One-Dimensional Electron and Thermal Transport in Suspended Carbon Nanotubes

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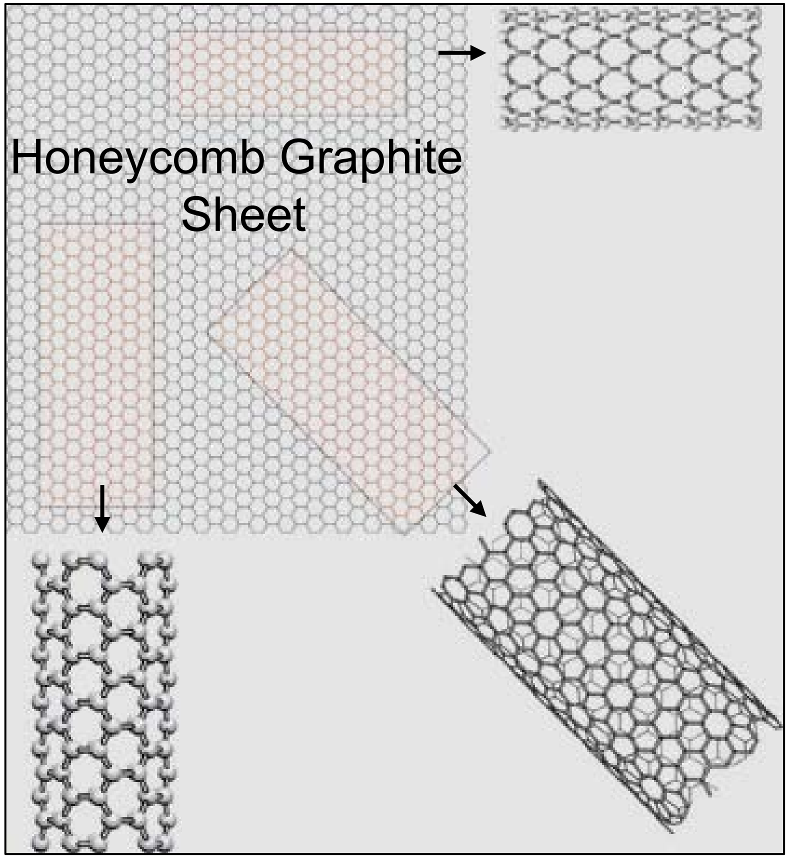
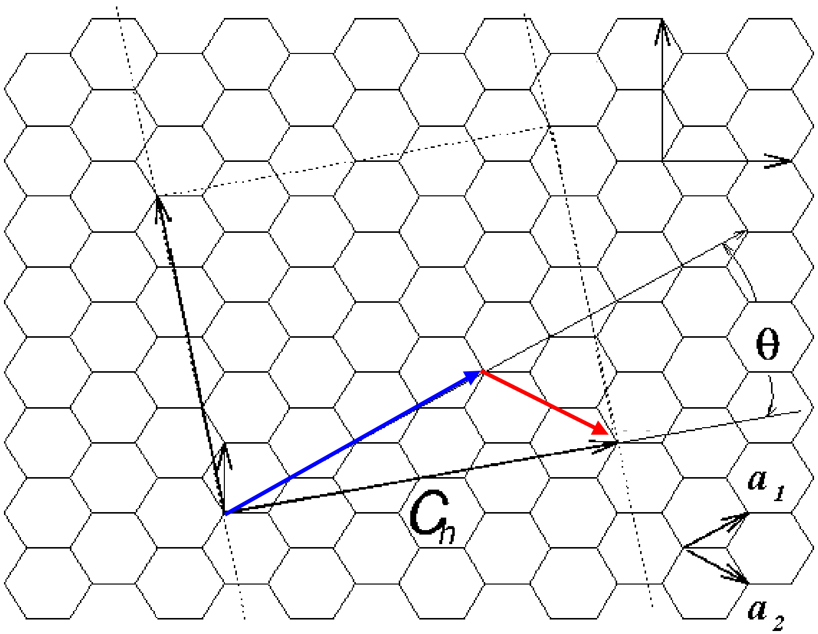
University of Texas, Austin

What is a Carbon Nanotube?

Imagine rolling a sheet of graphite into a seamless cylindrical tube.

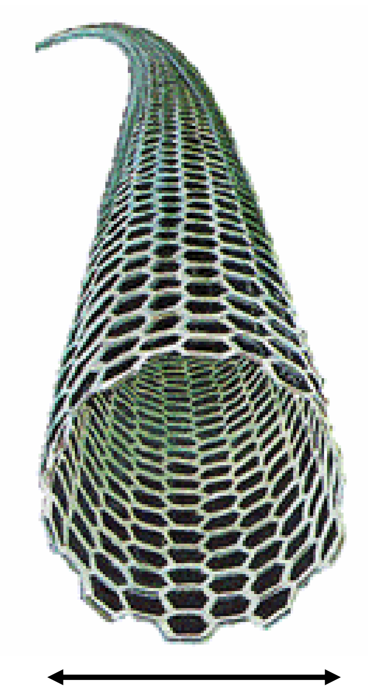


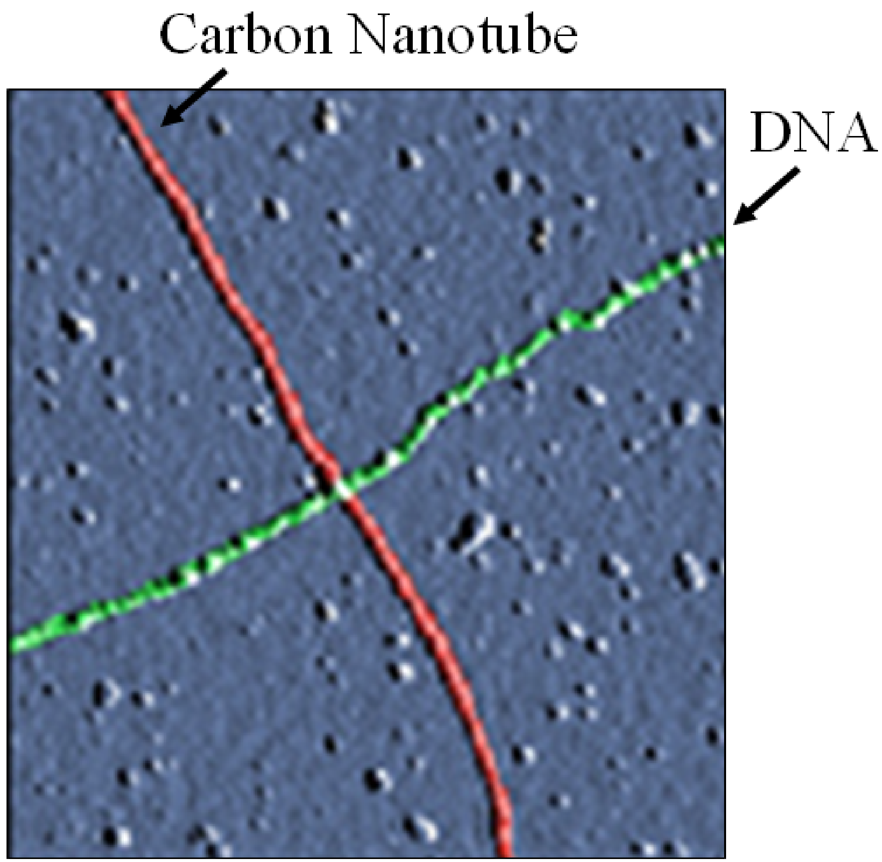


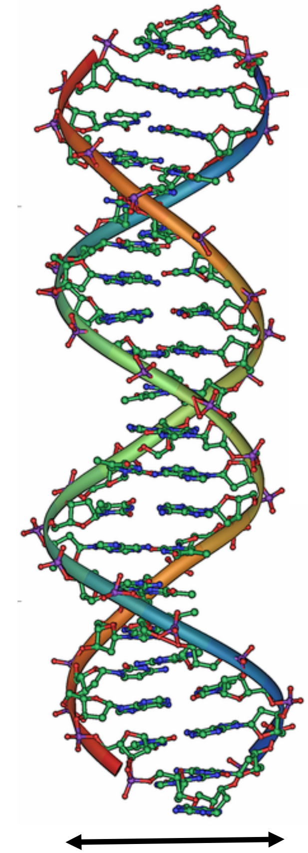
Chirality *(n,m)*:

$C_h = 4a_1 + 2a_2 = (4,2)$

Atomic Force Microscope (AFM)







Single Walled Carbon Nanotubes (SWNTs).

Bockrath, et al., Nano Lett., **2**, 187 (2002).

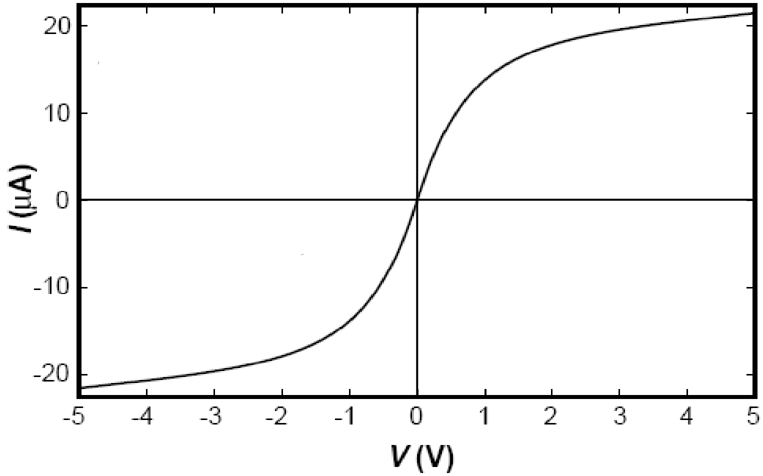
Why Study Carbon Nanotubes?

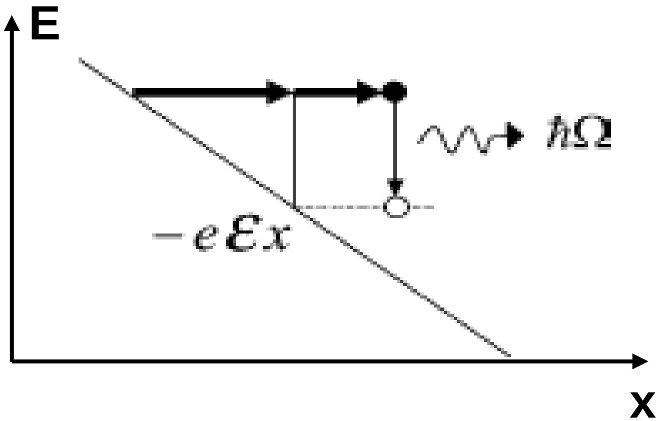
- 1nm in diameter, 1cm in length, aspect ratio ~10^7
- 100% surface-to-volume ratio
- 1 defect in 10^{12} C atoms => ballistic conduction
- High melting point ~3800^{o}C
- High Young's modulus 1TPa (> diameter)
- High electronic current carrying capacity (10^9A/cm^2) ~10^3 times higher than that of the noble metals
- Thermal conductivity 6600W/mK at room temperature is twice the maximum known bulk thermal conductor, isotropically pure diamond = 3320W/mK

Despite 46,000 publications, no large scale commercial applications of nanotubes

Review: High Field Transport

- Carbon nanotubes have extremely high current density threshold ~ $10^9 A/cm^2$.



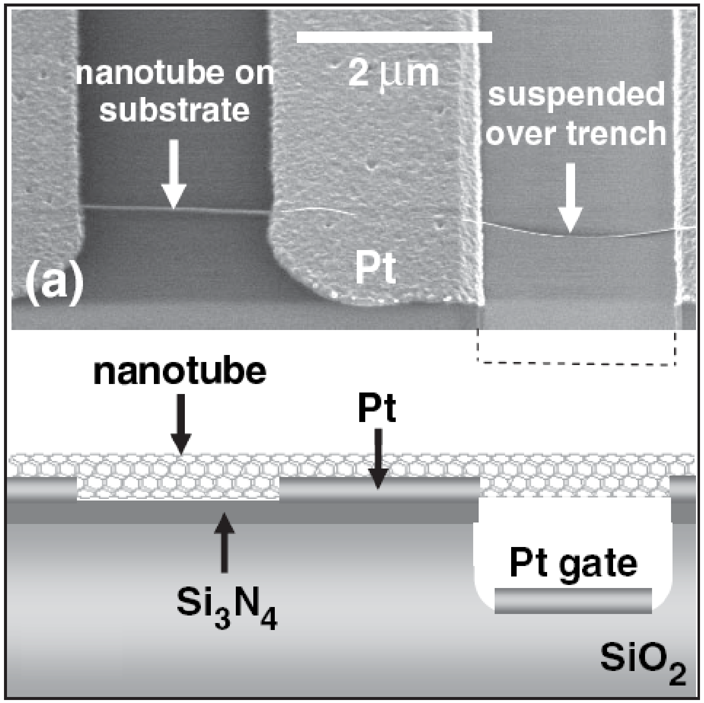


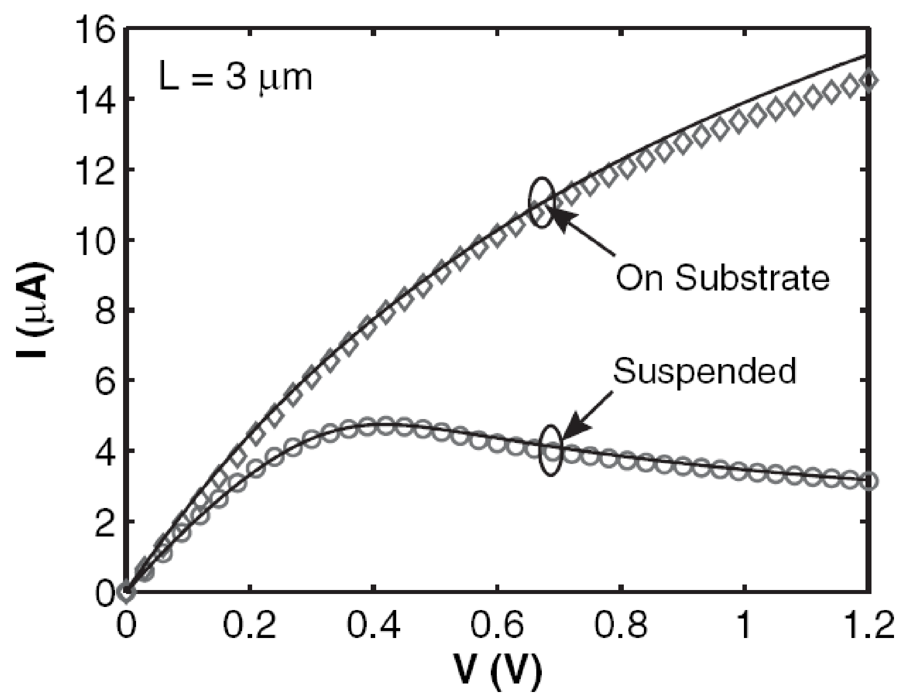
- Yao *et al.* proposed *G* band optical phonon emission.

Yao *et al*. PRL **84,** 2941 (2000).

Radosavljevic, *et al,* PRB, **64**, 241307 (2001).

