Université de Strasbourg

Institut de Physique et Chimie des Matériaux de Strasbourg

Optical spectroscopy as a probe of charge and energy transfer in two-dimensional materials

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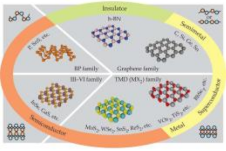
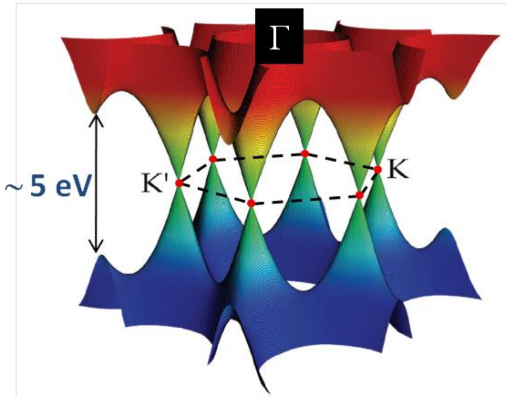
New Frontiers in 2D materials Winterschool/Workshop
Villard de Lans, January 16, 2017



Graphene and 2D materials at IPCMS

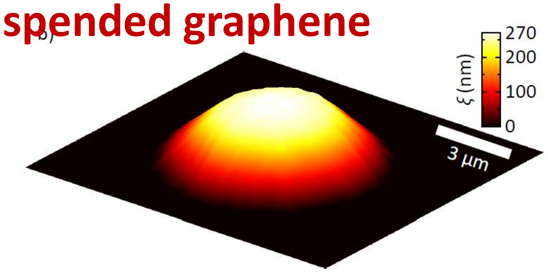
• *Cross-disciplinary work on graphene and 2DM since 2012*

- 6 Permanent staff, 5 Postdocs + 9 PhD (currently, 1 + 4)
- Nanofabrication facility (StNano, 180 m^2)
- Optical spectroscopy, optoelectronics, optomechanics, electron transport, spintronics, chemtronics, straintronics…

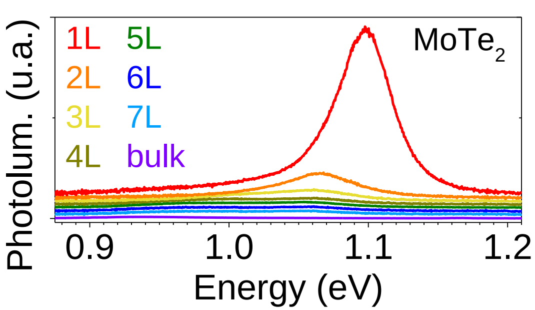


Fundamental properties

- **Suspended graphene**

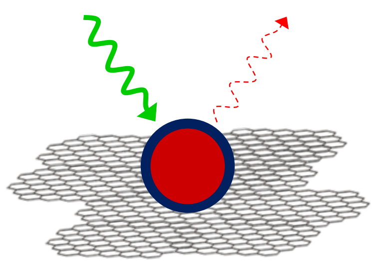


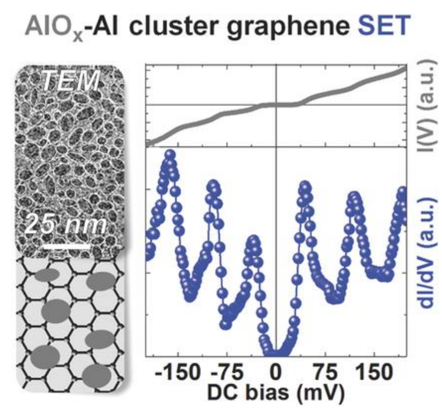
- **Transition metal dichalcogenides**



Devices, Hybrid Systems, Heterostructures

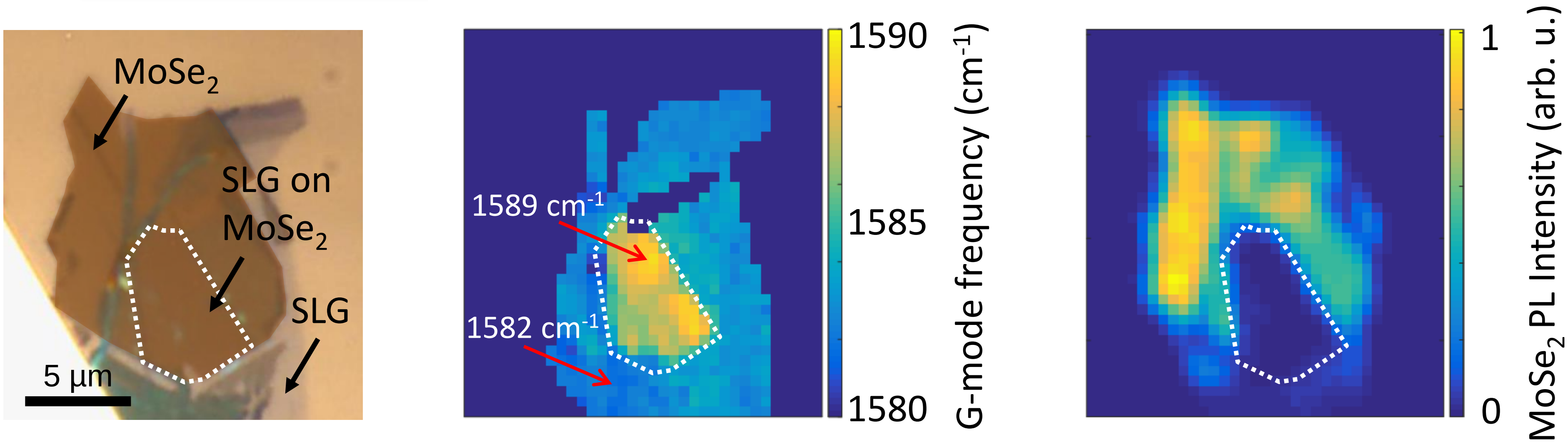
- Field-effect transistors, memories, sensors
- 2DM-nanoemitter hybrids
- van der Waals heterostructures
- Gr-based tunnel junctions



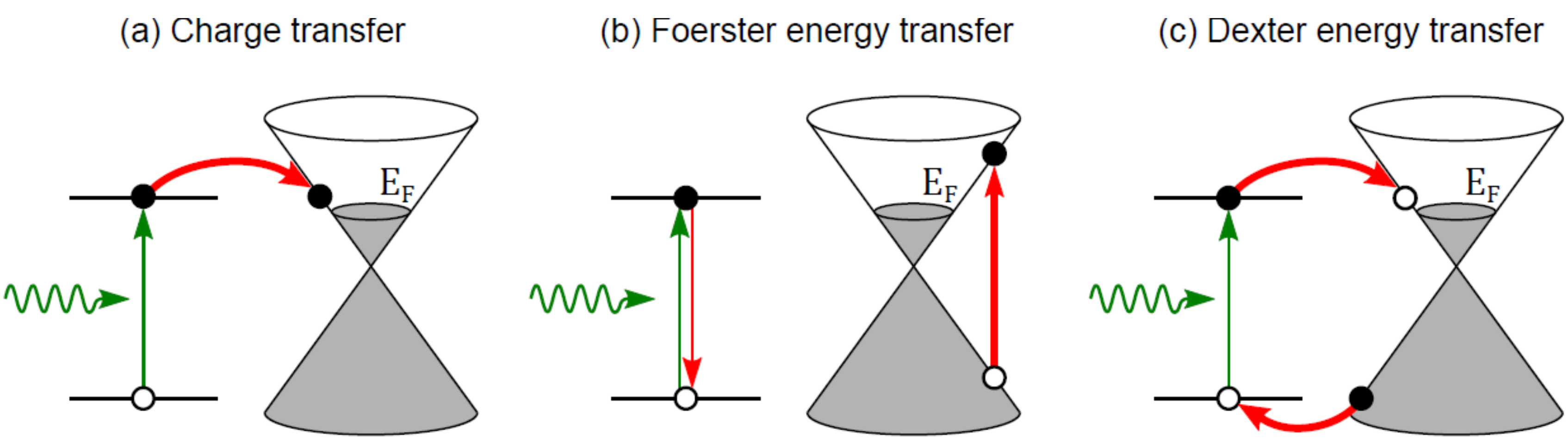


Advanced Mat. DOI: 10.1002/adma.201604837

Let us try to understand this…

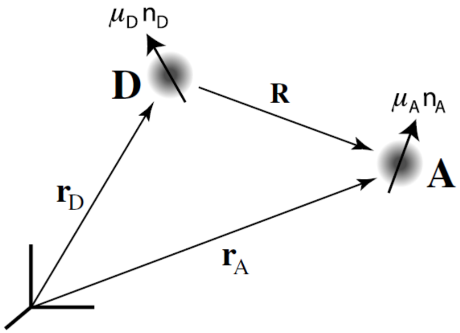


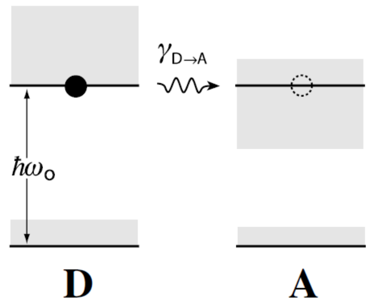
Data : G. Froehlicher, E. Lorchat, SB (in preparation)



…and discuss what this can be useful for.

Förster energy transfer: near field dipole-diople interaction





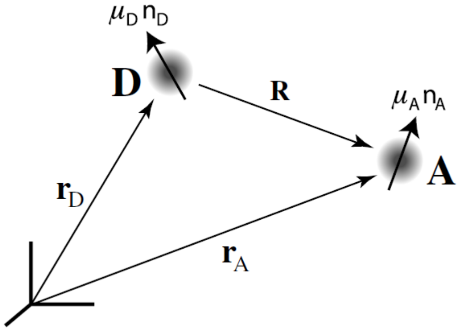
$$\frac{\gamma_{D\to A}}{\gamma_0} = \frac{P_{D\to A}}{P_0}$$

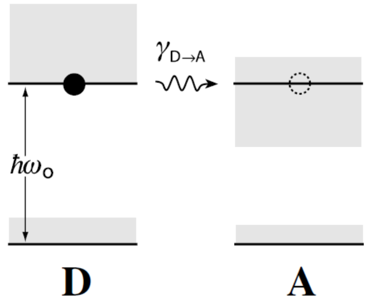
$$\mathbf{E}_D = \frac{1}{4\pi\varepsilon_0}\left[k^2(\mathbf{r}\wedge\boldsymbol{\mu}_D)\wedge\boldsymbol{\mu}_D\,\frac{e^{ikr}}{r^2} + \left(\frac{3\mathbf{r}(\mathbf{r}.\boldsymbol{\mu}_D)}{r^2} - \boldsymbol{\mu}_D\right)\left(\frac{1}{r^3} - \frac{ik}{r^2}\right)e^{ikr}\right]$$

Th. Förster Annalen der Physik **437**, 55 (1948)
Novotny, Hecht Principles of Nano Optics, Ch 8

R_0 : Förster radius

Förster energy transfer: near field dipole-diople interaction





$$\frac{\gamma_{\mathrm{D}\to\mathrm{A}}}{\gamma_0} = \frac{P_{\mathrm{D}\to\mathrm{A}}}{P_0}$$

$$\mathbf{E}_D = \frac{1}{4\pi\varepsilon_0}\left[k^2(\mathbf{r}\wedge\boldsymbol{\mu}_D)\wedge\boldsymbol{\mu}_D\frac{e^{ikr}}{r^2} + \left(\frac{3\mathbf{r}(\mathbf{r}.\boldsymbol{\mu}_D)}{r^2} - \boldsymbol{\mu}_D\right)\left(\frac{1}{r^3} - \frac{ik}{r^2}\right)e^{ikr}\right]$$

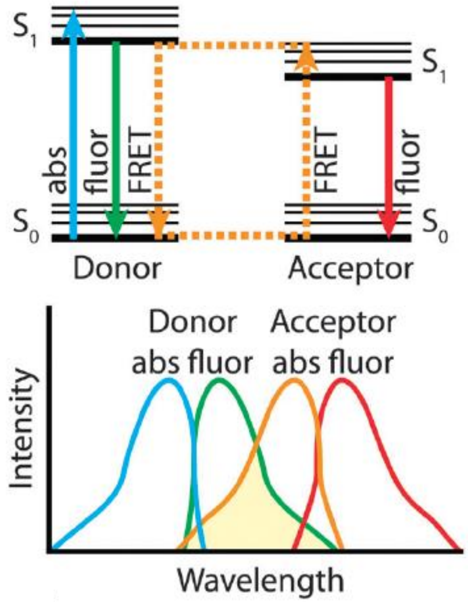
$$P_{\mathrm{D}\to\mathrm{A}} = -\frac{1}{2}\int_{V_{\mathrm{A}}} \mathrm{Re}\{\mathbf{j}_{\mathrm{A}}^{*}\cdot\mathbf{E}_{\mathrm{D}}\}\,\mathrm{d}V \approx \frac{\omega_0}{2}\,\mathrm{Im}\{\alpha_{\mathrm{A}}\}\left|\mathbf{n}_{\mathrm{A}}\cdot\mathbf{E}_{\mathrm{D}}(\mathbf{r}_{\mathrm{A}})\right|^2$$

$$\frac{\gamma_{\mathrm{D}\to\mathrm{A}}}{\gamma_0} = \left[\frac{R_0}{R}\right]^6 \qquad R_0^6 = \frac{9c^4\kappa^2}{8\pi}\int_0^\infty \frac{f_{\mathrm{D}}(\omega)\,\sigma_{\mathrm{A}}(\omega)}{n^4(\omega)\,\omega^4}\,\mathrm{d}\omega$$

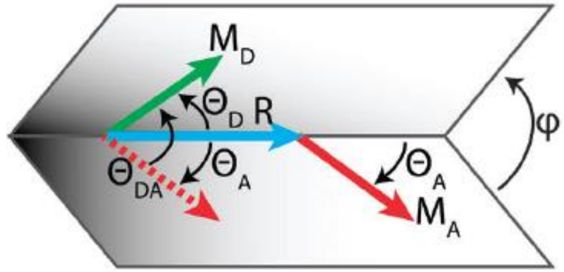
Th. Förster Annalen der Physik **437**, 55 (1948)
Novotny, Hecht Principles of Nano Optics, Ch 8

R_0 : Förster radius

FRET: Distance sensing at the single molecule level

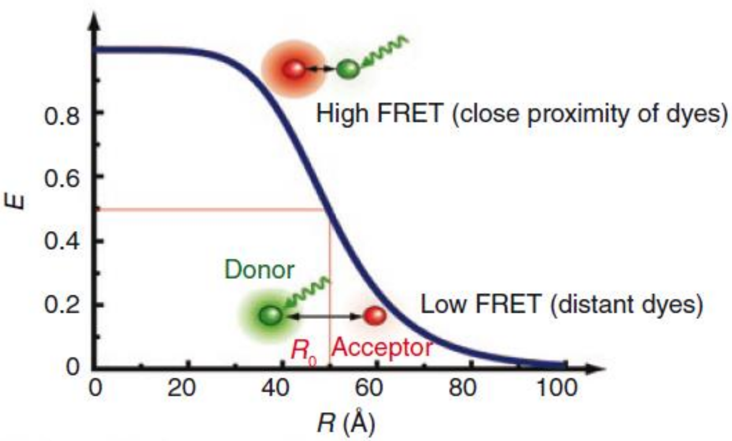


Chem.Soc.Rev., **43**, 1144 (2014)

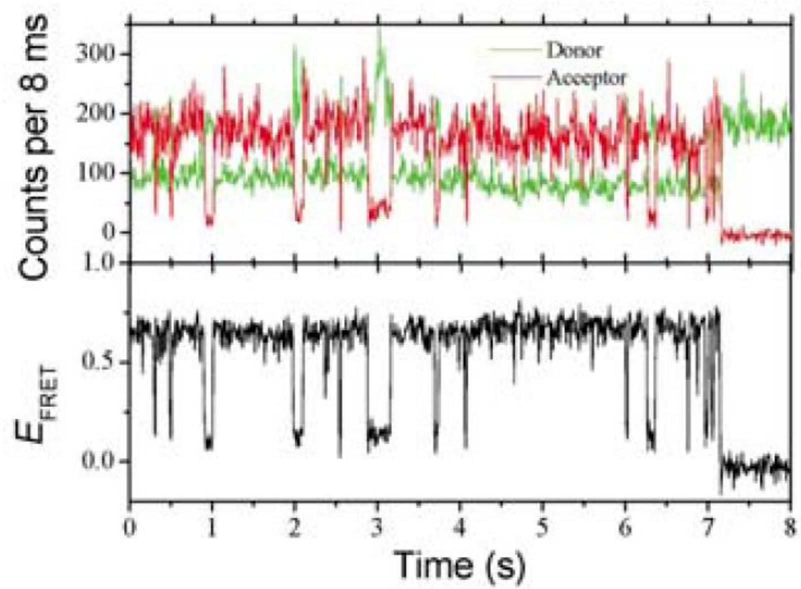


$$R_0^6 = \frac{9c^4\kappa^2}{8\pi}\int_0^\infty \frac{f_D(\omega)\,\sigma_A(\omega)}{n^4(\omega)\,\omega^4}\,d\omega$$

$$\eta = \frac{\gamma_0}{\gamma_0 + \gamma_{D\to A}} = \left[1 + \left(\frac{R_0}{R}\right)^6\right]^{-1}$$



Nature Methods, **5**, 507 (2008)



Nature structural biology **10**, 93 (2003)

Förster and Dexter energy transfer

$$(D^*, A) \rightarrow (D, A^*)$$

$$U = \langle \Psi_i | \hat{V} | \Psi_f \rangle$$

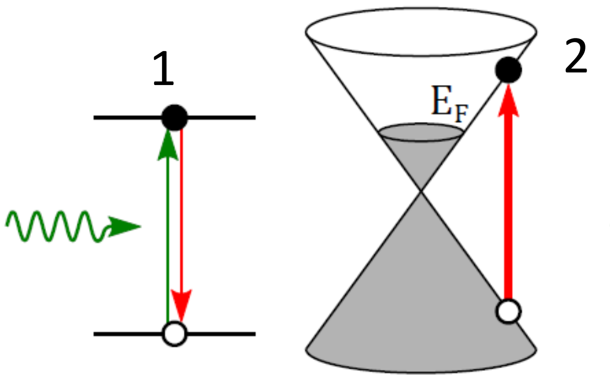
$$U = \langle \Psi_{D^*}(1)\Psi_A(2)|\hat{V}|\Psi_D(1)\Psi_{A^*}(2)\rangle - \langle \Psi_{D^*}(1)\Psi_A(2)|\hat{V}|\Psi_D(2)\Psi_{A^*}(1)\rangle$$

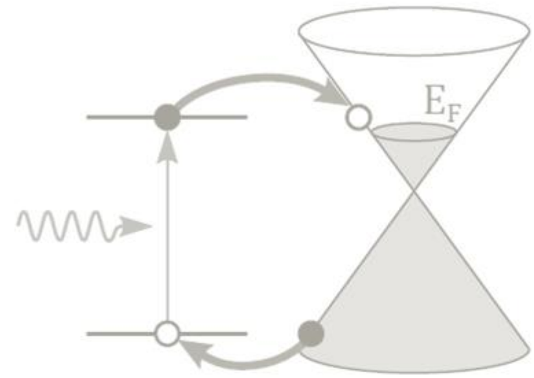
Coulomb (FRET) term

- ✓ 'Long' range (power law)
- ✓ Implies spectral overlap

Exchange (Dexter) term

- ✓ Short range (exponential, idem CT)
- ✓ Implies overlap of molecular orbitals





A Govorov, PL Hernandez Martinez, HV Demir
Understanding and Modeling Förster-type Resonance Energy Transfer (FRET), Springer 2016

Photoinduced Charge Transfer and Energy Transfer

Key near-field phenomena in nano-optoelectronic devices

Affect:

- (photo)excited states dynamics
- Fermi energies/doping levels

Sensitive to:

- donor-acceptor distance
- dimensionality
- band alignment
- excitonic effects
- Fermi energies/doping levels

How to probe charge and energy transfer ?

Experimental techniques:

- Raman spectroscopy (CT)
- Photoluminescence spectroscopy (CT & ET)
- Non-linear (pump-probe) spectroscopy (CT & ET)

Devices:

- Nanofabrication
- Custom devices
- Electrical control

Today's menu

I. Introduction

- Two-dimensional materials (2DM)
- Semiconductor nanostructures
- Hybrid and van der Waals heterostructures
- Optoelectronic devices
- Optical spectroscopies

II. Near-field coupling in hybrid heterostructures

- Energy transfer: distance scaling, dimensionality, screening
- Electrical control of near-field coupling

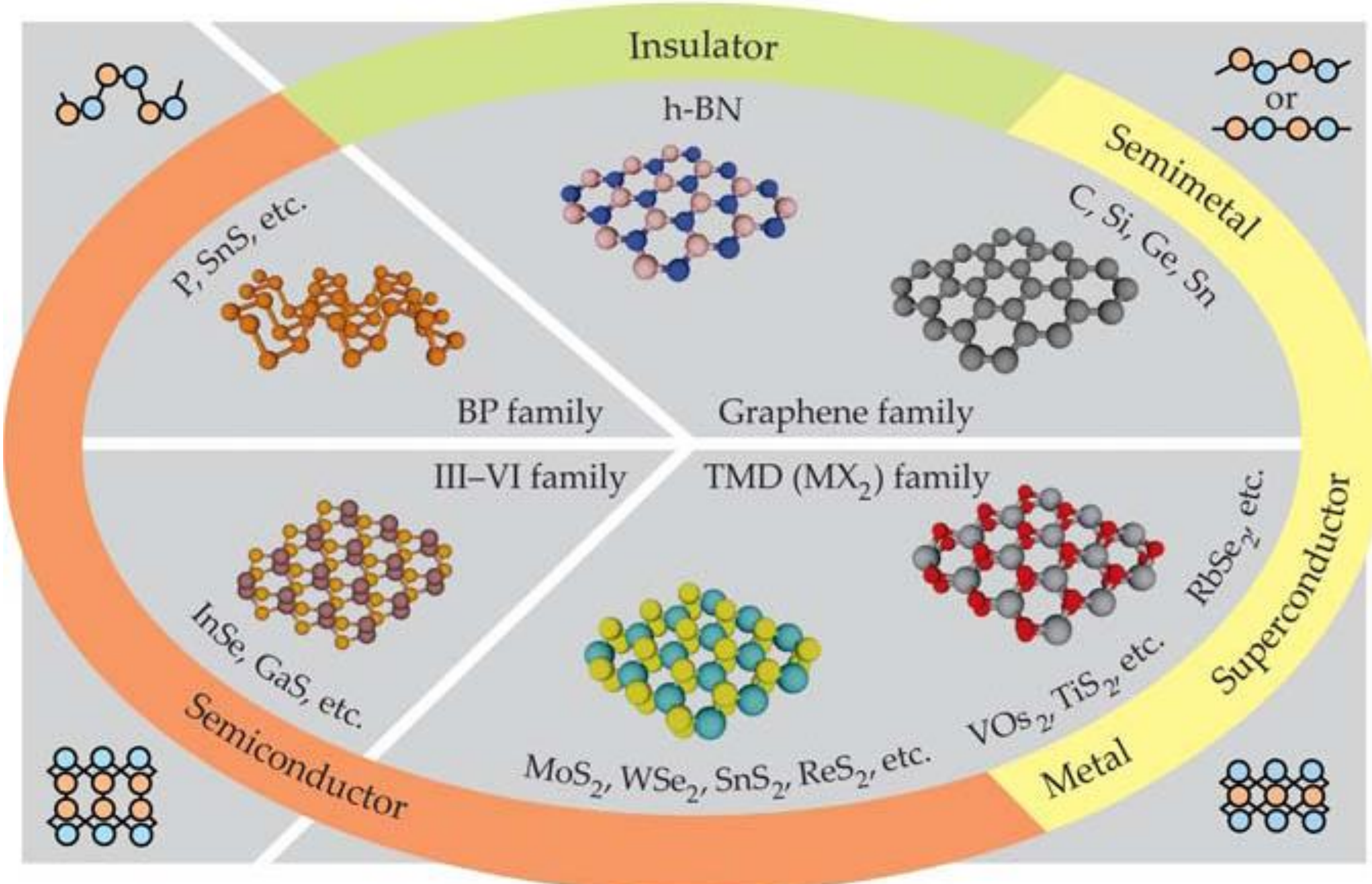
III. Near-field coupling in van der Waals Heterostructures

- TMD-TMD heterostructures
- Charge vs energy transfer in graphene-TMD heterostructures

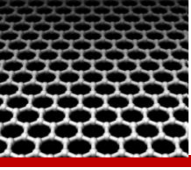
IV. Conclusion and outlook

- Novel optoelectronic devices
- Towards opto-electro-mechanics

Introducing 2D materials



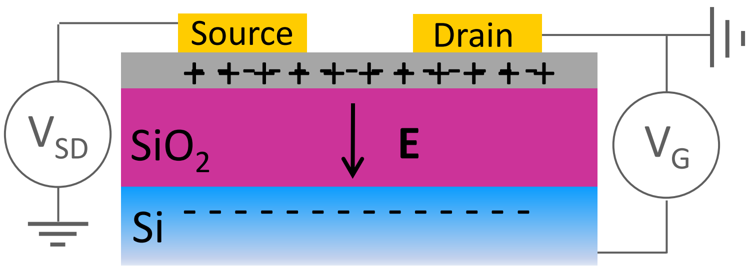
Ajayan, Kim, Banerjee - Physics Today (2016)

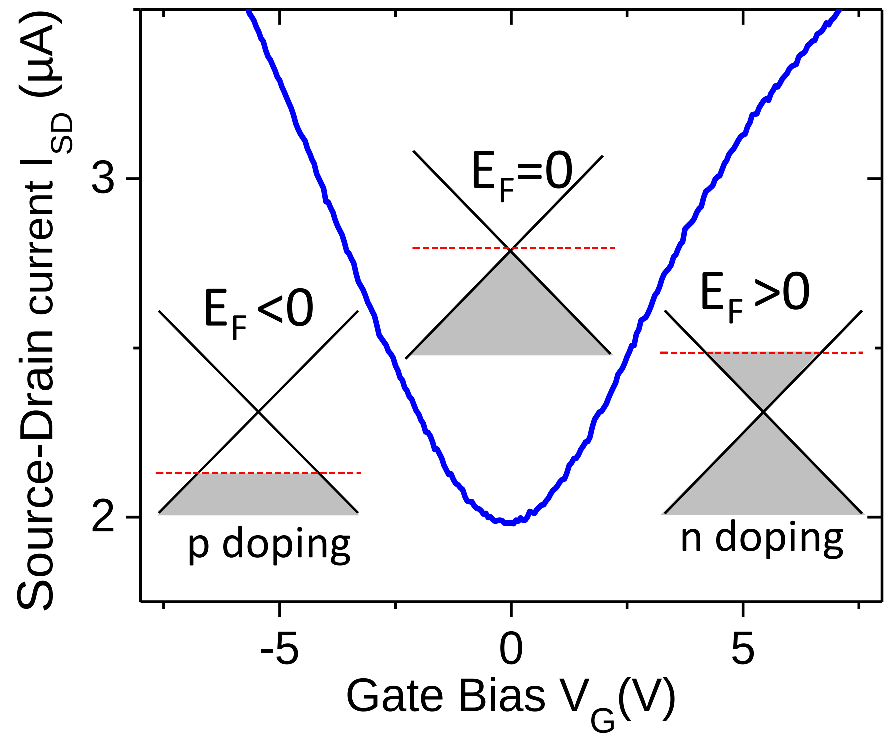


Graphene: a unique, tunable 2D electron gas

- ✓ quantum electron transport (QHE)
- ✓ electron-phonon coupling
- ✓ electromechanics
- ✓ optoelectronics

Electric field effect





1st observation: Novoselov *et al.*, Science (2004)

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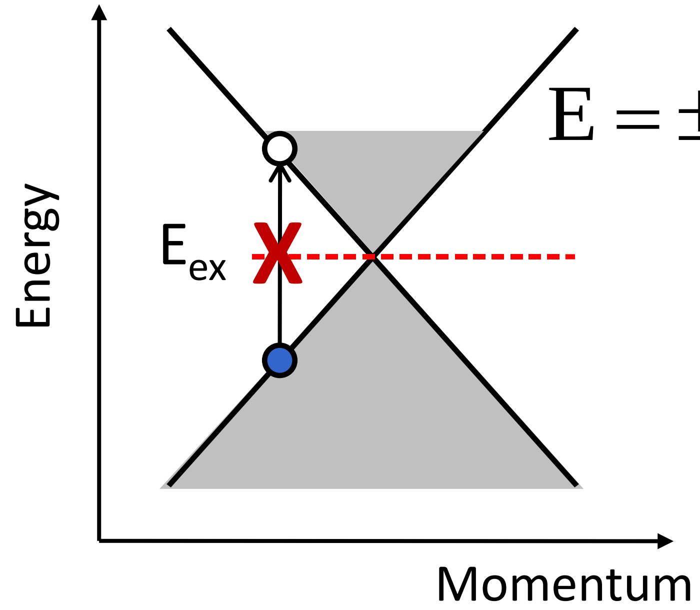
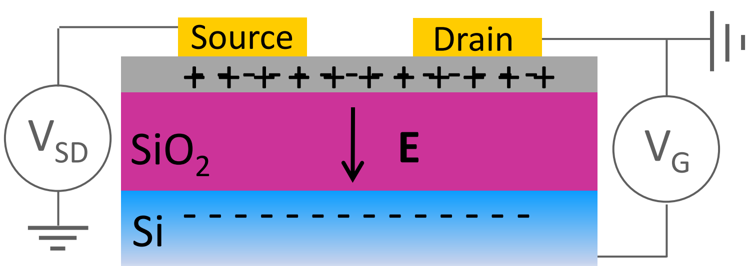
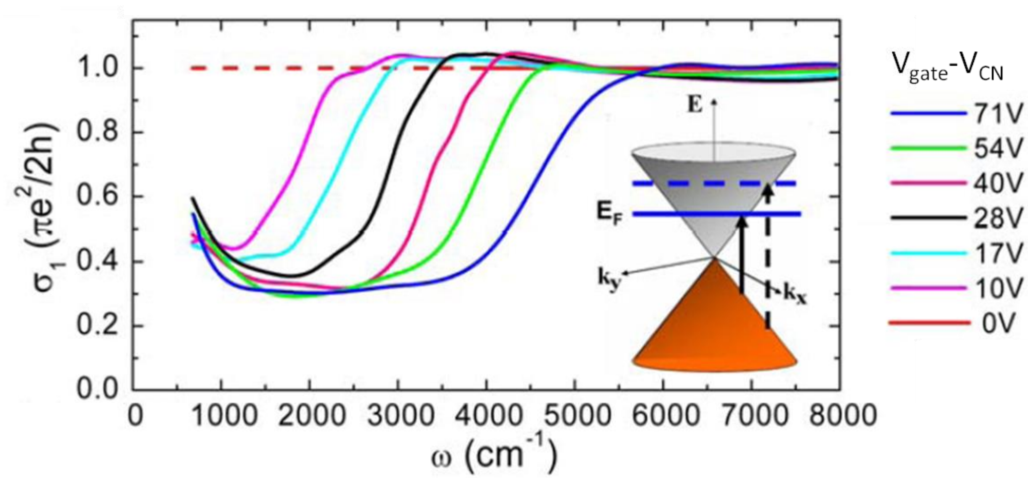


Electric field effect

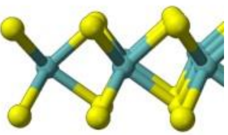


1st observation: Novoselov *et al.*, Science (2004)

$\rightarrow$ *Absorption edge at E~2E$_F$*



Z.Q. Li at al. Nature Physics (2008)
F. Wang *et al. Science* (2008)



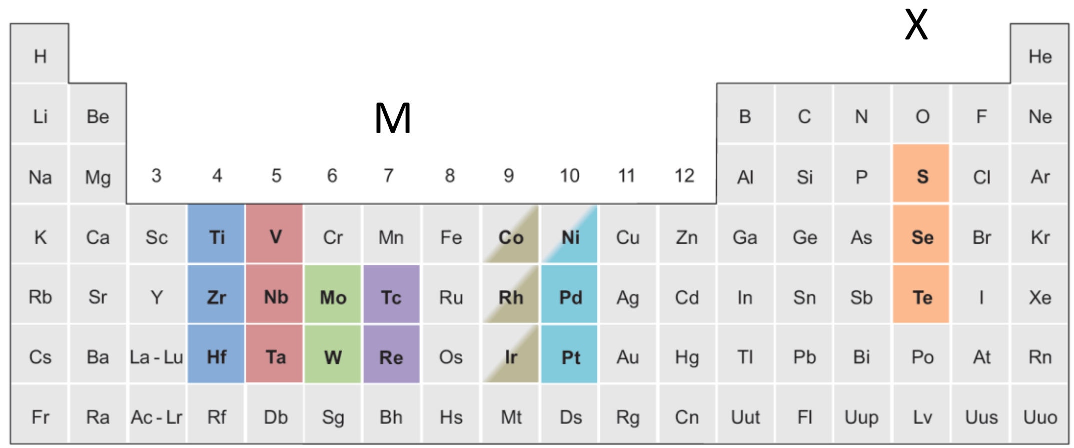
Introducing Transition Metal Dichalcogenides

- MX_2 with M = Mo, W, Re,…
  X = S, Se, Te
- Well documented in the bulk

Wilson and Yoffe Adv. Phys. 1969

- In this talk:

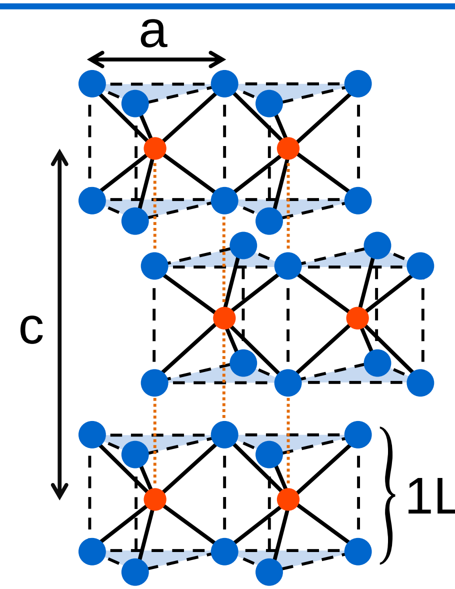
Semiconducting MX_2 only

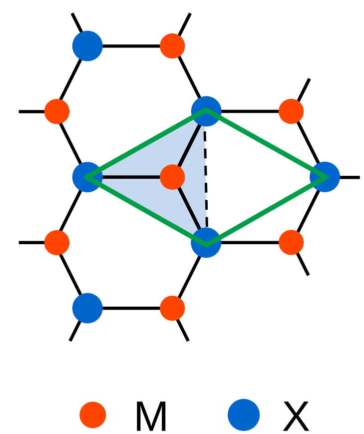


M. Chhowalla *et al.*, Nat. Chem. **5**, 263 (2013)

- Trigonal prismatic phase
- 2*Hc*-MX_2 (AbA,BaB stacking)

→ MoS_2, $MoSe_2$, WS_2, WSe_2, $MoTe_2$

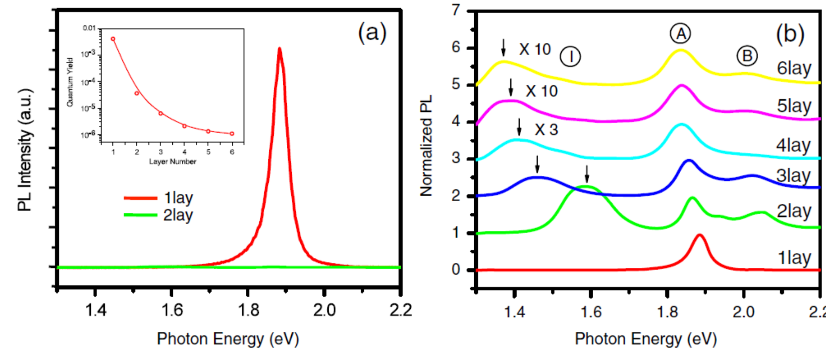




Some remarkable properties of *2Hc*-TMD

Photonics

- Indirect (bulk) to direct (1L) bandgap♦
- Tightly bound excions (trions, biexcitons)♣
- Single photon emitters*
- Towards large PL quantum yields♠



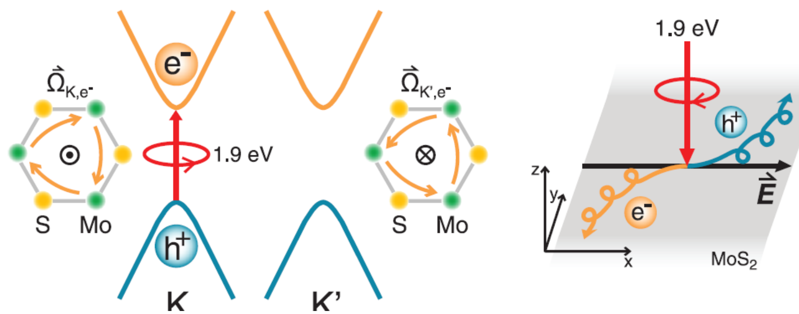
K. F. Mak, PRL **105**, 136805 (2010)

Valleytronics

- All optical valley polarization

Mak *et al.* + Zeng *et al.*, Nat. Nano 2012

- Valley-Hall effect

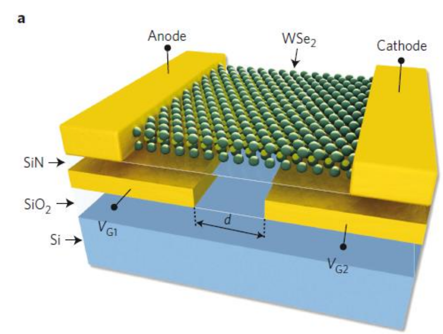


Mak *et al.* Science 2014

Optoelectronics

- Photodetection, electroluminescence, photovoltaics
- Type II van der Waals heterostructures

(Seattle, ICFO, Columbia, Berkeley, Manchester, MIT, Vienna, EPFL, U. Kansas,...)

