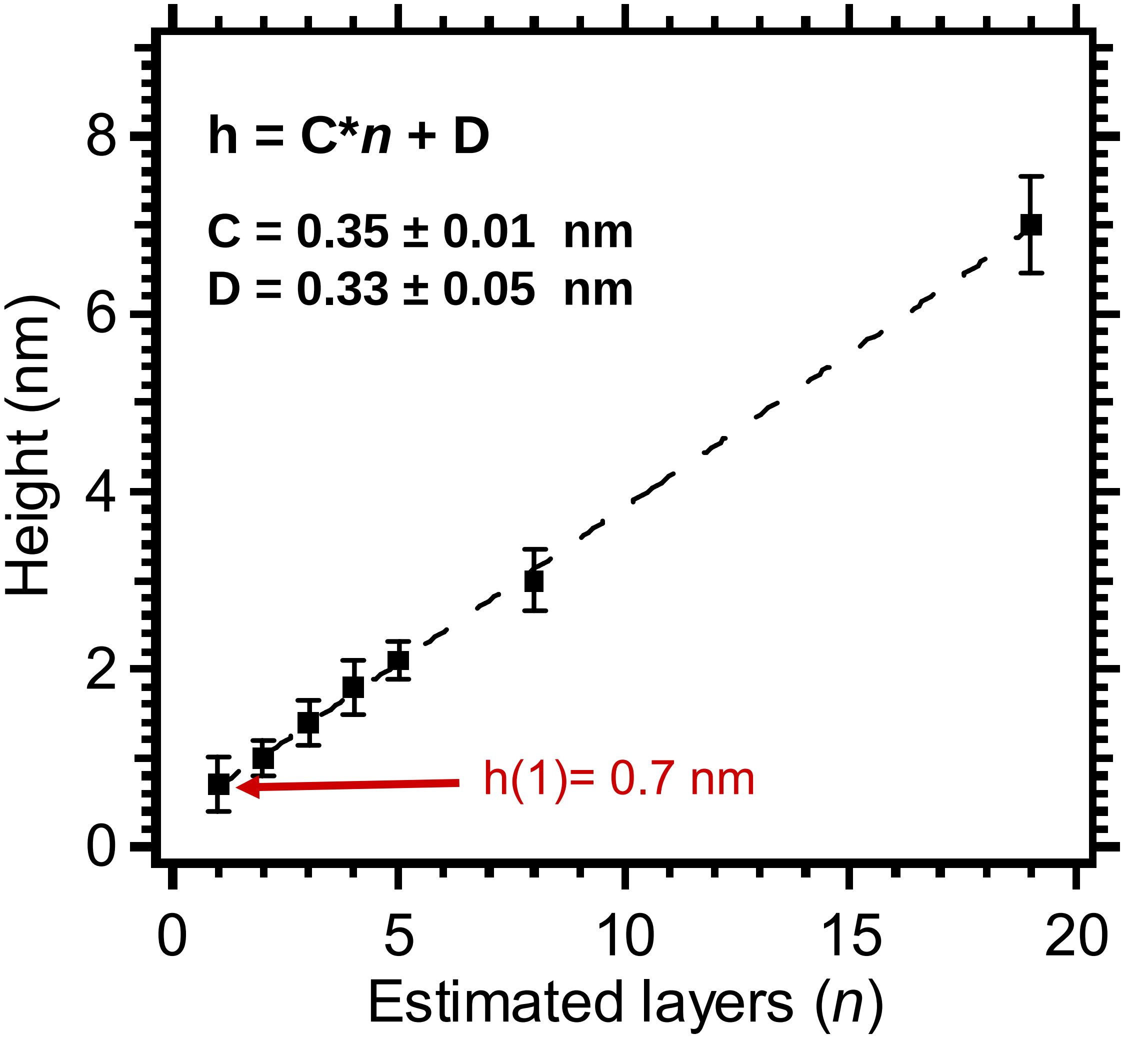
a) Plane view and b) electron diffraction pattern showing six-fold symmetry. In (a), the nGL has small contrast relative to the carbon TEM grid. Angles θ, θ' in the figure are 120°, the angle between basal plane vectors in graphite

