UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI FISICA

Spectroscopy of adsorbates and the role of interfacial interactions

Guido Fratesi

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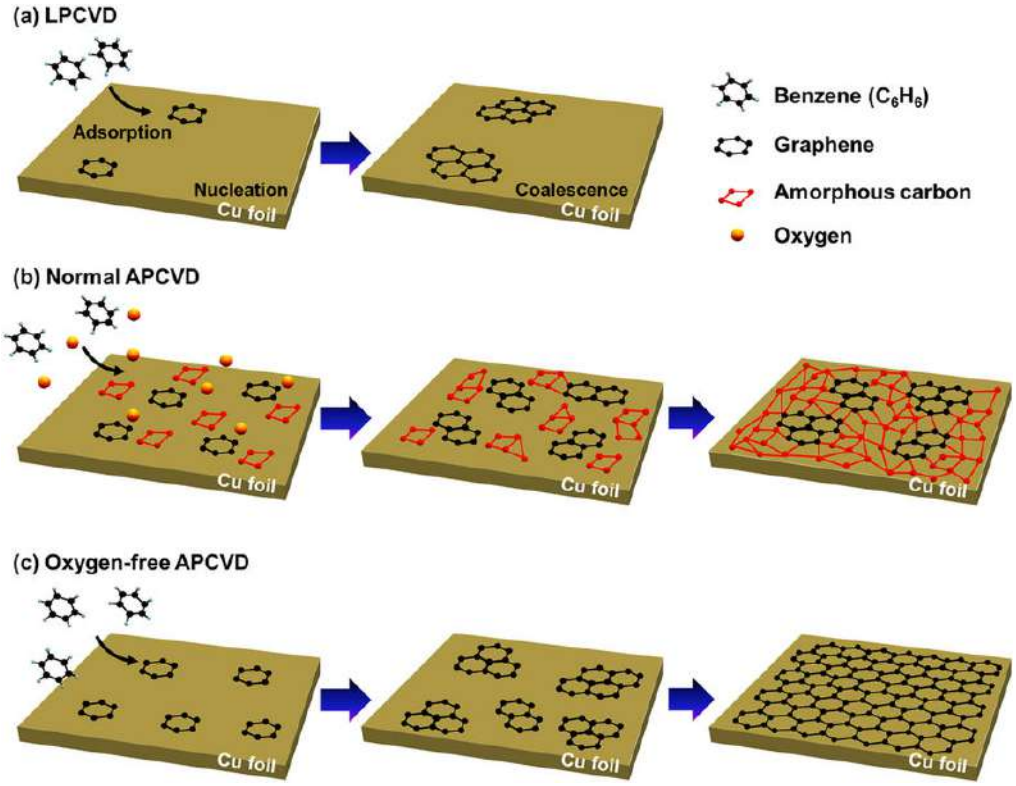
Substrate/adsorbate interfaces

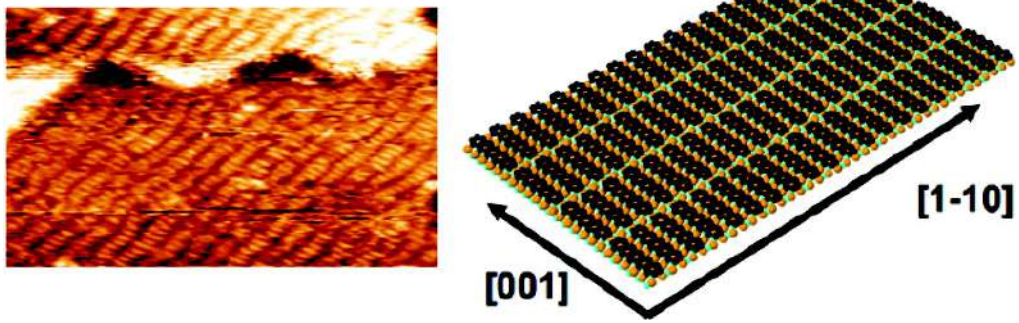
Graphene growth on Copper

J. Jang et al., Scientific Reports 5, 17955 (2015)



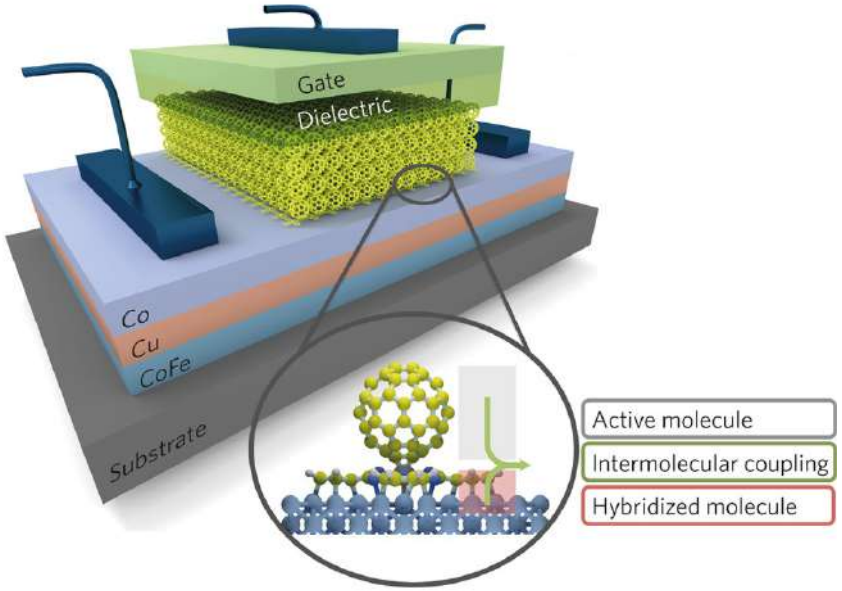
Pentacene molecules on titania

V. Lanzilotto et al., JPCC 115, 4664 (2011)



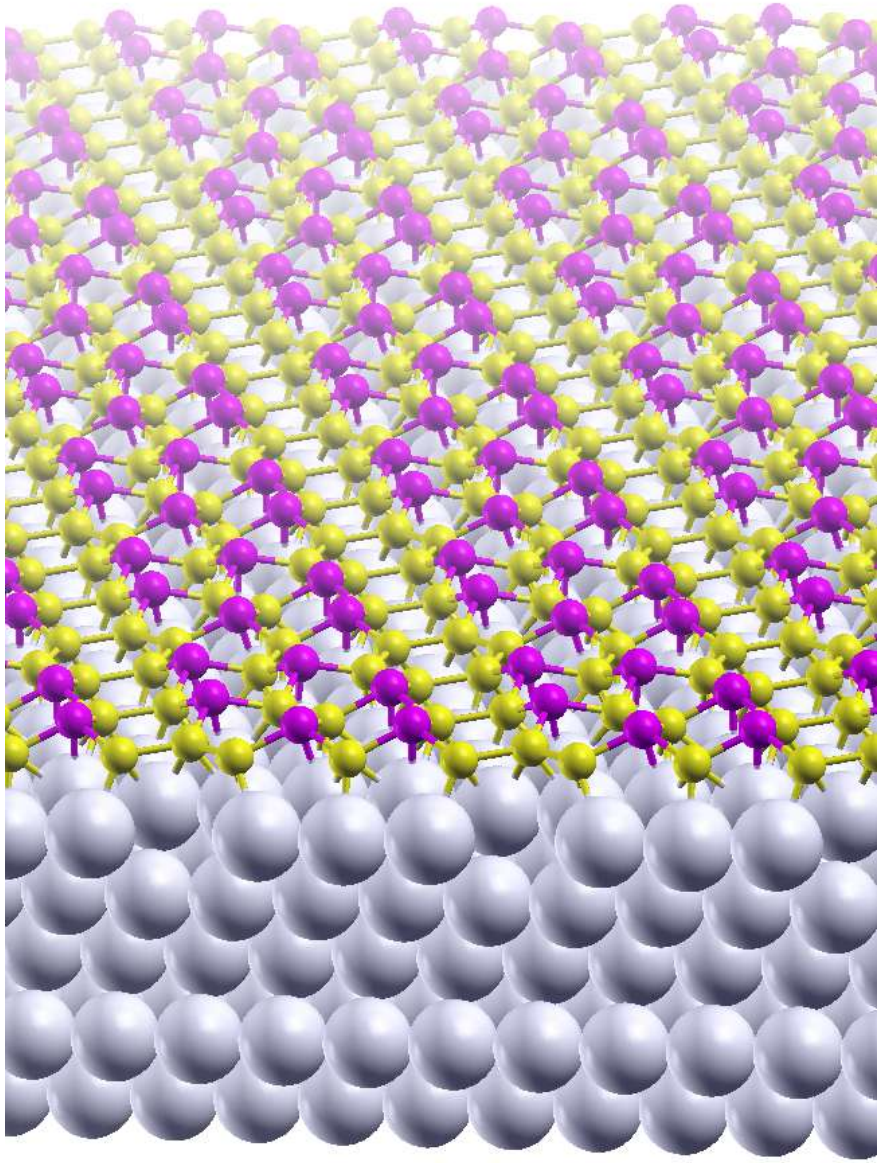
Molecular spintronic devices

M. Cinchetti et al., Nature Materials 16, 507 (2017)

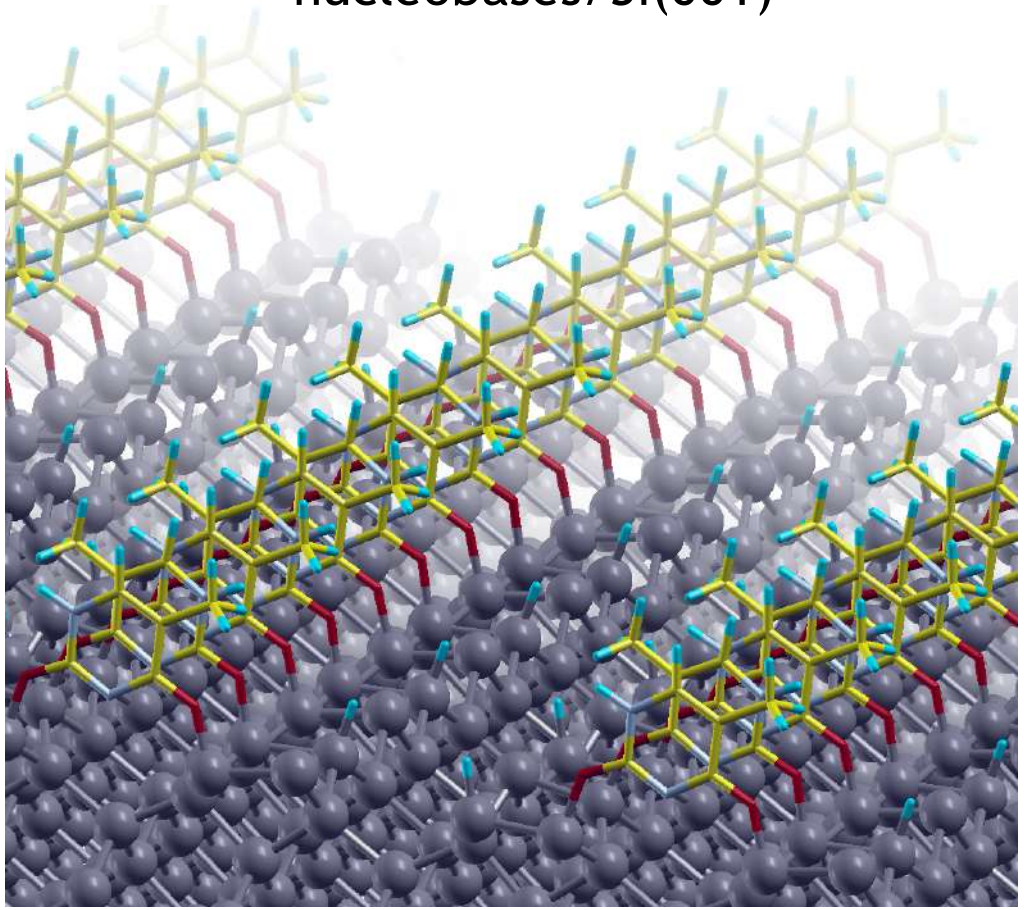


Outline

2D silicon/Ag(111)



Uracil-like
nucleobases/Si(001)



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The many electron problem and spectroscopy

- Density Functional Theory

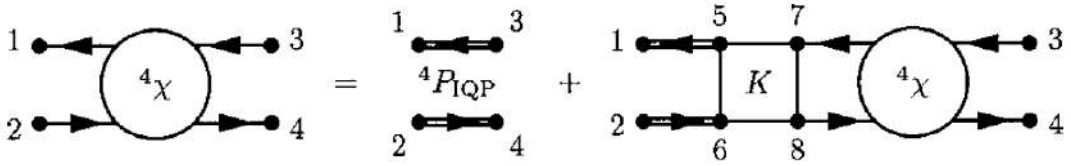
$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad \rightarrow \quad \rho(\mathbf{r})$$

  - ✔ No adjustable parameters
  - ✔ Systems with thousands of electrons
  - ✗ Needed approximations (e.g., quasi-local dependence)
  - ✗ In principle, a ground state theory

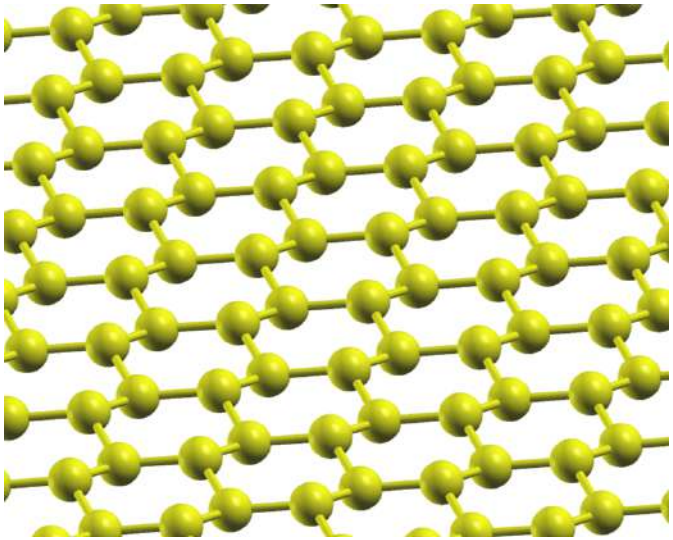
So what about spectroscopy?

