Low dimensional sp2 carbon materials: graphene and carbon nanotubes

Stéphane BERCIAUD
Institut de physique et chimie de matériaux de Strasbourg (IPCMS)
European Summer Campus, Strasbourg, July 3 2012
email: stephane.berciaud@ipcms.unistra.fr
Outline

I – A brief introduction to carbon materials
II – Timeline: Nanotube and Graphene Gold Rush
III – Overview of the basic properties of graphene
IV – Some major experimental results and applications
V – From Graphene to carbon nanotubes
VI – Probing individual carbon nanotubes
Two popular carbon allotropes

• Carbon (1s² 2s² 2p²)

sp³ hybridized carbon: Diamond
• one s orbital and 3 p orbitals
• 3-dimensional structure
• Covalent bonds
• Metastable
• Electrically insulating
• Extremely robust
Two popular carbon allotropes

• Carbon (1s² 2s² 2p²)

sp² hybridized carbon: Graphite
• one s orbital and two p orbitals (in plane)
• pz is not hybridized and contains one electron
• 2-dimensional covalent structure + stacking
• Van der Waals interactions (out of plane)
• Cleavable but stiff and robust
• Excellent conductor (semi metal)

ABA Stacking

ABC Stacking

C.H. Lui Nature Physics 2011
Graphitic Materials

- Fullerenes (0D) → 1985 (Kroto, Curl, Smalley) → Nobel Prize 1996

- Single walled nanotubes (1D) → 1993 (NEC, IBM) → Kavli Prize 2008 (Iijima)

- Graphene (2D) → 2005 (Novoselov & Geim) → Nobel Prize 2010

- Graphite (3D) γράφειν: “to draw/ to write” Used since 4000 BC!

Adapted from Novoselov & Geim « the rise of graphene » Nat. Mater 6 184 (2007)
The graphene gold rush

- 1564: First graphite pencils
- 1859: Liquid suspension of graphene oxide (B. Brodie)
- 1947-1959: Electronic structure of graphite (Wallace, Slonczevski, Weiss, I)
- 1970’s: graphite intercalation compounds
- 1960’s-1990’s: Epitaxial graphene on SiC
- 1980’s-now: Fullerenes
- 1990’s-now: Carbon Nanotubes
  → Fascinating one dimensional systems
  → Many applications (bottleneck: contacts)
- Graphene: easier to pattern and contact
- Quasi 1D graphene ribbons ~ nanotubes
  → New experimental efforts
Late 90’s-early 2000’s :

• *Mesoscopic Graphite*
  T. Ebbesen *et al.*, R. Ruoff *et al.*, P. Kim *et al.*, W. de Heer *et al.*, etc...
  Nano-scrolls, nanocones, nanodisks, origami,...

• Several research proposals submitted for a "graphene-based electronics"
  (Georgia Tech., Manchester, Columbia, Cornell, MIT, etc...)

2004: First measurements on epitaxial multilayer graphene

2004: Electric field effect on 1 to 3 graphene layers
Novoselov, Geim *et al.* Science (2004)

2005: Observation of the "half integer" quantum hall effect on a graphene monolayer

2008-2010: Macroscopic growth of graphene
(B-H Hong *et al.*, J. Kong *et al.*, Ruoff *et al.*, J.M Tour *et al.*)
The graphene gold rush

Towards “industrial” production: several start-ups created

Source ISI Web of Knowledge (2010)
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"
Entering “Flatland”
Entering “Flatland”

**Introduction**

- Basic properties
- Making graphene... ...with scotch tape!
- Characterizing graphene

**Major breakthroughs**

- “Massless” Fermions
- Controlling graphene
- Towards applications
Atoms, molecules and solids

- In free space, all states are allowed for electrons
- In a crystal: the periodic boundary conditions give rise to a band structure with allowed and forbidden bands (bandgaps)
- Dispersion relation between electron momentum ($\mathbf{k}$) and energy ($E$)
  - Let us fill the bands...
Electrons in solids: band filling

Pauli principle (1925): at most one electron per quantum state

Conduction Band
- Empty states
- Fermi energy
- highest occupied electronic states
- $E_{\text{gap}}$

Valence Band
- occupied States

Insulator
- (wide gap $>5\text{eV}$)

Semiconductor
- (small gap $\sim1\text{eV}$)

Semi-metal
- Gapless

Metal
Electrons in solids: dimensionality matters!

