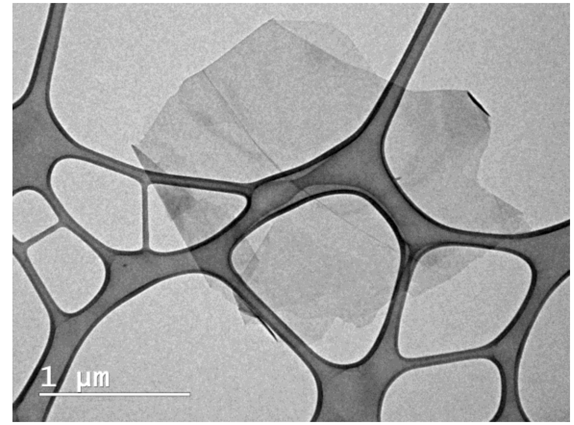
Graphene 2018
June 26 - 29
Dresden (Germany)
8th edition of the largest European Conference & Exhibition in Graphene and 2D Materials

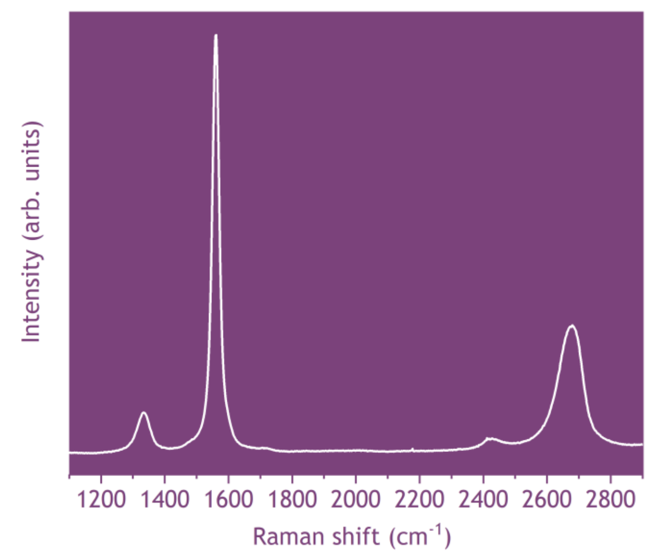
Macro, micro and nano-Raman spectroscopy in 2D systems: fundamentals and applications

Ado JORIO
Departamento de Física
Universidade Federal de Minas Gerais
BRAZIL

Laboratório de NANO.ESPECTROSCOPIA
UFMG

Macro-Raman spectroscopy





Pilot plant for mass-scale production of liquid-phase exfoliated graphene from natural graphite

Micro-Raman spectroscopy

nature COMMUNICATIONS

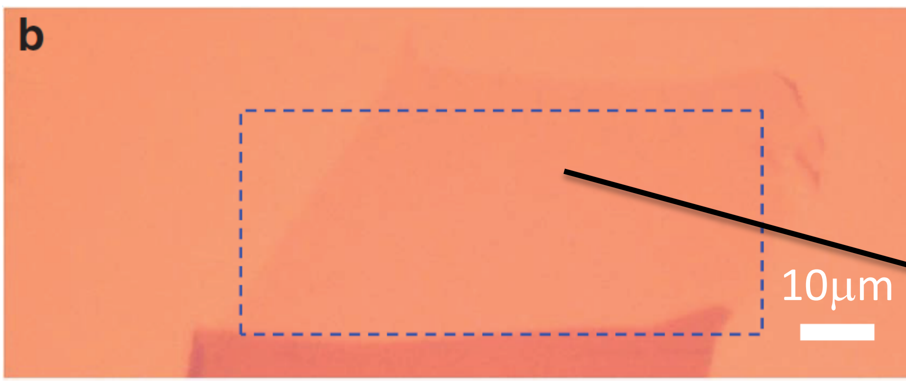
Received 2 May 2012 | Accepted 25 Jul 2012 | Published 28 Aug 2012

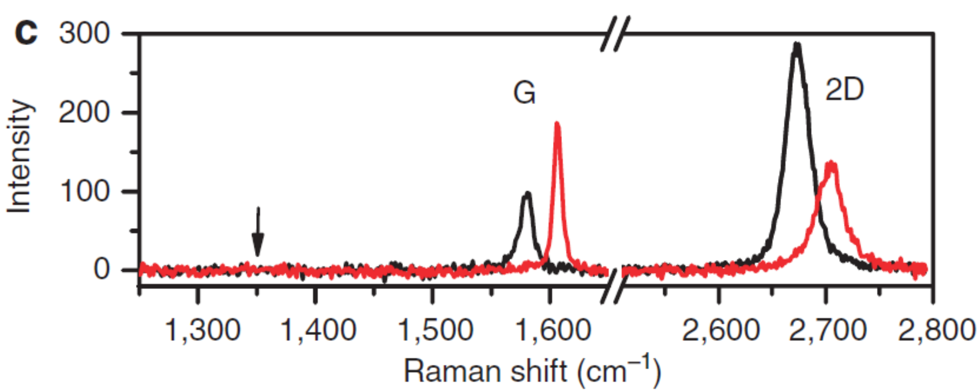
DOI: 10.1038/ncomms2022

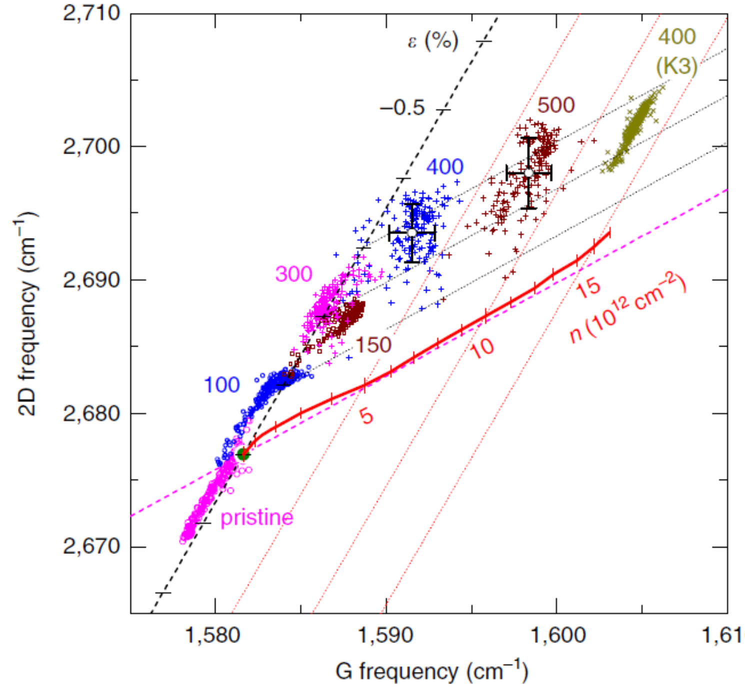
Optical separation of mechanical strain from charge doping in graphene

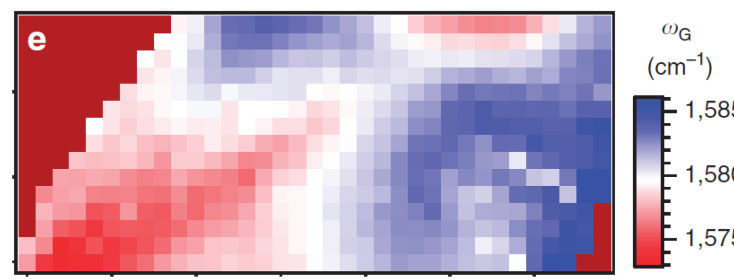
Ji Eun Lee[1,†], Gwanghyun Ahn[1], Jihye Shim[1], Young Sik Lee[1] & Sunmin Ryu[1]

[1]*Kyung Hee University, Republic of Korea*









1×1 μm² resolution
1μm² ~ 39.000.000 C atoms

Micro- vs. Nano-Raman spectroscopy

nature COMMUNICATIONS

Received 2 May 2012 | Accepted 25 Jul 2012 | Published 28 Aug 2012 DOI: 10.1038/ncomms2022

Optical separation of mechanical strain from charge doping in graphene

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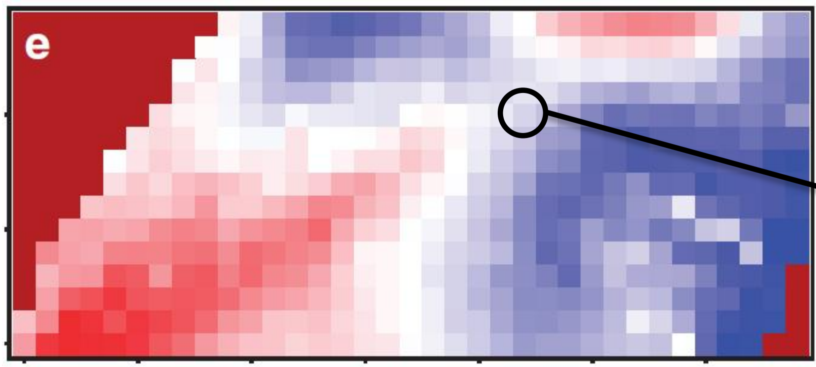
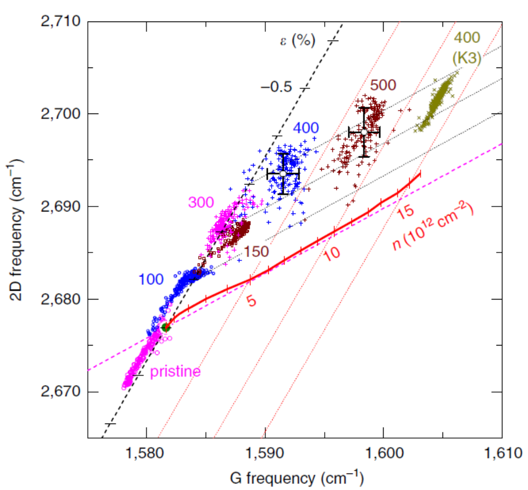
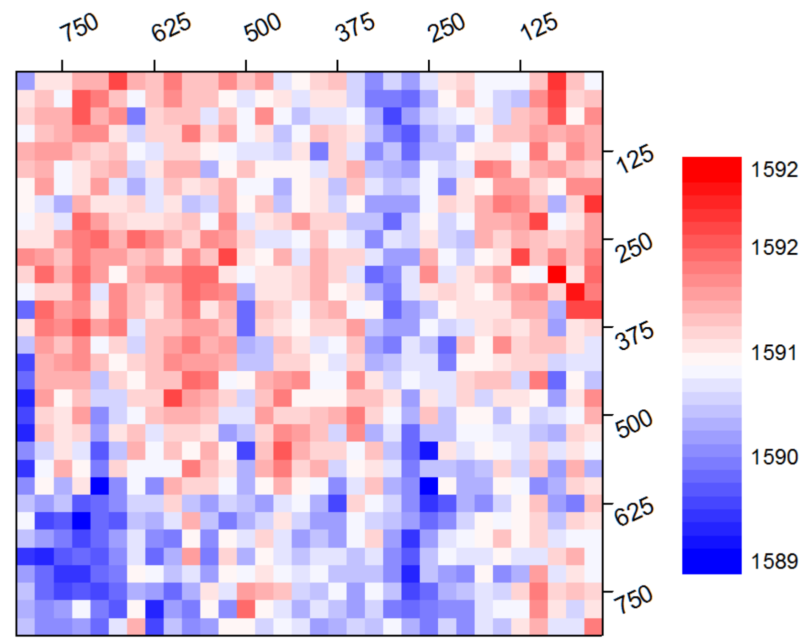




Our Nano-Raman spectroscopy on graphene
1024 points
5 sec / point (1h20min)
25×25 nm² resolution



Obs: micro and nano are placed together here for comparison only. They are not on the same sample

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graphene 2016
April 19-22, 2016 Genova (Italy)
6th edition of the largest European Conference & Exhibition in Graphene and 2D Materials

Metrology of defects and local temperature in graphene

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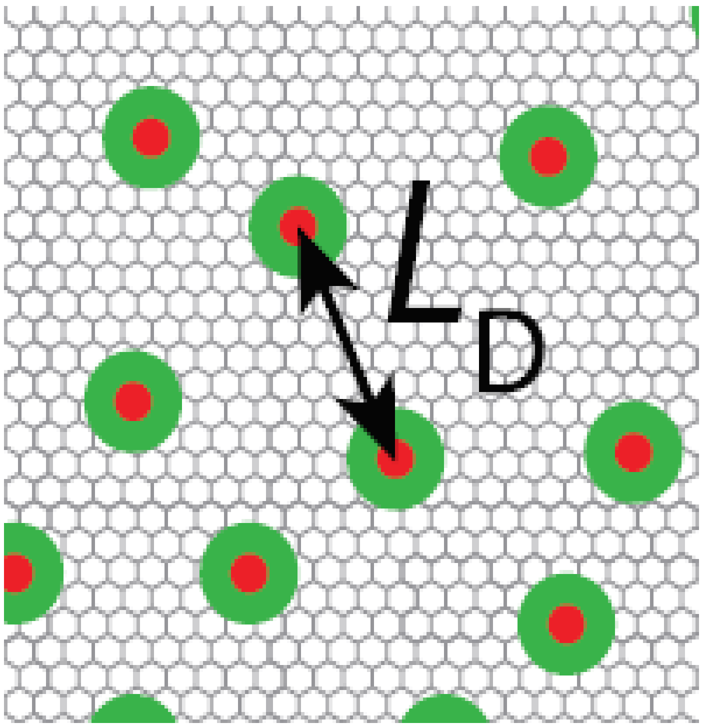
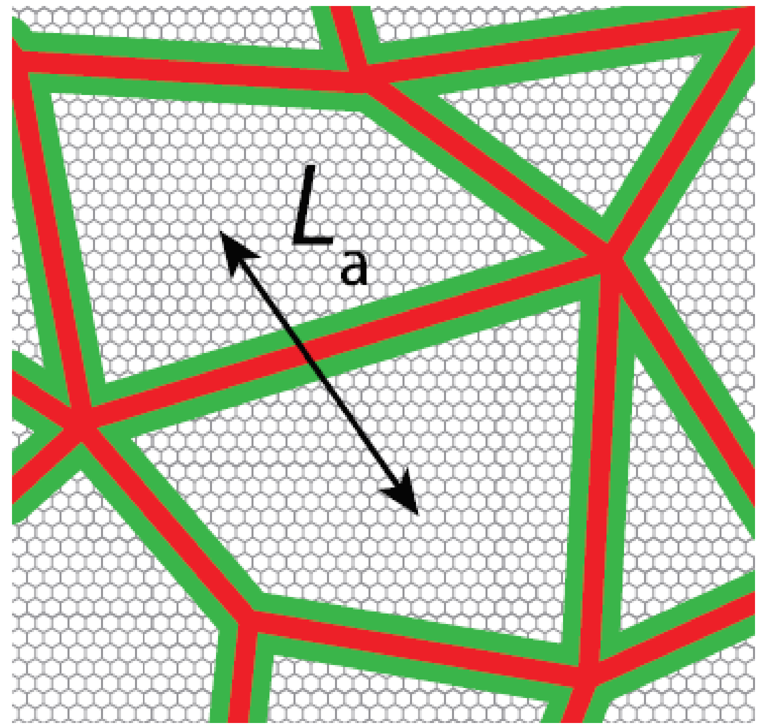
0D & 1D defects – two parameters

2D Mater. 4, 025039 (2017)