- Zero[th]-order expansion in the e-e interaction
  - 1-e excitations:

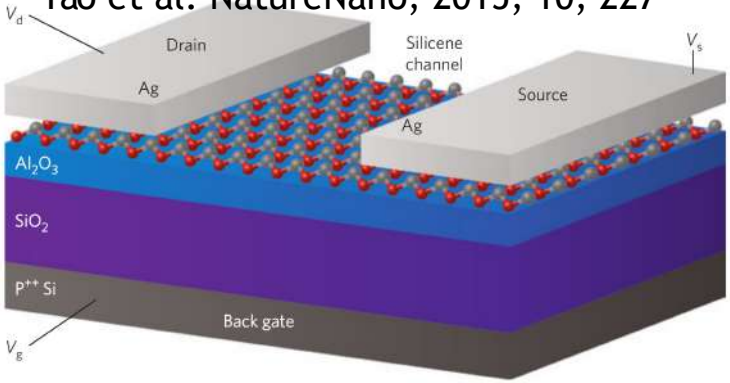
  - 2-e excitations:



“Silicene” = 2D honeycomb silicon

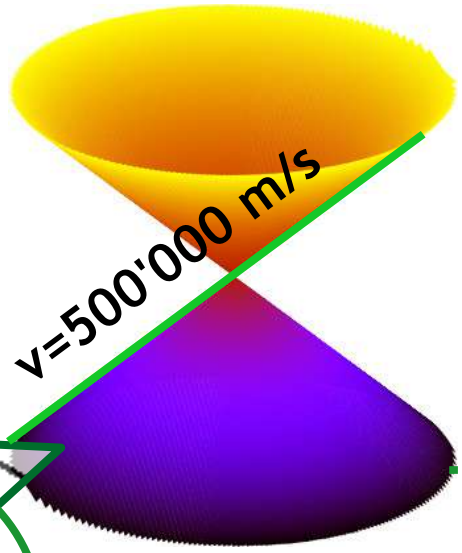


Tao et al. NatureNano, 2015, 10, 227



1994, 2009
Stability
(Theory)

2012
Dirac bands
on Ag(111)



2013-2014
Not for “4x4”

2015
Transistor
grown on Ag

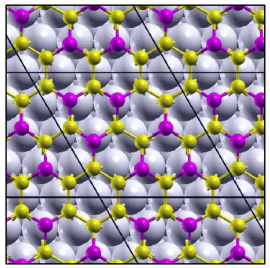
2015
Polymorphism
dependence?

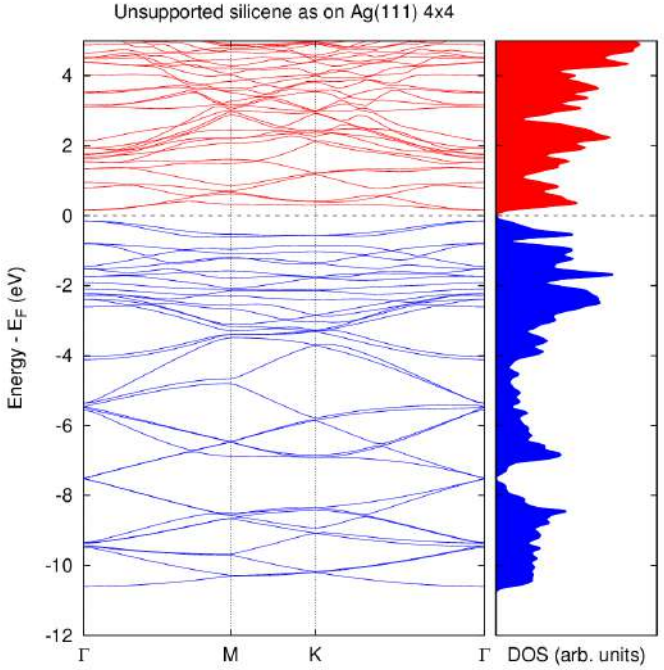
2017 More
“compelling
evidences” to
verify?

Silicene polymorphism

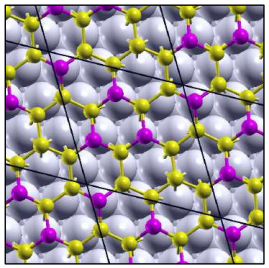
- Preparation conditions → different phases of silicene/Ag(111)
- <u>Free standing layers</u>: *Dirac character* .OR. *band gap opening*

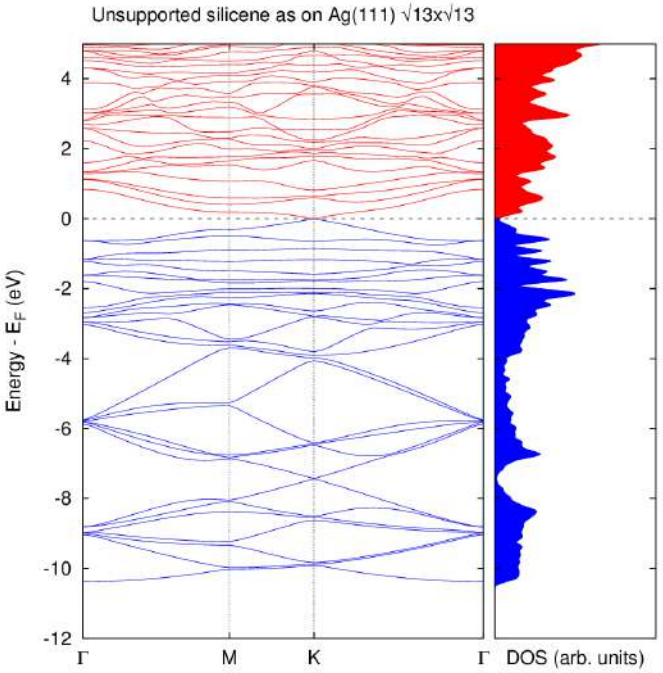
4x4



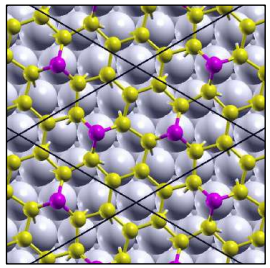


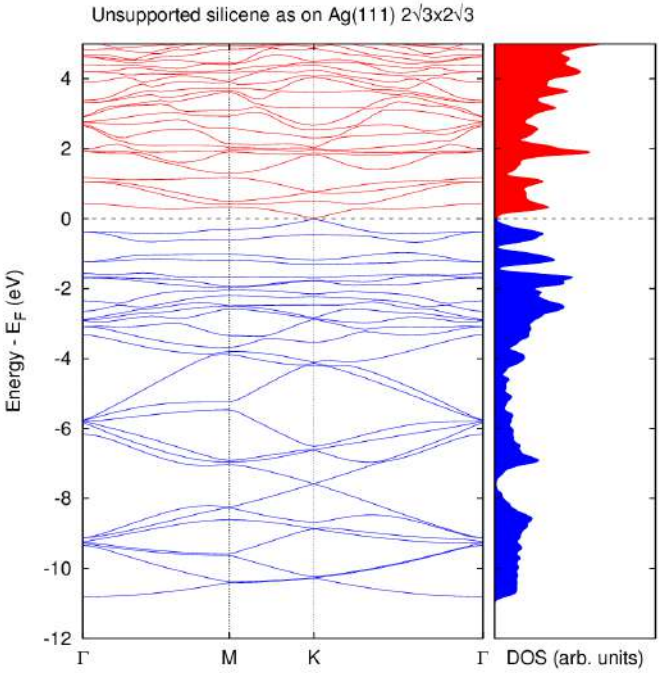
√13x√13





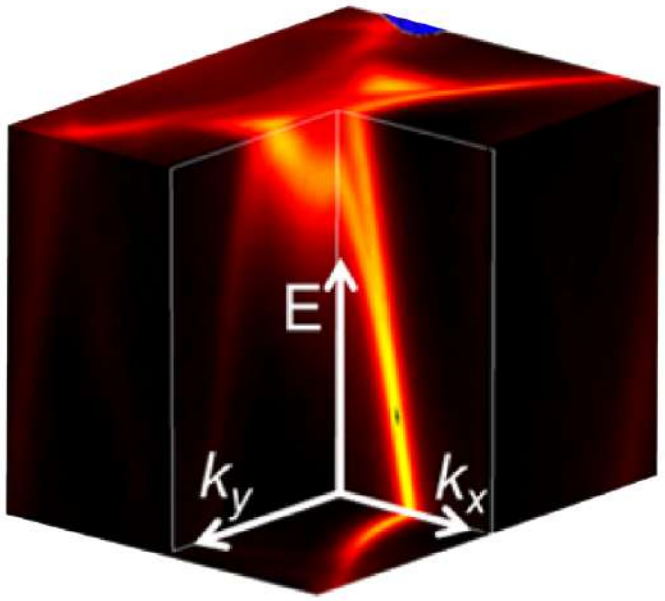
2√3x2√3

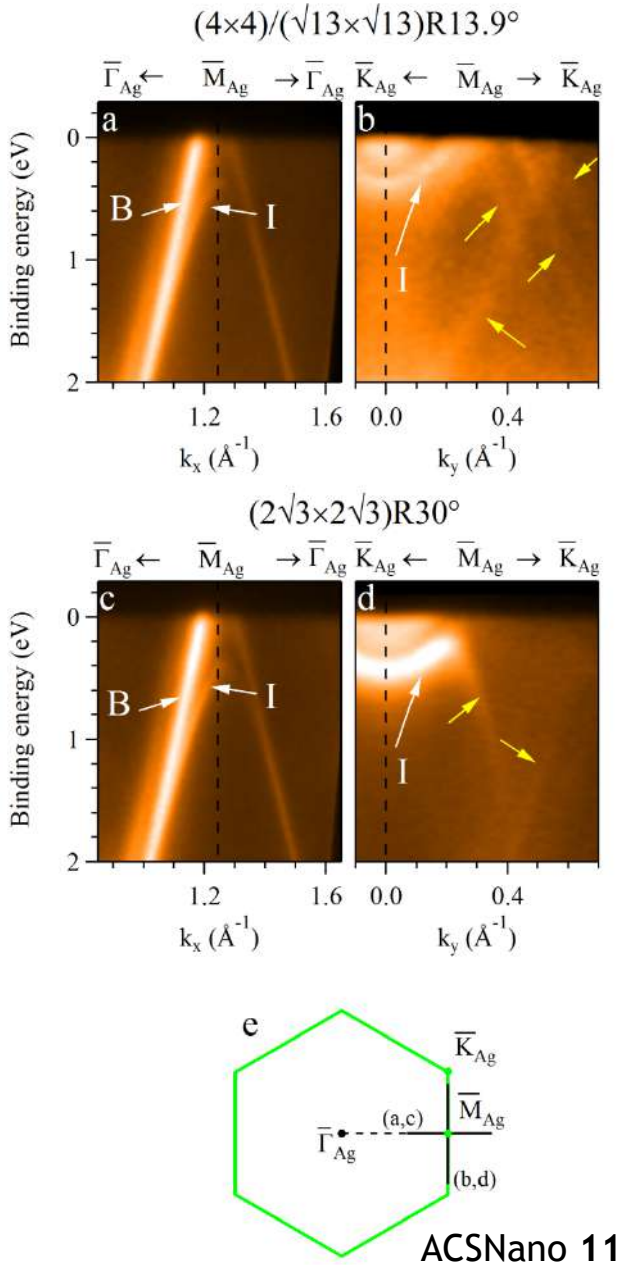




Angle-resolved photoemission (π bands?)

- Different phases, similar states:
  - Bulk and replicas
  - Interface (mostly Ag-sp)
  - Misunderstood as Dirac *cone*, it is a *saddle*

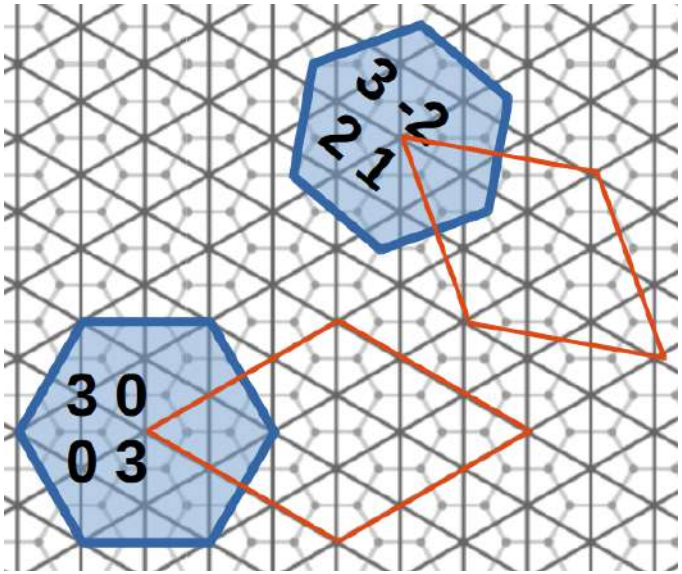


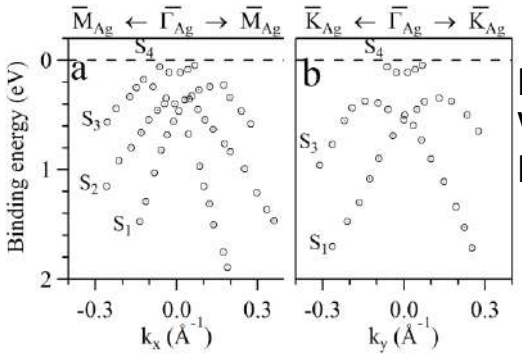


ACSNano **11**, 975 (2017)

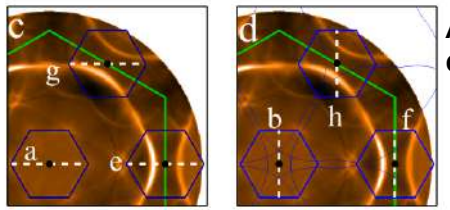
Angle-resolved photoemission (σ bands?)

