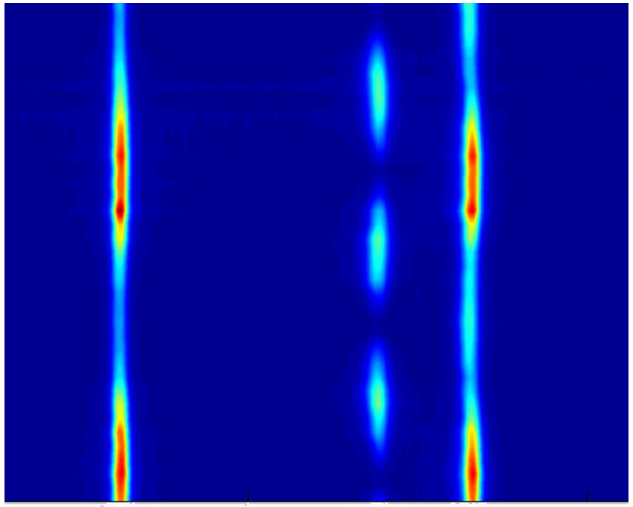
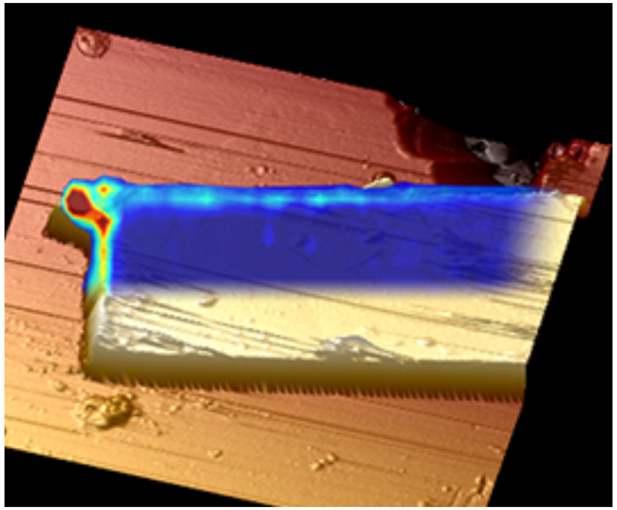
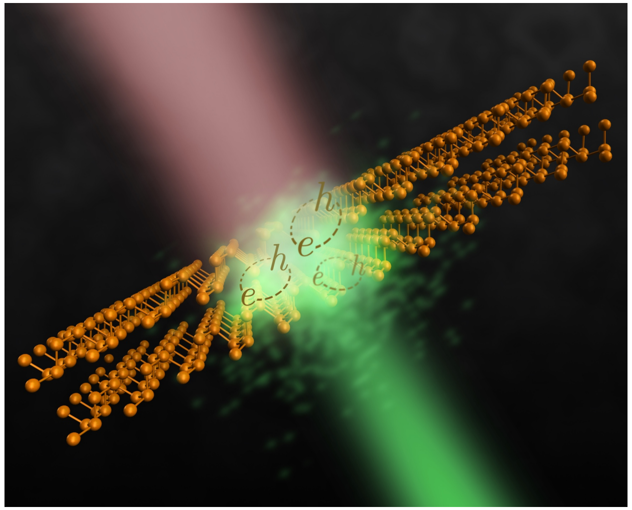
The Unusual Raman and Optical Properties of Black Phosphorus



ACS Nano 9, 4270 (2015)



Nature Commun. 7, 12191 (2016)



Adv. Mater. 28, 10693 (2016)

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MackGraphe

Talk outline

- Black phosphorus (BP): an anisotropic layered semiconductor
- Raman response in BP
  - Unusual dependence on light polarization
  - Edge phonons
- Nonlinear optical response in BP
  - Third-harmonic generation
- Conclusions

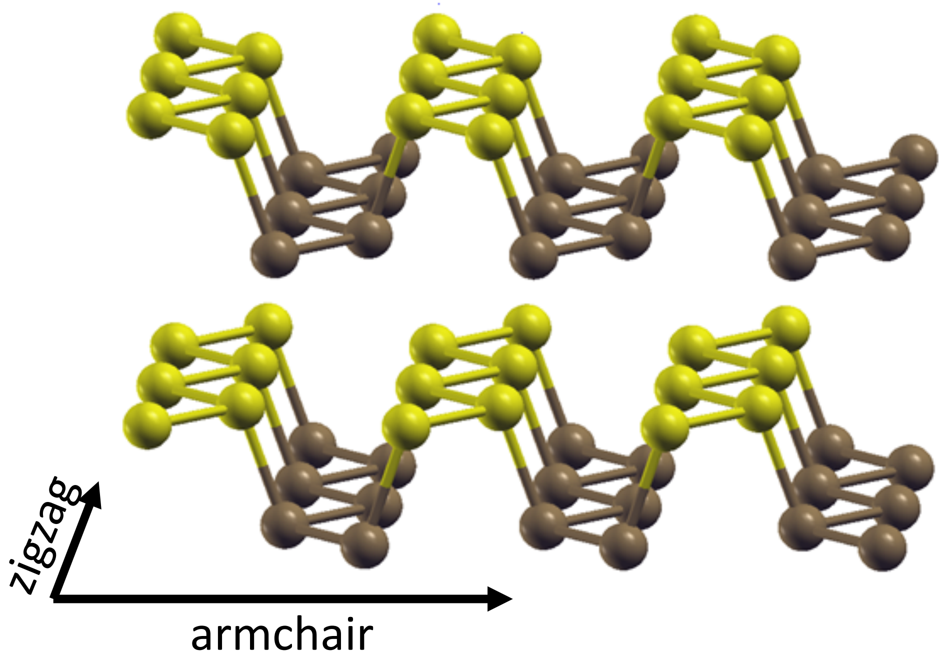
About MackGraphe

(Graphene and Nanomaterials Research Center)

- Located at the Mackenzie Presbyterian University, São Paulo, Brazil
- Began its activities in 2013
- Headquarters building opened on 2 march 2016
- 3 areas of interest: Photonics, Energy, Composite Materials
- **Positions available!**

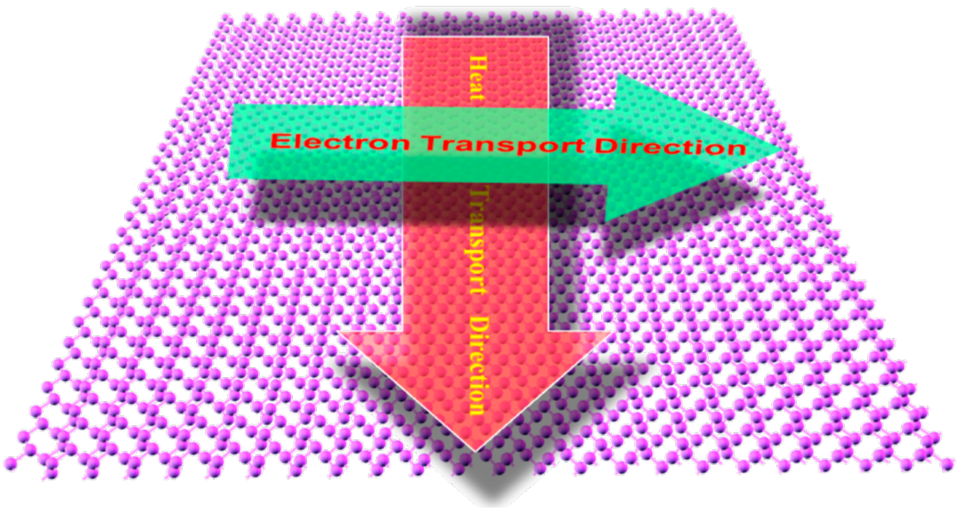
Black Phosphorus

- Highly anisotropic puckered structure
  - orthorhombic, point group D_{2h}, centrosymmetric

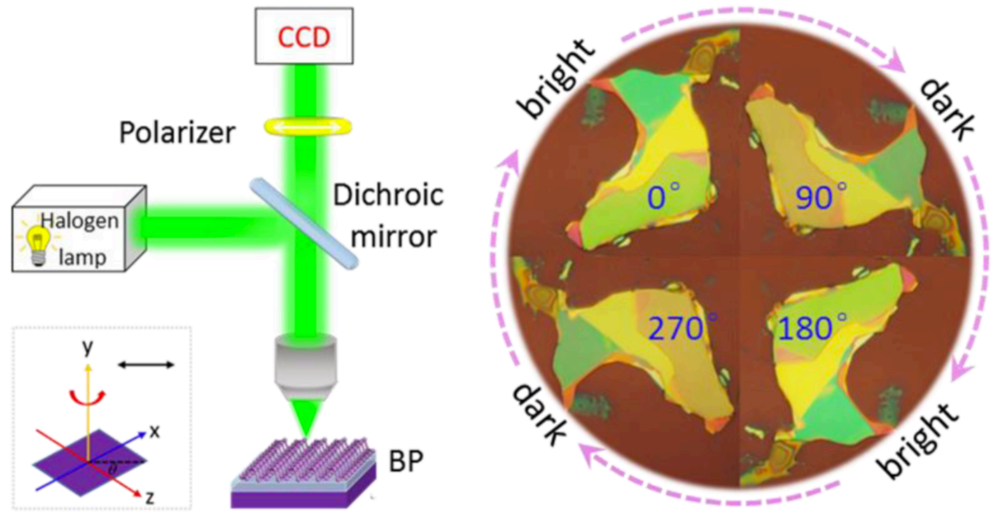


Highly anisotropic properties

Angle dependent heat & electronic conduction



Birefringence & linear dichroism



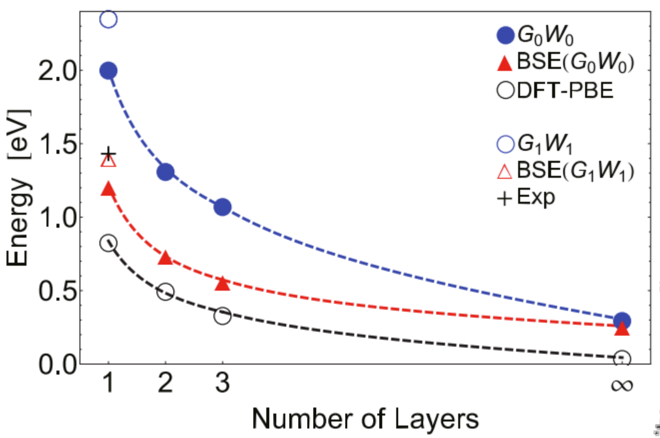
Fei et al., Nano Lett. 14, 6393−6399 (2014)

Mao et al., J. Am. Chem. Soc.138, 300−305 (2016)

