Excitons and exciton-phonon interactions in 2D MoS_2, WS_2 and WSe_2 studied by resonance Raman spectroscopy

and

Unusual angular dependence of the Raman spectra in Black phosphorus

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Outline

- ✓ Different types of excitons and excited states in MoS_2, WSe_2 and WS_2 by resonance Raman spectroscopy
- ✓ The double resonance Raman features and disorder induced bands in MoS_2
- ✓ Unusual angular dependence of the polarized Raman spectra of Black phosphorus

Raman spectroscopy in graphene and 2D materials

Disorder, defects, charges, edge structure, strain, number of layers, etc...

M. A. Pimenta et al., Phys. Chem. Chem. Phys. **9**, 1276 (2007)

L. M. Malard et al. , Phys Rep. **473**, 51-87 (2009)

Resonance Raman spectroscopy

Probes the electronic structure excitons and exciton-phonon interactions

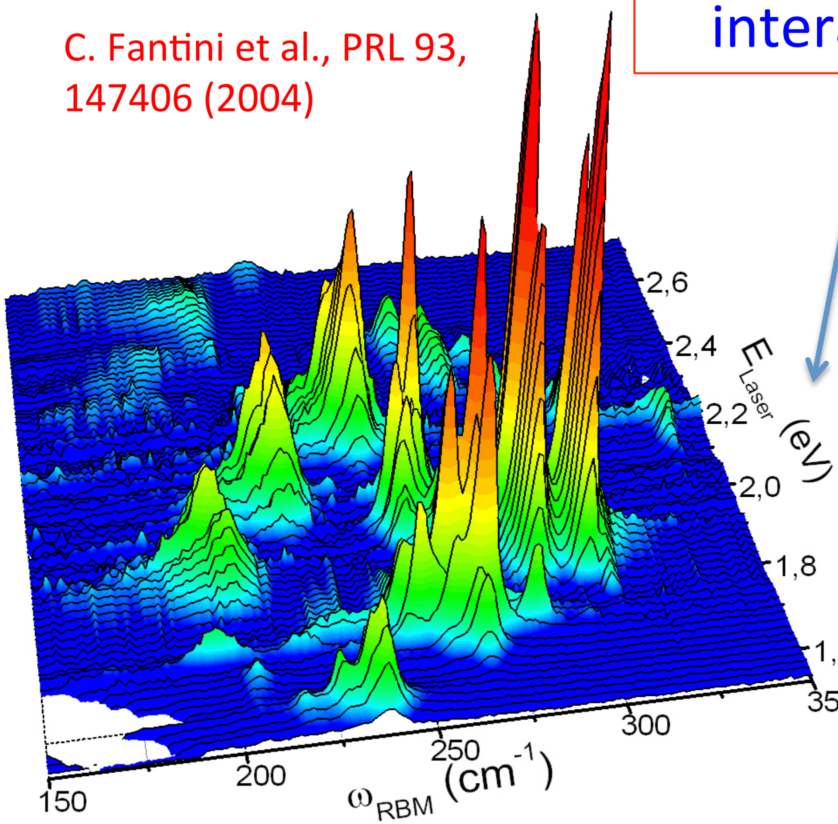
- **Ar-Kr laser, Dye laser (Rhodamine 6G, 110, DCM), Ti-sapphire, He-Cd, VERDI and Ar pump lasers**

325 a 850 nm
(1.45 a 3.81 eV)

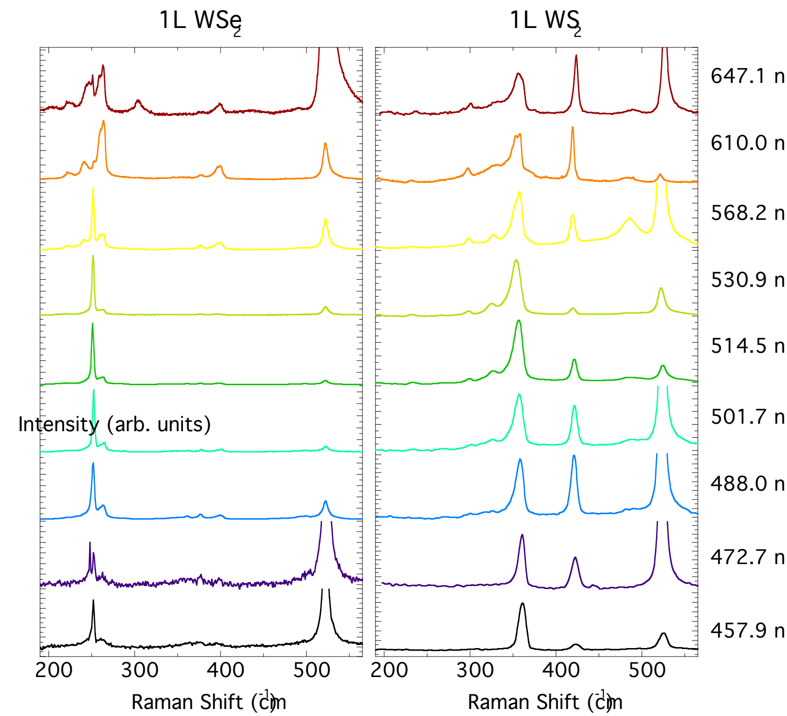
Resonance Raman spectroscopy

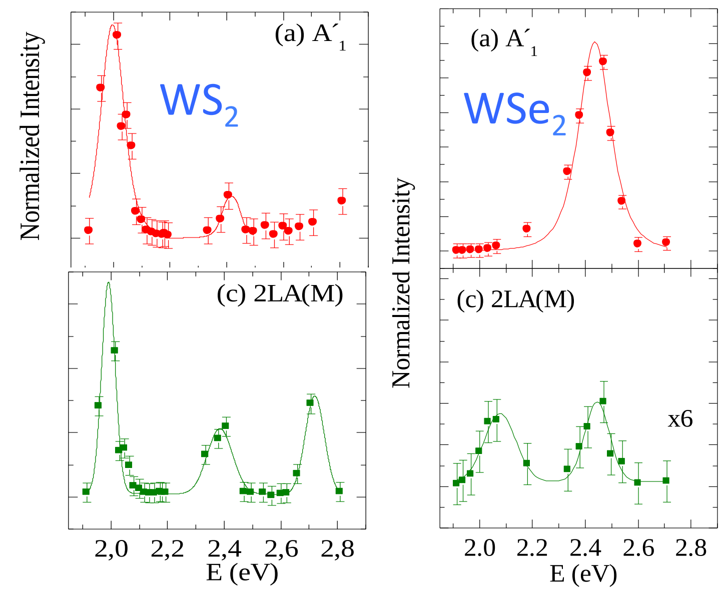
Excitons and exciton-phonon interactions

