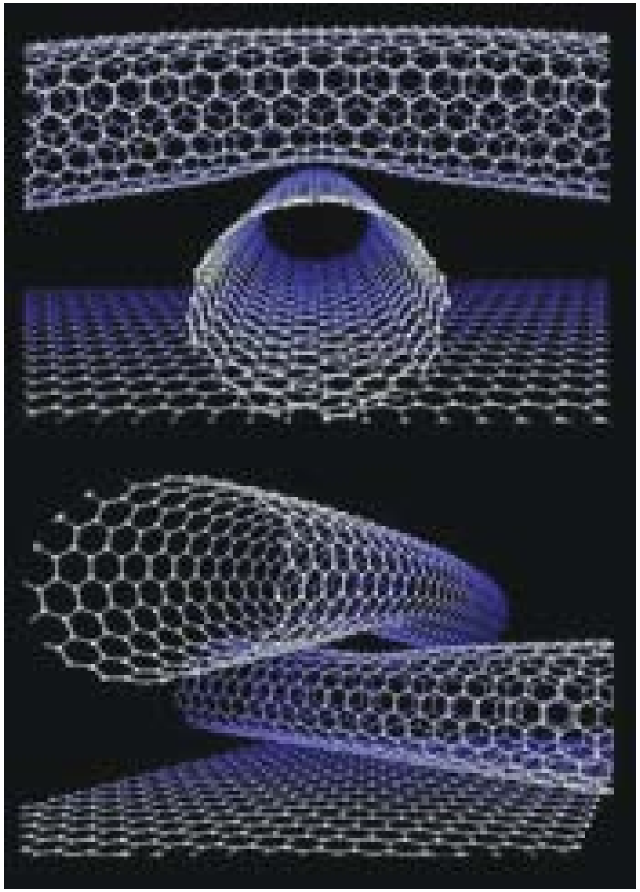
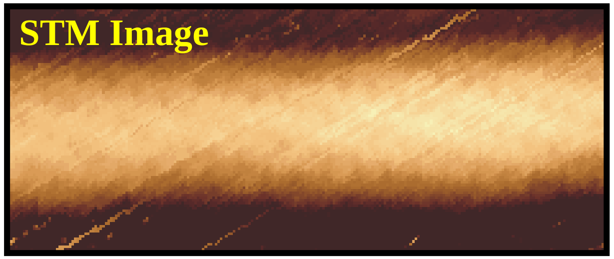
Nanomaterials

