Inelastic Light Scattering in Graphene
Time and Space Localization

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Outline

• Time localization
  – Stokes-anti-Stokes Correlation

• Space localization
  – Tip enhanced Raman Spectroscopy
Outline

• **Time localization**
  – **Stokes-anti-Stokes Correlation**

• **Space localization**
  – *Tip enhanced Raman Spectroscopy*
Tutorial Introduction

Stokes and anti-Stokes scattering processes
Inelastic Scattering of Light

\[ E_{\text{Laser}} - \Delta E_{\text{phonon}} \]

\[ E_{\text{elastic}} = E_{\text{Laser}} \]

\[ E_S = E_{\text{Laser}} - E_{\text{phonon}} \]
Inelastic Scattering of Light

\[ E_{\text{Laser}} - \Delta E_{\text{phonon}} = E_{\text{elastic}} = E_{\text{Laser}} - E_{\text{phonon}} \]

Graphene Raman spectrum

From Carozo

G band

From Samsonidze

Raman shift (cm\(^{-1}\))

G
Inelastic Scattering of Light

\[ E_{aS} = E_{\text{Laser}} + E_{\text{phonon}} \]

\[ E_{\text{elastic}} = E_{\text{Laser}} \]

\[ E_S = E_{\text{Laser}} - E_{\text{phonon}} \]

\[ \frac{I_S}{I_{aS}} \propto e^{E_{\text{phonon}}/k_BT} \]
Phonon - Quantum Harmonic Oscillator

\[ \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} Kx^2 \right] \Psi_n = E_n \Psi_n, \quad (n = 0, 1, 2, \ldots) \]

\[ \mathcal{H}|n\rangle = \hbar \omega [N + 1/2]|n\rangle = \hbar \omega (n + 1/2)|n\rangle \]

\[ N = a^\dagger a \]

\[ a^\dagger = \frac{p + i \omega mx}{\sqrt{2\hbar \omega m}} \]

\[ a = \frac{p - i \omega mx}{\sqrt{2\hbar \omega m}} \]

\[ a^\dagger|n\rangle = (n + 1)^{1/2}|n + 1\rangle \]

\[ a|n\rangle = n^{1/2}|n - 1\rangle, \quad (n \neq 0) \]

\[ \frac{I_S}{I_{aS}} \propto \frac{n + 1}{n} \]
The Stokes/anti-Stokes ratio in light scattering

The probability to annihilate or create a phonon depends on the phonon statistics, which is given by the Bose-Einstein boson distribution function

\[
\frac{I_S}{I_{aS}} \propto \frac{n + 1}{n}
\]

\[
\frac{I_{aS}}{I_S} = C \frac{n_0}{1 + n_0} = Ce^{\frac{E_q}{k_B T}}
\]

From \(I_S/I_{aS}\) you can get the temperature

\[
T = \frac{E_{ph}}{k_B \left[ \ln C - \ln \frac{I_{aS}}{I_S} \right]}
\]
Applications of $I_s/I_{as}$ ratio in nanoscience

A few examples from the graphene community
Phonon populations and electrical power dissipation in carbon nanotube transistors

Mathias Steiner¹, Marcus Freitag¹, Vasili Perebeinos¹, James C. Tsang³, Joshua P. Small¹,
Megumi Kinoshita¹, Dongning Yuan², Jie Liu² and Phaedon Avouris¹*

Carbon nanotubes and graphene are candidate materials for nanoscale electronic devices¹,². Both materials show weak acoustic phonon scattering and long mean free paths for low-energy charge carriers. However, high-energy carriers couple strongly to optical phonons³-⁴, which leads to current saturation⁵-⁶ and the generation of hot phonons⁷. A non-equilibrium phonon distribution has been invoked to explain the negative differential conductance observed in suspended metallic nanotubes⁸, while Raman studies have shown the electrical generation of hot G-phonons in metallic nanotubes⁹,¹⁰. Here, we
Thermal Conductivity of Graphene in Corbino Membrane Geometry