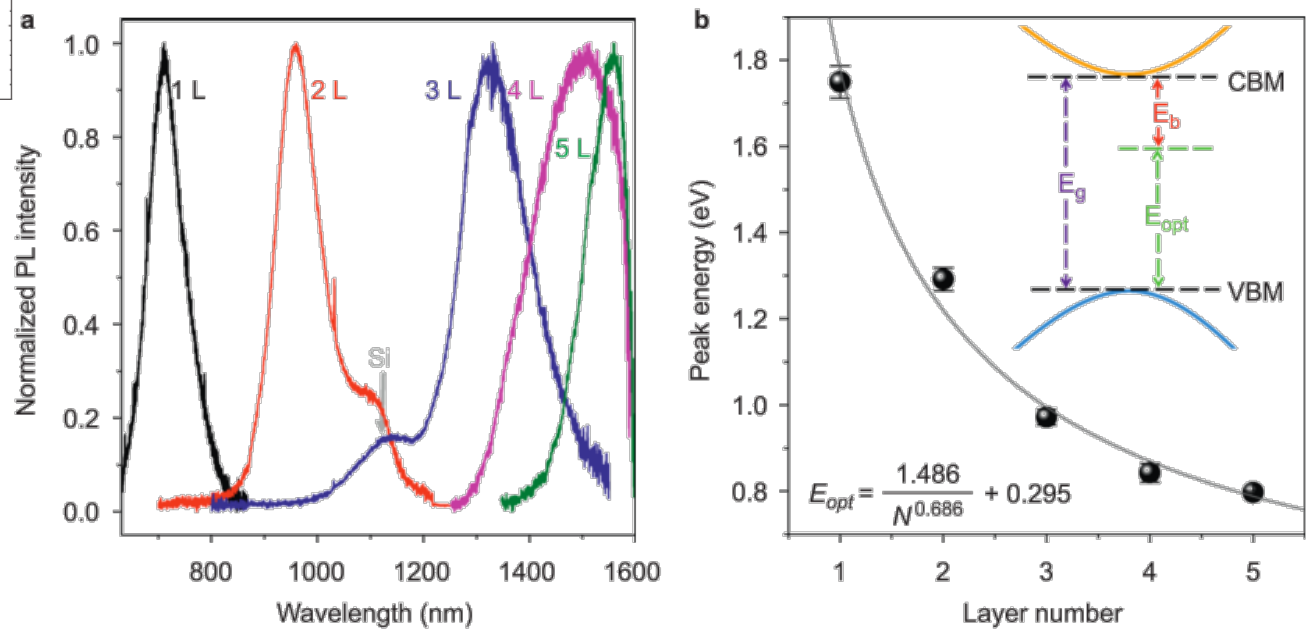
Black Phosphorus

- A direct bandgap semiconductor from bulk to the monolayer; gap increases with thickness reduction

Tran et al., Phys. Rev. B 89, 235319 (2014)



Highly bound (room temperature) excitons

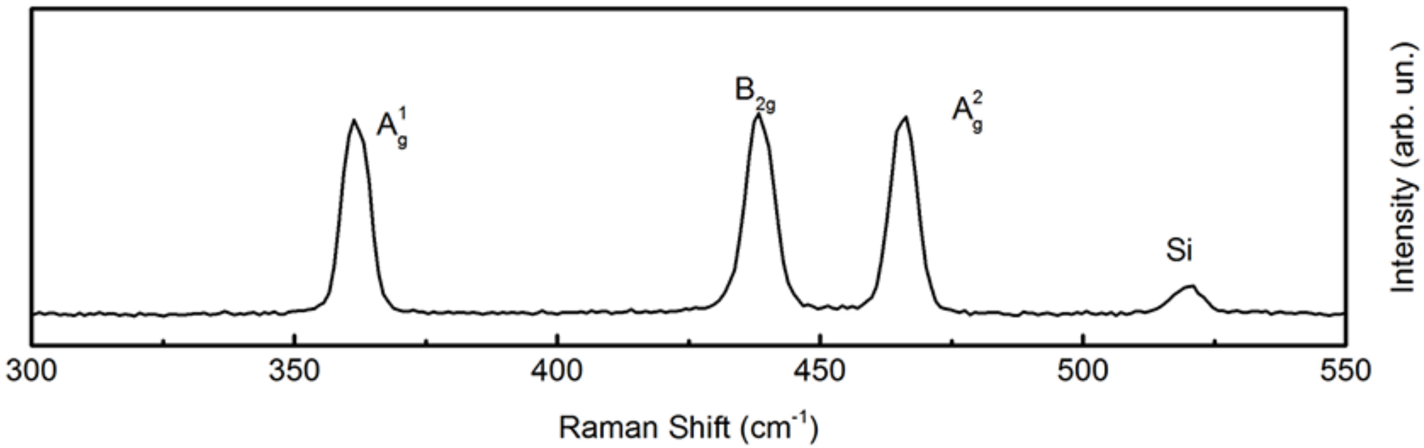


Yang et al., Light Science and Applications 4, e312 (2015)

Motivation to this work

- Properties suggest important applications in
  - Electronics
  - Optoelectronics
  - Photonics
- Thorough characterization of the crystal is imperative
- **Here:**
  - Polarized Raman characterization and identification of complex Raman tensor elements
  - Changes in Raman mode symmetries at the crystal edges
  - Enhanced nonlinear optical frequency conversion in few-layer flakes

Raman spectroscopy in black phosphorus

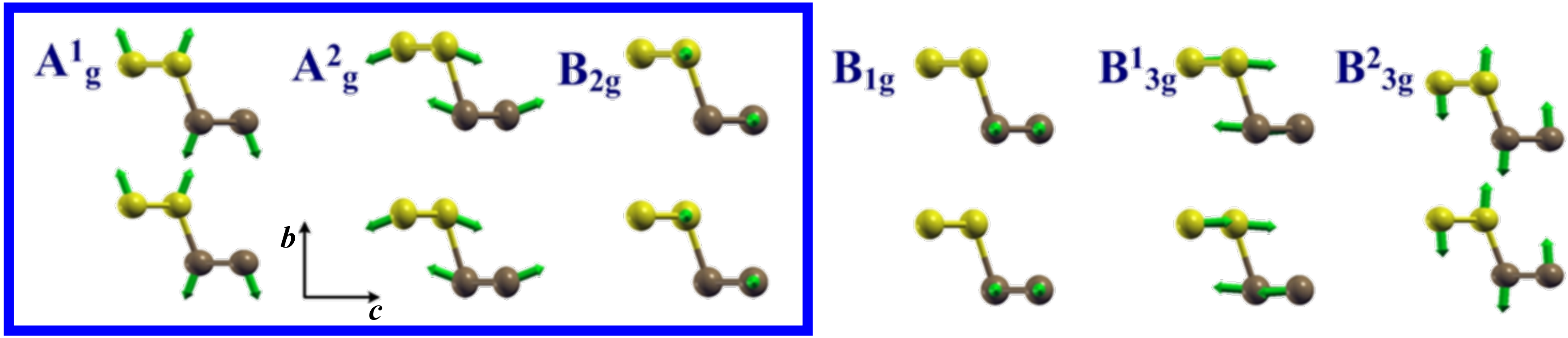


Soon: a review in Journal of Raman Spectroscopy

H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)   H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Raman modes in BP

- 6 Raman active modes



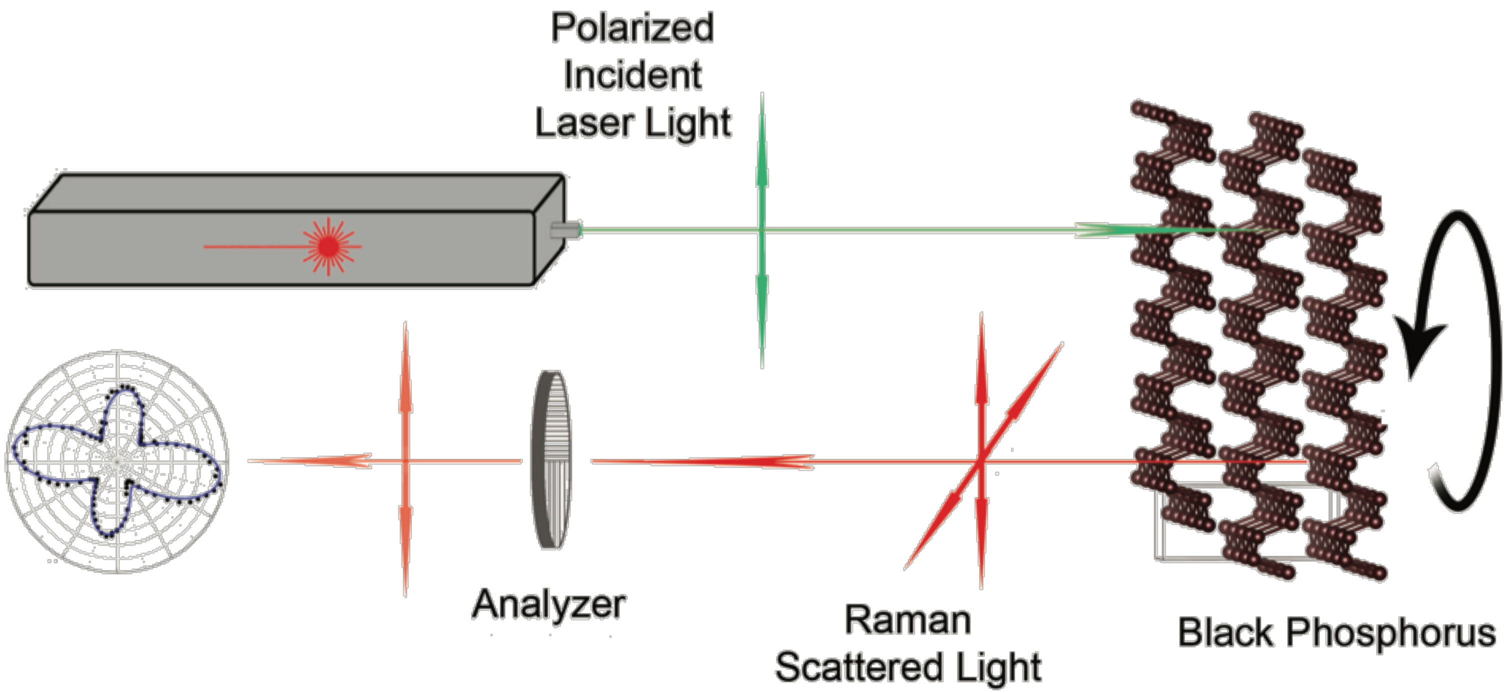
Light incident along *y*

Raman tensors obtained from the dielectric tensor:

$$R^k_{ij} = \frac{\partial \epsilon_{ij}}{\partial q^k} \qquad S_k \propto |\hat{\mathbf{e}}_i \cdot \overleftrightarrow{R}^k \cdot \hat{\mathbf{e}}_s|^2$$

Mode	A_g	B_{1g}	B_{2g}	B_{3g}
Tensor	$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ f & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & g \\ 0 & g & 0 \end{pmatrix}$

