(Nano)spectroscopic fingerprints of van der Waals interactions in 2D materials

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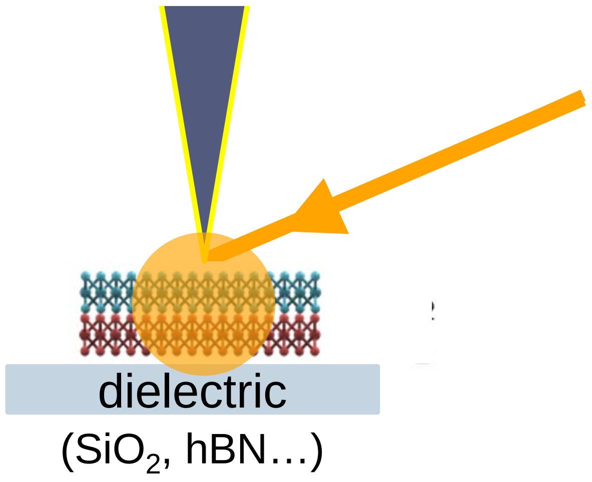
No. CZ.02.1.01/0.0/0.0/16_026/0008382
Carbon allotropes with rationalized nanointerfaces and nanolinks for environmental and biomedical applications

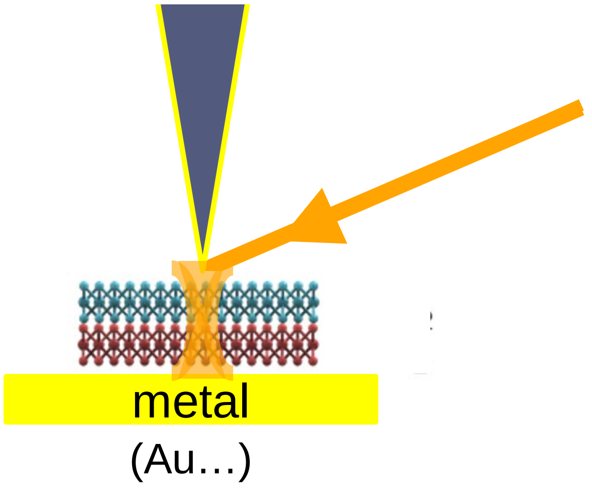
Topics

Gap-less tip-enhanced PL (TEPL)



- smaller enhancement
- worse resolution (~tip diameter)
- need for far-field signal subtraction
+ deliberate sample prep
+ less substrate influence
+ as-grown (Rodriguez et al. PSS-RRL 2019, 13, 1900381)

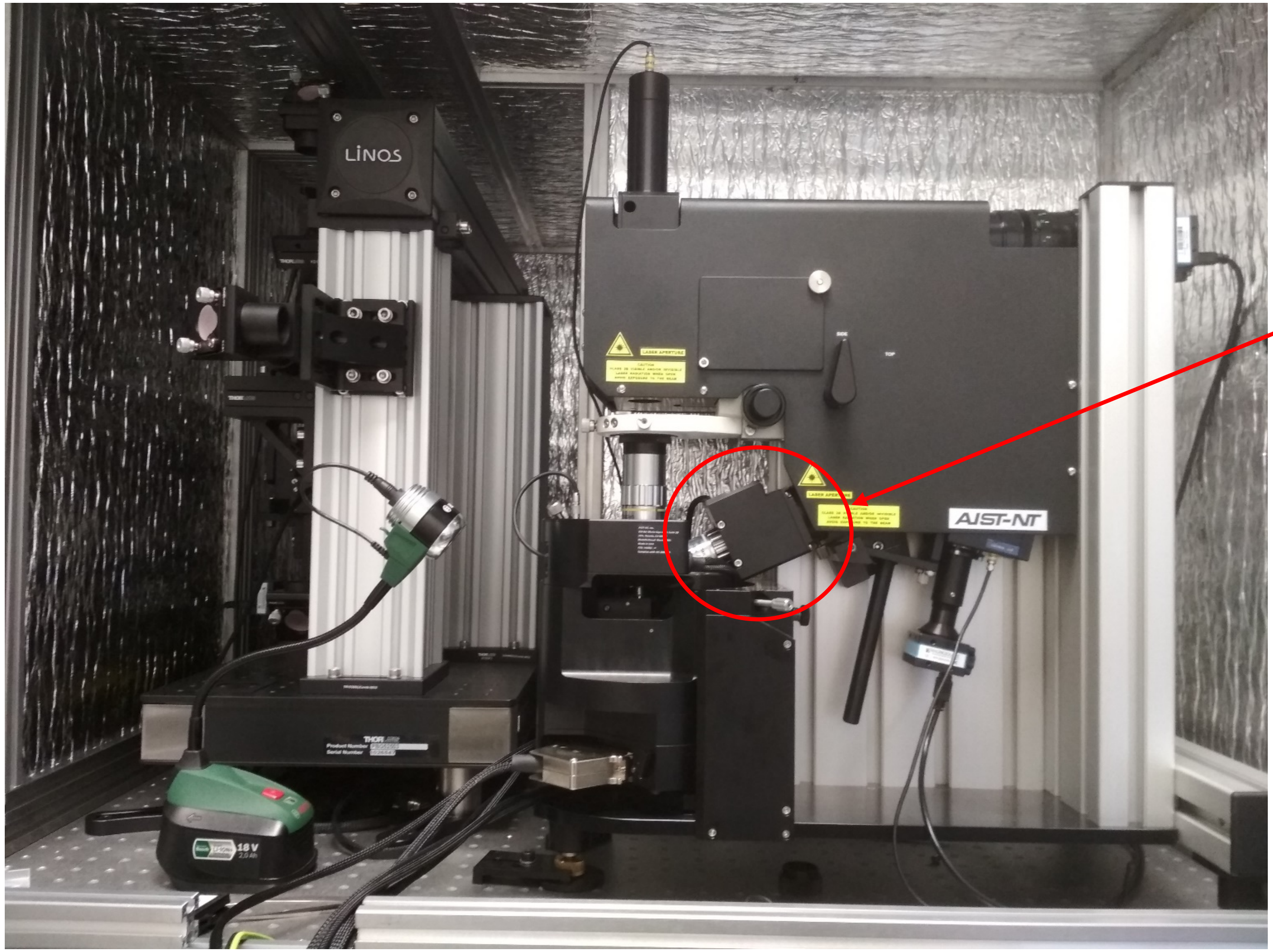
Gapped-mode tip-enhanced Raman (TERS)



+ larger enhancement
+ better resolution
- sample prep limitations
± potentially large substrate influence (Rodriguez et al. PRB 2022, 105, 195413)
+ large monolayers (Velický et al. JPCL 2020, 11, 6112)

Setup

Horiba LabRAM Nano (based on LabRAM EVO + AIST-NT OmegaScope + CombiScope)



side illumination

100x ULWD / 0.7 NA

30 x 30 x 30 μm objective piezo scanner

tips: visible apex AppNano Access-FM, Ag-sputtered

λ_{exc} : 532 / 633 nm

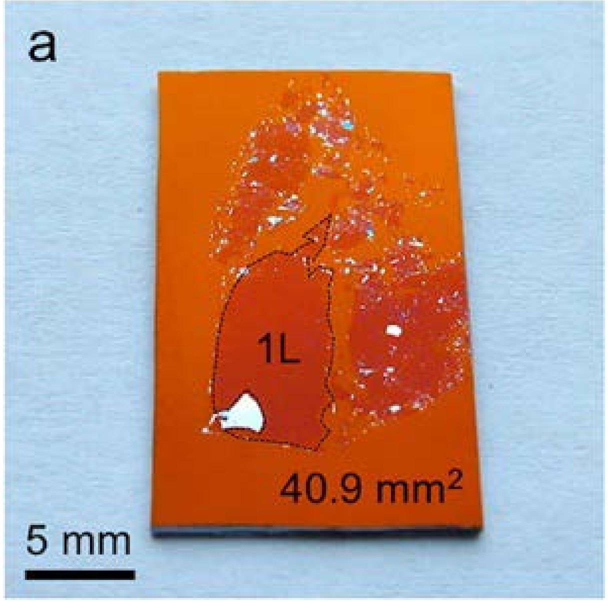
grating:
150 or 300 l/mm for TEPL
1800 l/mm for TERS

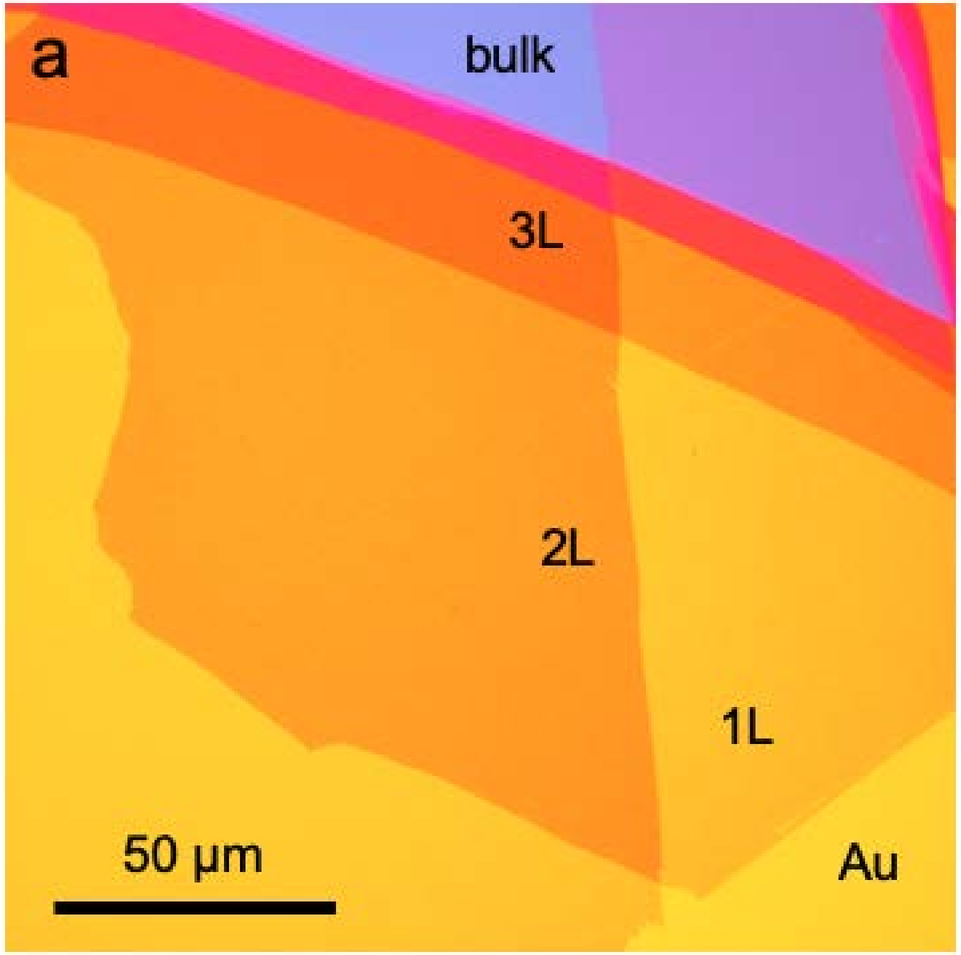
Outline

1. MoS_2 on Au
    - strong vs. weak interaction and their spatial heterogeneity (gapped mode TERS)
    - activation of Raman modes due to symmetry lowering (gapped mode TERS)
2. TMDC heterobilayers
    - interlayer excitons (gap-less TEPL)
    - interlayer phonons etc. (gapped mode TERS)

