Novel materials for energy applications: insight by ab-initio ground and excited state methods

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SIF Annual Conference
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INFN Sezione di Roma Tor Vergata

TOR VERGATA UNIVERSITÀ DEGLI STUDI DI ROMA

ETSF

Motivations & goals

Opto-electronics
Photo-voltaics
Photo-catalysis…

Goals :

- interpret spectroscopy data/experiments
- Find key parameters to improve devices performance w/o trial & error
- Predict new materials opto-electronic properties

Need to describe ground & excited-state properties (gaps, band-offsets, optical spectra..) in materials of different dimensionality

Parameter-free quantum-mechanical theories
DFT + post-DFT (MBPT)

DFT and post-DFT (MBPT) simulations

DFT

Kohn-Sham Equations

$$H_0(r)\varphi_{KS}(r) + v_{xc}(r)\varphi_{KS}(r) = \varepsilon_{KS}\varphi_{KS}(r)$$

Conduction Band

Ground-state properties
KS gaps underestimate the real QP ones

Valence Band

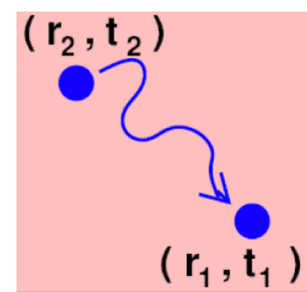
GW method

$$\varepsilon_i^{QP} \approx \varepsilon_i^{KS} + \langle \varphi_i^{KS} | \Sigma(\varepsilon_{nk}^{KS}) - V_{xc} | \varphi_i^{KS} \rangle$$

(One-shot G_oW_o or e-GW)

Conduction Band

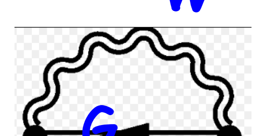
Electronic (transport) gaps



Quasi-particle Bandstructures

Valence Band

W

$\Sigma =$ 

Bethe-Salpeter Equation (BSE)

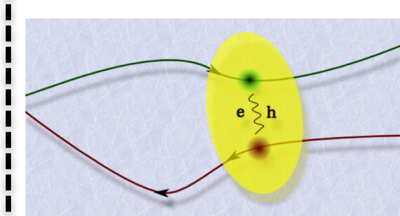
$$[H_{el} + H_{hole} + H_{el-hole}]A_\lambda = E_\lambda A_\lambda$$

$$Abs(\omega) \propto \sum_\lambda \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c\rangle \right|^2 \delta(E_\lambda - \omega)$$

Conduction Band

Excitons

Optical Gaps, spectra



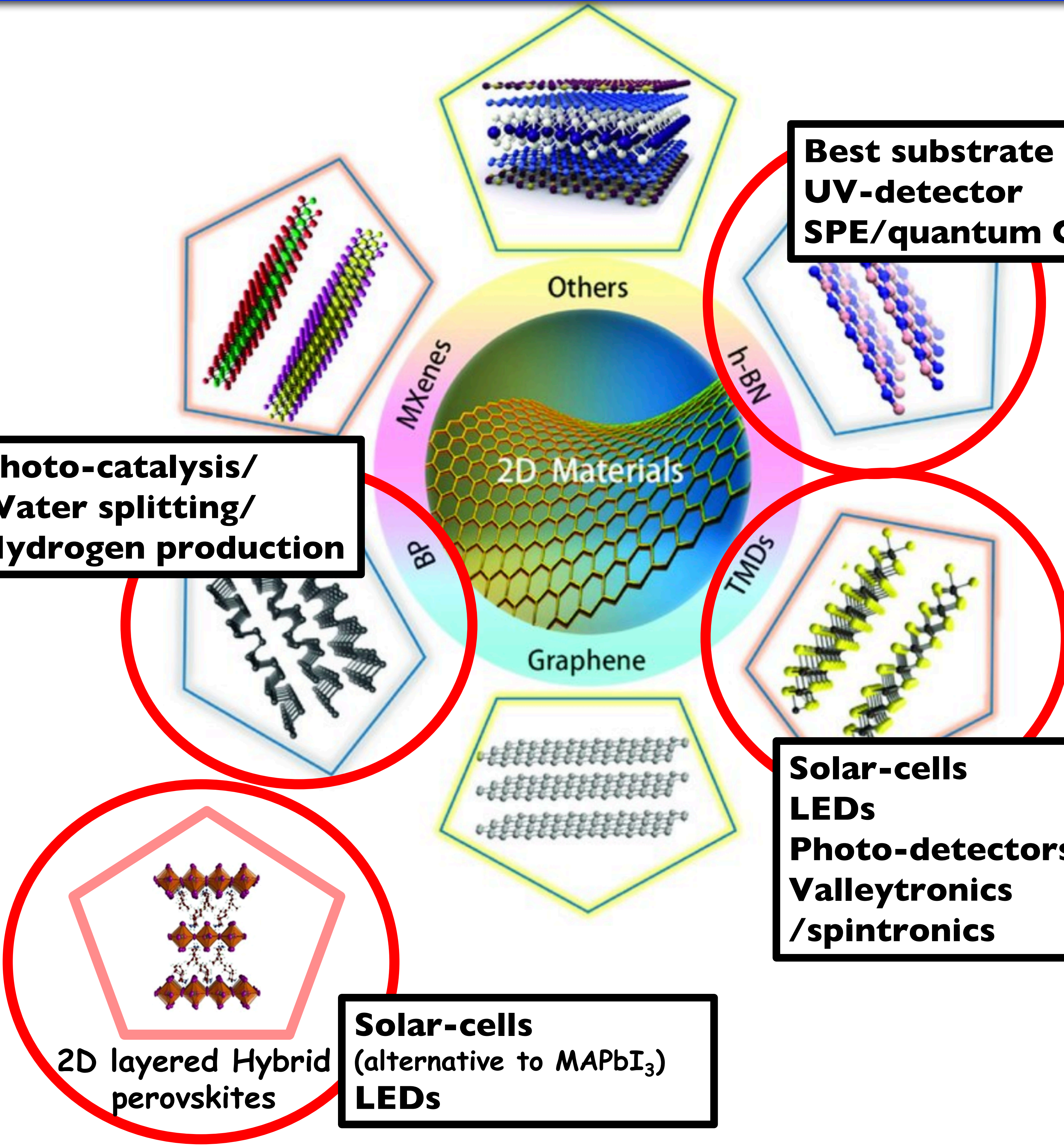
Valence Band

A_λ = excitonic eigenfunctions
E_λ = excitonic Eigenvalues

Yambo

Computational cost increases

Which Novel Materials? 2D/vdW/layered



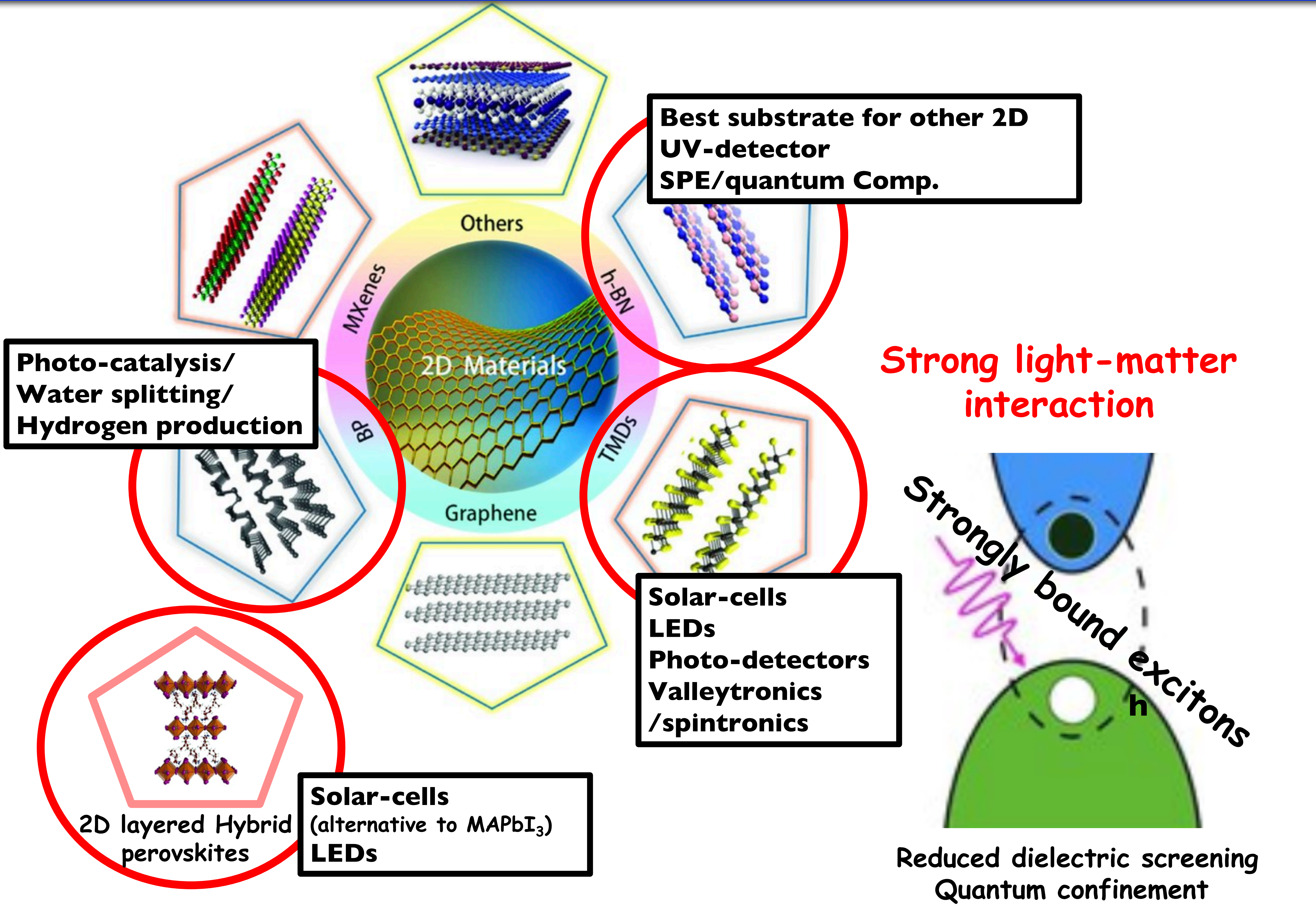
Best substrate for other 2D
UV-detector
SPE/quantum Comp.

Photo-catalysis/
Water splitting/
Hydrogen production

Solar-cells
LEDs
Photo-detectors
Valleytronics
/spintronics

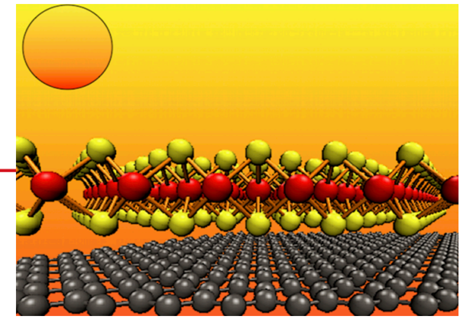
Solar-cells
(alternative to $MAPbI_3$)
LEDs

Which Novel Materials? 2D/vdW/layered



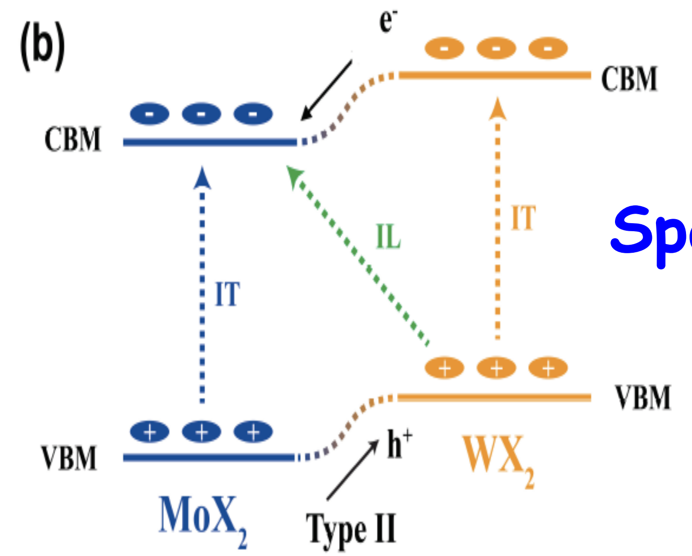
Group VI Transition Metal Dichalcogenides

NANO LETTERS 2013

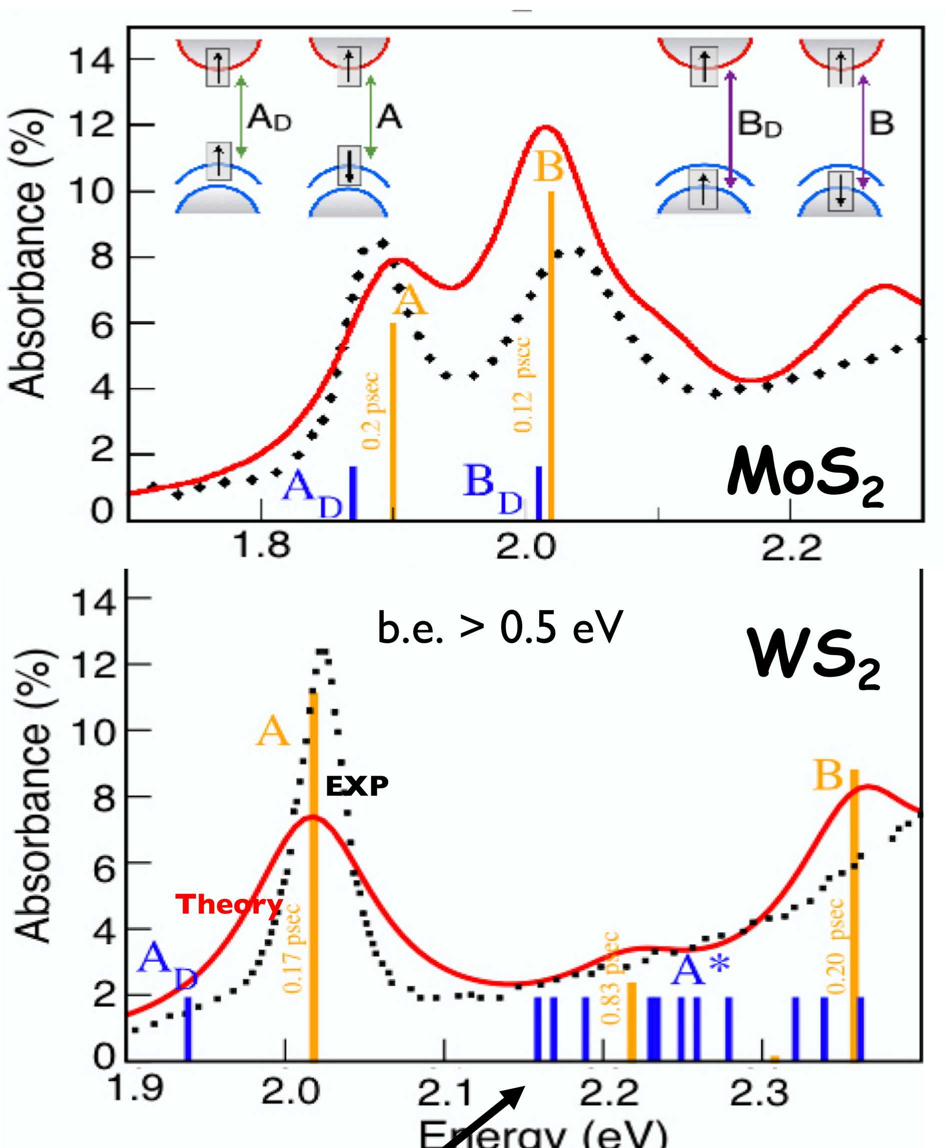


Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials

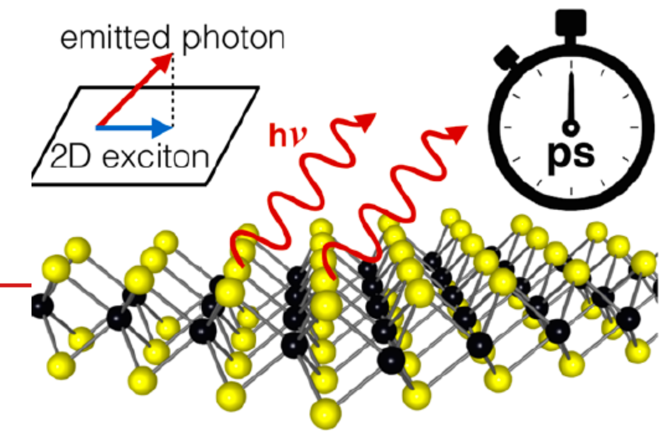
Marco Bernardi,[†] Maurizia Palummo,[†,‡] and Jeffrey C. Grossman*[,†]