Distance among 0D defects
Defect density

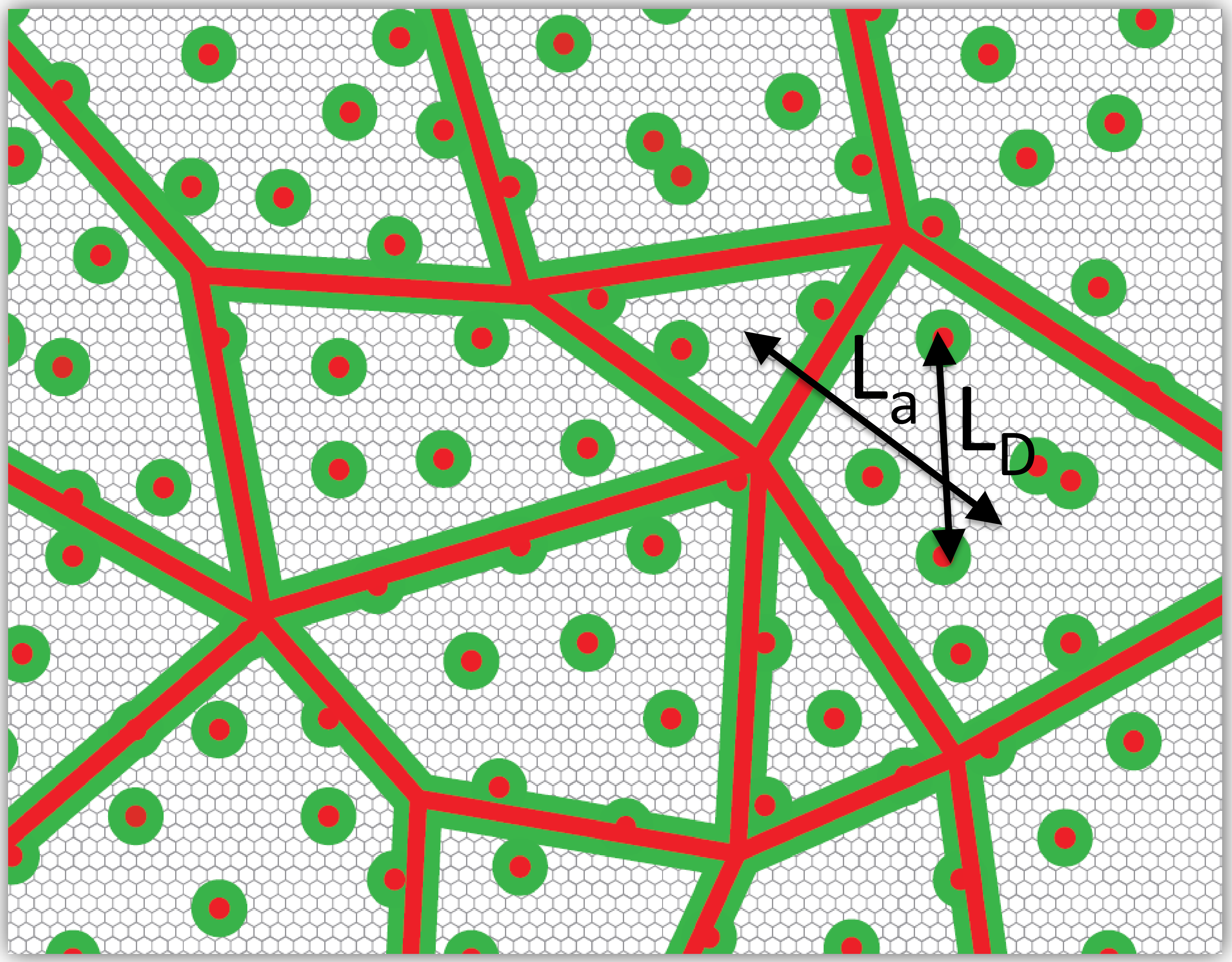


Distance among 1D defects
Crystallite sizes

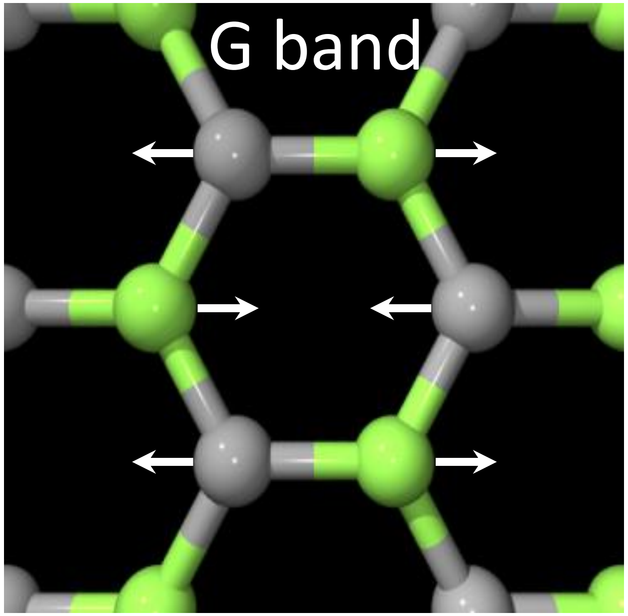


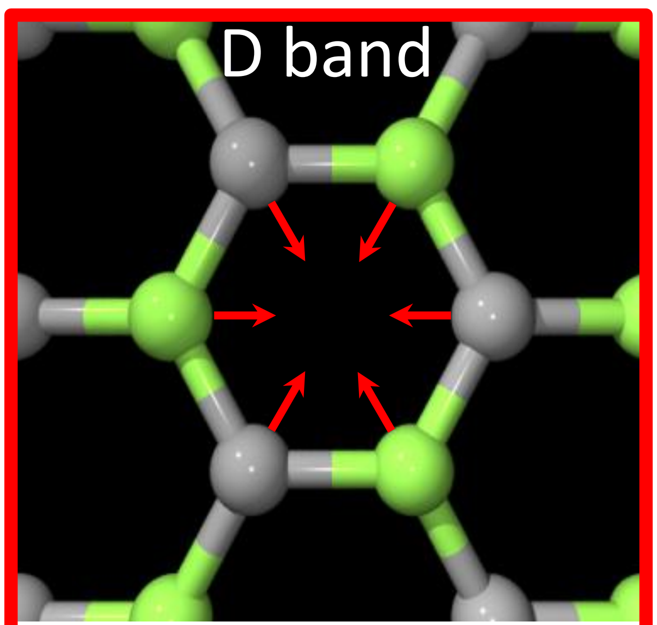
0D & 1D defects – two parameters

2D Mater. 4, 025039 (2017)



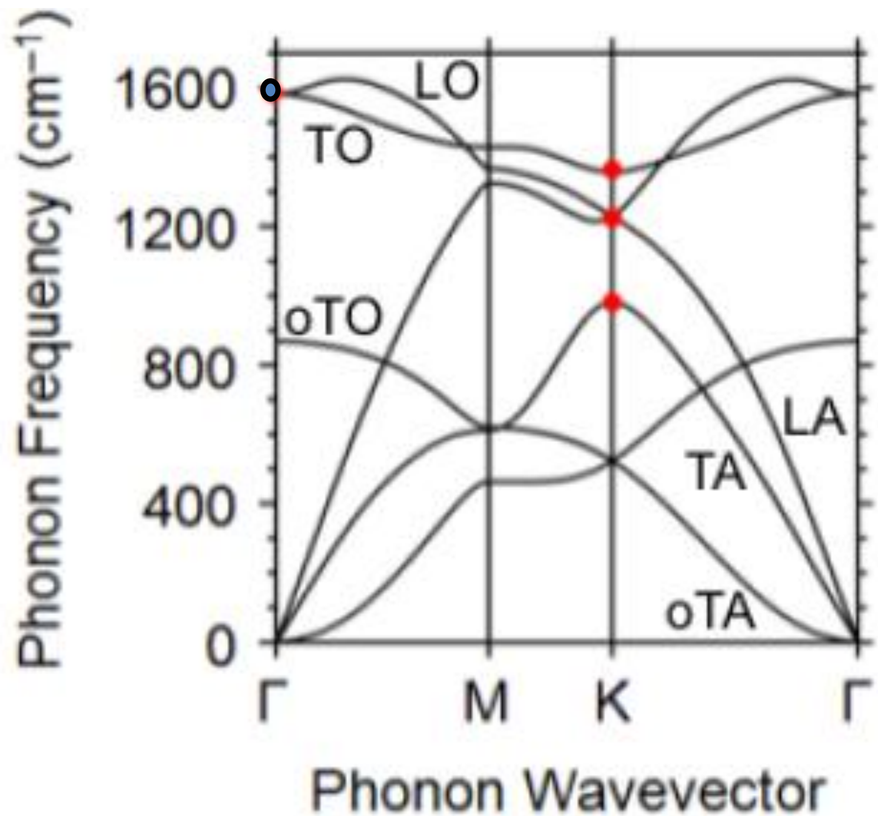
Two parameters: (1) Symmetry breaking



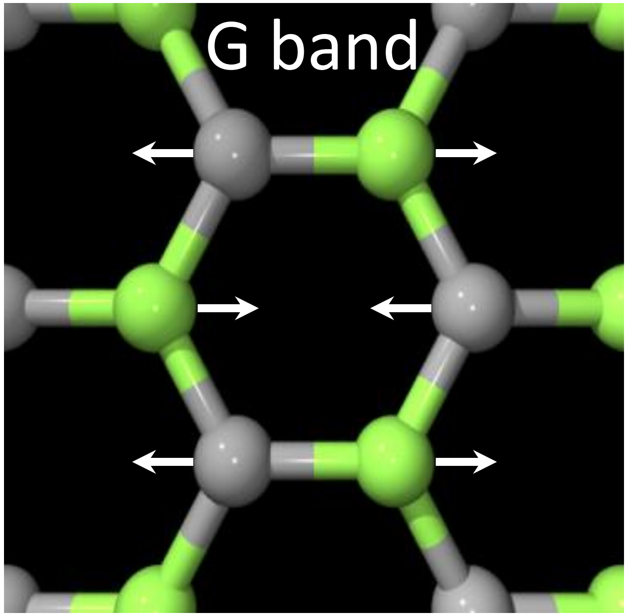


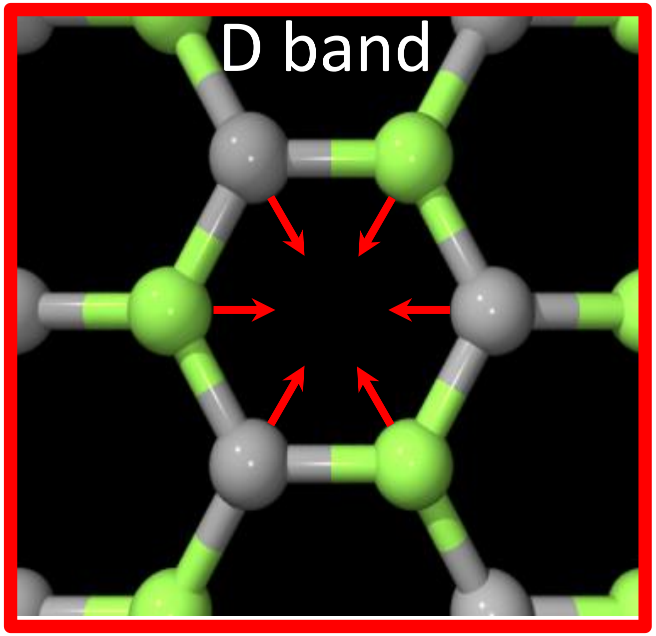
Activation of $q \neq 0$ and other symmetry forbidden modes

OBSERVATION OF NEW PEAKS

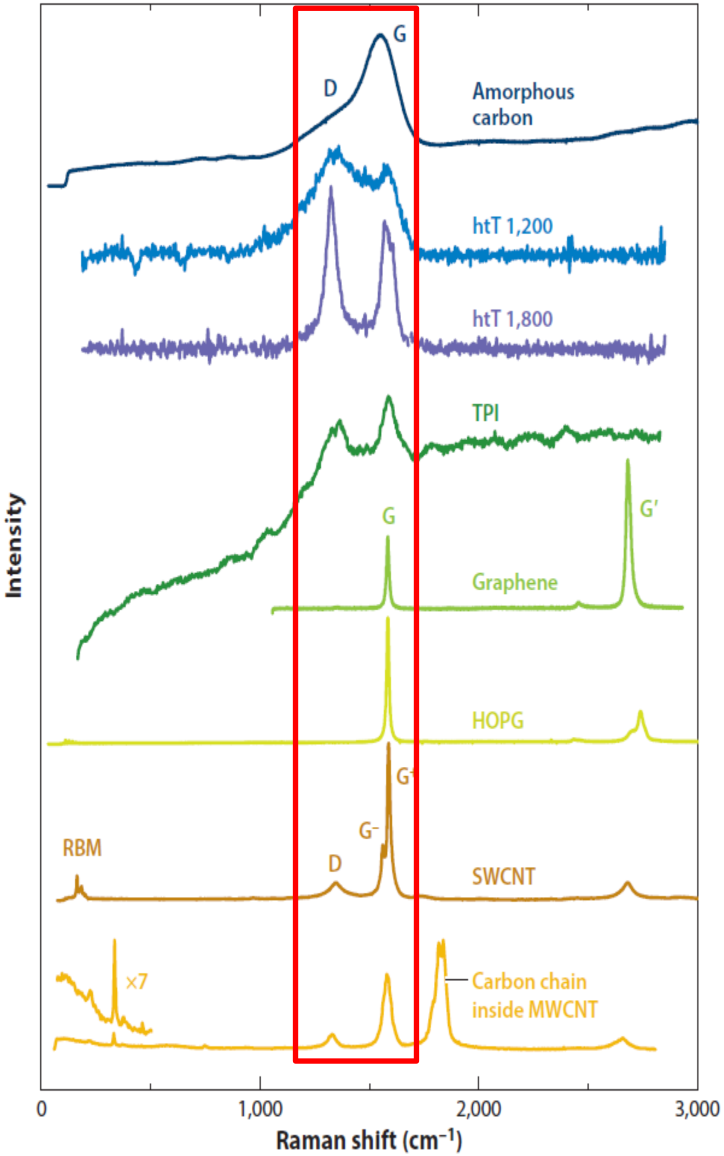


Two parameters: (1) Symmetry breaking

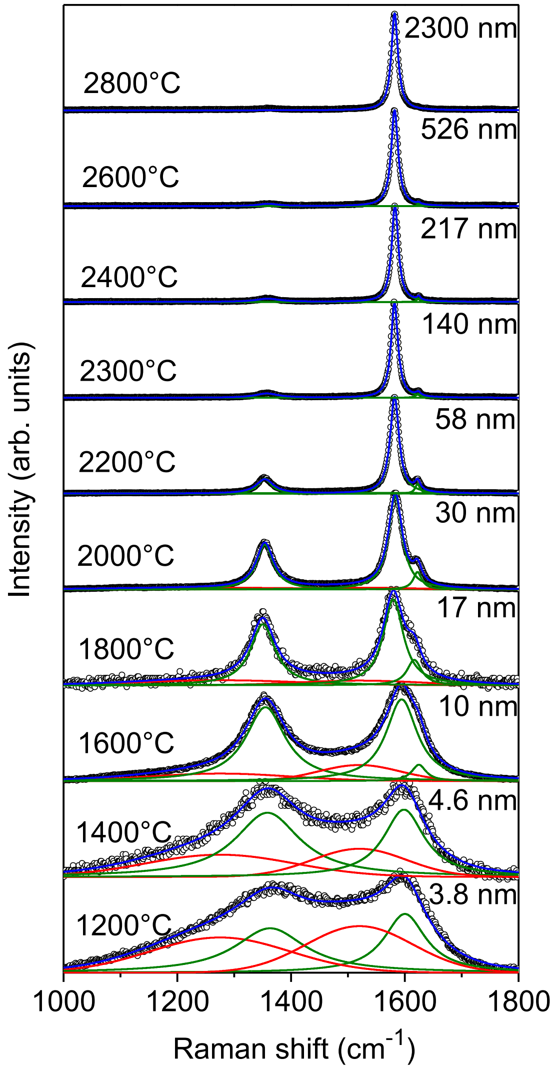


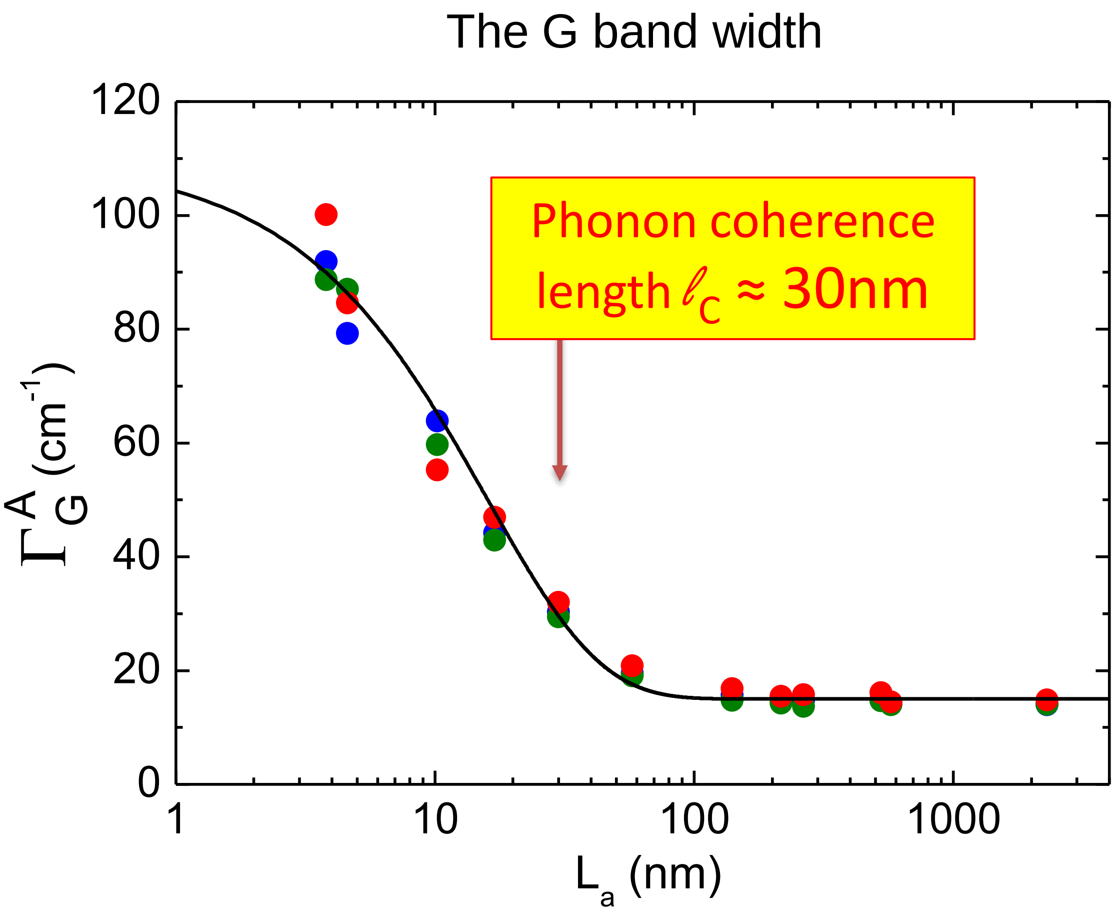


Jorio and Souza Filho ARMR (2016)



