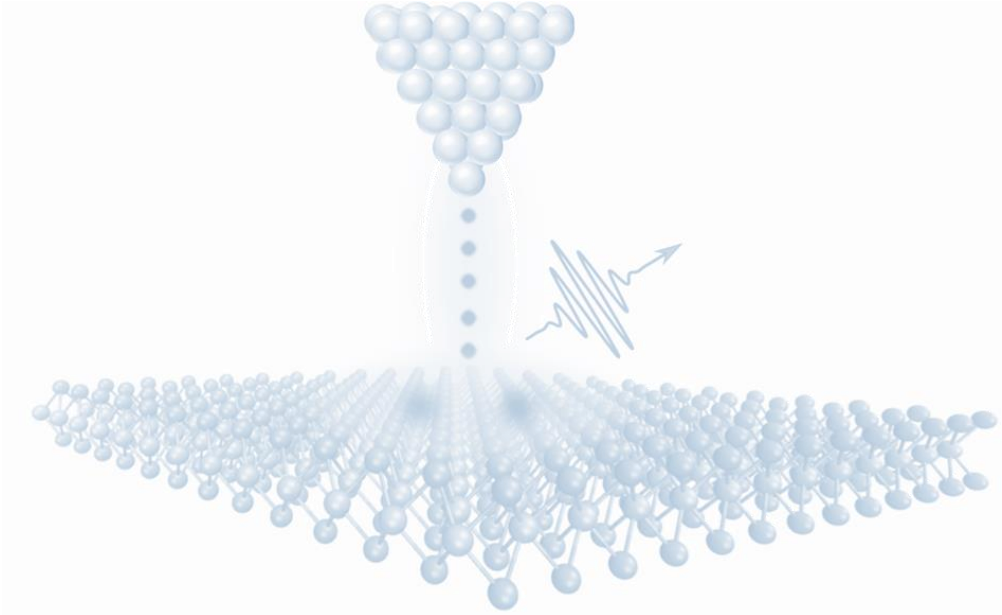
Université de Strasbourg

Institut de Physique et Chimie des Matériaux de Strasbourg

Optical spectroscopy and nanoscopy in 2D semiconductor/graphene van der Waals heterostructures



Stéphane BERCIAUD

Université de Strasbourg - CNRS - IPCMS - France

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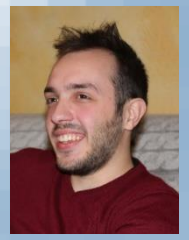
Quantum Nanophotonics| Benasque | March 14, 2023

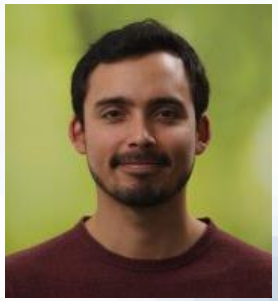
Acknowledgements

Team (as of 03/2023):
Loïc Moczko (PhD 2019-)
Aditi Moghe (PhD 2020-)
Joanna Wolff (PhD 2021-)
Arnaud Gloppe (CNRS)




More info https://fcbg.team

Previous members:
Luis E. Parra-López (joint PhD 2017-21)
Etienne Lorchat (PhD 2015-19)
Xin Zhang (Postdoc 2016-19)
G. Froehlicher (PhD 2013-2016)



Local Collaborators:
H. Majjad (IR) + StNano staff
M. Romeo (IR)
F. Fras (Unistra)
J.-F Dayen (Unistra)

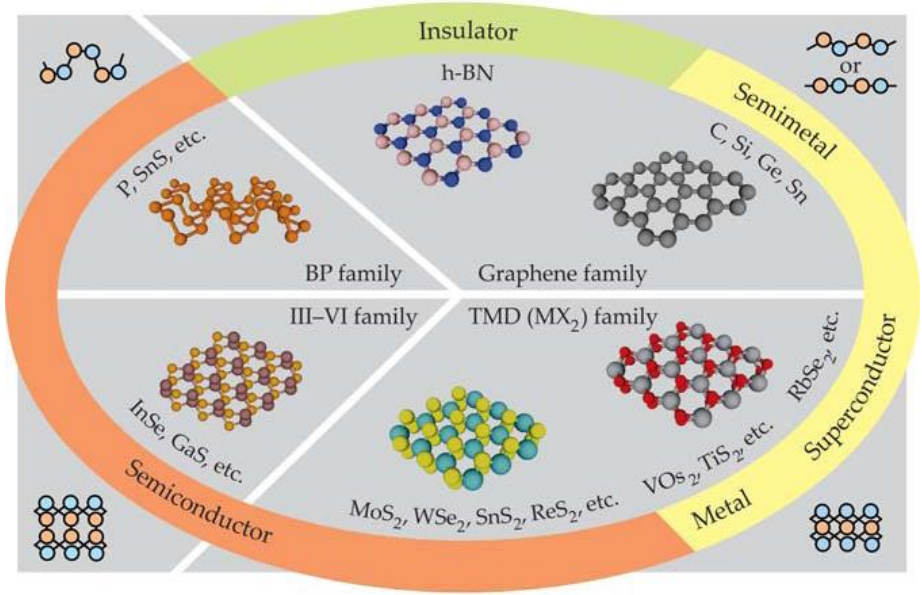
STM Team
G. Schull
A. Roslawska
F. Scheurer
V. Speisser



External collaborations
LPCNO-INSA Toulouse (**C. Robert, D. Lagarde, X. Marie**)
ISMO (**E. Le Moal** *et al.*)
ISIS (C. Genet *et al.*)
Uni. Luxembourg (S. Reichardt, L. Wirtz)
La Sapienza - Rome (T. Scopigno *et al.*)
NIMS (T. Taniguchi, K. Watanabe)

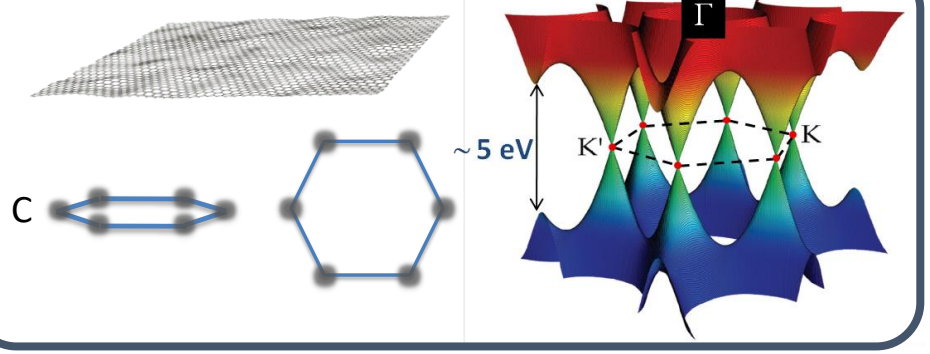
Funding:

Entering "Flatland"



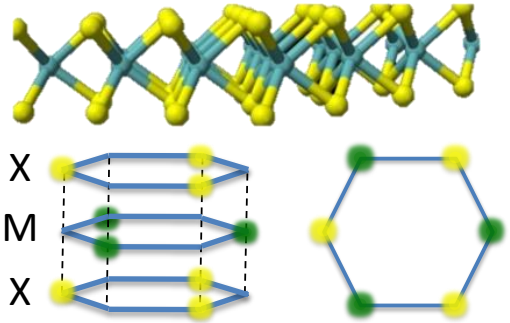
Ajayan, Kim, Banerjee - Physics Today (2016)

Graphene (semimetal)

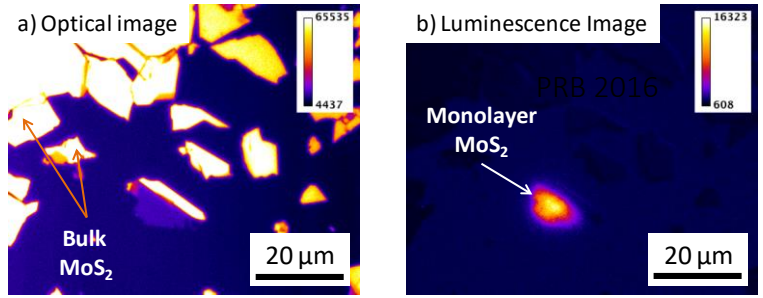


2H-TMD (semiconductors)

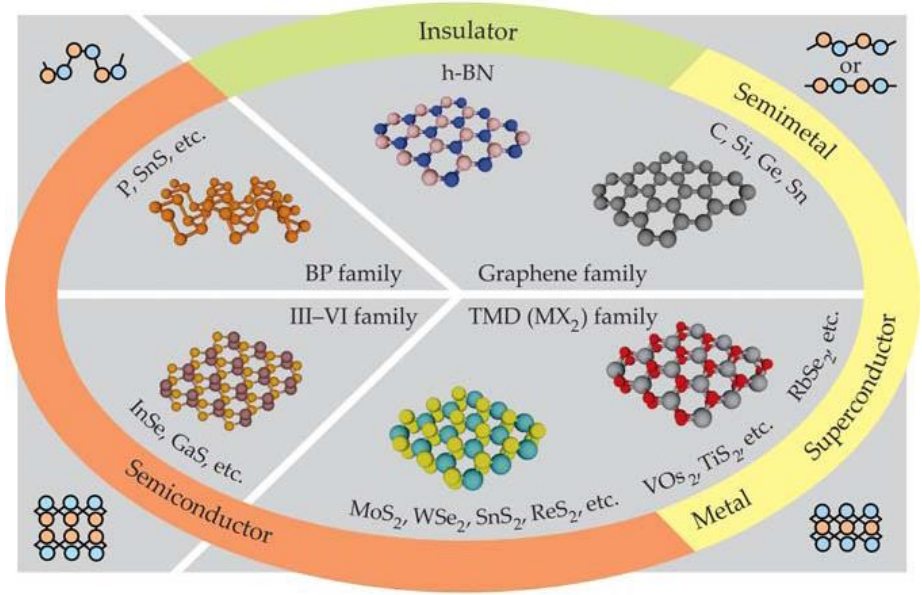
M= Mo, W X= S, Se, Te



Direct bandgap emission



Entering "Flatland"



Ajayan, Kim, Banerjee - Physics Today (2016)

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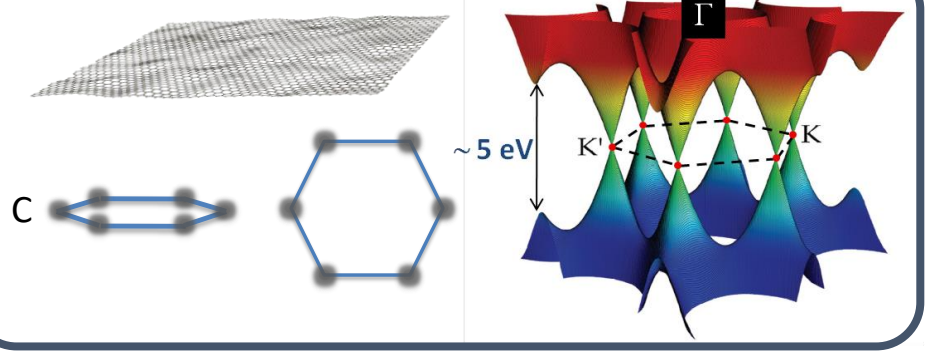

2H-TMD (semiconductors)

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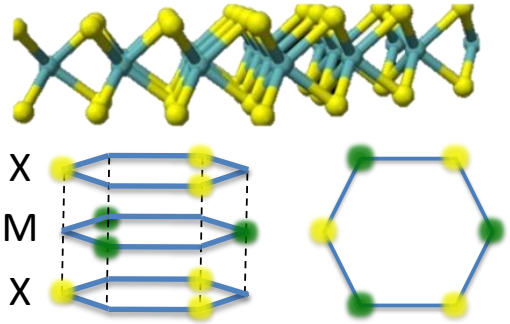
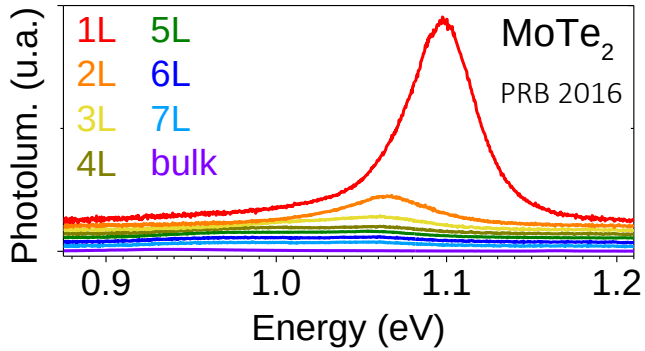
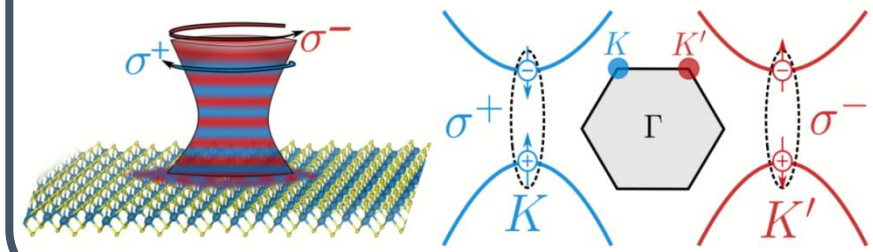


Direct bandgap emission



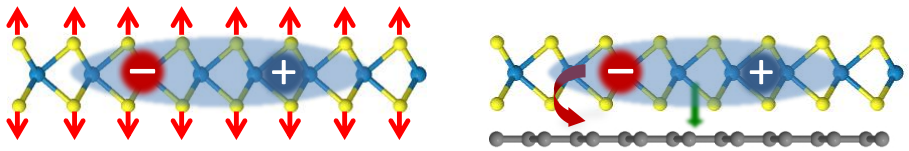
Helicity-dependent valley addressability



Who we are - What we do

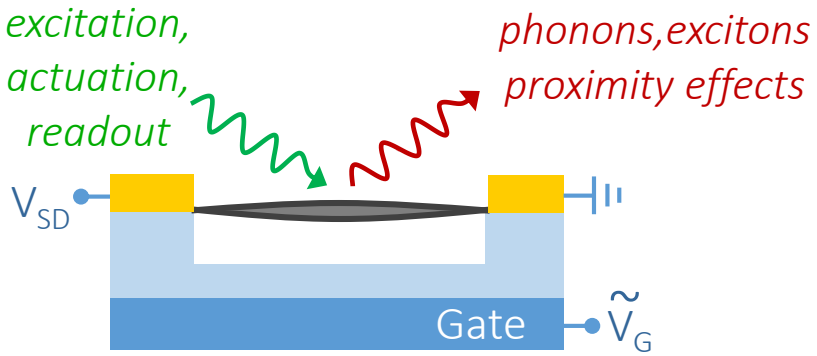
Nano-optics and low-D materials | fcbg.team

- Excitons, phonons and interfacial coupling in van der Waals heterostructures



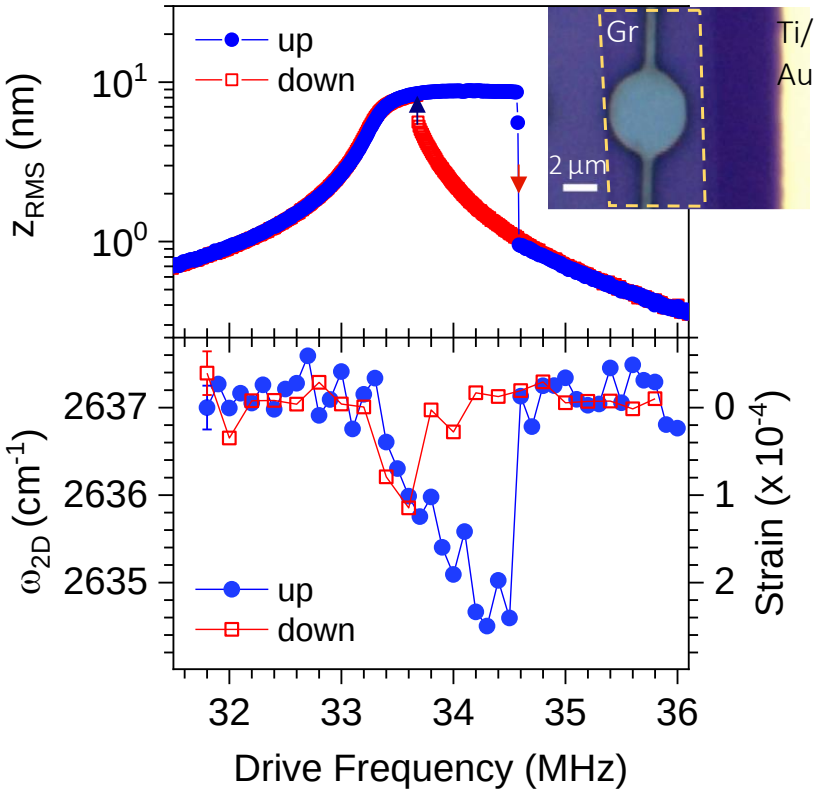
G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8**, 011007 (2018)

- Opto-electromechanics



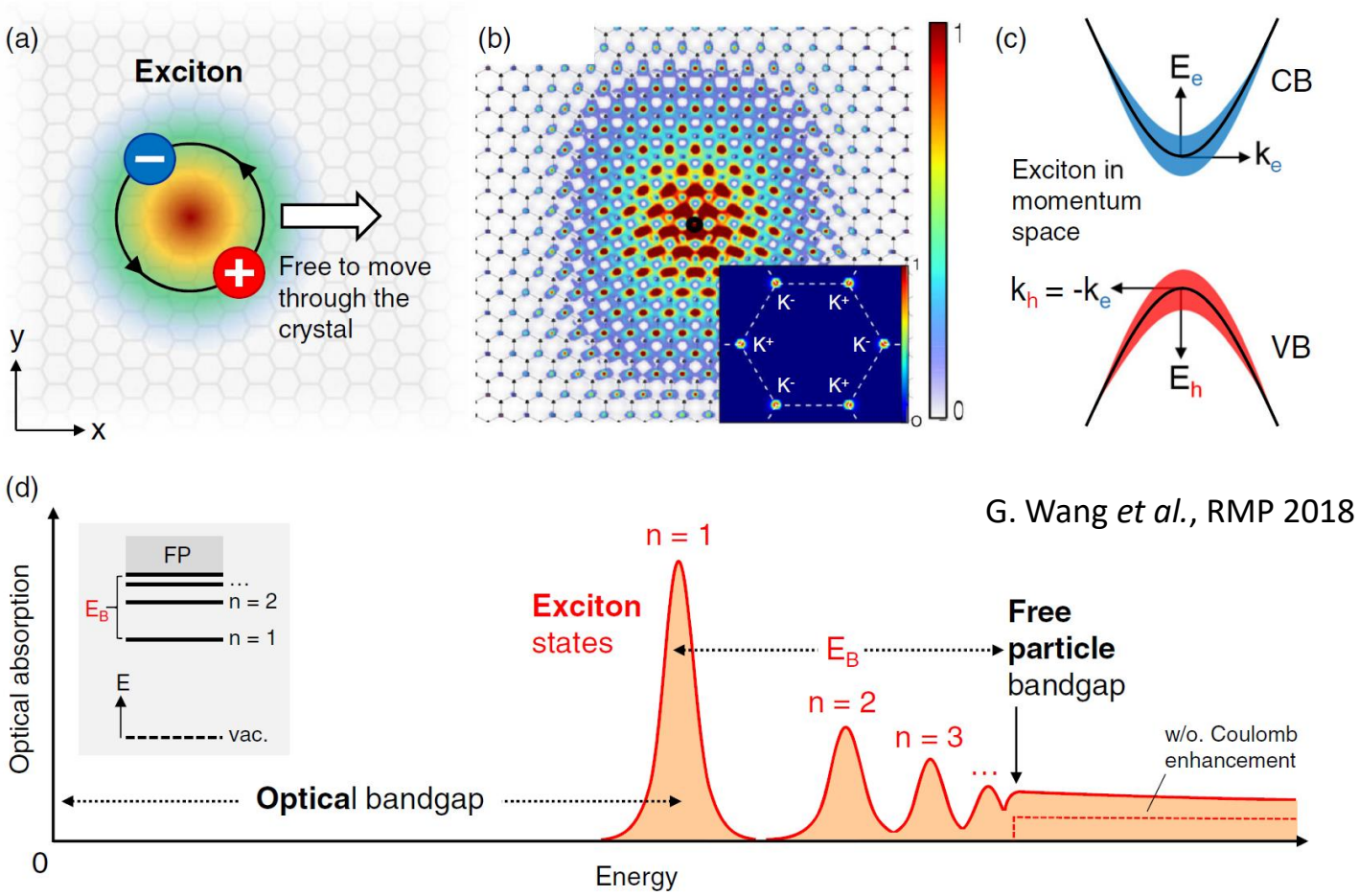
L. Moczko, PhD Thesis, J. Wolff PhD Thesis

