Bulk doping effects in hybrid organic/ inorganic systems from quantum mechanical first principles

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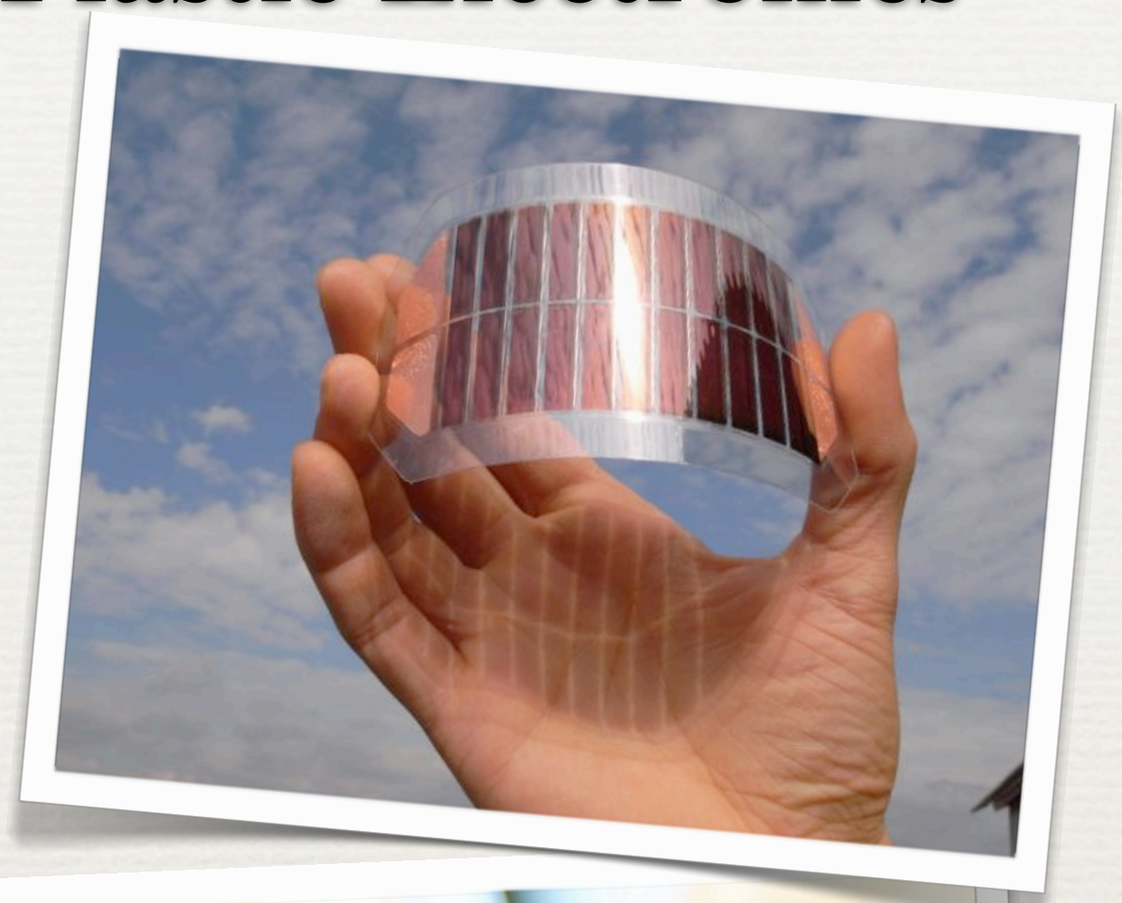
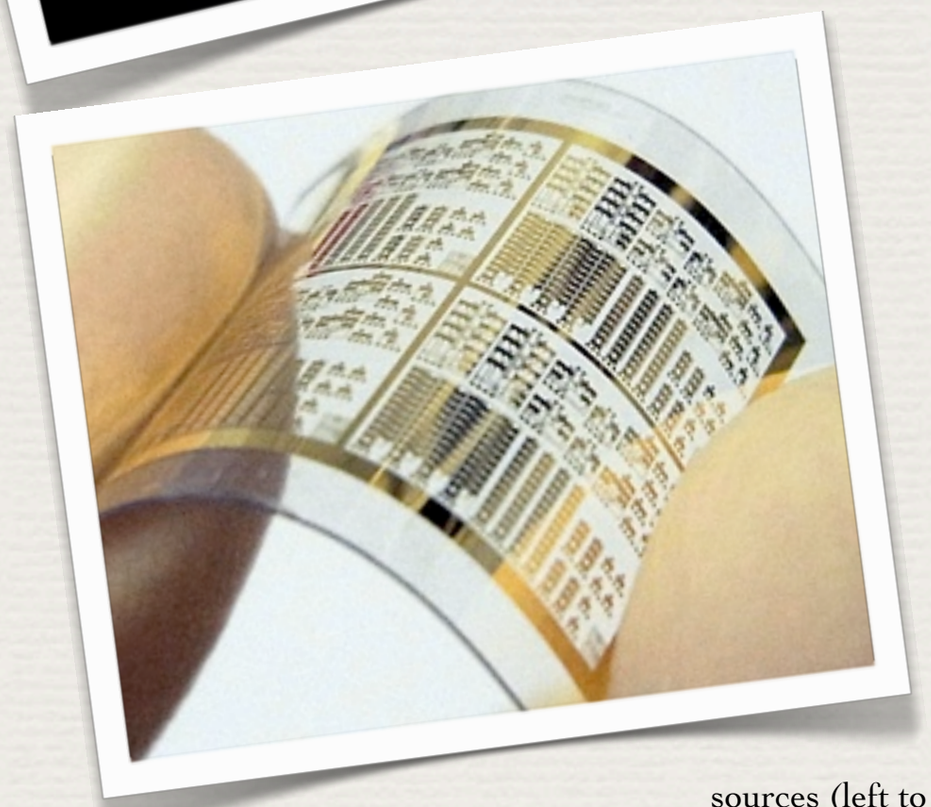
MAX-PLANCK-GESELLSCHAFT

HIOS

Unterstützt von / Supported by
Alexander von Humboldt
Stiftung/Foundation

Organic Electronics - Plastic Electronics





sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Organic Electronics - Plastic Electronics

Inorganic/organic interfaces are already present...

... and affect or determine device properties.

Can we understand and control them?

sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Hybrid Inorganic/Organic Interfaces (HIOS)

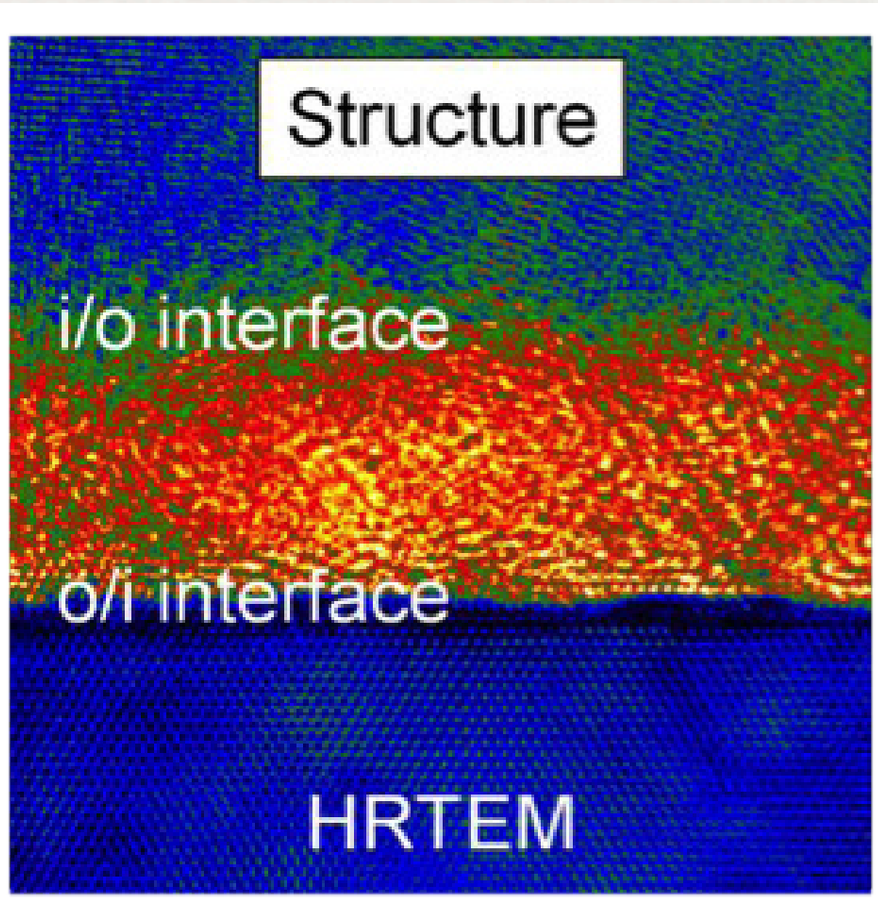
Combine the best of two worlds...

Hybrid electronics:
- make interface central

inorganic materials:
- stable crystal structures
- good growth control
- high charge carrier mobilities

organic materials:
- strong light matter coupling
- large chemical compound space

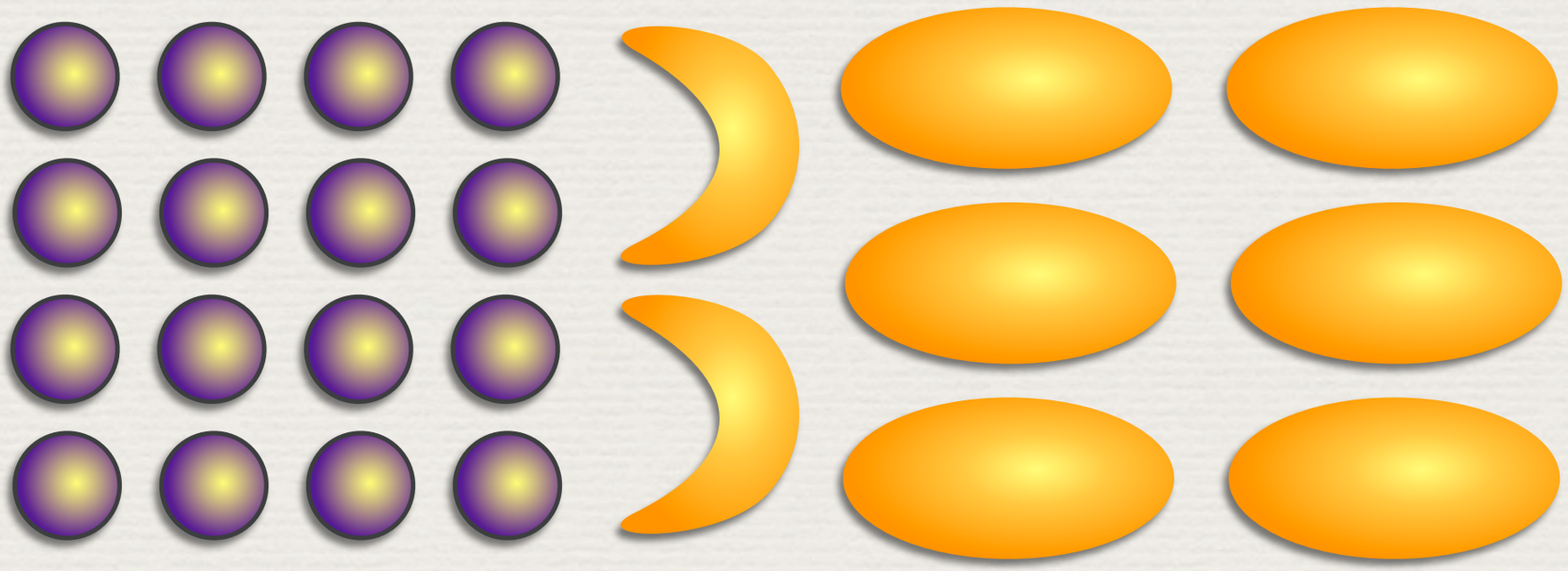
synergy or more!



ZnO/p-sexiphenyl
(courtesy of S. Blumstengel)

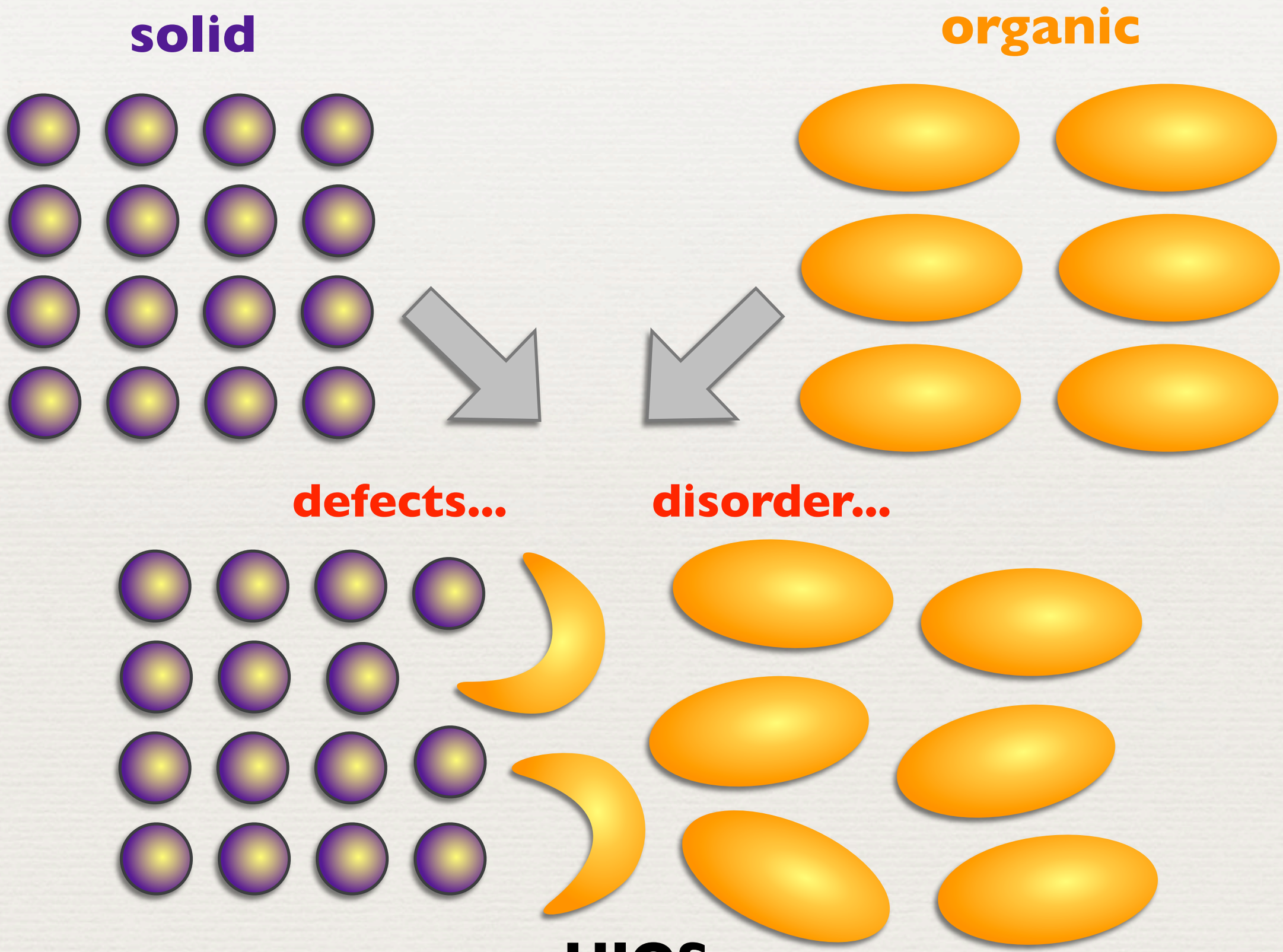
Potential for new physics at HIOS

- potential for new interface morphologies



HIOS

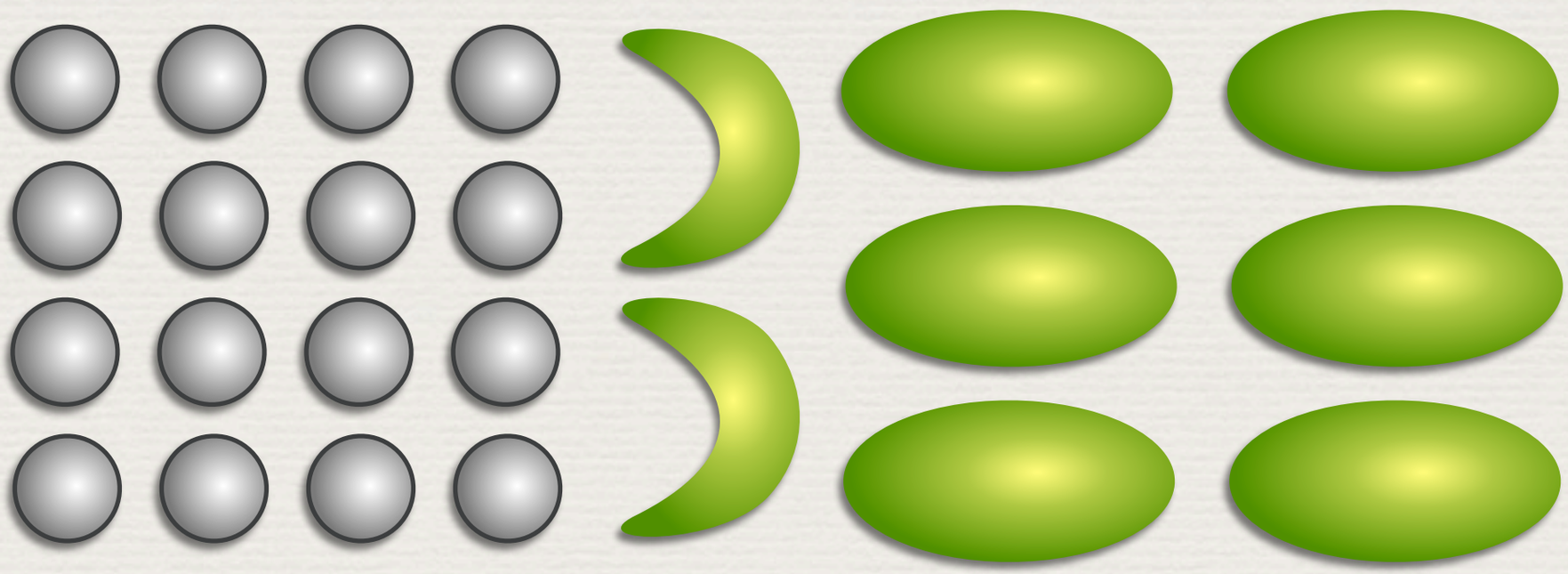
HIOS in reality - defects and disorder



Optimizing HIOS - the right combination

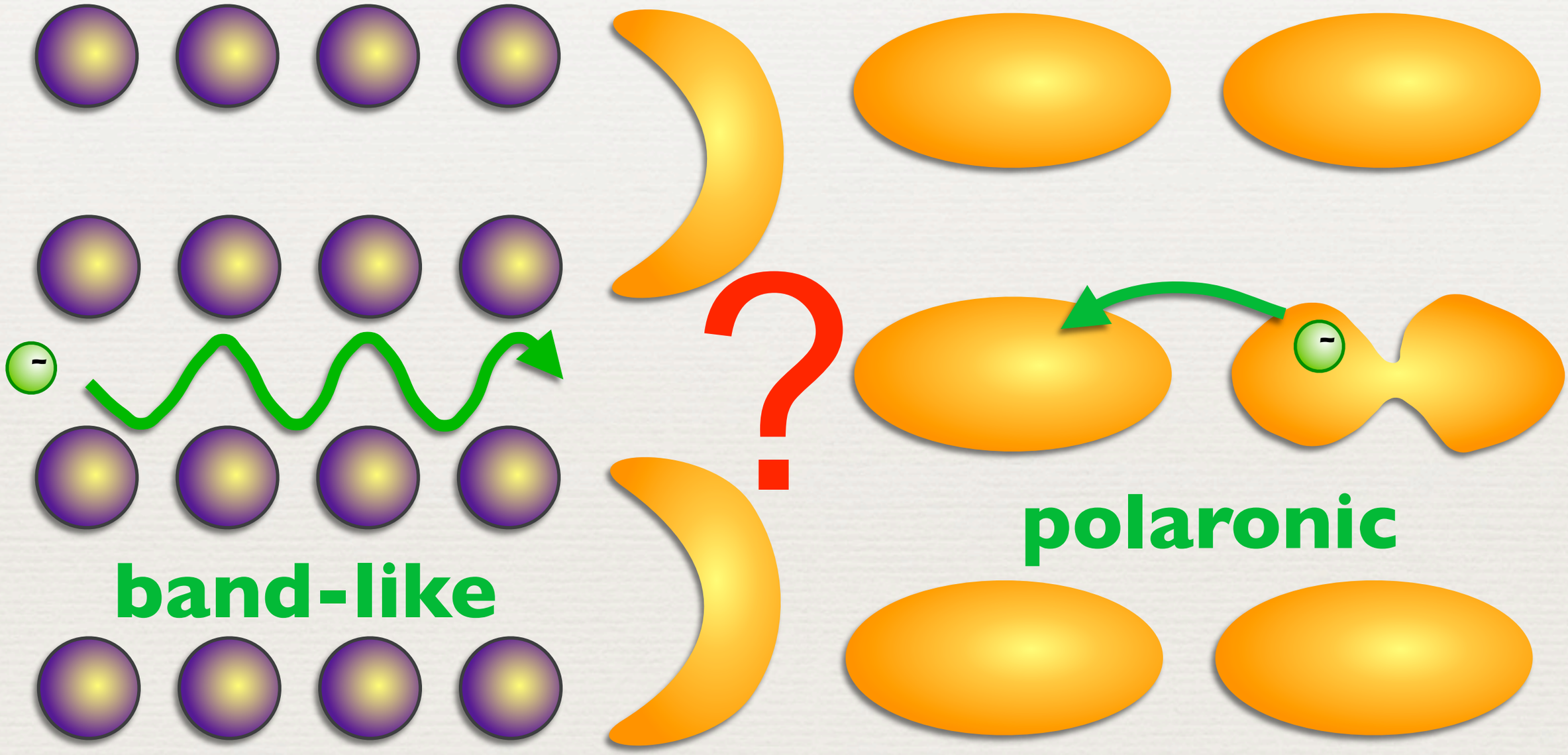
- **What is the right combination?**

- **Vast chemical compound space**



HIOS

Fundamental questions at HIOS interfaces



- **What is the nature of charge carriers?**
- **Do new quasiparticles emerge at interface?**