Inter-Layer Spatially indirect excitons



Excitons fine structure



NANO LETTERS 2015

Exciton Radiative Lifetimes in Two-Dimensional Transition Metal Dichalcogenides

Maurizia Palummo,[†] Marco Bernardi,[‡] and Jeffrey C. Grossman*[,§]

$$\tau_S(0)^{-1} = \frac{8\pi e^2 E_S(0)}{\hbar^2 c}\,\frac{\mu_S^2}{A_{uc}}$$

$$\langle \tau_S \rangle = \tau_S(0)\,\frac{3}{4}\left(\frac{E_S(0)^2}{2M_S c^2}\right)^{-1} k_B T$$

A_D order of ms

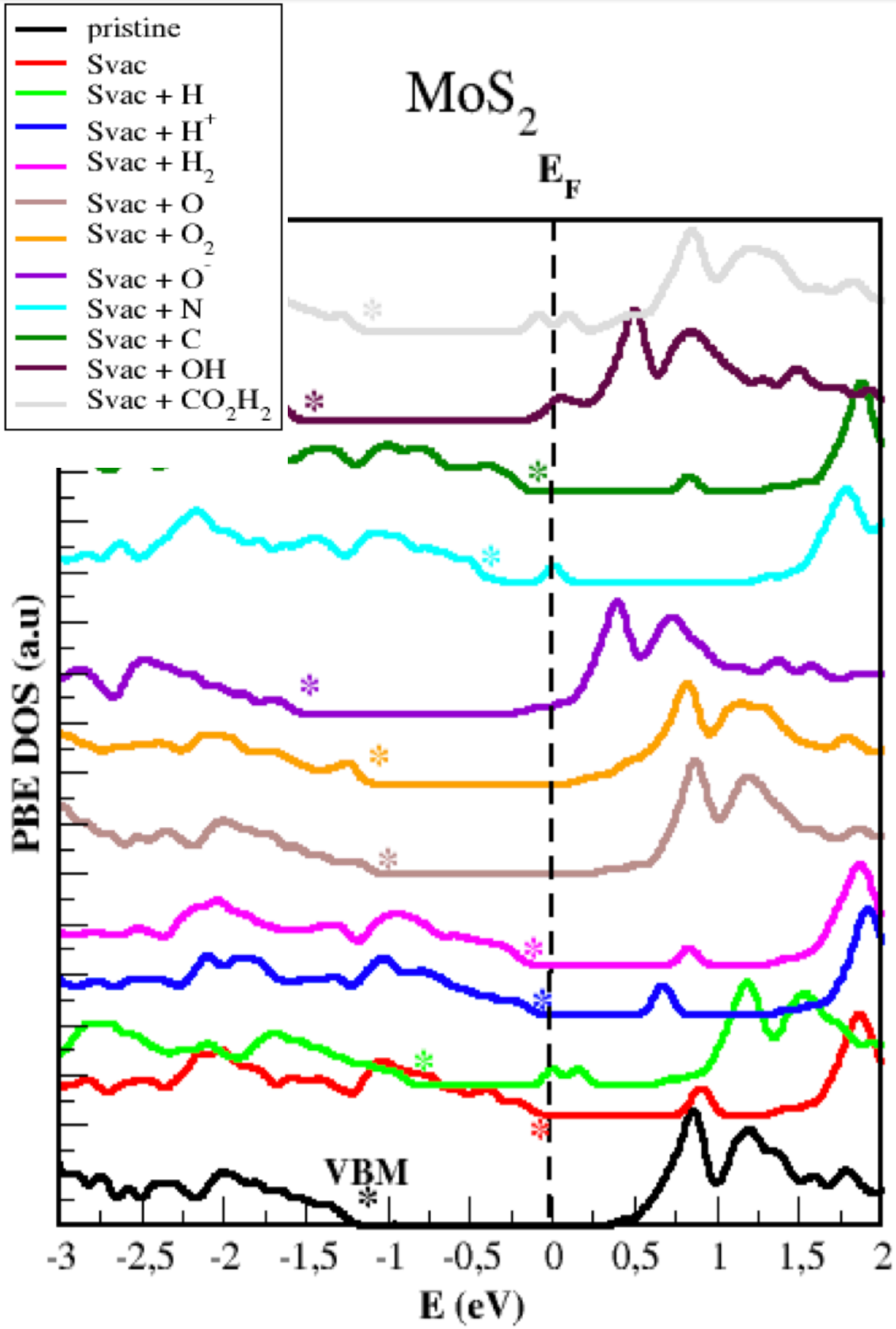
A 0.1-0.2 ps

A few ps at 4K

few ns at RT

IL excitons have much longer radiative lifetimes

Modulation of the electronic and optical properties of MoS_2-1L by defects/dopants



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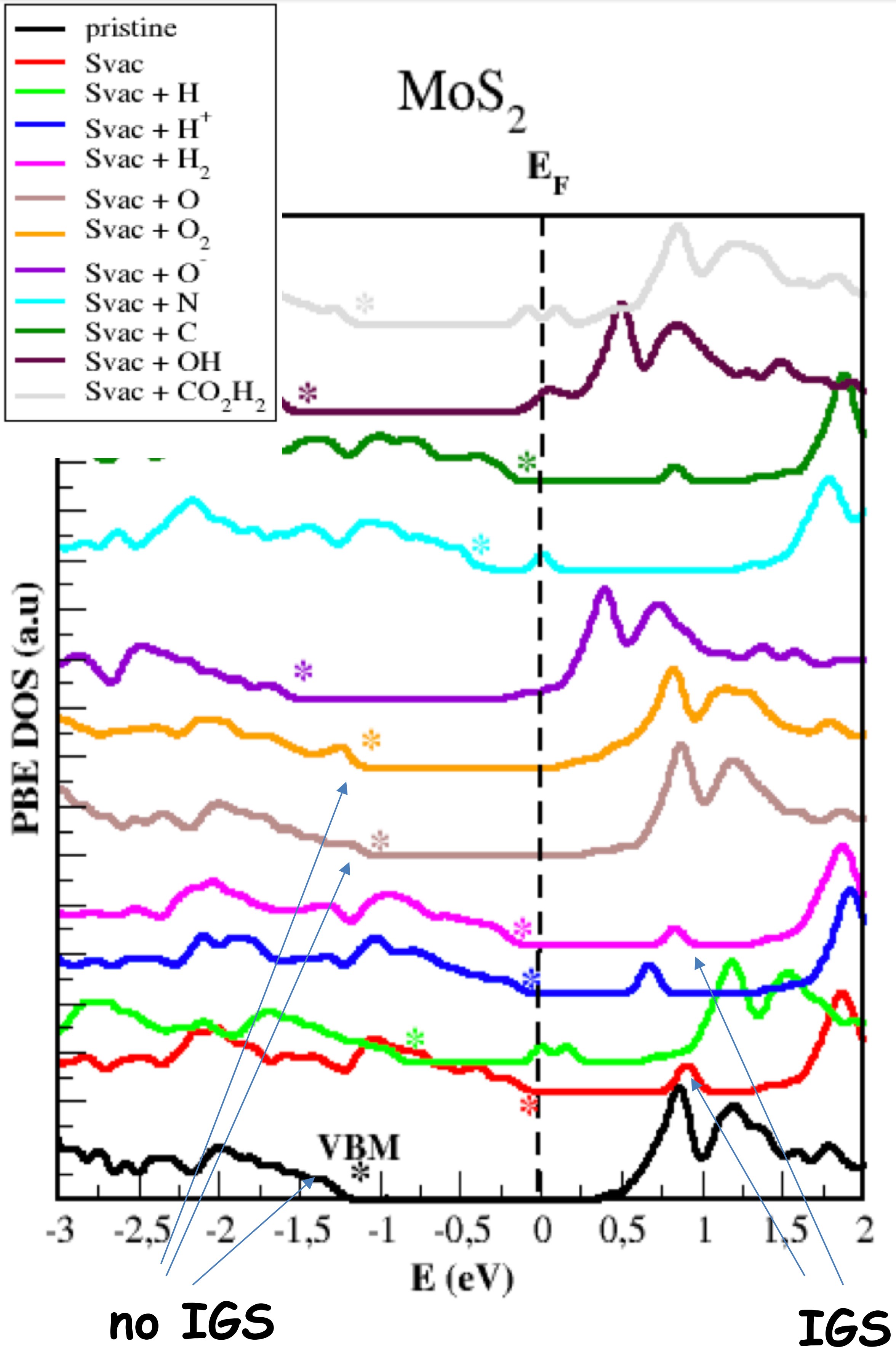

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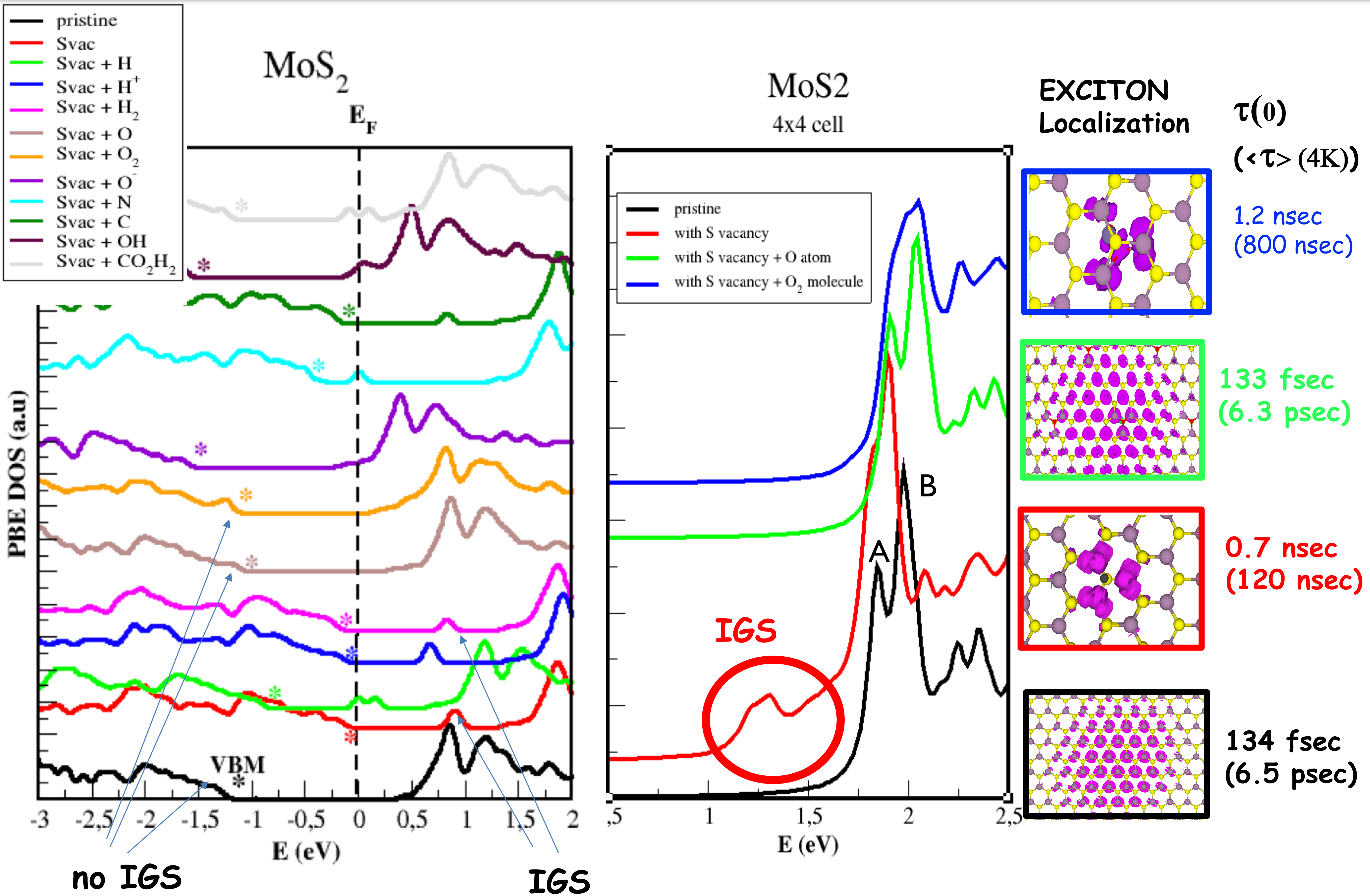

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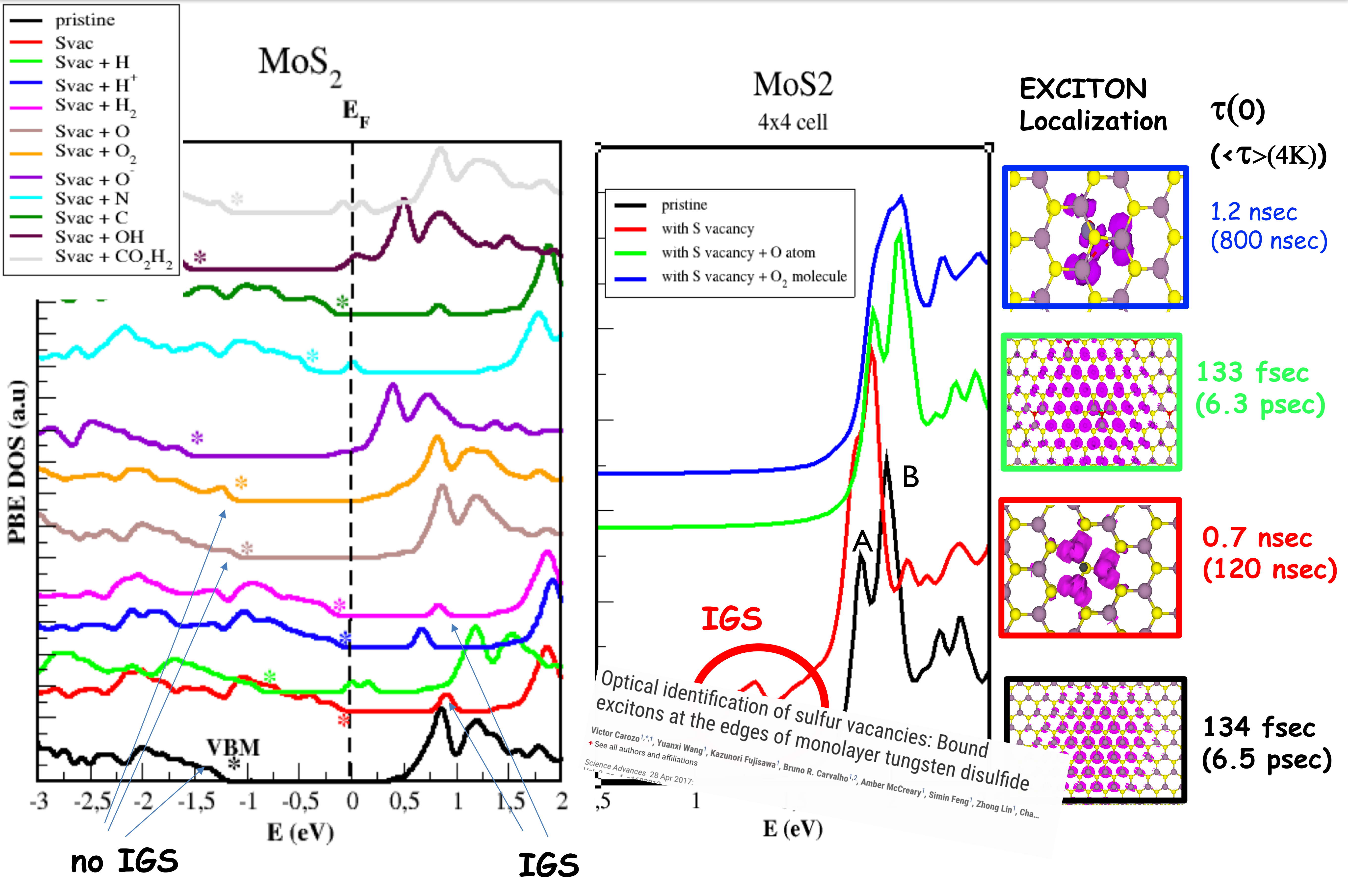