AFM z-scans of n=3 nGL



Film thicknes via averaging the step heights of ~100 line scans

*n*GL thickness *h(n)* vs assigned *n*

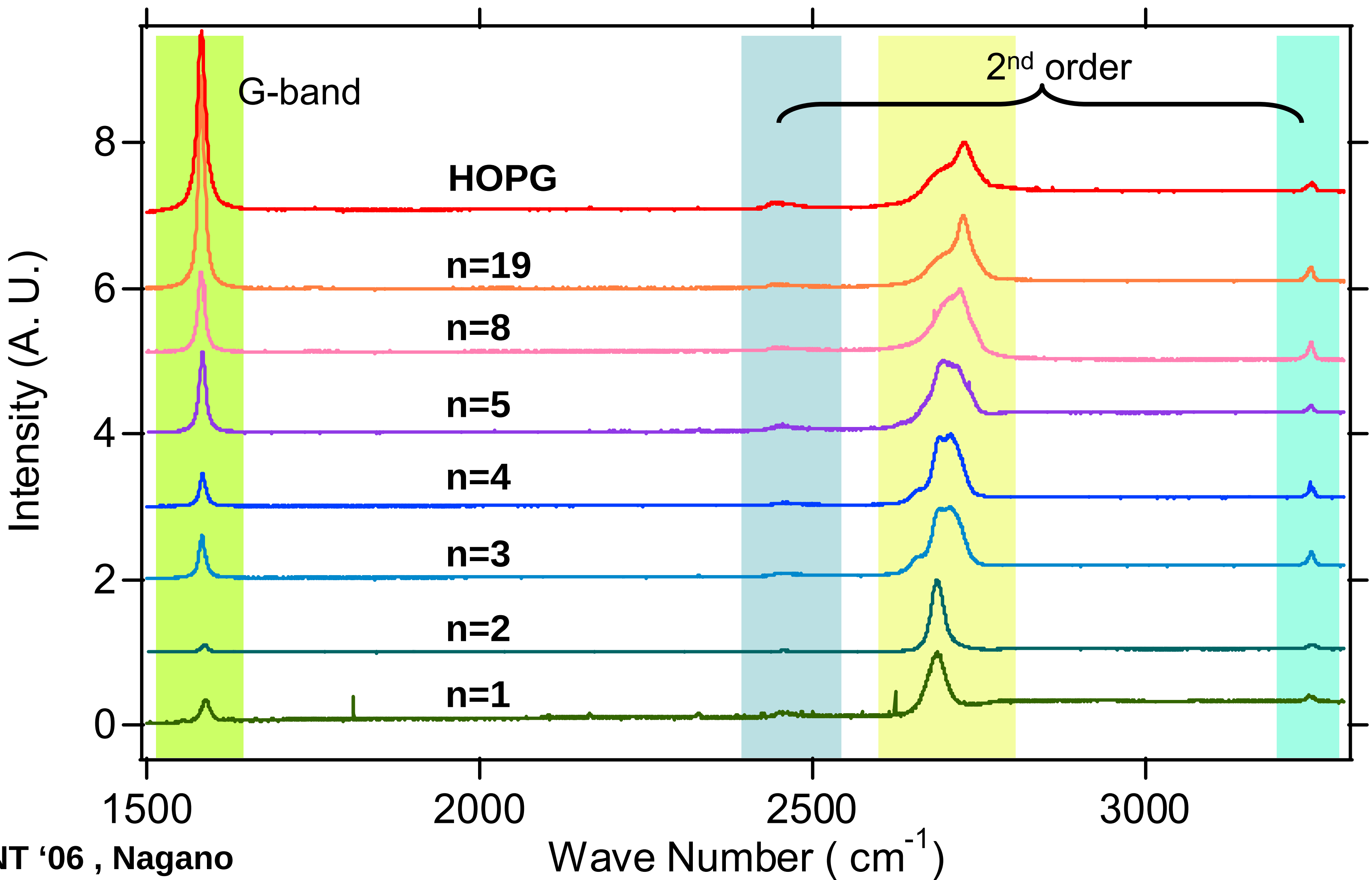


- AFM z-scan used to measure the height relative to substrate
- Least squares fit h vs n:

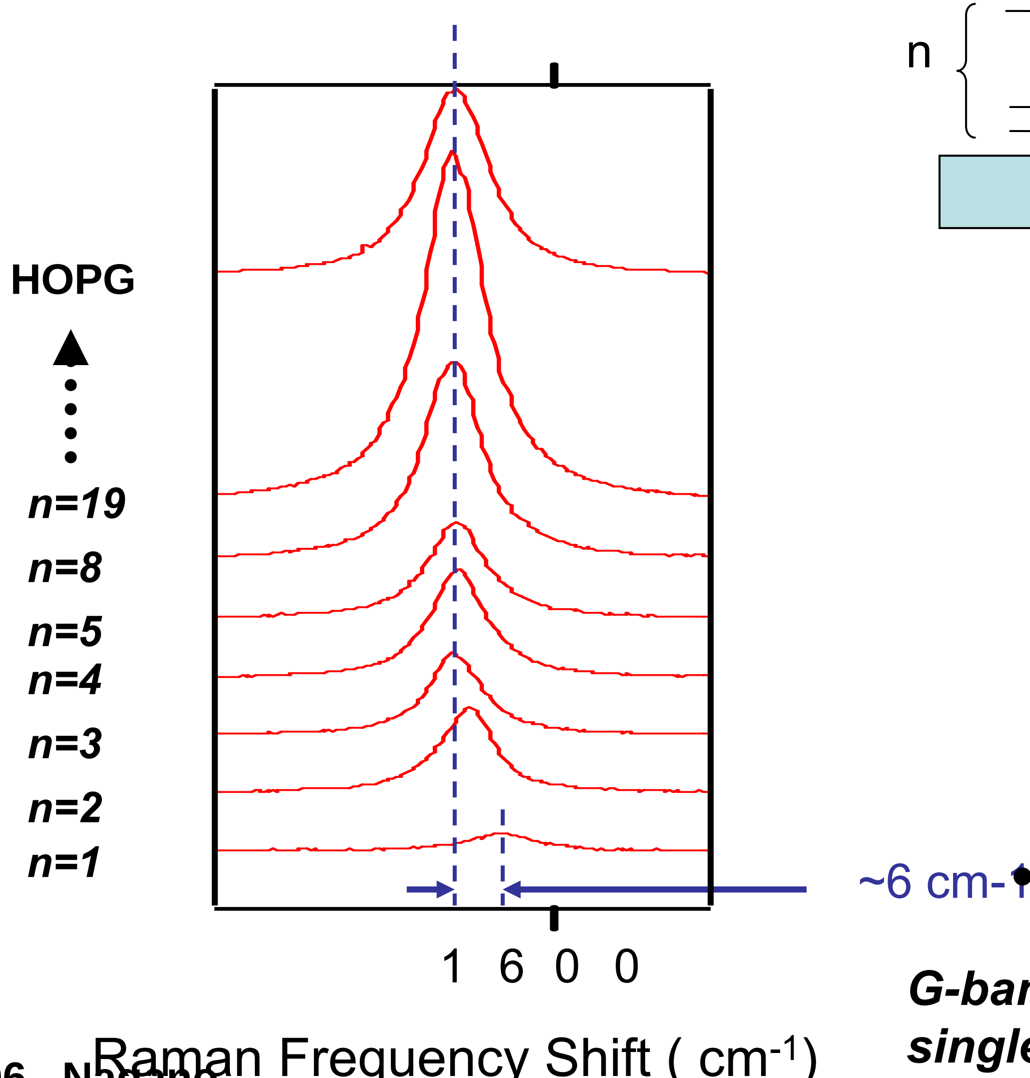
  Slope= 0.35 nm ; slightly larger than c/2=0.335 nm

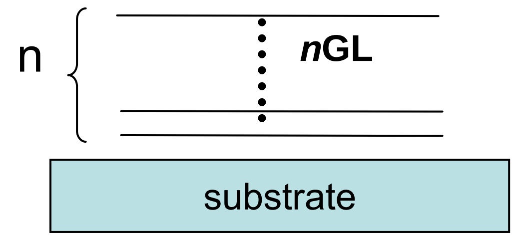
- h(1)= 0.35 + 0.33 = 0.68 nm extra thickness may reflect inherent difference in attractive AFM tip force