MoS_2 on Au

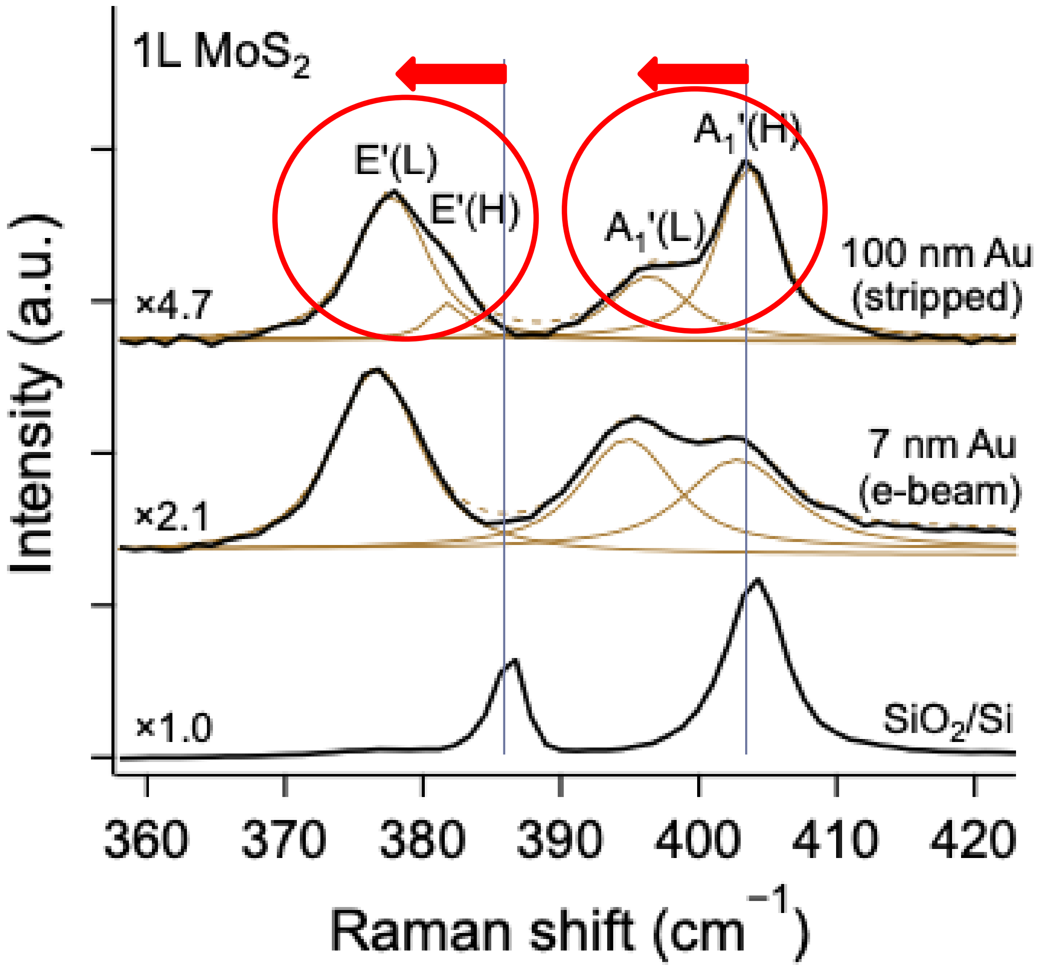
- large-area mechanical exfoliation
- MoS_2 exfoliated on Au (freshly) deposited at Si/SiO_2
- **strong MoS_2 – Au adhesion – high exfoliation gains**
- Au thicknes 3 - 100 nm
- sputtering / e-beam / stripped





Velicky et al. ACS Nano 2018, 12, 10463

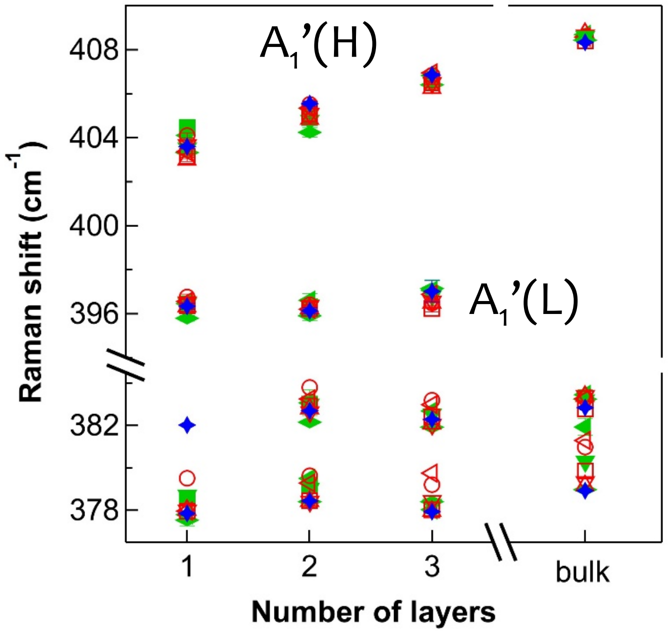
MoS_2 on Au

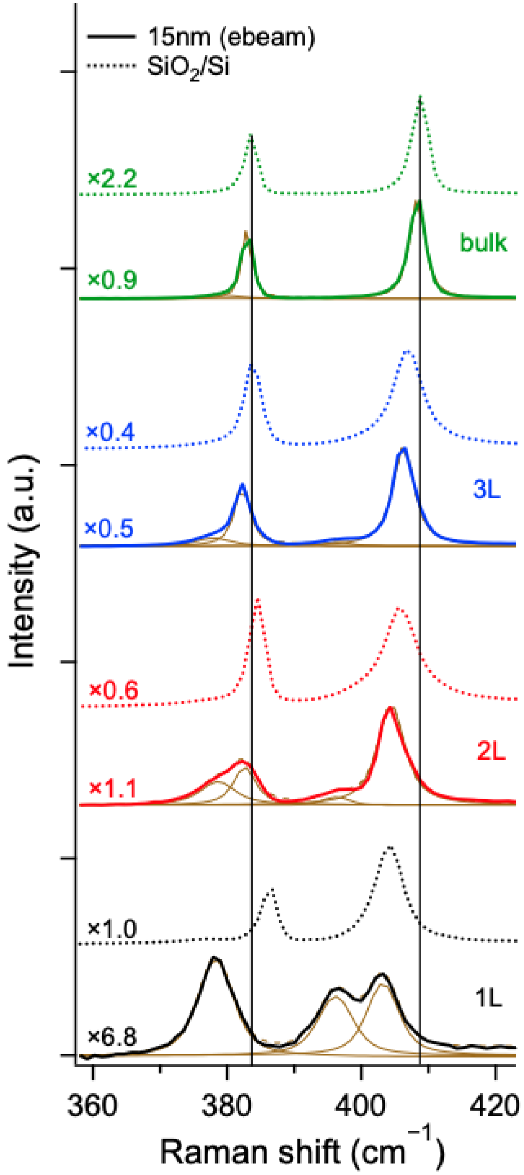


far-field Raman (532 nm)

- significant redshift of both E' and A_1'
- clear splitting of both bands (especially A_1')
- area ratio of the split peaks different for sample types/thicknesses

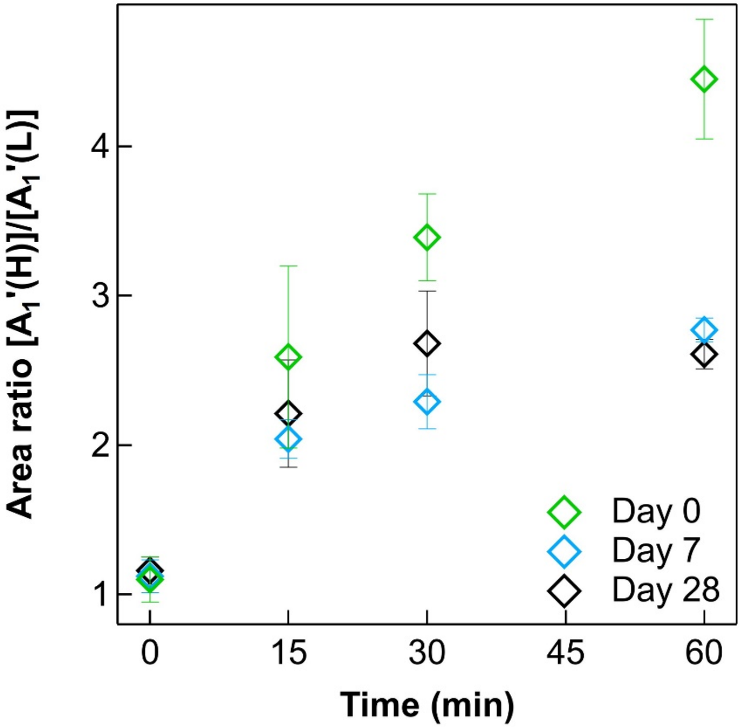
MoS_2 on Au





- A_1'(H) behaves as on Si/SiO_2
- A_1'(L) stays at roughly the same position/intensity

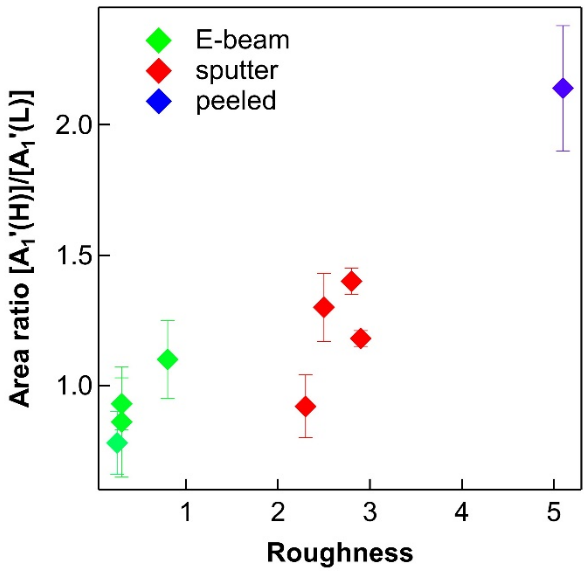
MoS_2 on Au



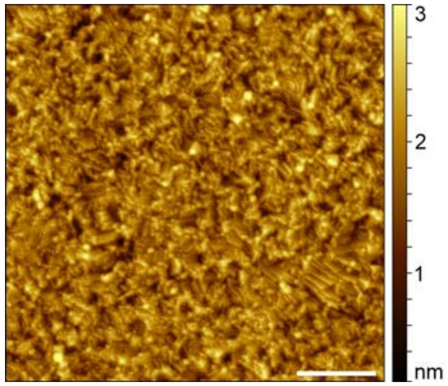
Exfoliation performed immediately after Au deposition / with 15-60 min delay:

- A_1'(H) intensity increases

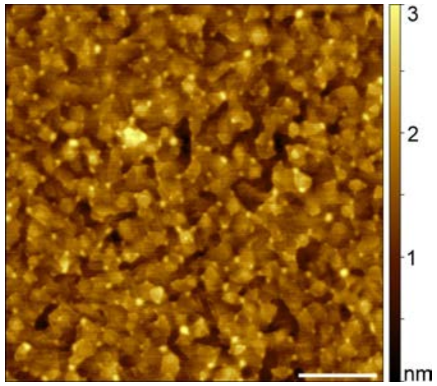
MoS_2 on Au



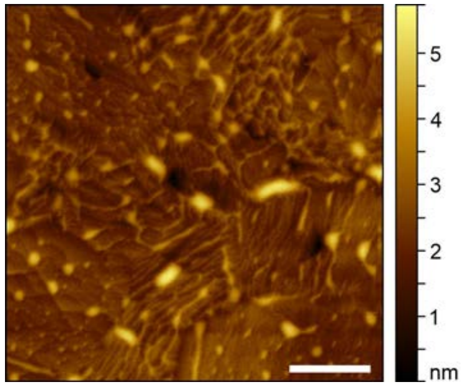
- increased roughness ⇨ increased A_1'(H)
- ? A_1'(L) caused by the substrate interaction



15 nm e-beam

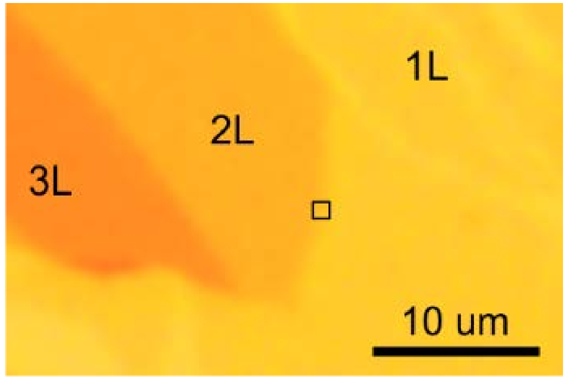


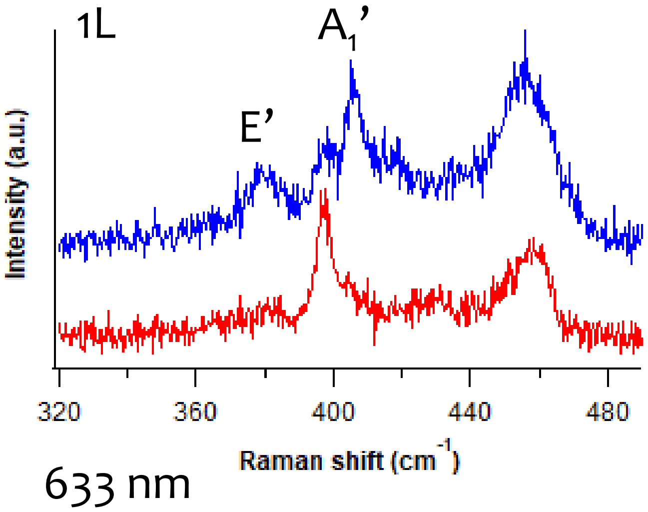
15 nm sputter



50 nm stripped

MoS_2 on Au

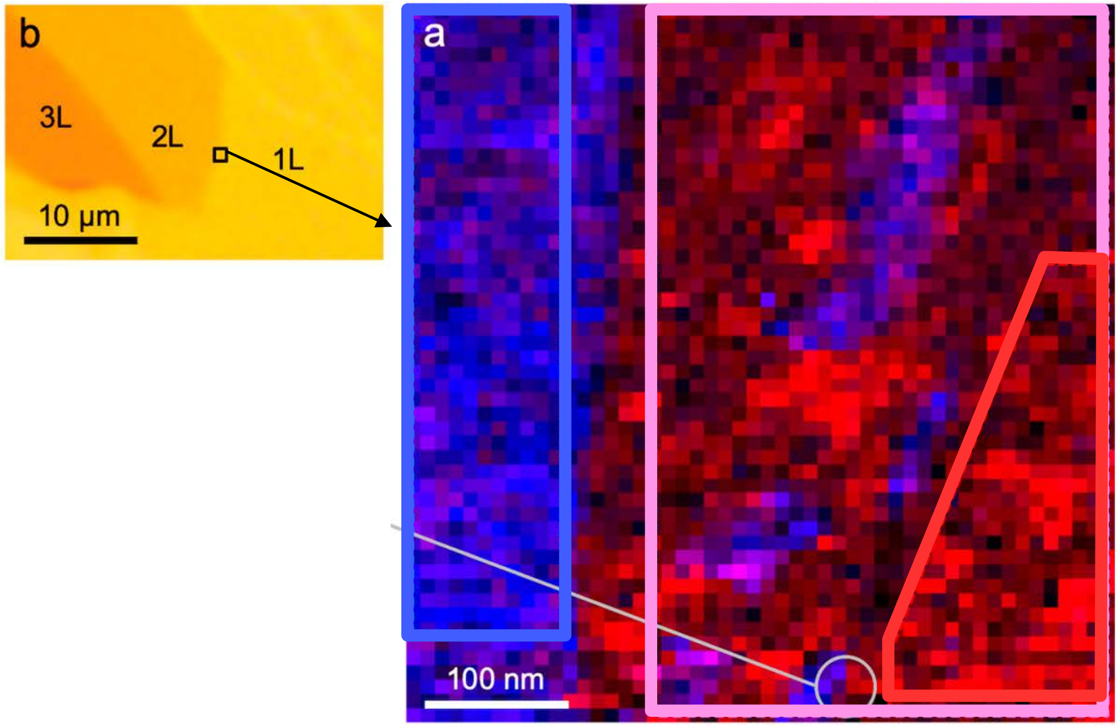




<u>*TERS (gapped mode)*</u>

- near-field (1s accumulation, 1800 l/mm gr.)
- no far-field visible
- extreme A_1' enhancement – out-of-plane mode

MoS_2 on Au

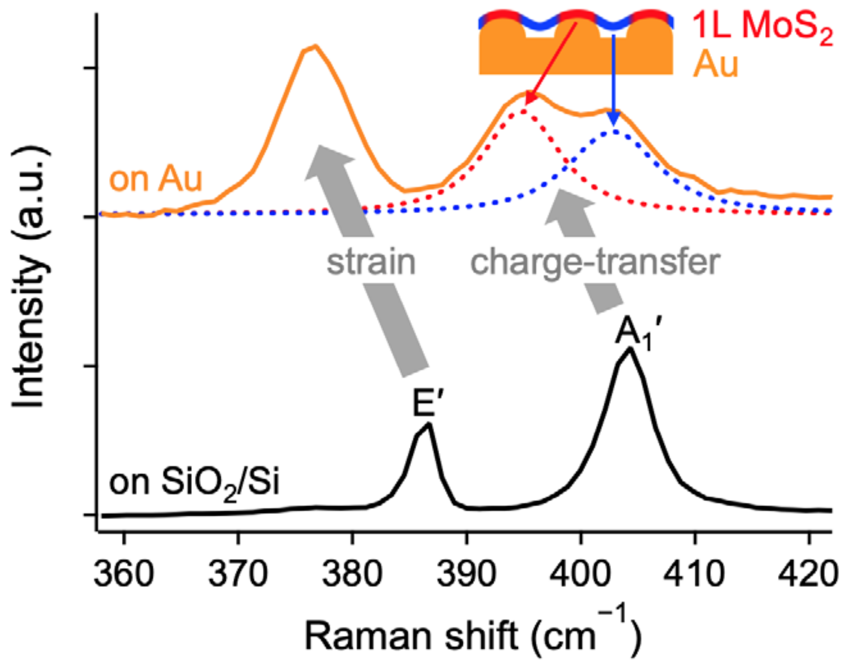


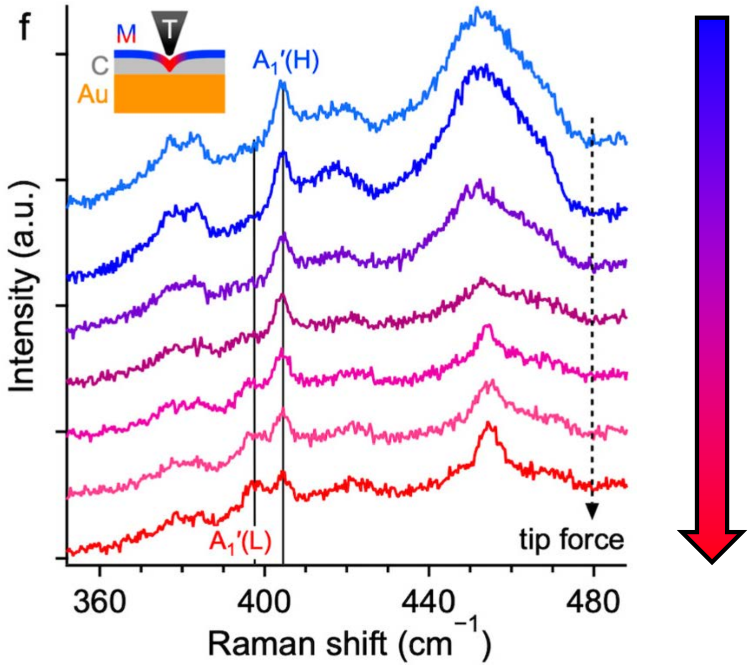
- TERS: lateral resolution ~ 10 nm
- splitting originates from small (x – x0 nm) patches, where 1L MoS_2-Au adhesion is weaker/stronger
- redshift of E'(L) and A_1'(L) – strain and doping, respectively

MoS_2 on Au

- increasing tip force

⇨ gradual appearance of A_1'(L)

