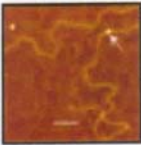
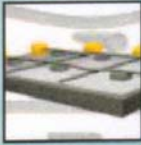



# Nanomaterials

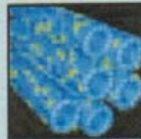
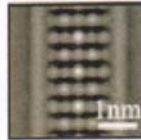
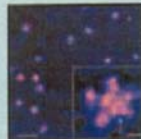

## Lecture 7: Carbon Nanomaterials

# Other Applications of Nanotubes

Other Uses for Nanotubes Beyond Electronics		Feasibility Ratings 0 = Science Fiction 2 = Demonstrated 4 = Ready for Market	
THE IDEA	OBSTACLES	FEASIBILITY	
 <p><b>Chemical and Genetic Probes</b> Tagged strand of DNA</p>	<p>A nanotube-tipped atomic force microscope can trace a strand of DNA and identify chemical markers that reveal which of several possible variants of a gene is present in the strand.</p>	<p>This is the only method yet invented for imaging the chemistry of a surface, but it is not yet used widely. So far it has been used only on relatively short pieces of DNA.</p>	<b>3</b>
 <p><b>Mechanical Memory</b> Nonvolatile RAM</p>	<p>A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to contact (the "on" state) and others to separate (the "off" state).</p>	<p>The switching speed of the device was not measured, but the speed limit for a mechanical memory is probably around one megahertz, which is much slower than conventional memory chips.</p>	<b>2</b>
 <p><b>Nanotweezers</b> Pincers five microns long</p>	<p>Two nanotubes, attached to electrodes on a glass rod, can be opened and closed by changing voltage. Such tweezers have been used to pick up and move objects that are 500 nanometers in size.</p>	<p>Although the tweezers can pick up objects that are large compared with their width, nanotubes are so sticky that most objects can't be released. And there are simpler ways to move such tiny objects.</p>	<b>2</b>

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

# Other Applications of Nanotubes

	<p><b>Supersensitive Sensors</b></p> <p>Oxygen sticks to tubes</p>	<p>Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens and other gases at room temperature, raising hopes for better chemical sensors.</p>	<p>Nanotubes are exquisitely sensitive to so many things (including oxygen and water) that they may not be able to distinguish one chemical or gas from another.</p>	<p><b>3</b></p>
	<p><b>Hydrogen and Ion Storage</b></p> <p>Atoms in hollow core</p>	<p>Nanotubes might store hydrogen in their hollow centers and release it gradually in efficient and inexpensive fuel cells. They can also hold lithium ions, which could lead to longer-lived batteries.</p>	<p>So far the best reports indicate 6.5 percent hydrogen uptake, which is not quite dense enough to make fuel cells economical. The work with lithium ions is still preliminary.</p>	<p><b>1</b></p>
	<p><b>Sharper Scanning Microscope</b></p> <p>Individual IgM antibodies</p>	<p>Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments' lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules.</p>	<p>Although commercially available, each tip is still made individually. The nanotube tips don't improve vertical resolution, but they do allow imaging deep pits in nanostructures that were previously hidden.</p>	<p><b>4</b></p>
	<p><b>Superstrong Materials</b></p> <p>Nanotube stress test</p>	<p>Embedded into a composite, nanotubes have enormous resilience and tensile strength and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake.</p>	<p>Nanotubes still cost 10 to 1,000 times more than the carbon fibers currently used in composites. And nanotubes are so smooth that they slip out of the matrix, allowing it to fracture easily.</p>	<p><b>0</b></p>

*Compiled by W. Wayt Gibbs, staff writer*

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

# Density of States

In general, the density of states in  $d$ -dimensions is:

$$D(E) = \left( \frac{L}{2\pi} \right)^d \int \frac{\delta(k(E) - k) dk^d}{|\nabla_k(E)|}$$

