Optical Properties and Electron-Phonon Interactions in Low-Dimensional Materials

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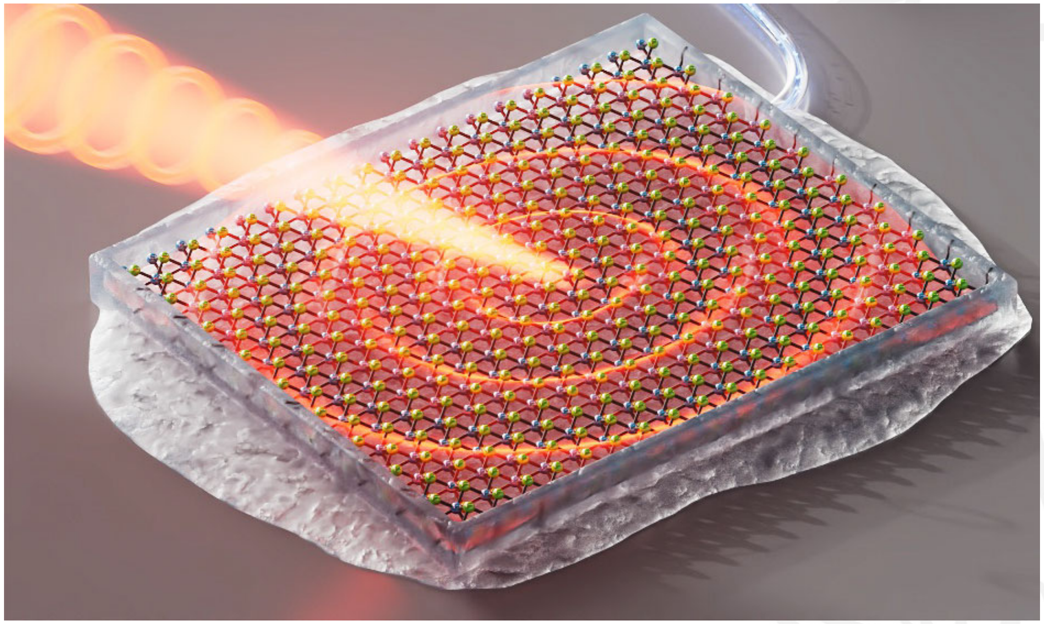
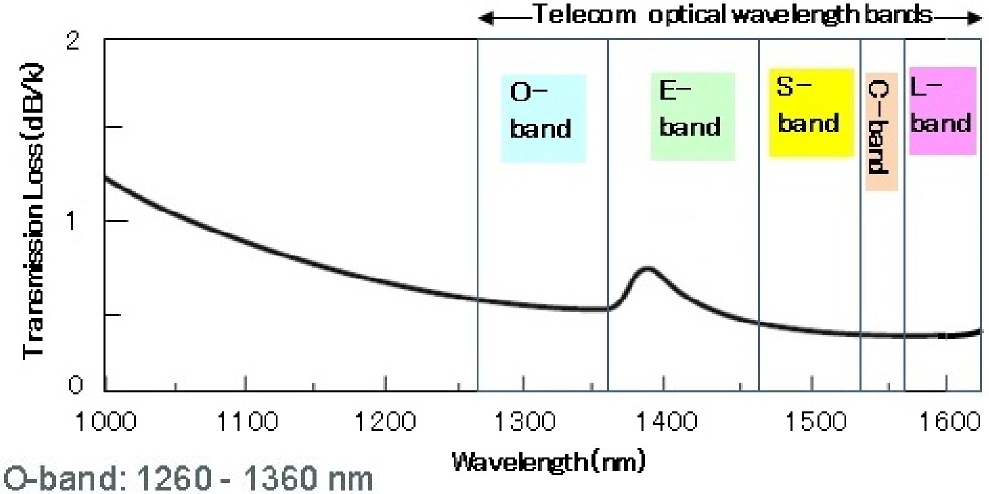


quest for 2D materials as quantum light generation

optical fiber attenuation



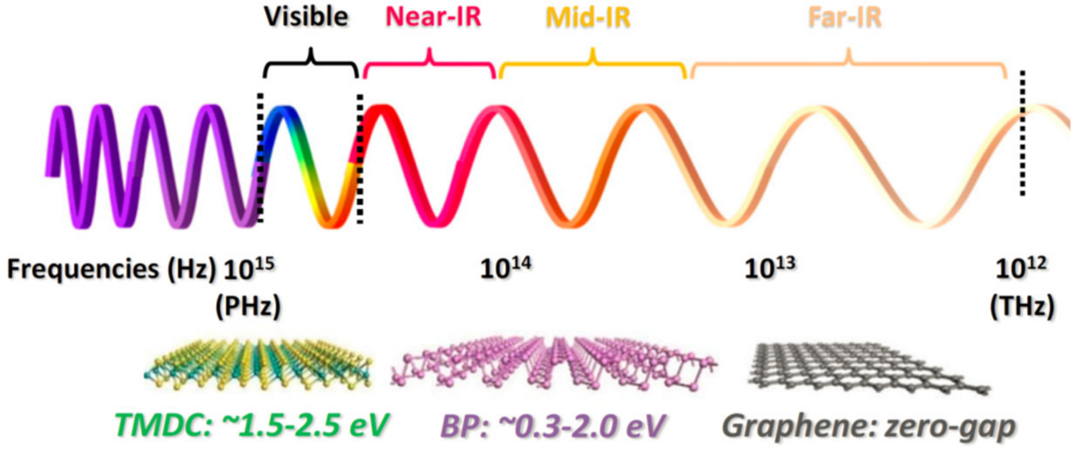
O-band: 1260 - 1360 nm

S-band: 1460 - 1530 nm

C-band: 1530 - 1565 nm

L-band: 1565 - 1625 nm

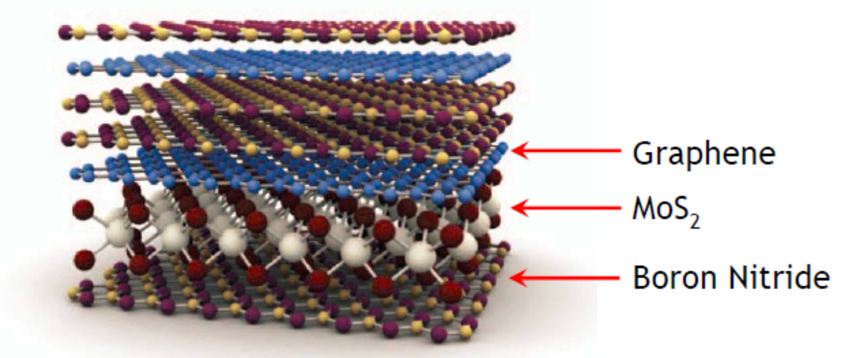
2D materials spectral range



Key Optical Properties of 2D Materials

- Extraordinary strong light-mater interaction
- Strong electron-hole interactions, exciton binding up to 500 meV
- Strong optical nonlinearity
- Optical tuning external electric field
- Dielectric environment engineering

A schematic of a 2D hetero-structure



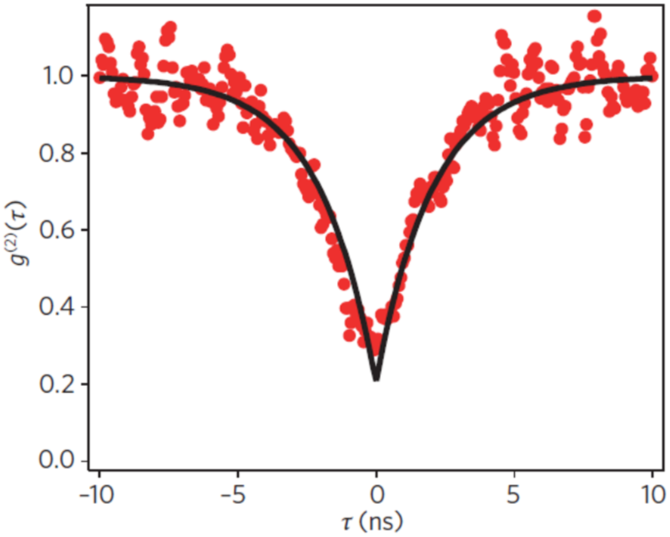
Novoselov et al, “A roadmap for graphene”, Nature 2012

single photon emitters in WSe_2

nature nanotechnology

JUNE 2015 VOL 10 NO 6
www.nature.com/naturenanotechnology

Single photons from single layers



Srivastava, et. al. Nature Nano **10**, 491 (2015)
He, et. al. Nature Nano **10**, 497 (2015)
Koperski, et. al. Nature Nano **10**, 503 (2015)
Chakraborty, et. al. Nature Nano **10**, 507 (2015)
Tonndorf, et. al. Optica **2**, 347 (2015)

news & views

METAL DICHALCOGENIDES

Two dimensions and one photon

Single-photon sources have been demonstrated in two-dimensional semiconductors.

V. Perebeinos

Nature Nano (2015)

Outline

1) Linear spectroscopy due to excitons and trions
2) Phonon-Assisted Indirect Exciton Ionization in 2D materials
3) Electron-phonon interactions in mono and bilayer graphene
4) Electron-phonon interactions in black phosphorous and 1D SbPS4

excitons in 3D, 2D, and 1D

$$E_n^{3D} = -E_0 \frac{1}{n^2},\ E_0 = 13.6\, eV \frac{m}{\varepsilon^2},\ a_B = 0.529\, \overset{0}{A}\, \varepsilon / m$$

$$E_n^{2D} = -E_0 \frac{1}{(n+1/2)^2}$$

GaAs: E_1=4.2meV (3D)

GaAs: E_1=16.8meV (2D)

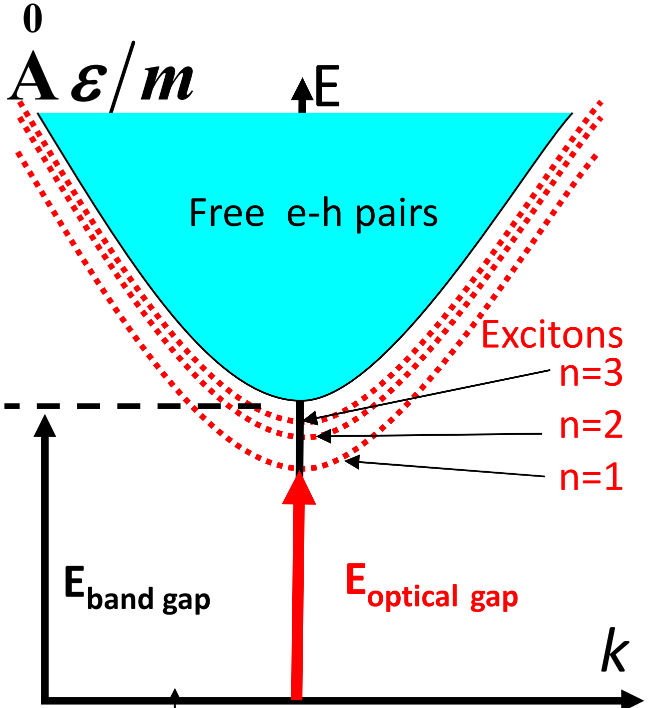
$$E_\lambda^{1D} \propto -E_0\, ln\left(\frac{d}{a_B}\right)$$

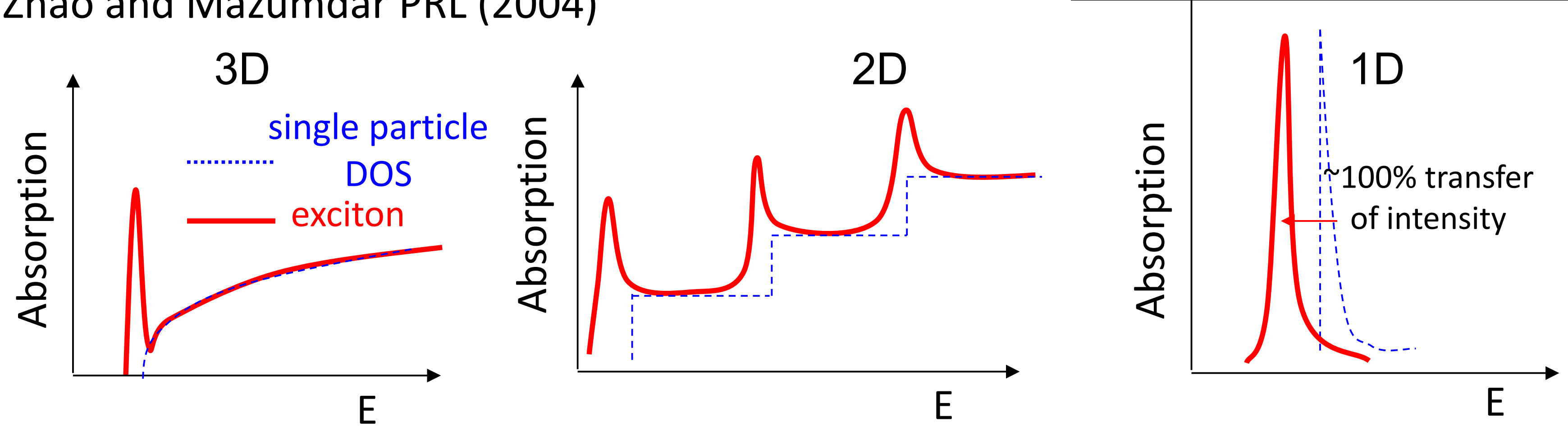
CNT E_1~500meV (1D)

$E_B \sim 1/(d\varepsilon^{1.4})$

Perebeinos et. al. *PRL (2004)*

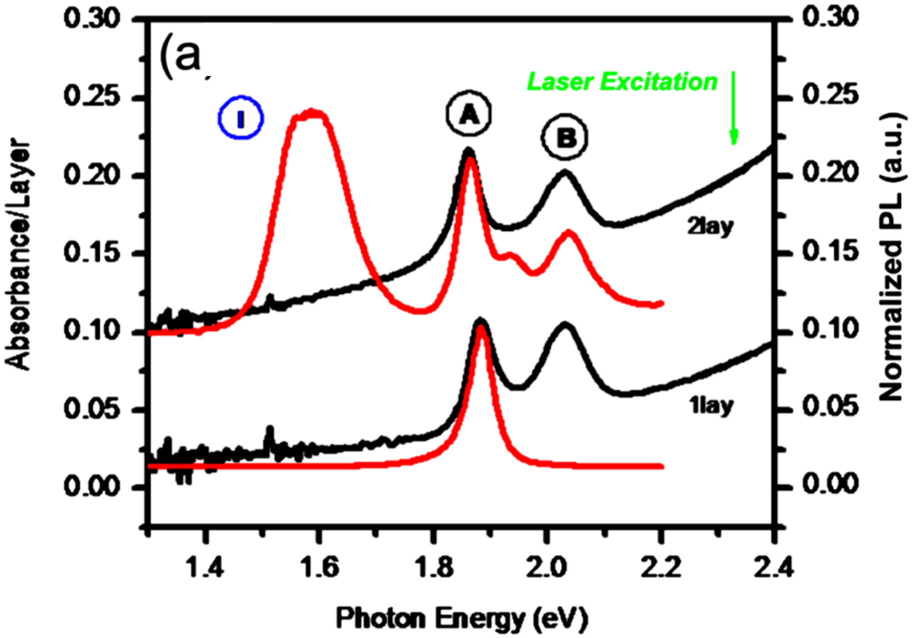
See also: Zhao and Mazumdar PRL (2004)