Atomistic understanding of molecules@surfaces

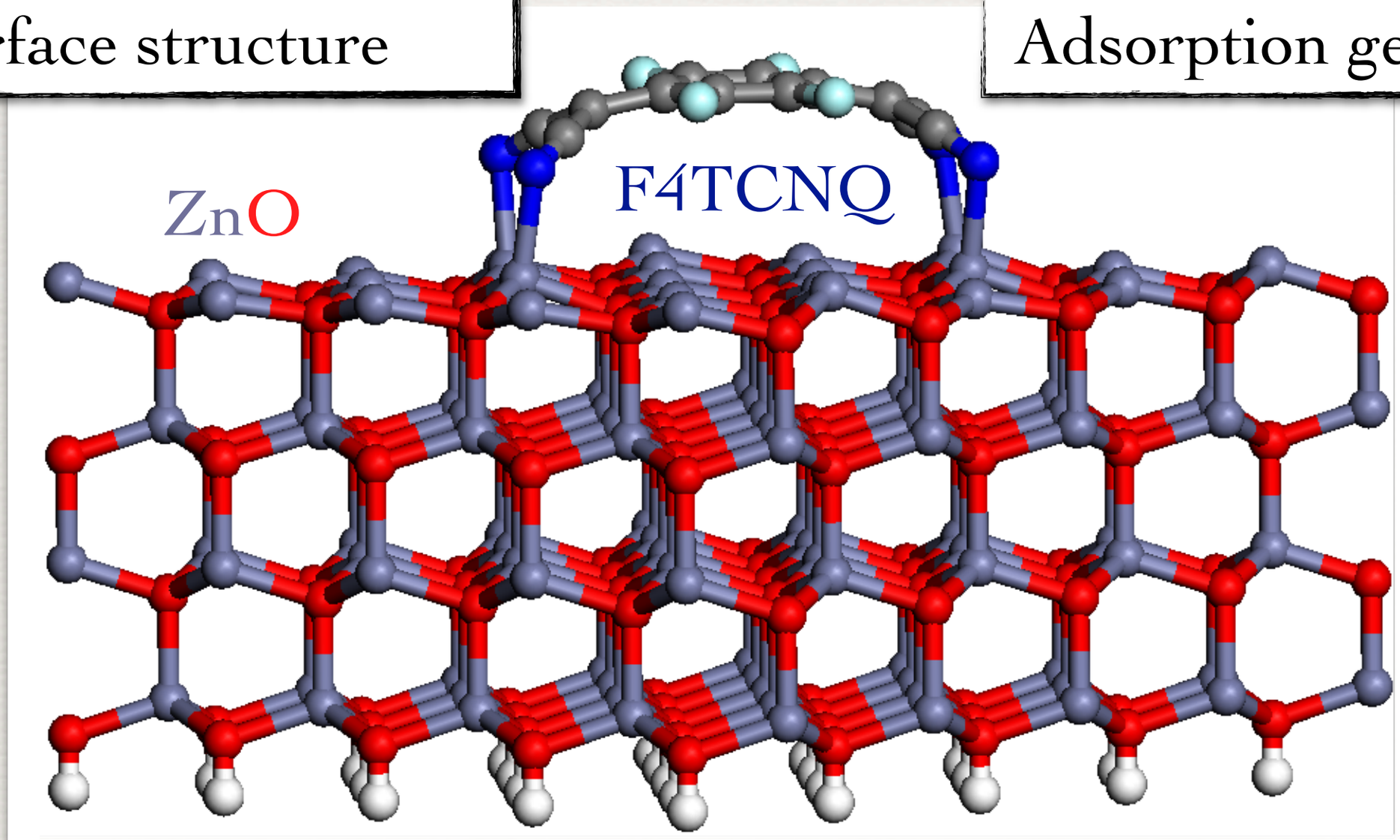
Charge transfer

Level alignment

Van der Waals interaction

Surface structure

Adsorption geometry



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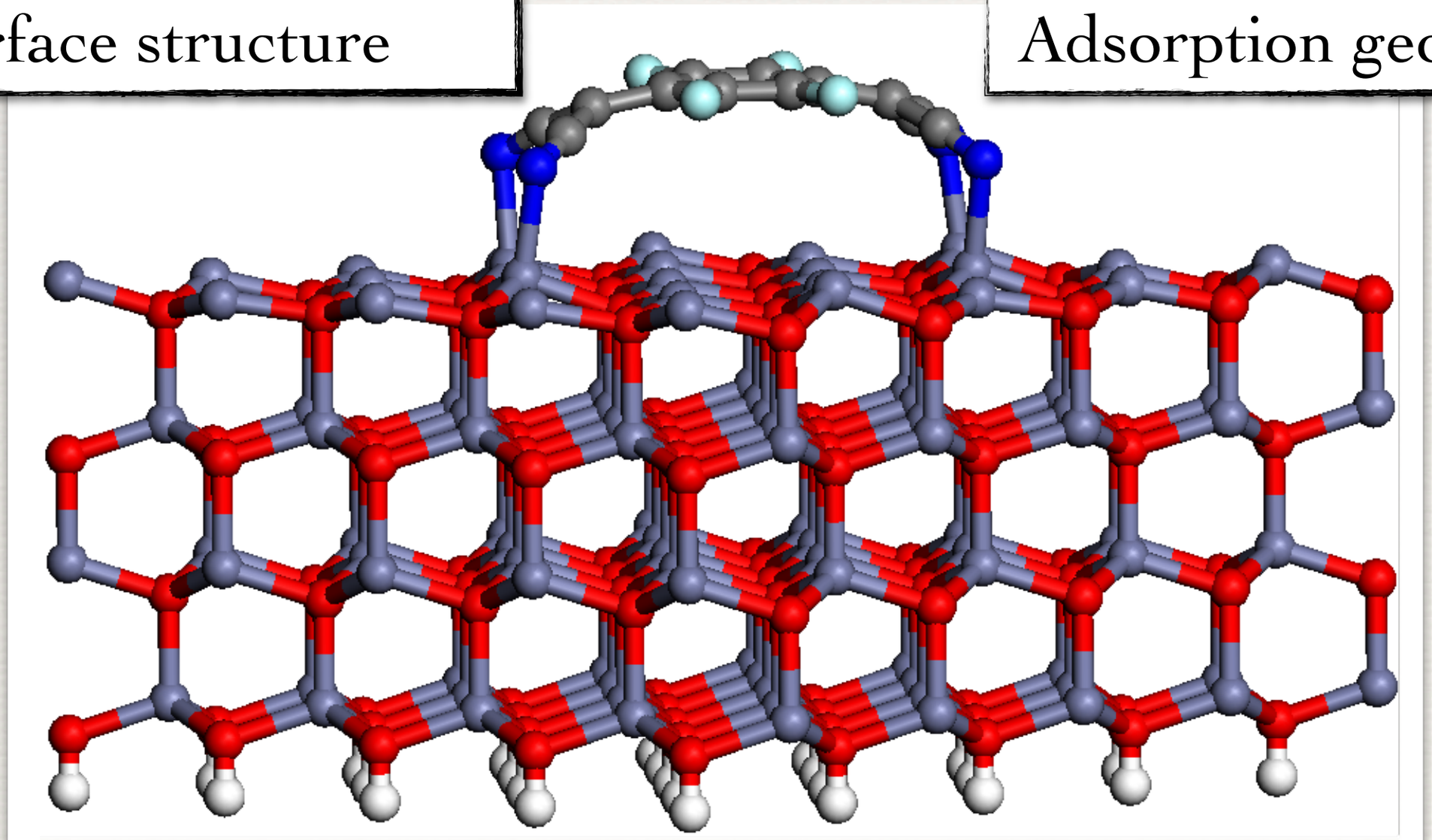
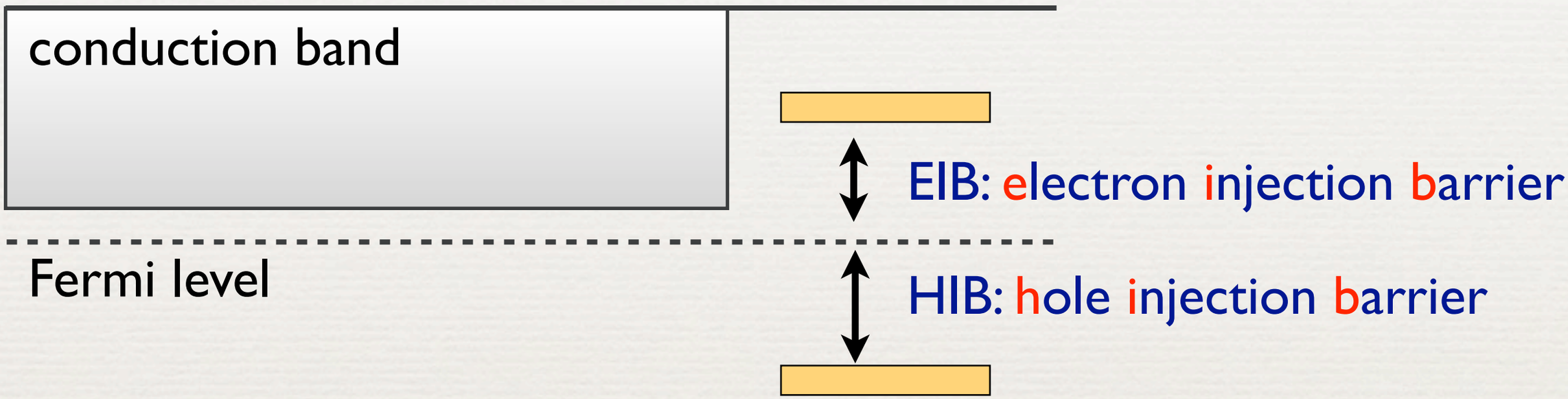


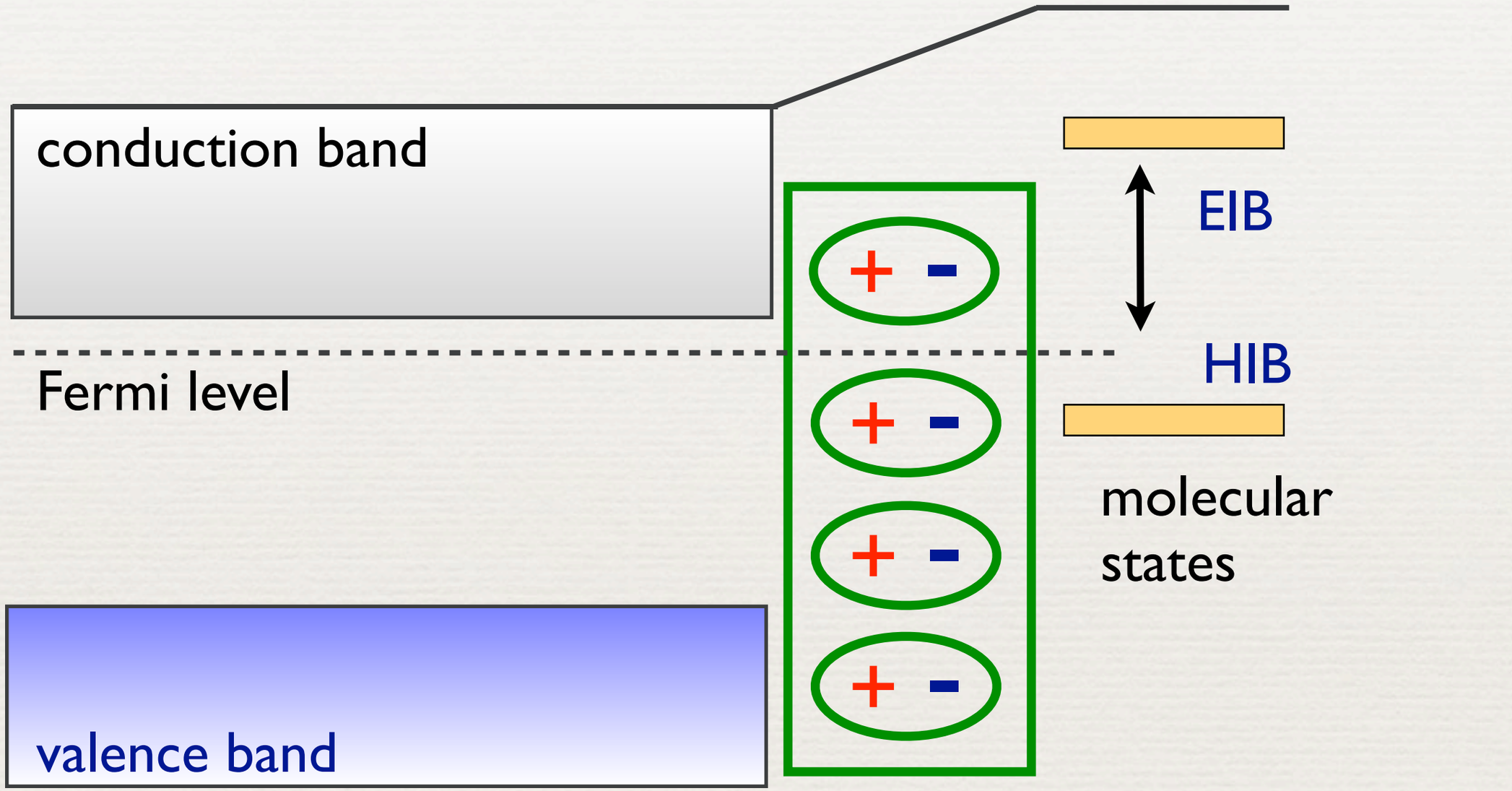
Level alignment at interface



injection limited current:

$$j \propto AT^2 \exp\left(-\frac{\text{charge injection barrier}}{k_B T}\right)$$

Modifying level alignment at interface



interface layer to adjust level alignment

Modifying level alignment at interface

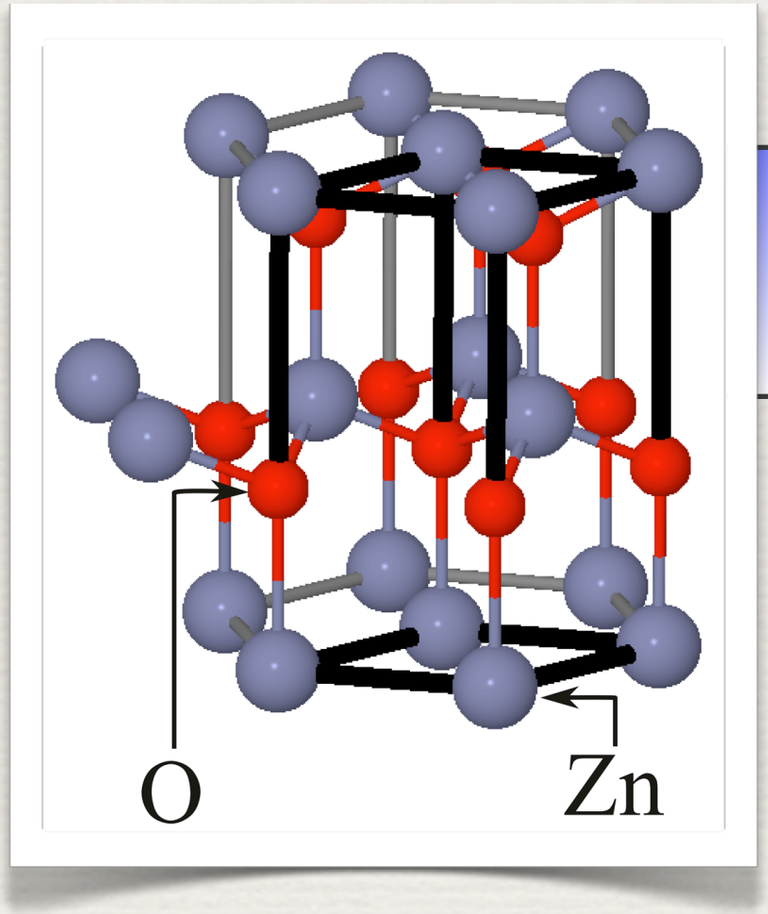
conduction band

Fermi level

EIB

HIB

molecular states

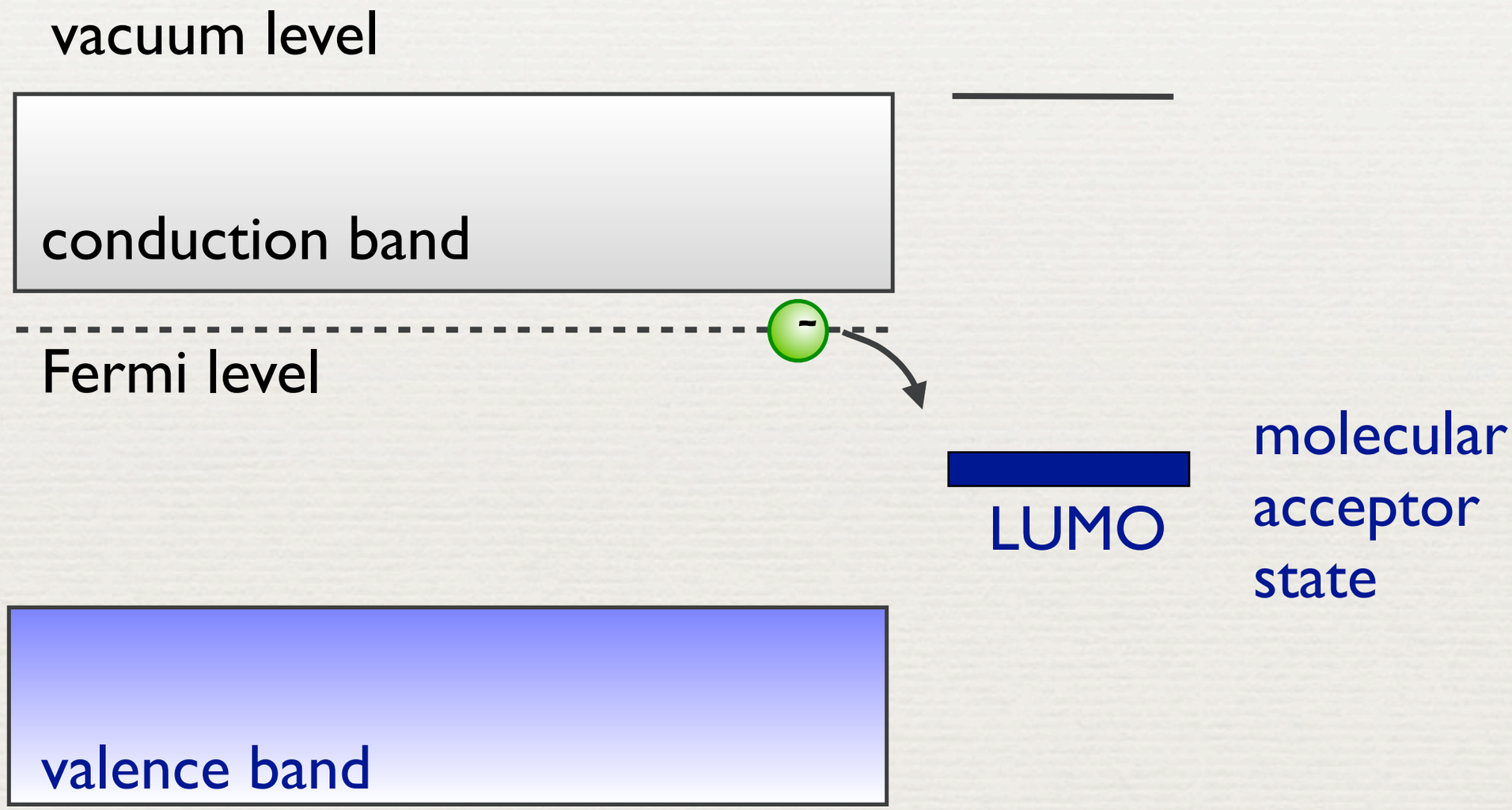


ZnO

e.g. acceptor F4TCNQ (tetrafluoro-tetracyano quinodimethan)

Charge transfer induced work function increase

High doping ⇒ flat bands ⇒ metallic regime



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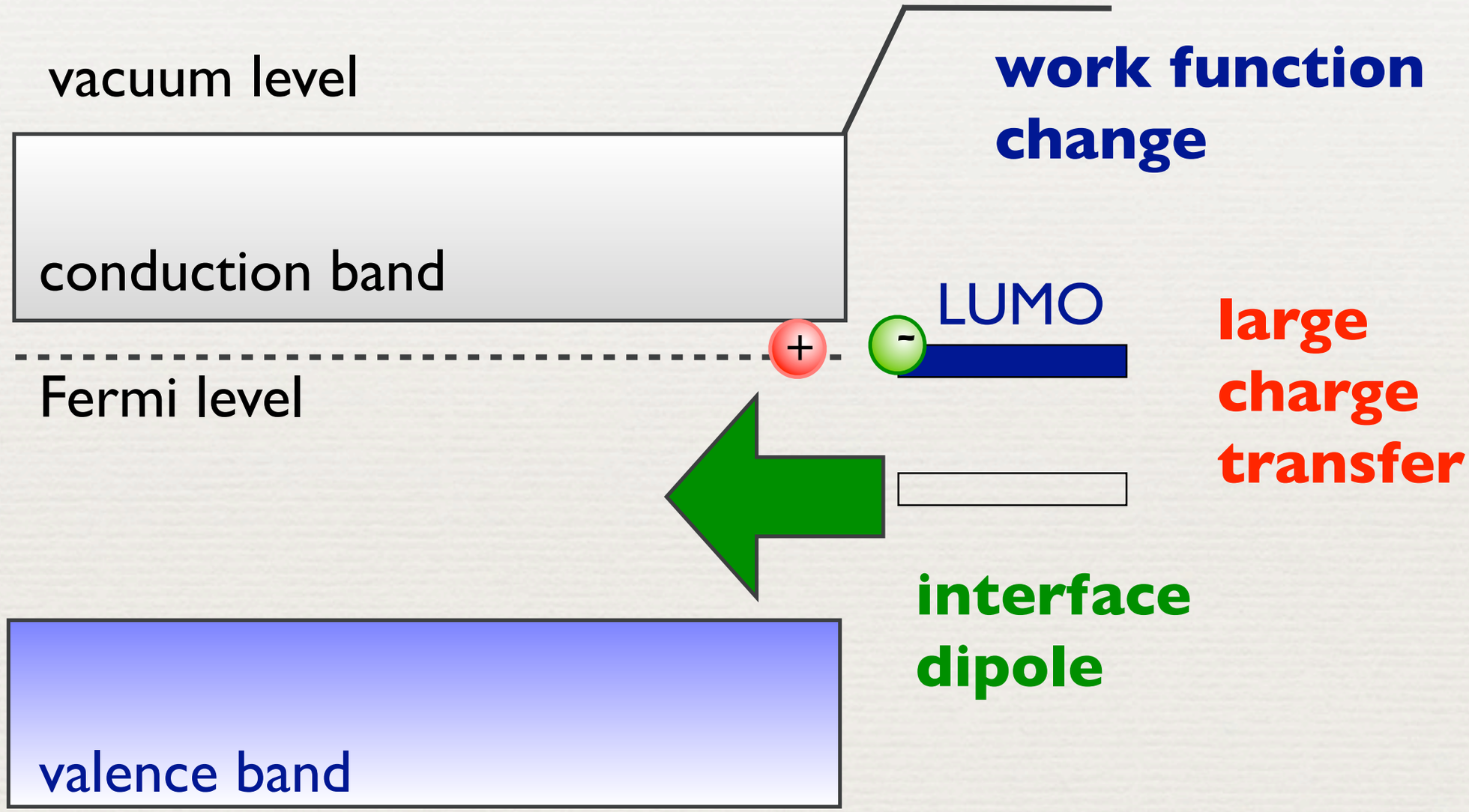
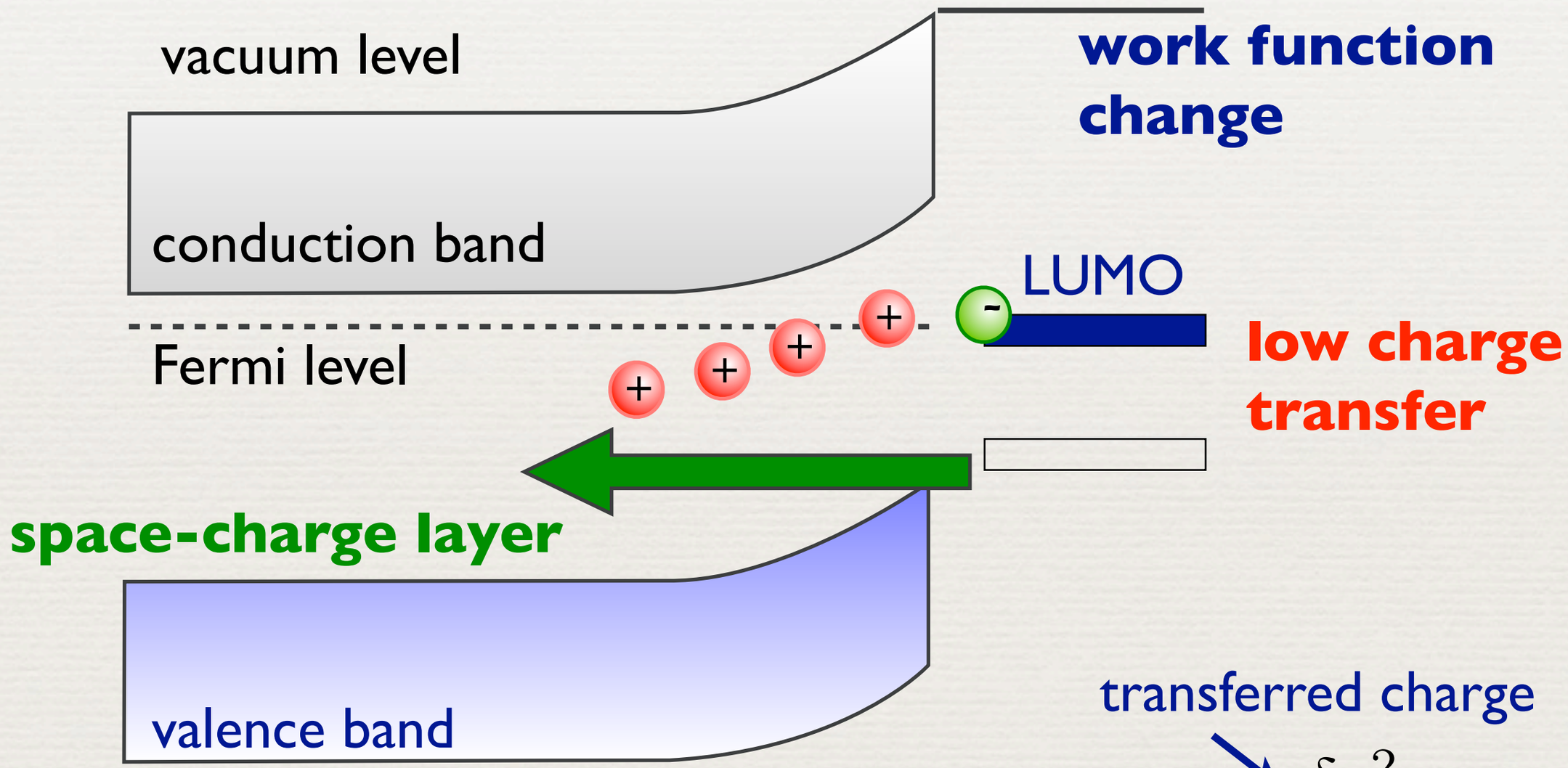