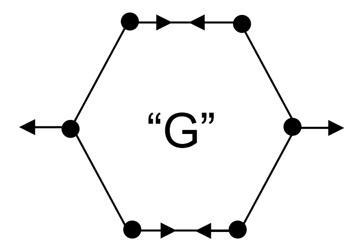
High Freq. Raman Spectrum of *n*GLs



G-band vs n

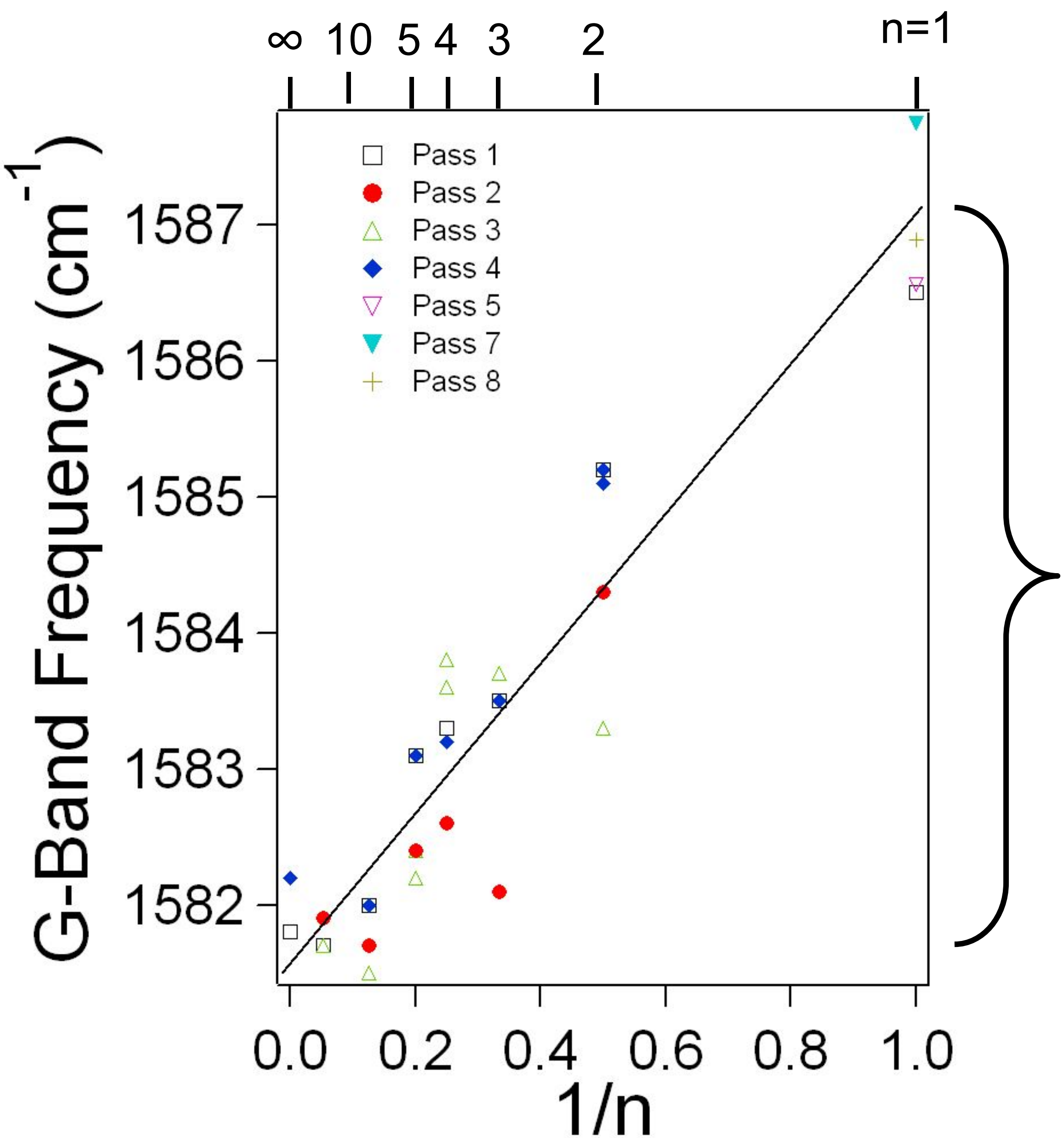


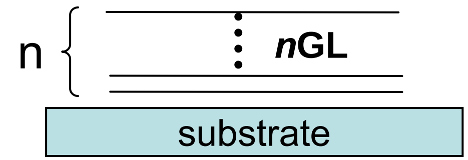




G-bands are all well fit with a single Lorentzian (Voight analysis)