Clement Faugeras,†,* Blaise Faugeras,‡ Milan Orlita,†,‡ M. Potemski,† Rahul R. Nair,§ and A. K. Geim§

VOL. 4 • NO. 4 • 1889–1892 • 2010 ACSNANO

ABSTRACT  Local laser excitation and temperature readout from the intensity ratio of Stokes to anti-Stokes Raman scattering signals are employed to study the thermal properties of a large graphene membrane. The concluded value of the heat conductivity coefficient $\kappa \approx 600 \text{ W/(m-K)}$ is smaller than previously reported but still validates the conclusion that graphene is a very good thermal conductor.

$$T = \frac{E_{ph}}{k_B \left[ \ln C - \ln \frac{I_{as}}{I_S} \right]}$$

![Graph showing intensity and temperature measurements against Raman shift and distance from the center.](Image)

- $P = 6.2 \text{ mW}$
- $\lambda_{exc} = 632.8 \text{ nm}$
- $r = 21 \mu m$
- $r = 15 \mu m$
- $r = 0 \mu m$
- $P_{laser} = 6.2 \text{ mW}$
- $T_{edge} = 295 \text{ K}$
Electron and Optical Phonon Temperatures in Electrically Biased Graphene

Stéphane Berciaud,¹,²,∗ Melinda Y. Han,³ Kin Fai Mak,¹ Louis E. Brus,² Philip Kim,⁴ and Tony F. Heinz¹,†

We examine the intrinsic energy dissipation steps in electrically biased graphene channels. By combining *in-situ* measurements of the spontaneous optical emission with a Raman spectroscopy study of the graphene sample under conditions of current flow, we obtain independent information on the energy distribution of the electrons and phonons. The electrons and holes contributing to light emission are found

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\[ T = \frac{E_{ph}}{k_B \left[ \ln C - \ln \frac{I_{as}}{I_S} \right]} \]
Phonon Anharmonicities in Graphite and Graphene

Nicola Bonini, Michele Lazzeri, Nicola Marzari, and Francesco Mauri

We determine from first principles the finite-temperature properties—linewidths, line shifts, and lifetimes—of the key vibrational modes that dominate inelastic losses in graphitic materials. In graphite, the phonon linewidth of the Raman-active $E_{2g}$ mode is found to decrease with temperature; such anomalous behavior is driven entirely by electron-phonon interactions, and does not appear in the nearly degenerate infrared-active $E_{1u}$ mode. In graphene, the phonon anharmonic lifetimes and decay channels of the $A_1'$ mode at $K$ dominate over $E_{2g}$ at $\Gamma$ and couple strongly with acoustic phonons, highlighting how ballistic transport in carbon-based interconnects requires careful engineering of phonon decays and thermalization.
Phonon Anharmonicities in Graphite and Graphene

Nicola Bonini, Michele Lazzeri, Nicola Marzari, and Francesco Mauri

Implies $\tau = 3$ ps
Direct Measurement of the Lifetime of Optical Phonons in Single-Walled Carbon Nanotubes

Daohua Song,¹ Feng Wang,¹,* Gordana Dukovic,² M. Zheng,³ E. D. Semke,³ Louis E. Brus,² and Tony F. Heinz¹,†

Time-resolved anti-Stokes Raman spectroscopy has been applied to probe the dynamics of optical phonons created in single-walled carbon nanotubes by femtosecond laser excitation. From measurement of the decay of the anti-Stokes Raman signal in semiconducting nanotubes of (6, 5) chiral index, a room-temperature lifetime for $G$-mode phonons of $1.1 \pm 0.2$ ps has been determined. This lifetime, which reflects the anharmonic coupling of the $G$-mode phonons to lower-frequency phonons, is important in assessing the role of nonequilibrium phonon populations in high-field transport phenomena.

\[ \tau = 1.1 \text{ps} \text{ implies } \Gamma = 4.8\text{cm}^{-1} \text{ (FWHM)} \]
Joint density of electronic states for one isolated single-wall carbon nanotube studied by resonant Raman scattering