- Different phases, similar states:
  - Bulk and replicas
  - Interface (mostly Ag-sp)
  - Differences originate from the relative orientation of reciprocal space lattices

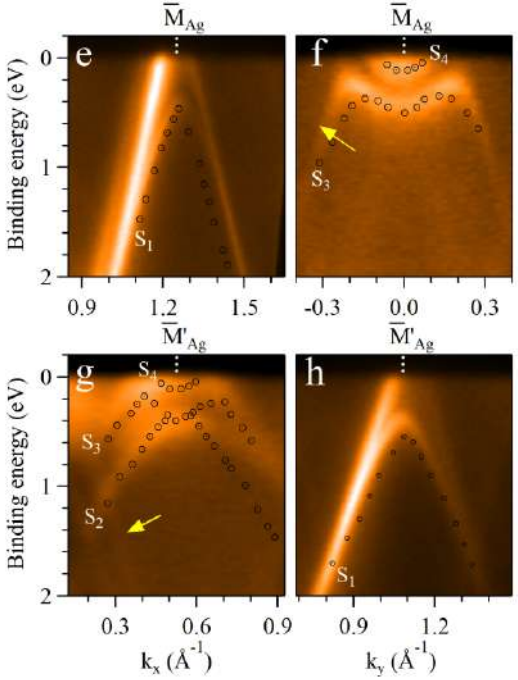




Data from Wang et al., PRB 92, 205427



ACSNano **11**, 975 (2017)

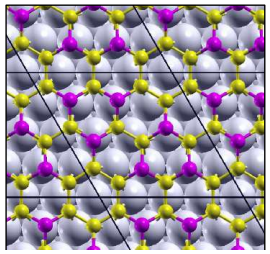
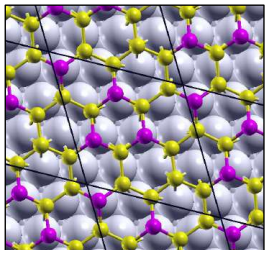
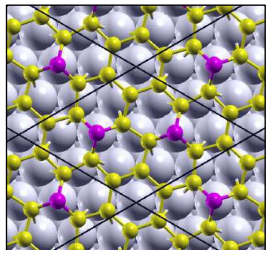


Silicene polymorphism

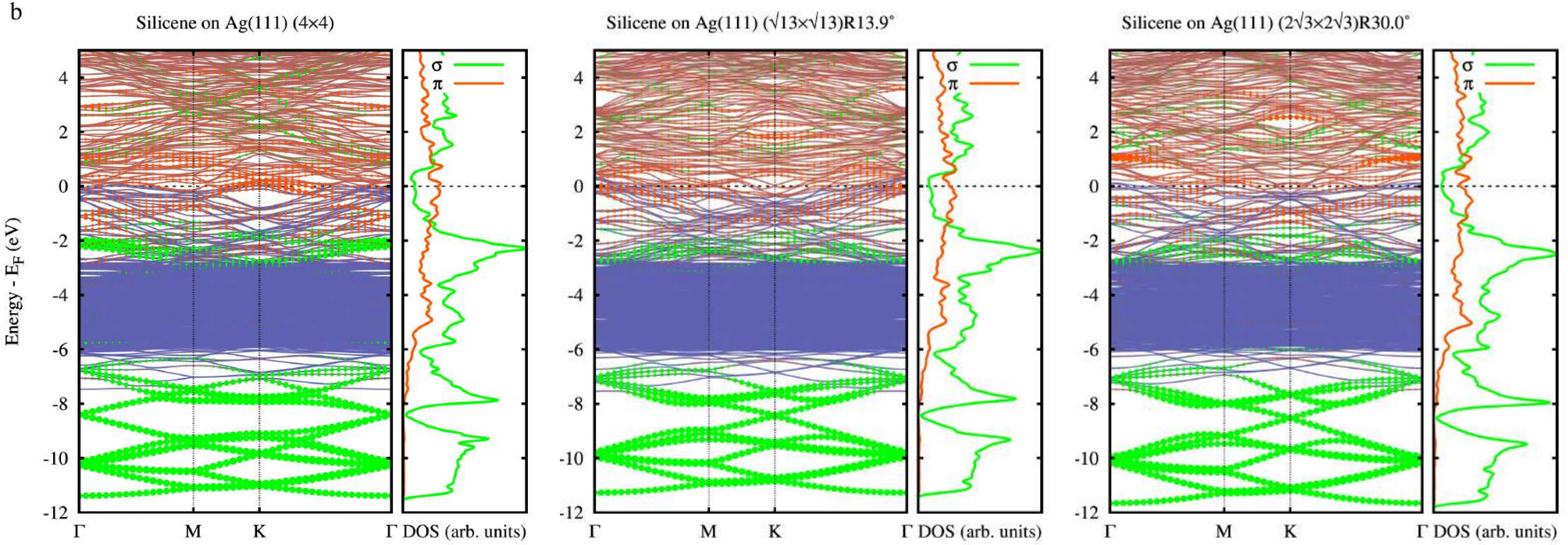
- Preparation conditions → different phases of silicene/Ag(111)
- Supported layers: very similar electronic structure (hybridization!)

ACSNano **11**, 975 (2017)

4x4 $\sqrt{13}$x$\sqrt{13}$ 2$\sqrt{3}$x2$\sqrt{3}$

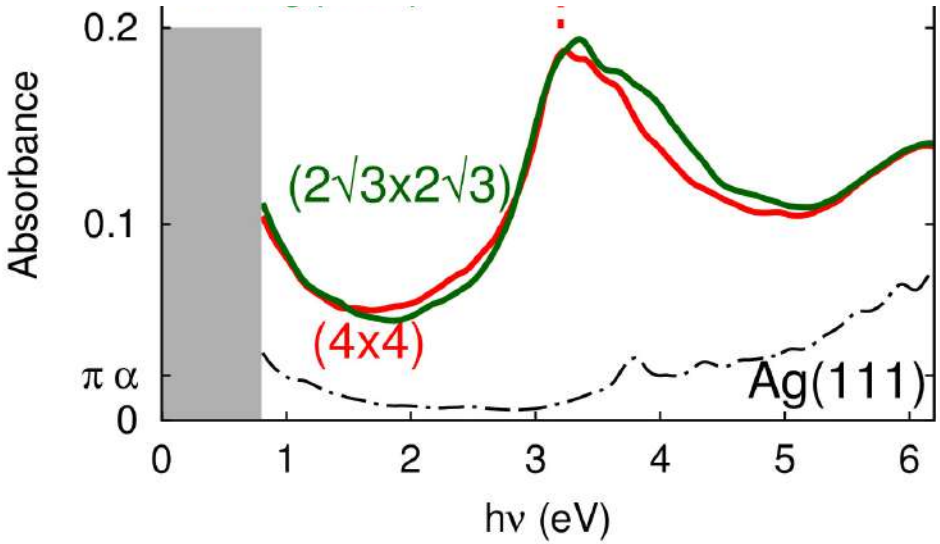
b



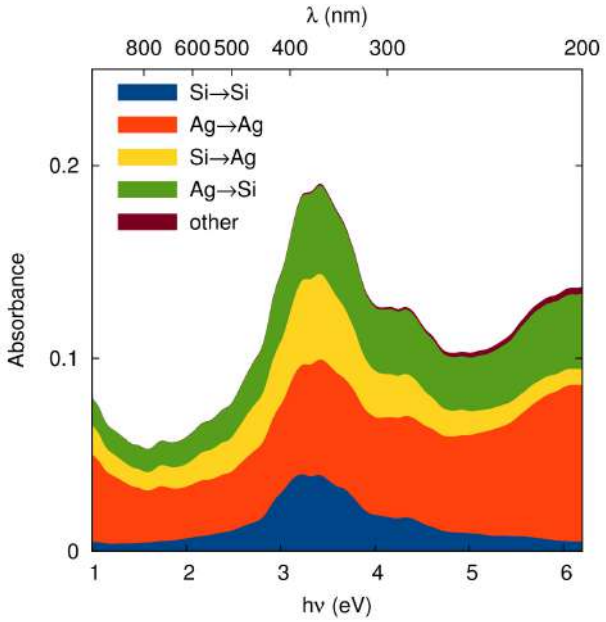
Optical spectra and charge carriers

- Silicene features almost independent of the phase

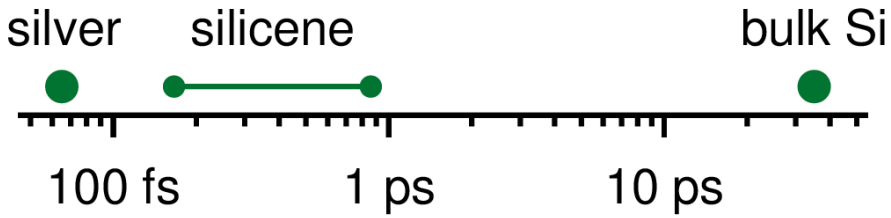
PRB **92**, 165427 (2015)



- Light absorption due to hybrid states *<u>mostly located on Ag</u>*

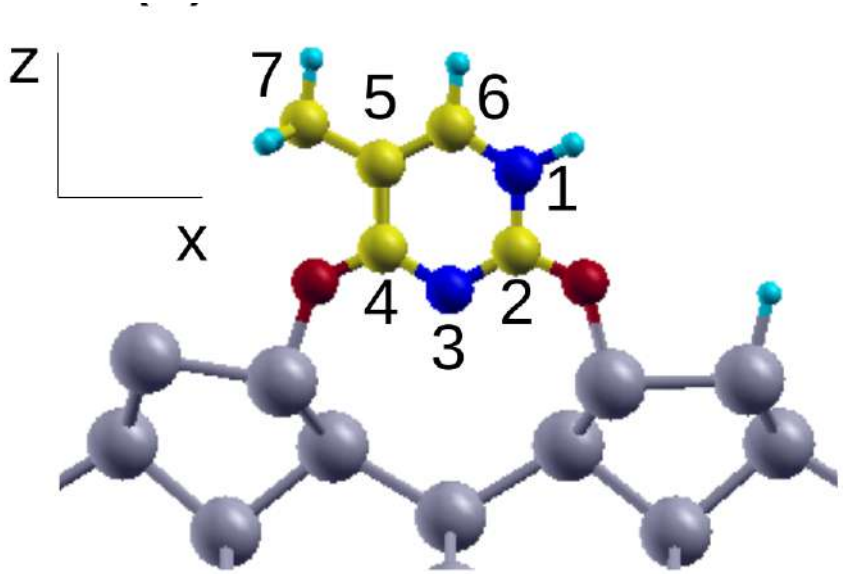


Relaxation times (by pump&probe):



- Metallic character of photogenerated charge carriers

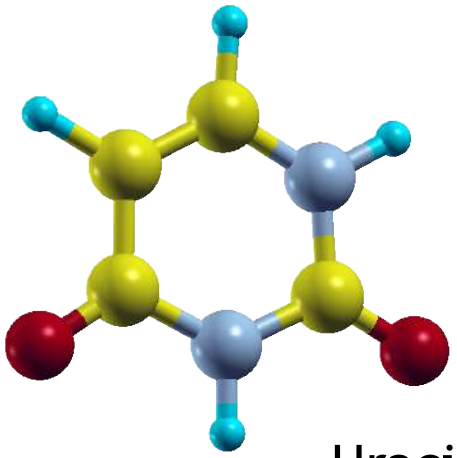
Uracil-like nucleobases on Si(001)



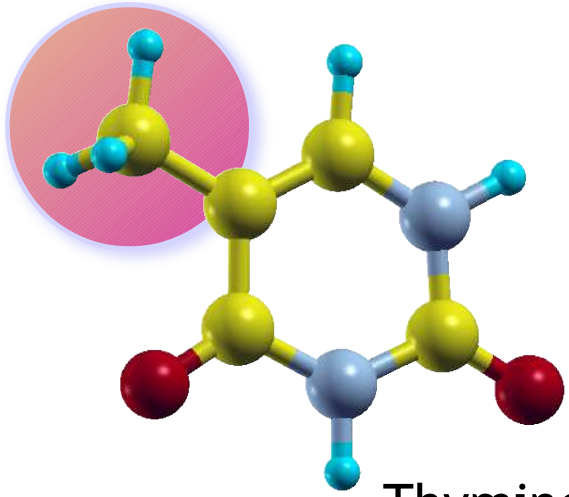
- Non-destructive tools
- Reflection anisotropy spectroscopy (RAS):

$$\frac{\Delta R}{R}(\omega) = \frac{R_x - R_y}{(R_x + R_y)/2}(\omega)$$

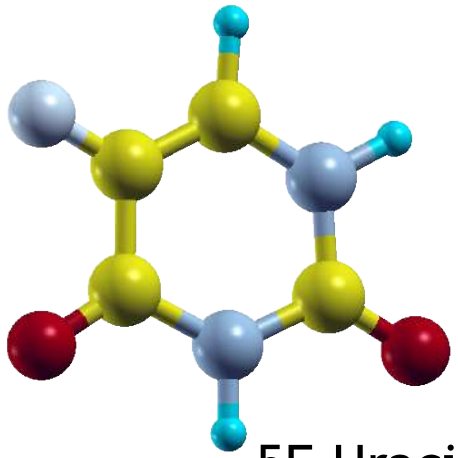
- Fingerprinting chemical substitutions for molecular recognition?