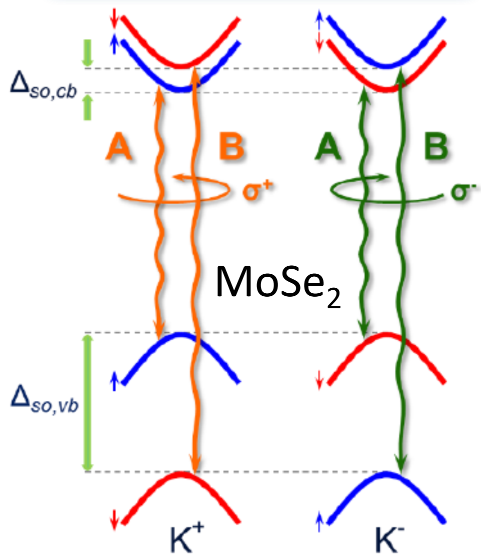


Nat. Nano 2014 (TU Vienna, MIT, Seattle)

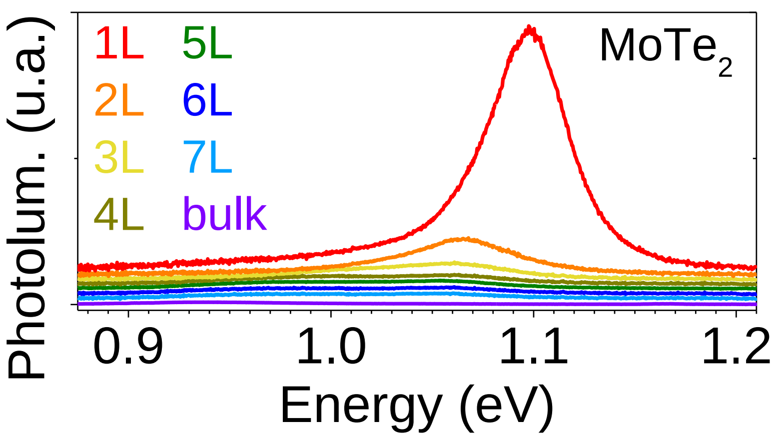
♦ ♣ Columia, Berkeley, Case Western, Hong Kong, INSA Toulouse, Vanderbilt, LNCMI, Geneva...
*Nat Nano 2015 (ETH, Rochester, LNCMI, Hefei/Seattle) ♠Amani et al. Science 2015

Basic optical properties of TMD

Spin-valley locking

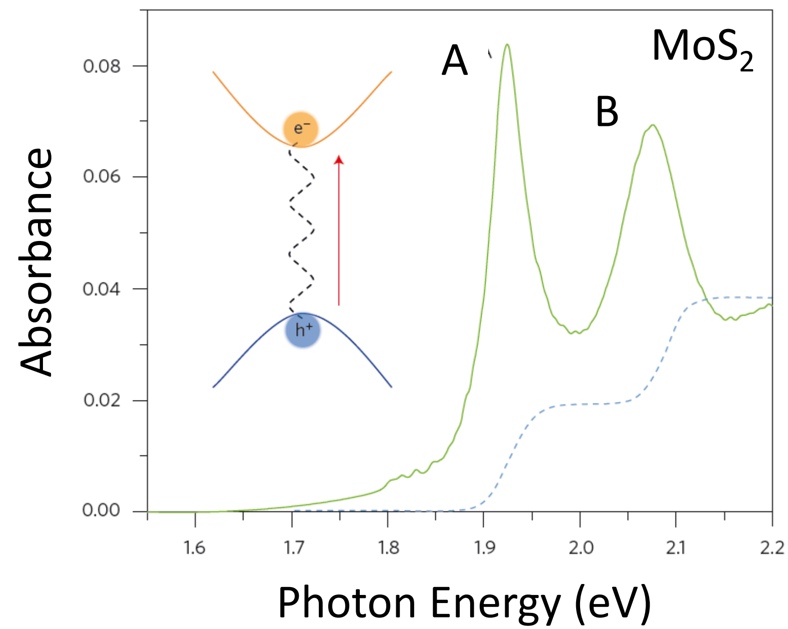


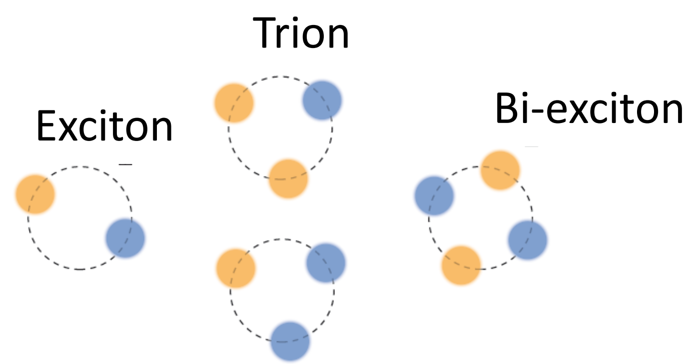
Koperski *et al.* arXiv:1612.05879 (review)



Froehlicher *et al.*, PRB 2016 (also Ruppert NL 2014, Lezama NL 2015)

Excitonic Effects

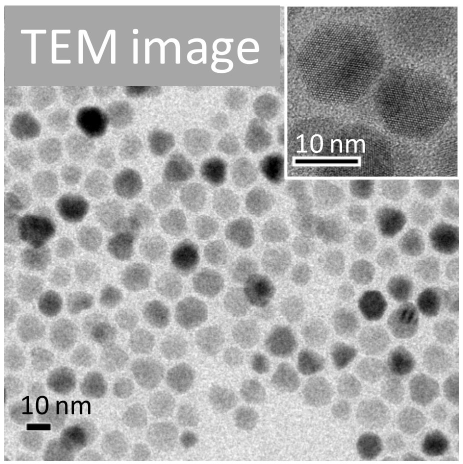


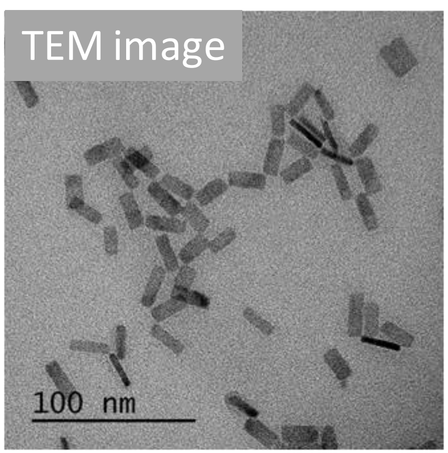


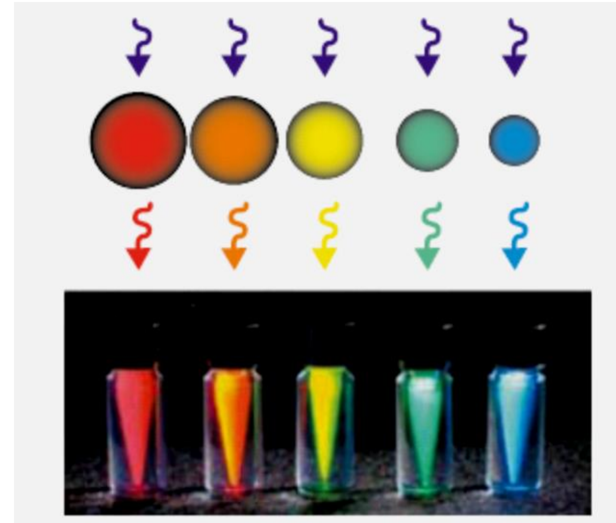
Mak & Shan, Nat. Photon. 2016 (review)

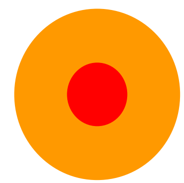
30+ years of colloidal semiconductor nanostructures

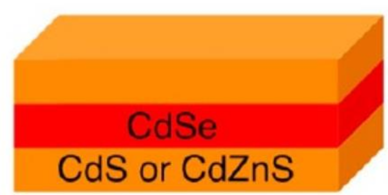
- Quantum dots (0D), rods (~1D), wells (2D)
- Size and shape tunable properties
- Broadband absorption / narrow emission











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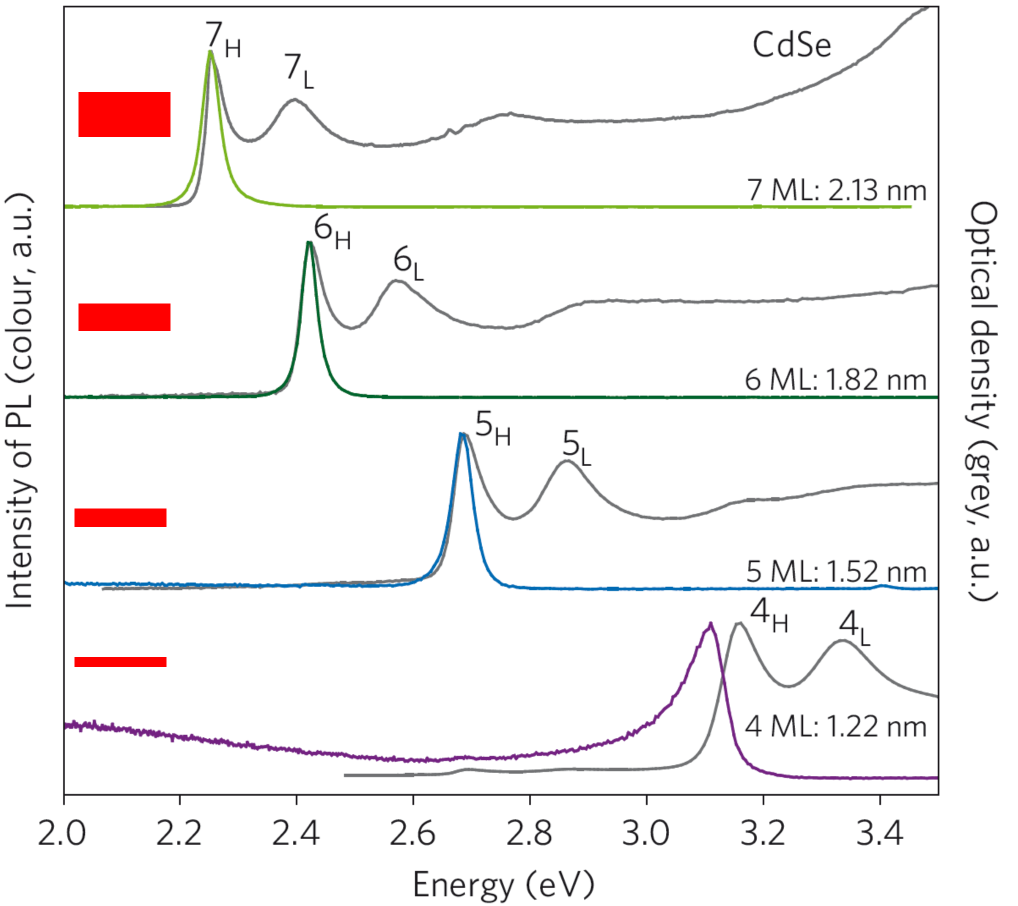
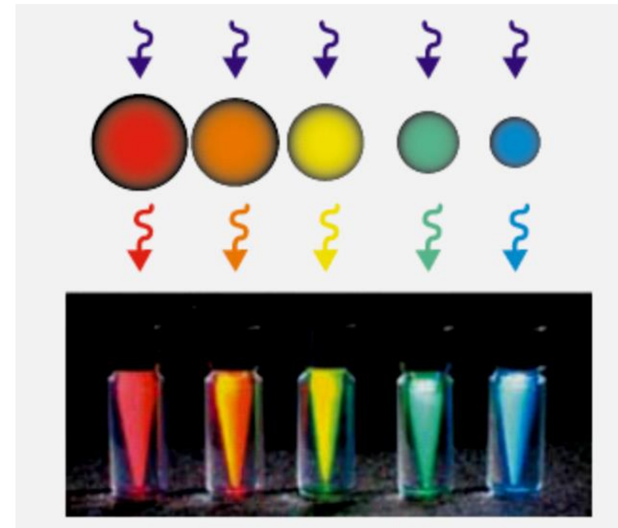
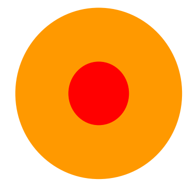
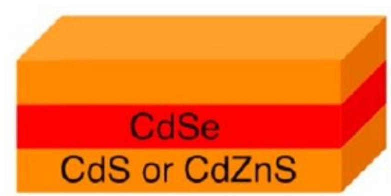




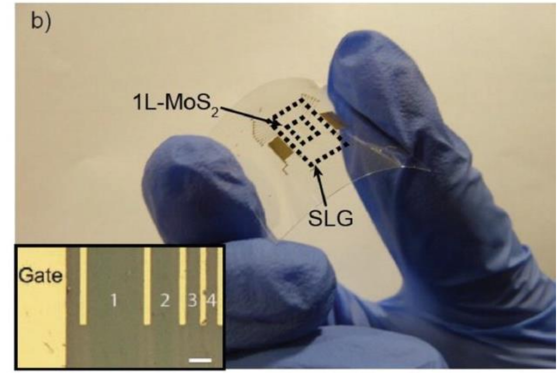




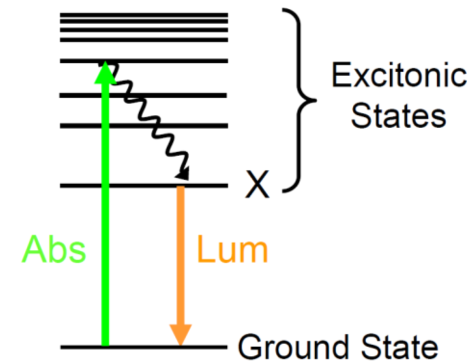
Ithurria *et al.* Nat. Mater. **10**, 936-941 (2011)

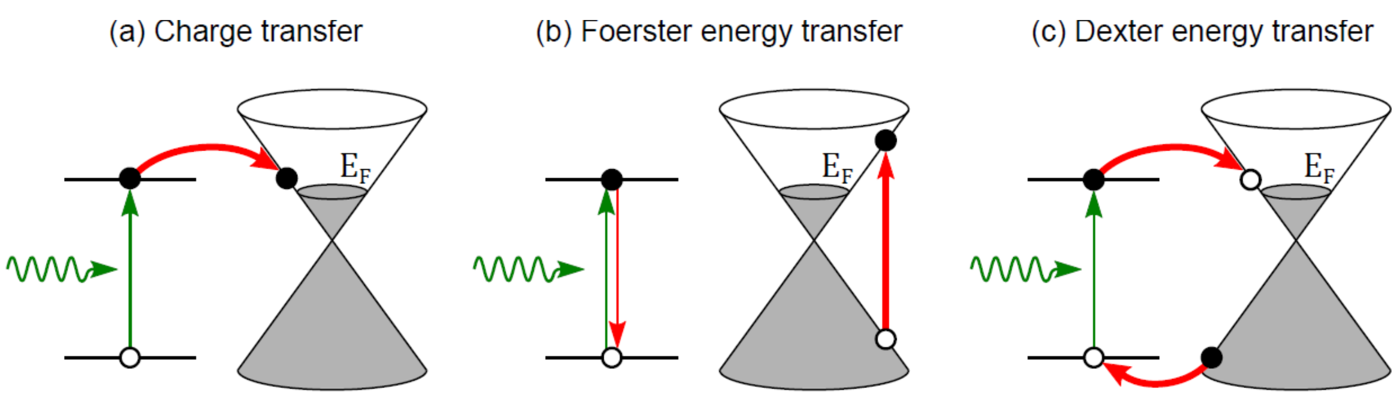
Hybrid systems and heterostructures: why the interest?

- *Graphene: 2D semi-metallic channel*
  - ✓ Quasi-transparent (~2% absorption per layer)
  - ✓ High carrier mobility and large carrier density
- *TMD: atomically thin semiconducting channel*
  - ✓ Strong light matter interaction
  - ✓ Tunable properties



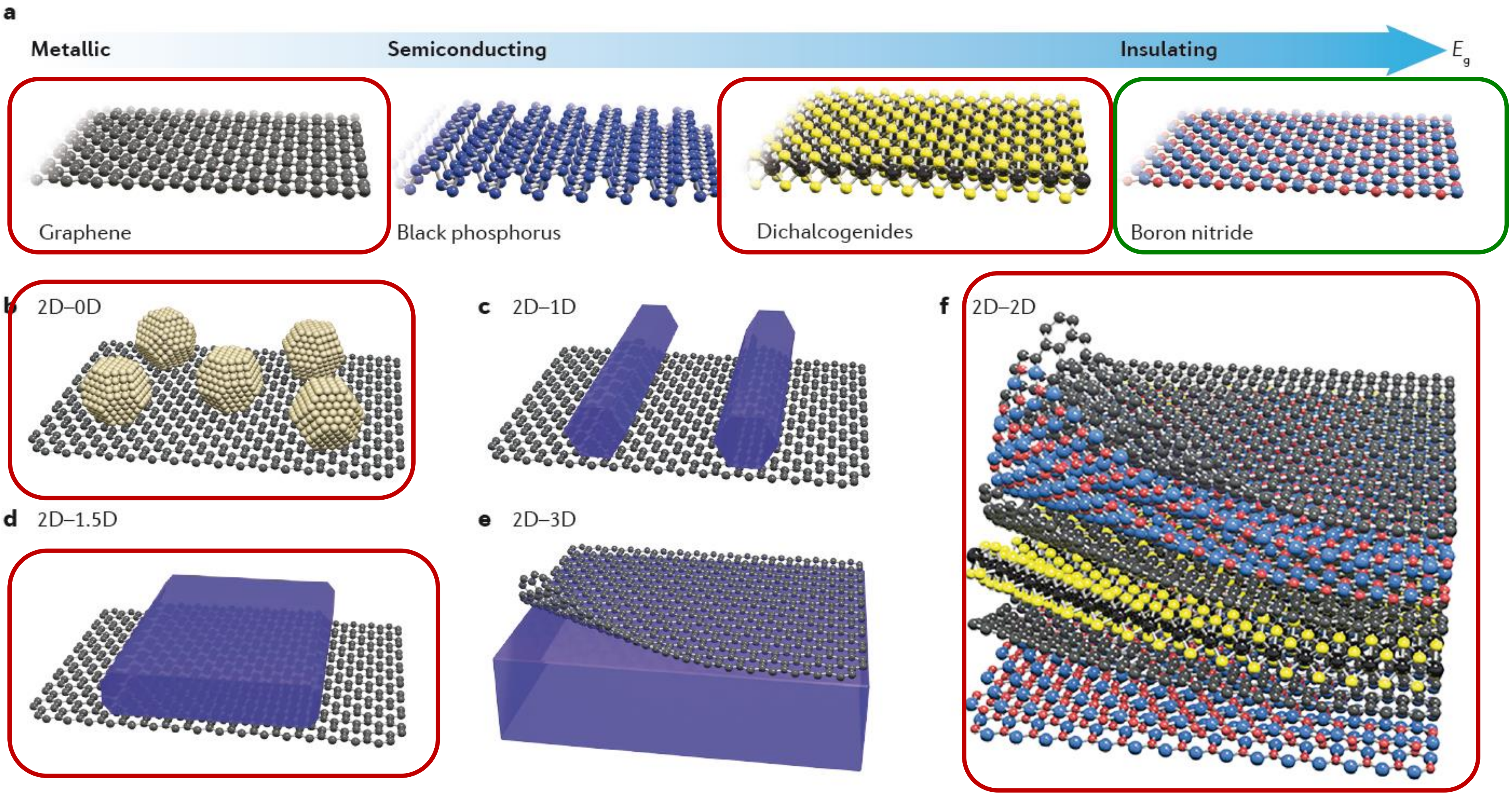
- *Semiconductor nanostuctures: 0D, 1D, 2D*
  - ✓ Broadband absorption & size tunable emission
  - ✓ Highly photostable





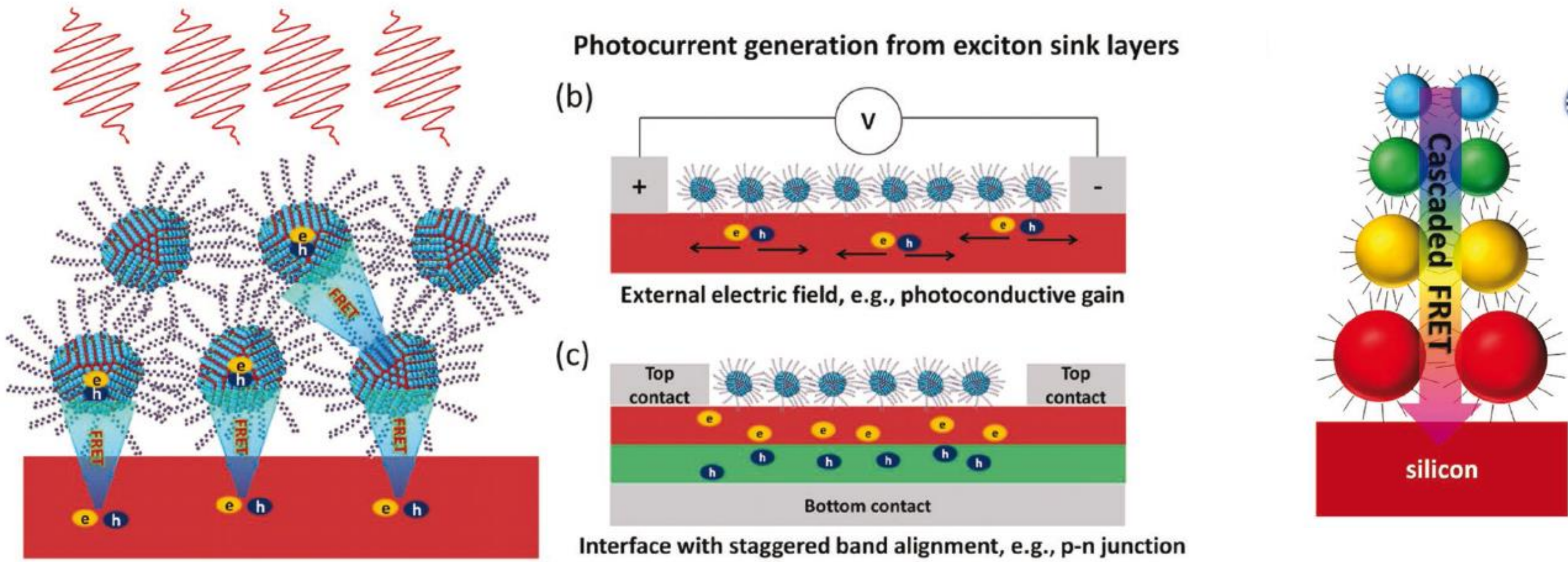
➢ *Harnessing near-field interactions in new optoelectronic devices*

Hybrid systems and heterostructures



Y. Liu *et al.*, Nature Review Materials doi: 10.1038/natrevmats.2016.42

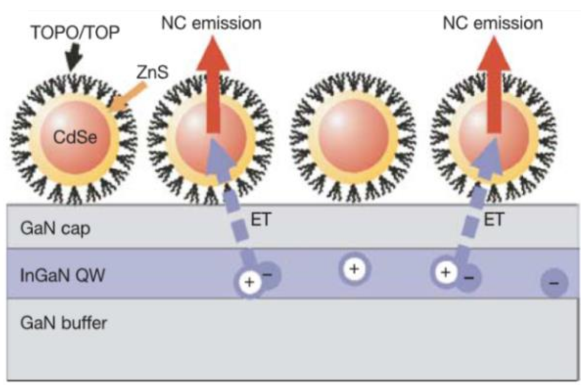
FRET in hybrid optoelectronic devices



B. Guzelturk & HV Demir Advanced Functional Materials 10.1002/adfm.201603311

Energy Transfer Pumping

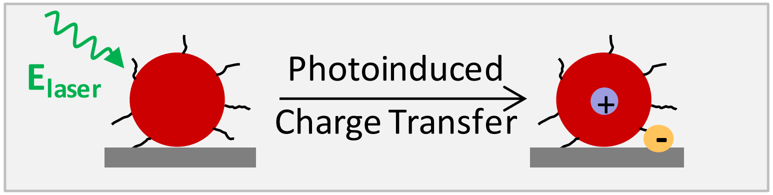
Achermann *et al.*
Nature (2004)
(Los Alamos)



+ Energy/exciton funnelling
Substrate sensitization
Color conversion
Long Range (>> 1 nm)

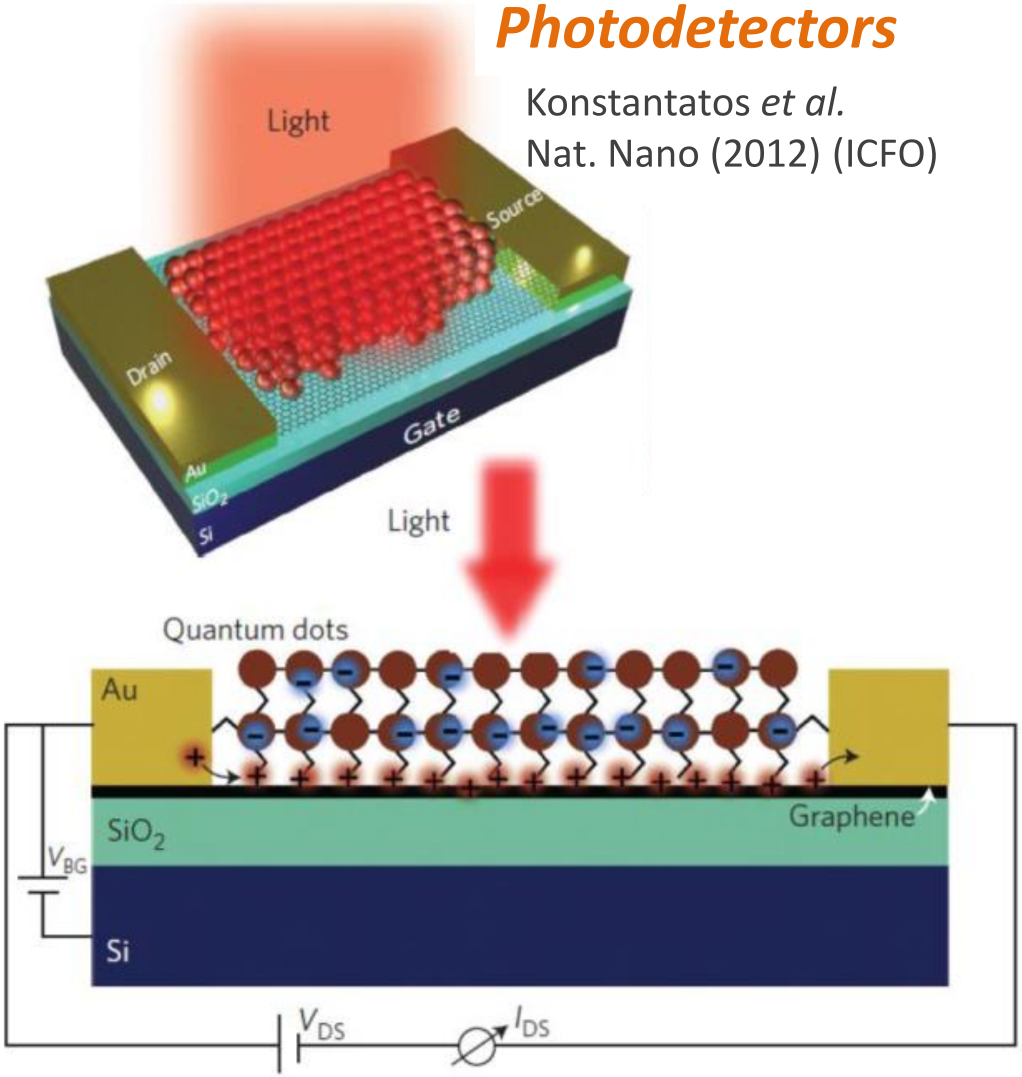
− How to separate
the transferred excitons?

Charge Transfer in hybrid photodetectors



High gain Photodetectors

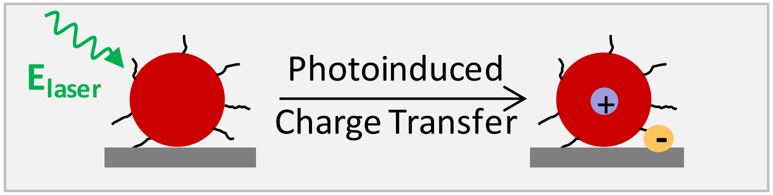
Konstantatos *et al.*
Nat. Nano (2012) (ICFO)



+ Photodetection
  Short range (< 1 nm)
  → Selectivity/Sensitivity
  Processability

− Short range…
  Highly sensitive to:
  ✓ Surface states
  ✓ Adsorbates
  ✓ Interfaces/ligands

Charge Transfer in hybrid photodetectors



High gain Photodetectors

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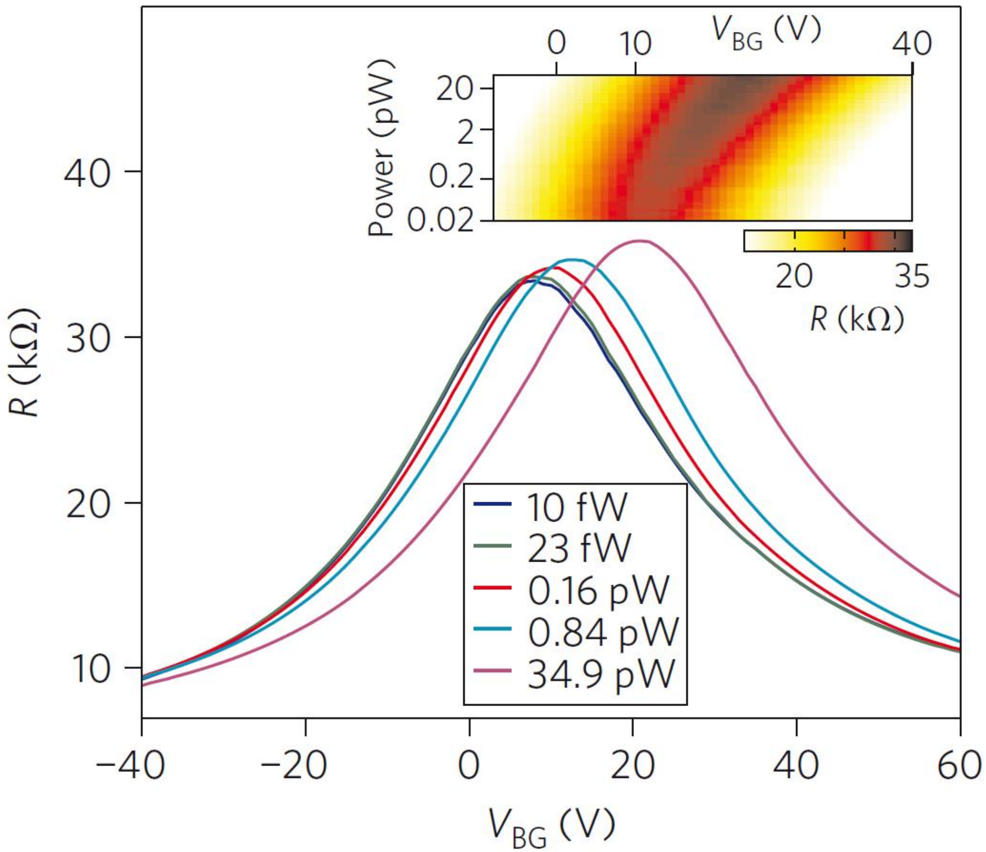

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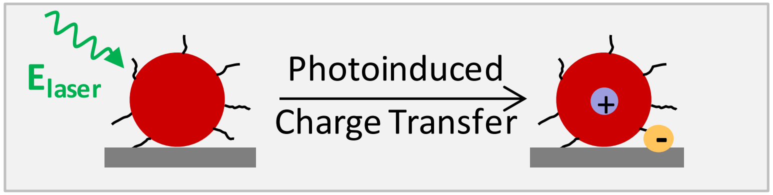
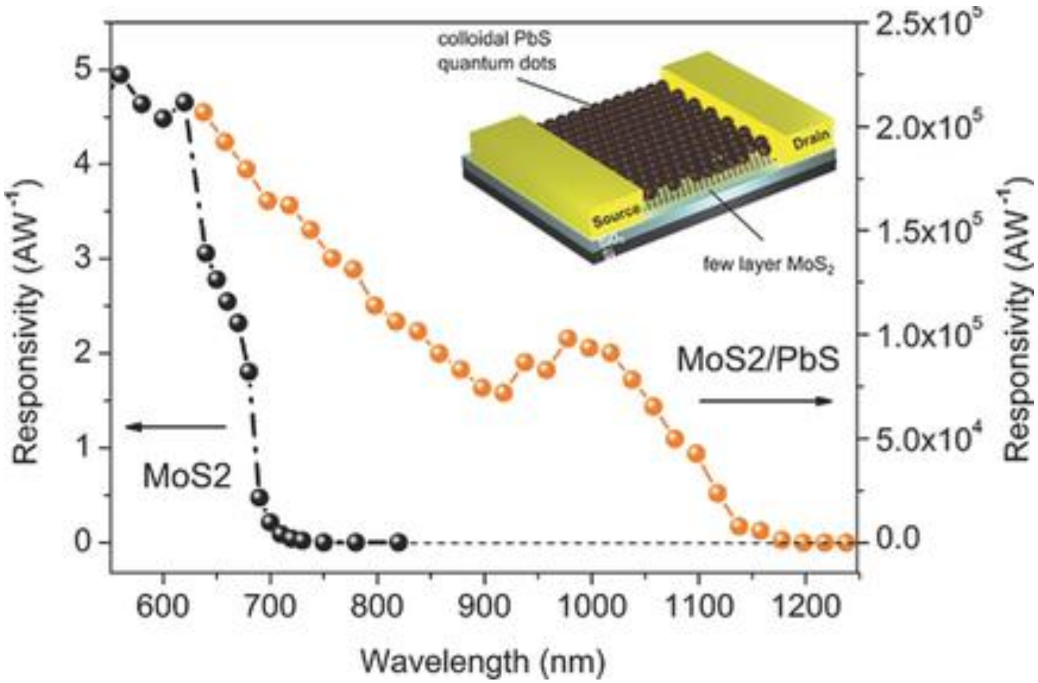


High gain Photodetectors

Kufer *et al.*
Advanced Mat. (2015)



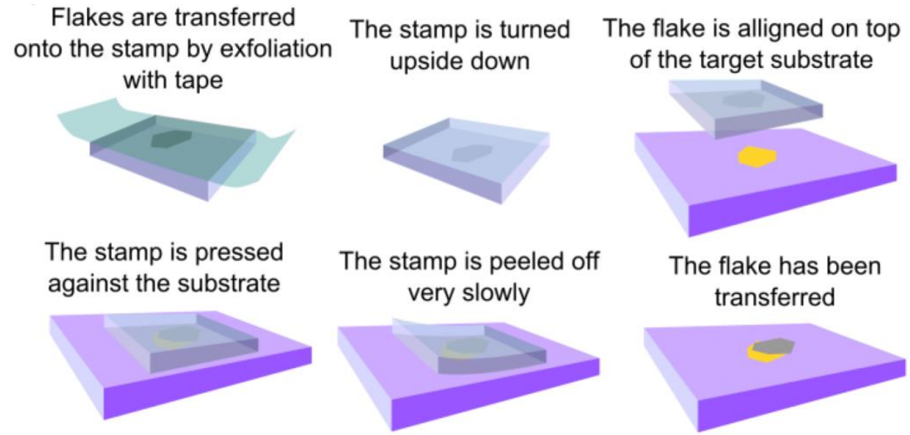
+ Photodetection
Short range (< 1 nm)
→ Selectivity/Sensitivity
Processability

− Short range…
Highly sensitive to:
- ✓ Surface states
- ✓ Adsorbates
- ✓ Interfaces/ligands

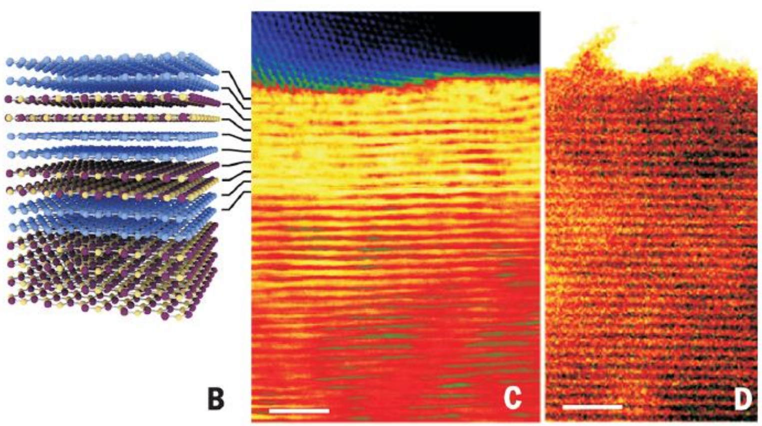
van der Waals Heterostructures

- ✓ No dangling bounds
- ✓ No lattice mismatch issues
- ✓ Rotational degree of freedom

- 2010 : Graphene on hBN
- 2017 : wet or dry transfer, pick up and lift,…
- Numerous possibilities!