A. Jorio,1 A. G. Souza Filho,1,4 G. Dresselhaus,3 M. S. Dresselhaus,1,2 R. Saito,5 J. H. Hafner,6 C. M. Lieber,6 F. M. Martinaga,7 M. S. S. Dantas,7 and M. A. Pimenta7

Resonant Raman scattering (RRS) measurements made with a tunable laser provide a highly reliable technique to study the shape of the joint density of electronic states (JDOS) of isolated single-wall carbon nanotubes (SWNTs). RRS can be used to determine the energy value for the one-dimensional (1D) van Hove
Electronic transition energy $E_{ii}$ for an isolated $(n,m)$ single-wall carbon nanotube obtained by anti-Stokes/Stokes resonant Raman intensity ratio

A. G. Souza Filho,1,2 A. Jorio,1 J. H. Hafner,3 C. M. Lieber,3 R. Saito,4 M. A. Pimenta,5 G. Dresselhaus,6 and M. S. Dresselhaus1,7

A resonant Raman study of the anti-Stokes and Stokes spectra for individual isolated single-wall carbon nanotubes is presented. The observed asymmetry between the anti-Stokes and Stokes spectra is analyzed within the framework of resonant Raman scattering theory, thereby providing a method for accurately determining the transition energy between van Hove singularities $E_{ii}$ in the electronic density of states and unambiguously

anti-Stokes resonance
Problems with $I_s/I_{as}$

the Stokes – anti-Stokes (SaS) correlation
Stokes and anti-Stokes Raman scattering processes

\[ n_0 = \frac{1}{e^{\frac{E_g}{k_B T}} - 1} \]

Stokes

\[ \omega_{\text{Laser}} \rightarrow \omega_{\text{phonon}} \rightarrow \omega_{\text{S}} = \omega_{\text{Laser}} - \omega_{\text{phonon}} \]

anti-Stokes

\[ \omega_{\text{Laser}} \rightarrow \omega_{\text{phonon}} \rightarrow \omega_{\text{aS}} = \omega_{\text{Laser}} + \omega_{\text{phonon}} \]
Correlation between the Stokes and anti-Stokes components in inelastic scattering of light

D. N. Klyshko

M. V. Lomonosov State University, Moscow
(Submitted September 9, 1976)
Kvantovaya Elektron. (Moscow) 4, 1341–1350 (June 1977)

\[ \omega_S = \omega_{\text{Laser}} - \omega_{\text{phonon}} \]

\[ \omega_{\text{aS}} = \omega_{\text{Laser}} + \omega_{\text{phonon}} \]
Is the SaS correlation playing a role?

Nat. Nanotech (2009)

PRL100, 225503 (2008)

ACS Nano 4, 1889 (2010)

PRB 63, 245416 (2001)
Optical-Phonon Resonances with Saddle-Point Excitons in Twisted-Bilayer Graphene

Ado Jorio,*,†,‡ Mark Kasperczyk,† Nick Clark,¶ Elke Neu,§ Patrick Maletinsky,§ Aravind Vijayaraghavan,¶ and Lukas Novotny†

$$E^{vHs} = E_0 \cos(3\theta) \rightarrow E_0 = 3.9\text{eV}$$

Saddle points and the 2D density of states

M point is a saddle point

from R. Saito

Mak, Shan, Heinz
PRL106, 046401 (2011)

Sanders et al.
JPCM 25, 144201 (2013)
The Occurrence of Singularities in the Elastic Frequency Distribution of a Crystal

Léon Van Hove
Institute for Advanced Study, Princeton, New Jersey
(Received December 5, 1952)

\[(S, i = 1) \quad \varepsilon_1 = -\varepsilon_2 = \pm 1,\]

\[g(\nu) = C - \frac{v_0}{Z\lambda a} \log \left| \frac{1 - \frac{\nu}{\nu_c}}{1 - \frac{\nu}{\nu_c}} \right| + 0(\nu - \nu_c)\]

The Band Theory of Graphite

P. R. Wallace*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario
(Received December 19, 1946)
Engineering the M point location with twisted bilayer graphene - superlattice
Engineering the M point location with twisted bilayer graphene - superlattice

The $\theta$ dependence of the saddle (M) point

Optical absorption

$E^{\text{vHs}} = E_0 \cos(3\theta)$
Building superlattices by folding graphene into itself

Graphene
SiO$_2$ substrate

Scanning direction of an AFM tip

Building superlattices by folding graphene into itself

Moiré patterns in tBLG

STM image

Cancado et al. PRB 2007

TEM image

By M. Terrones

Electron diffract.