Uracil



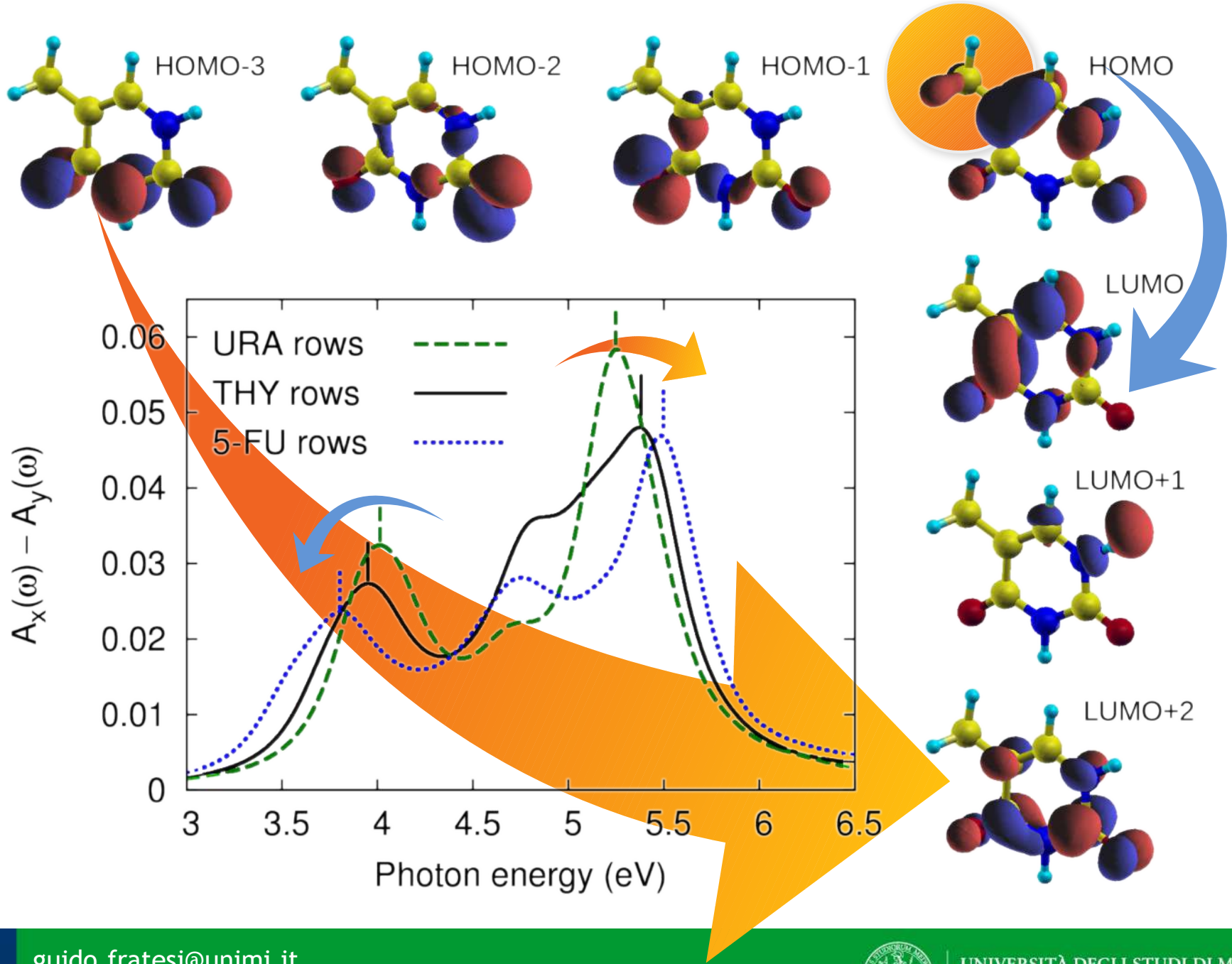
Thymine



5F-Uracil

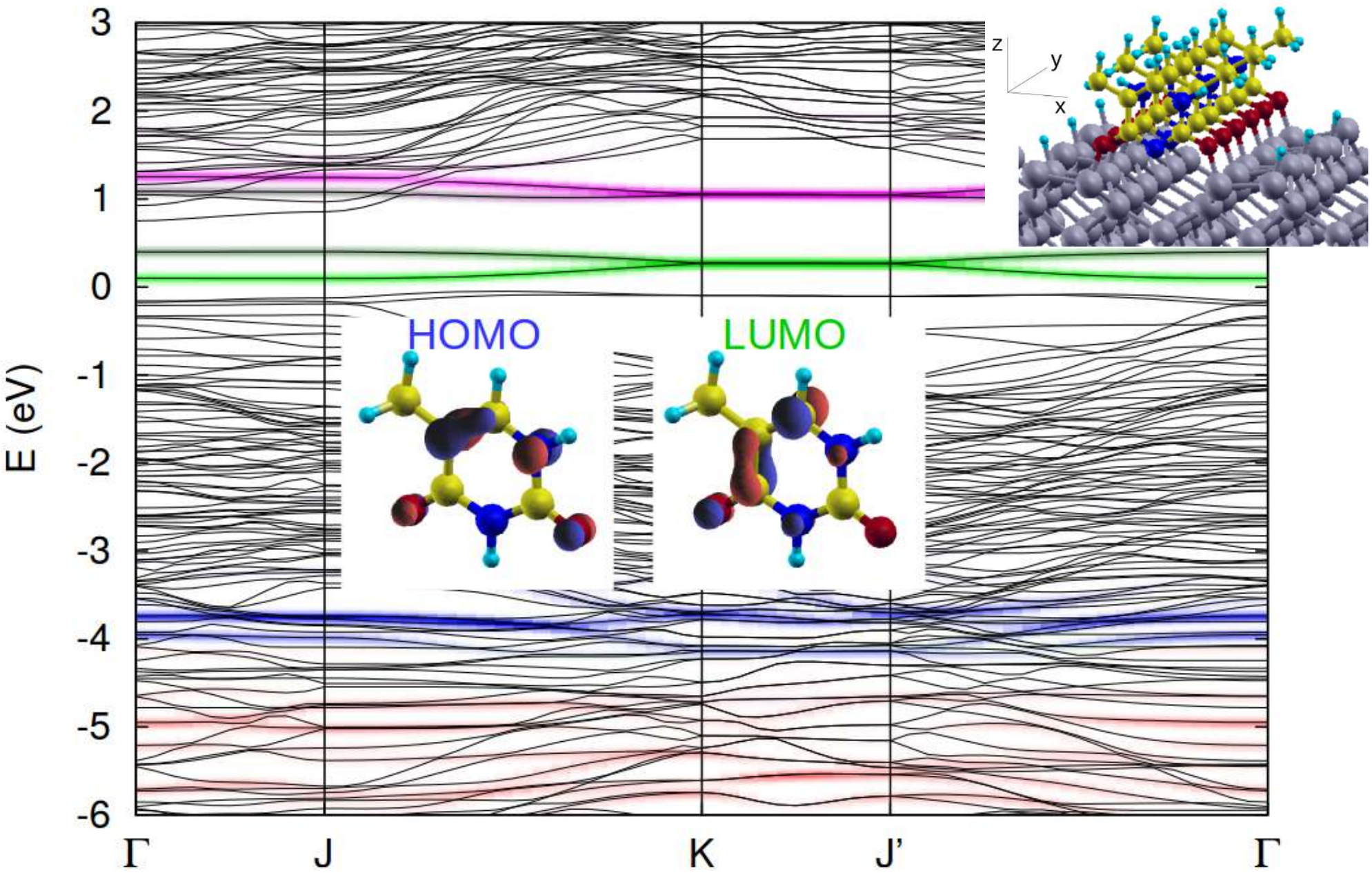
Expected chemical sensitivity

PRB **95**, 075437 (2017)



Thymine/Si(001) band structure

PRB **95**, 075437 (2017)



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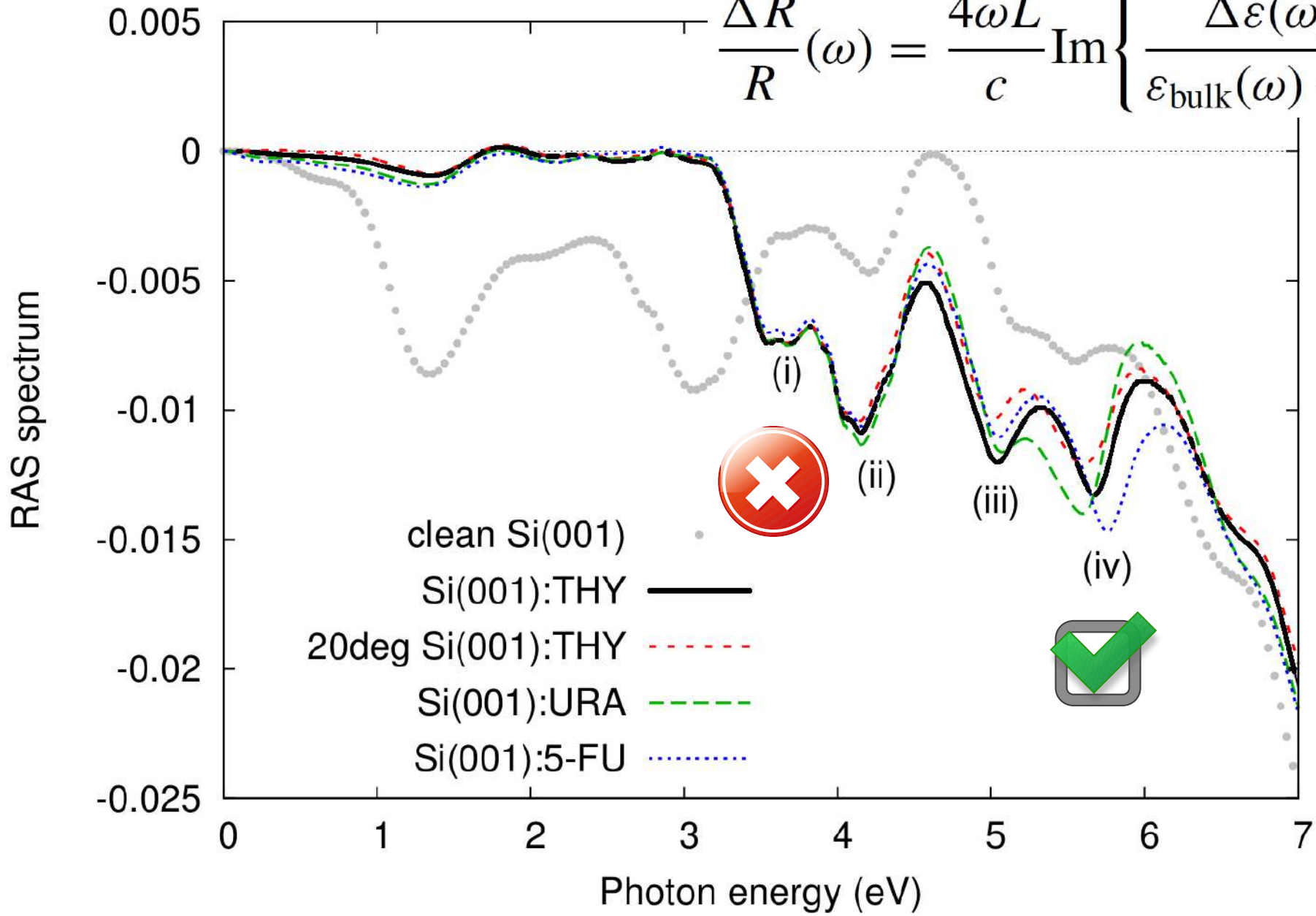
Reflection anisotropy spectroscopy (RAS)

PRB **95**, 075437 (2017)

$$\frac{\Delta R}{R}(\omega) = \frac{4\omega L}{c}\mathrm{Im}\left\{\frac{\Delta\varepsilon(\omega)}{\varepsilon_{\mathrm{bulk}}(\omega) - 1}\right\}$$



Reflection anisotropy spectroscopy (RAS)

PRB **95**, 075437 (2017)

- Simpler absorption spectrum:

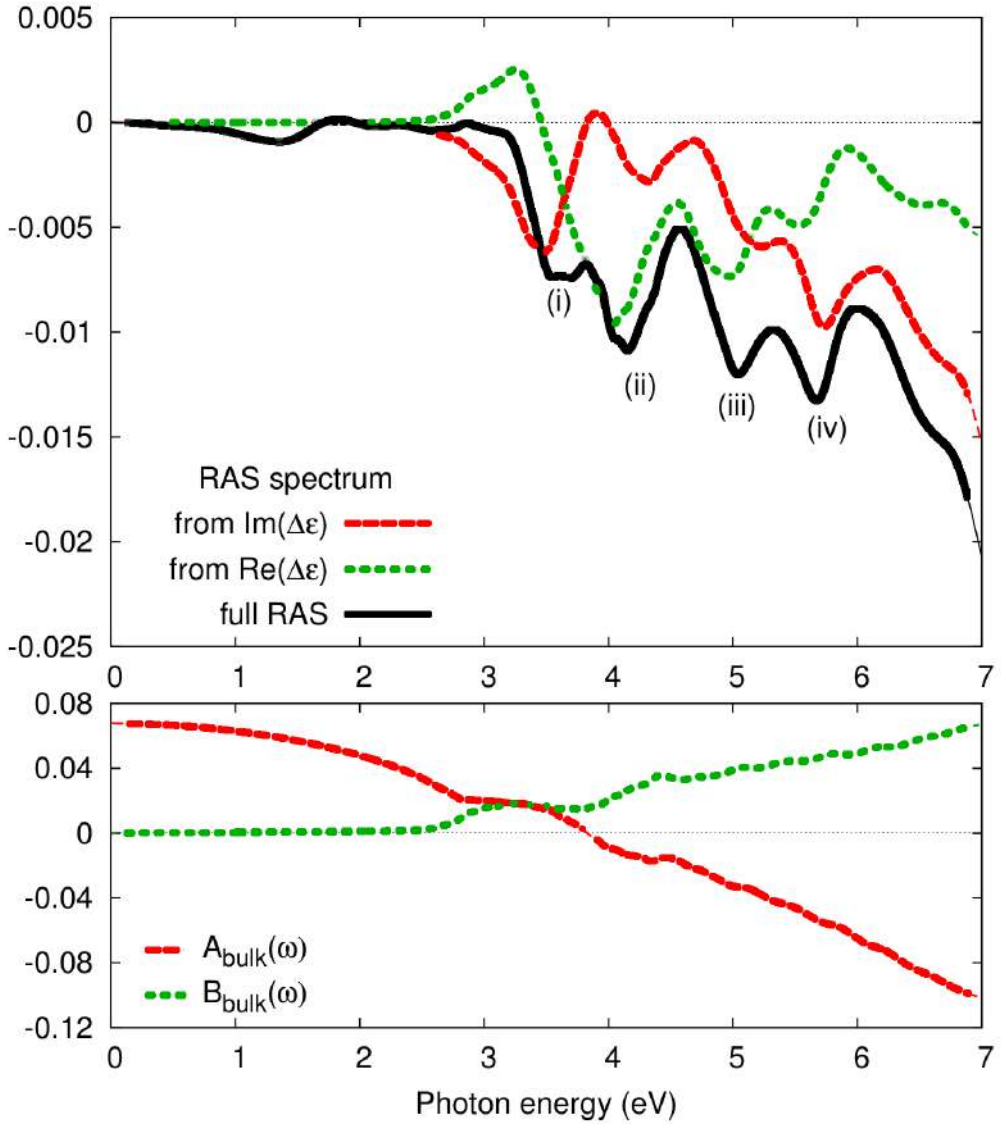
$$A_j(\omega) = \frac{\omega L}{c}\mathrm{Im}[\varepsilon_{jj}(\omega)]$$

- From the RAS:

$$\frac{\Delta R}{R}(\omega) = \frac{4\omega L}{c}\mathrm{Im}\left\{\frac{\Delta\varepsilon(\omega)}{\varepsilon_{\mathrm{bulk}}(\omega) - 1}\right\}$$

$$= \frac{4\omega L}{c}[A_{\mathrm{bulk}}\Delta\varepsilon'' - B_{\mathrm{bulk}}\Delta\varepsilon']$$

$$\Delta A = A_x - A_y$$



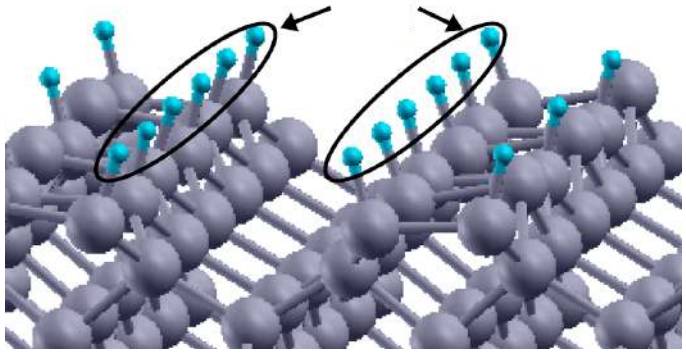
Reflection anisotropy spectroscopy (RAS)