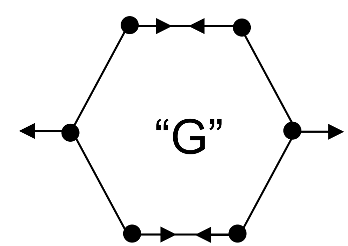
G-Band Frequency vs 1/n



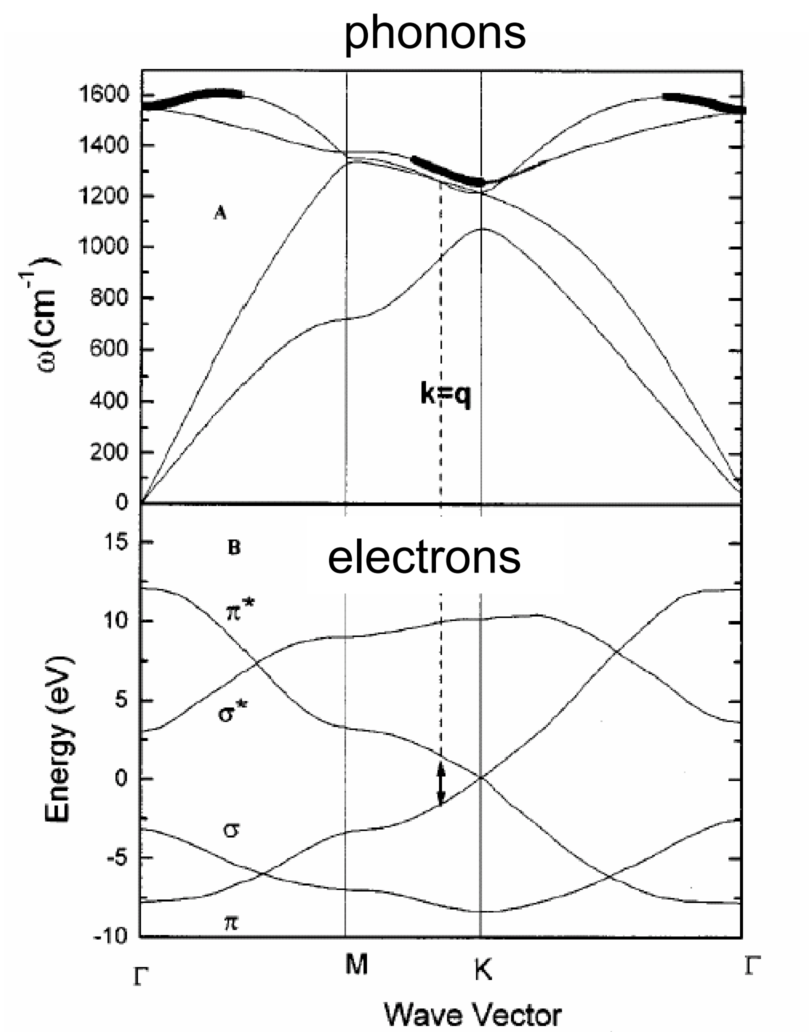


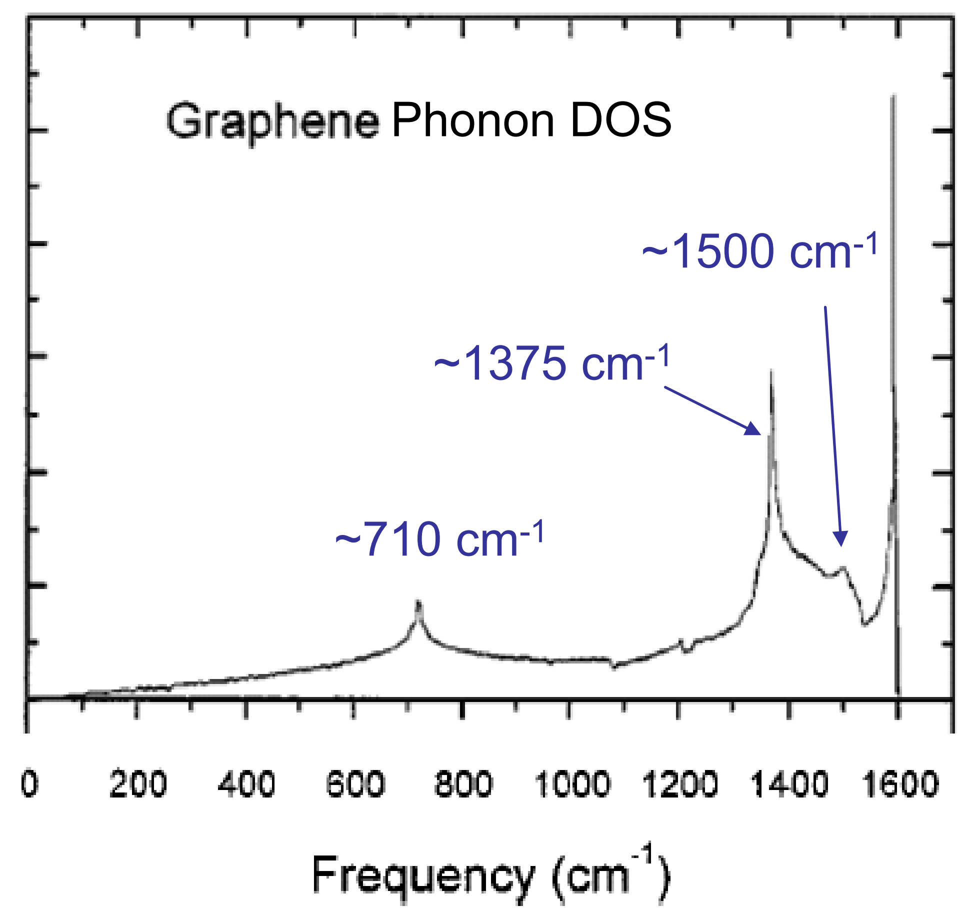
$\omega_G \sim 1/n$

5.5 cm^{-1}



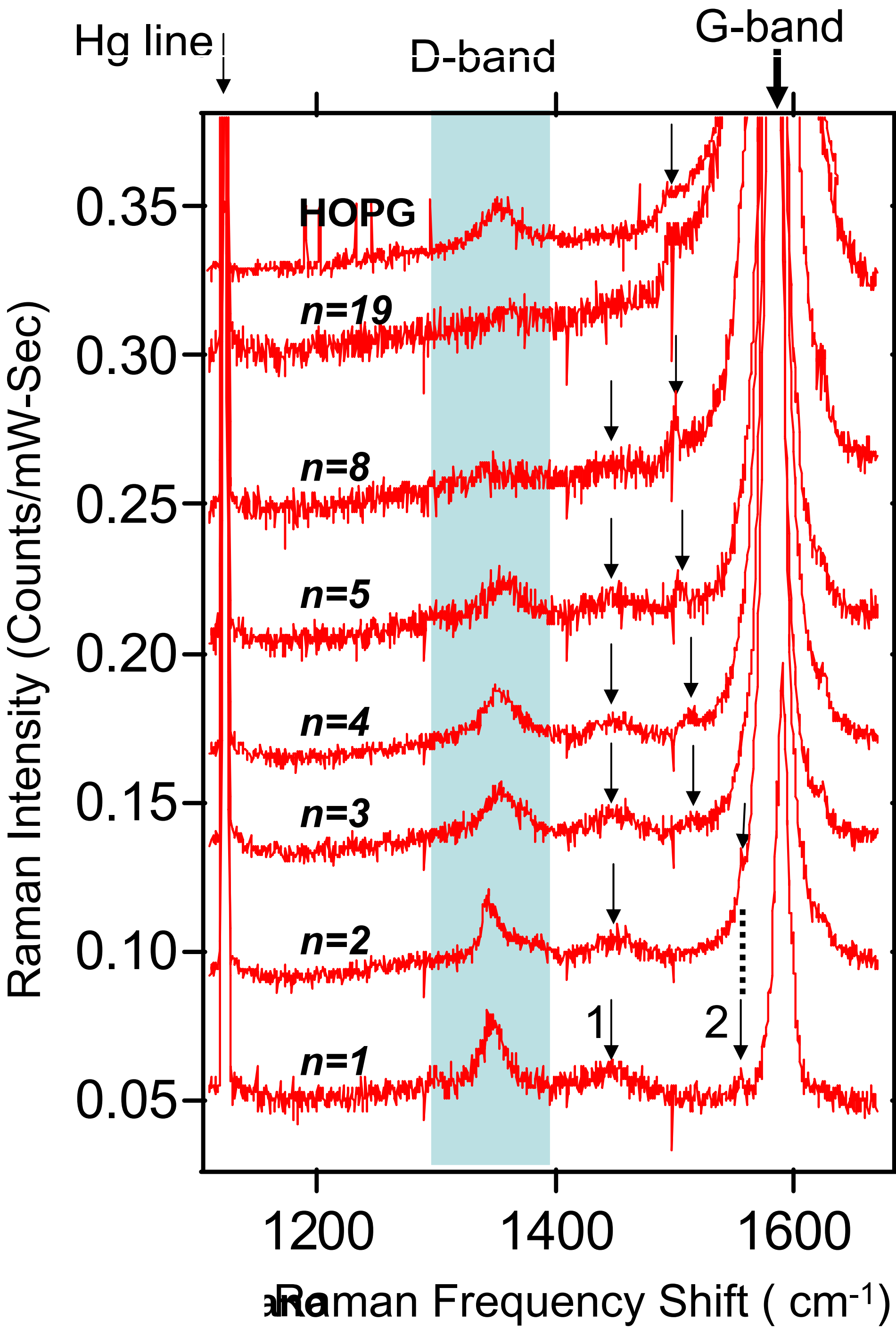
Phonon and Electron Dispersion in Graphene