The Resonance Raman effect

\[
\frac{I(G)}{I(G_{SLG})} = \left\vert \frac{M}{(E_L - E_{vHs} - i\gamma)(E_L - E_{vHs} - \hbar\omega_G - i\gamma)} \right\vert^2
\]

G band
from Samsonidze

Rotation angle $\theta$ from atomic resolution AFM
The Resonance Raman effect

$$E_{\nu Hs} = E_0 \cos(3\theta) \rightarrow E_0 = 3.9 \text{eV}$$
Optical-Phonon Resonances with Saddle-Point Excitons in Twisted-Bilayer Graphene

Ado Jorio,*,†,‡ Mark Kasperekzyk,† Nick Clark,§ Elke Neu,§ Patrick Maletinsky,§ Aravind Vijayaraghavan,¶ and Lukas Novotny†

E^{vHs}_v = E_0 \cos(3\theta) \rightarrow E_0 = 3.9\text{eV}

aS (633nm) resonance and Laser power dependence

- **HeNe 8 mW**

- **Reference**
  - AB-BLG

- **Intensity (counts/s)**

- **Raman shift (cm⁻¹)**

### tBLG vs. AB-stacked BLG
**different laser power behavior**

- **tBLG**
  - Iₐₜ / P_laser (counts/s.mW)

- **AB-BLG**
  - Iₐₜ / P_laser (counts/s.mW)

- **P_laser (mW)**
Can the $I_{as}/I_S$ behavior in tBLG be due to $n_0$?

$$\frac{I_{as}}{I_S} = C \frac{n_0}{1 + n_0}$$

$$T = \frac{E_{ph}}{k_B \left[ \ln C - \ln \frac{I_{as}}{I_S} \right]}$$

$T \rightarrow 295\text{ K as } P_L \rightarrow 0.$
Can the $I_{as}/I_S$ behavior in tBLG be due to $n_0$?

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\]
Identification of the $SaS$ correlation

Correlation between the Stokes and anti-Stokes components in inelastic scattering of light

D. N. Klyshko

M. V. Lomonosov State University, Moscow
(Submitted September 9, 1976)
Kvantovaya Elektron. (Moscow) 4, 1341–1350 (June 1977)
Macroscopic non-classical states and terahertz quantum processing in room-temperature diamond

K. C. Lee¹, B. J. Sussman²*, M. R. Sprague¹, P. Michelberger¹, K. F. Reim¹, J. Nunn¹, N. K. Langford¹, P. J. Bustard¹², D. Jaksch¹³ and I. A. Walmsley¹*
S and aS in diamond

LASER
130 fs pump
\( \lambda_{\text{laser}} = 785 \text{nm} \)

Band pass filter
786/22nm

diamond

Notch filter
785/39nm

Band pass
880/40nm

Band pass
716/20nm

Stokes detector
anti-Stokes detector

Stokes

anti-Stokes

\(~P^2\)

\(\sim P\)

\(x5\)

Photon Counts/s

P (mW)

Correlation function $g^2(0)$

- LASER
  - 130 fs pump
  - $\lambda_{\text{laser}} = 785\text{nm}$

- Band pass filter 786/22nm

- diamond

- Notch filter 785/39nm

- Band pass 880/40nm

- TIME DELAY DETECTOR

Correlation function $g^{(2)}(0)$

- LASER: 130 fs pump, $\lambda_{\text{laser}} = 785\text{nm}$
- Band pass filter: 786/22nm
- Notch filter: 785/39nm
- Diamond
- Band pass filter: 880/40nm
- TIME DELAY DETECTOR

$$g^{(2)}_{S,AS}(0)$$

- $g^{(2)}_{S,AS}(0) = 2 \rightarrow$ aleatory; thermal
- $g^{(2)}_{S,AS}(0) > 2 \rightarrow$ quantum correlated