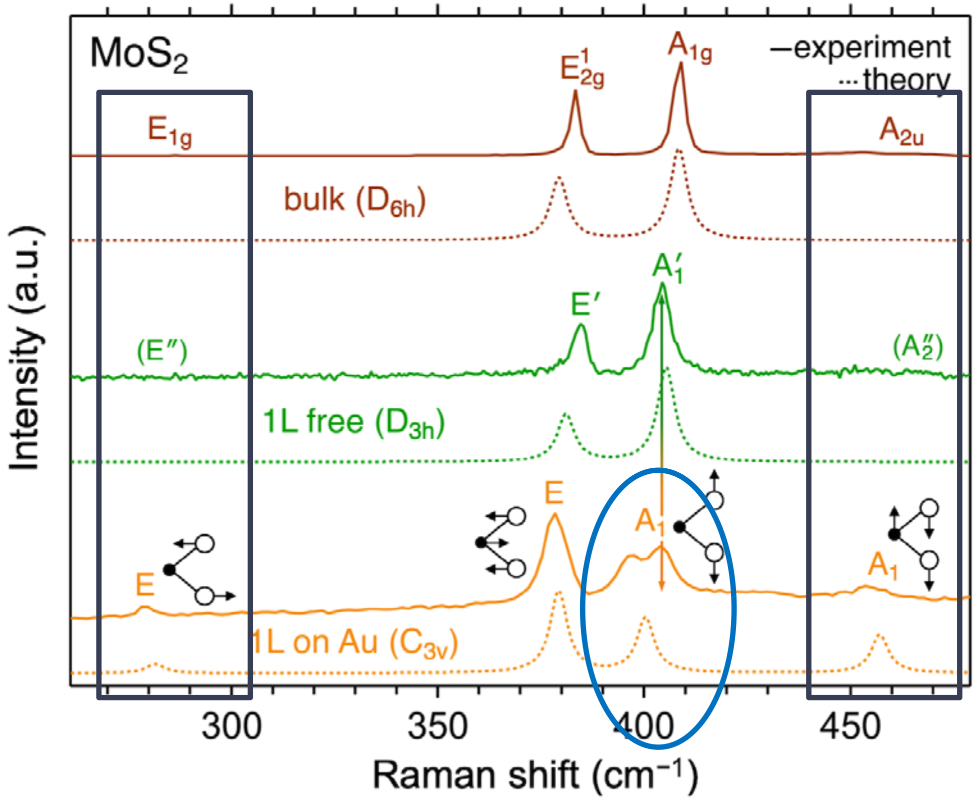


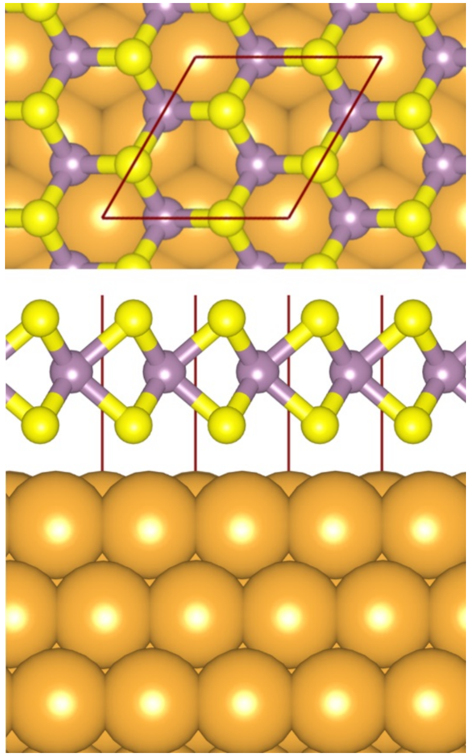


Velický *et al.* J. Phys. Chem. Lett. 2020, 11, 6112.

MoS_2 on Au

Activation of Raman modes due to symmetry change upon strong interaction with Au substrate

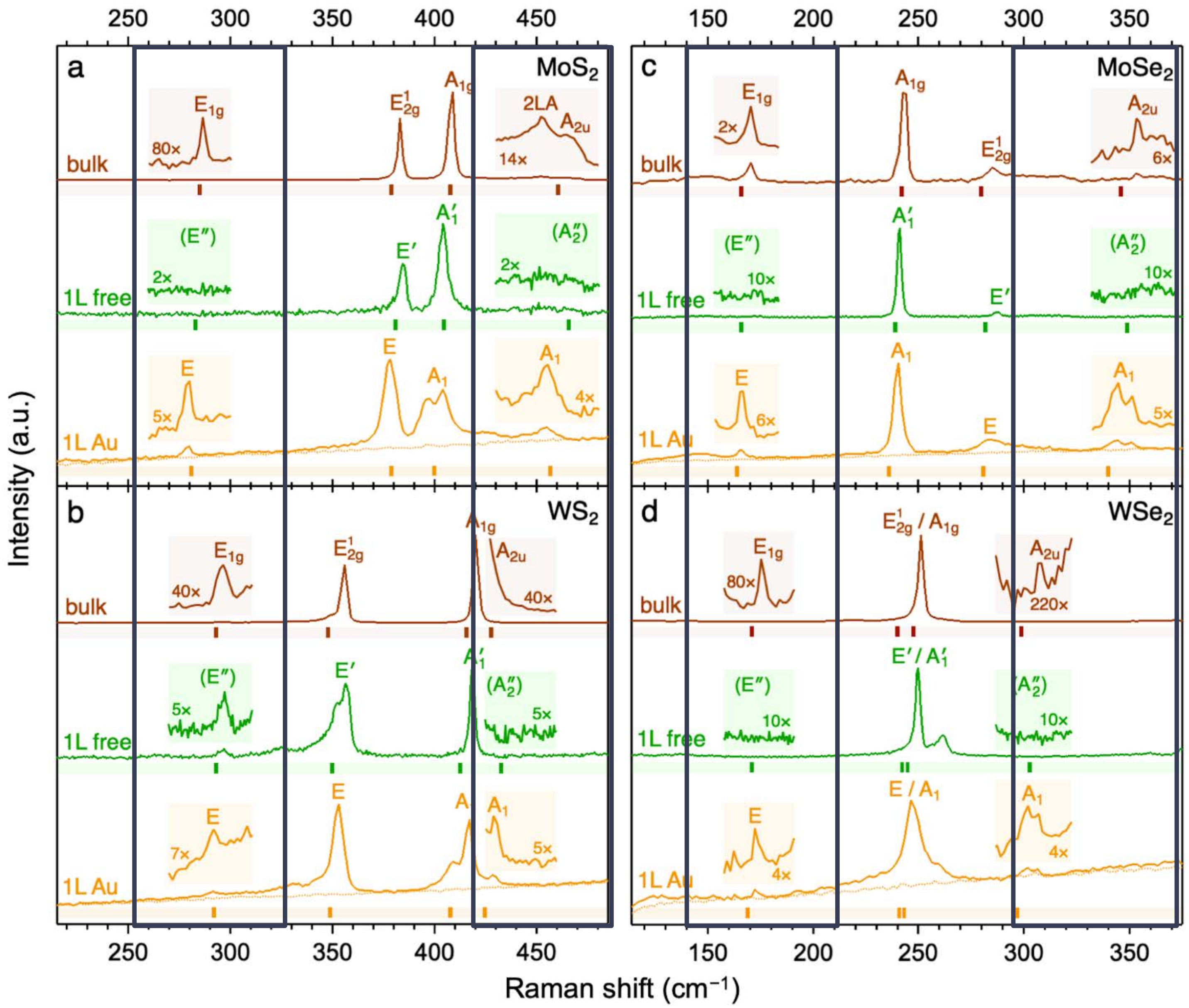




- activation of geometry (E) and symmetry-forbidden (A_1) modes due to symmetry lowering
- downshift of A_1 mode (at 400 cm^{-1}); predicted also by theory (only one mode; i.e. the splitting is indeed from spatial heterogeneity only!

Rodriguez et al. PRB 2022, 105, 195413

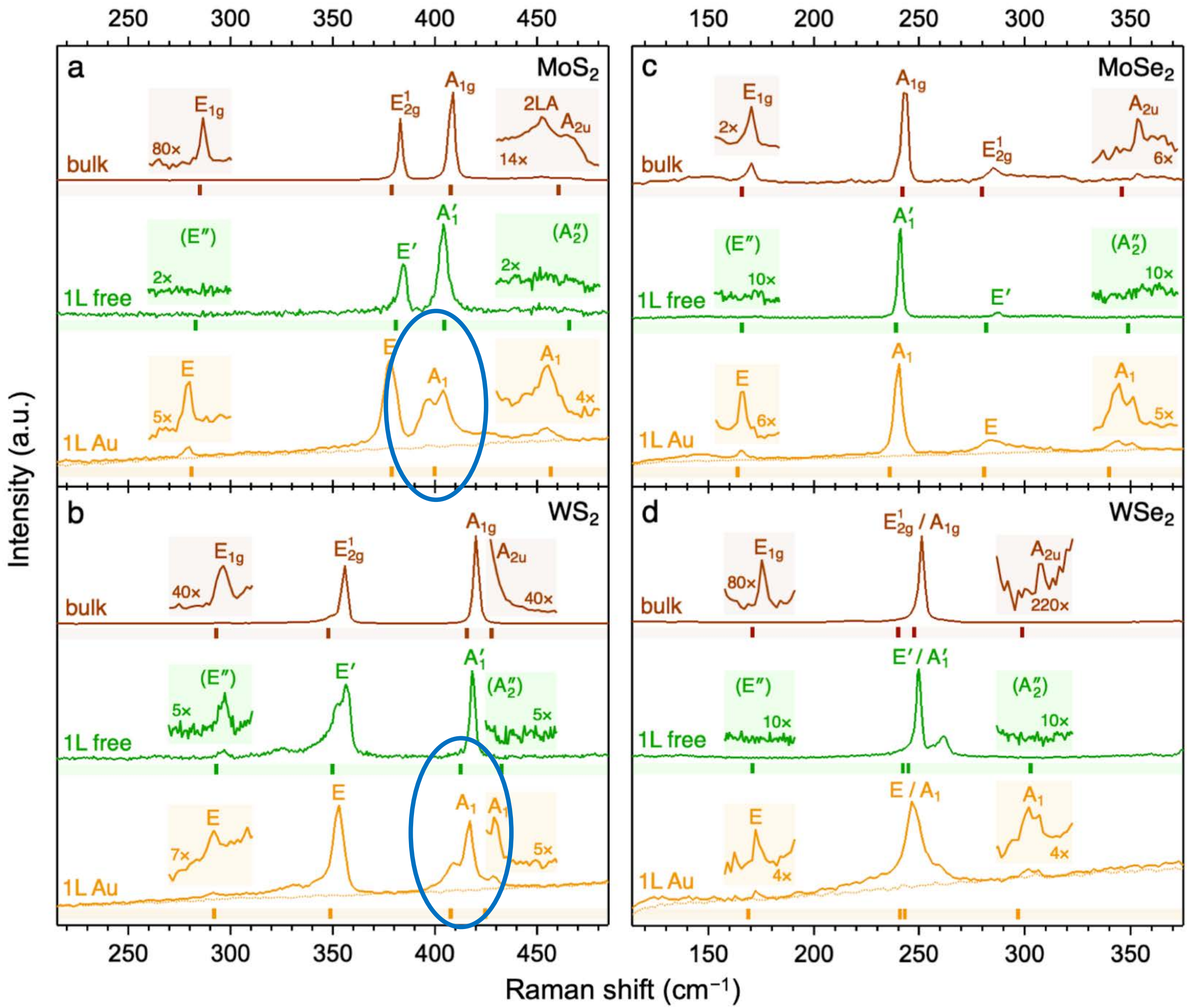
MX_2 on Au



- activation of geometry (E) and symmetry-forbidden (A_1) modes due to symmetry lowering