Electron density of states (DOS) \( \rho(E) = \frac{dN(E)}{dE} \)

Number of states with energy \( E \in [E, E+dE] \)

**Parabolic bands** (effective mass approximation)

\[ E - E_0 = \frac{p^2}{2m_{\text{eff}}} = \frac{(\hbar k)^2}{2m_{\text{eff}}} \]

**Linear bands**

\[ E - E_0 = \hbar k \nu_{\text{Fermi}} \]

**Density of States**

- **3D**
  \( \rho(E) \propto \sqrt{E - E_0} \)

- **2D**
  \( \rho(E) = \text{const} \)

- **1D**
  \( \rho(E) \propto \frac{1}{\sqrt{E - E_0}} \)
The electronic structure of graphene

**Electronic Structure known since 1947***

**Tight binding approach** (up to 2\textsuperscript{nd} nearest neighbor)
- \(\pi\) and \(\pi^*\) bands (valence and conduction bands)
- Two atoms per unit cell (two sublattices)
- Nearest neighbor hopping: \(t \sim 2.8\) eV
- 2\textsuperscript{nd} nearest neighbor hopping: \(t' \sim 0.1\) eV
→ Electron-hole asymmetry

\[ E_{\pm}(\mathbf{k}) = \pm t\sqrt{3} + f(\mathbf{k}) - t'f(\mathbf{k}) \]

\[ f(\mathbf{k}) = 2\cos(\sqrt{3}k_ya) + 4\cos\left(\frac{\sqrt{3}}{2}k_ya\right)\cos\left(\frac{3}{2}k_xa\right) \]

---

Massless Fermions in graphene

1 electron per \( p_z \) orbital

⇒ Half-filled bands: Fermi level at the K and K' points (in undoped graphene)

⇒ Graphene is a Semi-metal

**Linear low energy dispersion “Dirac Cones”**

→ Formally identical to that of photons: \( m_{\text{eff}} = 0 \)

→ “Relativistic” electrons with \( v_{Fermi} = 10^6 \text{ m s}^{-1} \approx 3.3 \times 10^{-3} c \)

Cf. Lecture by Klaus Richter Friday morning
“Unstoppable” fermions

For massless relativistic particles
• Absence of back-scattering in a defect-free sample
• Klein tunnelling:
  → Crossing a potential barrier with a 100% probability
  → Different from tunnelling by a massive particle (exponential probability)

Experimental realization: Héterojunctions

B. Huard et al. PRL (2008)
Are 2D crystals stable?

**Long range fluctuations make 2D systems unstable**
- Coupling between bending and stretching modes stabilizes 2D membranes
- Microscopic ripples on the graphene surface?

**Stability in a 3D world**
- **Bottom-up approach**: growth on a substrate (CVD or epitaxy)
- **Top-down approach**: mechanical exfoliation
- Graphene is ultraflat on an ultraflat substrate (Lui et al. Nature 2009)
- Effect on rippling on the electronic properties of graphene?
Observation of 2D crystals

“Top-Down” approach: mechanical exfoliation of mesoscopic graphite (MIT, Cornell, Columbia, Manchester)
In 2005, the Manchester team introduces the “scotch tape method”!

Monolayer $h=0.9$ nm
Folder monolayer $h'=h+0.35$ nm

Unambiguous fingerprint of graphene?

Observation 2D atomic crystals
(a) NbSe$_2$, (b) graphite, (c) Bi$_2$Sr$_2$CaCu$_2$O$_x$, (d) MoS$_2$

K. Novoselov et al. Two-dimensional atomic crystals PNAS (2005)
Micro-mechanical exfoliation using adhesive tape!

Low yield, but
Very high quality samples

- Scientific American @ Columbia University

K. S. Novoselov et al. PNAS (2005)
... and a good bit of patience

- Tape Residues
- Graphite
- ~ 10 layers
- SiO₂
- Si
- 200 µm
... and a good bit of patience
A graphene monolayer (0.34nm thin) induces an appreciable contrast.
Device fabrication in the clean room

- electron beam lithography
- patterning by plasma etching
- metal deposition (contacts)
- wirebonding
- measurements ...