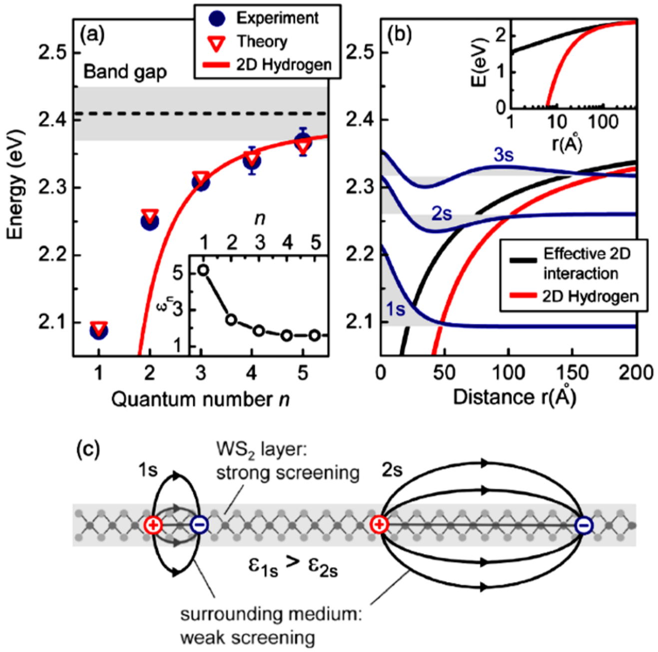


Avouris, Freitag, Perebeinos, *Nature Photonics* **2**, 341 (2008)

excitons in transition metal dichalcogenides



K.F. Mak, et al., Phys. Rev. Lett. ***105****, 136805 (2010)*



A. Chernikov, et al., Phys. Rev. Lett. ***113****, 076802 (2014)*

Excitons and trions with large binding energies

Experiments:

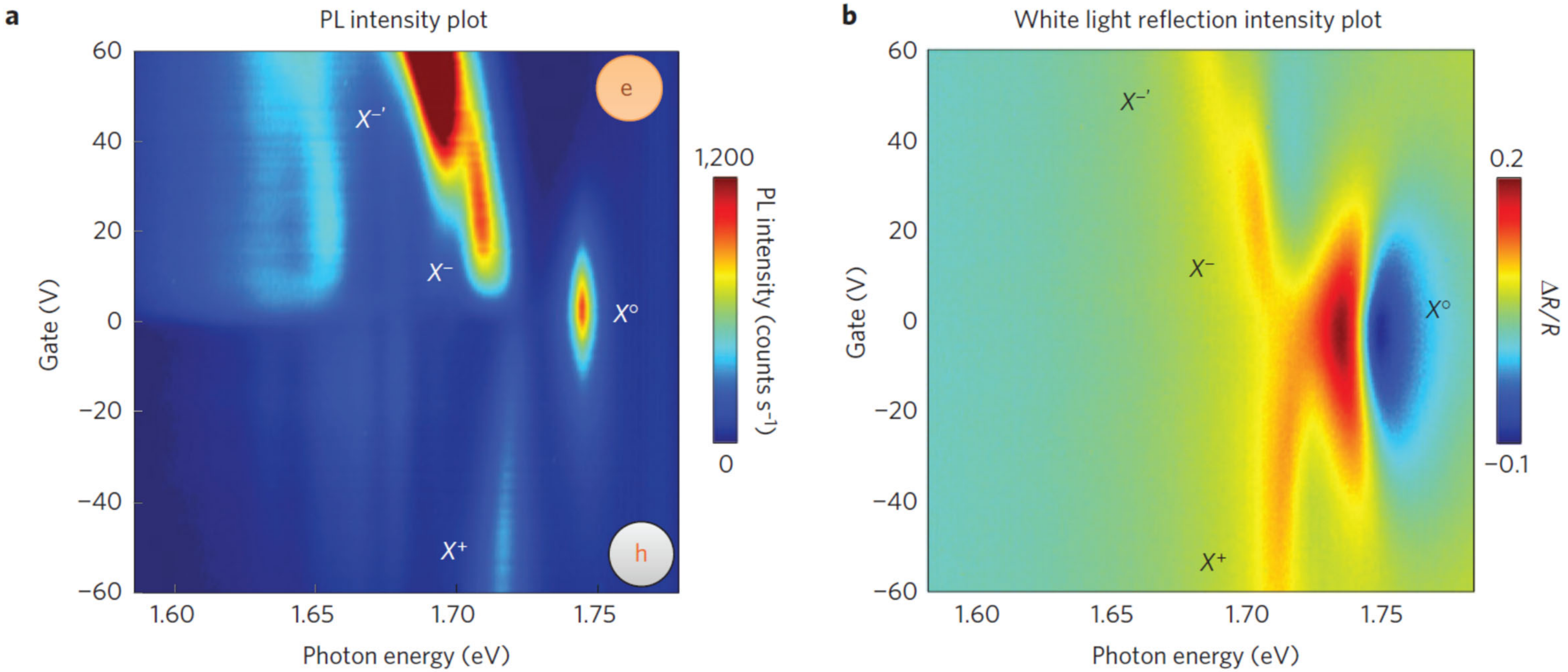
- *K. F. Mak, et al., Nat. Mater.* ***12****, 207 (2013)*
- *Z. Ye, et al., Nature* ***513****, 214 (2014)*

Theory:

- *T. C. Berkelbach, et al., Phys. Rev. B* ***88****, 045318 (2013)*
- *D. Y. Qiu, et al., Phys. Rev. Lett.* ***111****, 216805 (2013)*

and many others…

trions in transition metal dichalcogenides



X. Xu, W. Yao, D. Xiao, T. Heinz, Nat. Physics ***10****, 343 (2014)*

theoretical approach for excitons

$$|n\boldsymbol{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\nu,i} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_i} a_{n\boldsymbol{k}\nu} |\nu, \boldsymbol{R}_i\rangle$$

single-particle basis set

$$\Delta_{vc\boldsymbol{k}} A^S_{vc\boldsymbol{k}} + \sum_{v'c'\boldsymbol{k}'} \mathcal{K}_{vc\boldsymbol{k},v'c'\boldsymbol{k}'} A^S_{v'c'\boldsymbol{k}'} = \Omega_S A^S_{vc\boldsymbol{k}}$$

Bethe-Salpeter equation for
two-particle wavefunction

$$\mathcal{K}_{vc\boldsymbol{k},v'c'\boldsymbol{k}'} = \mathcal{K}^{\mathrm{d}}_{vc\boldsymbol{k},v'c'\boldsymbol{k}'} + \mathcal{K}^{\mathrm{x}}_{vc\boldsymbol{k},v'c'\boldsymbol{k}'}$$

interaction kernel:
direct and exchange Coulomb potentials

$$W\left(\left|\boldsymbol{R}^{\nu\nu'}_{ij}\right|\right) = \frac{e^2}{8\varepsilon_0 r_0}\left[H_0\left(\frac{\varepsilon\left|\boldsymbol{R}^{\nu\nu'}_{ij}\right|}{r_0}\right) - Y_0\left(\frac{\varepsilon\left|\boldsymbol{R}^{\nu\nu'}_{ij}\right|}{r_0}\right)\right]$$

the Struve and Bessel functions

$$r_0 = 2\pi\,\chi_{2\mathrm{D}}$$

screening from 2D material: χ_{2D}=6.5 Å

$$\varepsilon = (\varepsilon_1 + \varepsilon_2)/2$$

screening from the background:
ε_1 and ε_2 are above and below the 2D material

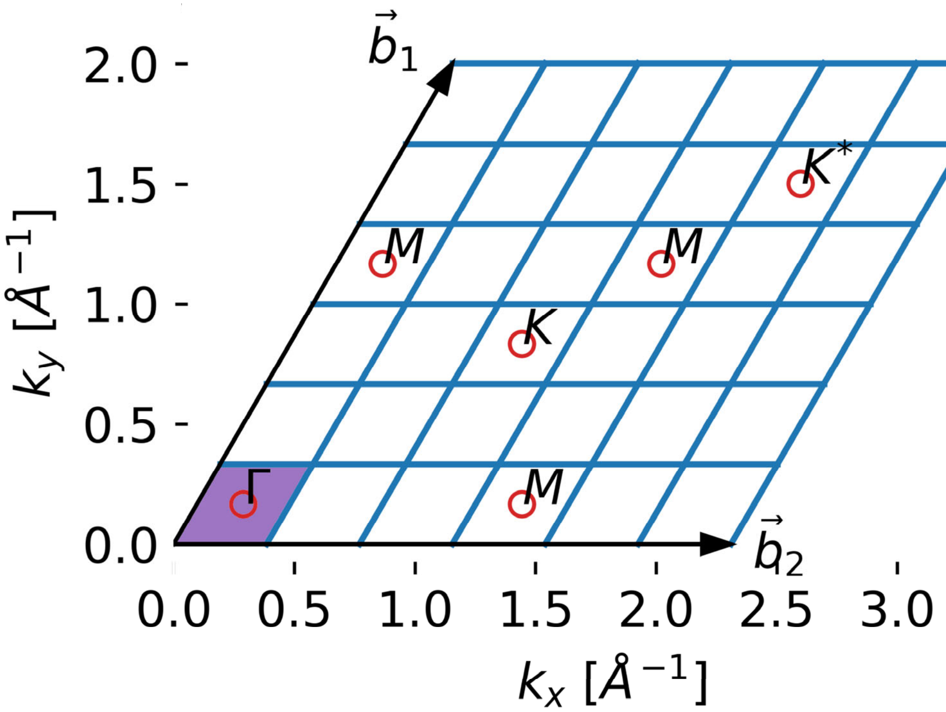
$$|\Psi_S\rangle = \sum_{vc\boldsymbol{k}} A^S_{vc\boldsymbol{k}} \hat{c}^{\dagger}_{c\boldsymbol{k}} \hat{c}_{v\boldsymbol{k}} |\mathrm{GS}\rangle$$

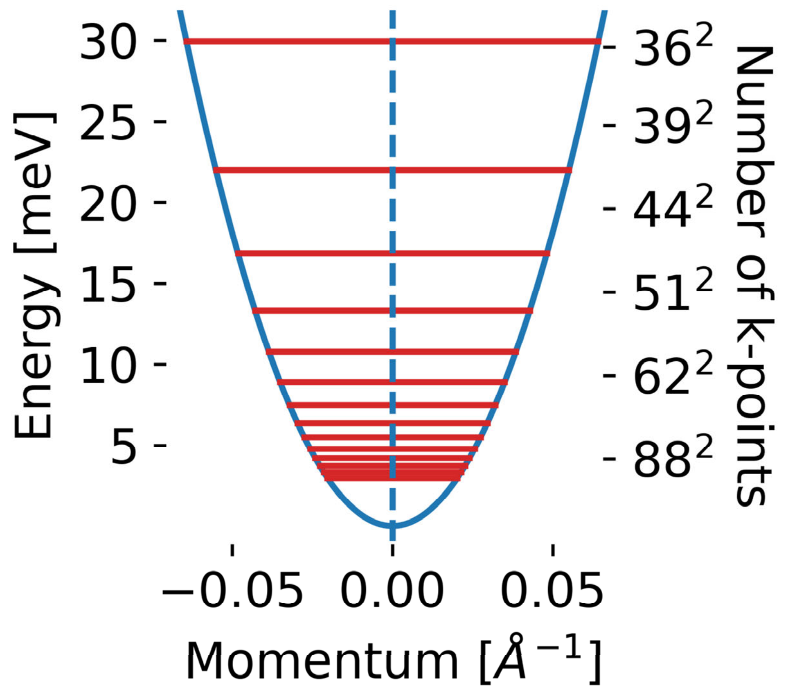
exciton two-particle wavefunction

$$\alpha(\omega) = \frac{e^2\pi}{\varepsilon_0 c\omega}\frac{1}{A}\sum_S \left|\sum_{vc\boldsymbol{k}} A^S_{vc\boldsymbol{k}} d_{vc}(\boldsymbol{k})\right|^2 \delta(\hbar\omega - \Omega_S)$$

absorption spectra

trions calculations



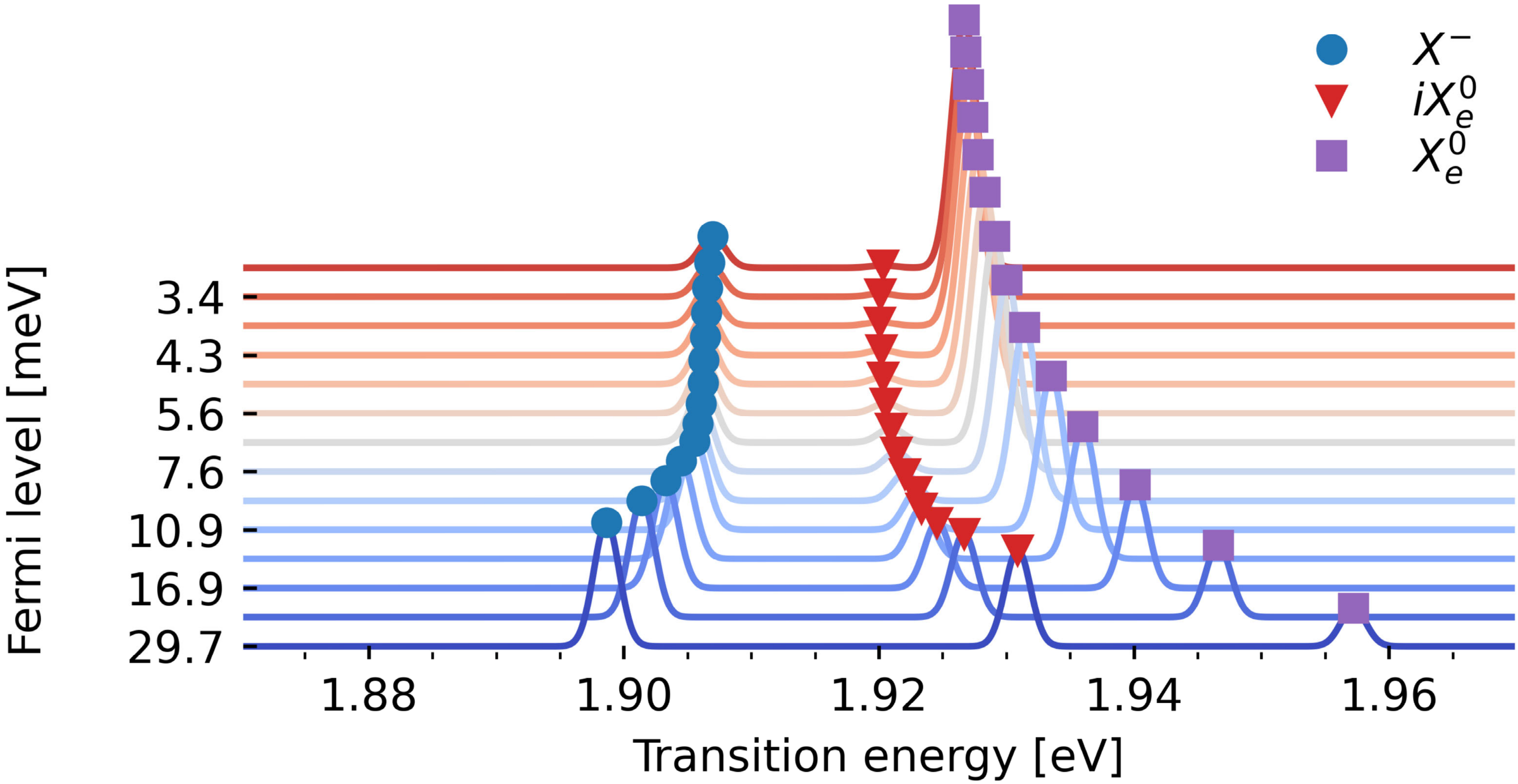


Trion Hamiltonian:

$$\left\langle vc_1c_2 | H^{Trion} | v'c_1'c_2' \right\rangle = \langle vc_1c_2|H_{kin}|vc_1c_2\rangle + \langle vc_1c_2|H_{c1c2}|vc_1'c_2'\rangle + \langle vc_1c_2|H_{c1v}|v'c_1'c_2\rangle + \langle vc_1c_2|H_{c2v}|v'c_1c_2'\rangle$$