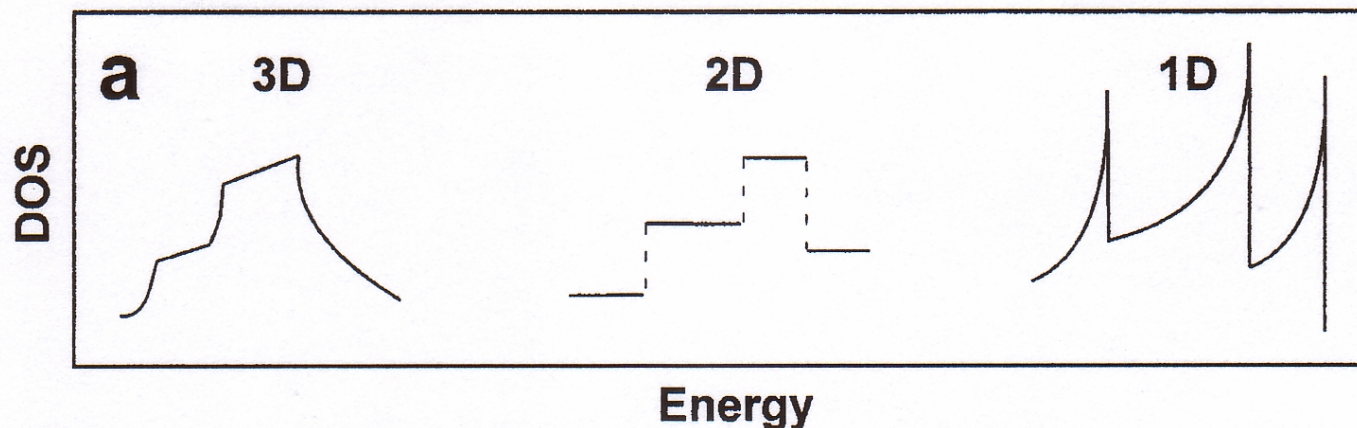
At band edges,  $|\nabla_k(E)| = 0$

→ van Hove singularities in the density of states

T. W. Odom, *et al.*, *J. Phys. Chem. B*, **104**, 2794 (2000).

## Nanotube 1-D Density of States

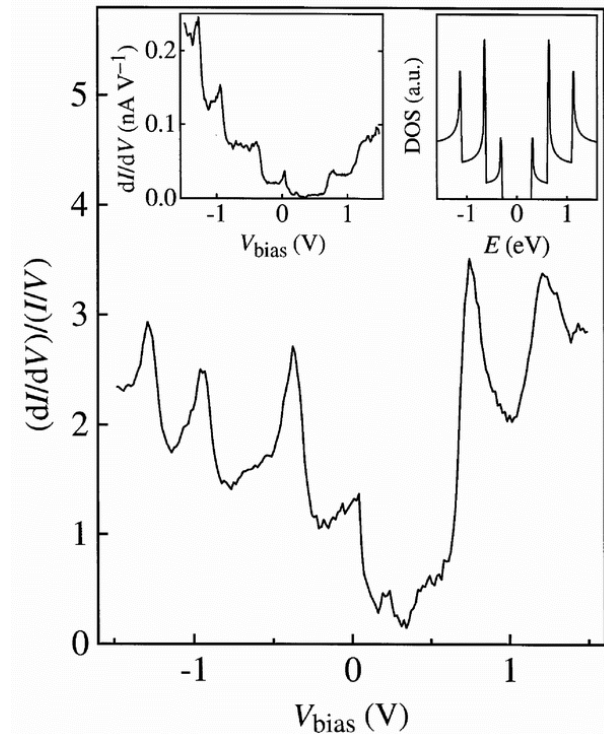
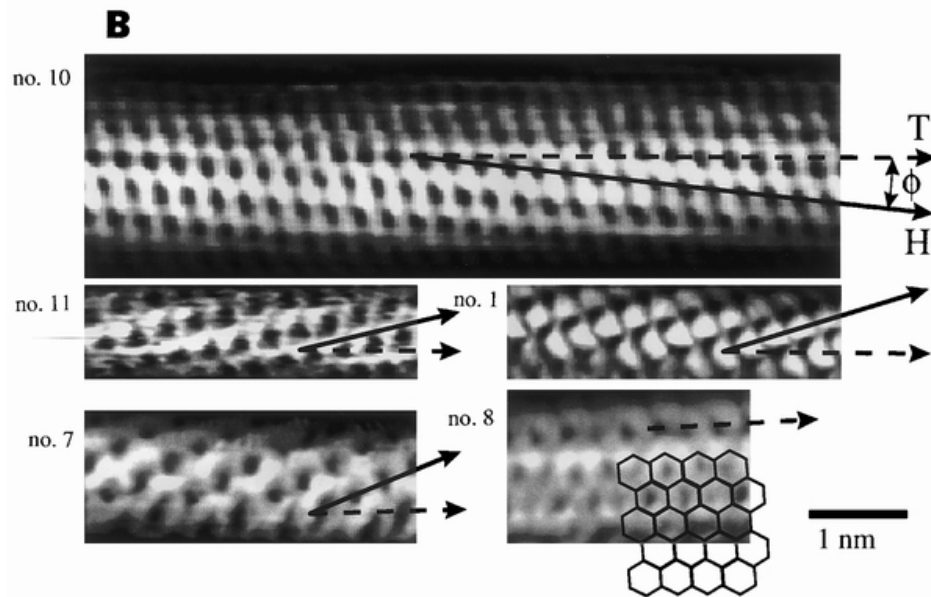
The van Hove singularities assume different forms based on the dimensionality of the system:



The 1-D nature of nanotubes leads to peaks in the density of states.

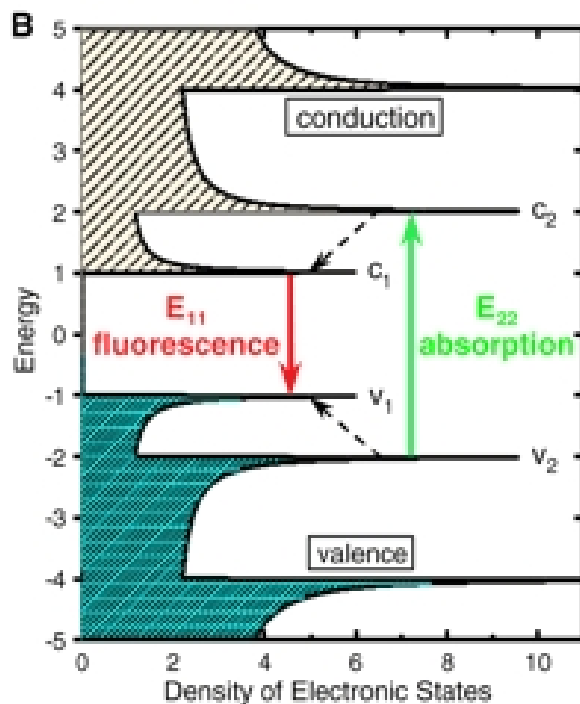
T. W. Odom, *et al.*, *J. Phys. Chem. B*, **104**, 2794 (2000).

# STM Measurements of Nanotube van Hove Singularities



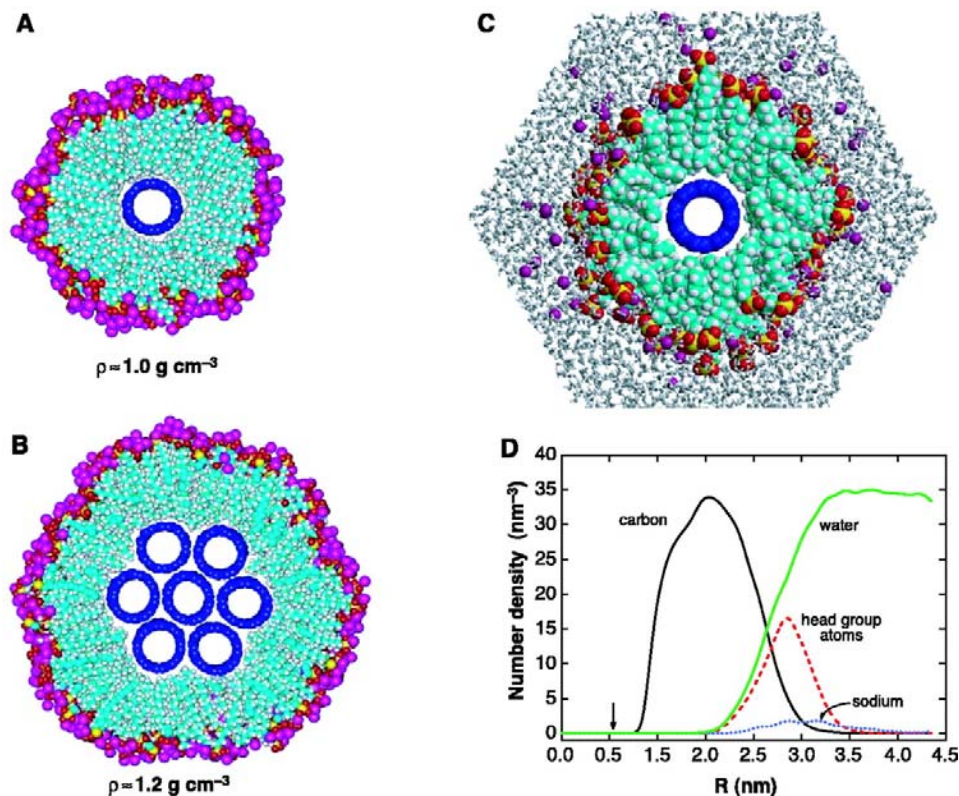
J. W. G. Wilder, *et al.*, *Nature*, **391**, 59 (1998).