Dynamically enhanced strain in a graphene resonator



X. Zhang, *et al.*, Nat. Commun. **11**, 5526 (2020)

Tightly bound excitons in TMDs

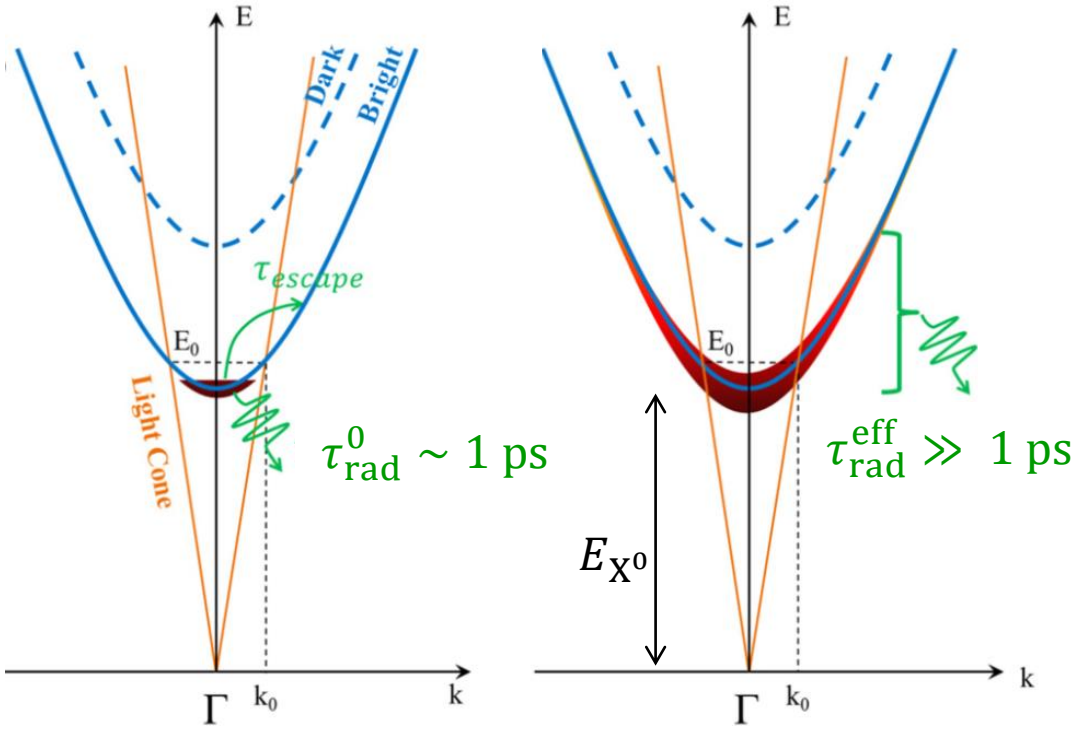


G. Wang *et al.*, RMP 2018

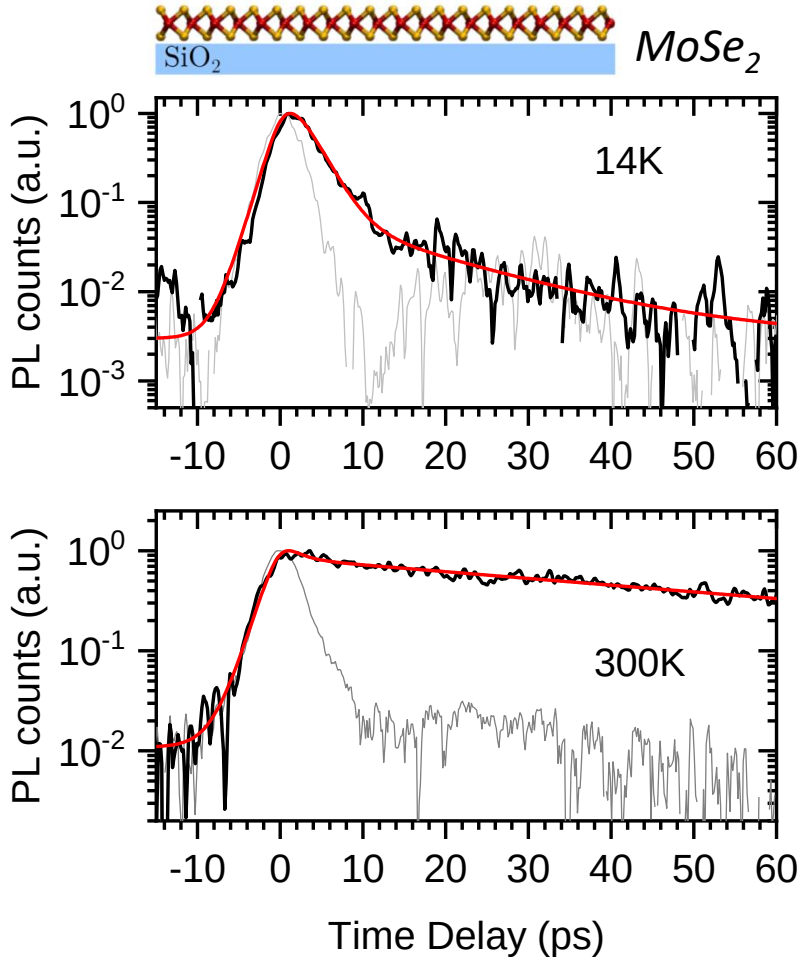
$$E_b = \frac{e^2}{2\pi\,\varepsilon\,a_0} \approx 500\ \text{meV} \qquad a_0 = \frac{4\pi\varepsilon\,\hbar^2}{\mu e^2} \approx 1\ \text{nm}$$

μ: exciton reduced mass
ε: dielectric constant

Temperature-dependent exciton dynamics



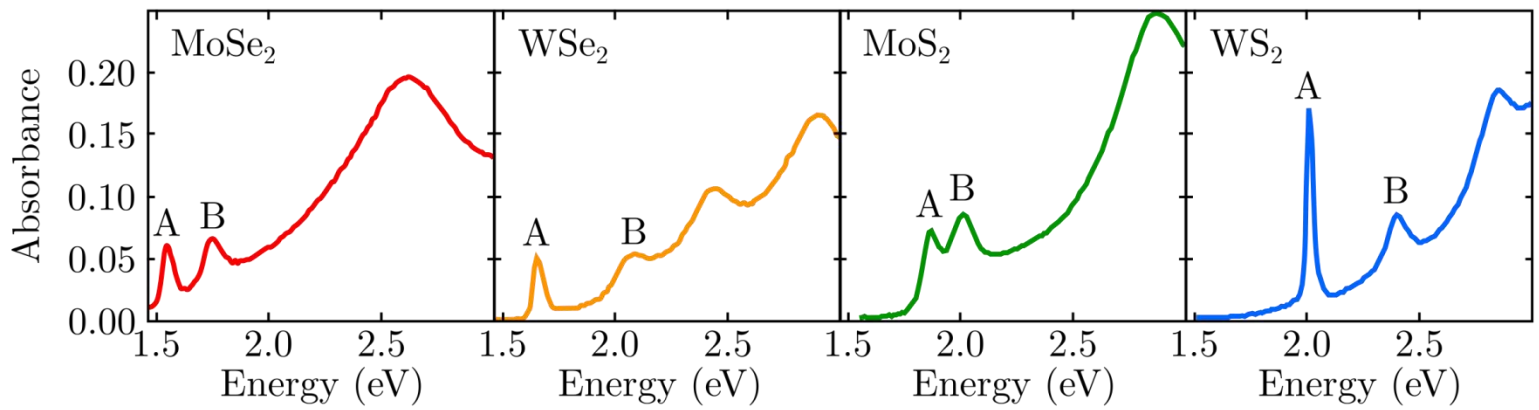
C. Robert *et al.* PRB, **93**, 205423 (2016)

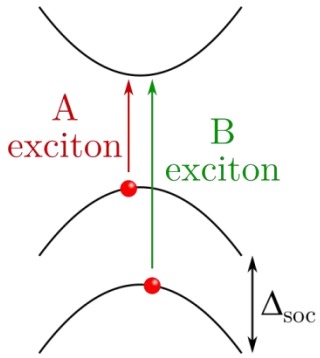


$$\tau^0_{rad} = \frac{1}{2\Gamma^0_{rad}} = \frac{\hbar\,\varepsilon}{2k_0}\left(\frac{E_{X^0}}{e\hbar v}\right)^2 a_0^2 \qquad \tau^{eff}_{rad} = \frac{3}{2}\frac{k_B T}{E_0}\tau^0_{rad}$$

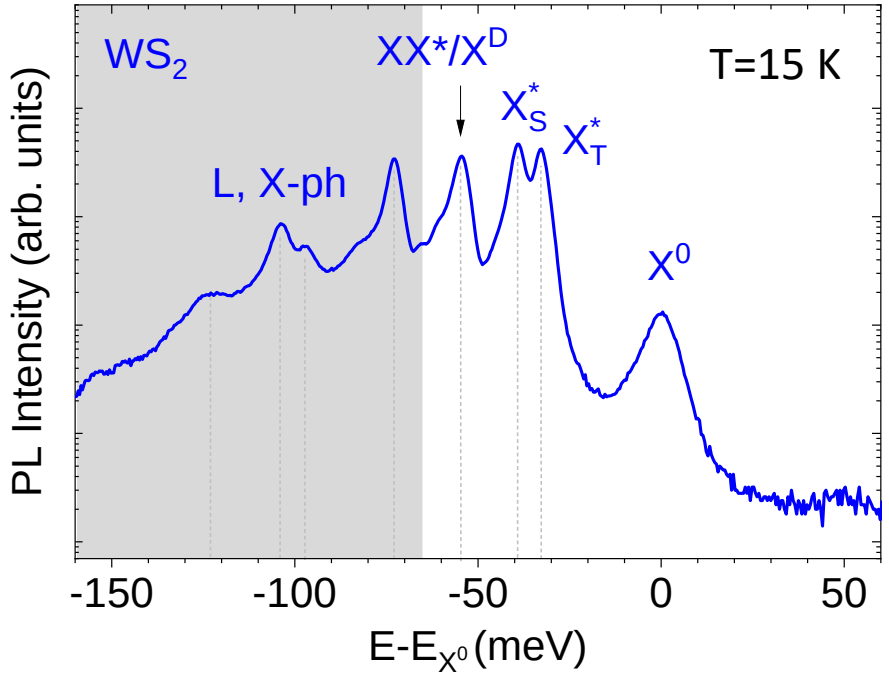
Collaboration : INSA Toulouse
(C. Robert, D. Lagarde, X. Marie)

Light absorption and emission in TMDs





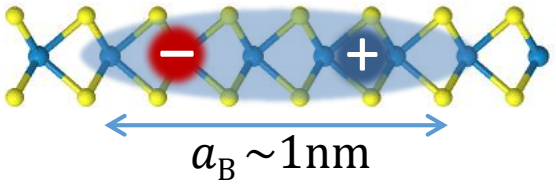
Y.Li *et al.* Phys. Rev. B **90**, 205422, 2014



- $\tau_{X^0} \ll \tau_{X^*}, \tau_{XX^*}, \tau_{X^D}, \tau_L$
- *A spectroscopist's paradise?*

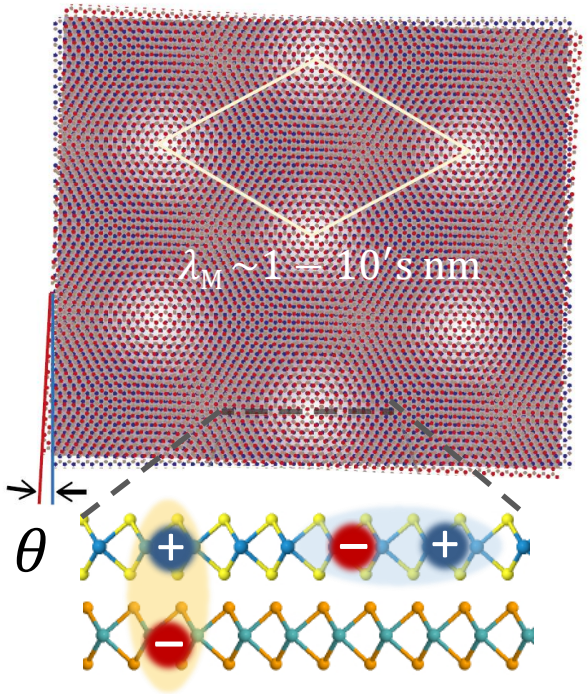
or…too complicated PL spectra?

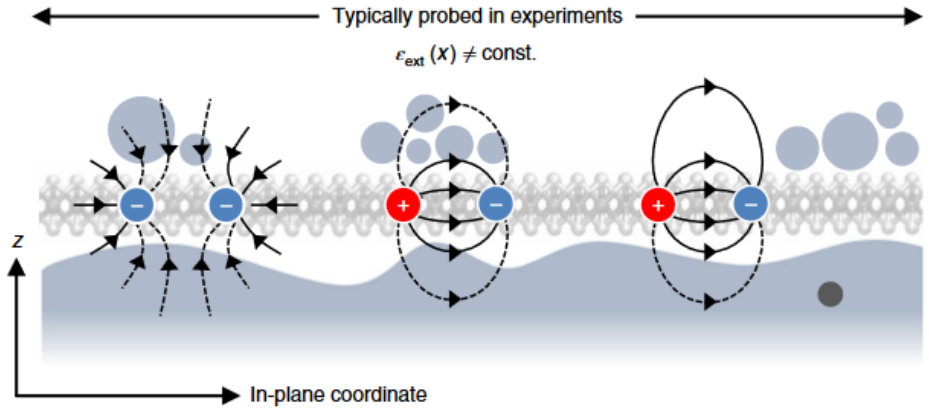
Rich exciton physics…governed by nanoscale phenomena



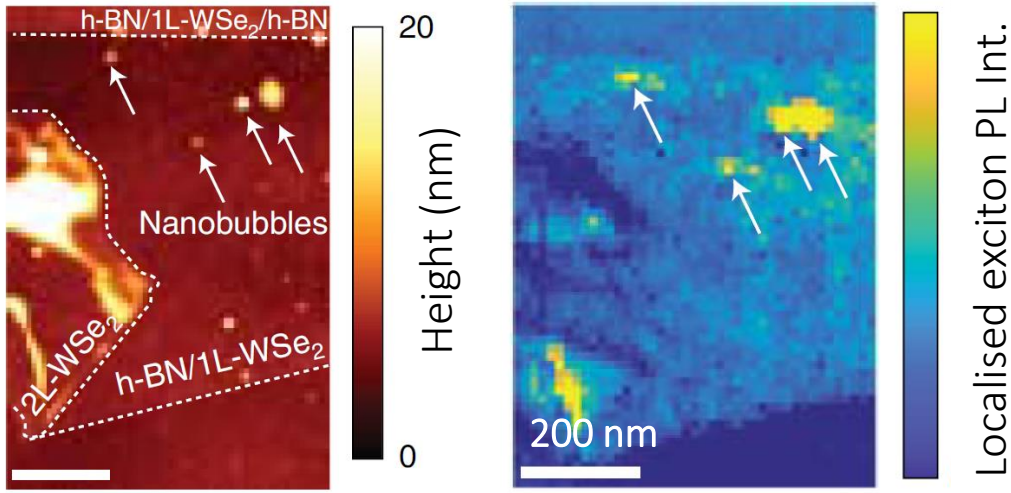
- Dielectric disorder
- Residual doping
- Strain gradients
- (too many?) defects
- Atomic reconstruction
- …

K. Seyler *et al.*, Nature **567**, 66 (2019)





A. Raja *et al.*, Nat. Nano **14**, 832 (2019)



T. Darlington *et al.*, Nat. Nano. 15, 854 (2020)

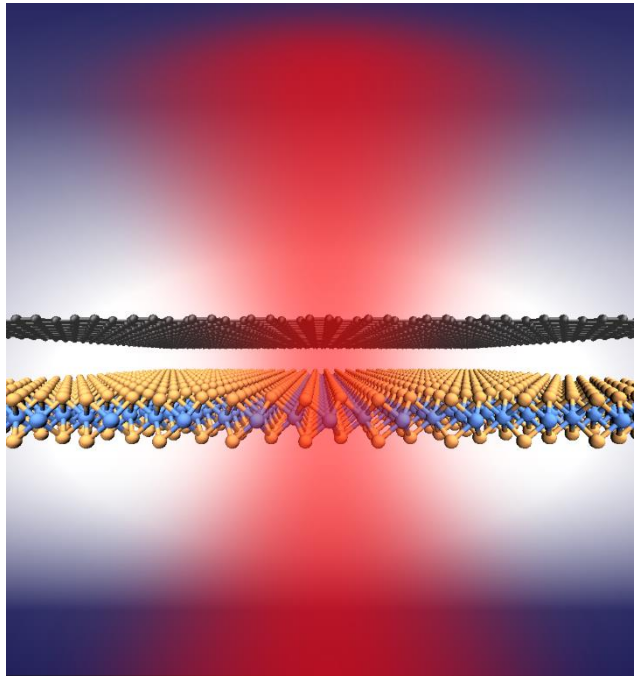
Main objective: Tailoring the properties of excitons at ultimate scales (sub-nm, sub-ps)

Our approach:

- van der Waals engineering
- STM-based quantum photonics in atomically-resolved van der Waals materials

Today's menu

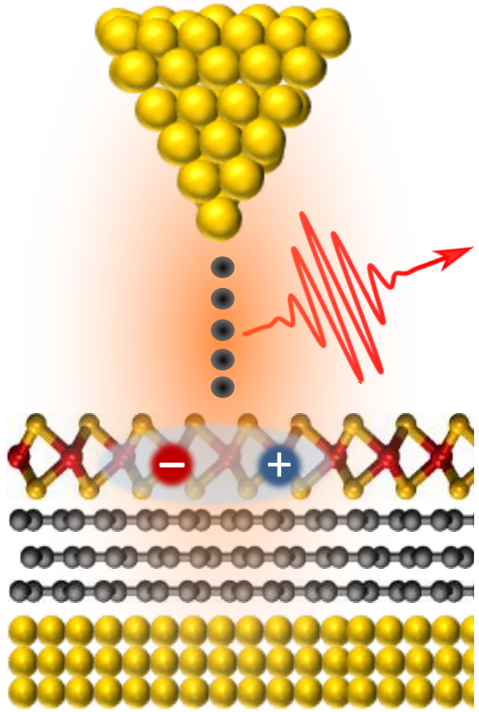
Tailoring interfacial coupling



G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8,** 011007 (2018)

E. Lorchat*, L. Parra-López* *et al.* Nature Nanotechnology **15**, 283 (2020)

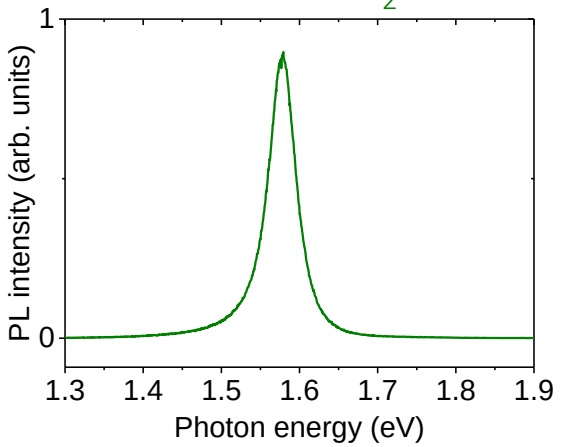
Tip-induced luminescence

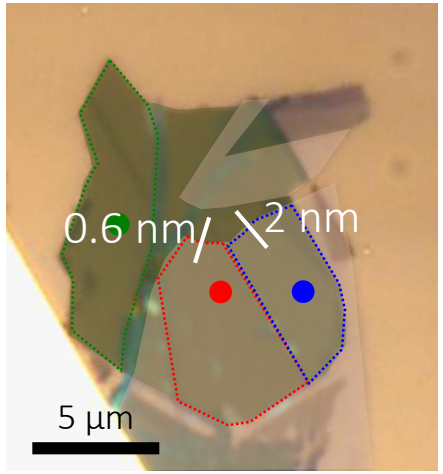


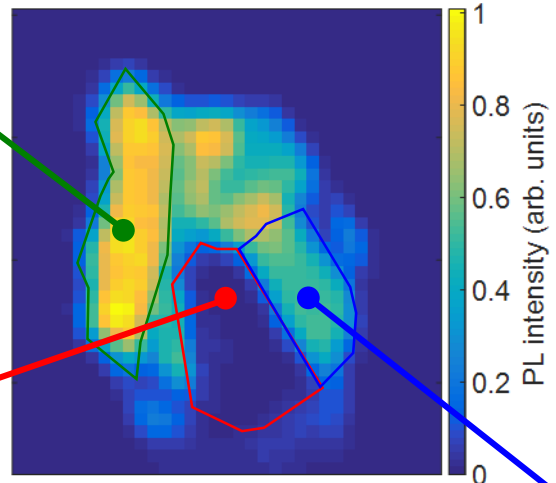
L. Parra-López *et al.* Nature Materials (in press, 2023)
see also: arXiv:2204.14022

Massive PL quenching at room T

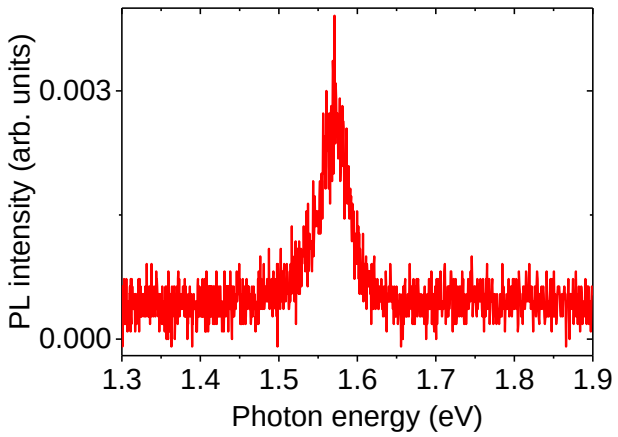
Bare $MoSe_2$





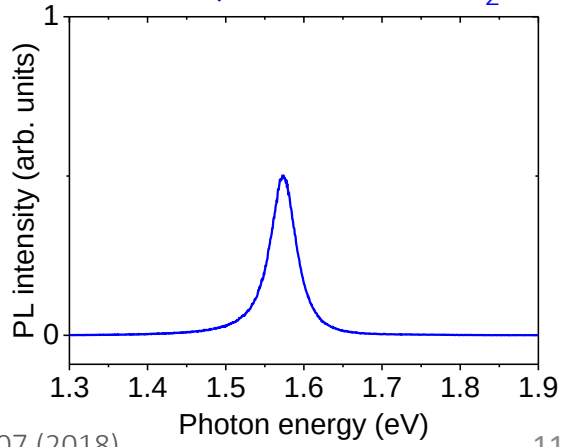


Coupled Gr/$MoSe_2$



➡ Quenching factor ~ 300

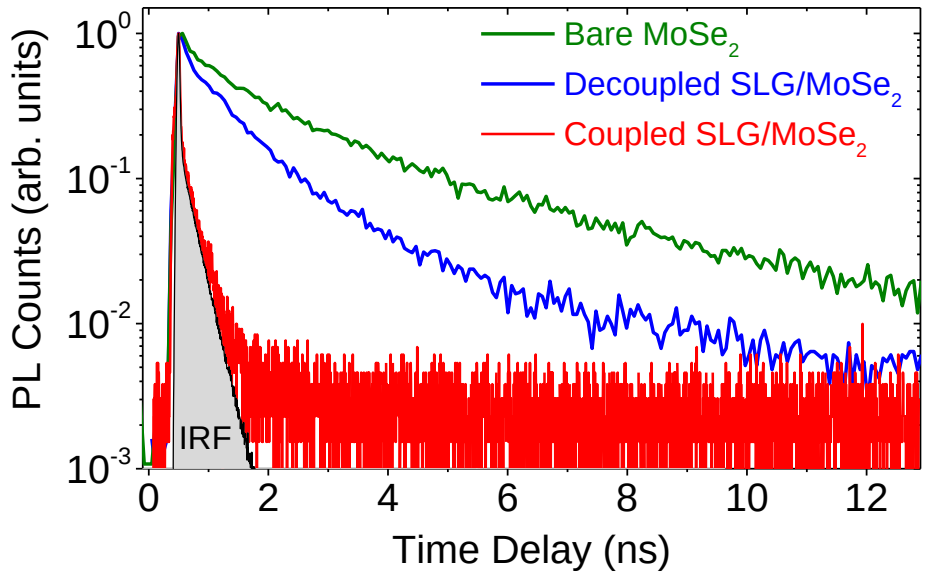
Decoupled Gr/$MoSe_2$



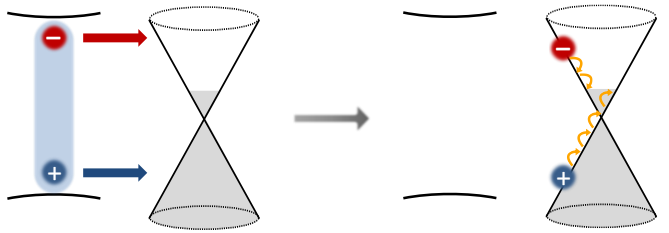
G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8,** 011007 (2018)