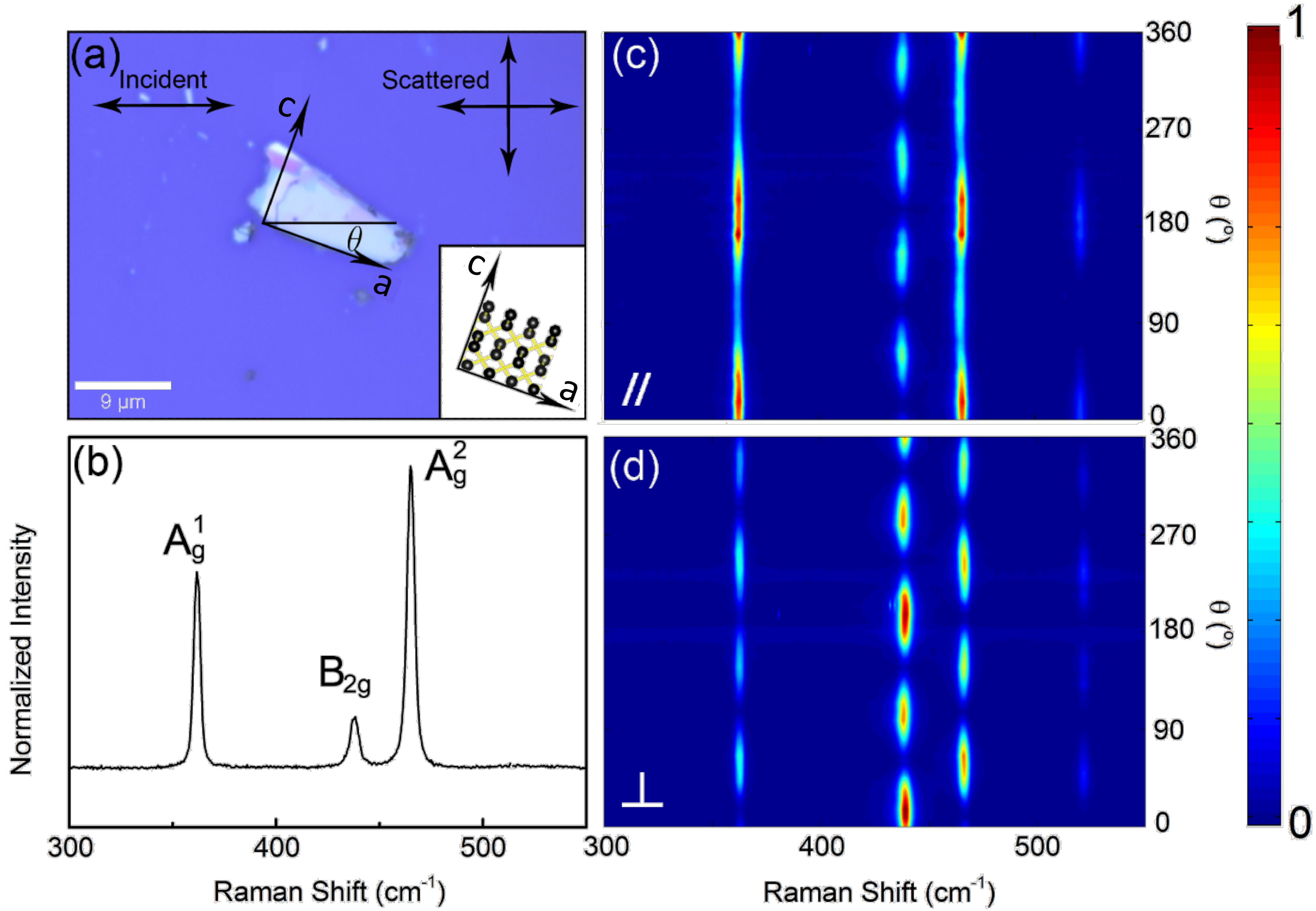
Polarized Raman spectroscopy



- Parallel configuration: $\hat{e}_i \parallel \hat{e}_s$
- Orthogonal configuration: $\hat{e}_i \perp \hat{e}_s$

H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

Polarized Raman spectroscopy: results



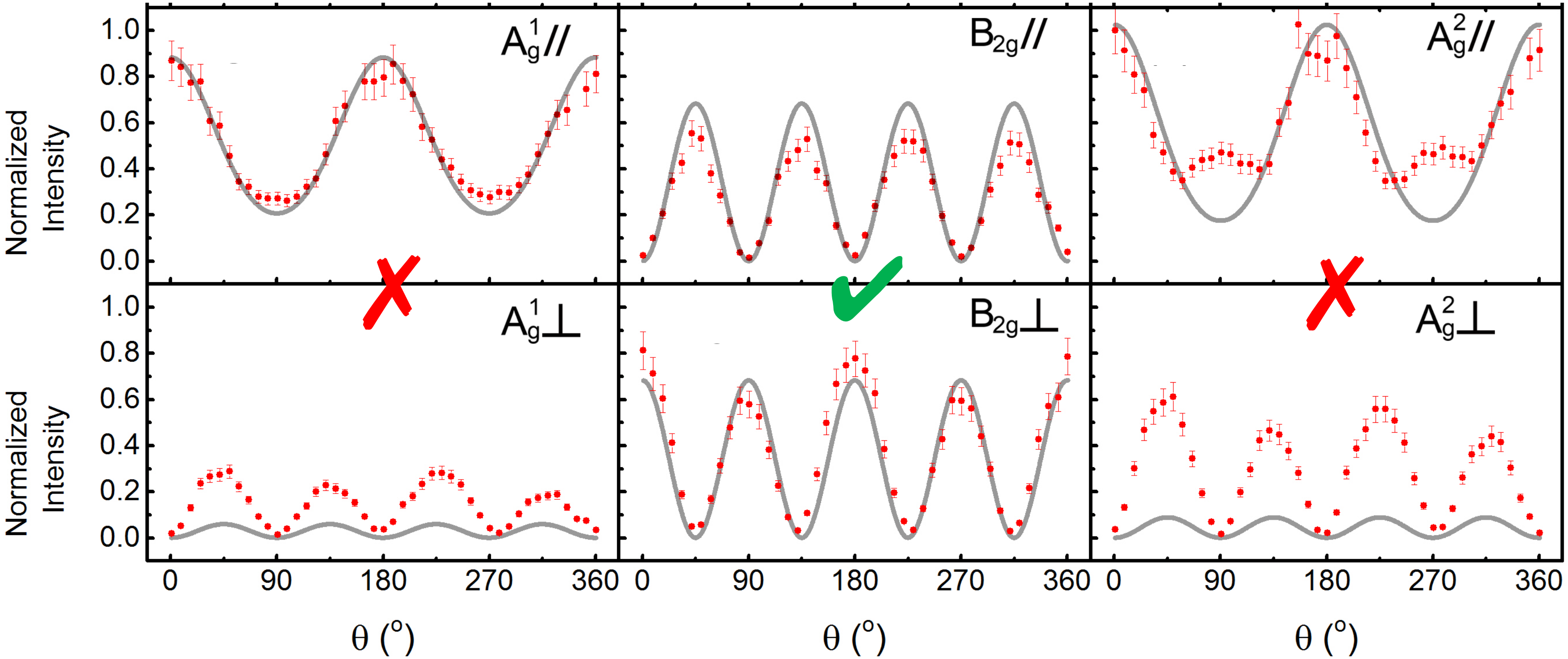
H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

Polarized Raman spectroscopy: conventional analysis

Mode	A_g	B_{2g}
Tensor	$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ f & 0 & 0 \end{pmatrix}$

$$S^{\parallel}_{A_g} = (a.\cos^2\theta + c.\sin^2\theta)^2 \qquad S^{\parallel}_{B_{2g}} = (2f.\sin\theta\cos\theta)^2$$

$$S^{\perp}_{A_g} = (a-c)^2\sin^2\theta\cos^2\theta \qquad S^{\perp}_{B_{2g}} = (f.\cos 2\theta)^2$$



H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

Unusual angular dependence of the Raman response in BP

$$R_{ij}^{k} = \frac{\partial \epsilon_{ij}}{\partial q^k} = \frac{\partial \epsilon'_{ij}}{\partial q^k} + i\frac{\partial \epsilon''_{ij}}{\partial q^k}$$

$$a = |a|e^{i\phi_a}, \quad c = |c|e^{i\phi_c}, \quad f = |f|e^{i\phi_f}$$

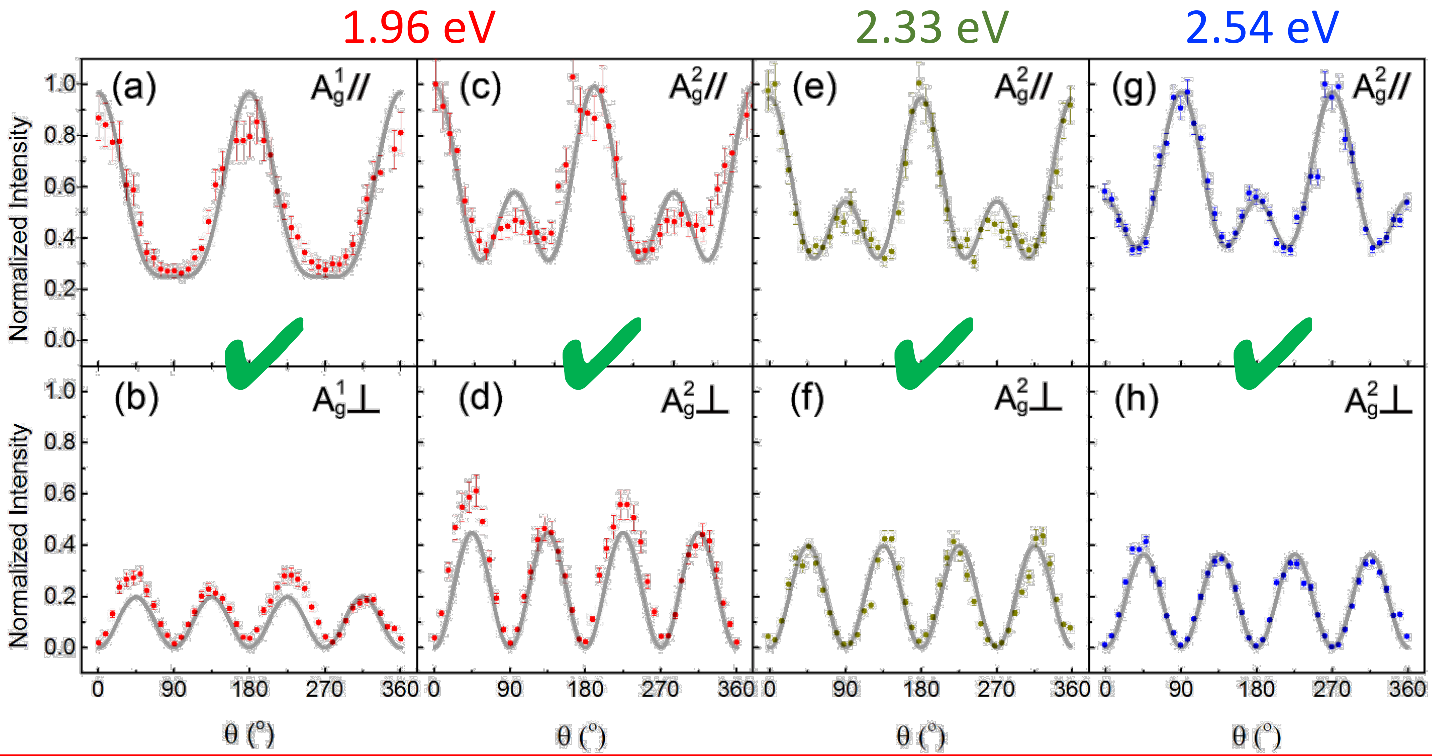
$$S_{A_g}^{\parallel} = (|a|cos^2\theta + |c|cos\phi_{ac}sin^2\theta)^2 + c^2 sin^4\theta sin^2\phi_{ac}$$