StNano Clean Room (Strasbourg)
Graphene Devices

Field effect transistors

Source

Drain

Graphene

Hall cross

Freestanding device


© M. Han (Columbia U.)
The field effect

- \( V_{SD} \neq 0 \rightarrow \text{source-drain current} 
- \text{Si/SiO}_2/\text{graphene: parallel plate capacitor} 
  \rightarrow \text{Gate-controlled} \ I_{SD}
- V_G = 0 \rightarrow \text{“universal” minimal conductivity} 
- V_G > 0 \rightarrow \text{hole current} 
- V_G < 0 \rightarrow \text{electron current}

First observed on a \( \sim 3 \) layer sample by Novoselov, Geim et al. (Science 2004)

Much of graphene’s potential arises from its great CONTROLLABILITY
Graphene in a magnetic field

- Quantized motion of electrons in a $\perp$ magnetic field
  → Formation of Landau levels
- In a 2D “parabolic” electron gas
  → Equidistant levels separated by:

$$E_n = \hbar \omega_C \left(n + \frac{1}{2}\right) \quad \omega_C = eB/m^*$$

Graphene: linear dispersion ($E = \hbar k \nu_F$):

$$E_n = \text{sgn}(n) \sqrt{2e\hbar \nu_F^2 B |n|}$$

$$\omega_C \propto \sqrt{B}$$

- NON-équidistant levels
- Scaling as $\sqrt{|n|}$
- Half filled level at $E=0$

McClure Phys Rev. (1959)
Quantum hall effect in graphene

“Classical” Hall effect
Transverse current in the presence of $\mathbf{B} \perp$

Quantum Regime (K. von Klitzing, Nobel 1985)
• When crossing a Landau Level
  ✓ Zero longitudinal resistivity $\rho_{xx}$
  ✓ Quantized plateau of Hall conductivity $\sigma_{xy}$

In practice:
Filling by electric field effect at constant $\mathbf{B}$

$\rho_{xx}(k \Omega)$ $\sigma_{xy}(4e^2/h)$

Half integer quantum hall effect
$\rightarrow$ hallmark of graphene

High resolution structural characterization

- Scanning tunneling microscopy (STM)
- Electron microscopy (TEM)
  - Atomic resolution
  - “Invasive methods”

Measurement of a tunnel current

E. Stolyarova et al. PNAS (2007)


Visualizing graphene’s band structure

Angle resolved photoemission spectroscopy (ARPES)

\[ \hbar \omega_{\text{phot}} = E(k) + W_{\text{ion}} + \delta E_C \]

\[ \hbar k_{\text{phot}}^\parallel = \hbar k_i^\parallel - \hbar k_f^\parallel \]

Bostwick et al., Nature Physics (2007)
Optical absorption and Raman spectroscopy

- Diffraction limited spatial resolution: micro-spectroscopy
- Mapping capabilities
- Easily combined with other measurements (electron transport)
- "Macro" versions also available for samples with large enough areas
- Electrical access, Magnetic Field, Low Temperature,...

A. Ferrari (Cambridge), A. Geim and k. Novoselov (Manchester), D. Basov (UCSD) T. Heinz & L. Brus Groups (Columbia), F. Wang Group (Berkeley), J. Kong & M. Dresselhaus (MIT), M. Pimenta & A. Jorio (UFMG, Brazil), Berlin groups (Reich, Thomsen, Maultzsch), H. Cheong (Korea), + French groups
Optical Spectroscopy of Graphene

Absorbance: \( \varepsilon = \pi \frac{e^2}{\hbar c} \approx 2.3\% \)

Linear Bands in 2 dimensions:
\( \rightarrow \varepsilon(\omega) \) is constant

- **Visible**: Measurement of the Number of layers
- **UV**: trigonal warping & many body effects
- **Infra-Red**: Gate tunable absorption edge

From Graphene to Graphite

Zone folding approach

- Electronic Structure of graphene multilayers from cuts in the 3D electron dispersion of graphite along the $k_z$ direction at quantized values of $k_z$.
- Single and Bi-Layer band structures can be seen as building blocks for the band structure of multi-layer graphene.
- Analogous method for nanotubes

Finer effects

- Influence of stacking ABA $\neq$ ABC
- Many Body effects (saddle point excitons)
- Electron-phonon coupling: Fano Physics
- Gate tunable absorption

Vibrational properties

Phonon dispersion (3 acoustic and 3 optical modes)

Energy and momentum conservation
✓ for a one phonon process

\[ \hbar \omega_{in} = \hbar \omega_{out} + \hbar \omega_{\text{phonon}} \]
\[ k_{in} = k_{out} + q_{\text{phonon}} \]
\[ k_{in} \approx k_{out} \approx 0 \Rightarrow q_{\text{phonon}} = 0 \]

G mode: \( \Gamma \) point LO and TO phonons

✓ Processes with \( q_{\text{phonon}} \neq 0 \)?