Picosecond energy transfer

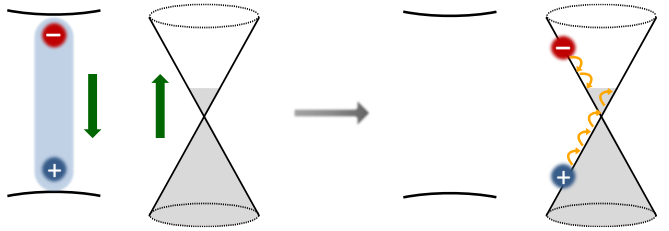
T=300 K



Tunelling mediated processes (short range)



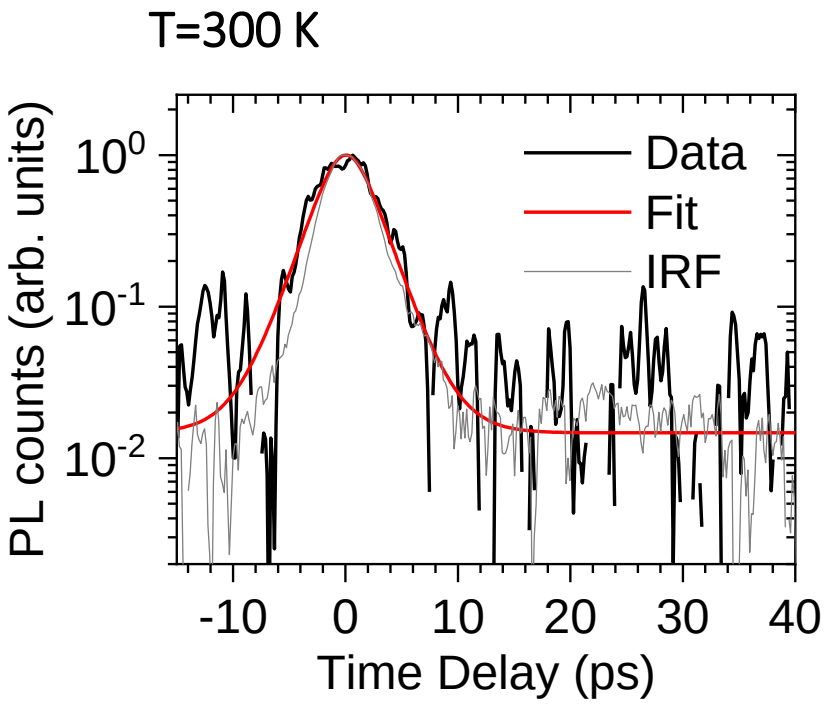
Dipole-dipole interaction (longer range)



- Long exciton lifetime in TMD monolayers at 300 K
  → Graphene induces massive quenching

For details, see: G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8**, 011007 (2018)

Picosecond energy transfer



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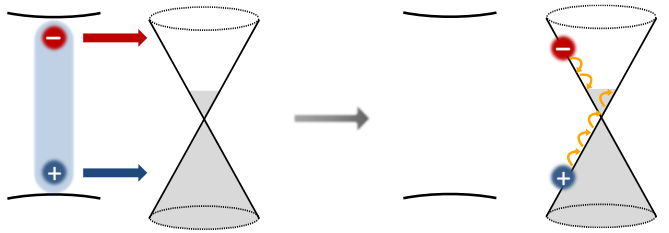

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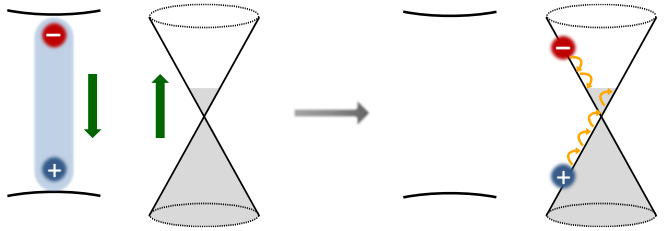
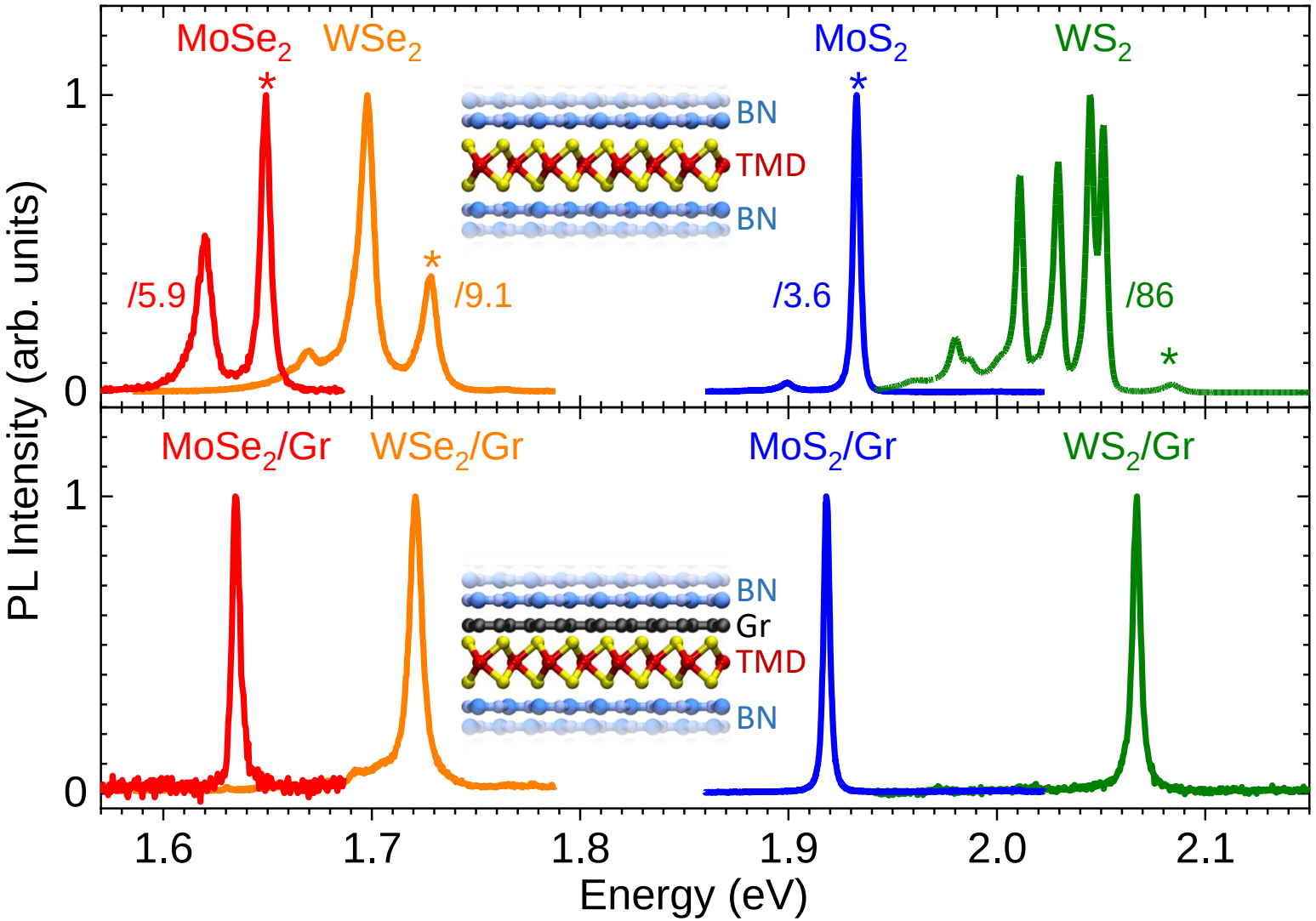


- Long exciton lifetime in TMD monolayers at 300 K
  → Graphene induces massive quenching

→ *Question: what happens at low temperature?*

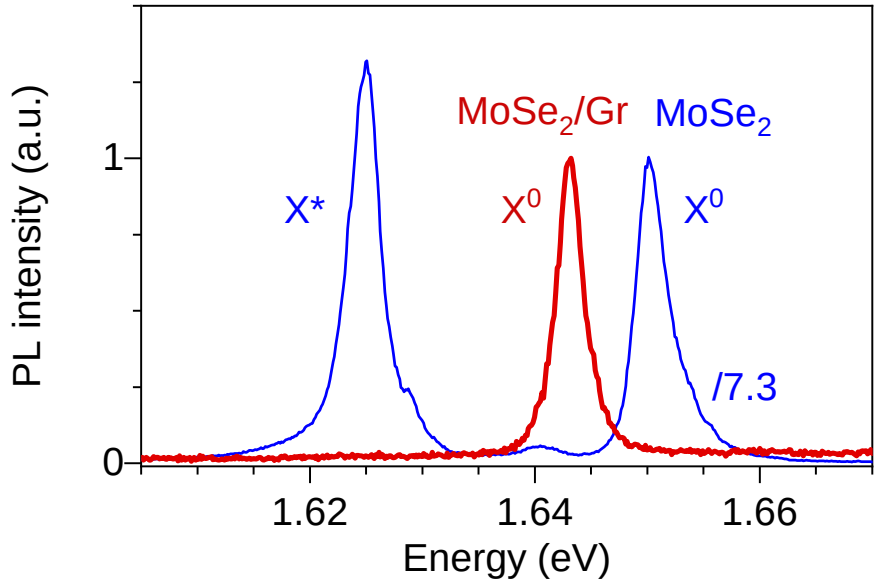
For details, see: G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8**, 011007 (2018)

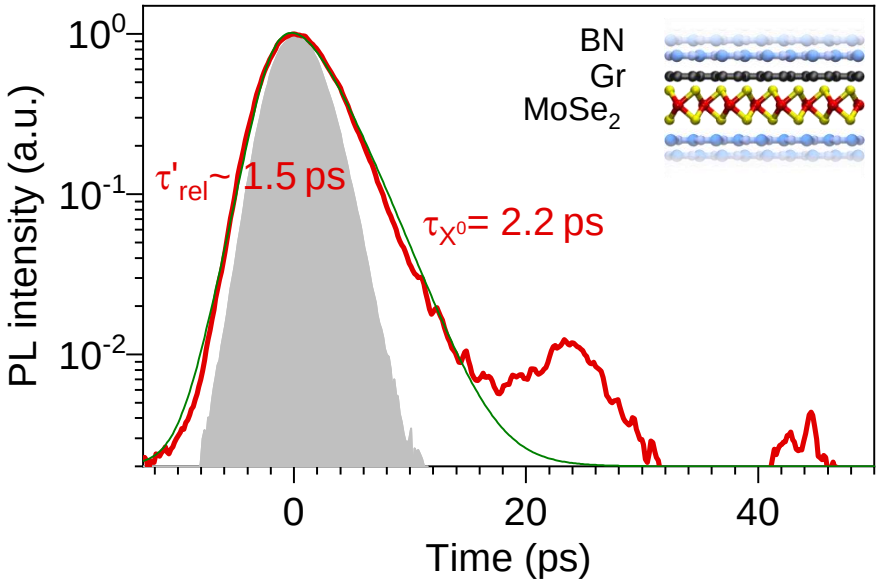
Answer: graphene ‘filters’ TMD PL spectra



E. Lorchat*, L. Parra-López* *et al.* Nature Nanotechnology **15**, 283 (2020)

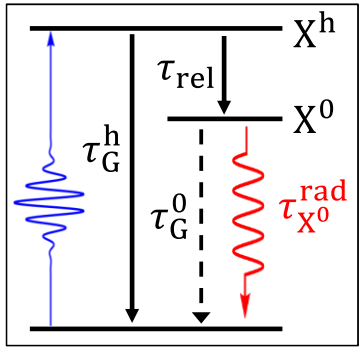
Estimating the exciton transfer time



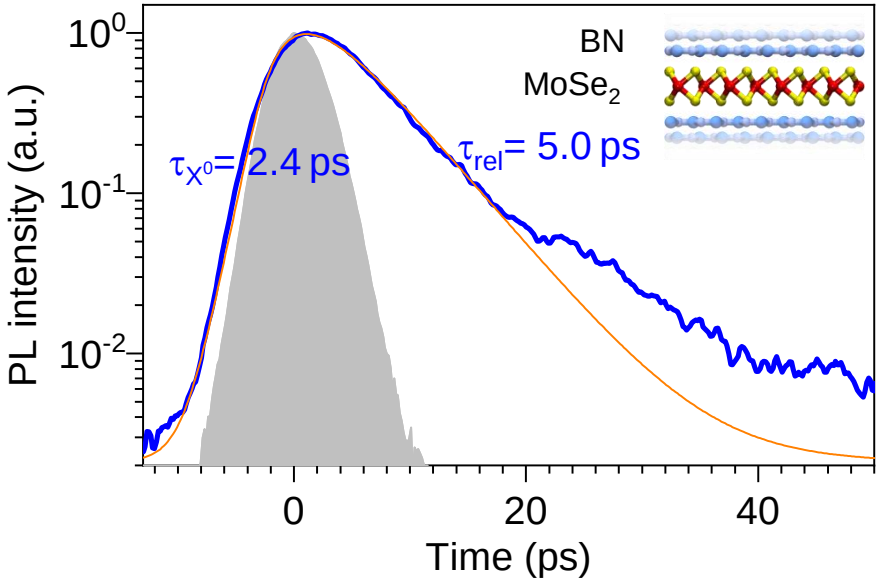


- $\tau_G^0 = \frac{\tau_{X^0}^{rad}\,\tau_{X^0}}{\tau_{X^0}^{rad} - \tau_{X^0}} \sim 4$ ps
- $\eta_{X^0} = \frac{\tau_G^0}{\tau_{X^0}^{rad} + \tau_G^0} \sim 50\%$

$\rightarrow \tau_G^h \gg \tau_G^0$



➢ *Energy dependent exciton transfer*



Partial conclusion

✓ *Selective ps energy transfer yields bright, narrow line emission*

→ Microscopic mechanism?

→ Electrical control, cavity control

✓ *A 2D semiconductor coupled to a quasi-transparent 2D electrode*

→Towards fast (up to ~ THz emission rate) electroluminescent devices approaching the homogeneous limit

nature nanotechnology

ARTICLES

https://doi.org/10.1038/s41565-020-0644-2

Check for updates

Filtering the photoluminescence spectra of atomically thin semiconductors with graphene

Etienne Lorchat[1,5], Luis E. Parra López[1,5], Cédric Robert[2], Delphine Lagarde[2], Guillaume Froehlicher[1], Takashi Taniguchi[3], Kenji Watanabe[3], Xavier Marie[2,4] and Stéphane Berciaud[1,4]

RESEARCH ARTICLE | PHYSICS

Picosecond energy transfer in a transition metal dichalcogenide–graphene heterostructure revealed by transient Raman spectroscopy

Carino Ferrante, Giorgio Di Battista, Luis E. Parra López, Giovanni Batignani, Etienne Lorchat, Alessandra Virga, Stéphane Berciaud, and Tullio Scopigno -4 Authors Info & Affiliations

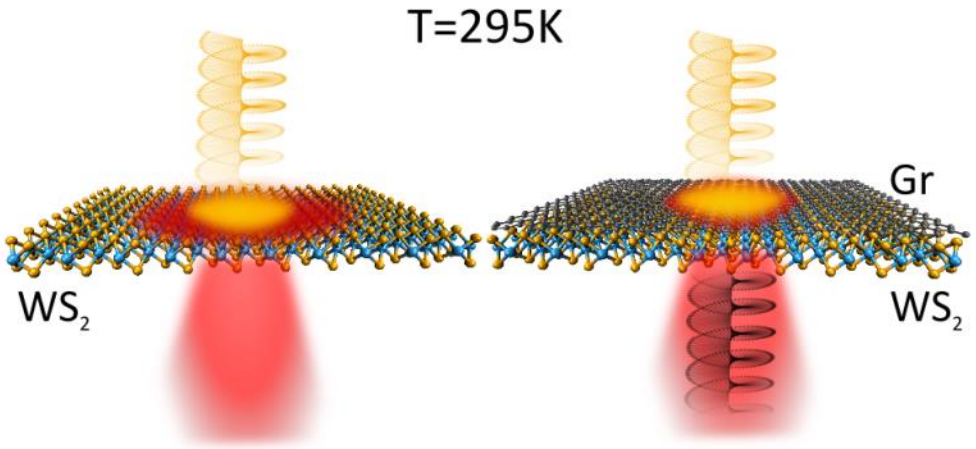
April 5, 2022 | 119 (15) e2119726119 | https://doi.org/10.1073/pnas.2119726119

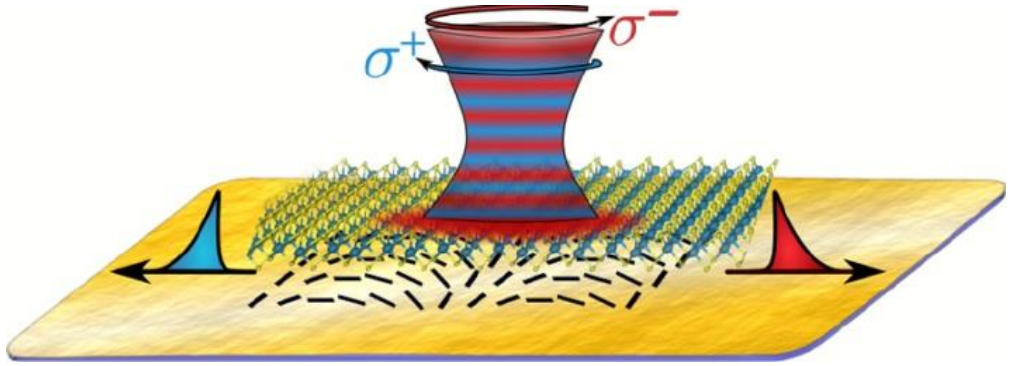
C. Ferrante *et al.*, PNAS **119**, e2119726119 (2022)

Going further

➢ *Chiral optics and valleytronics* *(with C. Genet, S. Azzini, T. Chervy, T. Ebbesen)*

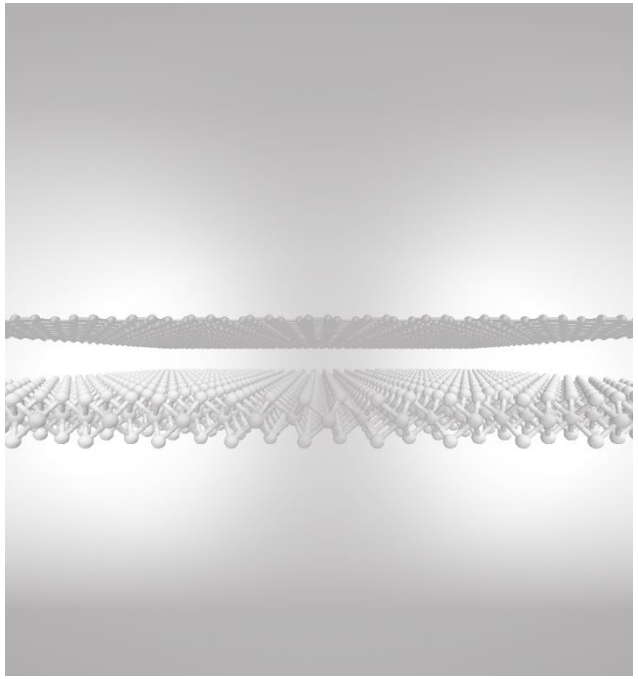
E. Lorchat*, S. Azzini*, T. Chervy *et al.*, ACS Photonics 5, 5047 (2018) | T. Chervy*, S. Azzini*, *et al.*, ACS Photonics 5, 1281 (2018)