Two parameters: (2) Phonon confinement



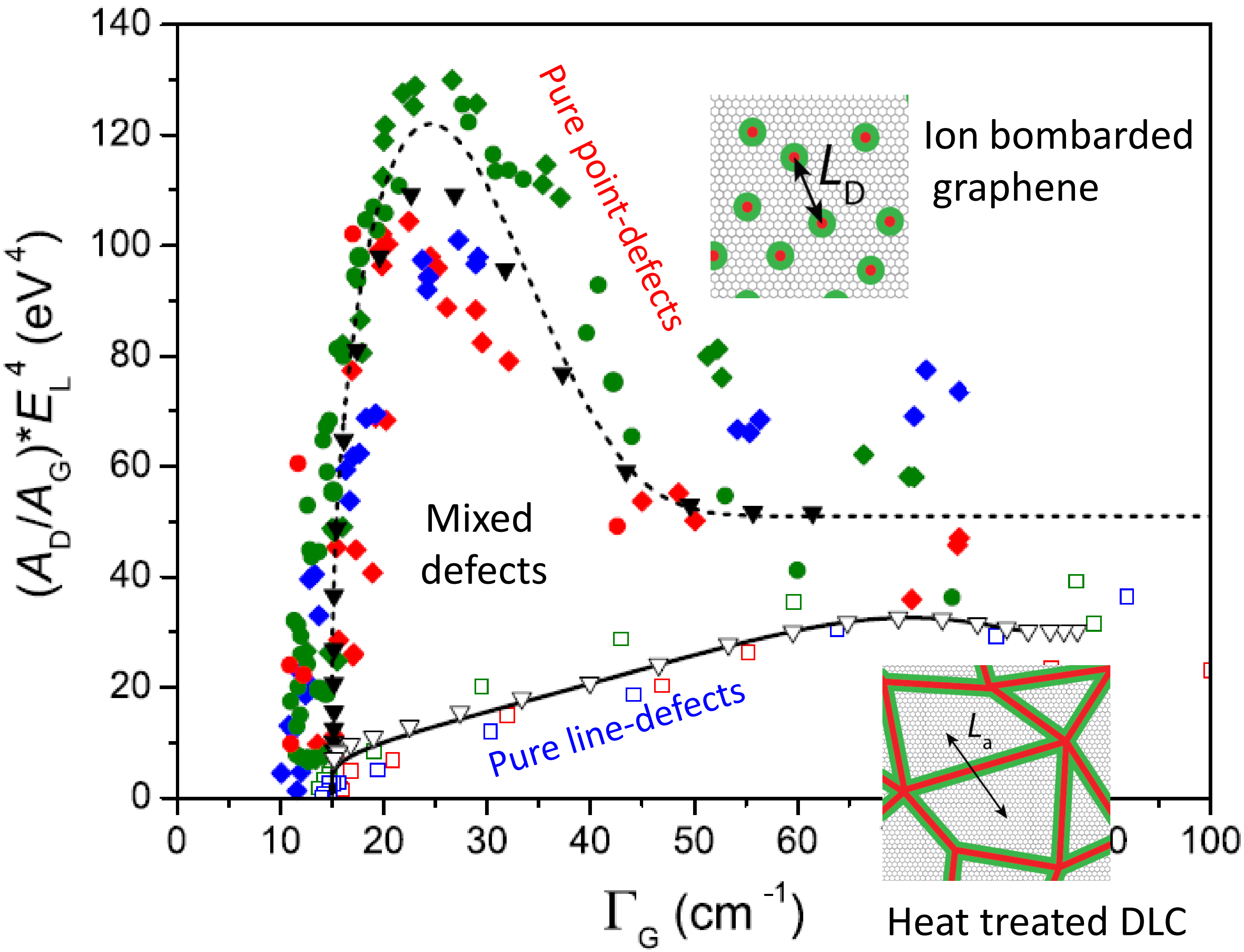


$$\Gamma_G^{\mathbb{A}}(L_a) = \Gamma_G^{\mathbb{A}}(\infty) + C\,e^{-L_a/(\ell_C/2)}$$

J. Ribeiro Soares et al. Carbon 95 646-652 (2015)

Raman phase diagram (micro)

2D Mater. 4, 025039 (2017)



Raman phase diagram (micro)

$$L_D^2\ (\text{nm}^2) = \frac{(4.3 \pm 1.3) \times 10^3}{E_L^4}\left(\frac{I_D}{I_G}\right)^{-1}$$

Lucchese-Cançado

Carbon 48, 1592 (2010)

NanoLett 11, 3190 (2011)

Not good for $L_D < 7$ nm

Tuinstra-Cançado

JCP53 (1970)

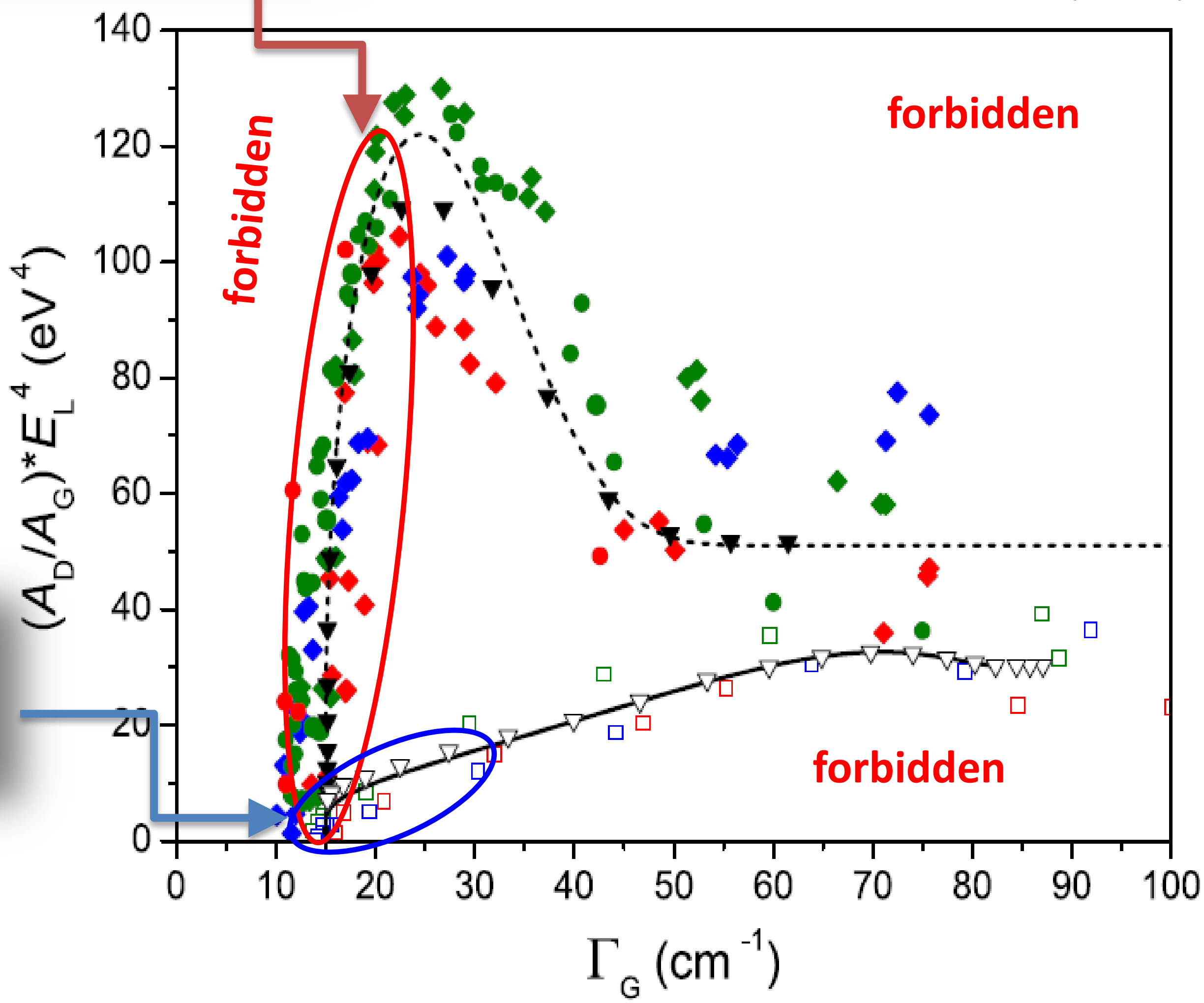
APL88, 163106 (2006)

$$L_a(\text{nm}) = \frac{560}{E_l^4}\left(\frac{I_D}{I_G}\right)^{-1}$$

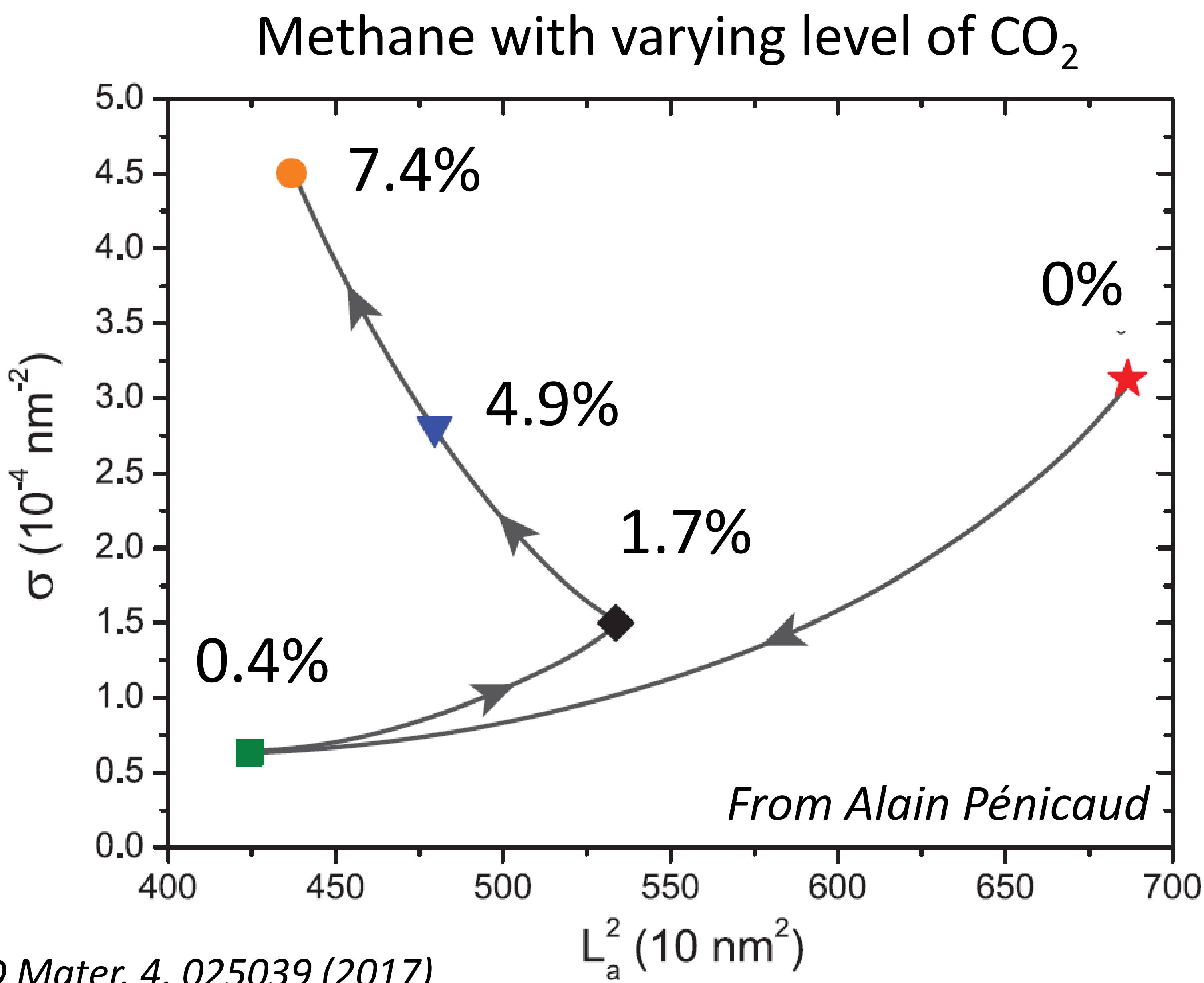
Not good for $L_a < 30$nm

VALID FULL RANGE

Riberiro-Soares et al. *Carbon* 95 646 (2015)



Characterizing CVD grown graphene from natural gas

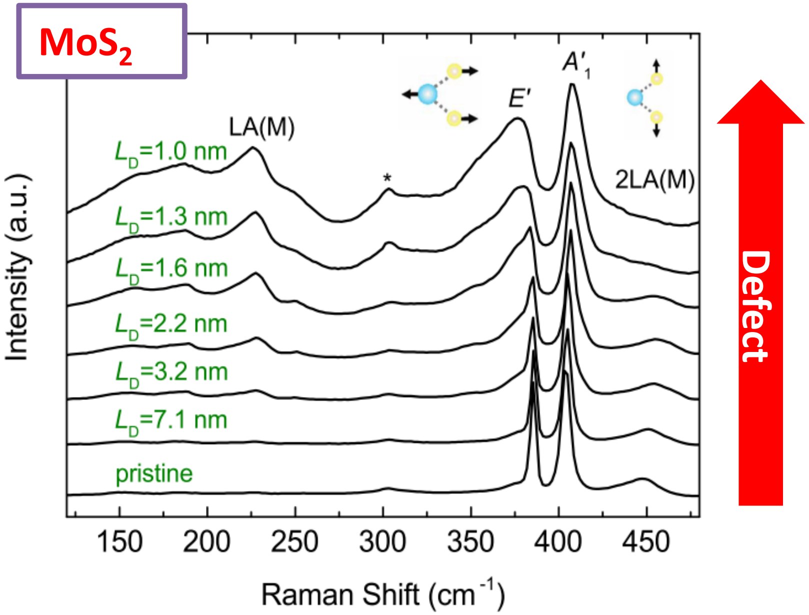


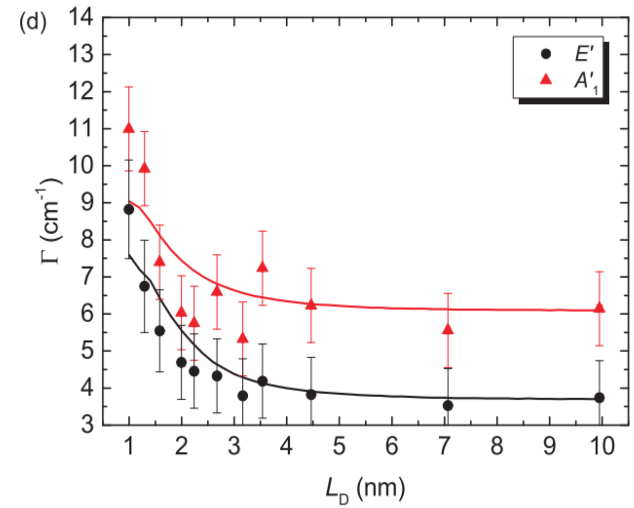
2D Mater. 4, 025039 (2017)