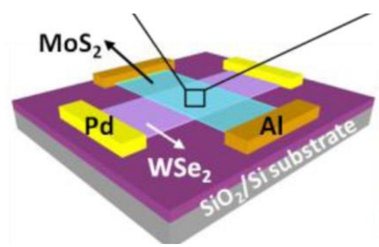
Castellanos-Gomez *et al.* 2D Materials **1** 011002 (2014)

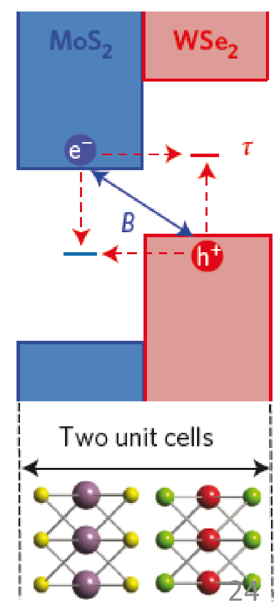


Haigh, Gorbachev *et al.*, Nature Materials 2012
Manchester Group

Atomically thin p-n junctions

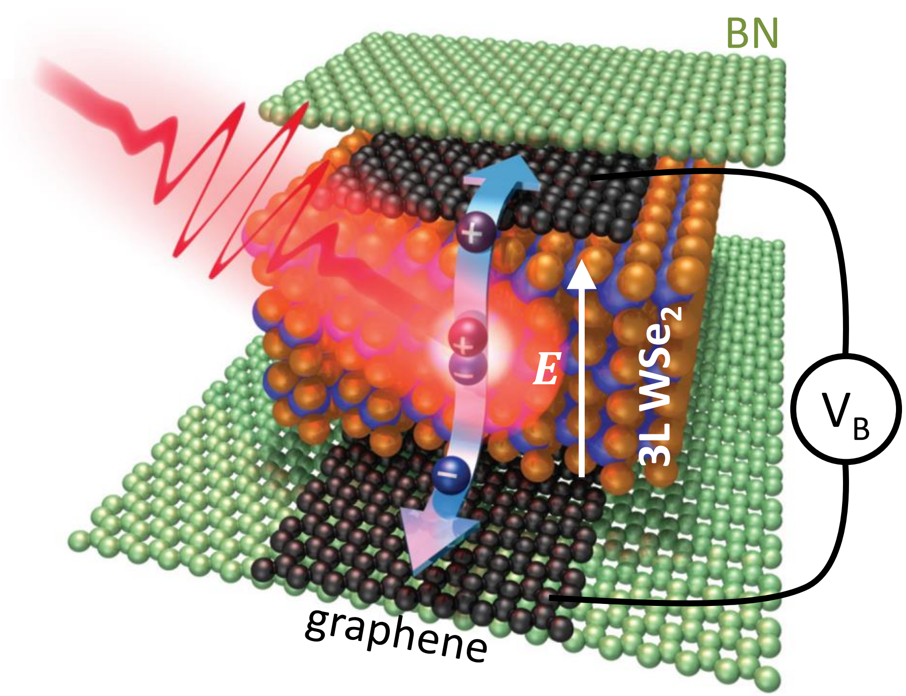
C-H Lee *et al.*
Nat. Nano (2014)
(Columbia)





Optoelectronic devices based on vdWH: key mechanisms

BN/Gr/WSe_2/Gr/BN



M. Massicotte *et al.*, Nat. Nano. 11, 42 (2016)

- ✓ Photoactive material: **WSe_2**
- ✓ Electrical contacts: **graphene**
- ✓ Electric field: **V_B**

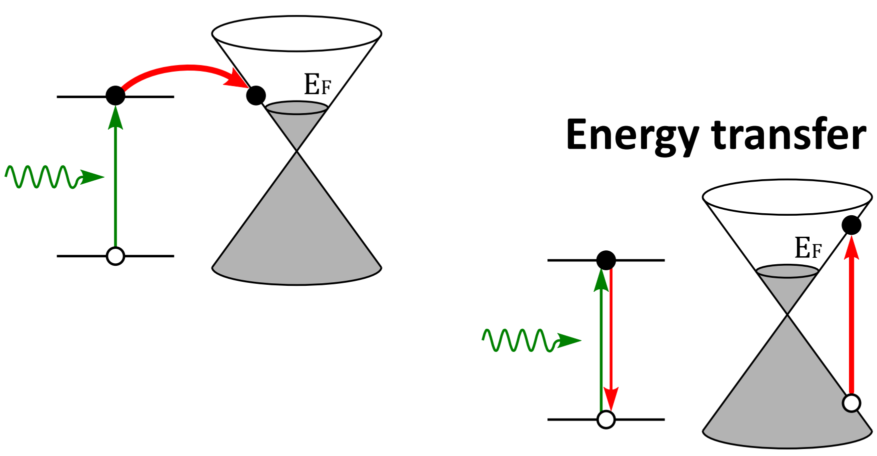
⚠ Atomic dimensions ≠ conventional heterostructures

1. Exciton formation
2. Exciton dissociation
3. Charge transport
4. Interfacial transfer

+ losses: exciton recombination

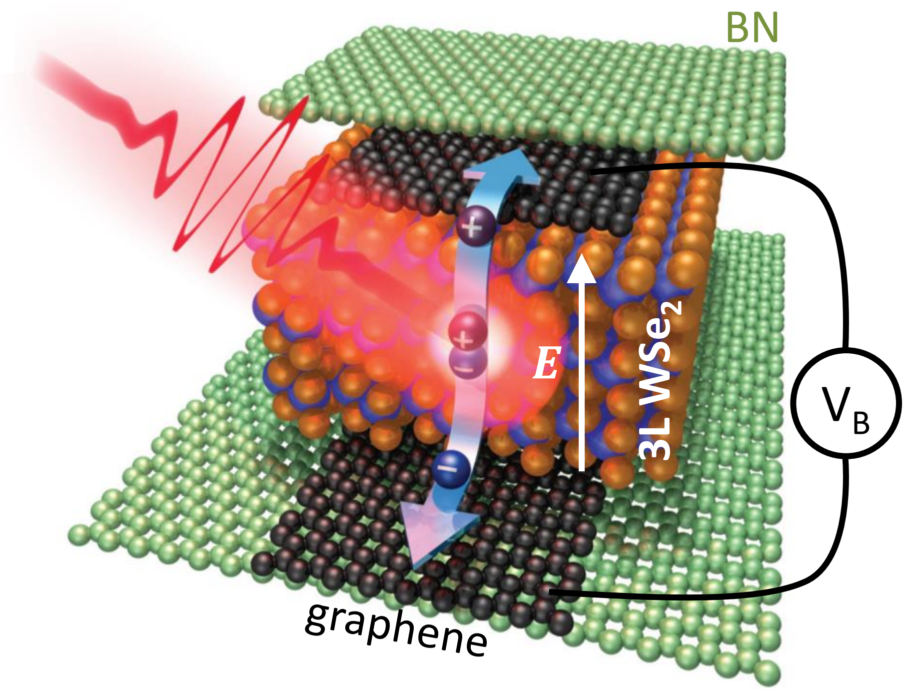
Charge transfer

Energy transfer



Optoelectronic devices based on vdWHs: key mechanisms

BN/Gr/WSe_2/Gr/BN



M. Massicotte *et al.*, Nat. Nano. 11, 42 (2016)

1. Exciton formation
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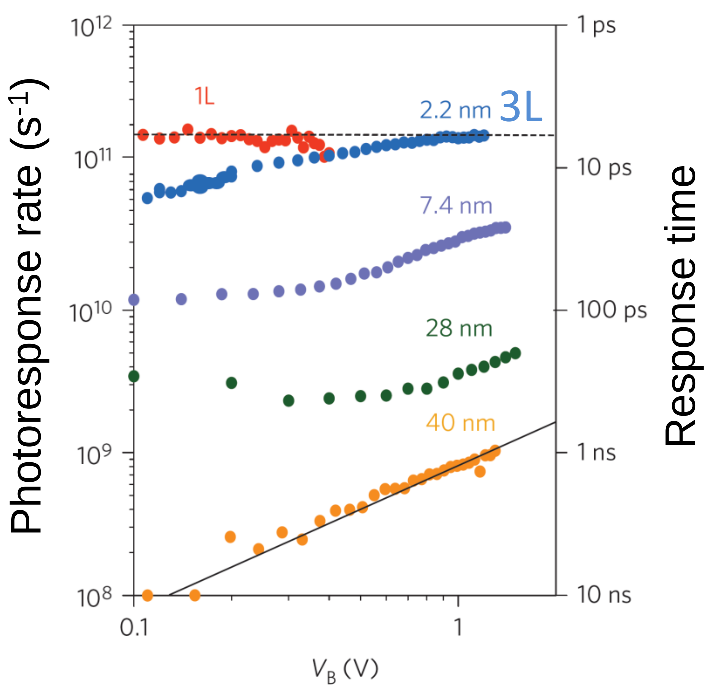
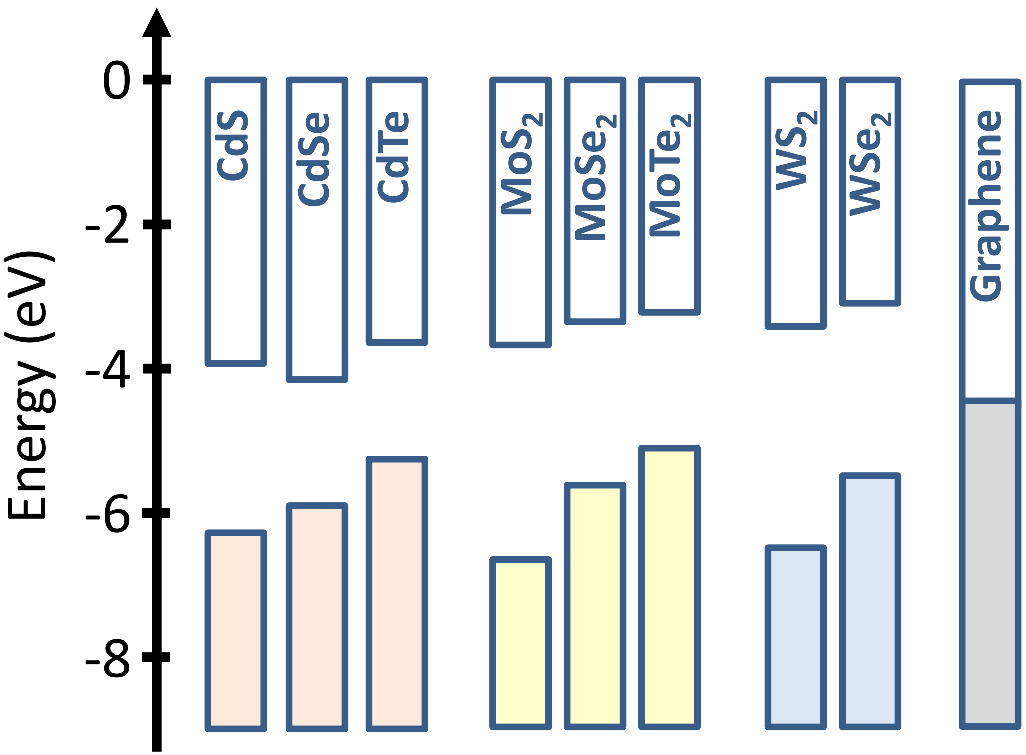


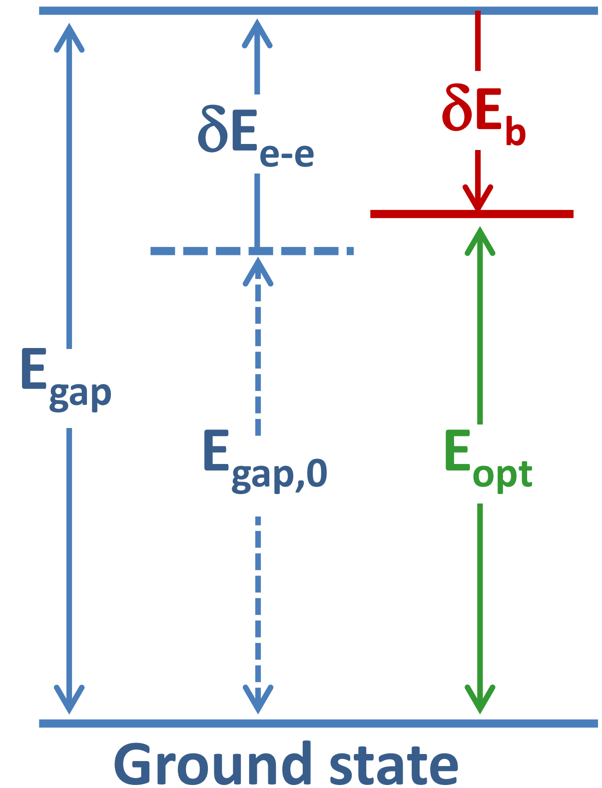
- ✓ Photoactive material: **WSe_2**
- ✓ Electrical contacts: **graphene**
- ✓ Electric field: **V_B**

Band alignment and excitonic effects

Type I (CdSe/ZnS) or II (CdSe/CdTe) Heterojunctions

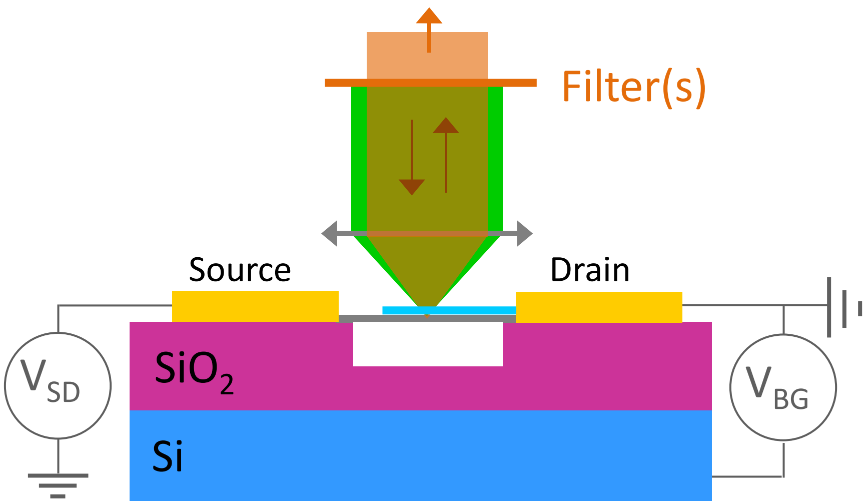


Optical Gap < Transport Gap



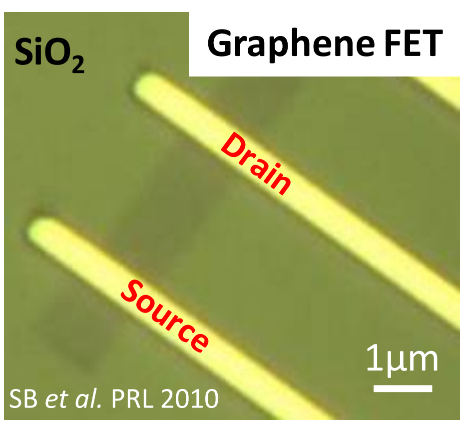
TMD: Y. Liang et al., APL **103**, 42106 (2013), M. Ugeda *et al.*, Nat. Mater. **5**, 1091 (2014)
Graphene: Y.-J. Yu *et al.*, Nano Lett. **9**, 3430 (2008), II-VI semicond : Norris et al. Science 2008

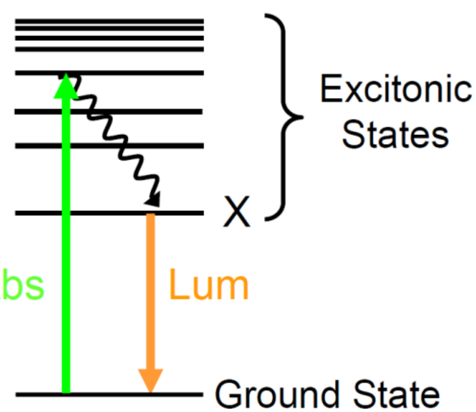
Our experimental approach

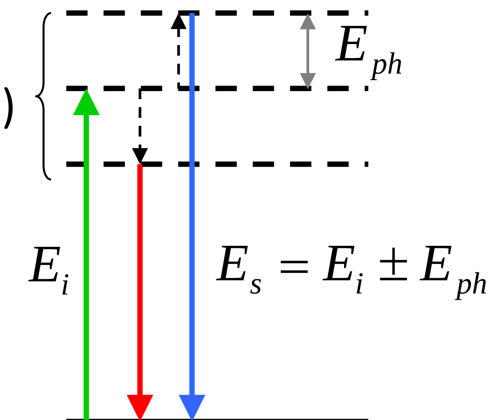


Graphene, TMD, hybrid system, heterostructure,…

- ***(micro)-optical spectroscopy***
  → Photoluminescence, Raman,…
- ***Exciton dynamics***
  → Time correlated photon counting
- ***Nanofabrication***
  → Optoelectronics
  → (electro-)optomechanics







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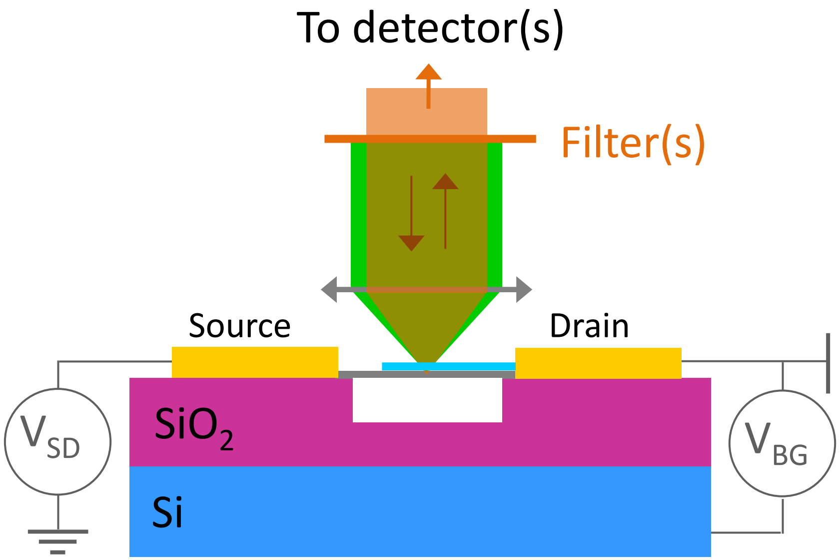
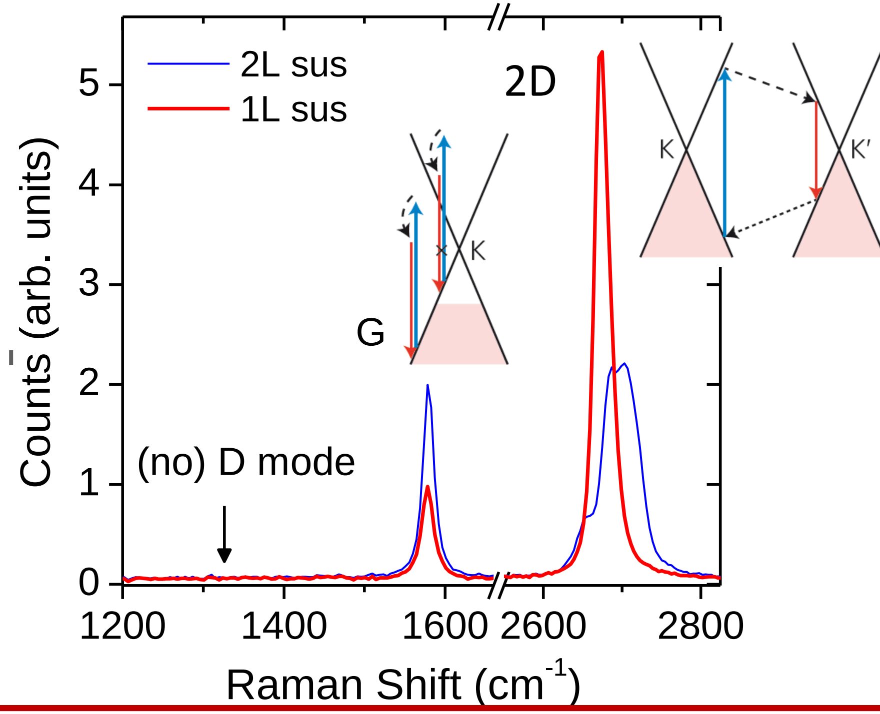
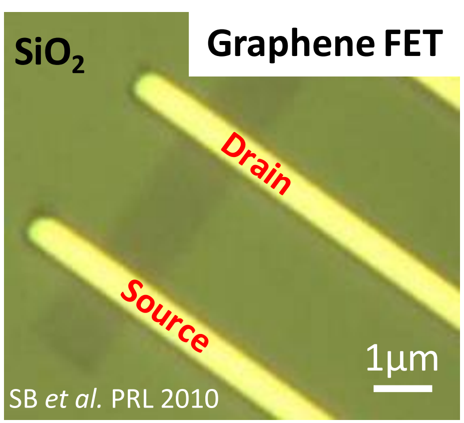
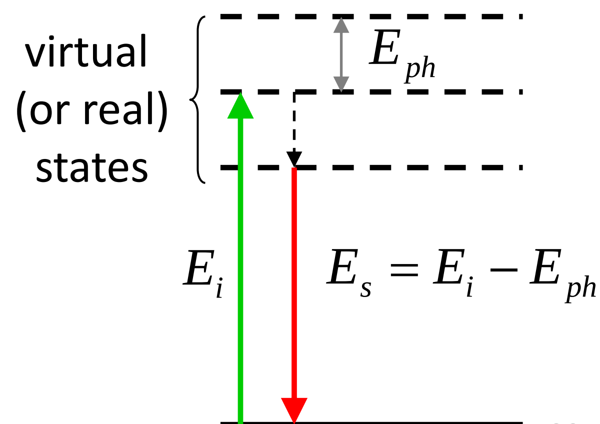


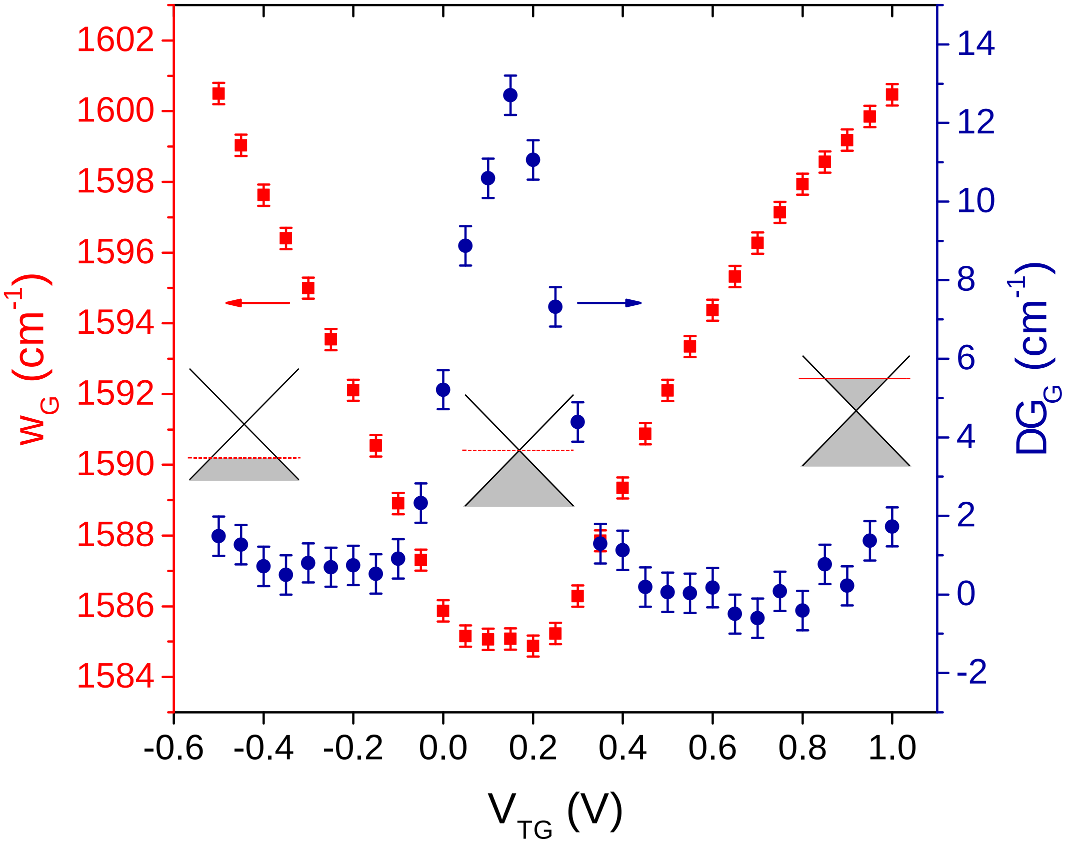
Graphene, TMD, hybrid system, heterostructure,...



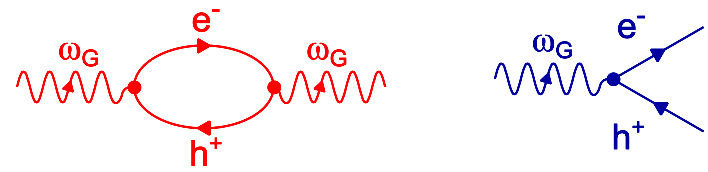


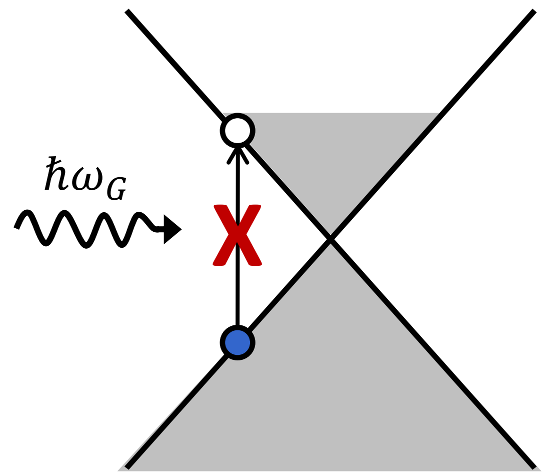


Electron-phonon coupling and Raman spectroscopy



G phonon renormalization





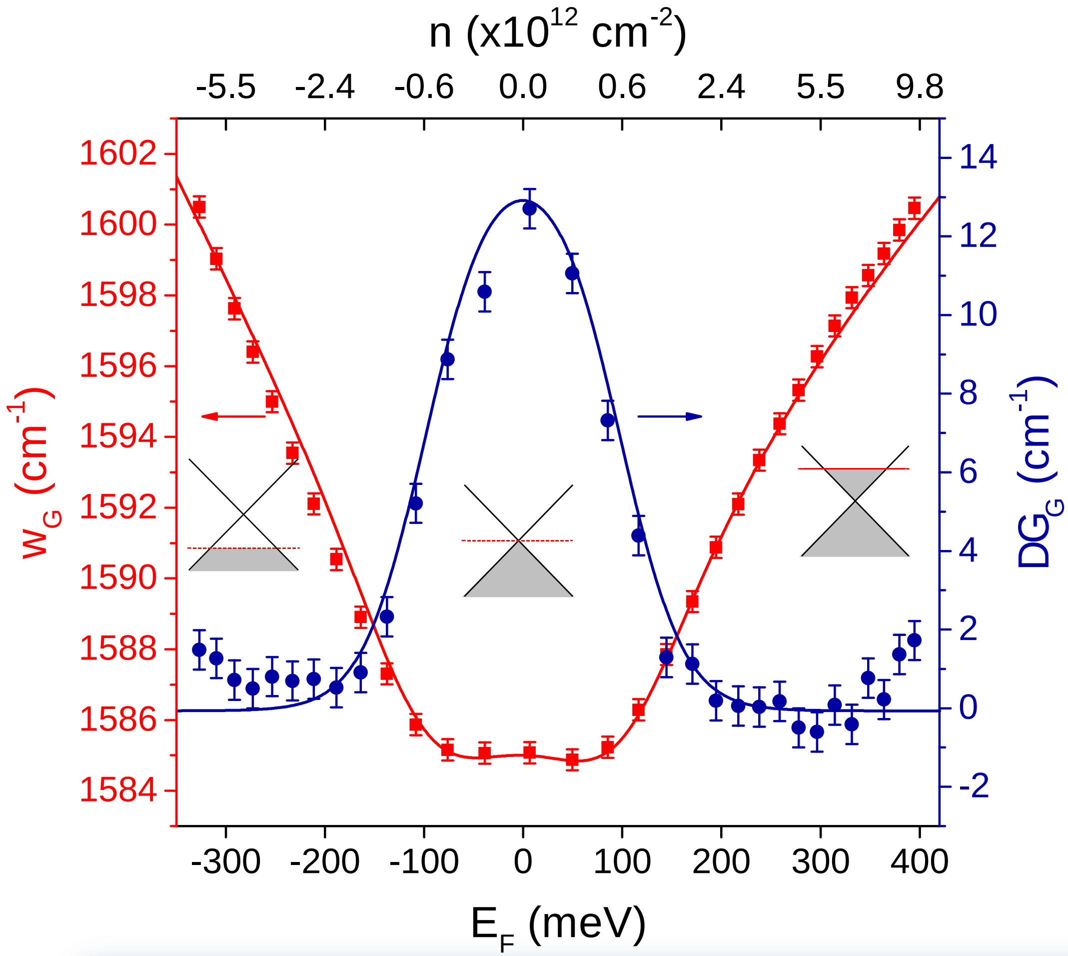
$\lambda_\Gamma = 0.031$

$$\Delta\omega_G = \omega_G - \omega_G^0 = \frac{\lambda_\Gamma}{2\pi\hbar} P \int_{-\infty}^{+\infty} \frac{[f(E-E_F) - f(E)]E^2 \,\mathrm{sgn}(E)}{E^2 - (\hbar\omega_G^0)^2/4} \mathrm{d}E + \Delta\omega_G^A$$

$$\Delta\Gamma_G = \Gamma_G - \Gamma_0 = \frac{\lambda_\Gamma}{4}\left[f\left(\frac{-\hbar\omega_G^0}{2} - E_F\right) - f\left(\frac{\hbar\omega_G^0}{2} - E_F\right)\right]$$

Data. G. Froehlicher & SB PRB 2015
See also: M. Lazzeri & F. Mauri, PRL **97**, 266407 (2006)
S. Pisana *et al.,* Nat. Mat. **6**, 198 (2007)
J. Yan et *al.*, PRL **98**, 166802 (2007)

Electron-phonon coupling and Raman spectroscopy



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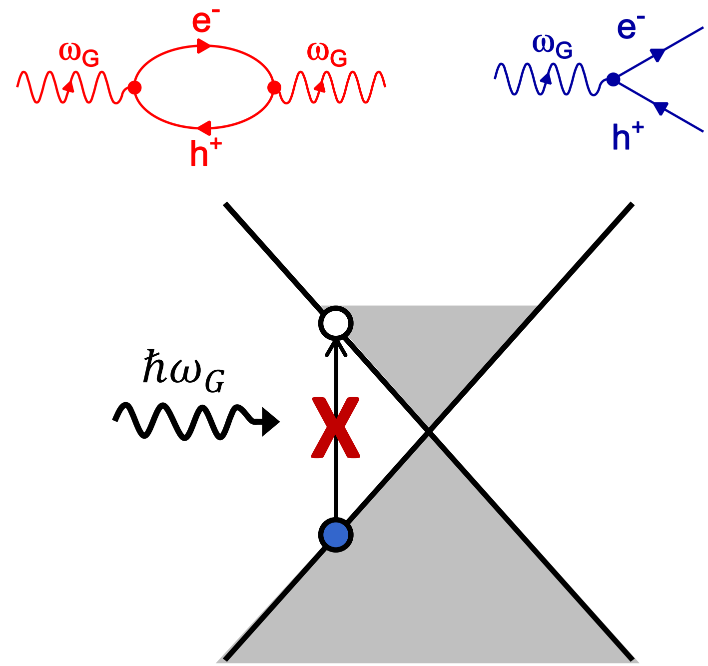

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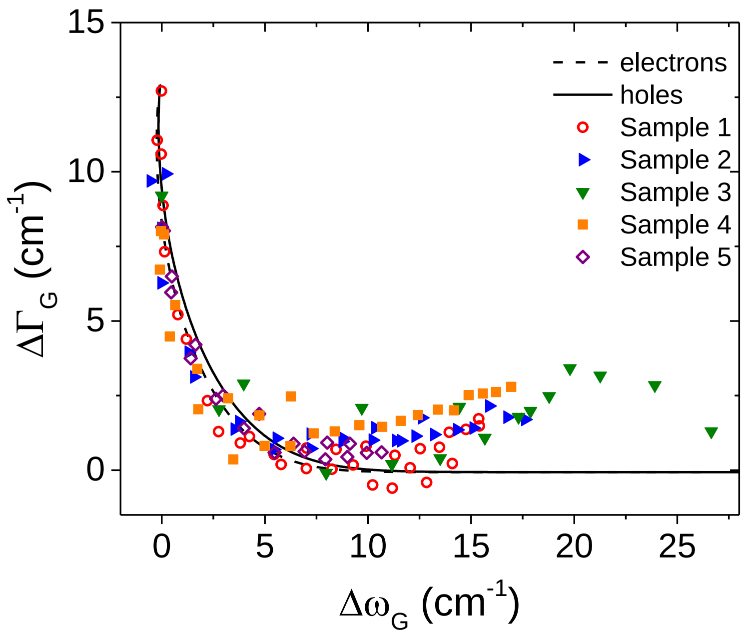
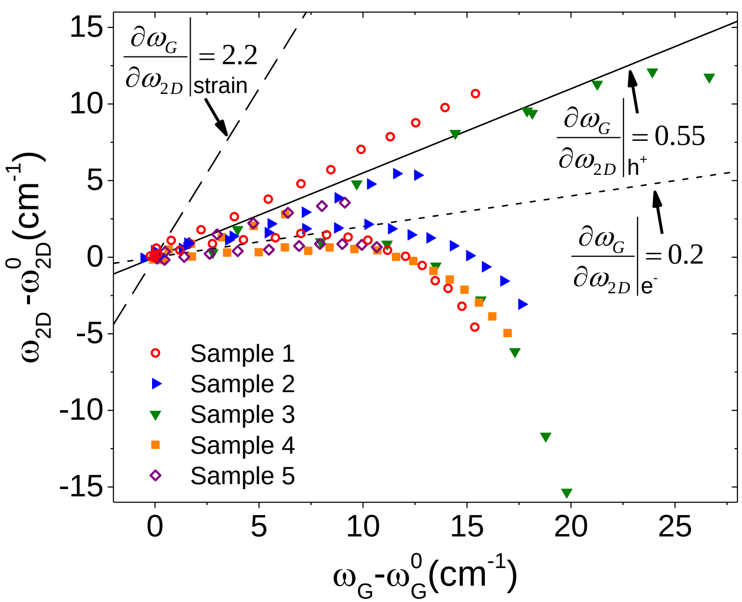
S. Pisana *et al.*, Nat. Mat. **6**, 198 (2007)
J. Yan et *al.*, PRL **98**, 166802 (2007)

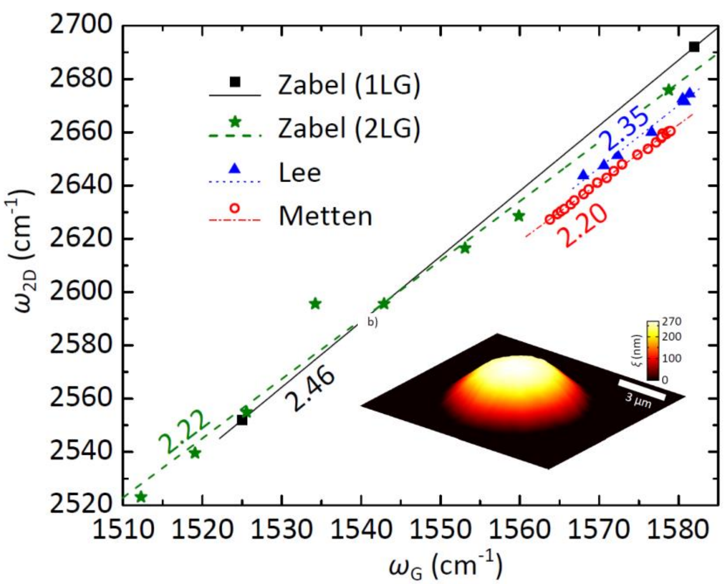
Separating doping and strain

Doping





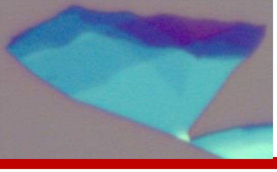
Strain

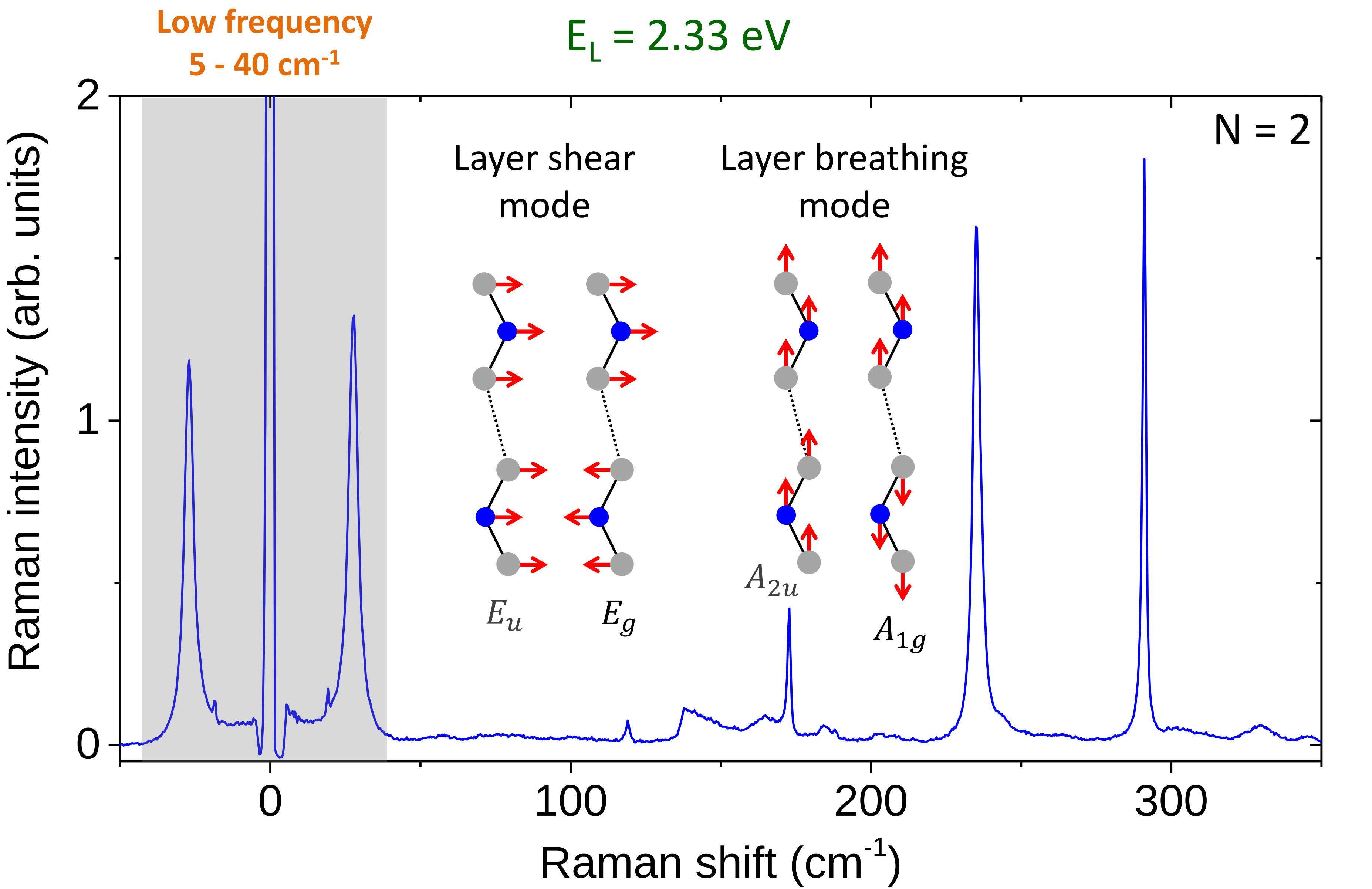


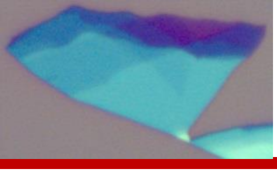
Well-defined and useful correlations between Raman parameters

Data : Froehlicher & Berciaud, PRB 2015
Metten *et al.*, PRApplied 2014
Zabel *et al.*, Nano Lett 2012
Lee *et al.*, Nano Lett 2012
See also : A. Das *et al.*, Nat Nano 2008
Lee *et al.*, Nat Comm 2012