# Implications of van Hove Singularities for Nanotube Optical Properties



S. M. Bachilo, *et al.*, *Science*, **298**, 2361 (2002).

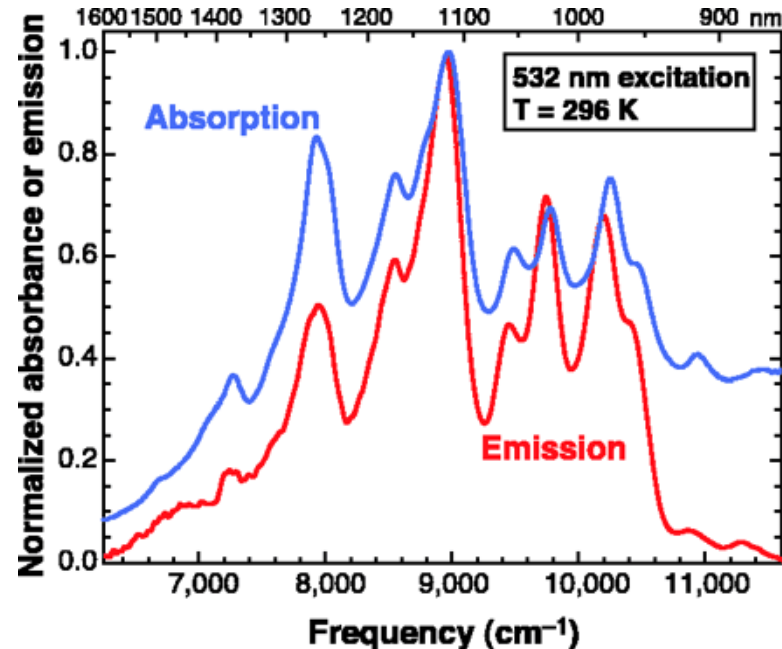
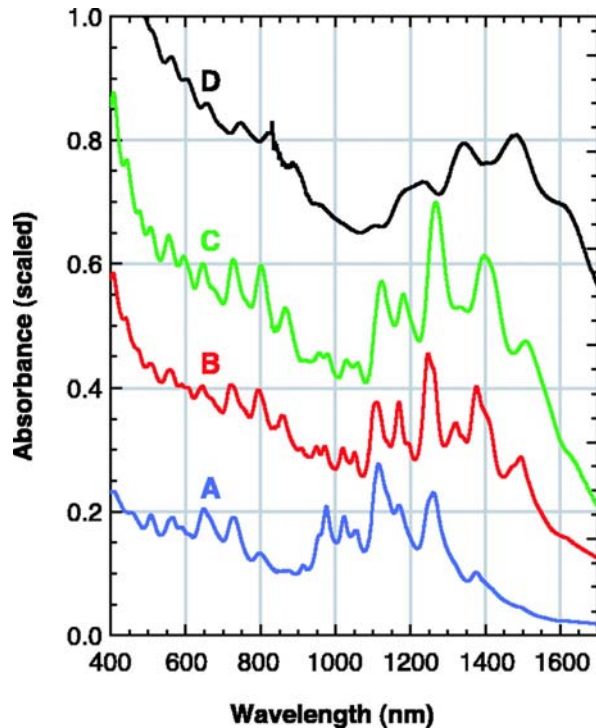
# Separating Carbon Nanotubes in Solution



M. J. O'Connell, *et al.*, *Science*, **297**, 593 (2002).

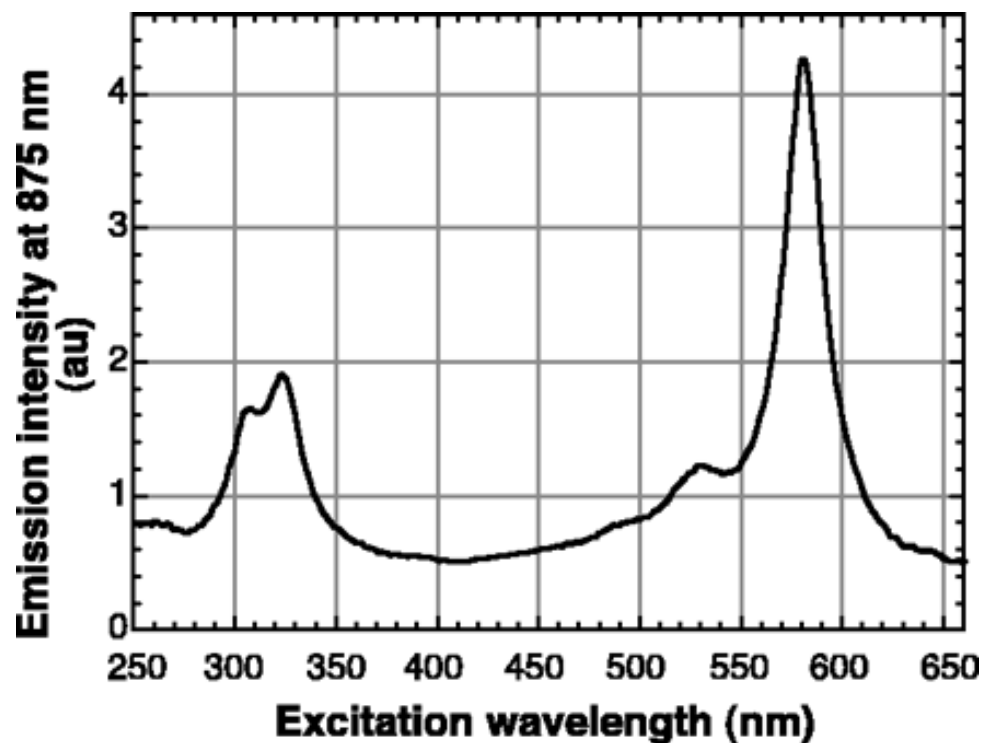


# Band Gap Absorption and Fluorescence from Individual Single-Walled Carbon Nanotubes



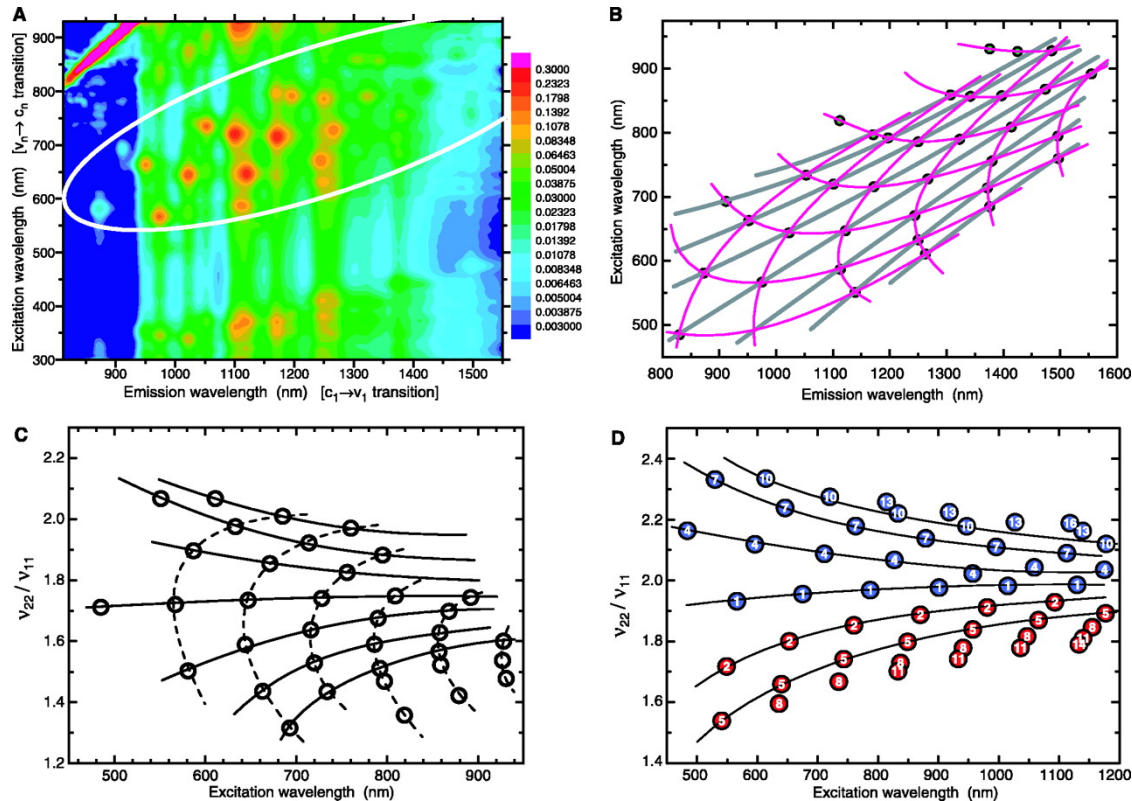
M. J. O'Connell, *et al.*, *Science*, **297**, 593 (2002).