Review: High Field Transport





- Suspended nanotubes with low contact resistance show negative differential conductance.
  - Landauer Model

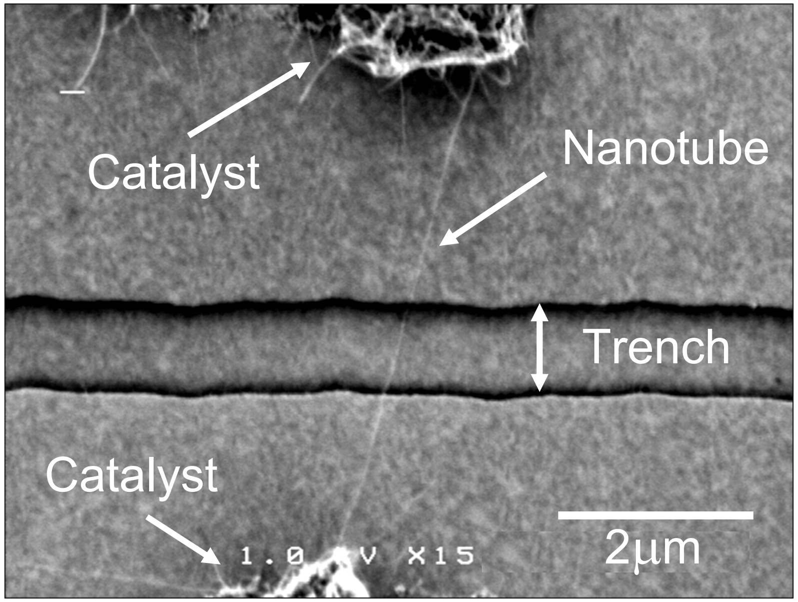
Pop, *et al.* PRL **95,** 155505 (2005)

Using Raman Spectroscopy…

What is the temperature of the nanotube at each point on the I-V curve?

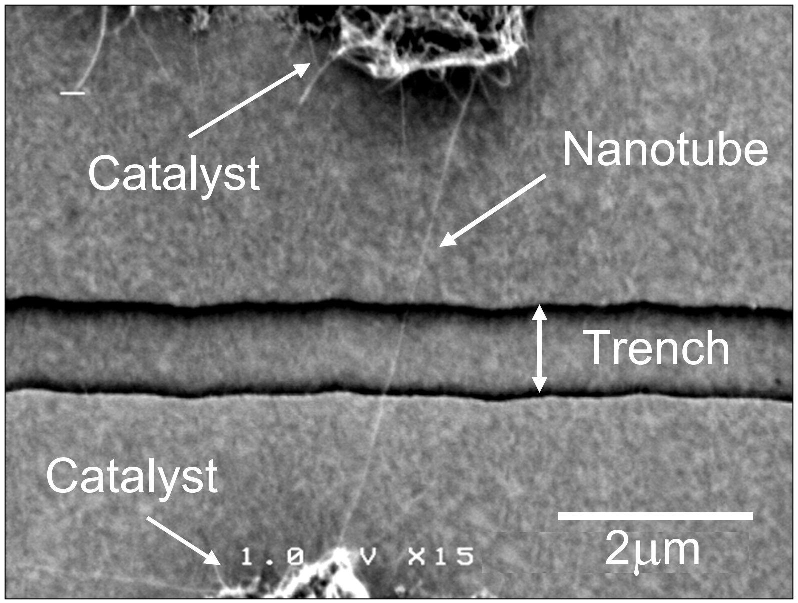
Can we observe optical phonon emission?

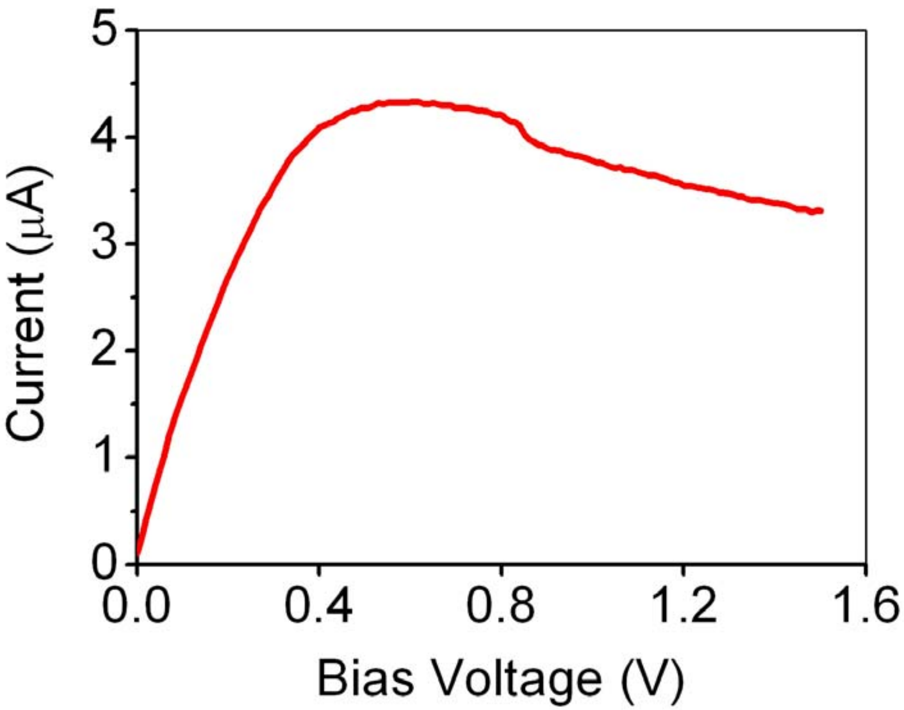
Sample Fabrication



- Pt electrodes deposited on top of trenches etched in Si/SiO_2.
- Catalyst patterned lithographically
- Nanotubes are growth in a mixture of methane and hydrogen over the wafer at 800°C.
- Measure the nanotubes, as-grown.

Negative Differential Conductance

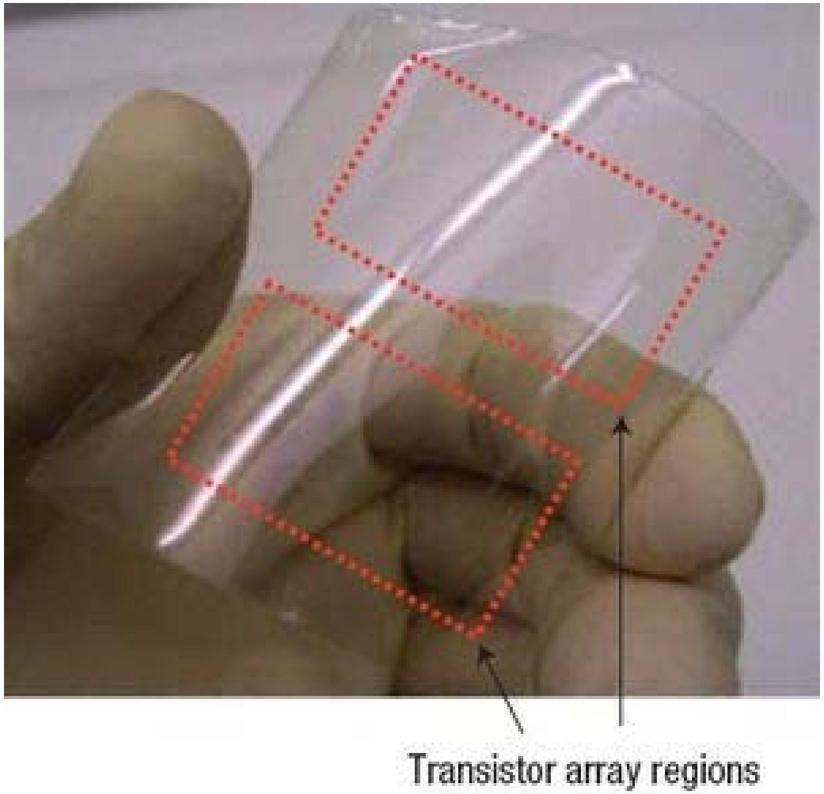




- Selected individual metallic nanotubes exhibiting NDC
- Pristine, highly crystalline, as-grown nanotubes
- Measure the intrinsic properties of nanotube

Carbon Nanotube Applications

Space Elevator



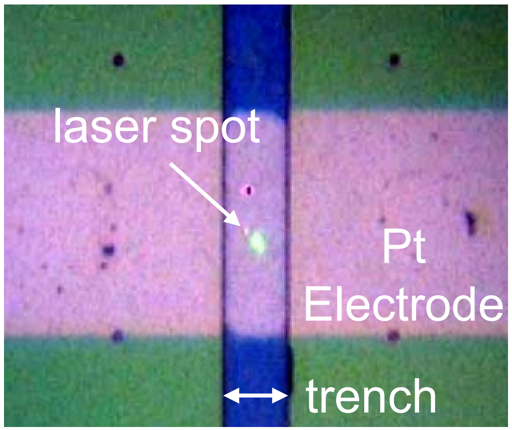
Flexible Electronics

Source: IEEE Spectrum, Aug 2005

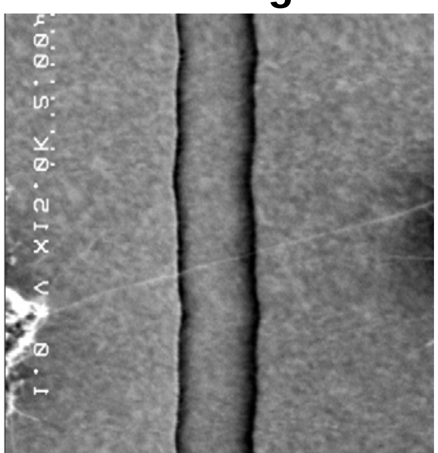
Ju, et al., Nature 2007

Experimental Setup

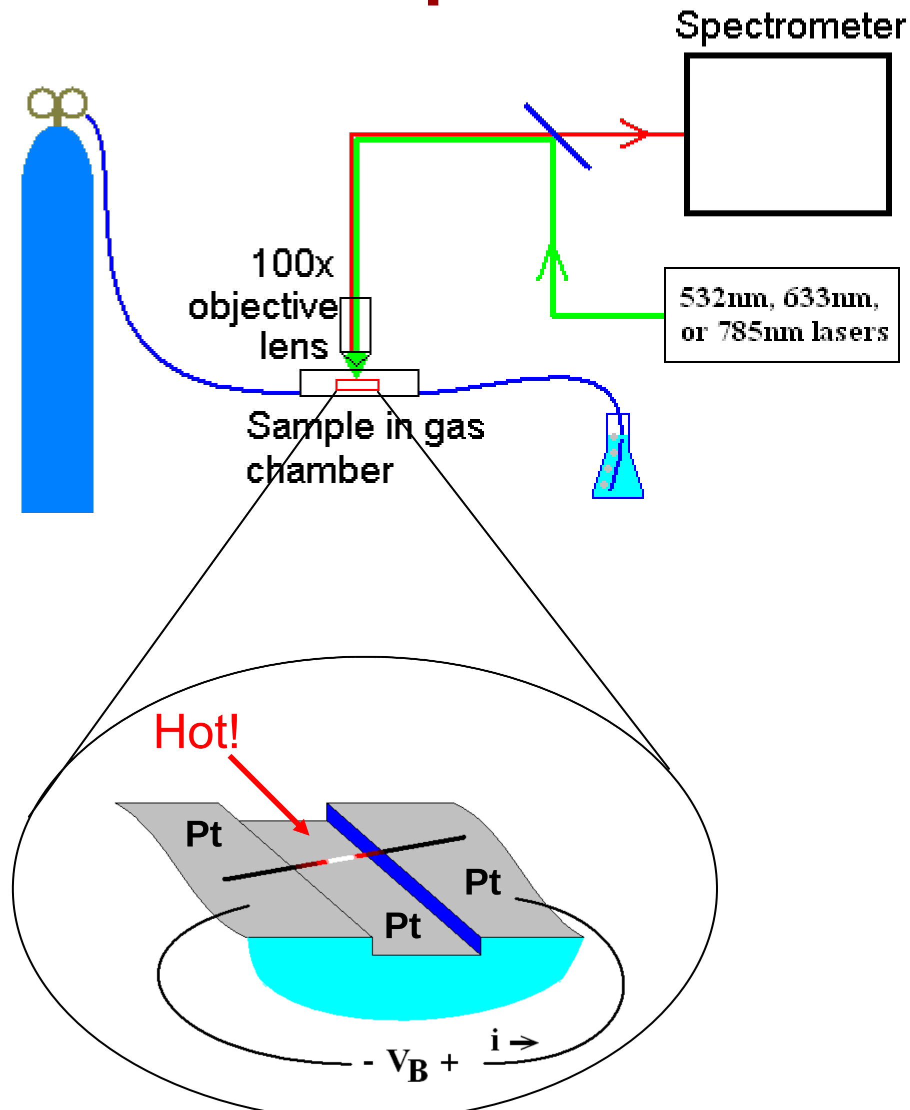
Optical Microscope Image:



SEM Image:

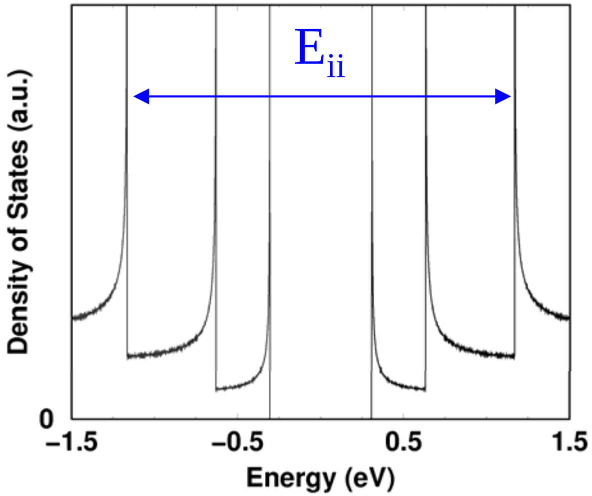


Our device (example)

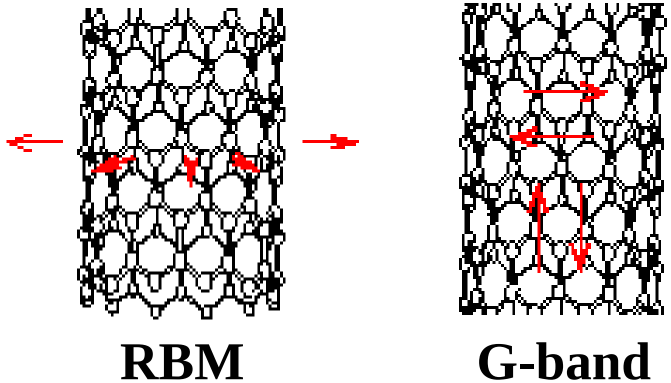


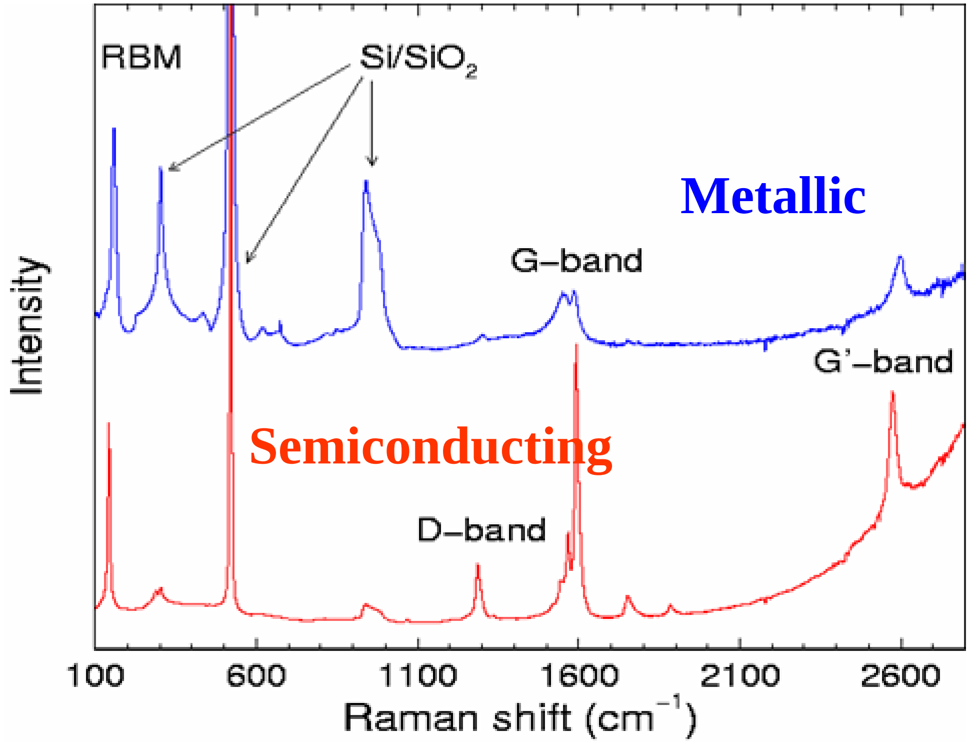
Single Nanotube Raman Spectroscopy

Despite the extremely small geometric cross-section the Raman signal from a single isolated nanotube can be observed.