Raman Spectrum of bilayer $MoTe_2$







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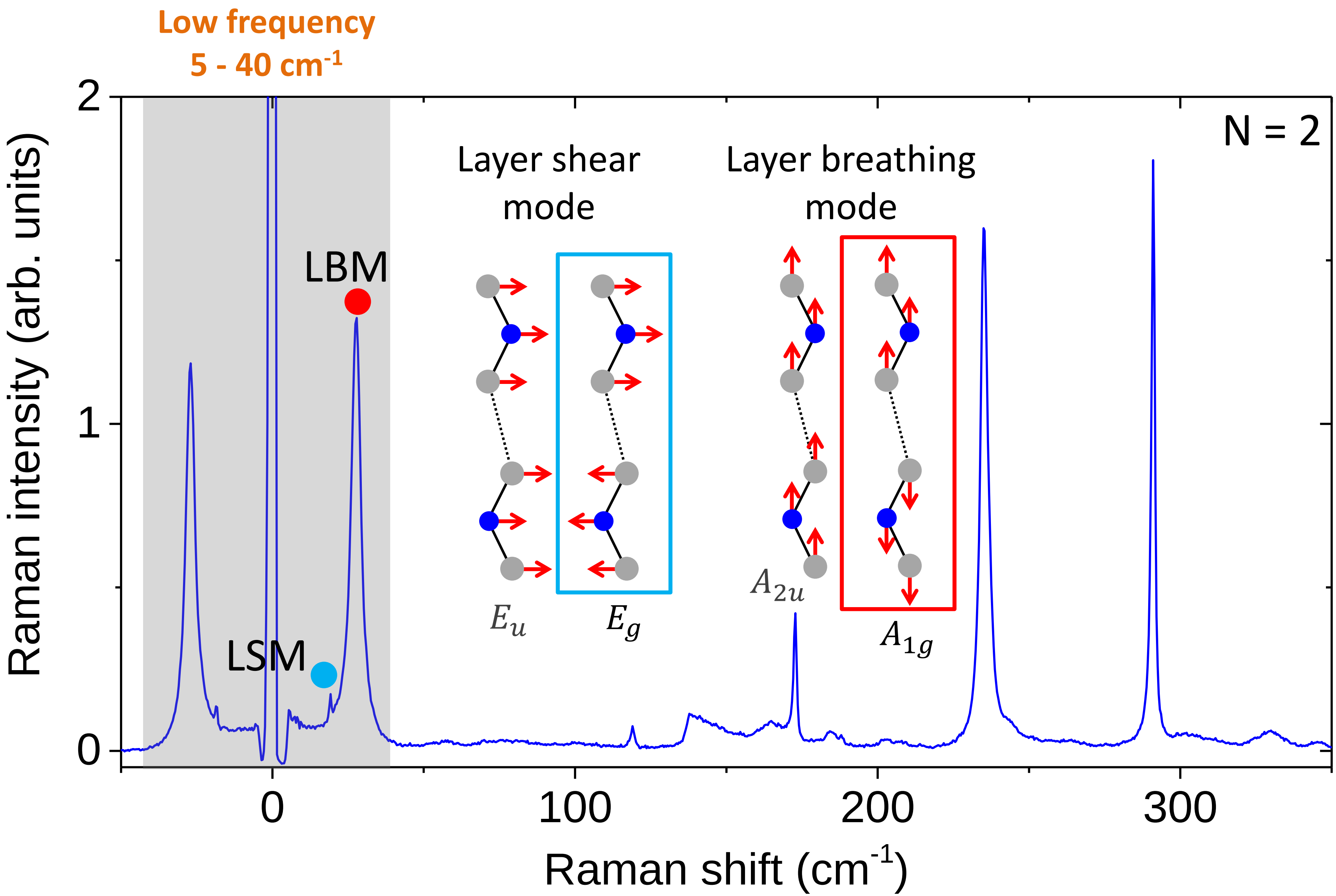

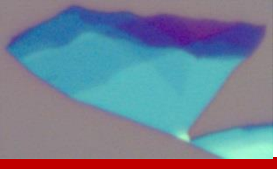

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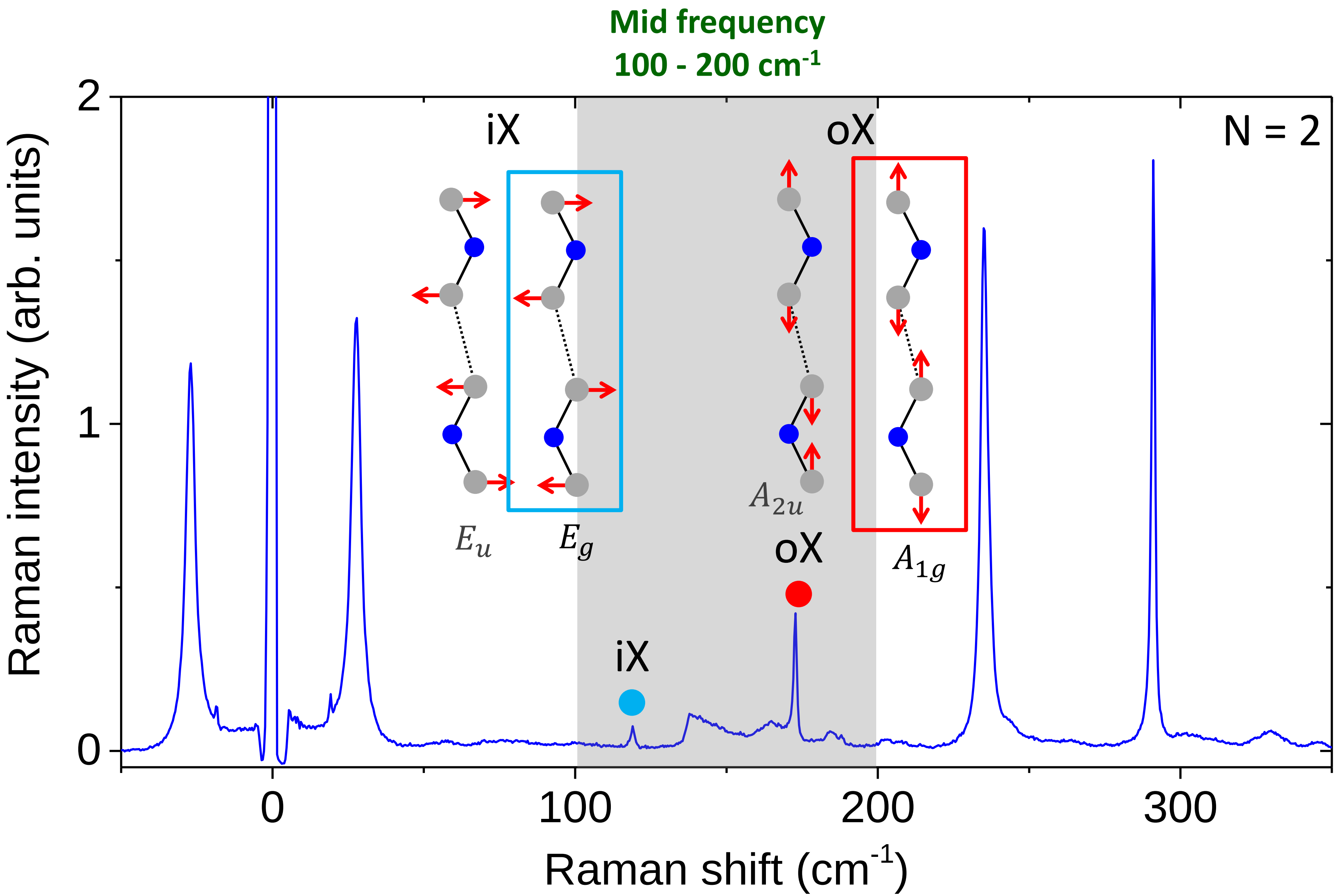

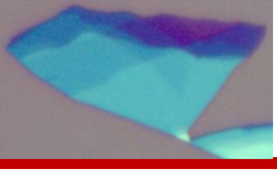

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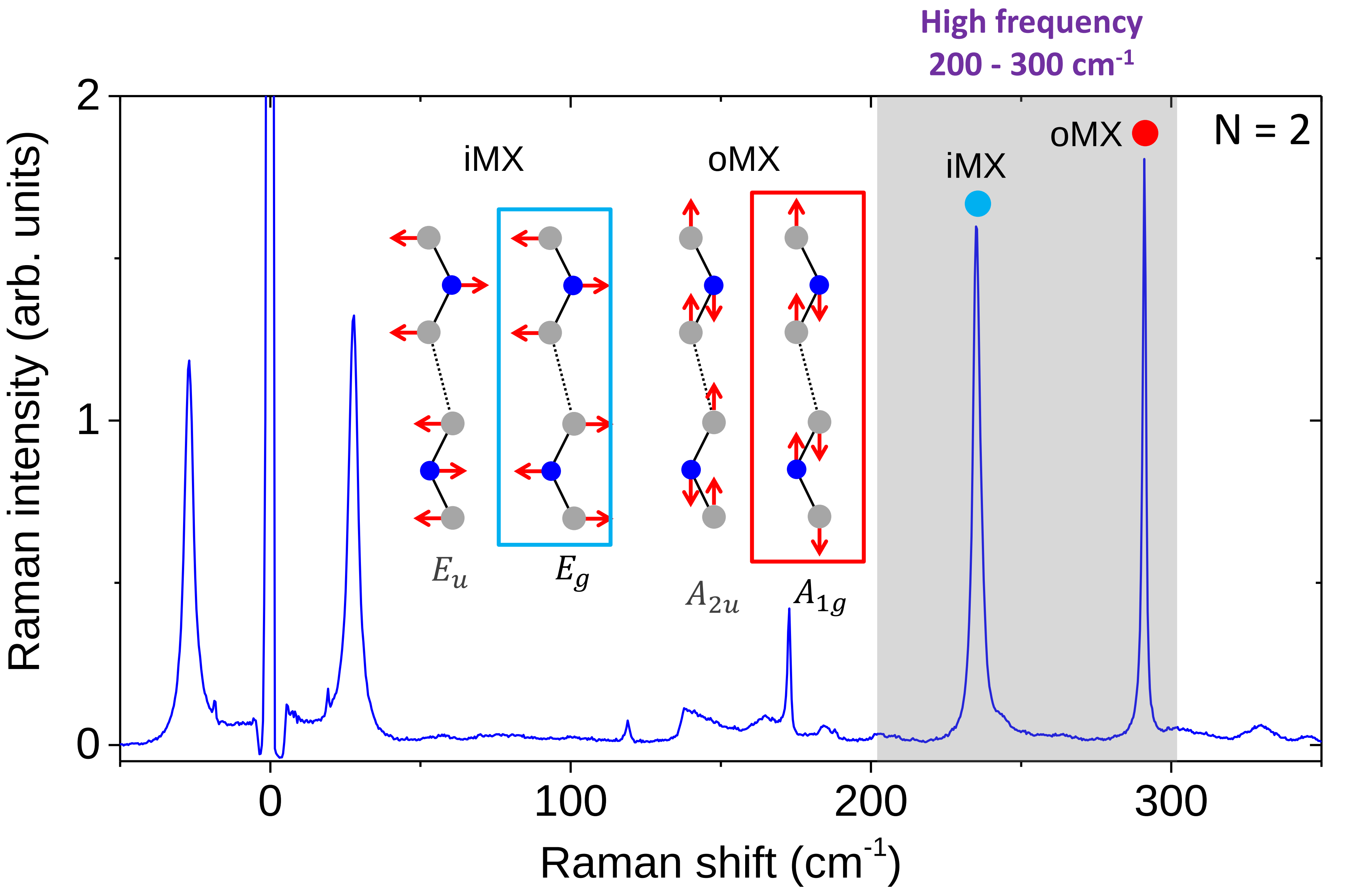

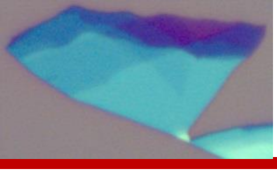

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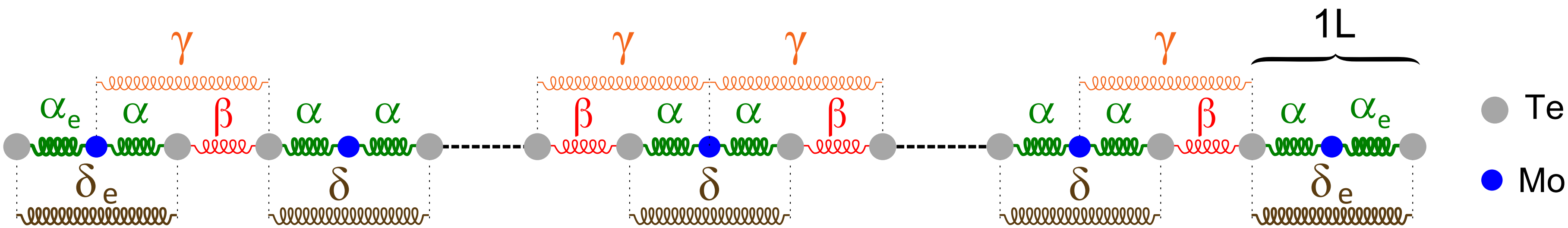
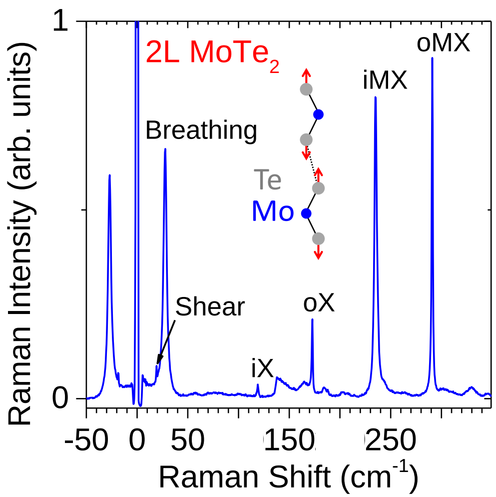
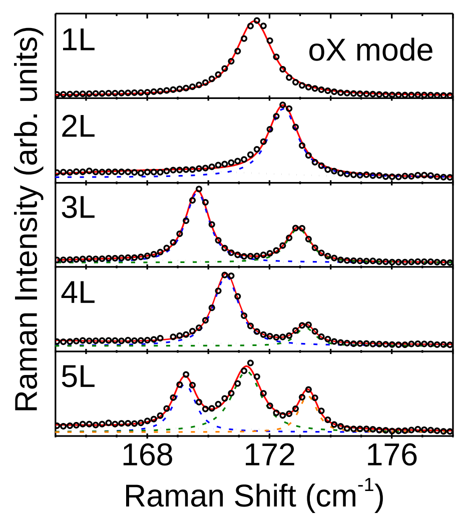
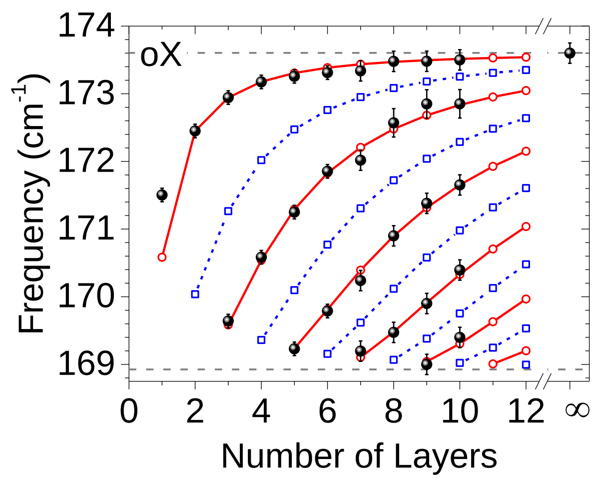


Luo *et al.*, PRB **88**, 075320 (2013)

✓ Interlayer interactions: Davydov splitting and unified description of the phonon modes



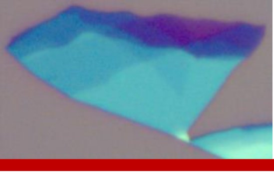




Froehlicher *et al.*, Nano Lett. **15**, 6481 2015 ($MoTe_2$), Lorchat et al. ACS Nano 2016 (ReS_2 and $ReSe_2$)

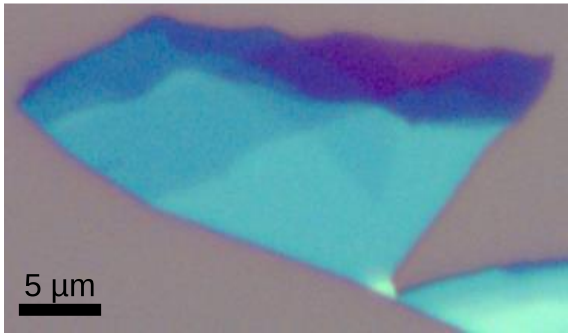
Related works:

- M. Grzeszczyk *et al.*, 2D Materials **3**, 25010 (2016) ($MoTe_2$)
- Q. J. Song *et al.*, PRB **93**, 115409 (2016) ($MoTe_2$)
- K. Kim *et al.*, ACS Nano **10**, 8113 (2016) ($MoSe_2$)

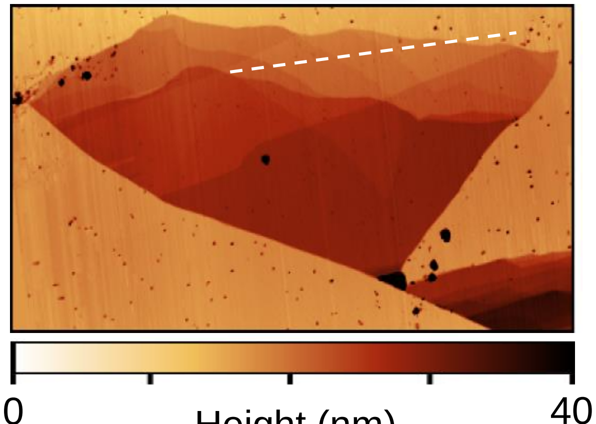


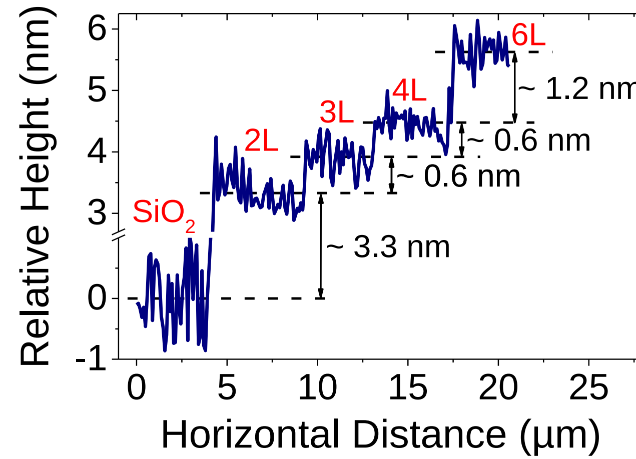
Hyperspectral Imaging of N-layer $MoTe_2$

Optical image

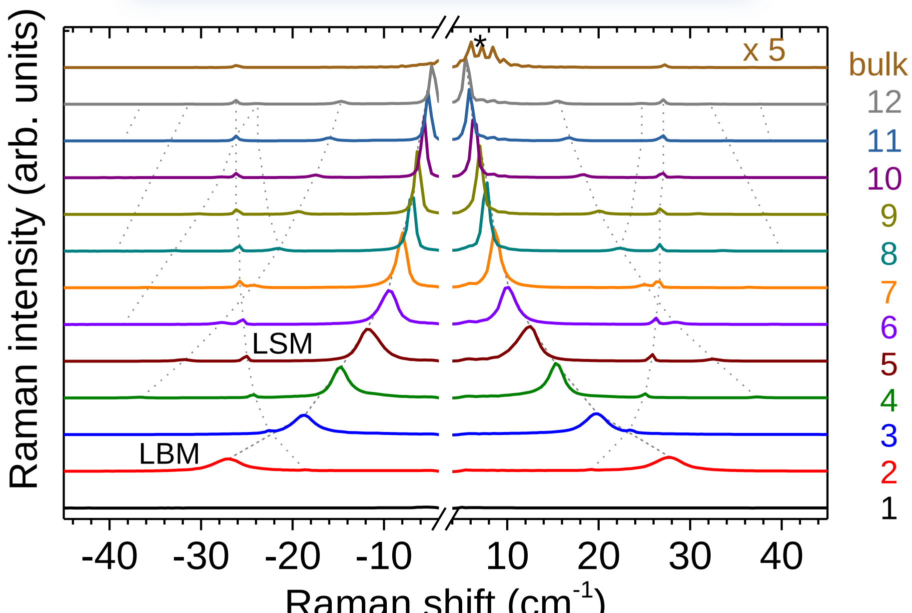


AFM image

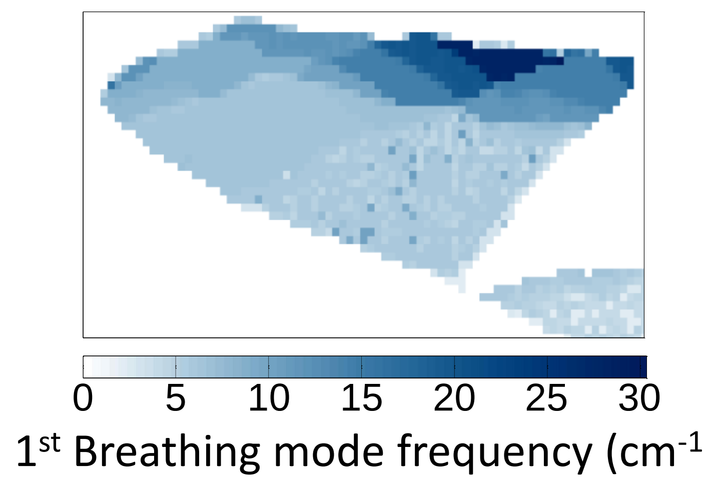


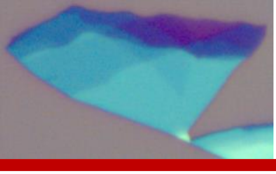


Low Frequency Interlayer Modes

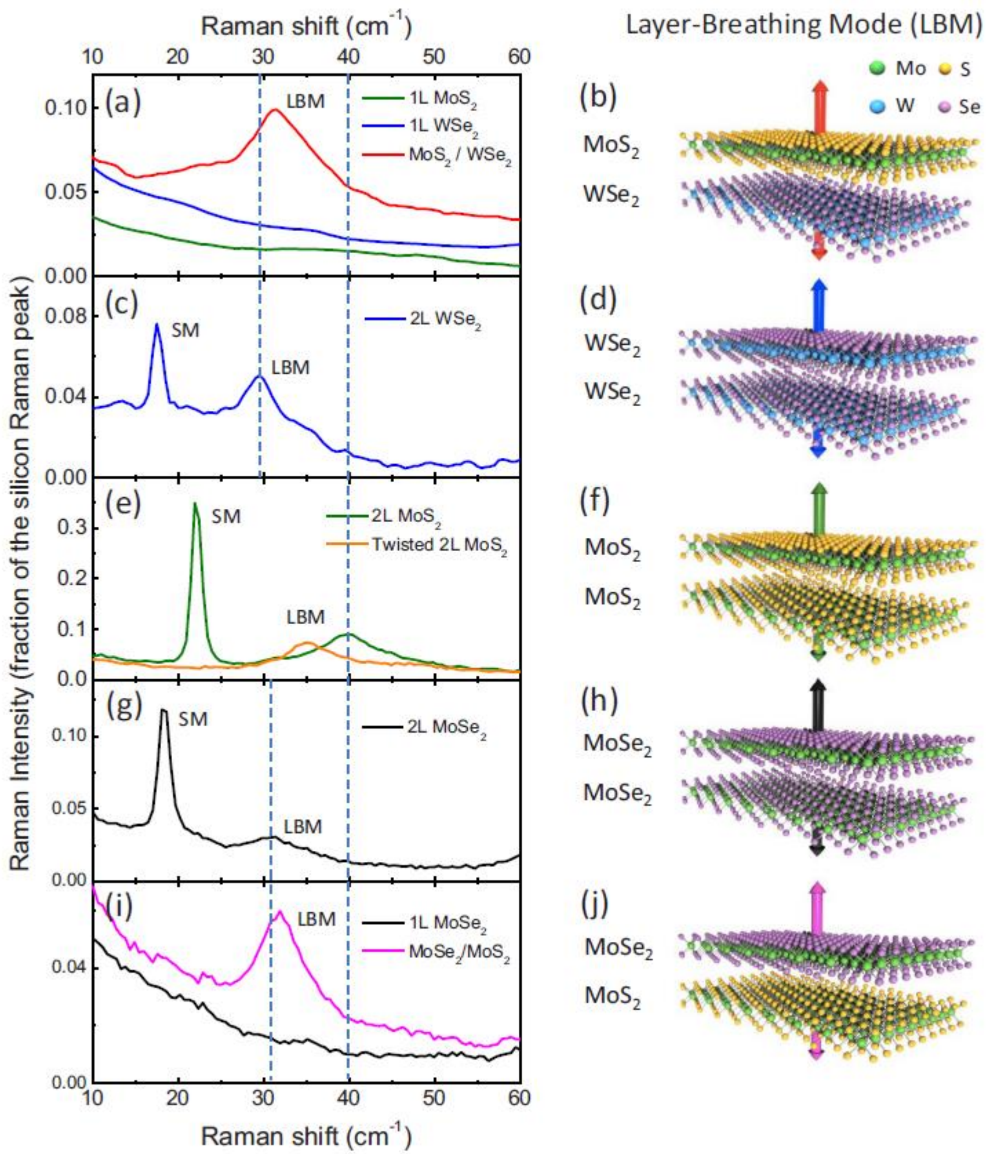


Hyperspectral Raman map





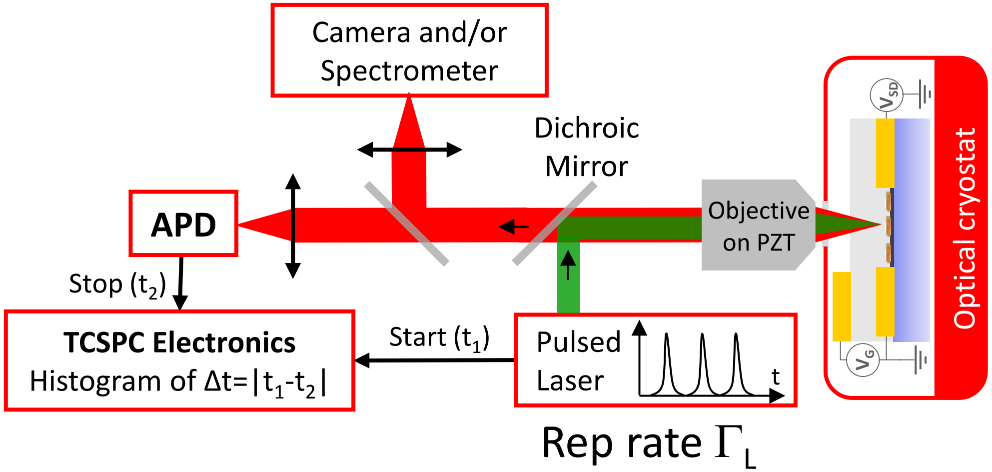
Interlayer modes in van der Waals Heterostructures

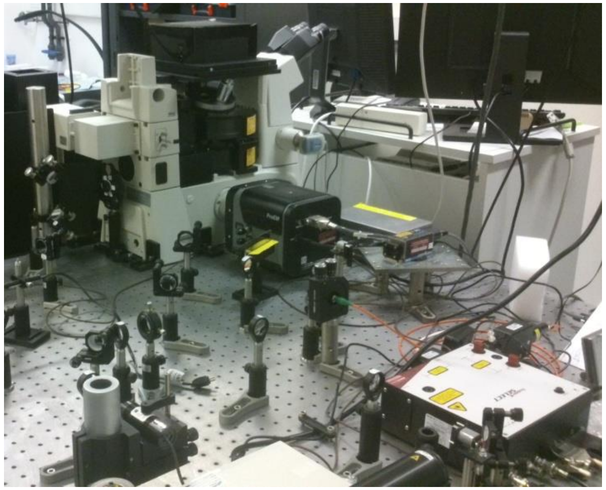


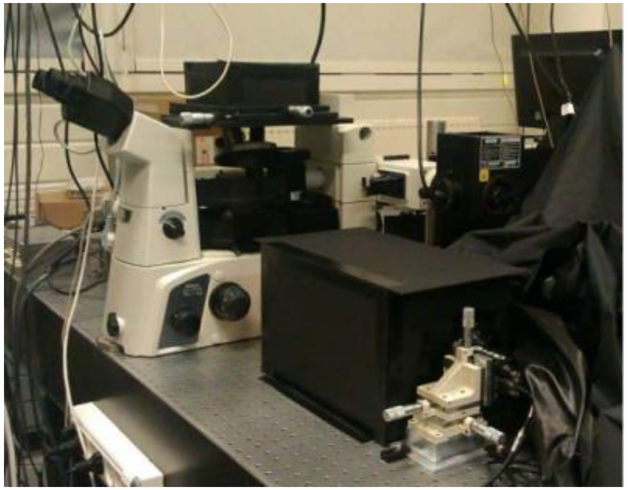
C.H Lui *et al.*, PRB **91,** 165403 (2015)

(Time resolved) photoluminescence

- Tunable pulsed laser
pulse width : 100 fs → 70 ps
rep.rate 100 kHz → 80 MHz)
- Fast avalanche photodiode
(resolution ≈ 50 ps)
- Photon counting board







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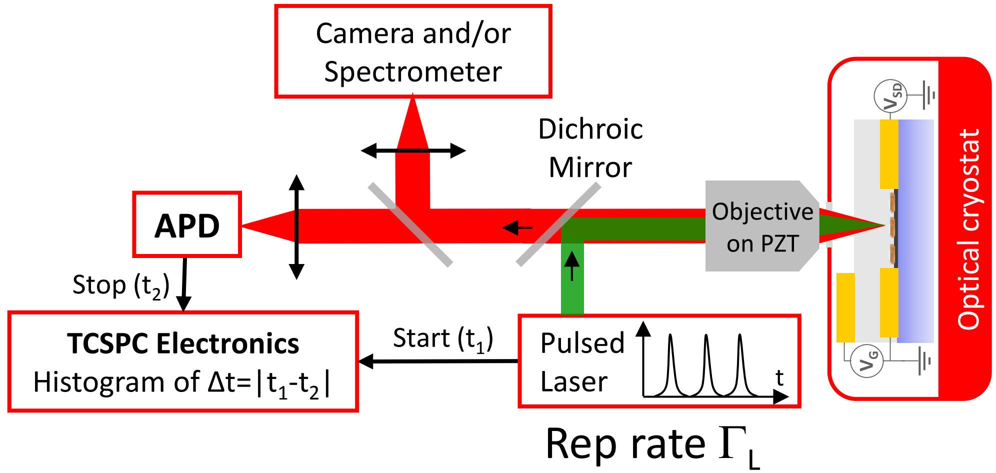
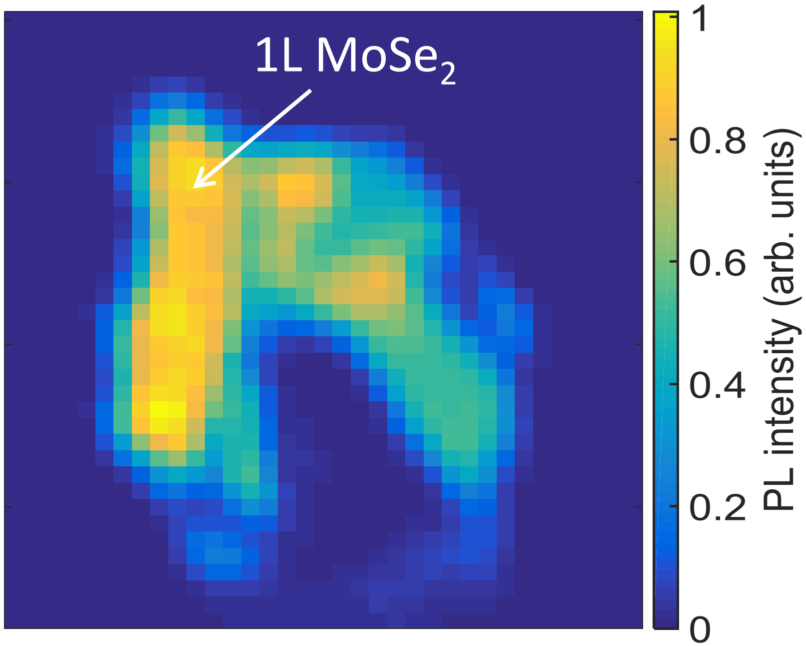
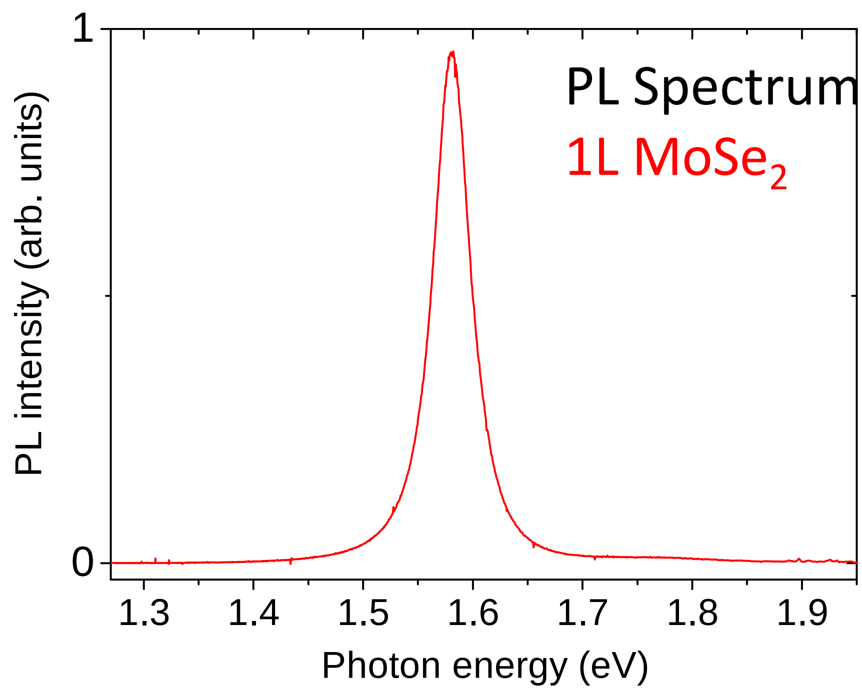






(Time resolved) photoluminescence

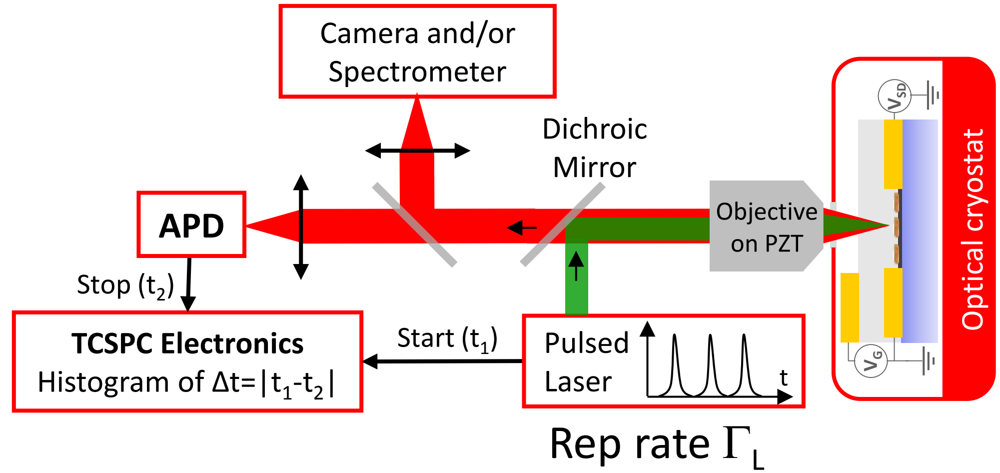
- ➢ Tunable pulsed laser

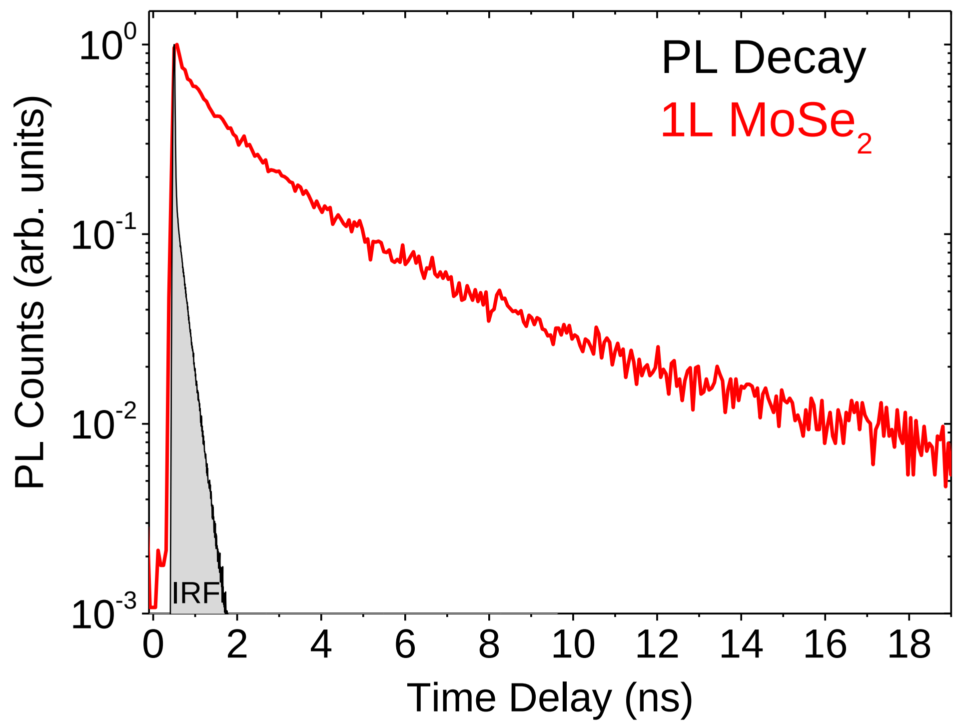
pulse width : 100 fs → 70 ps
rep.rate 100 kHz → 80 MHz)

- ➢ Fast avalanche photodiode

(resolution ≈ 50 ps)

- ➢ Photon counting board

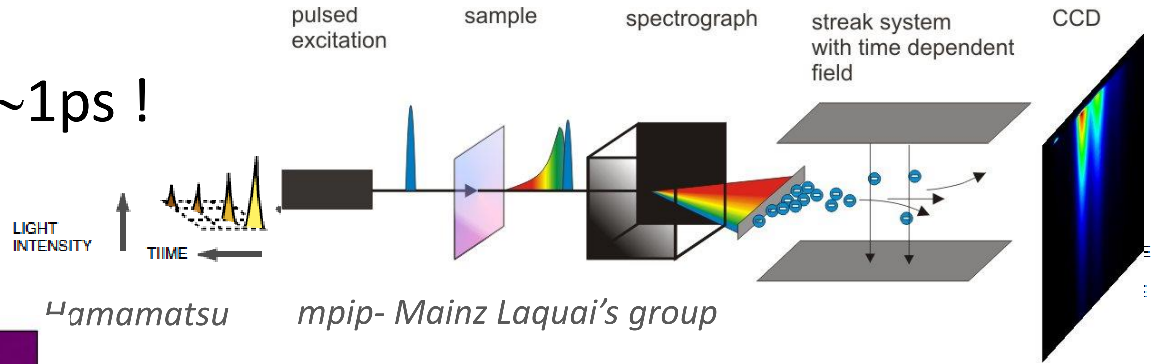


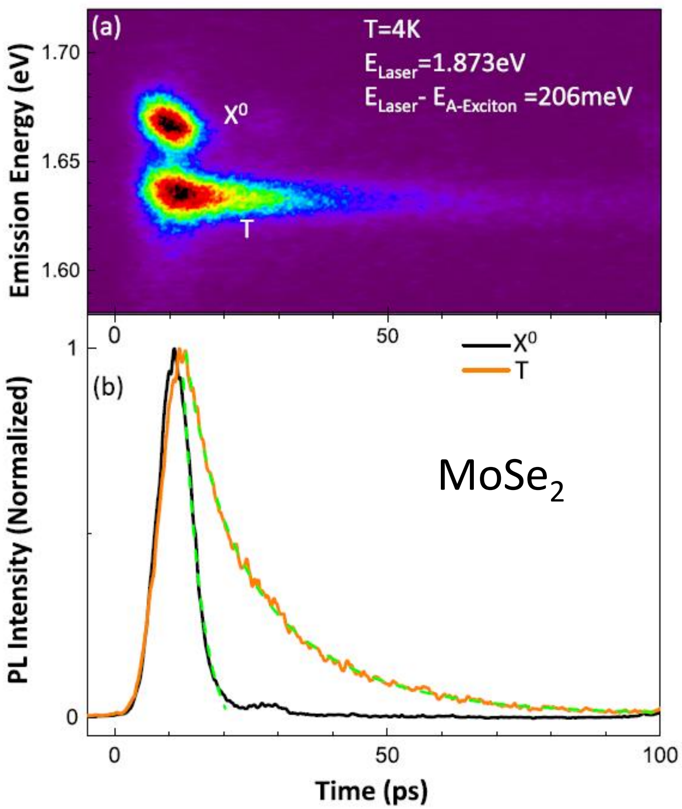


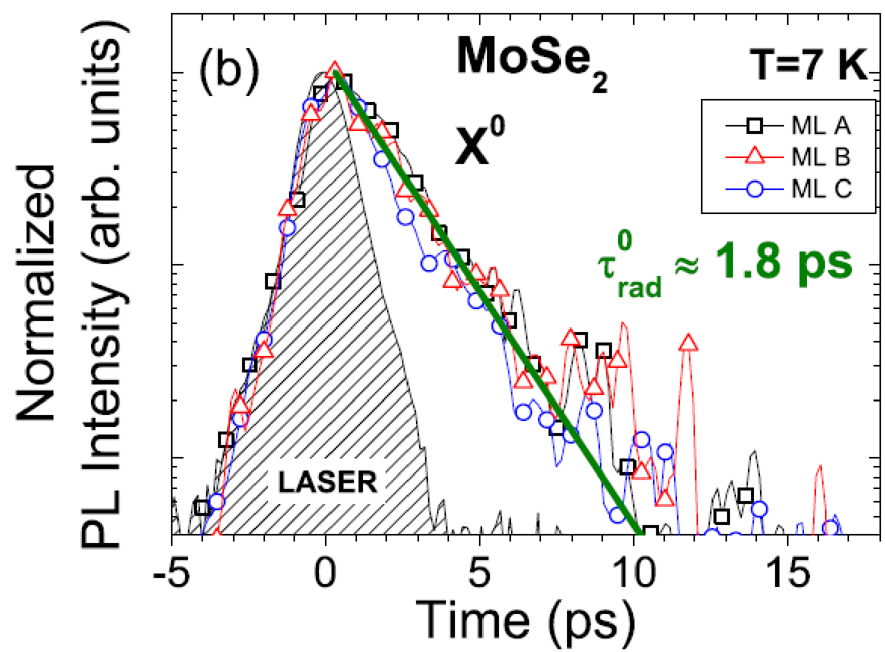
Streak Camera: an optical oscilloscope

Spectroscopy + TRPL

Time resolution down to ~1ps !