C. Fantini et al., PRL 93, 147406 (2004)



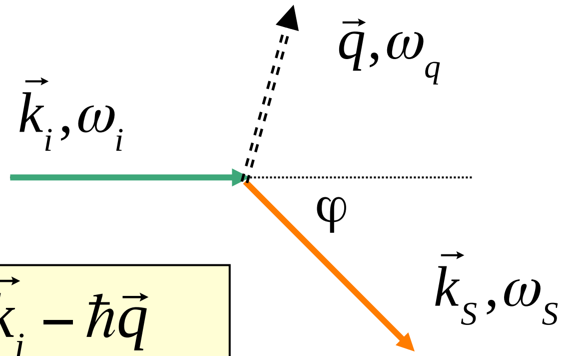
Phonons





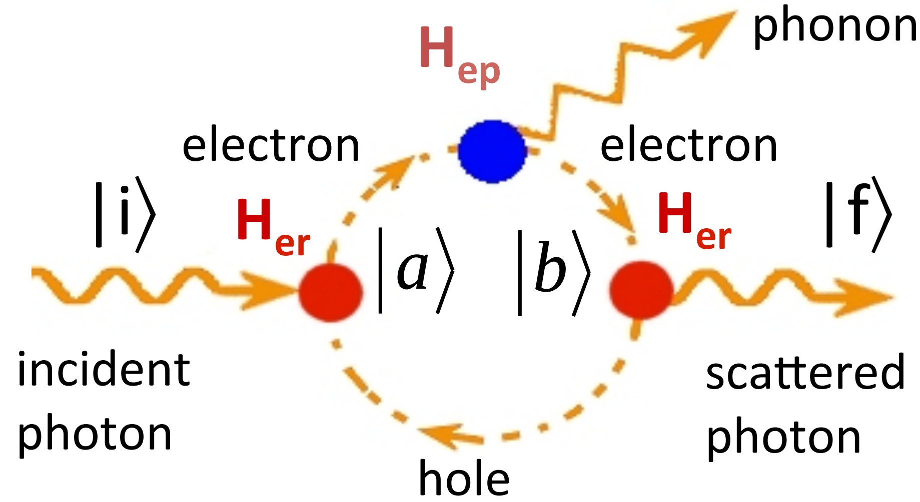
Raman excitation profile

Raman scattering



$$\hbar\vec{k}_S = \hbar\vec{k}_i - \hbar\vec{q}$$

$$\hbar\omega_S = \hbar\omega_i - \hbar\omega_q$$



Raman intensity → transition probability per unit time

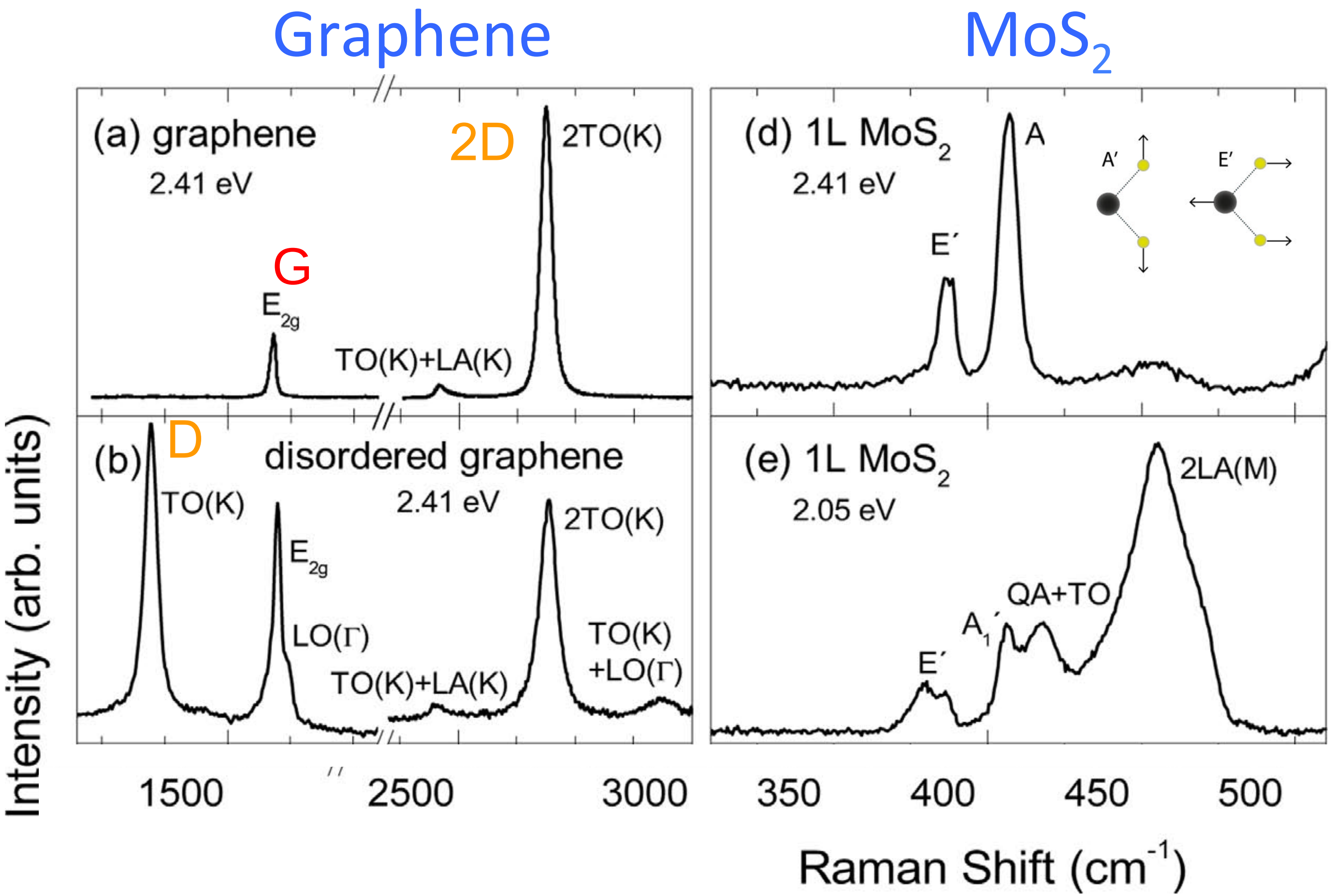
$$I(E_i) = C\left|\sum_{a,b}\frac{\langle f|H_{e-r}|b\rangle\langle b|H_{e-ph}|a\rangle\langle a|H_{e-r}|i\rangle}{(E_i - E_a - i\gamma)(E_i - E_b - i\gamma)}\right|^2$$

$E_i - E_a = \hbar\omega_i - \Delta\varepsilon$ → resonance with incident photon

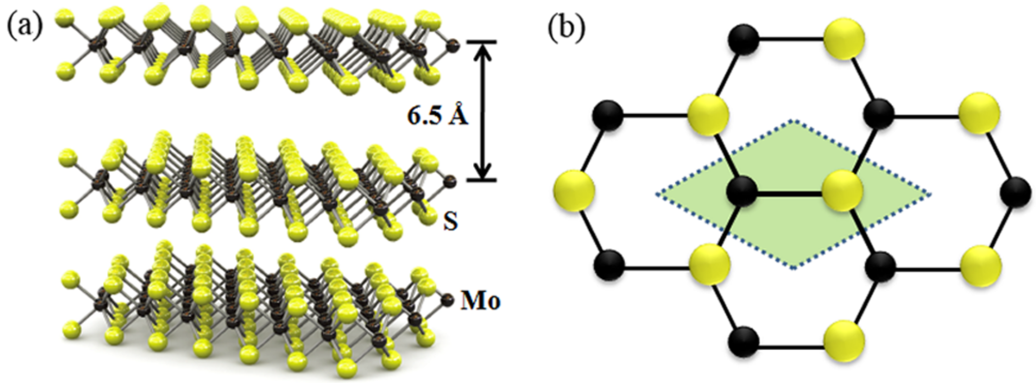
$E_i - E_b = \hbar\omega_i \mp \hbar\omega_q - \Delta\varepsilon = \hbar\omega_s - \Delta\varepsilon$ → resonance with scattered photon