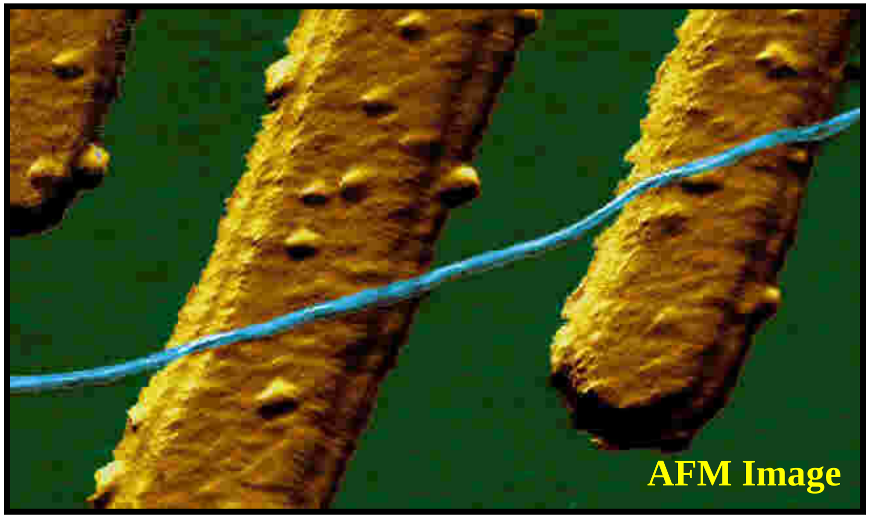
Lecture 8: Carbon Nanomaterials

Carbon Nanomaterials

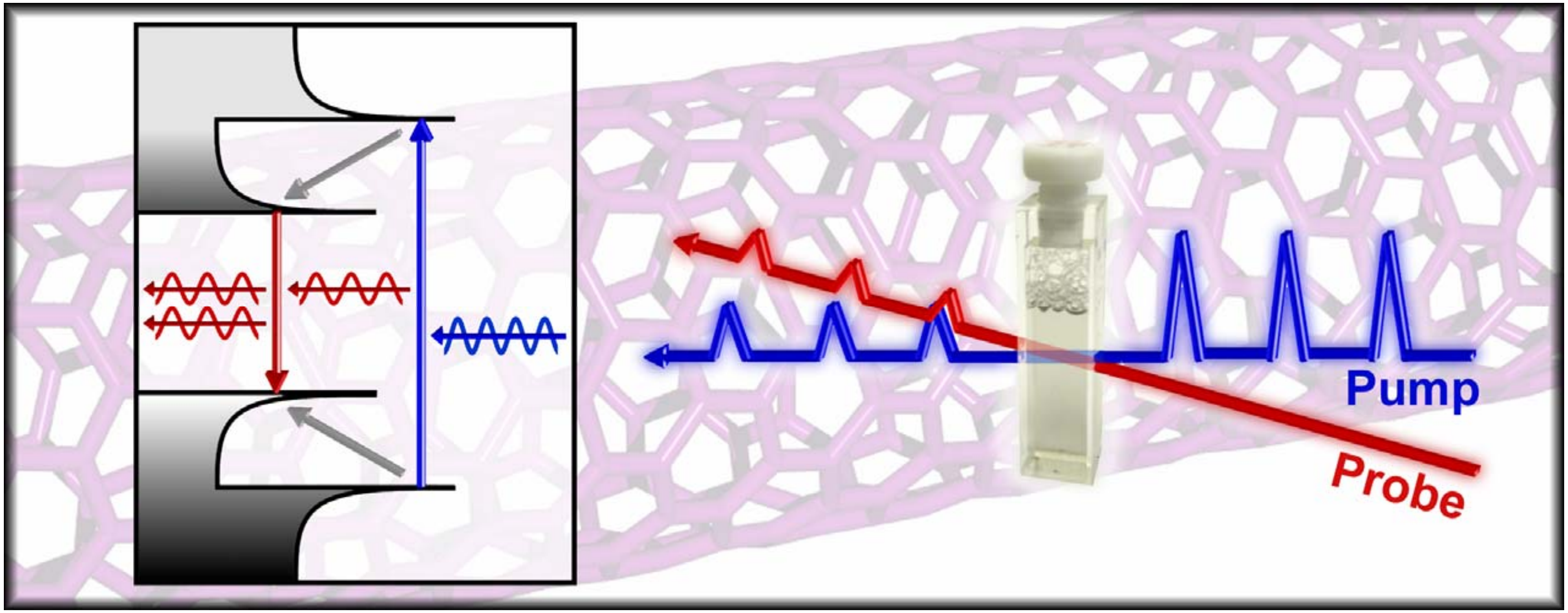




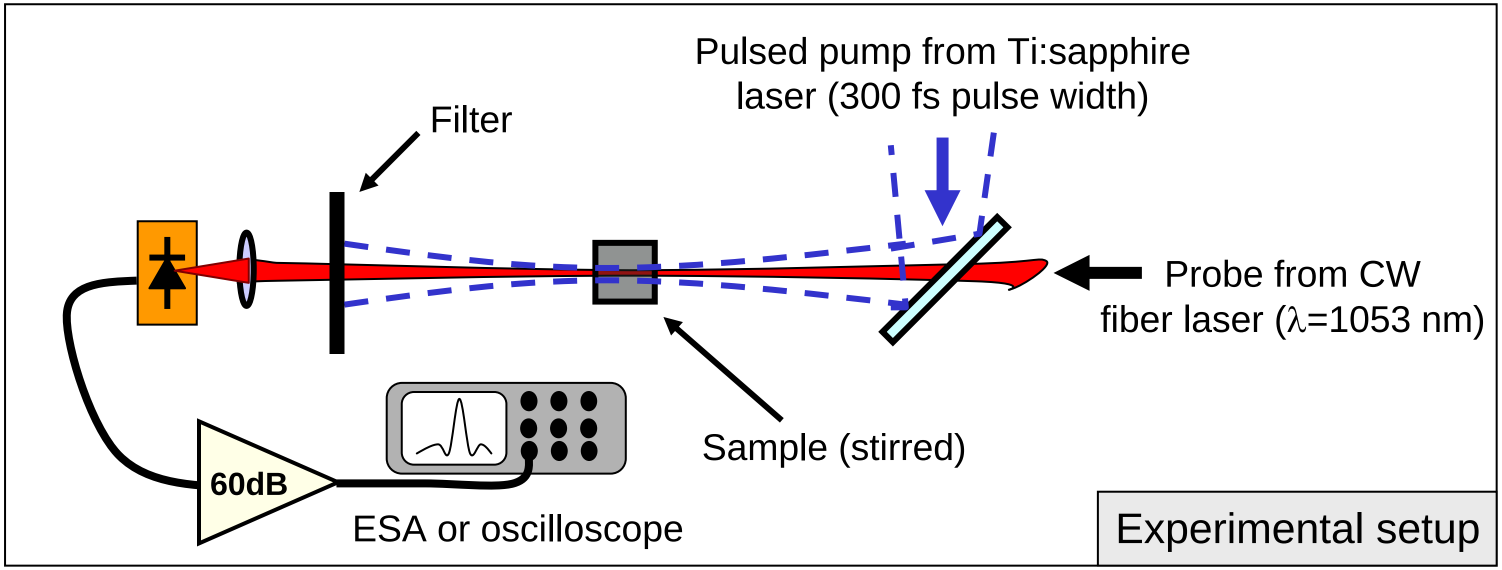
7 nm

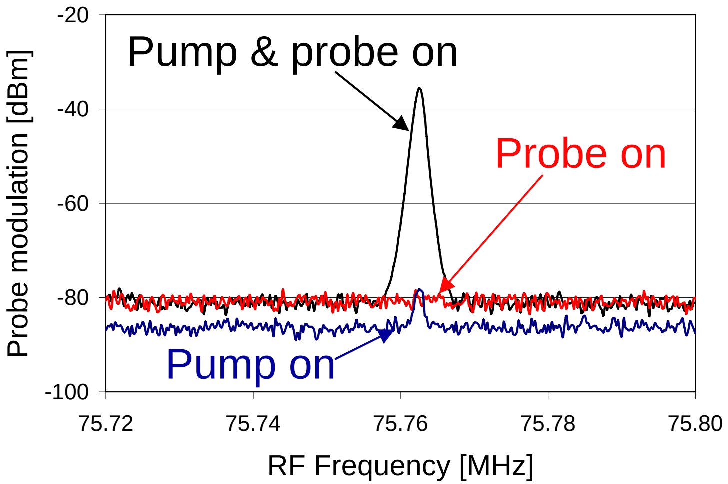


Characterization of Stimulated Emission from Encapsulated SWNTs

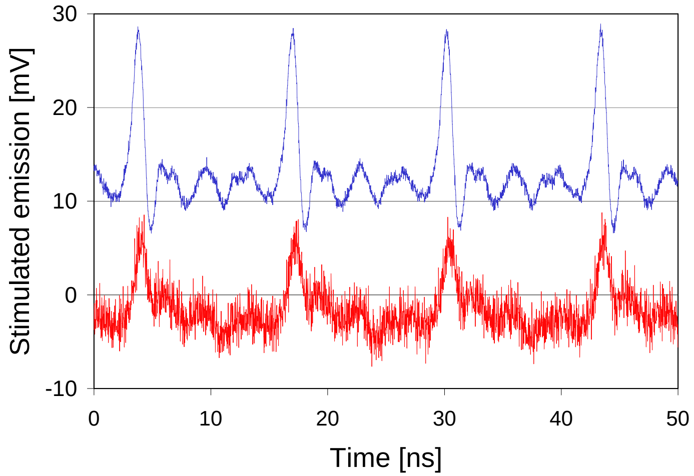


M. S. Arnold, *et al.*, *Nano Letters*, **3**, 1549 (2003).



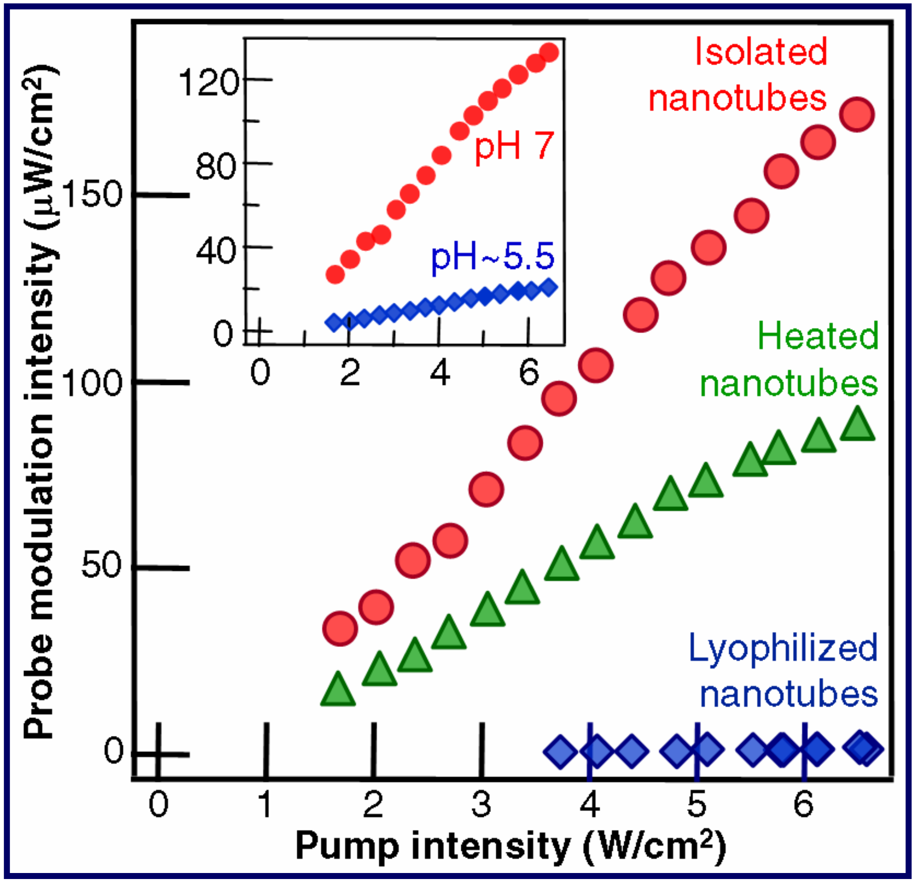


Probe modulation in frequency domain



Temporal response of probe modulation

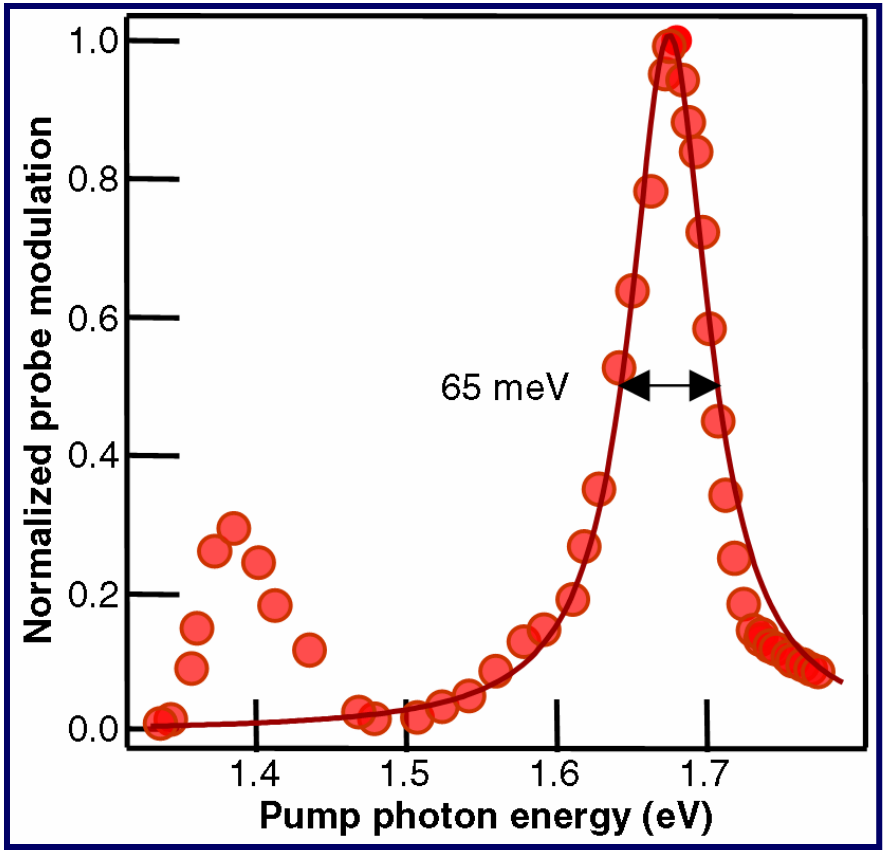
Effect of Aggregation and pH



- Aggregation of isolated nanotubes by lyophilization and re-suspension drastically reduces probe modulation intensity by a factor of 122.
- Photobleaching disappears at acidic pH and is reversibly restored at neutral and basic pH, consistent with protonation of nanotube sidewalls at acidic pH.