Formation of space-charge layer

low doping ⇒ band bending



macroscopic dimensions:
100nm for $N_D=10^{17}cm^{-3}$

transferred charge

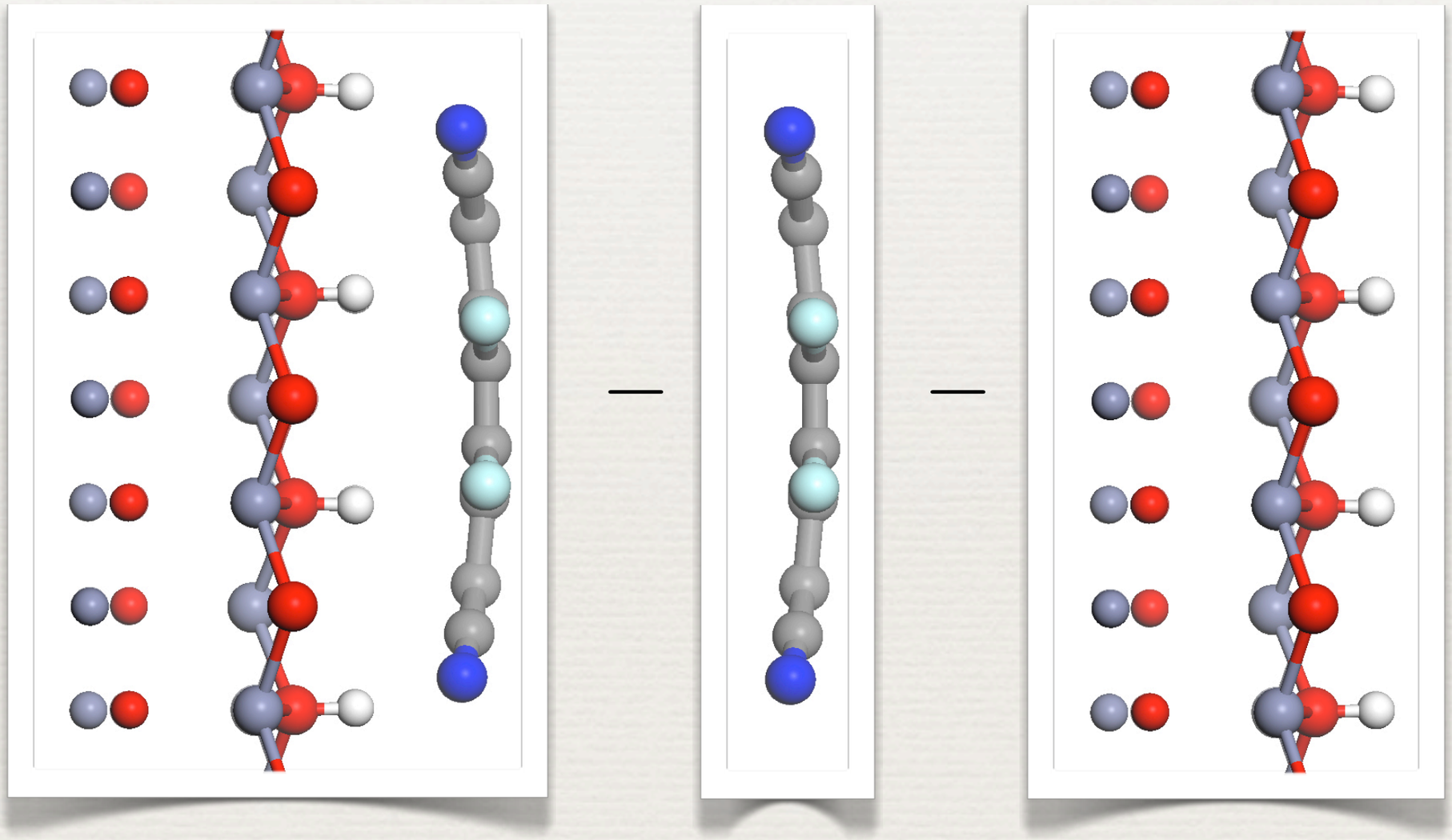
$$\Delta\Phi_{\mathrm{BB}} = \frac{\delta q^2}{2\varepsilon_0\varepsilon N_D}$$

bulk doping concentration

Quantum mechanical treatment

adsorption energy:

$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf}$$



Density-Functional Theory (DFT)

Our Code: FHI-aims [1]

All-electron DFT and beyond code developed in the Fritz-Haber-Institut

- Accurate numerical atomic orbital basis sets:

$$\varphi_i(\vec{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

- Massively scalable, massively parrallel
- DFT functionals: LDA, PBE, hybrids (HSE), ...
- pairwise van der Waals (vdW) scheme [2]:

$$E_{\mathrm{vdW}} = -\sum_{B>A} f_{damp} \frac{C_6^{AB}[n]}{R_{AB}^6}$$

density-dependent C_6 coefficient

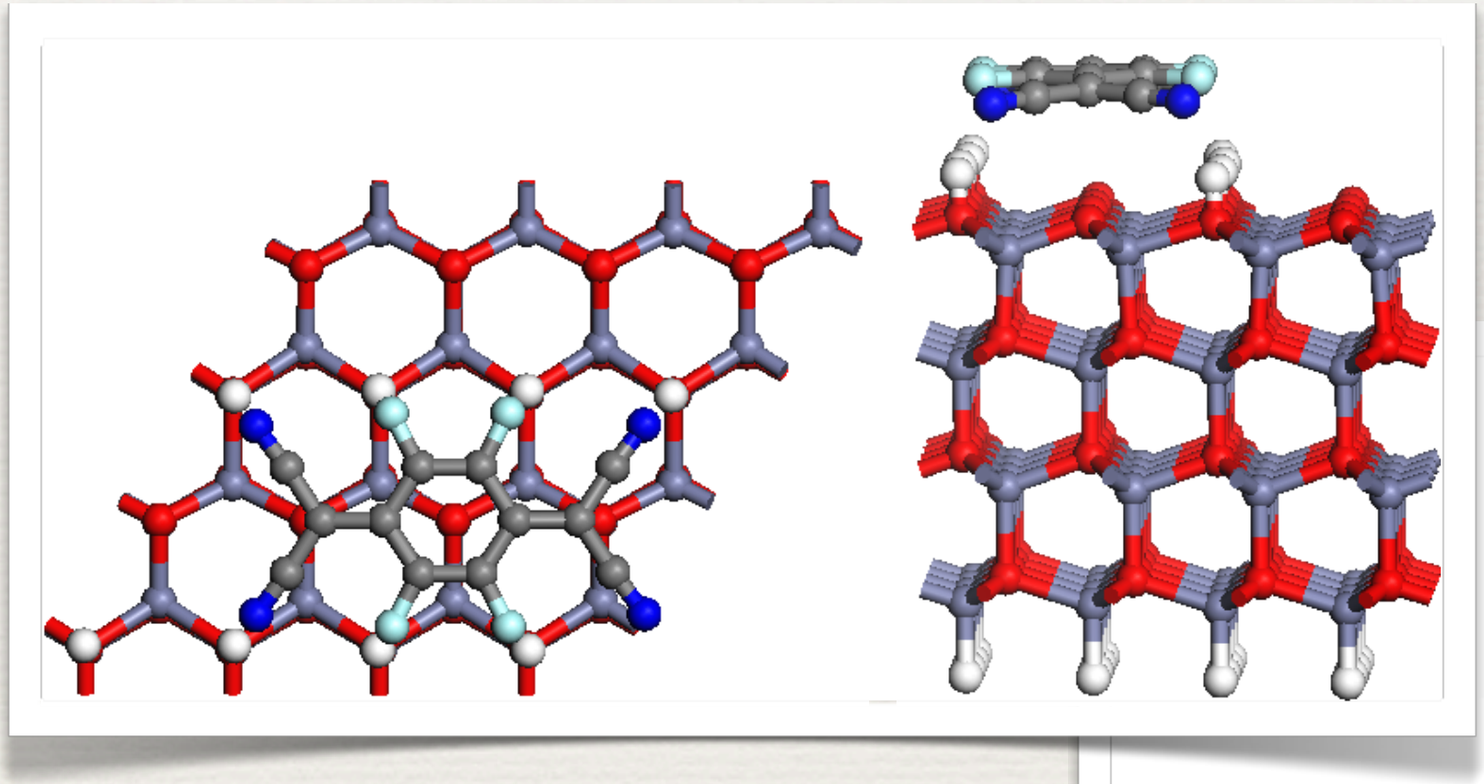
distance between atoms *A* and *B*

[1] V. Blum et al. Comp. Phys. Comm. ***180****, 2175 (2009)*
[2] A. Tkatchenko and M. Scheffler Phys. Rev. Lett. ***102****, 073005 (2009)*

Adsorption geometries and energies

$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf}$$

F4TCNQ on hydrogen terminated ZnO(000-1)

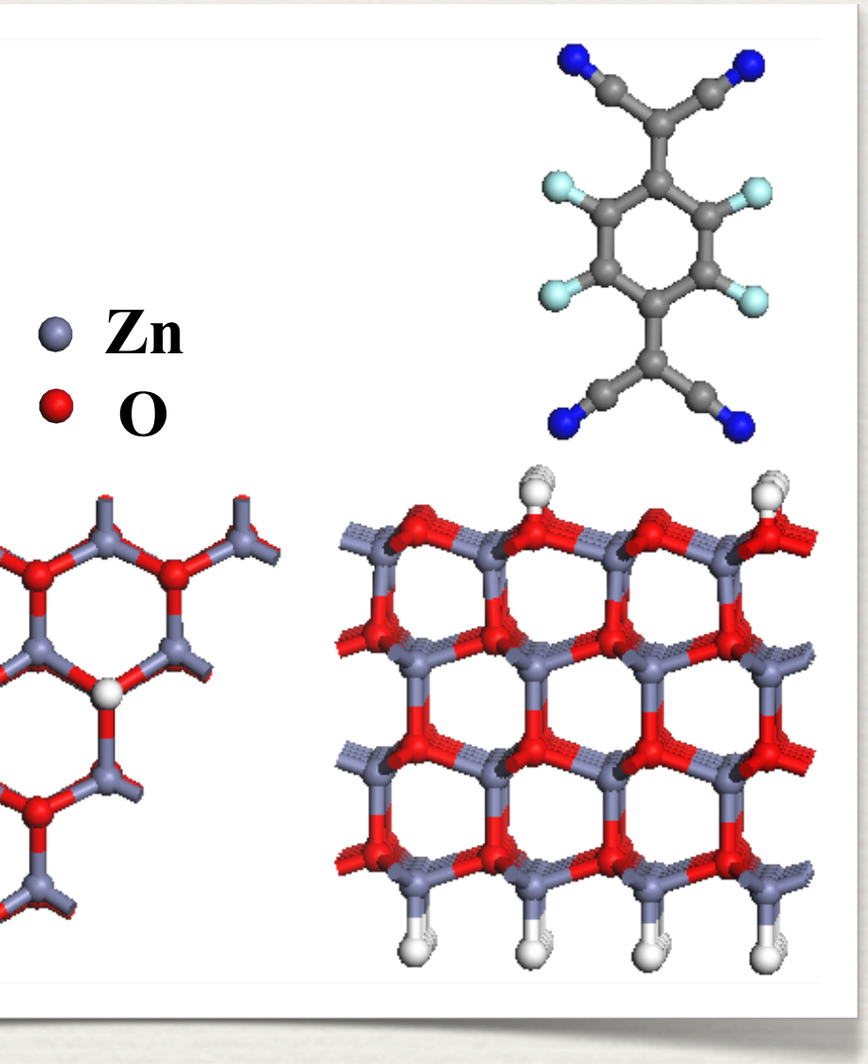


$E^{ads} = 1.84$ eV

flat-lying

upright

$E^{ads} = 0.40$ eV

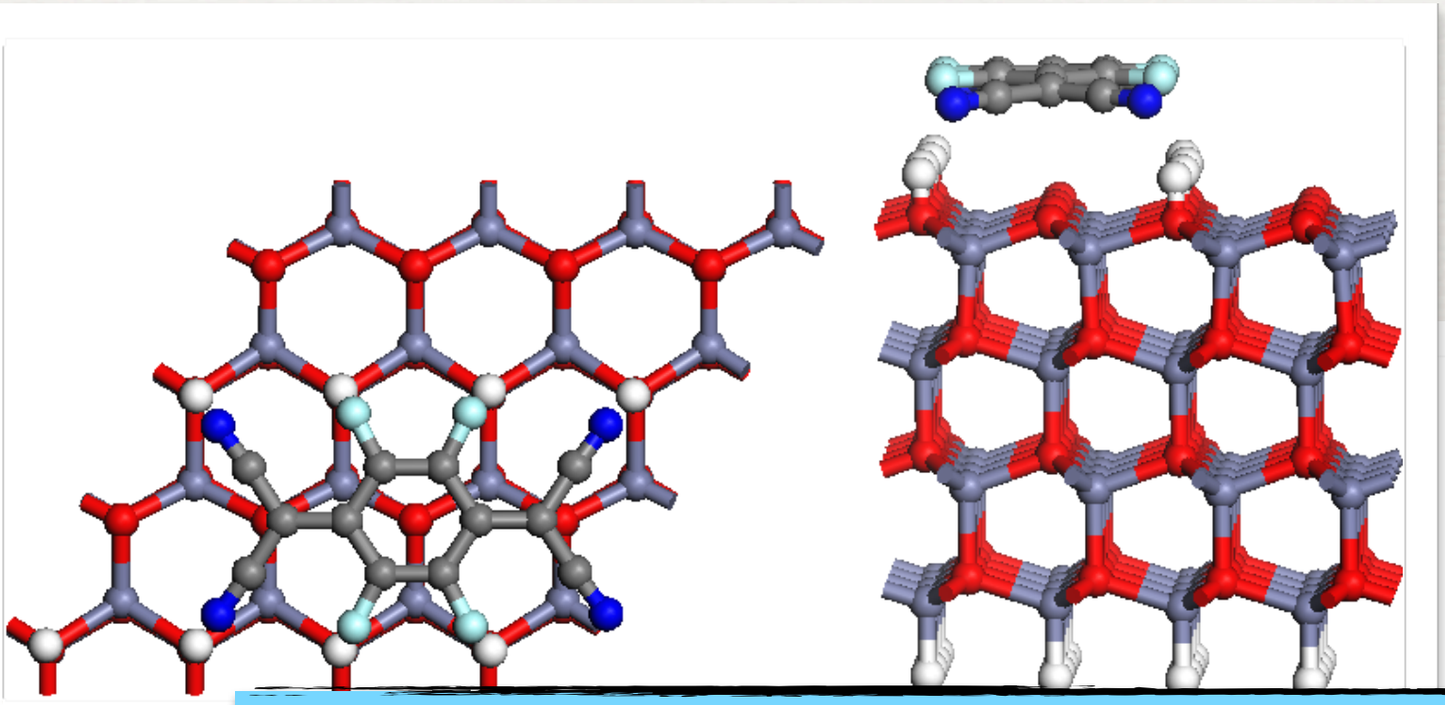


all energies: HSE*+vdW^{scr}

Adsorption geometries and energies

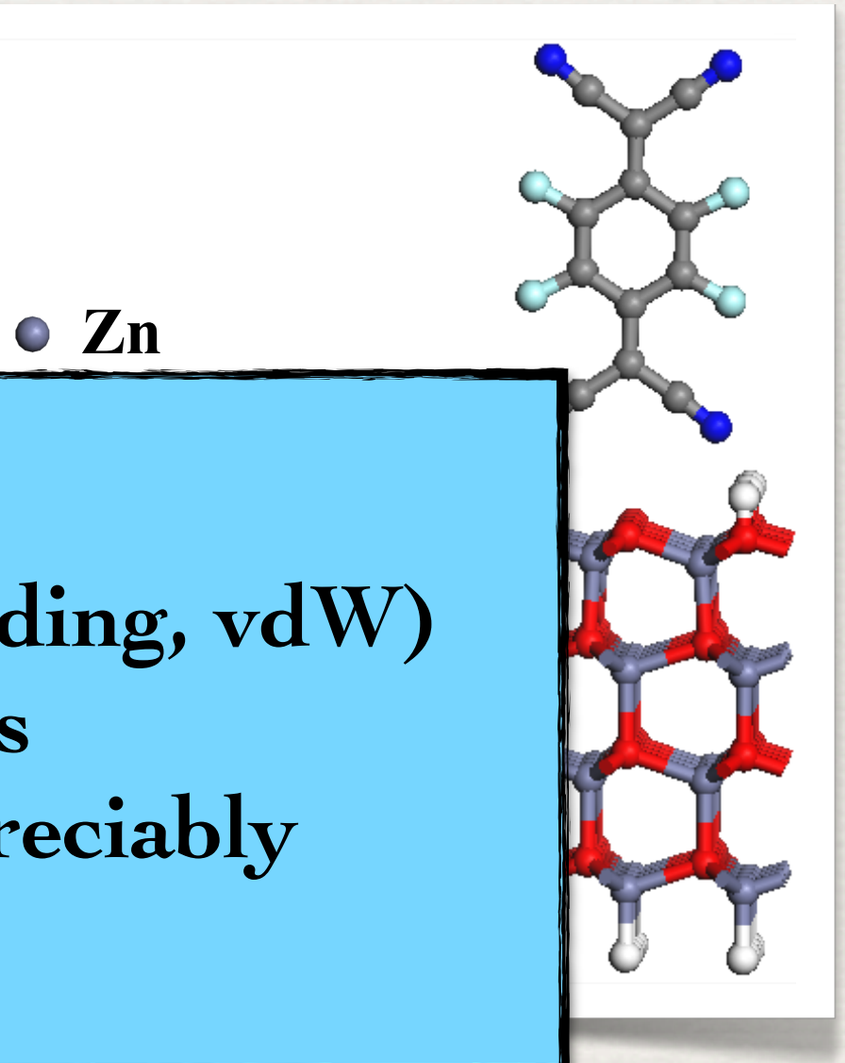
$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf}$$

F4TCNQ on hydrogen terminated ZnO(000-1)



upright

$$E^{ads} = 0.40 \text{ eV}$$



Structural features:

- **weak binding (hydrogen bonding, vdW)**
- **CN groups bind to hydrogens**
- **F4TCNQ does not bend appreciably (unlike on metals)**

all ene

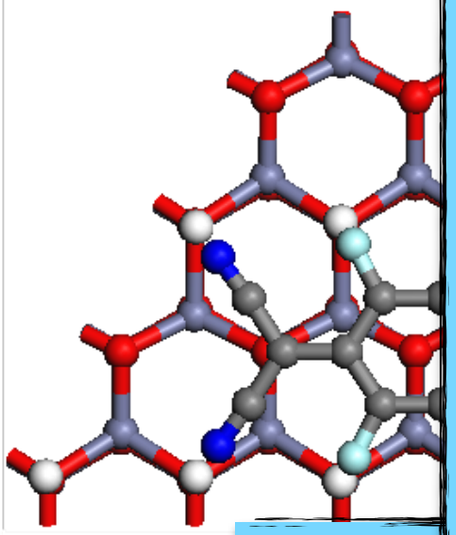
Adsorption geometries and energies

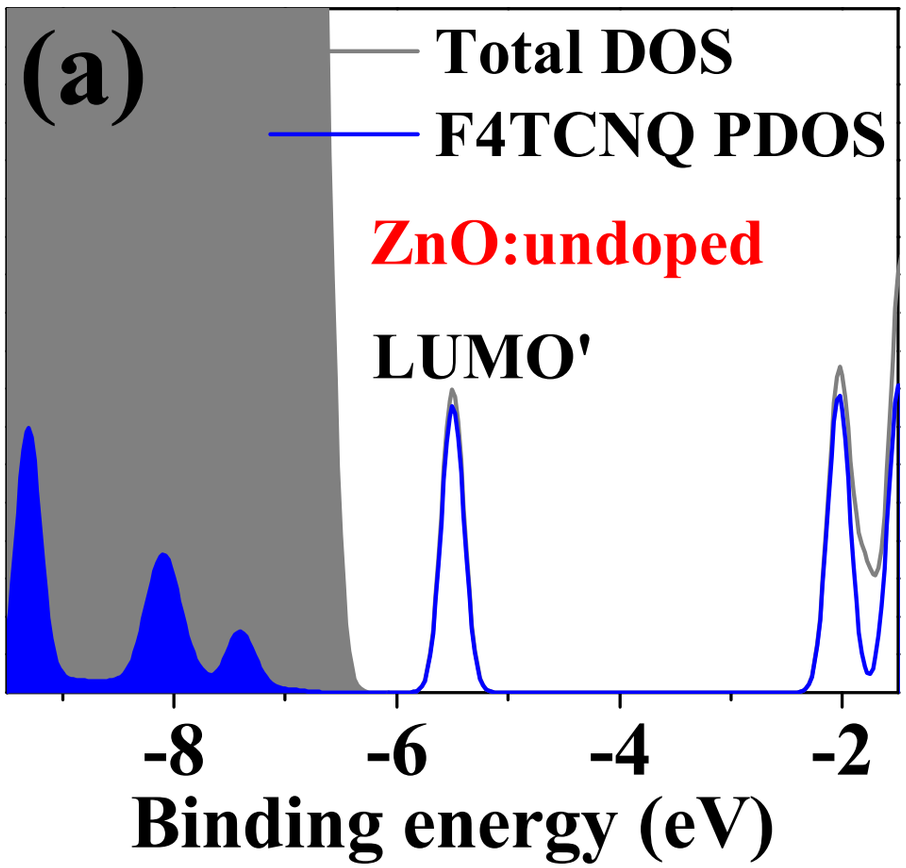
$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf}$$

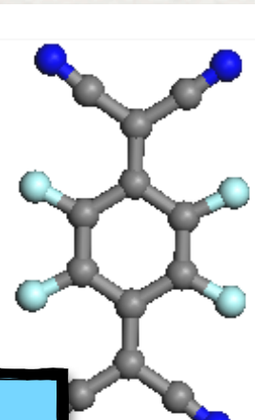
F4T 0-1)

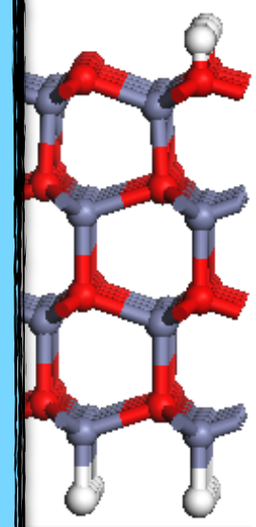
upright

= 0.40 eV









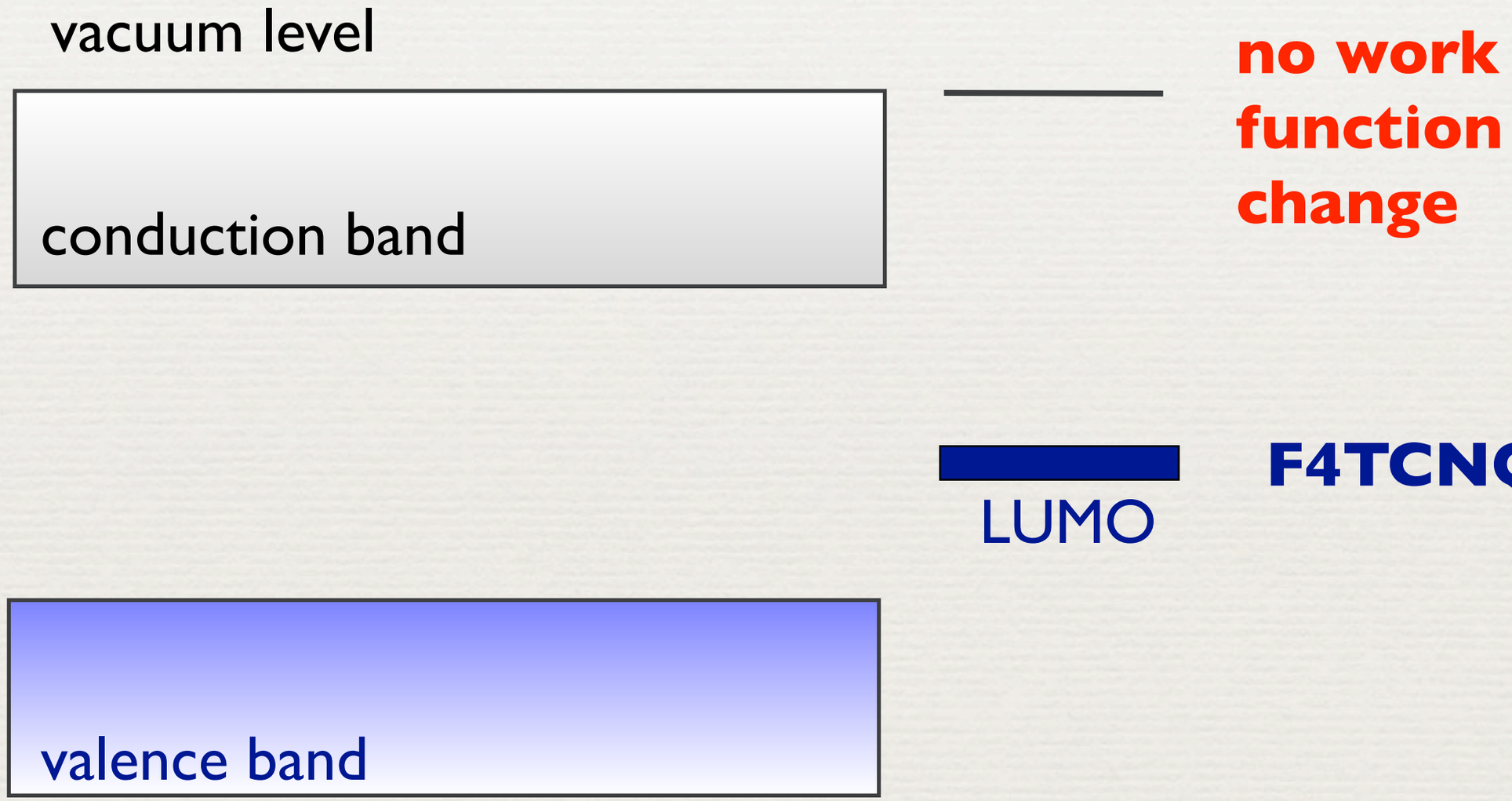
Str

- CN groups bind to hydrogens
- F4TCNQ does not bend appreciably (unlike on metals)