Graph showing $g^{(2)}_{S,AS}(0)$ against $P$ (mW) and $\Delta t$ (ns) with data points and trend line.
Theory for the SaS correlation

and

The generalization of the Bose-Einstein phonon statistics \( (n_0) \)
for the inelastic scattering of light
The physical model

\[ \hat{H} = \omega_0 \hat{a}^\dagger \hat{a} + \nu \hat{c}^\dagger \hat{c} + \omega_S \hat{b}_S^\dagger \hat{b}_S + \omega_{aS} \hat{b}_{aS}^\dagger \hat{b}_{aS} \]
\[ + \lambda_S (\hat{a} \hat{c}^\dagger \hat{b}_S^\dagger + h.c.) + \lambda_{aS} (\hat{a} \hat{c} \hat{b}_{aS}^\dagger + h.c.) \]

\[ \omega_{aS,S} = \omega_0 \pm \nu, \quad \hbar = 1 \]

\( \lambda_S \) and \( \lambda_{aS} \) are the coupling constants.

\[(\hat{a}, \hat{a}^\dagger) \rightarrow |\alpha| \quad |\alpha|^2 \text{ the mean number of incident photons.} \]

\[ P_L = \mathcal{A}|\alpha|^2 \quad \mathcal{A} \text{ constant depending on the laser energy.} \]

Time evolution (Lindblad master equation)

\[ \frac{d}{dt} \hat{\rho} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}(\hat{\rho}) \]

\[ \mathcal{L} = \mathcal{L}_b + \mathcal{L}_c, \text{ with:} \]

\[ \mathcal{L}_b(\hat{\rho}) = -\sum_{x=S,aS} \gamma_x (\hat{b}_x^\dagger \hat{b}_x \hat{\rho} + \hat{\rho} \hat{b}_x^\dagger \hat{b}_x - 2\hat{b}_x \hat{\rho} \hat{b}_x^\dagger) \]

\[ \mathcal{L}_c(\hat{\rho}) = -\gamma_c (n_0 + 1)(\hat{c}^\dagger \hat{c} \hat{\rho} + \hat{\rho} \hat{c}^\dagger \hat{c} - 2\hat{c} \hat{\rho} \hat{c}^\dagger) \]

\[ -\gamma_c n_0 (\hat{c}^\dagger \hat{c} \hat{\rho} + \hat{\rho} \hat{c}^\dagger \hat{c} - 2\hat{c}^\dagger \hat{\rho} \hat{c}), \]

\[ \gamma_S \quad S \text{ photons} \]

\[ \gamma_{aS} \quad aS \text{ photons} \]

\[ \gamma_c \quad \text{phonons} \]

decay rates

Proportional to inverse of coherence time

Time evolution (Lindblad master equation)

\[
\frac{d}{dt} \hat{\rho} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}(\hat{\rho})
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\]

\[\quad -\gamma_c n_0 (\hat{c} \hat{c}^\dagger \hat{\rho} + \hat{\rho} \hat{c} \hat{c}^\dagger - 2\hat{c}^\dagger \hat{\rho} \hat{c}),\]

\[
\langle n_{S,aS} \rangle = \langle \hat{b}_{S,aS}^\dagger \hat{b}_{S,aS} \rangle \quad \langle n_c \rangle = \langle \hat{c}^\dagger \hat{c} \rangle \quad g^2(0) = \frac{\langle \hat{b}_{aS}^\dagger \hat{b}_{aS}^\dagger \hat{b}_S \hat{b}_S \rangle}{\langle \hat{b}_S^\dagger \hat{b}_S \rangle \langle \hat{b}_{aS}^\dagger \hat{b}_{aS} \rangle}
\]