• Two phonons with opposite momenta
  → Symmetry allowed

• One phonon and one elastic collision on a defect
  → Symmetry forbidden

D and 2D modes
TO phonons near \( K \) and \( K' \)

Venezuela et al. PRB (2011)
Strong coupling to zone center ($\Gamma$) and zone edge ($K$) phonons

Highly sensitive probe of:
→ Number of Layers
→ Doping level, Disorder, Strain
→ Temperature

Gate tunable electron-phonon coupling

A Shift of the Fermi Energy induces:

i) G Phonon renormalization: $\omega_G \uparrow$ when $|E_F| \uparrow$

ii) Narrowing of the G mode linewidth

• Strong coupling to resonant e-h pair generation
  → Reduced Landau Damping when $|E_F| \neq 0$

J. Yan et al., PRL 98, 166802 (2007)
Even better with freestanding graphene!

The underlying SiO$_2$ has a negative impact on electron transport

- Unintentional doping
- Residual charge inhomogeneity (puddles)
- Coupling to substrate polar phonons

“Ultra clean” freestanding samples

- Quasi ballistic transport
- Approaching the Dirac point

Mobility $\mu = \frac{\sigma}{n e}$ improved by a factor $\sim 10$

$\mu \sim 200,000$ cm$^2$ V$^{-1}$ S$^{-1}$ at T = 300K

Mechanical properties of freestanding graphene

- **Intrinsic strength of 43 N/m for a monolayer!**
  - A 1m² graphene hammock would support...a 4.4 kg cat!!!

- **Electromechanical micro resonators:**
  - RF modulation of the gate bias
    - Vibration → variation of the capacitance
    - Resonant current modulation
    - Mass sensor (2. $10^{-21}$ g)

C. Lee et al., Science (2008)

J.S. Bunch et al., Science (2007)
Boron Nitride: best substrate so far

Hexagonal BN: small (1.7%) lattice mismatch wrt graphene
Large band gap $\sim 6$ eV: good gating material

- Excellent transport properties (fractional quantum hall effect)
- Large doping levels attainable without collapsing
- State of the art for high performance devices

C. Dean Nature Nanotechnology (2010)
Bandgap Engineering in Graphene

**Bilayer Graphene**

→ Gate tunable Bandgap (up to 250meV)

**Graphene Nanoribbons**

→ Size tunable Bandgap
  - e-beam lithography (Columbia, IBM,...)
  - Chemical derivation (Stanford, Rice, Mainz,...)
→ from expandable graphite + sonication
→ “Unzipping” carbon nanotubes
→ Bottom-up fabrication (polycyclic aromatic hydrocarbons)

Feng Wang et al. (Berkeley), Nature **459**, 820 (2009)

Han et al. PRL **97**, 206805 (2007)


Cai et al. Nature **466**, 470 (2010)
Graphene: Towards “Real” Applications

- **Large Scale Production (CVD growth on Cu foils)**

  - Graphene electrodes
    - Transparent & flexible
    - Graphene could replace ITO
    - Application to solar cell technology

  - A. Reina Nano Lett. 9, 30 (2008)
  - X. Li et al. Science 324, 1312 (2009)
Diameter, chirality & electronic structure given by two integers \((n,m)\): 
- \(1/3\) Metallic tubes (non-luminescent) if \(\nu = \text{mod}(n-m,3)=0\)
- \(2/3\) Semiconducting tubes (luminescent, \(\eta \sim 1\%\)) if \(\nu = \text{mod}(n-m,3)=1,2\)

- Strong Coulomb interactions between electrons and holes in 1D systems 
  \(\rightarrow\) Enhanced excitonic effects