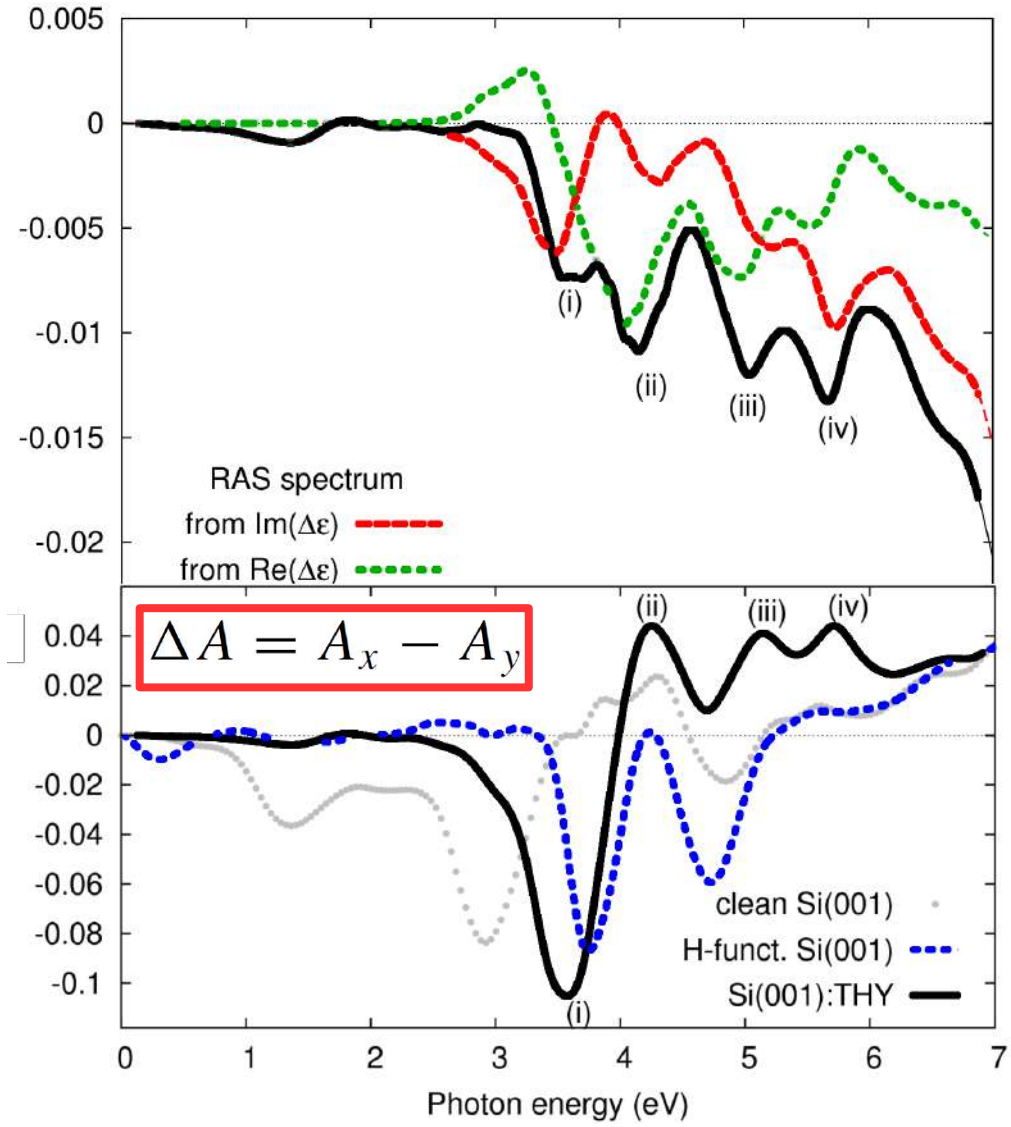
PRB **95**, 075437 (2017)

- Simpler absorption spectrum:

$$A_j(\omega) = \frac{\omega L}{c}\mathrm{Im}[\varepsilon_{jj}(\omega)]$$

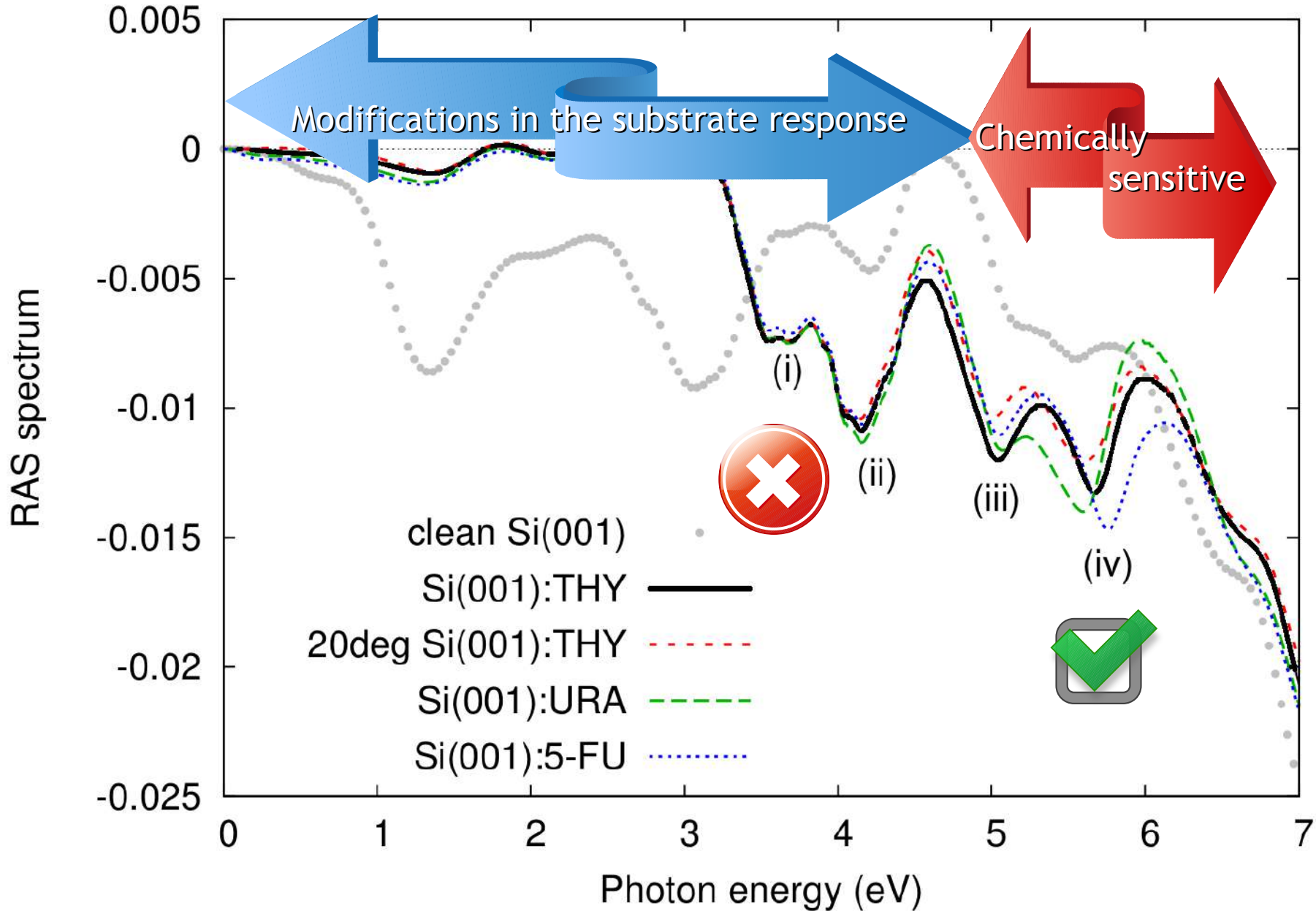
- Peak (i): purely substrate origin
  - Opposite sign than expected for HOMO → LUMO molecular transitions
  - Reproduced with … H!





Reflection anisotropy spectroscopy (RAS)

PRB **95**, 075437 (2017)



Conclusions & Acknowledgments

- Twofold role of interfaces:
  - Substrate → adsorbates
    e.g. Ag → silicene
  - Substrate ← adsorbates
    e.g. Si(001) ← molecules

- Ab initio as a valuable tool:
  - Interpretation and analysis
  - Prediction/suggestion

Theory @ UNIMI
Elena Molteni, Giovanni Onida

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CNR - Istituto di Struttura della Materia, Trieste
Sincrotrone Elettra, Trieste
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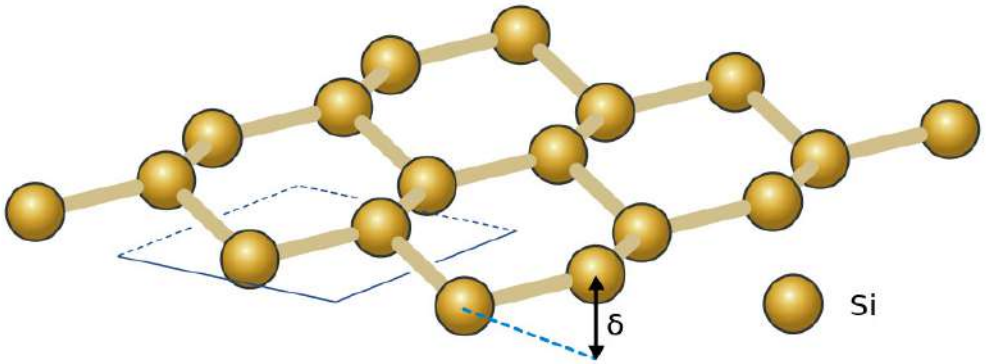
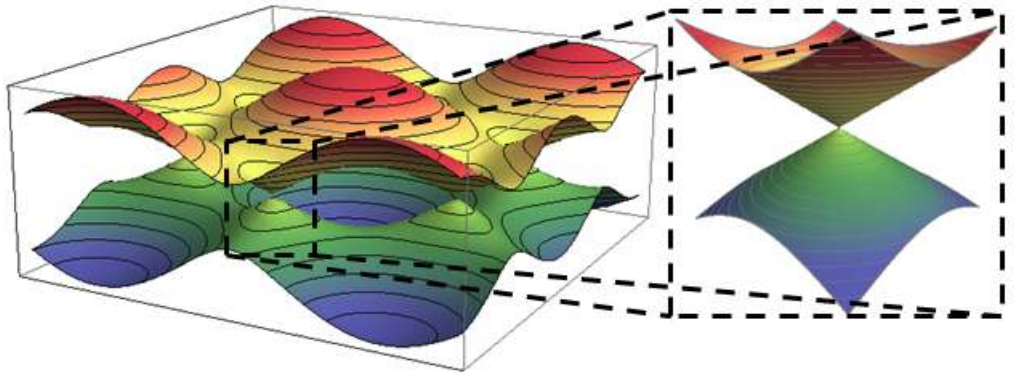
Thank you for your attention!

Extra slides

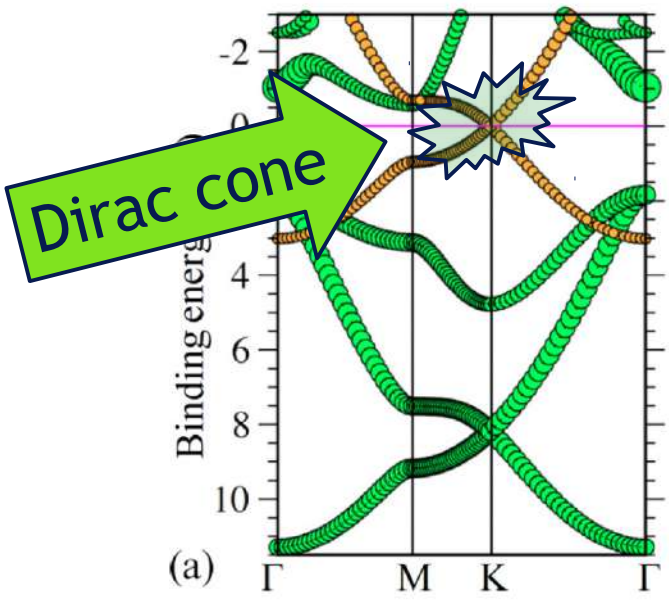
Potentials of silicene



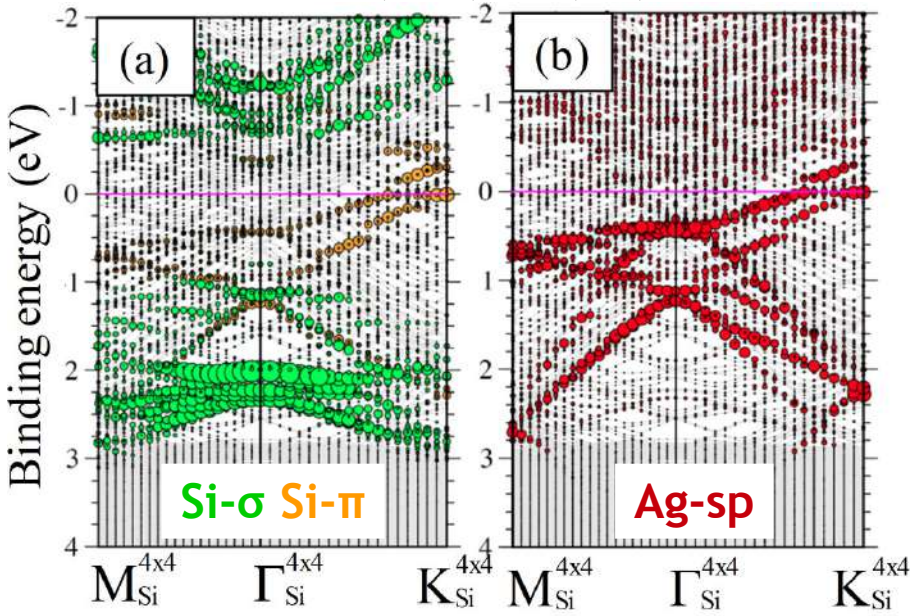
- Ease of integration
- Massless charge carriers
- On-demand properties