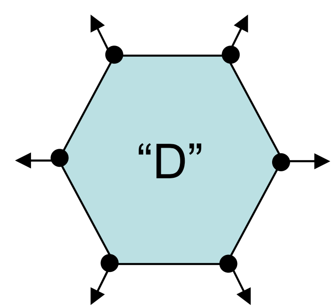


c.f., C. Mapeli et al., Politecnico di Milano (1998) in A. Ferrari and J. Robertson, Phys Rev B61 (2000)

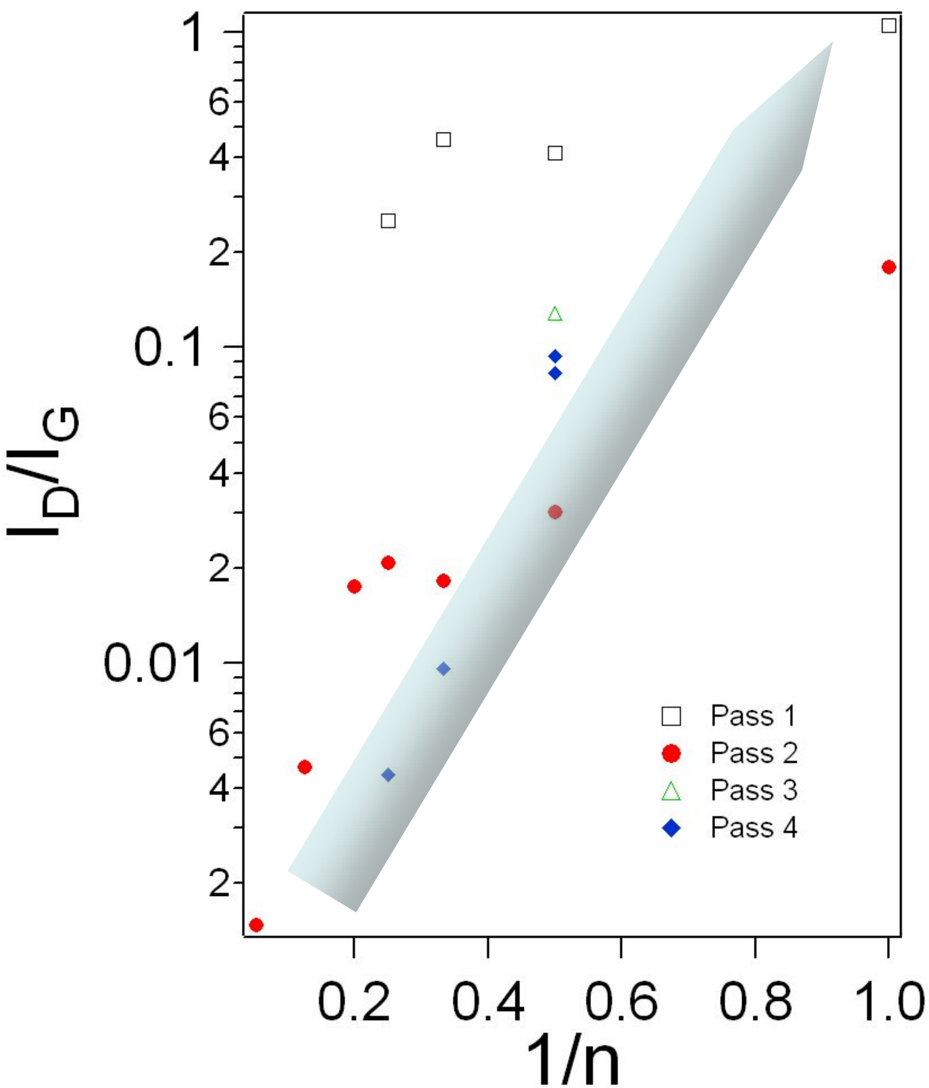
Other weak 1st order Scattering

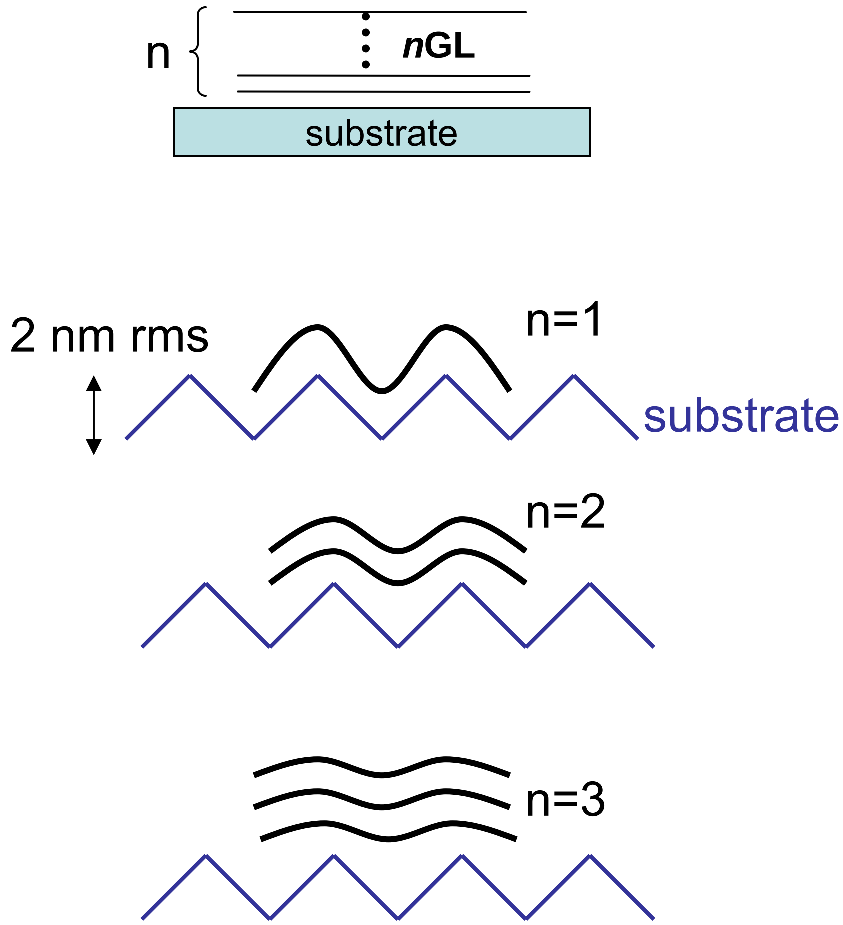


"D"=Disorder-induced Scattering
•Dispersive mode •Zone edge mode •Intensity decreases with increasing n