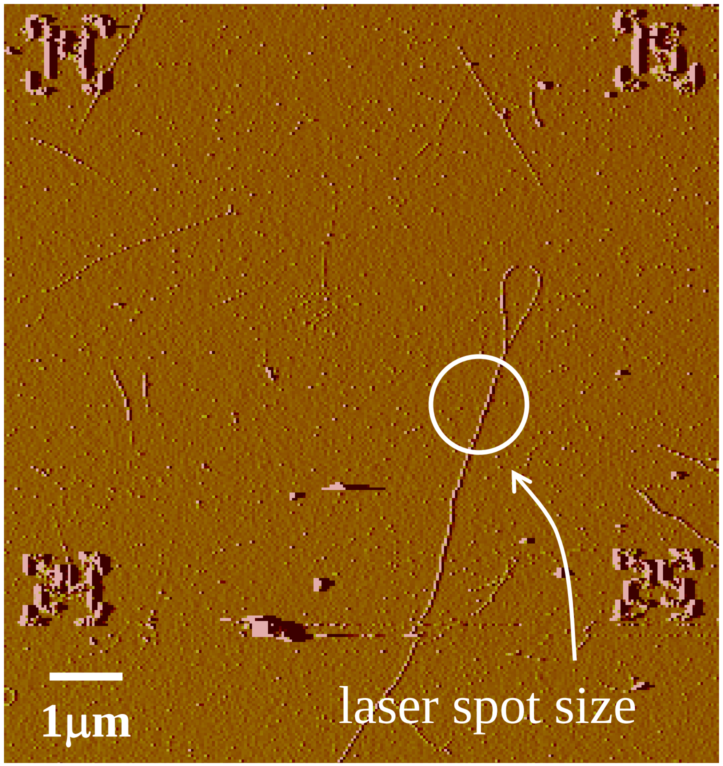
- 10^5 enhancement in scattering cross-section due to singularities in the DOS
- Resonance occurs when $E_{laser}=E_{ii}$
- Only observe nanotubes that are resonant with E_{laser}



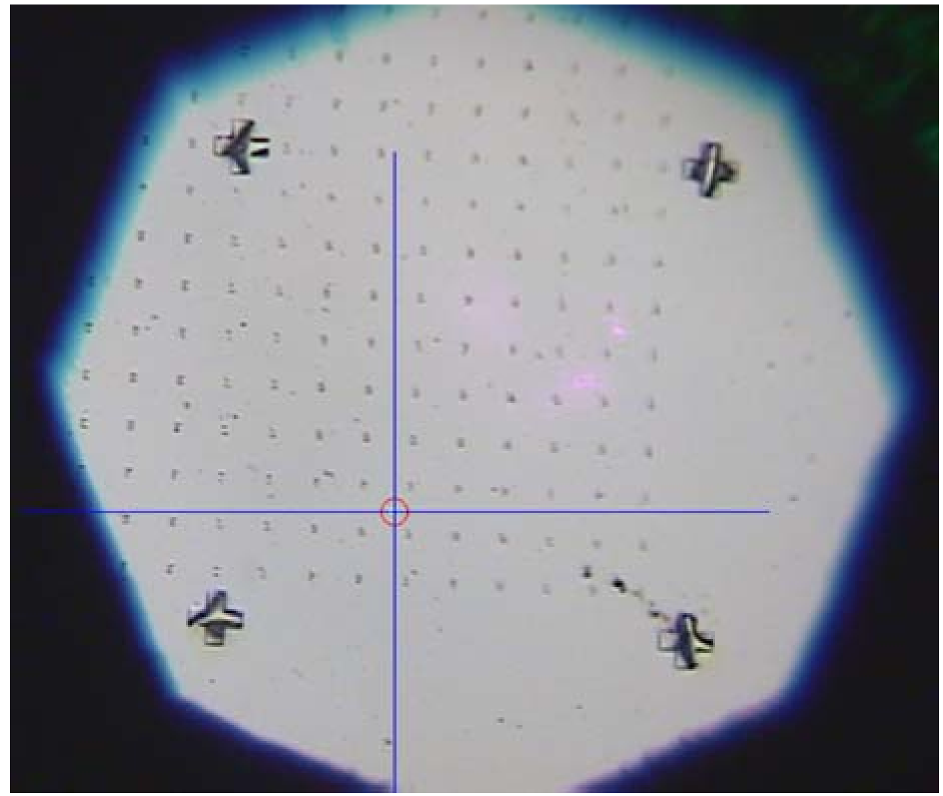


Jorio, *et al*., PRL, **86**, 1118 (2001)

Nanotubes on a Substrate with Grid Patterned by *e*-Beam Lithography

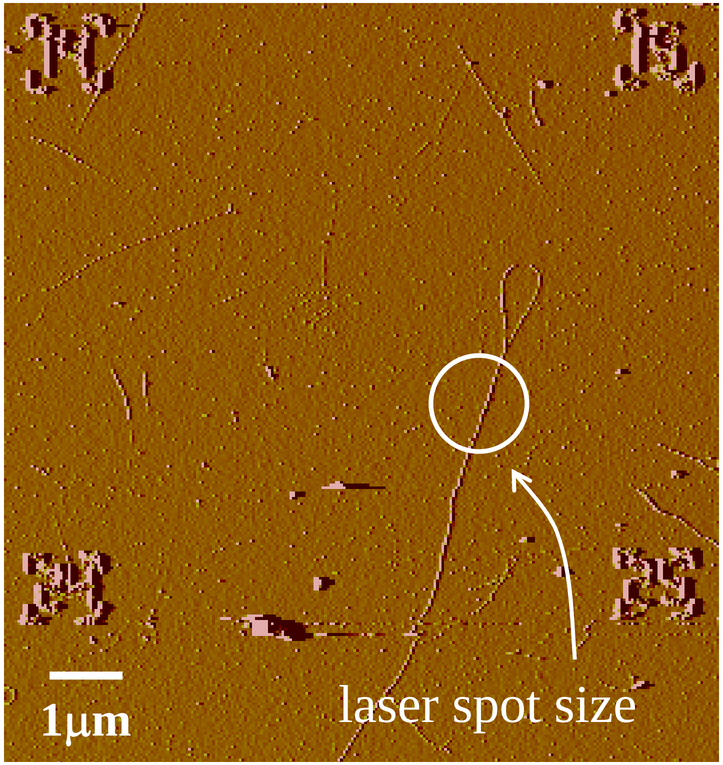


AFM Image

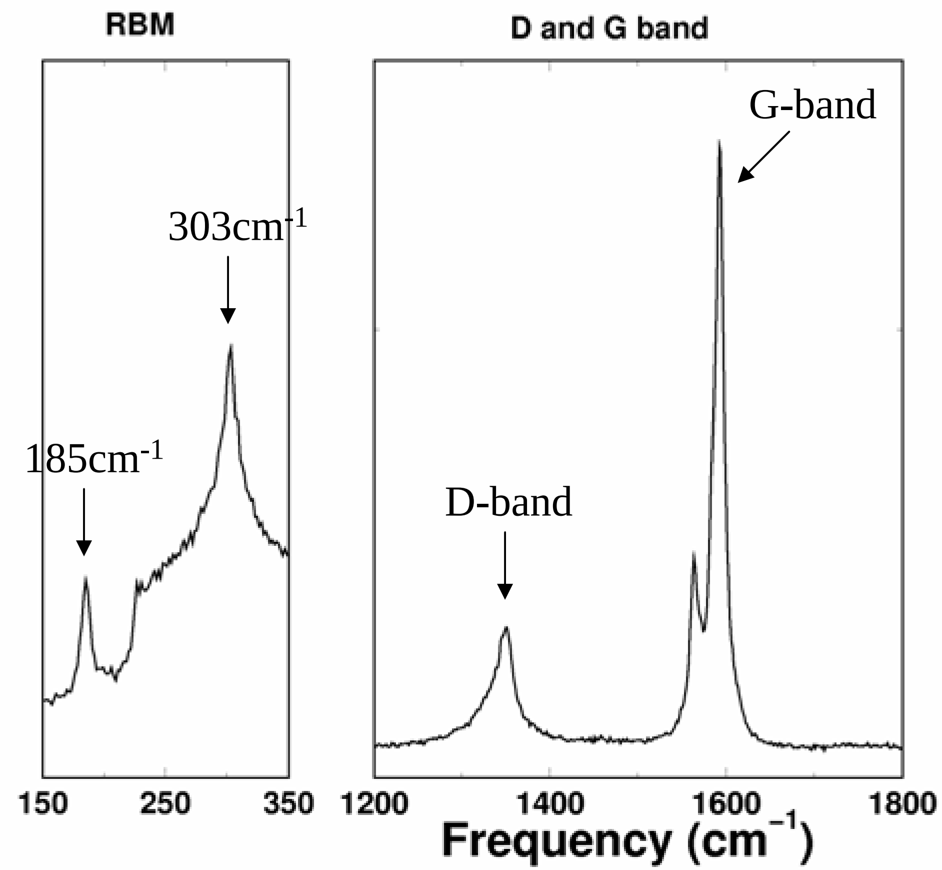


Optical Image

Raman Spectroscopy of Individual Nanotube on a Substrate with Grid



AFM Image



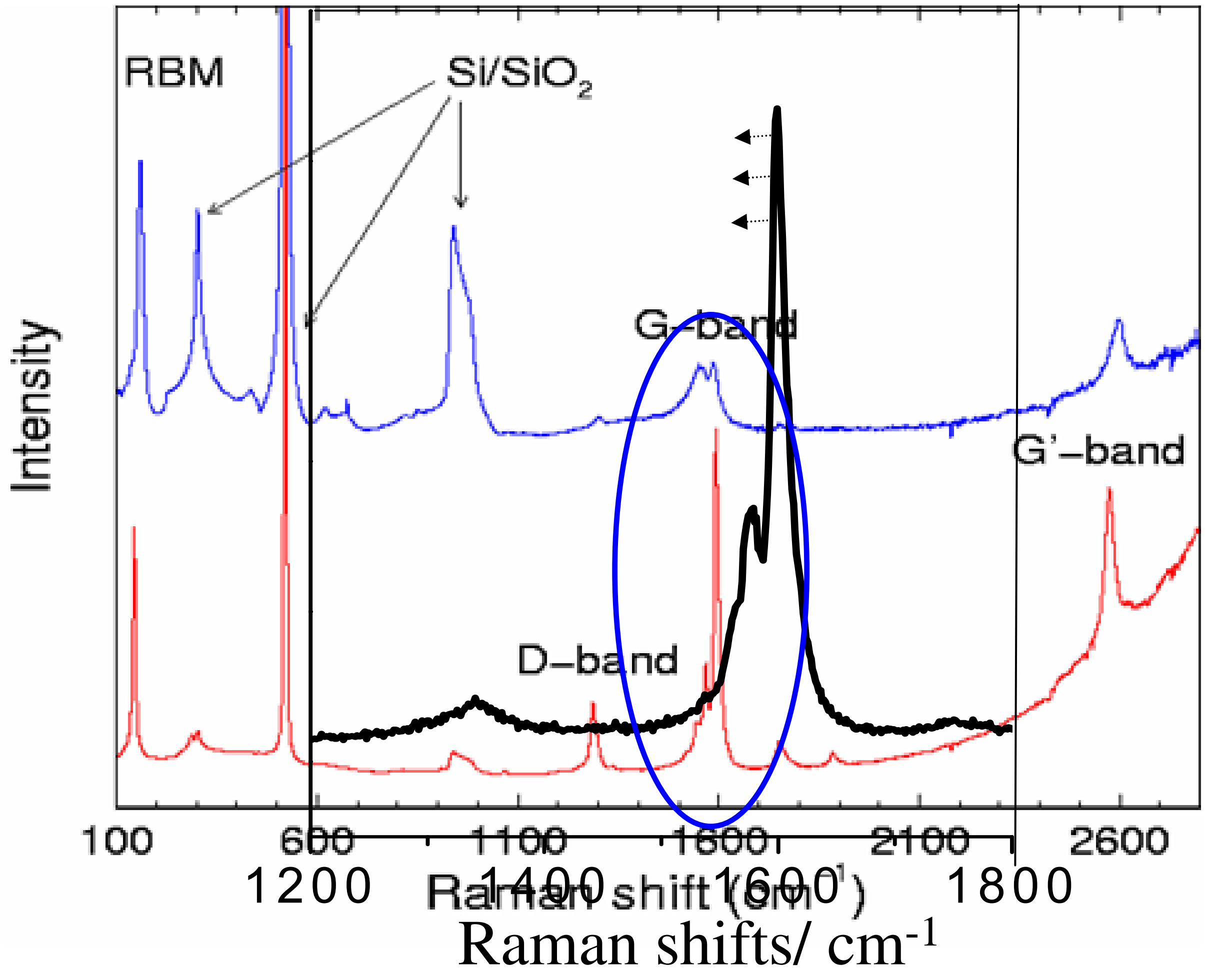
Raman Spectrum

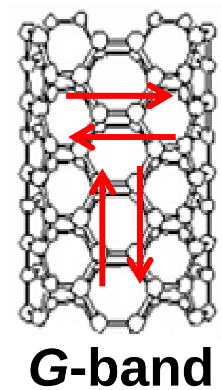
Raman tells us:

- Metal / Semiconducting nature → *G* Band lineshape
- Diameter (±5%) → Inverse to RBM
- Electronic transition energies (E_{ii}) → Laser Energy
- Rough chirality *(n,m)* → E_{ii} and ω_{RBM}
- Orientation of a nanotube → Polarized Raman Intensity
- Defect concentration → *D* Band Intensity
- Strain / Temperature effects → *G* band frequency shift
- Non-contact
- Non-destructive

Raman Spectra

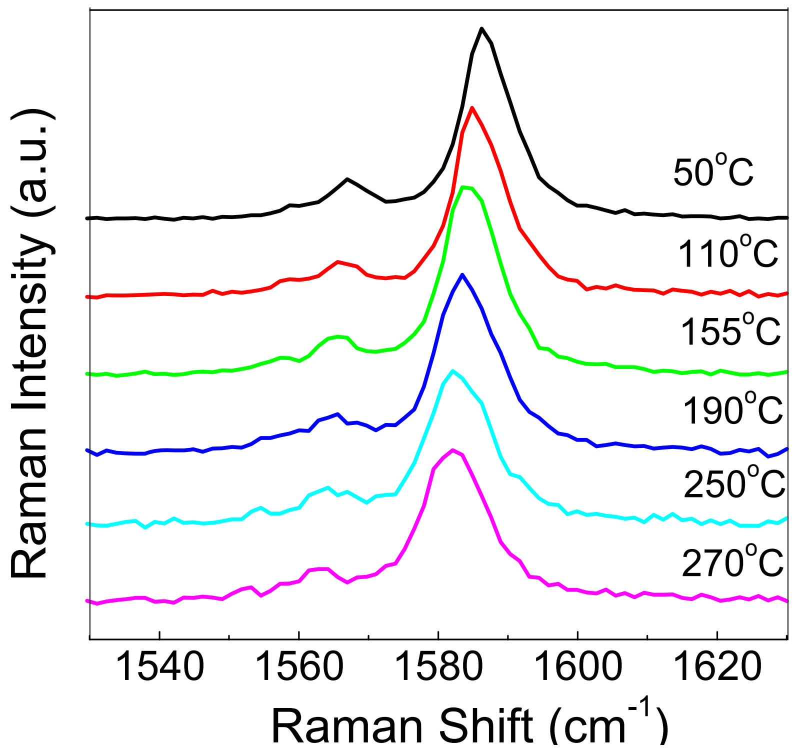
- Downshift of the *G*-band is caused by thermal expansion when the laser heats the nanotube and lengthens the interatomic C-C length.