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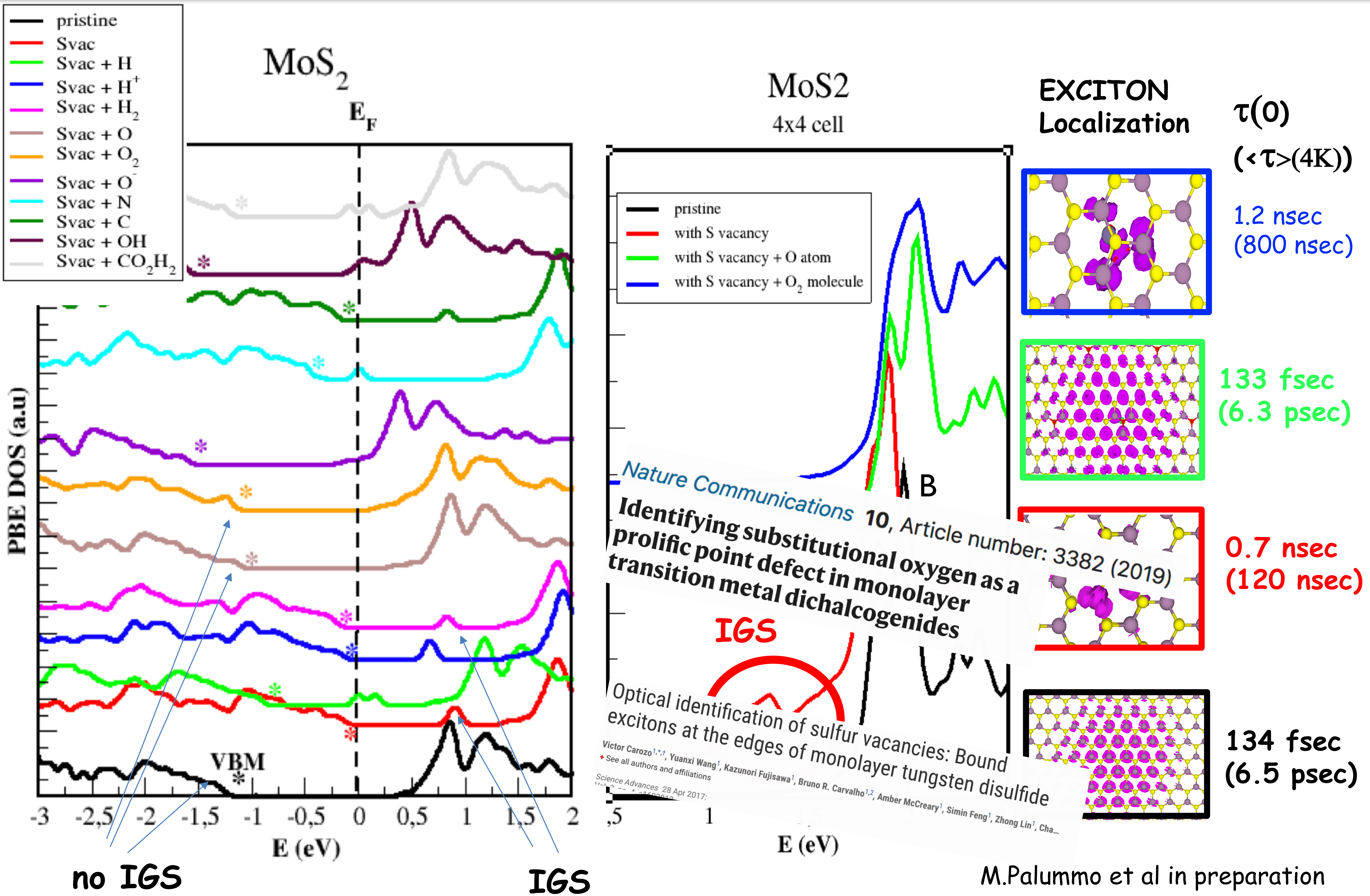


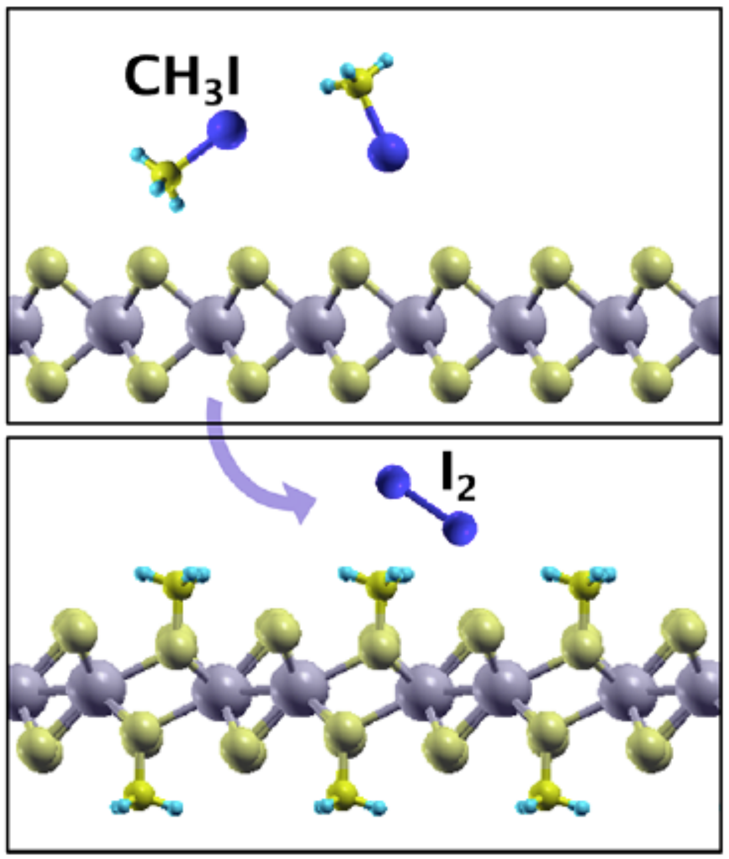
M.Palummo et al in preparation

Tayloring the electronic and optical properties of MS_2 by covalent molecular functionalization

Methyl-iodine precursors allow covalent functionalization of pristine hexagonal MS_2 M = Mo, W

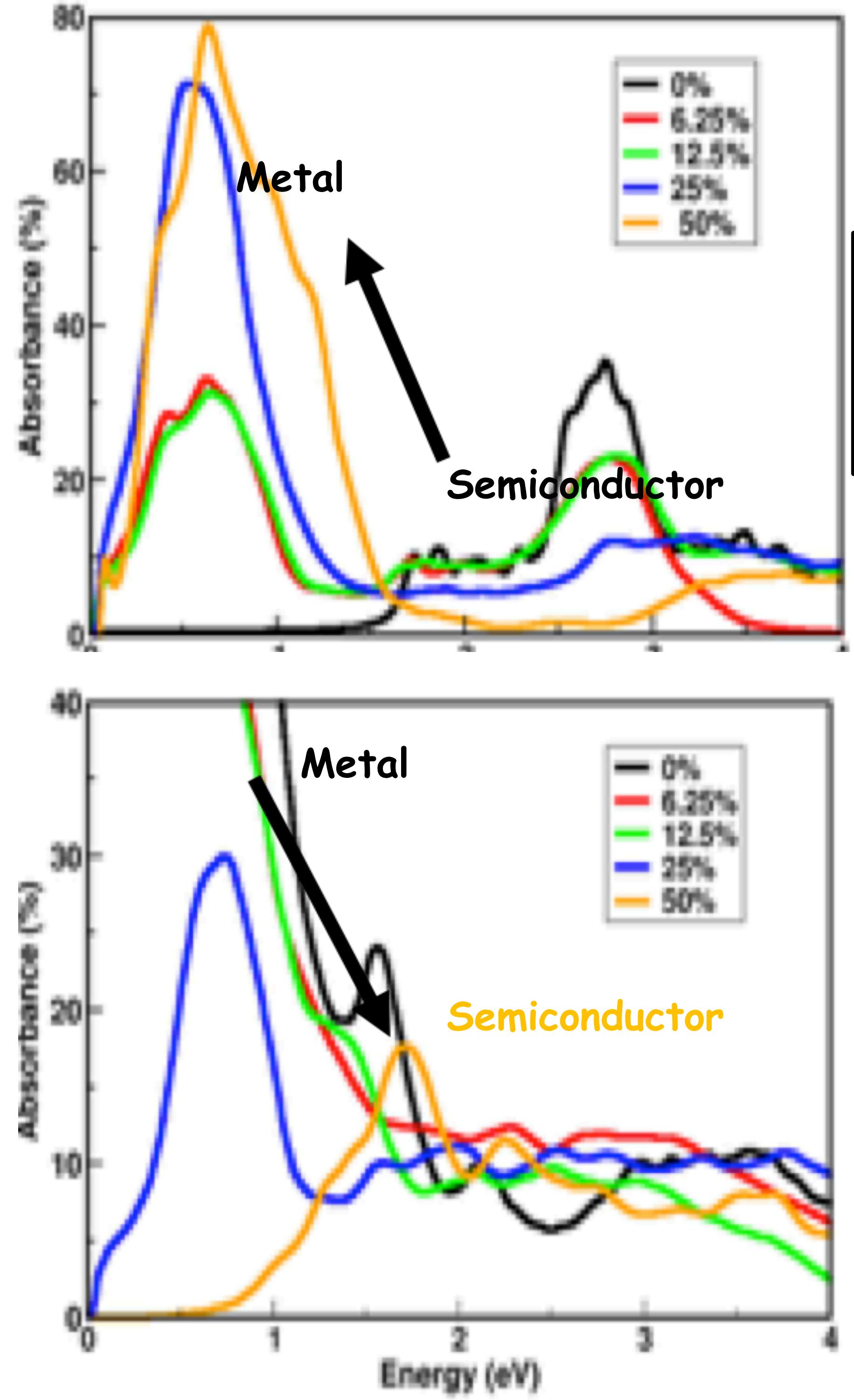
D. Voiry et al Nat chem 2015

2H Hexagonal



T' Tegragonal-distorted

It can induces the stabilization of the pristine T' phase which is very interesting for QSH effects /TI properties/ Excitons condensation

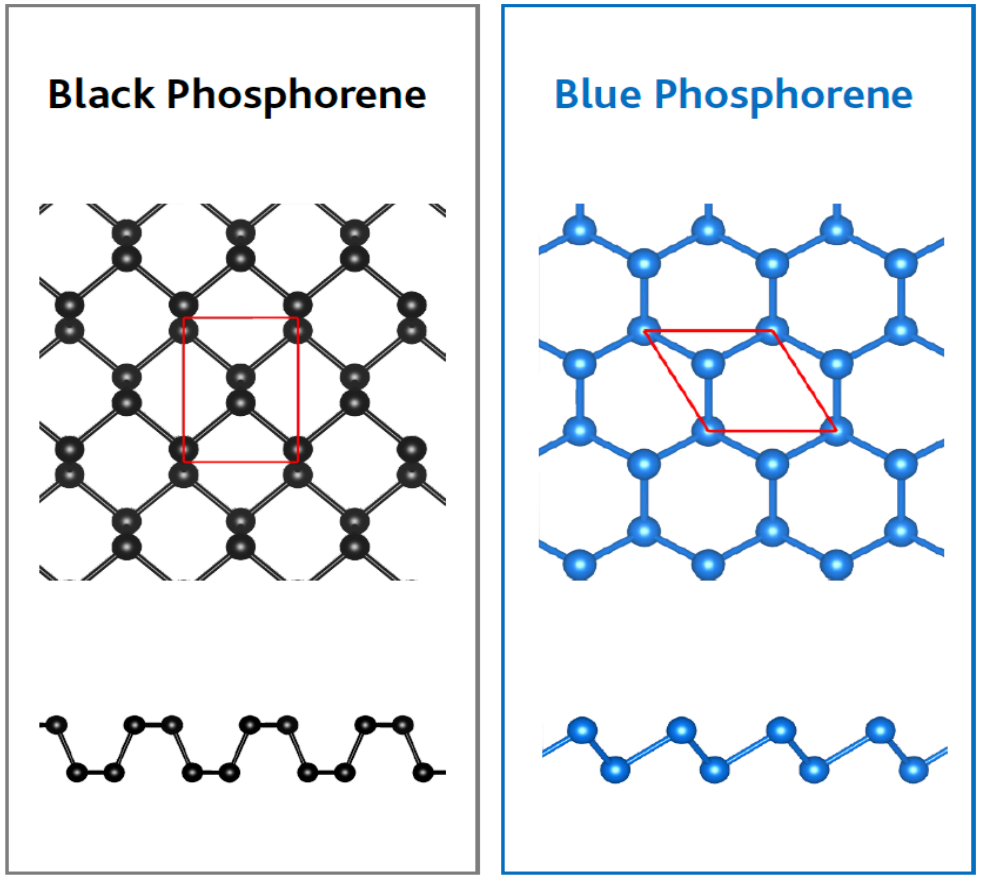


MoS_2-2H Hexagonal

MoS_2 -T' Tegragonal-distorted

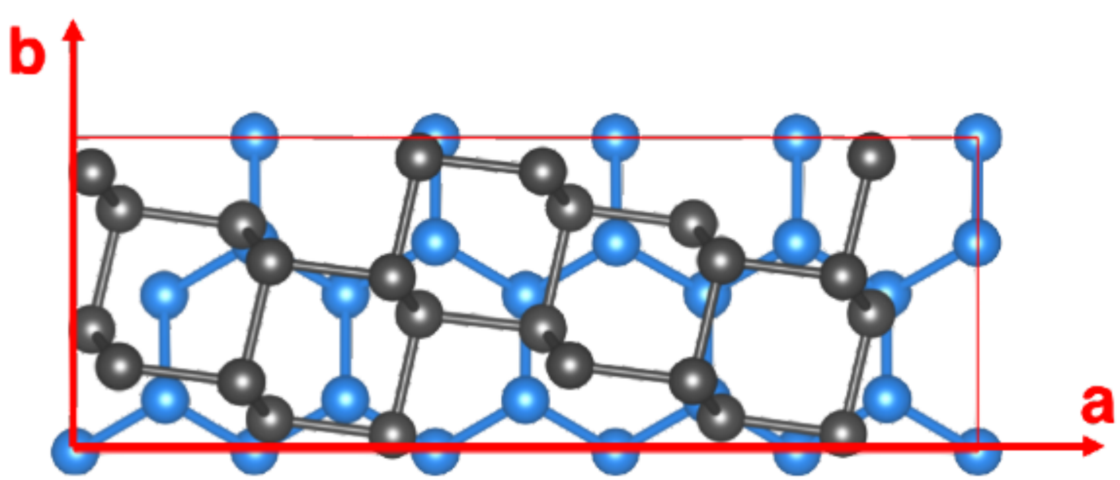
MP, A. D'Auria JC Grossman G. Cicero Journal of Physics: Condensed Matter 2019

Spatially indirect excitons in Black/Blue phosporene bilayer



Direct gap GoWo 2.1 eV
Main Optical peak 1.6 eV

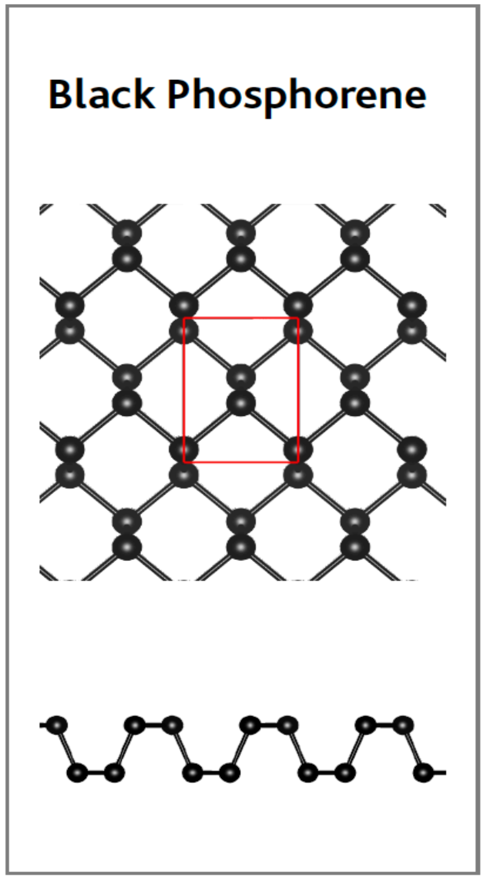
Indirect gap GoWo 3.45 eV
Main Optical peak 3.0 eV



Bilayer is stable Negative cohesive energy
Almost zero Strain (< 1%)