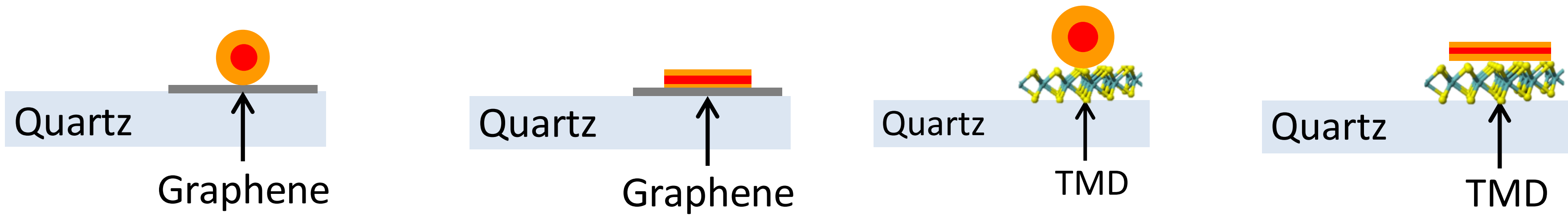




Data from Insa Toulouse : G. Wang et al. APL 2015 & C. Robert et al. PRB 2016

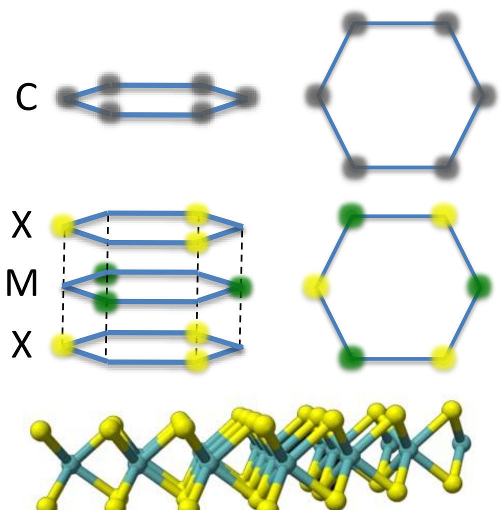
Outline

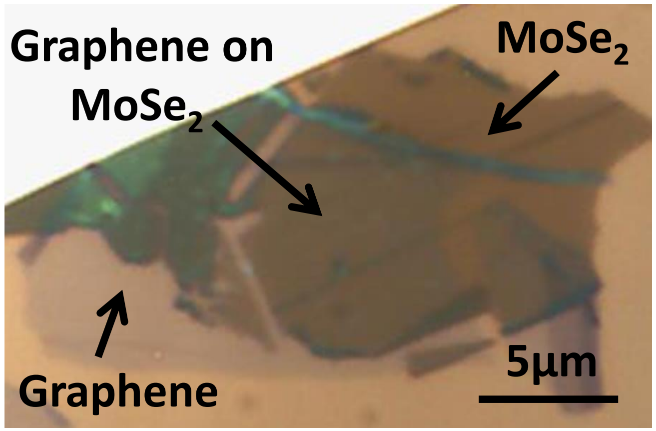
- *Near-field coupling in hybrid heterostructures*



✓ Distance dependence
✓ Dimensionality effects
✓ Dielectric screening
✓ Elecrical control

- *Charge and energy transfer in van der Waals heterostructures*

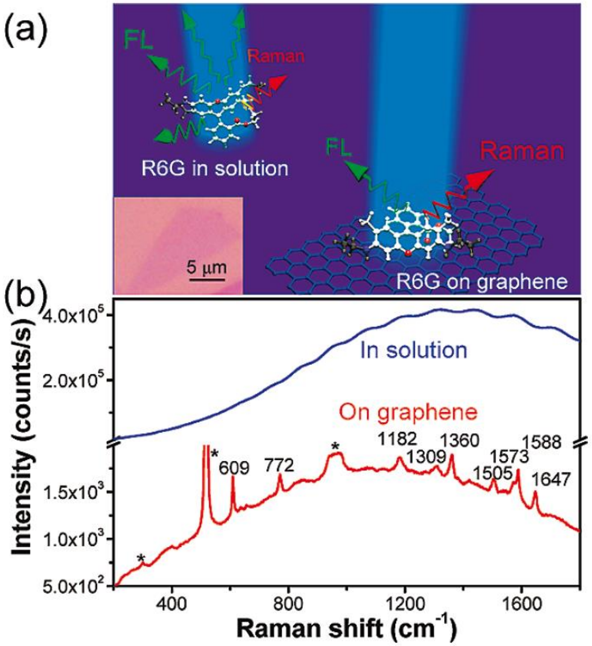




Nano-emitter graphene FRET

Useful for Raman studies

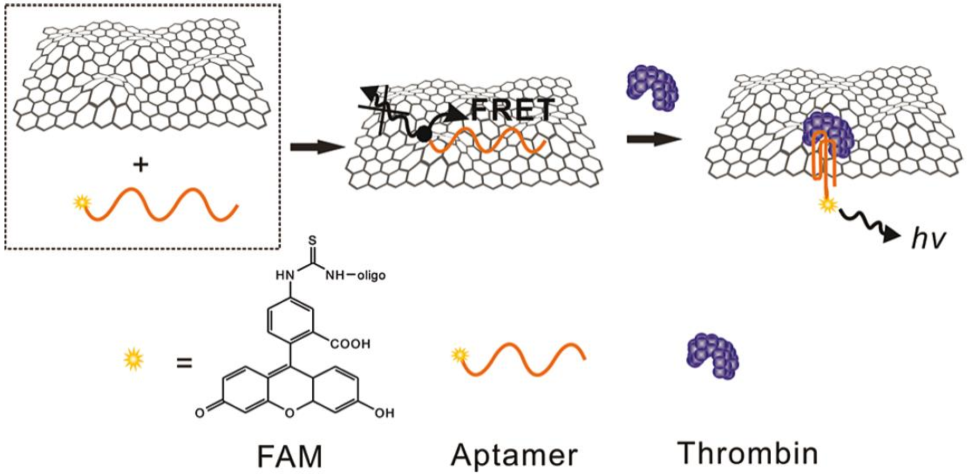
Xie *et al.*, JACS 2009



Aptasensors

Chang et al. Anal Chem 2010

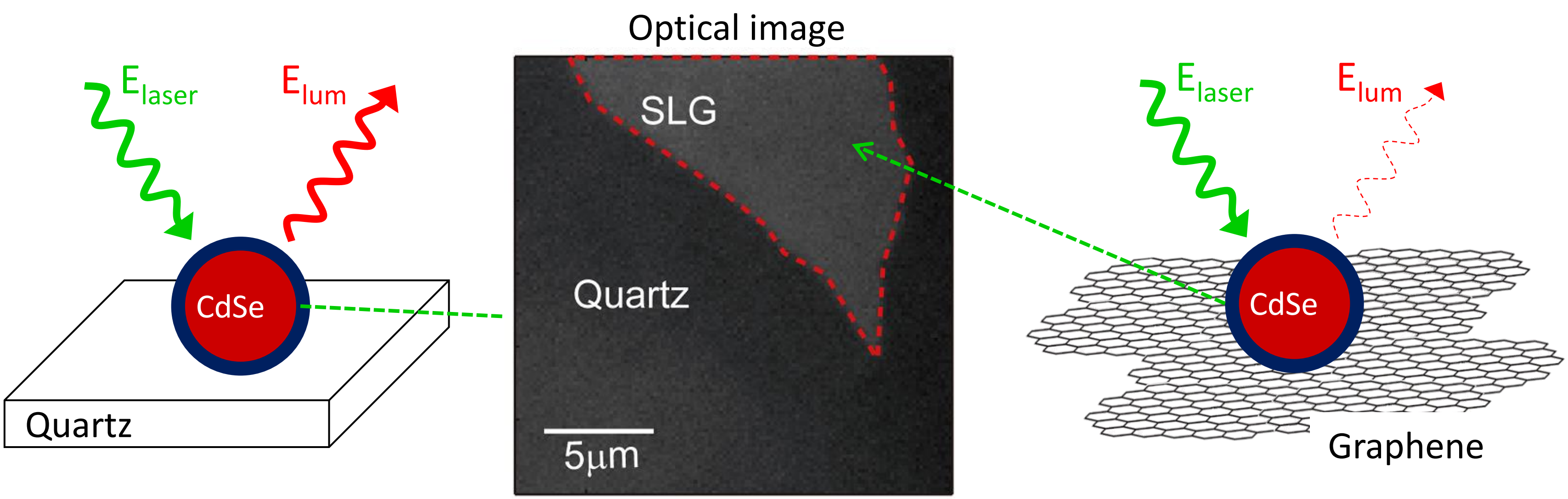
Scheme 1. Schematic Demonstration of Graphene FRET Aptasensor and the Detection Mechanism for Thrombin[a]



- ➢ First theoretical studies: Swathi and Sebastian J. Chem. Phys. 2008 & 2009
- ✓ Single particle studies ?
- ✓ Distance dependence ? Dimensionality effects ?
- ✓ Electrical control ?

Energy transfer between individual nanocrystals and graphene

- Core/shell nanocrystals on graphene : wide field fluorescence microscopy
- "Proof of concept" experiment: evidence for efficient energy transfer



Z. Chen, S. Berciaud *et al.* ACS Nano (2010)

Energy transfer between individual nanocrystals and graphene

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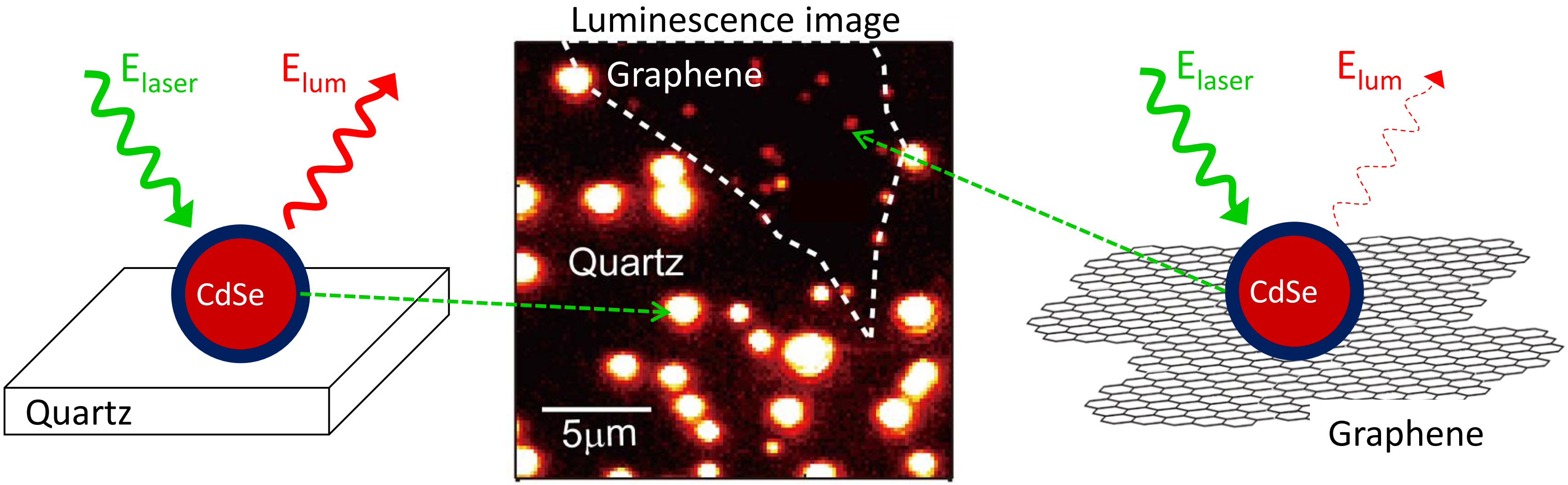

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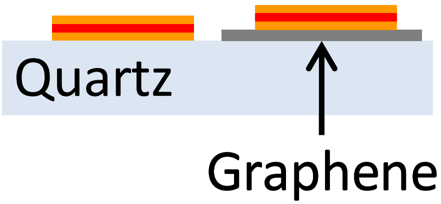
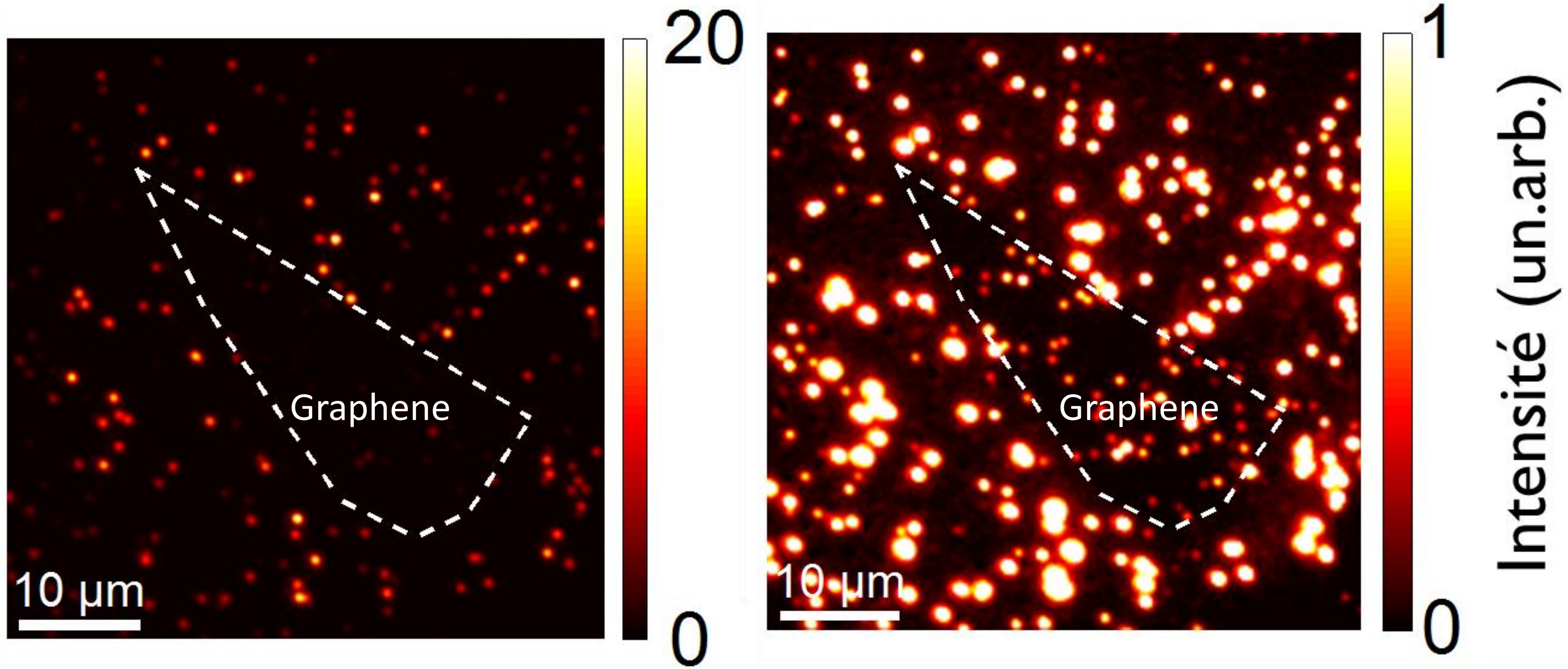
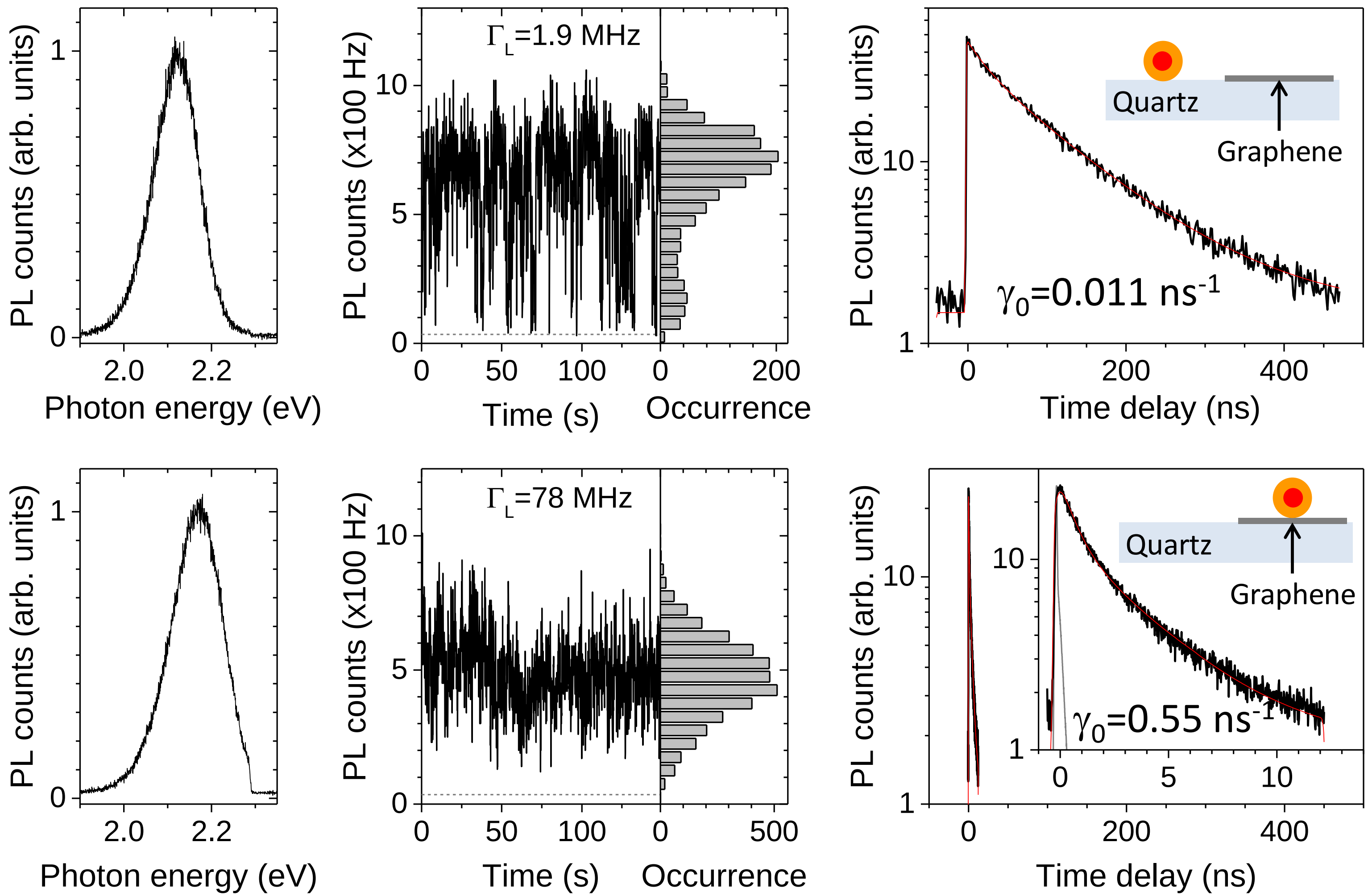


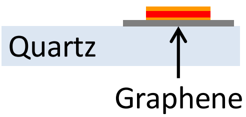


Energy transfer between individual **nanocrystals** and graphene

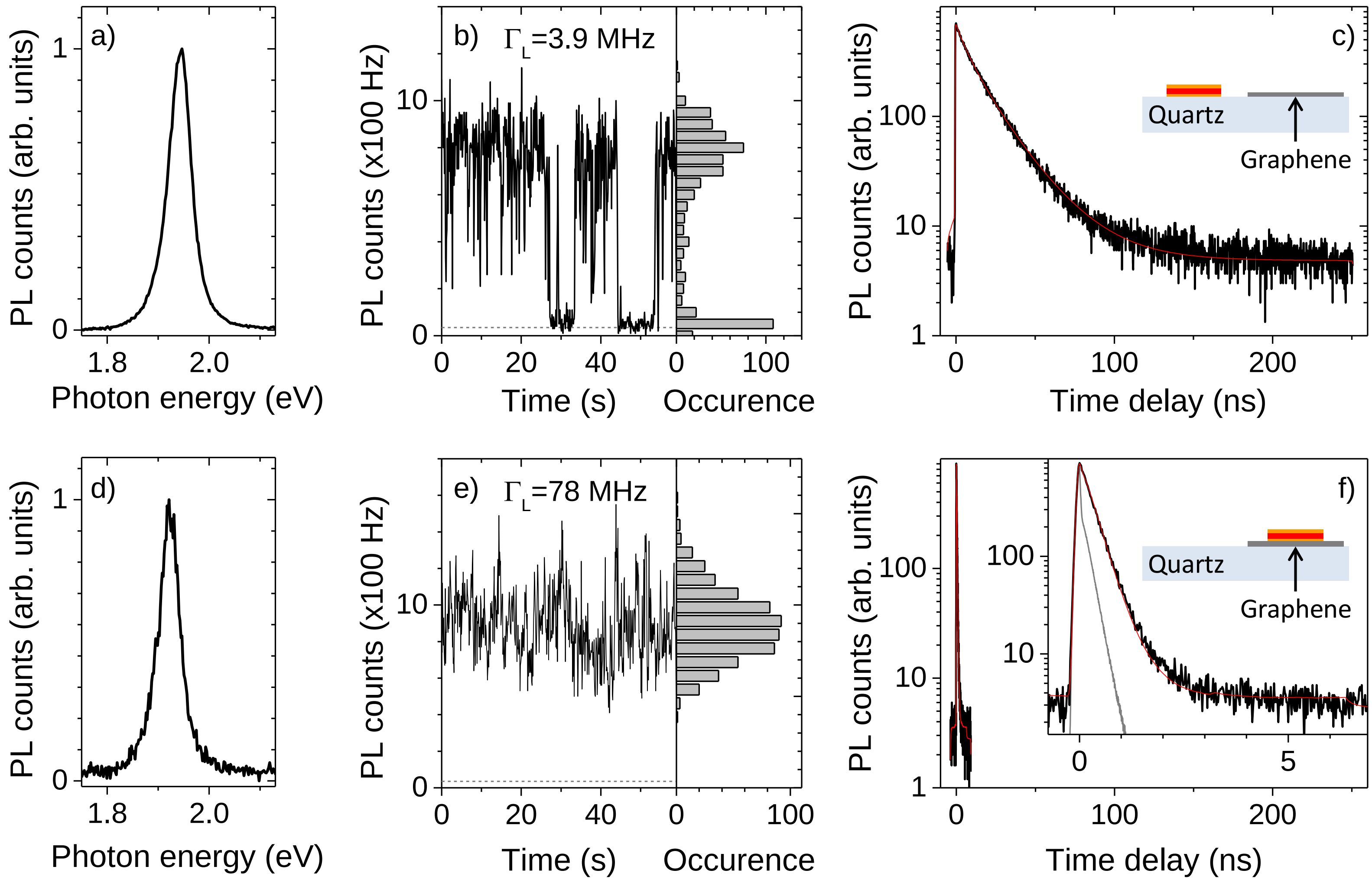


- Much faster decay on graphene and Reduced photoinduced blinking
- Energy transfer efficiency > 95%

F. Federspiel *et al.* Nano Letters **15**, 1252 (2015)



Energy transfer between individual nanoplatelets and graphene



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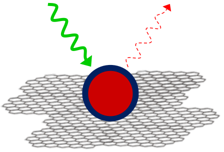
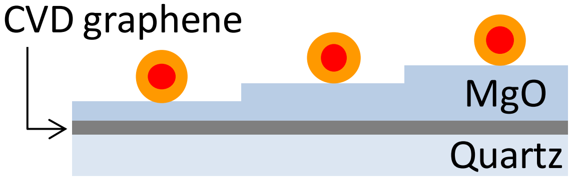
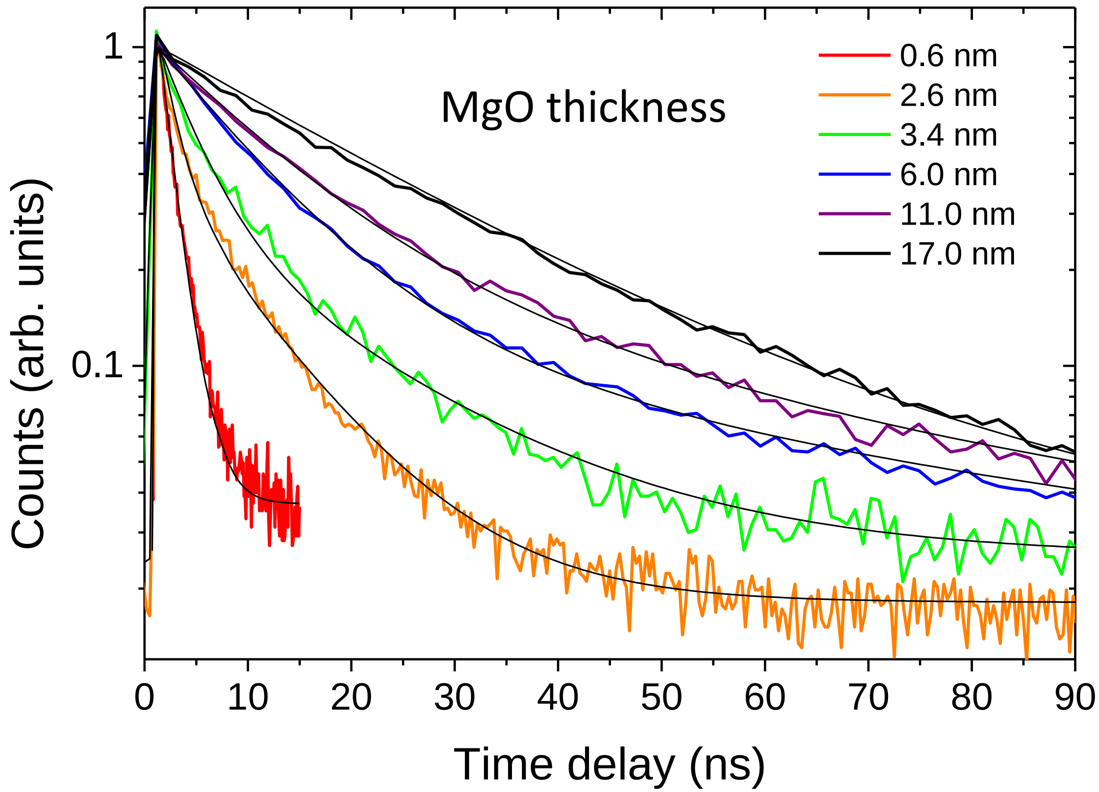
F. Federspiel *et al.* Nano Letters **15**, 1252 (2015)



Distance scaling of the energy transfer rate

- Mechanically exfoliated graphene monolayers on quartz
- CdSe/CdS nanocrystals (B. Dubertret, ESPCI)
- Smooth MgO films grown by MBE (D. Halley, IPCMS)
- Characterization by Raman spectroscopy and AFM





Epitaxial growth of MgO on graphene:
F. Godel *et al.* (Nanotechnology 2013)

F. Federspiel *et al.* Nano Letters **15,** 1252 (2015)

Distance scaling of the energy transfer rate

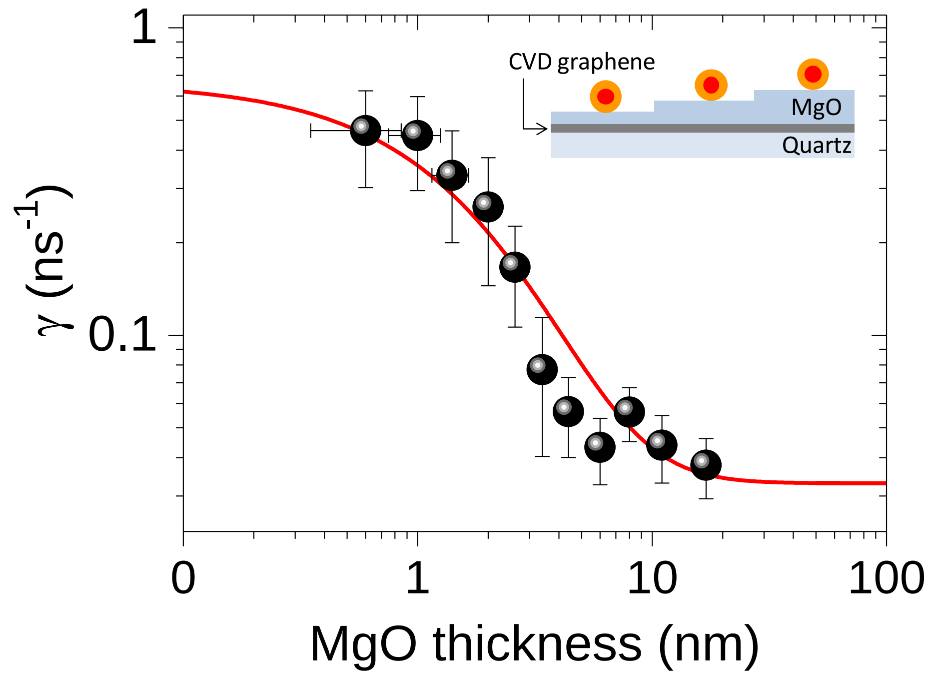
0D-2D Förster Energy Transfer*

$$\gamma = \gamma_0 \left[1 + \left(\frac{z_0}{z + r_0} \right)^4 \right]$$

r_0 (TEM)= 4.75 ± 1 nm
z_0 (theory)~ 12 nm

$$N_{em} = \frac{\gamma_0}{\gamma} N_{abs}$$

$$\Rightarrow N_{em}\,\gamma = const.$$

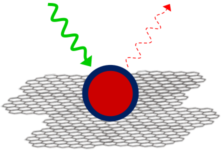


r_0= 5.5 nm, z_0= 11.5 nm

Demonstration of a graphene-based molecular ruler (1/d^4 scaling)

*Kühn J. Chem Phys 1970
Chance, Prock, Silbey Adv. Chem. Phys. **37** 65 (1978)

F. Federspiel *et al.* Nano Letters **15**, 1252 (2015)



Distance scaling of the energy transfer rate

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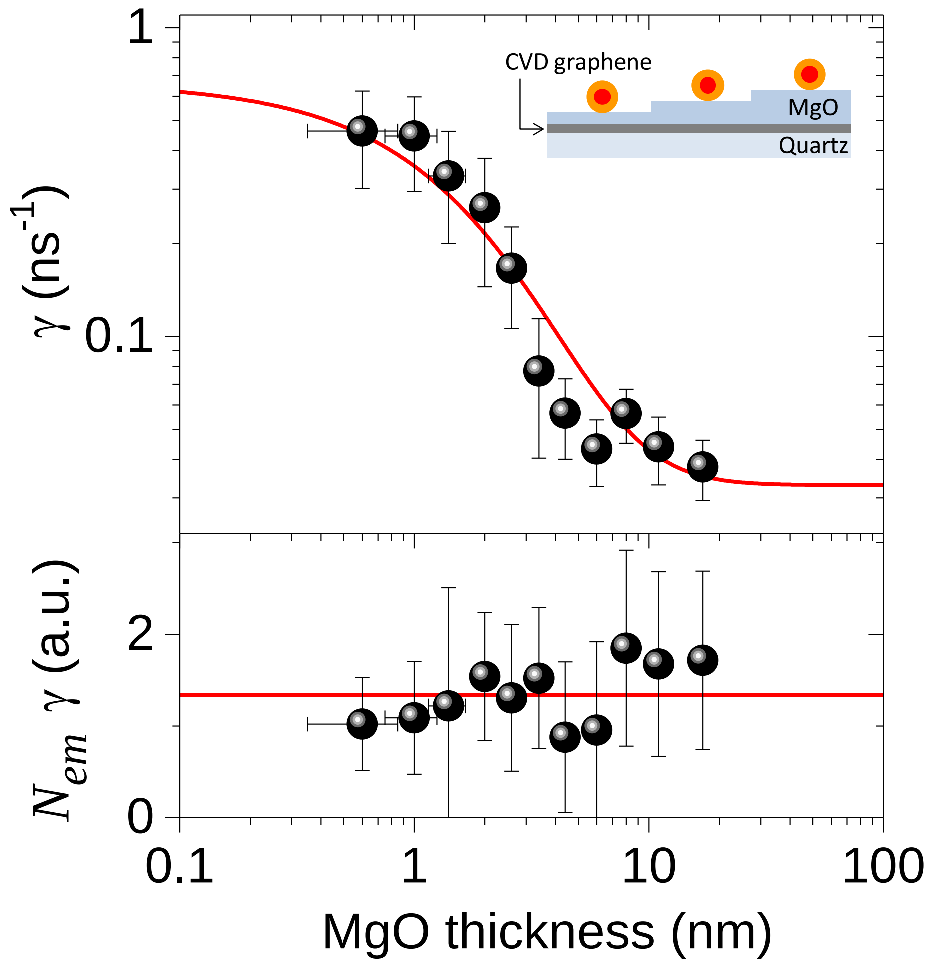

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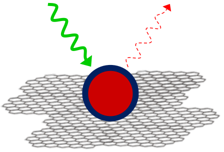


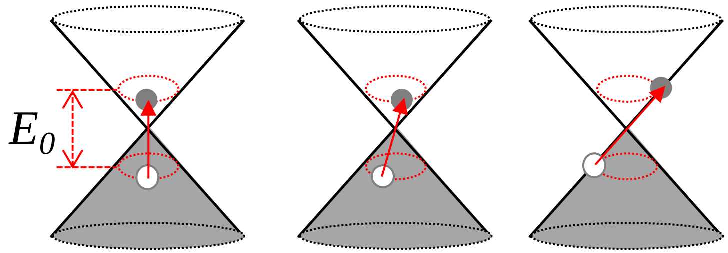
Dimensionality matters: platelets vs. dots

0D - Graphene

$$\gamma_T \propto \int_0^{q_{max}} dq \frac{q^3 e^{-2qd}}{\sqrt{q_{max}^2 - q^2}}$$

$$q_{max} = \frac{E_0}{\hbar v_F}$$

For d>>1/q_{max} ≈ 0.3 nm → $\gamma_T \propto \frac{1}{d^4}$



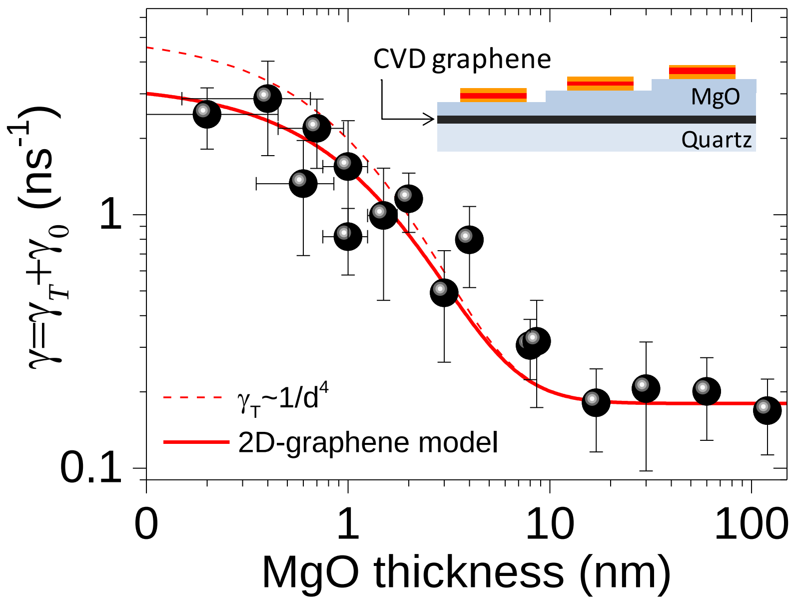
2D - Graphene

$$\Lambda = \frac{h}{\sqrt{2 m_x k_B T}} \approx 7.5\,\text{nm}$$

d >> 1/q_{max}

L_x,L_y>Λ and L_z<<d

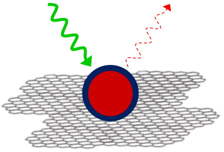
$$\gamma_T \propto \int_0^{\infty} dq\, q^3 e^{-2qd} e^{-\left(\frac{\Lambda q}{2\pi}\right)^2}$$