$$S_{A_g}^{\perp} = [(|a| - |c|cos\phi_{ac})^2 + |c|^2 sin^2\phi_{ac}]sin^2\theta cos^2\theta$$

$$S_{B_{2g}}^{\parallel} = (2|f|sin\theta cos\theta)^2$$

$$S_{B_{2g}}^{\perp} = (|f|cos2\theta)^2$$

Dichroism: Complex values of the Raman tensors



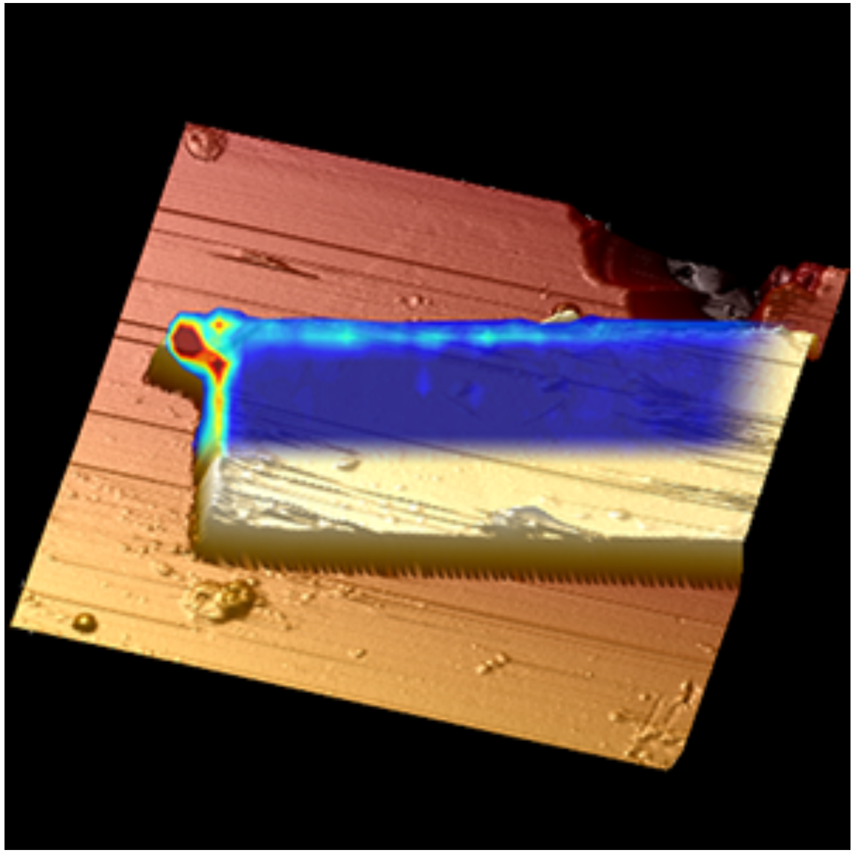
H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

Unusual angular dependence of the Raman response in BP

- Later work showed need to account also for
  - Flake thickness [Kim et al., Nanoscale 7 , 18708 (2015)] [Ling et al., Nano Lett 16, 2260 (2016)]
- Same trend also observed in other layered materials
  - $ReS_2/ReSe_2$ [Lorchat et al., ACS Nano 10, 2752–2760 (2016)]
  - WTe_2 [Song et al., Scientific Reports 6, 29254 (2016)]

H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

Edge phonons in BP

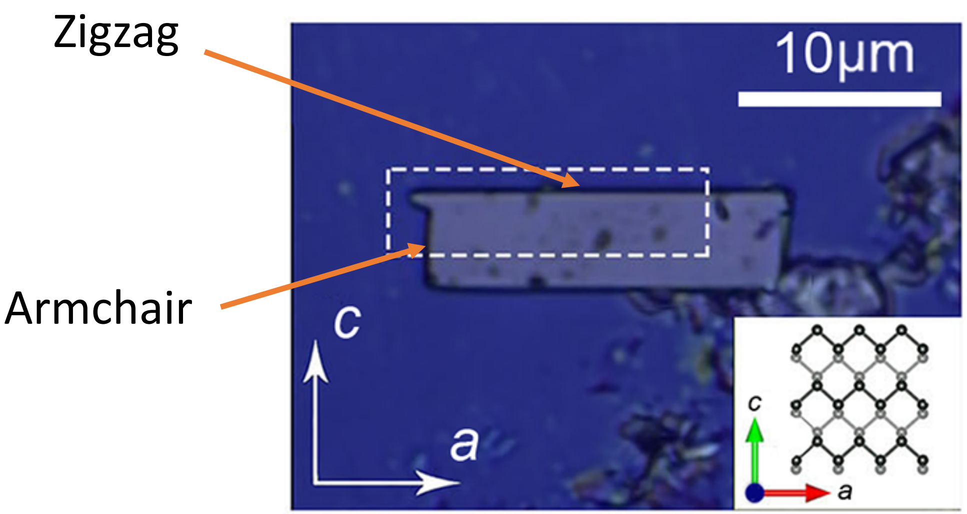


- Polarized Raman maps across BP flakes revealed anomalous mode appearance at the edges
- Mode appearance also depends on the edge type: zigzag or armchair

H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Edge phonons in BP: experiment

- Selected flakes exhibit well defined edge character



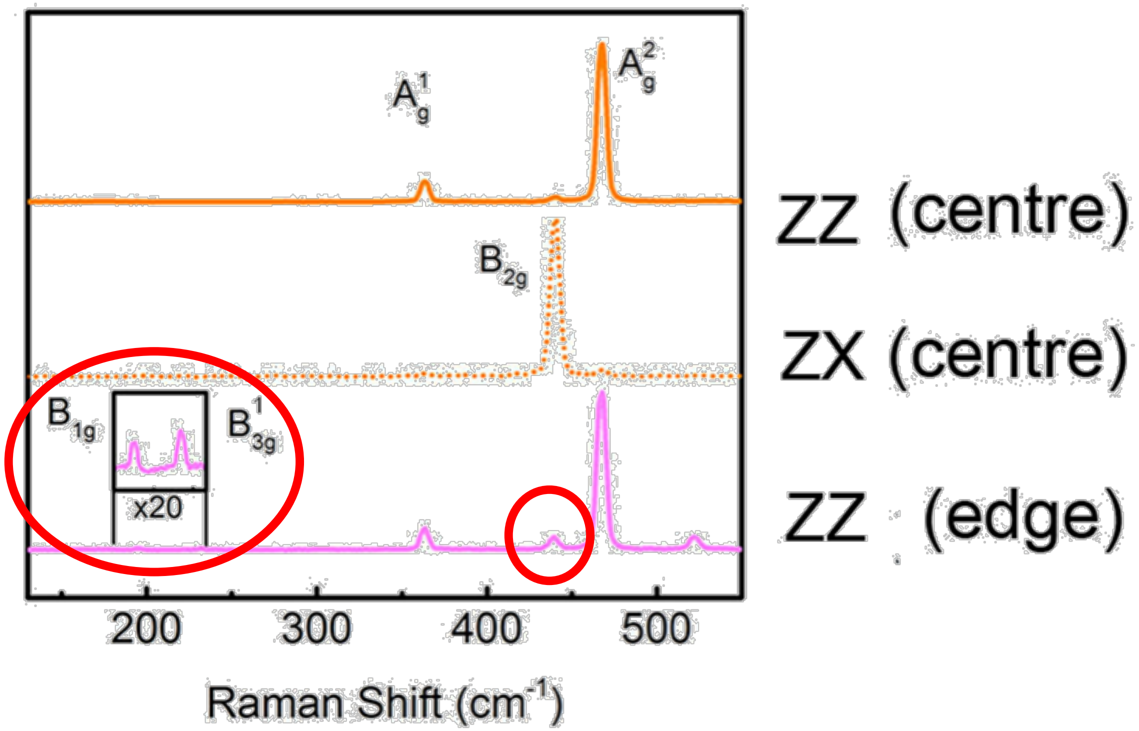
- Incident polarization X (// to *a*) or Z (// to *c*)
- Analysed polarization X or Z
- Analysed polarization configurations
  - Parallel: XX, ZZ
  - Orthogonal: XZ, ZX

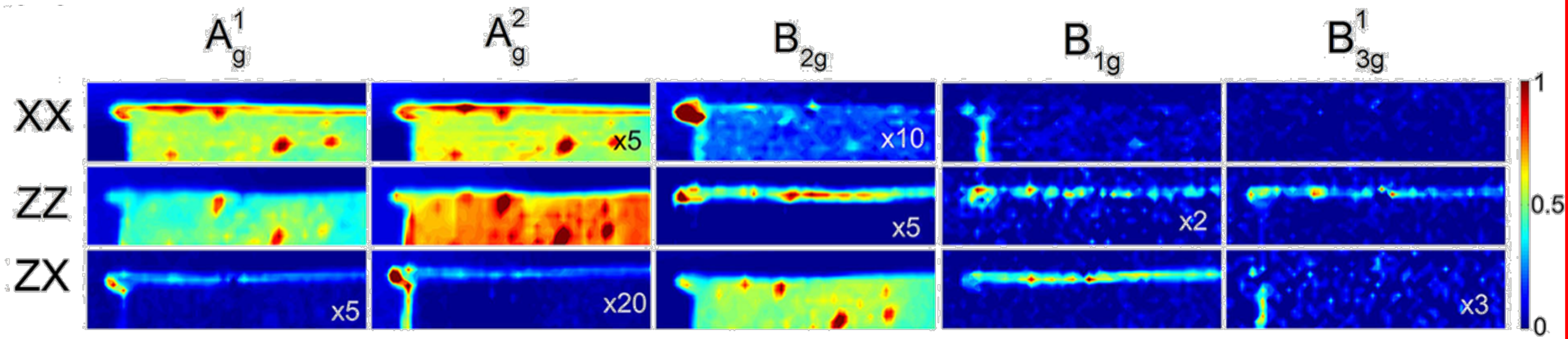
Bulk phonons

A_g => (XX) and (ZZ)
B_{2g} => (XZ) and (ZX)
B_{1g}, B_{3g} not visible

H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Edge phonons in BP: results