## Excitation at the $E_{22}$ Transition



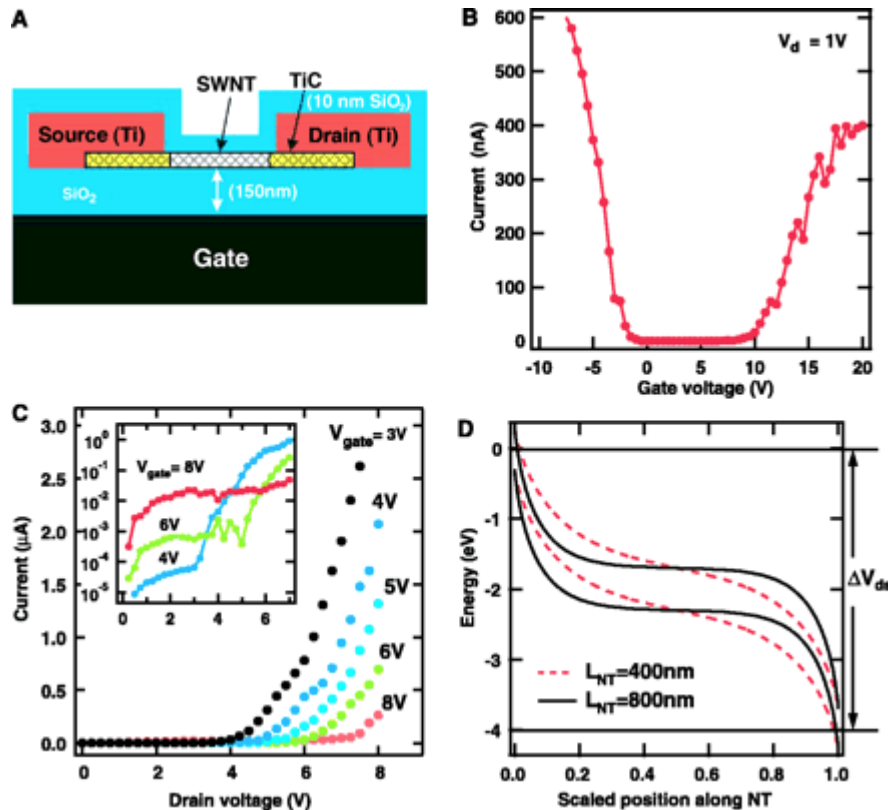
M. J. O'Connell, *et al.*, *Science*, **297**, 593 (2002).

# Structure-Assigned Optical Spectra



S. M. Bachilo, *et al.*, *Science*, **298**, 2361 (2002).

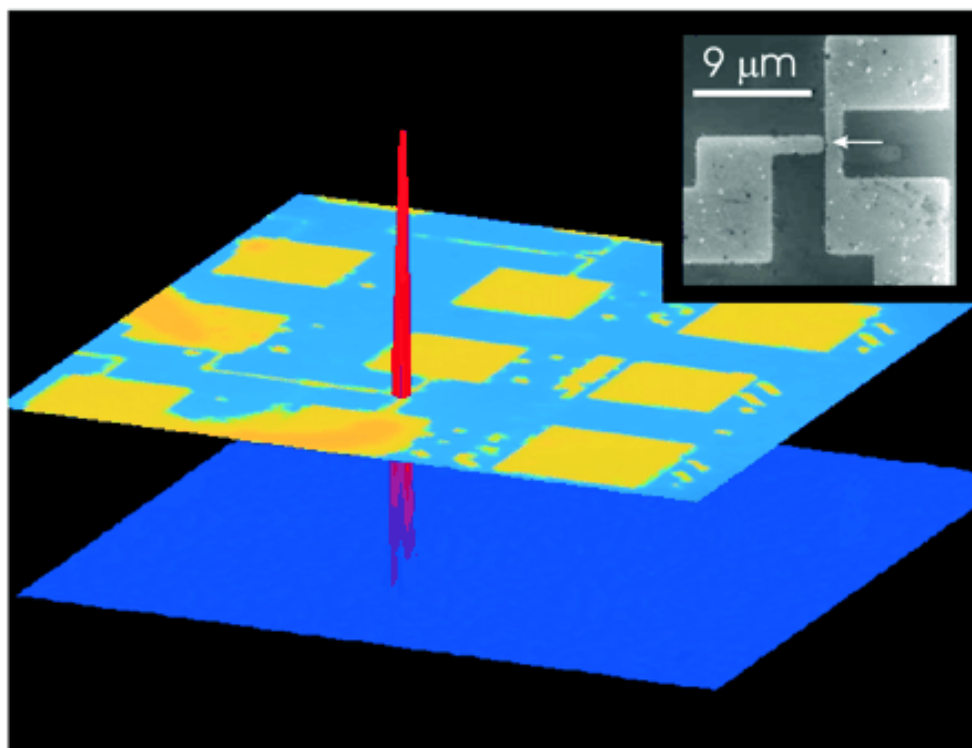
# Ambipolar Carbon Nanotube FET



**Fig. 1.** (A) Schematic diagram of the ambipolar s-SWNT device structure. (B) Electrical characterization of a typical ambipolar device. A plot of the drain current versus  $V_g$  for a grounded source and a small drain potential of 1 V is shown. The data indicate ambipolar behavior. (C) Plot of the drain current versus  $V_d$  for a grounded source and a gate potential of 5 V for the device used in the optical measurements. The inset shows the data on a logarithmic scale. (D) Calculated band structure for carbon nanotube FET devices with  $V_d = 4$  V and  $V_g$  halfway between the source and drain voltages.