Today's menu

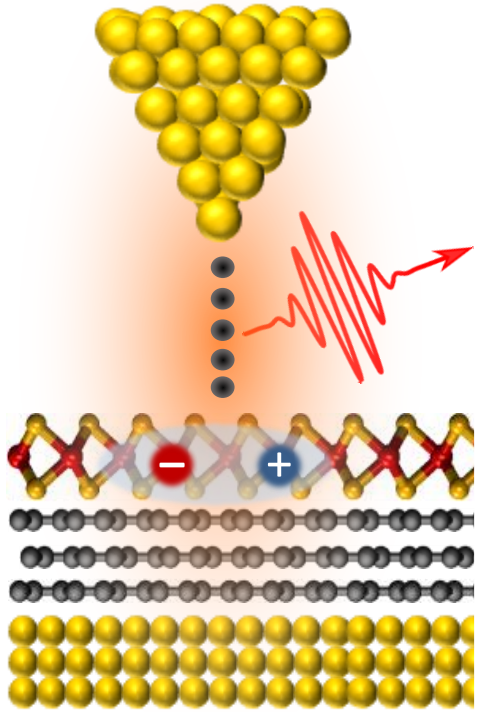
Tailoring interfacial coupling



G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8**, 011007 (2018)

E. Lorchat*, L. Parra-López* *et al.* Nature Nanotechnology **15**, 283 (2020)

Tip-induced luminescence

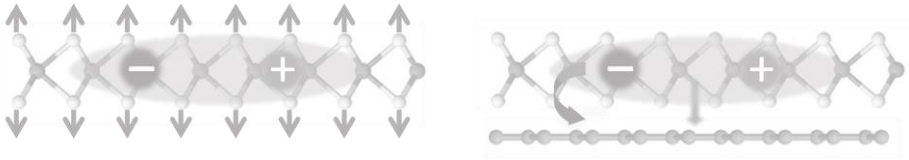


L. Parra-López *et al.* Nature Materials (in press, 2023)
see also: arXiv:2204.14022

Who we are - What we do

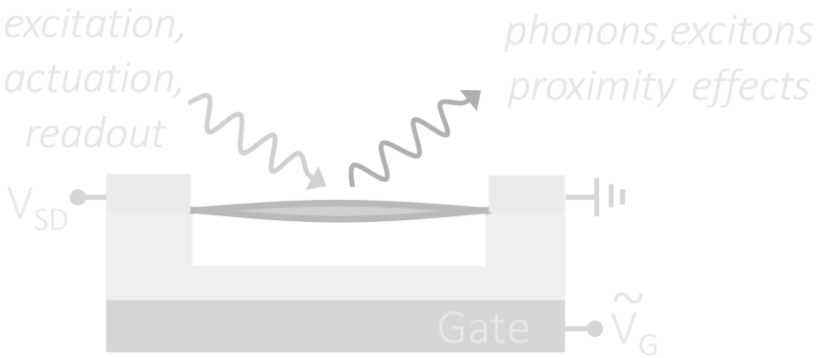
Nano-optics and low-D materials (S. Berciaud, A. Gloppe)

• Excitons, phonons and interfacial coupling in van der Waals heterostructures



G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8**, 011007 (2018)

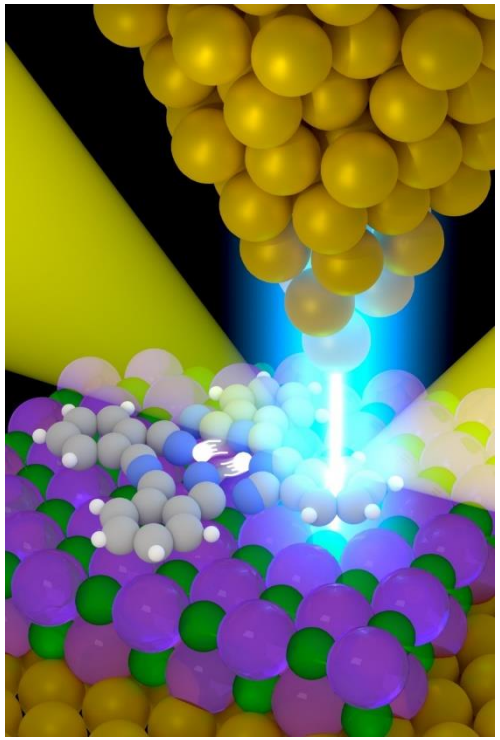
• (Magno)-opto-electro-mechanics



X. Zhang *et al.*, Nature Communications **11**, 5526 (2020)
L. Moczko, PhD Thesis J. Wolff PhD Thesis

Scanning Tunnelling Microscopy (STM) team (G. Schull *et al.*)

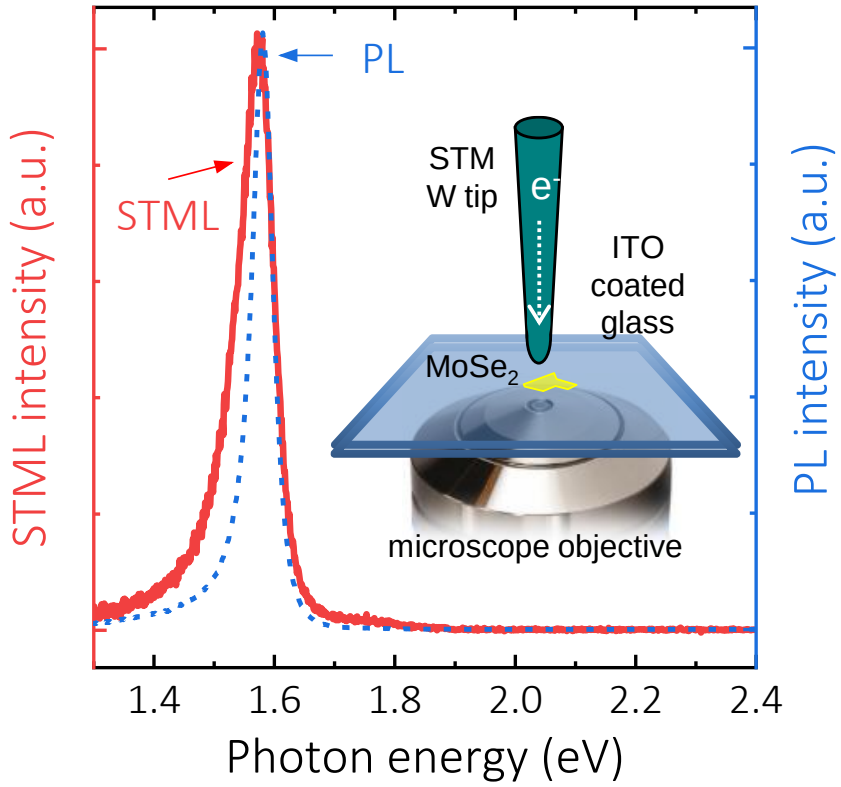
- Single molecule luminescence
  - ✓ Induced by the tunneling current (e- in, photon out)
  - ✓ Enhanced by the STM tip (photon in/ photon out)



http://www-ipcms.u-strasbg.fr/stmipcms/

STM-induced luminescence (STML) from a TMD monolayer

300 K – ambient air

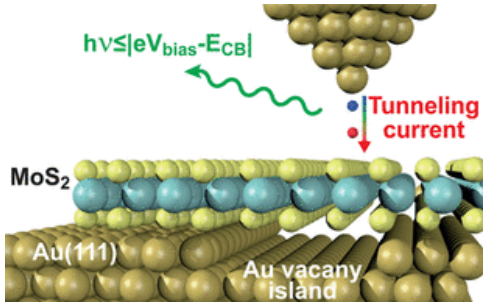


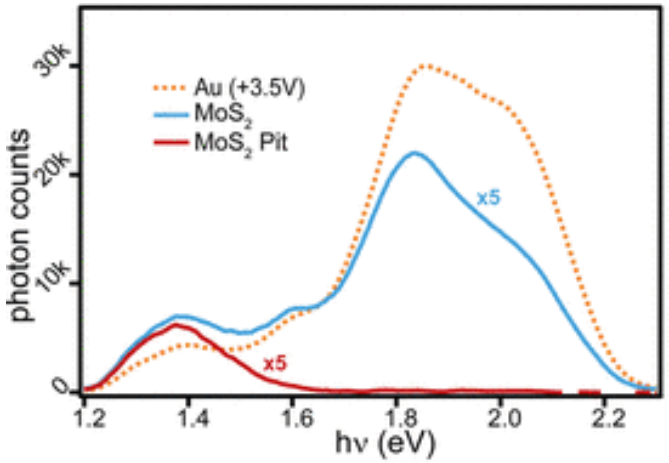
D. Pommier *et al.,* PRL **123**, 027402 (2019)
R. J. Peña Román *et al.,* PRB **106**, 085419 (2022), Nano Lett **22**, 9244 (2022)
Collaboration ISMO-IPCMS (PI: E. Le Moal)

See also: R. J. Peña Román *et al.,* Nanoscale **12**, 13460 (2020)
R. Péchou *et al.,* ACS Photonics **7**, 3061 (2020)

4K – ultra high vacuum (UHV)

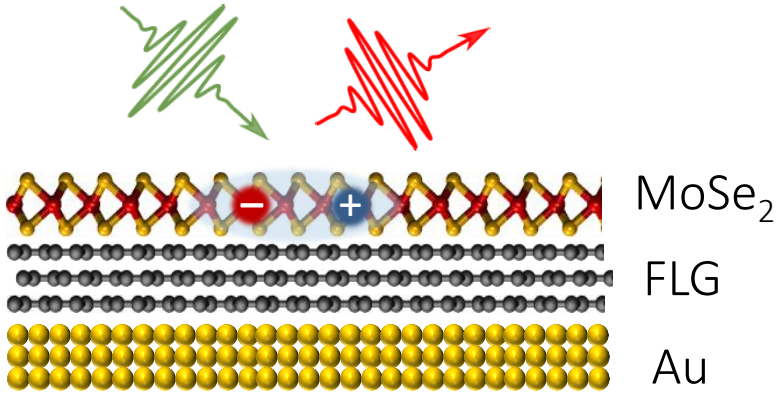
Defect-mediated broad, extrinsic emission

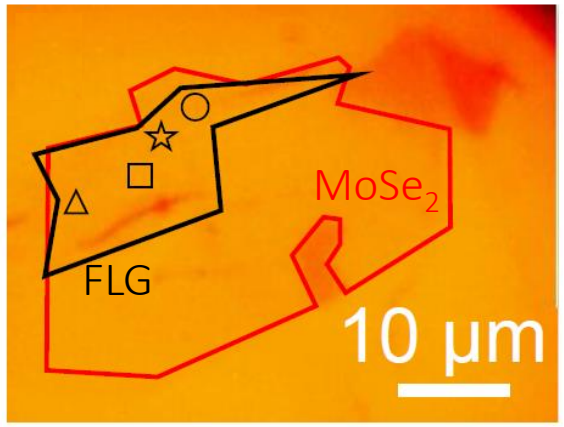




N. Krane *et al.*, Nano Lett **16**, 5163 (2016)
See also: B. Schuler *et al.*, Science Advances **6**, eabb5988 (2020)

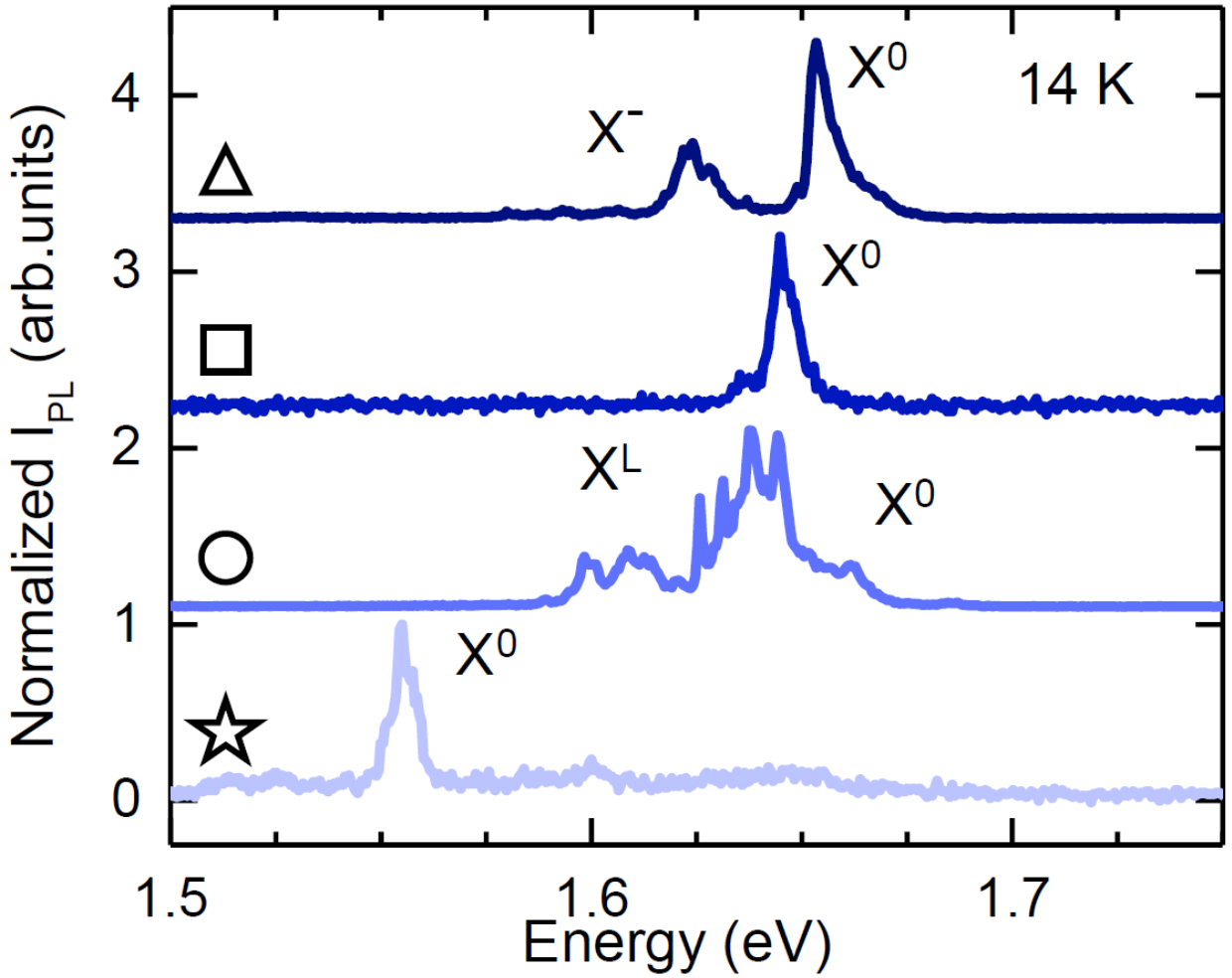
TMD/Graphene/Au: a model system for STML?



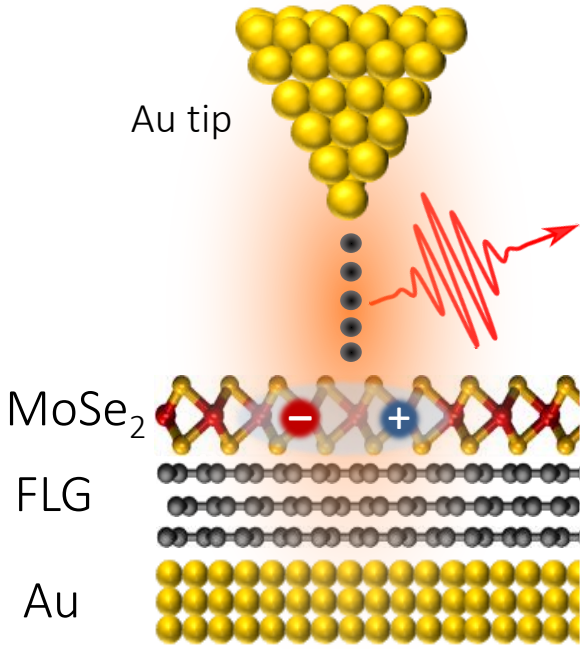


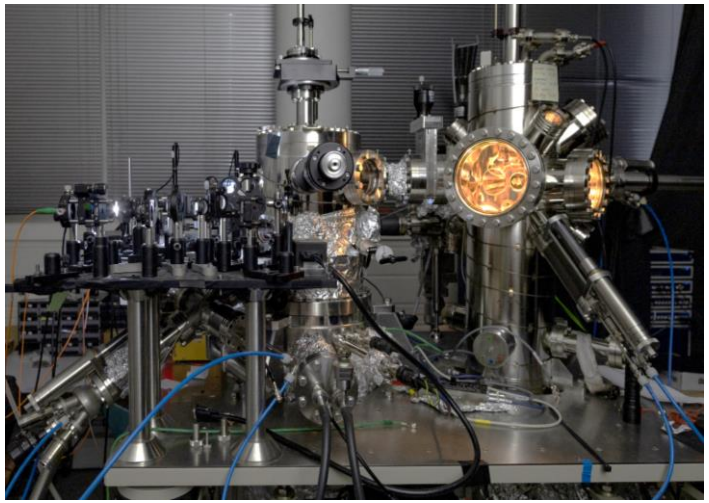
- Annealing induces local strain gradients
- Resolving this complexity using STML?

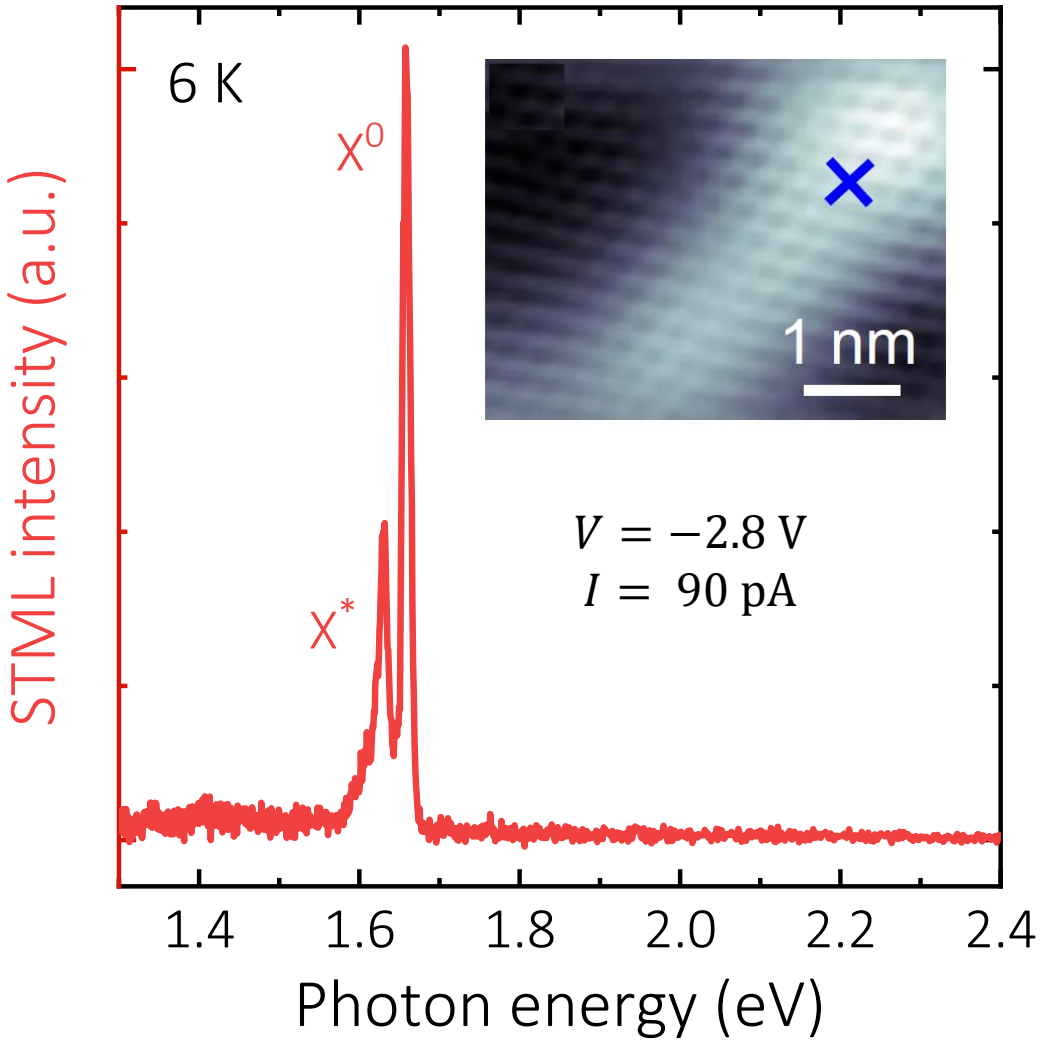
µPL characterization post annealing at 200 °C



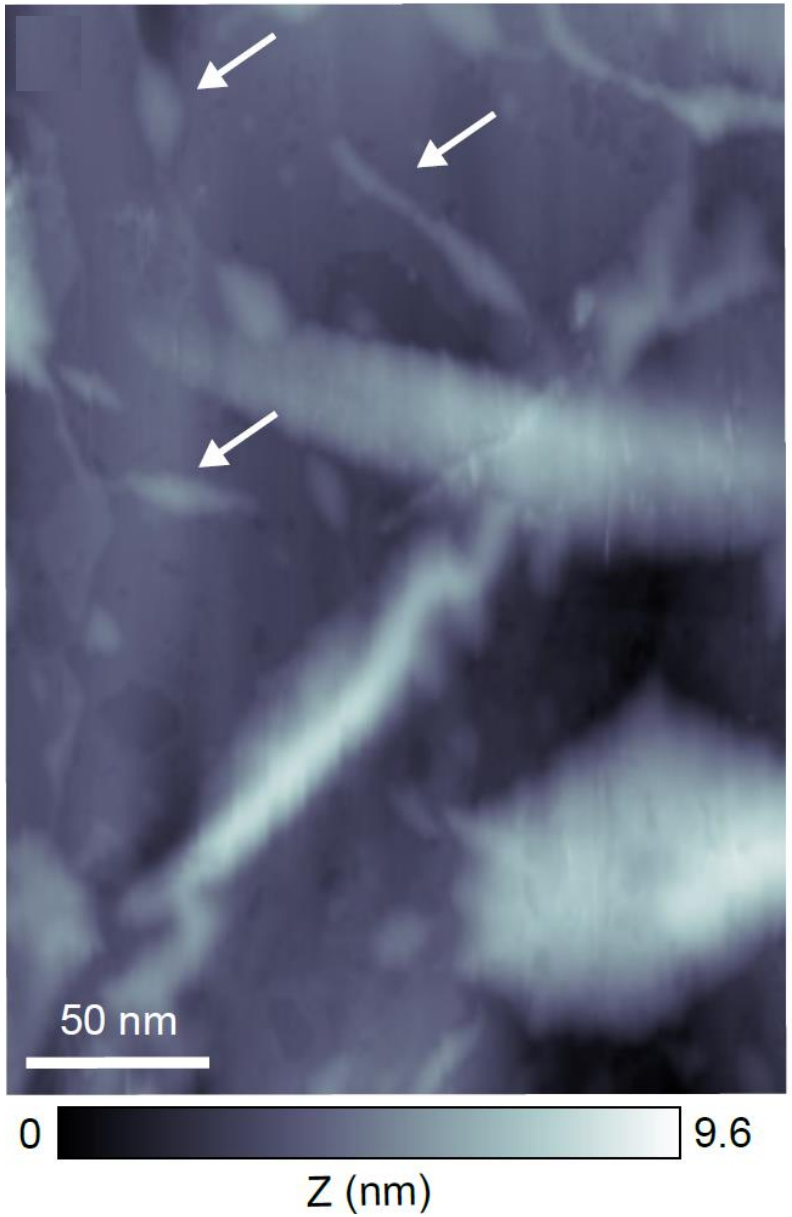
STM-induced luminescence from an atomically-resolved TMD