S,aS population  phonon population  SaS correlation function

S and aS Population

$$\langle n_{S,aS} \rangle = \langle \hat{b}_{S,aS}^\dagger \hat{b}_{S,aS} \rangle$$

$$n_0 = \frac{1}{e^{E_q/k_B T} - 1}$$

$$P_0 \approx A\gamma\gamma_c/2\lambda^2 \text{ for } \gamma/\gamma_c \gg n_0$$

[Graph showing populations as a function of $P_L/P_0$]

S and $aS$ Population and $SaS$ correlation

\[ \langle n_{s,as} \rangle = \langle \hat{b}_{s,as}^\dagger \hat{b}_{s,as} \rangle \]

\[ P_0 \approx A \gamma \gamma_c / 2\lambda^2 \quad \text{for} \quad \gamma / \gamma_c \gg n_0 \]
S and aS population – theory vs. experiment

Perfect modeling of the results from diamond!

\[ P_0 \approx A \gamma \gamma_c / 2 \lambda^2 \text{ for } \gamma / \gamma_c \gg n_0 \]

[Graph and equation]
SaS correlation – theory vs. experiment

Diamond experiment

Perfect modeling of the results from diamond!

\[ P_0 \approx \mathcal{A} \gamma \gamma_c / 2\lambda^2 \text{ for } \gamma / \gamma_c \gg n_0 \]

$I_{aS} / I_S$ ratio  

Figure of merit

Generalization of $I_{aS} / I_S$ ratio

\[
\frac{\langle n_{aS} \rangle_{ss}}{\langle n_S \rangle_{ss}} = \frac{n_0}{n_0 + 1} \exp \left[ \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right]
\]

\[
\frac{I_{aS}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right]
\]

$C' = C_{aS}/C_S$.

$I_{S,aS} = C_{S,aS} \langle n_{S,aS} \rangle_{ss}$

Approximations

$\gamma/\gamma_c \gg n_0$

$\lambda_S = \lambda_{aS} = \lambda$

$\gamma_S = \gamma_{aS} = \gamma$

\[ \frac{I_{as}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2}{\gamma \gamma_c} \frac{P_L}{A} \right] \]

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>( C' )</th>
<th>( C_{SaS} \equiv (\lambda^2/\gamma \gamma_c)A^{-1} \text{[mW}^{-1}] )</th>
<th>( T \text{[K]} )</th>
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<tr>
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<td>(10 ± 1)</td>
<td>(2.13 ± 1.04) \times 10^{-5}</td>
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\[
\frac{I_{aS}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2}{\gamma \gamma_c} \frac{P_L}{A} \right]
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\[ \frac{I_{as}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2}{\gamma \gamma_c} \frac{P_L}{A} \right] \]

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Figure of Merit

Concluding remarks

You can differentiate correlated $SaS$ and uncorrelated $S+aS$ phenomena from intensity measurements!

- Generalization of the Bose-Einstein phonon distribution function

$$n_0 = \frac{1}{e^{E_g/k_B T} - 1}$$

for Stokes and anti-Stokes light scattering

$$\frac{I_{aS}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right]$$
Outline

• Time localization
  – Stokes-anti-Stokes Correlation

• Space localization
  – *Tip enhanced Raman Spectroscopy*
Tip Enhanced Raman Spectroscopy
special resolution beyond the diffraction limit

Conventional microscope

“Near-field” microscope


The system

- “Home-built” system – it can make nanomanipulation, scanning probe microscopies (AFM, STM…) and optical spectroscopies (Raman, Rayleigh, photoluminescence…) in situ.