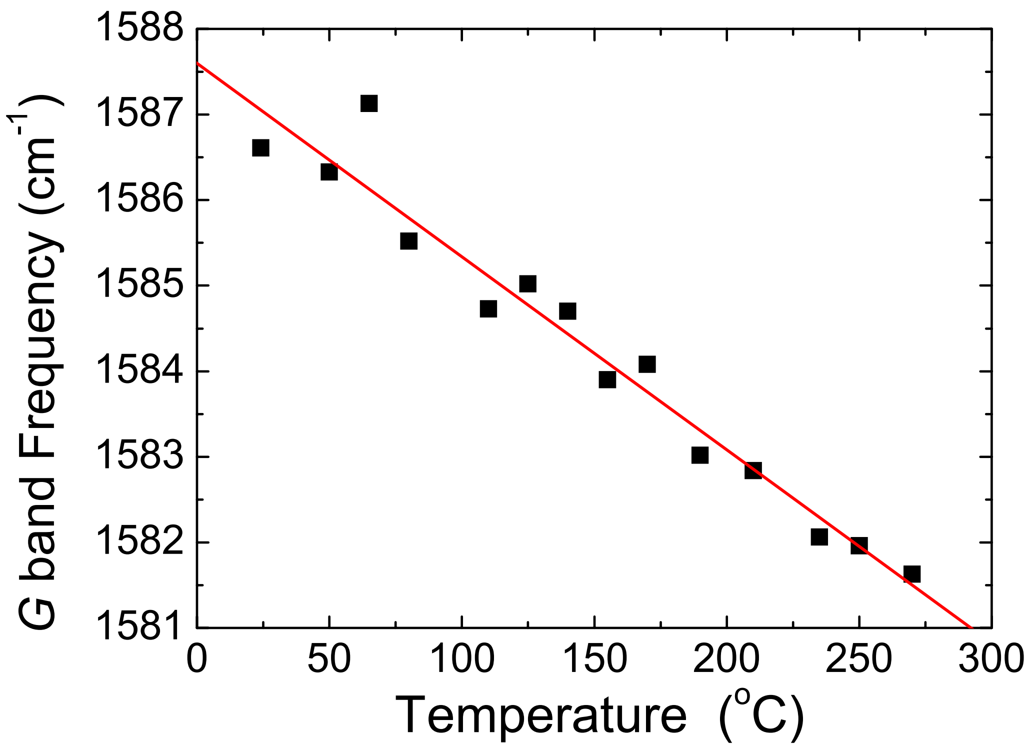




Jorio, *et al.*, PRL, **86**, 1118 (2001)

Temperature Coefficient of *G* band





TOC= -0.044cm^{-1}/K, Atashbar, *et. al., App. Phys. Lett.* 86, 123112 (2005)

TOC= -0.042cm^{-1}/K, H. D. Li, *et. al., App. Phys.* 76, 2053 (2000)

TOC= -0.028cm^{-1}/K, Huang, *et. al., App. Phys.* 84, 4022 (1998)

I.K. Hsu, *et. al.,* App. Phys. Lett. 92, 063119 (2008)

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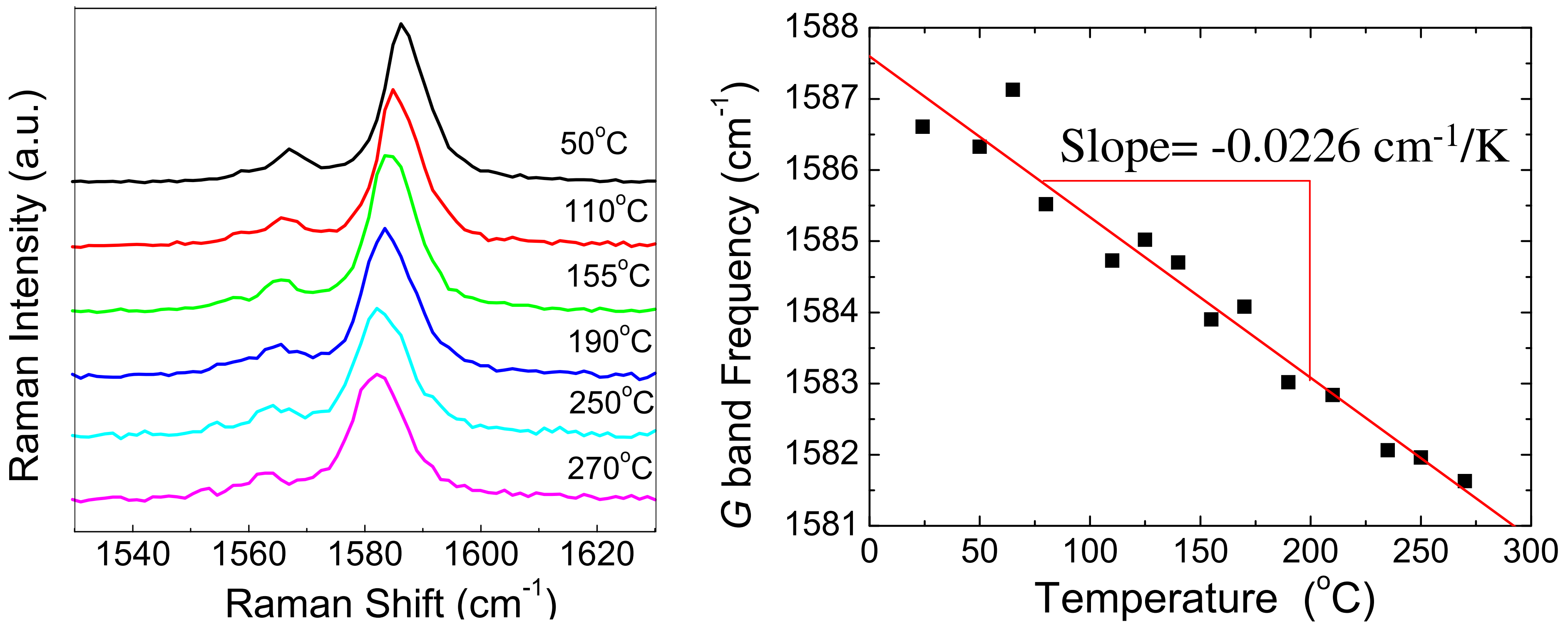

Temperature coefficient of *G* band shifts= -0.0226 cm^{-1}/K

TOC= -0.044 cm^{-1}/K, Atashbar, *et. al., App. Phys. Lett.* 86, 123112 (2005)
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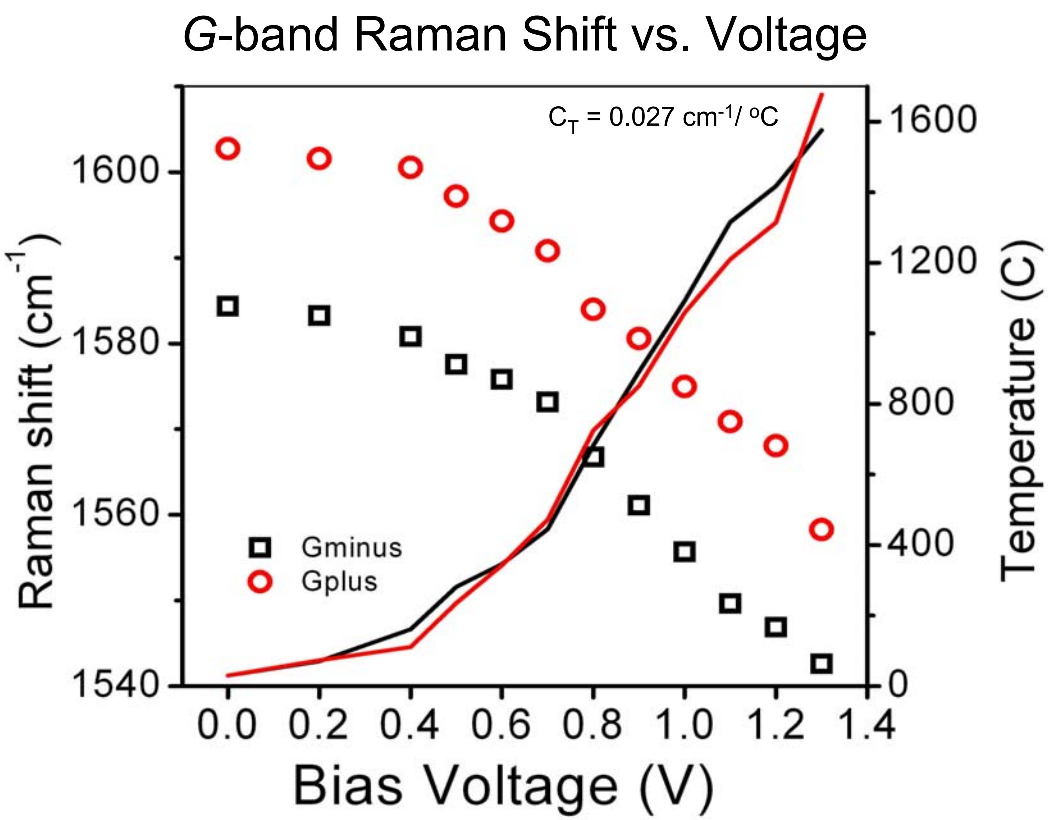
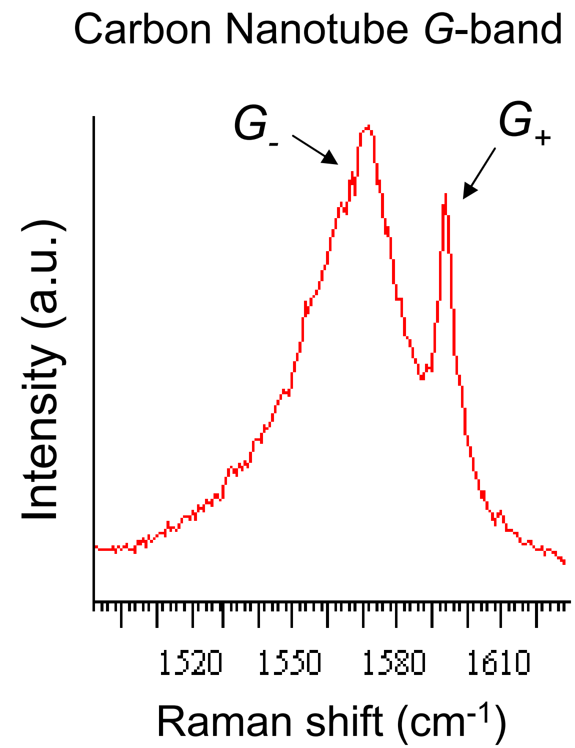
Electrical Heating



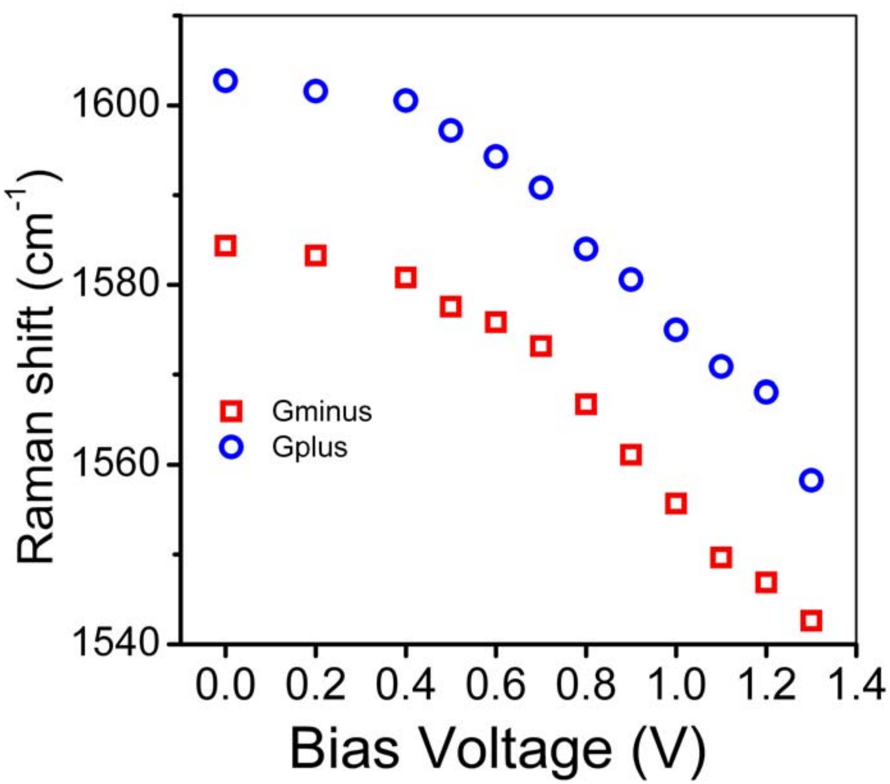


Nanotube reaches 1600ºC at high voltage bias

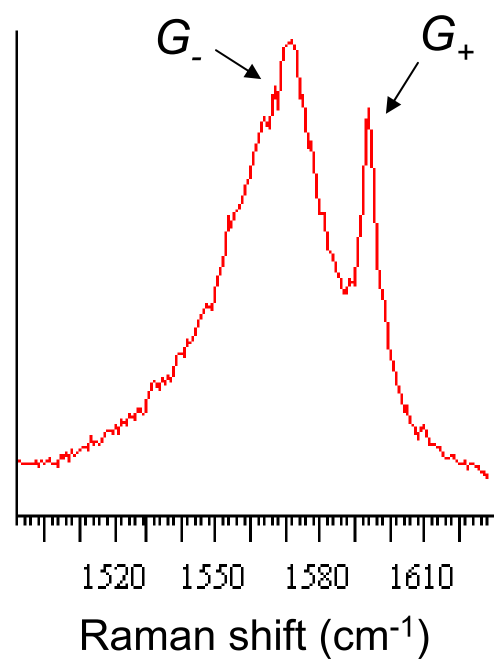
Bushmaker *et al*. Nano Lett. **7,** 3618 (2007)