Quasi-1D Systems: rolled-up graphene sheets

**Here:**

\((6,4)\) **S-SWNT**

\(d = 0.7\text{nm}, \theta = 23\ \text{deg}\)
1991: First observation of a multiwalled nanotube by Iijima
1992: Zone folding approach (Saito and Dresselhaus)
1993: First Single walled nanotubes observed (Iijima, Bethune)
1993-1996: Large Scale Synthesis (Ebbesen, Iijima, Rice...)
Mechanical and thermal properties
1997: Raman Radial Breathing mode (RBM)
1998: STM images, first nanotubes Transitors (IBM, Delft)
1999-2005: Breakthroughs in 1D transport in nanotubes
Nanotube devices, NEMS, etc...
2002: Observation of luminescence from individualized tubes
Optical structure assignment (Bachillo, Weisman, Smalley)
2003: Observation of individual tubes (Rochester)
2005: Observation of excitons (Columbia, Berlin) predicted in 1996 by Ando
2005-2006: Combined TEM and optical studies (Montpellier, Columbia)
2006-2010: Major advances in nanotube sorting
Band structure of carbon nanotubes

- Quantification of the transverse momentum
- SWNT sub-bands defined by equidistant cutting lines in the 2D graphene dispersion
- Metallic nanotube if the cutting line crosses K

$$\delta k_t = \frac{2}{d}$$

$$d = a\sqrt{n^2 + m^2 + nm}$$

$$a = 0.249 \text{ nm}$$
Metallic and Semiconducting SWNTs: (simplest) one electron picture

\[ E_0 = 2 \frac{\gamma_0 a}{\sqrt{3} d_t} \]

**M-SWNTs: \( \nu = 0 \)**

- \( M_{11} = 3 E_0 \)
- \( M_{22} = 6 E_0 \)

**S-SWNTs: \( \nu = \pm 1 \)**

- \( S_{11} = E_0 \)
- \( S_{22} = 2 E_0 \)
- \( S_{33} = 4 E_0 \)
- \( S_{44} = 5 E_0 \)

**M- and S- SWNTs with similar diameters have very different transition energies:**

\[ \nu = \text{mod} \ (n-m,3) \]

\( \rightarrow \) Combined measurements \((d_t \ M_{ii}, \ S_{ii})\)
For a given chiral angle $\theta$, “cutting lines” equidistant from $K$ cut different energy contours.

→ Splitting of $M_{ii}$ transitions into $M_{ii}^+$ and $M_{ii}^-$

→ “Family behavior” ($v=1$ and $v=-1$ have different $s_{i+1,i+1}/s_{ii}$ ratios)
Kataura Plot ($E_{ij}$ vs. $d_t$)

First introduced by Kataura et al., Synthetic Metals 103, 2555 (1999)
Optical Properties of Carbon Nanotubes

1D Density of states dominated by sharp van Hove singularities \( \propto (E - E_{ii})^{-1/2} \)

- **Metallic SWNTs**
- **Semiconducting SWNTs:**

- One electron picture
  \[ \rightarrow \text{Band to band optical transitions} \]
Excitonic effects in Carbon Nanotubes

- K-K' degeneracy lifting: 4 singlet + 12 triplet states
- Transverse excitons ($E_{ij}^{TB}$)
- “Rydberg” States

In practice the lowest optically active exciton carries most of the oscillator strength

Th: IBM, S. Louie Group (Berkeley), Kane & Mele (U. Penn), E. Molinari group (U. Modena), Zhao & Mazumdar (Az. State U.), T. Ando (Tokyo), etc...
F. Wang et al., PRL 99 227401 (2007) (M-SWNTs)
1D Excitons in Semiconducting SWNTs

- Two photon absorption couples to an excited excitonic state above the bright exciton.
- Exciton photophysics in SWNTs: a very active research field.

Exciton manifold? Exciton lifetime? exciton mobility? Multiple excitons vs multiexcitons? Role of the local environment? How to improve the luminescence quantum yield?

Optical characterization of individual SWNTs

• **Luminescence Spectroscopy**  
  (Rice, Rochester, Ottawa, Los Alamos, Munich, Bordeaux, Kyoto,...)  
  → Limited to individual Semiconducting SWNTs

  ![S22=2.18eV, S11=1.27eV, 57meV, 20meV](image)


• **Absorption Spectroscopy**  
  (Bordeaux, Berkeley)  
  → Semiconducting & Metallic SWNTs  
  → Limited spectral Range

  ![S11=1.27eV, S22=2.18eV, 57meV, 20meV](image)


• **Raman Scattering Spectroscopy**  
  (MIT+Belo Horizonte, Columbia, TU Berlin, Rochester,...)  
  → Semiconducting & Metallic SWNTs  
  → Weak signal  
  → Indirect method (fitting procedure)
One dimensional effect: polarization dependence