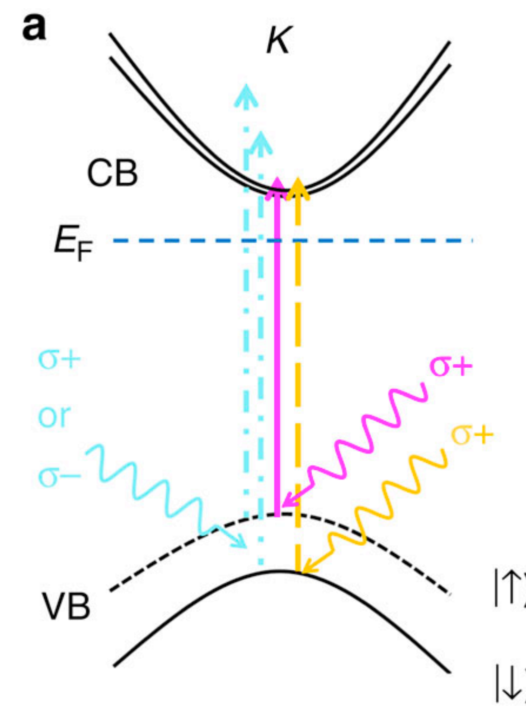
Comparing Raman spectra of Graphene and MoS_2

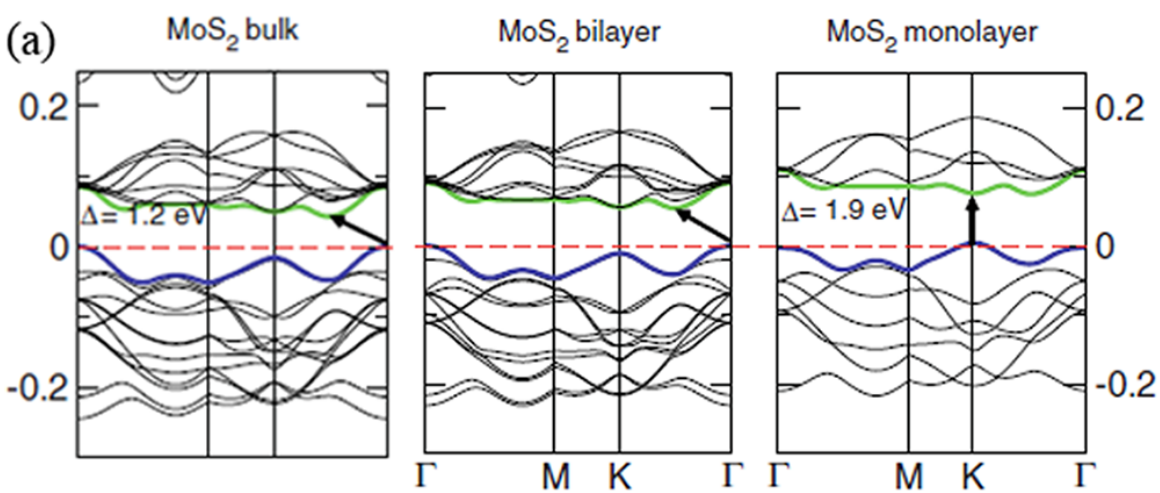
M. A. Pimenta et al. Acc. Chem. Res. Vol. 48, 41–47 (2015)



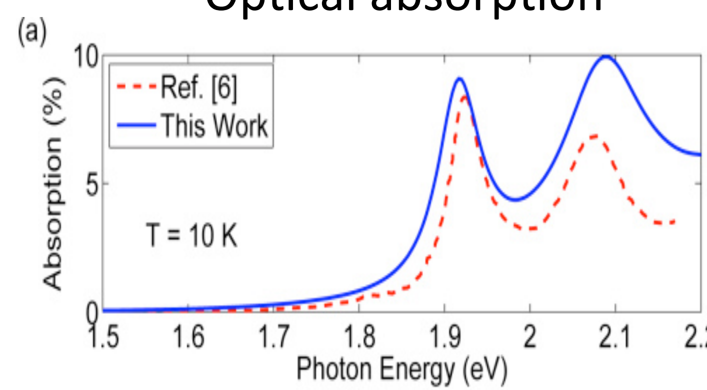
Optical transitions in MoS_2, WS_2, WSe_2