Electrical Heating

G-band Raman Shift vs. Voltage



Carbon Nanotube *G*-band



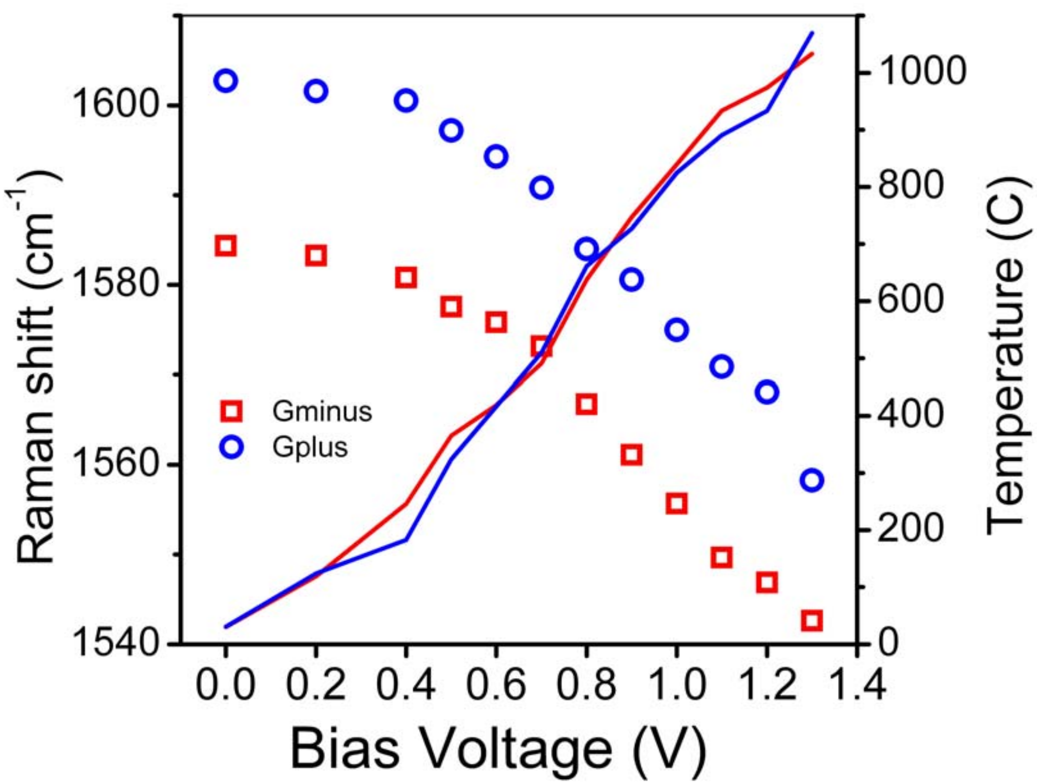
Nanotube reaches 1000°C at high voltage bias, with quadratic fit.

Chiashi, et al, Jpn. J. Appl. Phys., **47**, 2010 (2008).

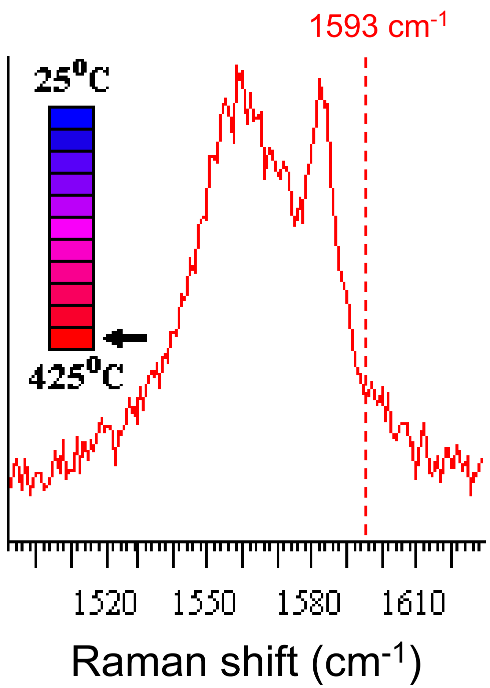
Bushmaker *et al*. Nano Lett. **7,** 3618 (2007)

Electrical Heating

G-band Raman Shift vs. Voltage



Carbon Nanotube *G*-band



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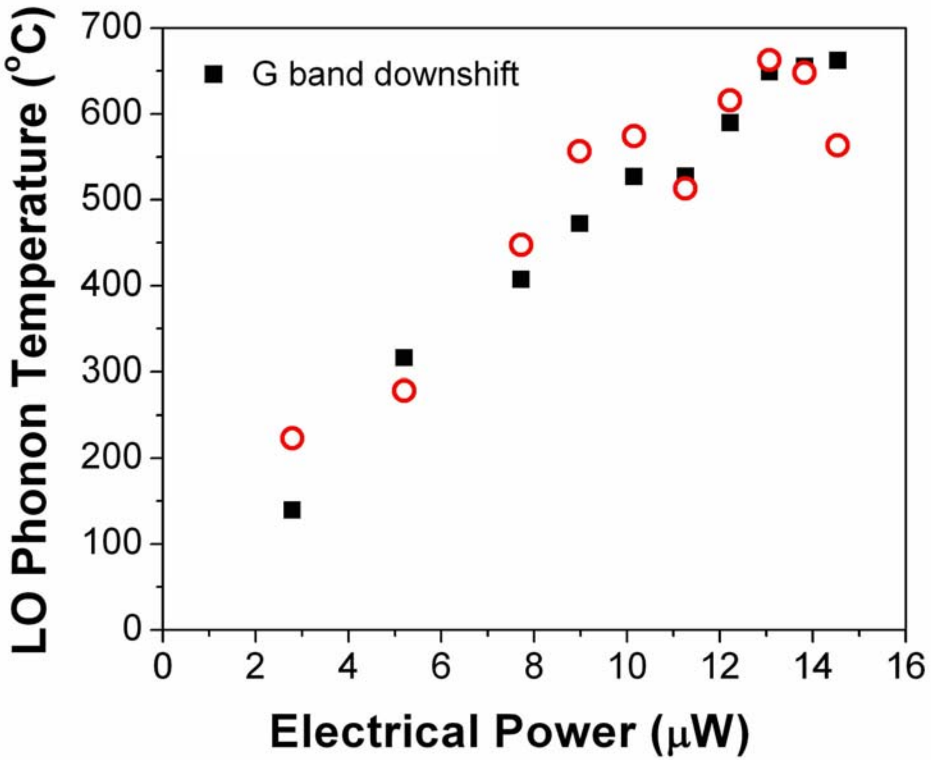
Bushmaker *et al*. Nano Lett. **7,** 3618 (2007)

Comparison of Raman Downshift vs. Stokes/AS Temperature Measurement



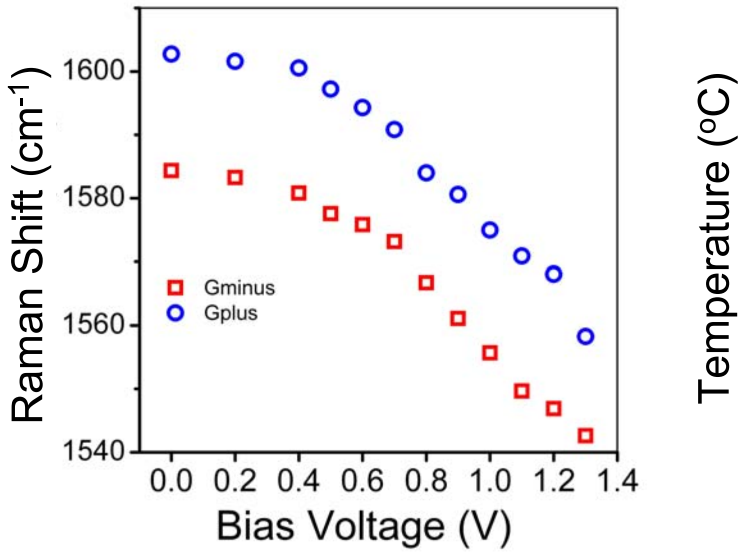
Anti-Stokes thermal factor:

$$e^{-E_{ph}/k_B T}$$

High temperatures were corroborated with AS spectroscopy

Bushmaker *et al*. Nano Lett. **7,** 3618 (2007)

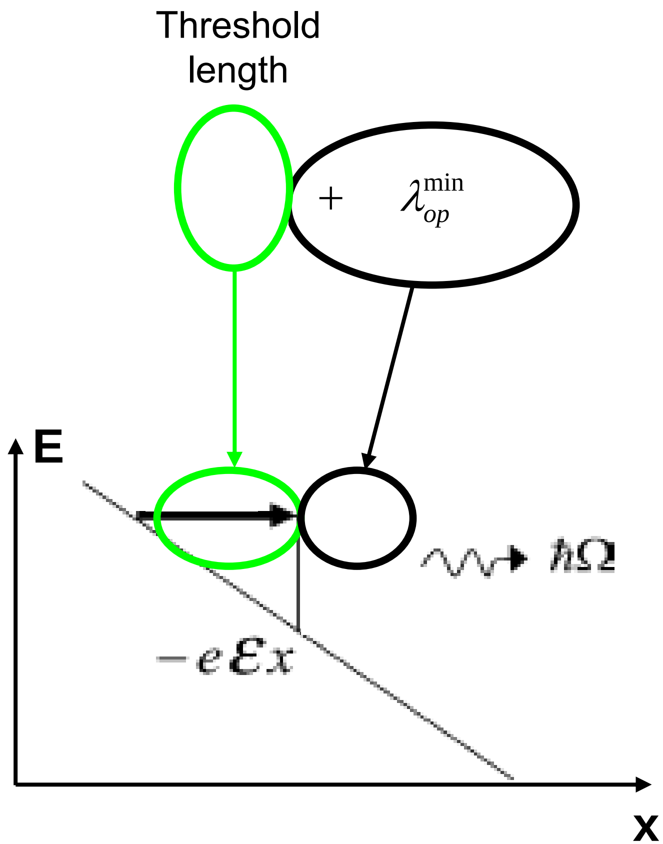
G_+ (TO) Preferential Heating



- Preferential shift indicates large non-equilibrium phonon populations
  - G_+ @ 1000°C
  - G_- @ 40°C
- An extreme state of thermal non-equilibrium

Bushmaker *et al*. Nano Lett. **7** 3618 (2007)

Optical Phonon Emission



- Electrons must exceed threshold phonon energy.
- And then, travel a little bit more before scattering.

Park, *et al.* Nano Lett. **4**, 517 (2004)
Yao *et al*. PRL **84** 2941 (2000)

Electron Transport Model

- The Landauer Model: (Pop, Mann, Park, Yao, and others)

$$R(V,T) = R_c + \frac{h}{4q^2}\left[\frac{L}{\lambda_{eff}(V,T)} + 1\right]$$

Phonon scattering contribution

Quantum Conductance

- Matthiessen's Rule:

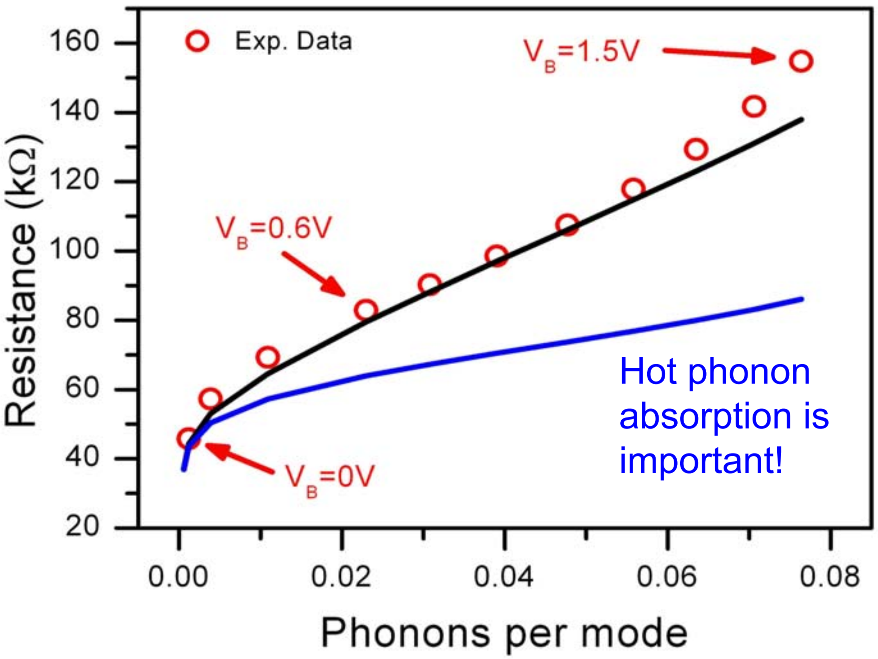
$$\lambda_{eff}^{-1} = \lambda_{ac}^{-1} + \lambda_{op,ems}^{-1} + \lambda_{op,abs}^{-1}$$

Dominant contribution to high bias scattering and nanotube heating

$$\lambda_{op,abs} = \lambda_{op}^{min} \cdot \frac{1}{\langle N(T_{OP}) \rangle}$$

Park *et al.* Nano Lett. **4** 517 (2004)
Yao *et al.* PRL **84** 2941 (2000)
Javey *et al.* PRL **92** 106804 (2004)
Pop *et al.* PRL **95** 155505 (2005)

Results of the Model



Sample	Length (μm)	M/SC	Down-shift	d_t (nm)	λ_{op}^{min} (nm)
1	0.5	M	G_+	-	18
2	2	M	G_-	1.70	26
3	1	M	G_+	-	35
4	2	SC	G_+	2.01	9
5	0.5	M	G_+	-	28

Confirms literature values for λ_{op}^{min} ~ 15 – 30 nm

Park *et al*. Nano Lett. **4** 517 (2004)
Yao *et al*. PRL **84** 2941 (2000)
Javey *et al*. PRL **92** 106804 (2004)
Pop *et al*. PRL **95** 155505 (2005)

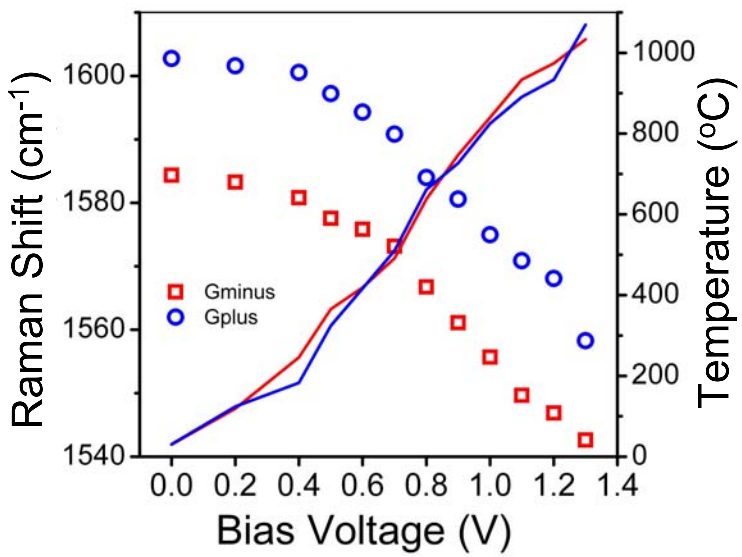
Apply the Landauer model:

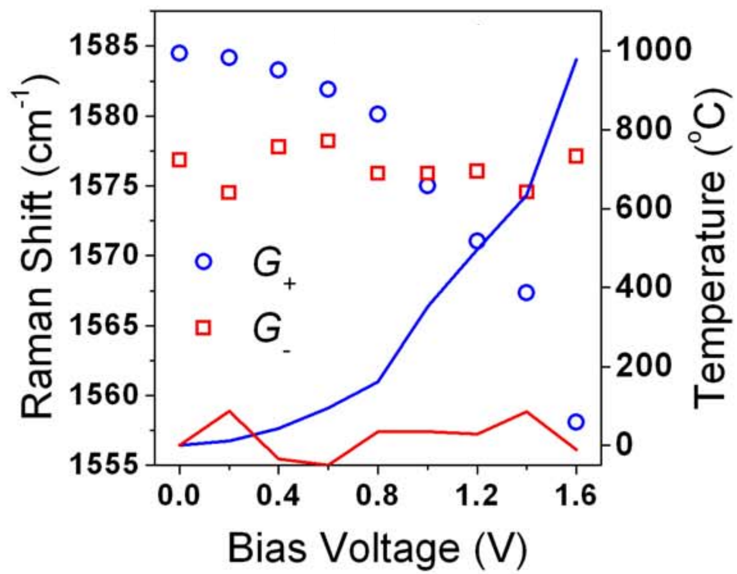
R_C , λ_{op}^{min} = fitting parameters

$$R(V,T) = R_c + \frac{h}{4q^2}\left[\frac{L}{\lambda_{eff}(V,T)} + 1\right]$$

Bushmaker *et al*. Nano Lett. **7** 3618 (2007)

G_+ Preferential Heating

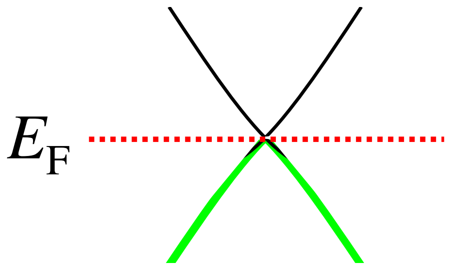


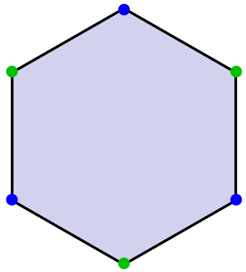


Why is there preferential heating of only one phonon mode?

Bushmaker *et al.* Nano Lett. **7** (2007)

The Kohn Anomaly



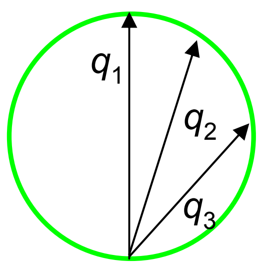


$$E_{\mathrm{TOT}} = \int_{-\infty}^{E_{\mathrm{F}}} E \cdot D(E)\, dE$$

- Strong coupling of electrons and phonons at the Fermi energy.
- Atomic displacements create dynamic bandgap, which lowers the energy of the phonons.

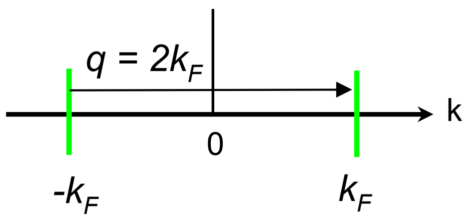
The Kohn Anomaly in 1D

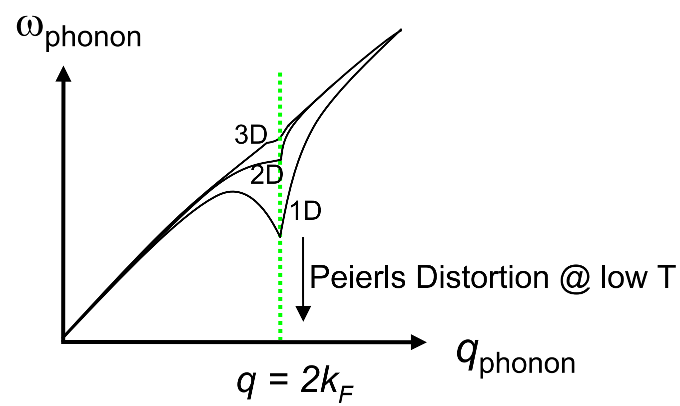
Fermi surface in 2D



$q_1 \neq q_2 \neq q_3 \leq 2k_F$

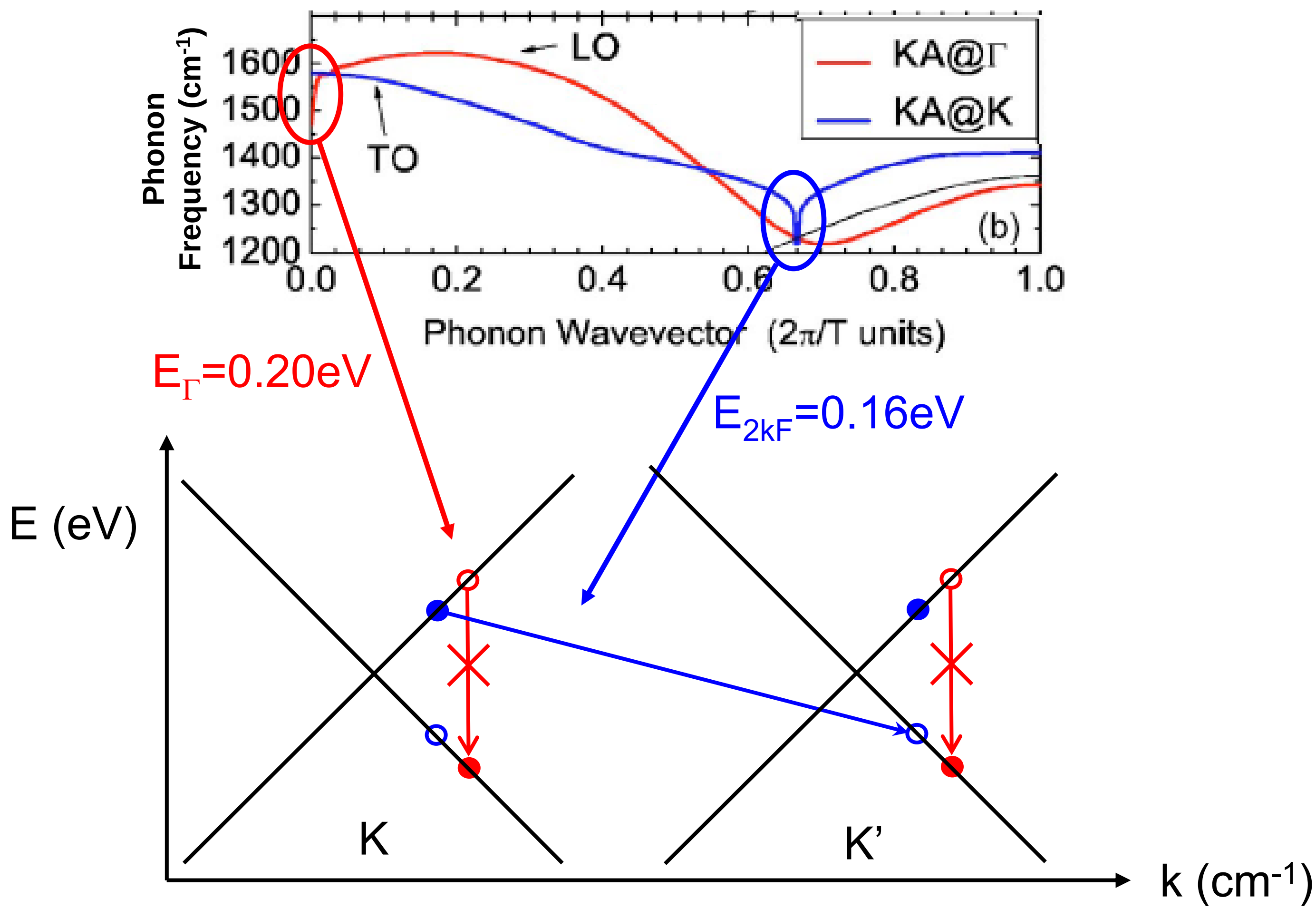
Fermi surface in 1D





- The Kohn anomaly is exacerbated in 1D because of the limited number of phonon and electronic states.
- At low temperatures the phonon frequency reduced to zero resulting in a permanent lattice (Peierls) distortion.

Preferential Electron-Phonon Coupling

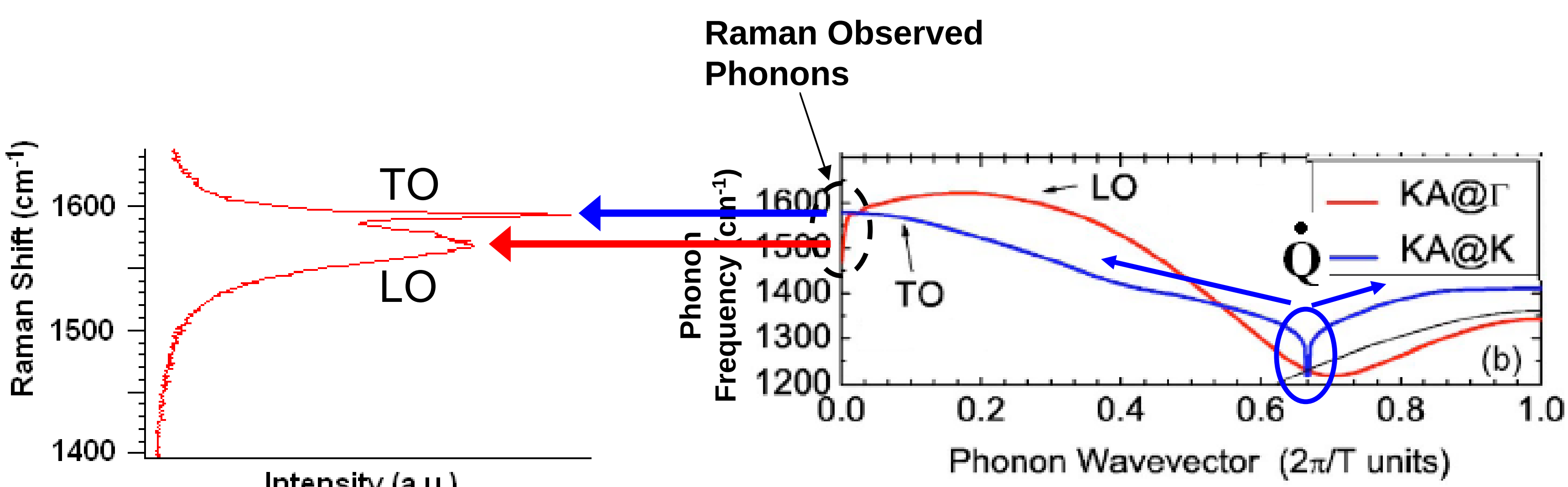


$E_{2kF} < E_{\Gamma} \Longrightarrow$ Only TO phonons are emitted

Piscanec *et al.* Phys. Rev. B **75** 35427 (2007)

Observation of $2K_F$ Optical Phonon Preferential Coupling

- $2k_F$ phonons are heated
- Each phonon band is expected to be in thermal equilibrium
- We observe the temperature of the bands with Raman spectroscopy
- The TO band is preferentially heated



Our data

Piscanec *et al.* Phys. Rev. B **75** 35427 (2007)

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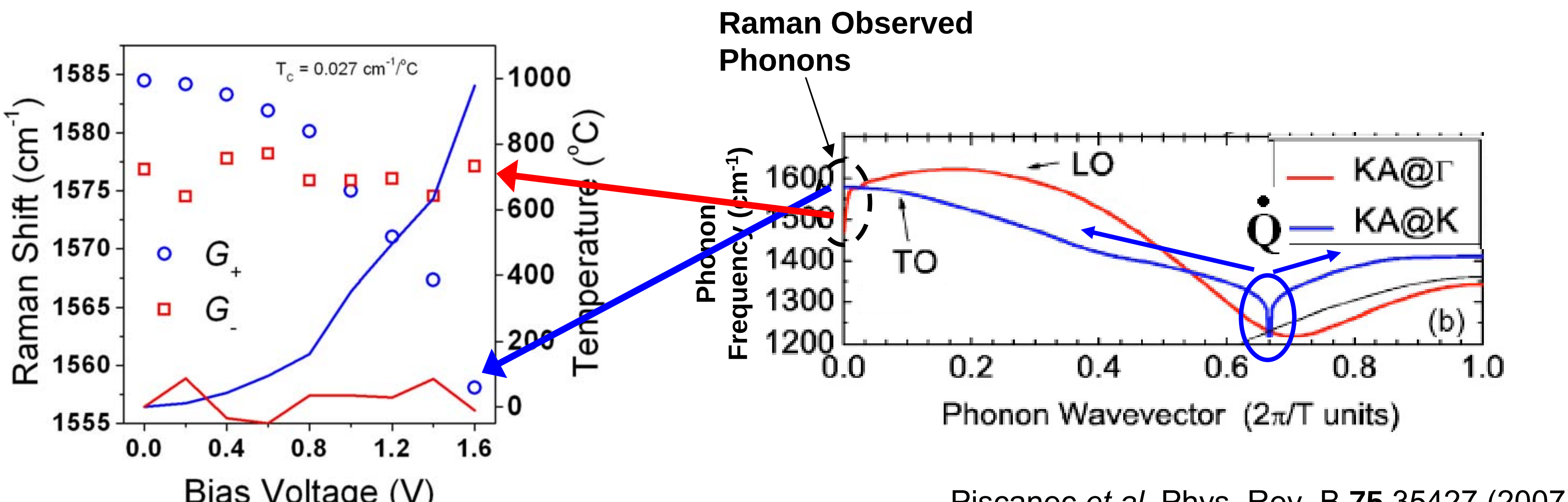
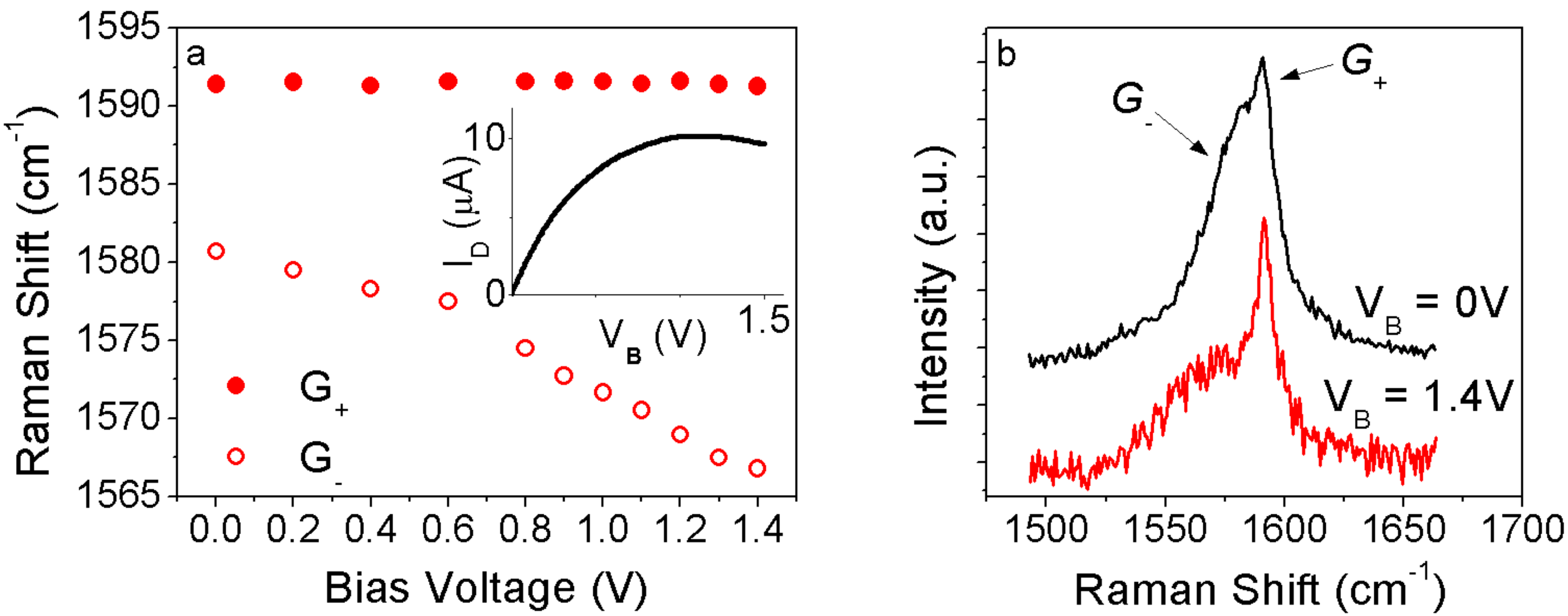