- The optical spectroscopy can be performed in the far- and near-field regimes, with a maximum resolution of 10nm.
The system
The system
The system
Network for NanoSpectroscopy

Scan head UFC

Scan head fabrication

Scan head Inmetro
Amplifier to drive piezoelectric for SPM

Gain: 1V / nA
Noise: 5mV (out)

STM HOPG

600nm x 600nm

2µm x 2µm
Touché project

Hardware, Software e Computational imaging
Software for Raman imaging

Imagens de hiperespectro geradas a partir de 4.096 espectros Raman. Os pontos marcados pelo nº. 1 nas imagens representam a posição de aquisição do espectro Raman exibido.
Nanoantenna fabrication

PI 1105968-0 & BR 1020120333040

EELS

BR 1020120269732

280 nm
150 nm
1.93 eV

Electron Energy Loss (eV)
Tip Enhanced Raman Spectroscopy

In collaboration with Lukas Novotny

Hartschuh et al.
90, 095503 (2003)

L. G. Cançado et al.,
Phys. Rev. Letters
103, 186101 (2009)

Tip Enhanced Raman Spectroscopy in “2D”

Tip Enhanced Raman Spectroscopy in “2D”
TERS on 2D graphene

At the edge

TERS on graphene

At the center

At the edge

TERS on graphene

At the center

At the edge

Tip approach curves

Distance

Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)
Calculation for Raman Scattering

\[ S \propto V \left| \hat{e} \cdot \vec{\alpha} \vec{E} \right|^2 \]

Valid for incoherent Raman

*Beams et al. PRL 113, 186101 (2014)*
*Cancado et al. PRX 4, 031054 (2014)*
Calculation for spatially coherent near-field Raman

\[ S(r_0) \propto \int \int \hat{G}^*(r_1) \hat{G}(r_2) \langle \vec{p}(r_1)^* \vec{p}(r_2) \rangle \, d^3r_1 \, d^3r_2 \]

\[ = \int \int \langle \hat{\alpha}_{r_1}^* \hat{\alpha}_{r_2} \rangle \left[ \hat{G}(r_1) \vec{E}(r_1) \right]^* \hat{G}(r_2) \vec{E}(r_2) \, d^3r_1 \, d^3r_2 \]

\[ \text{Beams et al. PRL 113, 186101 (2014) & Cancado et al. PRX 4, 031054 (2014)} \]
Calculation for spatially coherent near-field Raman

Tip approach curves

Phonon symmetry dependent spatial coherence

Tip approach curves

Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)
Phonon symmetry dependent spatial coherence

Tip approach curves

Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)
Phonon symmetry dependent spatial coherence

\[ S(r_0) \propto \int \int \hat{\tilde{G}}^*(r_1) \hat{\tilde{G}}(r_2) \langle \tilde{p}(r_1)^* \tilde{p}(r_2) \rangle \, d^3r_1d^3r_2 \]

\[ = \int \int \langle \hat{\alpha}_{r_1}^* \hat{\alpha}_{r_2} \rangle \left[ \hat{G}(r_1) \hat{E}(r_1) \right]^* \hat{G}(r_2) \hat{E}(r_2) \, d^3r_1d^3r_2 \]

\[ \tilde{\alpha}_r \propto \tilde{\pi}(r) \]

\[ D \]

**Figure:**

- **Coherence length**: \( L_C = 30 \text{ nm} \)
- **Distance (nm)**
- **Normalized Raman signal**
  - **\( \tilde{\alpha}_r = 4 \)**
  - **\( L_C = 30 \text{ nm} \)**
  - **\( r_{\text{tip}} = 17 \text{ nm} \)**

**Graphs:**

- **(a)** \( L_c = 0 \text{ nm} \)
- **(b)** \( L_c = 15 \text{ nm} \)
- **(c)** \( L_c = 30 \text{ nm} \)
- **(d)** \( L_c = 45 \text{ nm} \)

**References:**

- Beams et al. PRL 113, 186101 (2014)
- Cancado et al. PRX 4, 031054 (2014)
The relevance of phonon coherence length
Phonon coherence length ($\ell_C$) and $L_a$

the G band width

\[ \Gamma_G^A(L_a) = \Gamma_G^A(\infty) + C e^{-L_a/(\ell_C/2)} \]

$\Gamma_G^A(\infty) = 15 \text{ cm}^{-1}$

$C = 95 \text{ cm}^{-1}$

$\ell_C(\infty) = 32 \text{ nm}$

\[ L_a = \frac{\ell_C}{2} \ln \left[ \frac{C}{\Gamma_G^A(L_a) - \Gamma_G^A(\infty)} \right] \]
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