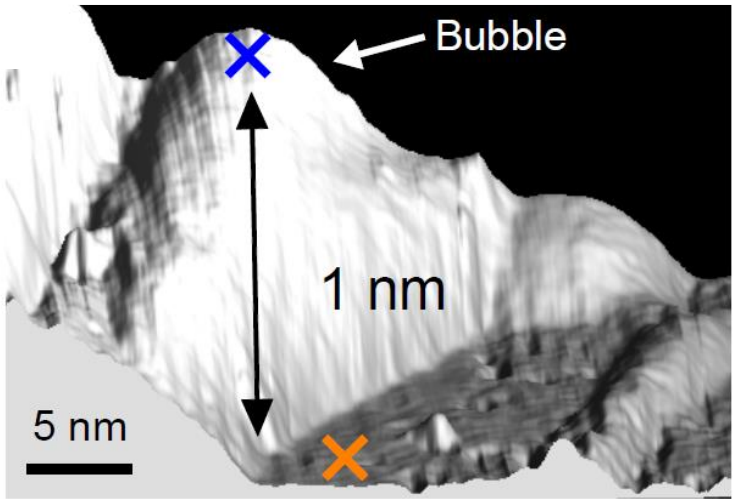


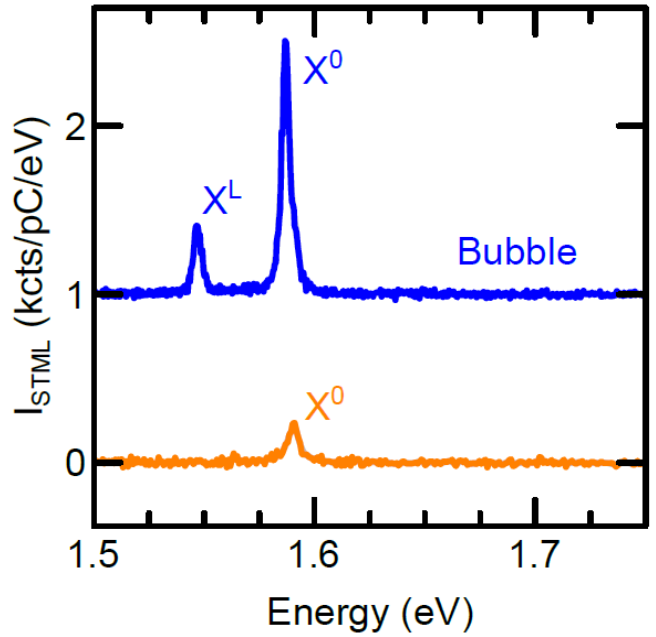




Spatially-resolved STML in an inhomogeneous nanoscale landscape

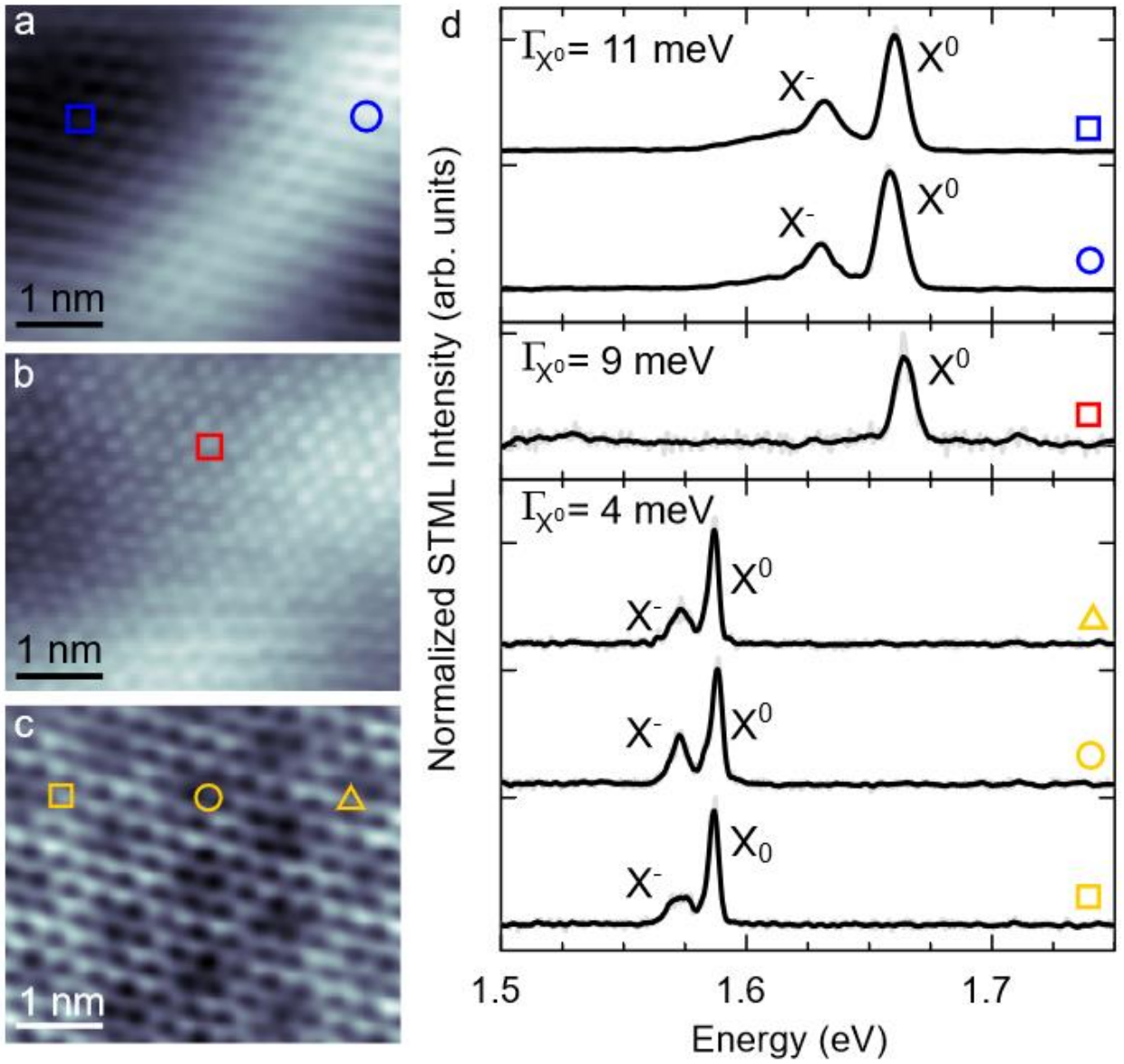






The STML spectrum varies strongly for an in-plane displacement of ≈ 5 nm
→ Upper bound of the spatial resolution

STML on atomically-resolved areas



Weakly coupled TMD/Gr/Au

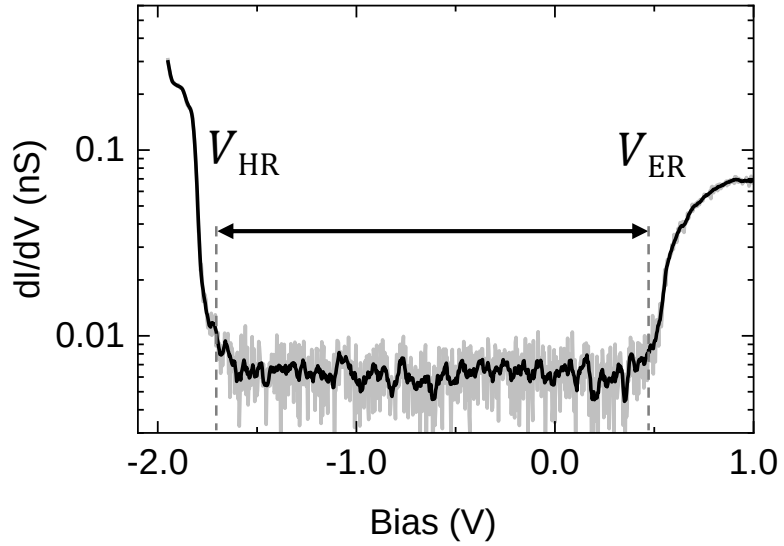
Coupled TMD/Gr
→ weaker coupling to Au

Coupled TMD/Gr/Au

$$\lambda_M \lesssim a_B$$

No expected spatial modulation of the excitonic characteristics

Proposed STML mechanism



How to understand E_G^{STS} ?

$E_G^{STS} = e(V_{HR} - V_{ER}) = 2.17$ eV

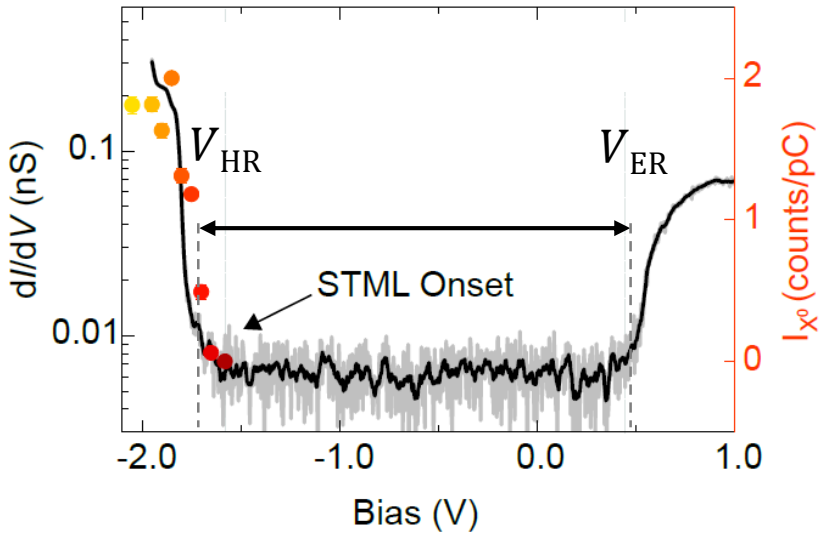
$E_G^{STS} - E_{X^0} = 0.52$ eV

$E_b \approx 150$ meV in $MoSe_2$/Gr*

*M. Goryca *et al.*, Nat. Commun. **10**, 4172 (2019)
*E. Lorchat, L. E. Parra López et al. Nature Nano **15**, 283 (2020)

See also M. Ugeda *et al.,* Nat. Mater. **13**, 1091 (2014) (PL + STS)

Proposed STML mechanism



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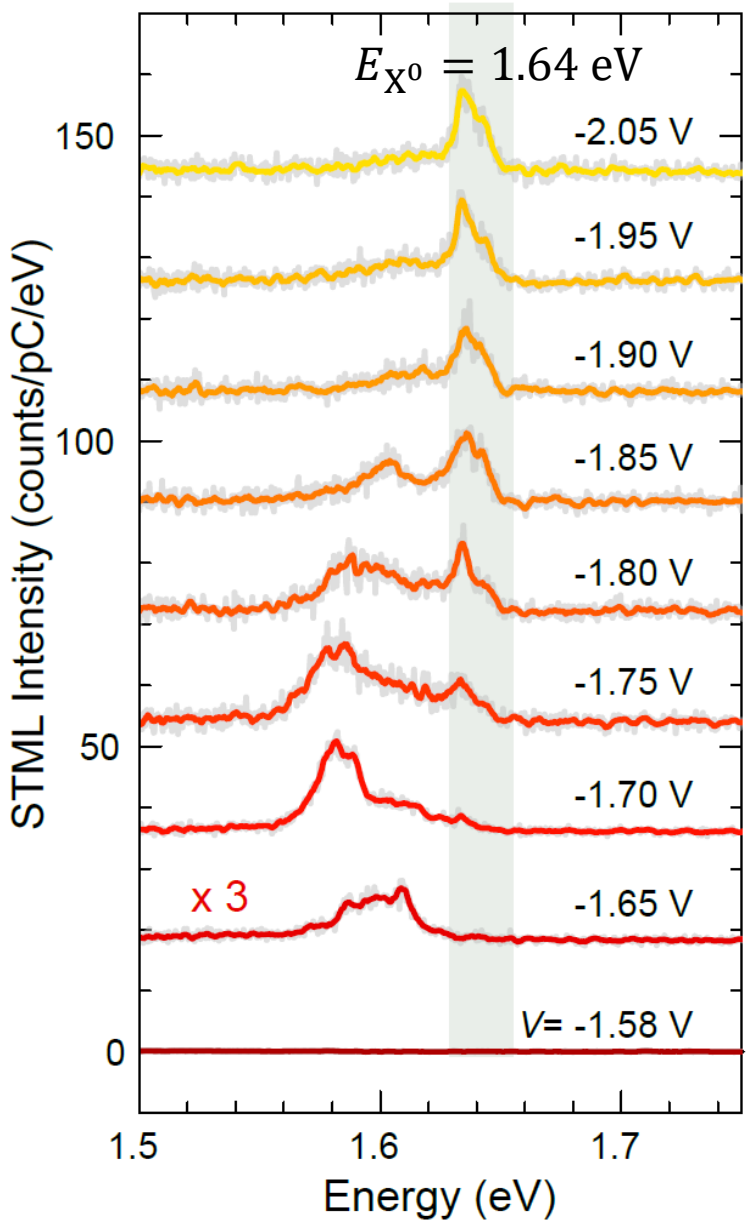

*M. Goryca *et al.*, Nat. Commun. **10**, 4172 (2019)
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See also M. Ugeda *et al.*, Nat. Mater. **13**, 1091 (2014) (PL + STS)

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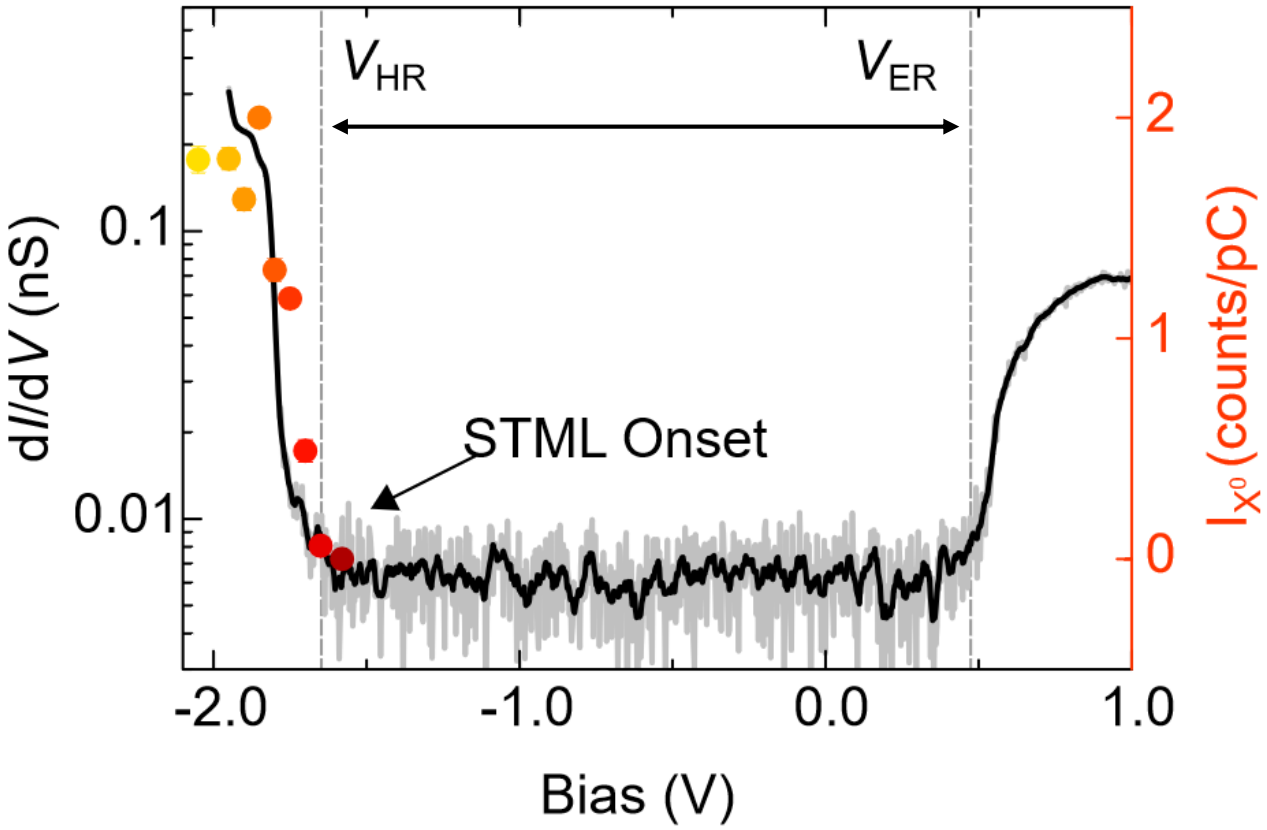
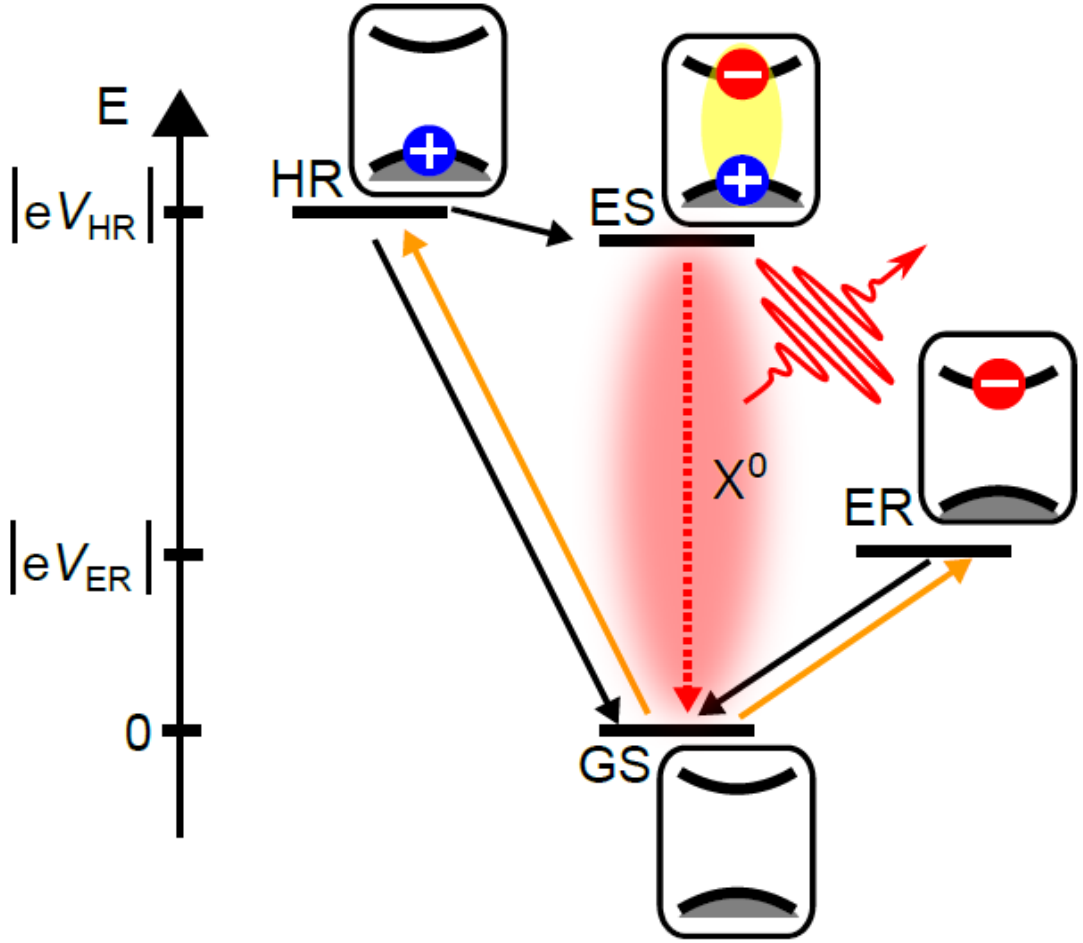




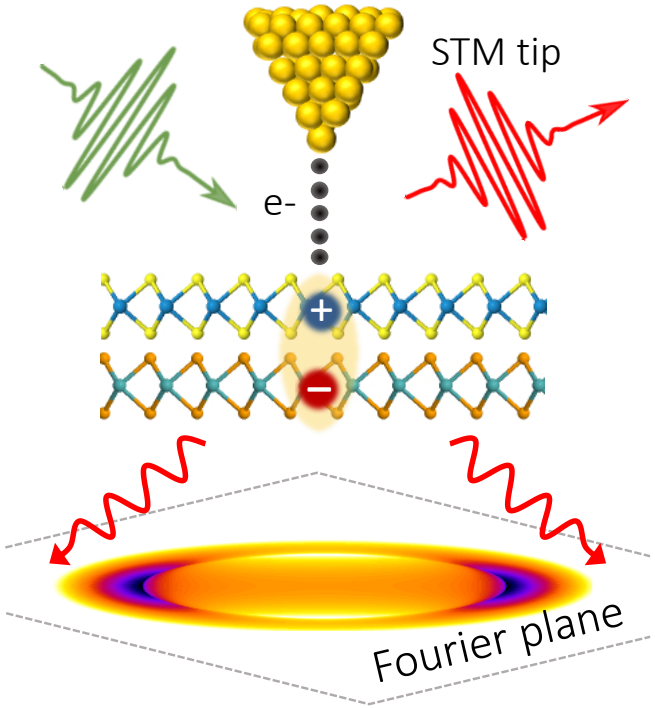
Conclusions and outlook

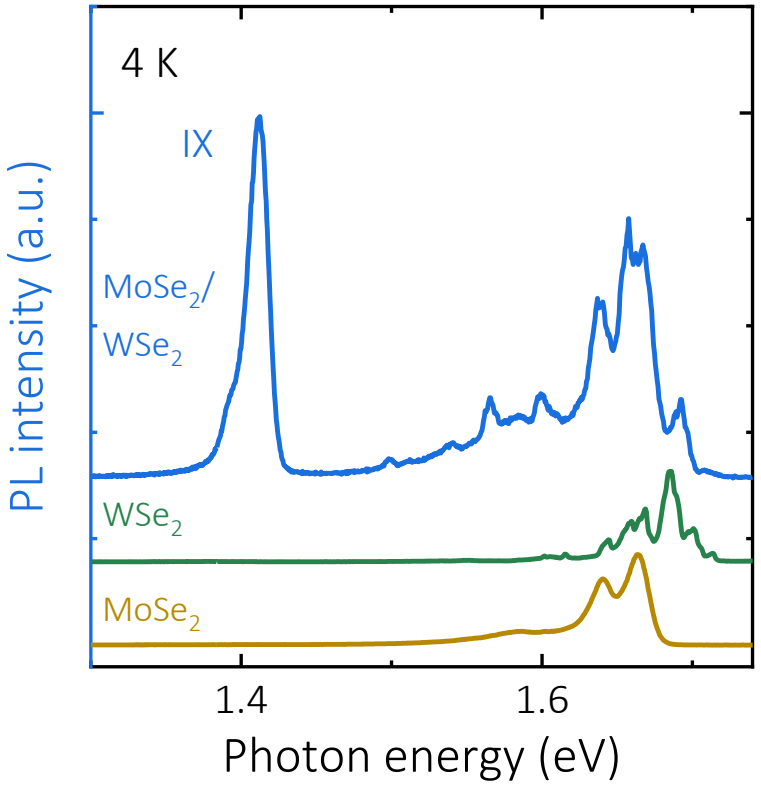
- Hyperspectral mapping
- Spatial resolution
- Exciton diffusion
- Tip-enhanced PL
- Time-resolved studies

- Sample/interface optimization?
- Do we need plasmonic enhancement?
- Can we further exploit it?