Piscanec *et al.* Phys. Rev. B **75** 35427 (2007)

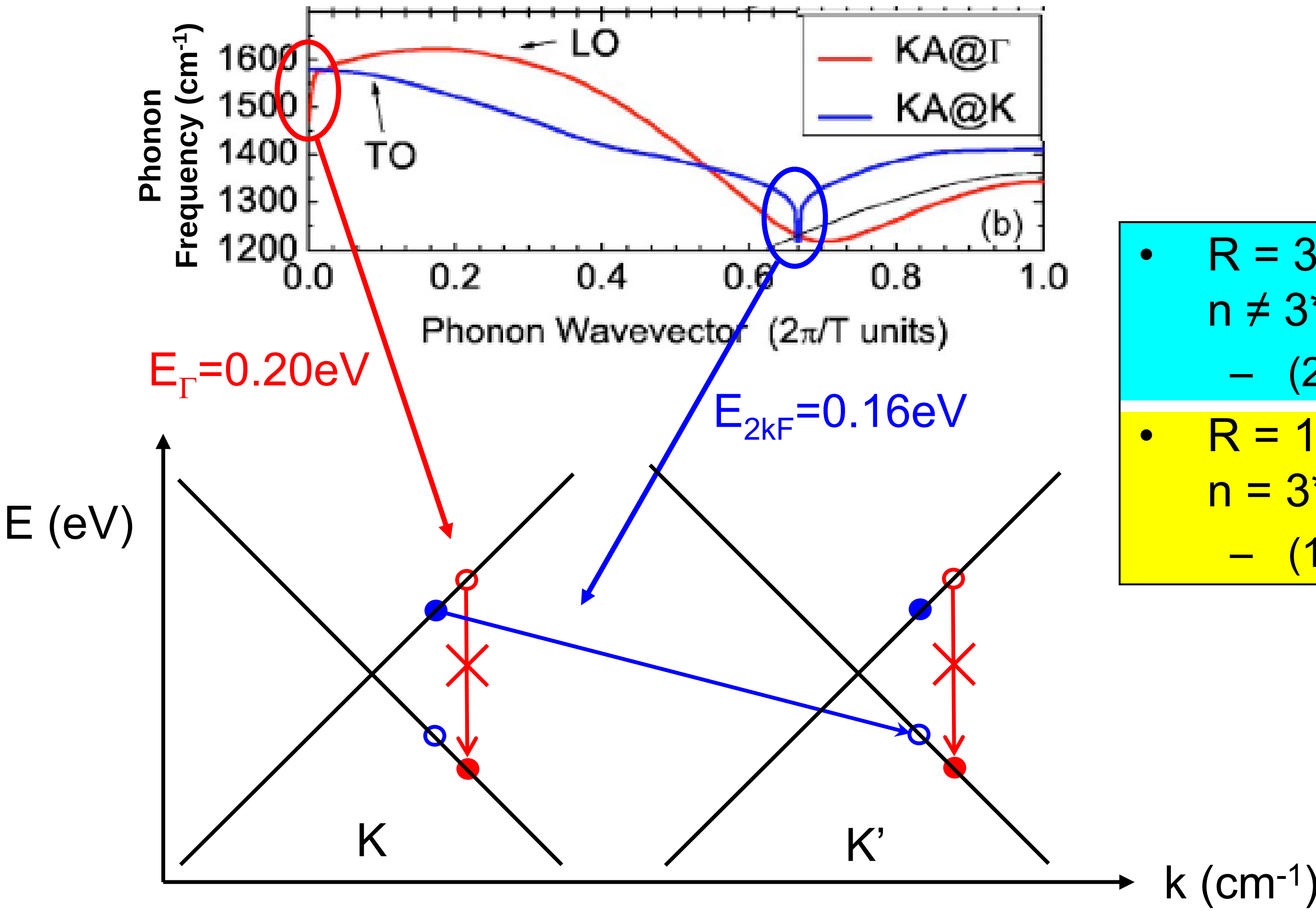
Sometimes, Only G_- (LO) is Heated



- Even less frequently, only G_- is heated (1 tube)
- Theory: rare chirality with non-Raman active TO phonon branch
  - Results in observation of heating in only LO branch
- Two types of metallic nanotubes: R = 1,3
  - LO heating is observed in R = 1 nanotubes

Bushmaker *et al*. Nano Lett. **7** 3618 (2007)

Preferential G_- (LO) Heating

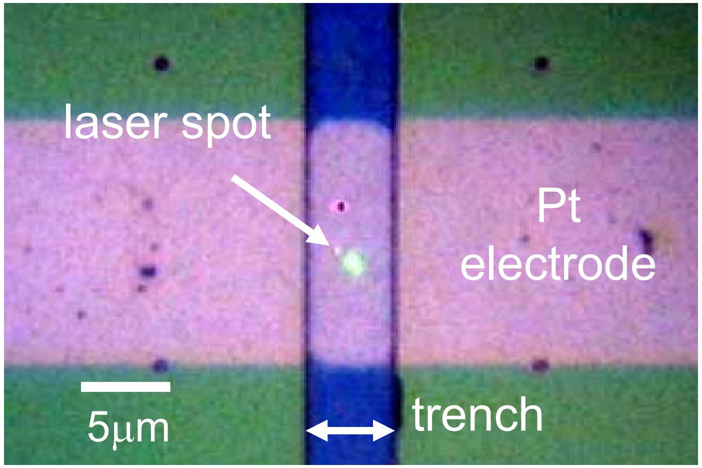


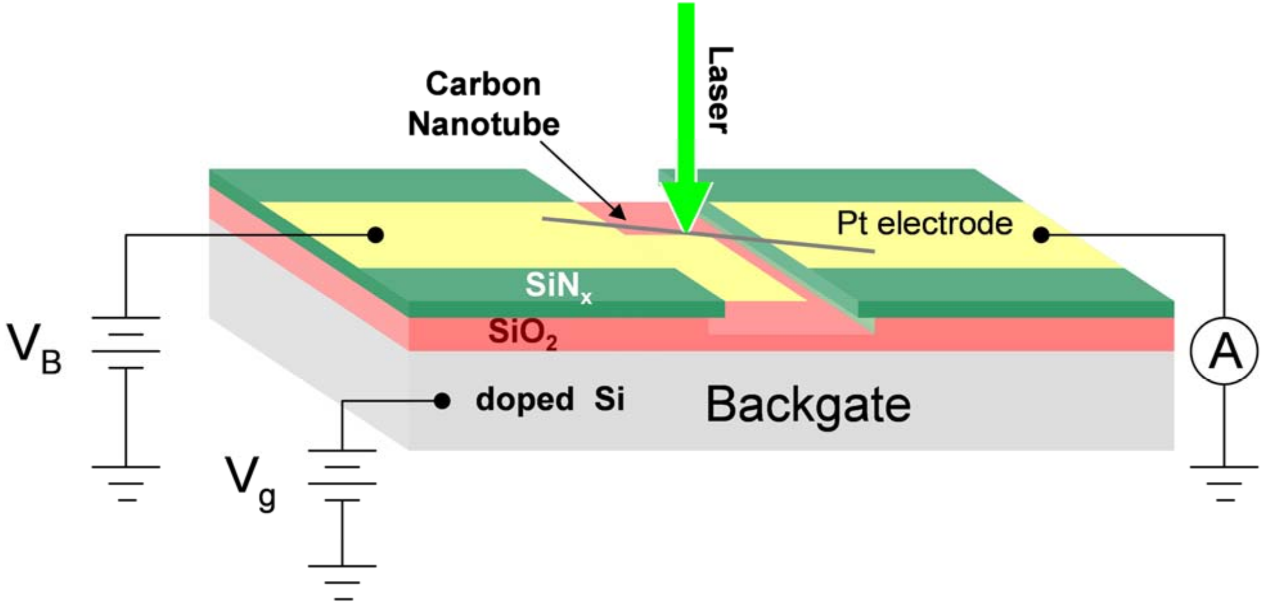
- R = 3 Armchair tubes ***or*** n ≠ 3**i* tubes
  - (2/3 of m-CNTs)
- R = 1 Non-armchair ***and*** n = 3**i* tubes
  - (1/3 of m-CNTs)

E_Γ only $\Longrightarrow$ Only LO phonons are emitted

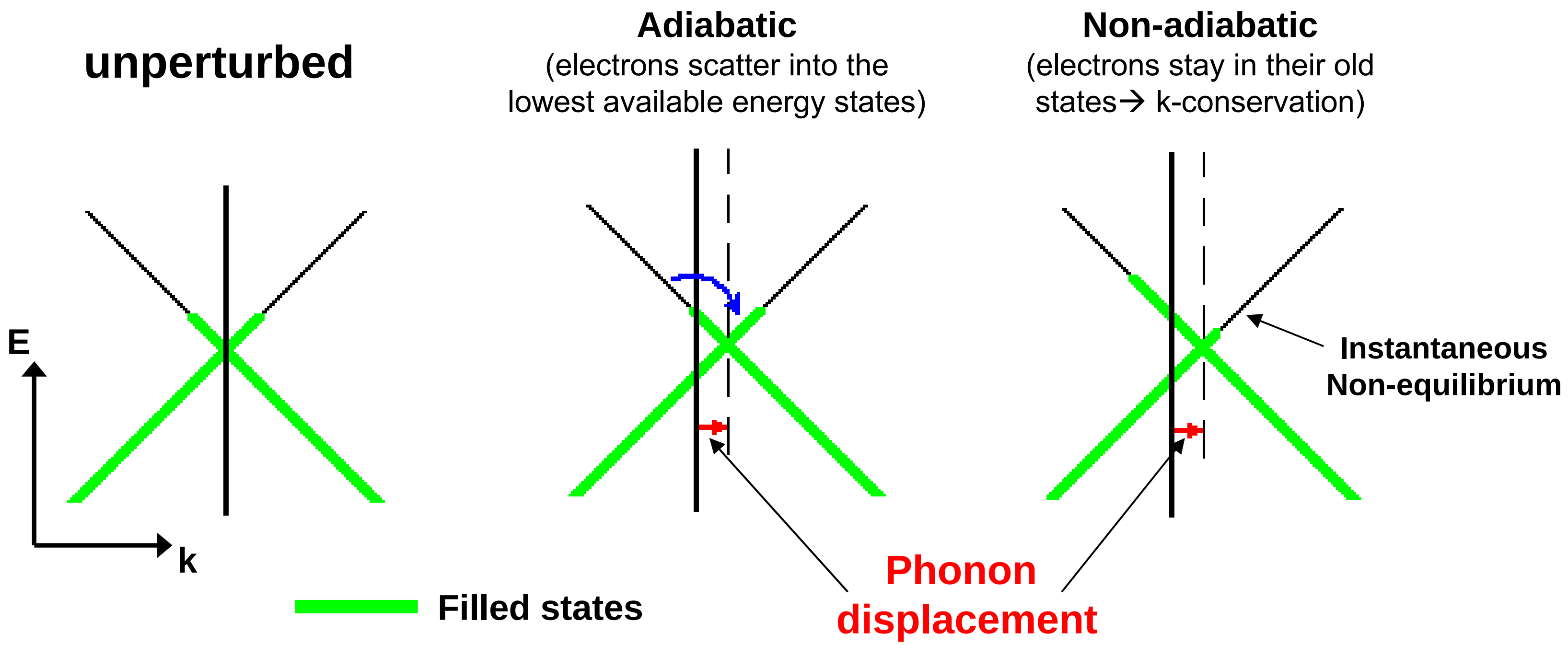
Piscanec *et al.* Phys. Rev. B **75** 35427 (2007)

Gate Voltage



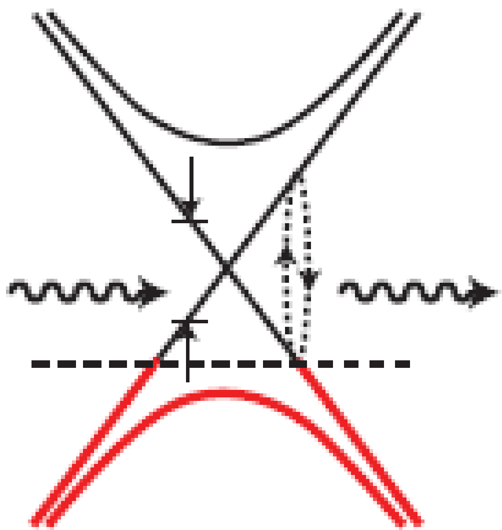


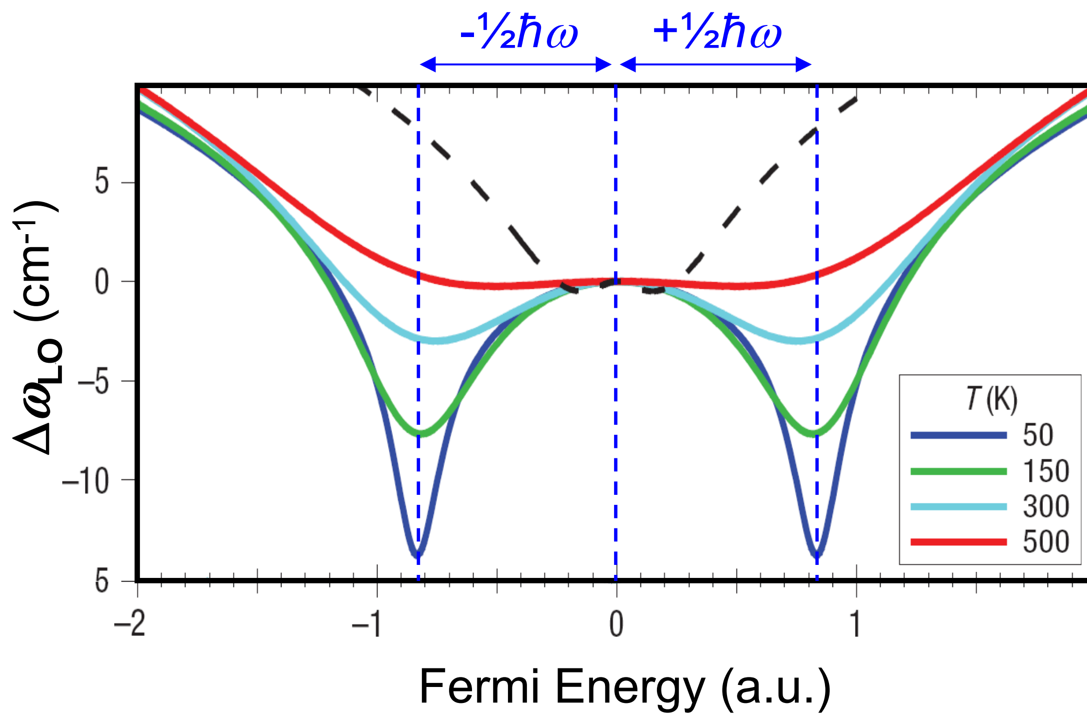
Born-Oppenheimer Approximation



- The approximation: Electrons equilibrate to the instantaneous ground state faster than the atoms vibrate.
- Approximation breaks down in SWNTs
  - 1.) fast vibrational motion (τ_{OP} = 0.02ps)
  - 2.) long electron lifetimes ($\tau_{electron}$ = 2ps)