M. ReFiorentin , G. Cicero, M. Palummo PRM 2020

Spatially indirect excitons in Black/Blue phosporene bilayer



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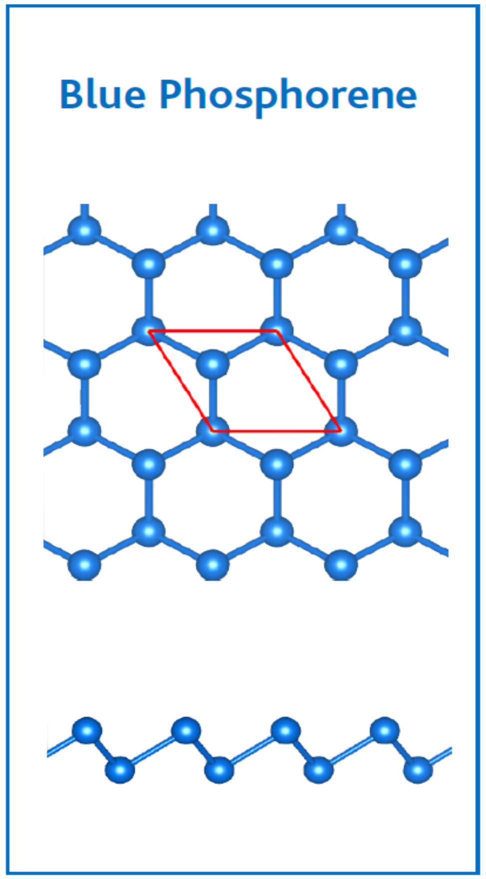

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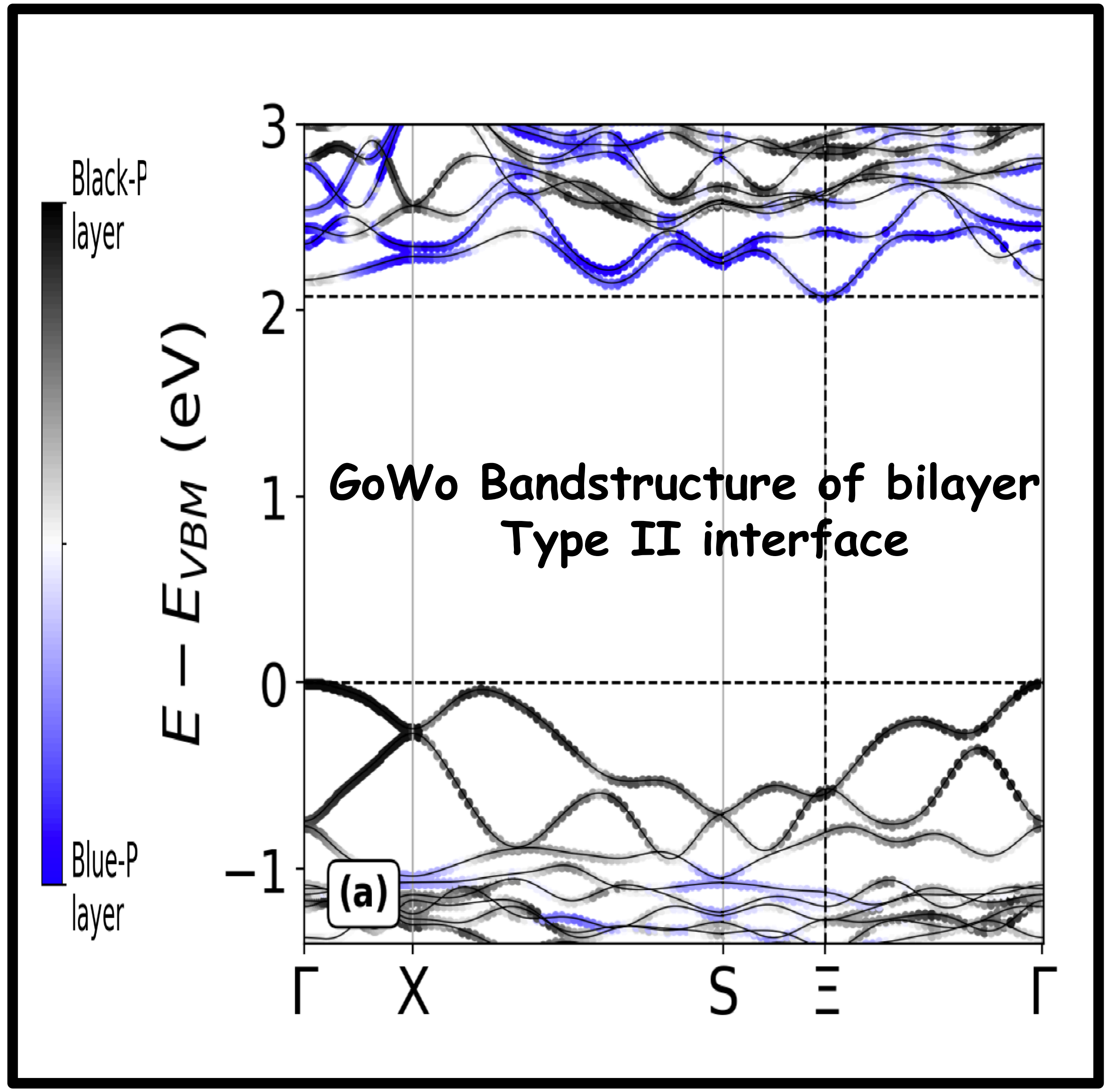
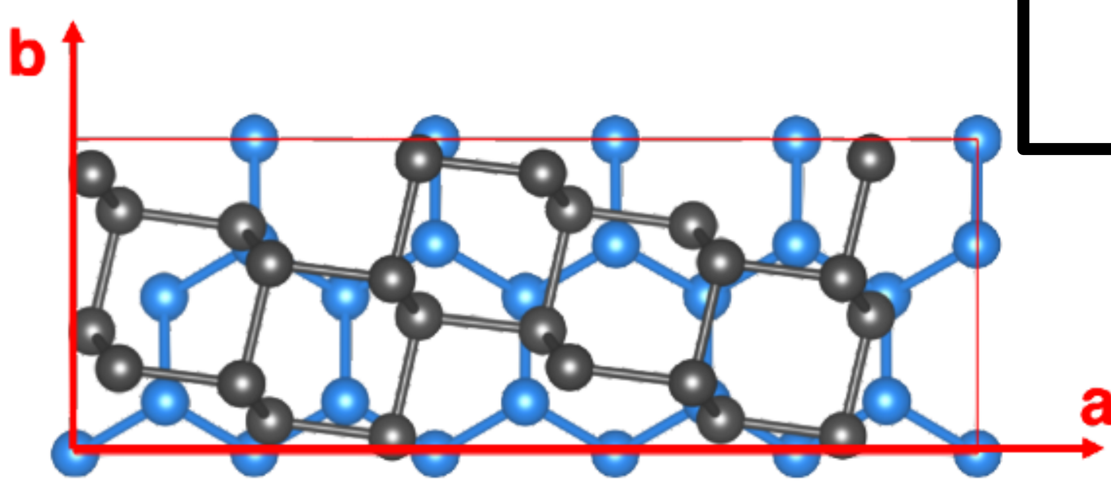


Bilayer with strain Indirect gap



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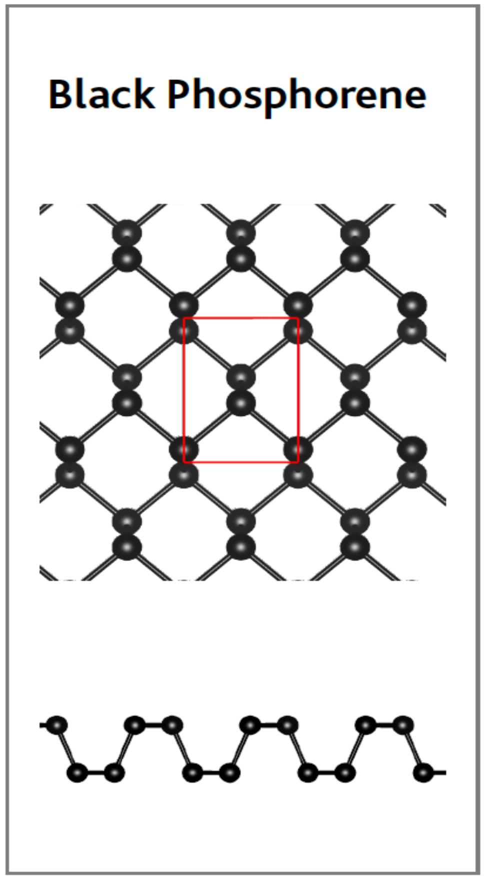

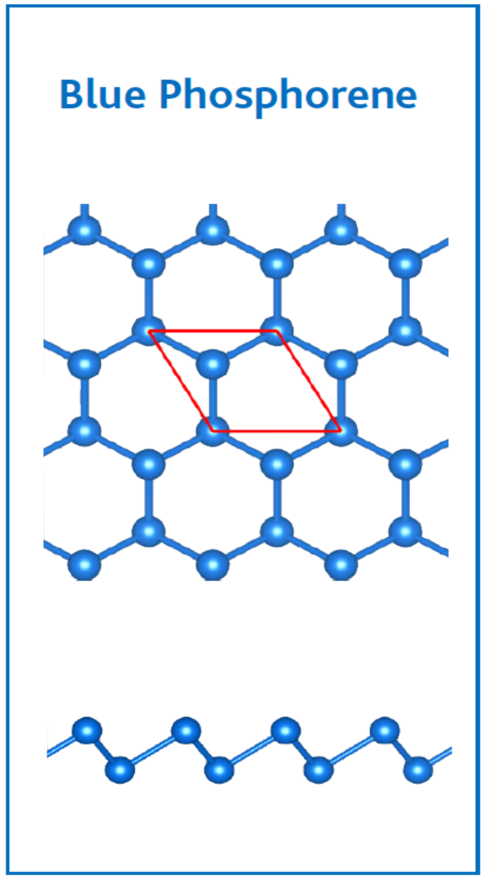

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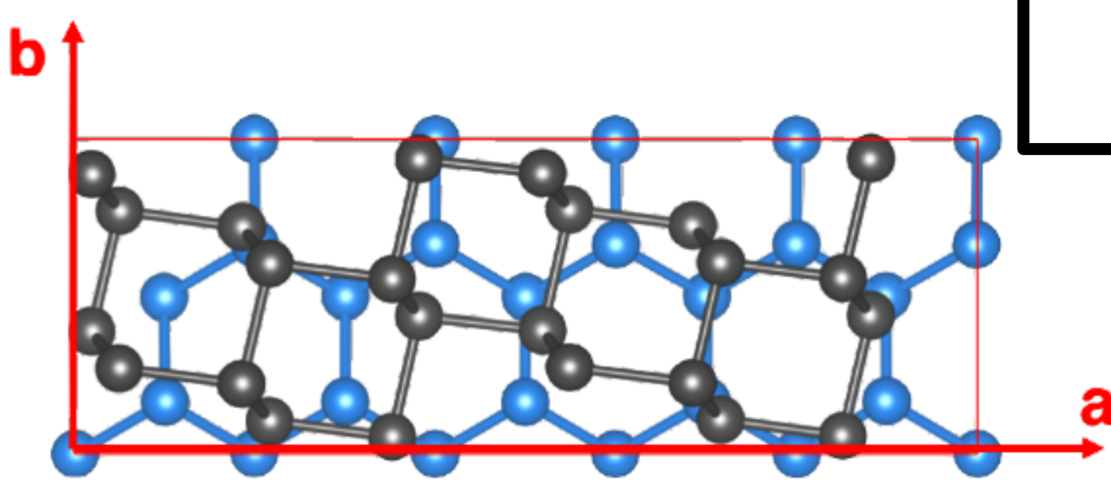

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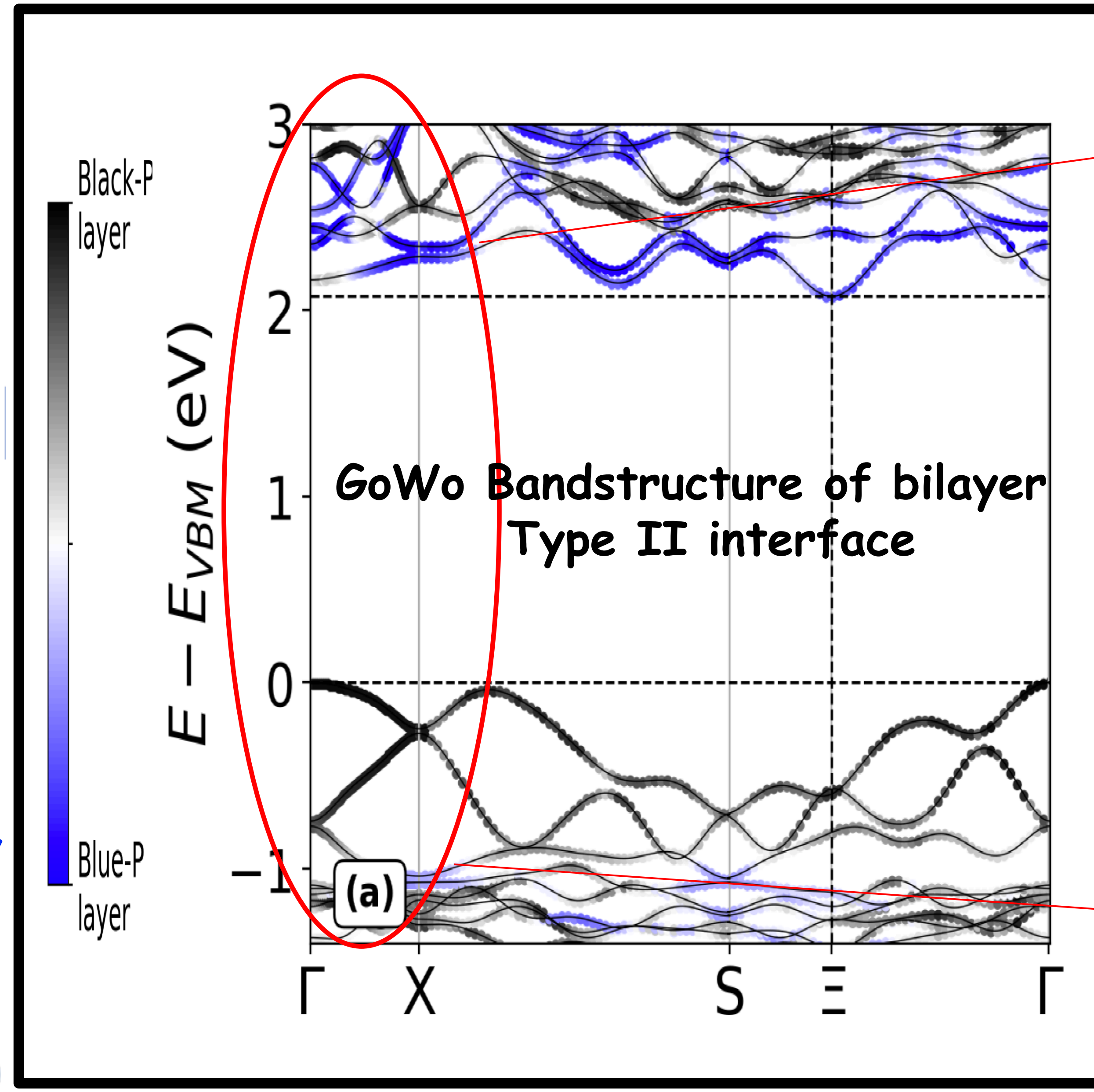
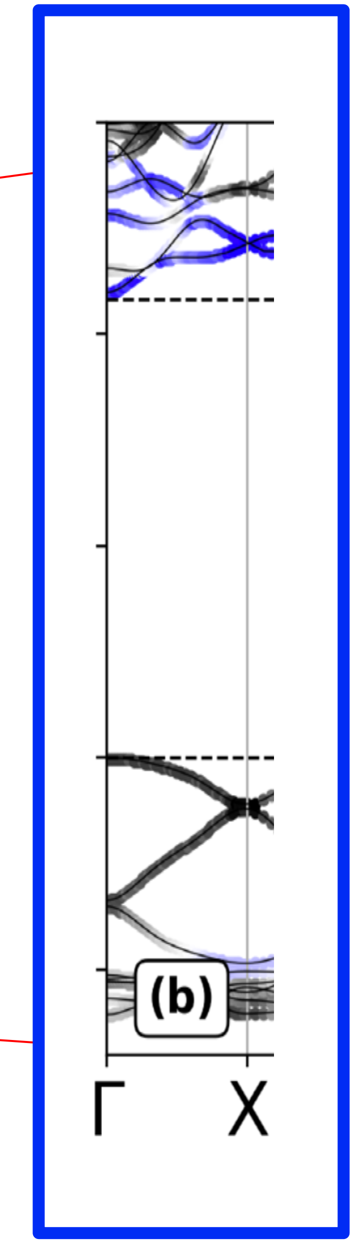