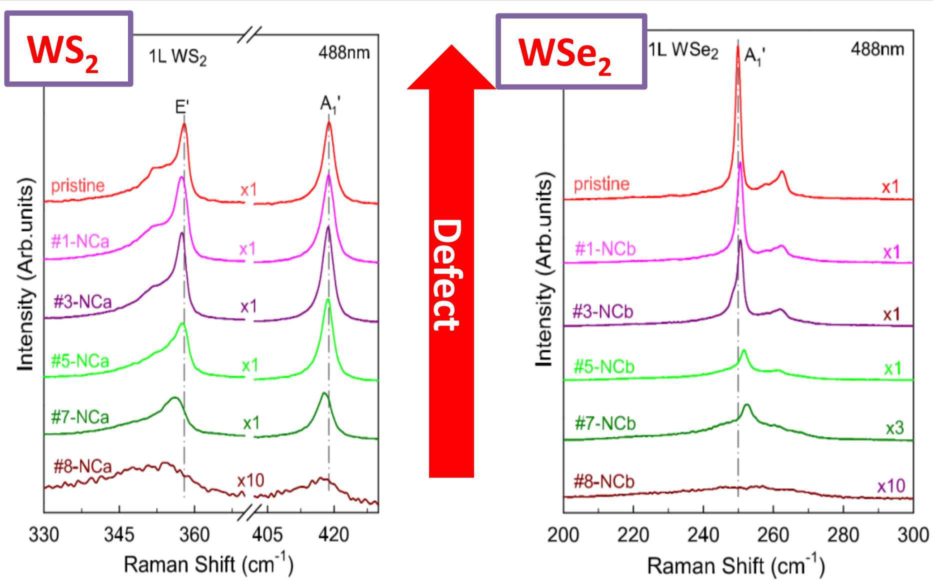
Raman Spectrum of Defective TMDs (micro)

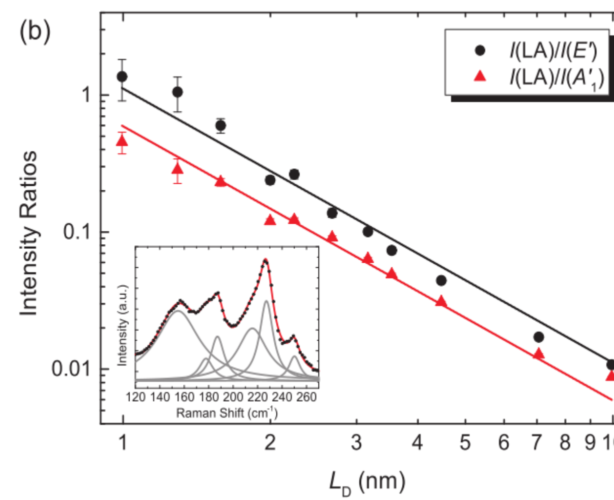
Center for 2-Dimensional and Layered Materials, Penn State

By Mauricio Terrones





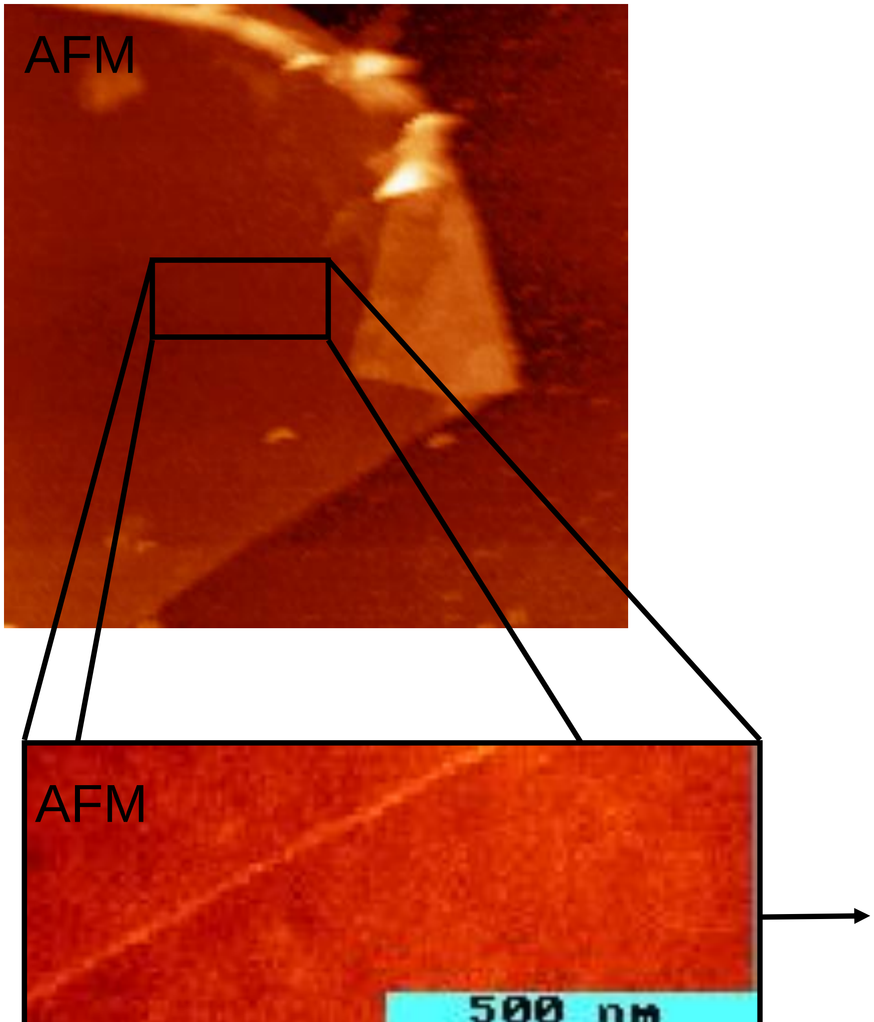




Width of 1st order mode and LA band intensity works as I_D/I_G in Graphene

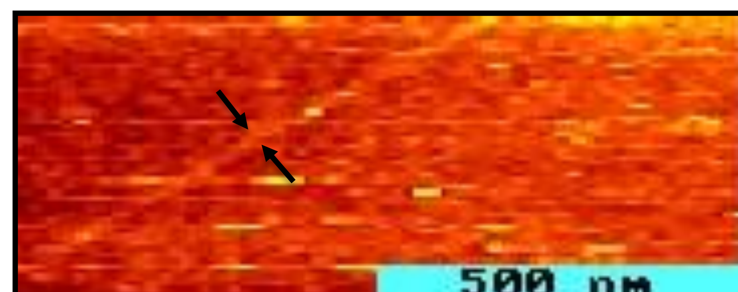
S. Mignuzzi, Phys. Rev. B, (2015), W. Shi, 2D Mater. (2016)

CROSSING THE DIFFRACTION LIMIT (nano)
Optical (D band) imaging of a graphene step



D band image with 20nm resolution

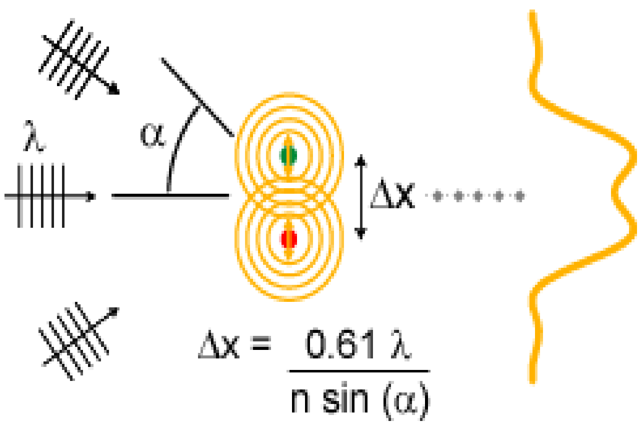
D band optical image



By Huihong Qian, Ado Jorio and Achim Hartschuh (2004). Umpublished.

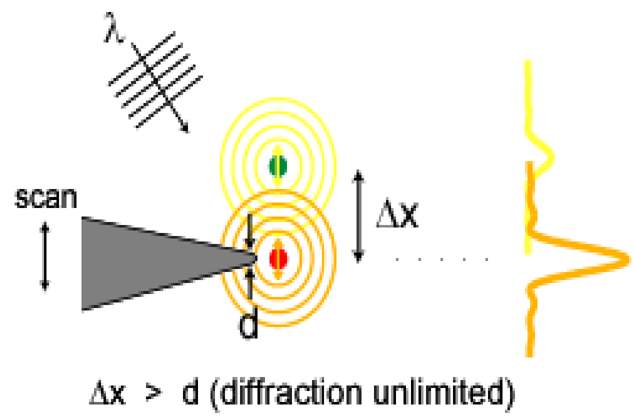
Tip Enhanced (nano)Raman Spectroscopy
special resolution beyond the diffraction limit

Conventional microscope



Abbé, Arch. Mikrosk., Anat.,(1873).

"Near-field" microscope

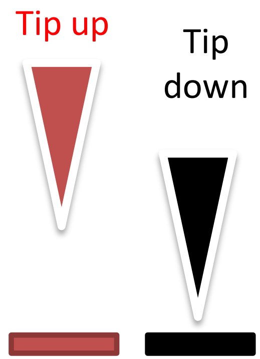


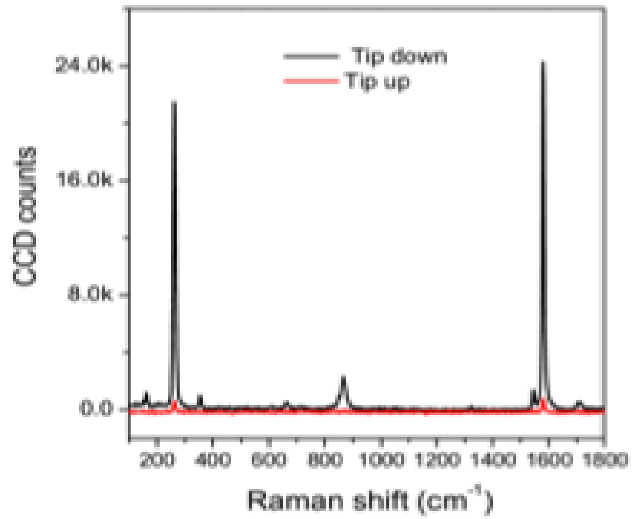
Wessel, JOSA B, (1985).
Novotny et al., Ultramicroscopy, (1998).

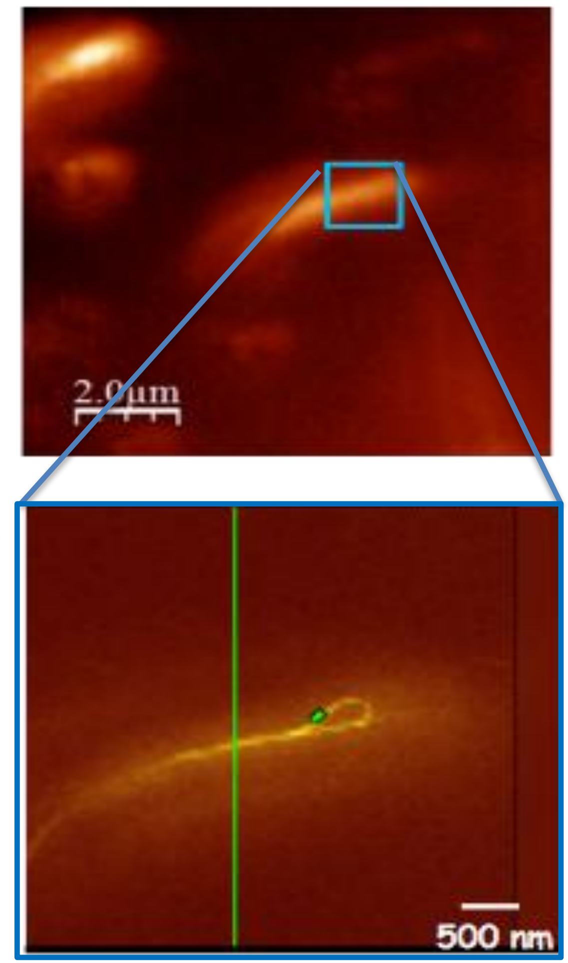
Important contributors to TERS development: Zenobi (ETH), Volker (Jena), Novotny (ETH), Kawata (Japan), Hartschuh (Munich), Dong (China) and many others…

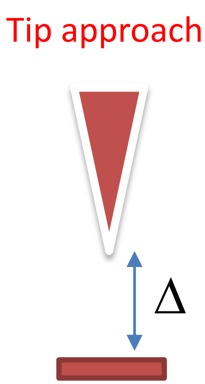
Tip up (micro) – Tip down (nano)