M. S. Arnold, *et al.*, *Nano Letters*, **3**, 1549 (2003).

Pump Spectral Dependence



- The measured E_{22} transition width of 65 meV is consistent with fast electron-electron scattering on the 300 fs time scale.
- The feature near 1.4 eV is likely due to a Raman effect (the measured difference between pump and probe energies is ~ 1600 cm^{-1}, which matches the G-band Raman mode in SWNTs).

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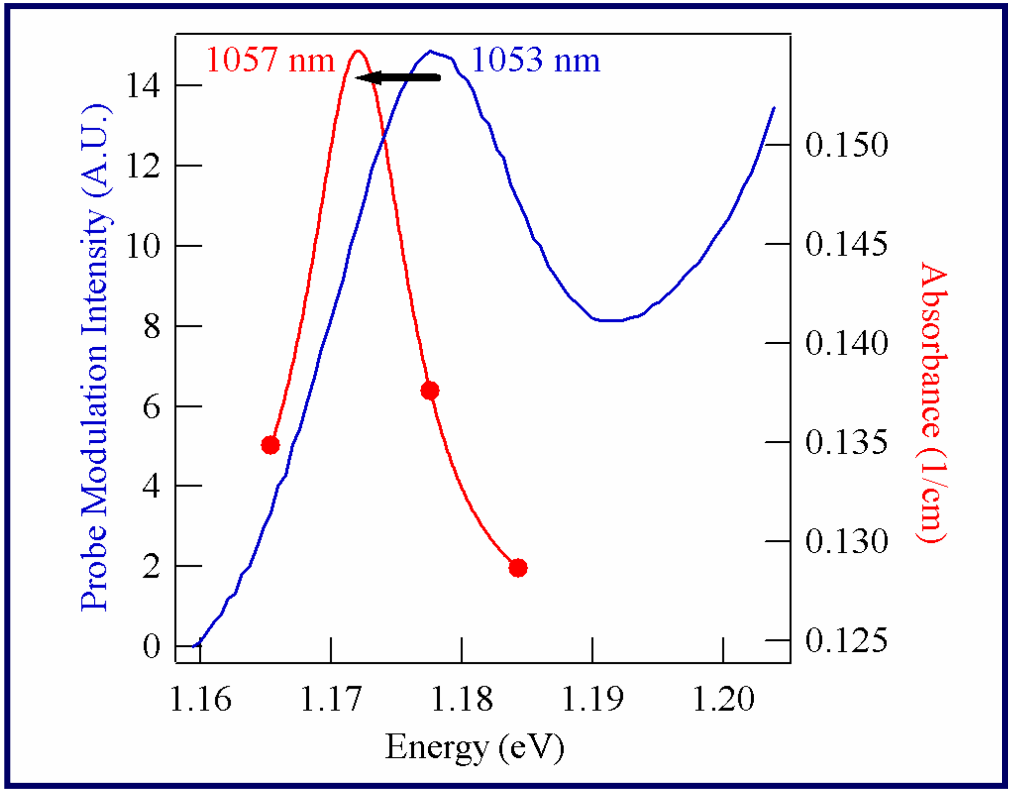
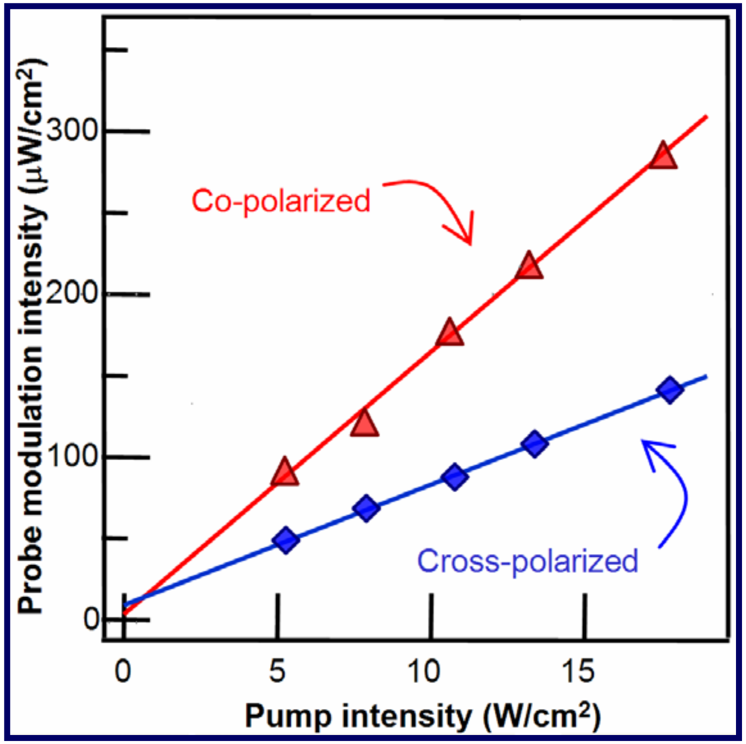
Probe Spectral Dependence



- The probe modulation spectrum is slightly red-shifted from the absorbance spectrum by 45 cm^{-1}.
- From a Lorentzian fit, the width of the E_{11} transition is only 10 meV compared with 65 meV as measured for the E_{22} transition.