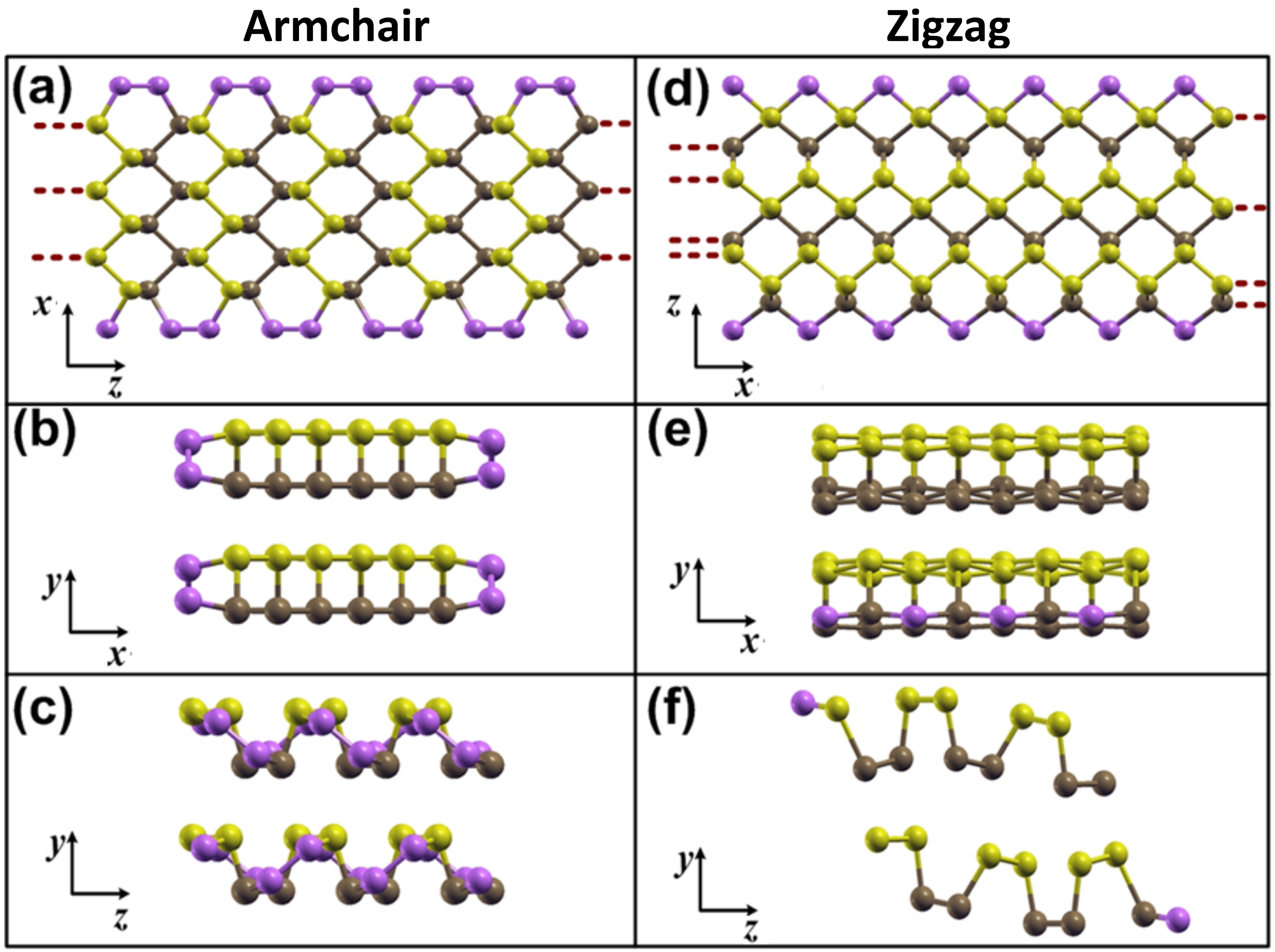




H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

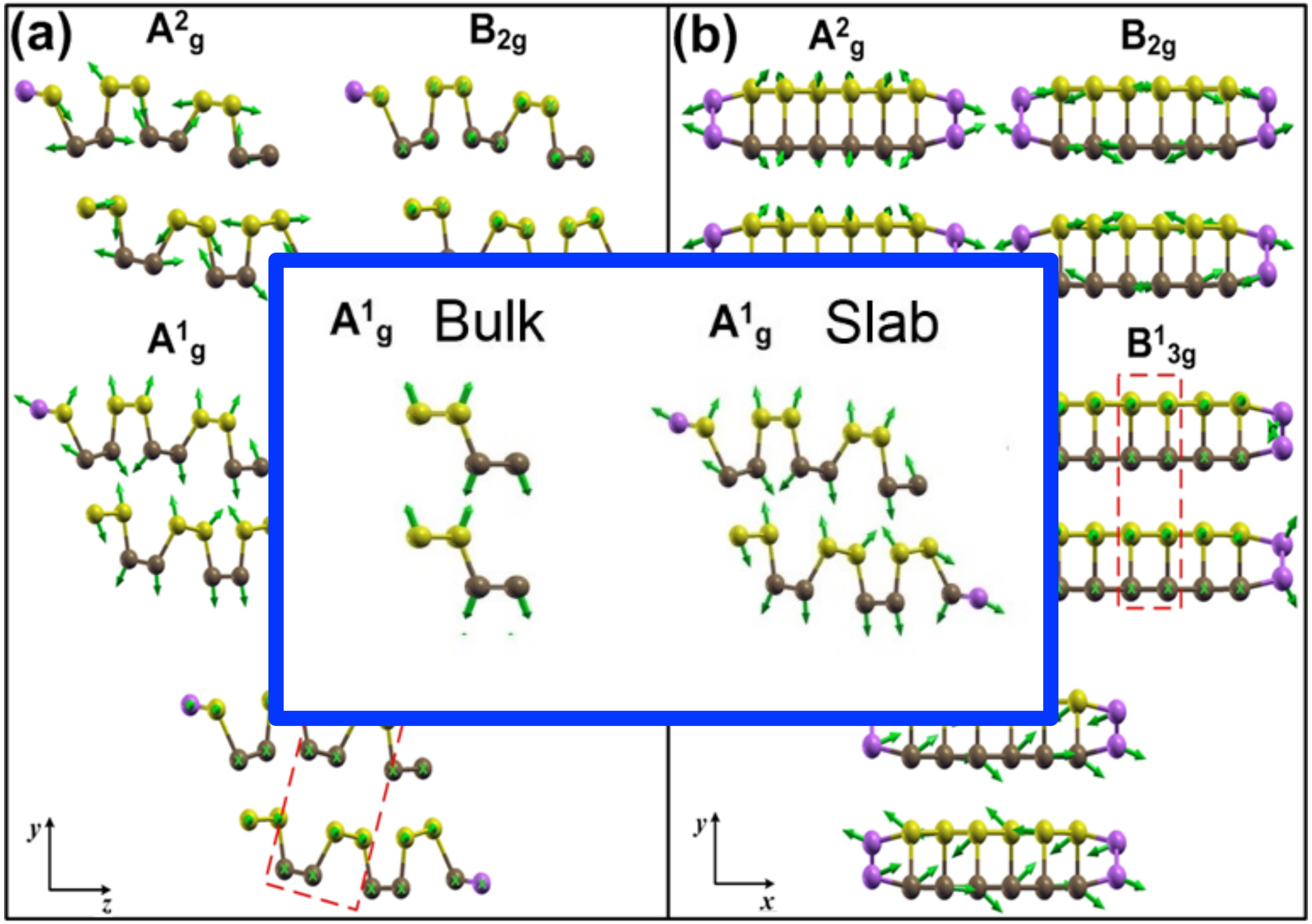
Modelling the edges with density functional theory (DFT)

- BP slabs with zigzag and armchair surfaces simulated by DFT
- Atomic rearrangements



H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Origin of edge phonons



- Atomic rearrangements ➔ deviations in atomic displacements at the edges

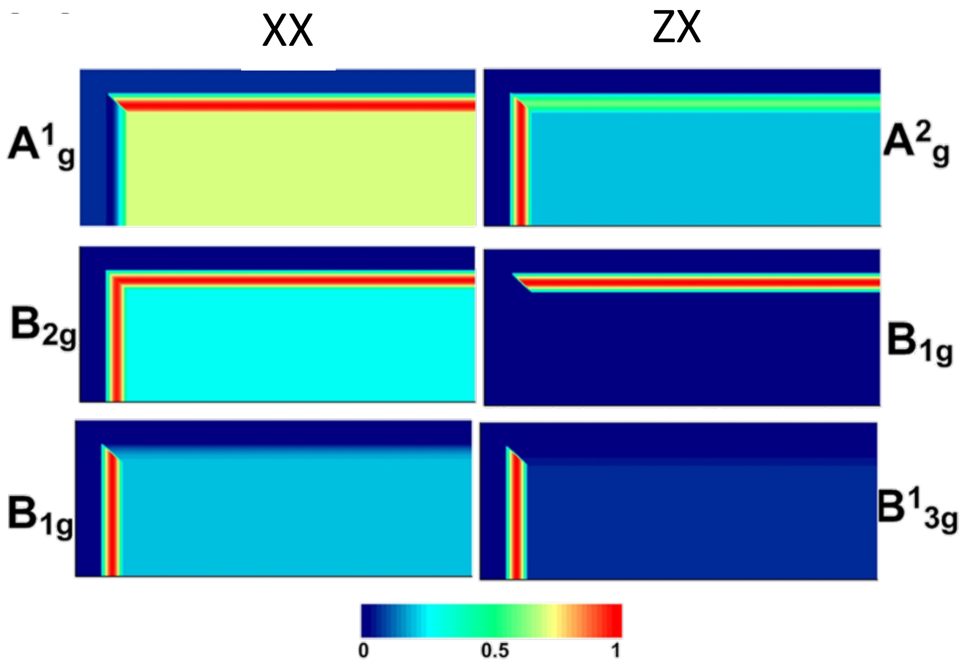
H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Raman tensors at BP edges calculated by DFPT

- Using density functional perturbation theory (DFPT), the dielectric tensor and the Raman intensities for the relaxed structures were evaluated for each mode

$$I^{\nu} \propto |\mathbf{e}_i \; . \; A^{\nu} \; . \; \mathbf{e}_s|^2 \frac{1}{\omega_{\nu}}(n_{\nu}+1)$$

Polarized Raman edge effects reproduced:



Intensity (a.u.)