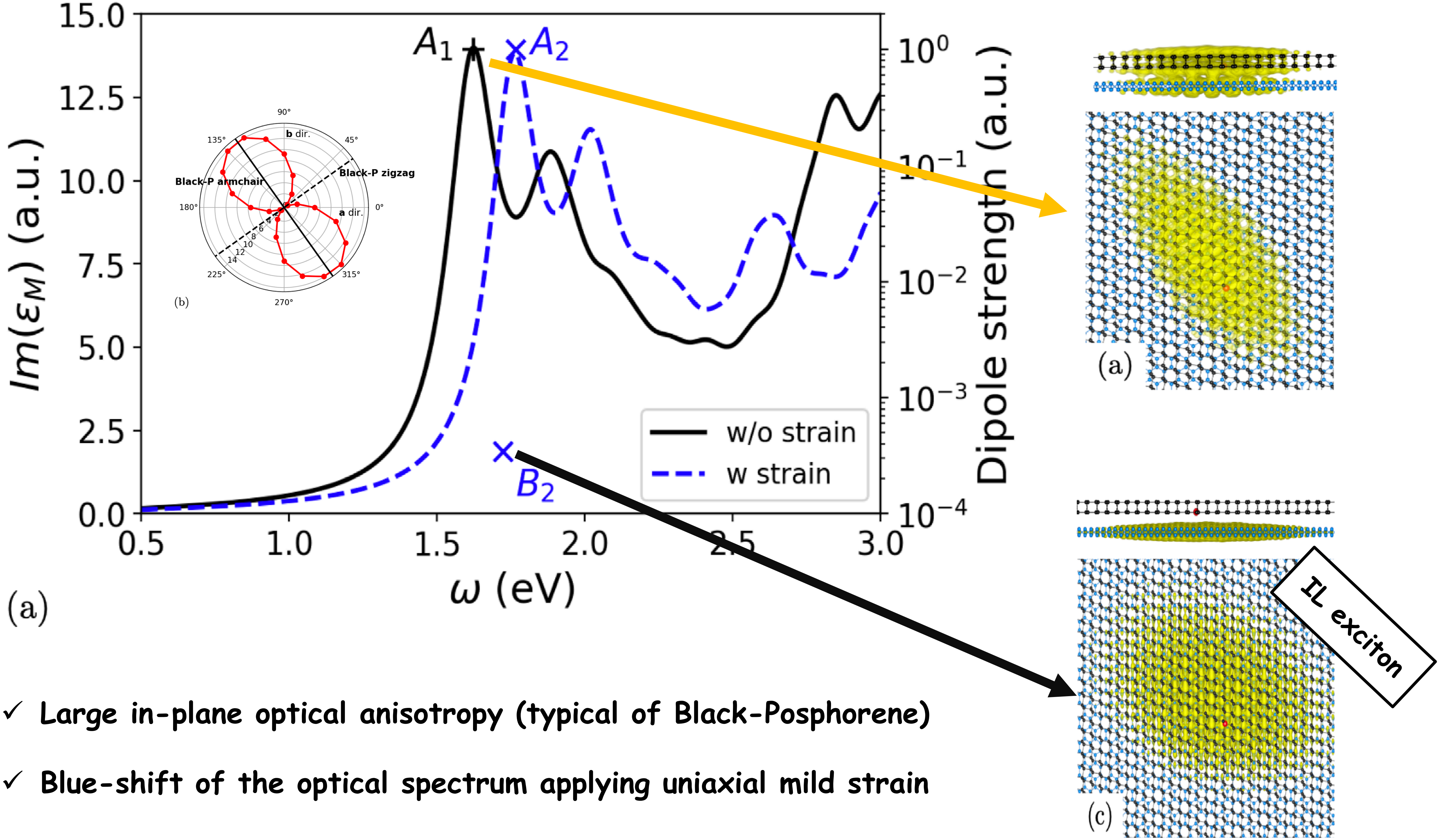


Bilayer with strain Indirect gap

Bilayer with 2% uniaxial strain along a Direct gap

M. ReFiorentin , G. Cicero, M. Palummo PRM 2020

Spatially indirect excitons in Black/Blue phosporene bilayer



- ✓ **Large in-plane optical anisotropy (typical of Black-Posphorene)**
- ✓ **Blue-shift of the optical spectrum applying uniaxial mild strain**
- ✓ **Spatially indirect exciton with very low oscillator strenght (longer lifetime)**

M. ReFiorentin G. Cicero, M. Palummo PRM 2020

Excitons Engineering by changing stacking and twisting angle: the case of BN bilayer

Unconventional superconductivity in magic-angle graphene superlattices

Yuan Cao, Valla Fatemi, Shiang Fang, Kenji Watanabe, Takashi Taniguchi, Efthimios Kaxiras & Pablo Jarillo-Herrero

Nature **556**, 43–50(2018) | Cite this article

Excitons Engineering by changing stacking and twisting angle: the case of BN bilayer

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...axiras & Pablo

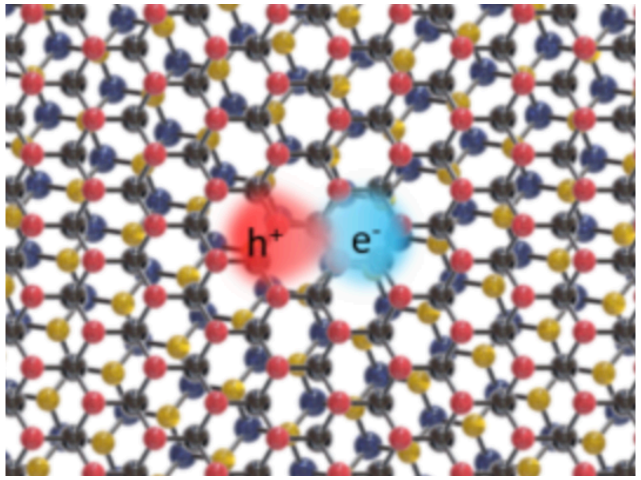
Letter | Published: 25 February 2019

Evidence for moiré excitons in van der Waals heterostructures

Kha Tran, Galan Moody, Fengcheng Wu, Xiaobo Lu, Junho Choi, Kyounghwan Kim, Amritesh Rai, Daniel A. Sanchez, Jiamin Quan, Akshay Singh, Jacob Embley, André Zepeda, Marshall Campbell, Travis Autry, Takashi Taniguchi, Kenji Watanabe, Nanshu Lu, Sanjay K. Banerjee, Kevin L. Silverman, Suenne Kim, Emanuel Tutuc, Li Yang, Allan H. MacDonald & Xiaoqin Li

Nature **567**, 71–75(2019) | Cite this article

TWINTRONICS



Moiré excitons

> 1400 works on google sch. in the last 2 years

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axiras & Pablo

Letter | Published: 25 February 2019

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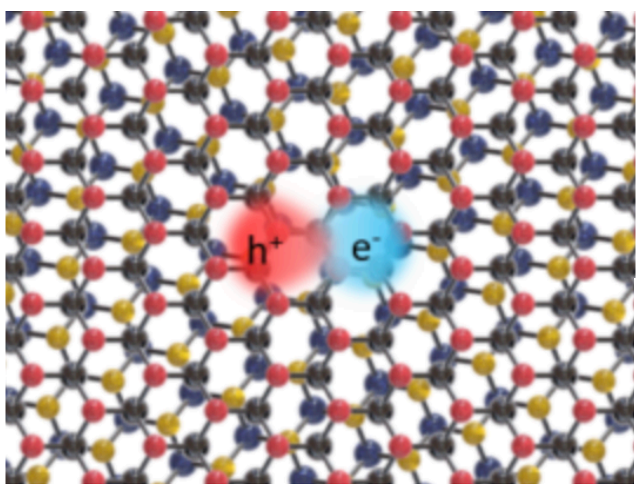

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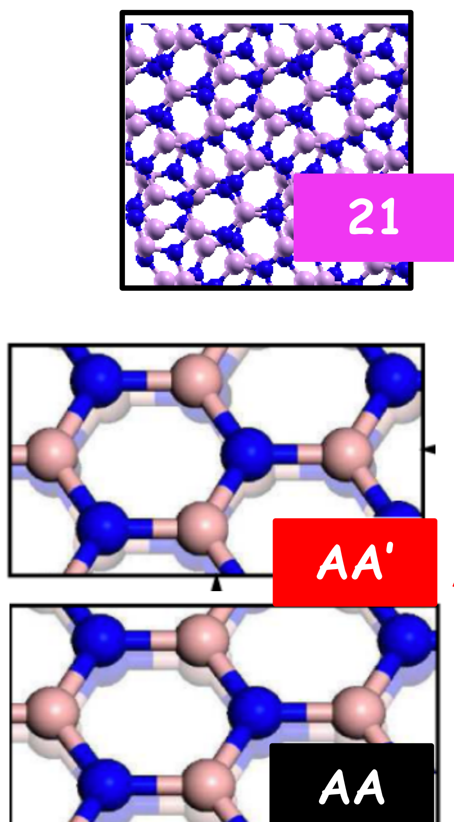
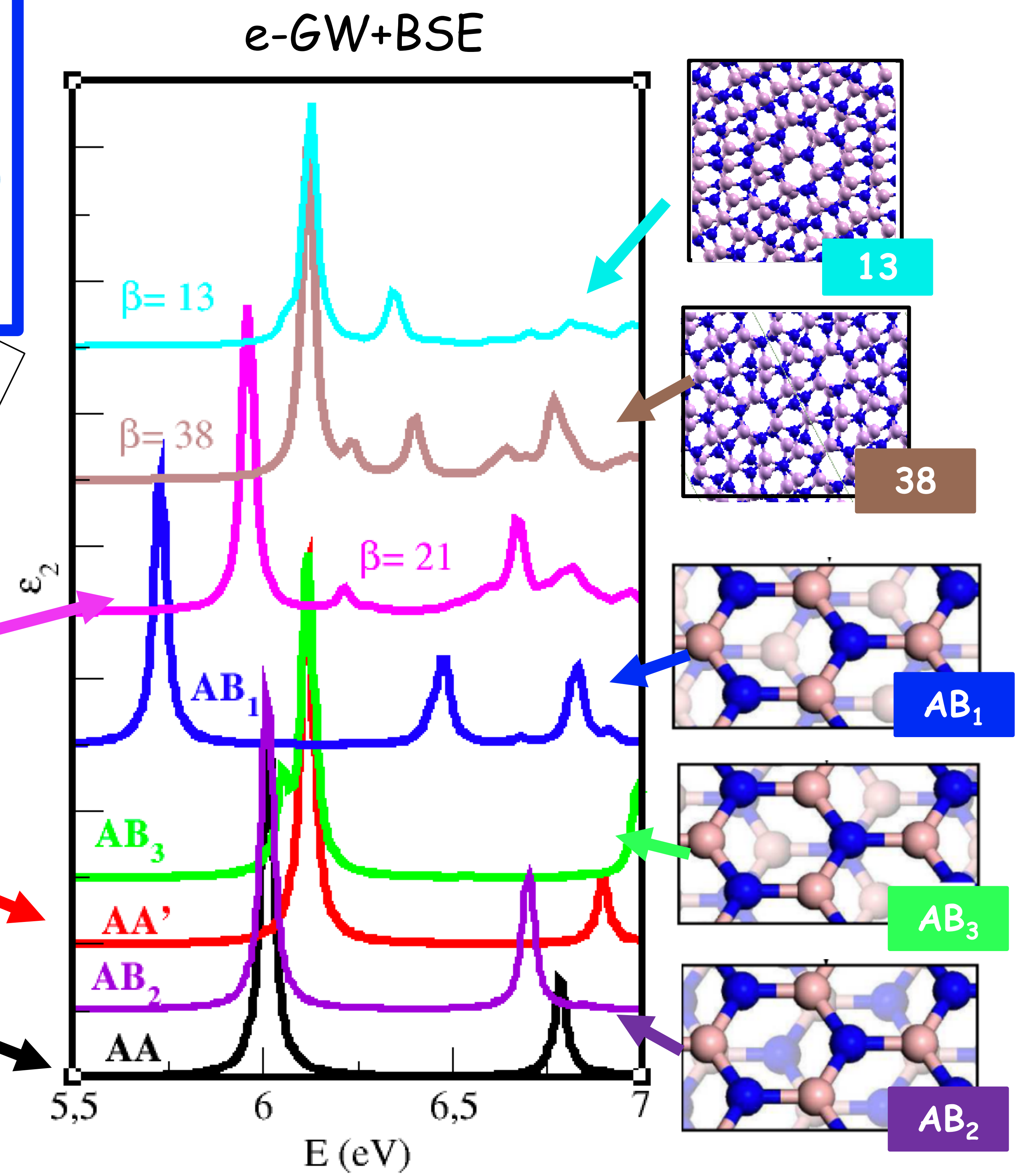
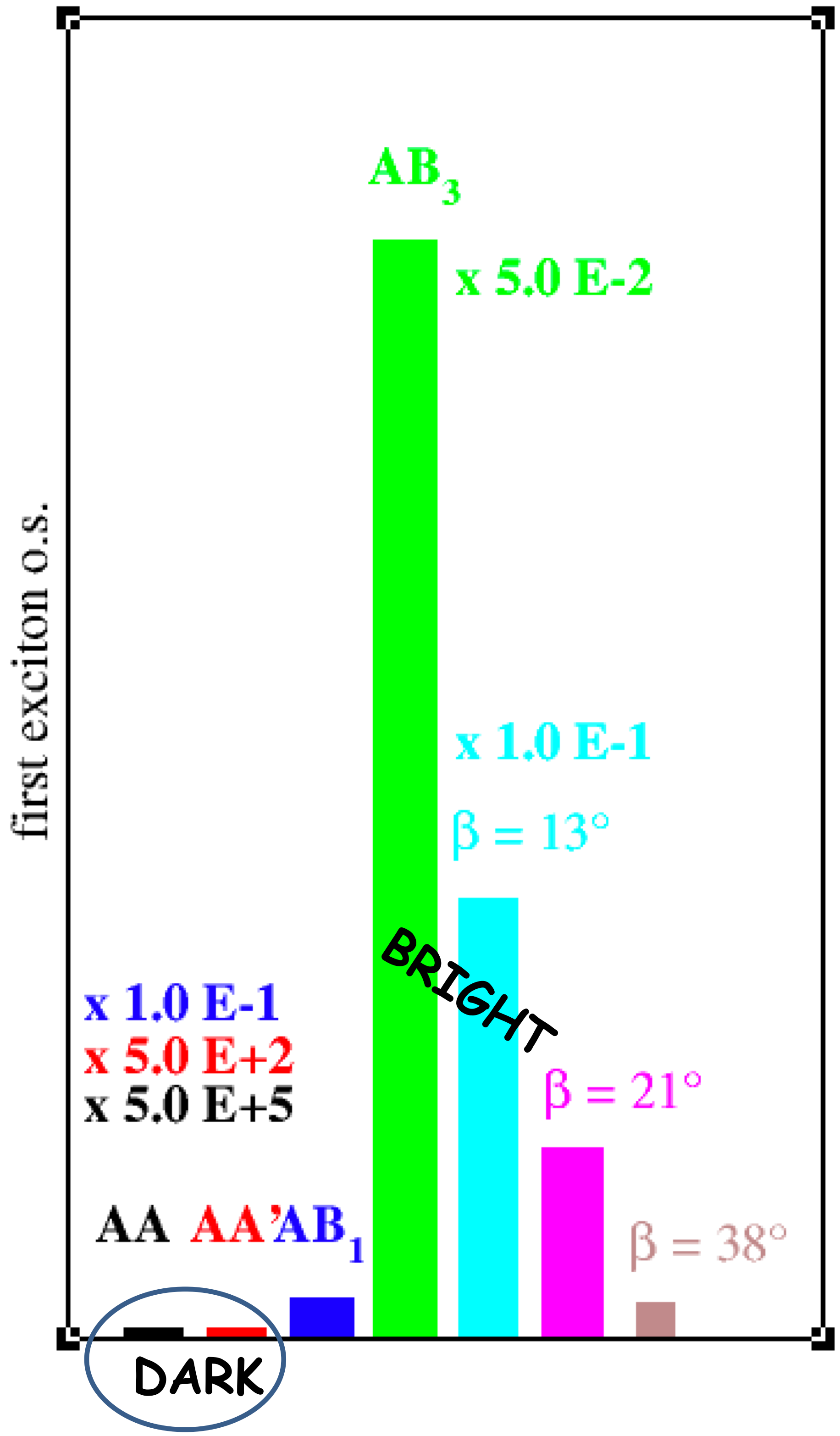