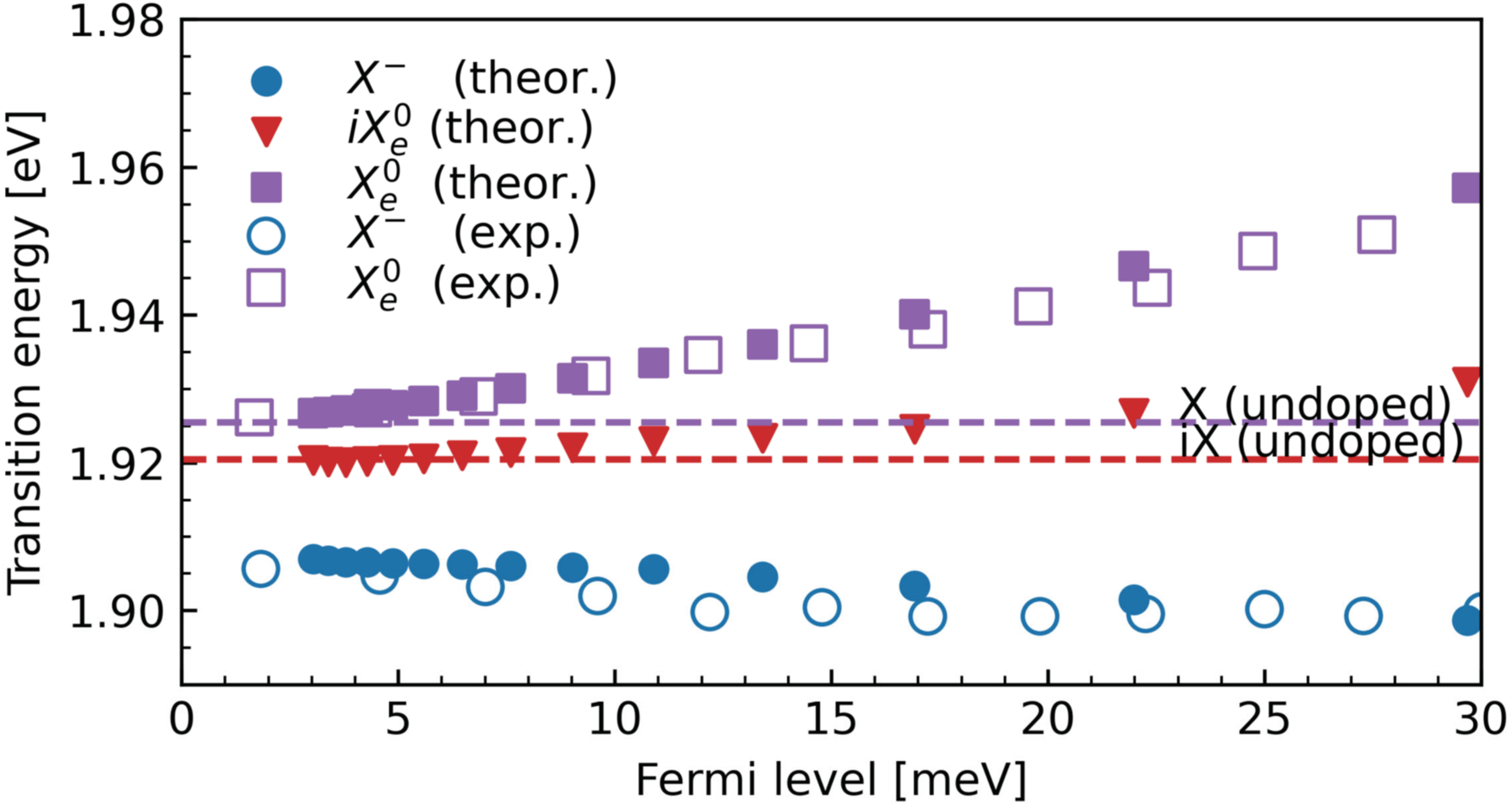
$$\langle T,\mathbf{K}|\mathbf{p}|c,\mathbf{K}\rangle = \sum_{vc_1c_2} A^{(T,\mathbf{K})}_{vc_1c_2}(\mathbf{p}_{vc_1}\delta_{c\mathbf{K},c_2} - \mathbf{p}_{vc_2}\delta_{c\mathbf{K},c_1})$$

doping dependence of linear absorption spectra in MoS_2



Zhumagulov, et. al. *Phys. Rev. B* **101**, 245433 (2020)

Doping dependence of trions and excitons

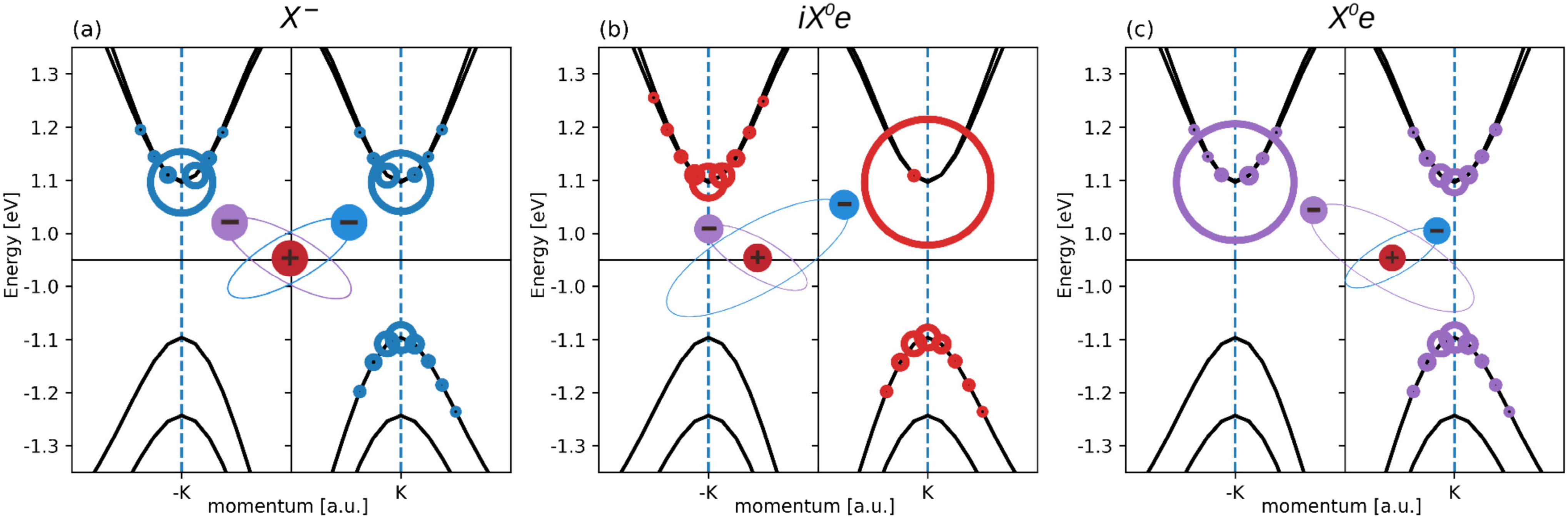


Exp: K.F. Mak, et. al. *Nat. Materials* **12**, 207 (2012)
Theory: Zhumagulov, et. al. *Phys. Rev. B* **101**, 245433 (2020)

Three-particle wavefunctions

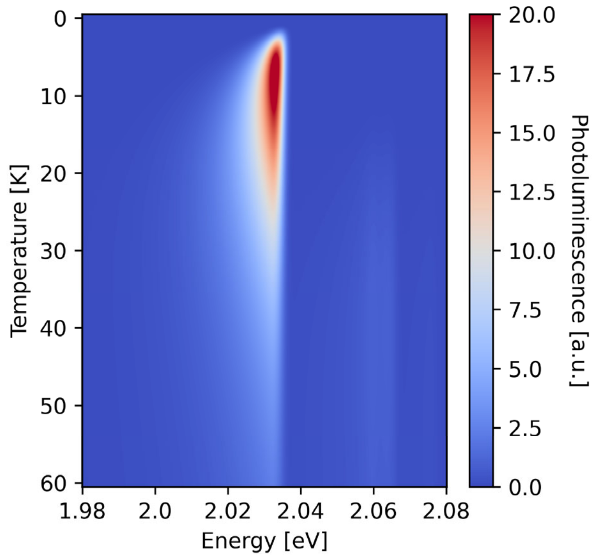
Structure of trion states: single-particle density of states

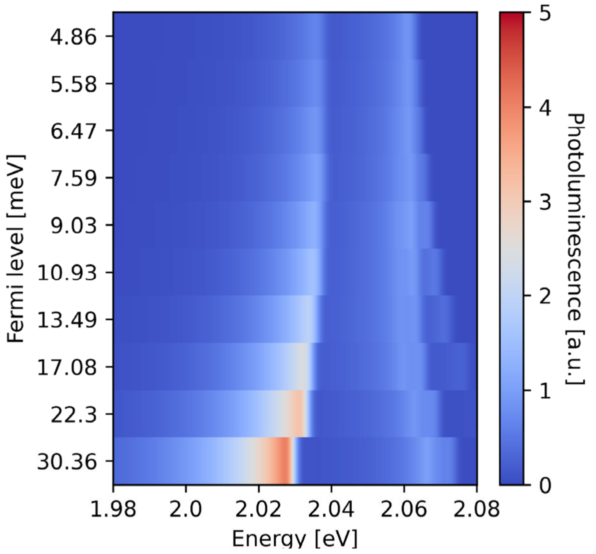
circle positions - contributing state, circle radius - weight

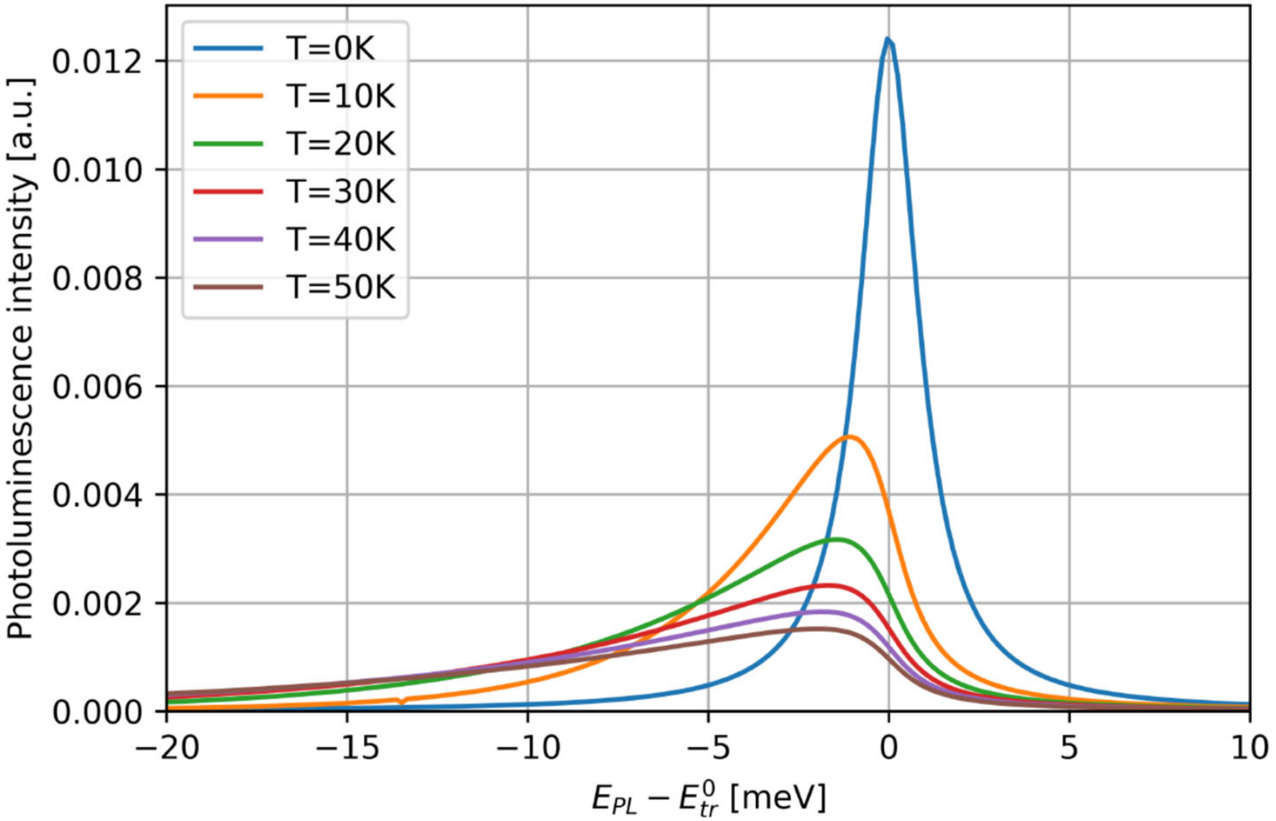


Zhumagulov, et. al. *Phys. Rev. B* **101**, 245433 (2020)

Temperature dependence of PL spectrum





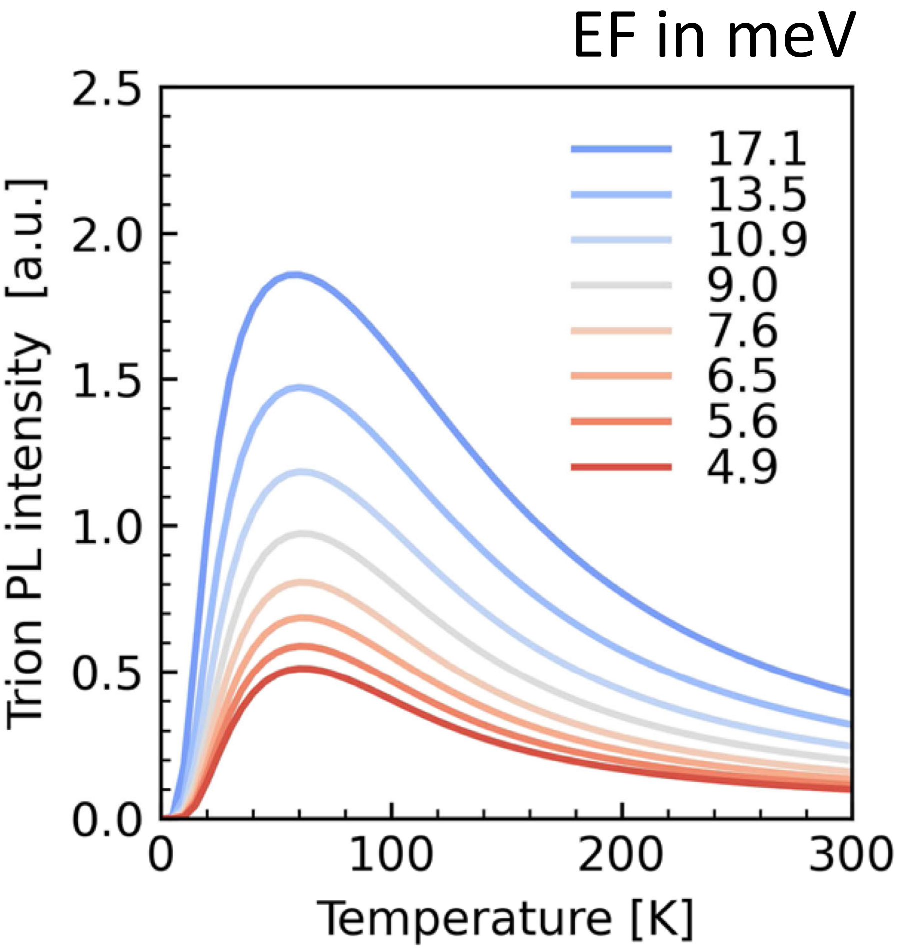


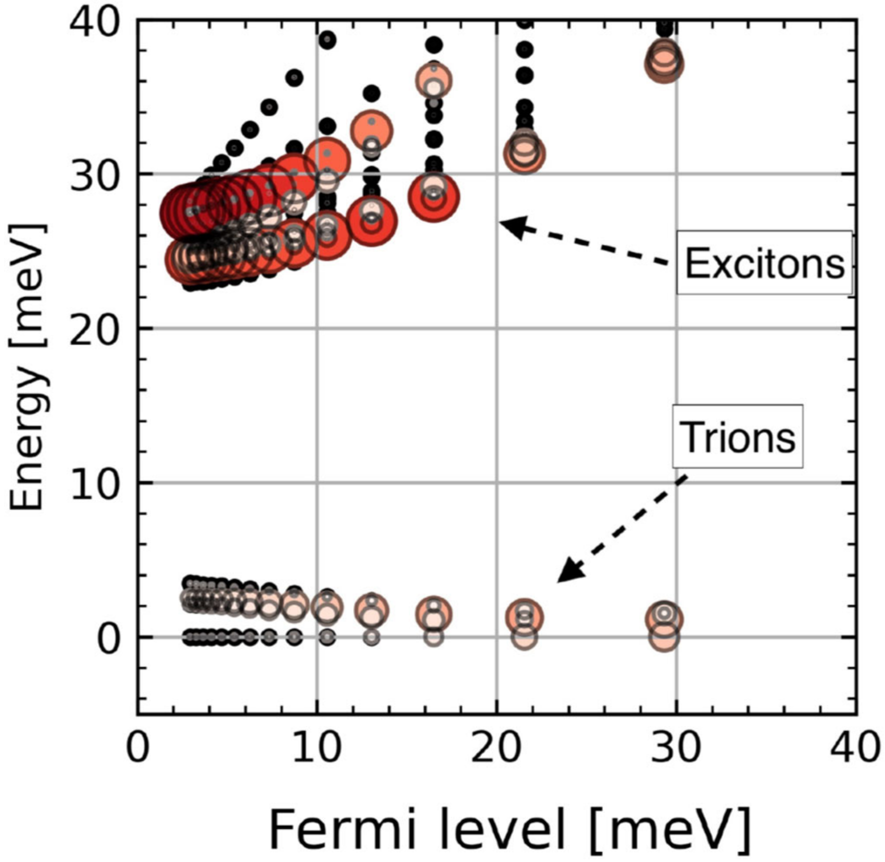
$$\Omega\left(|T,\mathbf{K}\rangle \to |c,\mathbf{K}\rangle\right) = E^{(T,\mathbf{K})} - \varepsilon_{(c,\mathbf{K})}$$

$$L(E) \sim \sum_{(c\mathbf{K},T\mathbf{K})} |\langle T,\mathbf{K}|\mathbf{p}|c,\mathbf{K}\rangle|^2 \times \delta(E - \Omega\left(|T,\mathbf{K}\rangle \to |c,\mathbf{K}\rangle\right)) \;\; w(q)$$

$$w(q) = \frac{1}{Z} e^{-\frac{E_T(q)}{kT}} \qquad Z = \int_{BZ} e^{-\frac{E_T(q)}{kT}}$$