STML in twsited TMD heterobilayers

- Localised and moiré exitons



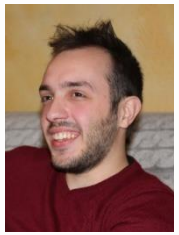


More info: arXiv:2204.14022
Nature Materials (2023) doi:10.1038/s41563-023-01494-4

ANR Project *TEXTURES* | IPCMS – ISMO
PhD or Postdoc positions available

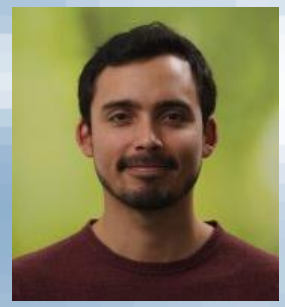
Acknowledgements

Team (as of 01/2023):
Loïc Moczko (PhD 2019-)
Aditi Moghe (PhD 2020-)
Joanna Wolff (PhD 2021-)
Arnaud Gloppe (CNRS)




More info https://fcbg.team

Previous members:
Luis E. Parra-López (joint PhD 2017-21)
Etienne Lorchat (PhD 2015-19)
Xin Zhang (Postdoc 2016-19)
G. Froehlicher (PhD 2013-2016)



Local Collaborators:
H. Majjad (IR) + StNano staff
M. Romeo (IR)
F. Fras (Unistra)
J.-F Dayen (Unistra)

STM Team
G. Schull
A. Roslawska
F. Scheurer
V. Speisser



External collaborations
LPCNO-INSA Toulouse (**C. Robert, D. Lagarde, X. Marie**)
ISMO (**E. Le Moal** *et al.*)
ISIS (C. Genet *et al.*)
Uni. Luxembourg (S. Reichardt, L. Wirtz)
La Sapienza - Rome (T. Scopigno *et al.*)
NIMS (T. Taniguchi, K. Watanabe)

Funding:

cnrs GDR Groupement de recherche
HOWDI Low dimensional van der Waals heterostructures

Thematic School: Advanced physics of van der Waals heterostructures

Sept 23rd, Oct 1st 2023, Roscoff, France

Topics: vdW stack fabrication, advanced characterization, electronic properties, phonons, e-ph interactions, quantum transport, optical properties, spintronics, 2D magnetism, twistronics, 2D-Quantum technologies, …

Confirmed speakers:

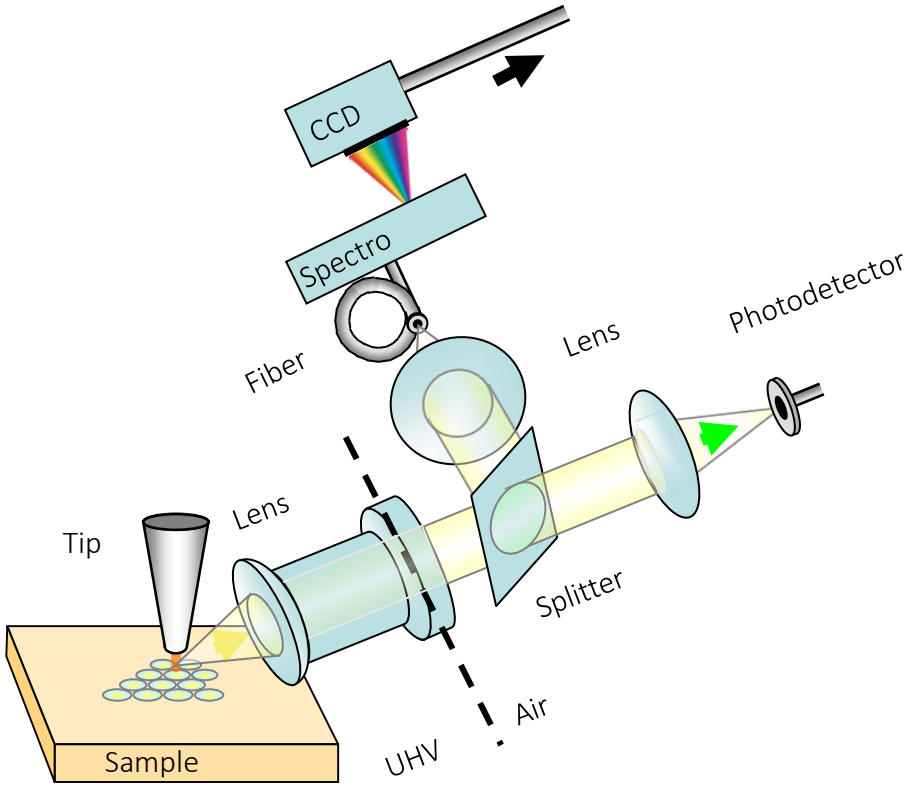
Alexey CHERNIKOV (TU Dresden, Germany)
Johann CORAUX (Institut Néel, France)
Dimitri EFETOV (LMU, Germany)
Marta GALBIATI (Universidad de Valencia, Spain)
Mark GOERBIG (LPS, France)
Roman GORBACHEV (NGI, UK)
Thomas IHN (ETH, Switzeland)
Jeewhan KIM (MIT, USA)
Janina MAULTZSCH (FAU, Germany)
Jose LADO (Aalto University, Finland)
Sylvain LATIL (IRAMIS, France)
Rebeca RIBEIRO (C2N, France)
Stephan ROCHE (ICN2, Spain)
Christoph STAMPFER (RWTH Aachen, Germany)
Xiaodong XU (University of Washington, USA)

DEAD LINE
APRIL 15TH

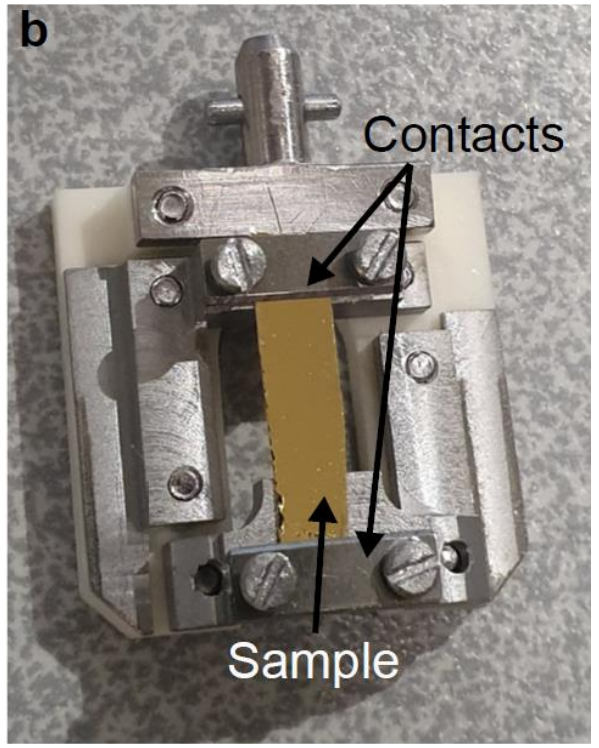
Committee: Ch. VOISIN, S. BERCIAUD, B. DLUBAK, A. LOISEAU, A. RESERBAT-PLANTEY, C. ROBERT, P. SENEOR, Ch. STAMPFER

BACKUP SLIDES

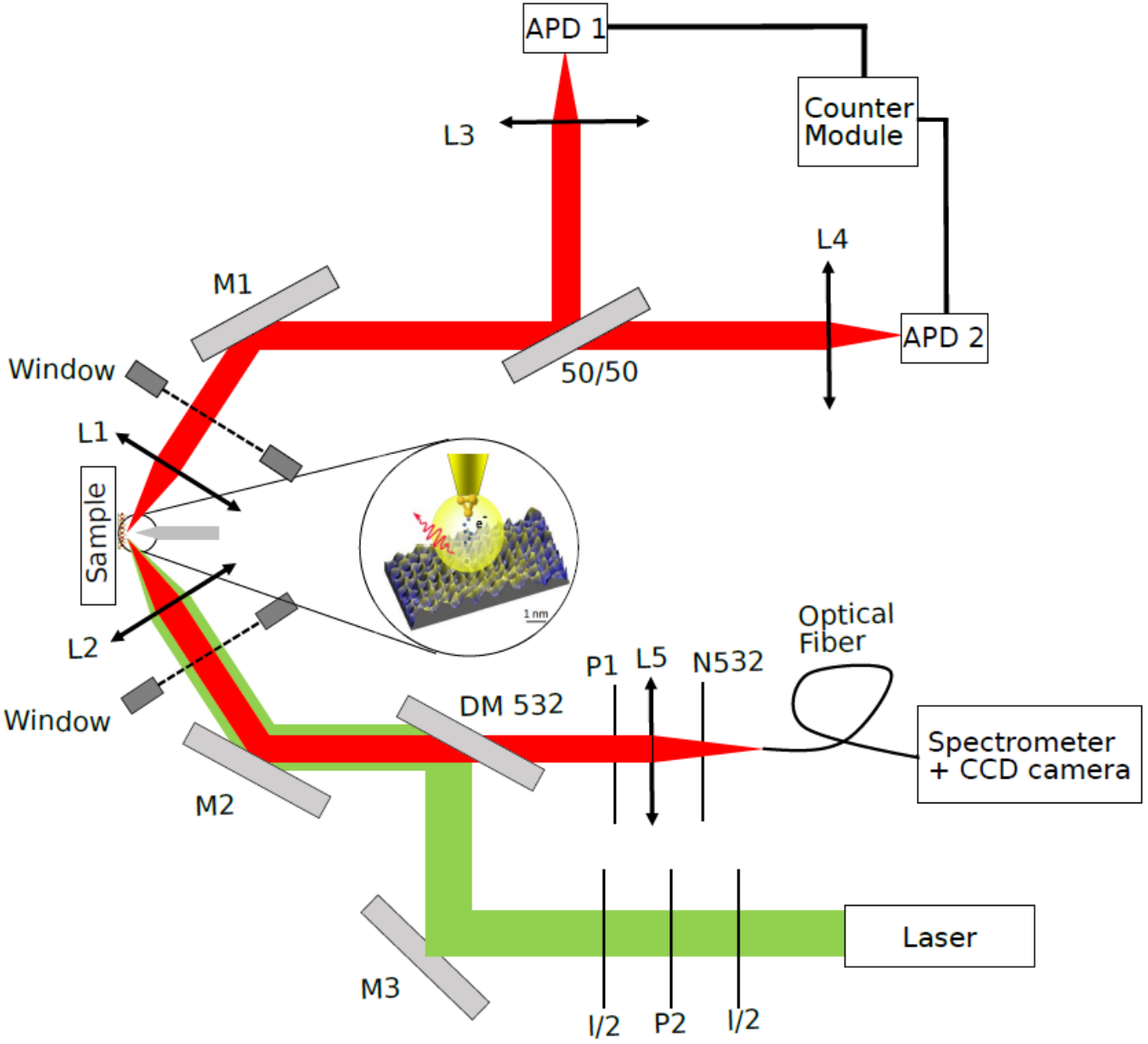
STML setup at IPCMS



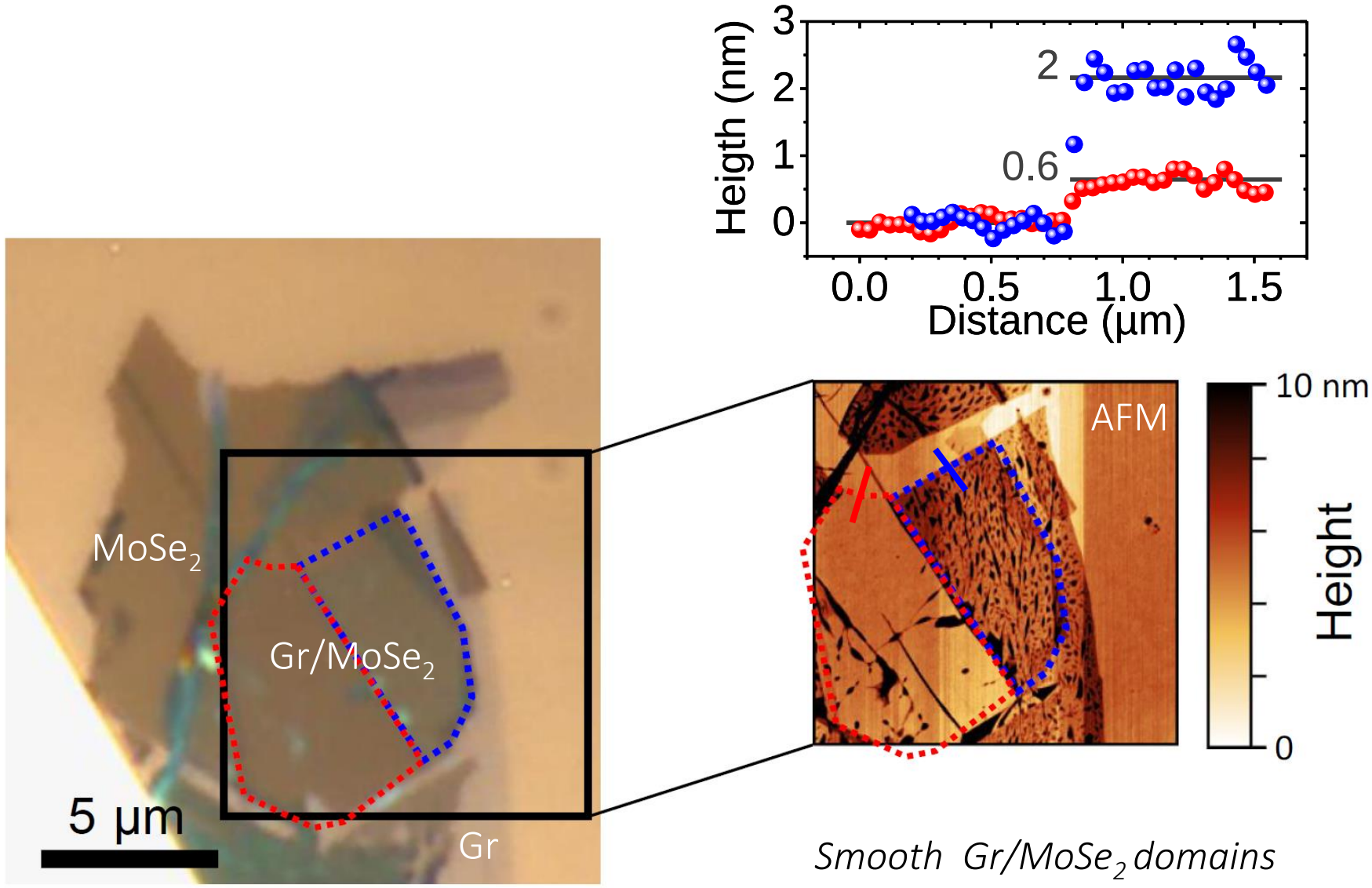
STM 4K



STML Setup


APD 1
L3
Counter Module
L4
M1
APD 2
Window
50/50
L1
Sample
L2
Window
Optical Fiber
P1
L5
N532
DM 532
Spectrometer + CCD camera
M2
Laser
M3
l/2
P2
l/2

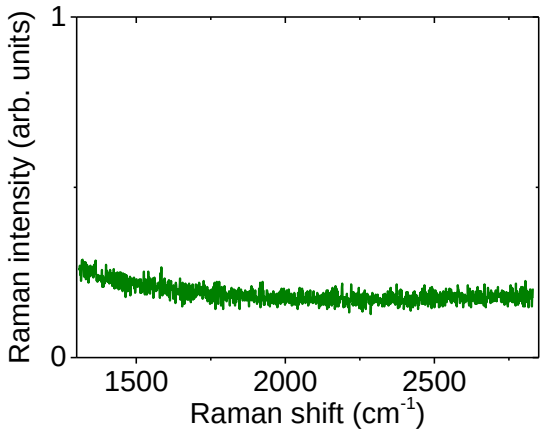
Atomic Force Microscopy



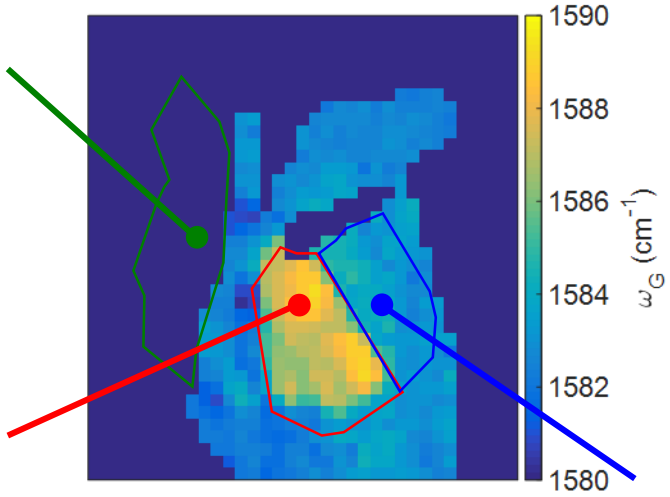
Smooth Gr/$MoSe_2$ domains

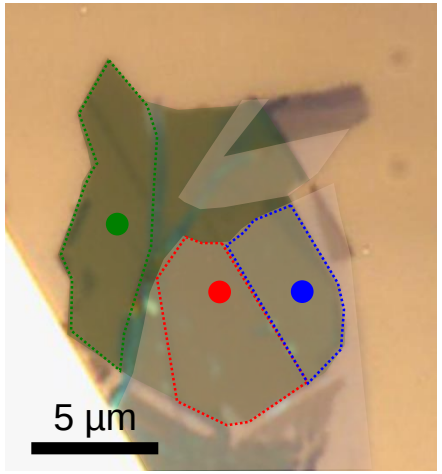
Raman mapping (graphene)