Confocal luminescence images with 2 orthogonal polarizations
Diffraction limited spot (~0.5 µm)

Maximum signal for $E \parallel$ tube axis
Strong depolarization effect for $E \perp$ tube axis
• **Isolated free-standing SWNTS**
  → Minimal environmental perturbations
  → Clear and “simple” spectroscopic features

Electronic transitions (Rayleigh)$^+$
→ Rapid determination of $d_t$ and $\theta$
→ Metallic or Semiconducting

Vibrational Properties (Raman)$^*$
→ $\omega_{RBM} \propto 1/d_t$
→ Chirality dependent e-ph coupling (G-mode)

Sfeir et al., Science 312, 554 (2006) (Rayleigh + TEM)
* Wu et al., PRL 98, 027402 (2007) (Rayleigh+Raman)
Semiconducting nanotubes

S-SWNTs with $d_t=1.5-2.0\text{nm}$: $S_{33}$ and $S_{44}$ transitions

- Chirality dependent $S_{44}/S_{33}$ ratio
- Sidebands at $\sim200\text{meV}$
  $\rightarrow$ Exciton-optical phonon coupling
  $\rightarrow$ High-order transitions $=$ Excitonic

- Bi-Modal (Narrow) G-mode
  $\rightarrow$ LO-TO phonon splitting

S. Berciaud et al. PRB 81, 041414(R) (2010)
**S-SWNTs: exciton vs. free-carriers models**

- **Excitonic model more appropriate**
  - $\gamma_{33} \sim 85$ meV
  - Very fast ($\sim 20$ fs) $S_{33} \rightarrow S_{22}$ decay
  - $\gamma_{33} \ll$ binding energy
  - $\rightarrow$ Exciton stability

\[ \sigma_{\text{Rayleigh}} \propto \omega^3 |\chi(\omega)|^2 \]

- Excitonic model (Lorentzian)
- Free-carriers model (band to band transitions in 1D)

\[ \chi(\omega) \propto \chi_B + \left[ (\omega - \omega_0) - i \frac{\gamma}{2} \right]^{-1} \]

\[ \chi_2(\omega) = \frac{\omega_p^2}{\omega^2} \frac{\sqrt{\eta + \sqrt{1 + \eta^2}}}{\sqrt{1 + \eta^2}}, \quad \eta = \frac{\omega - \omega_0}{\gamma/2} \]

\[ \chi_1(\omega) \quad \text{From Kramers-Krönig transform} \]
Metallic nanotubes

M-SWNTs with $d_t=2.5-2.75$ nm: $M_{22}$ transitions

- Chirality dependent $TW$ splitting and electron-phonon coupling*
- Broad and asymmetric G$^-$ feature
- No observable Phonon sidebands
  $\rightarrow$ Reduced strength of excitonic effects
  $\rightarrow$ PSBs (if any) overlap with band-to-band transitions

* Wu et al., PRL 98 027402 (2007)
S. Berciaud et al. PRB 81, 041414(R) (2010)
**M-SWNTS: exciton vs. free-carriers models**

![Graph](image)

- Reduced strength of excitons in 1-D Metals (No PSBs)
  
  **BUT** excitonic features remain observable

\[
\sigma_{\text{Rayleigh}} \propto \omega^3 |\chi(\omega)|^2
\]

- Excitonic model (Lorentzian)

\[
\chi(\omega) \propto \chi_B + [(\omega - \omega_0) - i\gamma/2]^{-1}
\]

- Free-carriers model
  (band to band transitions in 1D)

\[
\chi_2(\omega) = \frac{\omega_p^2}{\omega^2} \sqrt{\eta + \sqrt{1 + \eta^2}}, \quad \eta = \frac{\omega - \omega_0}{\gamma/2}
\]

\[
\chi_1(\omega) \quad \text{From Kramers-Krönig transform}
\]

→ Very fast (~20 fs) \(M_{22} \rightarrow M_{11}\) decay
→ Similar intersubband decay times in \(M\)- and \(S\)-SWNTS
A “new” feature in the Raman Spectra of $M$-SWNTs