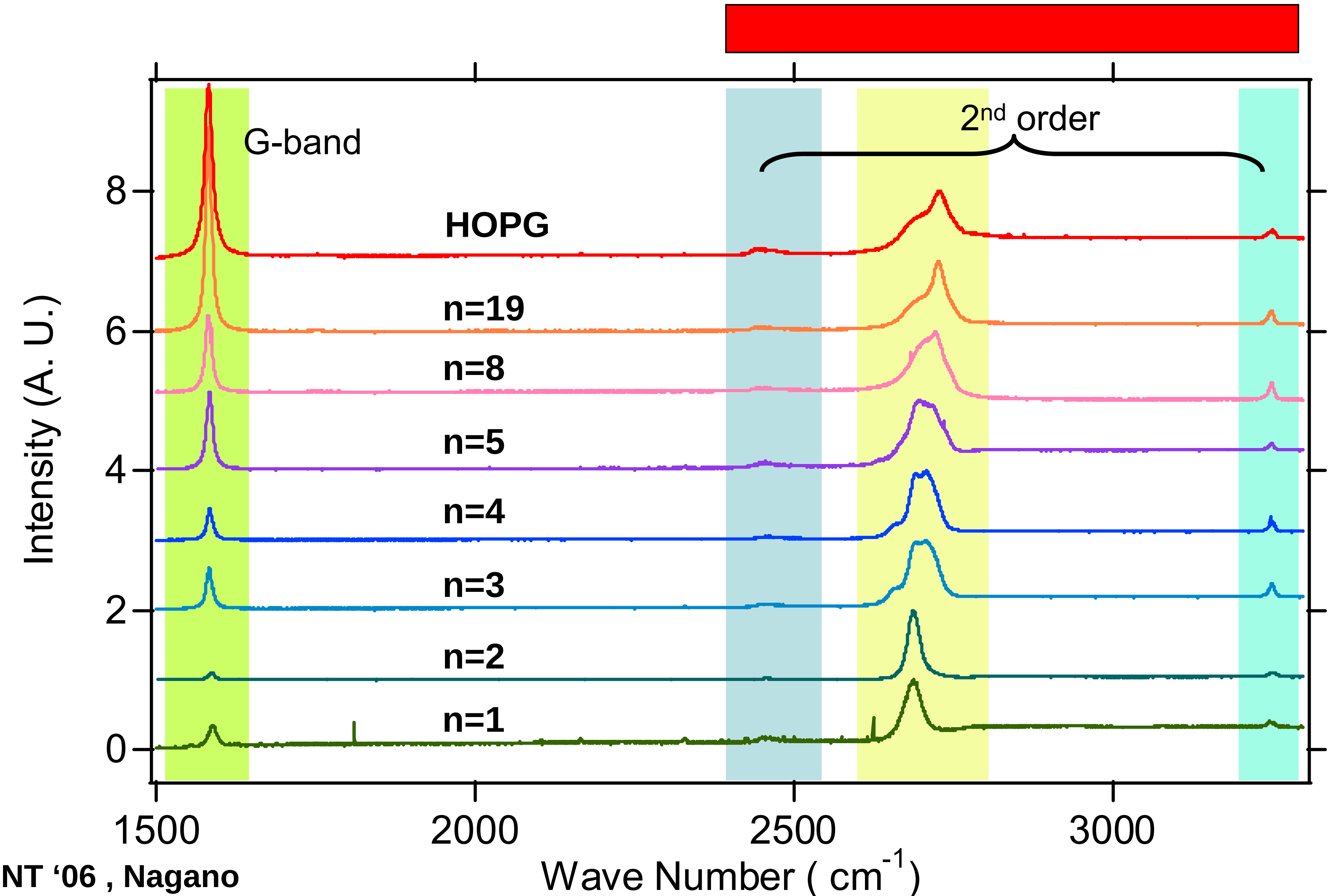


D/G Raman Band Intensity vs 1/n

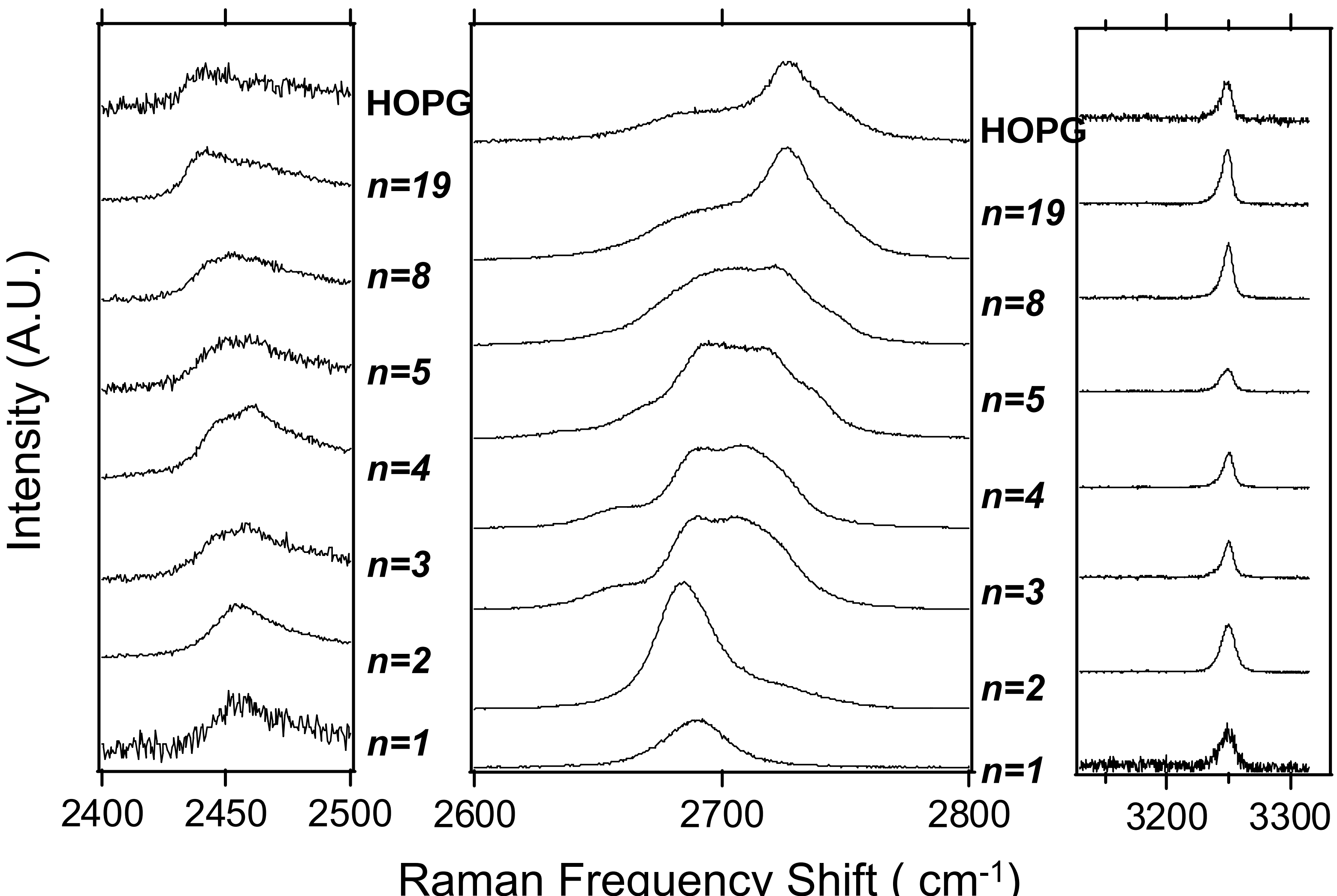




High Freq. Raman Spectrum of *n*GLs



2nd Order Raman Spectra of *n*GLs



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Summary: Chemical Sensors

- Carbon Nanotube and Semiconducting Nanowire FETs show great promise as real-time analytical tools
  - There is *much* to be learned about the sensing mechanism (charge transfer vs electronic scattering)
- HOWEVER, the SWNT cylindrical *shell* geometry should be the most sensitive. We find it is even sensitive to:
  - physisorption (with little or no charge transfer)
  - even collisions of inert gas atoms with the tube wall

Summary: Raman Scattering from nGLs

- Raman Scattering useful to characterize the number of layers in an *n*GL film
- 1st order G-band
  - Contains one Lorentzian