Swathi & Sebastian JCP 2008 & 2009
Gomez-Santos & Stauber PRB 2011
Gaudreau *et al.* Nano Lett 2013

D. M. Basko *et al.* EPJB 1999
Kos *et al.* PRB 2005

F. Federspiel *et al.* Nano Letters 15, 1252 (2015)
see also arXiv:1501.03401



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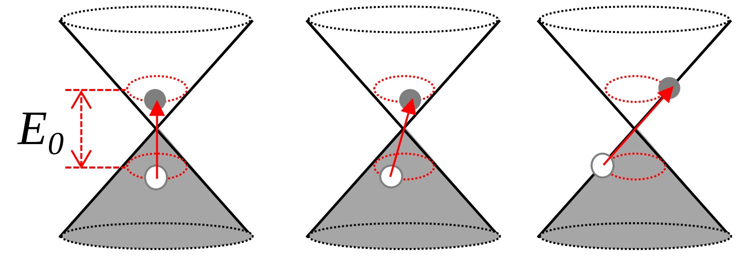

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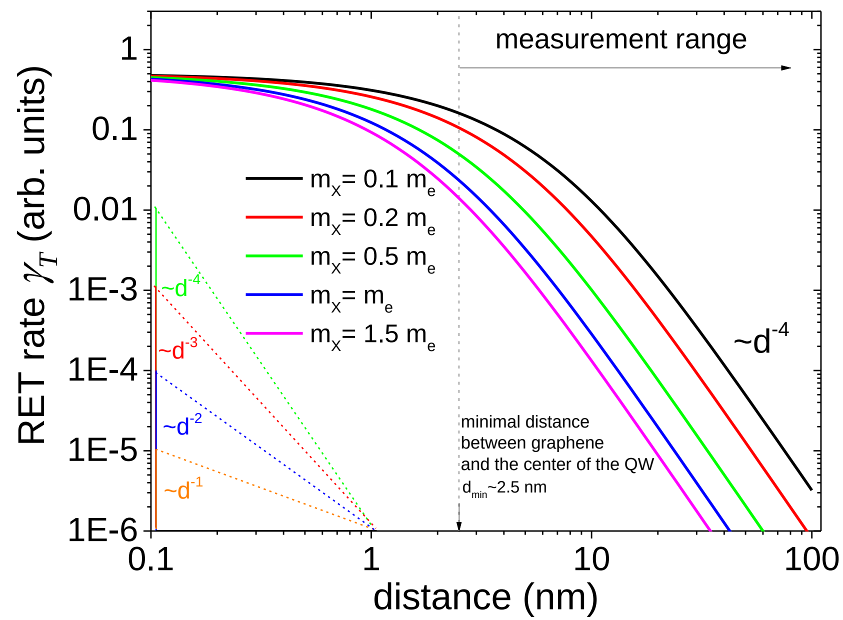

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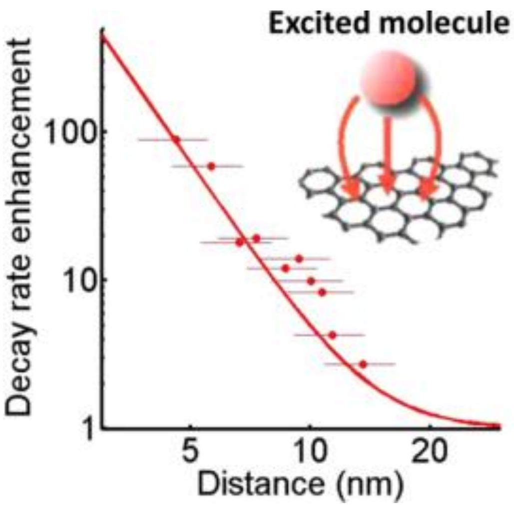
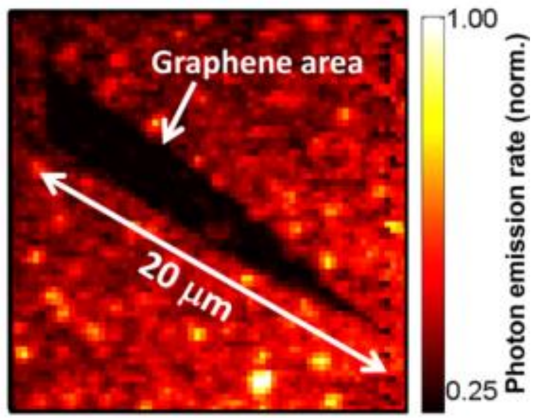
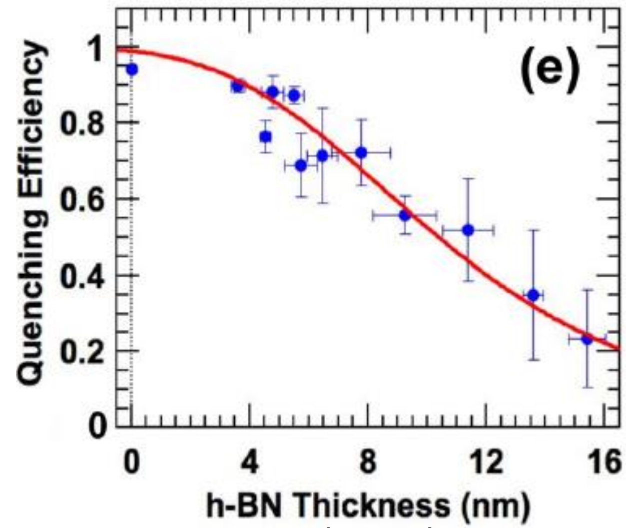
Kos *et al.* PRB 2005

F. Federspiel *et al.* Nano Letters 15, 1252 (2015)
see also arXiv:1501.03401

Related Results with other materials

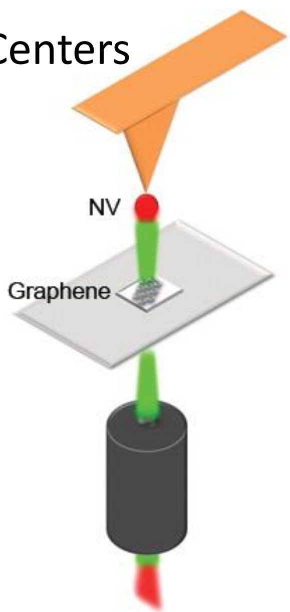


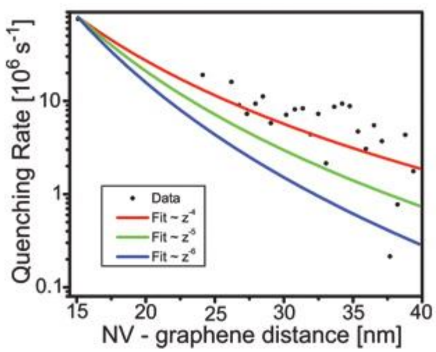


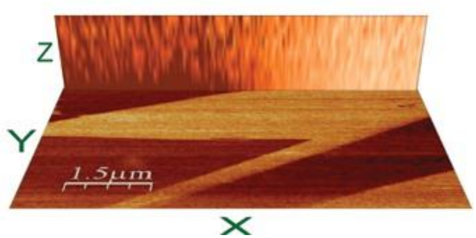


CdSe QD/hBN/$MoSe_2$

NV Centers







Distance dependence of FRET to graphene

Gaudreau *et al.* Nano Lett. **13**, 2030 (2013)

Tisler *et al.* Nano Lett. **13**, 3152 (2013)

Single Qdots on graphene

B. Rogez *et al.* JPCC 118, 18445 (2014)

O. Ajayi *et al.* APL 104 171101 (2014)

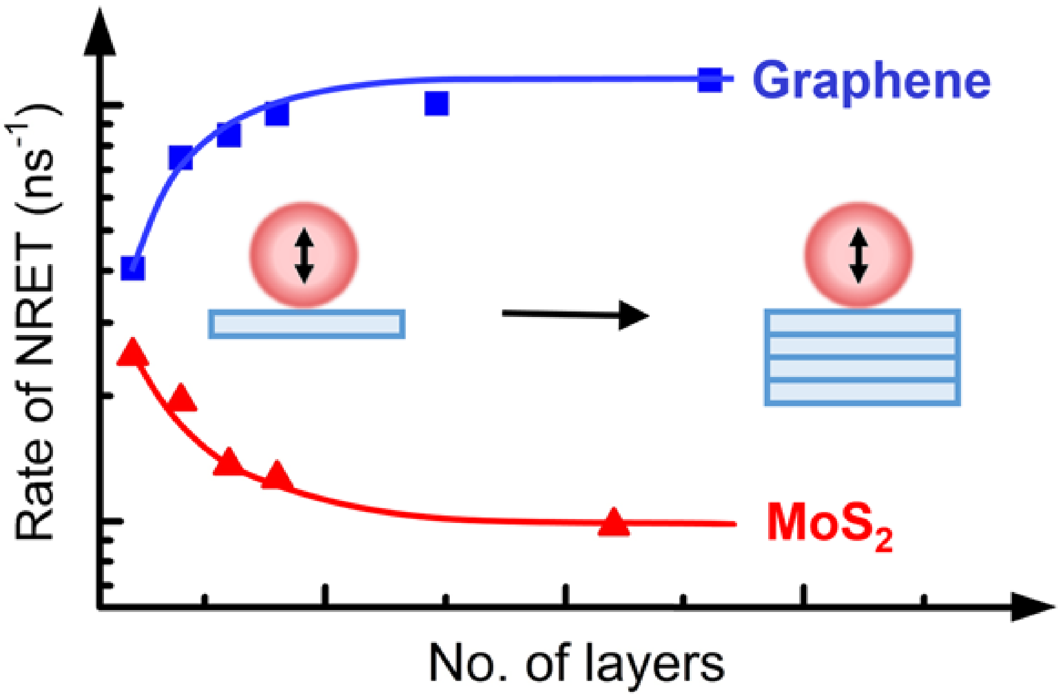
Distance dependence of FRET to TMDs

Goodfellow et al. APL 2015 (MoSe2)

TMD vs Graphene: Dielectric screening matters (1)

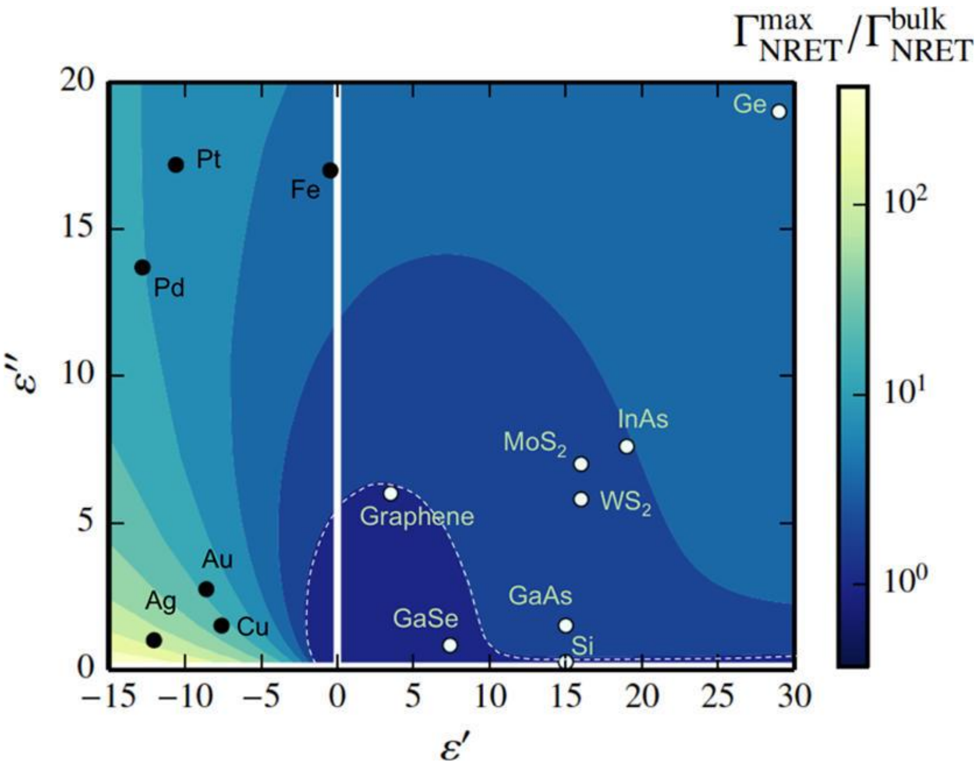
$$P_{\mathrm{D}\rightarrow\mathrm{A}} = -\frac{1}{2}\int_{V_{\mathrm{A}}} \mathrm{Re}\{\mathbf{j}_{\mathrm{A}}^{*}\cdot\mathbf{E}_{\mathrm{D}}\}\,\mathrm{d}V \approx \frac{\omega_0}{2}\,\mathrm{Im}\{\alpha_{\mathrm{A}}\}\left|\mathbf{n}_{\mathrm{A}}\cdot\mathbf{E}_{\mathrm{D}}(\mathbf{r}_{\mathrm{A}})\right|^2$$

- ✓ Imaginary part of the dielectric constant (A)
- ✓ $\mathbf{E}_D(_{\mathbf{r}A})$ depends also on epsilon and its anisotropy



Raja et al. Nano Letters 2016, see also: Z. Chen et al. ACS Nano 2010, F. Prins et al. Nano Lett 2014

TMD vs Graphene: Dielectric screening matters (2)



FRET to monolayer TMD is more efficient than FRET to bulk TMD

- Dielectric screening (ε')
- Optical absorption (ε'')
- Anisotropy ($\varepsilon_\perp$ vs $\varepsilon_{//}$)

FRET Engineering

Theoretical prediction(s):

Chance, Prock, Silbey 1970's

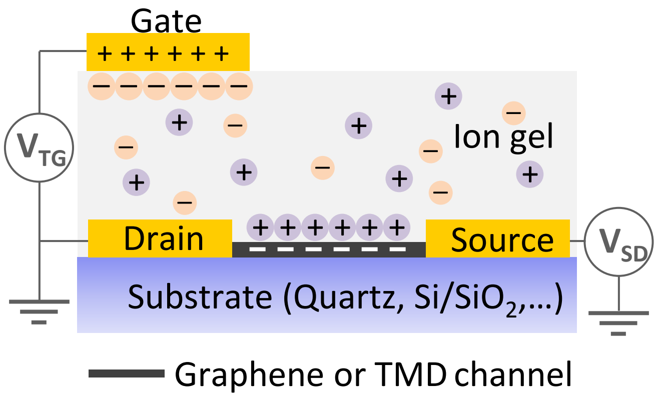
Gordon, Gartstein J. Phys Cond. Matter 2013

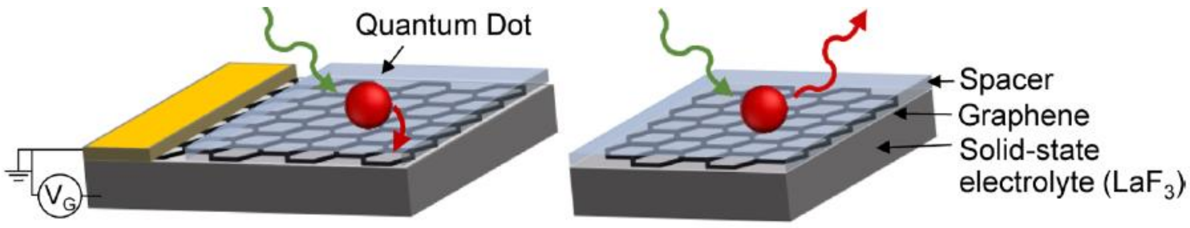
Experiments: QDs on MoS_2 layers

Prins *et al.*, Nano Letters 2014

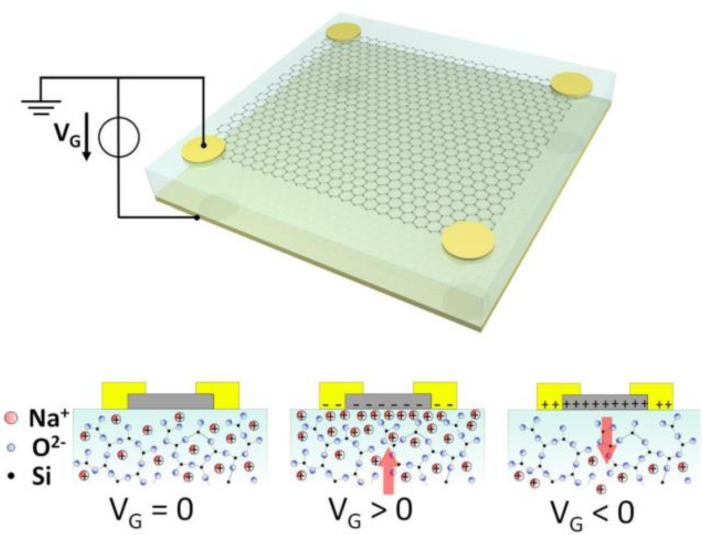
Raja *et al.*, Nano Letters 2016

Hybrid phototransistors: electrical Control of FRET

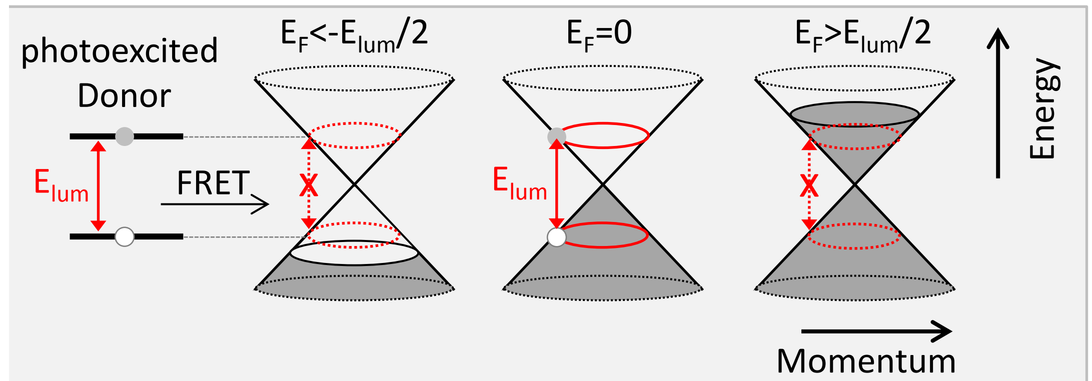




Lee *et al.* Nano Letters **14**, 7115 (2014)



Paradisi *et al.* APL 2015

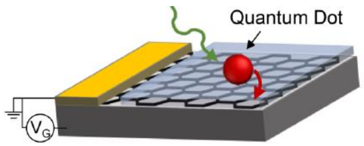


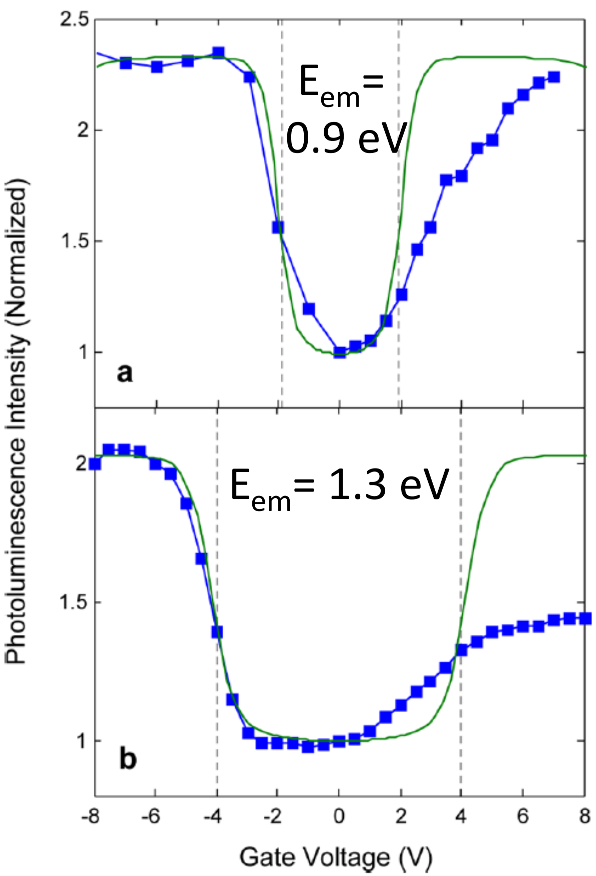
Fermi Energy shifts ~ 1 eV

Need for efficient gating methods

Electrical Control of FRET

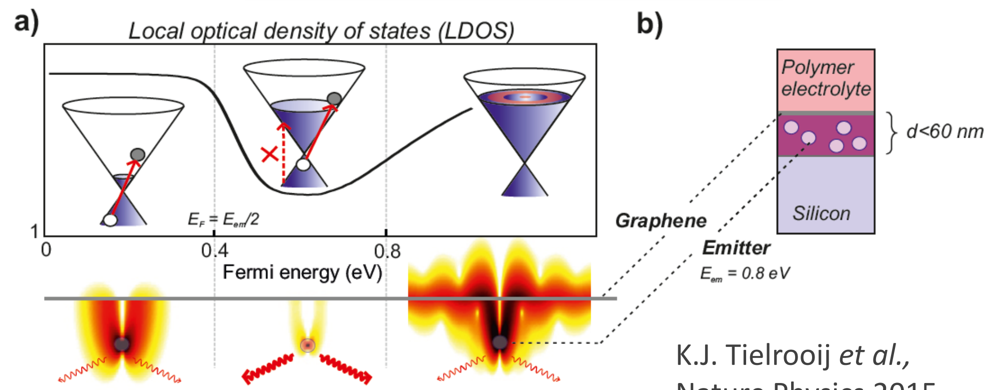
PbS nanocrystals on graphene



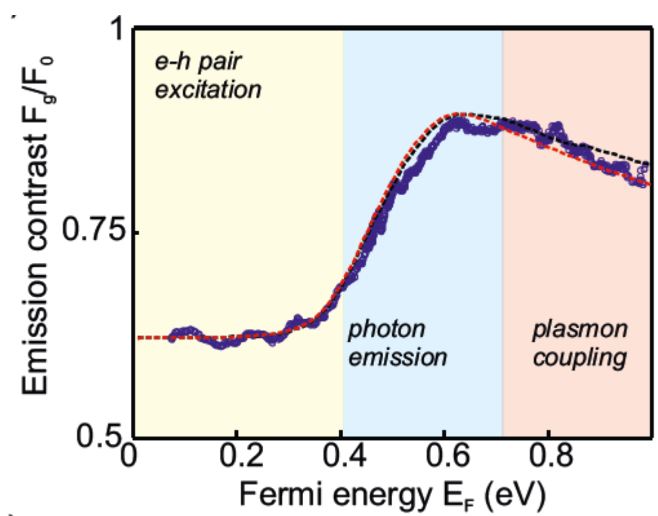


Lee *et al.* Nano Letters **14**, 7115 (2014)

Erbium ions on graphene

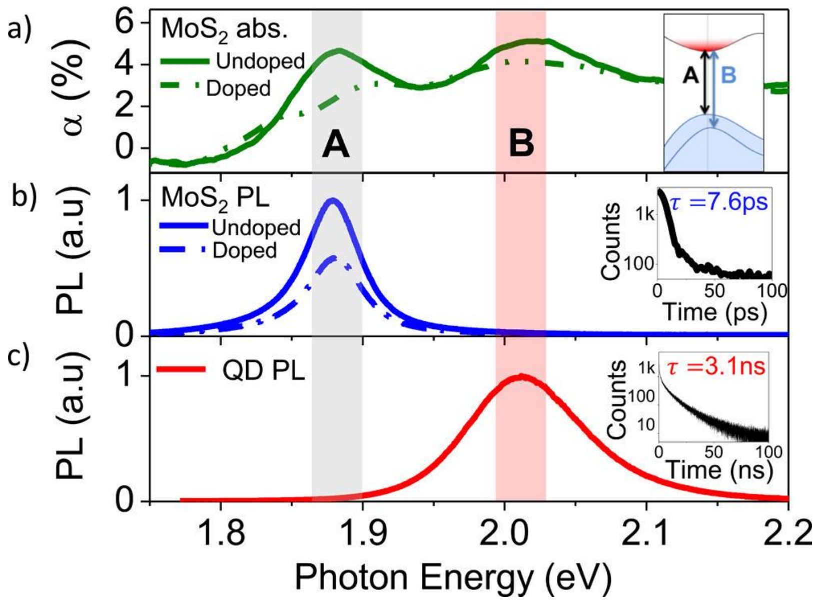


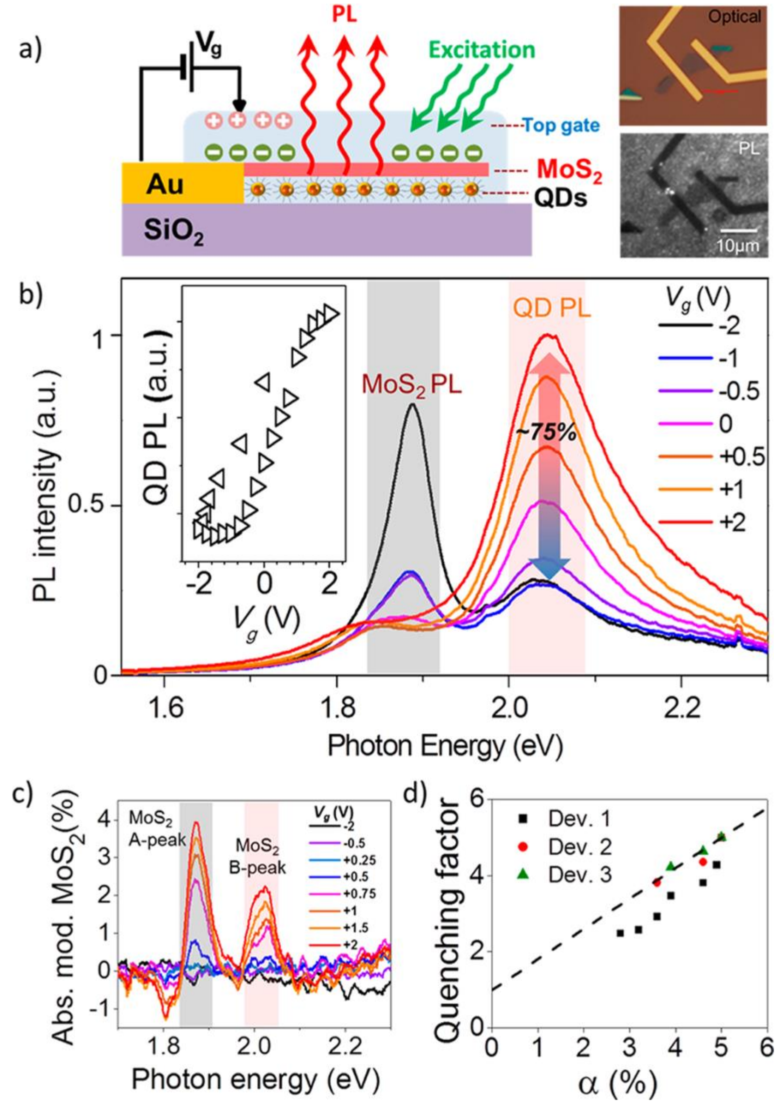
K.J. Tielrooij *et al.*, Nature Physics 2015



Coupling to graphene plasmons at high doping (E_F~E_{em})

Electrical Control of FRET in QD-TMD devices

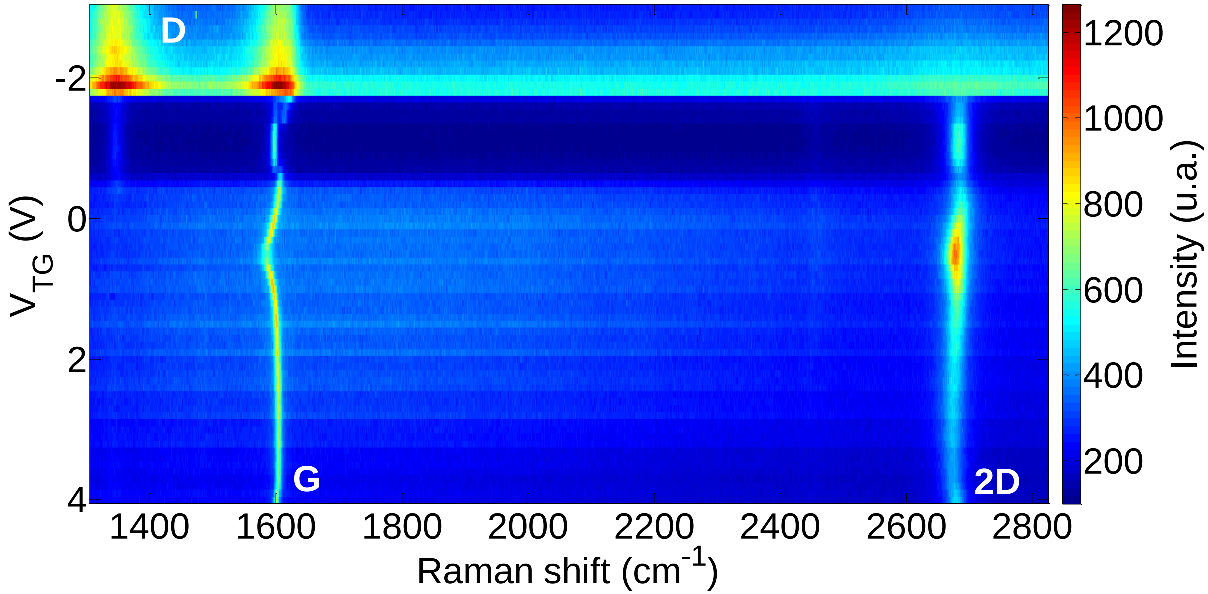


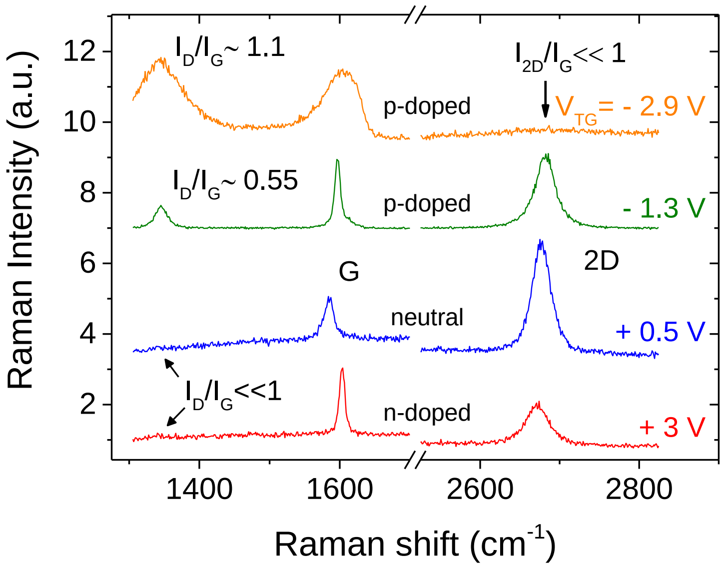


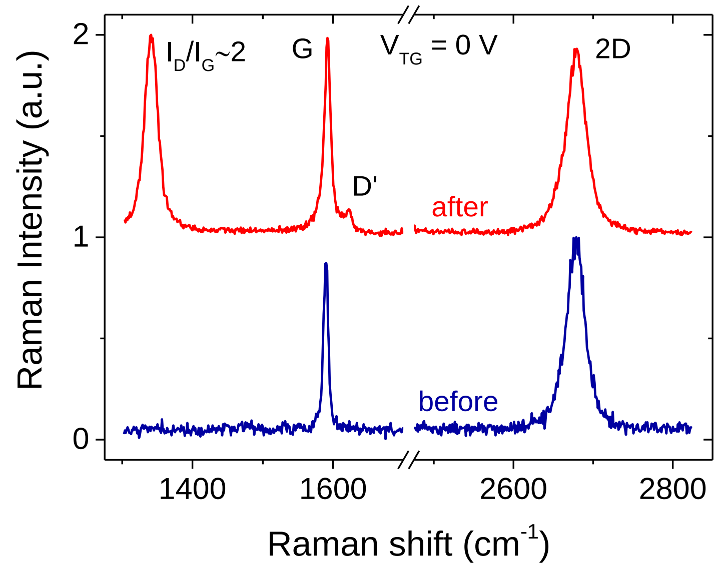
- *QD PL resonant with B exciton in MoS2*
- *Gate-induced absorption modulation in MoS_2*
  → Gate-induced modulation of the FRET Rate

Prasai *et al.,* Nano Lett. 2015 (K. Bolotin Group)

Beware of Polymer Electrolytes







Froehlicher & SB, PRB 2015

Partial conclusion

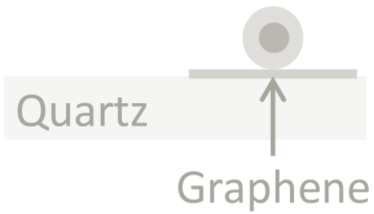
- Highly efficient « Förster-type » energy transfer (up to ~ 95%)
- Graphene-based molecular ruler at the single particle level
- Important role of dimensionality
- Electrical control : PL modulation by ~2x (graphene) up to 5x (MoS_2)
- Charge transfer $\rightarrow$ Photogating in Hybrid photodetectors

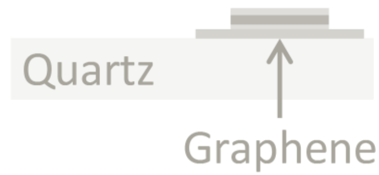
➢ Outlook:

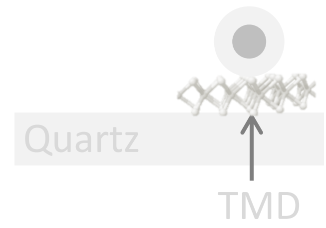
- Probing exciton dimensionality with FRET?
- Performance improvements with device engieering?