J. A. Misewich, *et al.*, *Science*, **300**, 783 (2003).

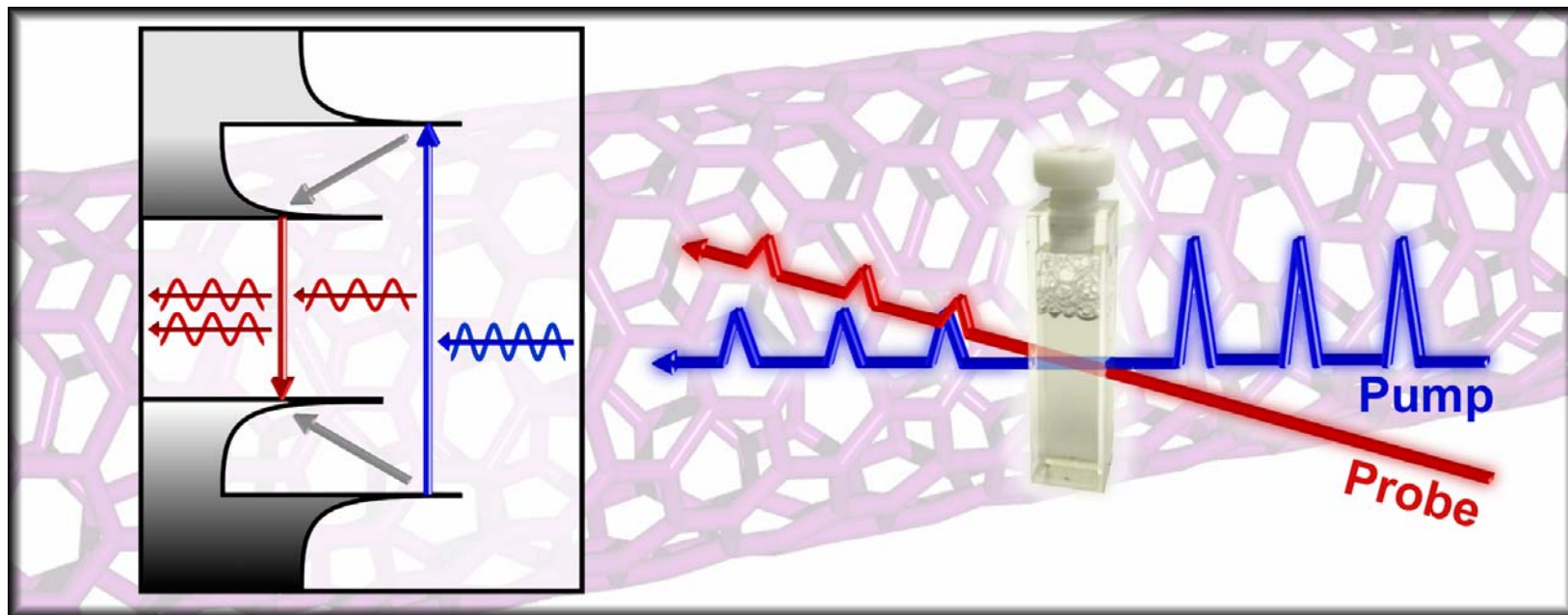
# Infrared Emission from an Ambipolar Nanotube FET



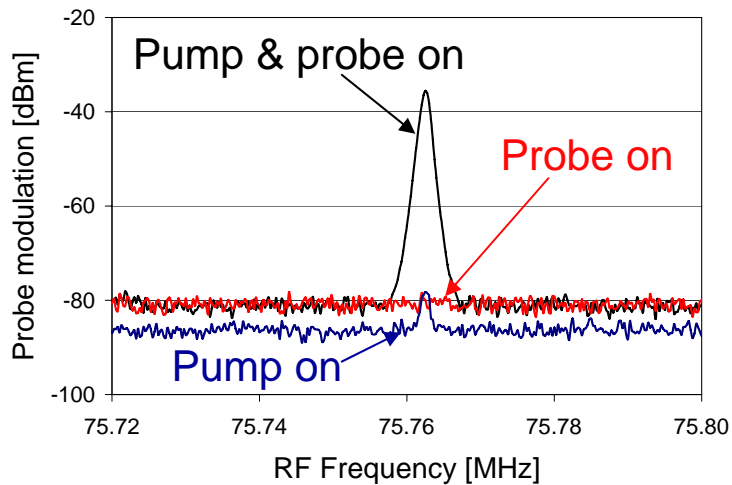
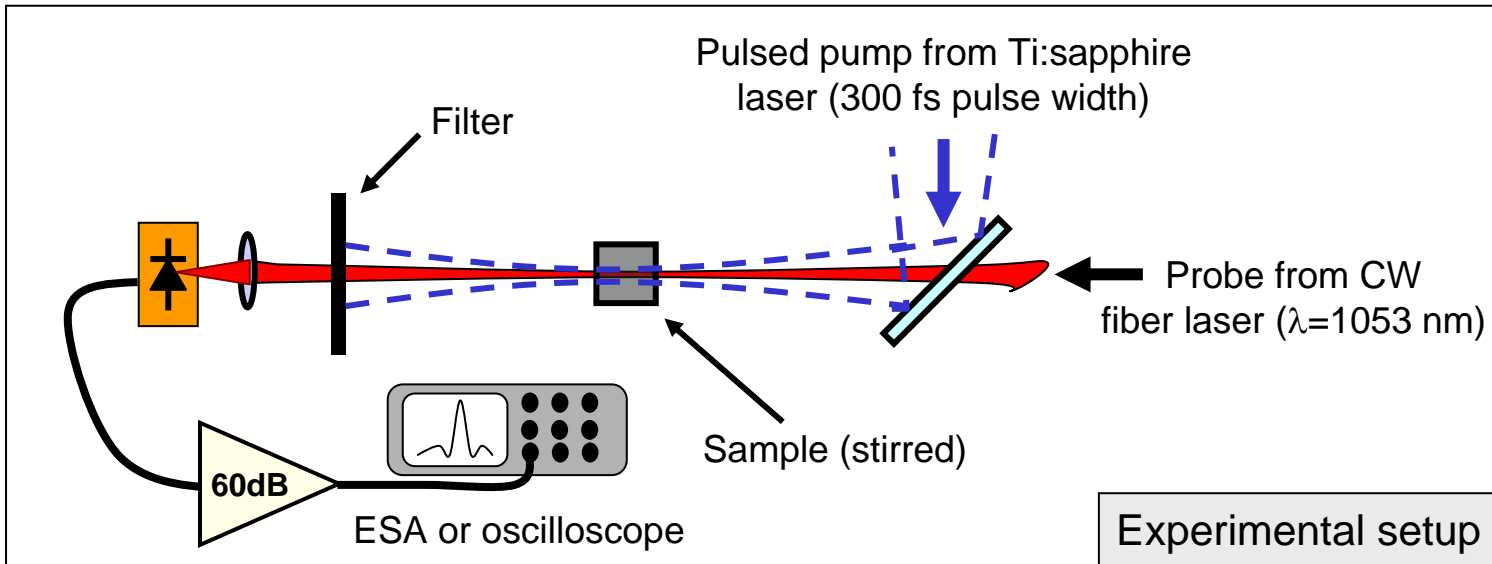
**Fig. 2.** Optical emission from an ambipolar carbon nanotube FET detected with an IR camera. The upper plane is a color-coded IR image of the carbon nanotube FET. The contact pads and thin wires leading to the carbon nanotube channel are shown in yellow. The lower plane is the surface plot of the IR emission image taken under conditions of simultaneous  $e^-$  and  $h^+$  injection into the carbon nanotube. The emission was localized at the position of the carbon nanotube. **(Inset)** SEM showing the device structure in the region of the nanotube emitter.