Silicene timeline

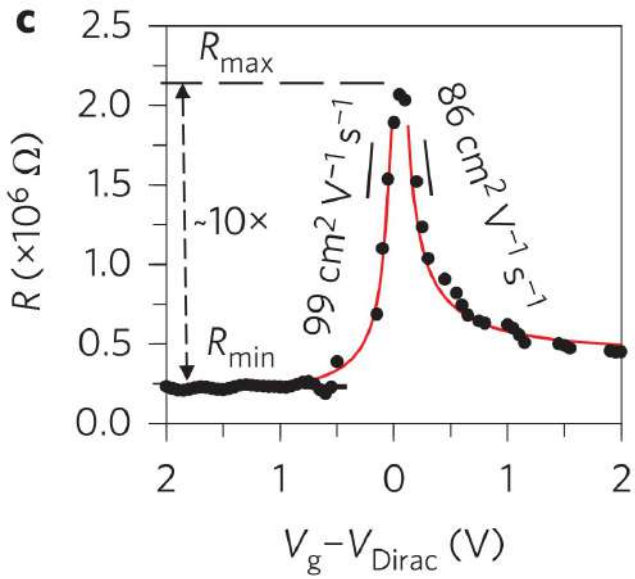


Mahatha et al., PRB, 2014, 89, 201416

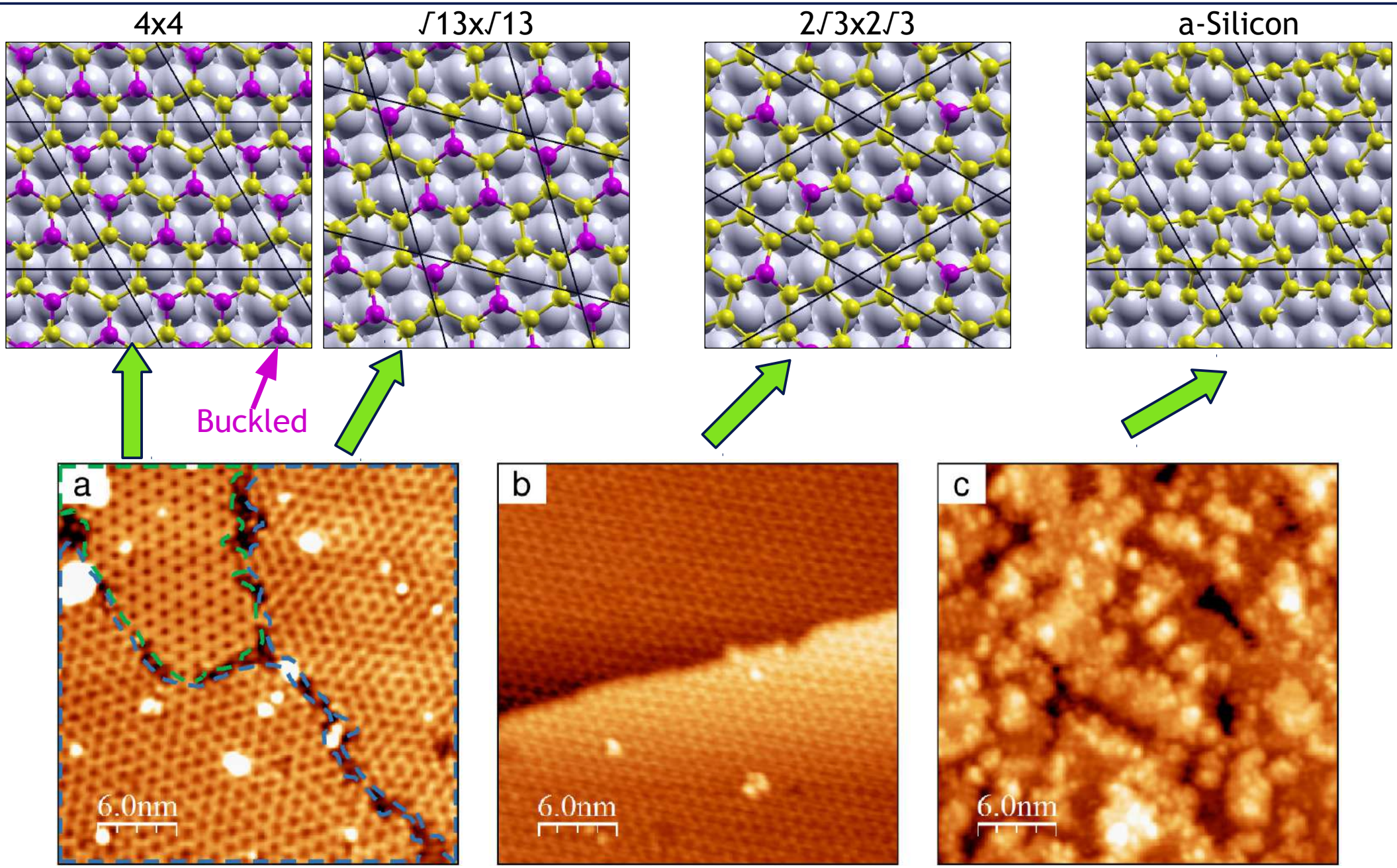


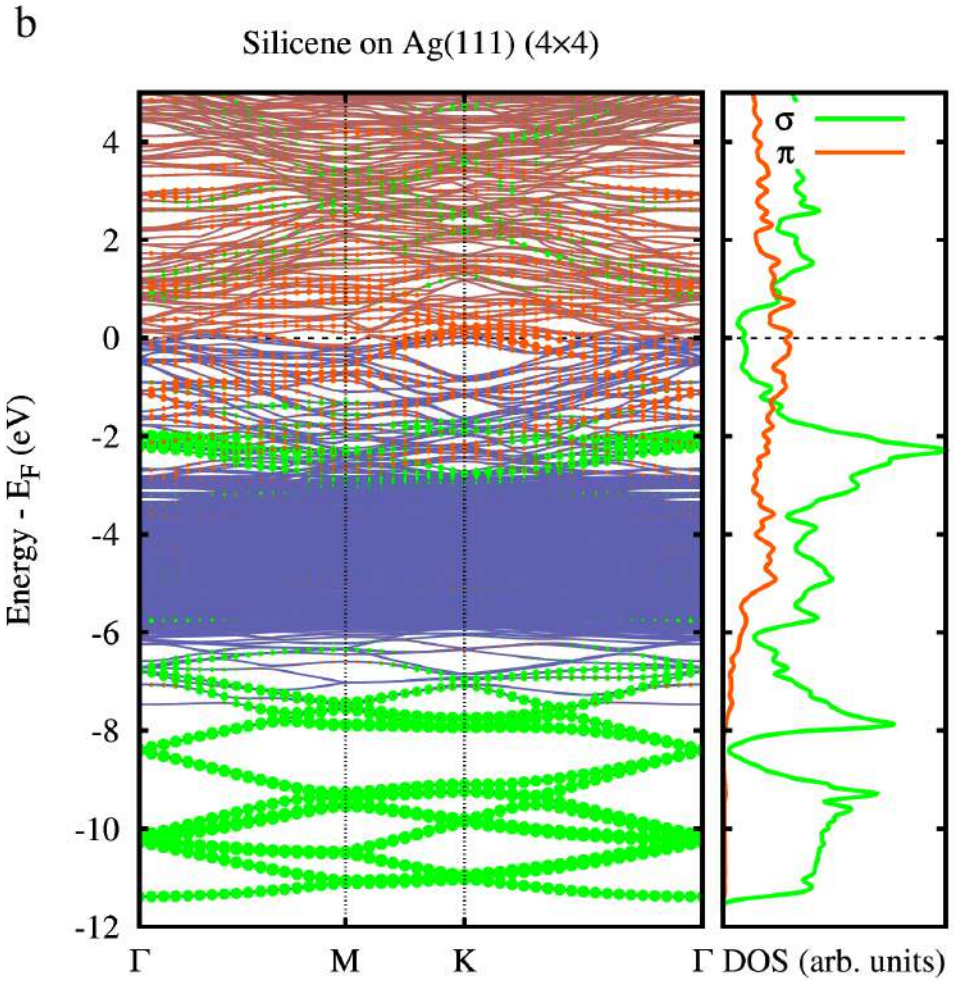
- 1994, 2009: stability (theory)
- 2010: synthesis on Ag
- 2012: Dirac bands on Ag(111)?
- 2013-2014: ***NO! too strong Si-Ag interaction***
- 2015: FET from Si/Ag(111)