  - G-band upshifts with decreasing n: $\omega_G(n) \sim \omega_{Graphite} + 7\ cm^{-1}(1/n)$
- 2nd Order bands
  - Stronger than G-band for n<5 (unusual behavior!)
  - Mid-freq band (~2700 cm-1) exhibits shape specific to *n*
  - ~2450 cm^{-1} and ~3250 cm^{-1} bands not sensitive to *n*
- D-bands
  - Intensity decreases exponentially with n
  - D-scattering may indicate an n-dependent bending of the thinnest films to conform to the substrate roughness
  - A weak ~1500 cm^{-1} D-band is also n-specific; downshifts with increasing n

Acknowledgements

n-Graphene Layer Films

Penn State:

Dr. Gugang Chen

Awnish Gupta

Prof S. Tadigadapa

Prasoon Joshi

SWNT Gas Sensors:

Prof K. Bolton, Chalmers/Goteborg

Prof Arne Rosen, Chalmers/Goteborg

Prof. G.D. Mahan, Penn State

Dr. Hugo Romero (U, Penn)

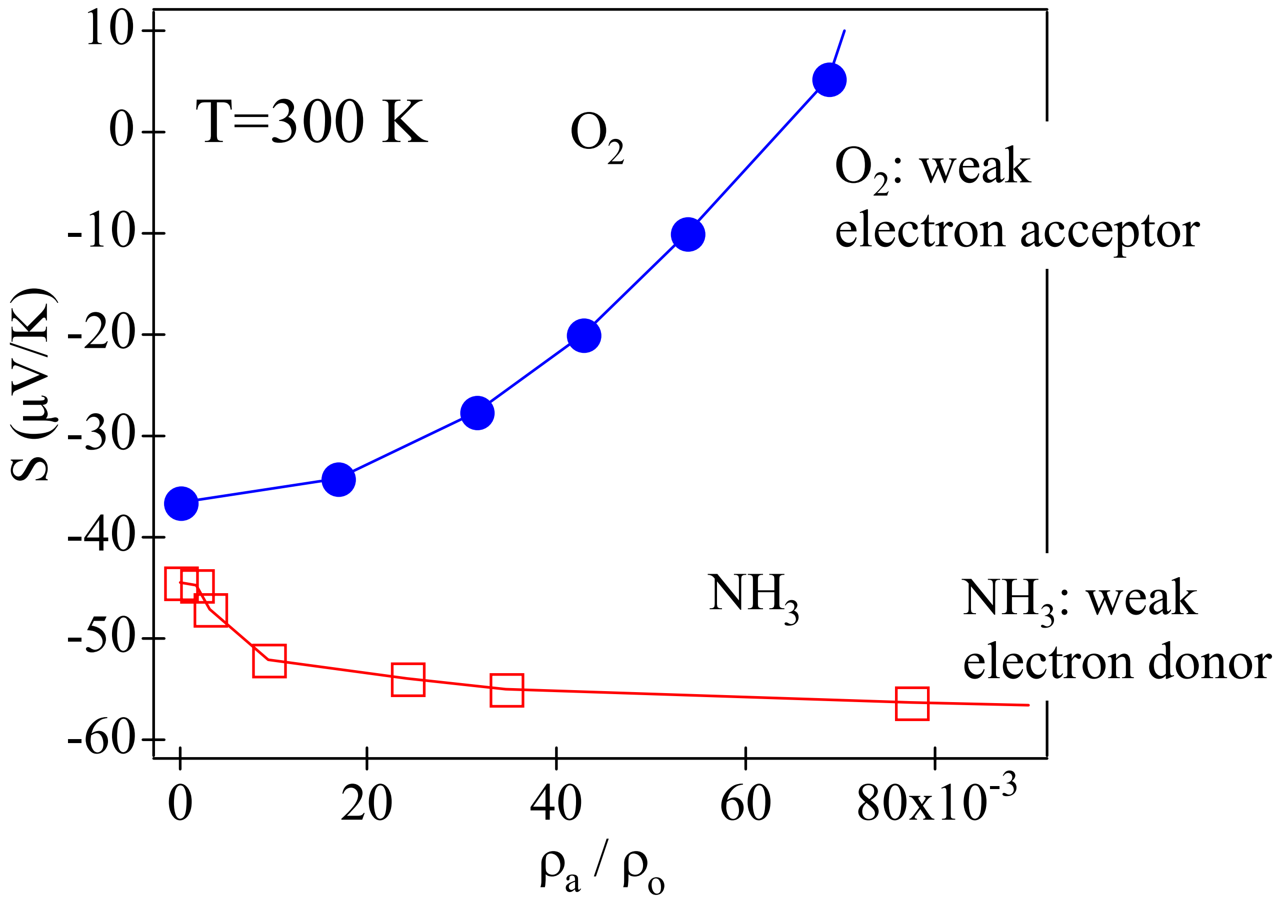
Prof. G. Sumanasekera (U. Lou'ville)