Bare $MoSe_2$

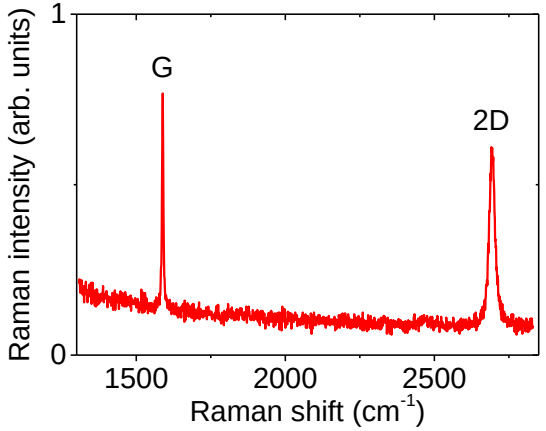


G-mode frequency



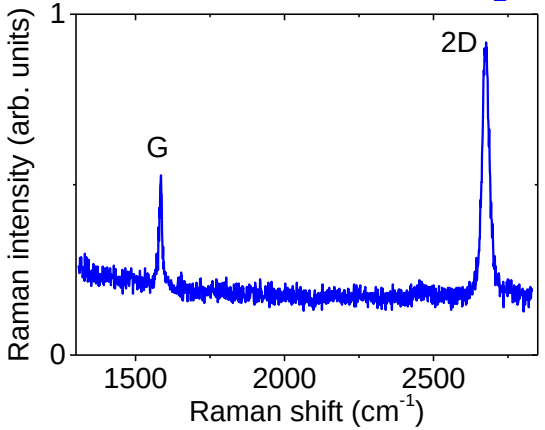


Coupled Gr/$MoSe_2$



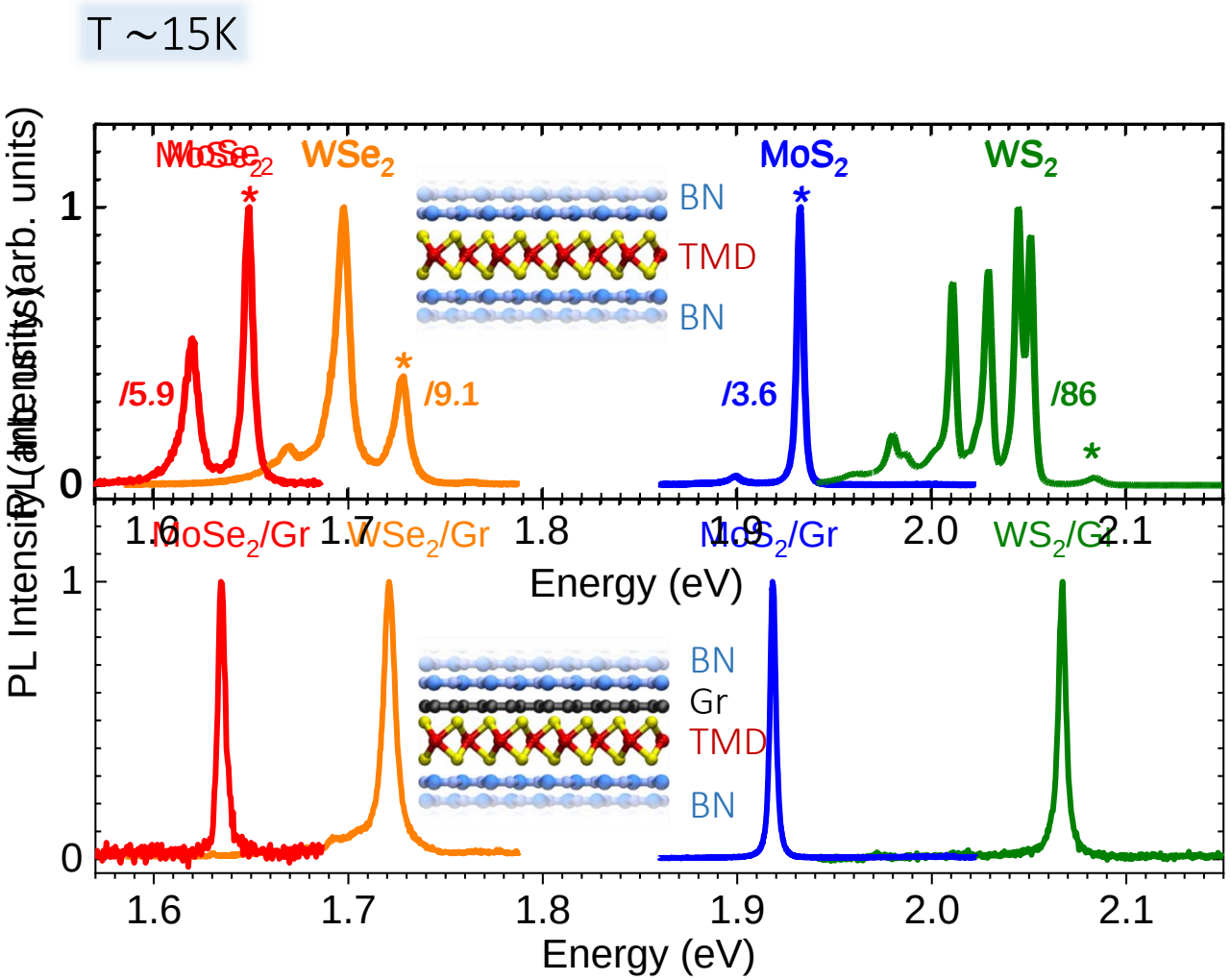
(Photo-induced) doping:
Slow, partly extrinsic effect
No impact on exciton dynamics

Decoupled Gr/$MoSe_2$



G. Froehlicher, E. Lorchat, S.B., Phys. Rev. X **8,** 011007 (2018)

TMD/Graphene: a model system for STML?



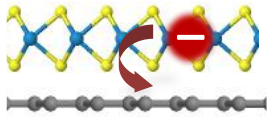
"Filtering effect"

- Neutralization + picosecond exciton transfer

→ Bright, single-line emission

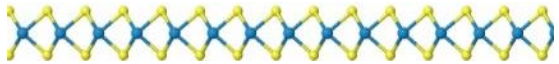
- Approaching the homogeneous linewidth
- Short X_0 lifetime ~ 2 ps
- Graphene as a smooth metallic contact

E. Lorchat*, L. Parra-López* *et al.* Nature Nanotechnology **15**, 283 (2020)
also Froehlicher, Lorchat Berciaud, PRX **8** 011007 2018 | Ferrante *et al.*, PNAS **119**, e2119726119 (2022)

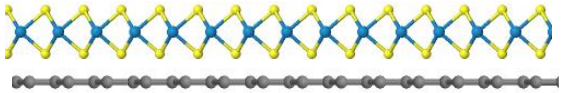


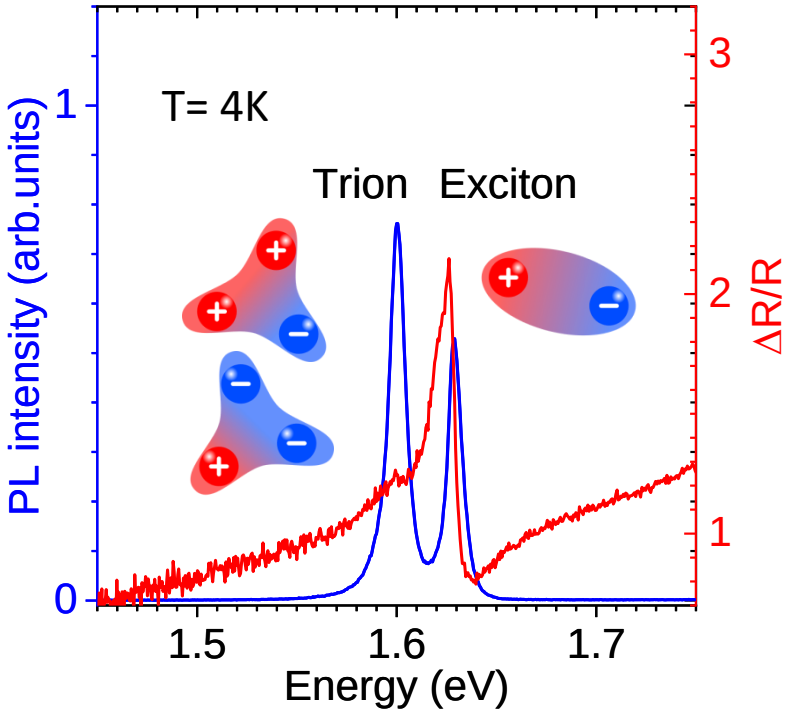
Neutralizing 2D semiconductors with graphene

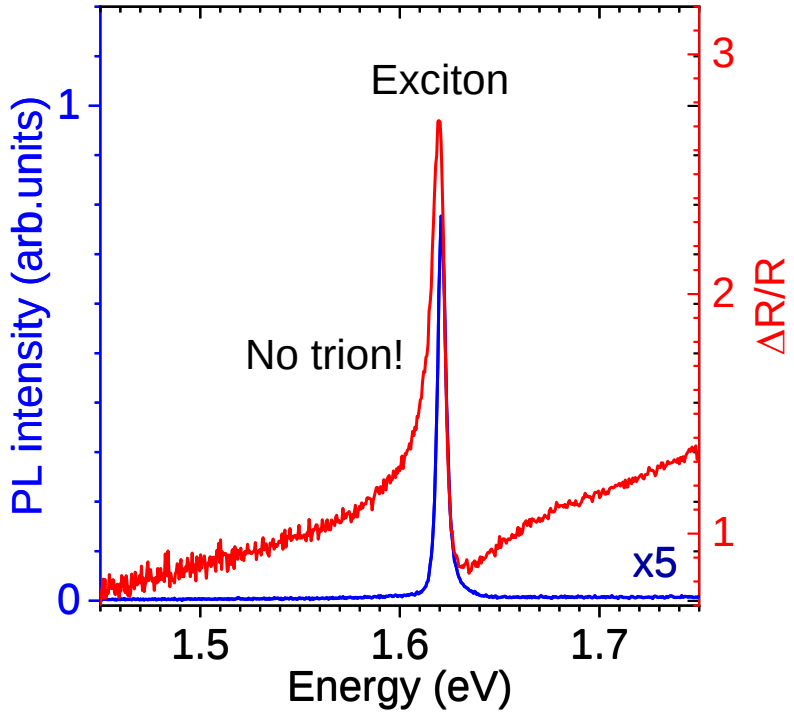
$MoSe_2$



$MoSe_2$/Gr

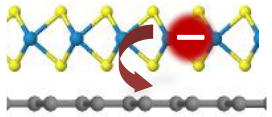






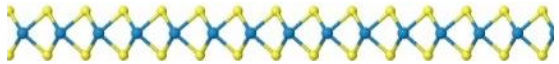
- $n \neq 0$ and graphene quenches trion emission?
- $n \neq 0$ and graphene quenches trion formation?
- $n = 0 \Rightarrow$ no trion!

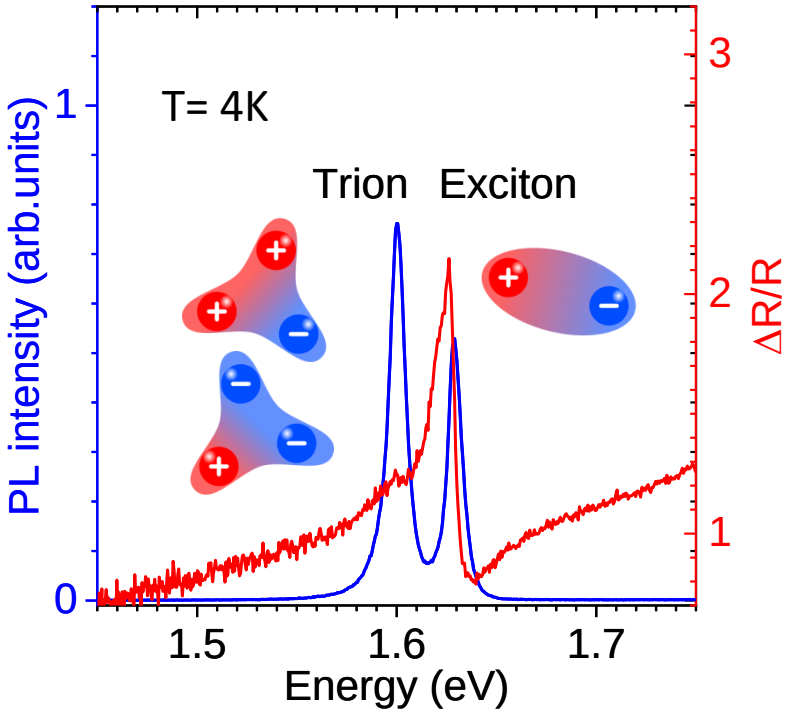
E. Lorchat*, L. Parra-López* *et al.* Nat. Nano. **15**, 283 (2020)
See also Hill et al. PRB (2017)



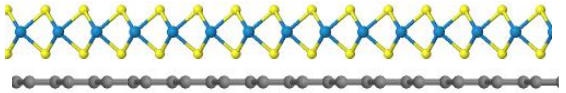
Neutralizing 2D semiconductors with graphene

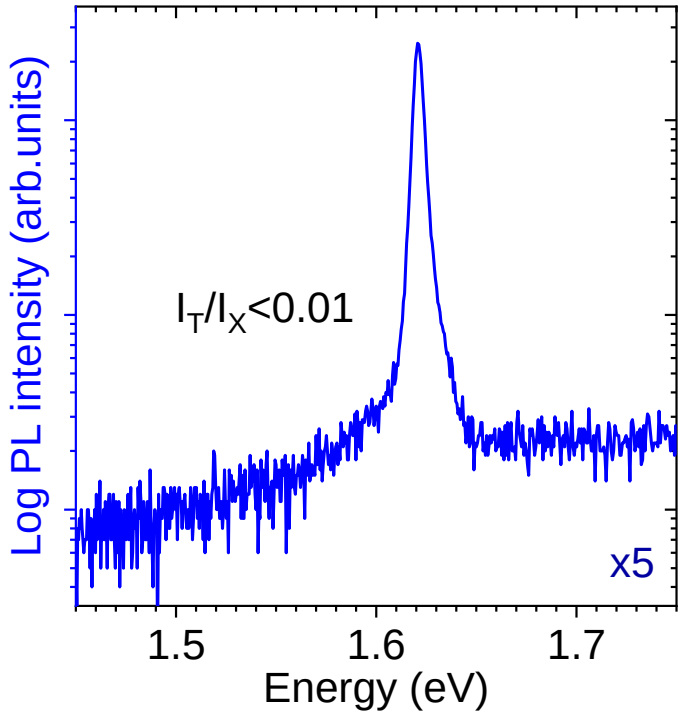
$MoSe_2$





$MoSe_2$/Gr

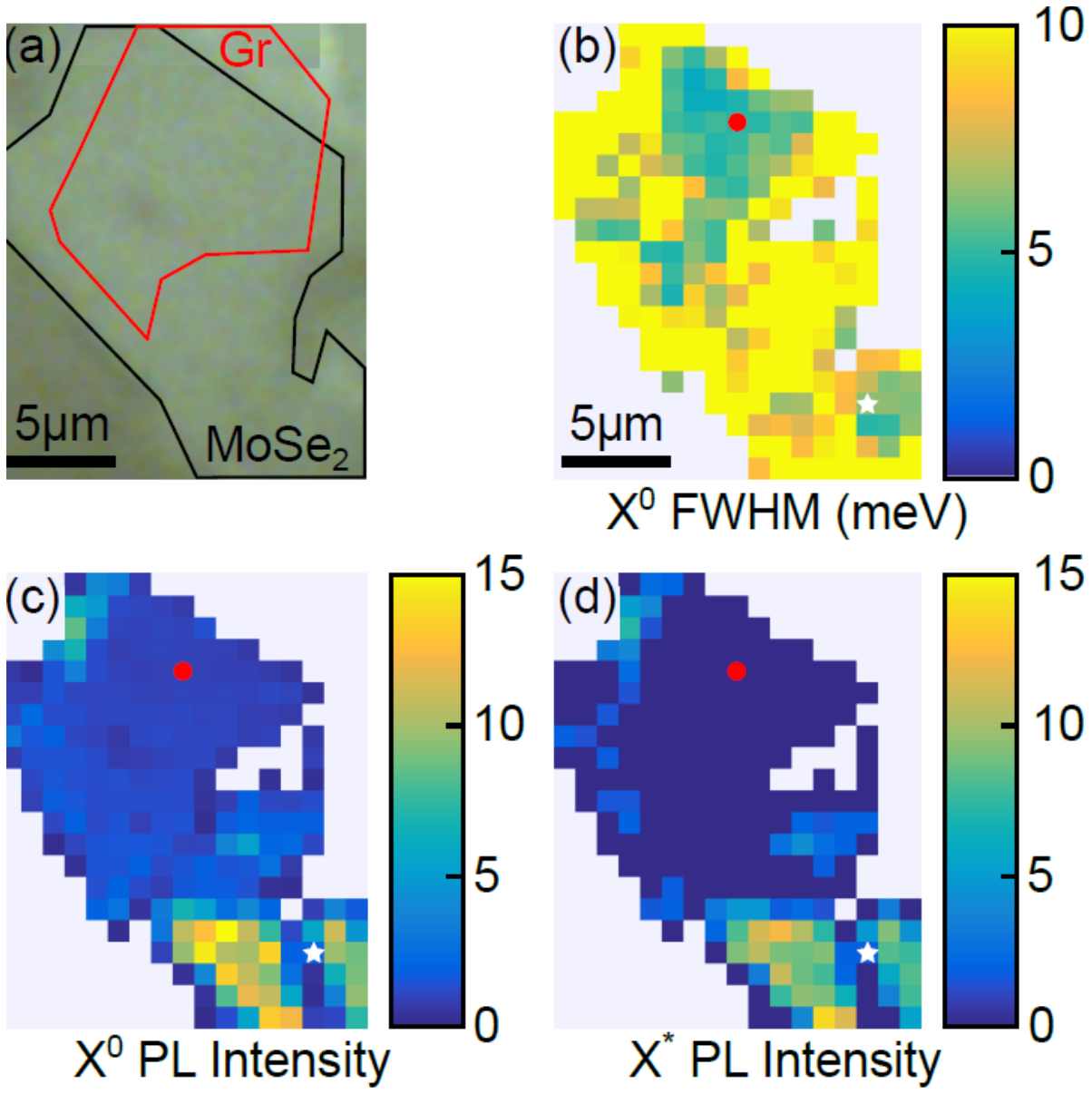




- $n \neq 0$ and graphene quenches trion emission?
- $n \neq 0$ and graphene quenches trion formation?
- $n = 0 \Rightarrow$ no trion!

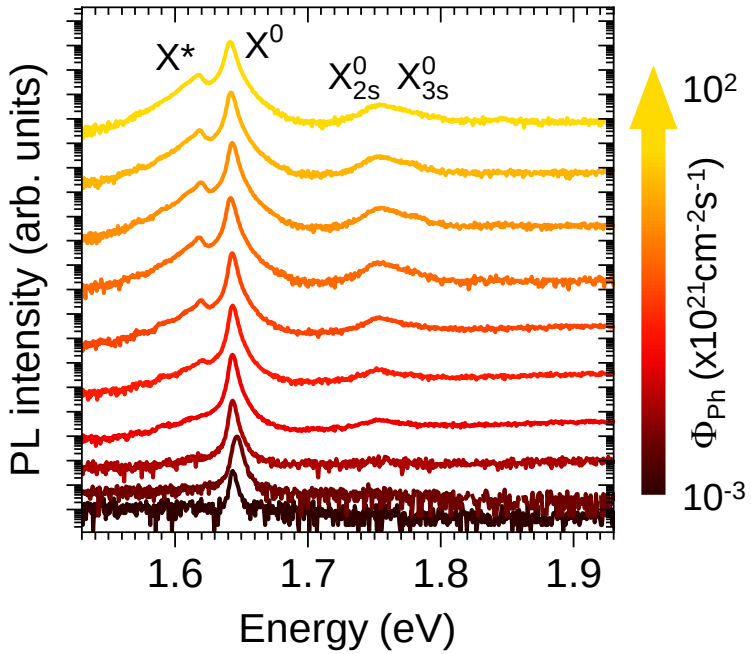
E. Lorchat*, L. Parra-López* *et al.* Nat. Nano. **15**, 283 (2020)
See also Hill et al. PRB (2017)

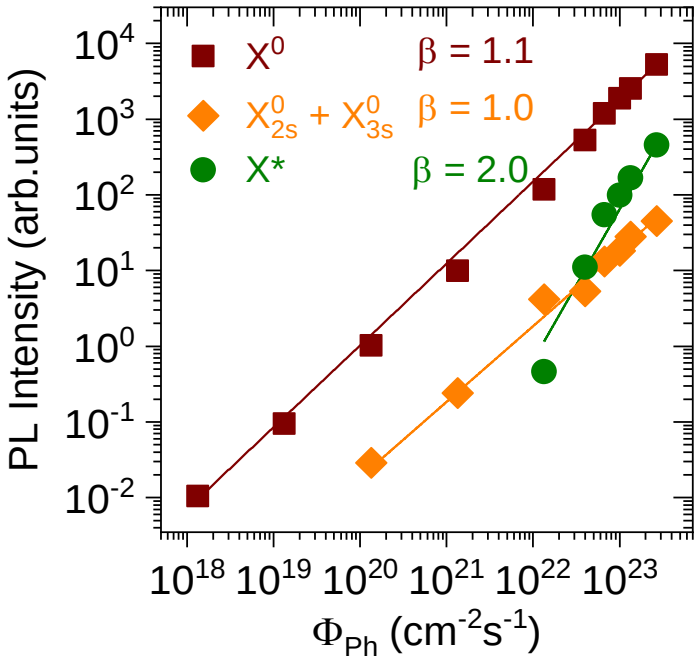
Spatial homogeneity

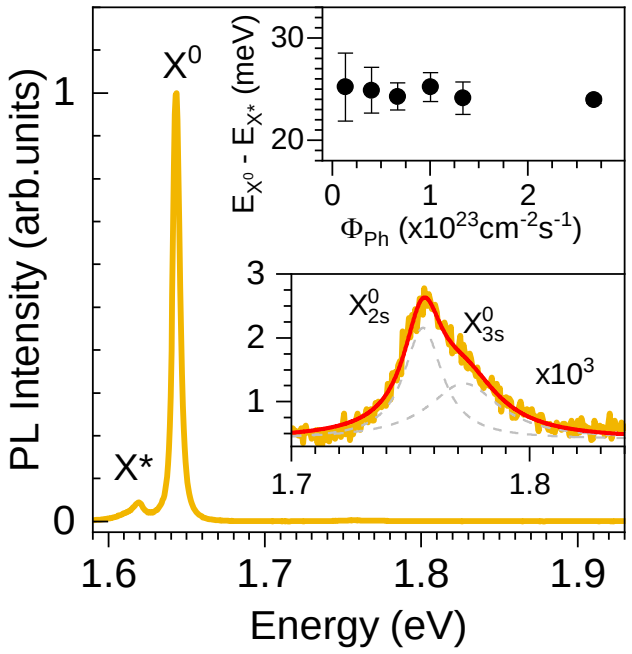


Photostability and dielectric screening

BN-capped $MoSe_2$/Gr, T= 4 K





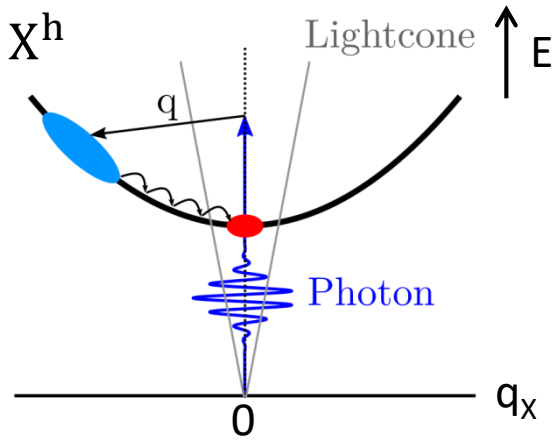


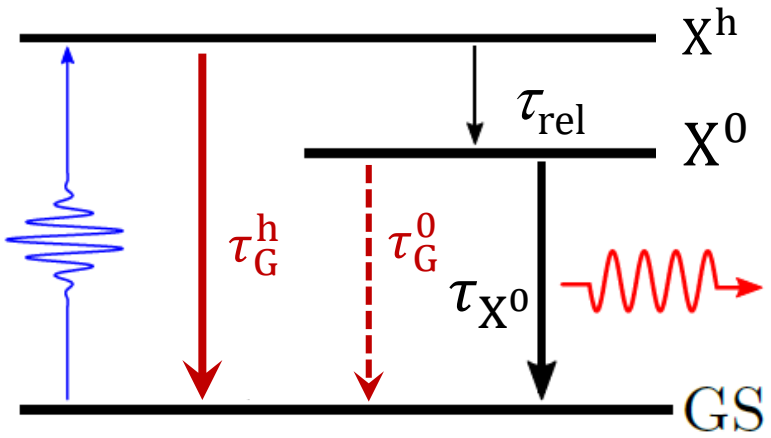
- Auger-mediated process → scales as Φ_{ph}^2
- TMD/Gr sustains larger photon fluxes than bare TMD monolayers
- Reduced Δ_{1s-2s} → reduced E_b by $\sim 30-50$ %