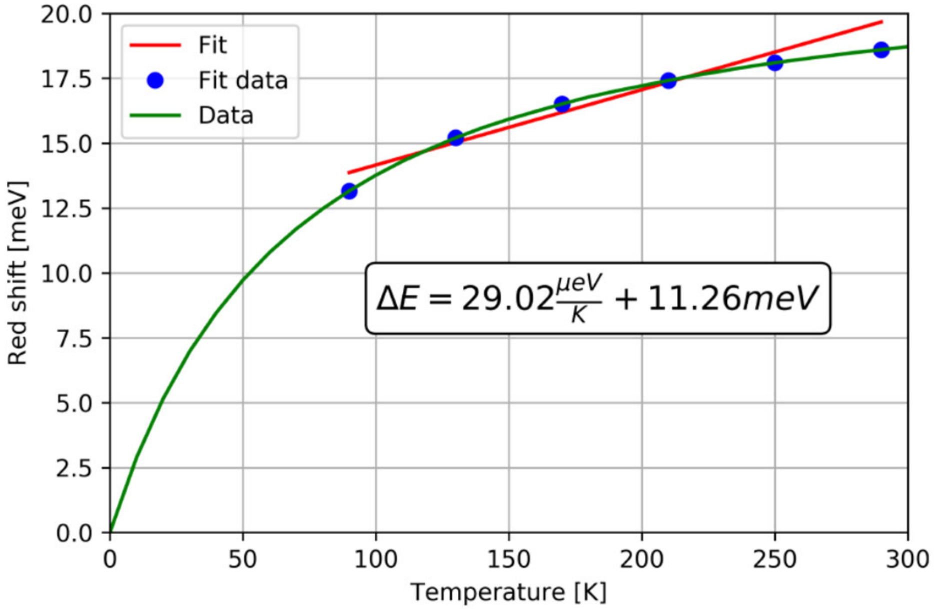
Temperature dependence of PL spectrum

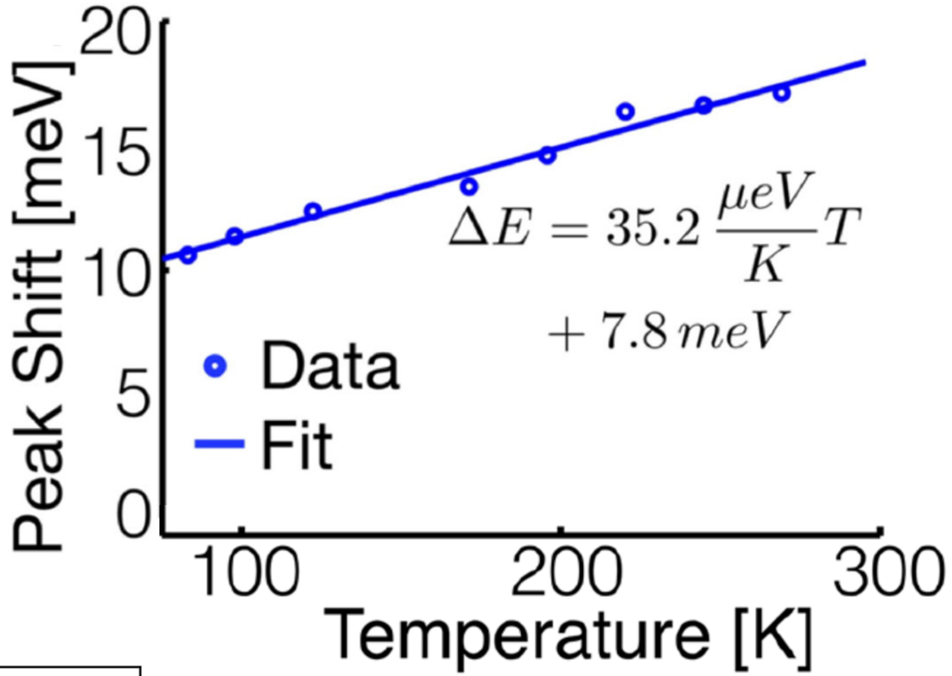


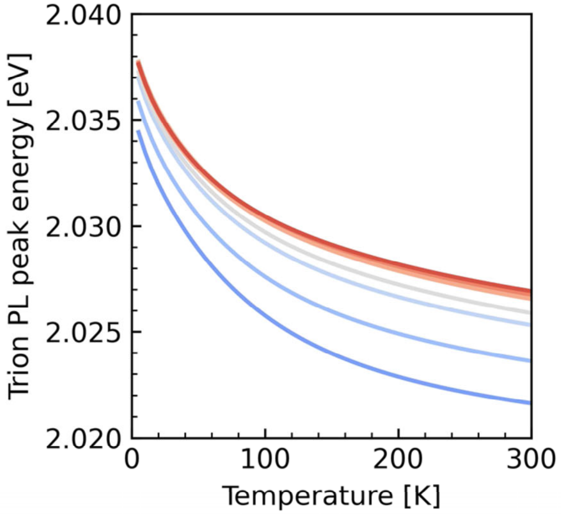


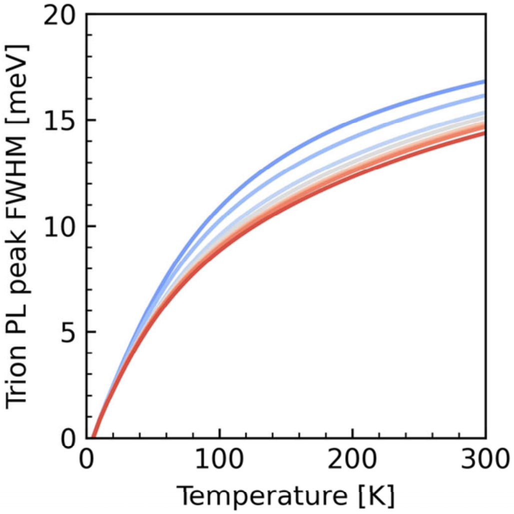
Zhumagulov, et. al. *J. Chem. Phys. Rev.* **153**, 044132 (2020)
Zhumagulov, et. al. Nanomaterials **12**, 3728 (2022)

comparison with the experiment









Exp: J. Christopher, et al. *Sci. Reports* (2017)

Theory: Zhumagulov, et. al. *J. Chem. Phys.* **153**, 044132 (2020)

Outline

1) Linear spectroscopy due to excitons and trions
2) Phonon-Assisted Indirect Exciton Ionization in 2D materials
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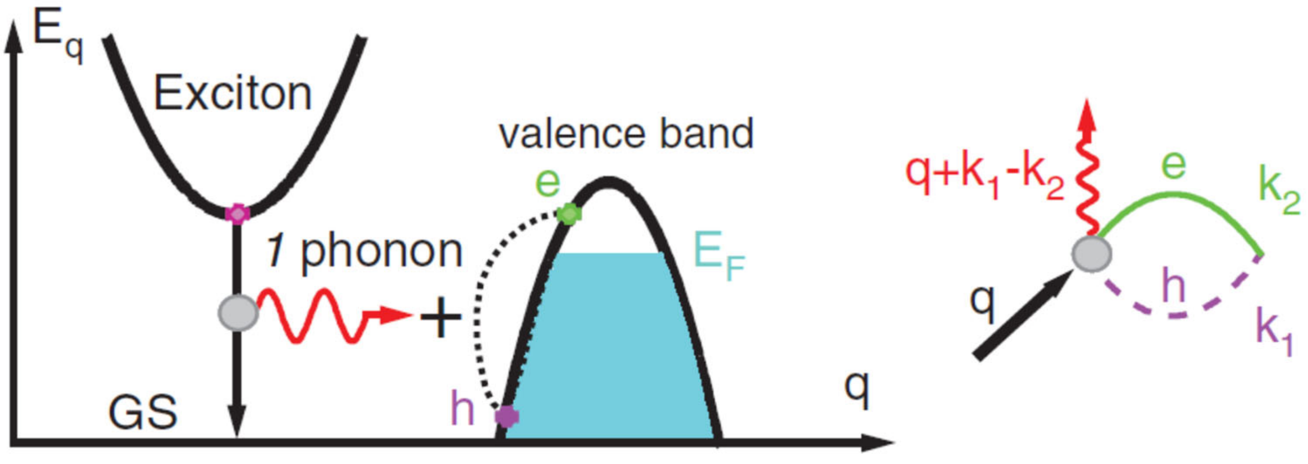
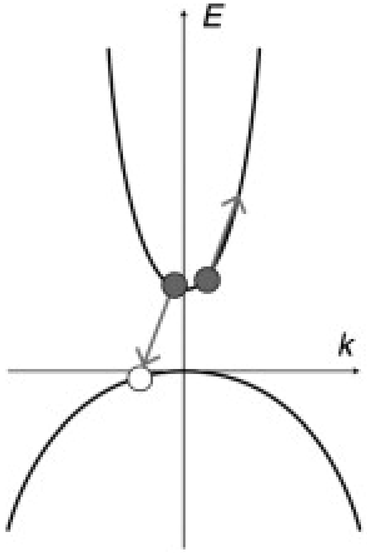
Phonon-Assisted Exciton Ionization



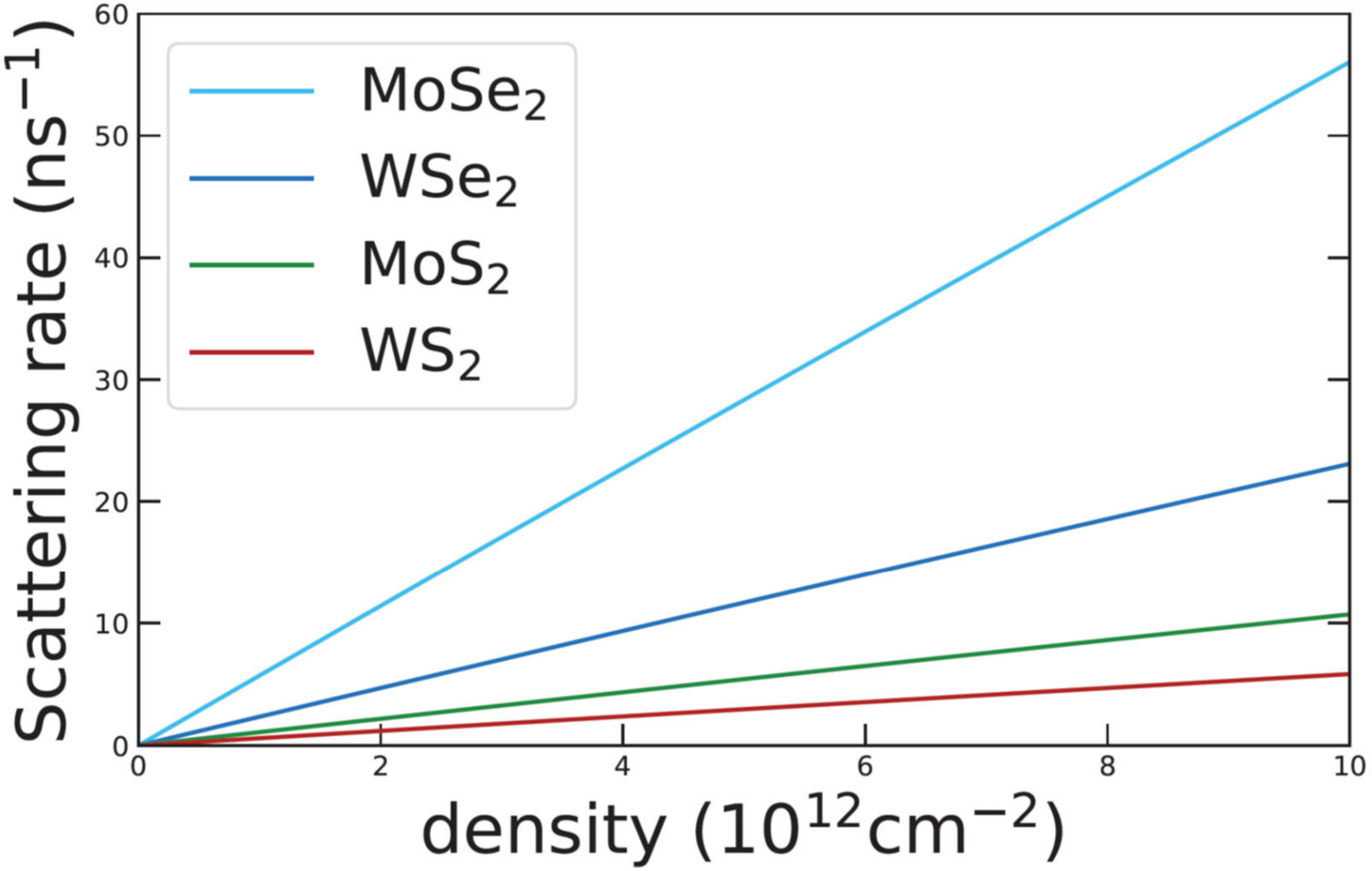
Auger decay



$$\frac{\hbar}{\tau} = \frac{2\pi g^2}{N^3} \sum_{c',\boldsymbol{k}',S,\boldsymbol{q}} f(\epsilon_{c_0\boldsymbol{k}'})\,[1-f(\epsilon_{c'\boldsymbol{k}'+\boldsymbol{q}})] \times \frac{\left|\sum_{cv\boldsymbol{k}} \mathcal{A}^{S\boldsymbol{q}}_{vc\boldsymbol{k}} U^{c',c_0,c,v}_{\boldsymbol{k}'+\boldsymbol{q},\boldsymbol{k}',\boldsymbol{k}+\boldsymbol{q},\boldsymbol{k}}\right|^2}{[\Omega_S(\boldsymbol{q})-\Omega_S(\boldsymbol{0})+\hbar\omega_{-\boldsymbol{q}}]^2} \times\delta\,[\epsilon_{c'\boldsymbol{k}'+\boldsymbol{q}} - \epsilon_{c_0\boldsymbol{k}'} + \hbar\omega_{-\boldsymbol{q}} - \Omega_S(\boldsymbol{0})]$$

Perebeinos, Avouris, Phys. Rev. Lett. 101, 057401 (2008)