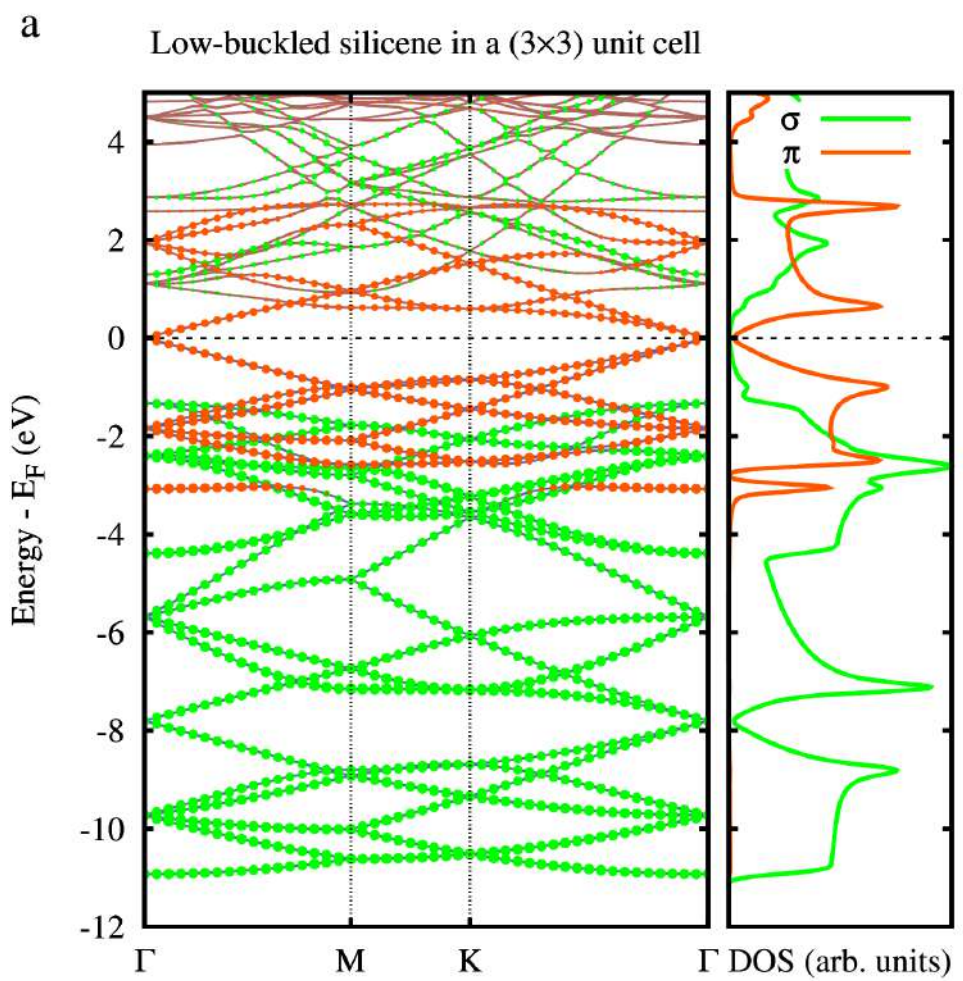
Tao et al. NatureNano, 2015, 10, 227



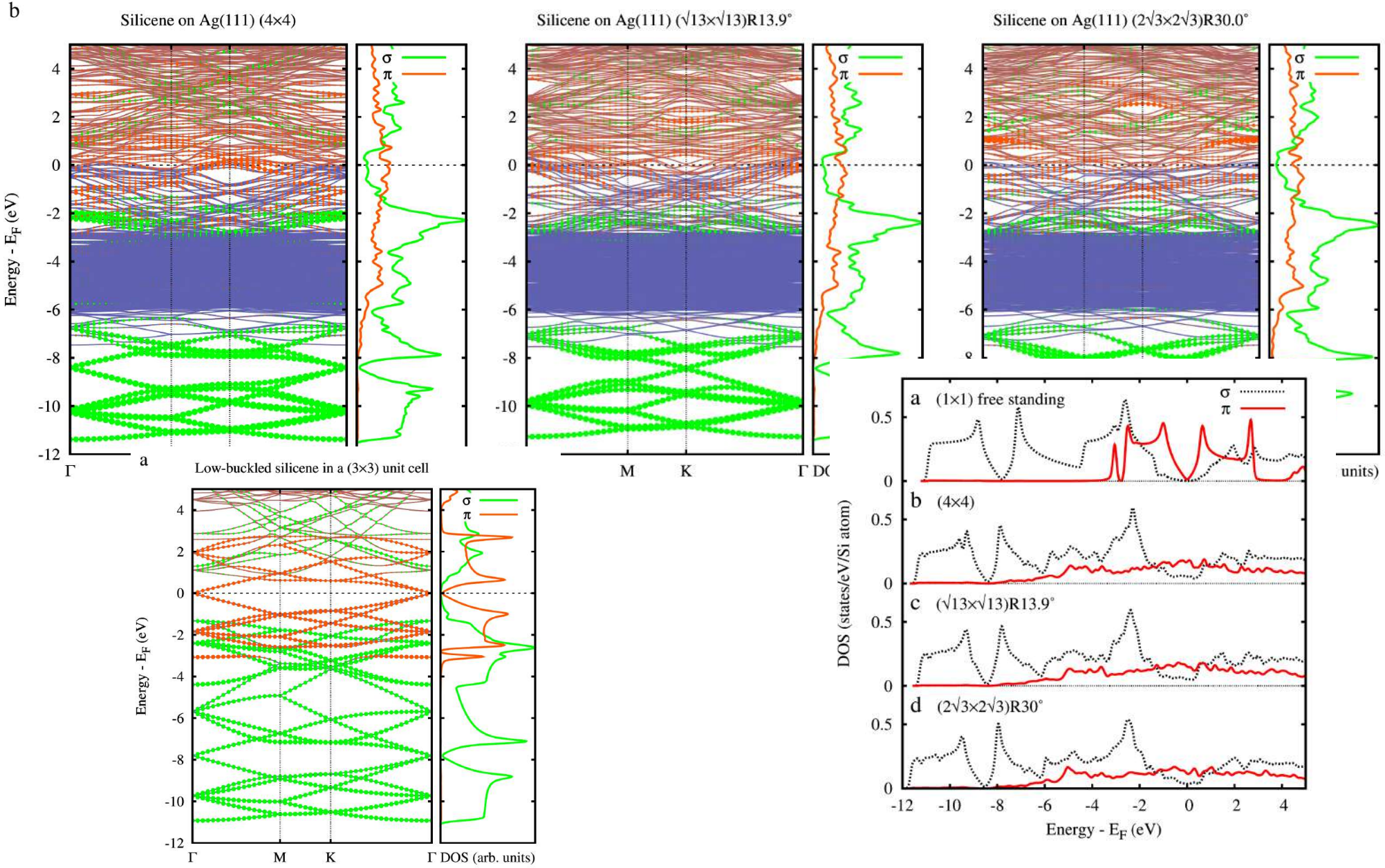
Different silicene polymorphs



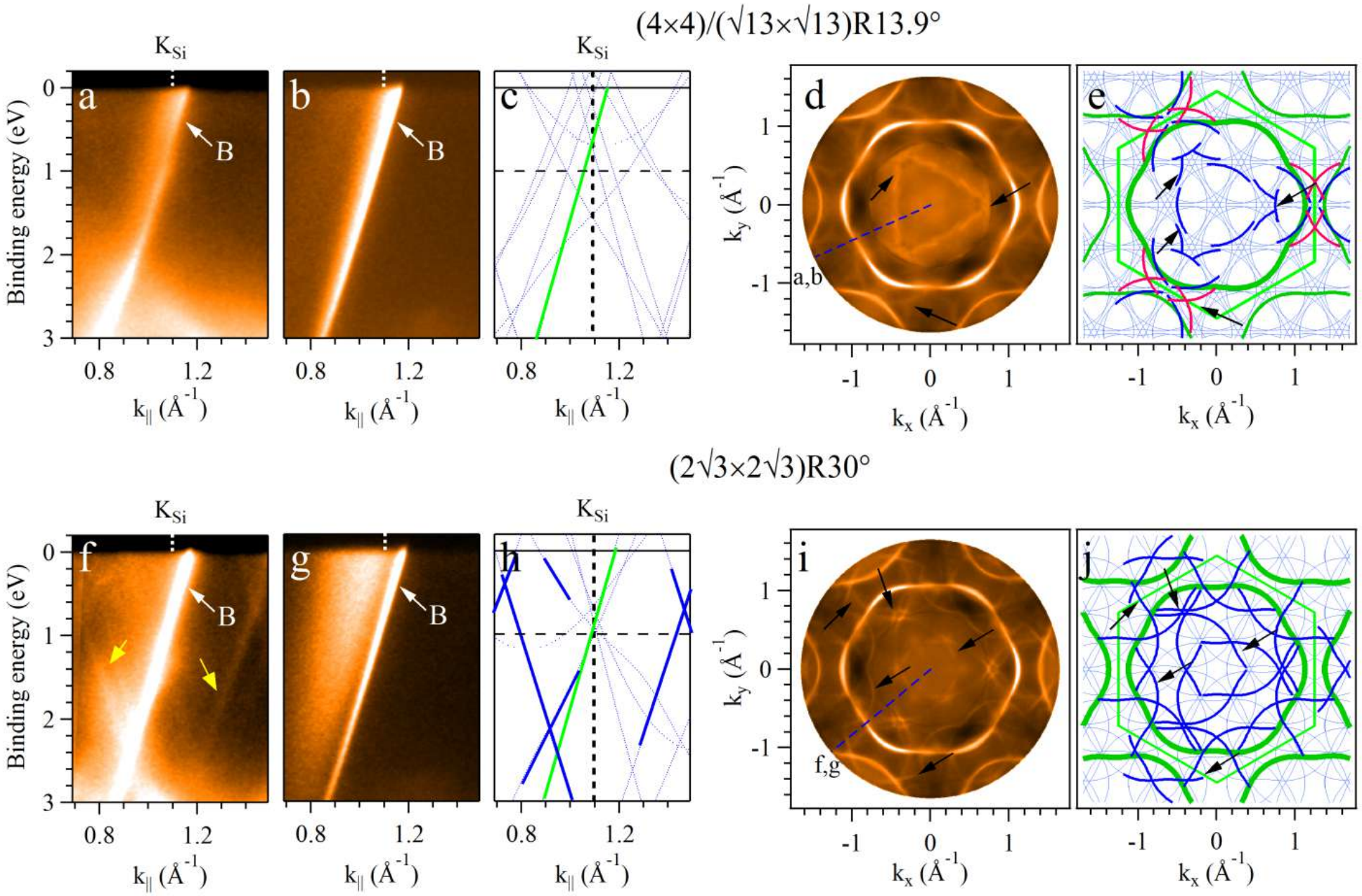

b
Silicene on Ag(111) (4×4)
Energy - E_F (eV)
4
2
0
-2
-4
-6
-8
-10
-12
Γ
M
K
Γ
DOS (arb. units)
σ
π


a
Low-buckled silicene in a (3×3) unit cell
Energy - E_F (eV)
4
2
0
-2
-4
-6
-8
-10
-12
Γ
M
K
Γ
DOS (arb. units)
σ
π

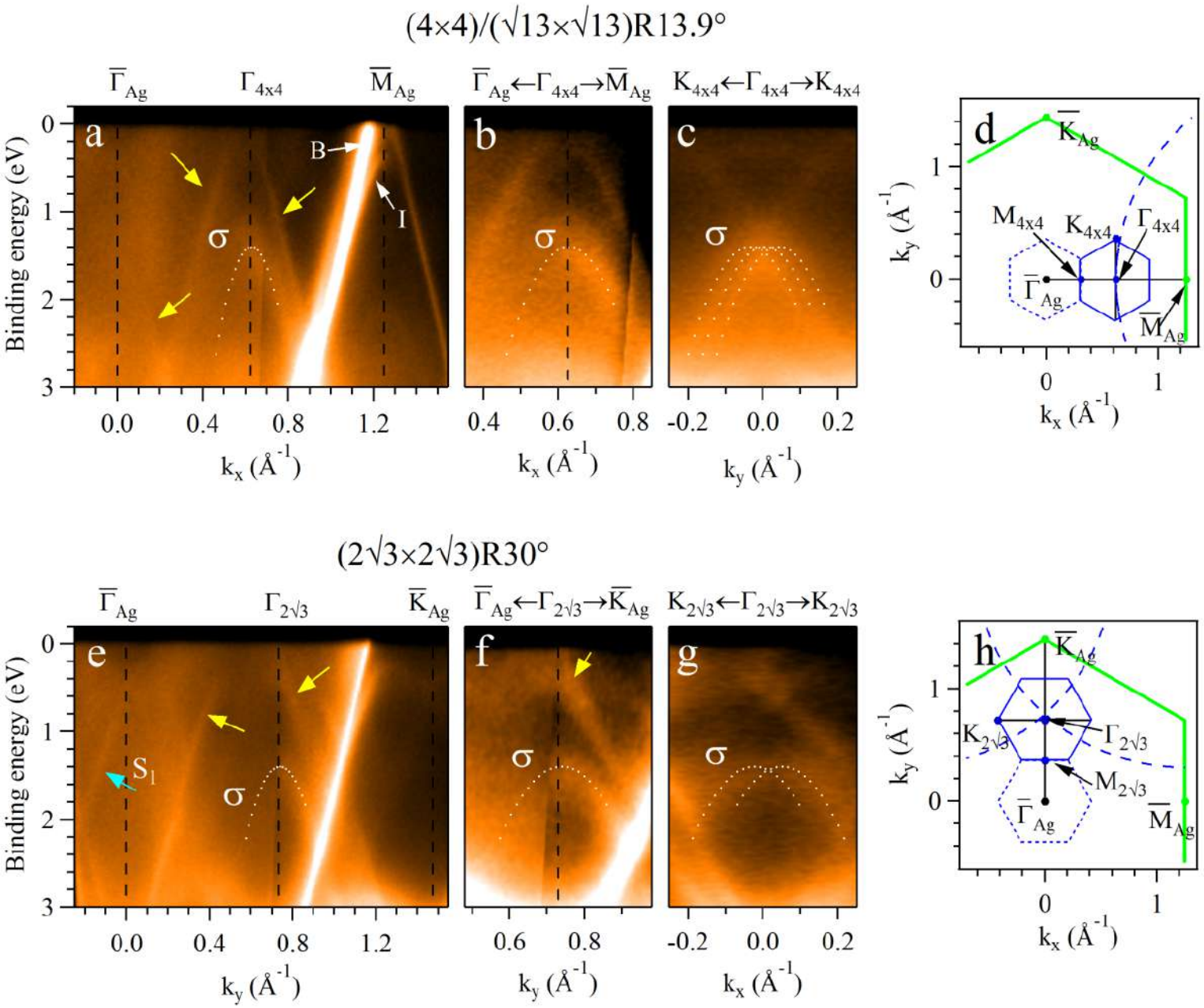
b


Silicene on Ag(111) (4×4)
Silicene on Ag(111) (√13×√13)R13.9°
Silicene on Ag(111) (2√3×2√3)R30.0°
Energy - E_F (eV)
σ
π
Γ
a
M
K
Γ DOS (arb. units)
Low-buckled silicene in a (3×3) unit cell
a (1×1) free standing
b (4×4)
c (√13×√13)R13.9°
d (2√3×2√3)R30°
DOS (states/eV/Si atom)
Energy - E_F (eV)

Angle-resolved photoemission (Dirac cones?)



Angle-resolved photoemission (again?)



Density functional theory simulations

- Silicene/Ag(111) slabs
- 5 layer-thick
- Geometries well established
  - Cinquanta et al., JPCC (2013) 117, 16719
- ***Kohn-Sham eigensystem (LDA)***

- ***Independent particle optical spectrum (IP-RPA)***
- (4x4) silicene
  - 12x12 K-point sampling
  - 380 empty states (>E_F+10eV)

$$\mathrm{Im}\varepsilon_{\mathrm{M}}(\omega) = \frac{16\pi}{\omega^2} \sum_{v,c,k} |\langle \psi_{vk} | \mathbf{v} | \psi_{ck} \rangle|^2 \delta(\epsilon_{ck} - \epsilon_{vk} - \omega)$$

$$A(\omega) = \mathrm{Im}\varepsilon_{\mathrm{M}}(\omega)\, \omega L/c$$

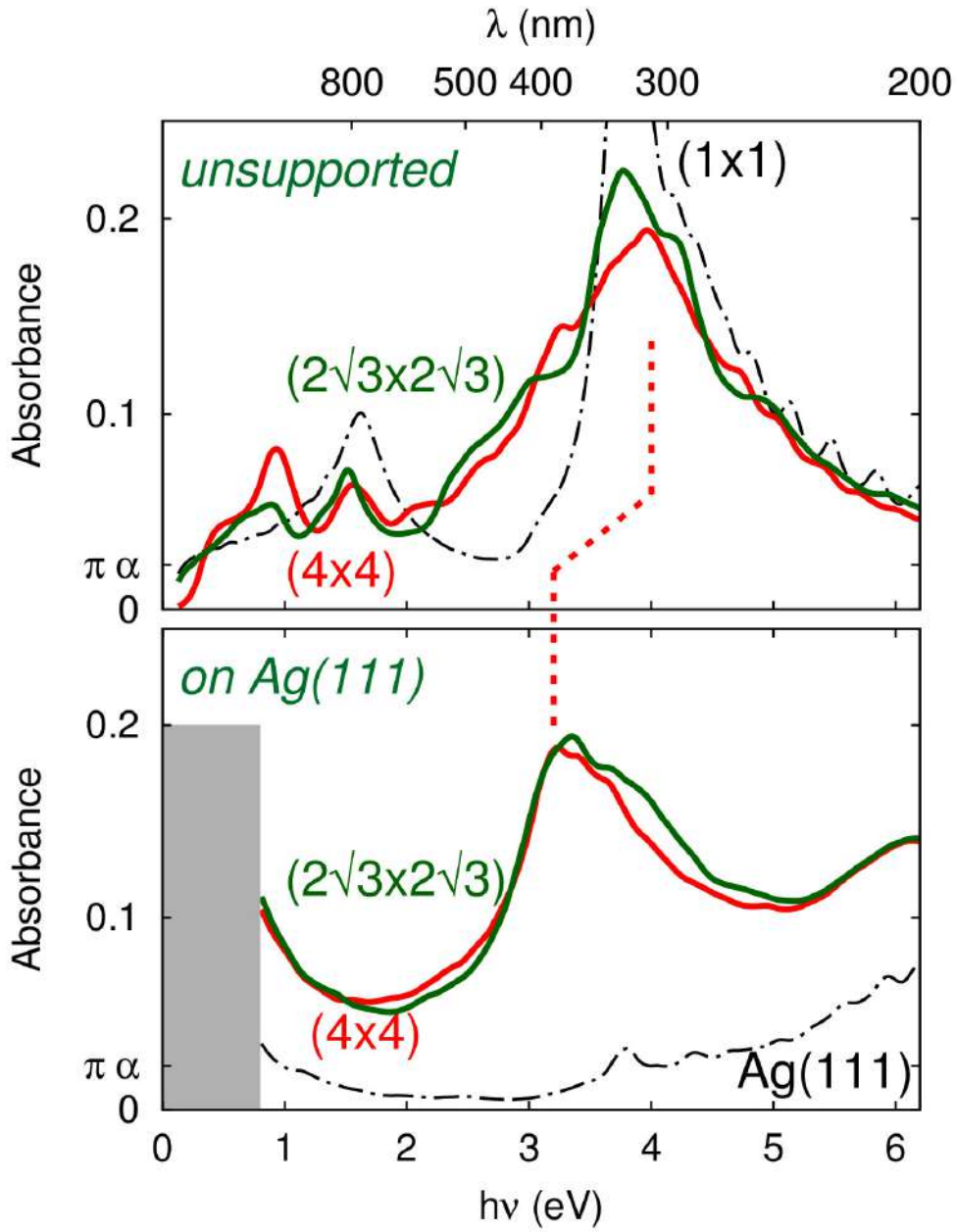
Optical absorbance

Effect of support (4x4)

- Distinguish features
  Silicene .vs. silver
- Non-additive
  - Redshift of the main peak
  - No more peak at ~1.6eV

Different phase (2√3x2√3)

- Similar observations!



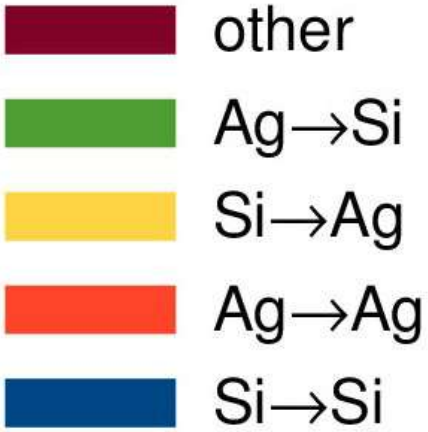
Optical absorbance - contributions

- Weights according to spacial localization, e.g.: $W_{ik}^{\mathrm{Si}} = \sum_{\phi \in \mathrm{Si}} |\langle \phi | \psi_{ik} \rangle|^2$

- Weighted contributions to the dielectric function, e.g.:

$$\mathrm{Im}\varepsilon_{\mathrm{M}}^{\mathrm{SiAg}}(\omega) = \frac{16\pi}{\omega^2} \sum_{v,c,k} W_{vk}^{\mathrm{Si}} W_{ck}^{\mathrm{Ag}} |\langle \psi_{vk} | \mathbf{v} | \psi_{ck} \rangle|^2 \delta(\epsilon_{ck} - \epsilon_{vk} - \omega)$$

- Multiple contributions:



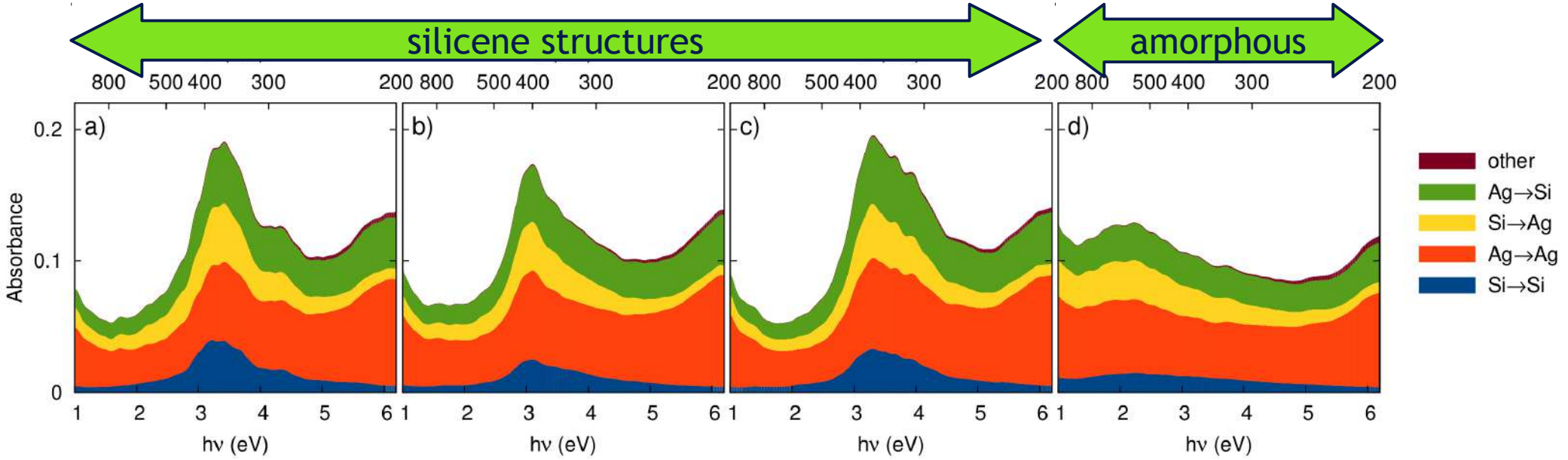
Optical absorbance - contributions

- 3-4eV peak:
  - Unequivocally attributed to silicene
  - Contribution of Ag states largely dominant