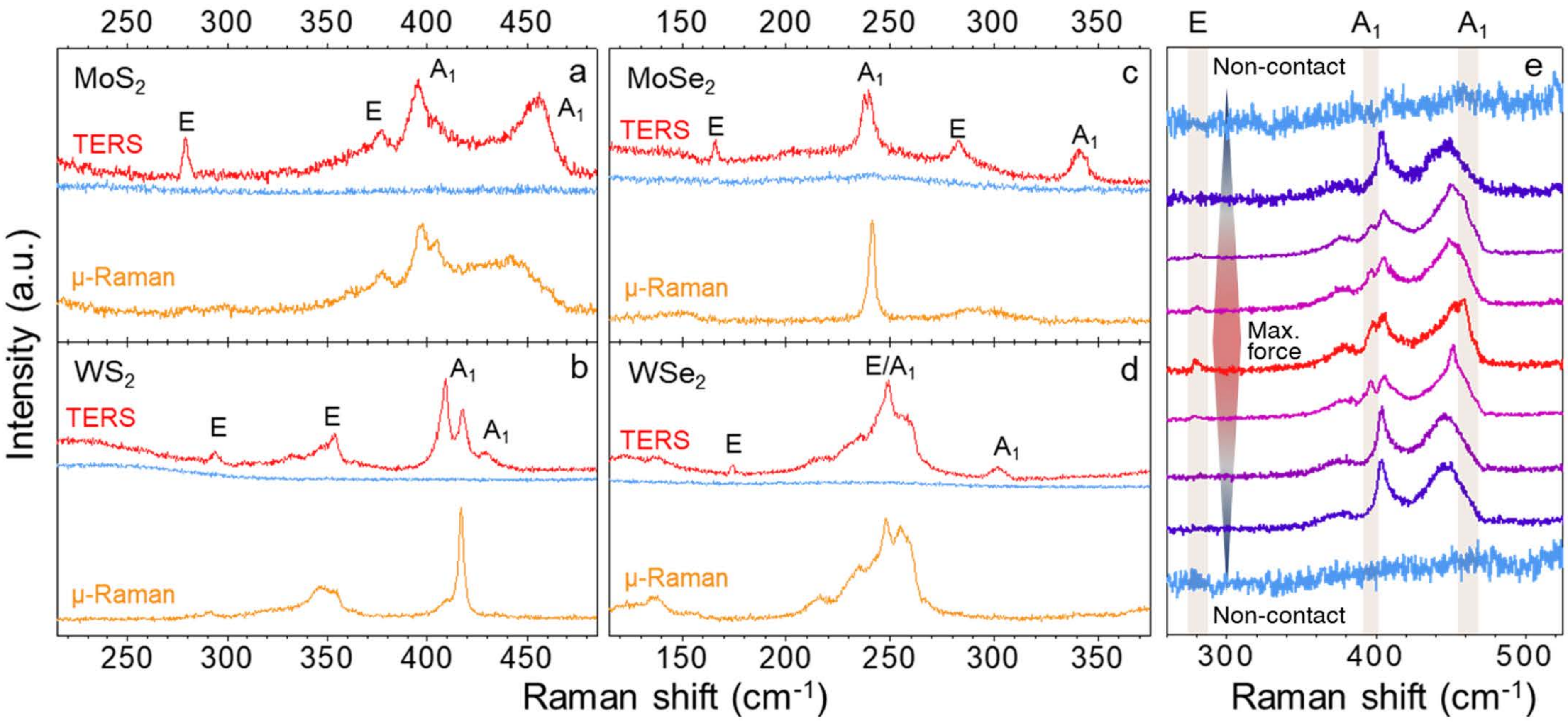
for all MX_2

MX_2 on Au



- activation of geometry (E) and symmetry-forbidden (A_1) modes due to symmetry lowering
- downshift of A_1 mode (at 400 cm^{-1}) also for WS_2
- for MSe_2 the A_1 mode interaction sensitivity is smaller

MX_2 on Au



- TMDCs on “aged” Au
- weaker interaction
- A_1 and E inactive

- TERS with stronger contact – mode activation

Rodriguez et al. PRB 2022, 105, 195413

Outline

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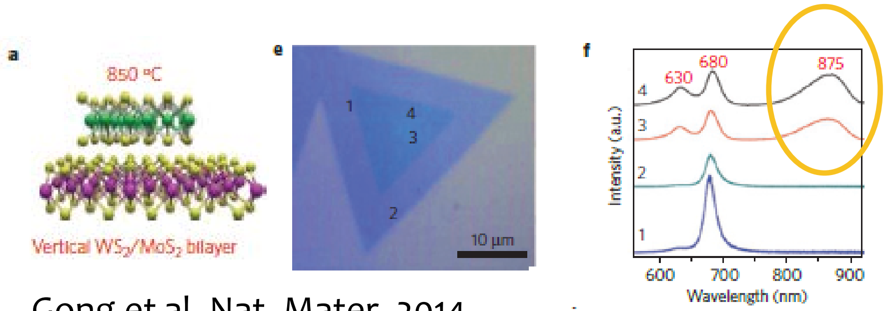
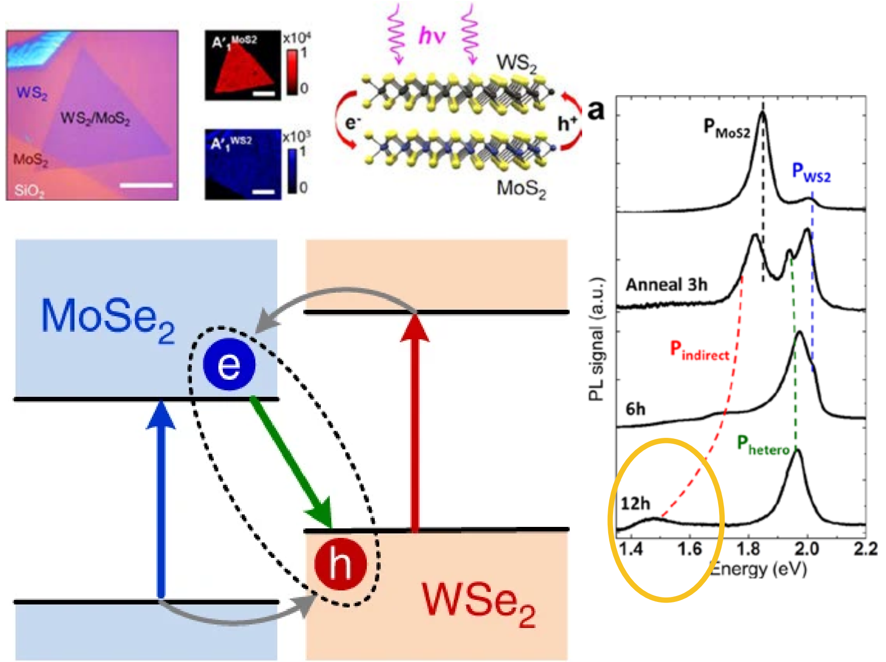
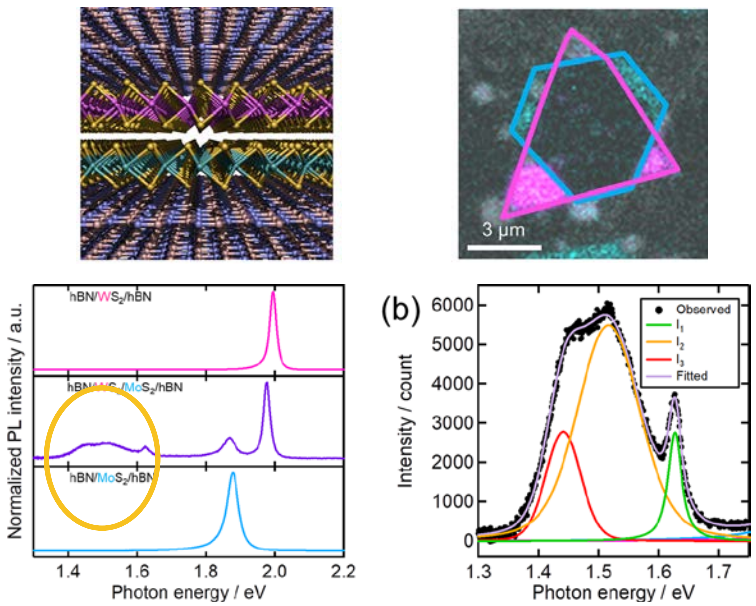
2. TMDC heterobilayers
    - interlayer excitons (gap-less TEPL)
    - interlayer phonons etc. (gapped mode TERS)

Gap-less TEPL on TMDC heterobilayers



Gong et al. Nat. Mater. 2014





Okada et al. ACS Nano 2018

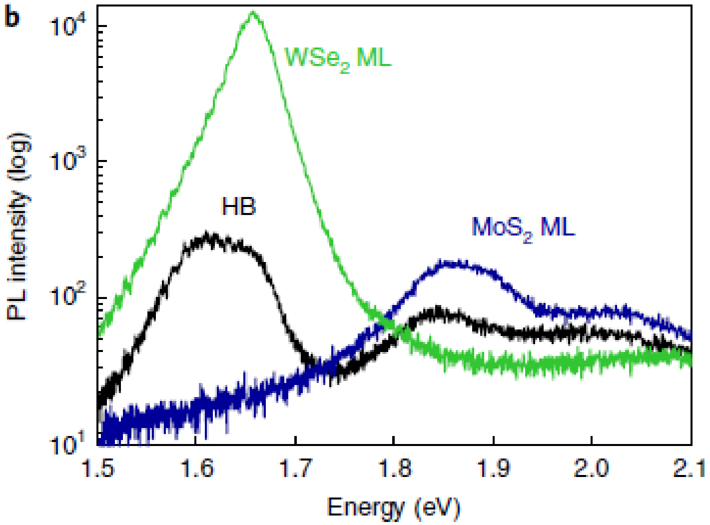
?

Interlayer exciton – spatial localization?

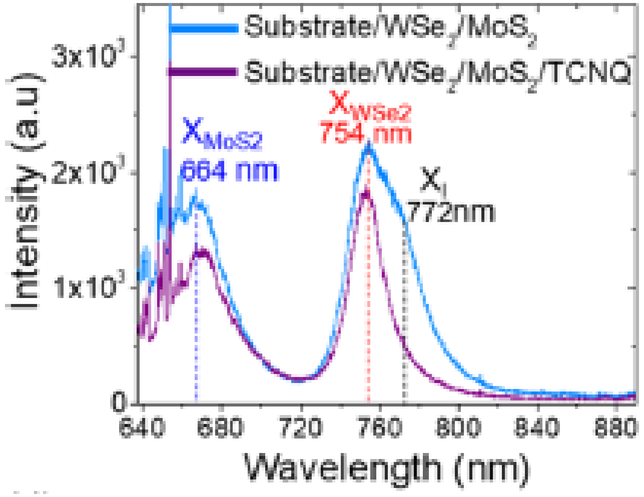
MoS_2-WS_2, $MoSe_2$-WSe_2 – spectral localization OK

but MoS_2-WSe_2 ?