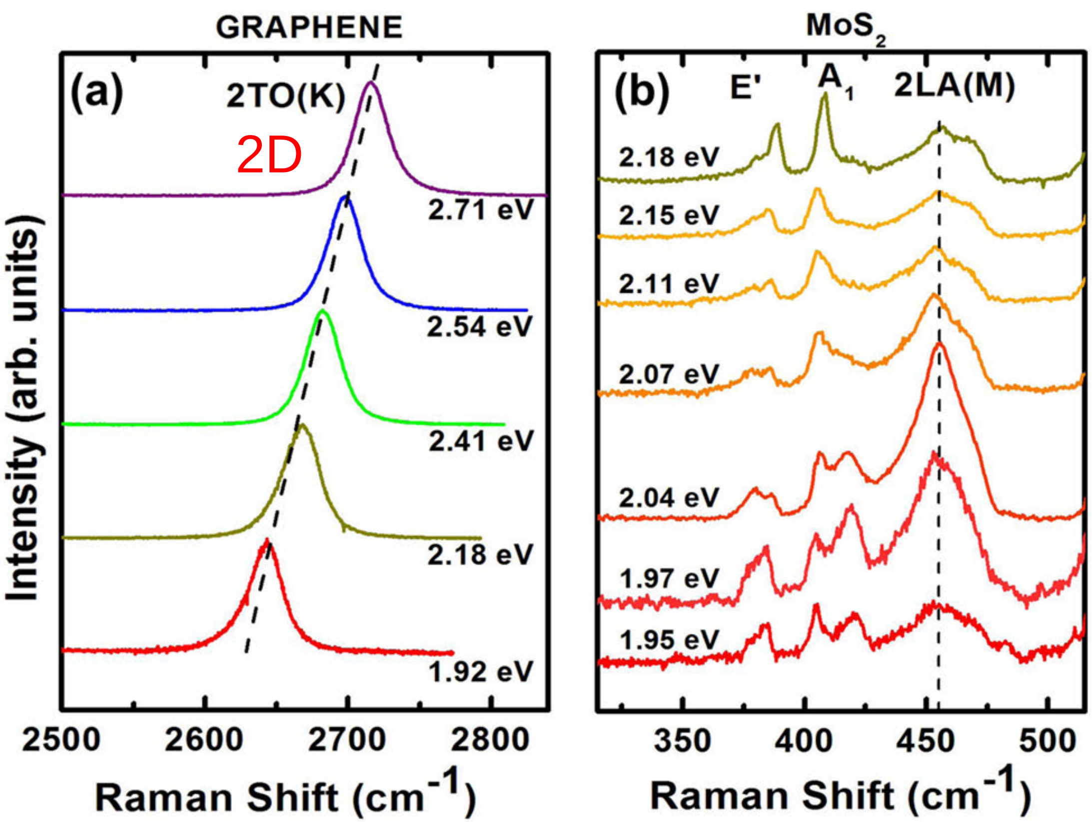




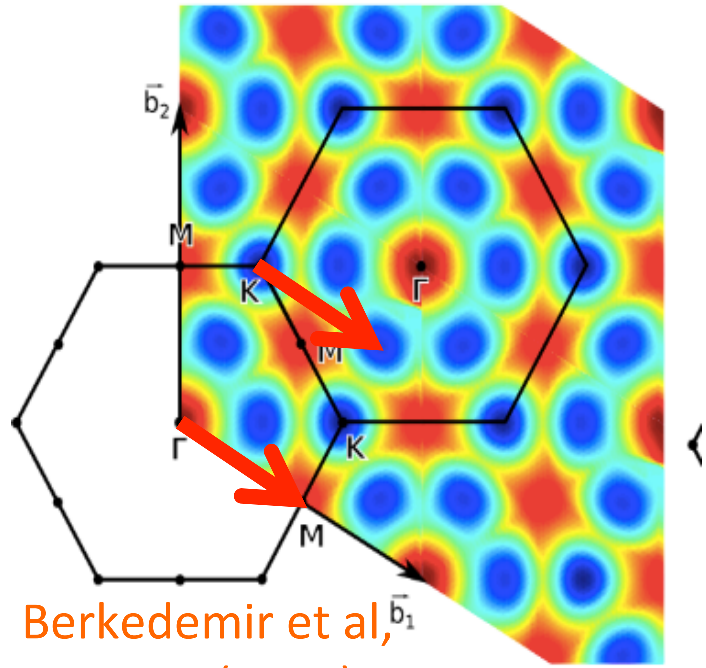
Optical absorption



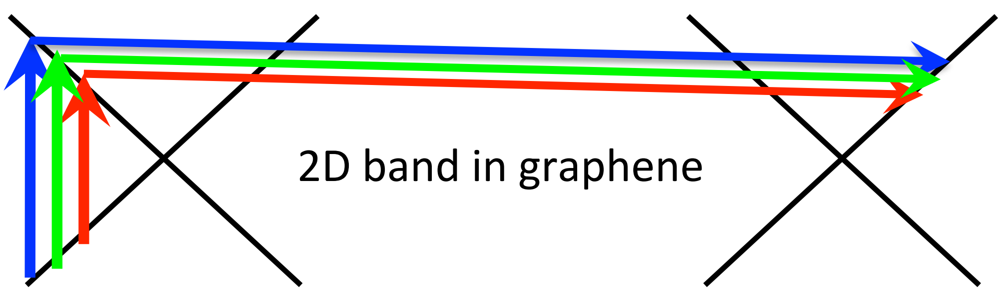
Double resonance Raman process in Graphene and MoS_2

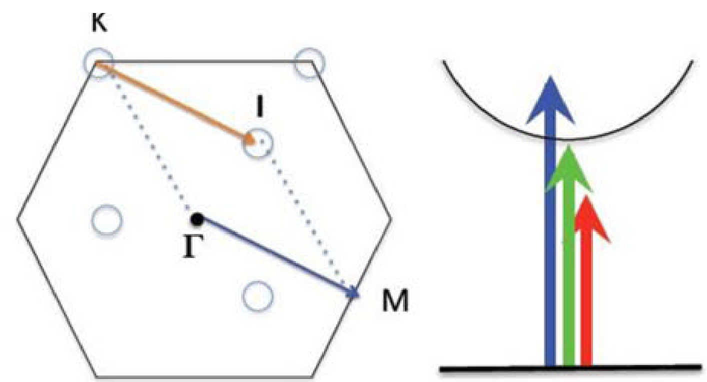


2LA(M) band in MoS_2



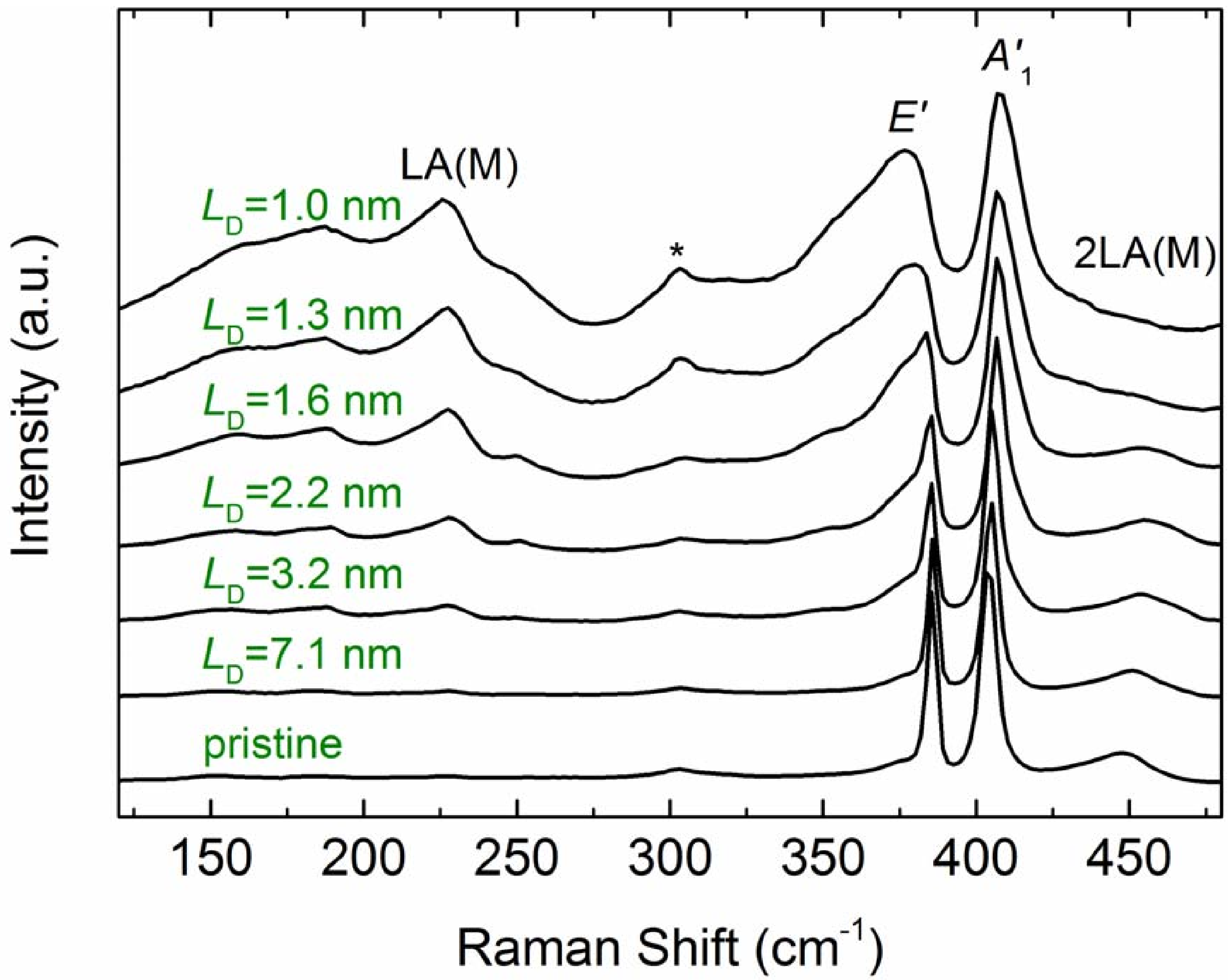
Berkedemir et al,
Sci. Rep. (2013)