Phonon-Assisted Exciton Ionization in 2D materials

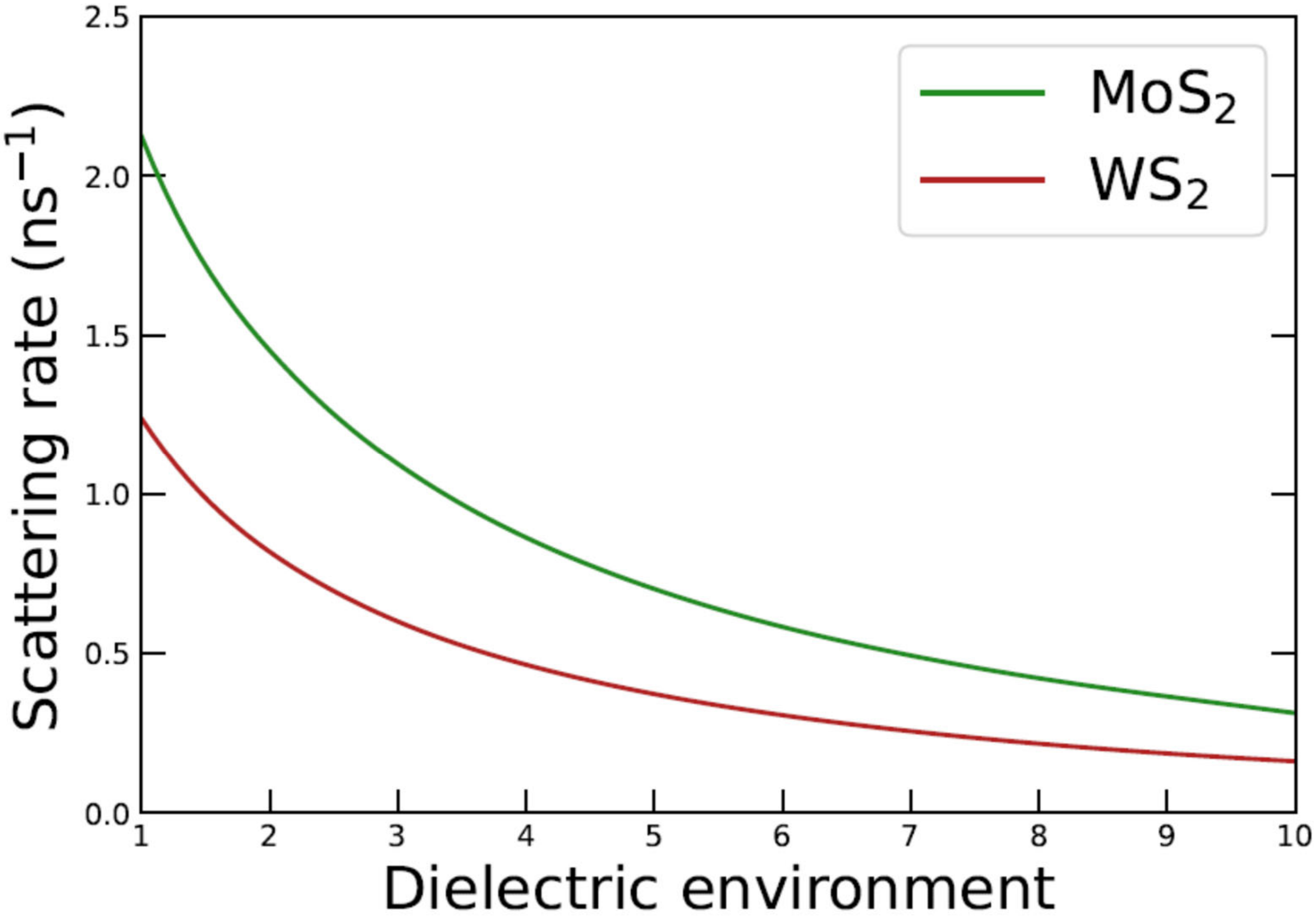


Exciton energies:

$MoSe_2$	1.58 eV
WSe_2	1.68 eV
MoS_2	1.90 eV
WS_2	2.03 eV

We use $\varepsilon = 3.0$ corresponding to the experimentally observable exciton binding energy of ~300 meV

Phonon-Assisted Exciton Ionization in 2D materials



In the single-particle limit, i.e. $\varepsilon = \infty$, phonon-assisted.

At fixed carrier density 10^{12} cm^{-2}

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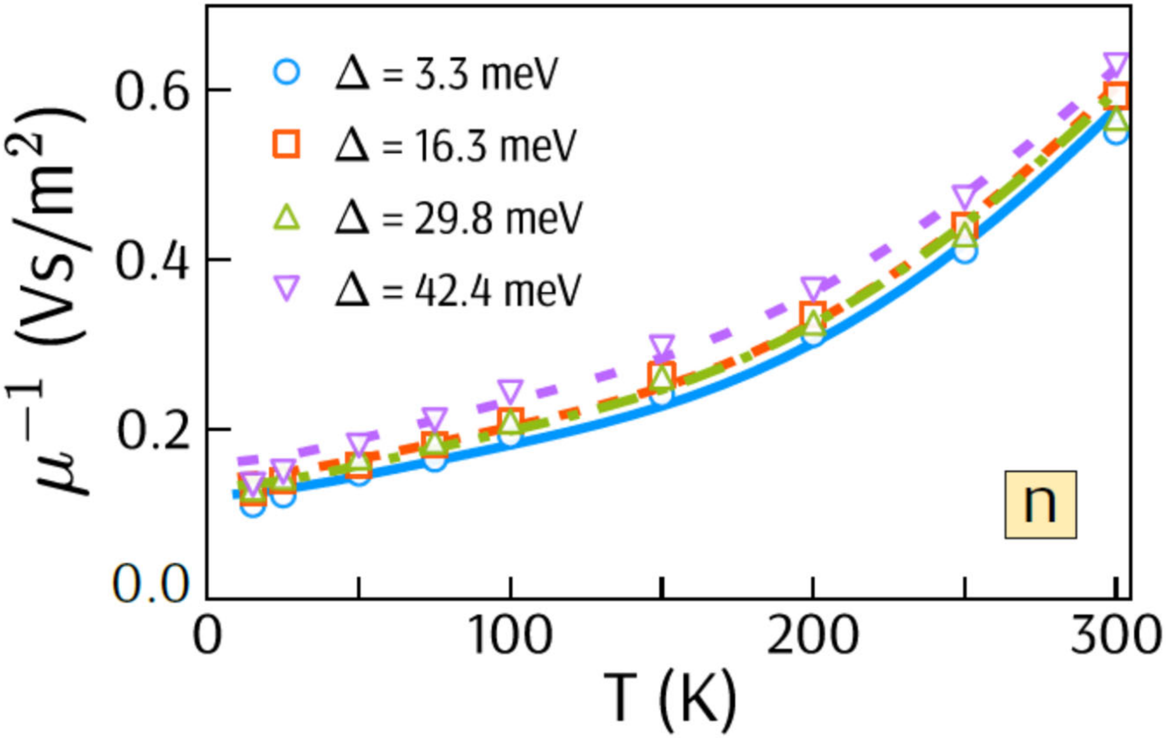
motivation

High quality monolayer graphene have higher room temperature mobility than AB-stacked bilayer graphene and exhibit stronger temperature dependence.



20,000 cm^2/Vs

Phonon scattering

100,000 cm^2/Vs

Coulomb impurity scattering

which phonon is responsible for in-plane transport?

$$eF\frac{\partial f_k}{\partial \hbar k} = -\sum_{k'} S_{kk'} f_k(1-f_{k'}) - S_{k'k} f_{k'}(1-f_k)$$

Boltzmann transport equation

Electron-phonon scattering

$$S^{\mu}_{kk'} = \left|\left\langle \psi_k \middle| H^{\mu}_{e-ph} \middle| \psi_{k'} \right\rangle\right|^2 \left[n_{k-k',\mu}\delta\left(E_{k'}-E_k+\hbar\omega_{k-k',\mu}\right) + \left(1+n_{k'-k,\mu}\right)\delta\left(E_{k'}-E_k-\hbar\omega_{k'-k,\mu}\right)\right]$$

$$t_{ij} = t_0 - g\delta r_{ij}, \qquad t_0 = 3.1\, eV, \qquad g = 5.3\, eV/Ang$$

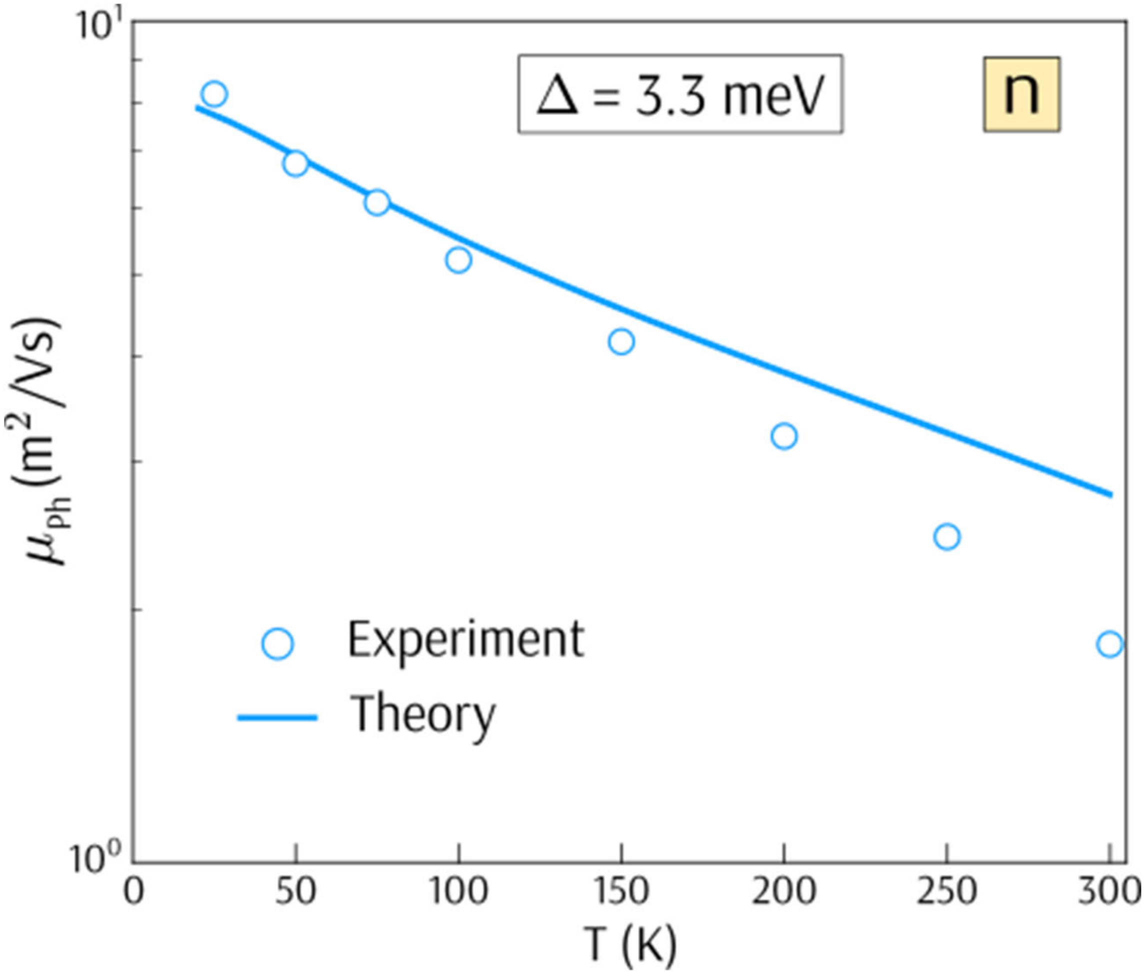
$$t_{ij} = t_\perp exp\left\{\left(-\frac{r_{ij}-h_0}{\lambda_z}\right)\right\} exp\left\{\left(-\left(\frac{\xi_{ij}}{\lambda_{xy}}\right)^{\alpha}\right)\right\}$$

Model parameters

Electron-phonon coupling: **Perebeinos et. al. PRL 109, 236604 (2012)**

Phonons: **Perebeinos and Tersoff, PRB 79, 241409(R) (2009)**

Intrinsic only phonon limited transport



Perfect match at low temperatures

Deviations at T> 150 K

Tan, Adinehloo, Hone, Perebeinos, PRL 128, 206602 (2022)

Surface Polar Phonon scattering in h-BN

Robust solution: Maxwell's equation for electric field

$$\varphi\left(\vec{\xi},z\right)=\sum_{\vec{q}}\varphi(z)e^{i\vec{q}.\vec{\xi}}\quad \omega_{SPP}=\omega_{TO}\sqrt{\frac{\varepsilon_0+\gamma(q)}{\varepsilon_\infty+\gamma(q)}}$$

$$\varphi(z)=\begin{cases}\varphi_0\cosh(q_z z) & |z|<h_s\\ Ae^{q(z-d)}+Be^{-q(z-h_s)} & h_s\le z<d\\ Ce^{-q(z-d)} & d\le z\end{cases}$$

$$\frac{1}{L^2}\frac{\hbar}{2\omega}=\int\frac{1}{4\pi}\frac{1}{2\omega}\left(\frac{\partial\epsilon}{\partial\omega}|\mathbf{E}_\perp|^2+\frac{\partial\epsilon}{\partial\omega}|\mathbf{E}_\parallel|^2\right)dr$$

$$|M_{\mathbf{kq}}|^2=(e\varphi_0)^2|\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k+q}}\rangle|^2$$

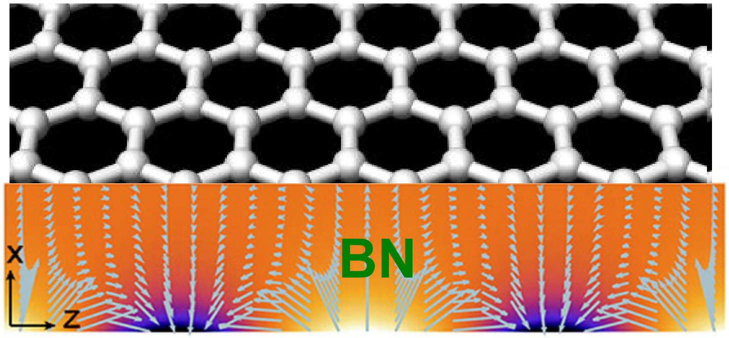
$$(e\varphi_0)^2=\frac{\pi e^2}{qA_CN_k}\hbar\omega\left(\frac{1}{\varepsilon_\infty+\gamma(q)}-\frac{1}{\varepsilon_0+\gamma(q)}\right)f^2$$

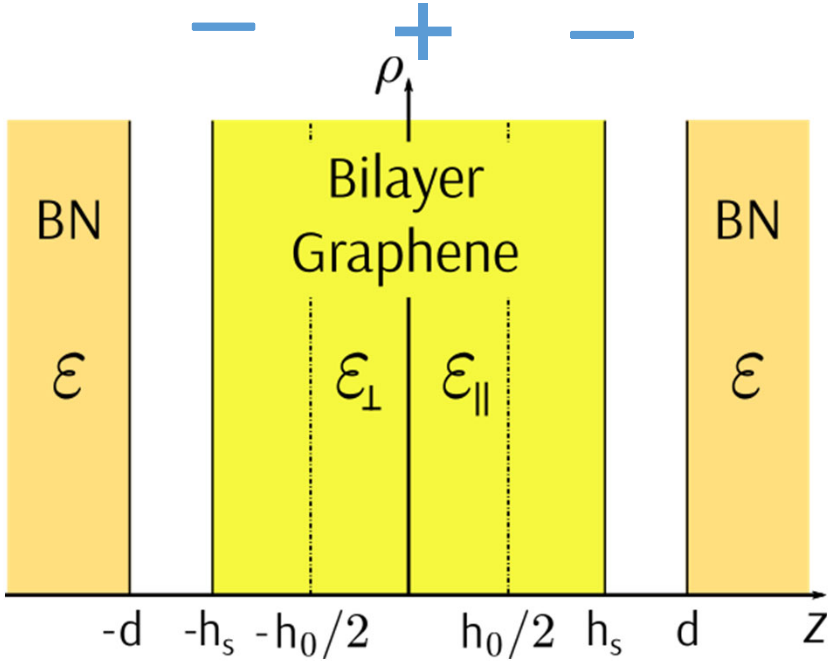
$$f^{-1}=\cosh\left(q_zh_s\right)\cosh\left(q(d-h_s)\right)\gamma_2(q),$$