M. S. Arnold, *et al.*, *Nano Letters*, **3**, 1549 (2003).

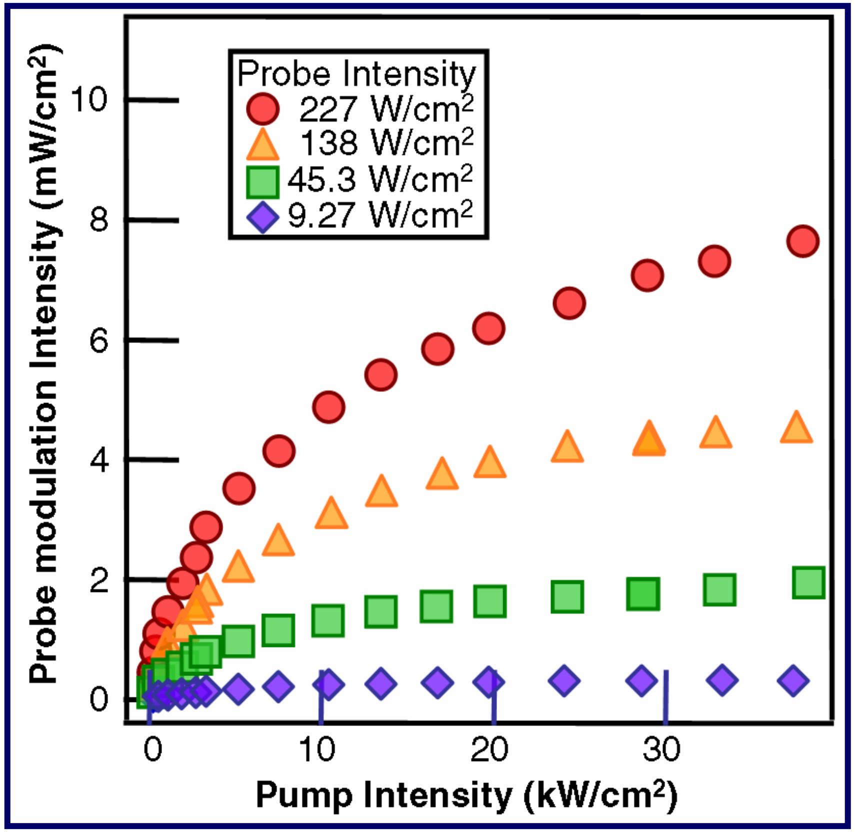
Polarization Dependence



Co-polarized pump and probe lead to greater photobleaching than cross-polarized as expected for a 1-D system.

M. S. Arnold, *et al.*, *Nano Letters*, **3**, 1549 (2003).

Pump Saturation Effects



- At low pump intensities below 10 W/cm^2, linear behavior is observed.
- Saturation of the probe modulation is consistent with:
  - ➢ Increased multi-particle Auger recombination for large carrier densities.
  - ➢ Exciton-exciton annihilation effects.
  - ➢ Saturation and filling of a finite number of states.

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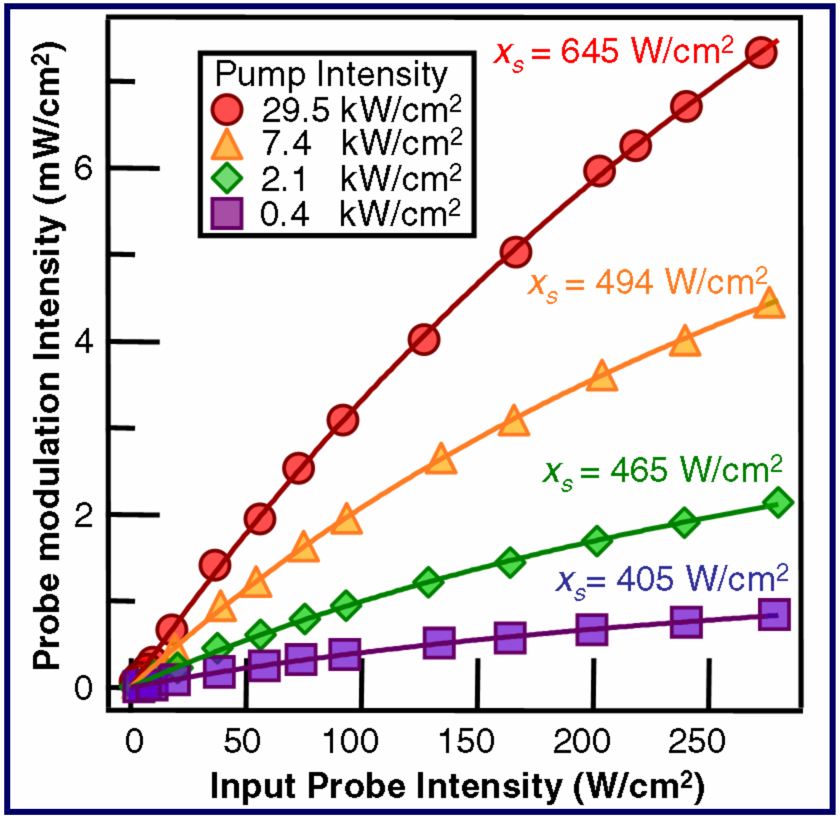
Probe Saturation Effects



- x_S corresponds to the probe intensity for which the rate of stimulated recombination is equal to the intrinsic rate of recombination.
- An increase in x_s at large pump intensities is consistent with an increase in the effective interband recombination rate due to enhanced Auger recombination for large carrier densities.