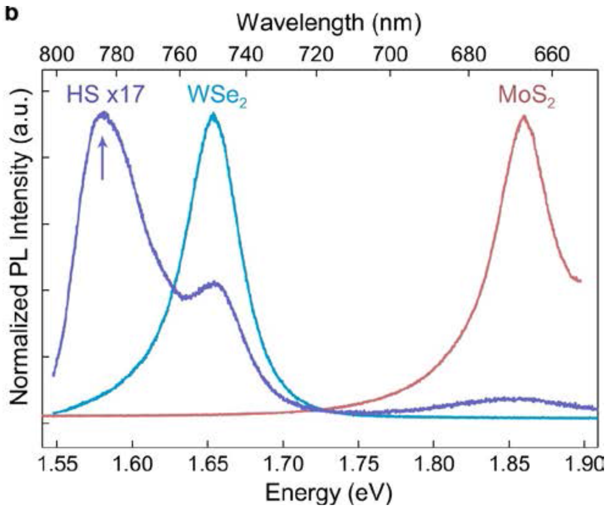
Gap-less TEPL on TMDC heterobilayers



Kunstmann et al. Nat. Phys. 2018



Ji et al. Nano Lett. 2020

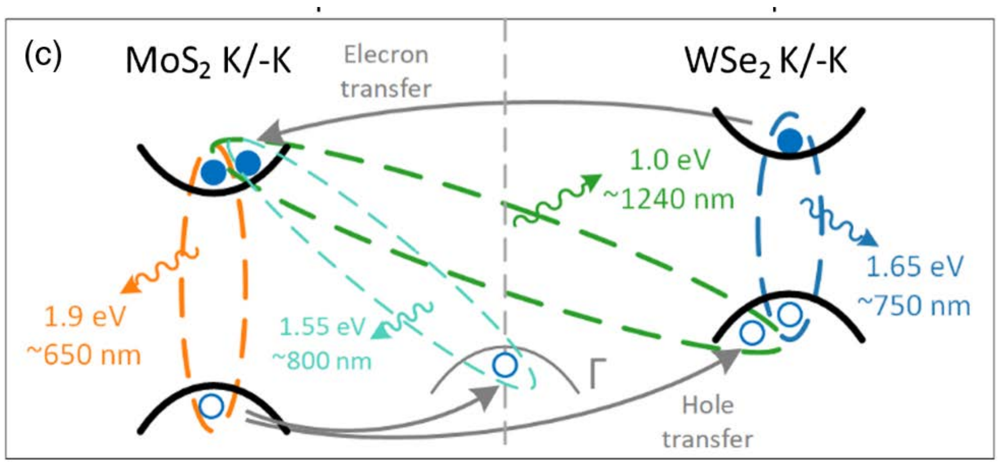


Unucheck et al. Nature 2018

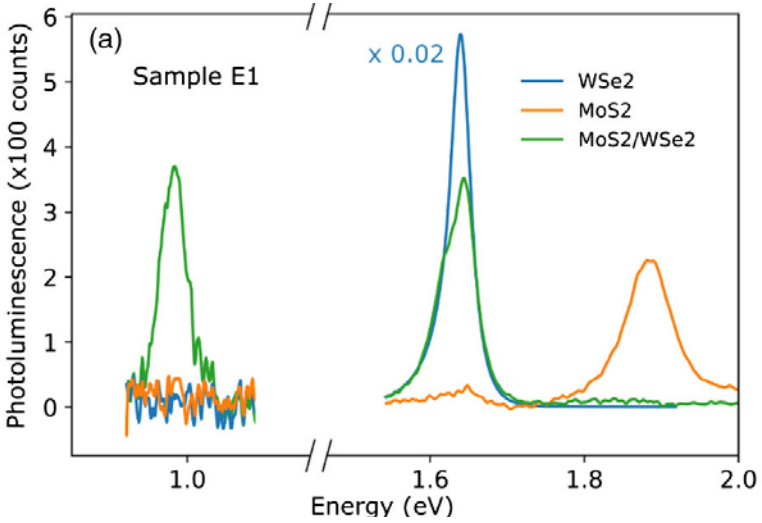
Interlayer exciton in MoS_2-WSe_2

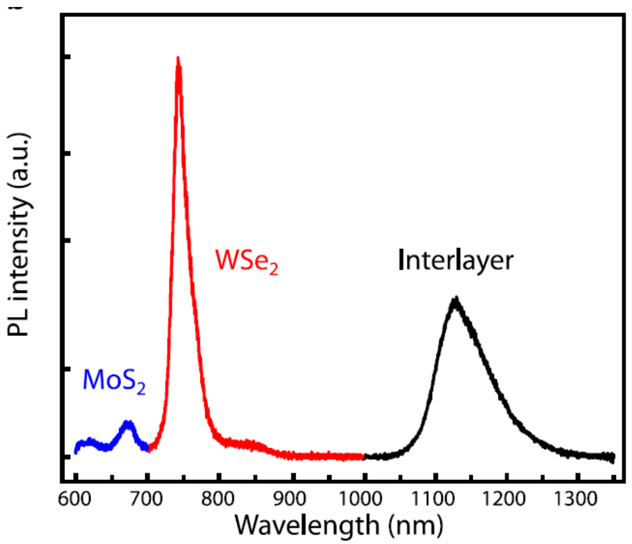
? ? ?

Gap-less TEPL on TMDC heterobilayers



Karni et al. PRL 2019

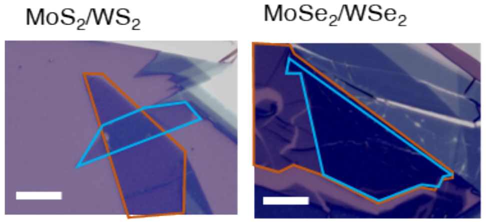




Huang et al. Nano Lett 2020

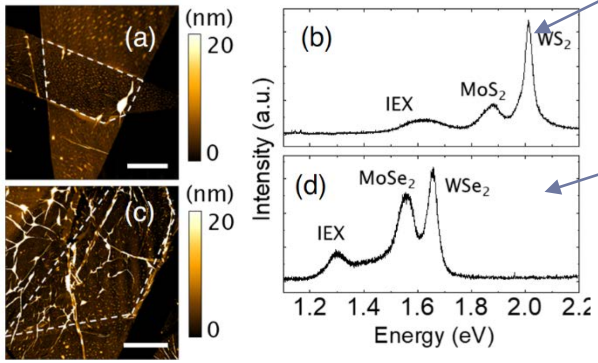
Interlayer exciton in MoS_2-WSe_2
? ? ?

Gap-less TEPL on TMDC heterobilayers

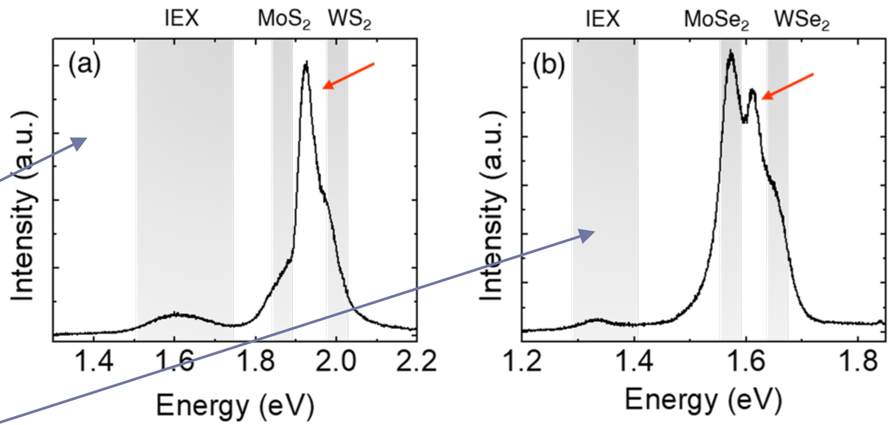


dry transfer

MoX$_2$ on top



μ-PL, 633 nm

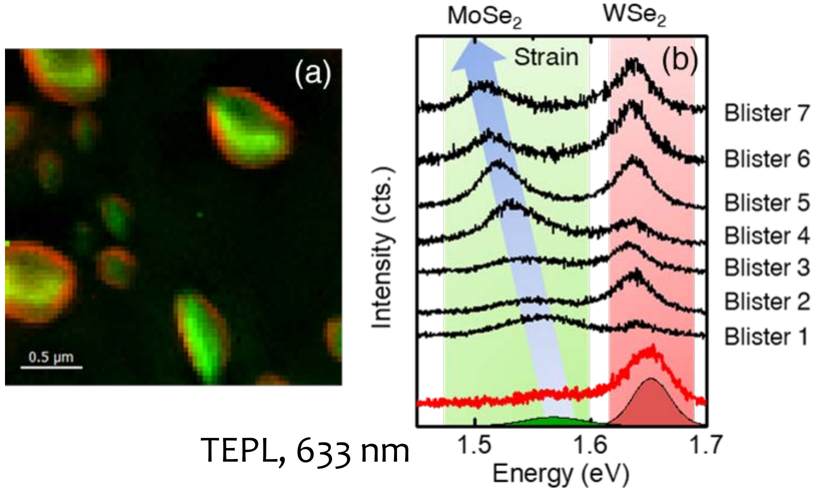


μ-PL, 633 nm

WX$_2$ on top

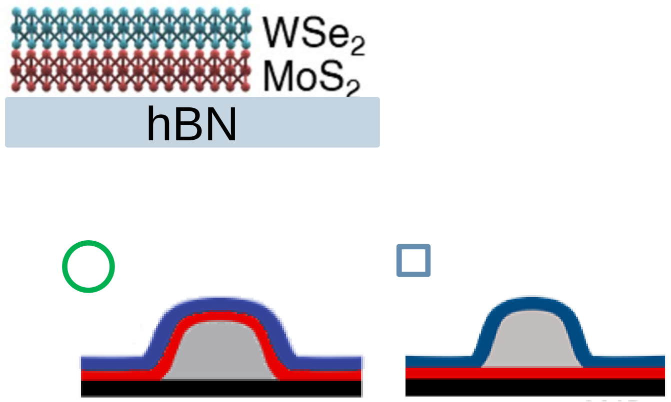
MoS_2-WS_2, $MoSe_2$-WSe_2 on SiO_2/Si

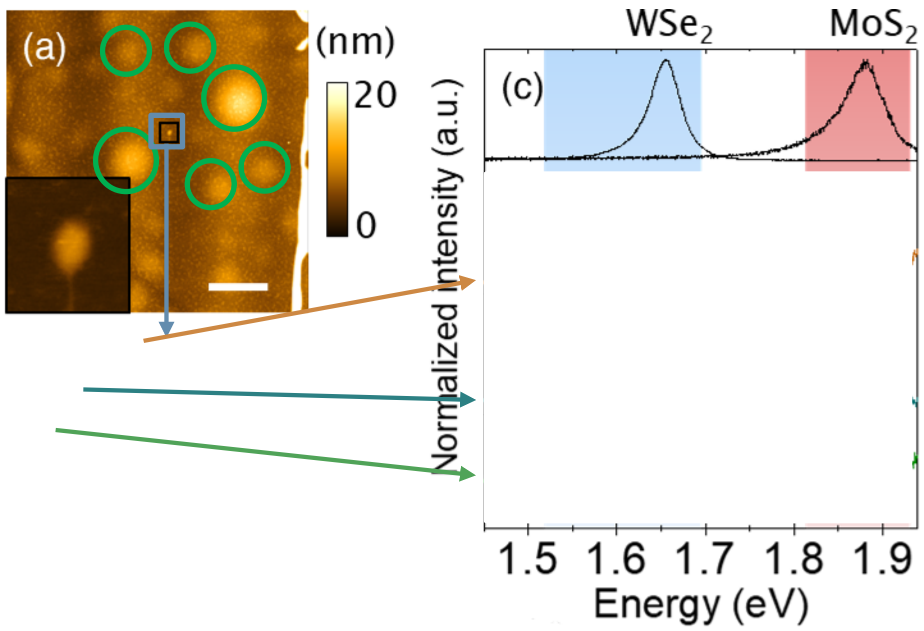
Local strain effects (redshift) on the PL of the top layer - bubbles, blisters