See also:
Hess
Fischetti
Konar, Frantini
V. Perebeinos et. al. Phys. Rev. B **81**, 195442 (2010)

Intuitive arguments

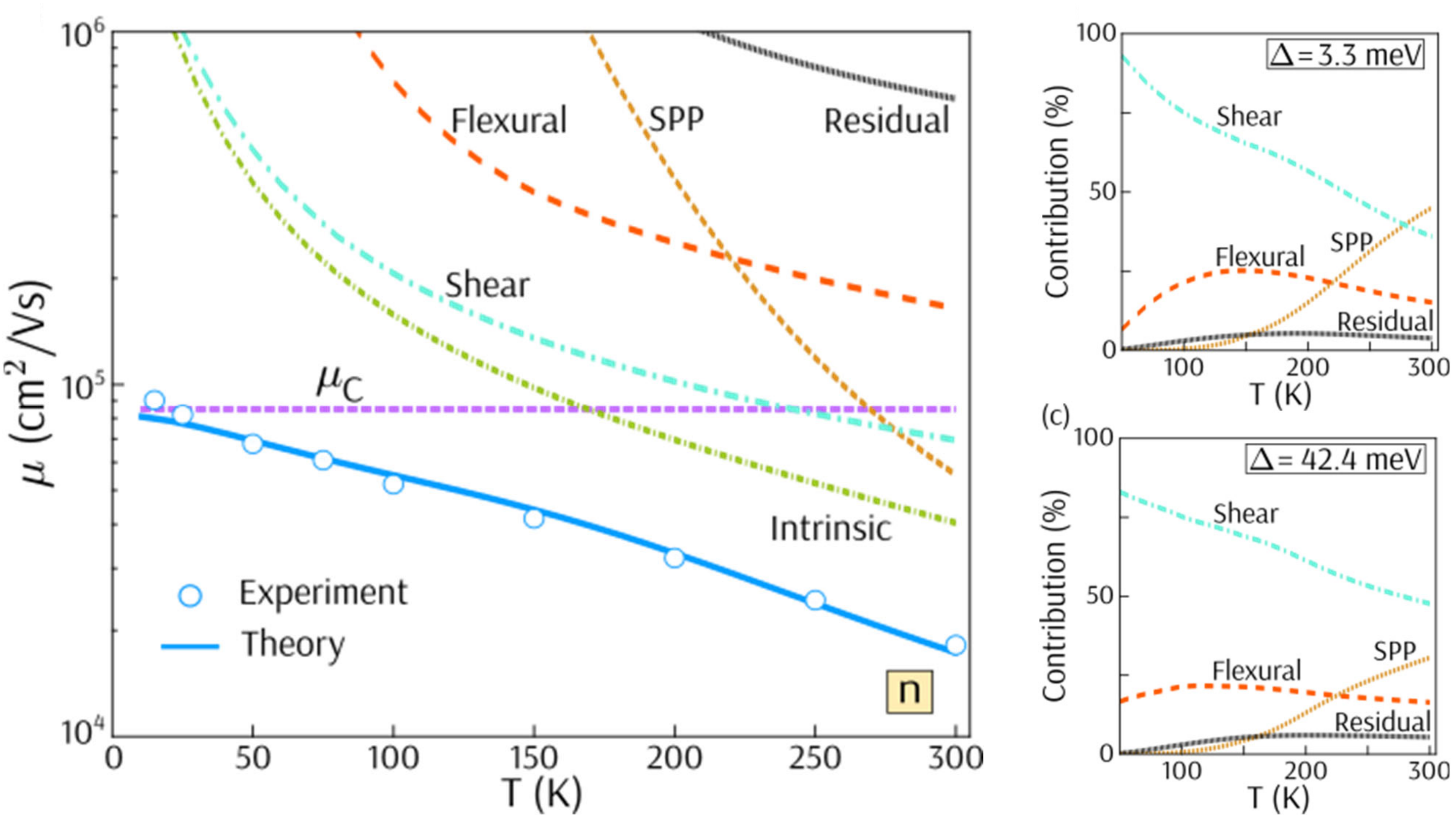
$$P(\vec{r}\,')\propto\frac{1}{\varepsilon_\infty+1}-\frac{1}{\varepsilon_0+1}\qquad V_{SPP}\left(q\right)\propto\frac{e^{-qz_0}}{\sqrt{q}}P$$





phonon-limited mobility in bilayer graphene

relative contributions of different modes



Tan, Adinehloo, Hone, Perebeinos, PRL 128, 206602 (2022)

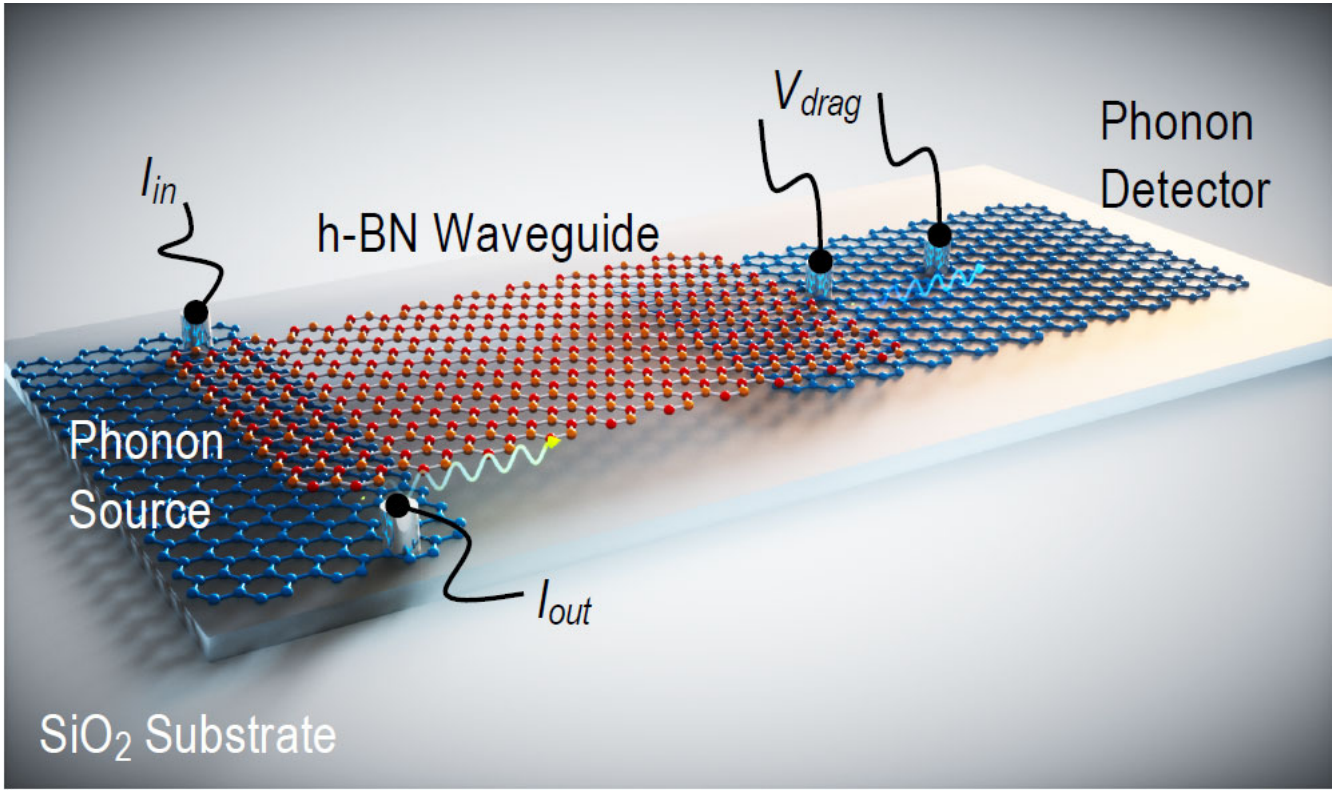
remote phonon sensing

make one phonon out of equilibrium: $n(q_0) = n_{eq}(q_0) + 1$

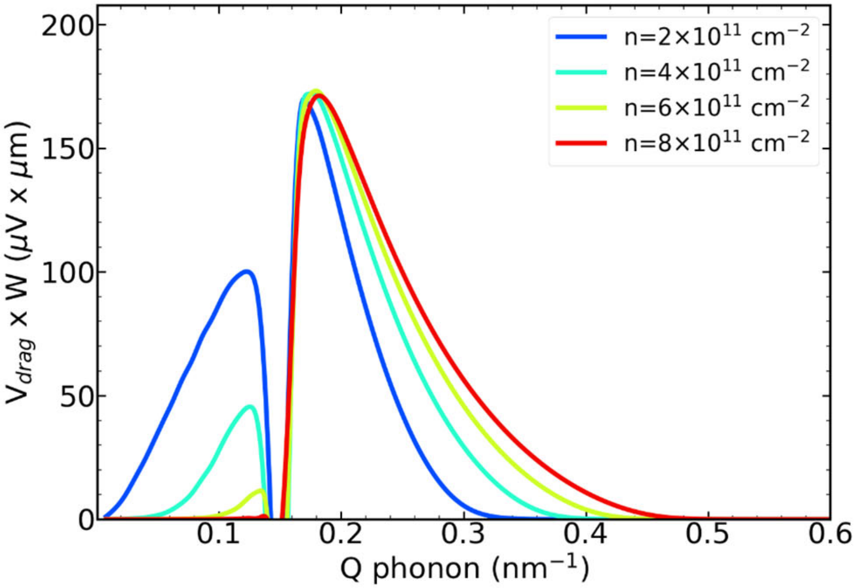
$$\vec{v}_\alpha(k)\frac{\partial f_\alpha(k,r)}{\partial \vec{r}} + e\vec{F}\frac{\partial f_\alpha(k,r)}{\partial \hbar\vec{k}} = \left(\frac{\partial f_\alpha(k)}{\partial t}\right)_{e-ph} + \left(\frac{\partial f_\alpha(k)}{\partial t}\right)_{imp}$$

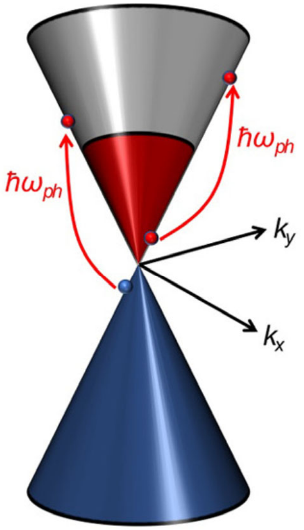
$$\vec{v}_\lambda(q)\frac{\partial n_\lambda(q,r)}{\partial \vec{r}} = \left(\frac{\partial n_\alpha(q)}{\partial t}\right)_{e-ph} + \left(\frac{\partial n_\alpha(q)}{\partial t}\right)_{ph-ph\&ph-imp}$$

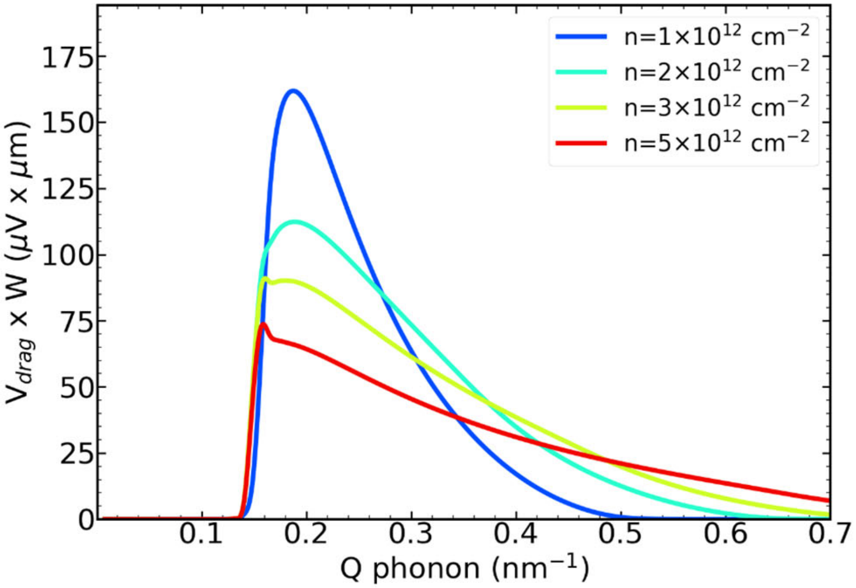
$$V_{drag} = \frac{e\sum_\alpha \int f_\alpha(k)v_\alpha(k)d\vec{k}}{\sigma W}$$

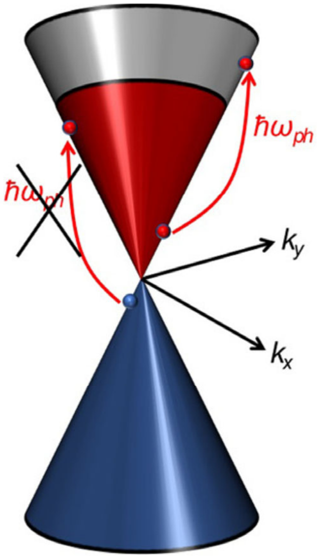


drag voltage in monolayer graphene on semi-infinite BN







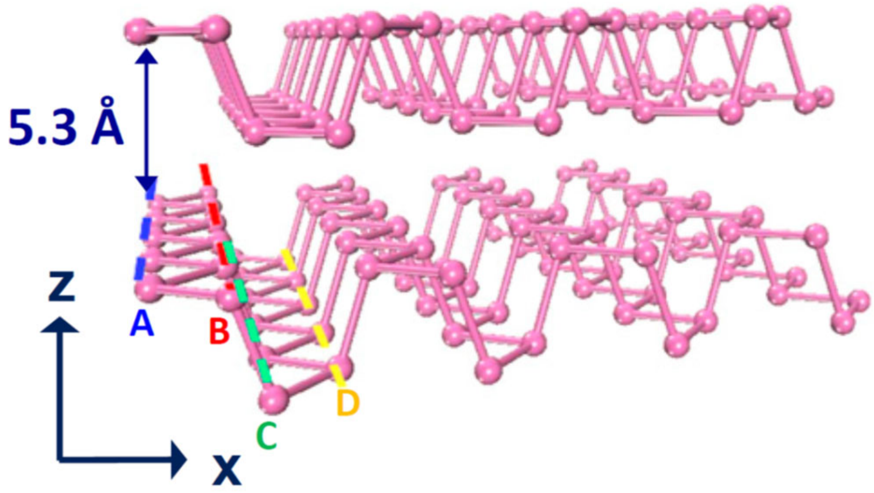


Kefayati, Bird, Perebeinos
PRB **106**, 155415 (2022)

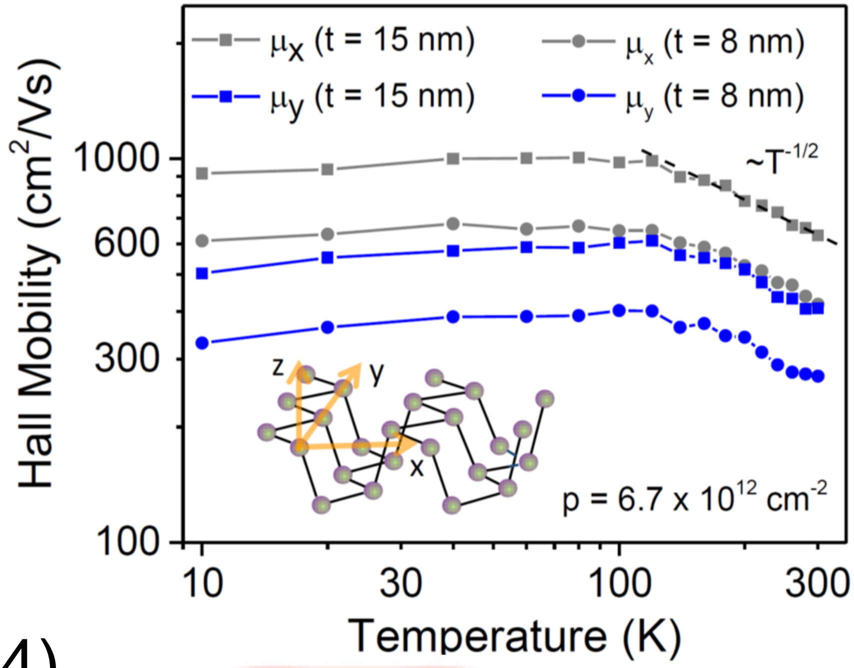
Outline

1) Linear spectroscopy due to excitons and trions
2) Phonon-Assisted Indirect Exciton Ionization in 2D materials
3) Electron-phonon interactions in mono and bilayer graphene
4) Electron-phonon interactions in black phosphorous and 1D SbPS4