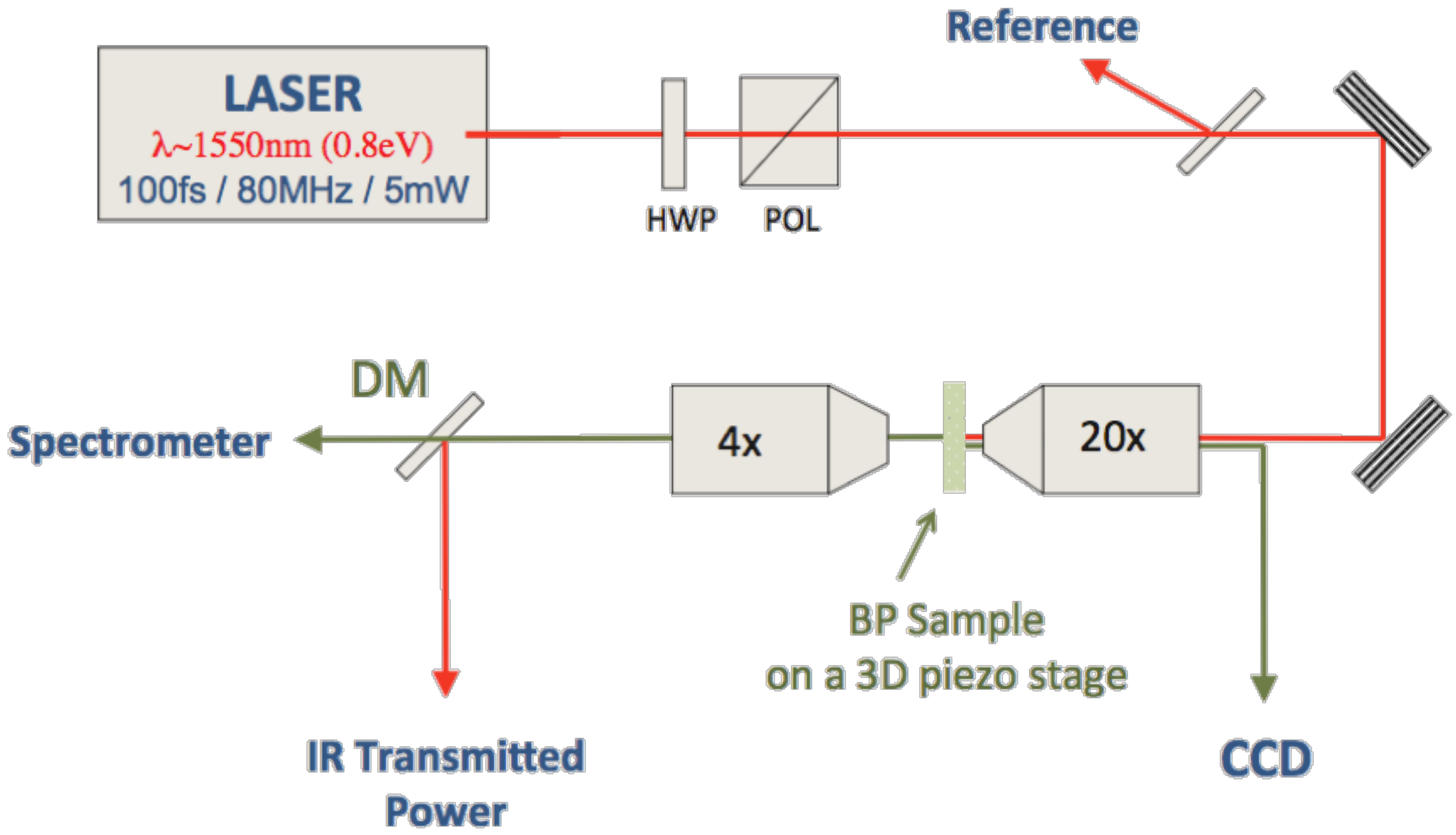
H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Nonlinear optical frequency conversion in black phosphorus

M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Sample preparation & experimental setup

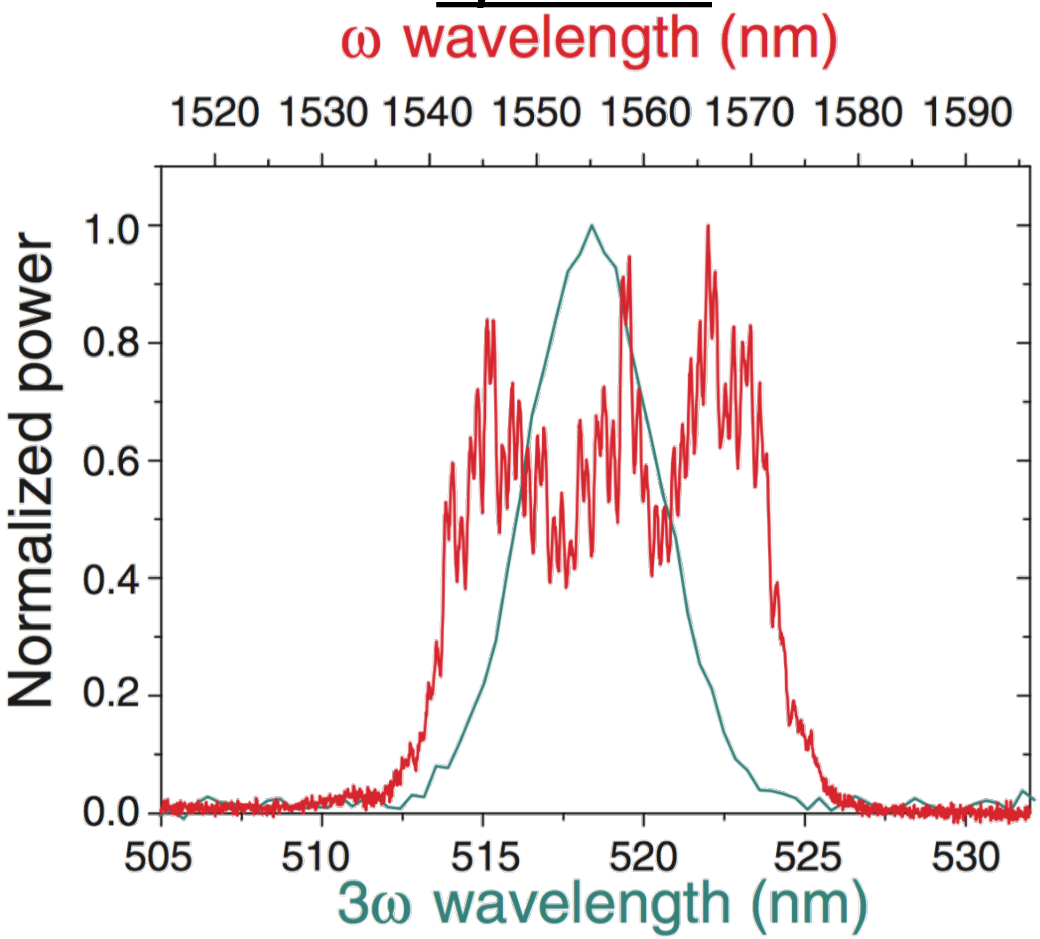
- Experimental setup



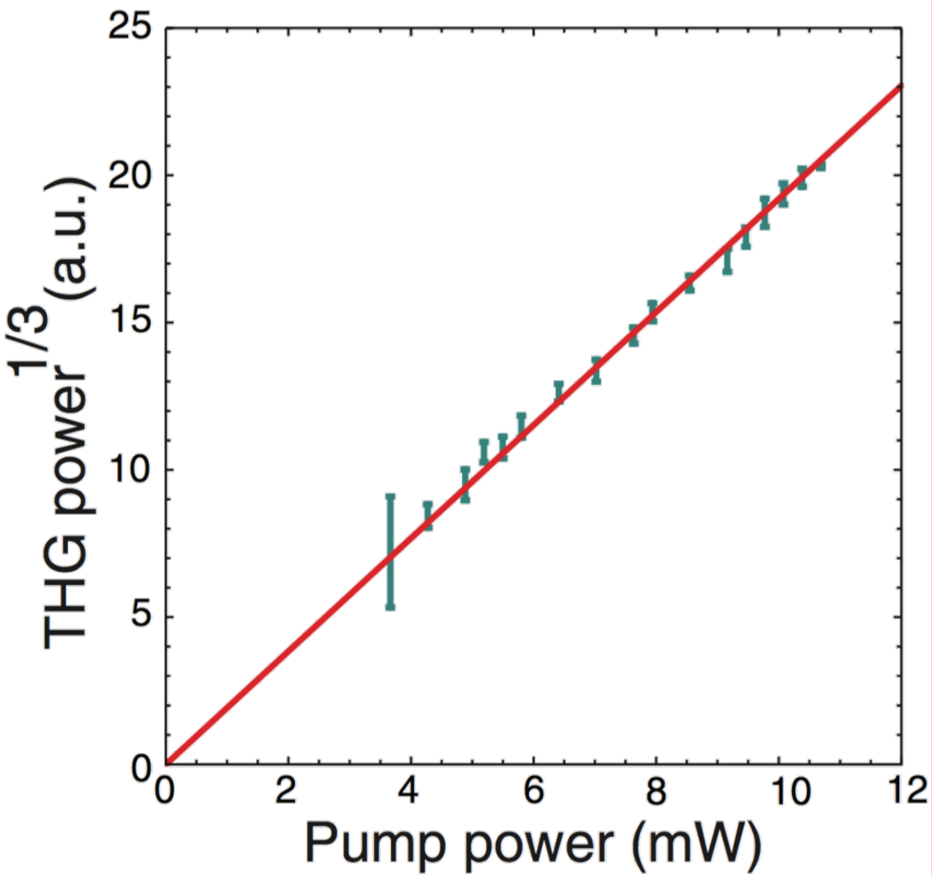
M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Nonlinear optical characterization - thick flake

Spectra



Power dependence

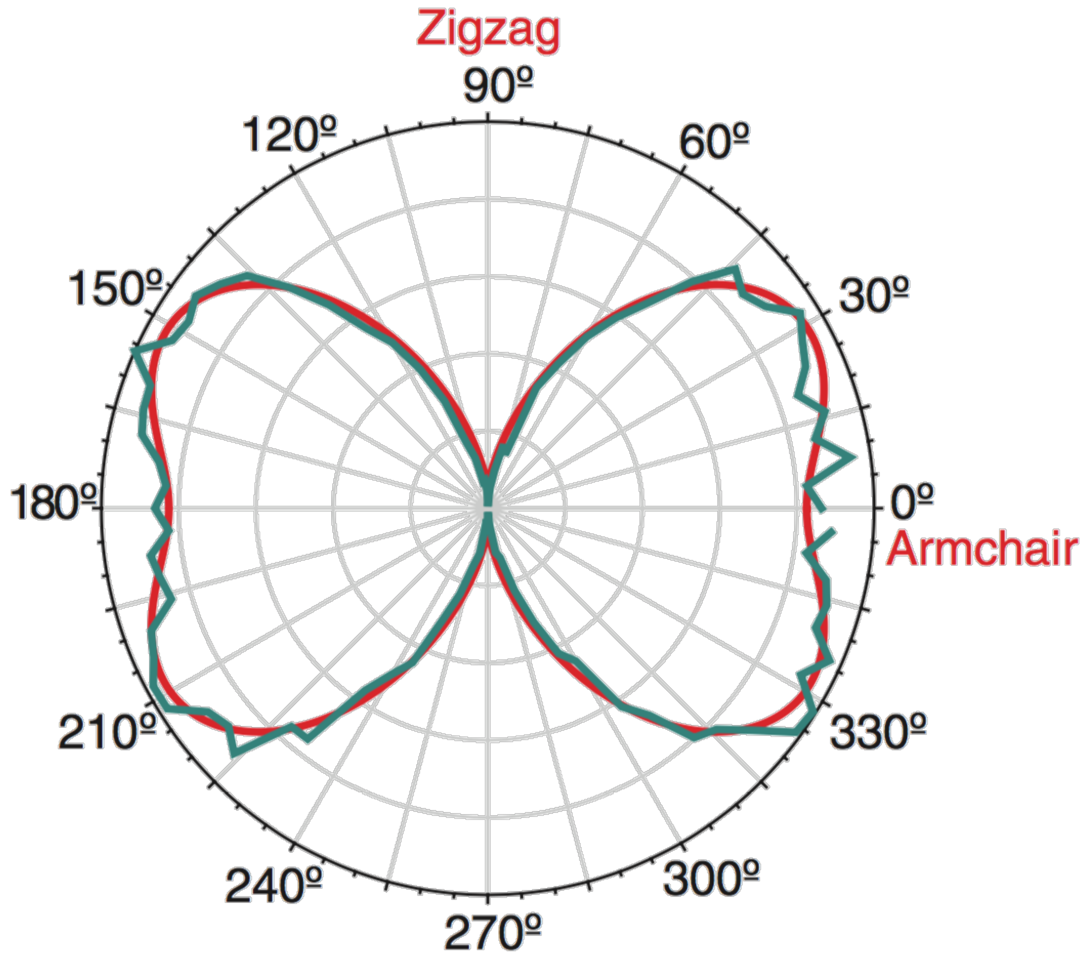


- Consistent with THG

M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Nonlinear optical characterization - thick flake