J. A. Misewich, *et al.*, *Science*, **300**, 783 (2003).

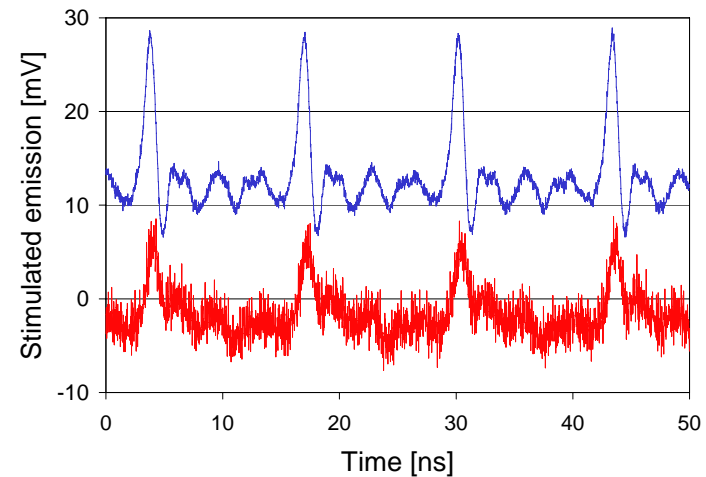
# Characterization of Stimulated Emission from Encapsulated SWNTs



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

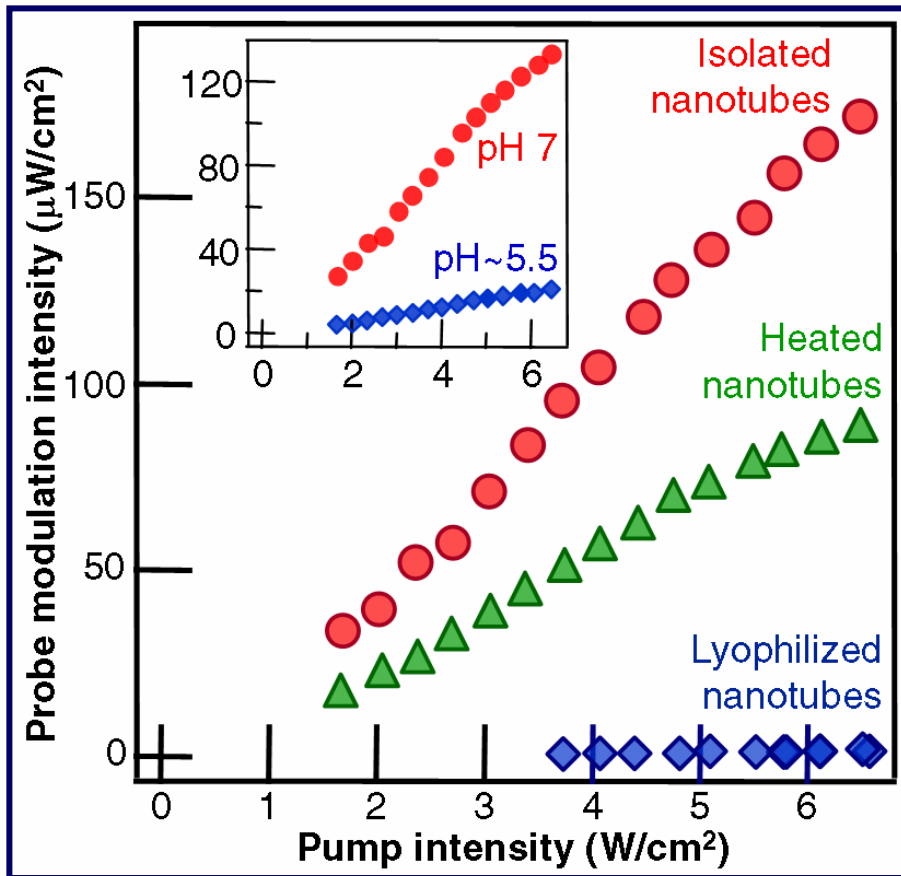


Probe modulation in frequency domain



Temporal response of probe modulation

# Effect of Aggregation and pH

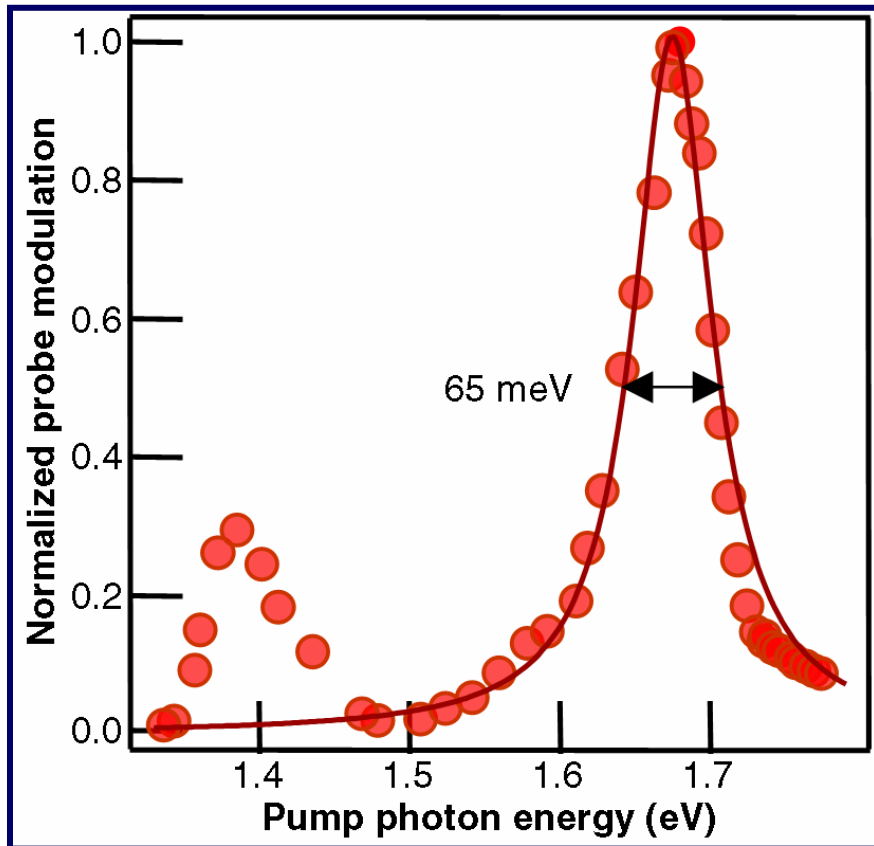


- Aggregation of isolated nanotubes by lyophilization and re-suspension drastically reduces probe modulation intensity by a factor of 122.
- Photobleaching disappears at acidic pH and is reversibly restored at neutral and basic pH, consistent with protonation of nanotube sidewalls at acidic pH.