A.Zobelli ,M. Amato, MP in preparation

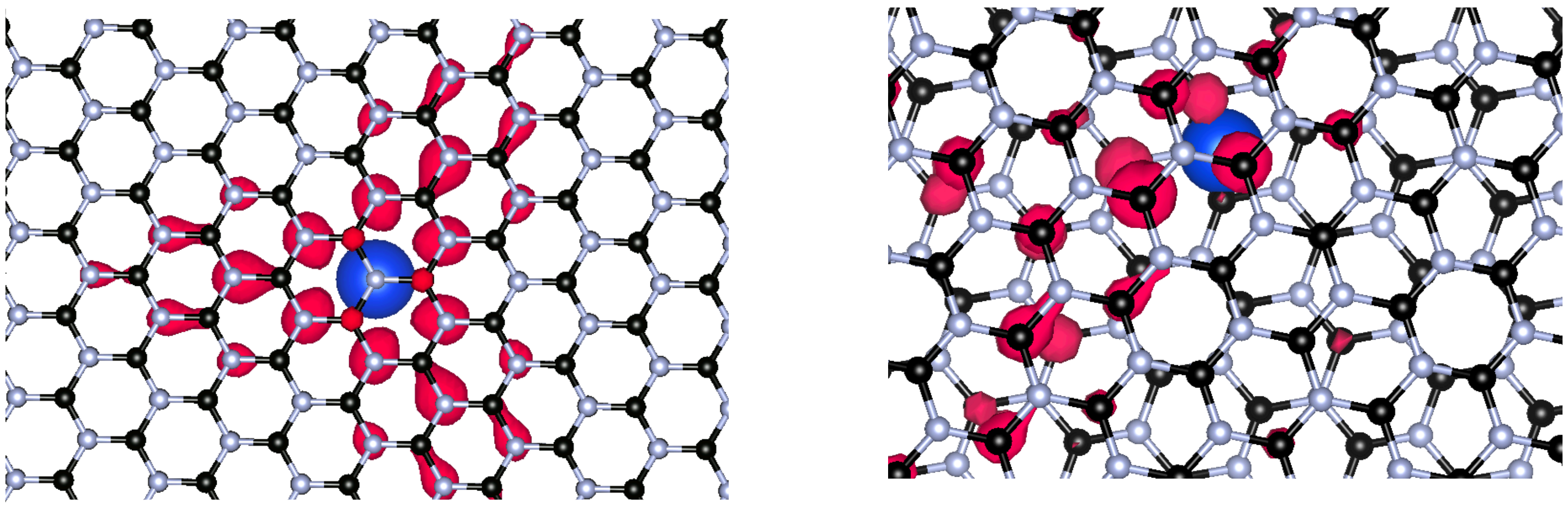
Twisting : from Dark to bright exciton



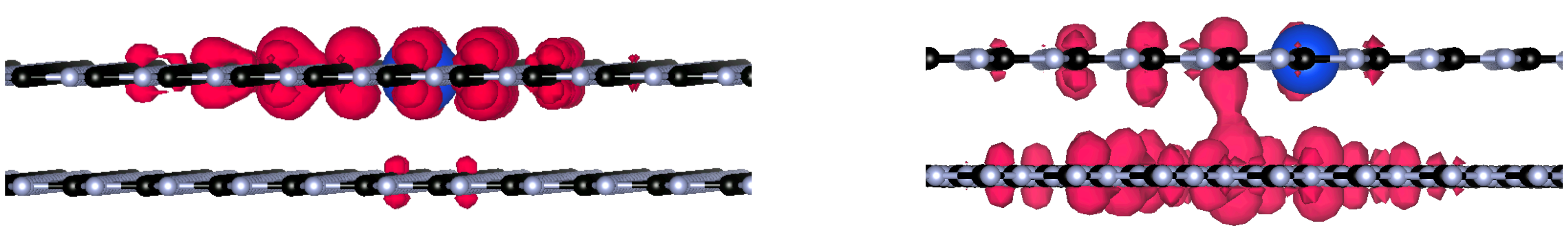
Exciton spatial distribution

AA' stacking

Moire
β =13°



TOP VIEWS

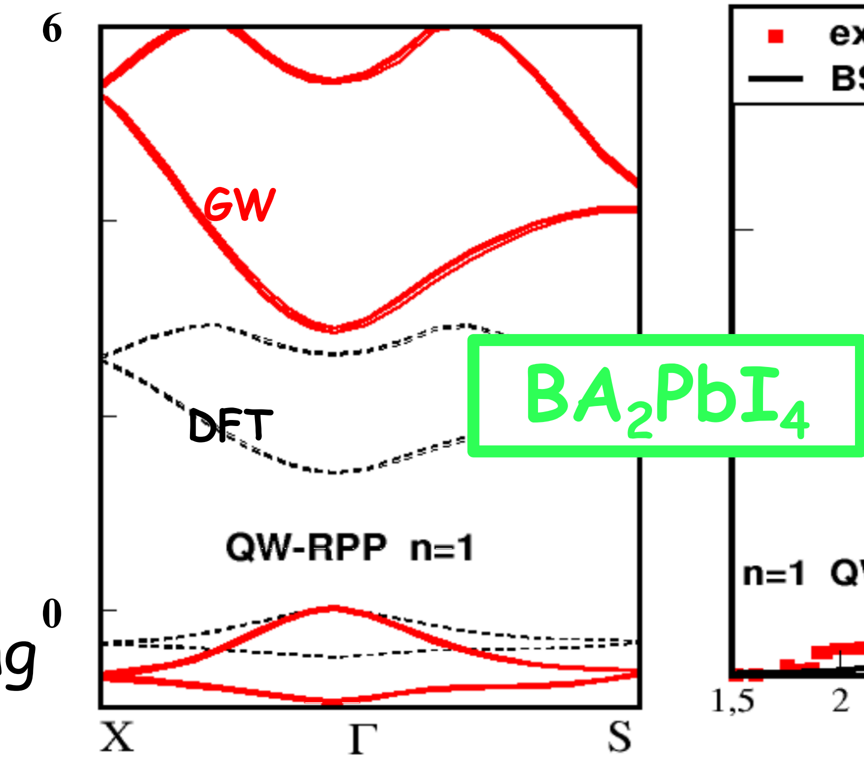


SIDE VIEWS

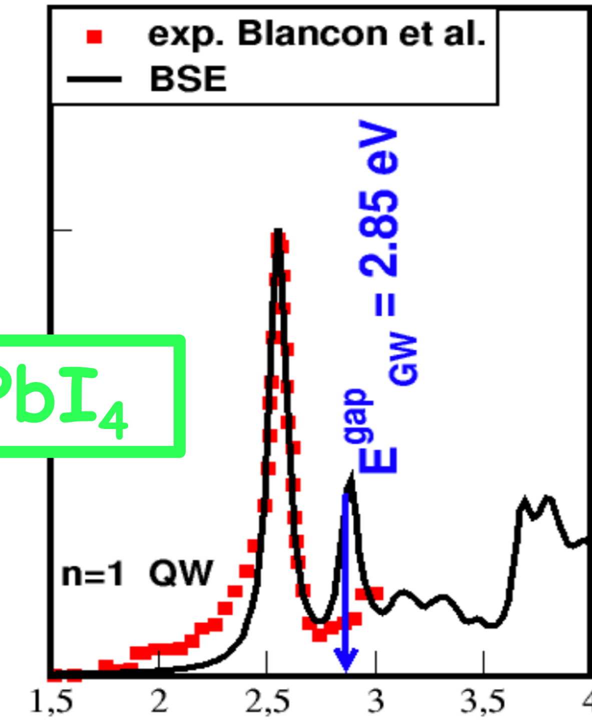
A.Zobelli et al. in preparation

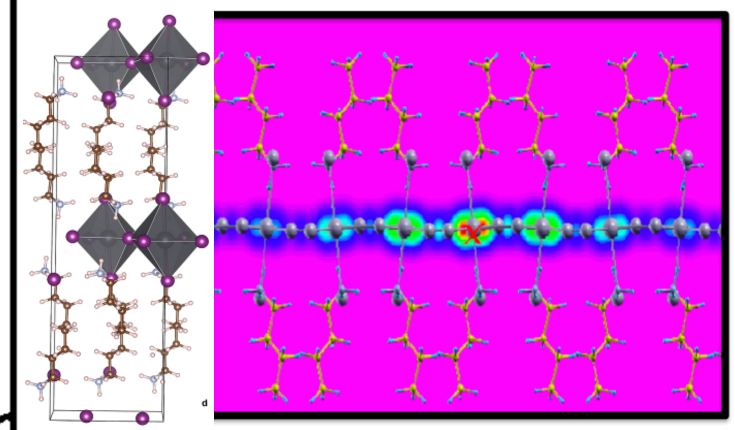
2D layered hybrid halide perovskites: BA_2PbI_4 and $BA_2MAPb_2I_7$

- ✓ Large band-gap renomalization due to correlation effects
- ✓ Large Rashba splitting (α =1 eV A) for $BA_2MAPb_2I_7$
- ✓ Strongly bound excitons
- ✓ e-h spatial distribution only in the inorganic layers and more laterally delocalized in n=2