  → Determination of $\tau_{X^0}^{rad} \propto E_b^{-2}$ in TMD/Gr

E. Lorchat*, L. Parra-López* *et al.* Nat. Nano. **15**, 283 (2020)

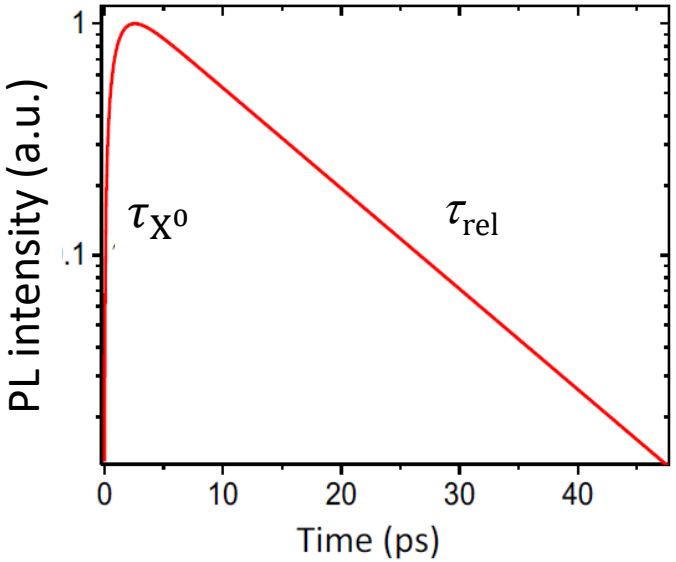
Low temperature exciton dynamics

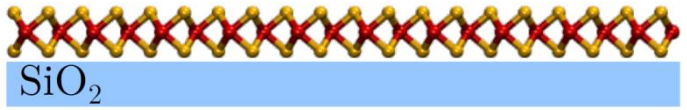




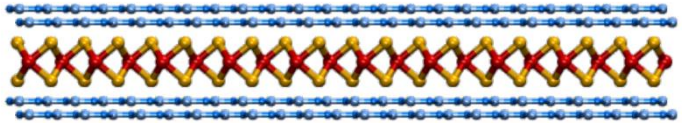
$$I(t) \propto \frac{n_h(0)}{\tau_{rel} - \tau_{X^0}} \left[\exp\left(-\frac{t}{\tau_{rel}}\right) - \exp\left(-\frac{t}{\tau_{X^0}}\right) \right]$$

$\tau_{rel} > \tau_{X^0}$





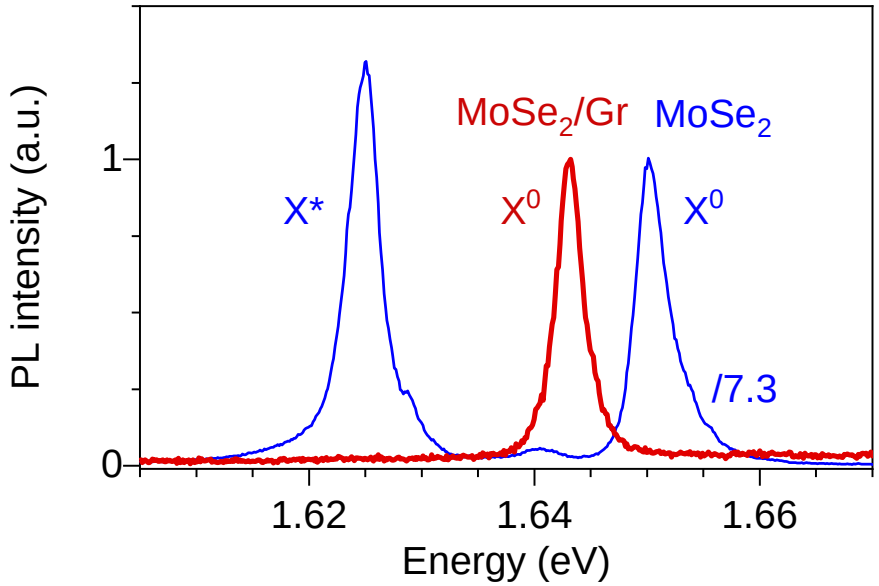
$\tau_{rel} < 1$ ps, $\tau_{X^0} \sim 2$ ps (i. e., 0.3 meV)

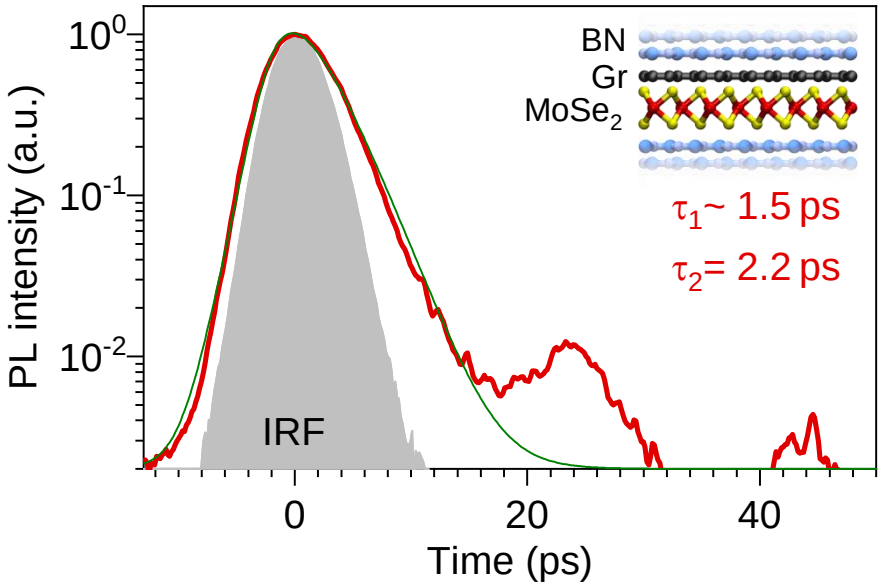


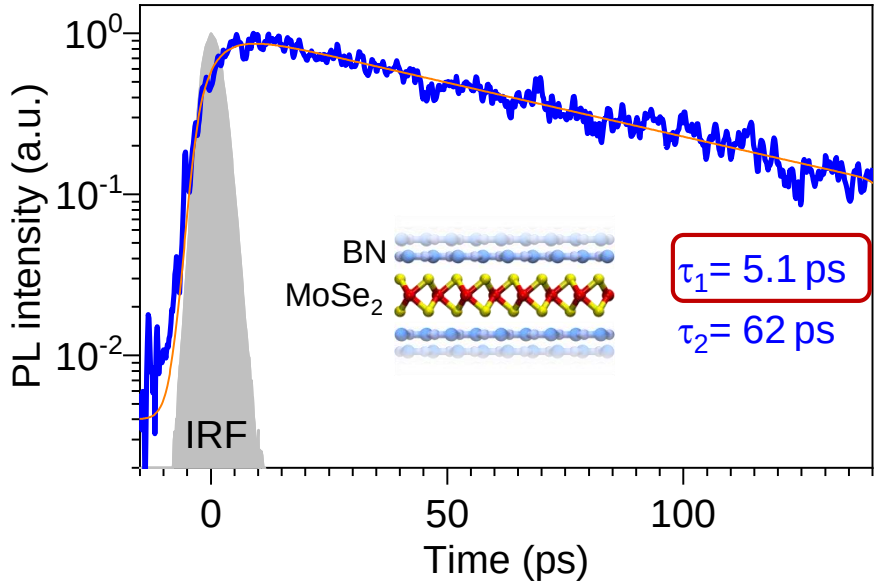
$\tau_{rel} \gg 1$ ps, $\tau_{X^0} \sim 1 - 10$ ps (i. e., $0.6 - 0.06$ meV)

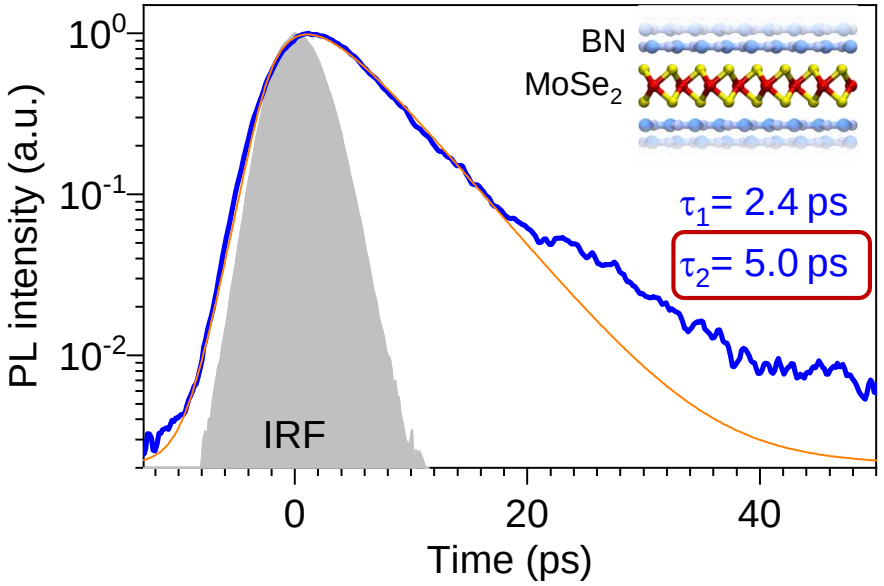
See H.H. Fang *et al.*, PRL (2019)

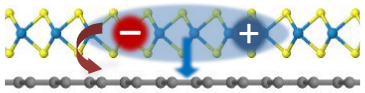
Exciton dynamics in BN-capped Gr/$MoSe_2$



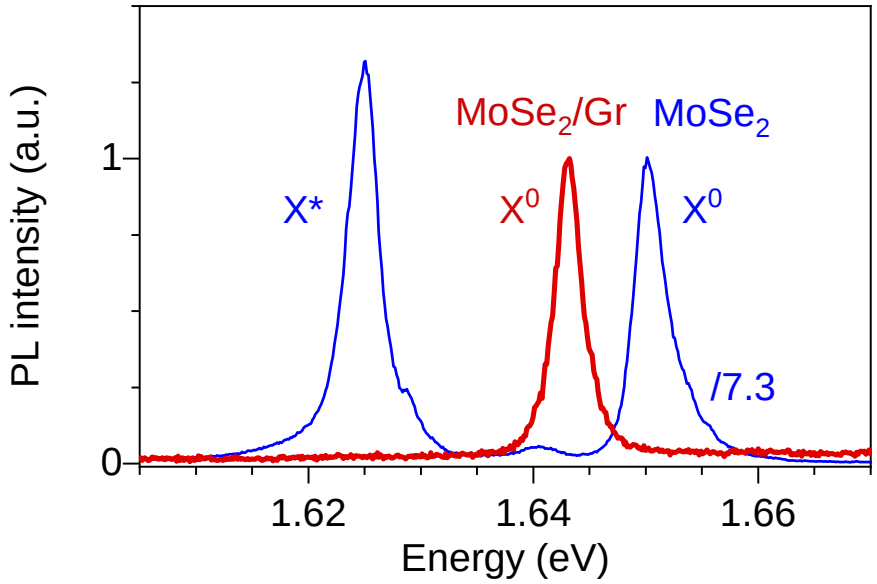


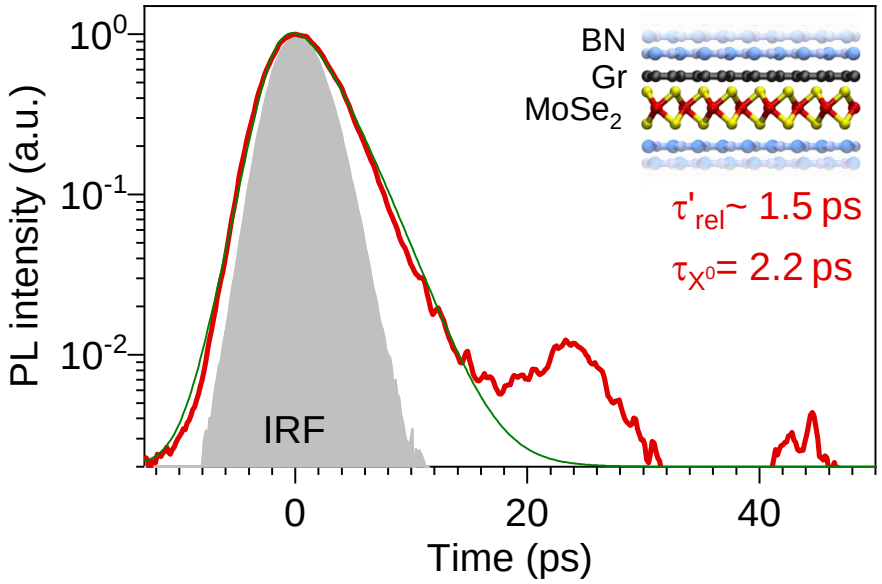


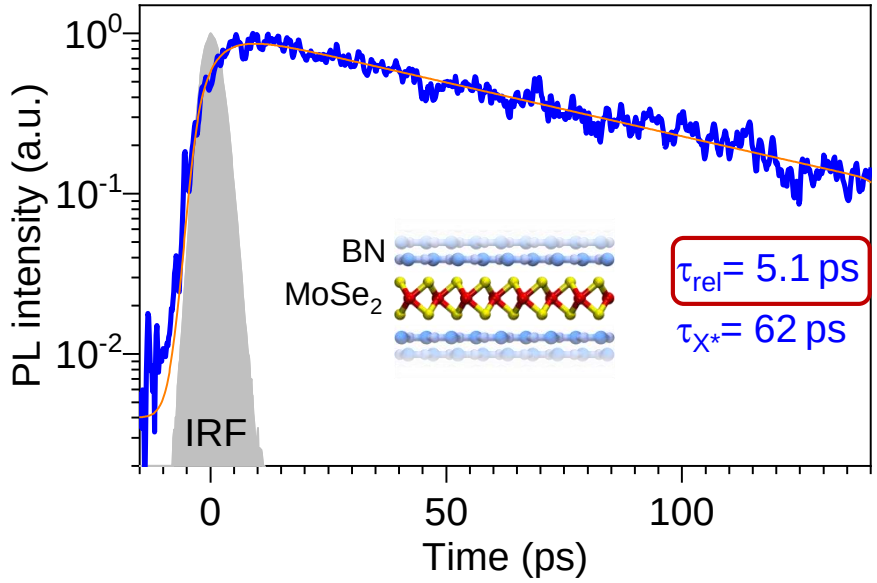


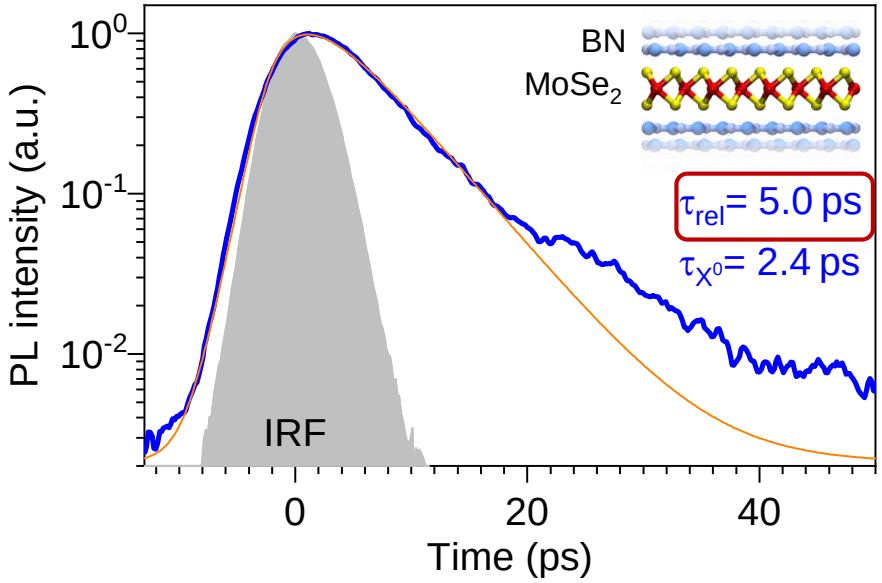


Exciton dynamics in BN-capped Gr/$MoSe_2$

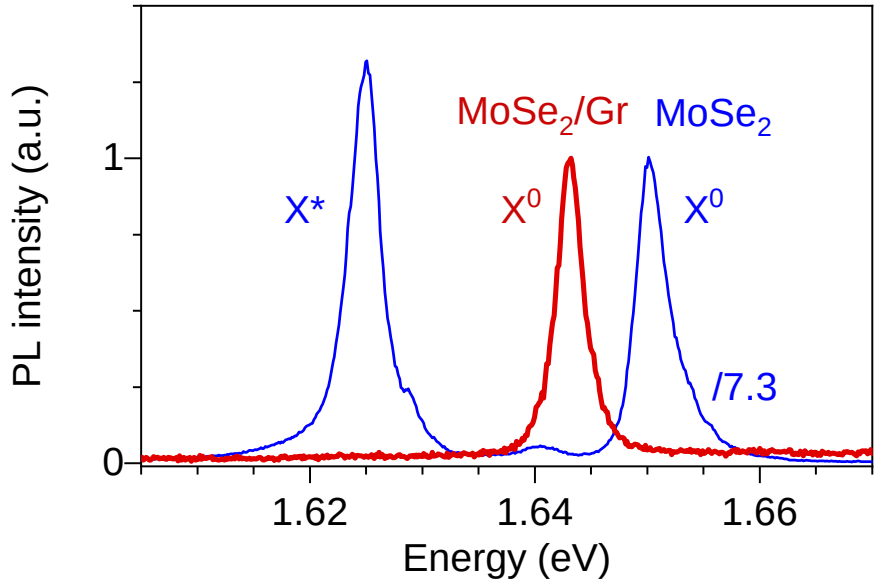


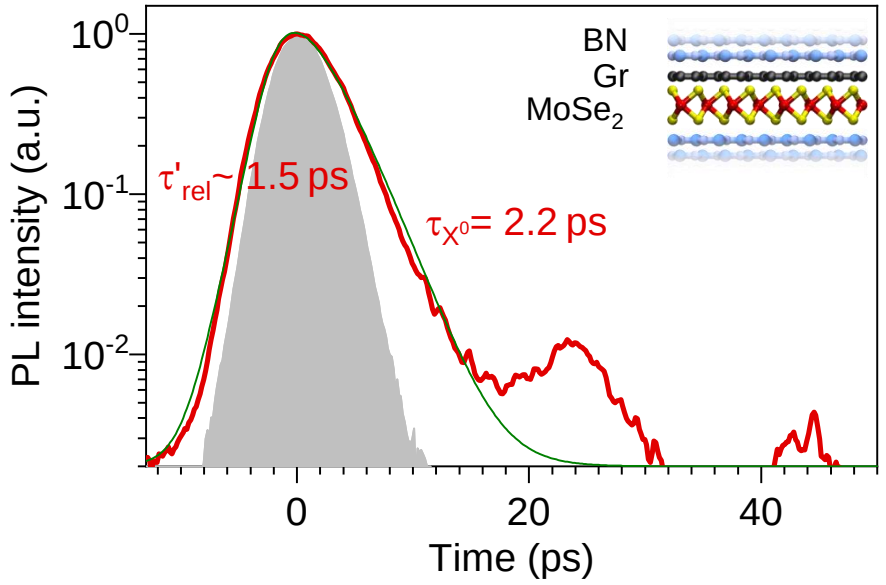






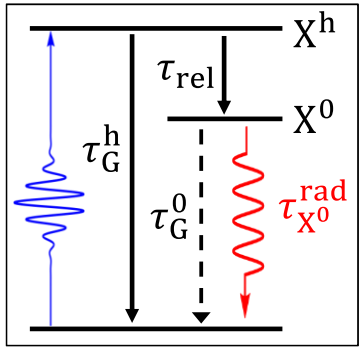
Evidence for hot exciton transfer





- $\tau_G^0 = \frac{\tau_{X^0}^{rad}\,\tau_{X^0}}{\tau_{X^0}^{rad} - \tau_{X^0}} \sim 4$ ps
- $\eta_{X^0} = \frac{\tau_G^0}{\tau_{X^0}^{rad} + \tau_G^0} \sim 50\%$

$\rightarrow \tau_G^h \gg \tau_G^0$



➢ *Energy dependent exciton transfer*