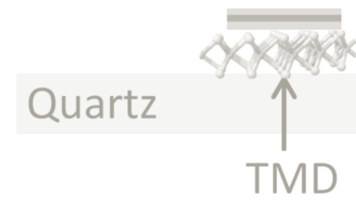
Outline

- *Near-field coupling in hybrid heterostructures*





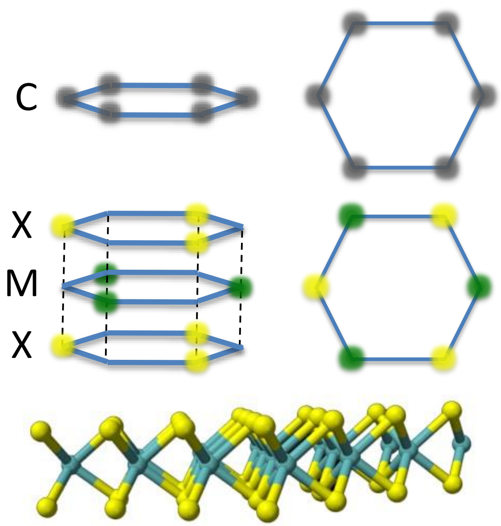


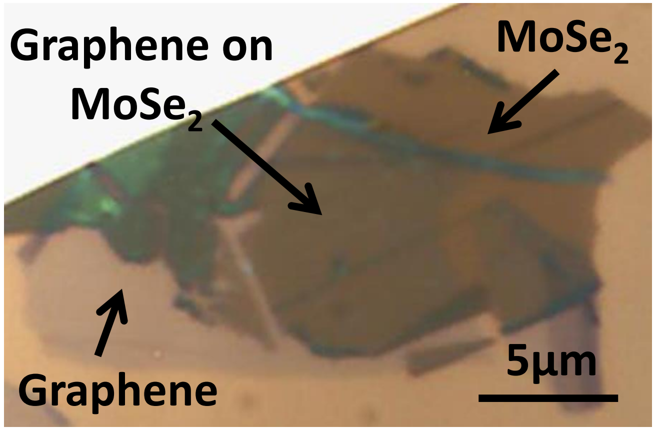


✓ Distance dependence
✓ Dimensionality effects

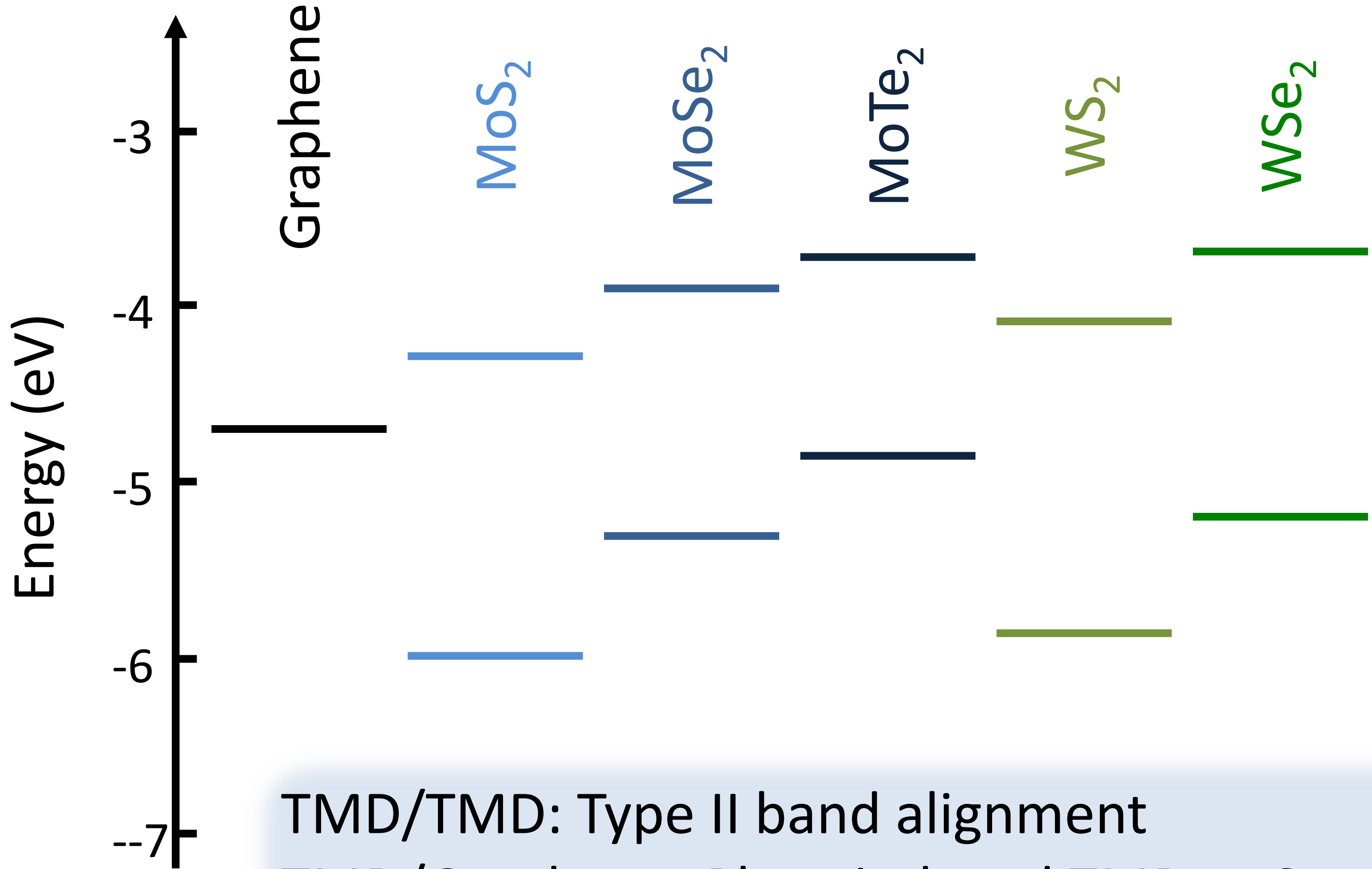
✓ Dielectric screening
✓ Elecrical control

- ***Charge and energy transfer in van der Waals heterostructures***





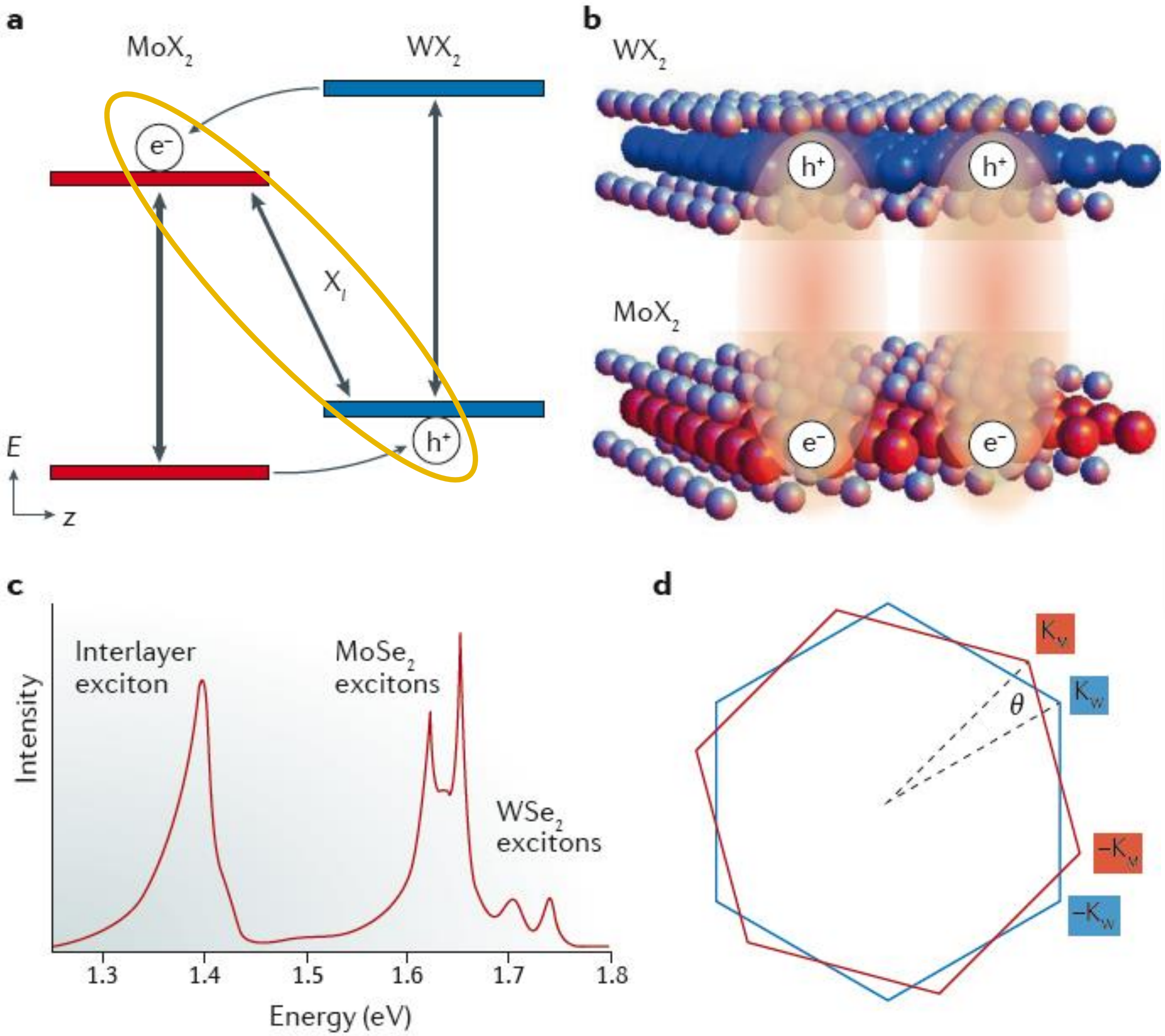
Band alignments



TMD/TMD: Type II band alignment
TMD/Graphene: Photoinduced TMD→ Gr e- transfer

TMD: Y. Liang et al., APL **103**, 42106 (2013), M. Ugeda *et al.*, Nat. Mater. **5**, 1091 (2014)
Graphene: Y.-J. Yu *et al.*, Nano Lett. **9**, 3430 (2008)

Interlayer excitons in TMD/TMD heterostructures

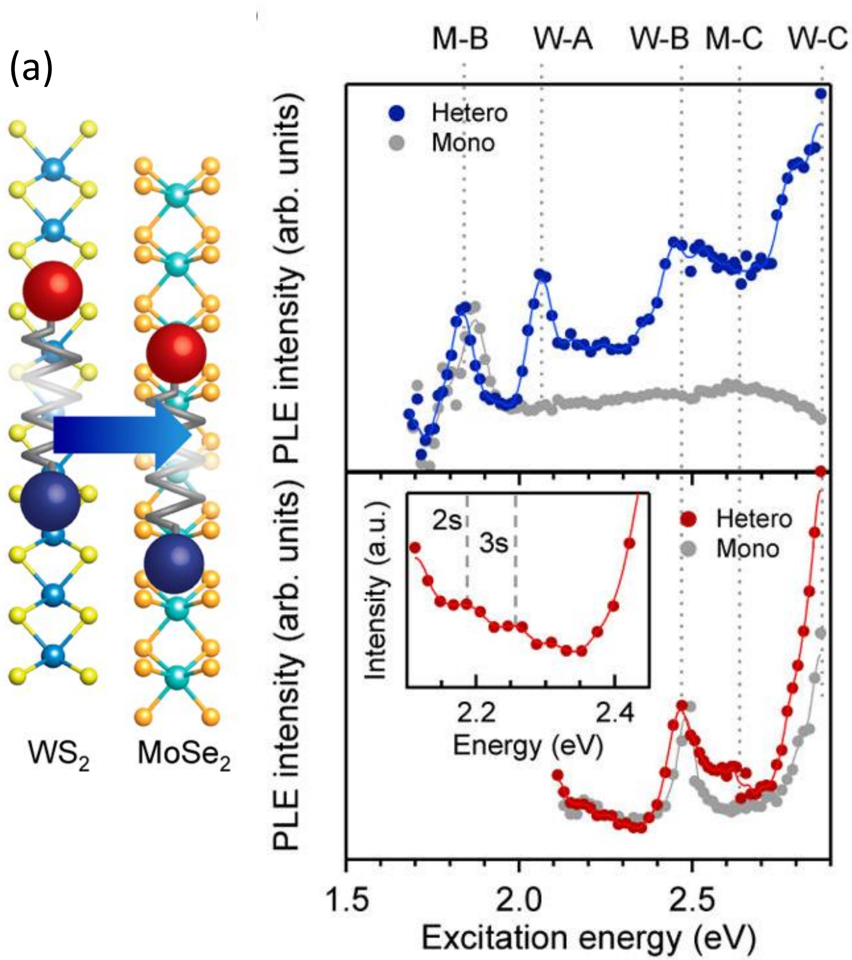


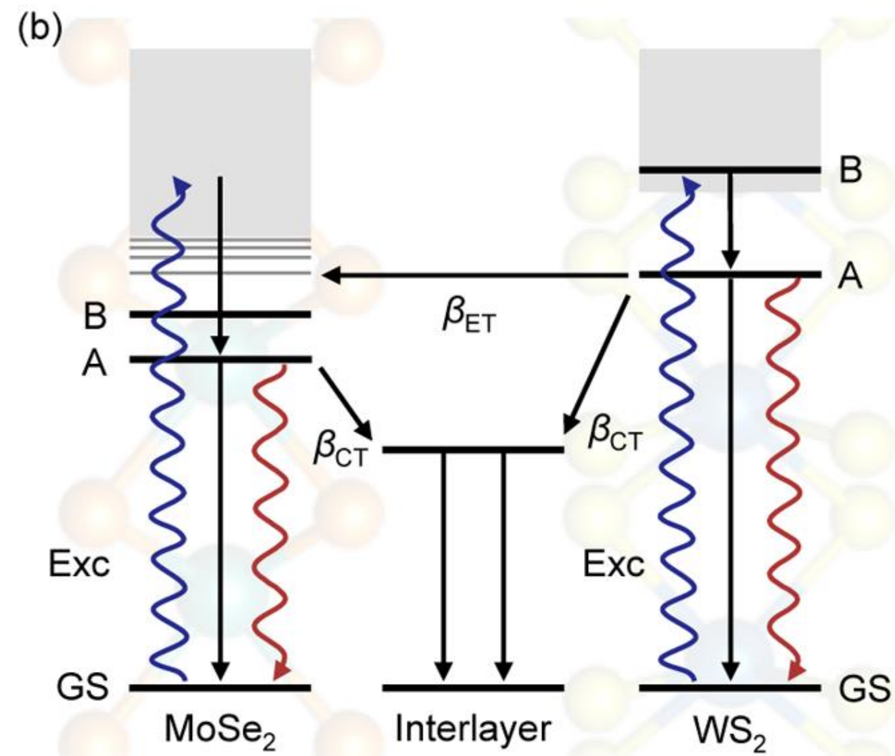
Ultrafast (<ps) formation
Long lived (>ns)
Valley polarized
Direct or indirect (θ)
PN Junctions

Fang *et al.*, PNAS 2014
Hong *et al.*, Nat Nano 2014
Lee *et al.*, Nat Nano 2014
Rivera *et al.*, Nat Comm 2015
Rivera *et al.*, Science 2016
Ceballos *et al.*, ACS Nano 2014
Ross *et al.*, Nano Lett 2017
…

Schaibley *et al.*, Nat. Rev. Materials doi:10.1038%2Fnatrevmats.2016.55

Energy Transfer in TMD/TMD heterostructures

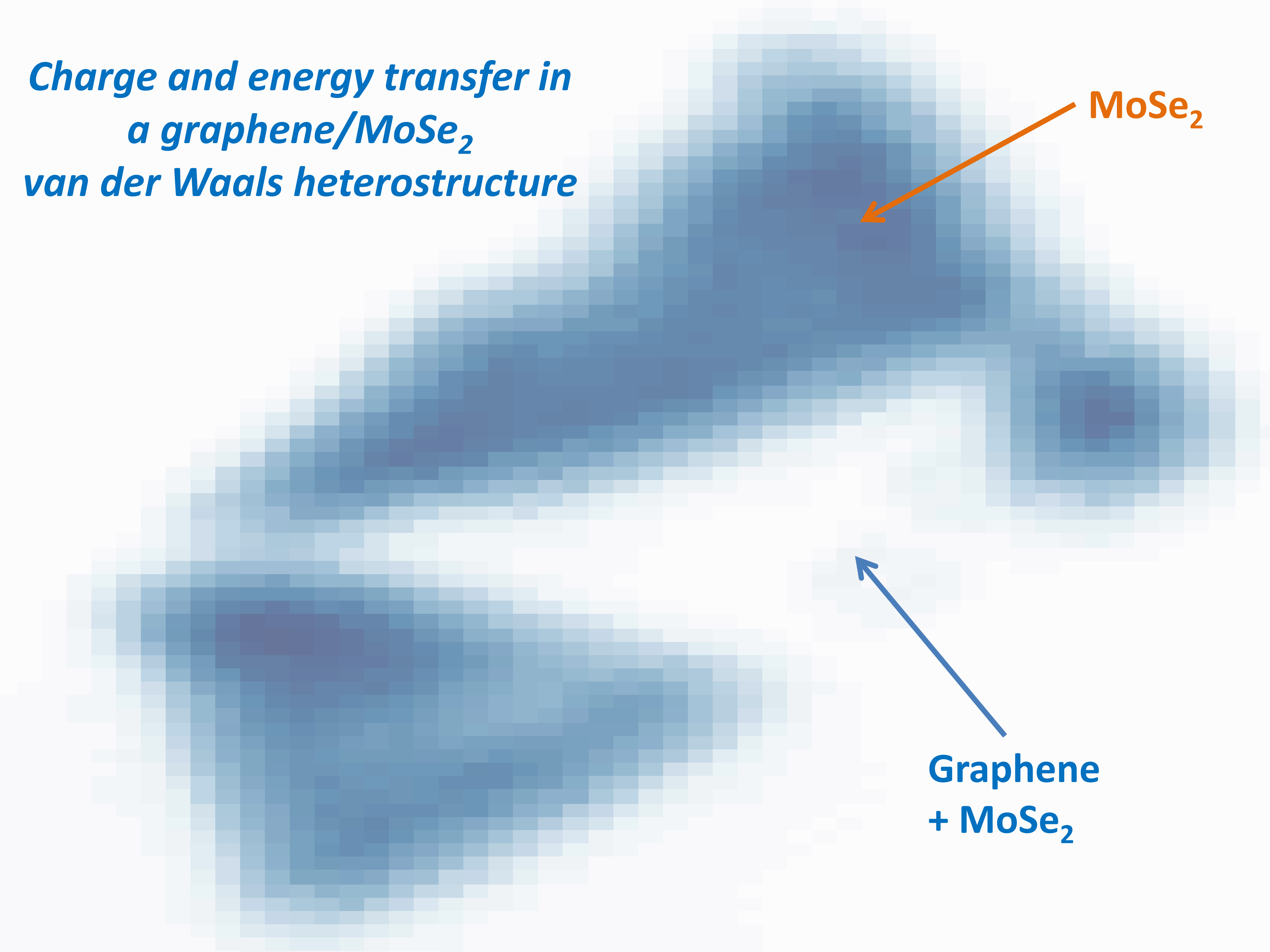


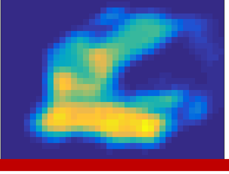


D. Kozawa *et al.*, Nano Lett. 2016

Open debate: competition between interlayer charge and energy transfer

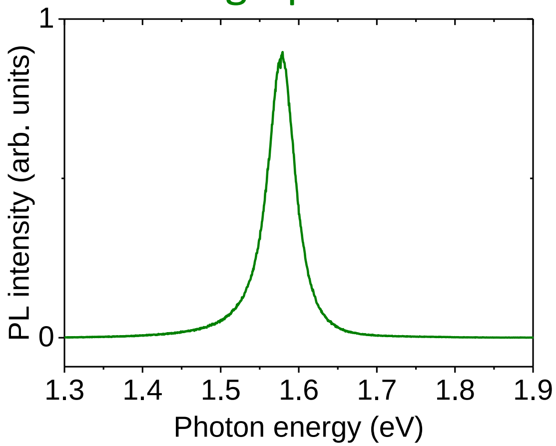
Charge and energy transfer in a graphene/$MoSe_2$ van der Waals heterostructure

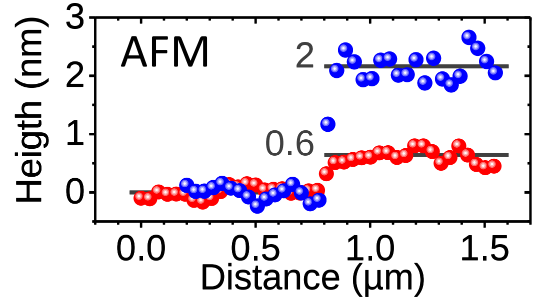


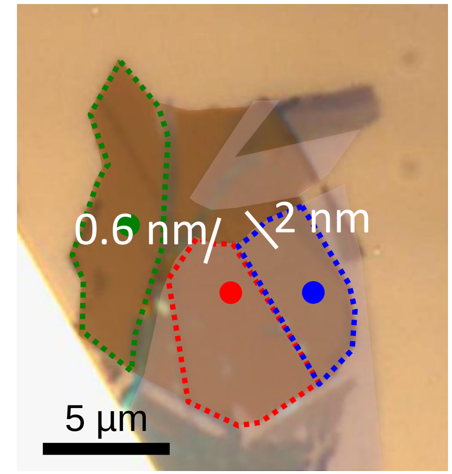


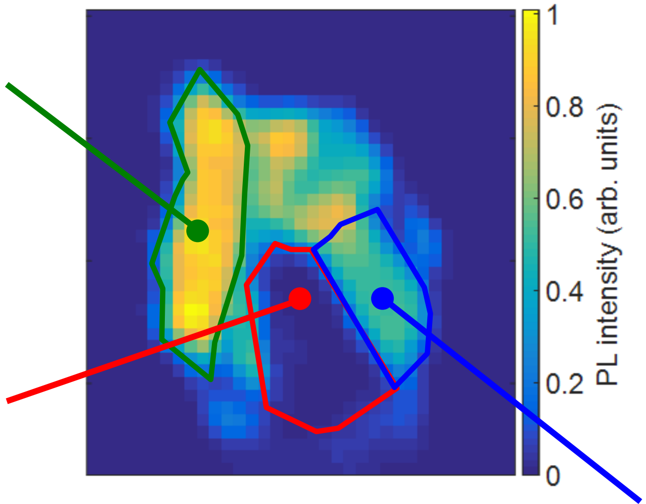
Photoluminescence mapping

No graphene

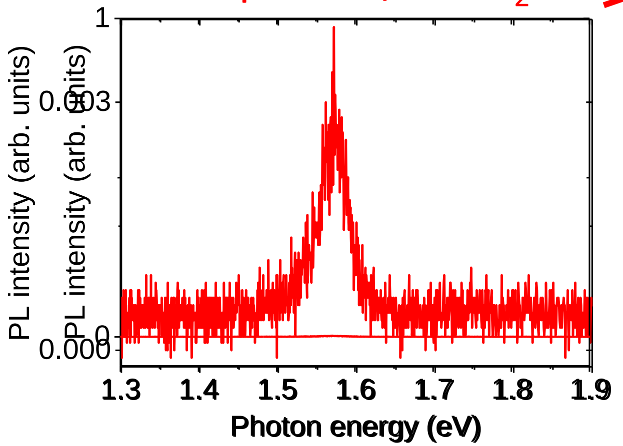






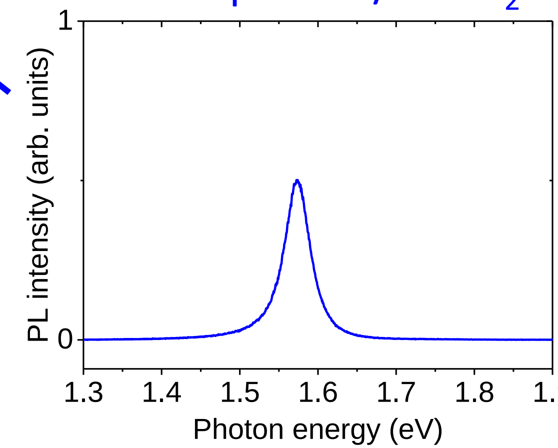


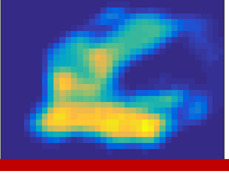
Coupled Gr/$MoSe_2$



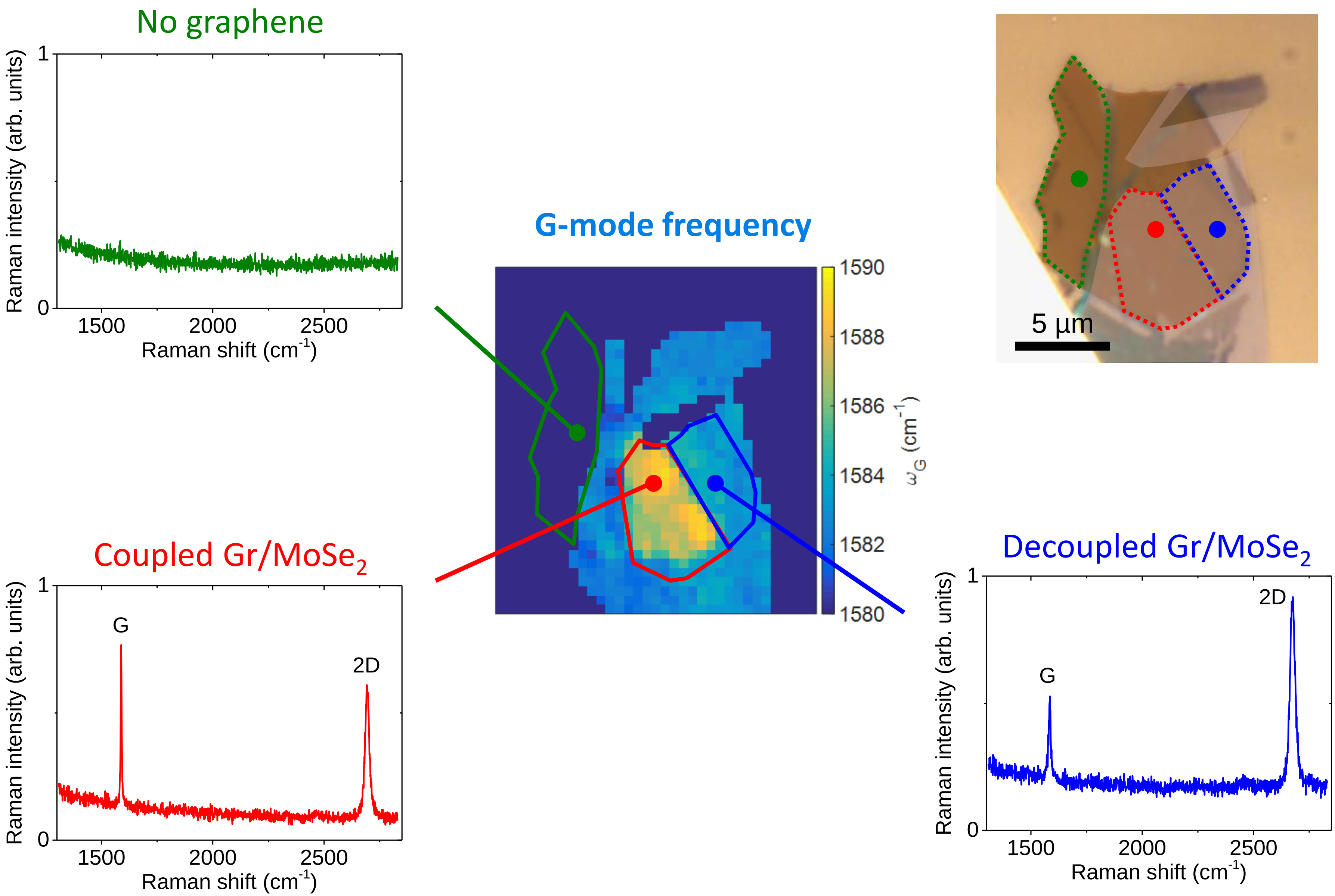
Strong PL Quenching ~ 300

Decoupled Gr/$MoSe_2$

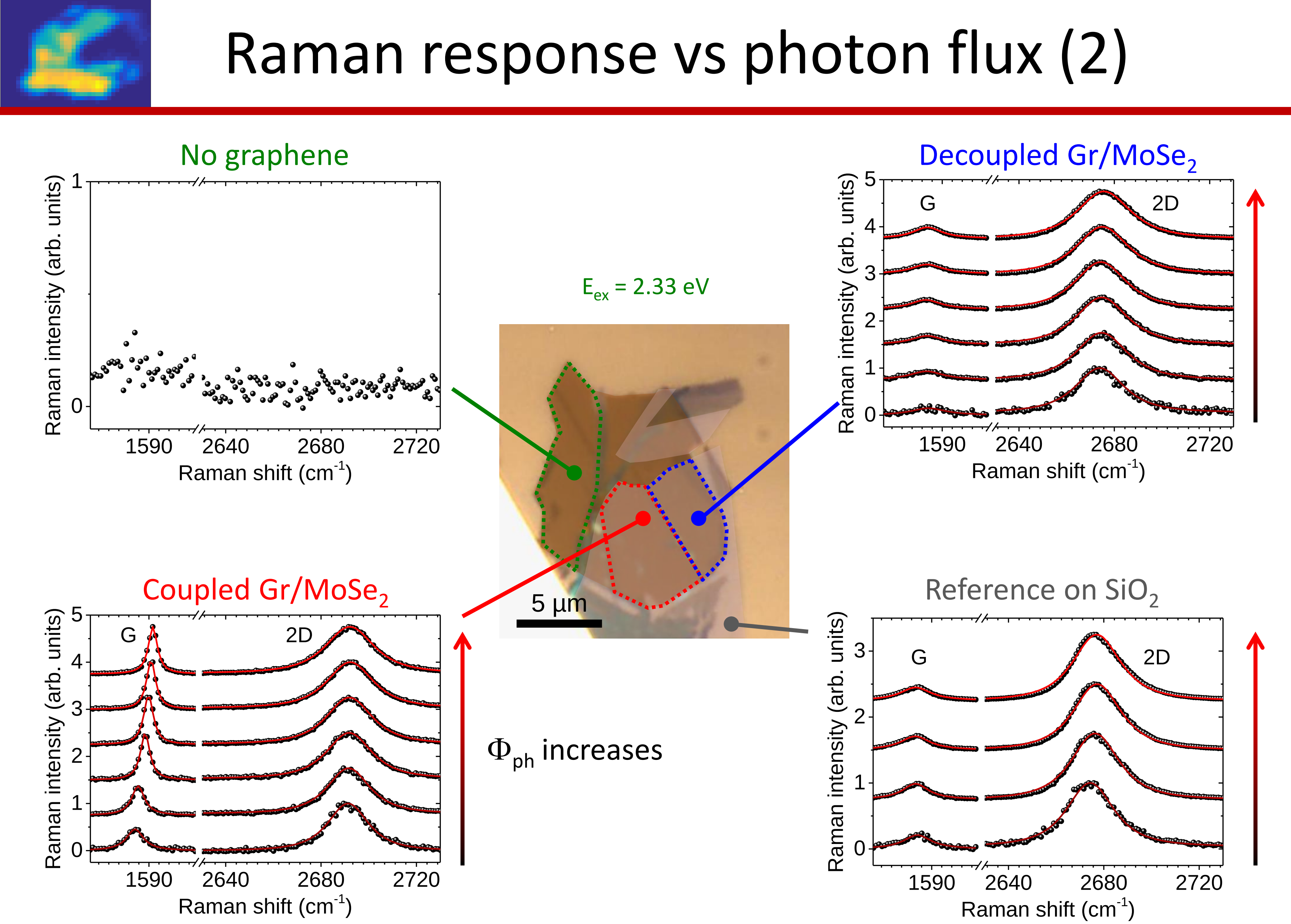


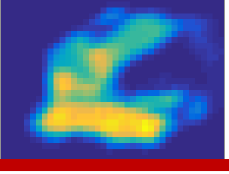


Raman mapping



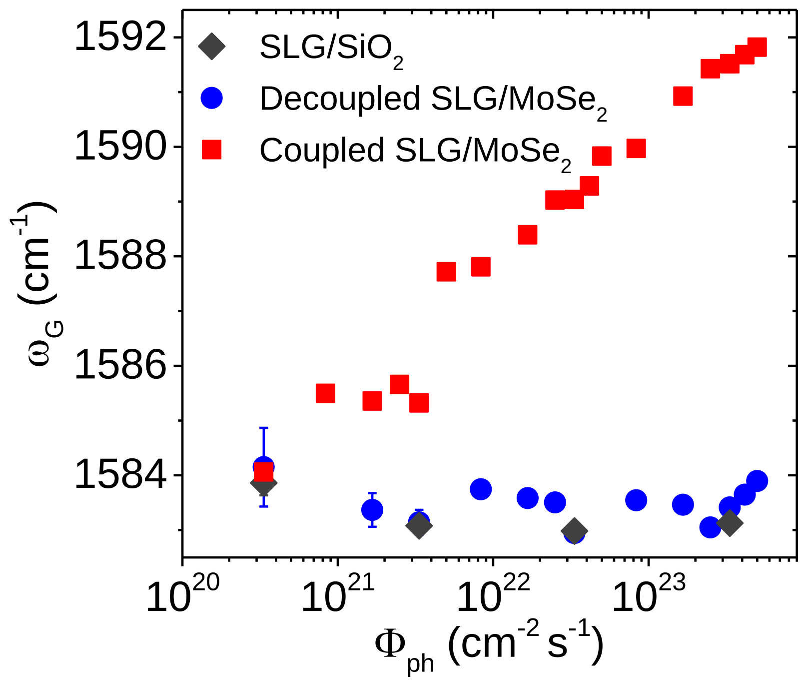
Raman response vs photon flux (2)



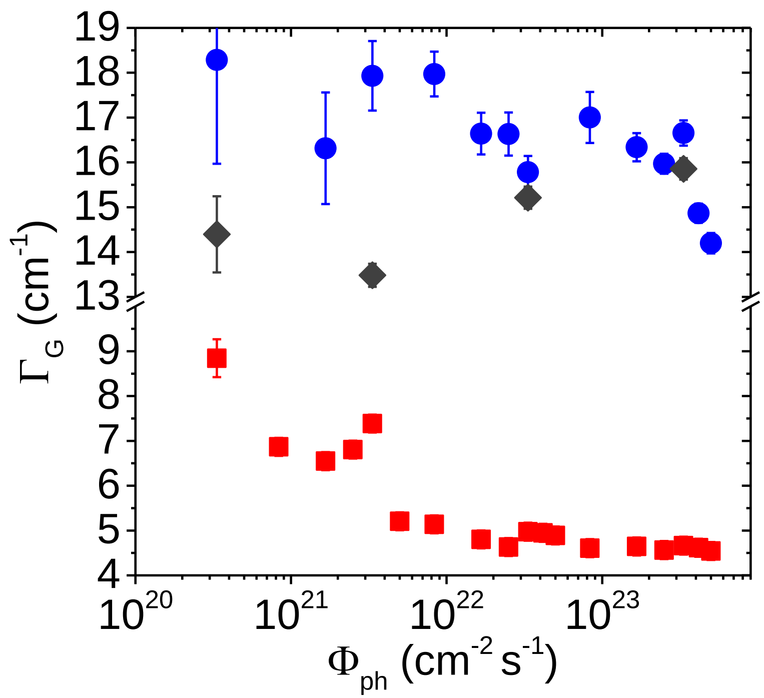


Raman response vs photon flux (2)

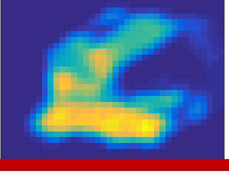
G-mode frequency



G-mode FWHM



➡ Clear signatures of photoinduced charge transfer



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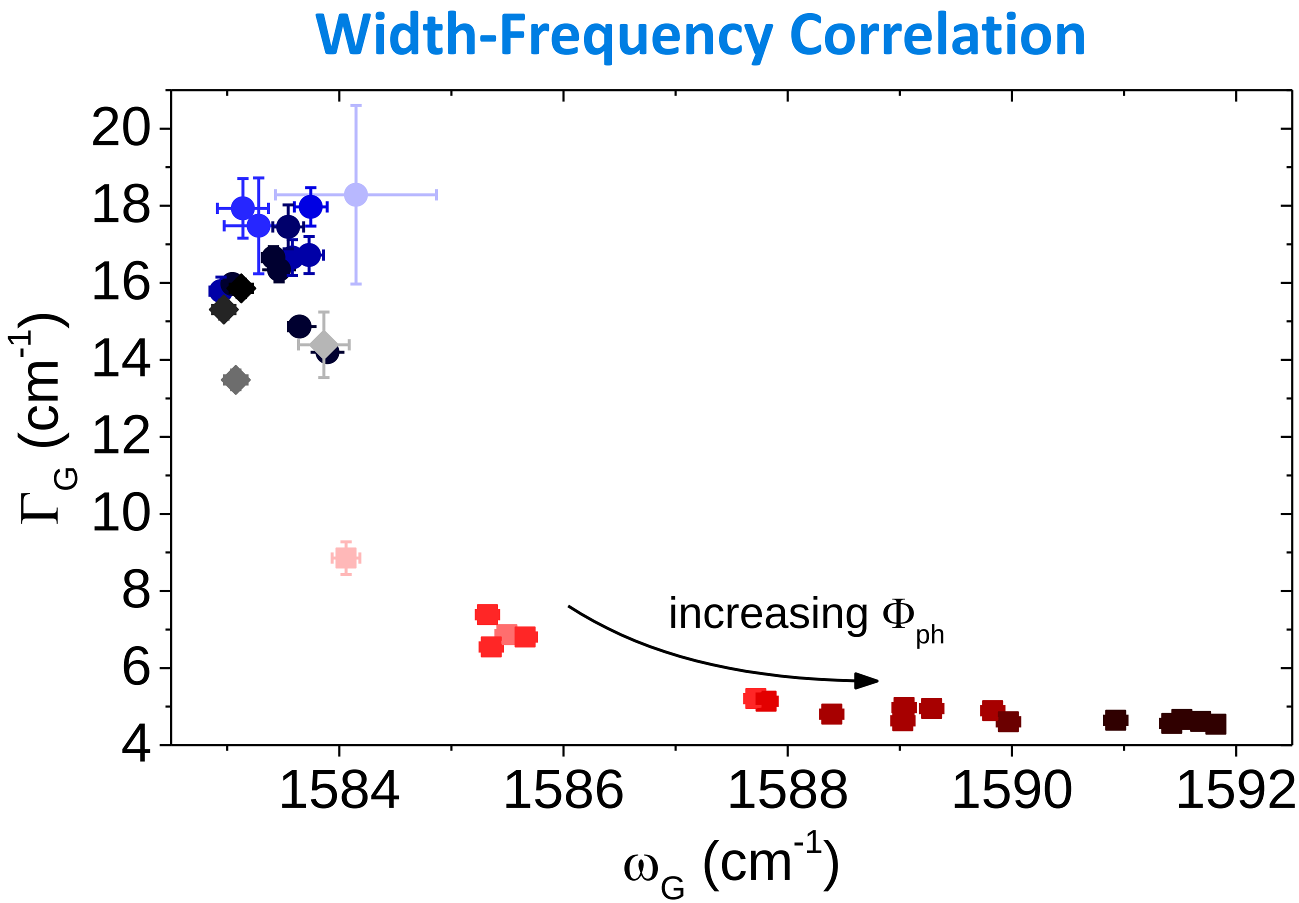
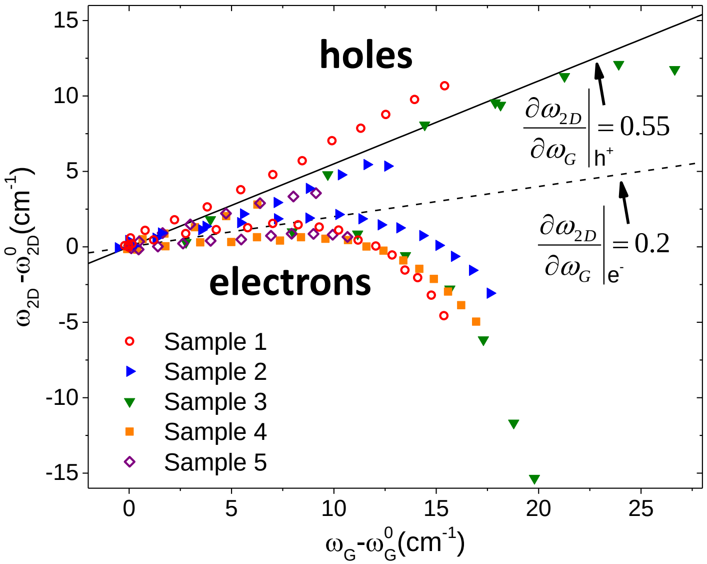
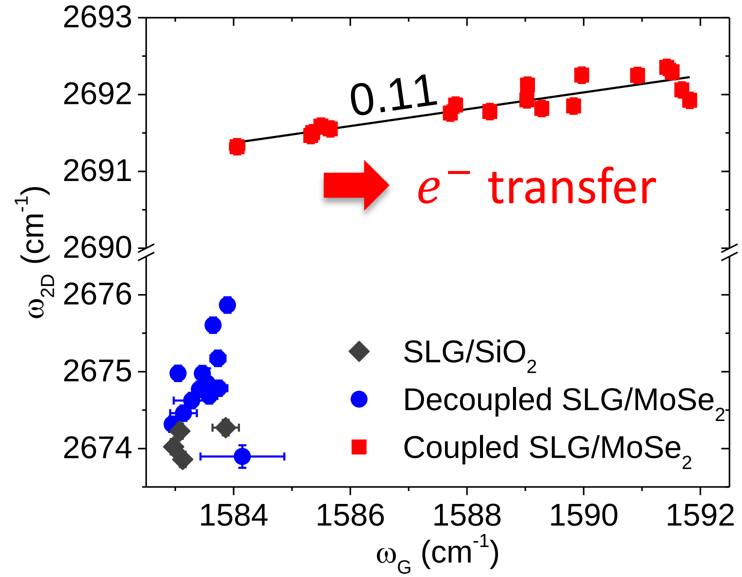