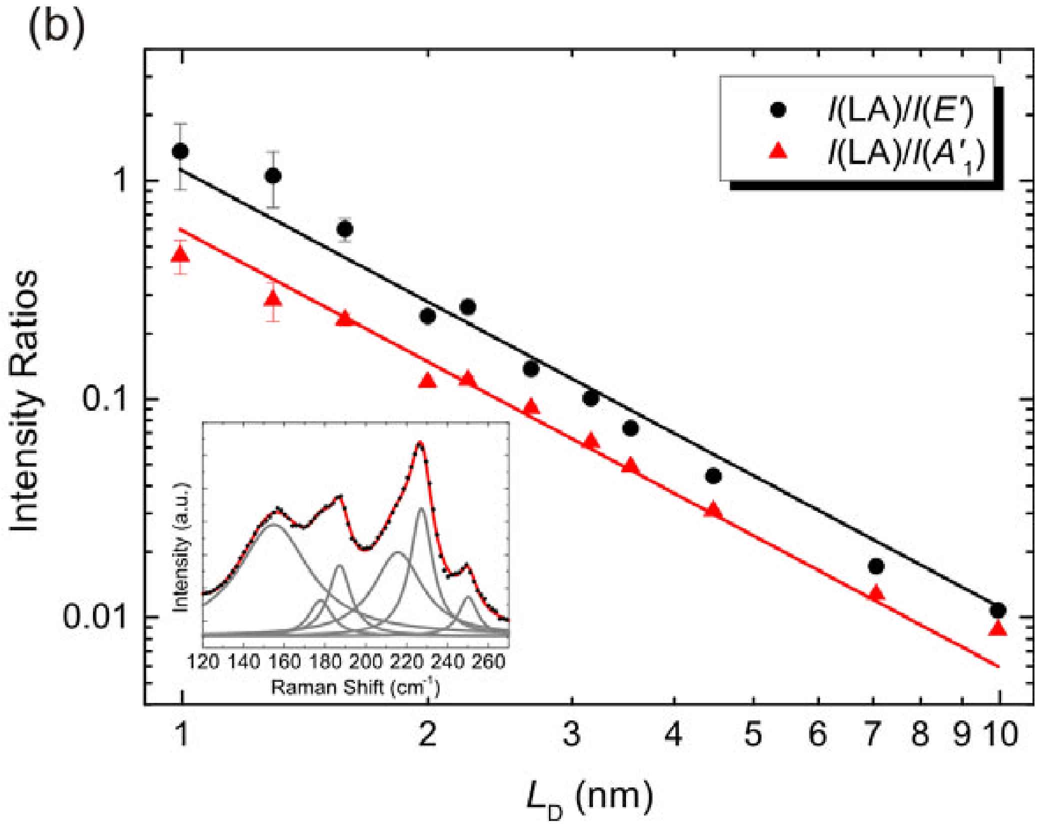


M. A. Pimenta et al., Accounts Chem. Res., Vol. 48 (1), pp 41–47 (2015)

Effect of disorder in the Raman scattering of single-layer MoS_2



S. Mignuzzi et al. , Phys Rev. B (2015), Vol. 91, 195411

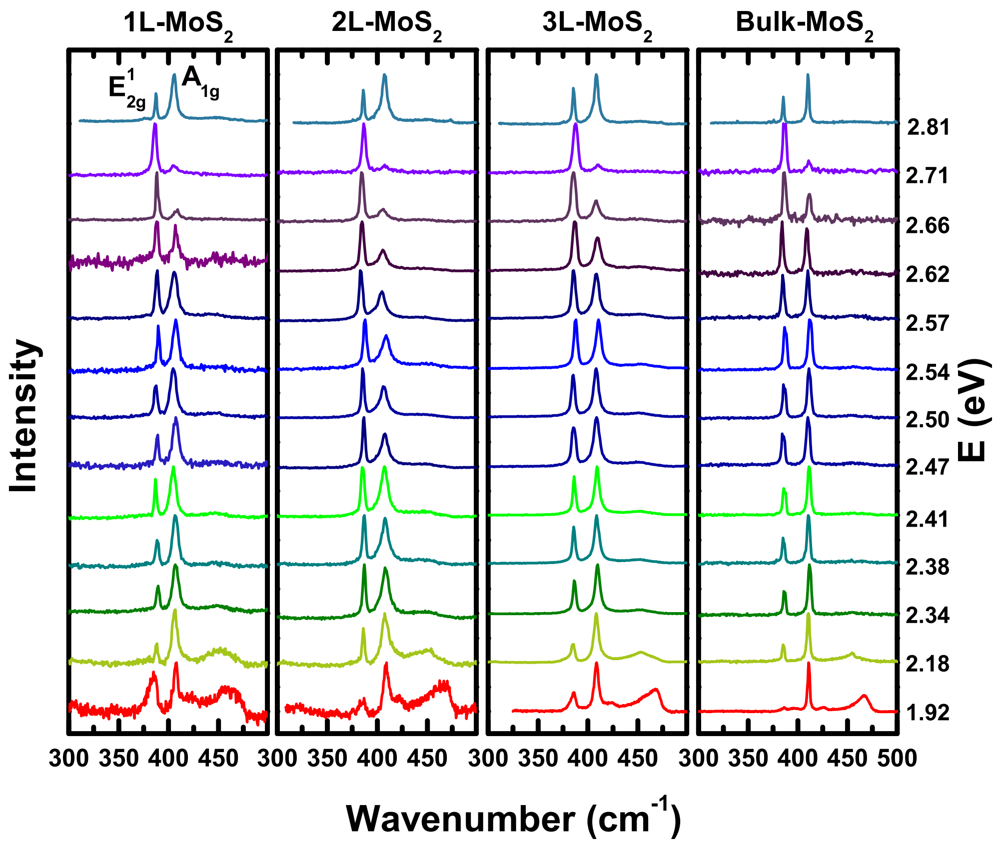


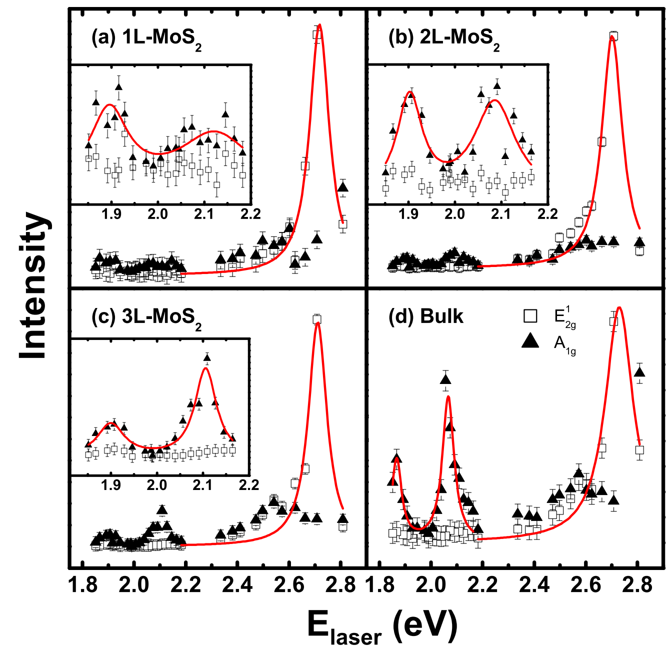
$$\frac{I(\mathrm{LA})}{I(\mathrm{X})} = \frac{\mathrm{C(X)}}{{L_\mathrm{D}}^2},$$

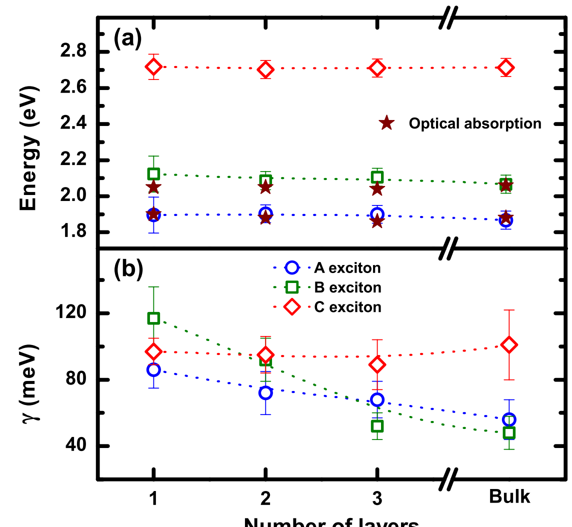
S. Mignuzzi et al.
Phys Rev. B (2015), Vol. 91, 195411

X = E' or A'_1, reveals that C(E') = 1.11±0.08 nm^2 and C(A'_1) = 0.59±0.03 nm^2.