all ene

F4TCNQ@ZnO in DFT

Our normal DFT calculations: undoped



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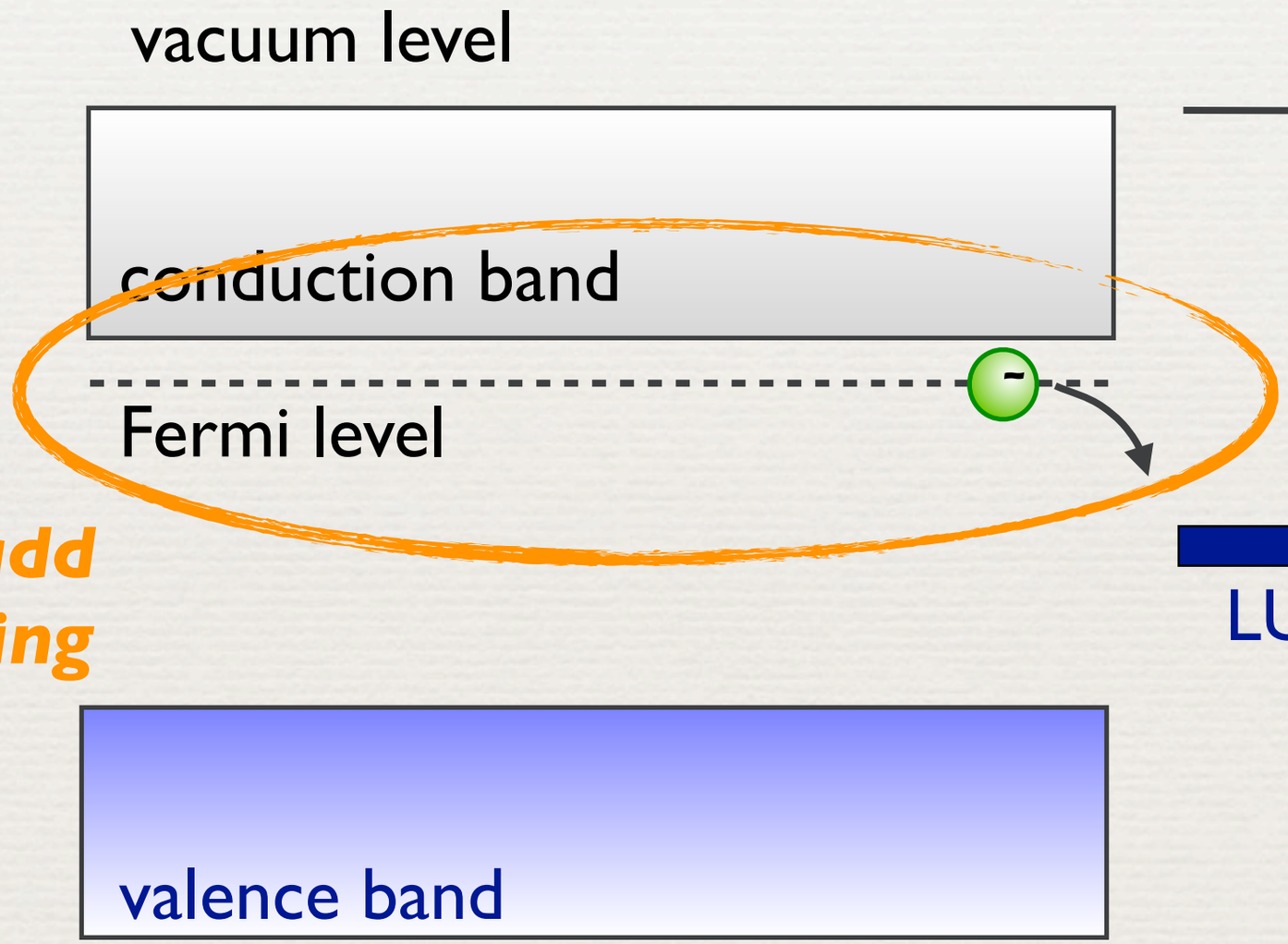


no work function change

need to add bulk doping

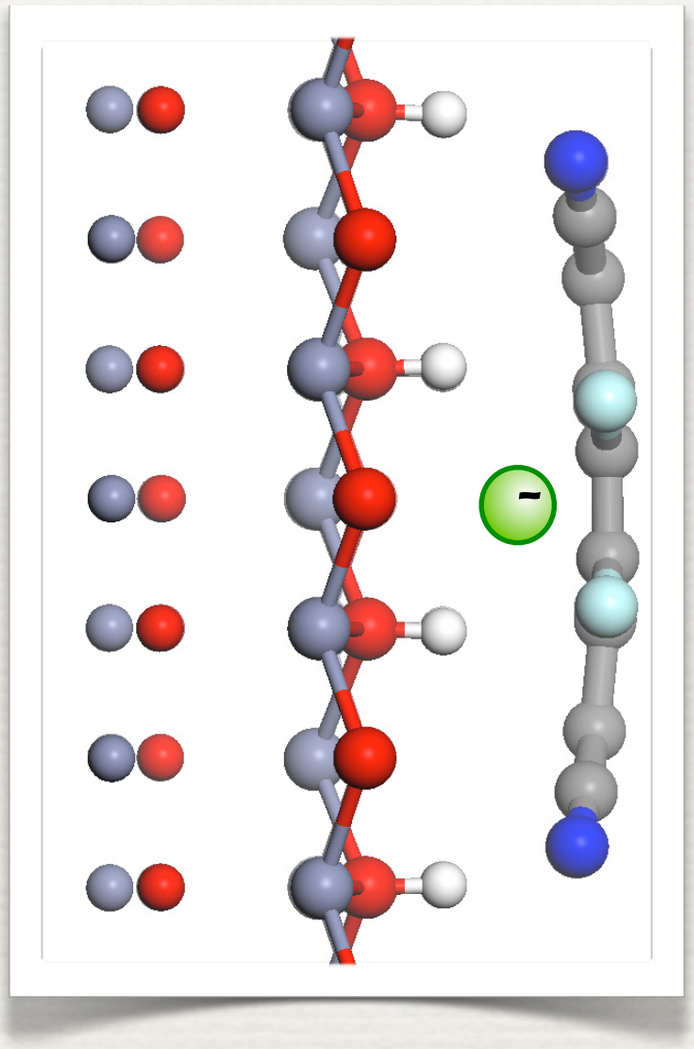
LUMO

F4TCNQ

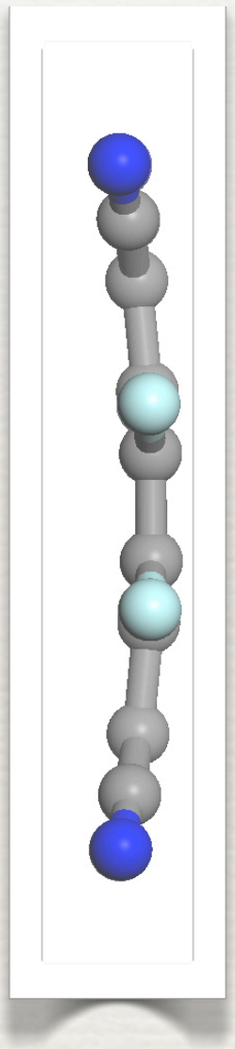
Step 1: add electrons to DFT calculation

adsorption energy:

$$E^{ads} =$$



$$-$$



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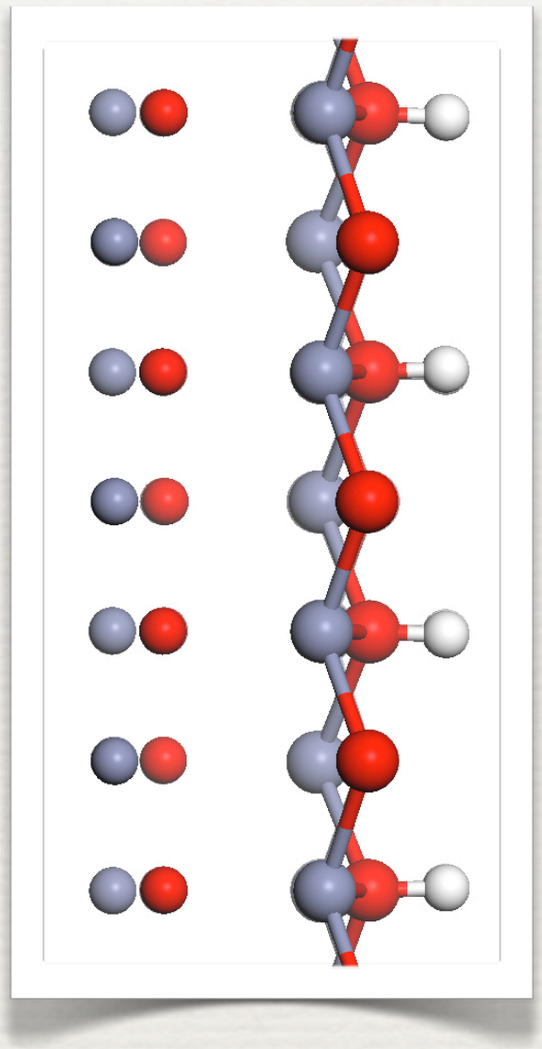


$$-$$ -

$$E^{ads}(q) = E^{mol@surf}(q) - E^{mol} - E^{surf} + q\Delta\epsilon_F$$

energy of electron reservoir

Adding electrons to surface calculations

adsorption energy:

$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf} + q\mu_e$$

chemical potential of electrons

Adding electrons to surface calculations

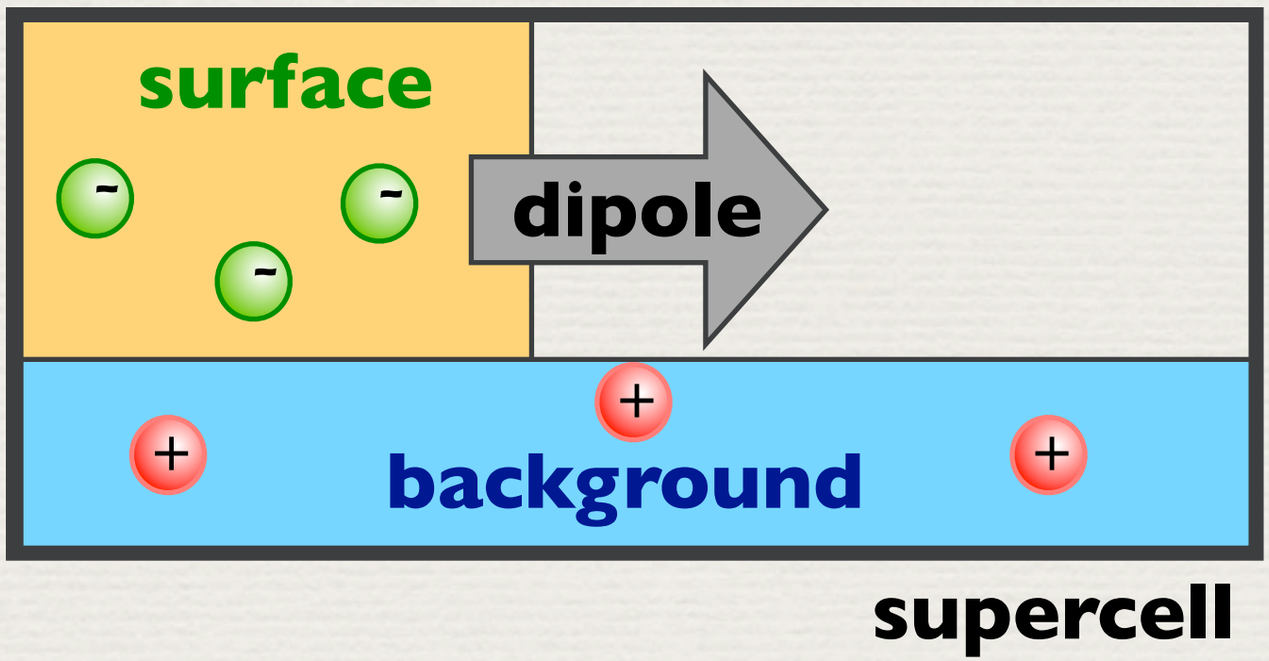
adsorption energy:

$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf} + q\mu_e$$

chemical potential of electrons

Adding electrons to supercells:

- requires compensating charge background



Adding electrons to surface calculations

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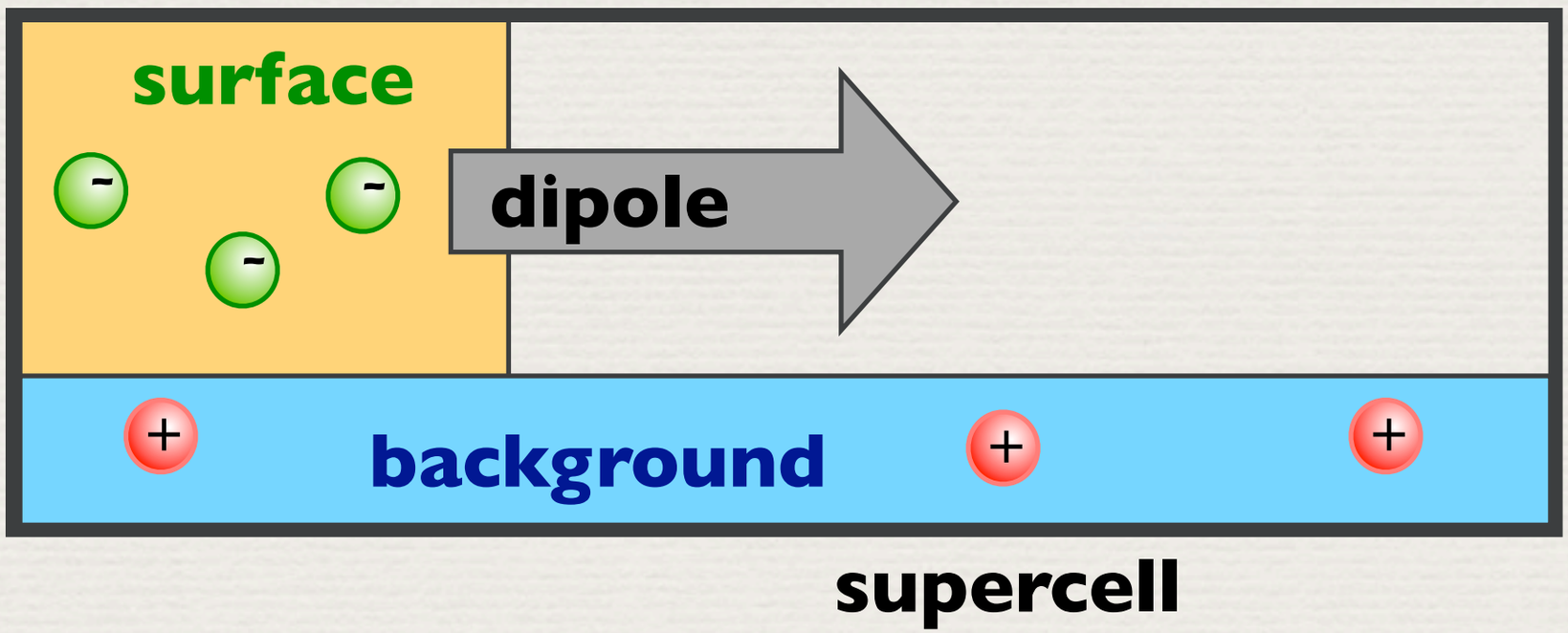

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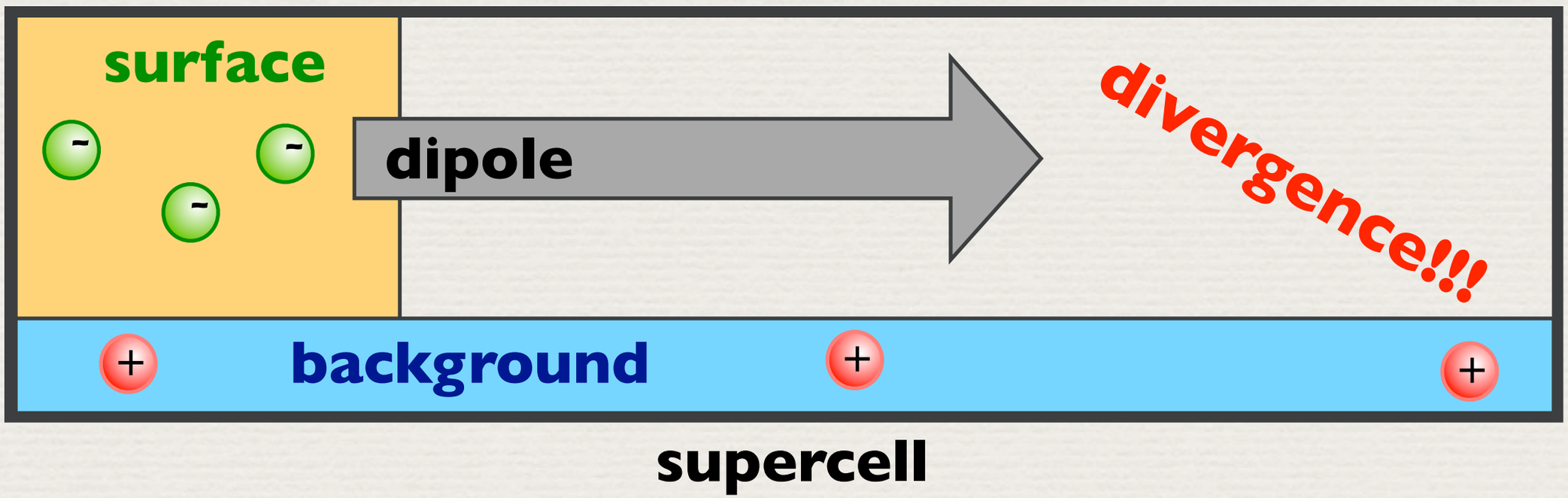


Adding electrons to surface calculations

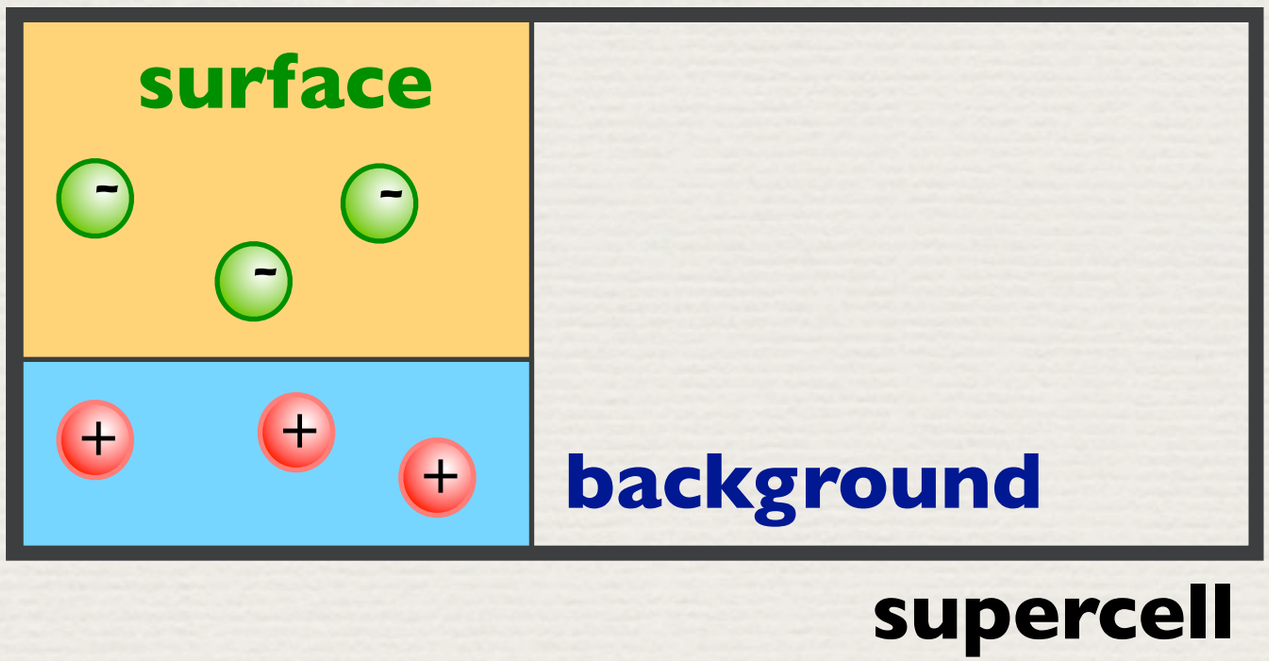
adsorption energy:

$$E^{ads} = E^{mol@surf} - E^{mol} - E^{surf} + q\mu_e$$

chemical potential of electrons

Adding electrons to supercells:

- we confine charge background (virtual crystal approximation)

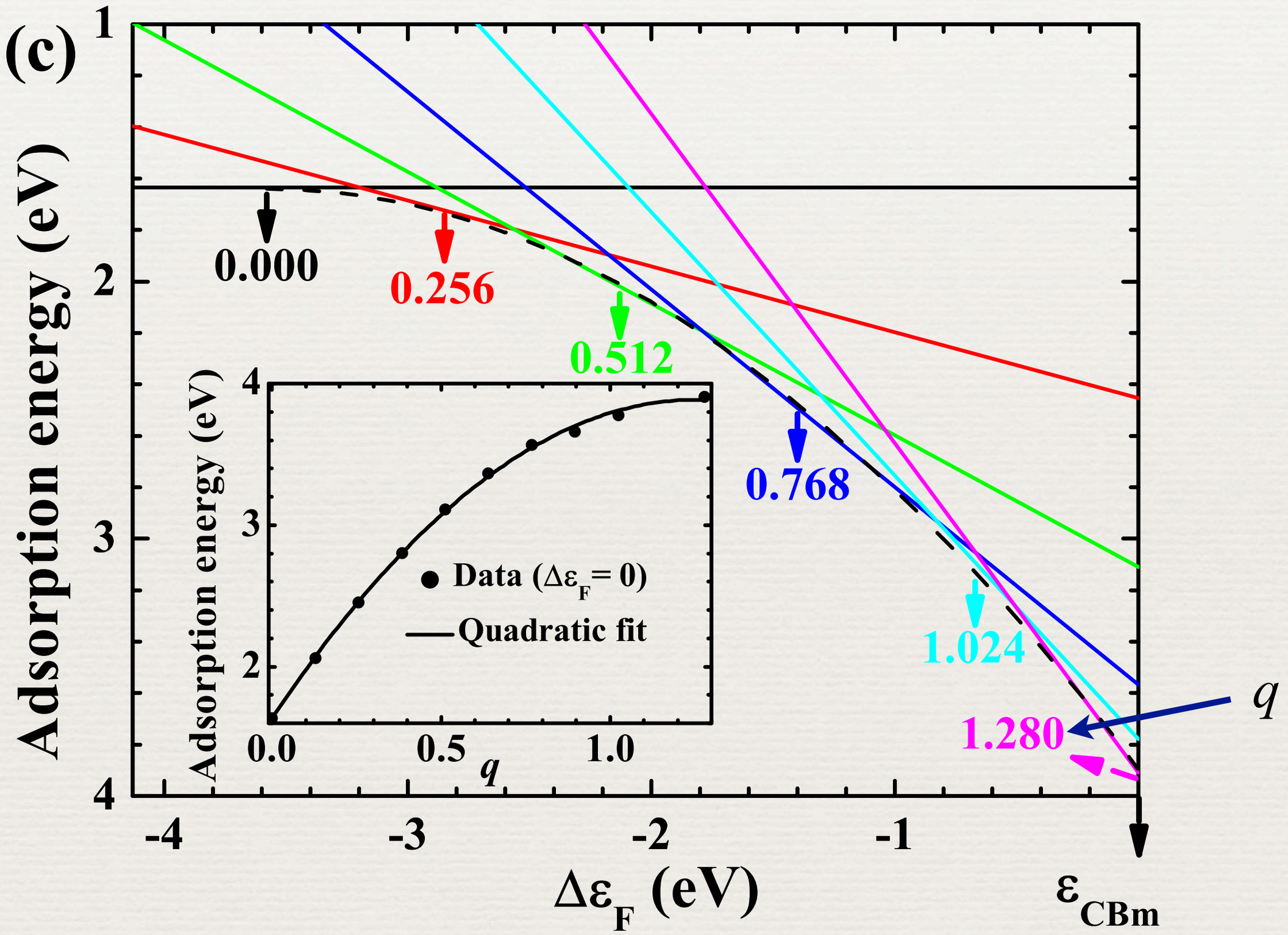


In our all-electron code:

- we change nuclear charge:

$$Z \rightarrow Z+\delta \quad (\delta \sim 10^{-2})$$

Adsorption energy as function of Fermi energy



Step 2: contribution from space charge region

Step 2a:

bulk doping concentration

$$\Delta\epsilon_{\mathrm{F}} \rightarrow N_D$$

- translate Fermi energy into doping dependence (standard semiconductor text book expressions)

Step 2b:

- introduce space charge region (add band bending contribution)

surface area **supercell length**

$$\Delta E_q^{\mathrm{ads}}(N_{\mathrm{D}}) = E_{\mathrm{ads}}^{\mathrm{DFT}}(q) - \underbrace{\frac{e^2}{6\varepsilon\varepsilon_0 N_{\mathrm{D}} A^2}|q|^3}_{\text{macroscopic band bending}} + \underbrace{\frac{e^2 d}{6\varepsilon\varepsilon_0 A}q^2}_{\text{spurious band bending in calculation}}$$