Dr. UnJeong Kim (Samsung)

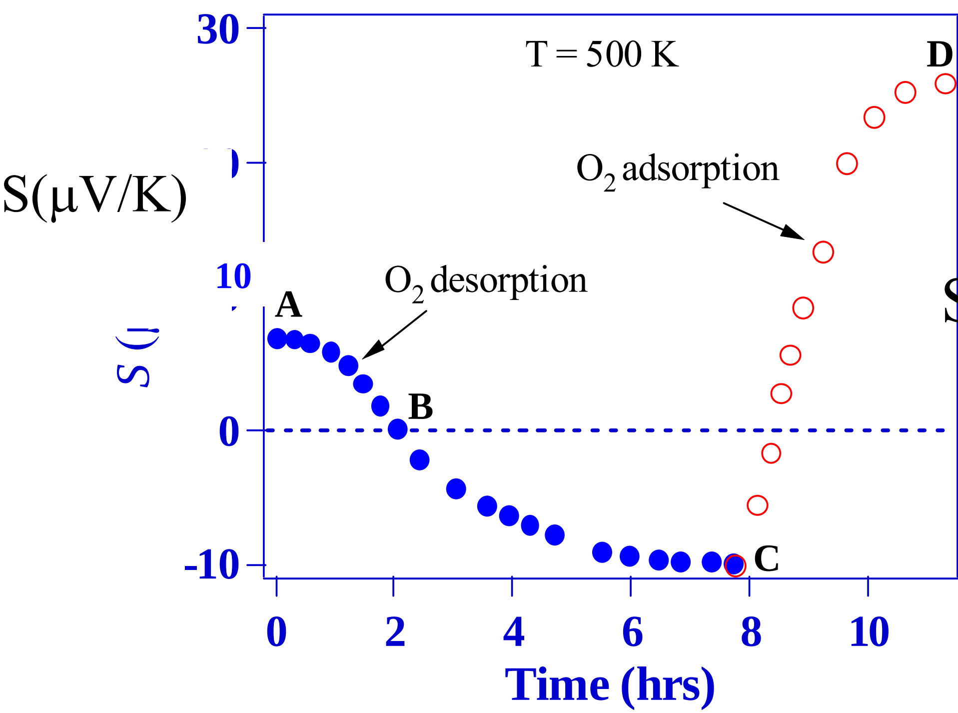
Funding/Support: United States National Science Foundation, Penn State Materials Research Institute, CarboLex, Inc.

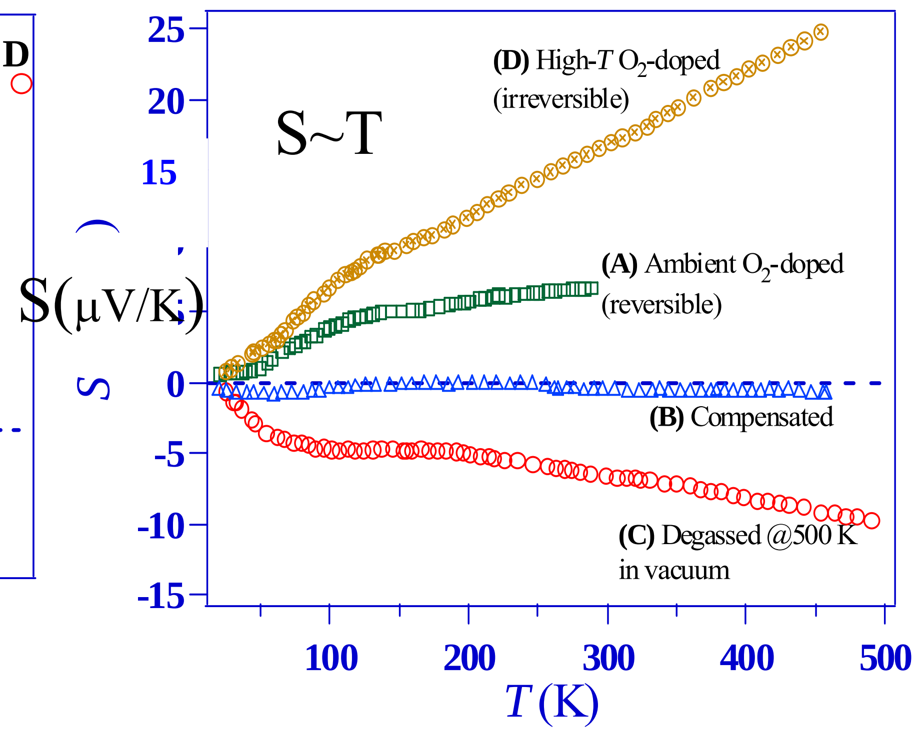
Supplementary Slides

(Non-Linear) Thermopower vs. Extra Resistance (Chemisorption)



Effects of Oxygen Exposure





P. G. Collins,..., A. Zettl, Science **287**, 1801 (2000)
G.U. Sumanasekera,...,P.C. Eklund, Phys. Rev. Lett. **85**, 1096 (2000)
K. Bradley *et al*, Phys. Rev. Lett. **85**, 4361 (2000)
H. Romero,..., P. C. Eklund, Phys. Rev. B., 65, 2054 (2002)