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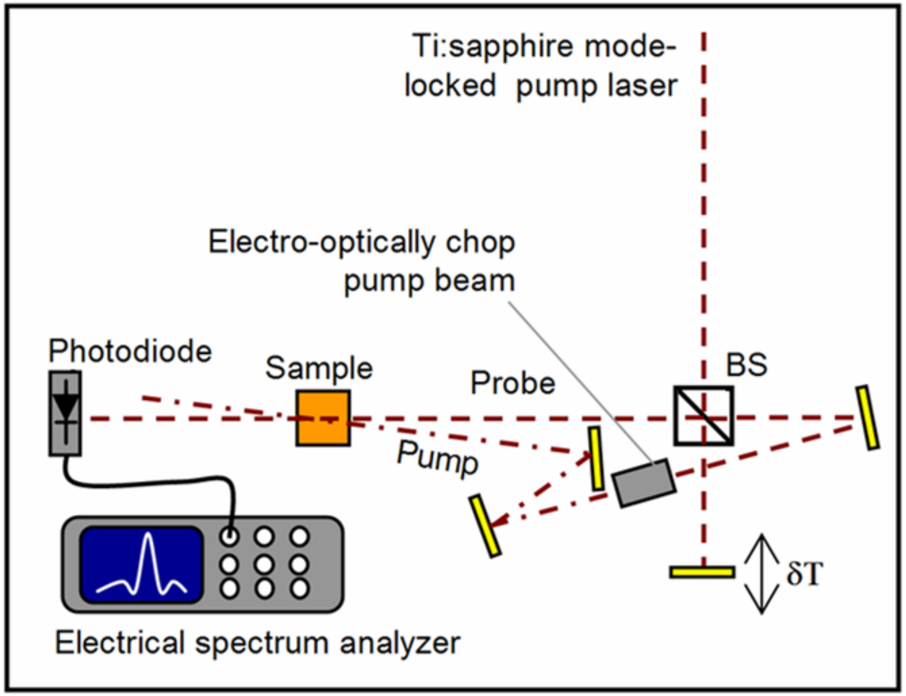
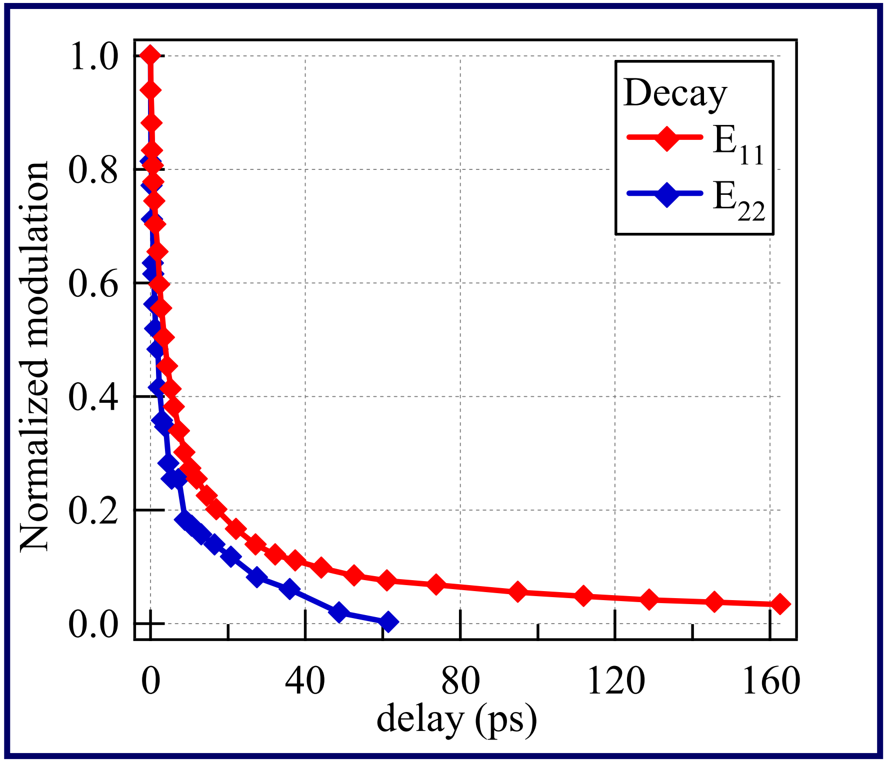
Degenerate Pump-Probe Measurements

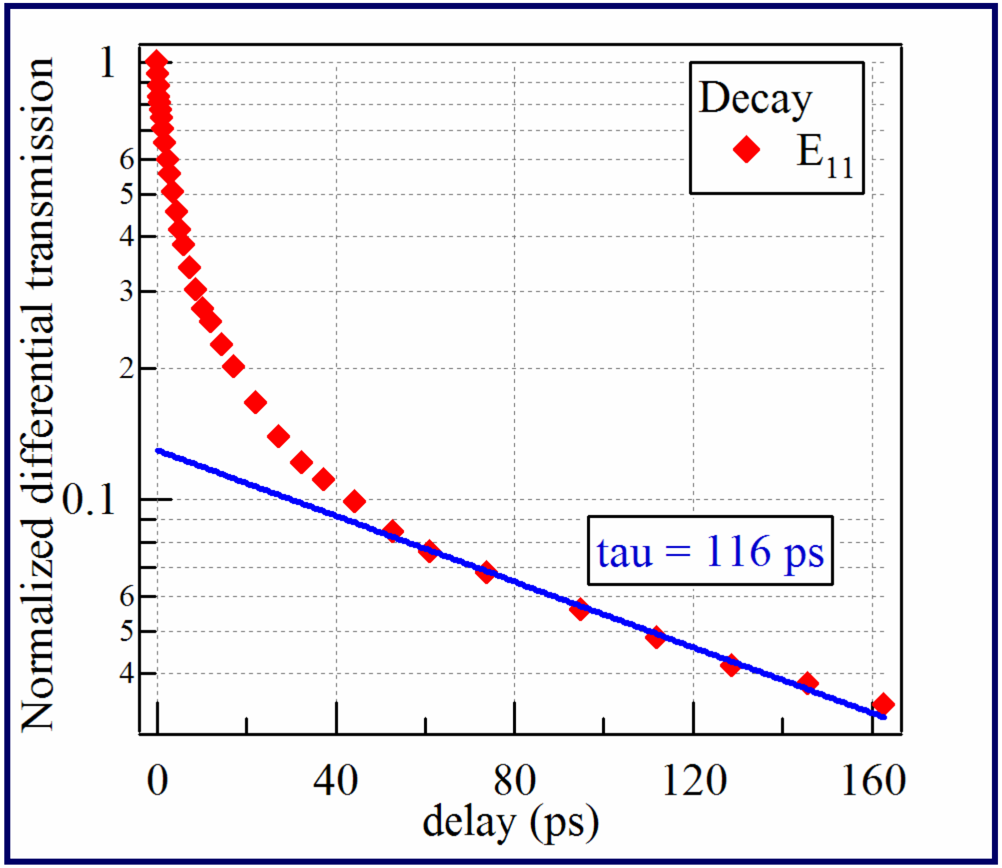


Degenerate pump-probe optical setup.



Time-resolved relaxation at E_{11} (975 nm) and E_{22} (740 nm) optical transitions.