Excitons and exciton-phonon coupling in MoS_2 by RRS





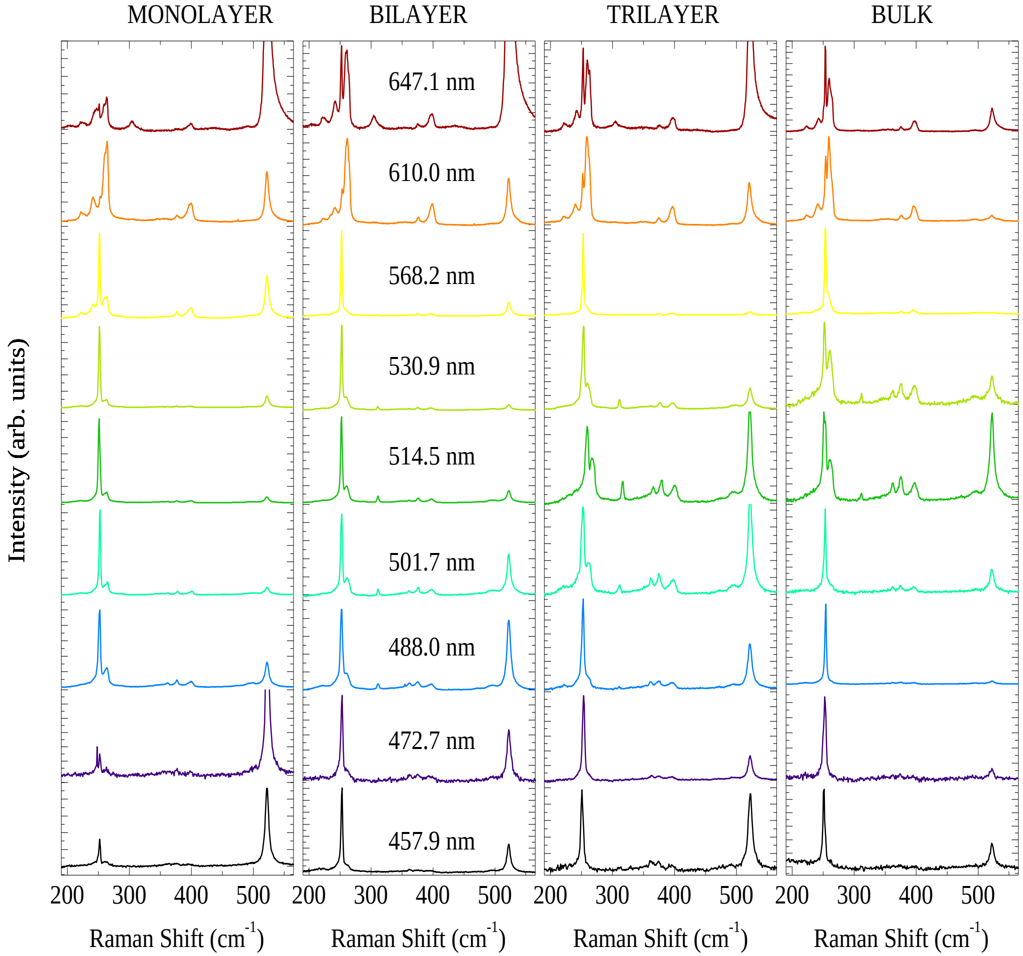


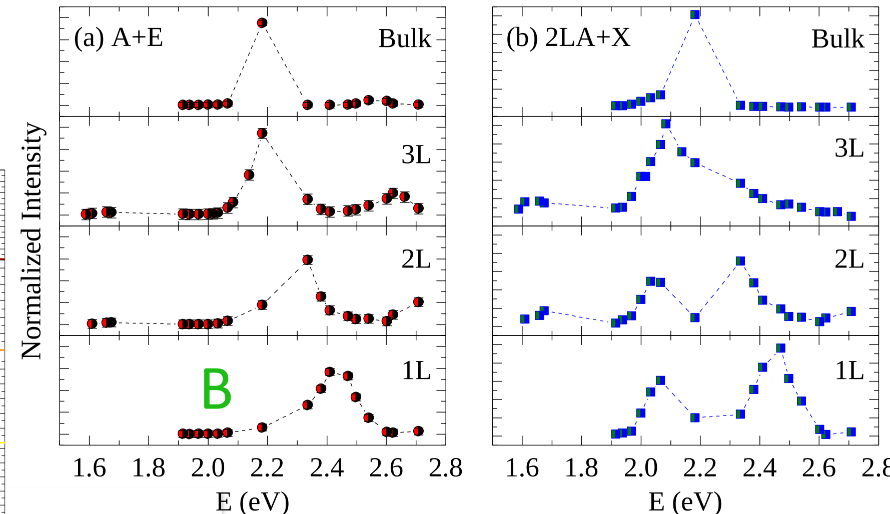
$$I(E_i) = C\left|\sum_{a,b}\frac{\langle f\,|H_{e-r}\,|b\rangle\langle b\,|H_{e-ph}\,|a\rangle\langle a\,|H_{e-r}\,|i\rangle}{(E_i - E_a - i\gamma)(E_i - E_b - i\gamma)}\right|^2$$

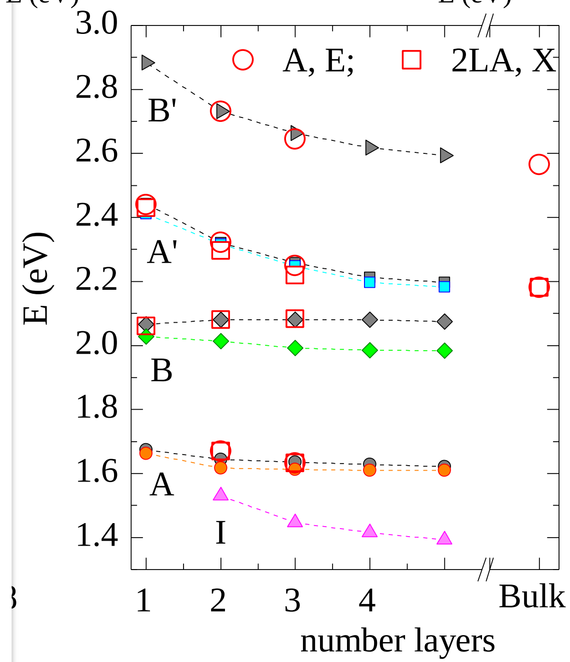
B. R. Carvalho et al. . Phys Rev. Letters 114, 136403 (2015)