Polarization dependence

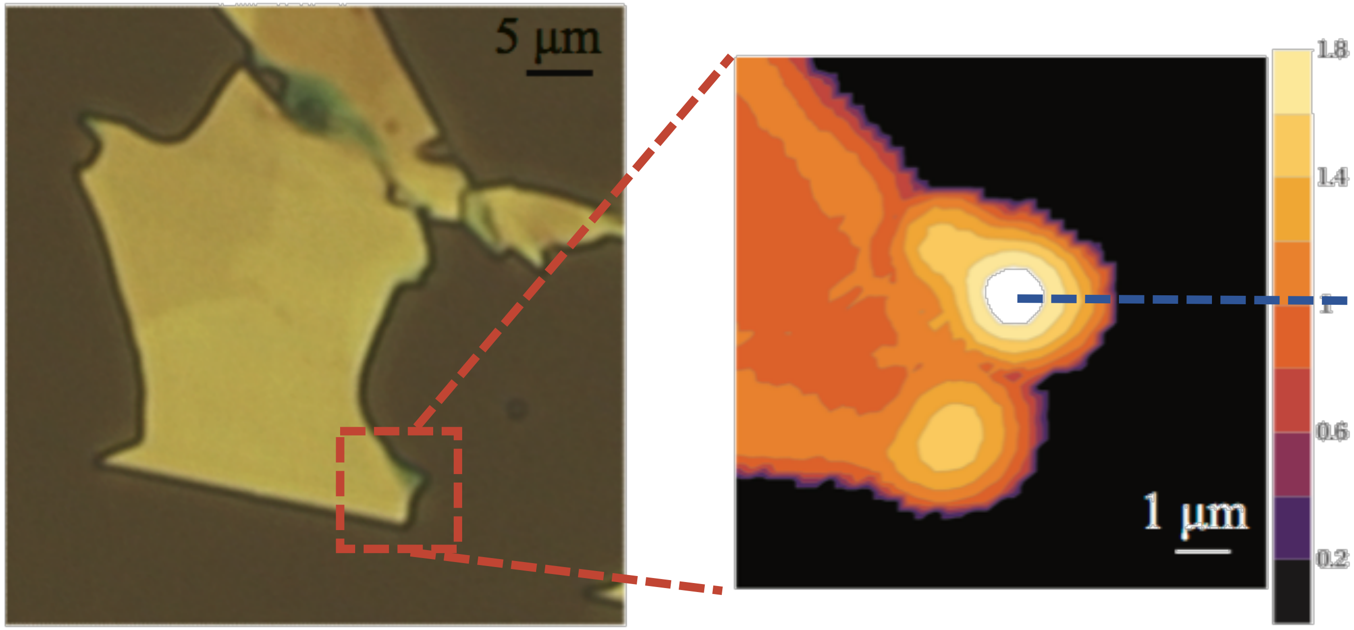


- Consistent with THG for point group D_{2h}

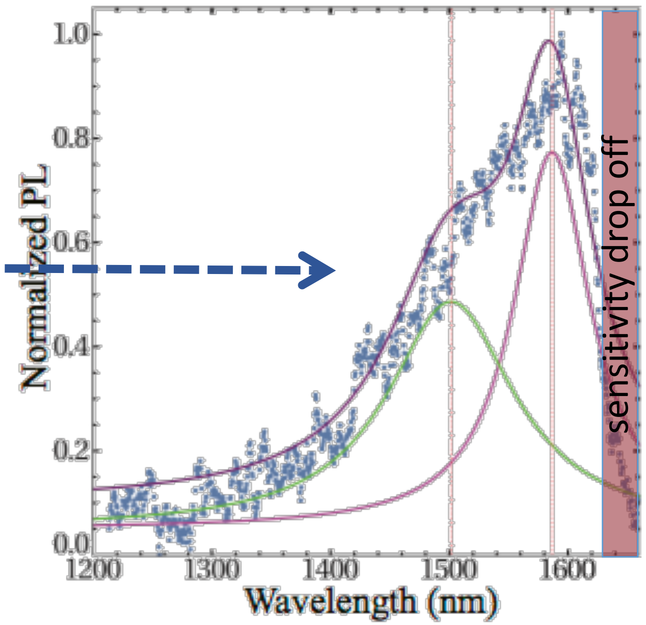
M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Nonlinear optical characterization - few-layer BP

Optical image *THG map*



Luminescence spectrum

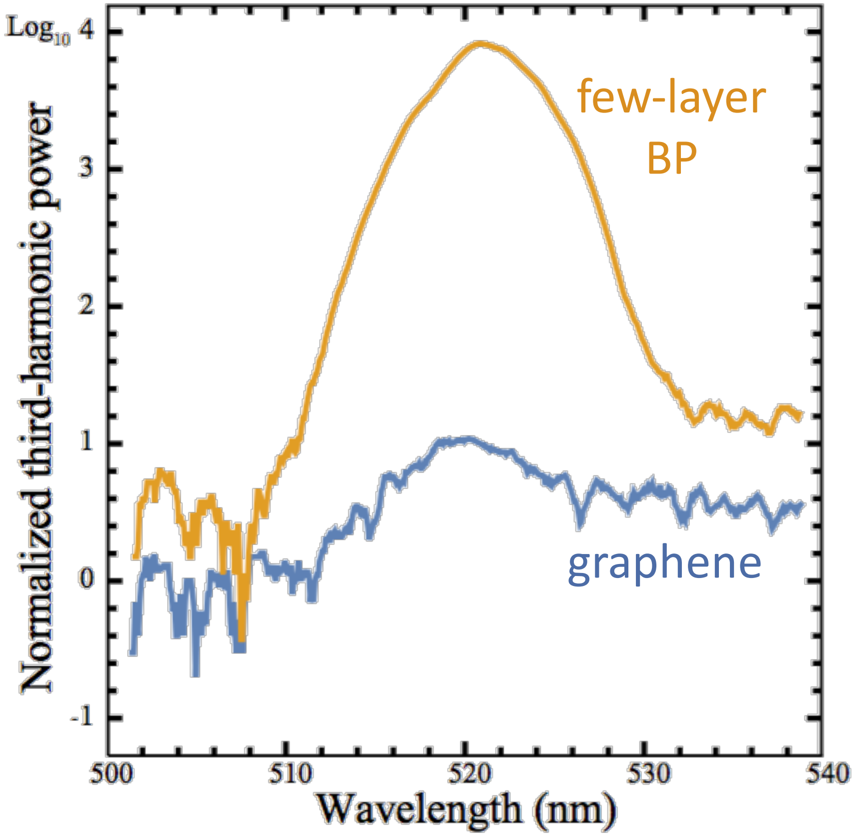


- Luminescence consistent with 4-5 BP layers

  [J. Yang *et al.*, Light: Science & Applications **4**, e312 (2015)]

- THG intensity an order of magnitude higher in the few layer region → resonant process?

Nonlinear susceptibility quantification



- Intensity with BP 3 orders of magnitude higher
- $\chi_S^{(3)}$ in BP ~28× higher than in graphene

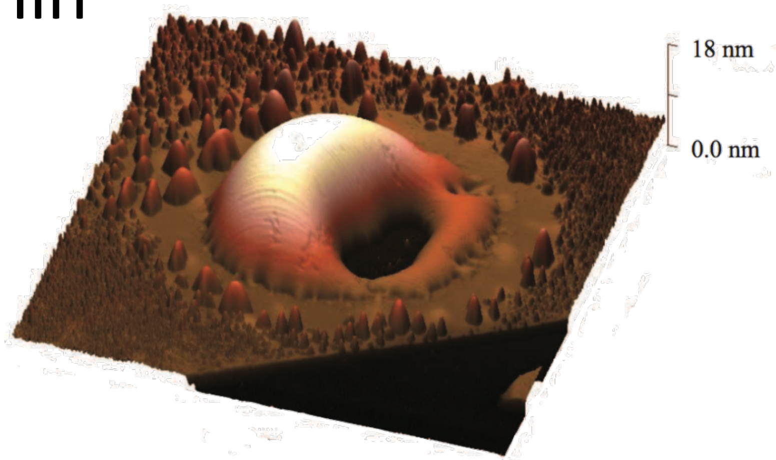
M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

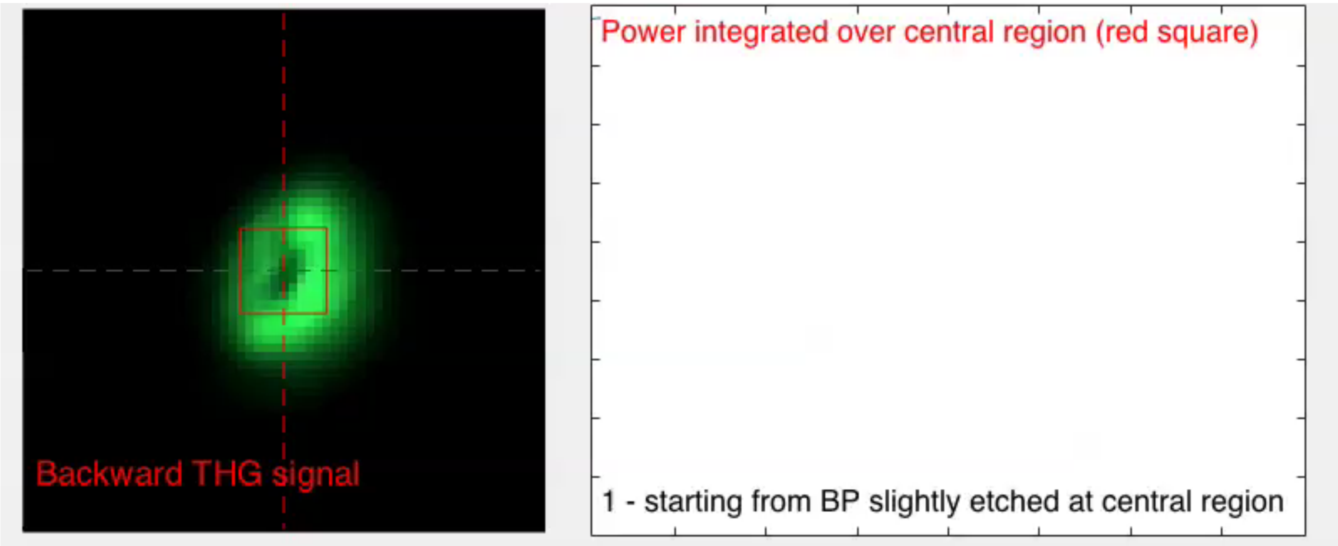
Laser thinning and simultaneous THG monitoring

- Fluences > 0.9 mJ/cm^2 found to thin BP flakes down

- THG can be simultaneously monitored:

AFM

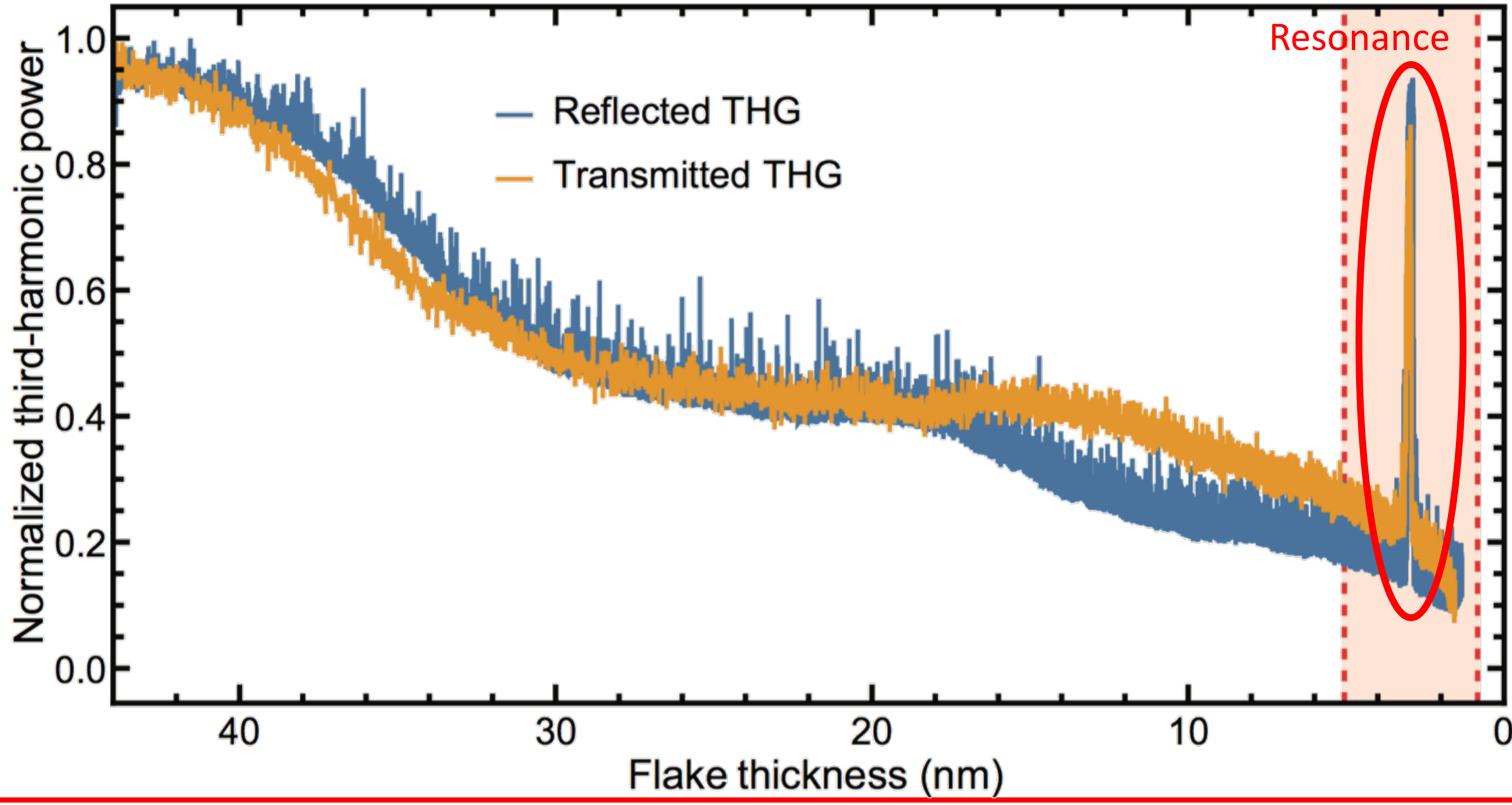




M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Laser thinning and simultaneous THG monitoring

- Average thinning rate calibrated from IR absorption



The origin of the enhanced nonlinearity

- Density functional theory suggests that the single particle picture is unable to reproduce resonance

- Preliminary exciton analysis, on the other hand, indicates a quasi-resonance for the few-layer thickness regime

M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Conclusions

- Black phosphorus presents a series of unusual properties
- Unusual polarized Raman scattering
  - Linear dichroism leads to complex Raman tensors
- Observation of edge phonons with anomalous symmetries
  - Local atomic rearrangement near the edges change atom displacements, generating new tensor elements
- Third-harmonic generation with drastic efficiency increase for few-layer thicknesses
  - (Quasi) resonance with excitonic states

H. B. Ribeiro et al., ACS Nano 9, 4270 (2015)

H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

M. Rodrigues et al., Adv. Mater. 28, 10693 (2016)

Acknowledgments: collaborators

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Antonio H. Castro Neto

Acknowledgments

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Mack Pesquisa

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

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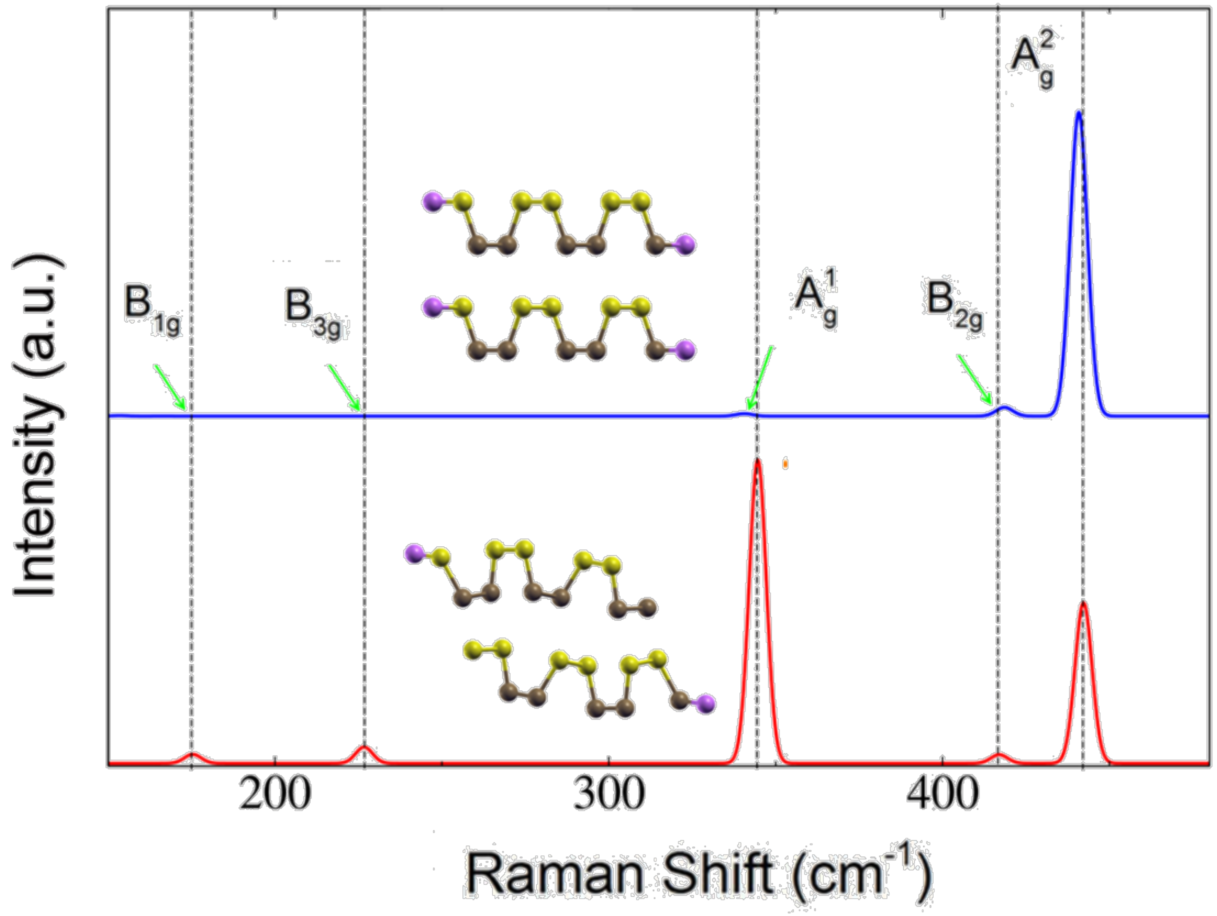
CENAPAD SP

LNNano
Laboratório Nacional de Nanotecnologia

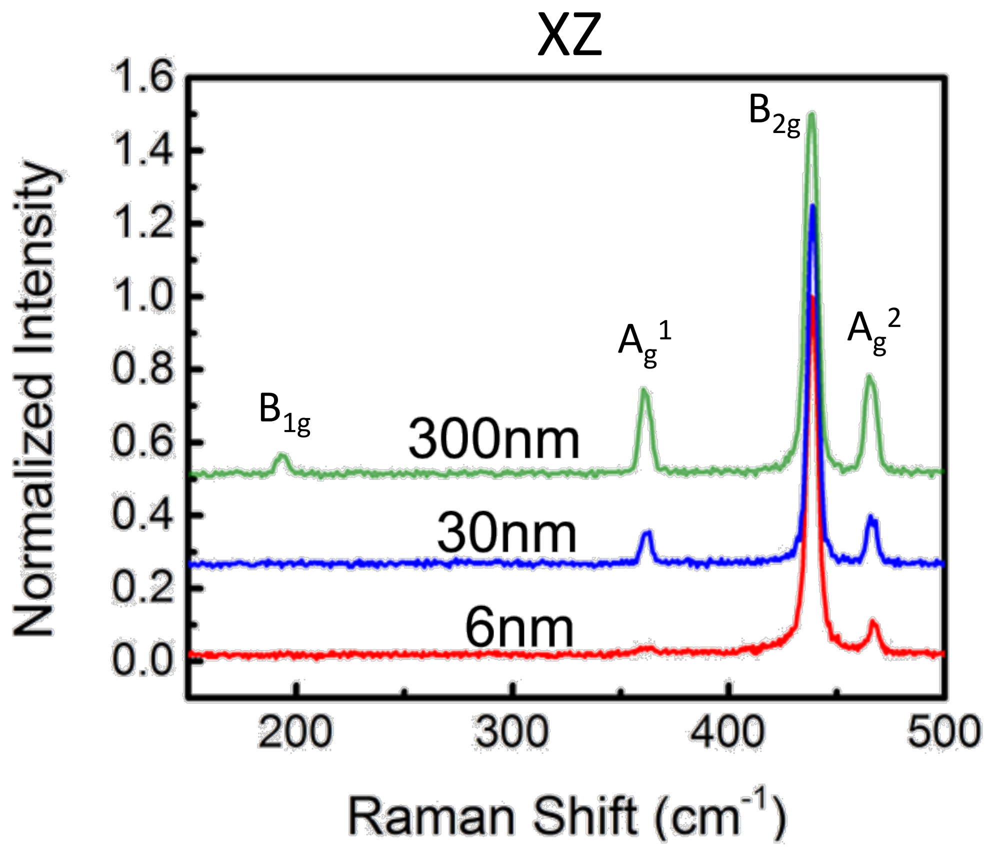
Truncated versus relaxed structure



- No edge effects observed in the truncated structure
- Edge phonons are, indeed, due to lattice relaxation

H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)

Edge phonons versus flake thickness



- Edge phonons still observed in the few-layer limit, even though with lower relative intensity

H. B. Ribeiro et al., Nature Commun. 7, 12191 (2016)