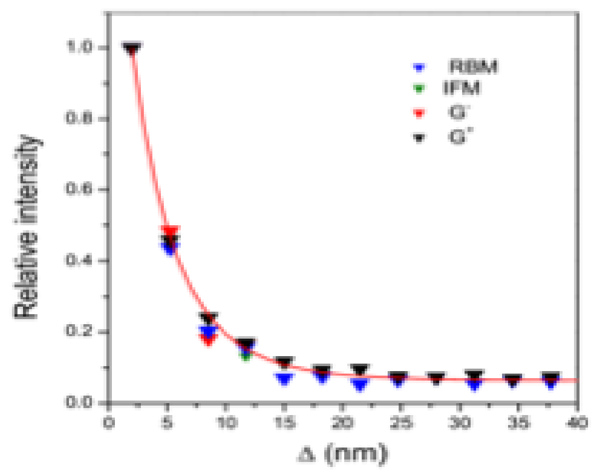
IN CARBONO NANOTUBES, FIRST MEASURED BY ACHIM HARTSCHUH, PRL 2003









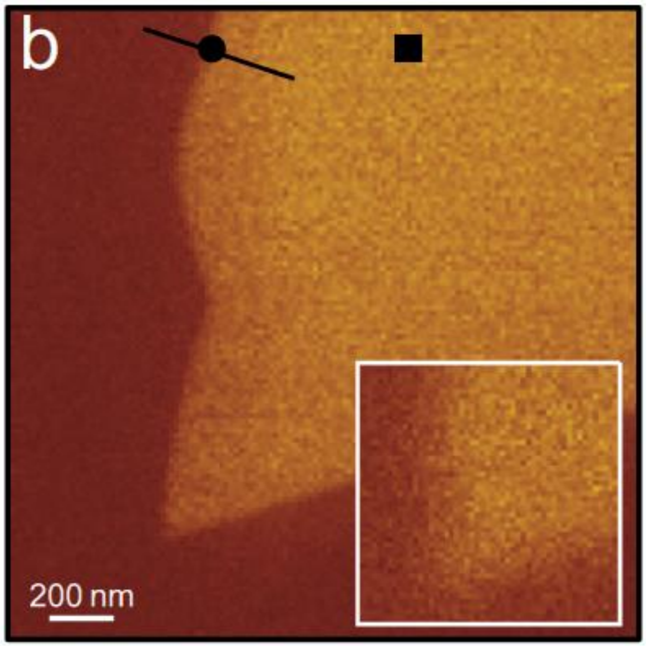


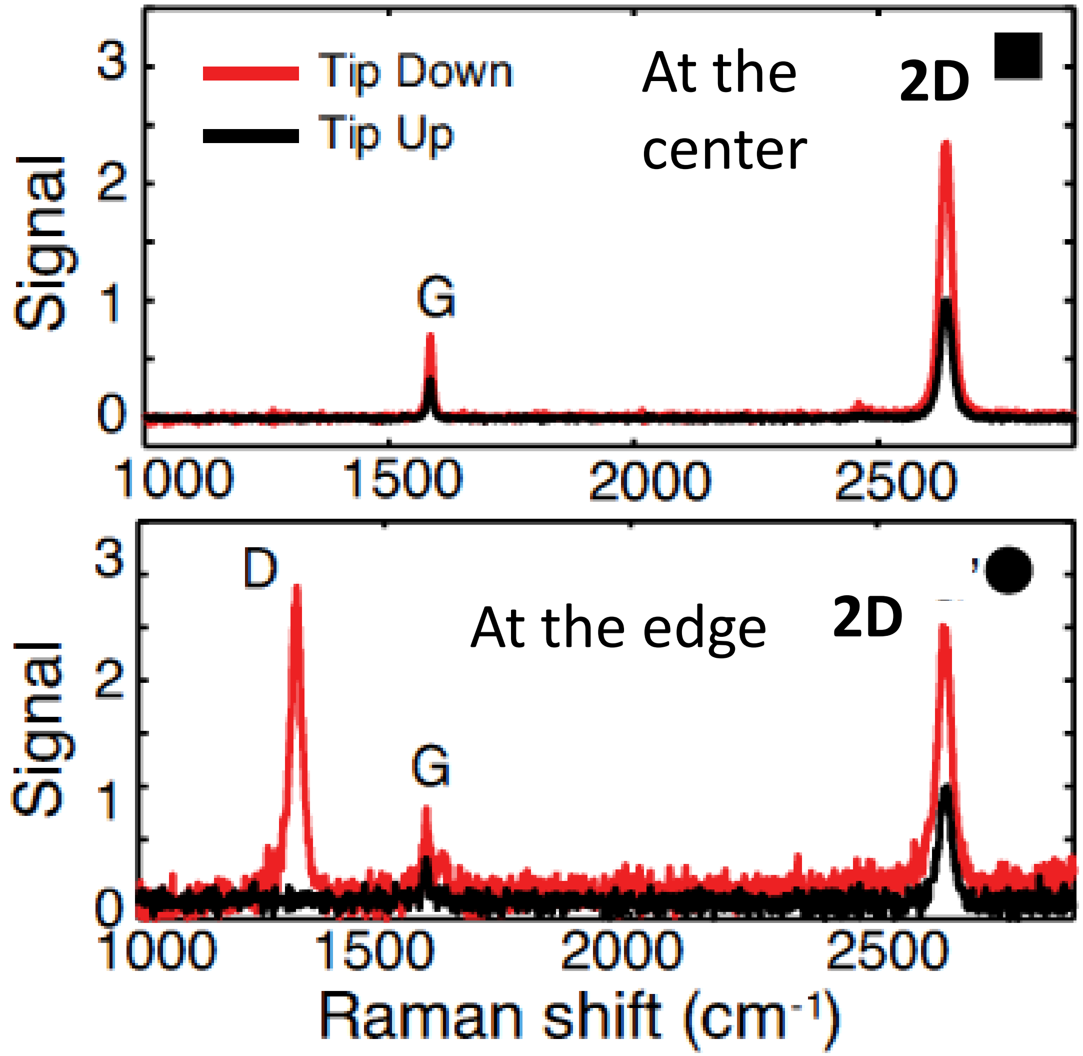
Cancado et al. PRL 103, 186101 (2009)

Jorio & Cancado
*PCCP **14**, 15246 (2012)*

The problem of TERS on 2D - graphene

10,000 enhancement on a 10,000 smaller area gives basically no spectral enhancement





Beams et al.
PRL 113, 186101 (2014)

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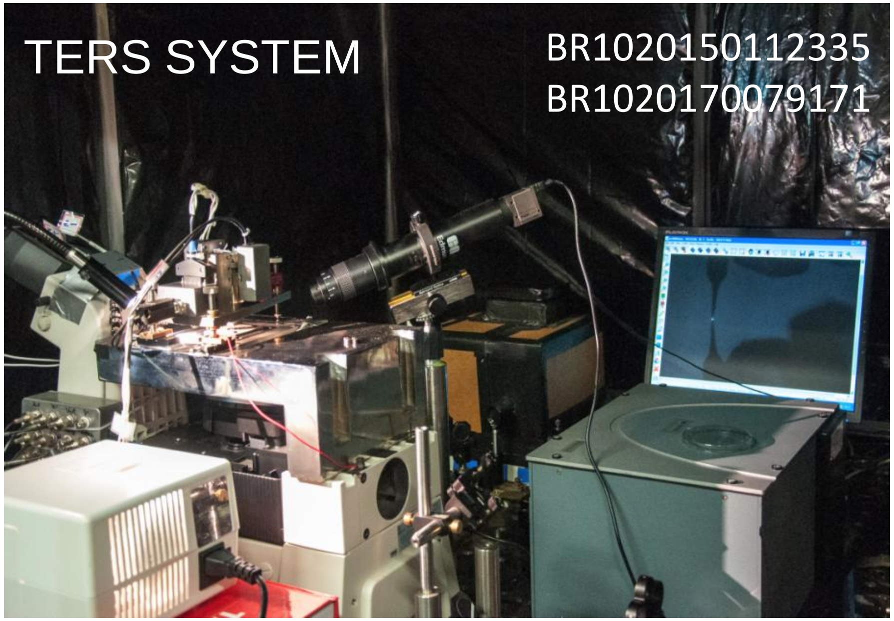
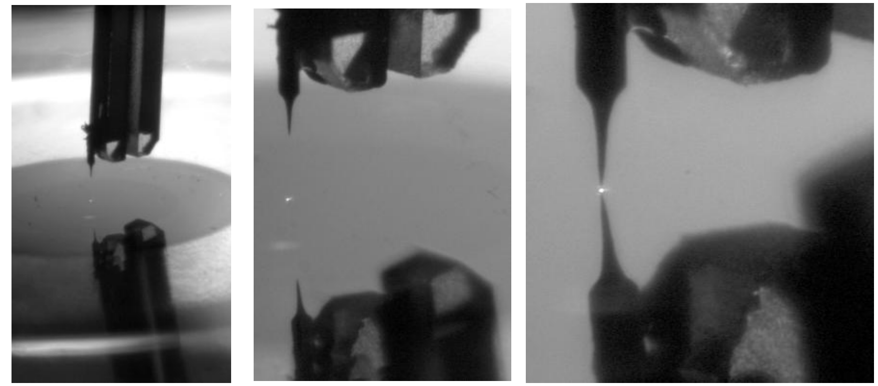
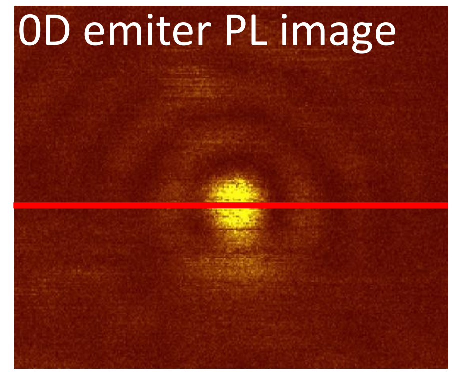
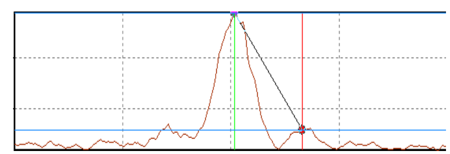
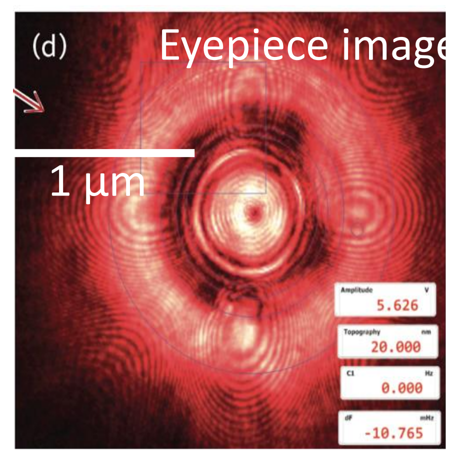
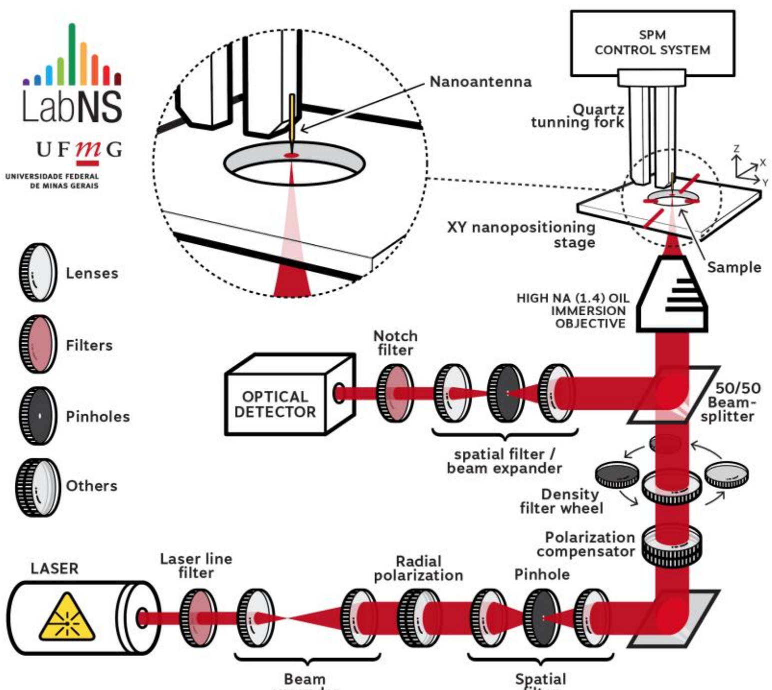










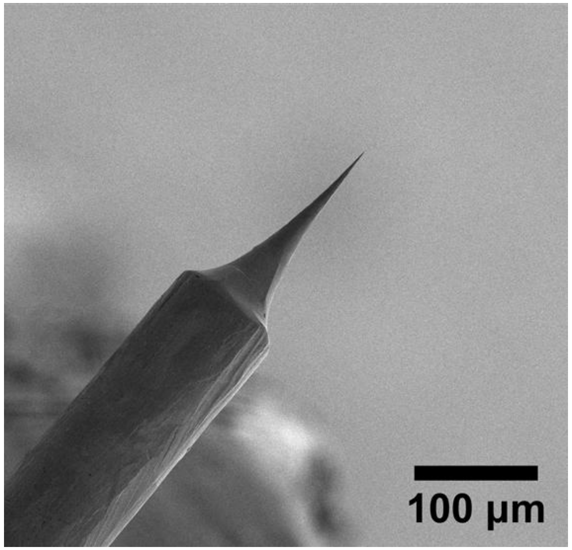


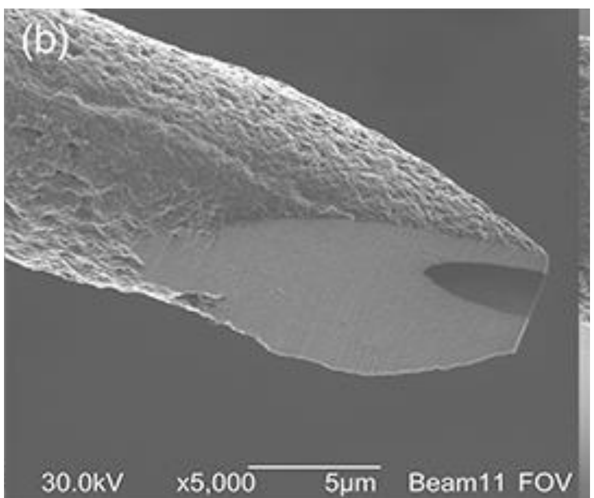
Radial polarized excitation field

Tip development

Chemical etched Au-tips

NIGHTMARE!



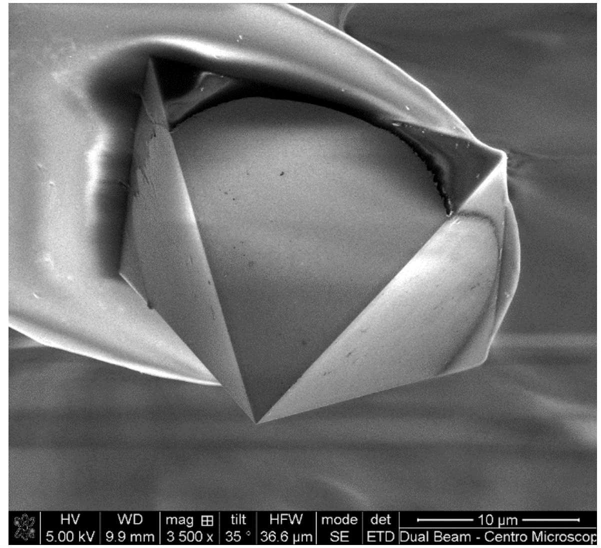


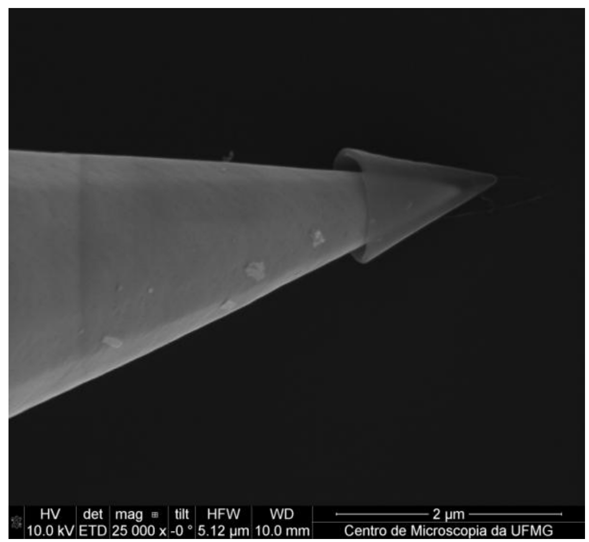
PI 1105968-0

BR 1020120333040

T. W. Johnson et al.

ACS Nano 6, 9168 (2012)





Cano-Marquez et al.

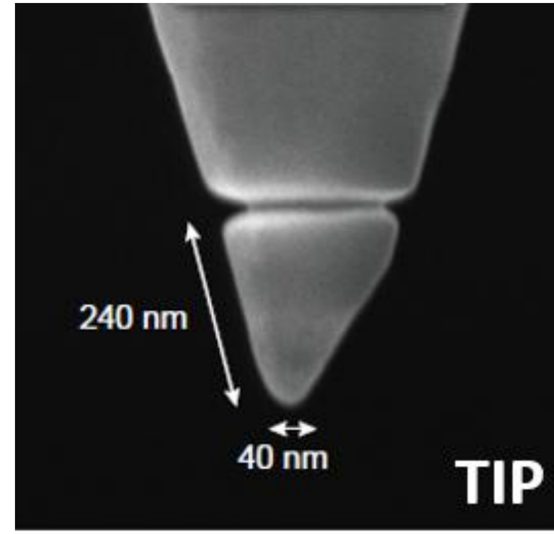
Scientific Reports, 5:10408 (2015)

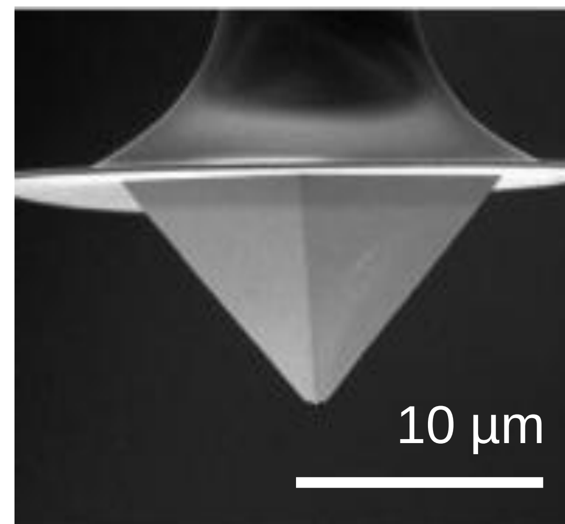
BR 1020120269732

T. L. Vasconcelos et al.,

ACS Nano 9, 6297 (2015)