Non-Adiabatic Phonon Renormalization

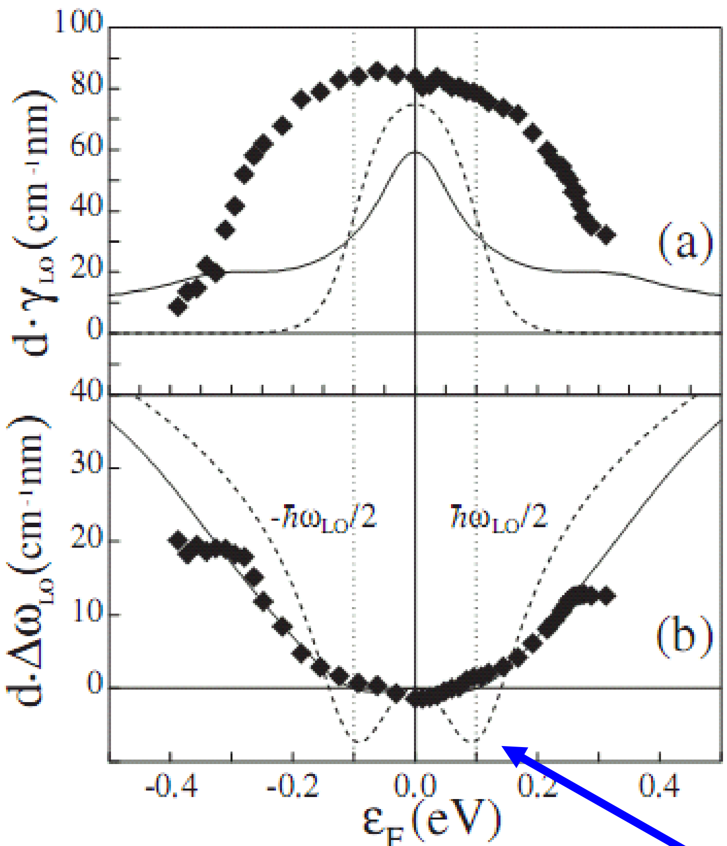




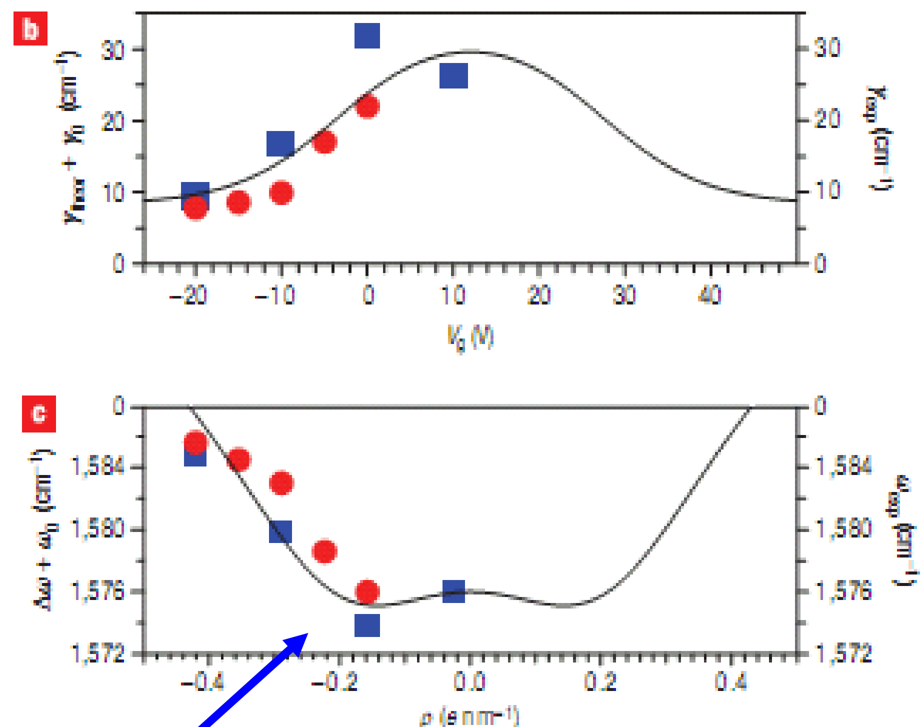
$$\omega_\Gamma = \sqrt{\frac{D_\Gamma^0}{M} + \frac{D_\Gamma^{KA}}{M}}$$

Caudal et al, PRB, **75**,115423 (2007)
Tsang et al, Nat. Phys. **2**, 725 (2005)

Comparison with Literature



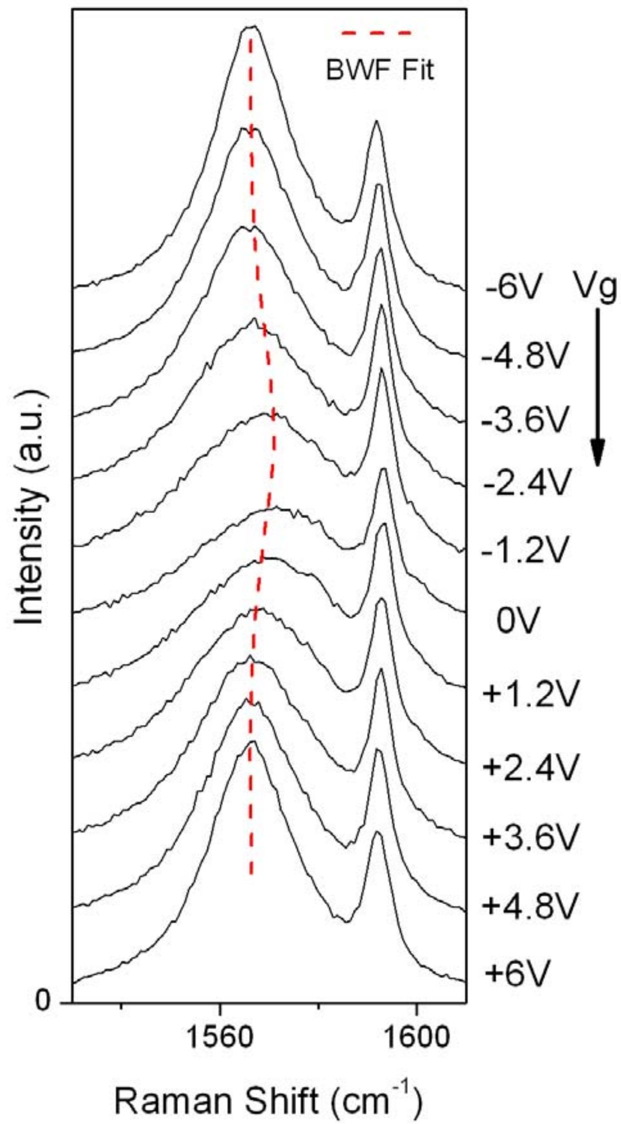
Das, mauri et al 2007



Tsang et al, Nat. Phys. **2**, 725 (2005)

"W" shape predicted by theory but not observed in experiment!

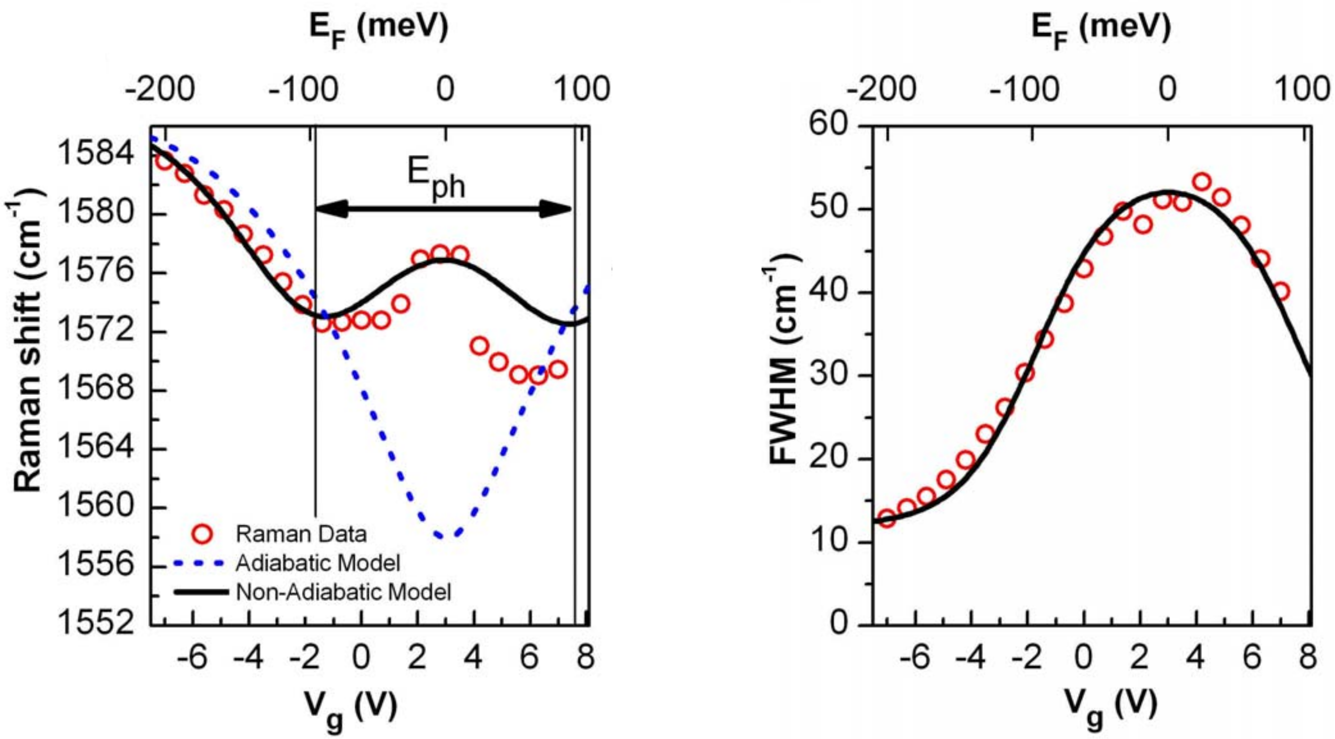
Gate Voltage Dependence



Our Devices:
- Few defects
- Suspended
- Long electron lifetimes

Bushmaker *et al*. Nano Lett. accepted (2008).

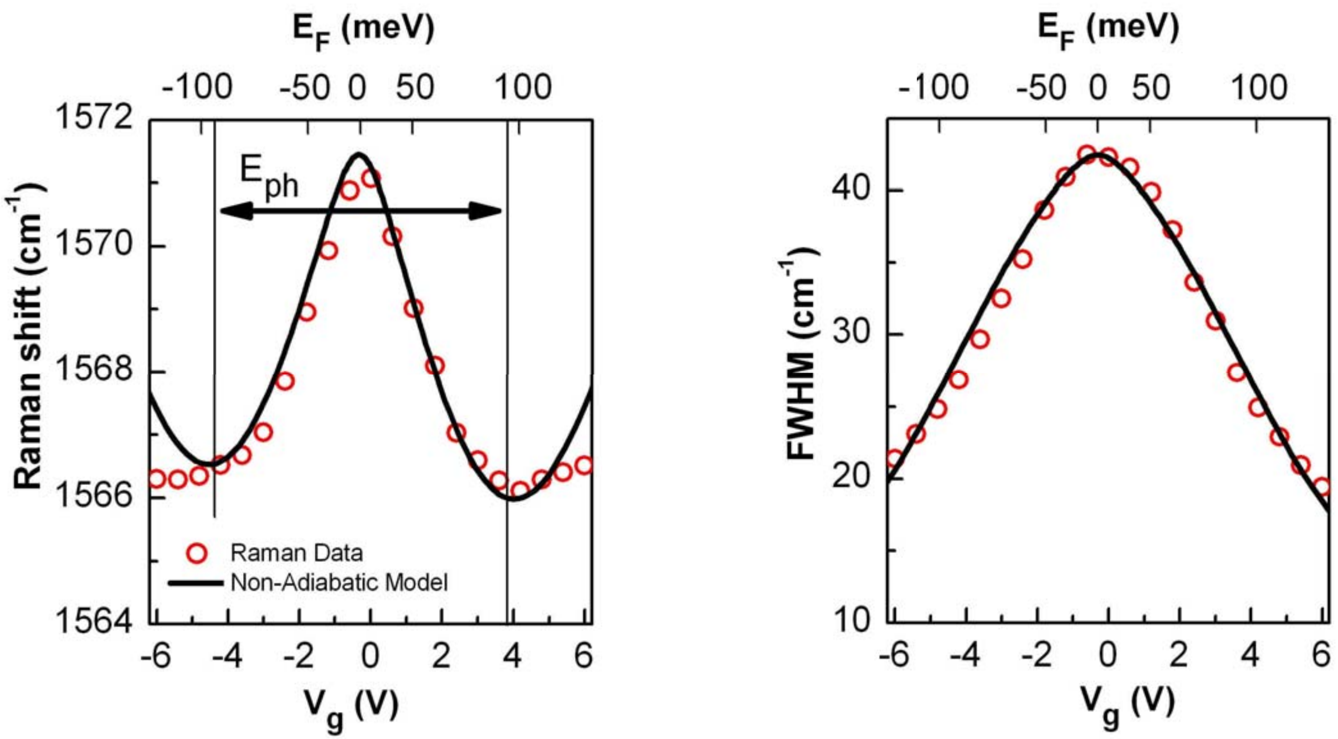
Gate Voltage Dependence



- "W" shape indicates breakdown of the BOA.
- Non-adiabatic model also predicts FWHM.

Bushmaker *et al*. Nano Lett. accepted (2008).

Gate Voltage Dependence



- “W” shape is more pronounced.
- Good agreement with FWHM.

Bushmaker *et al*. Nano Lett. accepted (2008).

Conclusion

- Carbon nanotubes provide an ideal system for studying 1D physics.
- Preferential heating, mode selective el-ph coupling, non-equilibrium phonon populations, negative differential conductance (NDC), caused by the Kohn anomalies.
- Breakdown of the Born-Oppenheimer approximation, due to long electron lifetimes.

Thank You

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