Rayleigh Spectrum

$E_{\text{Laser}} - M_{22}^- \approx 60 \text{ meV} \approx 500 \text{ cm}^{-1}$

$M_{22}^+ = 2.19 \text{ eV}$
$M_{22}^- = 2.08 \text{ eV}$
$E_{\text{Laser}} = 2.14 \text{ eV}$

Broad feature at 500 cm$^{-1}$

H. Farhat, S. Berciaud et al. PRL 107 157401 (2011)
Flat Raman Background in S-SWNTs

- No observed broad feature in S-SWNTs
Interpretation: Electronic Raman Scattering

- Inelastic Scattering involving a broad range of e-h quasi-particles
- **Resonant enhancement** for $E_S = M_{ii}^{-/+}$

In this picture, the low-energy continuum plays an essential role

→ No ERS expected in $S$-SWNTs
→ Anti-Stokes ERS can occur in $M$-SWNTs for $E_L < M_{ii}$

H. Farhat, S. Berciaud et al. PRL 107 157401 (2011)
Carbon nanotube opto-electronics

- **Size tunable “bandgap” emission**
  
  ![Absorption and Emission](image)

  Rice group: Science 297, 593 (2002)

- **Single photon emission**
  
  ![PL Intensity](image)

  Högele et al. PRL 100, 217401 (2008)

- **Electrically induced emission**
  
  ![Emission Diagram](image)

  IBM, Science 310, 1172 (2005)

  See also: Science 300, 783 (2003), Nature Nano. 5, 27 (2010)

- **Carrier multiplication in p-n junctions**
  
  ![Carrier Multiplication Diagram](image)

  Gabor et al., Science 325, 1367 (2009)
Outlook

• Fascinating phenomena occur in reduced dimensions
  ➢ Graphene: a truly 2-dimensional system
    • Massless dispersion
    • Easily processable
    • Gate tunable properties (high sensitivity)
    • Now available in macroscopic quantities for applications
  ➢ Carbon Nanotubes: model quasi 1D systems
    • Large variety of carbon nanotube species with distinct properties: all-optical structure assignment
    • Strong coulombic effects (excitons, ee interactions)
    • “Physics-rich” Raman spectra (especially for M-SWNTs)
    • Chirality sorted nanotubes are now available (great for applications)
The Rise of Graphene

The electronic properties of graphene

A. H. Castro Neto
Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215, USA

F. Guinea
Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

N. M. R. Peres
Center of Physics and Department of Physics, Universidade do Minho, P-4710-057, Braga, Portugal

K. S. Novoselov and A. K. Geim
Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, United Kingdom

(Published 14 January 2009)
P. Avouris, M. Freitag, V. Perebeinos,

**Carbon-nanotube photonics and optoelectronics**


Mildred S. Dresselhaus, Gene Dresselhaus, Riichiro Saito and Ado Jorio

**Exciton Photophysics of Carbon Nanotubes**

DOI:10.1146/annurev.physchem.58.032806.104628
Andre Geim: Nobel AND...igNobel Laureate!
For levitating a frog in a strong magnetic field
Also works with strawberries...
Broad and Asymmetric G Mode in M-SWNTs

Phonon Softening and Broadening

- Strong electron-phonon coupling
- Analogous physics in graphene

Origin of the G mode Asymmetry (a 10 year old debate*)

- Tube-tube interactions (only in bundles)?
- Incoherent superposition to a low-energy background?
- Fano interference with a continuum (low energy e-h pairs, plasmons)?

*Brown (PRB 2001), Paillet (PRL 2005), Oron Carl (Nano Lett 2005), Farhat (PRL 2007), Wu PRL (2007), etc...
How does ERS affect the G-mode lineshape?

*Fano interference between:*

- one discrete state (LO phonon)
- and a continuum of states (e-h pairs)

\[
I_{LO}(\omega) = I_0 \left[ \frac{q\Gamma_{LO} + (\omega - \omega_{LO})}{(\omega - \omega_{LO})^2 + \Gamma_{LO}^2} \right]^2
\]

\[
\frac{1}{q} = \frac{M_e}{M_{ph}} V_{e-ph}
\]

Related data: IR spectroscopy in gated bilayer graphene
How does ERS affect the G-mode lineshape?

The G-mode remains weakly asymmetric after subtraction of the ERS background.

- This asymmetry is an intrinsic feature of M-SWNTS
- \( q \approx -10 \) \( \Rightarrow \) The “phonon channel” largely dominates

H. Farhat, S. Berciaud et al. unpublished