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



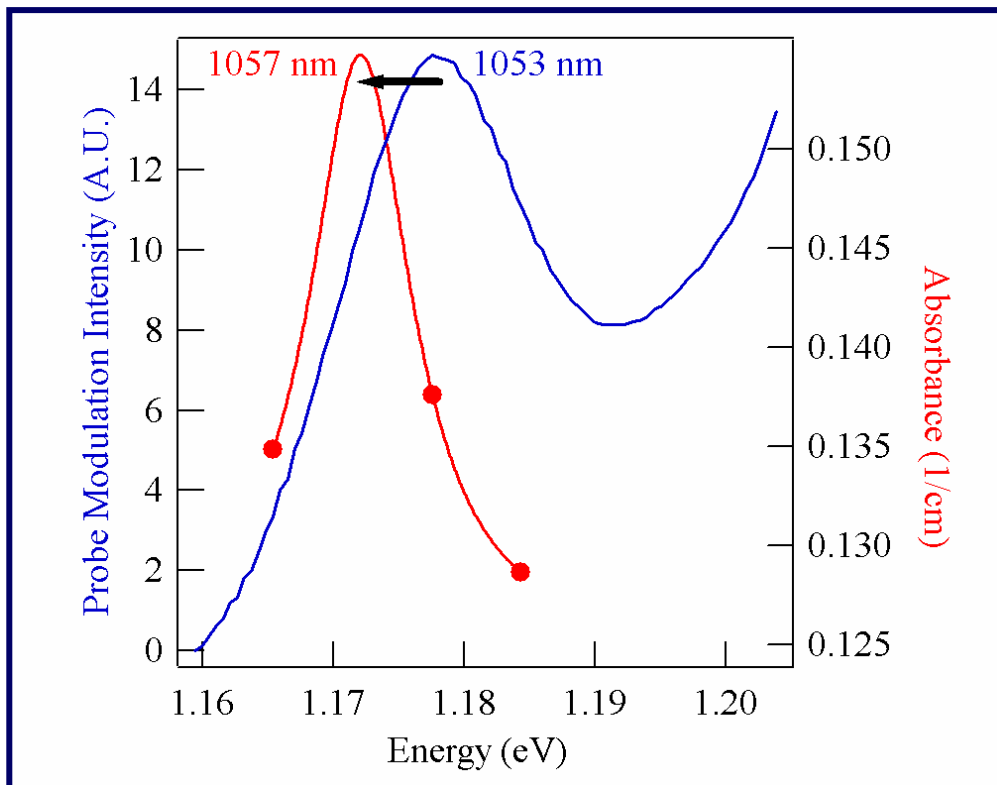
# Pump Spectral Dependence



- 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  $\sim 1600 \text{ cm}^{-1}$ , which matches the G-band Raman mode in SWNTs).

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

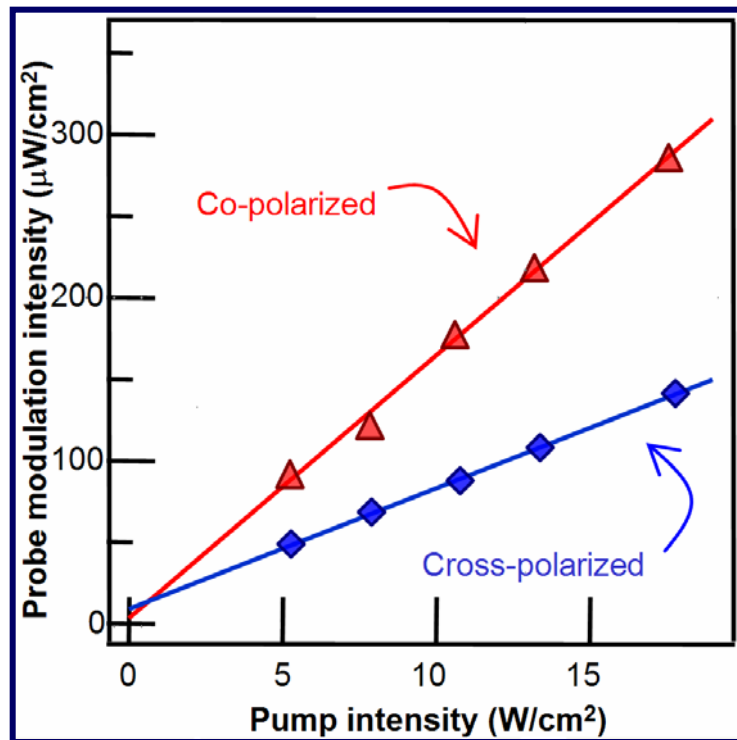
# Probe Spectral Dependence



- The probe modulation spectrum is slightly red-shifted from the absorbance spectrum by 45 cm<sup>-1</sup>.
- From a Lorentzian fit, the width of the E<sub>11</sub> transition is only 10 meV compared with 65 meV as measured for the E<sub>22</sub> transition.

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

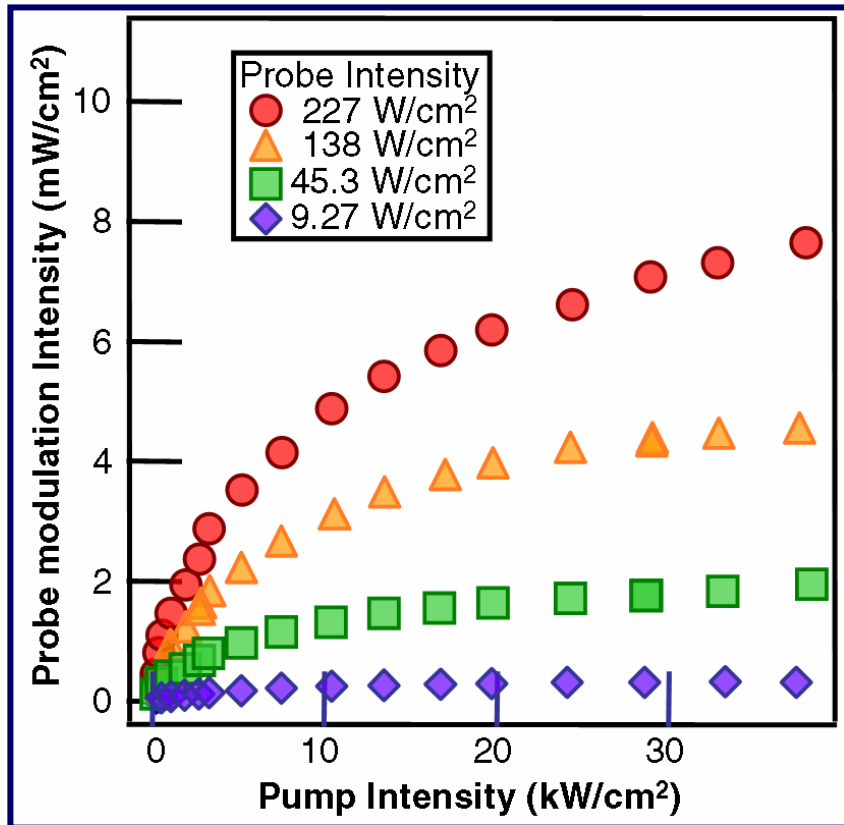
# Polarization Dependence



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).