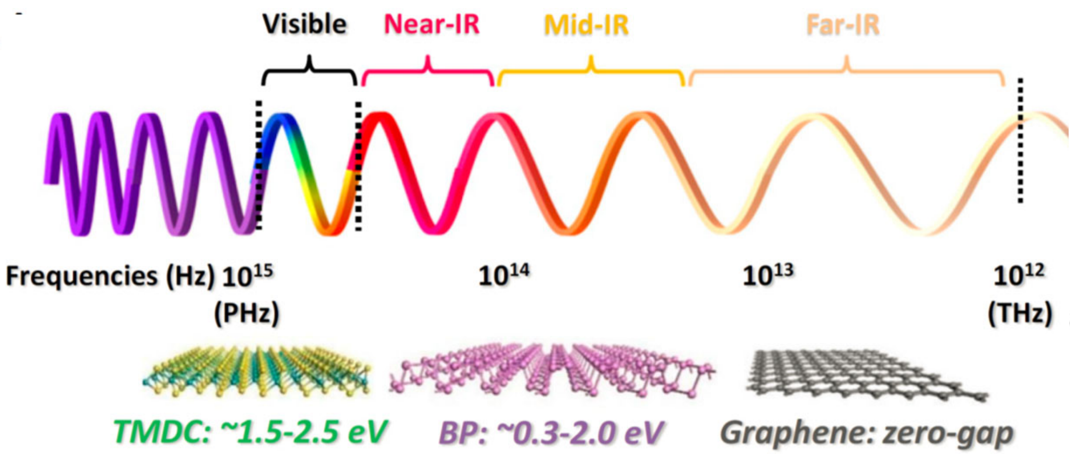
quest for other 2D materials: black phosphorous

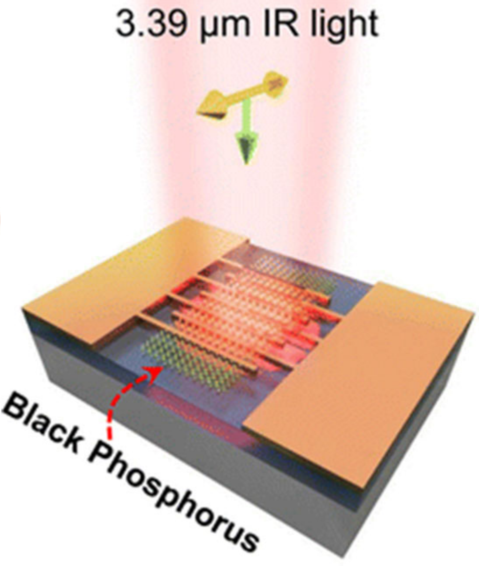


Ling et. al. PNAS (2015)



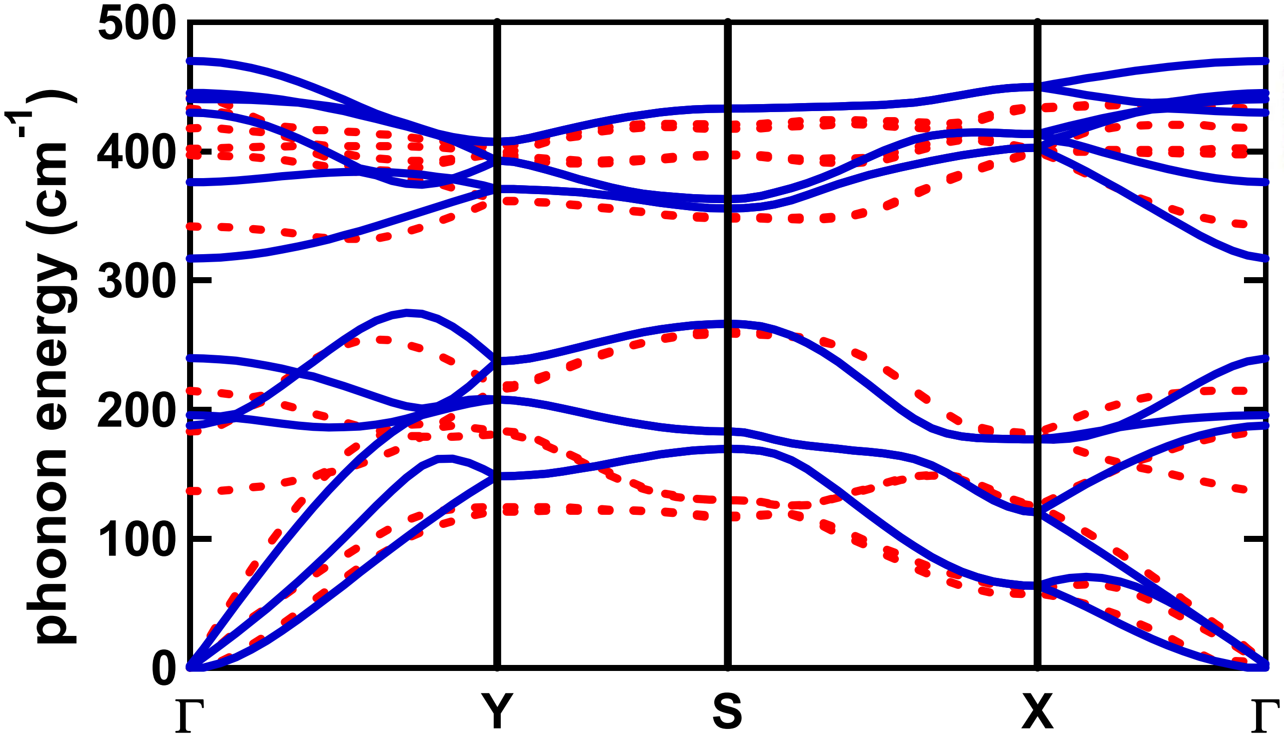
Xia et. al. Nature Com. (2014)





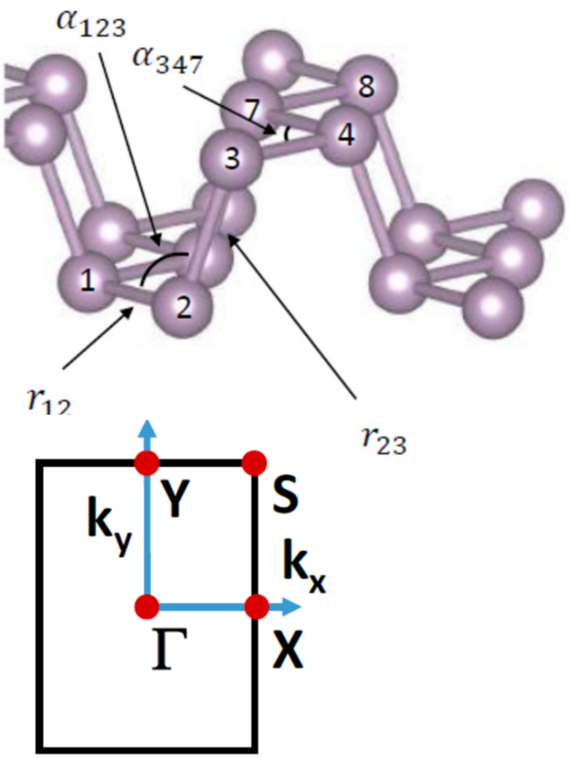
Guo et. al.
Nano Lett.
(2016)

Black Phosphorous: phonons



- - - Zhu & Tomanek PRL (2014)

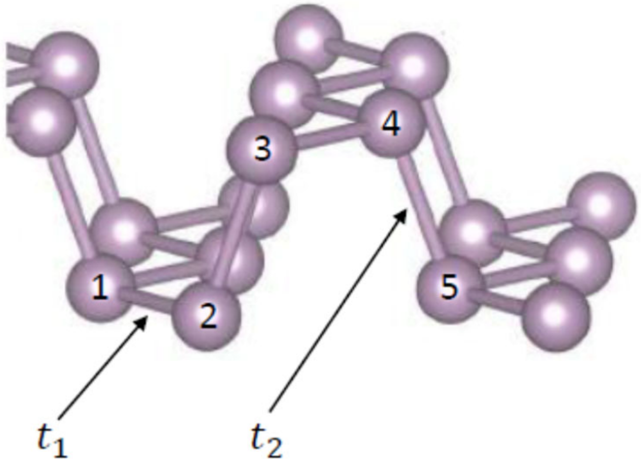
—— Keating two parameters model



$$H_{ph} = \frac{k_1}{2}(\delta r_{12}^2 + \delta r_{23}^2 + \cdots)$$

$$+\frac{k_2}{2}(\delta\alpha_{123}^2 + \delta\alpha_{347}^2 + \cdots)$$

Black Phosphorous: band structure

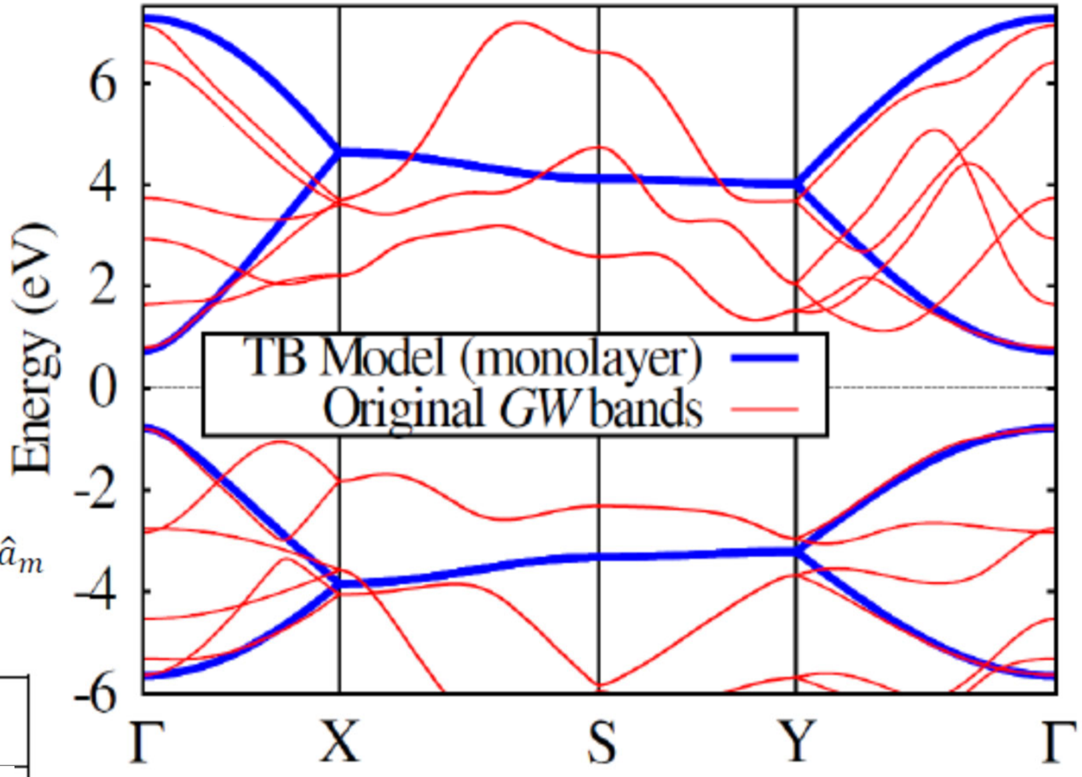


Tight binding:

$$\hat{H} = \sum_{i,k,l,m} t_1\, \hat{a}_i^+ \hat{a}_k + t_2\, \hat{a}_l^+ \hat{a}_m$$

Best fit:

t1, eV	t2, eV
-1.15	3.07



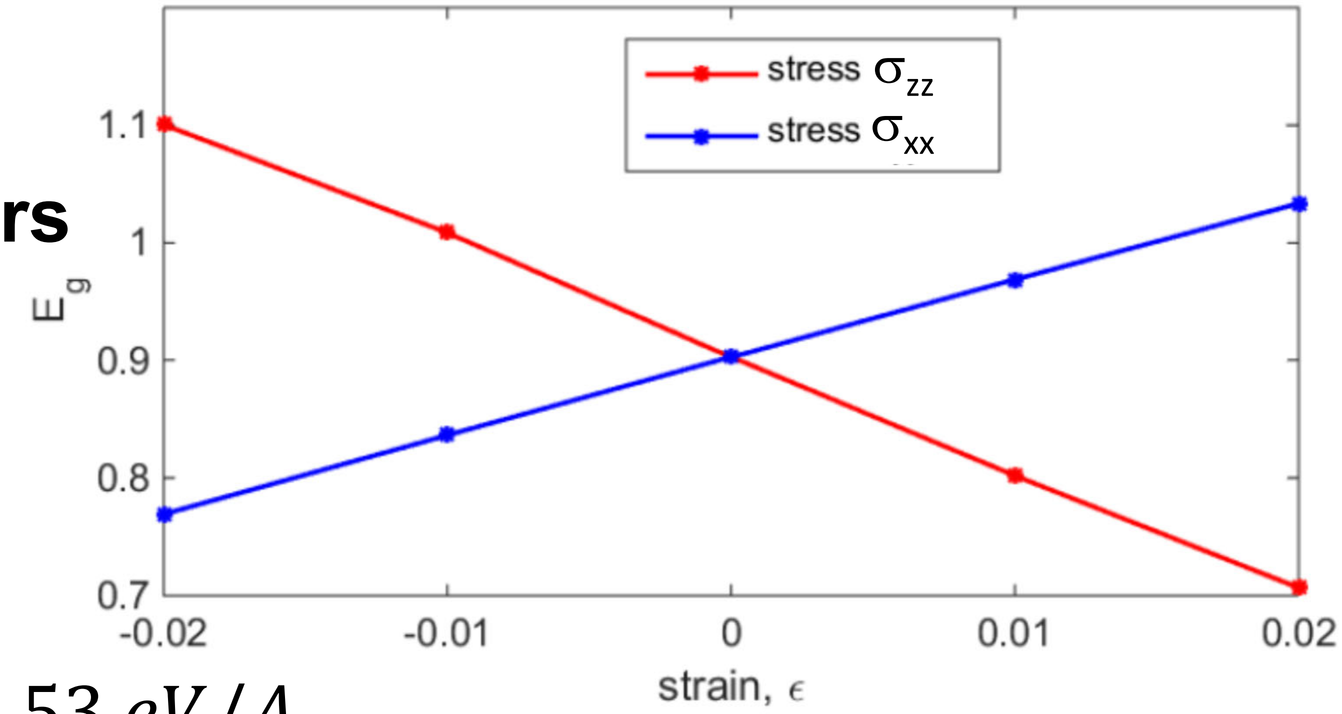
Rudenko et al, PRB (2014)