BR1020150103522





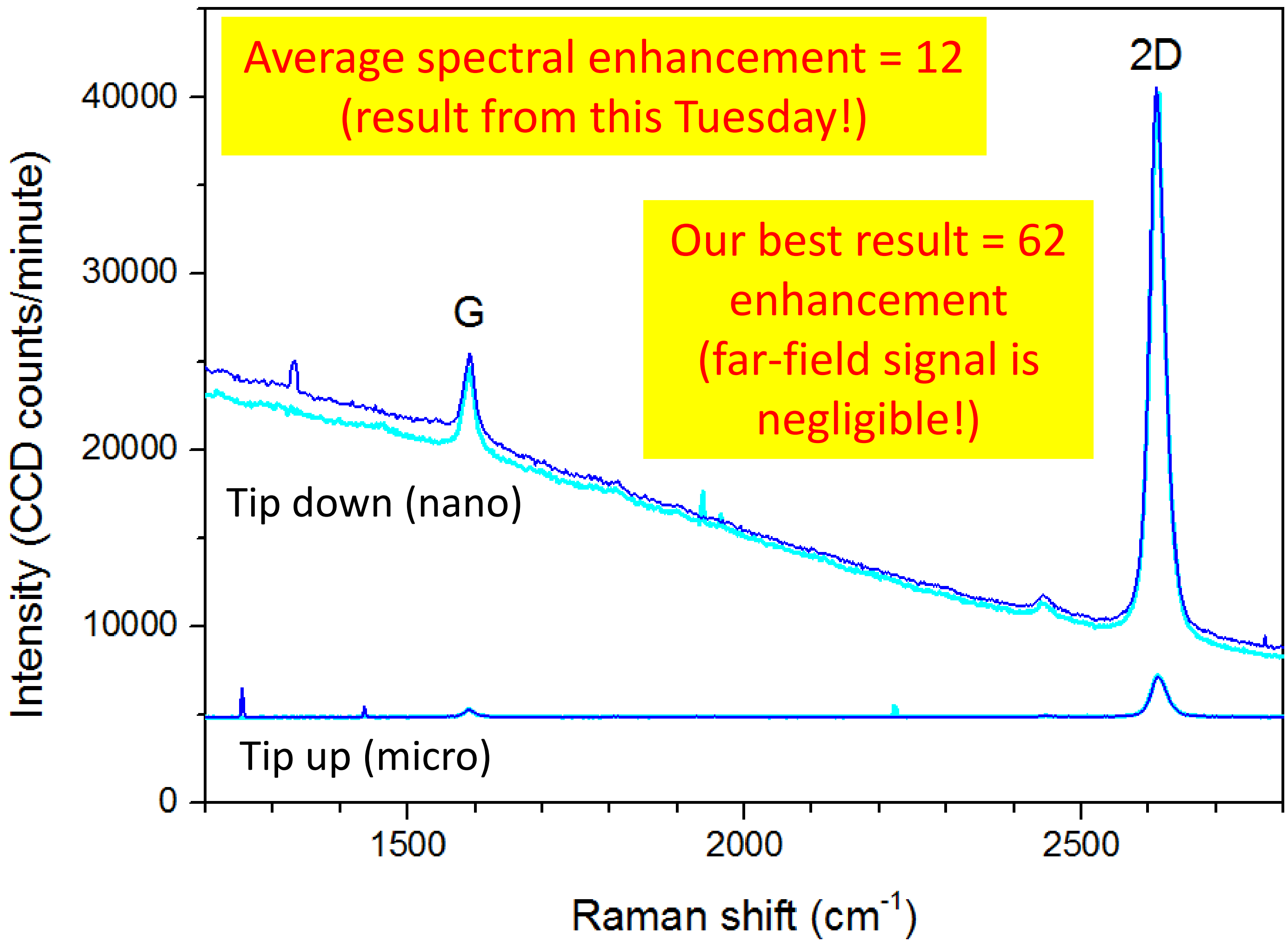
To appear in Adv. Opt. Mater.

BR1020150312032

BR1020160291267

Tip up (micro) – Tip down (nano)

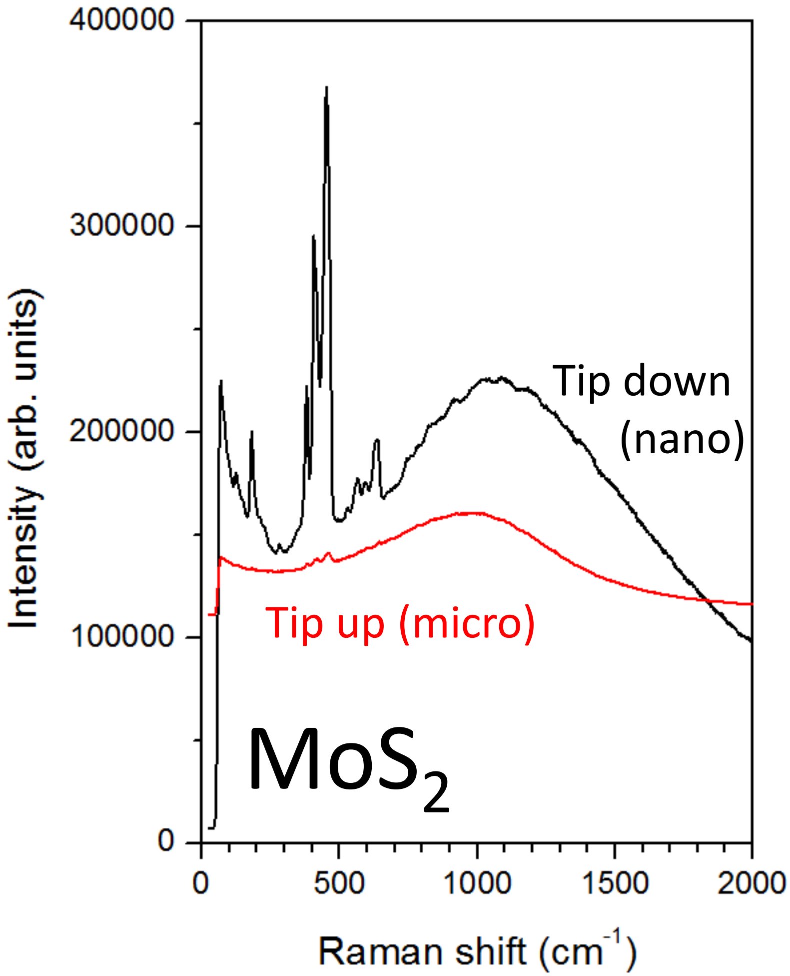
Raman on graphene

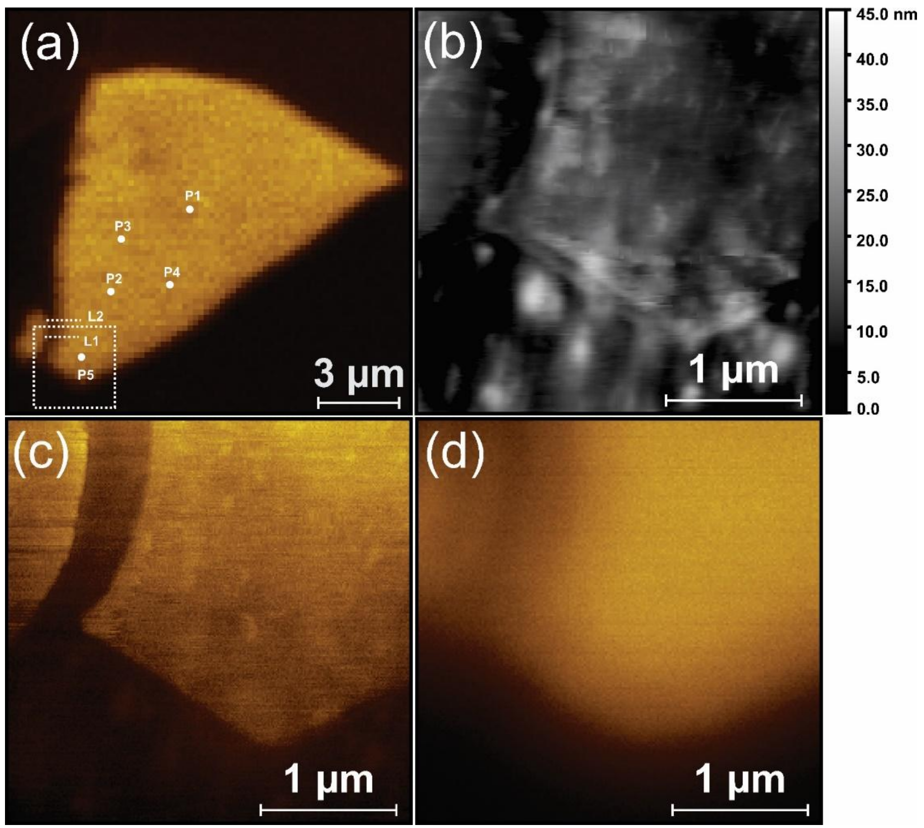


Tip up (micro) – Tip down (nano)

Raman on transition metal dichalcogenide

Average spectral enhancement = 60 (far-field signal is negligible!)

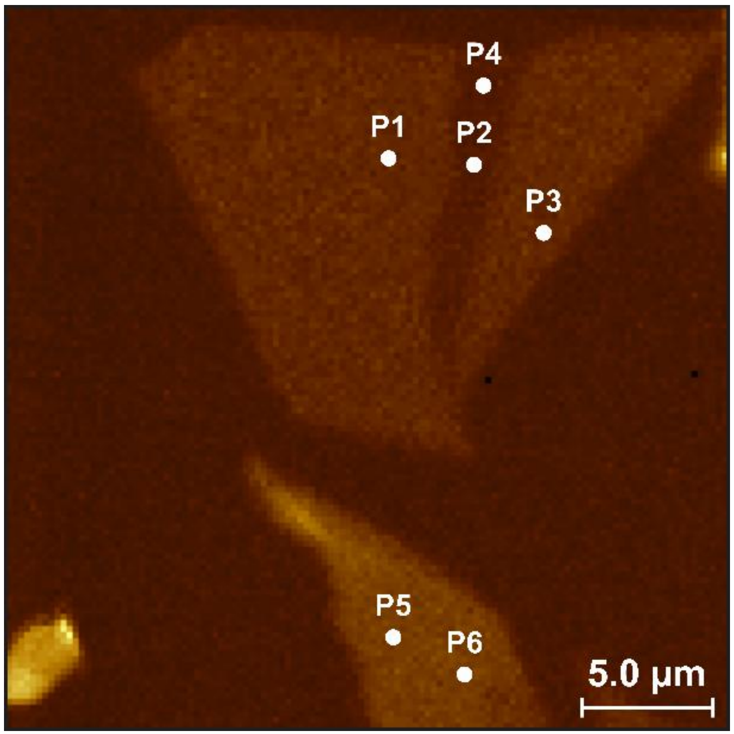


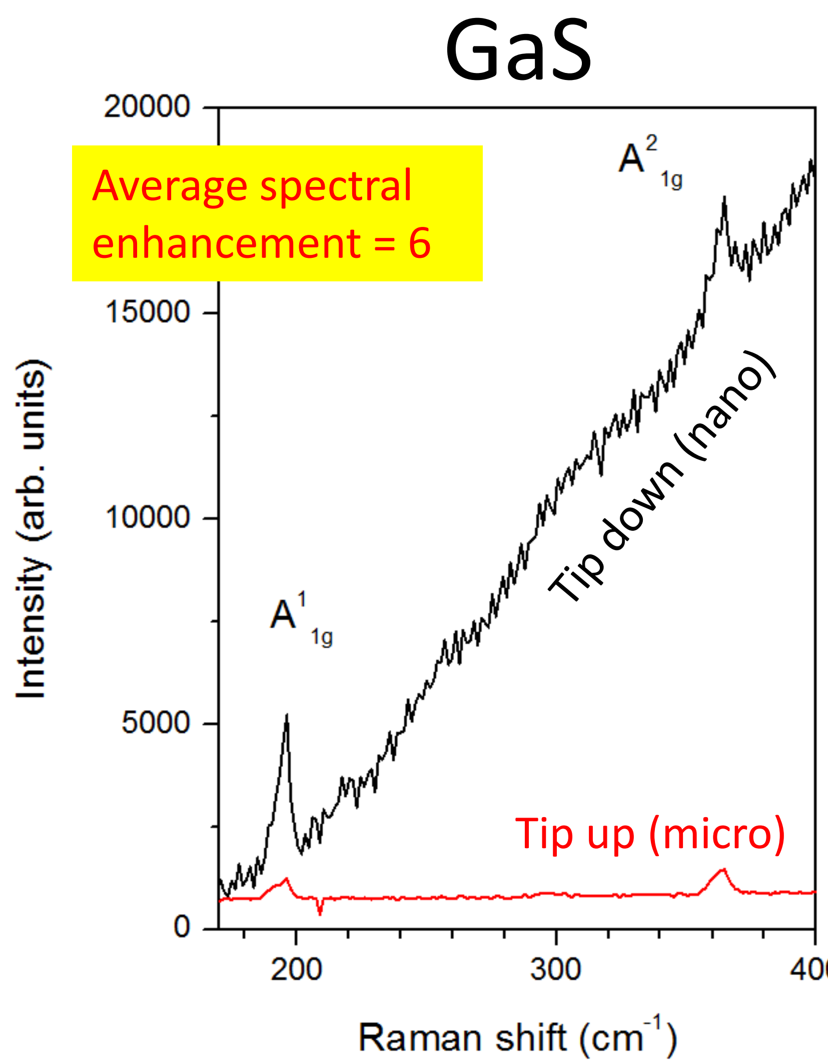


By Rafael Silva Alencar

Tip up (micro) – Tip down (nano)