TEPL, 633 nm

Gap-less TEPL on TMDC heterobilayers



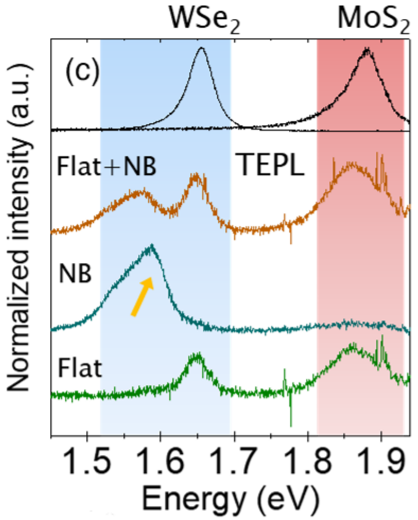


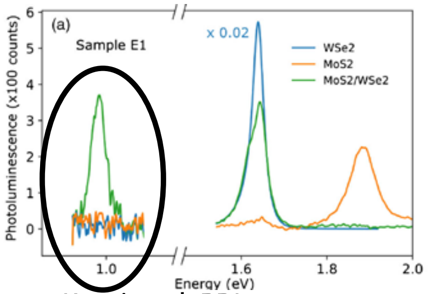
- nanobubbles, blisters (in the top layer): cause PL energy downshift (strain) and extreme intensity increase (decoupling of the layers)

- even a **single nanobubble of ~60 nm** can cause signals similar to reported interlayer excitons in MoS_2/WSe_2 – careful (re)assignment needed

Rodriguez *et al. 2D materials* 8, 025028 (2021)

Gap-less TEPL on TMDC heterobilayers

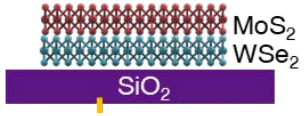


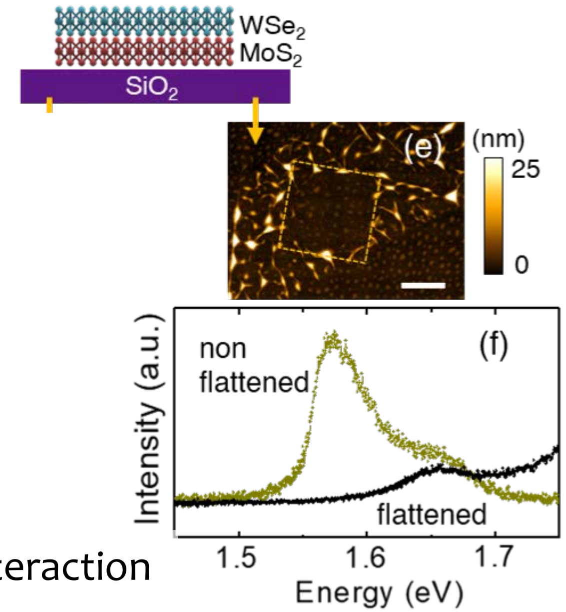


Karni et al. PRL 2019

Huang et al. Nano Lett 2020

Where is the interlayer exciton in MoS_2-WSe_2 ?

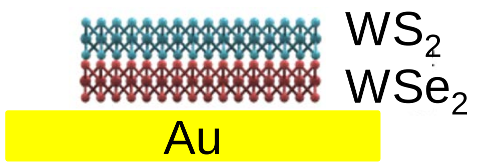




Moiré pattern ⬄ strong interaction

Rodriguez *et al. 2D materials* 8, 025028 (2021)

Gapped-mode TERS on TMDC heterobilayers



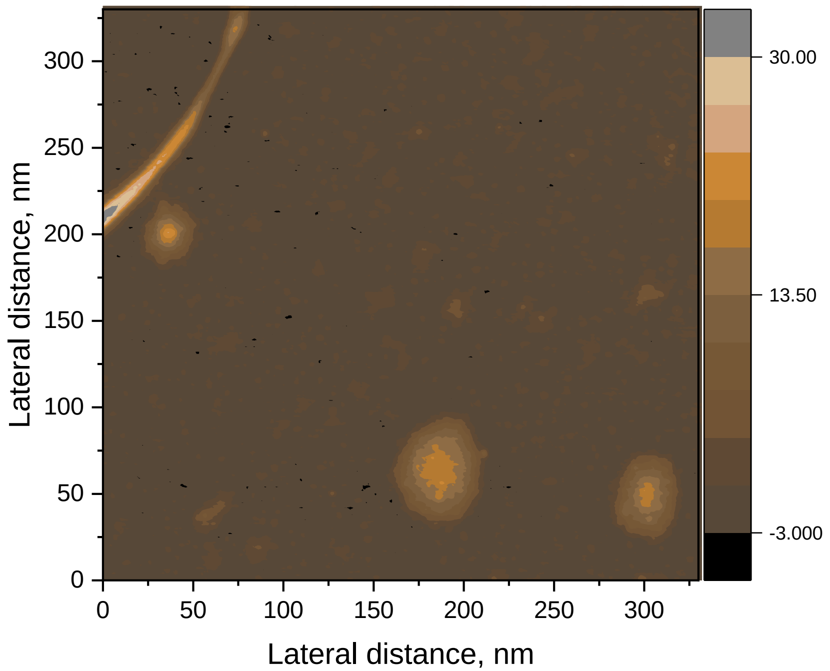
sample prep: PDMS stamping

tips: OMNI-TERS-SNC-Au

λ_{exc} : 785 nm

grating:
300 l/mm

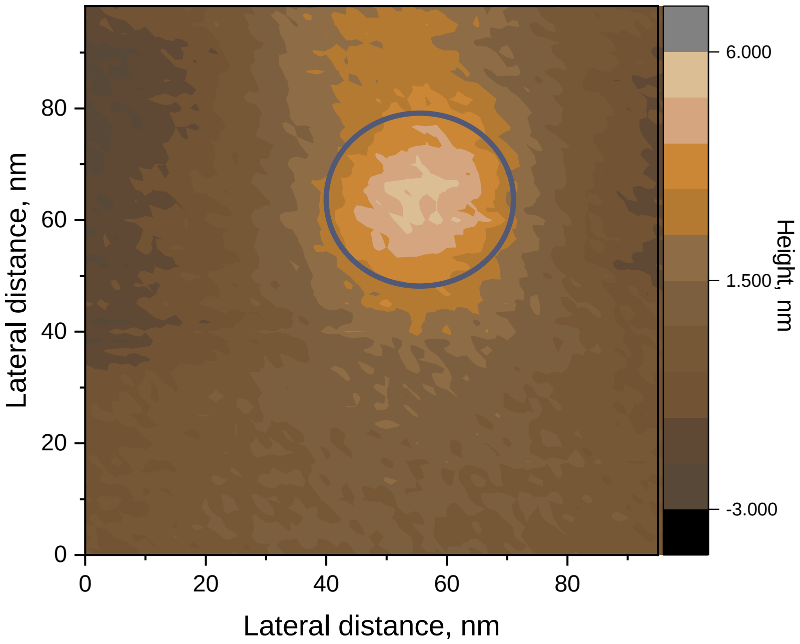
Bragg filters (OD 11, OptiGrate)
→ ultra-low frequency measurement