	E_g (eV)	m_{xh}	m_{yh}	m_{xe}	m_{ye}
GW Rudenko (2014)	1.60	-0.18	-1.14	0.17	0.85
our model	1.54	-0.15	-1.17	0.15	1.17

electron - phonon interaction

$$\widehat{H}_{el-ph} = \sum_{\substack{k_i,k_f,\\ q}} g_1\, M_1 \hat{a}^{+}_{k_f}\hat{a}_{k_i}(\hat{c}_q + \hat{c}^{+}_{-q})\, \hat{c}_q + g_2\, M_2 \hat{a}^{+}_{k_f}\hat{a}_{k_i}(\hat{c}_q + \hat{c}^{+}_{-q})\,) + c.c.$$

our DFT results



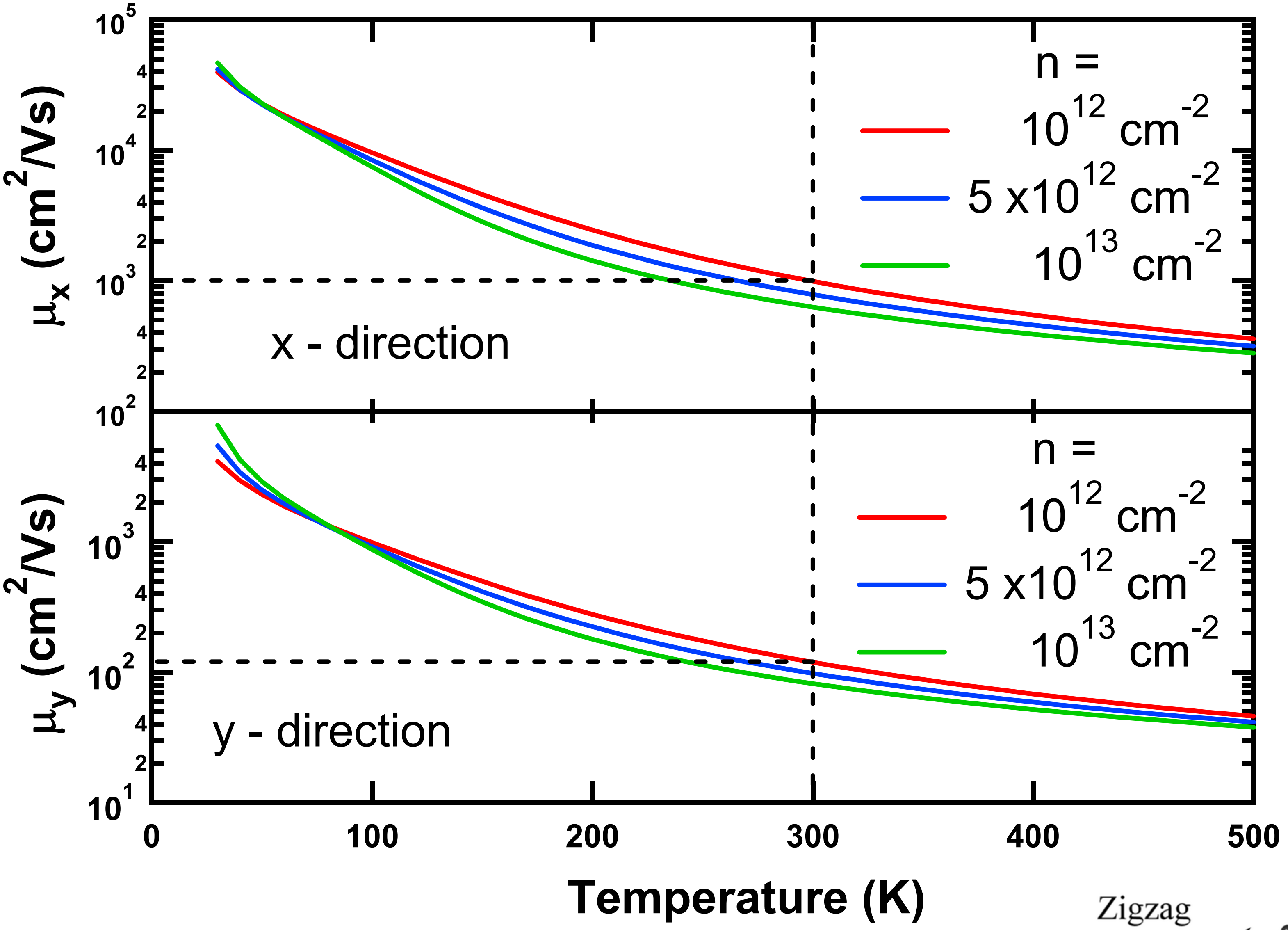
e-ph parameters

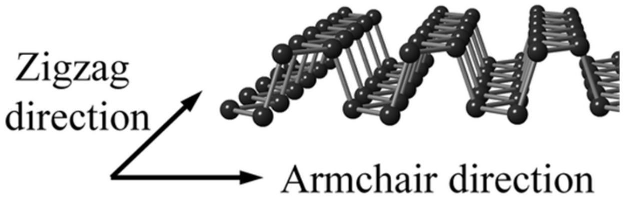
$$E_g = 2t_2 - 4|t_1|$$

$$g_1 = -\frac{\partial|t_1|}{\partial r_1} = 1.53\ eV/A$$

$$g_2 = -\frac{\partial|t_2|}{\partial r_2} = 2.46\ eV/A$$

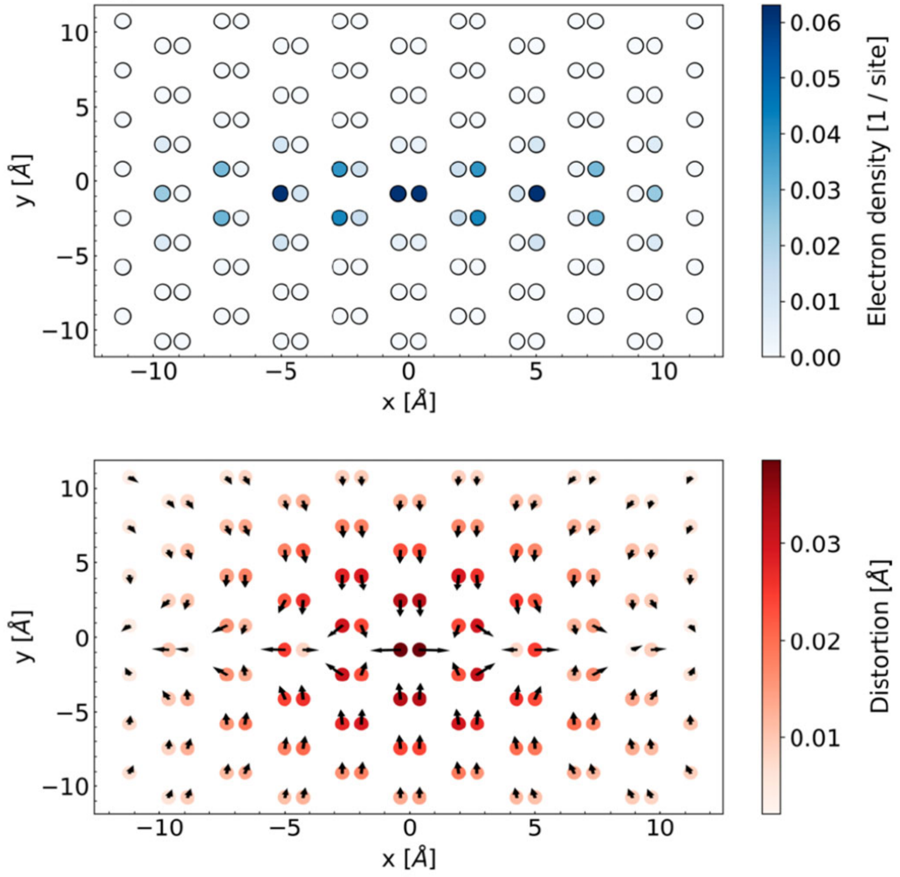
phonon limited low field mobility



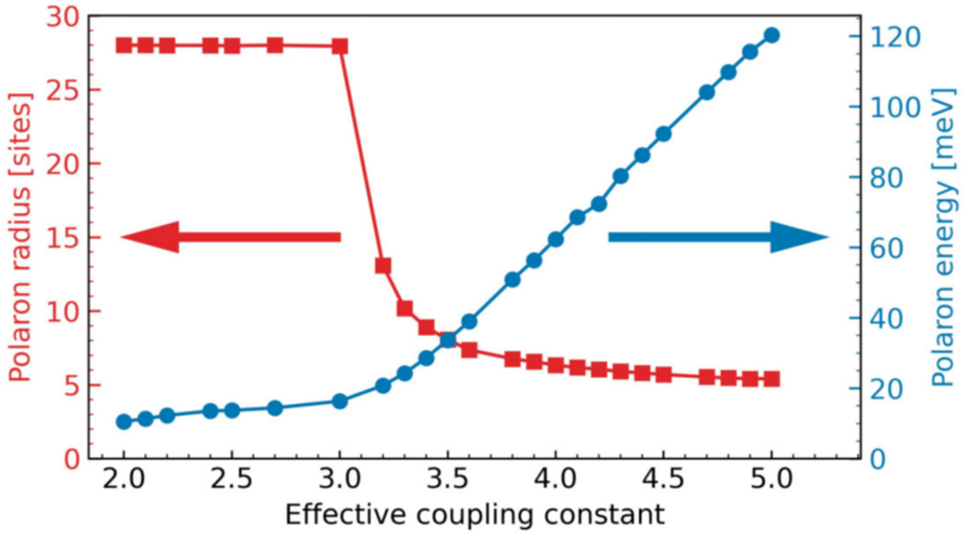


Y. Trushkov & VP, Phys. Rev B. 95, 075436 (2017)

Polarons in BP



$$\lambda_{\mathrm{eff}} = 4.5$$

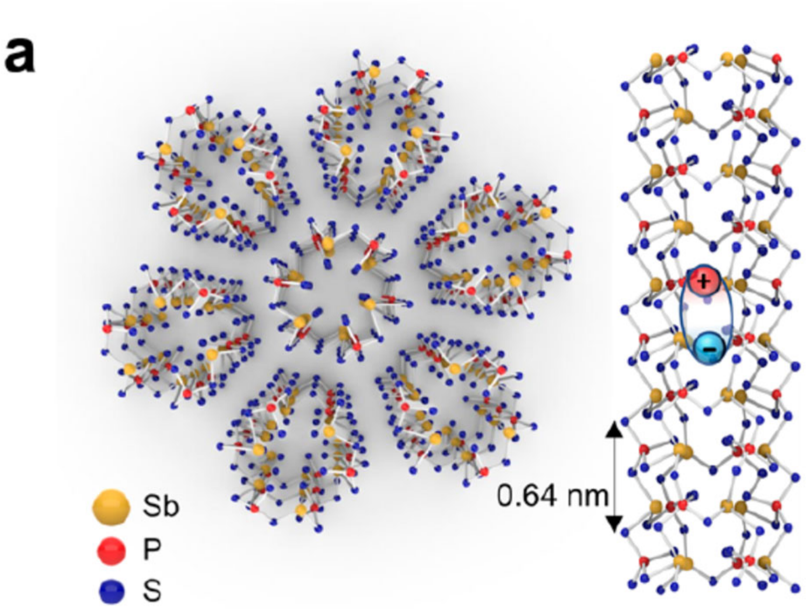


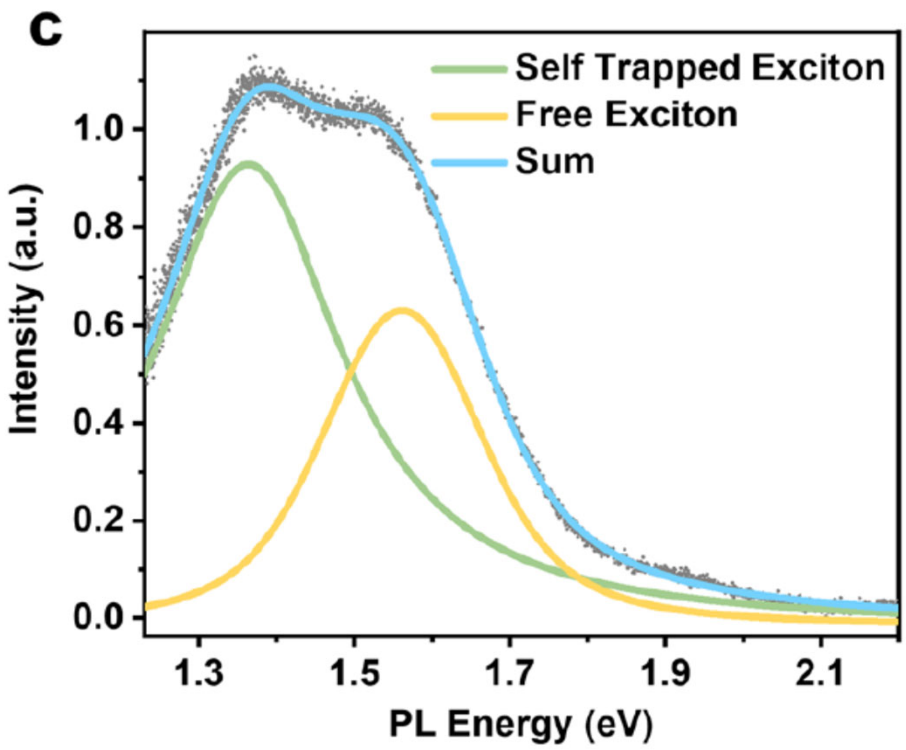
$$\lambda_{\mathrm{eff}} = \frac{1}{2k_1}\left(\frac{g_1^2}{|t_1|} + \frac{g_2^2}{|t_2|}\right) \approx 0.278$$

Neverov et. al. Phys. Rev Materials 5, 054008 (2021)
See also: Vasilchenko et. al.
J. Phys. Chem. Lett. 12, 4674 (2021)

Using parameters in Y. Trushkov & VP, Phys. Rev B. 95, 075436 (2017)

Polarons in 1D SbPS4



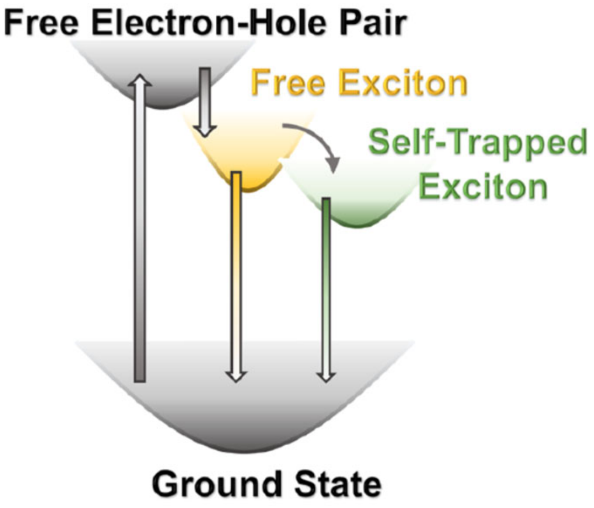


$$E_P = \sum_v \frac{C_v^2}{k_v}$$

polaron binding ~ 150 meV

$$E_b = A_b R^{\alpha-2} m^{\alpha-1} \varepsilon^{-\alpha}$$

exciton binding ~ 1 eV



Mahdikhany et. al. APL Mater. 12, 011112 (2024)

acknowledgment

AFOSR MURI

Optical response and polaritons in 2D materials:

Yaroslav Zhumagulov[2], *Dmitry Gulevich*[3], *Alexei Vagov*[3]

Polarons and e-ph interactions in BP:

Yuri Trushkov[4], *Viacheslav Neverov*[5] , *Alexander Lukyanov*[5], *Andrey Krasavin*[5]

Polarons in SbPS4:

Davoud Adinehloo[1], *Tai Kong*[6], *John Schaibley*[6], *et. al.*

Phonon-assisted Auger decay of excitons: *Benedict Scharf*[7]

Electron-phonon interactions in 2D materials: *Cheng Tan*[8], *Davoud Adinehloo*[1], *James Hone*[8], *Ali Keifayati*[1], *Jon Bird*[1]

[1]*Univeristy at Buffalo*, [2]*University of Regensburg*, [3]*ITMO, Sankt Petersburg*, [4]*Skoltech*, [5]*MEPhI*, [6]*University of Arizona*, [7]*Universität Würzburg*, [8]*Columbia University*

Summary

- 2D materials offer tunable and versatile solid-state material platform for quantum photonics and quantum phononics
- 2D materials optical response is dominated by excitons and trions described by two and three-particle Bethe-Salpeter and Tamm-Dancoff equations with predictive power
- Phonon-Assisted Indirect Exciton Ionization is predicted to have a sub ns lifetime at realistic doping levels
- Low dimensionality leads to enhanced polaronic effects in materials like SbPS4