Excited Excitonic States in WSe_2 observed by RRS

A, B, A' and B' excitons



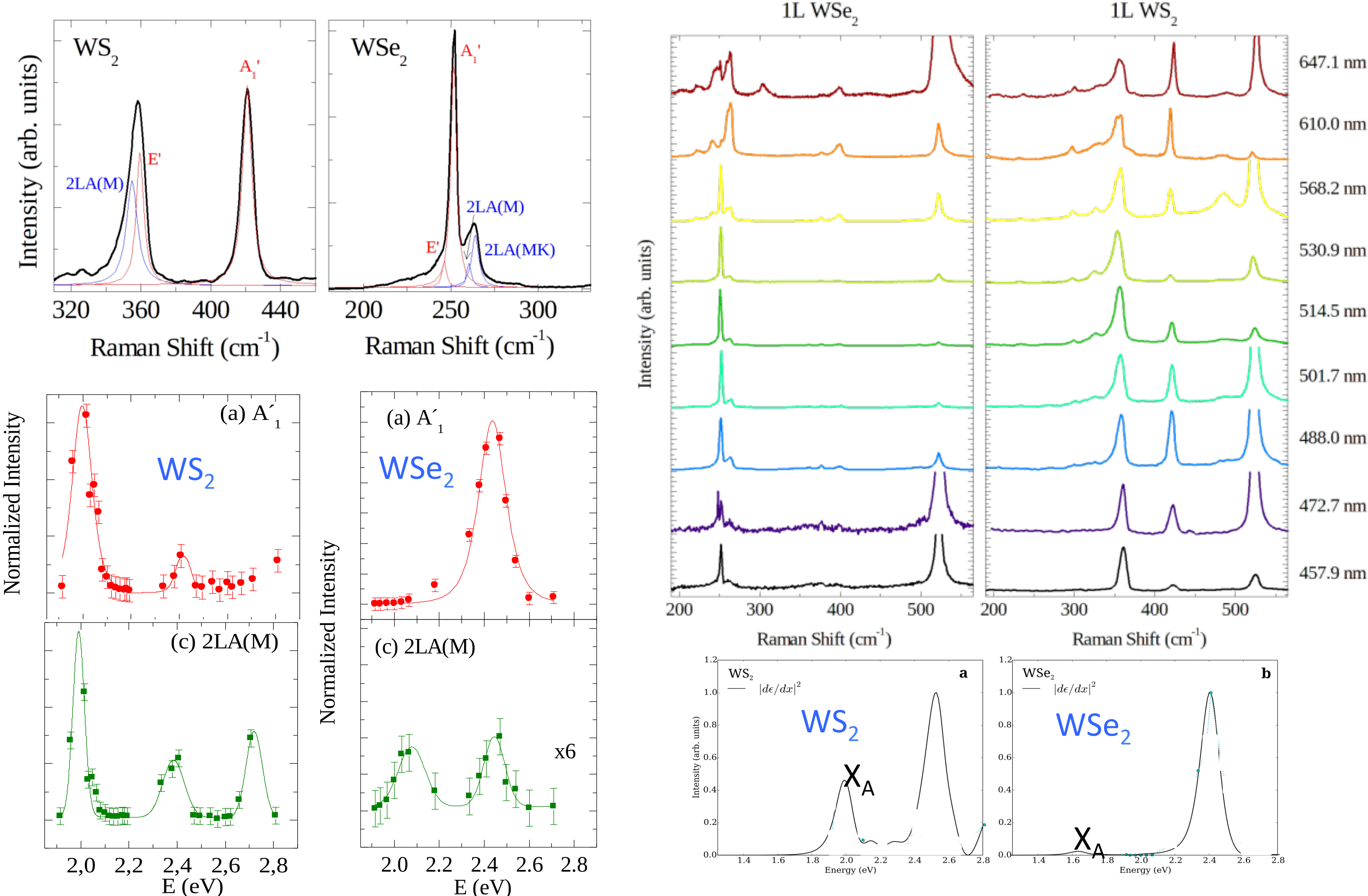




E. del Corro et al. ACS Nano, Vol 8, 9629 (2014)

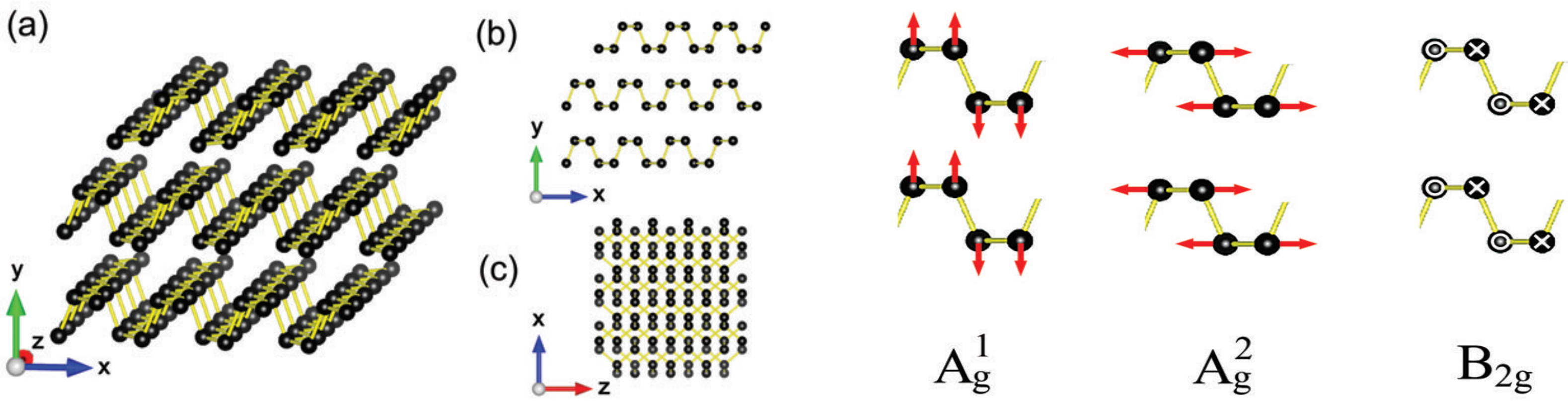
W. Zhao et al ACS Nano 7 , 791 2013

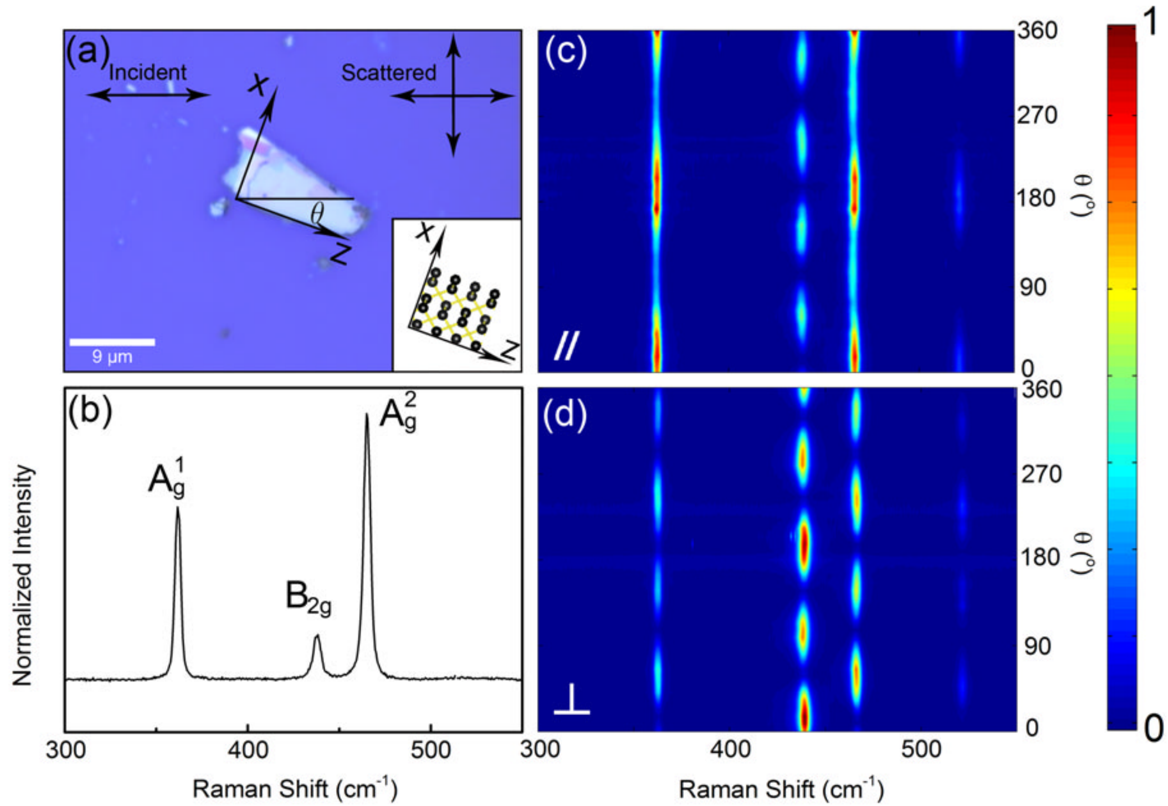
Resonance Raman studies in single layer WS_2 and WSe_2