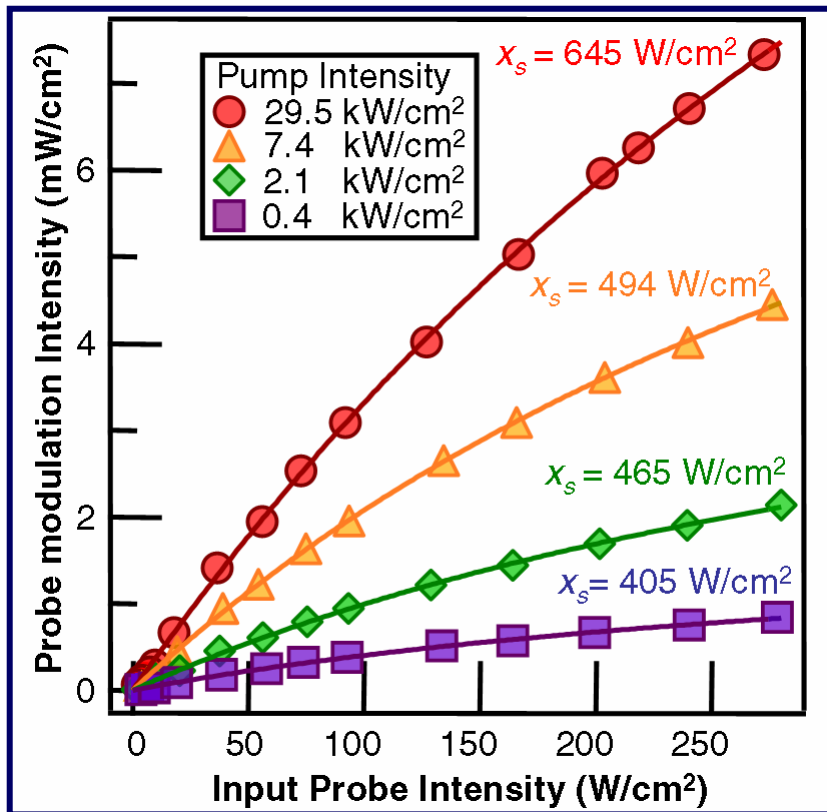
# Pump Saturation Effects



- At low pump intensities below 10 W/cm<sup>2</sup>, 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.

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

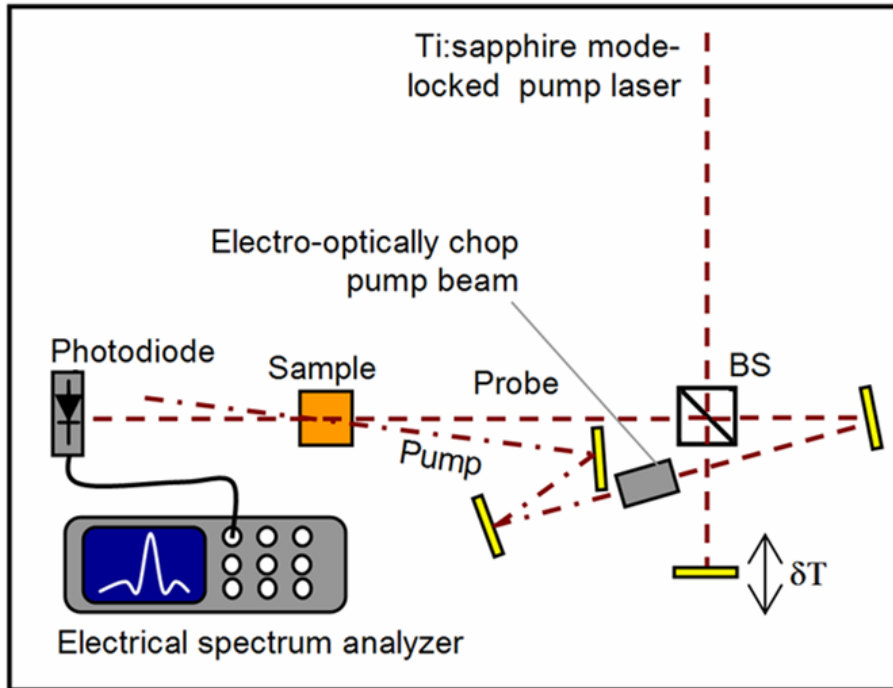
# Probe Saturation Effects



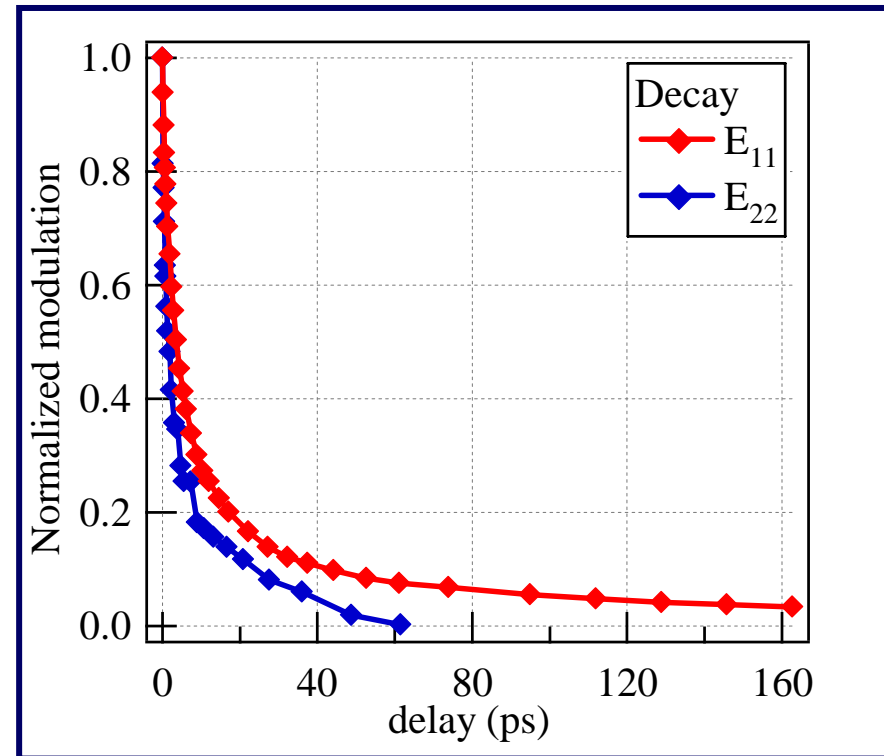
- $x_s$  corresponds to the probe intensity for which the rate of stimulated recombination is equal to the intrinsic rate of recombination.
- An increase in  $x_s$  at large pump intensities is consistent with an increase in the effective interband recombination rate due to enhanced Auger recombination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

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

# Degenerate Pump-Probe Measurements



Degenerate pump-probe optical setup.



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