➡ Clear signatures of photoinduced charge transfer

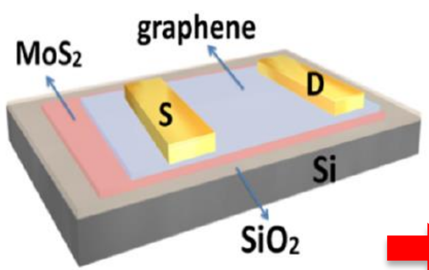
Evidence for TMD→ Gr electron transfer

- **2D and G mode correlations:** separation of strain and e⁻/h⁺ doping



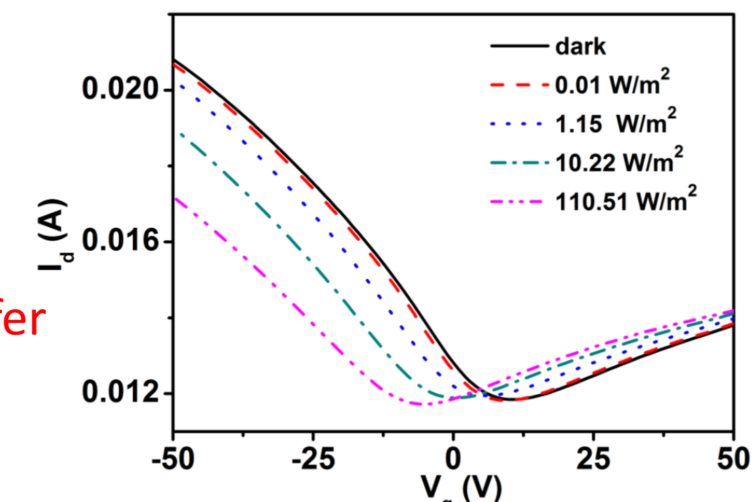


- **Comparison with Gr/MoS$_2$**

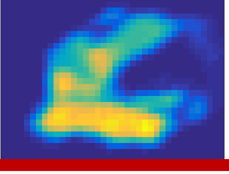


e^- transfer

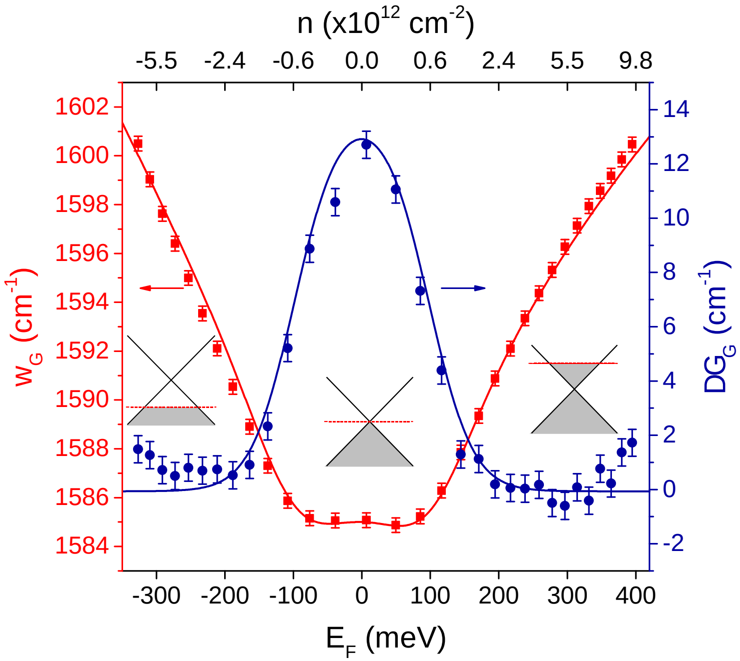
electrical measurements

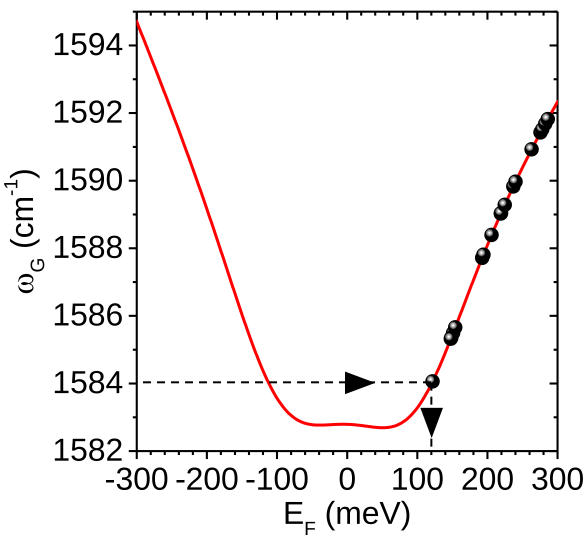


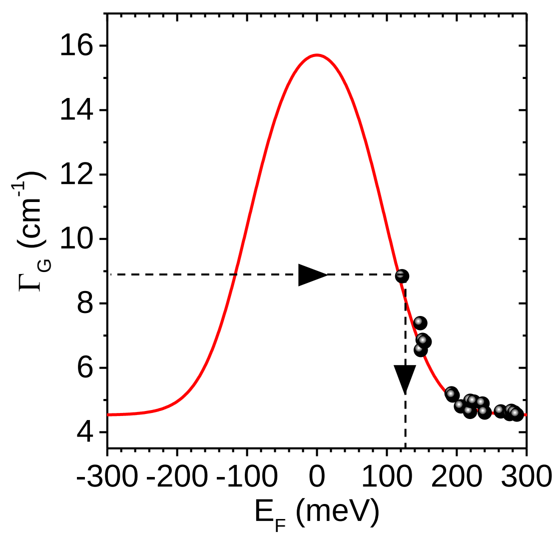
W. Zhang *et al.*, Scientific Reports **4**, 3826 (2014)

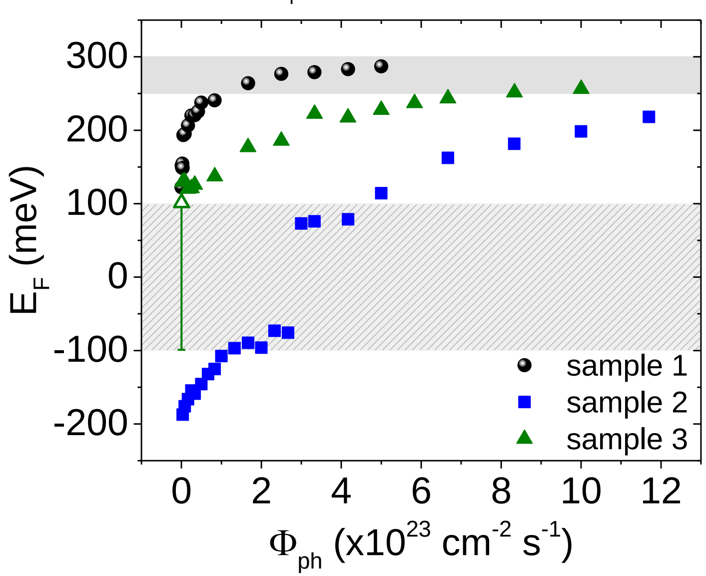


Quantifying photoinduced doping







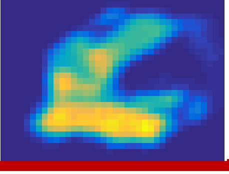


Saturation at $E_F \sim$ 250-300 meV

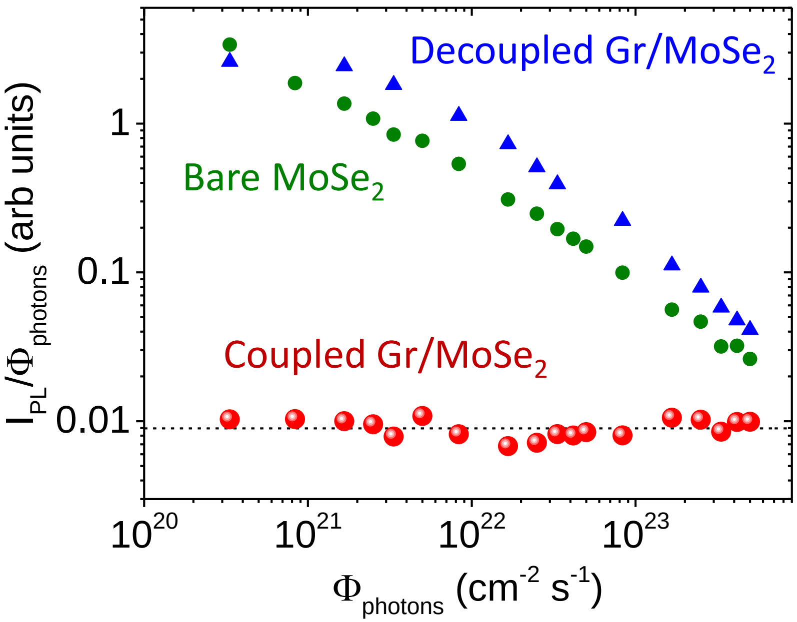
Does the ICT efficiency depend on E_F?

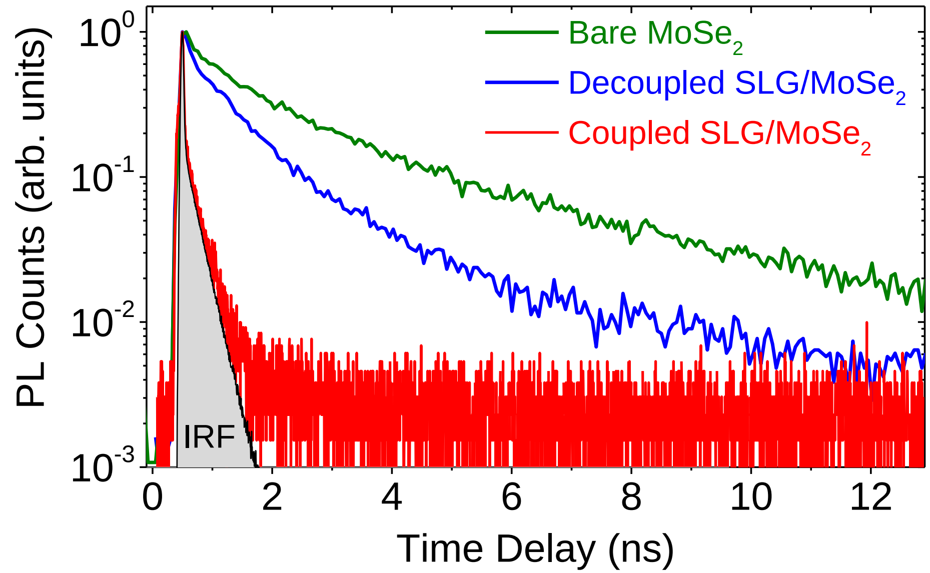
G. Froehlicher and SB, PRB **91**, 205413 (2015)

G. Froehlicher *et al.*, (in preparation, 2016)



PL vs $\Phi_{photons}$





- **PL saturation on bare and decoupled $MoSe_2$:**

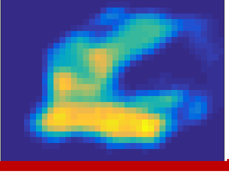
→ Exciton-Exciton Annihilation (EEA)

- **No PL saturation on Gr/$MoSe_2$**

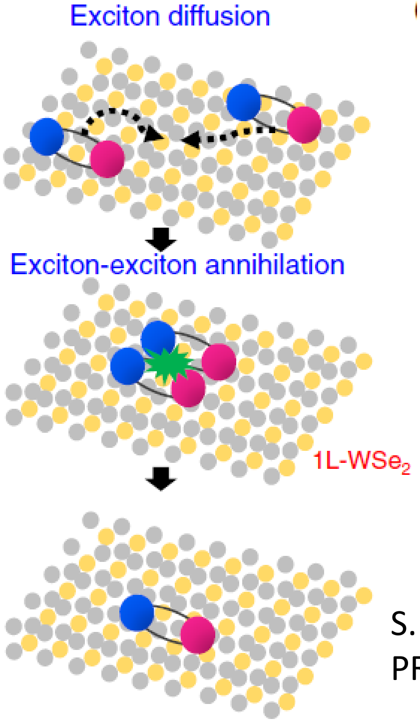
→ Drastic reduction of the excitonic lifetime (~ 1 ps)

→ **Charge *and* Energy Transfer?**

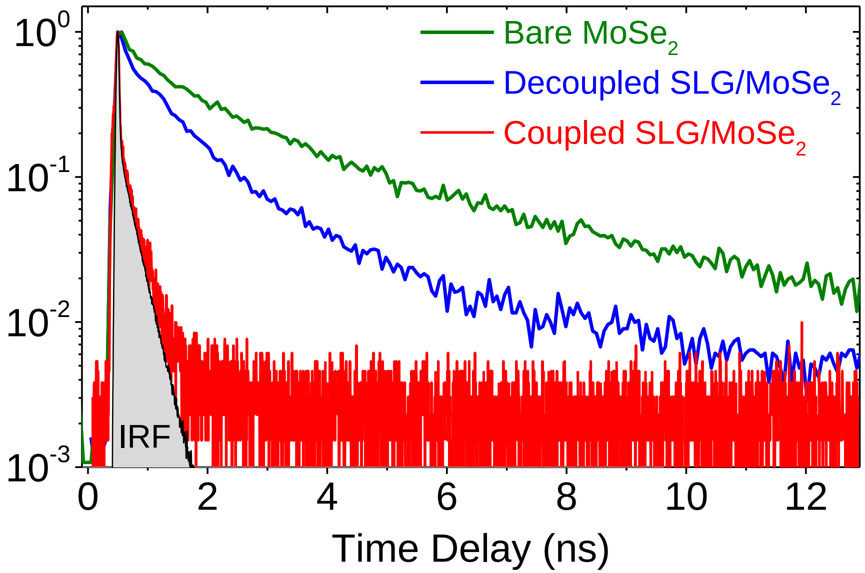
EEA: N. Kumar *et al.*, PRB **89**, 125427 (2014), S. Mouri *et al.*, PRB **90**, 155449 (2014), D. Sun *et al.*, Nano Lett. **14**, 5625 (2014)



PL vs $\Phi_{photons}$



S. Mouri *et al.*,
PRB 2014



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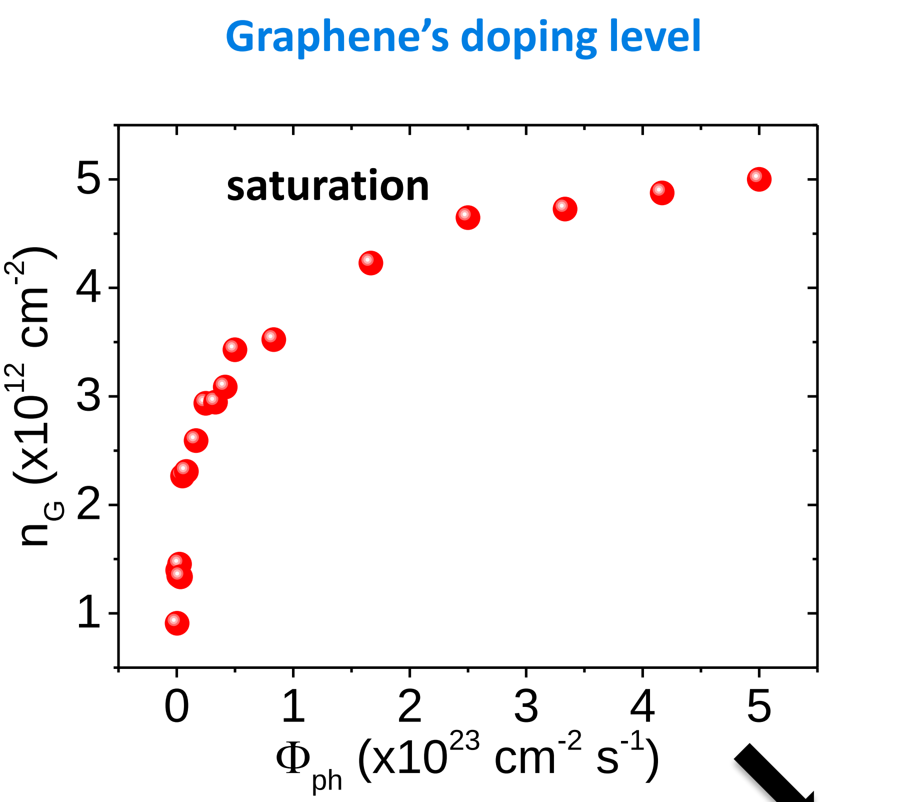
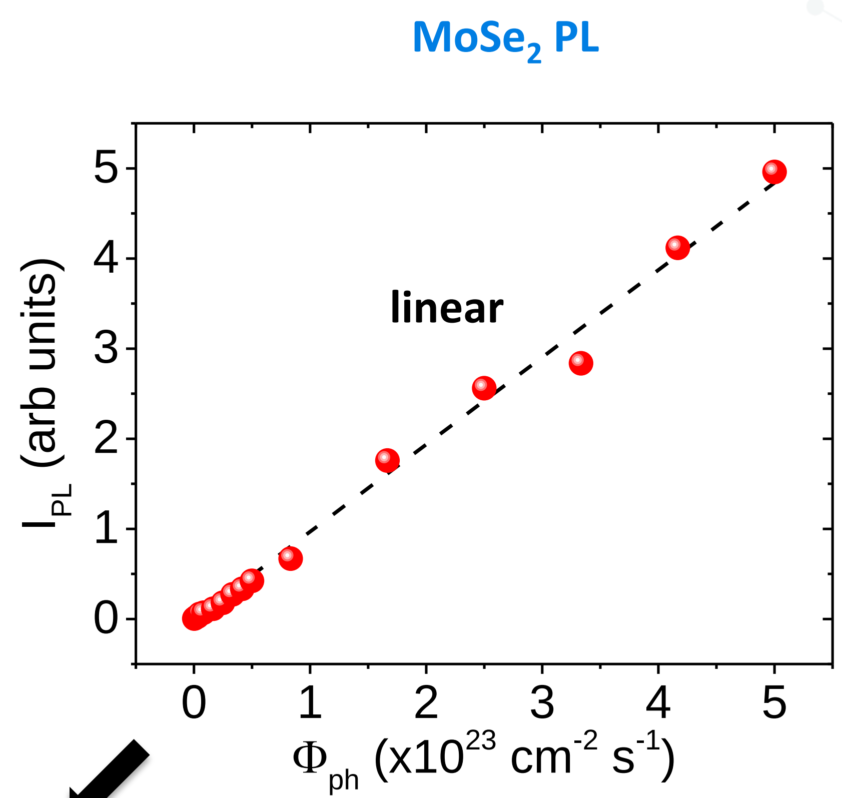
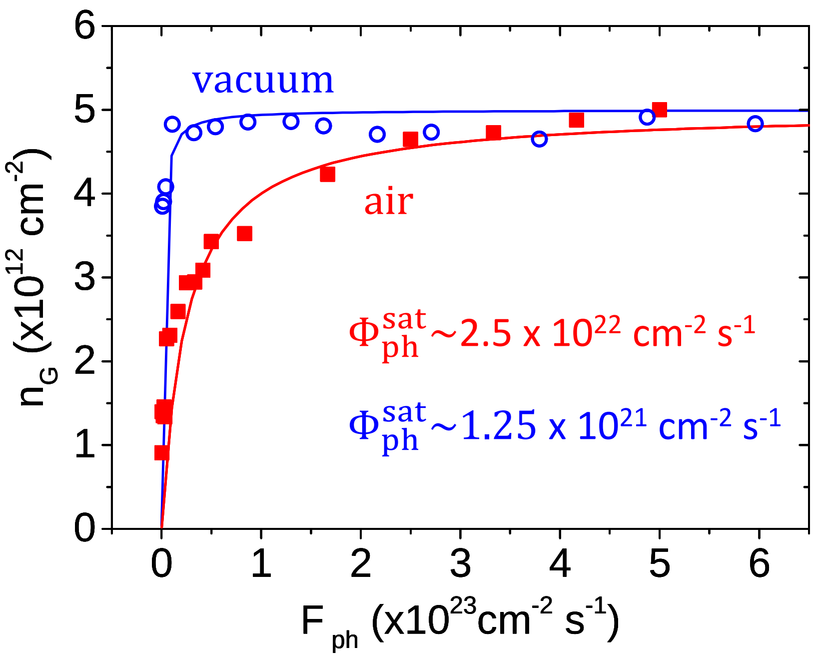
Photoluminescence vs Raman

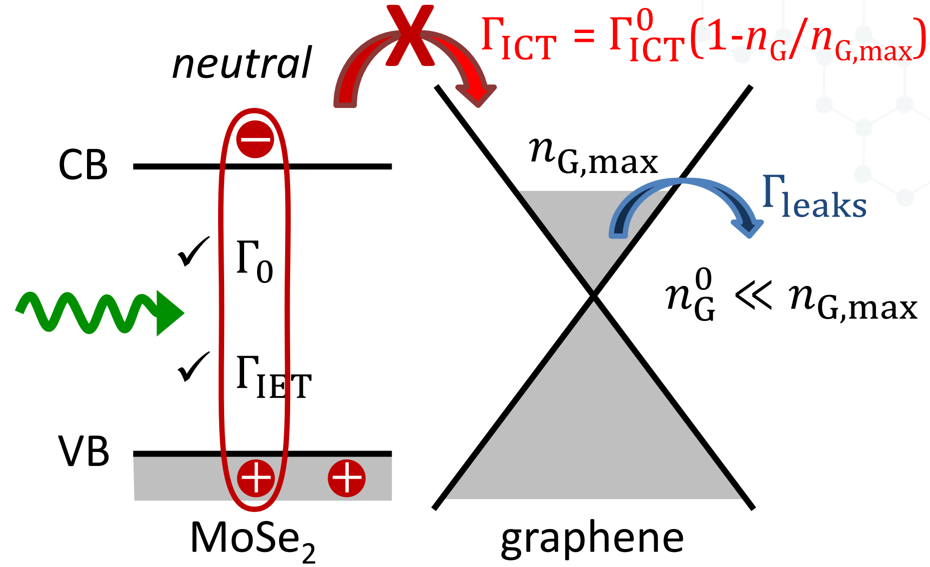




Cannot be explained using ICT only

Toy model

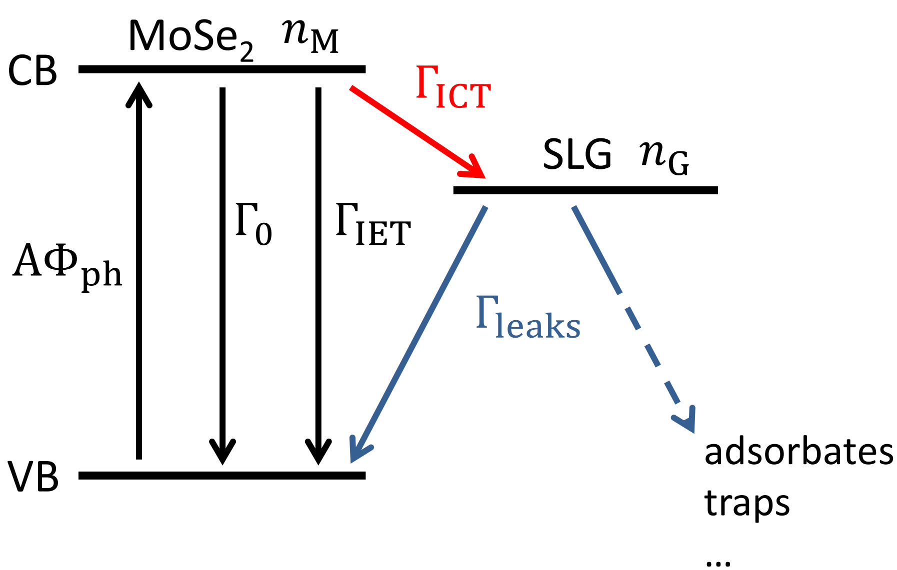




- At $\Phi_{ph} = 0, n_M = 0$ and $n_G = 0$
- $\Gamma_{IET} \gg \Gamma_{ICT}, \Gamma_0$

$$\langle n_M \rangle \approx \frac{A\Phi_{ph}}{\Gamma_{IET}}$$

$$\langle n_G \rangle \approx \frac{n_{G,max}}{1 + \Phi_{ph}^{sat}/\Phi_{ph}}$$

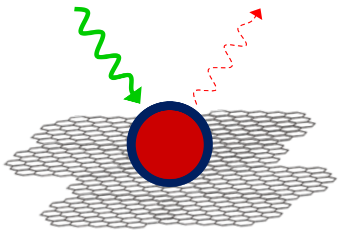


$\Gamma_{leaks} \downarrow$ $\sim 10^{12}$ s^{-1}

$$\Phi_{ph}^{sat} = \frac{\Gamma_{leaks}\Gamma_{IET}}{\Gamma_{ICT}^0}\frac{n_{G,max}}{A}$$

Conclusion

✓ **Efficient energy transfer from semiconductor nanostructures to 2D materials**



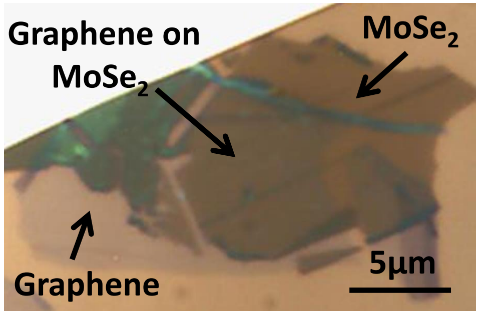
✓ Molecular rulers

✓ FRET as a probe of exciton dimensionality

✓ FRET engineering

✓ **Photoinduced e⁻ transfer from TMD to graphene**

→ Towards local photogating of graphene

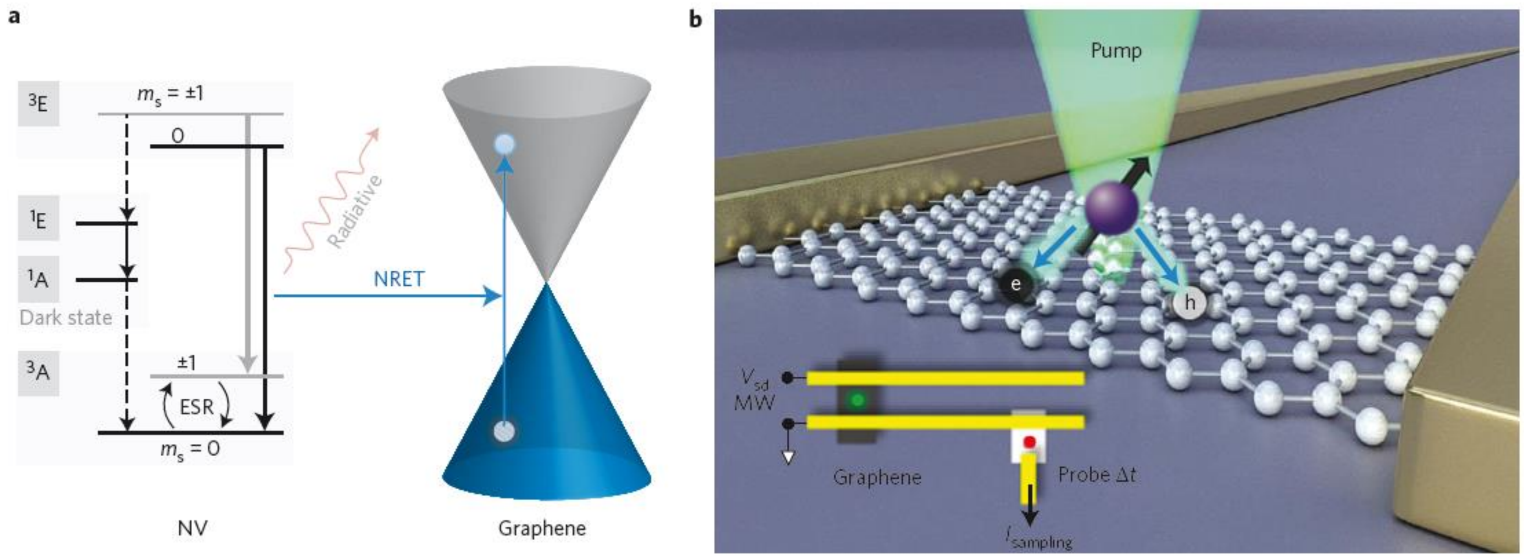


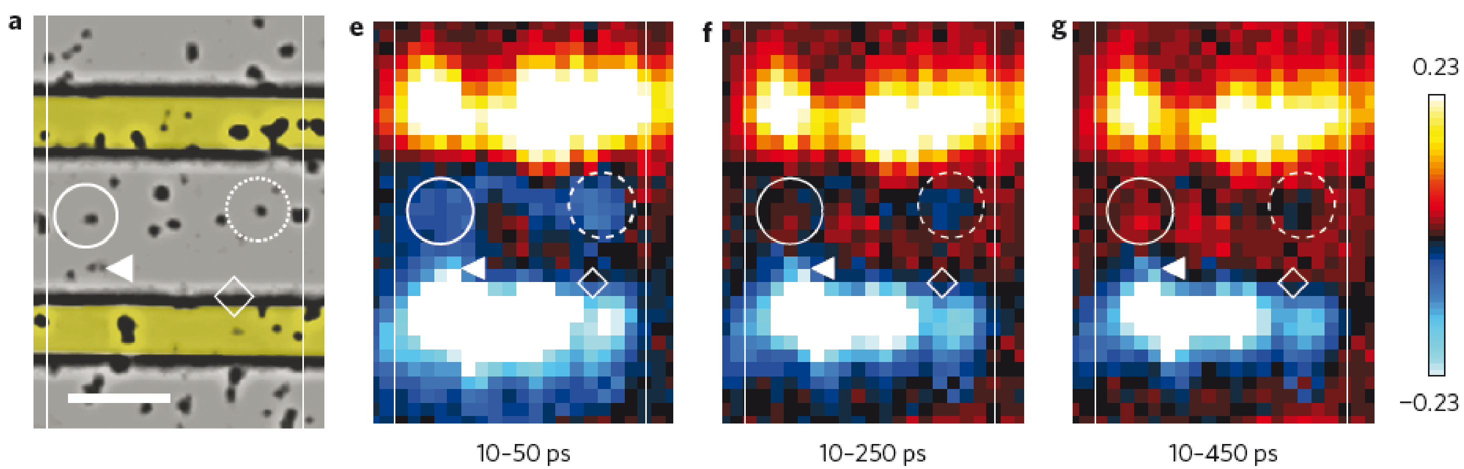
✓ **Fast IET is responsible for PL quenching**

✓ **IET is more efficient than ICT**

- **Open questions**
  - ✓ Energy transfer mechanism in Gr-TMD? In TMD-TMD?
  - ✓ Band alignment and excitonic effects?
  - ✓ …

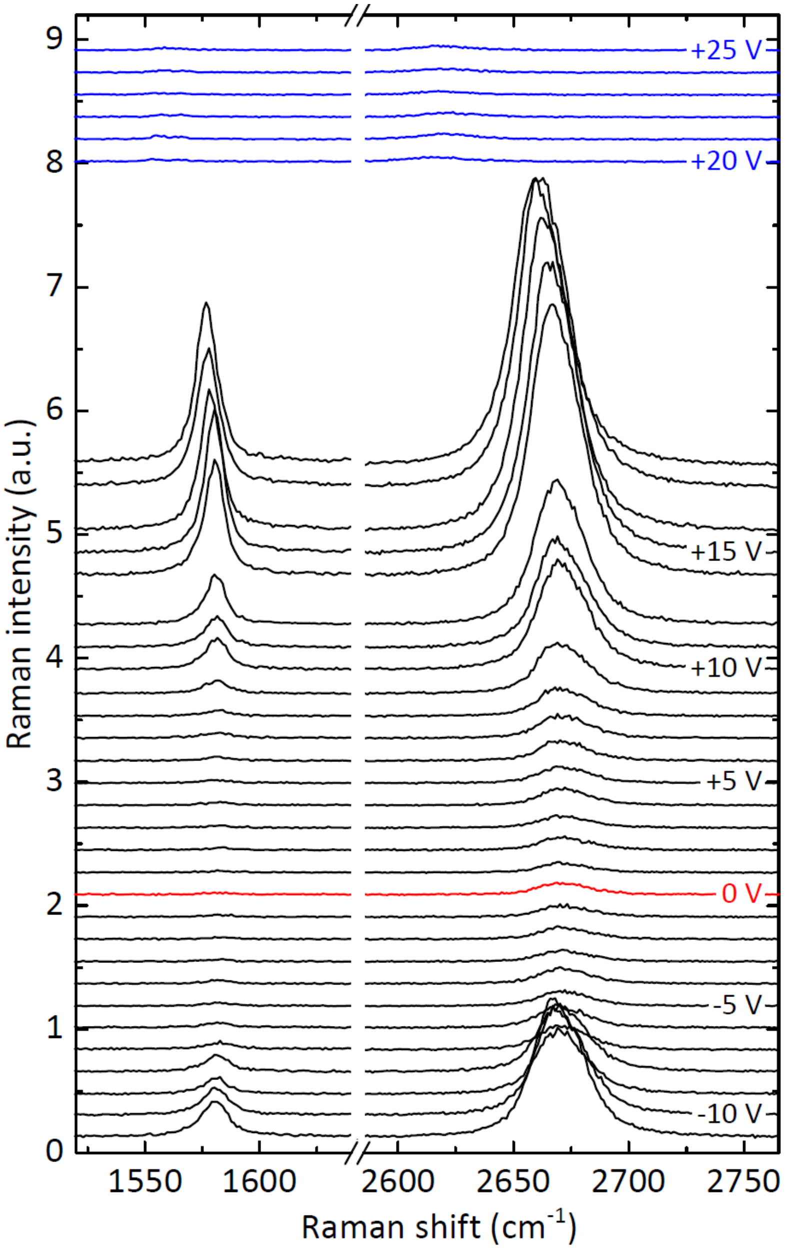
Outlook 1: FRET-induced electrical currents



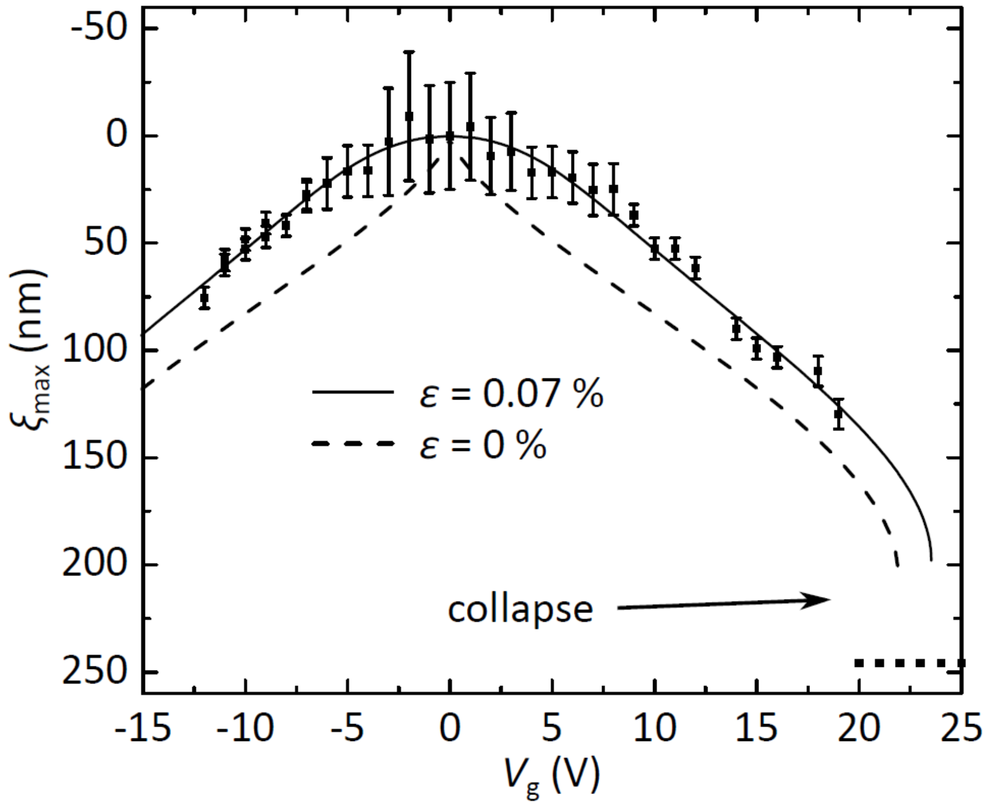


A. Brenneis *et al.* Nat. Nano 2015. (Holleitner group with Koppens group)

Outlook2: opto-electromechanics in 2DM

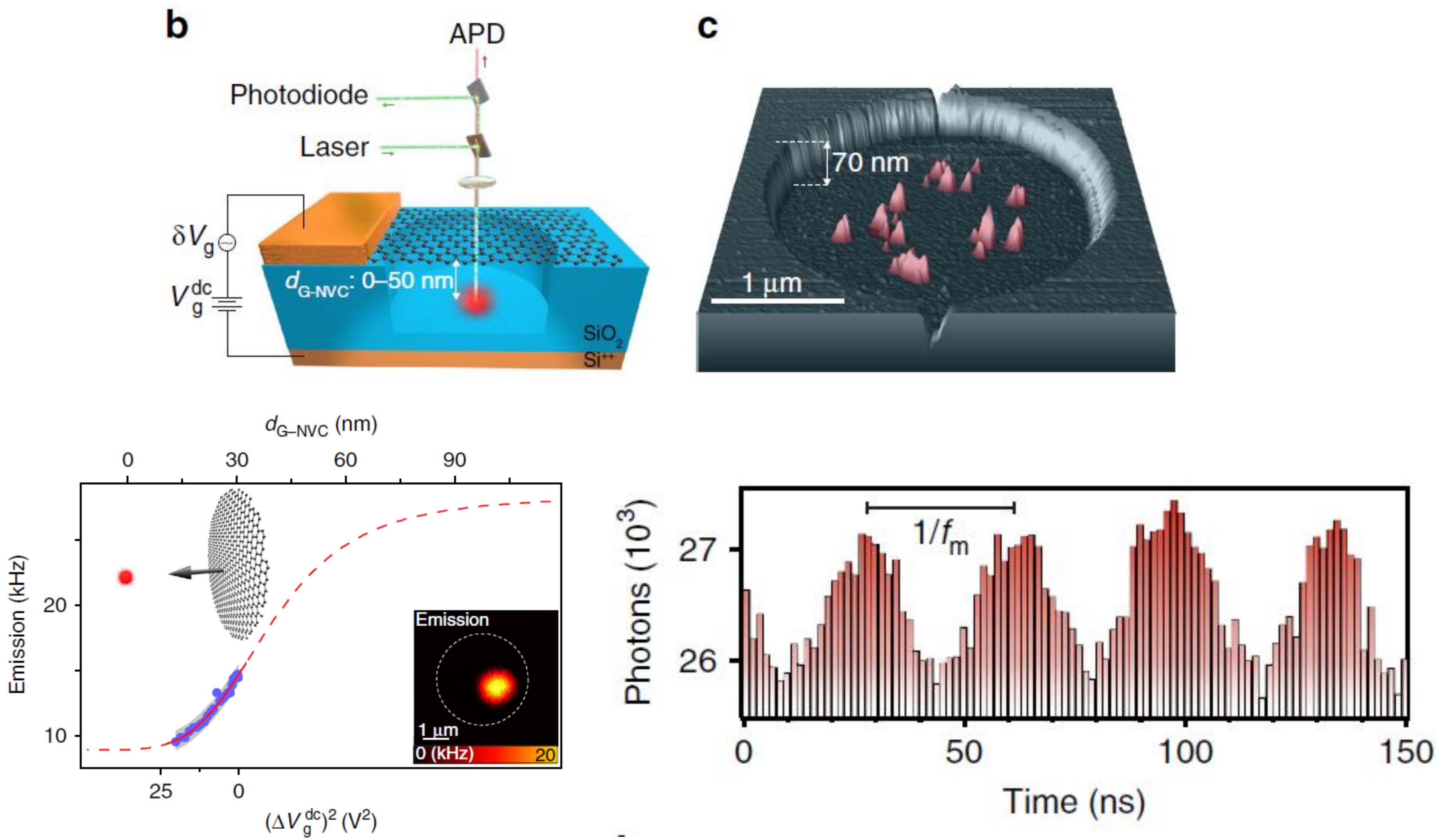


Deflection, strain, doping
Transport? Optomechanics?



D. Metten, G. Froehlicher and SB, 2D Materials **4** 014004 (2017)

Optoelectromechanical control of FRET



A. Reserbat-Platey, K. Schadler et al., Nat Comm. (2016) (Bachtold and Koppens groups)

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B. Doudin
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Michi Romeo
Pierre Gilliot
StNano Clean Room

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Emmanuel Lhuillier (INSP)
Benoît Dubertret

KRICT
Jeong-O Lee
Serin Park

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