E. Del Corro, A. Botello et al, (2015)

Unusual angular dependence of the Raman response in Black Phosphorus





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

Unusual angular dependence of the Raman response in Black Phosphorus

$$R_{ij}^{k} = \frac{\partial \epsilon_{ij}}{\partial q^{k}}$$

$$S_k \propto |\hat{\mathbf{e}}_i \cdot \overset{\leftrightarrow}{R^k} \cdot \hat{\mathbf{e}}_s|^2$$

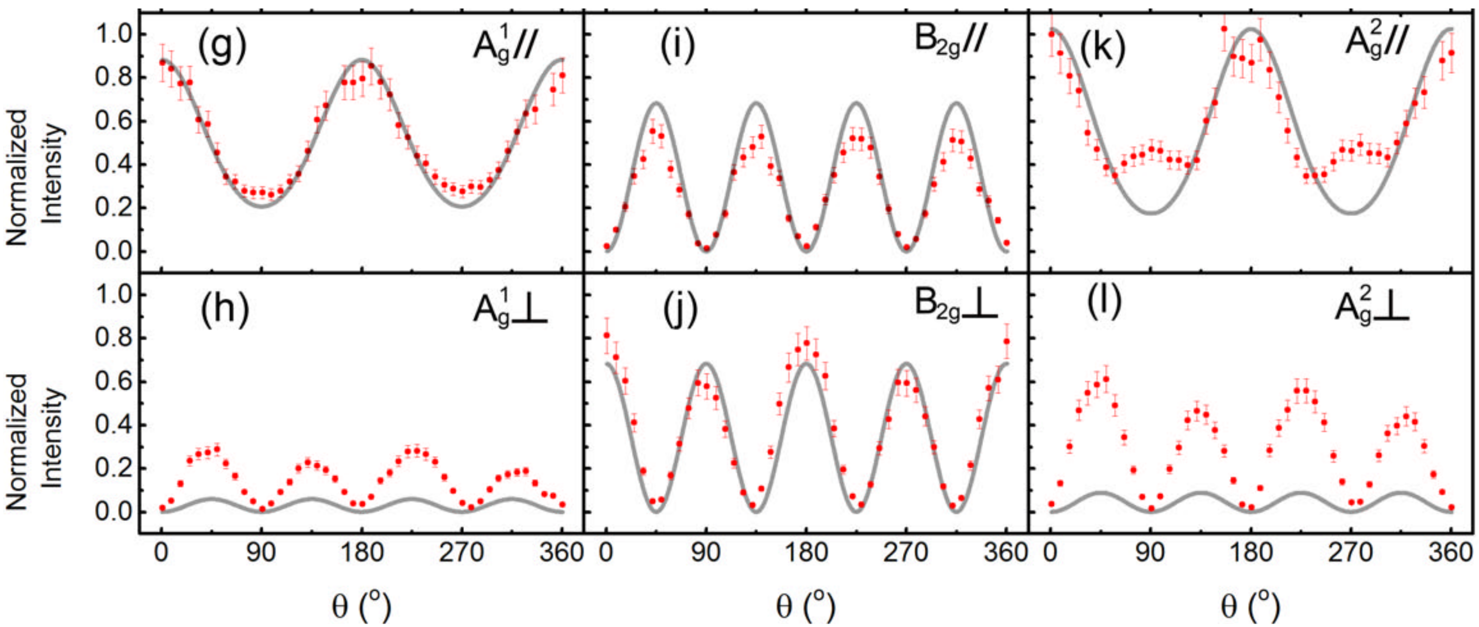
Mode	A_g	B_{2g}
Tensor	$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ f & 0 & 0 \end{pmatrix}$

$$S_{A_g}^{\parallel} = (asin^2\theta + ccos^2\theta)^2$$

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

$$S_{B_{2g}}^{\parallel} = (2fcos\theta sin\theta)^2$$

$$S_{B_{2g}}^{\perp} = [fcos(2\theta)]^2$$



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Unusual angular dependence of the Raman response in Black Phosphorus

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

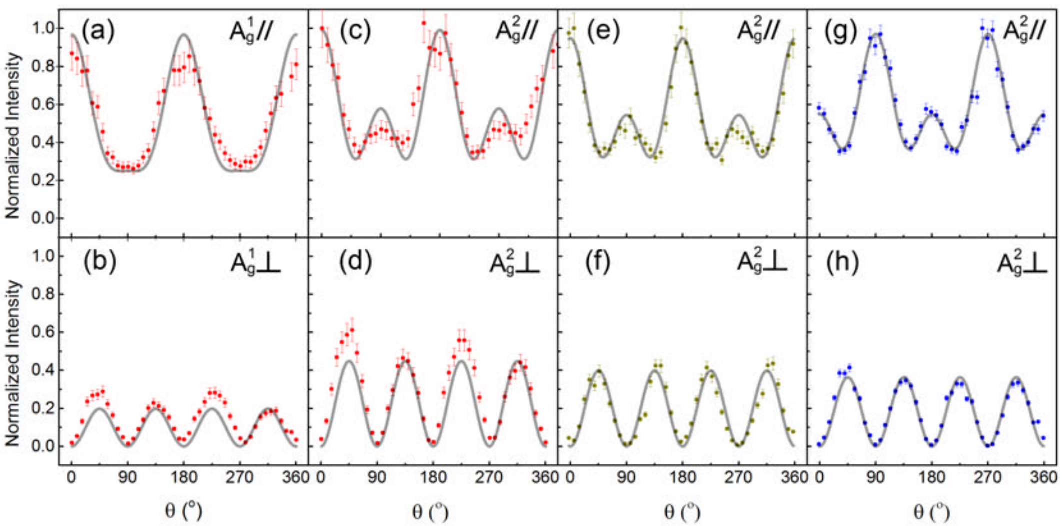
$$a = |a|e^{i\phi_a}, \quad c = |c|e^{i\phi_c}, \quad f = |f|e^{i\phi_f}$$

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

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

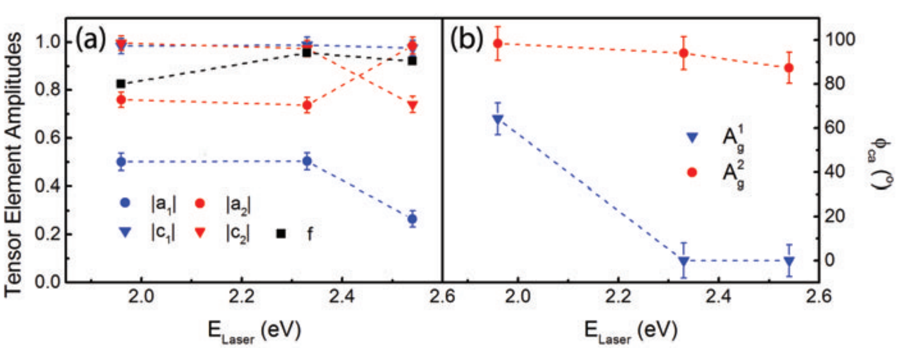
$$S_{B_{2g}}^{\parallel} = (2|f|sin\theta cos\theta)^2$$

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



Dichroism: Complex values of the Raman tensors

Anisotropy: Phase of the totally symmetric A_g Raman modes



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

Comparative Study of Raman Spectroscopy in Graphene and MoS_2-type Transition Metal Dichalcogenides

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Unusual angular dependence of the Raman response in Black Phosphorus

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

Origin of van Hove singularities in twisted bilayer graphene

H.B. Ribeiro et at, Carbon vol. 90, 138-145 (2015)