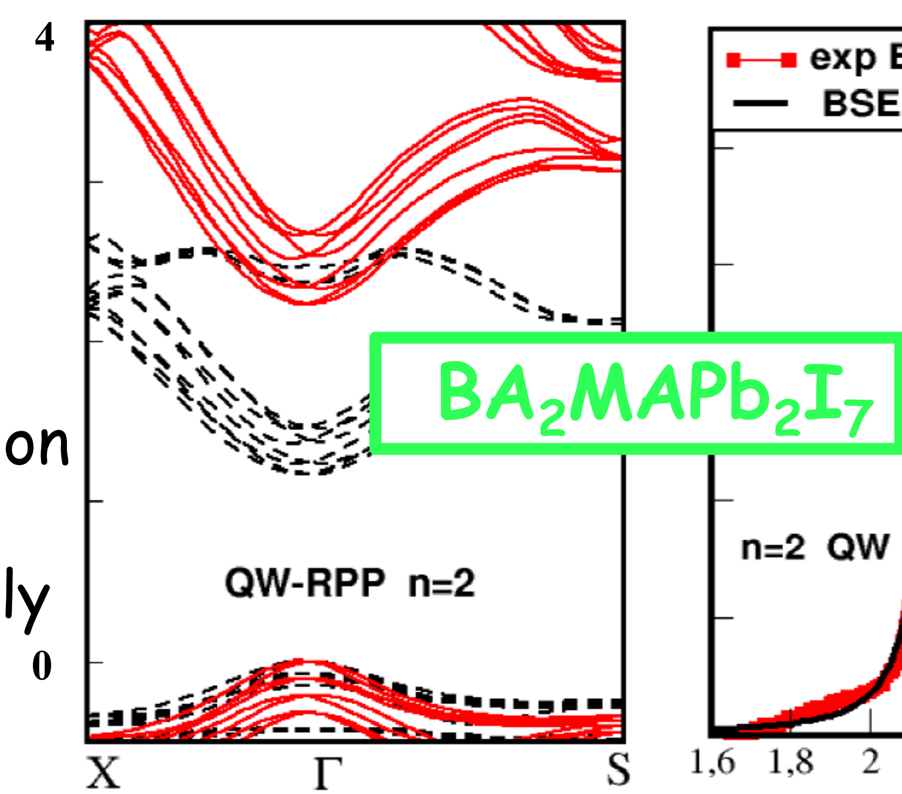
Theo. b.e. 300 meV



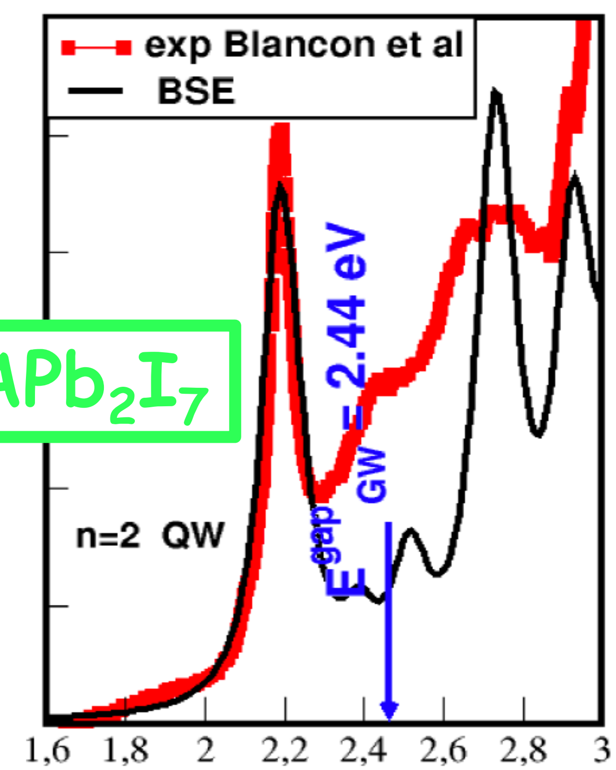


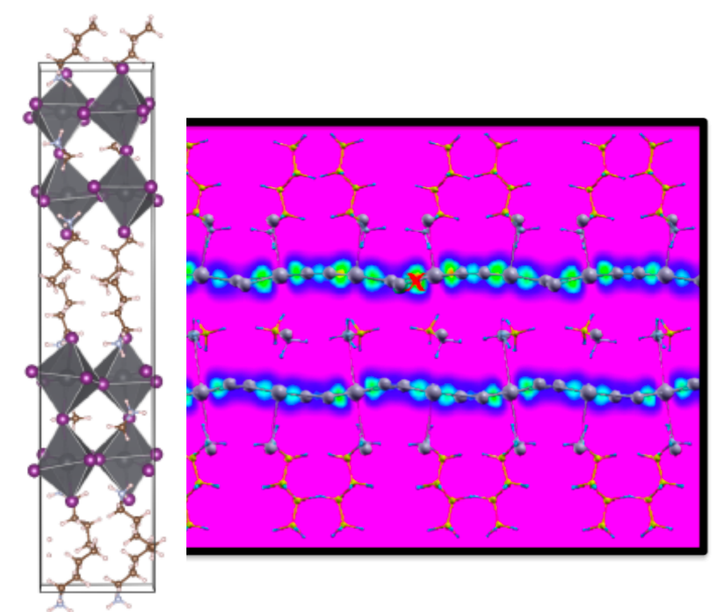
Dou et Science, 2015

Exciton spatial distribution fixing hole positon



Theo b.e. 260 meV

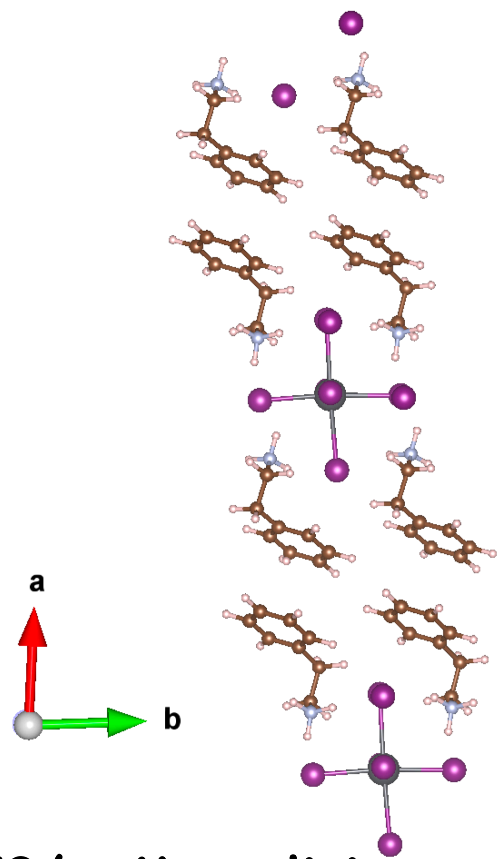




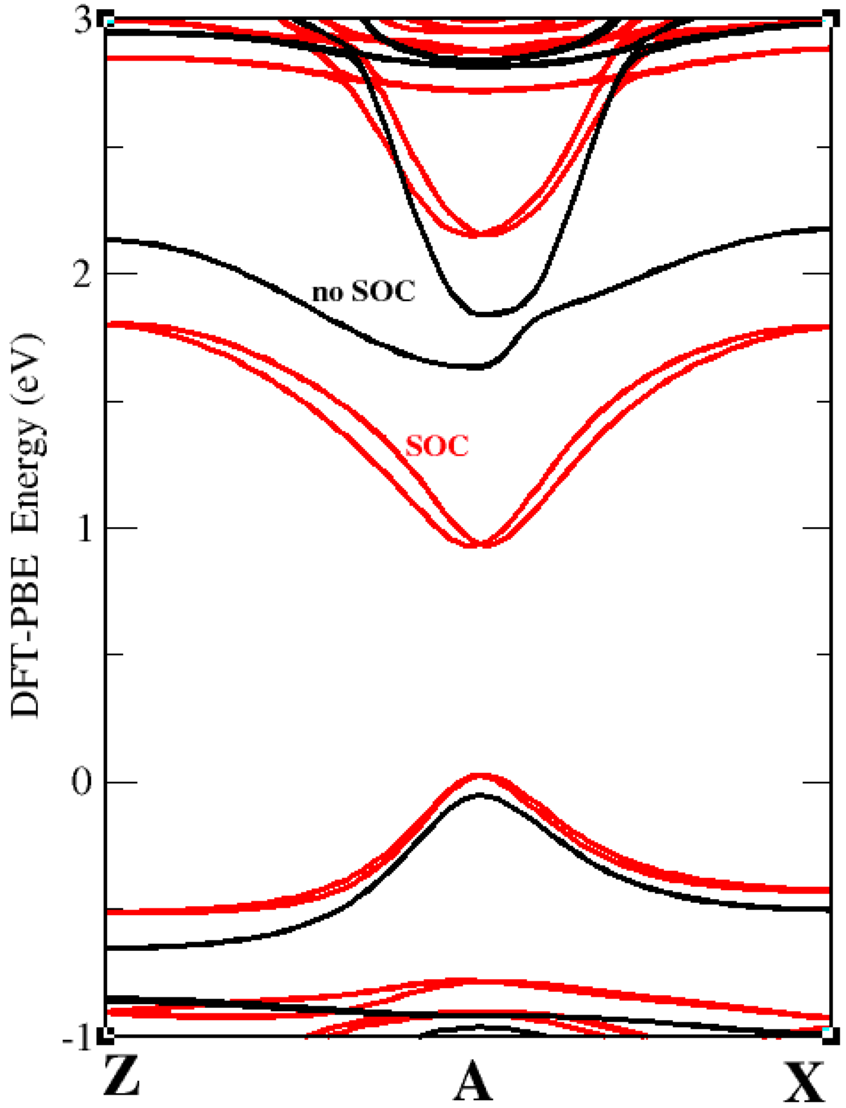
Soumpos at al Chem. Mater., 2016

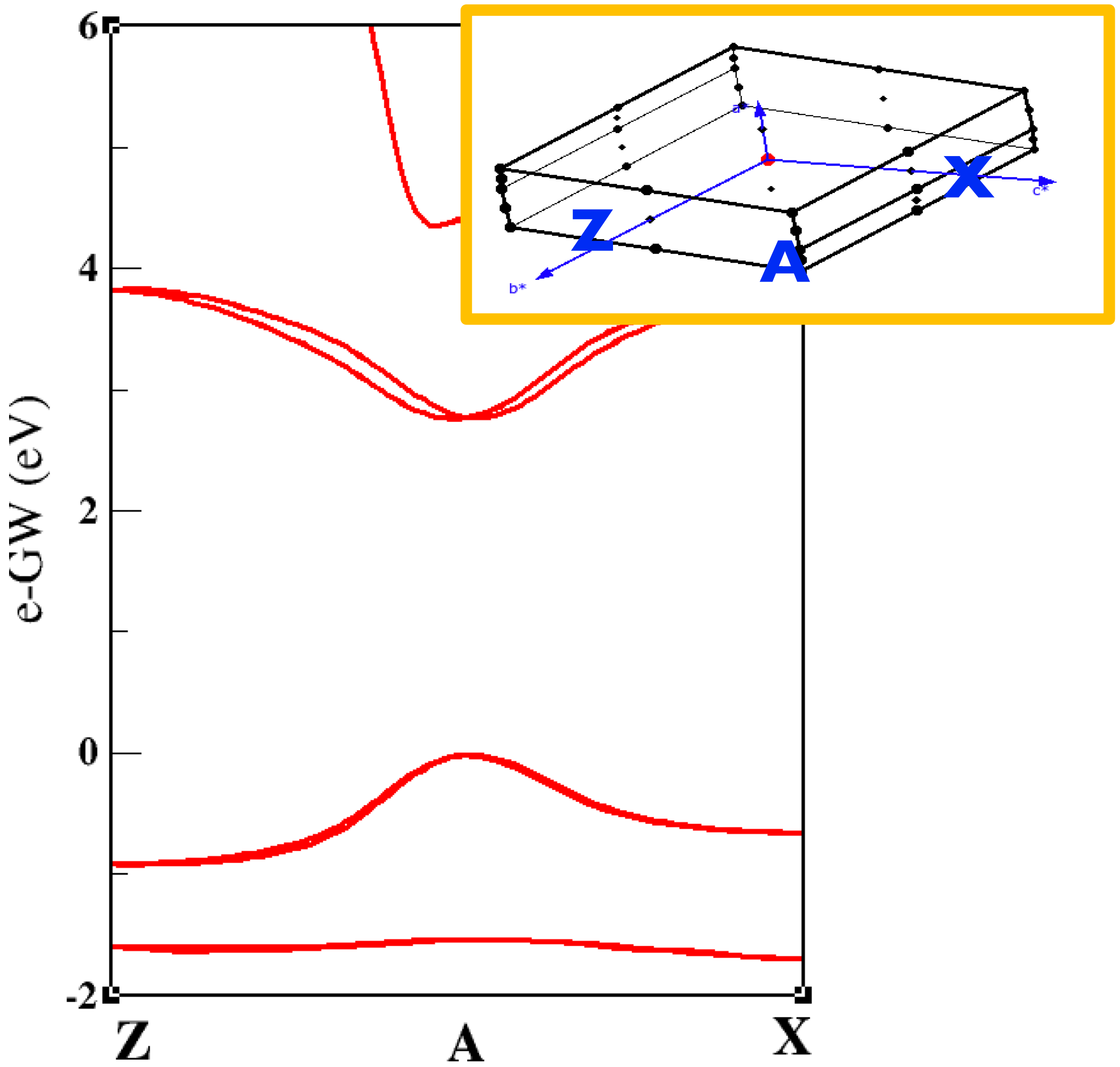
G.Giorgi, K. Yamashita, MP. JPCL 2018

2D layered hybrid halide perovskites: PEA_2PbI_4



C2/m Monoclinic
J. Calabrese
JACS 1991
&
F. Thouin et al
Nat Mat 2019

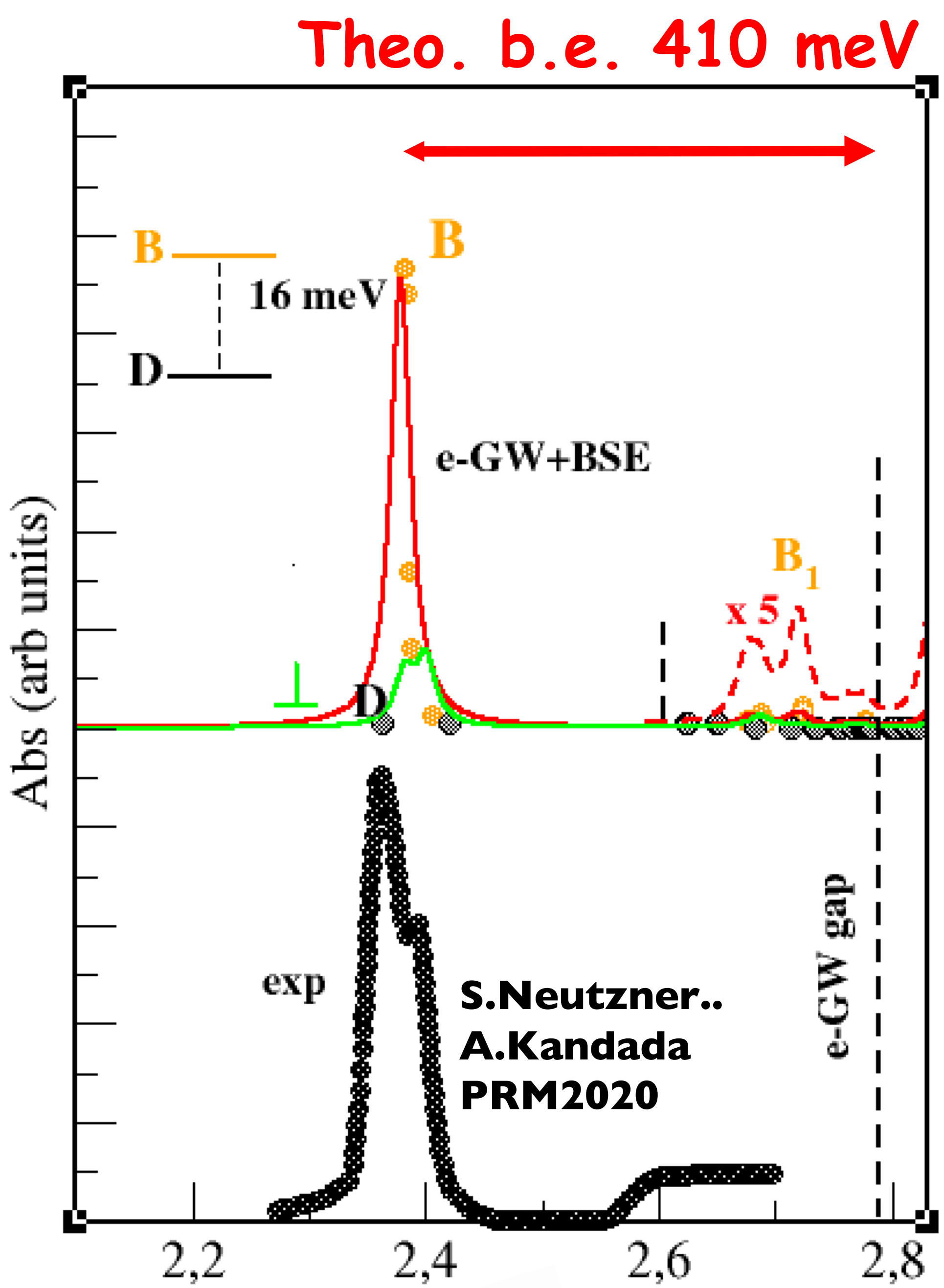


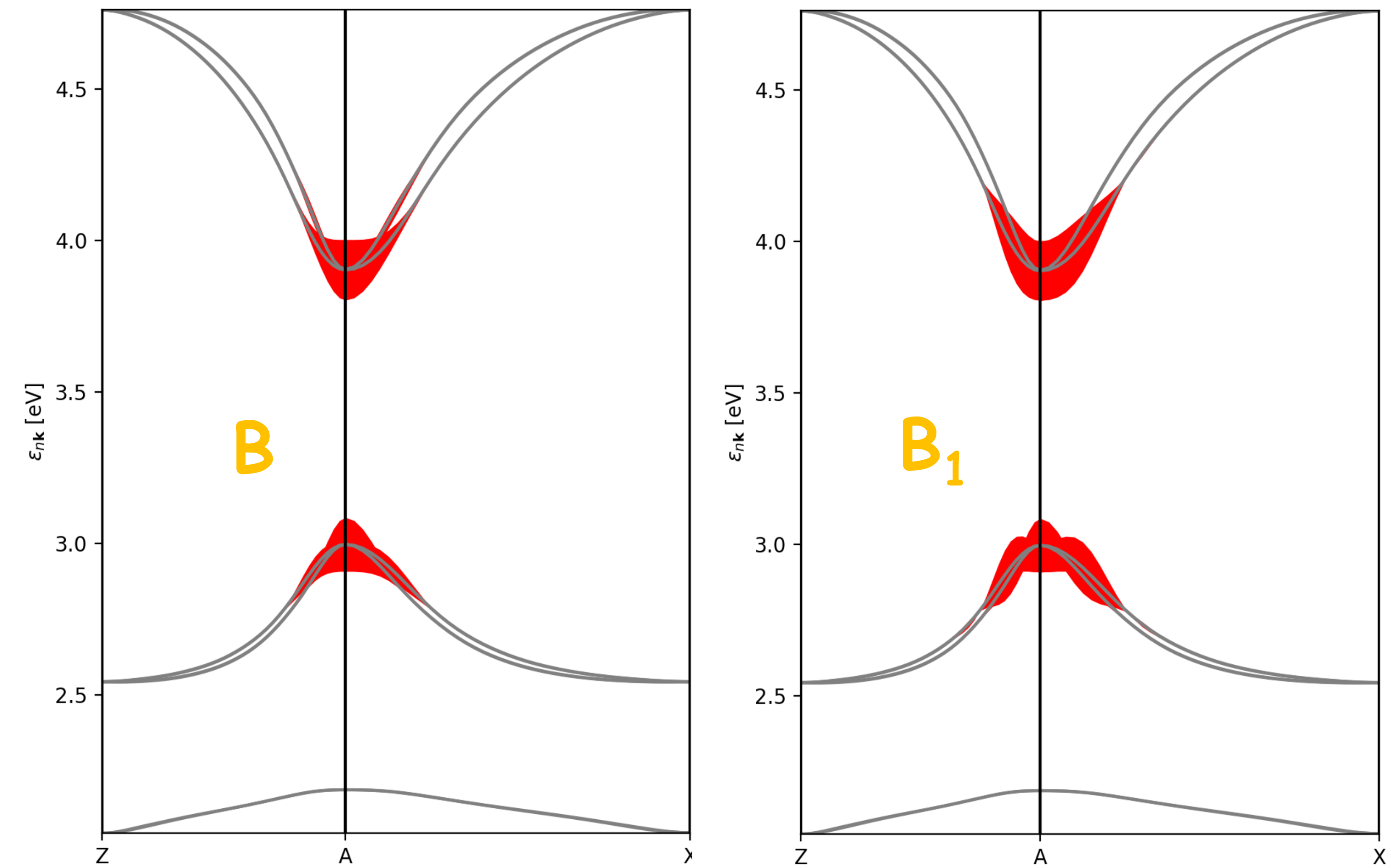


- ✓ **Valence : p of I + s of Pb, Conduction: p of Pb** (from pDOS not shown)
- ✓ **Strong influence of SOC both in VB & CB**
- ✓ **e-GW gap (with SOC) > about 1.5 eV of DFT-KS (with SOC)**

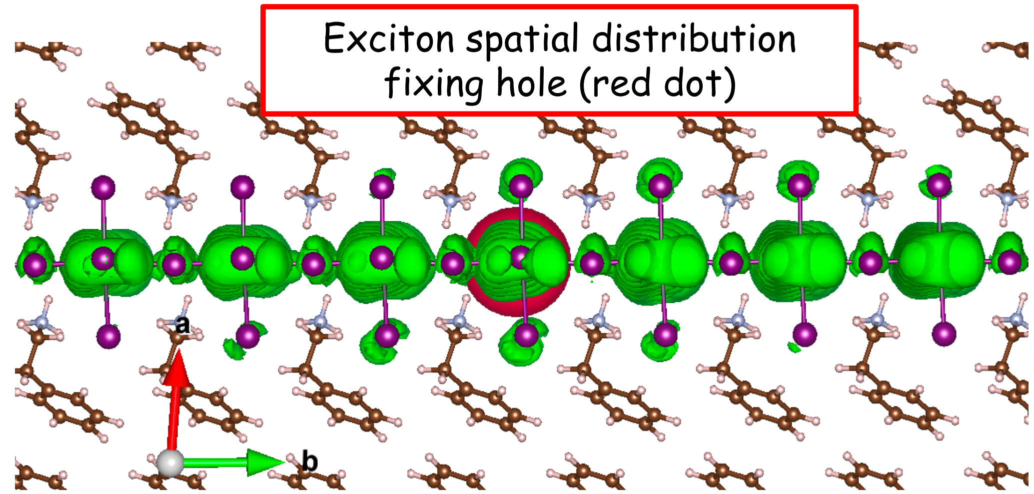
2D layered hybrid halide perovskites: PEA_2PbI_4

Theo. b.e. 410 meV





Exciton spatial distribution fixing hole (red dot)



Science Advances 07 Feb 2020:

Bright magnetic dipole radiation from two-dimensional lead-halide perovskites

Ryan A. DeCrescent, Naveen R. Venkatesan, Clayton J. ..., Rhys M. Kennard, Xie Zhang, Wen... Li, Xinhong Du, Michael L. Chabinyc, Rashid Zia and ...