Raman on transition metal monochalcogenide

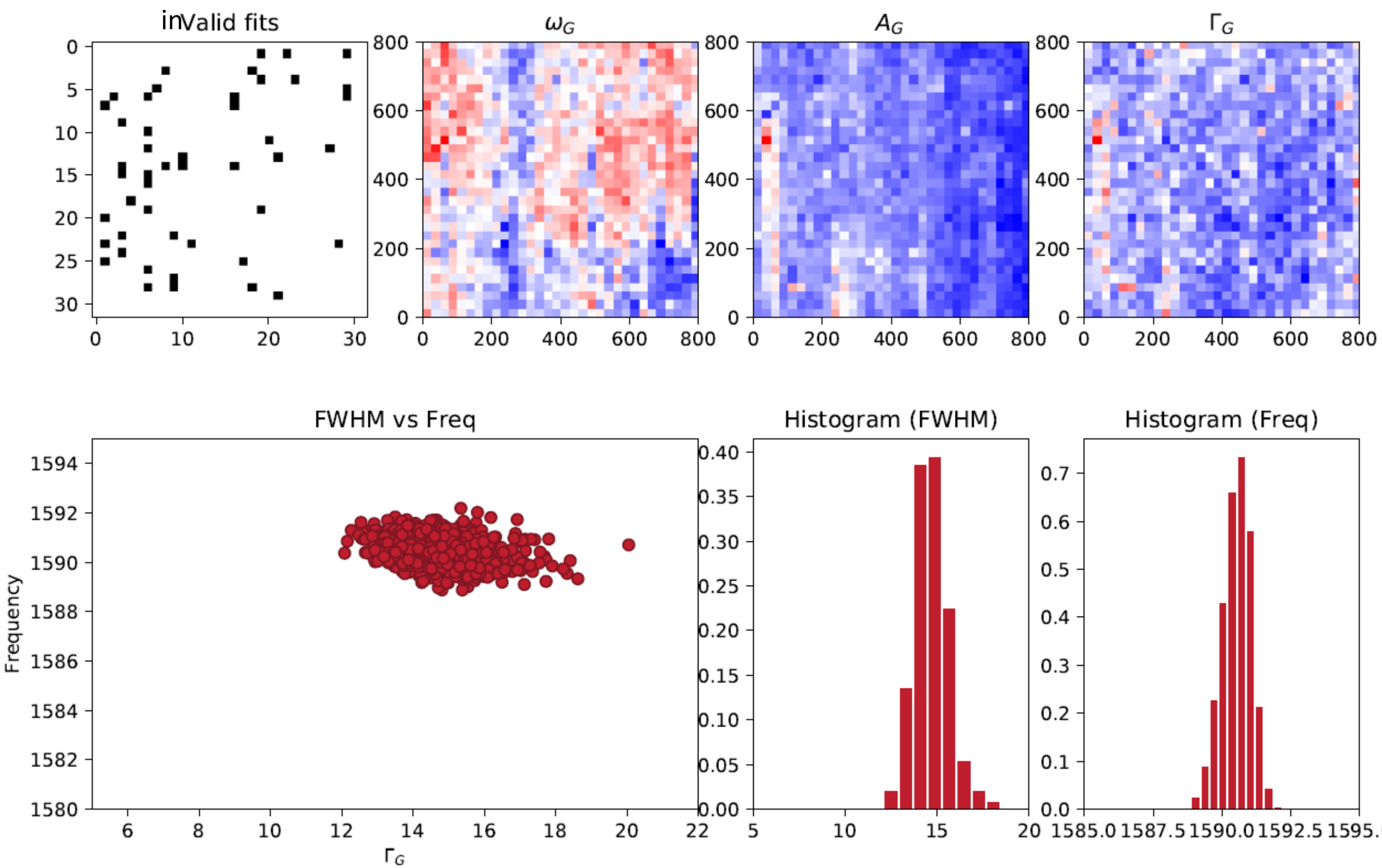




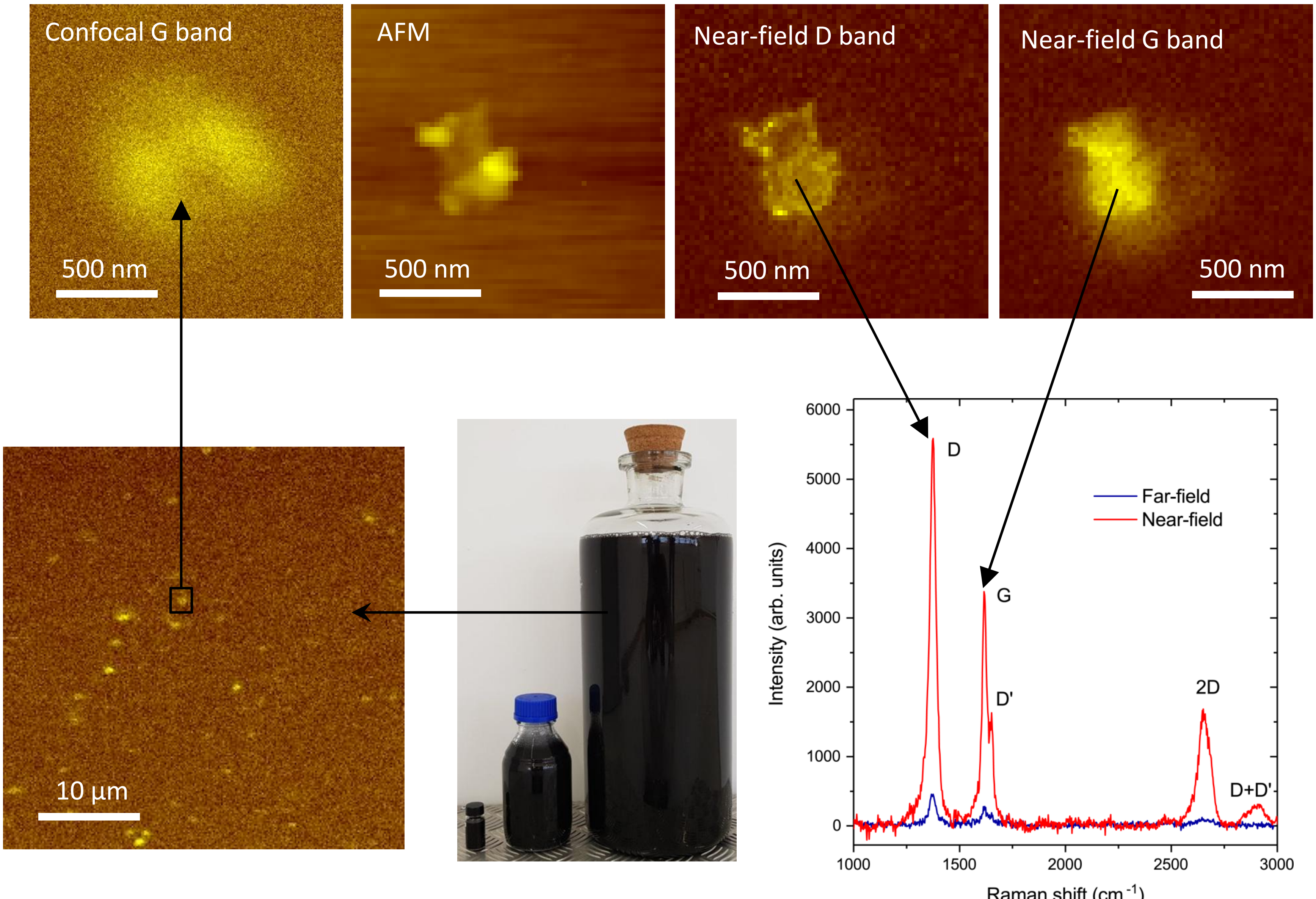
By Rafael Silva Alencar

Tip up (micro) – Tip down (nano)

Raman G band on graphene

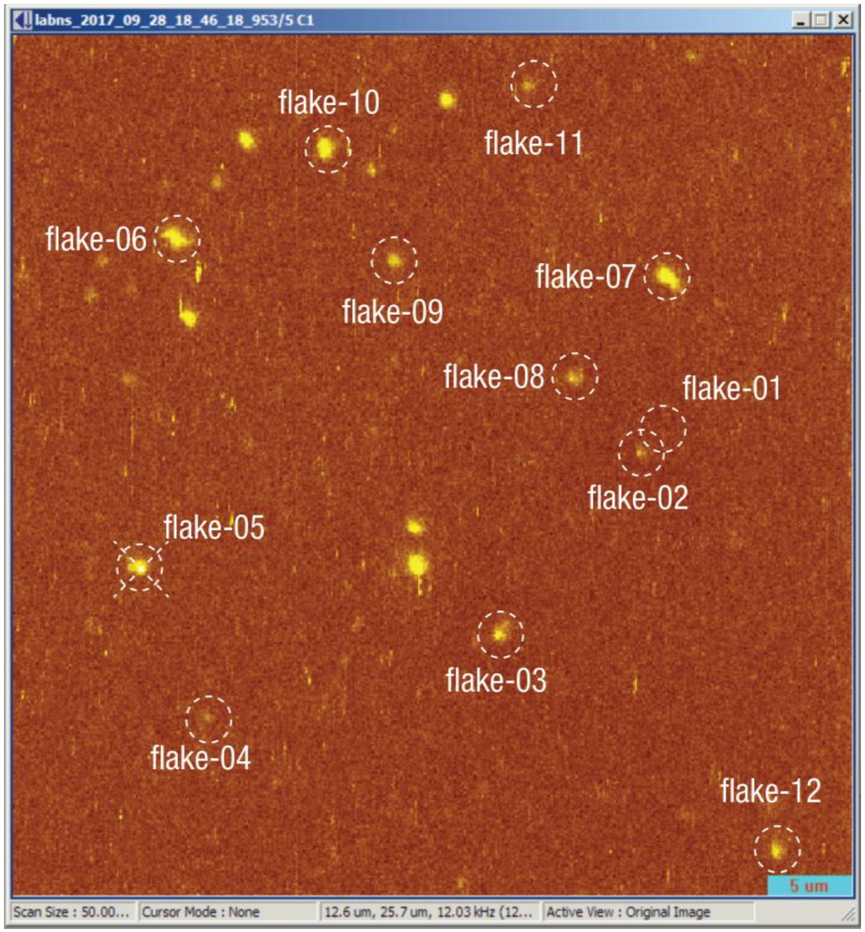


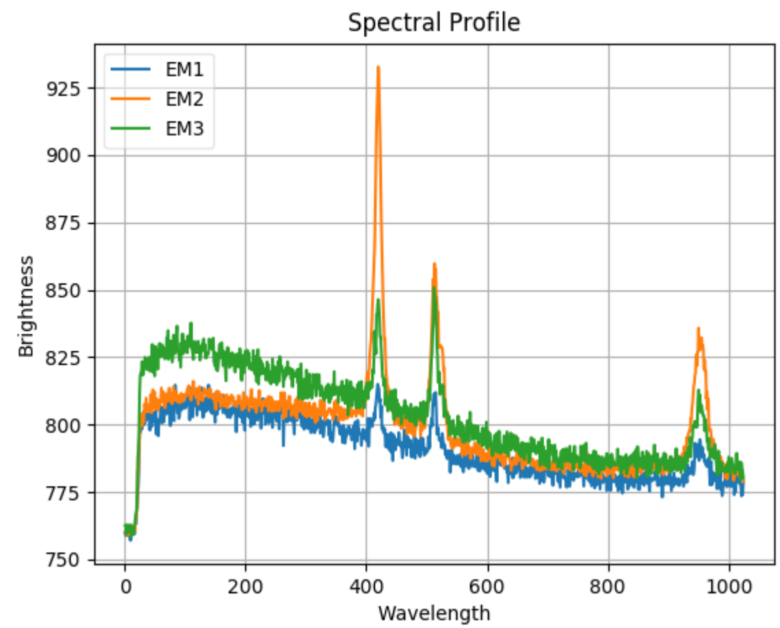
Nano-Raman of liquid-phase exfoliated graphene (nanoflakes) deposited on a glass coverslip

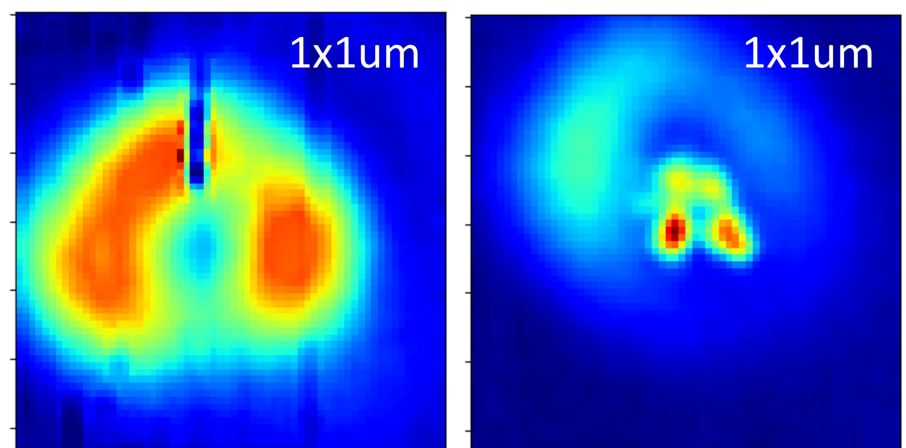


Cassiano Rabelo et al., submitted

Nano-Raman of liquid-phase exfoliated graphene (nanoflakes) deposited on a glass coverslip







Cassiano Rabelo et al., submitted

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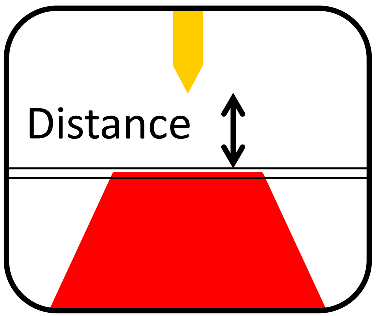
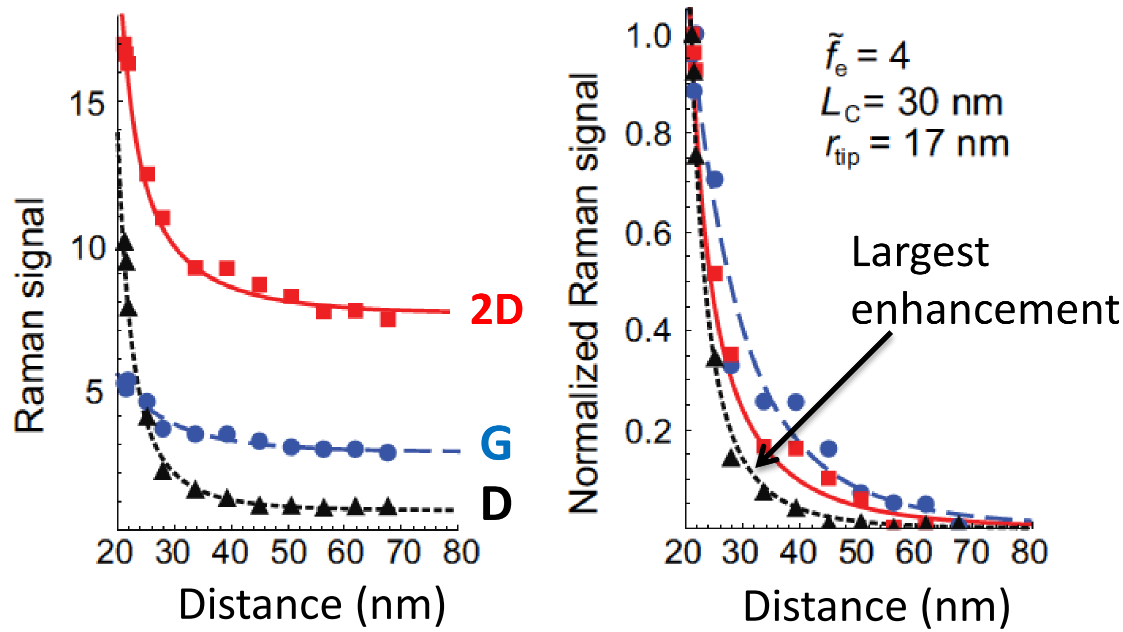
Spatially coherent near-field Raman

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

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

Tip approach curves





Phonon coherence length
ℓ_C = 30nm

Beams et al. PRL 113, 186101 (2014); Cancado et al. PRX 4, 031054 (2014)

Calculation for Raman Scattering

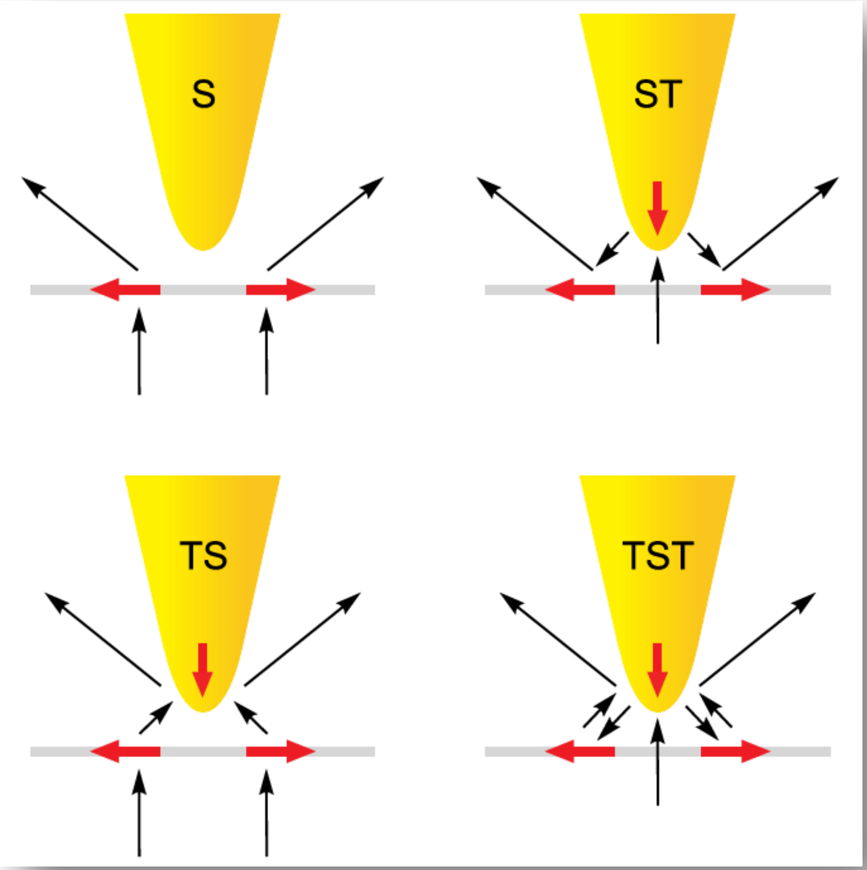
$$S \propto V \left| \hat{\epsilon} \cdot \overleftrightarrow{\alpha} \vec{E} \right|^2$$

Valid for incoherent Raman

Calculation for spatially coherent near-field Raman

$$S(r_0) \propto \int\int \overleftrightarrow{G}^*(r_1)\overleftrightarrow{G}(r_2)\left\langle \vec{p}(r_1)^*\vec{p}(r_2)\right\rangle d^3r_1 d^3r_2$$