Step 2: contribution from space charge region

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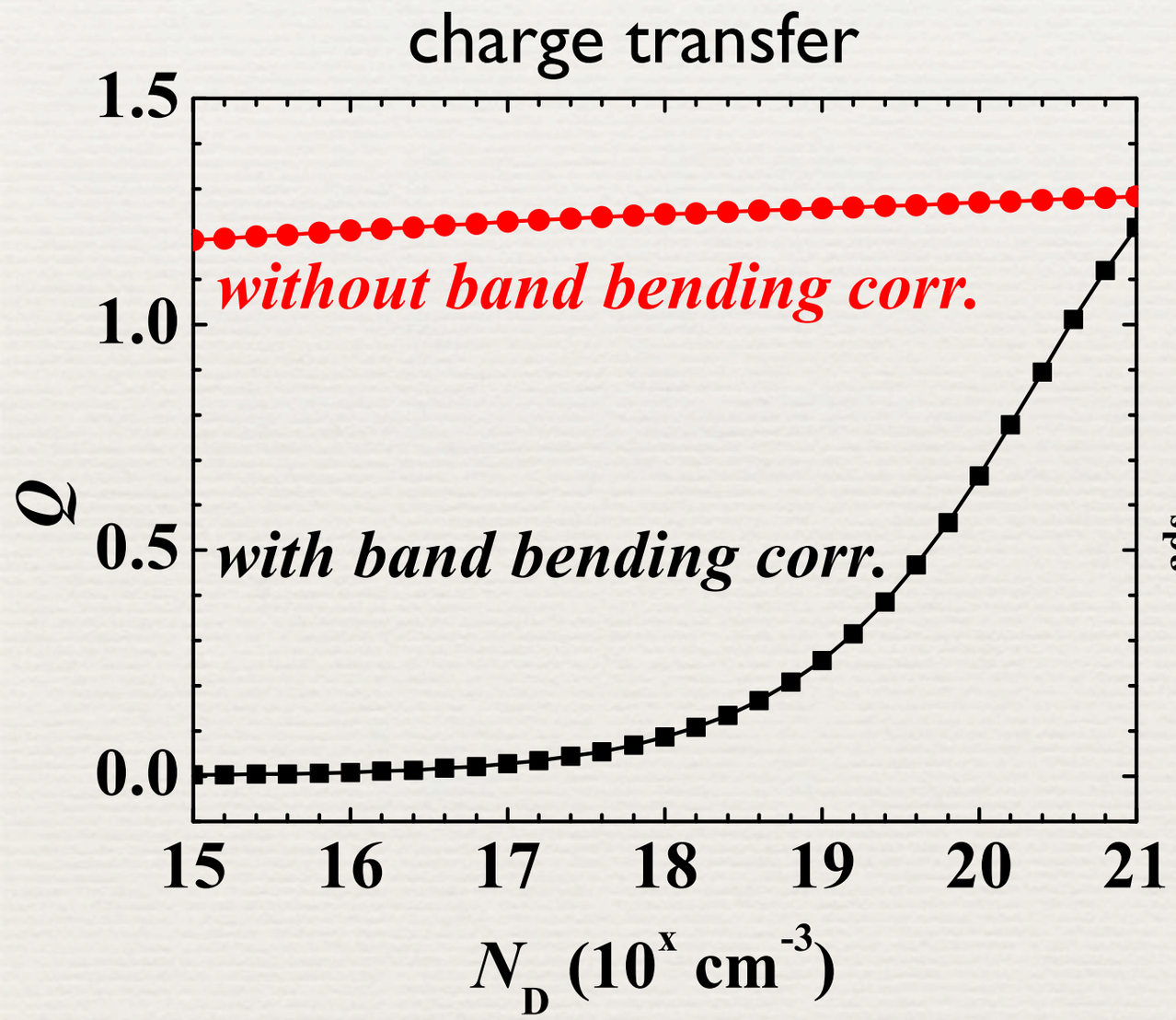
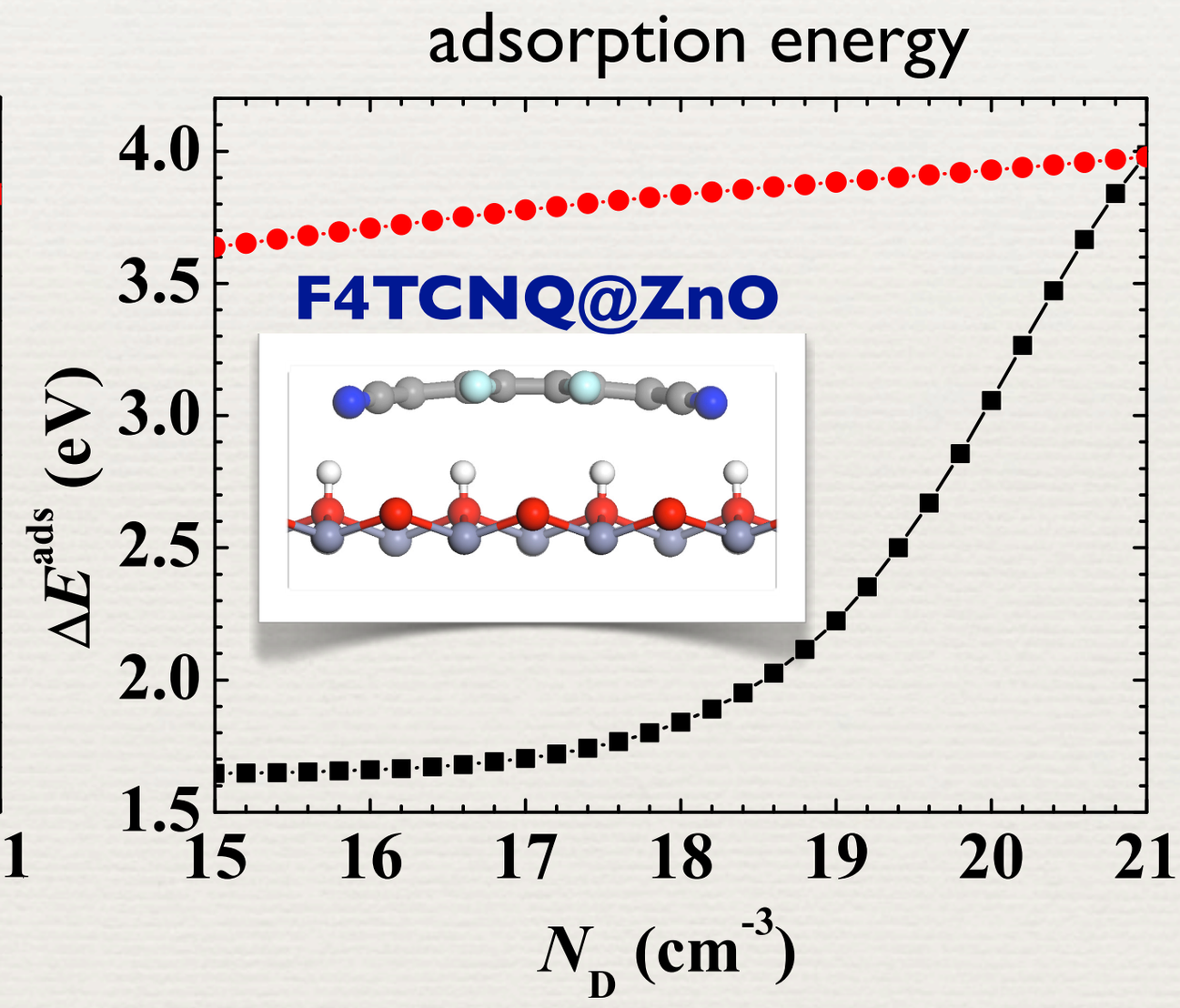
Step 2c:

- maximize $\Delta E_q^{\mathrm{ads}}(N_{\mathrm{D}})$ for optimal charge transfer *Q*

Introducing bulk doping into 1st principles

$$E^{ads}(N_D) = \underbrace{E^{mol@surf} - E^{mol} - E^{surf}}_{\text{microscopic: DFT}} + \underbrace{\Delta_{BB}(Q, N_D)}_{\text{macroscopic model}}$$





Y. Xu, O.T. Hofmann, R. Schlesinger, S. Winkler, J. Frisch, J. Niederhausen, A. Vollmer, S. Blumstengel, F. Henneberger, N. Koch, P. Rinke, and M. Scheffler, submitted to Phys. Rev. Lett

Introducing bulk doping into 1st principles

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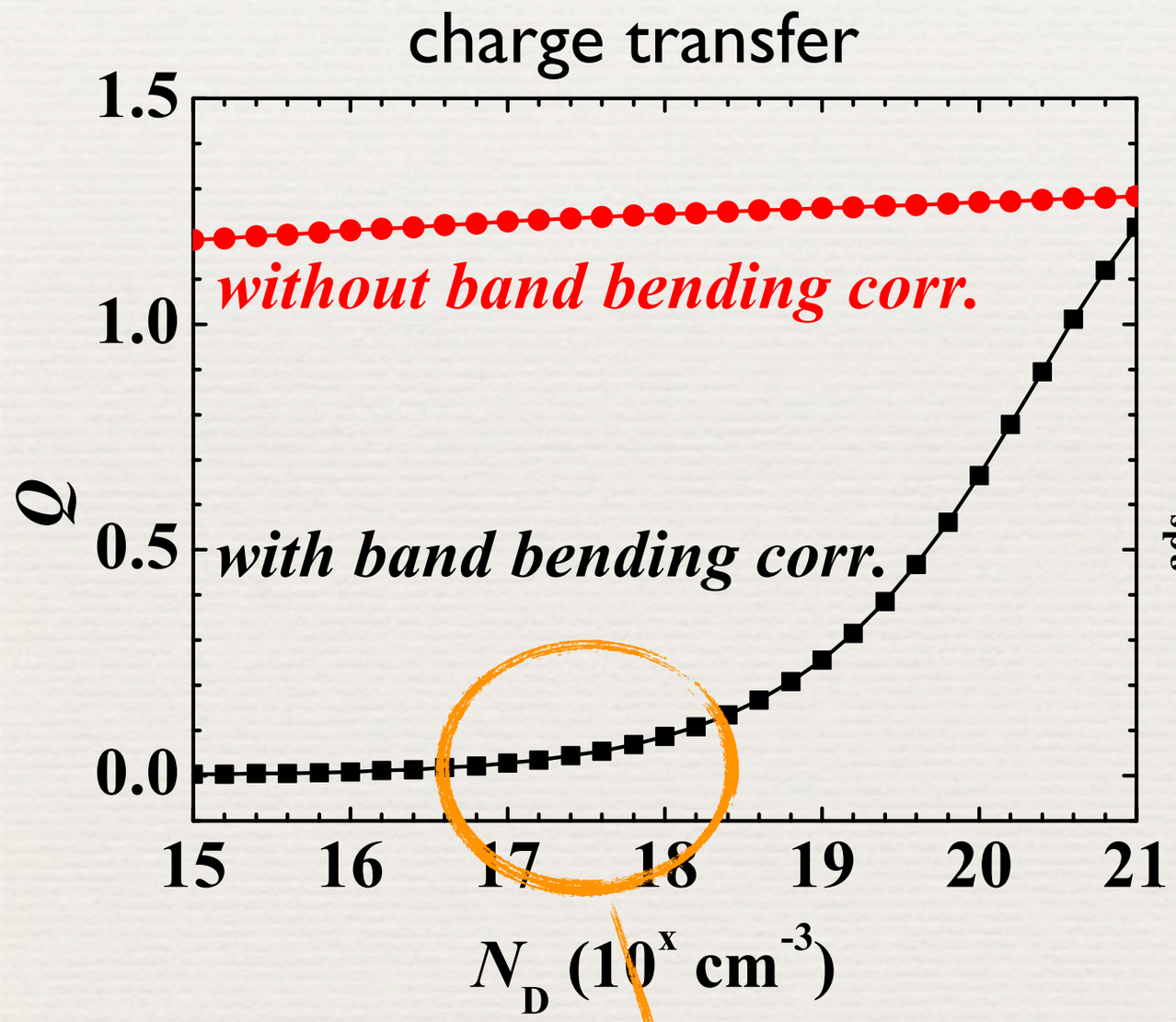
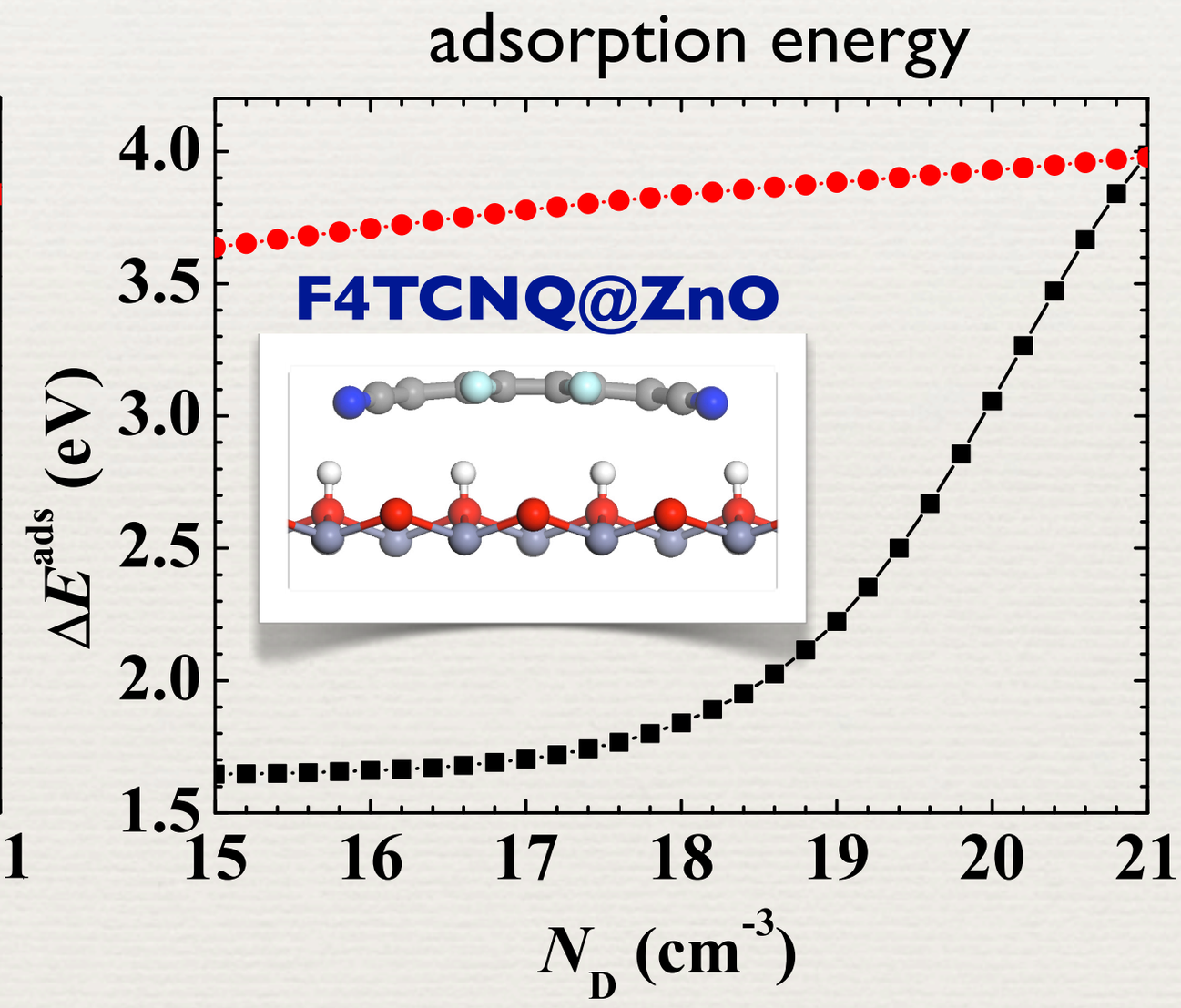
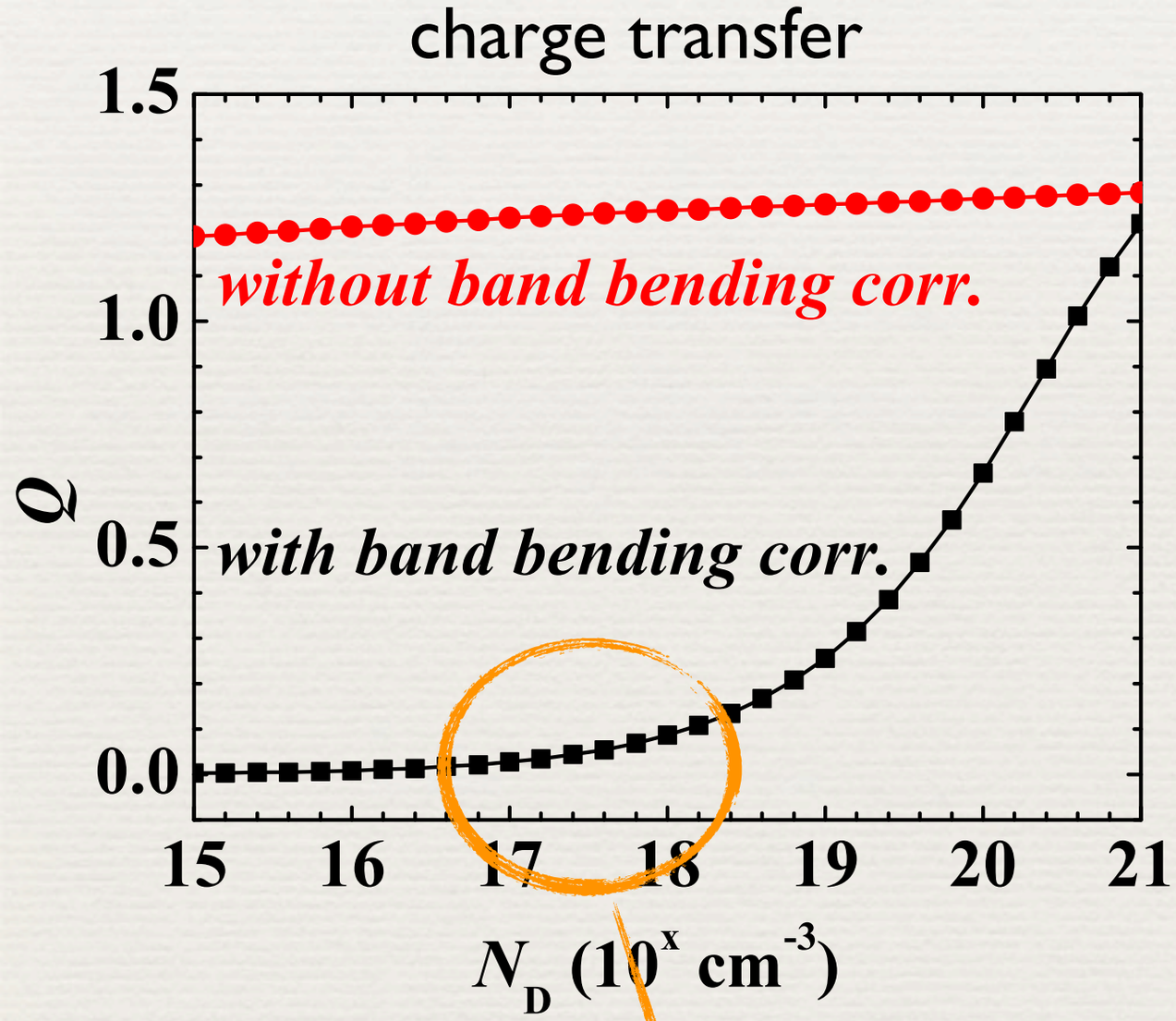


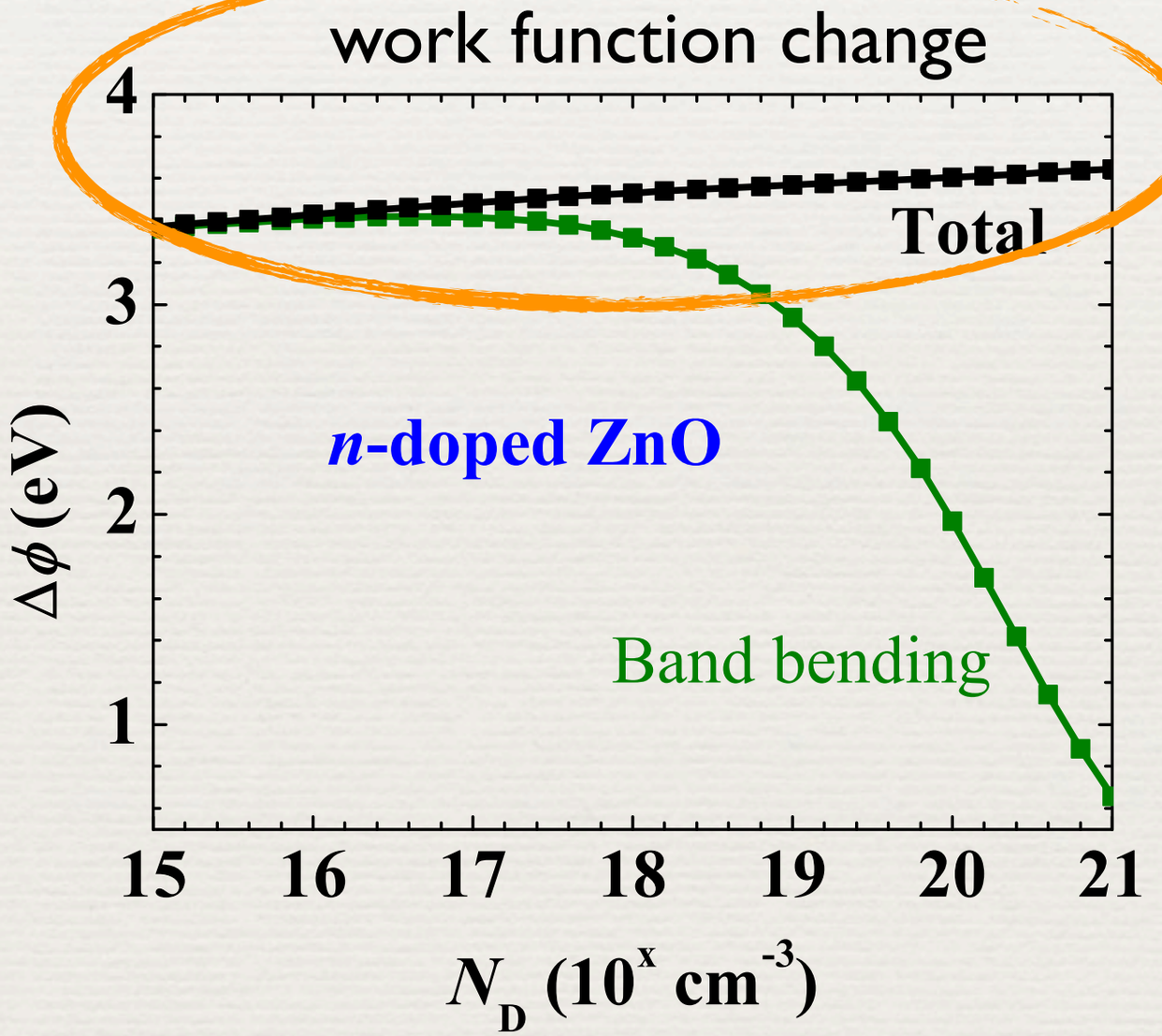


- small charge transfer

Adsorption energy and charge transfer

• large work function increase

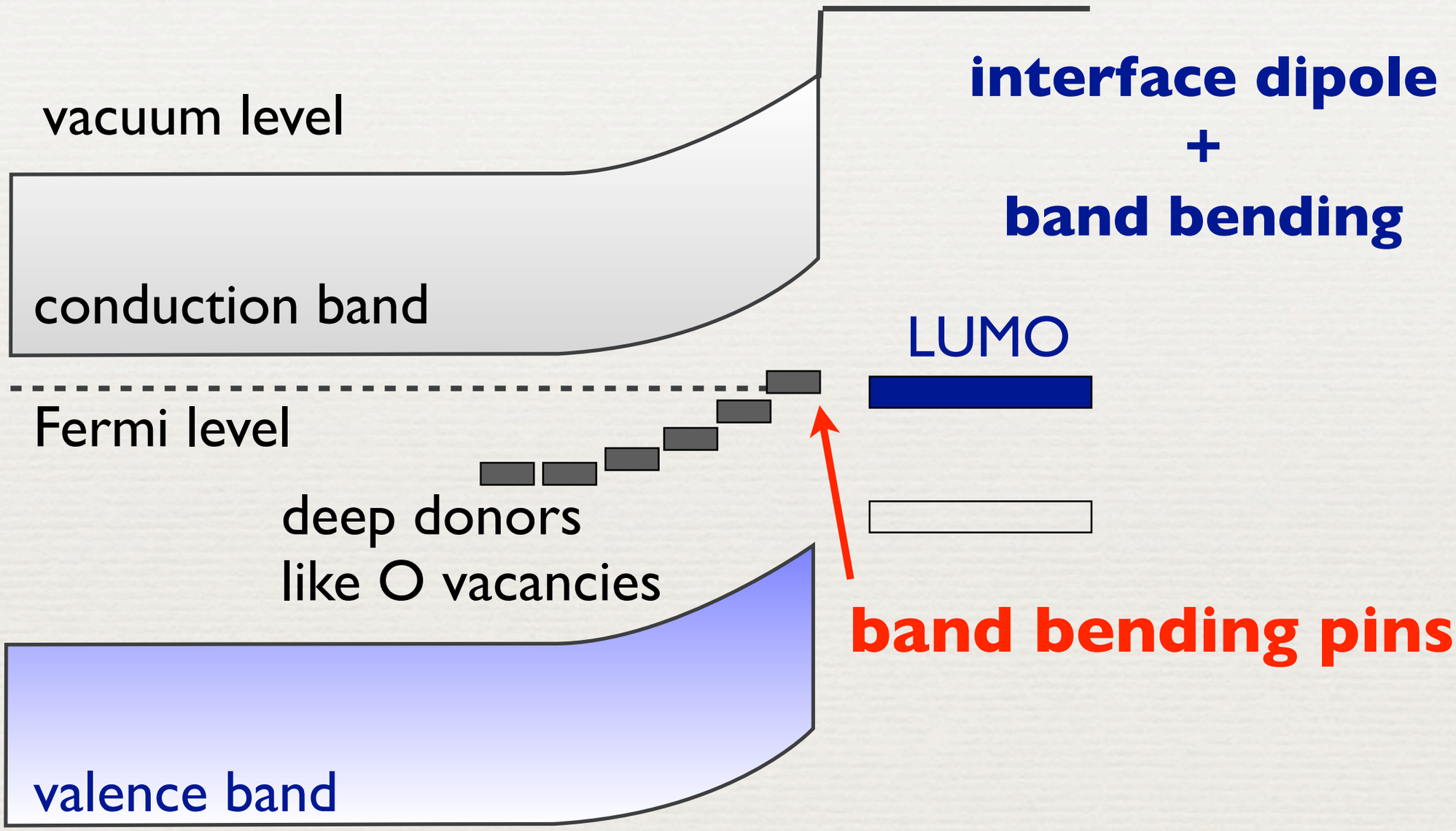




• small charge transfer

Formation of space-charge layer

low doping + deep donors ⇒ band bending pins



Work function increase in photoemission

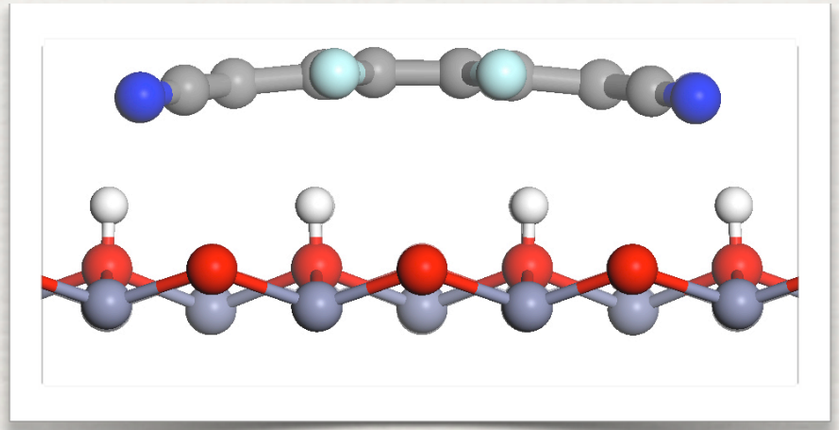
photoemission (UPS/XPS) in collaboration with:

Humboldt University Berlin

R. Schlesinger
J. Frisch
J. Niederhausen
S. Blumstengel
F. Henneberger
N. Koch

Synchrotron - BESSY II

S. Winkler
A. Vollmer



Experiment

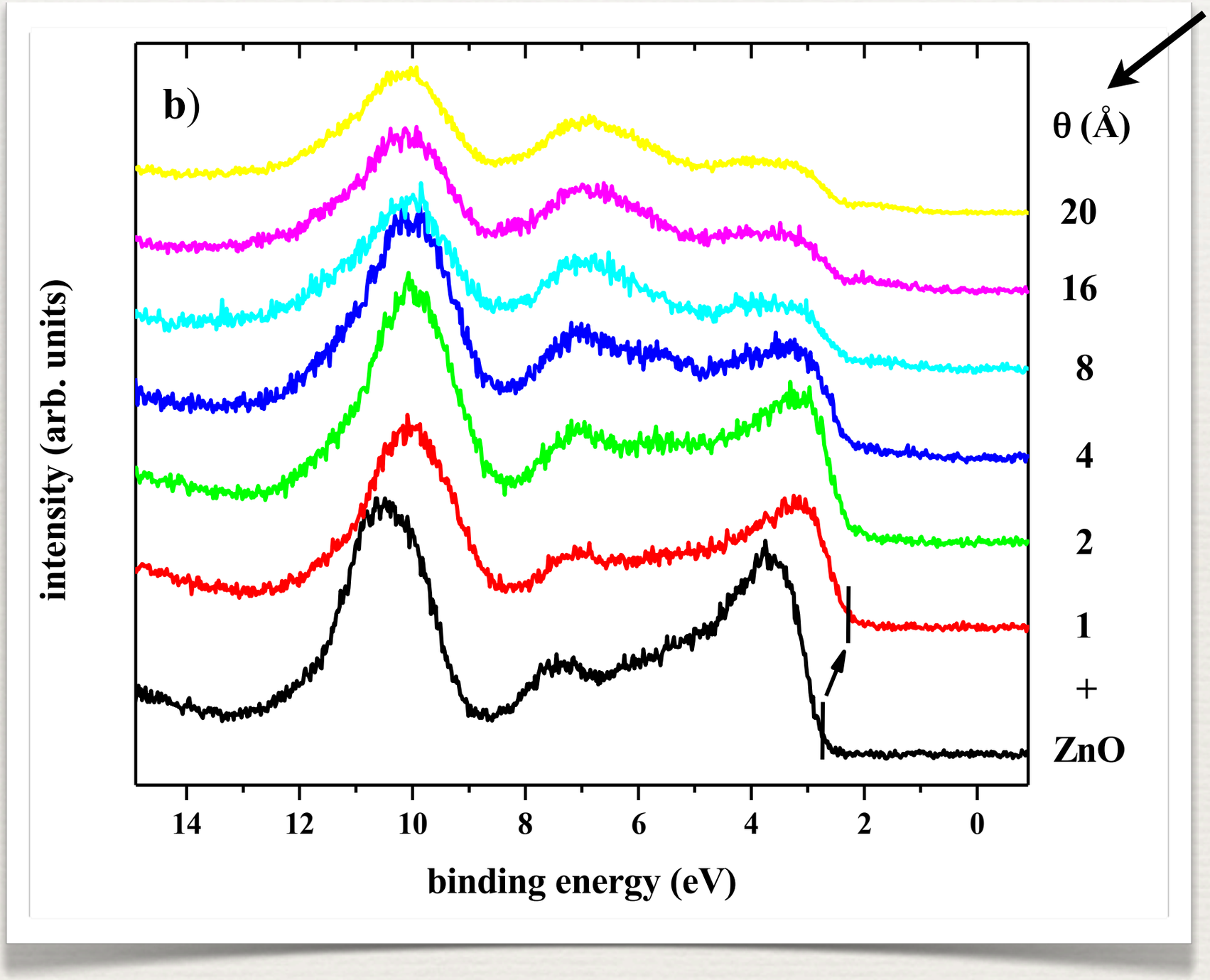
- work function increase: 1.4 eV
- minimal charge transfer

Collaborative Research Center "Hybrid Inorganic/ Organic Systems"

R. Schlesinger, Y. Xu, O. T. Hofmann, S. Winkler, J. Frisch, J. Niederhausen, A. Vollmer, S. Blumstengel, F. Henneberger, P. Rinke, M. Scheffler, and N. Koch, Phys. Rev. B 87, 155311 (2013)

F4TCNQ@ZnO - photoemission

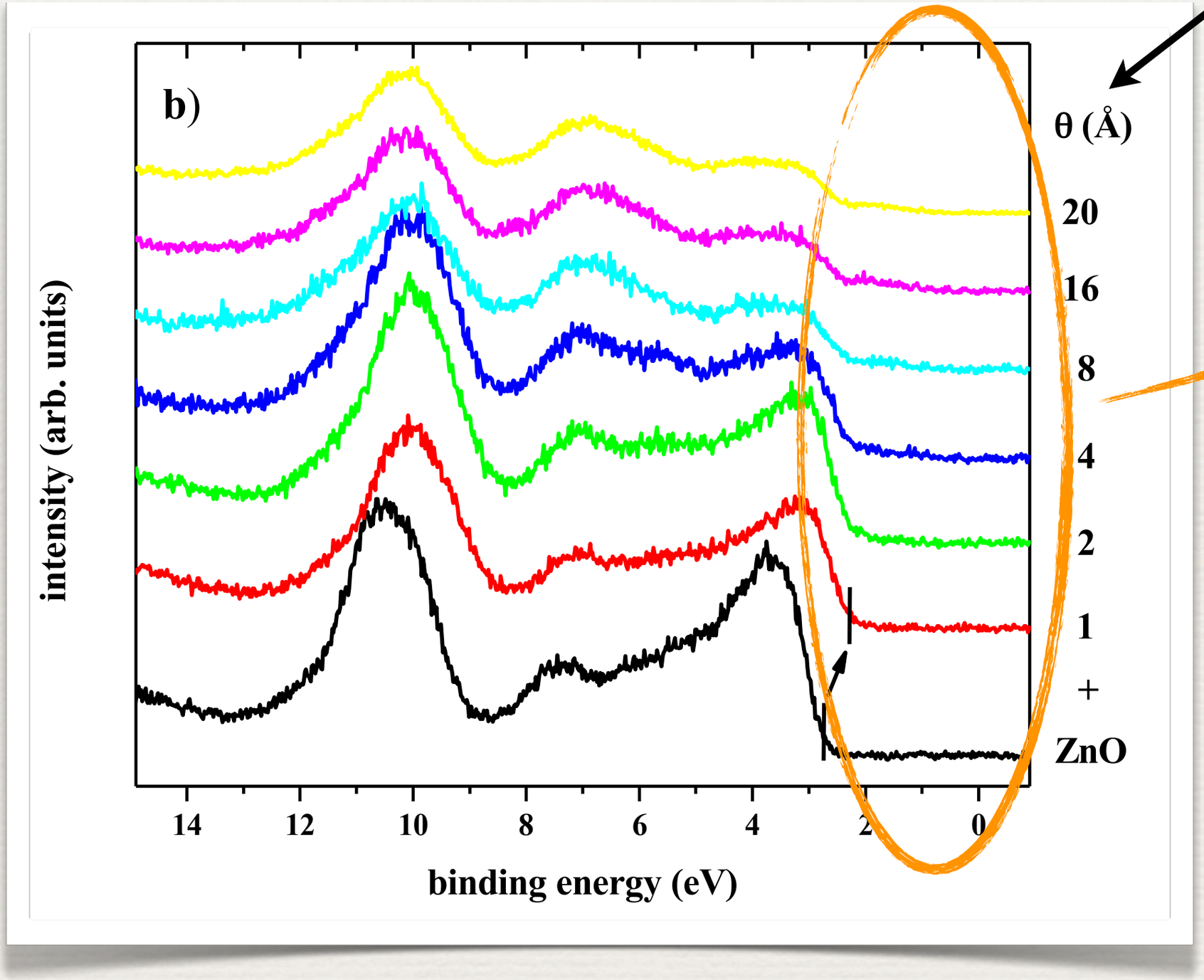
F4TCNQ@ZnO(00-10)



similar spectra for ZnO(0010)

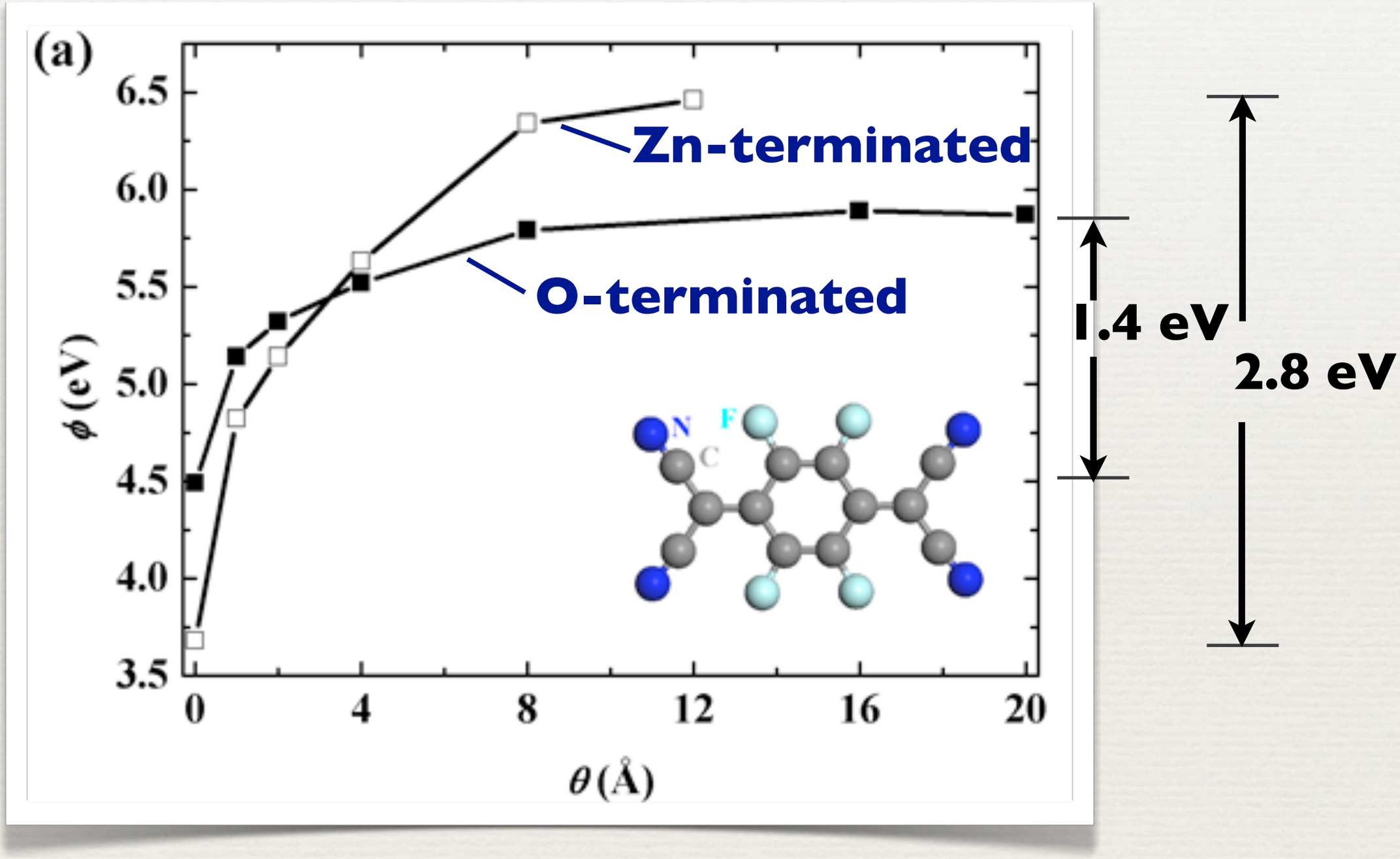
F4TCNQ@ZnO - photoemission

F4TCNQ@ZnO(00-10)



R. Schlesinger, et al., Phys. Rev. B **87**, 155311 (2013)

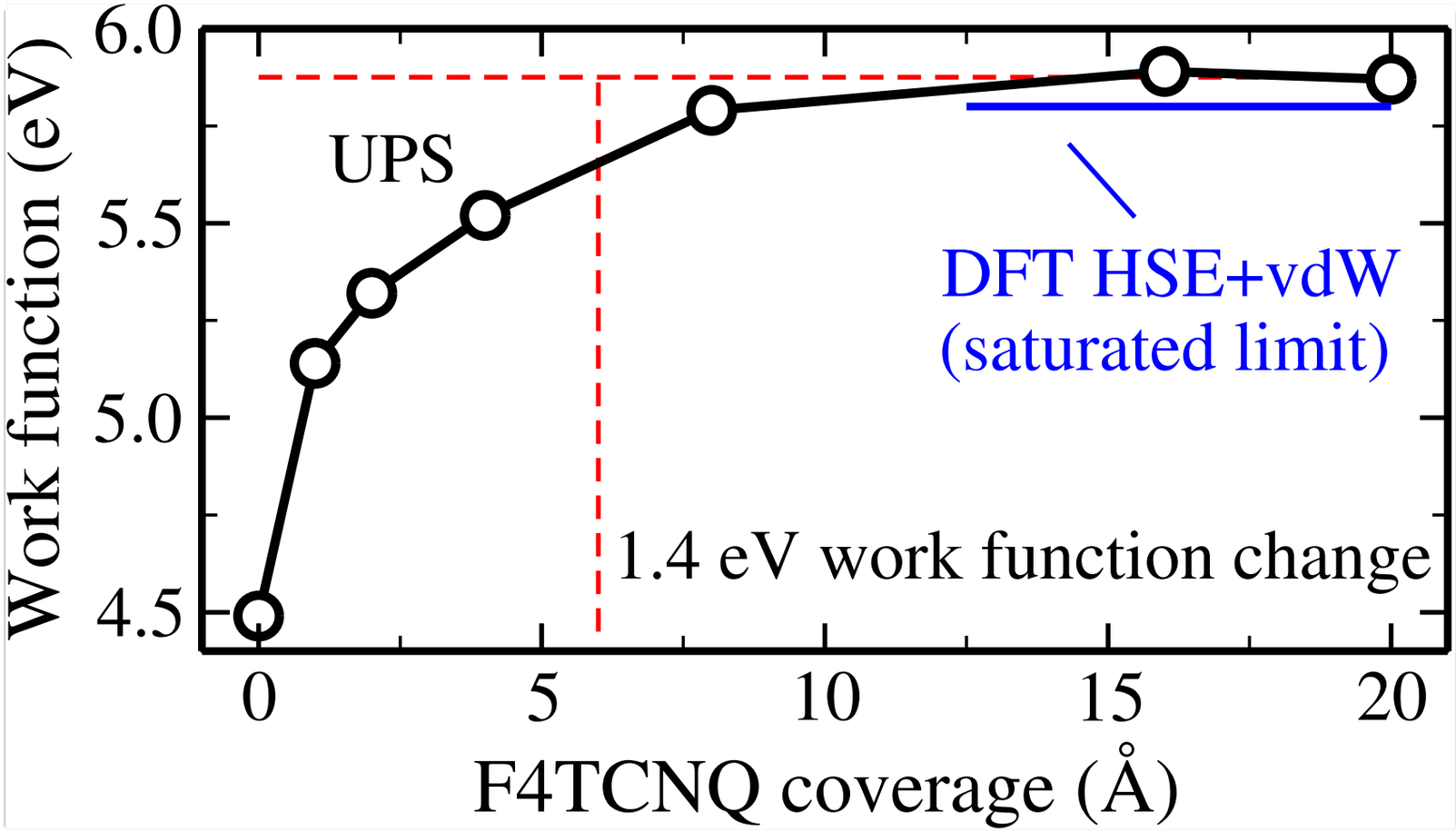
F4TCNQ@ZnO - photoemission

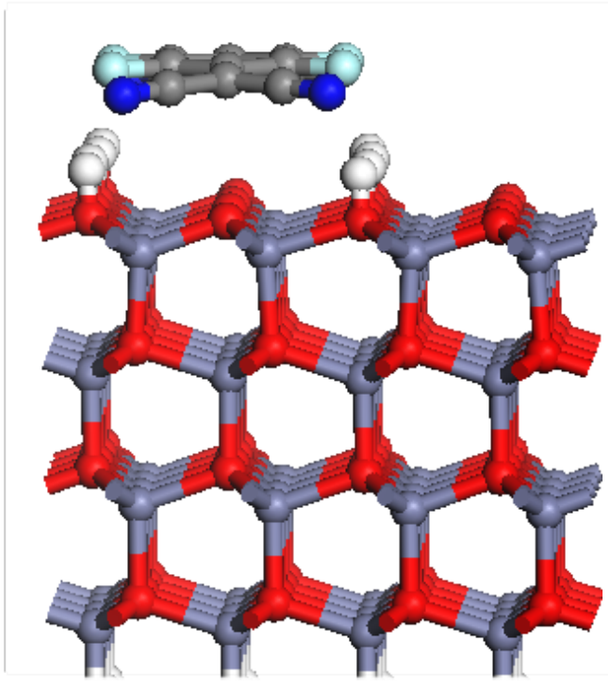


- **extraordinarily large work function changes**

R. Schlesinger, et al., Phys. Rev. B **87**, 155311 (2013)

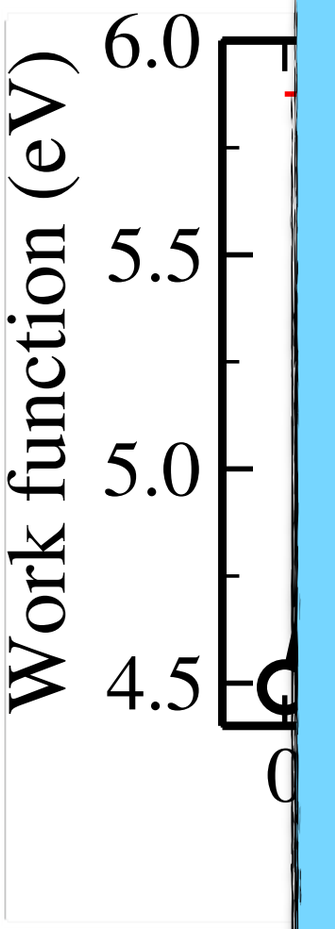
Workfunction of F4TCNQ@ZNO



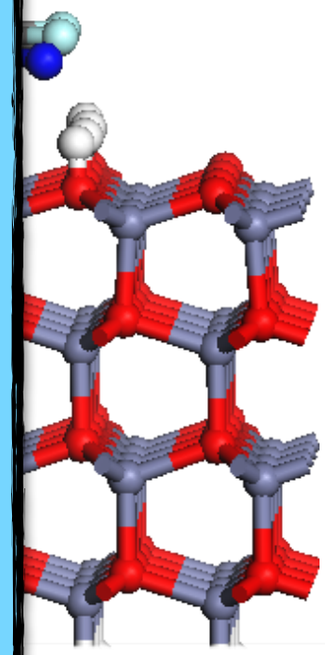


- DFT-HSE workfunction in good agreement with UPS

Workfunction of F4TCNQ@ZNO



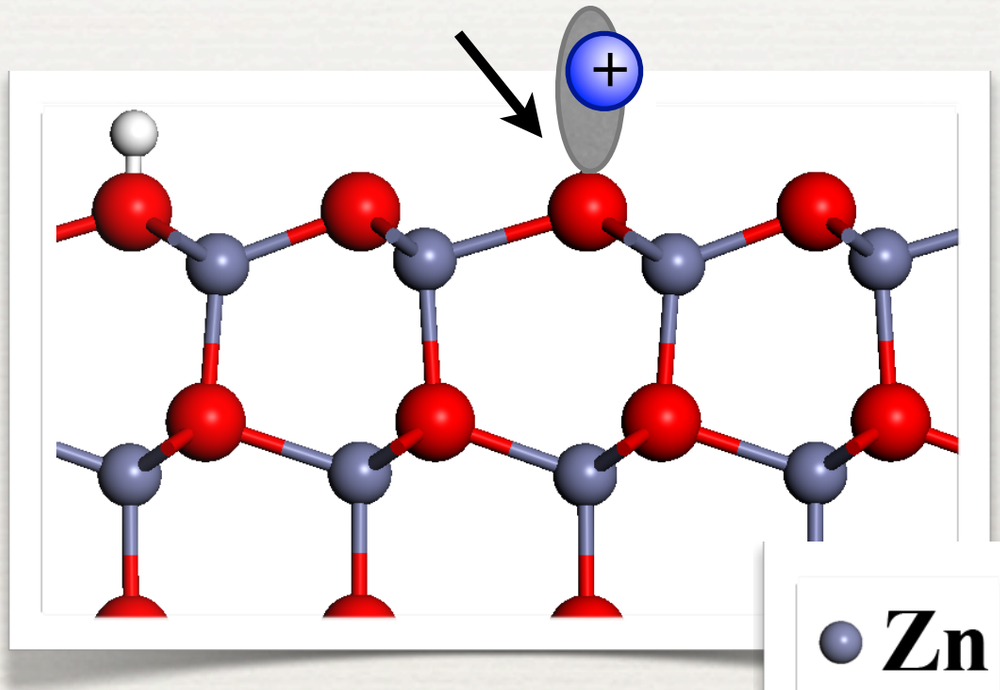
- work function change:
  - theory: ~3.5 eV
  - exper.: ~1.4 eV
- potential reasons for deviation:
  - photo voltage effect
  - deep defects pin band bending
  - hydrogen concentration at interface differs