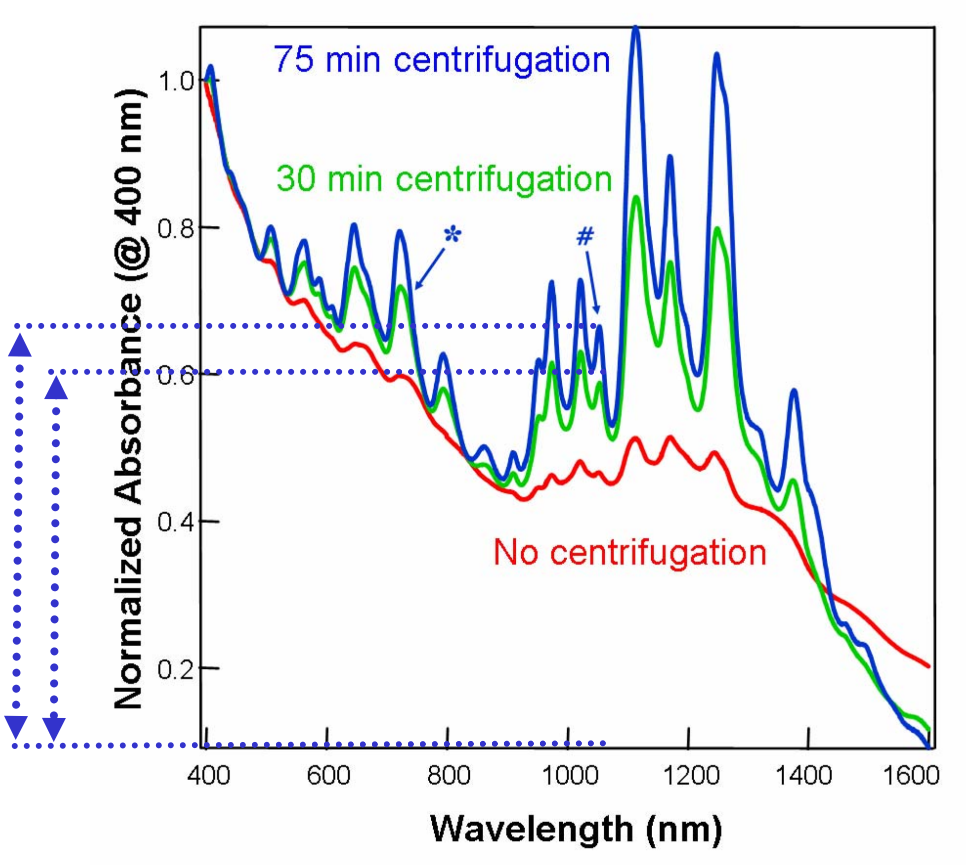
Temporal Relaxation at E_{11}



Semi-log relaxation at E_{11} (975 nm)

An Estimate of the Optical Gain

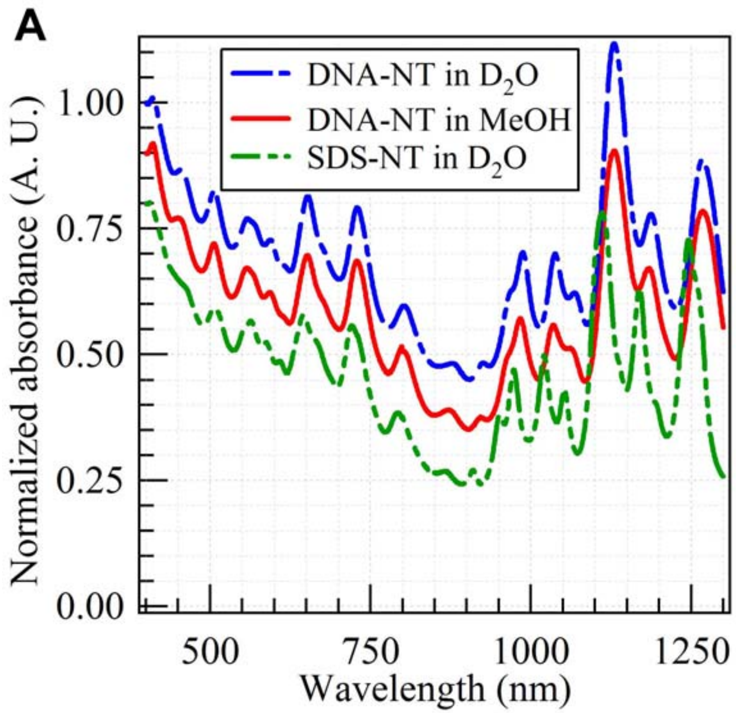
~ 10% instantaneous decrease in absorption



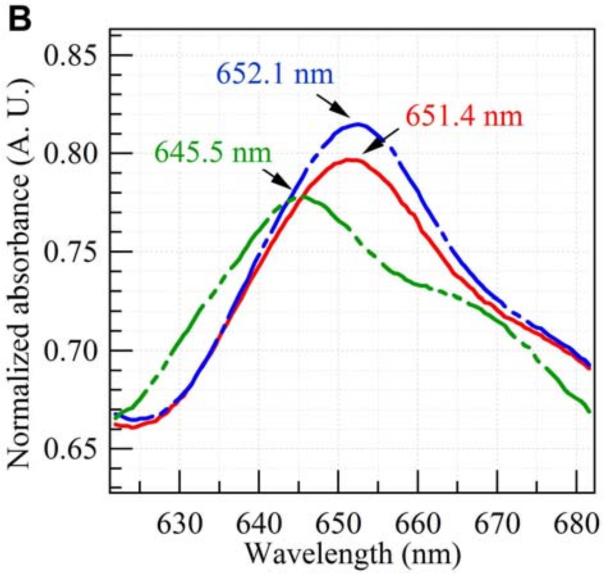
To reach optical transparency, SWNTs need to be separated by electronic bandstructure

Optical Absorption Spectra for DNA Encapsulated SWNTs

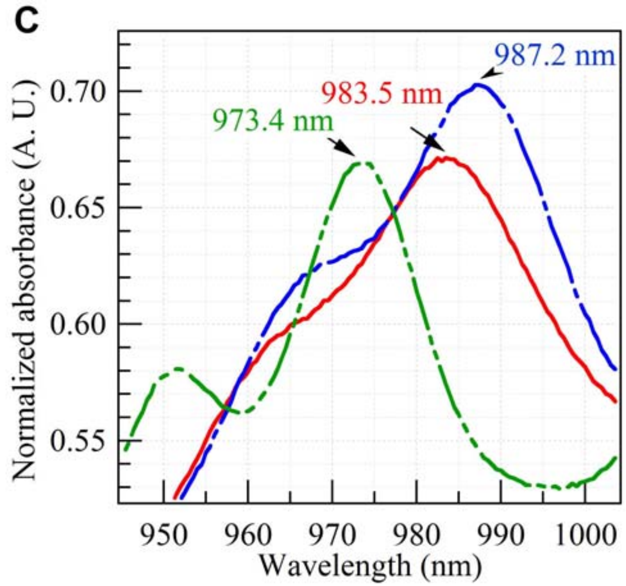
Optical absorbance spectrum:



E_{22} Transition:

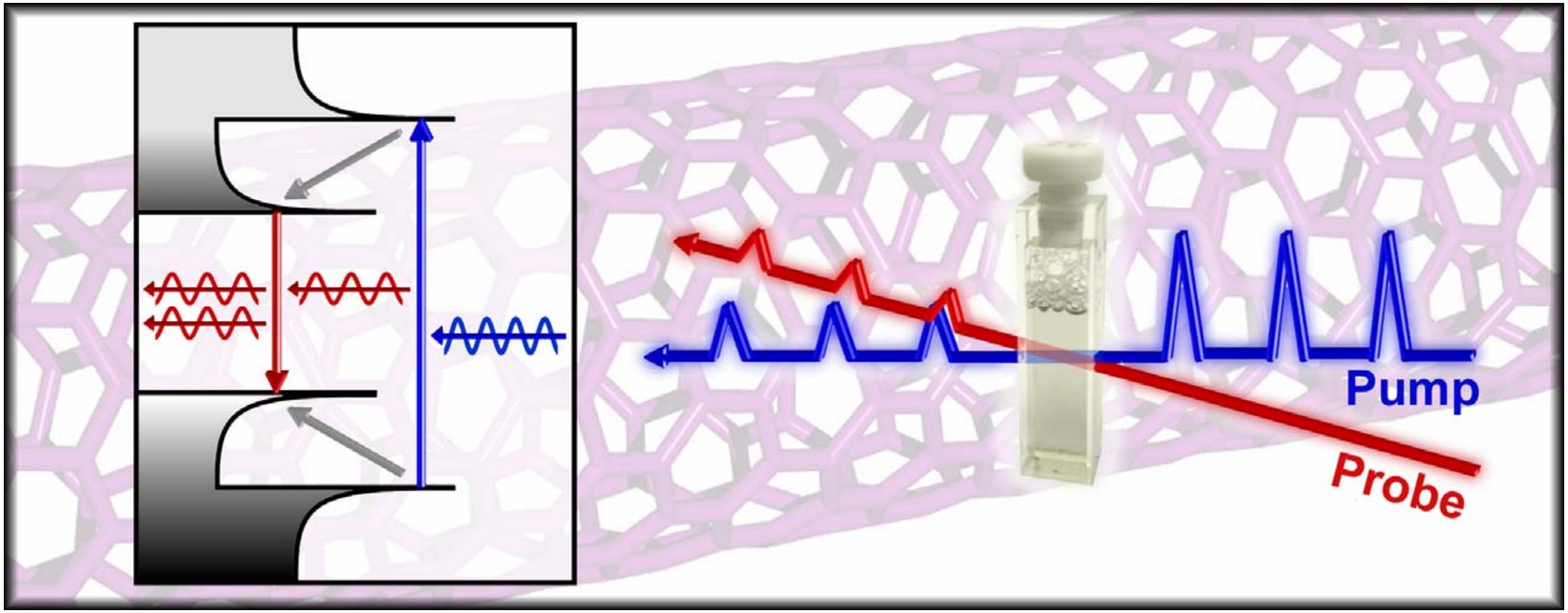


E_{11} Transition:



	E_{11} red-shift	**E_{22} red-shift**
SDS-NT in D_2O	0 meV	0 meV
DNA-NT in methanol	13.1 meV	17.4 meV
DNA-NT in D_2O	17.8 meV	19.4 meV

Characterization of Stimulated Emission from Encapsulated SWNTs



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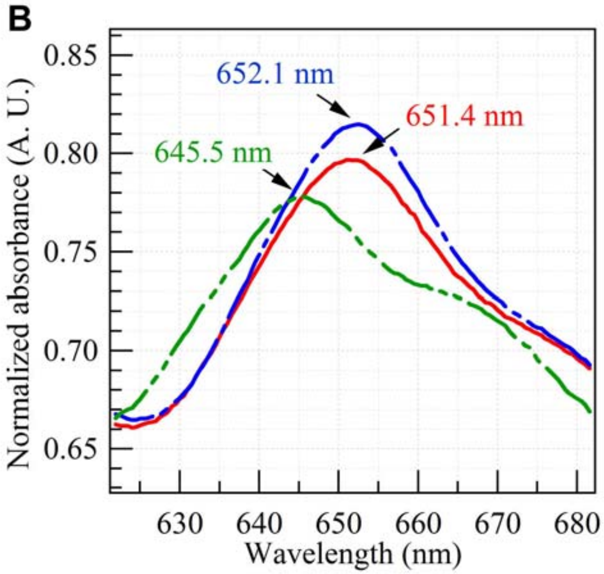
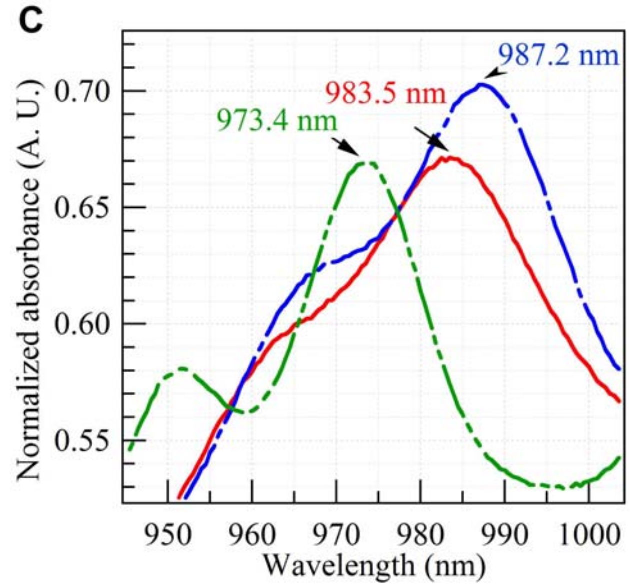
E_{22} Transition:



E_{11} Transition:



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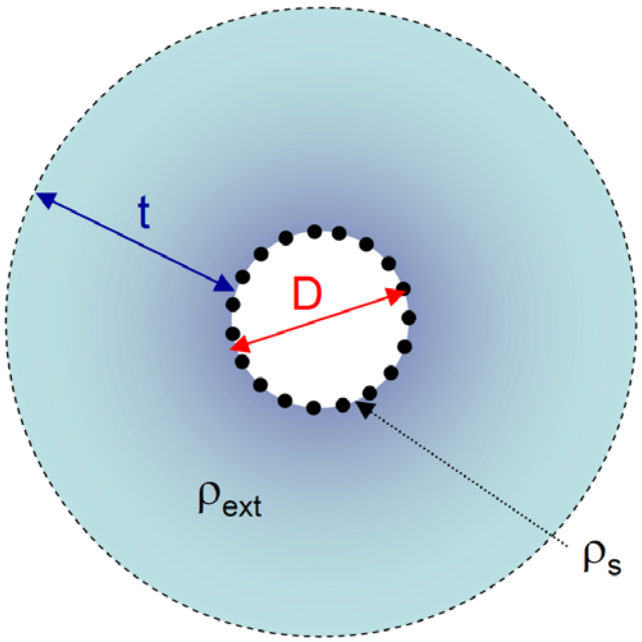
Density of DNA Encapsulated SWNTs



Density of SWNTs in vacuum:

$$\rho_{NT} := \frac{4\,\rho_s}{D}$$

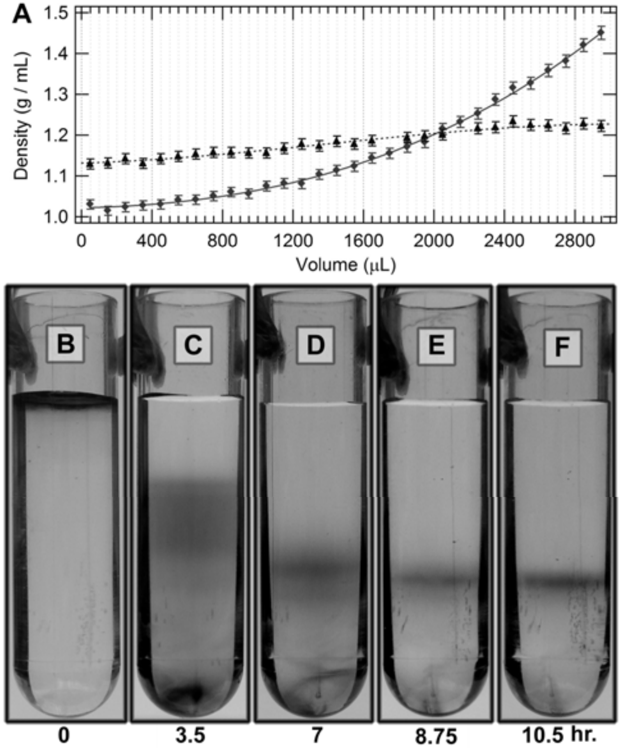
Density of DNA encapsulated SWNTs:

$$\rho_{NT} := \frac{\rho_s\,\pi\,D + \rho_{ext}\,\pi\left[\left(\frac{D}{2}+t\right)^2 - \frac{D^2}{4}\right]}{\pi\left(\frac{D}{2}+t\right)^2}$$