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

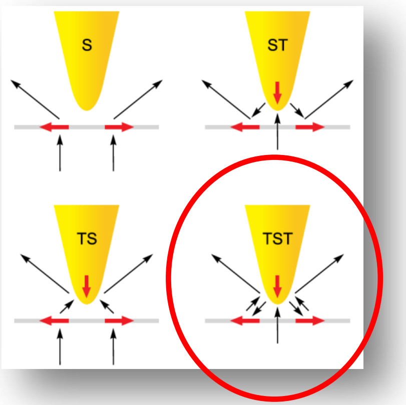


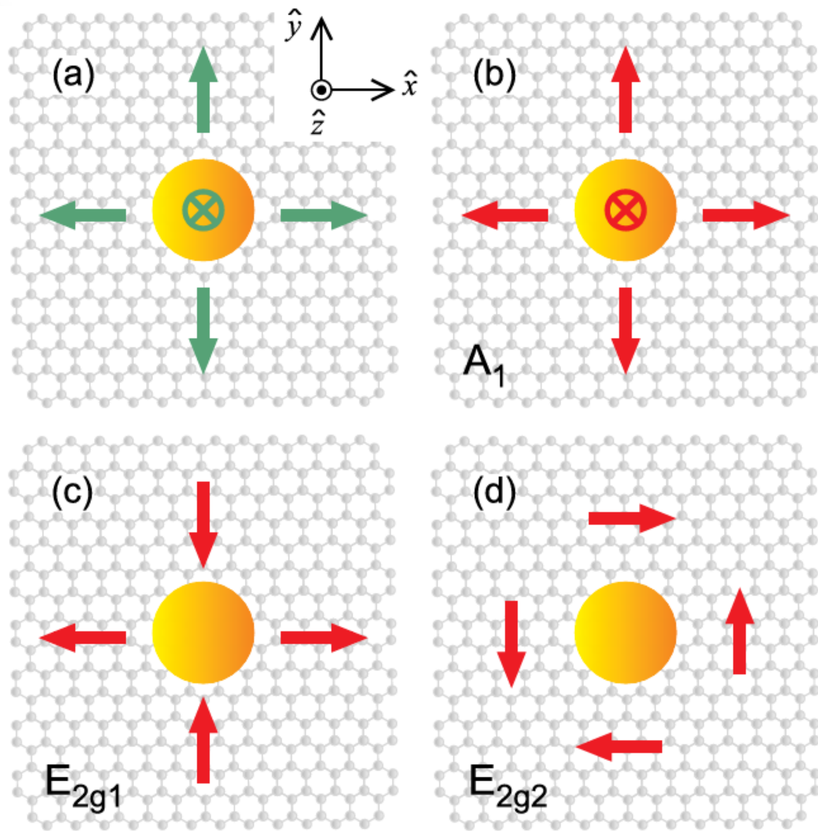
Beams et al. PRL 113, 186101 (2014) & Cancado et al. PRX 4, 031054 (2014)

Calculation for spatially coherent near-field Raman

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

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





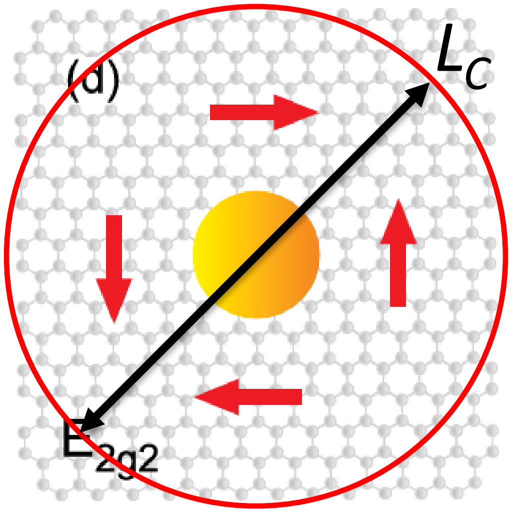
$$\overleftrightarrow{\alpha}^{\mathrm{D,G'}}(\mathrm{A_1}) = \alpha^{\mathrm{D,G'}}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

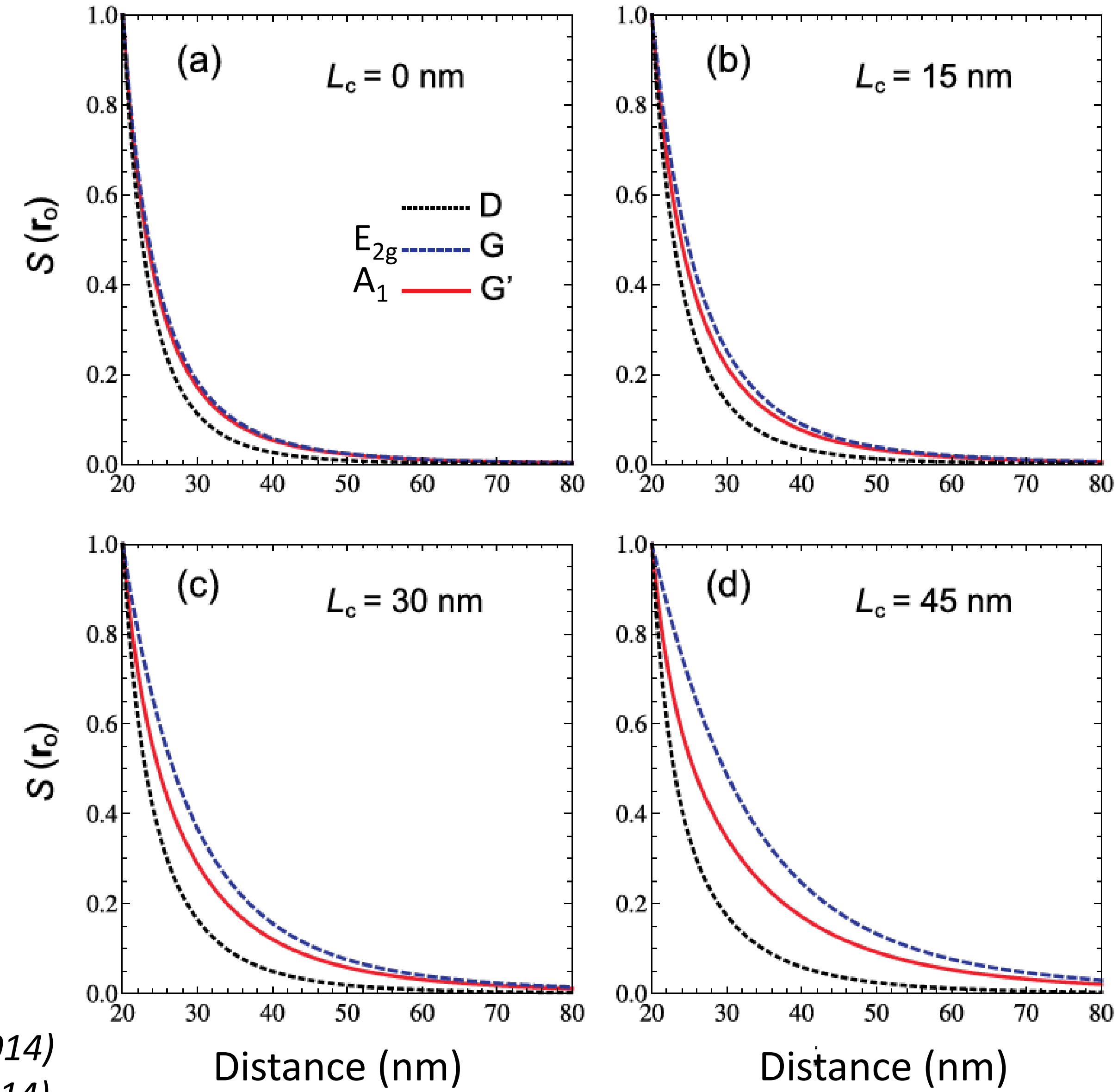
$$\overleftrightarrow{\alpha}^{\mathrm{G}}(\mathrm{E_{2g1}}) = \alpha^{\mathrm{G}}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\overleftrightarrow{\alpha}^{\mathrm{G}}(\mathrm{E_{2g2}}) = \alpha^{\mathrm{G}}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

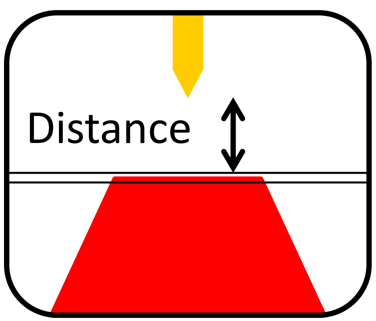
ams et al. PRL 113, 186101 (2014) & Cancado et al. PRX 4, 031054 (2014)

Calculation for spatially coherent near-field Raman





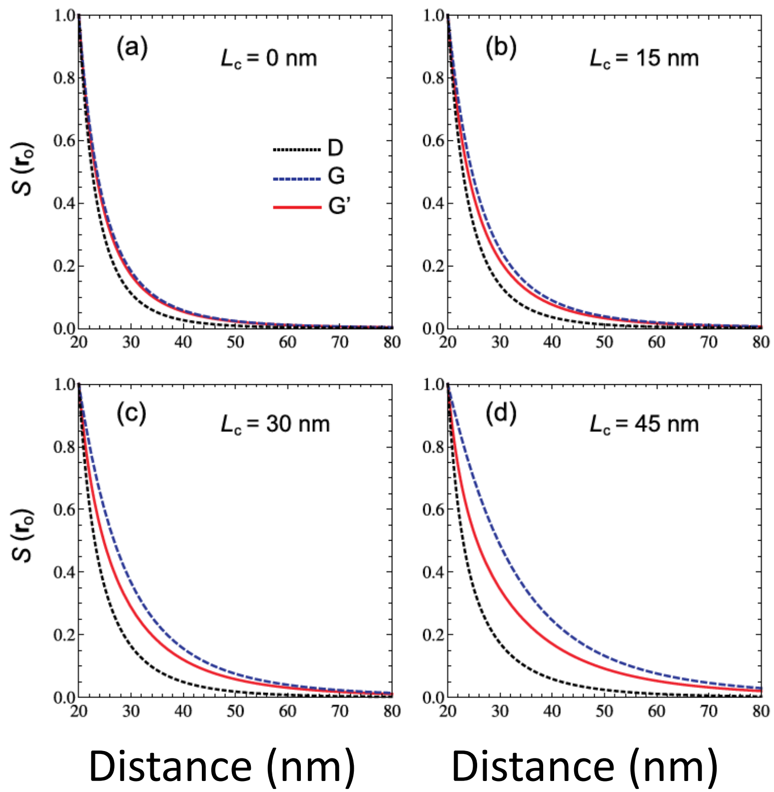
Tip approach curves

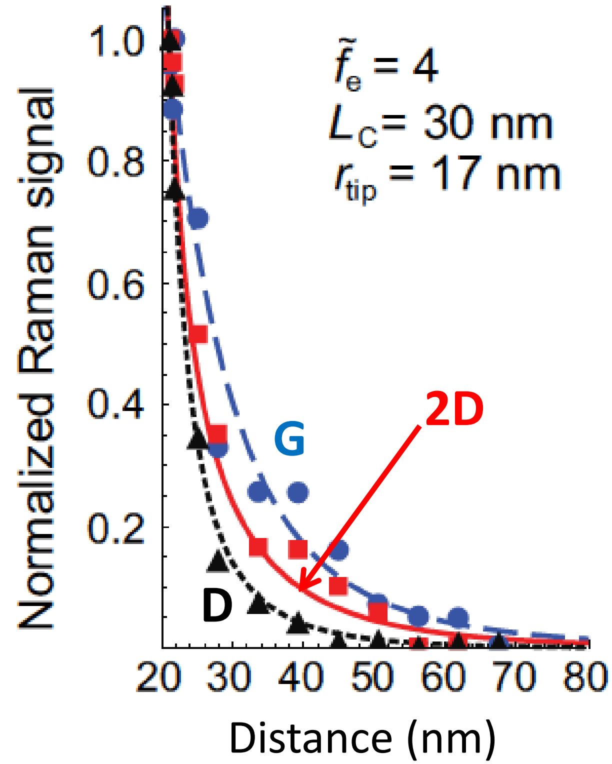


Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)

Phonon symmetry dependent spatial coherence

$$S(r_0) \propto \int\int \overleftrightarrow{G}^*(r_1)\overleftrightarrow{G}(r_2)\,\langle \vec{p}(r_1)^*\vec{p}(r_2)\rangle\, d^3r_1 d^3r_2$$
$$= \int\int \langle \overleftrightarrow{\alpha}^*_{r_1}\overleftrightarrow{\alpha}_{r_2}\rangle\,[\overleftrightarrow{G}(r_1)\vec{E}(r_1)]^*\overleftrightarrow{G}(r_2)\vec{E}(r_2) d^3r_1 d^3r_2$$





Coherence length

L_C = 30nm

Beams et al. PRL 113, 186101 (2014)

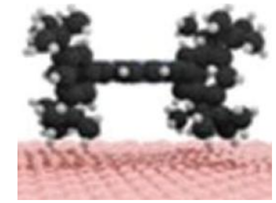
Cancado et al. PRX 4, 031054 (2014)

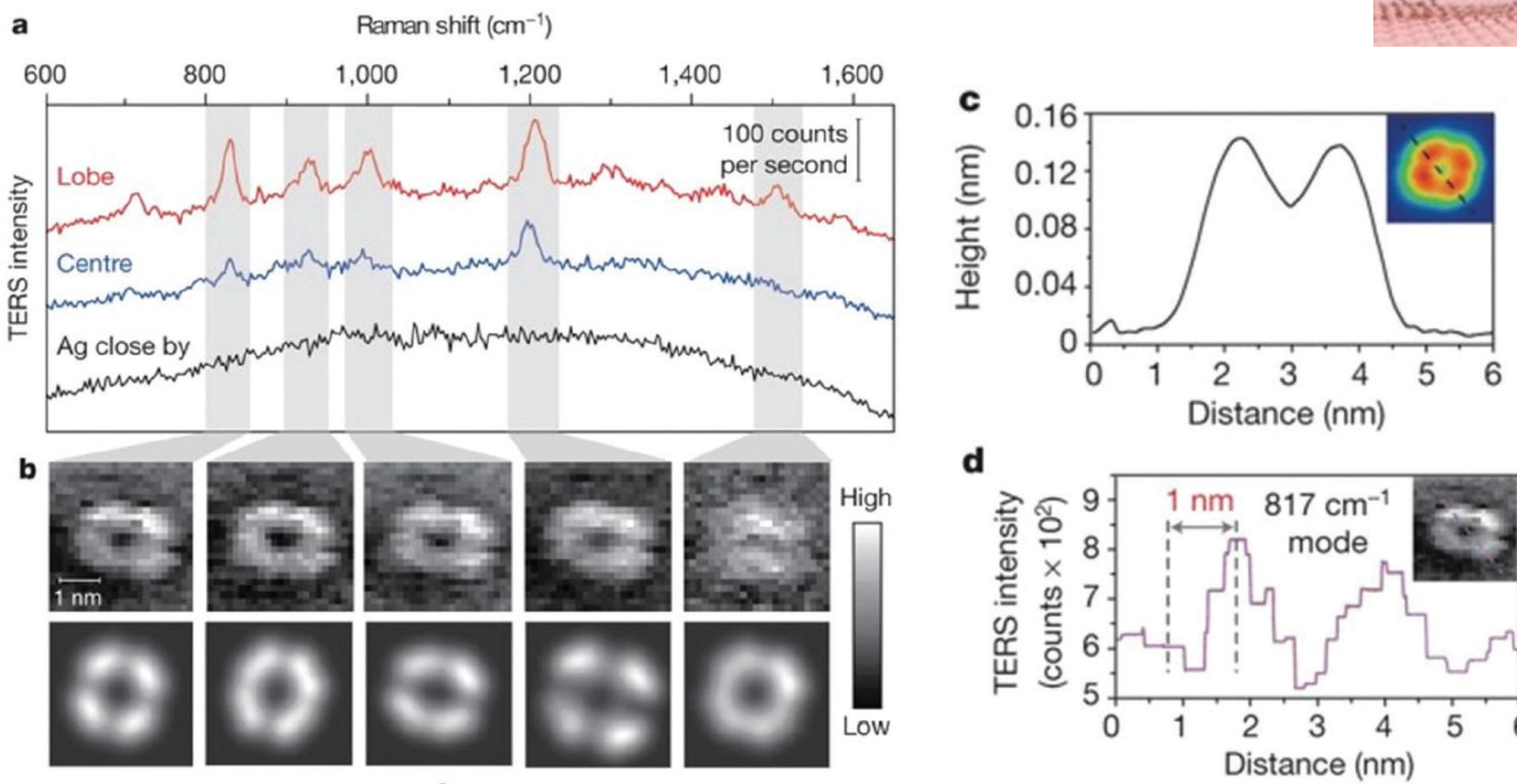
The future of nano-Raman
(reaching resolutions better than 1nm)

R. Zhang et al. Nature 498, 82–86 (2013)

Ultra high vacuum STM (gap mode)

tetrakis(3,5-ditertiarybutylphenyl)-porphyrin (H2TBPP) on Cu(111)





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