- DFT-FHSE workfunction in good agreement with UPS

H-deficient ZnO-O 2x1-H surface

O dangling bond



conduction band

Fermi level

-

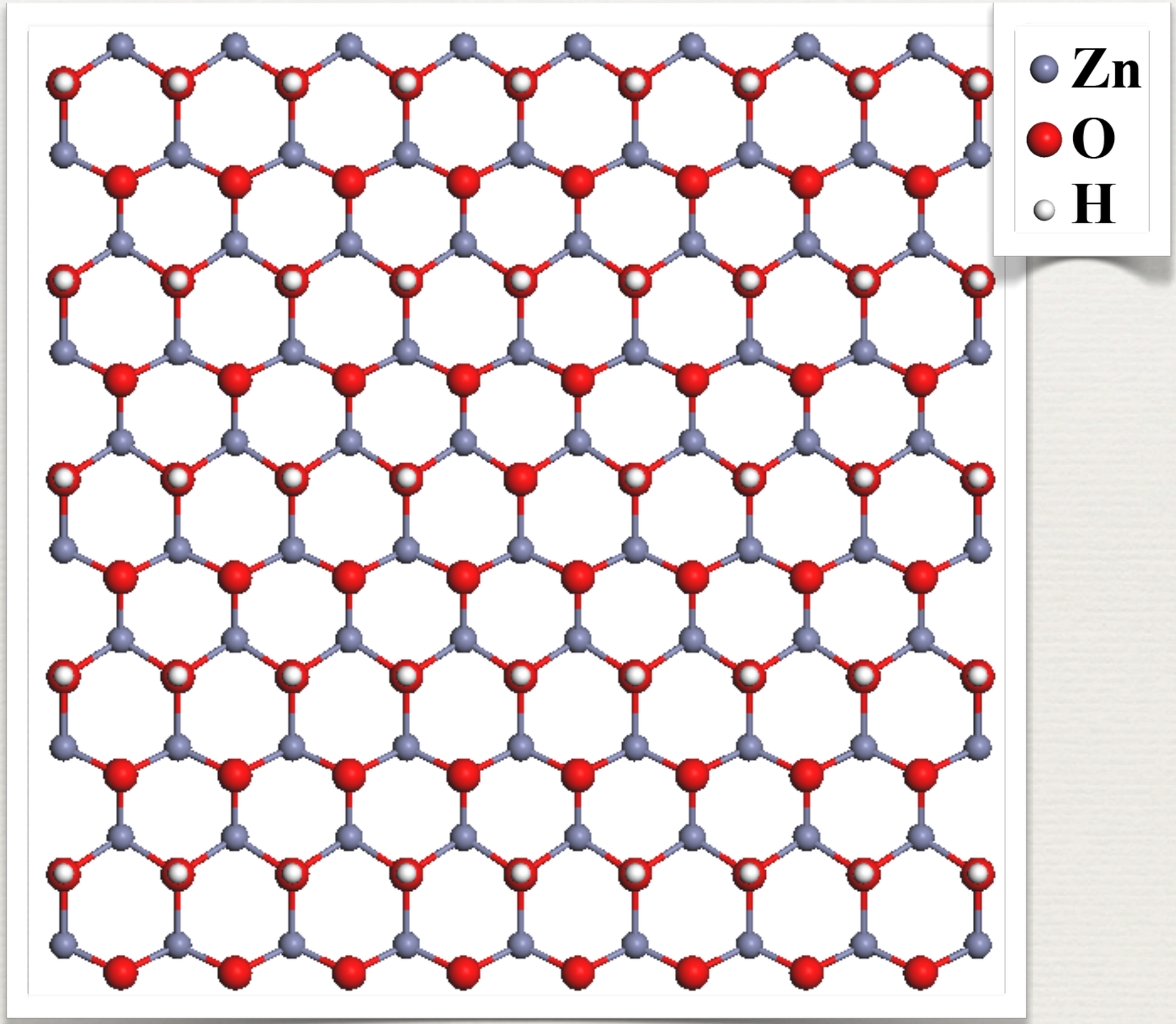
H removal

⇓

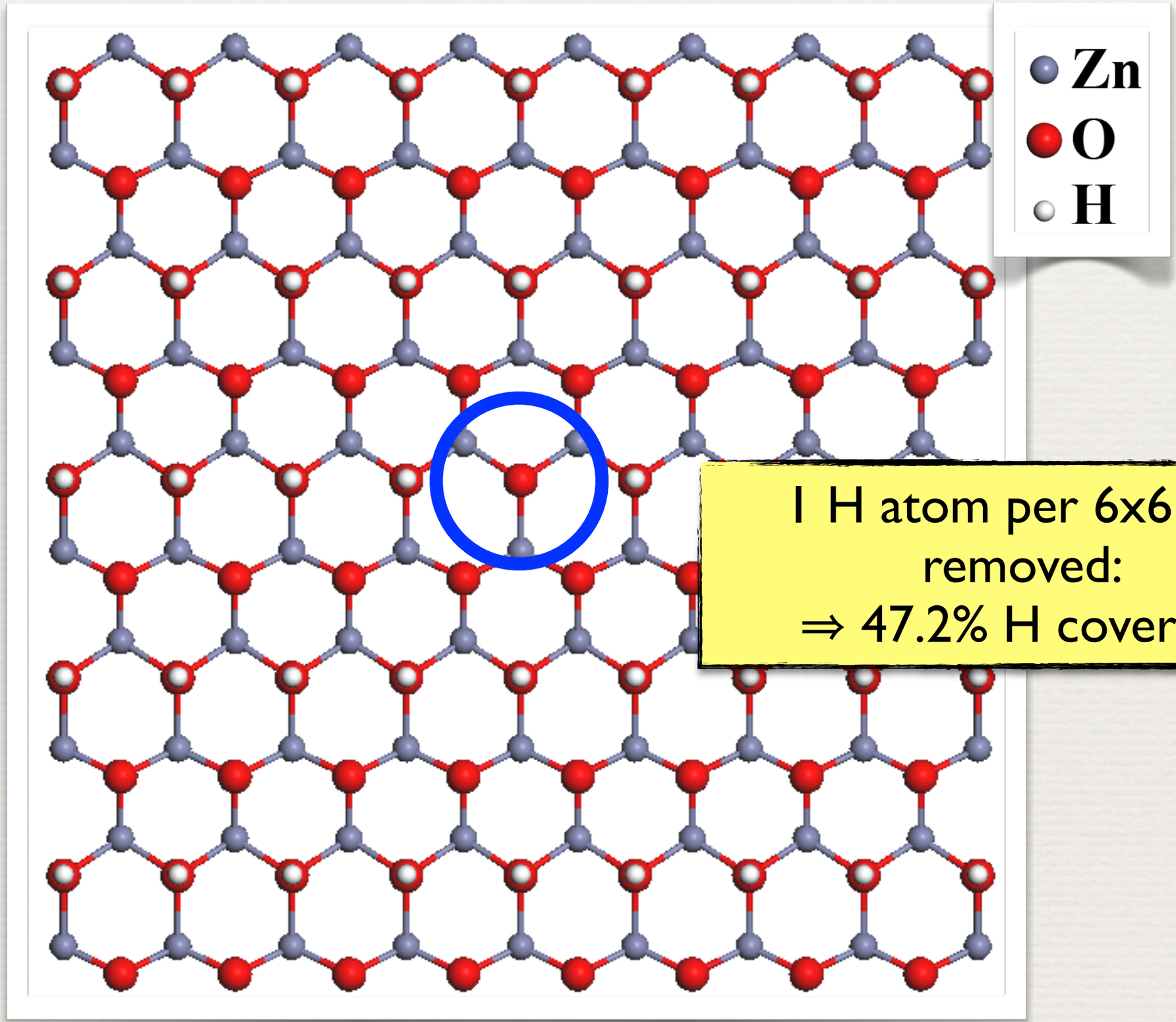
O dangling bonds

valence band

H-deficient ZnO-O 2x1-H surface



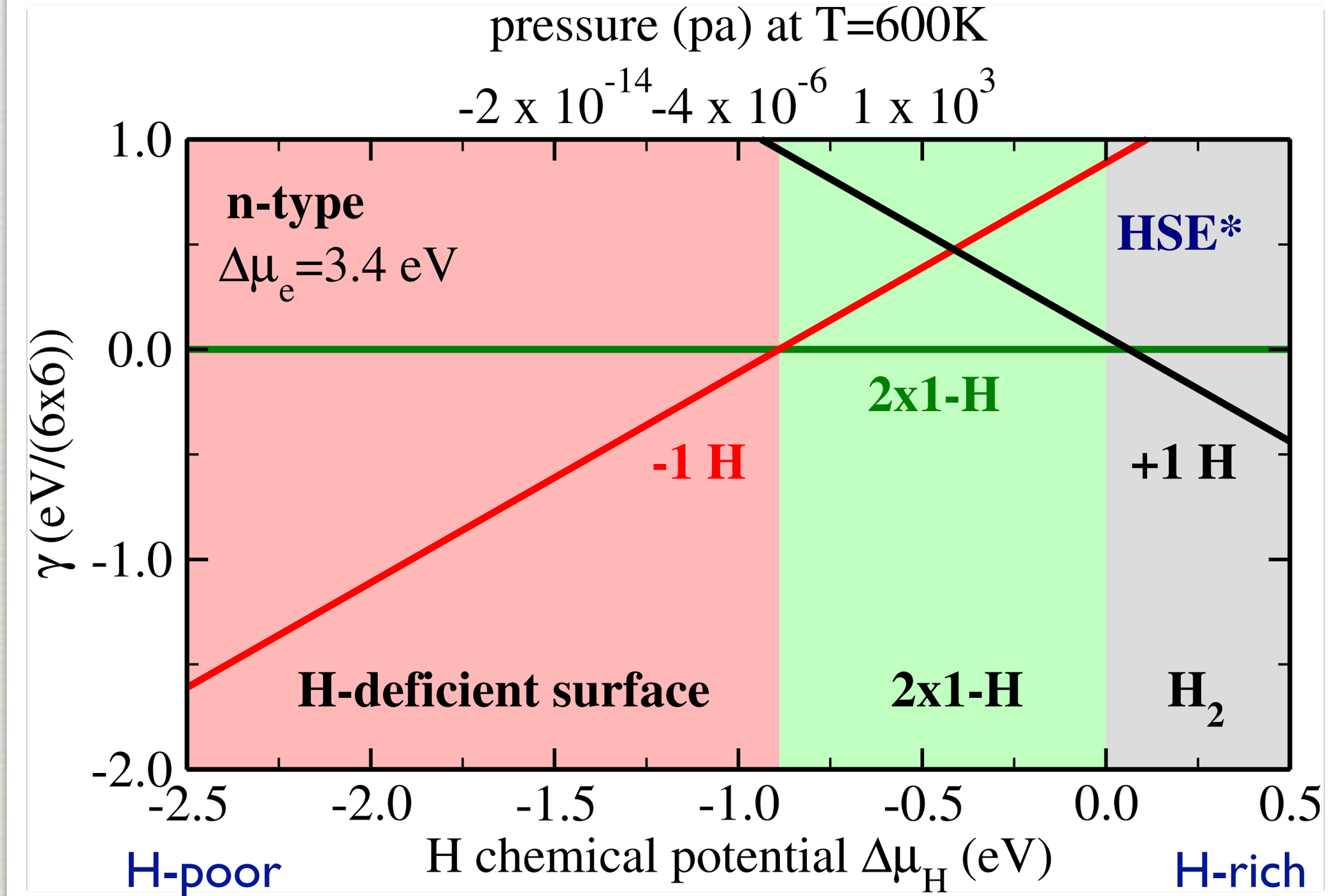
H-deficient ZnO-O 2x1-H surface



1 H atom per 6x6 cell removed:
⇒ 47.2% H coverage

ZnO-O in contact with H-reservoir

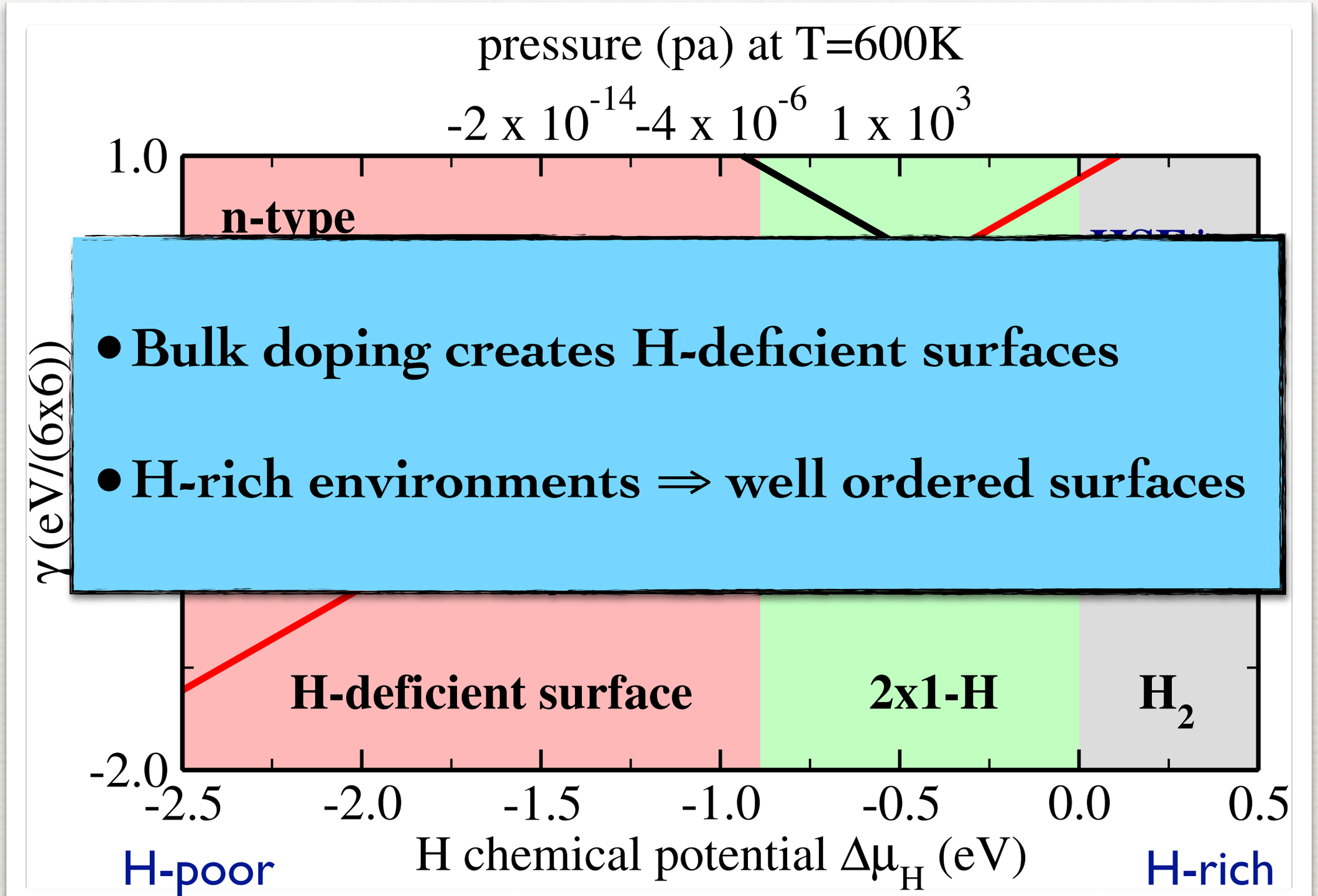
- H-deficient surfaces stabilized by n-type conditions



N. Moll, Y. Xu, O. Hofmann, P. Rinke, New J. Phys. in press

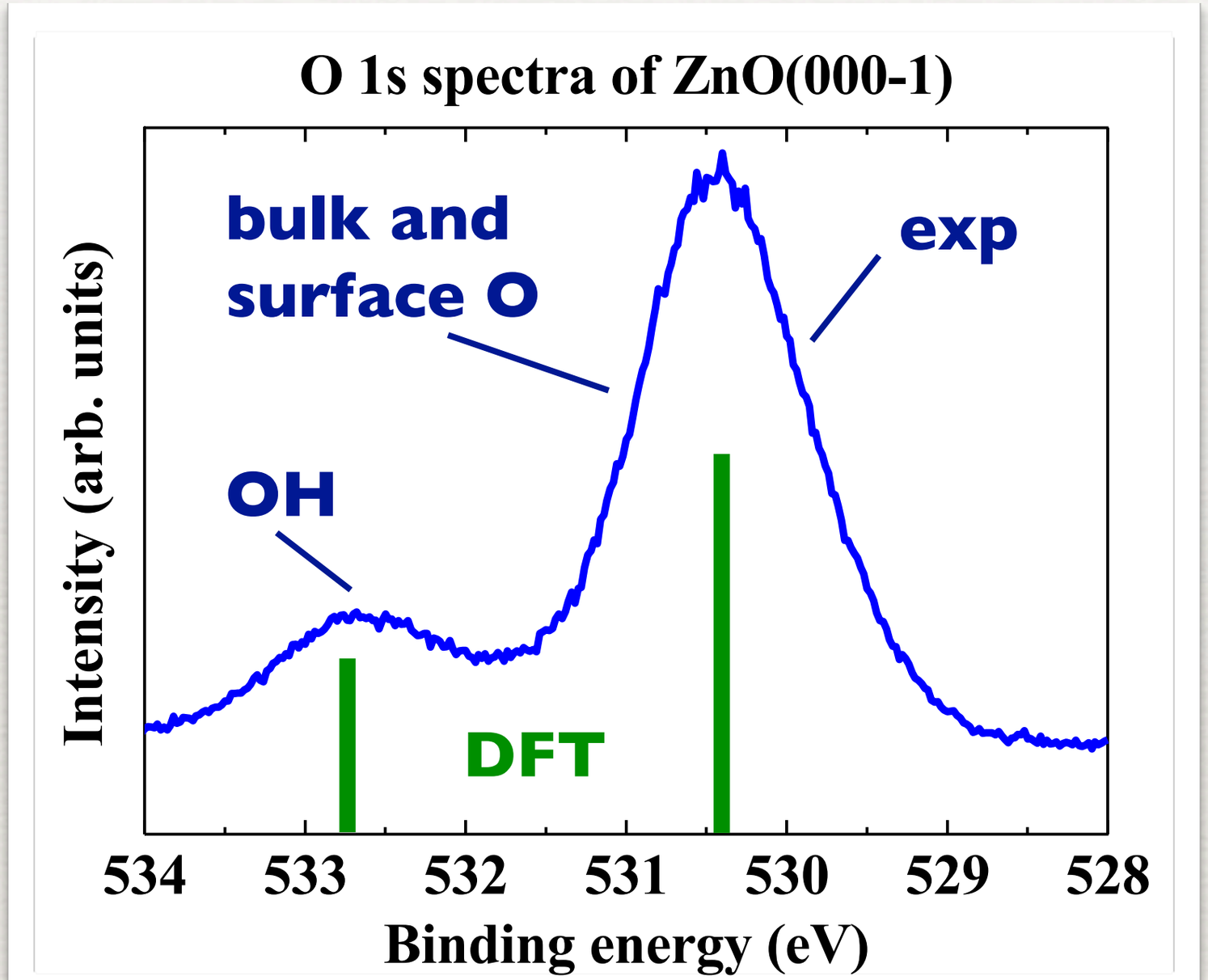
ZnO-O in contact with H-reservoir

- H-deficient surfaces stabilized by n-type conditions



N. Moll, Y. Xu, O. Hofmann, P. Rinke, New J. Phys. in press

Experimental evidence



	surf. core level shift
Exp.	2.0 eV
DFT	2.3 eV

peak weights:

- H-coverage ~30-40%

PBE Δ self-consistent field (SCF) calculations reveal:

- **only H-terminated structures match exp. core level shifts**

HIOS are fascinating systems

Charge transfer

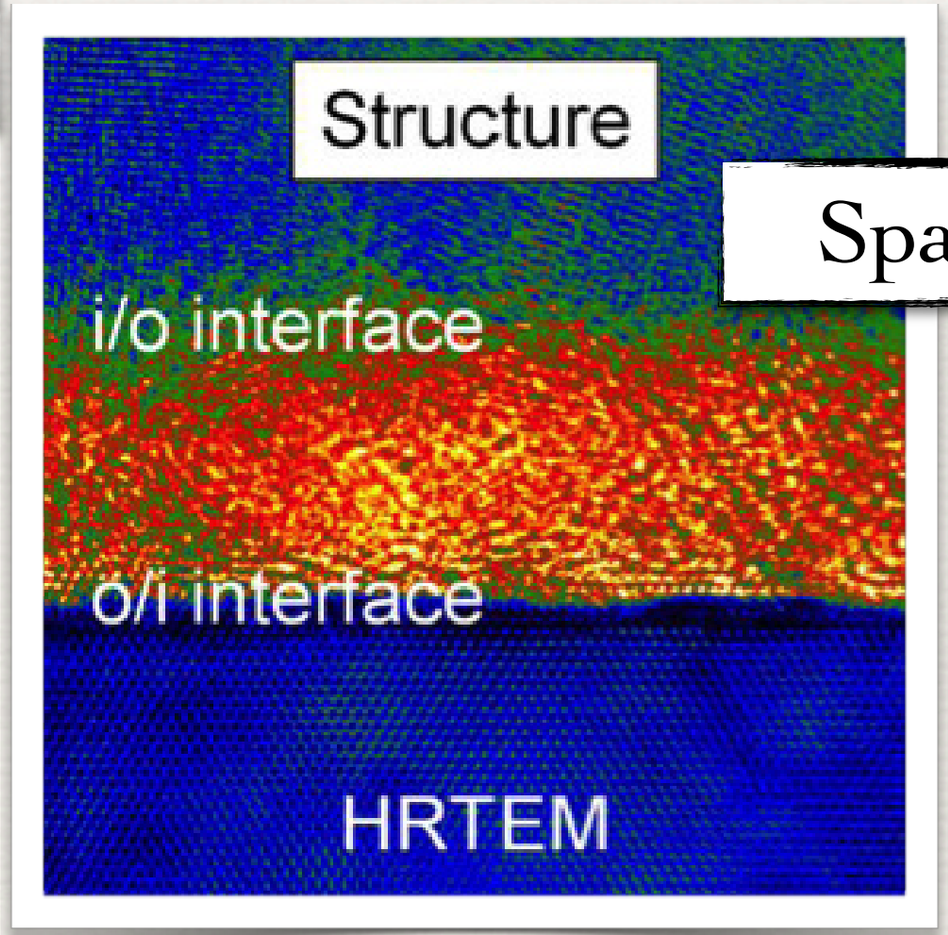
Level alignment

Van der Waals interaction

Surface structure

Adsorption geometry

Defects



Space-charge layers

Atomistic understanding of HIOS

Charge transfer

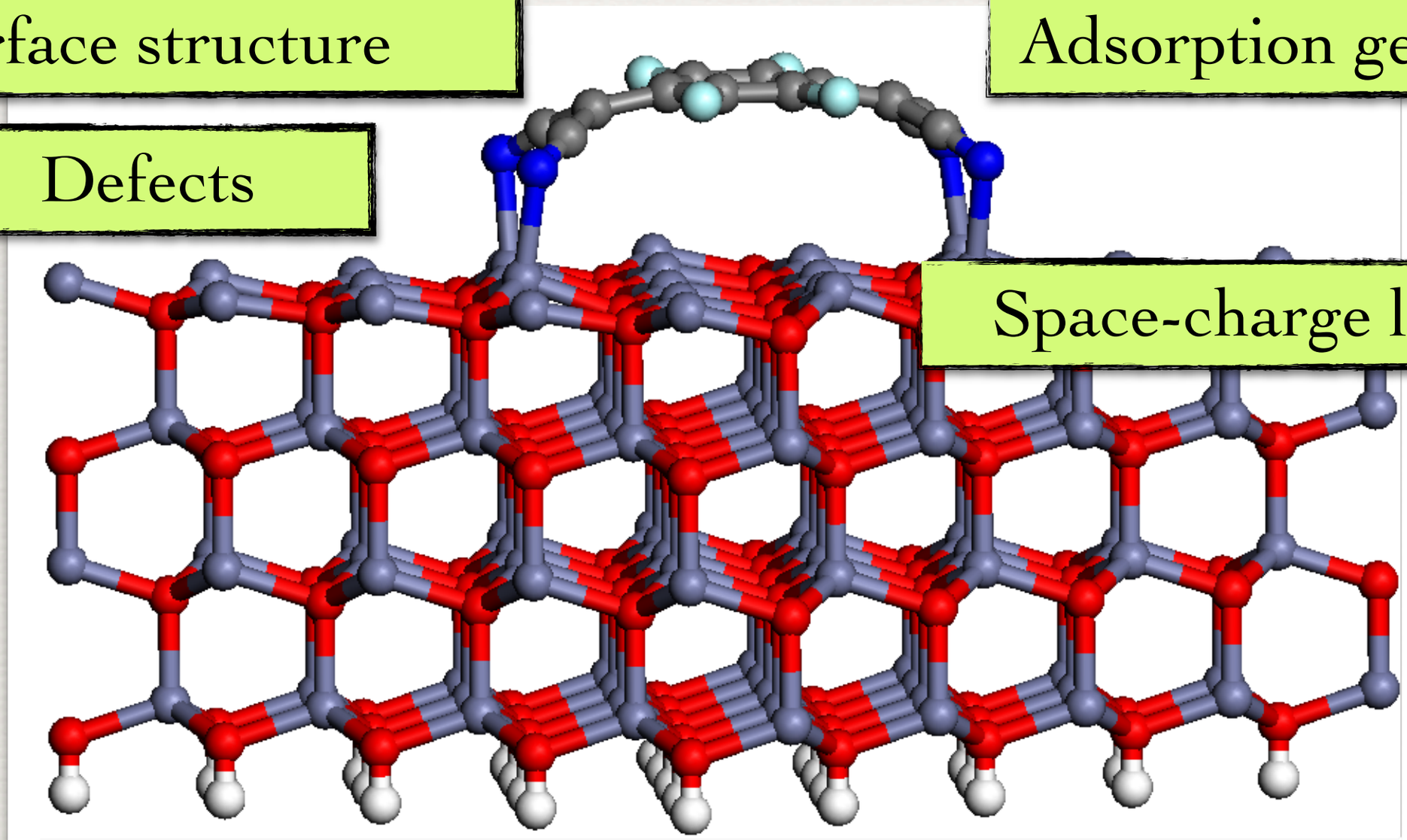
Level alignment

Van der Waals interaction

Surface structure

Adsorption geometry

Defects



Space-charge layers

Atomistic understanding of molecules@surfaces

Charge transfer

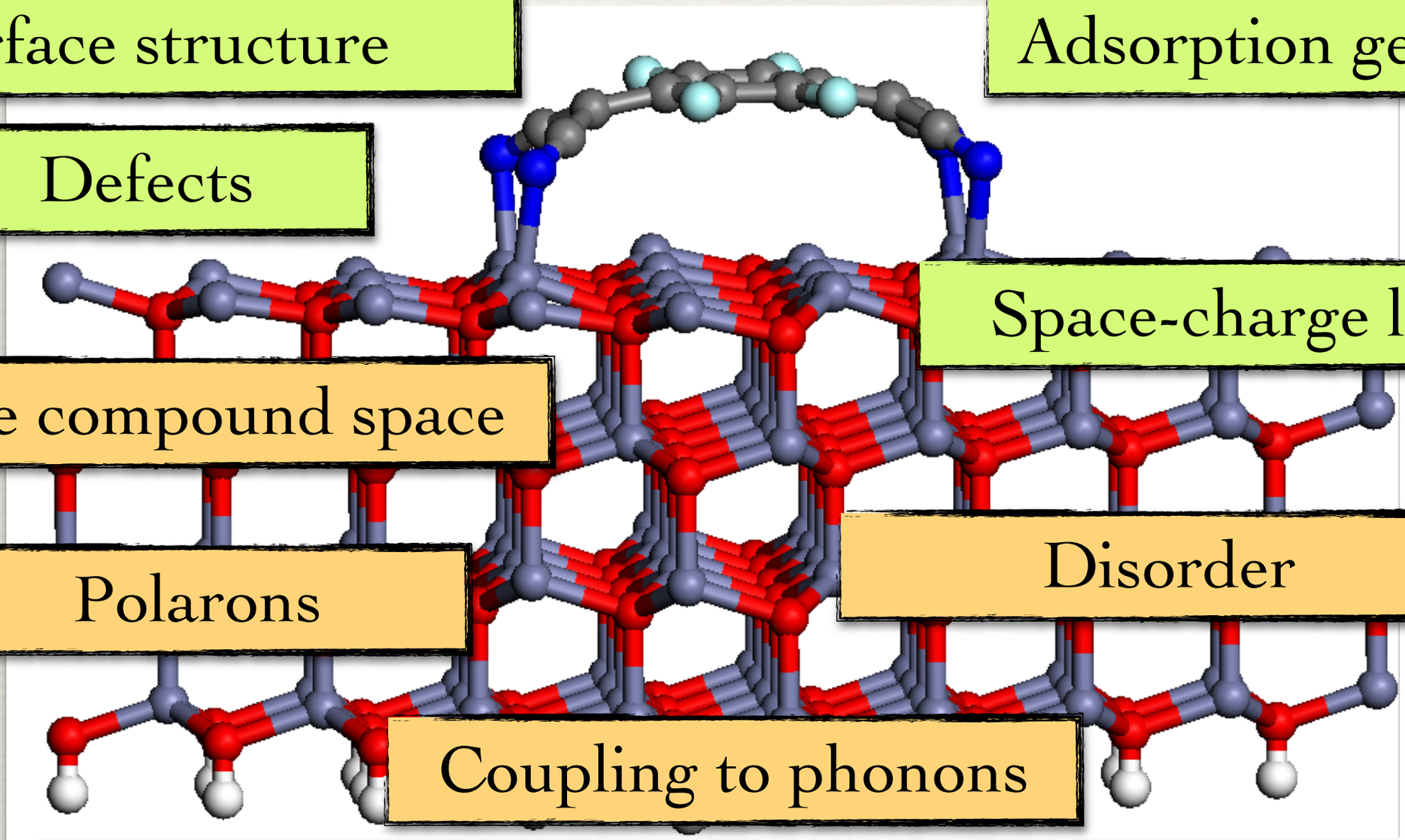
Level alignment

Van der Waals interaction

Surface structure

Adsorption geometry

Defects



Space-charge layers

Large compound space

Disorder

Polarons

Coupling to phonons

Acknowledgements

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Yong Xu
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Norina Richter
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F. Henneberger
N. Koch

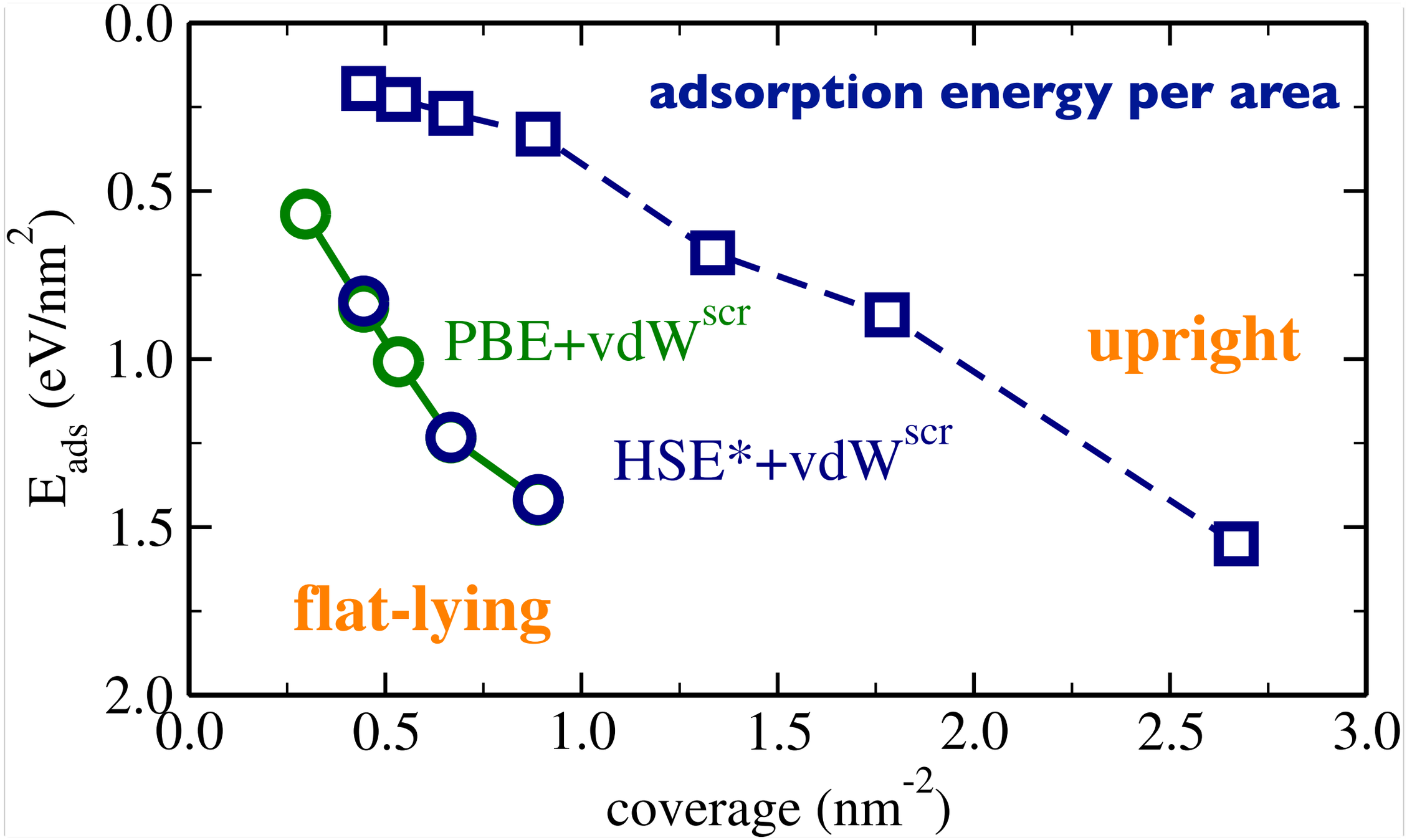
Helmholtz-Center Berlin - BESSY II

S. Winkler
A. Vollmer

HIOS

Thank you!

Adsorption geometries and energies



- **monolayer is composed of flat-lying molecules**
- **molecular orientation in layer random: disorder (no impact on electronic structure)**

Step 2: contribution from space charge region

Step 2a:

bulk doping concentration

- translate Fermi energy into doping dependence (standard semiconductor text book expressions)

$$\Delta\epsilon_{\mathrm{F}} \rightarrow N_D$$

$$\frac{N_{\mathrm{D}}}{1+2\exp(\frac{\Delta\epsilon_{\mathrm{F}}}{k_{\mathrm{B}}T})\exp(\frac{E_{\mathrm{d}}}{k_{\mathrm{B}}T})} = N_{\mathrm{C}}\frac{2}{\sqrt{\pi}}F_{1/2}(\frac{\Delta\epsilon_{\mathrm{F}}}{k_{\mathrm{B}}T})$$

donor binding energy (30 meV)

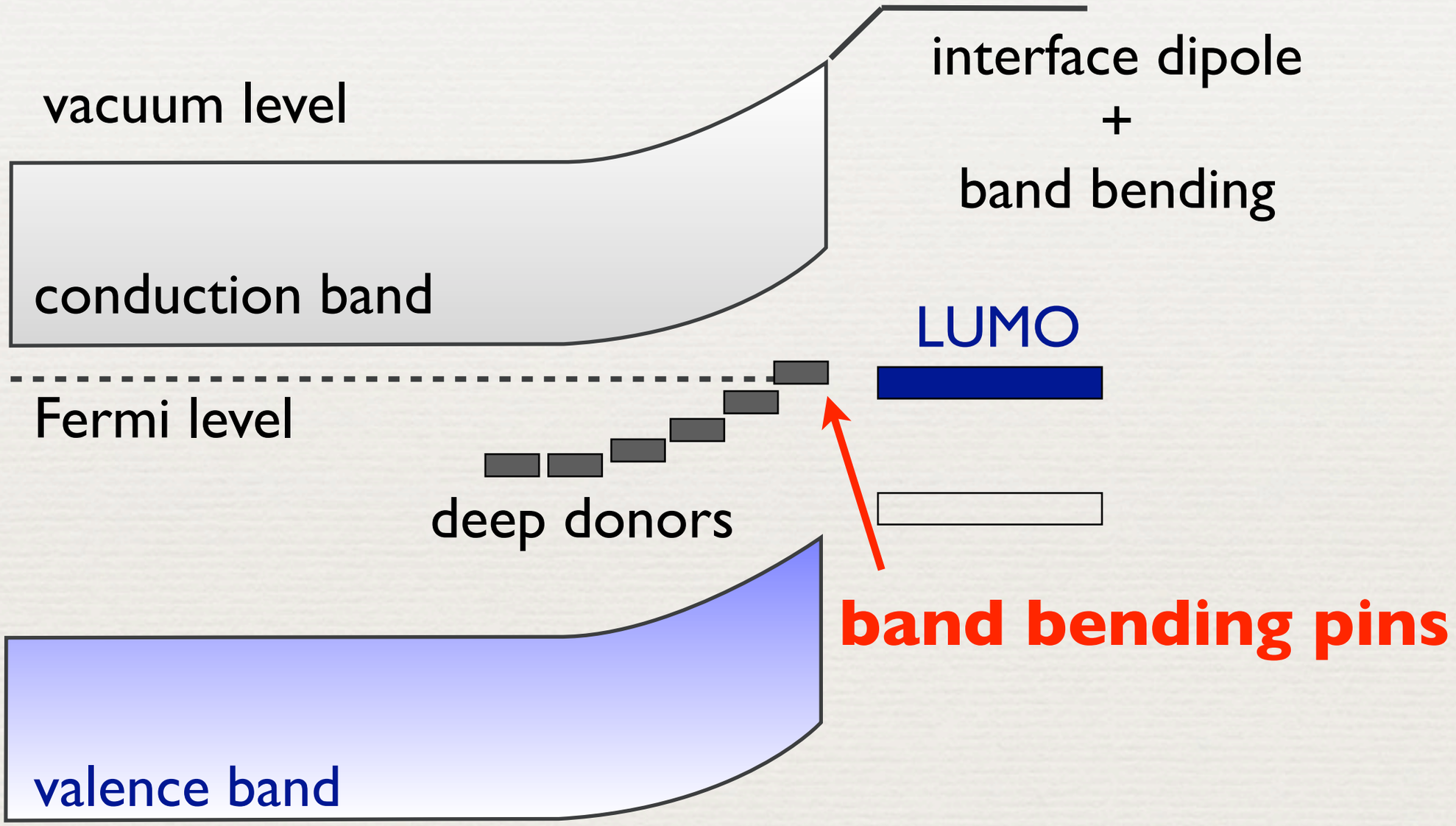
conduction band effective mass ($0.27\ m_e$)

$$N_{\mathrm{C}} = 2(\frac{2\pi m^* k_{\mathrm{B}}T}{h^2})^{\frac{3}{2}}$$

$$F_{1/2}(\eta_{\mathrm{F}}) = \int_0^\infty \frac{\eta^{1/2}\mathrm{d}\eta}{1+\exp(\eta-\eta_{\mathrm{F}})}$$

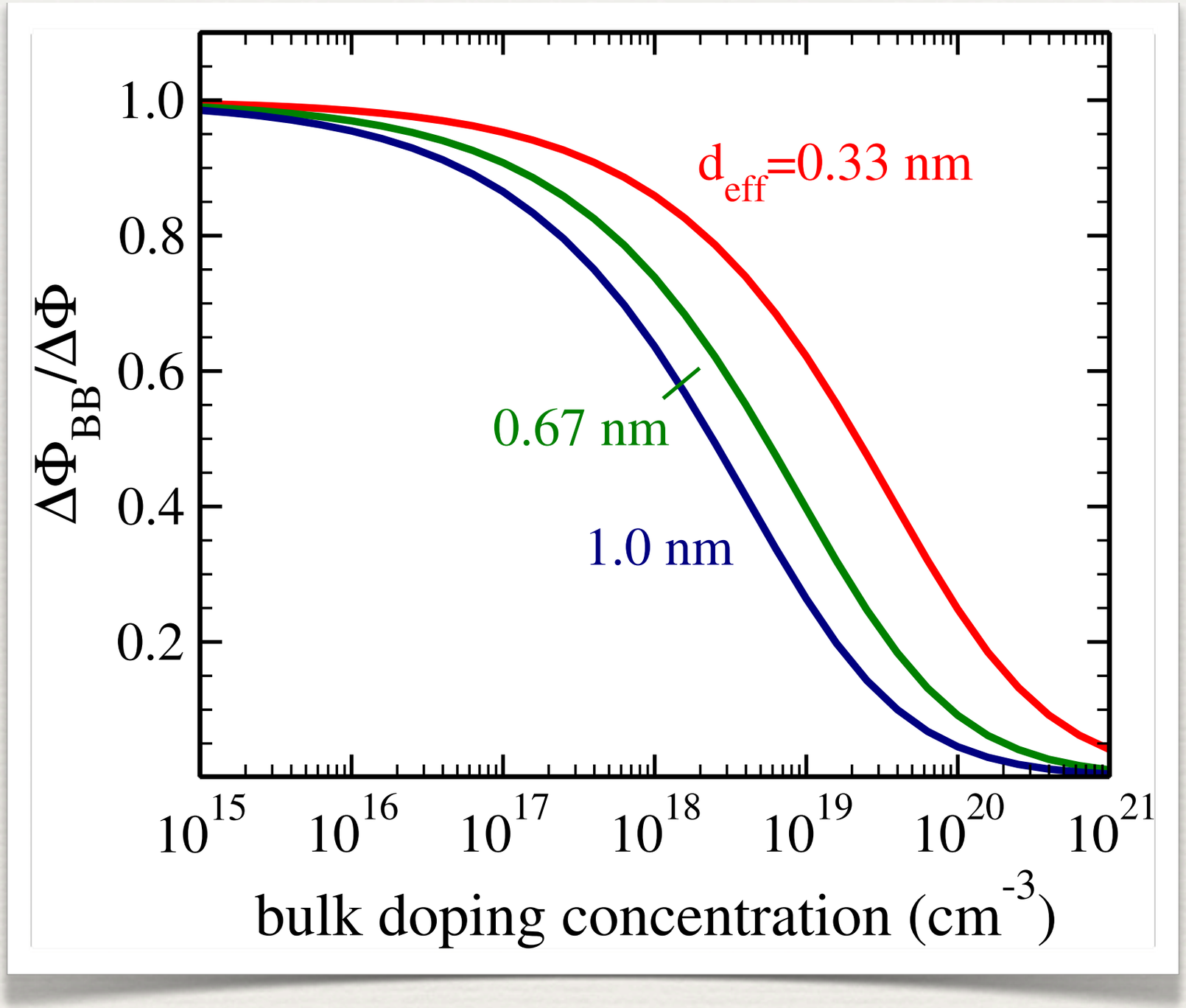
F4TCNQ@ZnO schematically

low doping + deep donors ⇒ band bending pins



F4TCNQ@ZnO schematically

$$\Delta\Phi = \Delta\Phi_{\mathrm{ID}} + \Delta\Phi_{\mathrm{BB}} = \frac{\delta q}{\varepsilon_0} d_{eff} + \frac{\delta q^2}{2\varepsilon_0 \varepsilon N_D}$$



R. Schlesinger, et al., Phys. Rev. B **87**, 155311 (2013)

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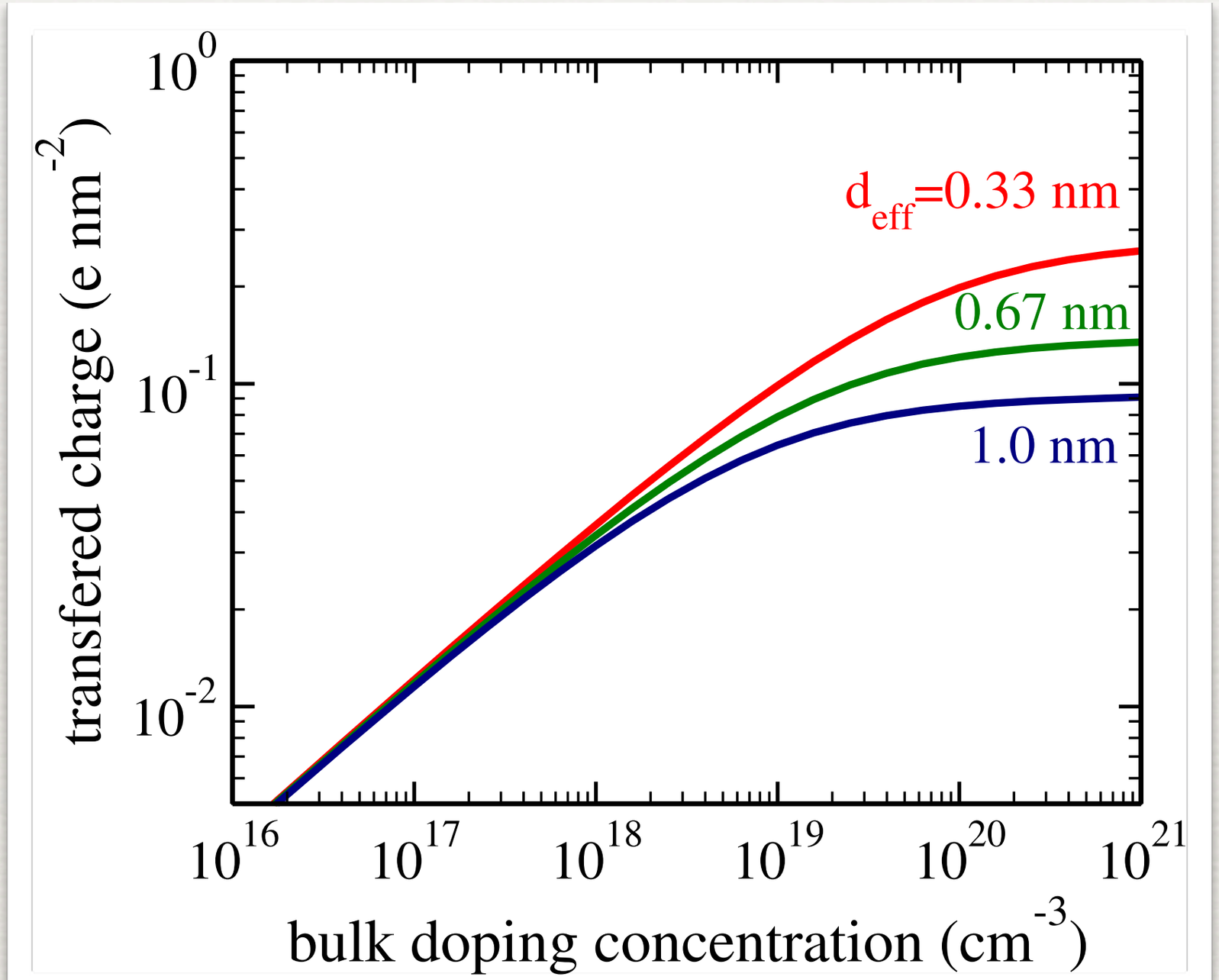

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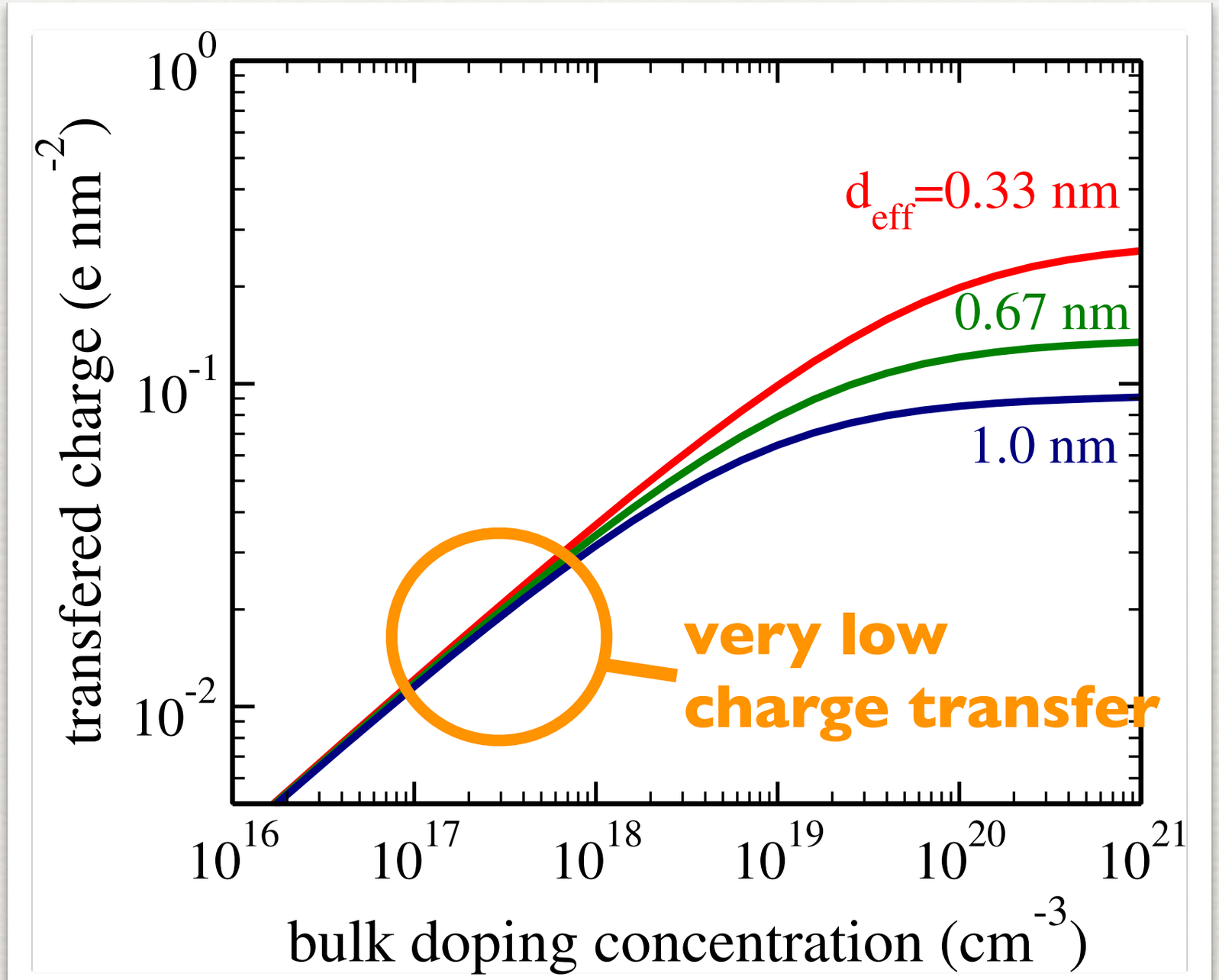

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