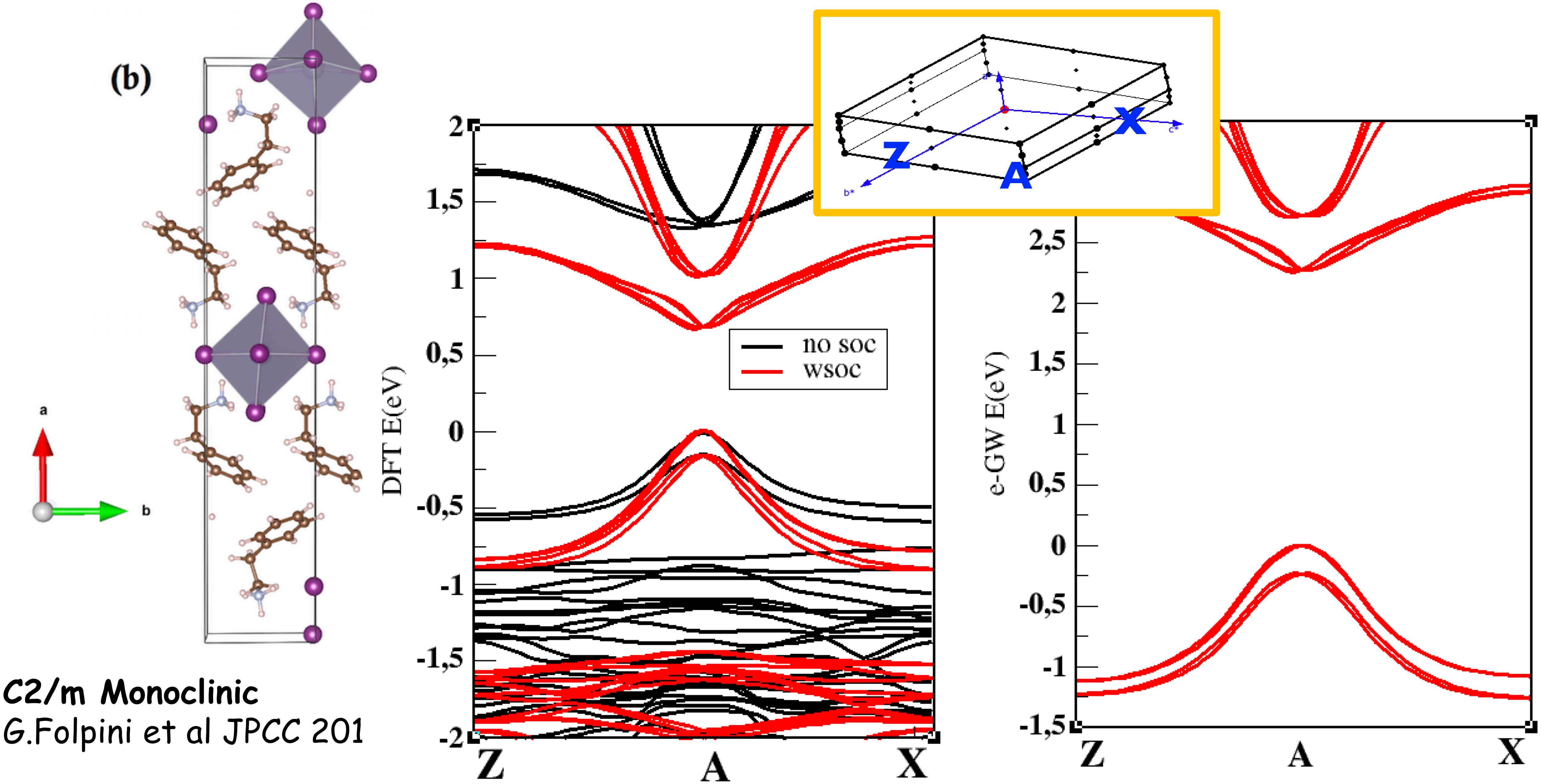
ACS Photonics 2018, 5, 10, 4179–4185

Tunable Out-of-Plane Excitons in 2D Single-Crystal Perovskites

Antonio Fieramosca, Luisa De Marco*, Marco Passoni, Laura Polimeno, Aurora Rizzo, Barbara L. T. Rosa, Giuseppe Cruciani, Lorenzo Dominici, Milena De Giorgi, Giuseppe Gigli, Lucio C. Andreani, Dario Gerace*, Dario Ballarini*, and Daniele Sanvitto

Strong out-of-plane exciton

2D layered hybrid halide perovskites: PEA_2SnI_4

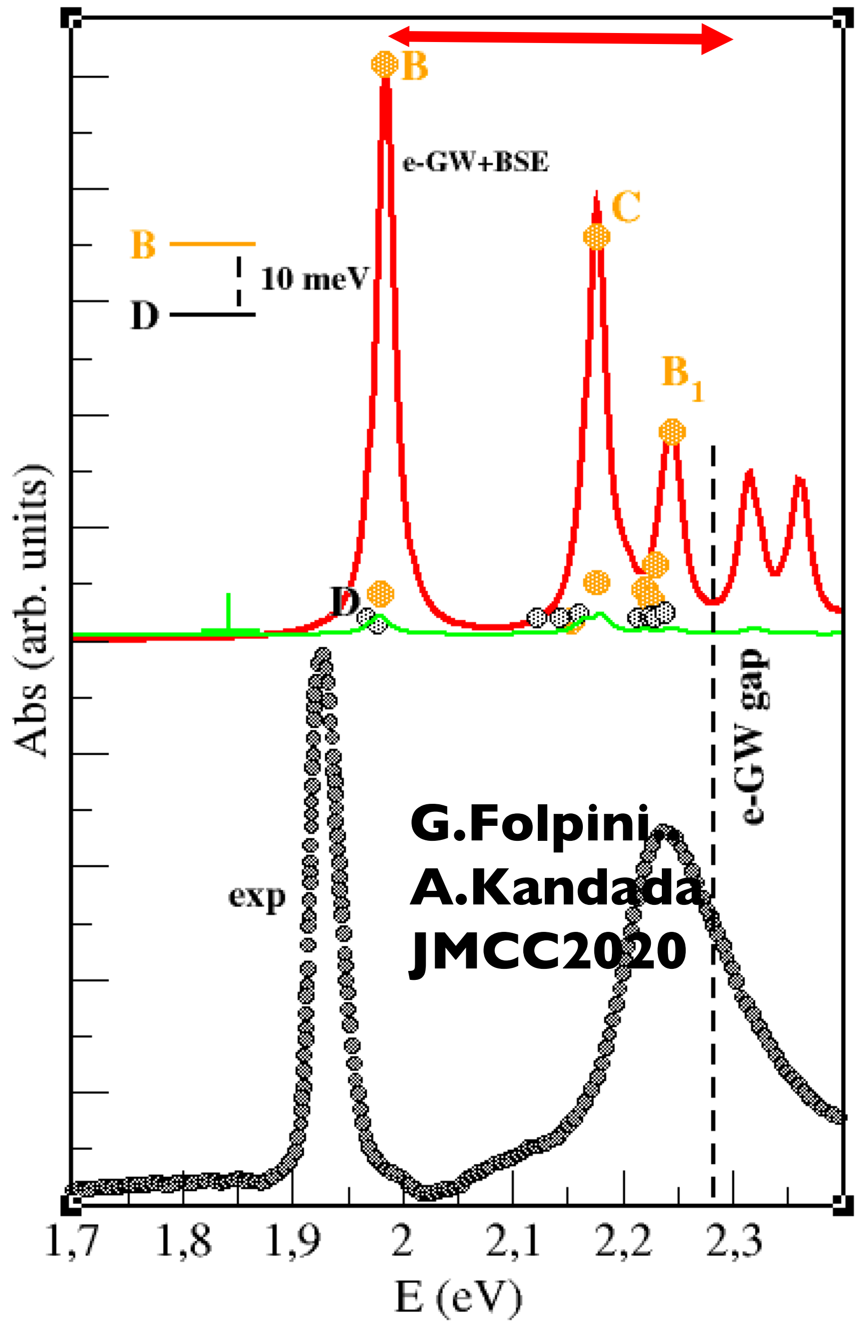


C2/m Monoclinic
G.Folpini et al JPCC 201

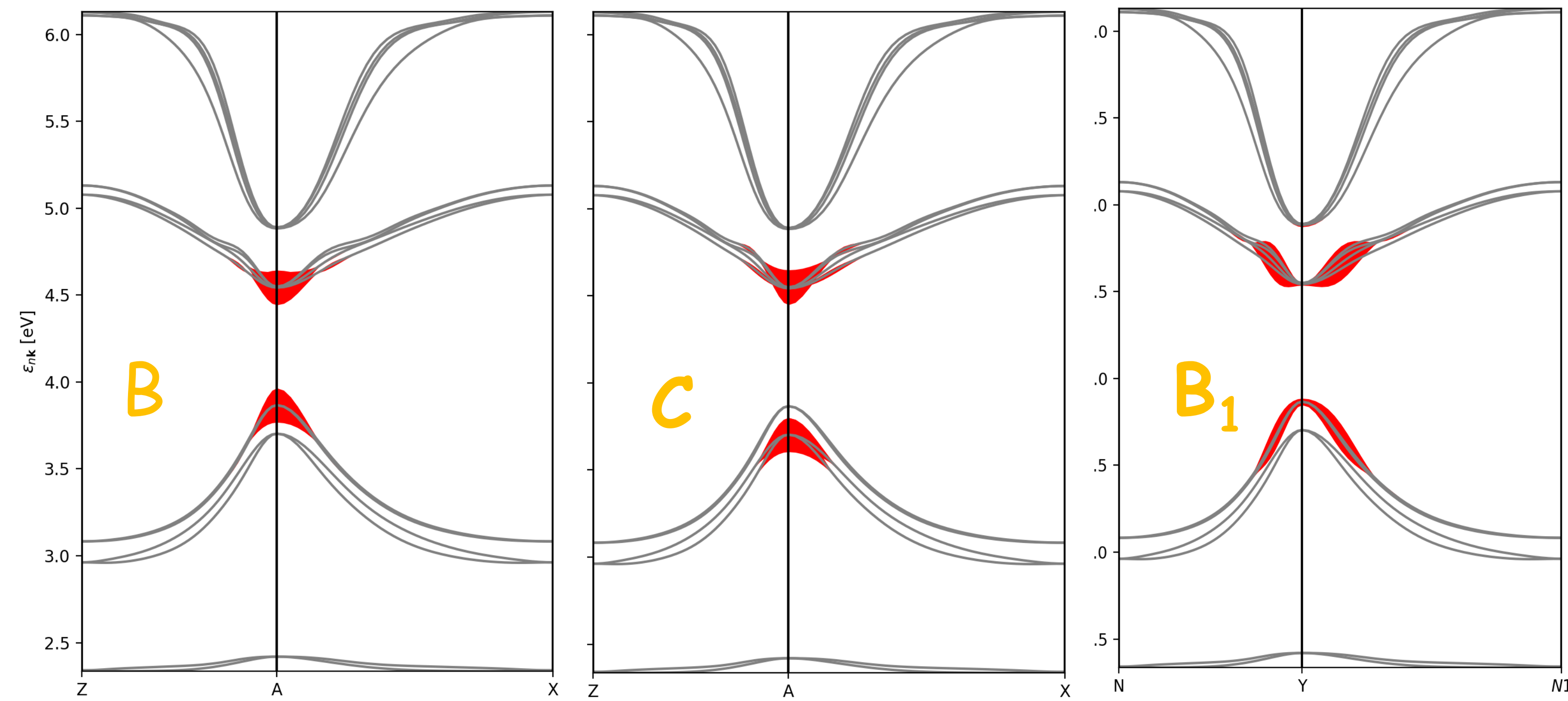
- ✓ **Valence : p of I, Conduction : p of Sn** (from pDOS not shown)
- ✓ **Splittings due to SOC < than for the case of Pb**
- ✓ **e-GW gap (with SOC) >> DFT-KS (with SOC)**

2D layered hybrid halide perovskites: PEA_2SnI_4

Theo. b.e. 300 meV



out-of-plane exciton < of PEA_2PbI_4



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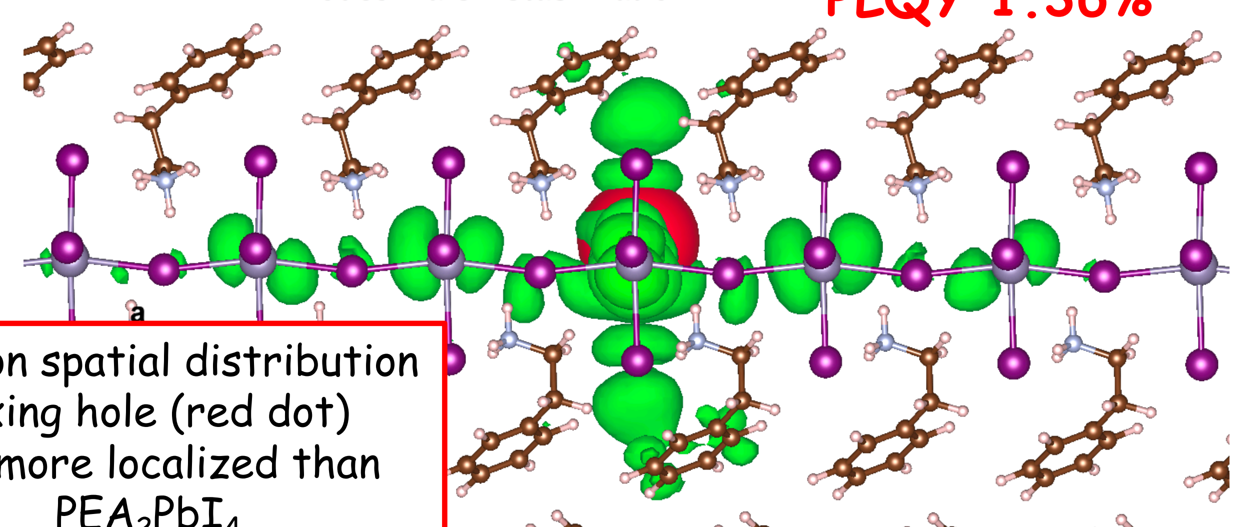

Exciton spatial distribution fixing hole (red dot) e-h more localized than PEA_2PbI_4

G. Folpini , M.Palummo, .. G. Giorgi A. Kandada in preparation

Conclusions

With a lot of HPC resources and a lot of patience to converge GW+BSE results, useful info regarding quasi-particles and excitons in layered/2D materials can be obtained

But there are 2 lacking important ingredients in what I have shown

EXCITON-phonon

Theory of phonon-assisted luminescence in solids: Application to hexagonal boron nitride

E. Cannuccia, B. Monserrat, and C. Attaccalite
Phys. Rev. B **99**, 081109(R) – Published 8 February 2019

Exciton-Phonon Coupling in the Ultraviolet Absorption and Emission Spectra of Bulk Hexagonal Boron Nitride

Fulvio Paleari, Henrique P. C. Miranda, Alejandro Molina-Sánchez, and Ludger Wirtz
Phys. Rev. Lett. **122**, 187401 – Published 7 May 2019

Exciton-Phonon Interaction and Relaxation Times from First Principles

Hsiao-Yi Chen, Davide Sangalli, and Marco Bernardi
Phys. Rev. Lett. **125**, 107401 – Published 31 August 2020

EXCITON dynamics - non-equilibrium Green functions approach

Nonequilibrium optical properties in semiconductors from first principles: A combined theoretical and experimental study of bulk silicon

Davide Sangalli, Stefano Dal Conte, Cristian Manzoni, Giulio Ce
Phys. Rev. B **93**, 195205 – Published 13 May 2016

First-principles approach to excitons in time-resolved and angle-resolved photoemission spectra

E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci
Phys. Rev. B **94**, 245303 – Published 6 December 2016

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Ab Initio Calculations of Ultrashort Carrier Dynamics in Two-Dimensional Materials: Valley Depolarization in Single-Layer WSe_2

Alejandro Molina-Sánchez[*†⊥], Davide Sangalli[‡], Ludger Wirtz[†], and Andrea Marini[‡]

Many-body perturbation theory calculations using the yambo code

D Sangalli[1,16], A Ferretti[2,16], H Miranda[3], C Attaccalite[4,16], I Marri[2], E Cannuccia[5,6], P Melo[7,16], M Marsili[8], F Paleari[9], A Marrazzo[10], G Prandini[10], P Bonfà[11], M O Atambo[2,12], F Affinito[11], M Palummo[5,16], A Molina-Sánchez[13], C Hogan[5,14,16], M Grüning[15,16], D Varsano[2,16] and A Marini[1,16] — Hide full author list

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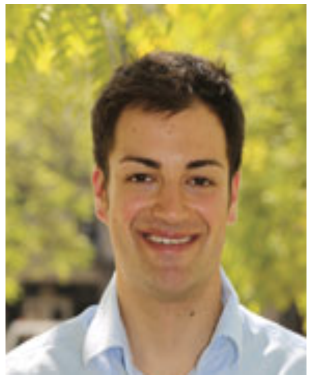

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THANK YOU FOR ATTENTION!