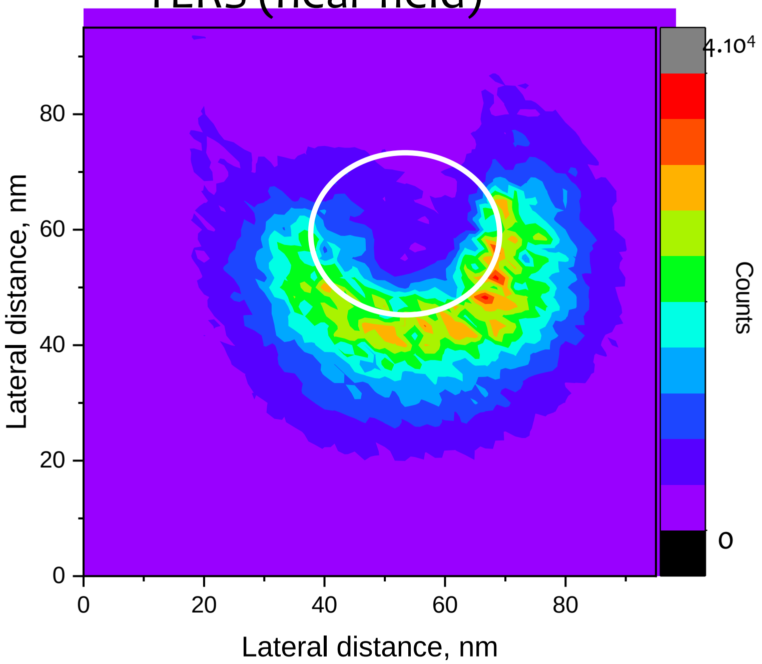
AFM topography

Gapped-mode TERS on TMDC heterobilayers

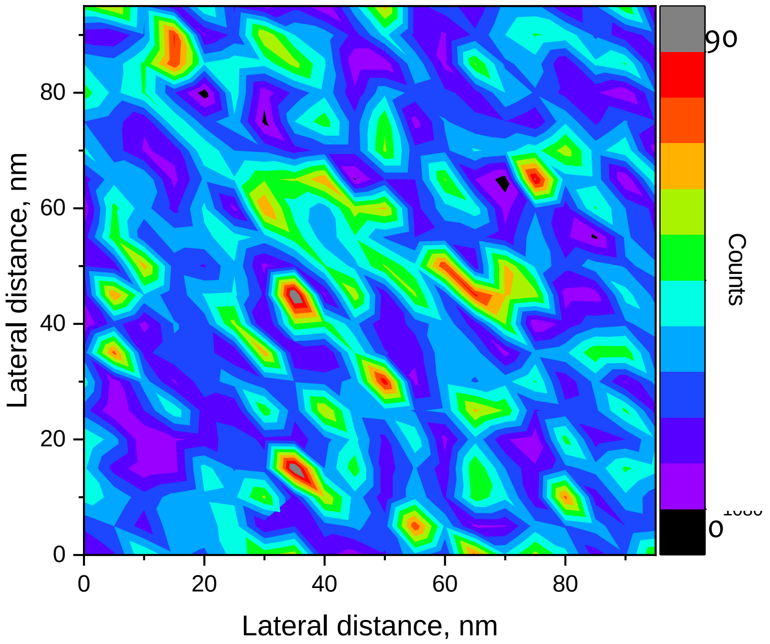
AFM topography



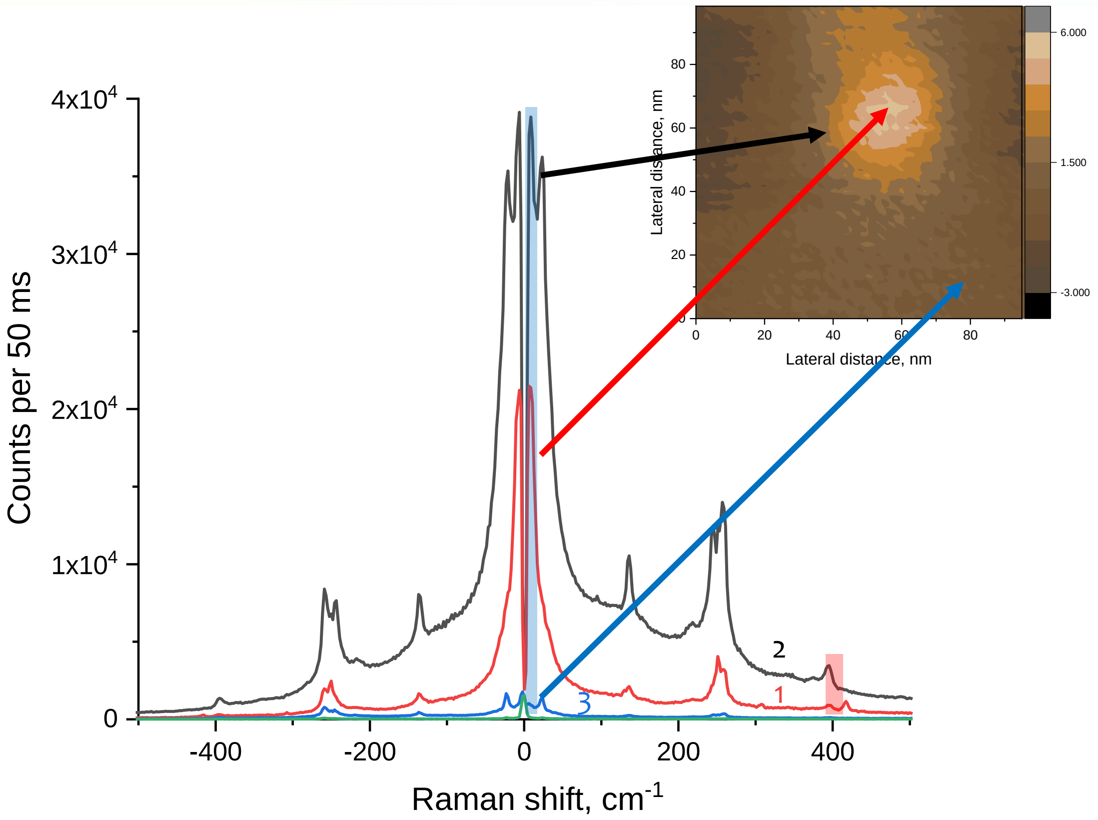
TERS (near field)

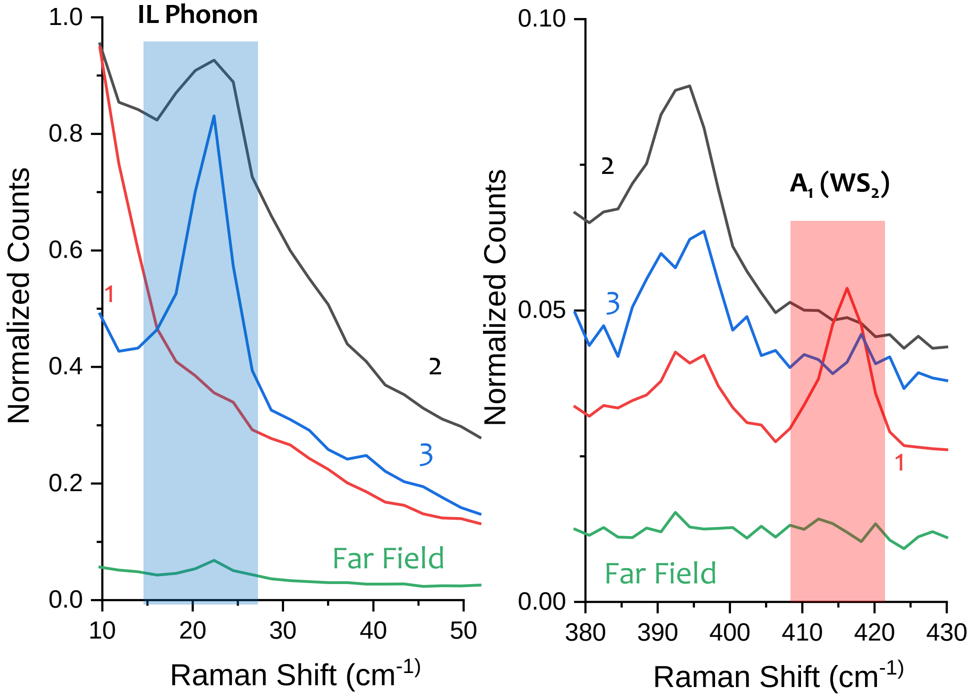


far field

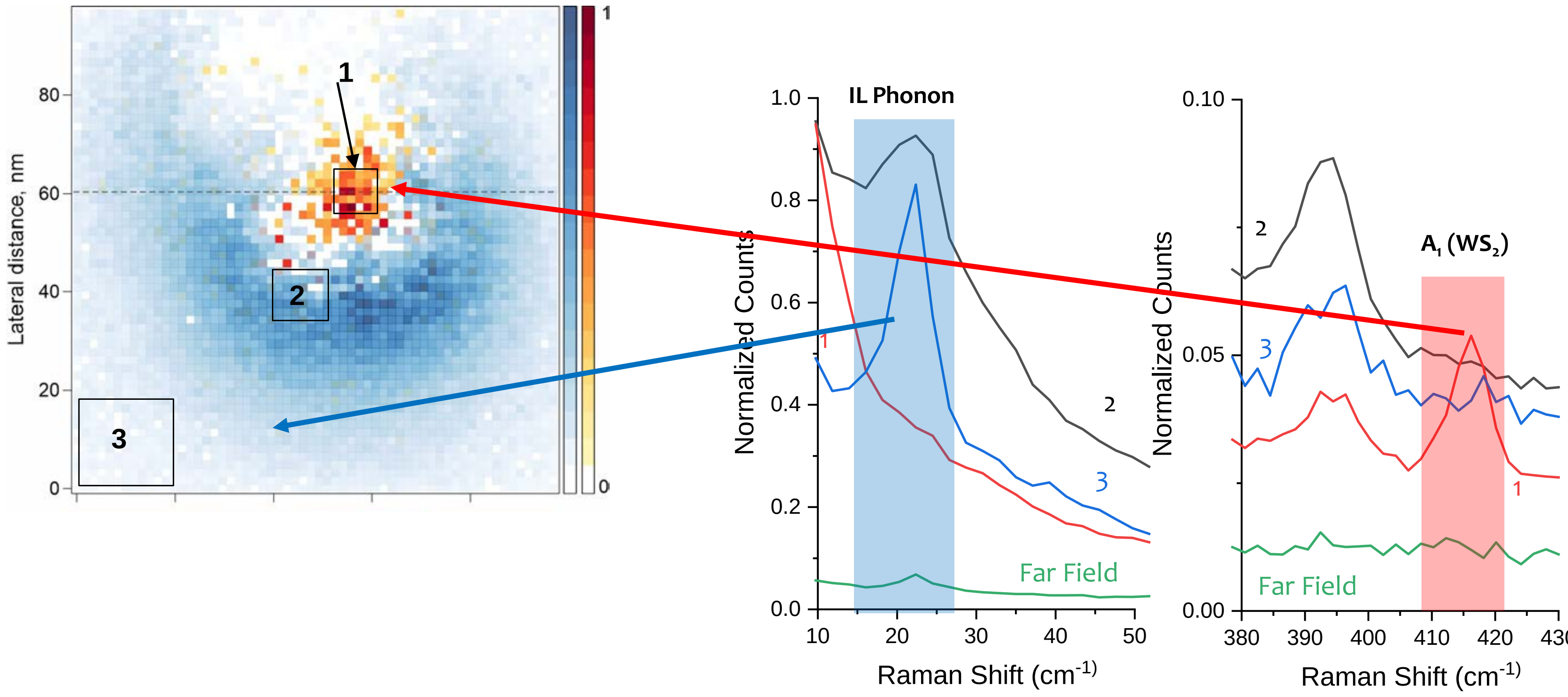


Gapped-mode TERS on TMDC heterobilayers



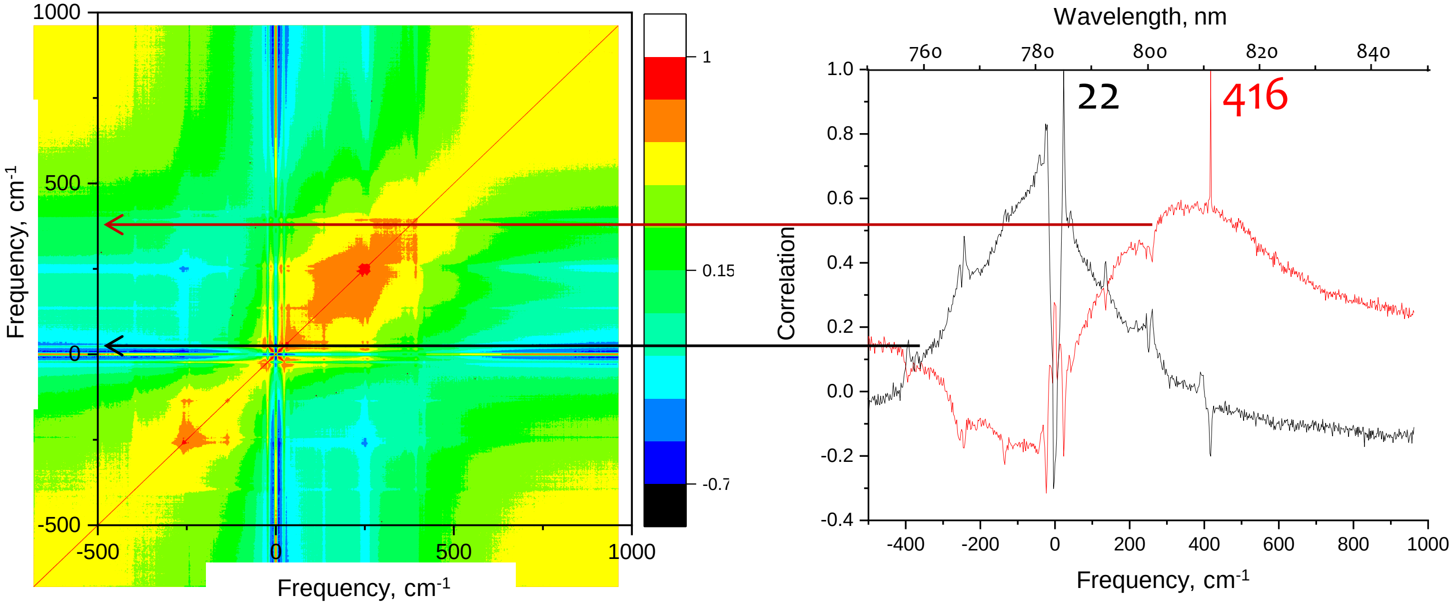


Gapped-mode TERS on TMDC heterobilayers



Rodriguez *et al. J. Phys. Chem. Lett.* 2022, 13, 5854

Gapped-mode TERS on TMDC heterobilayers



- IL phonon (~22 cm^{-1}) anticorrelates A_1 mode of WS_2 (416 cm^{-1})
- (anti)correlation of phonons with exciton – tool for investigating exciton-phonon coupling

correlation coefficient (also called Pearson's correlation coefficient (PCC), r_{xy}) is calculated for each Raman shift

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}}$$

where x_i and y_i are the Raman spectrum intensities at **x** and **y** Raman shifts

Rodriguez *et al. J. Phys. Chem. Lett.* 2022, 13, 5854

Conclusions

High lateral resolution is beneficial when interpreting spectroscopy

(Raman, PL) data in 2D materials!

Thank you for your attention!