ρ_s = areal density of graphite = 7.66×10^{-8} g/cm^2
ρ_{ext} = volume density of hydrated DNA in iodixanol = 1.12 g/cm^3

M. S. Arnold, *et al.*, *Nano Letters*, **5**, 713 (2005).

Density Gradient Centrifugation of DNA Encapsulated SWNTs



Density of DNA encapsulated SWNTs:
1.11 – 1.17 g/cm^3

→ DNA hydration layer thickness of 2 – 3 nm

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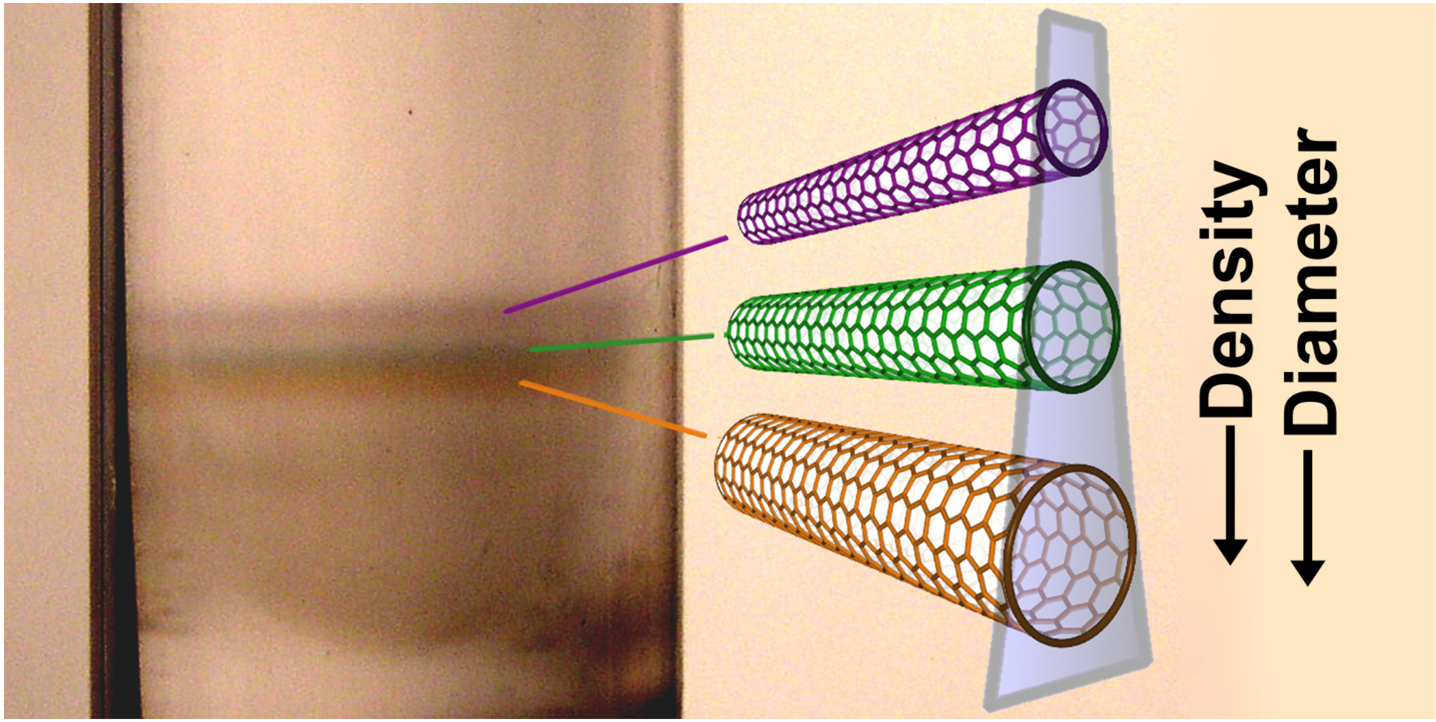
Separation of DNA Encapsulated SWNTs by Diameter



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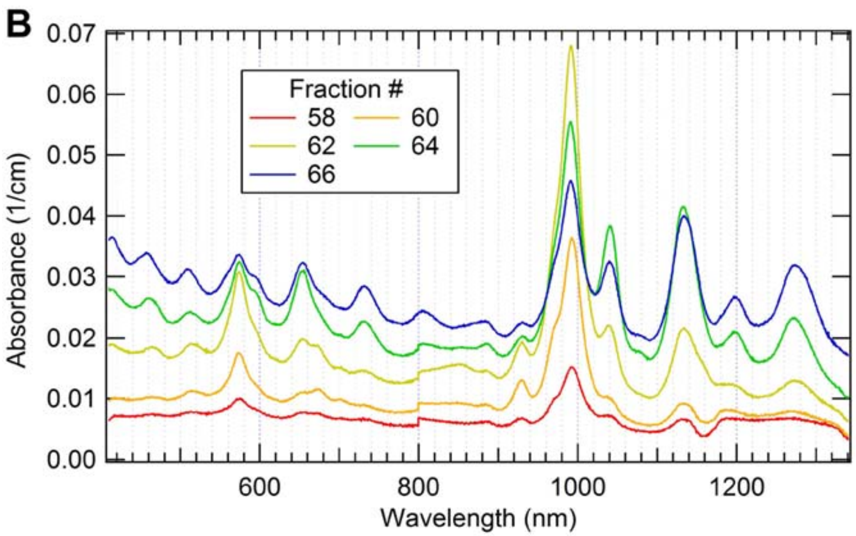
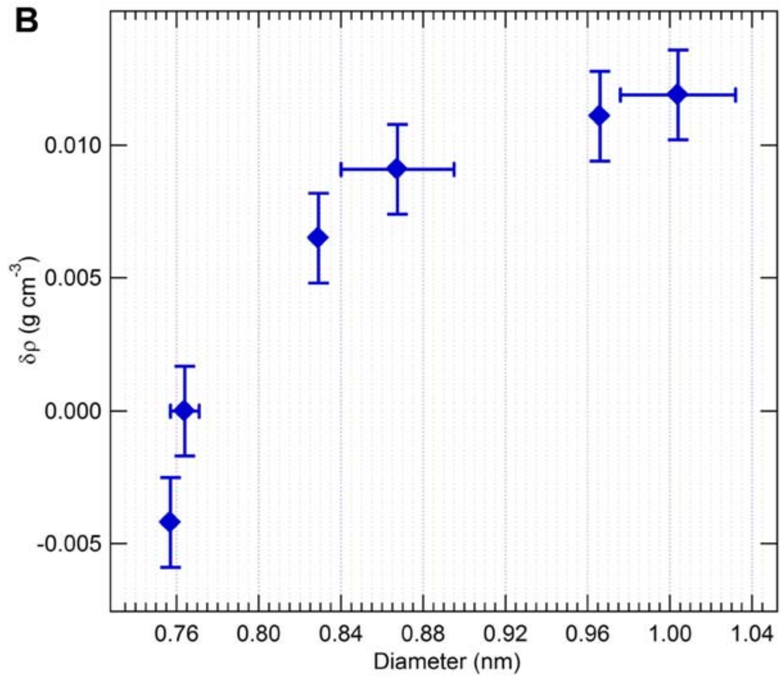
Correlating Diameter and Density





- Density of DNA encapsulated SWNTs increases with increasing diameter.
- Separation is most effective at small diameters.

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