➔ ***Signature of silicene electronic structure, but delocalized***

- Similar to amorphous silicon

➔ ***Dimensionality effect***

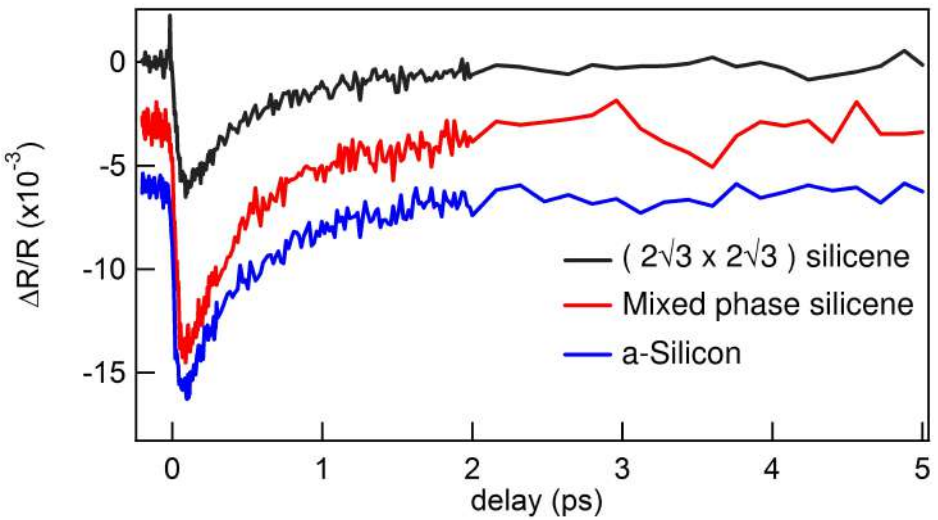


Charge carrier dynamics

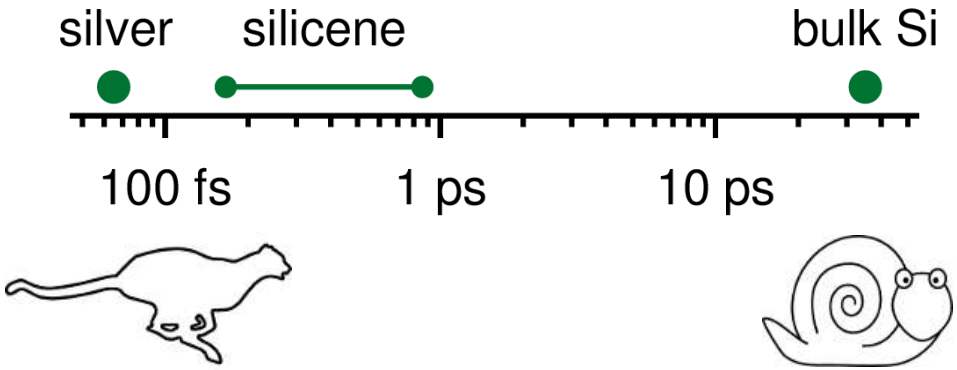
- Transient reflectance
  - Excitation (λ=500nm pulse)

    … *time delay* …
  - Reflectance (λ=340nm)

→ Relaxation times (±20fs)

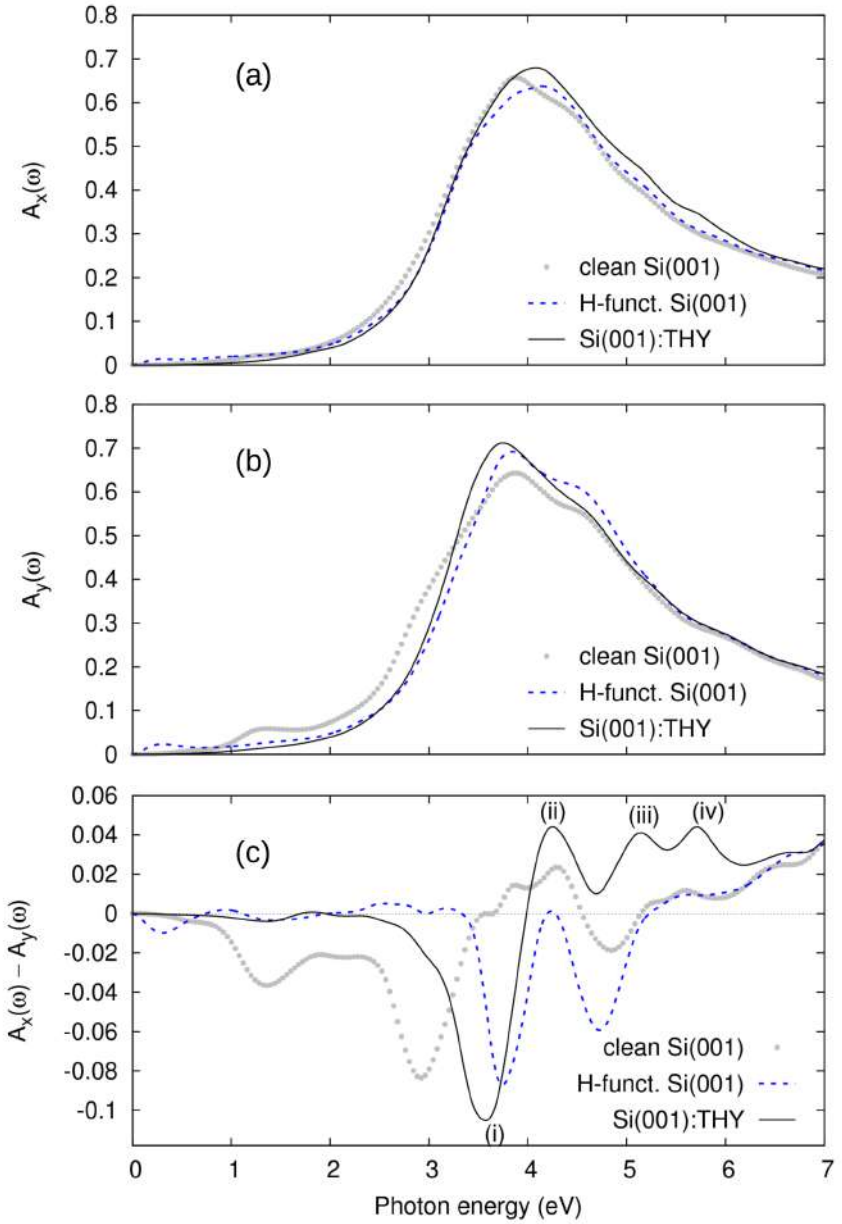


Relaxation times:



- Fast relaxation channels
  - Wavefunction delocalization → ***metallic-like*** channels
- Independent of specific structure
  - Dimensionality effect

Optical absorbance spectra



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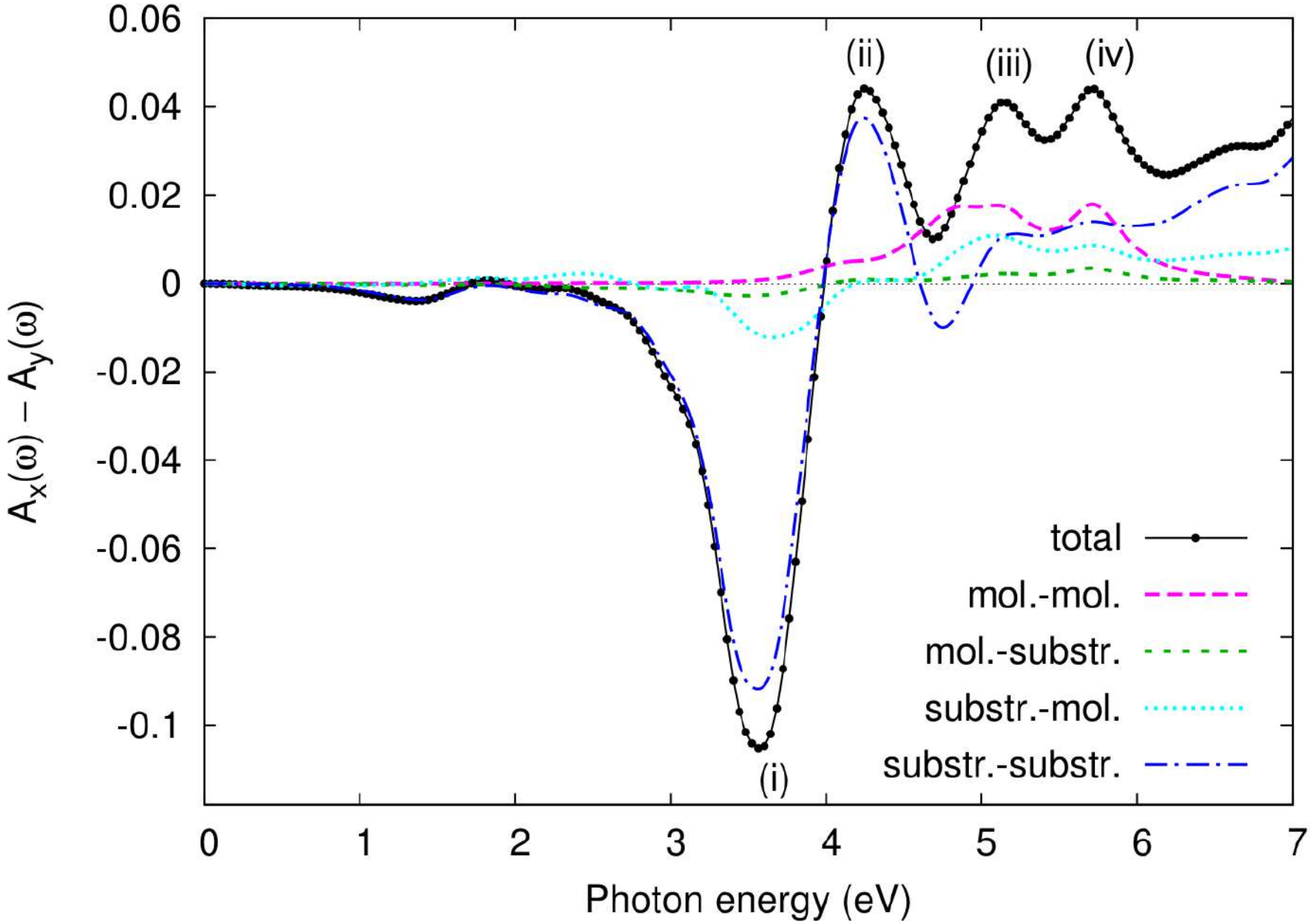
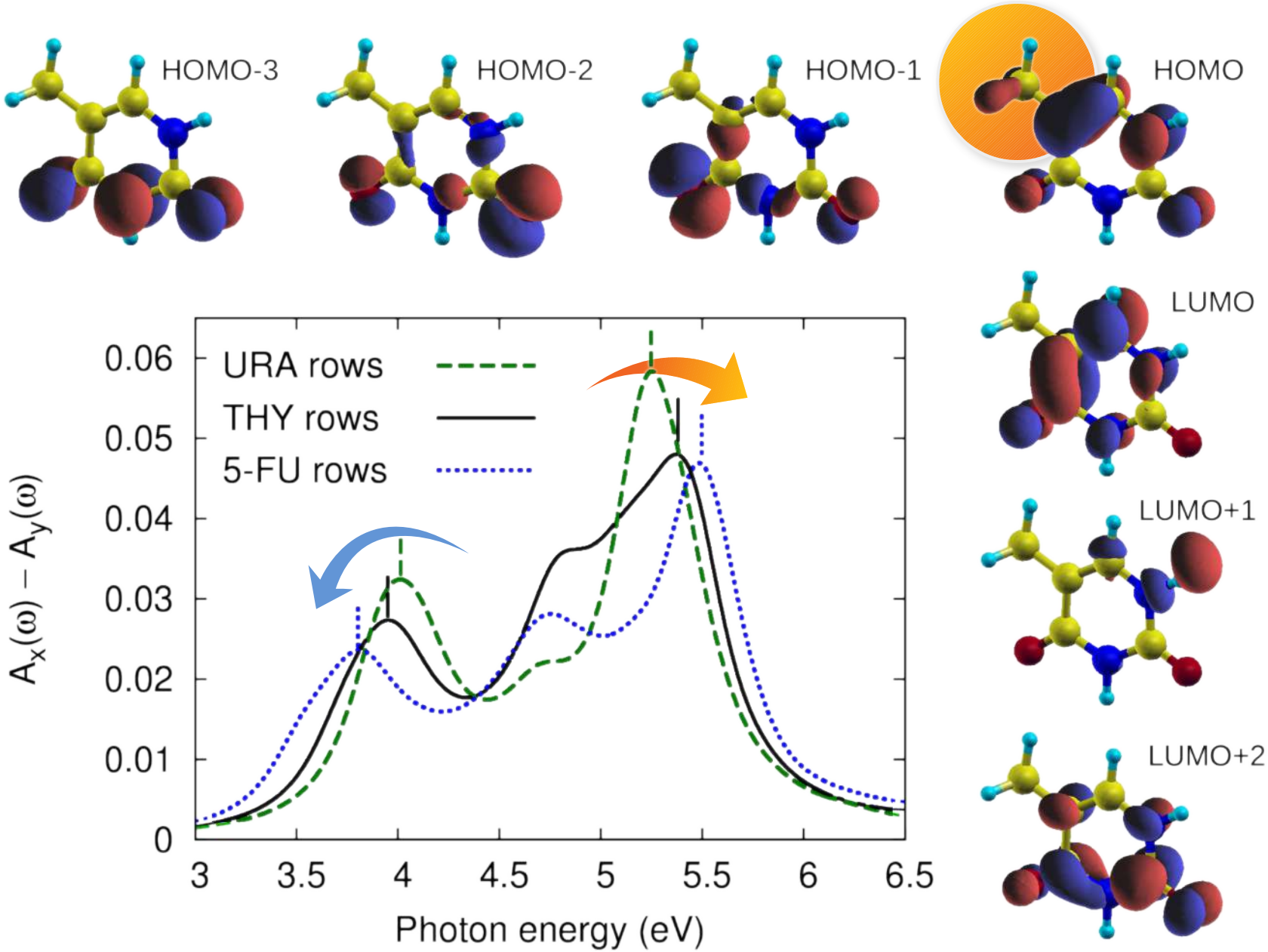
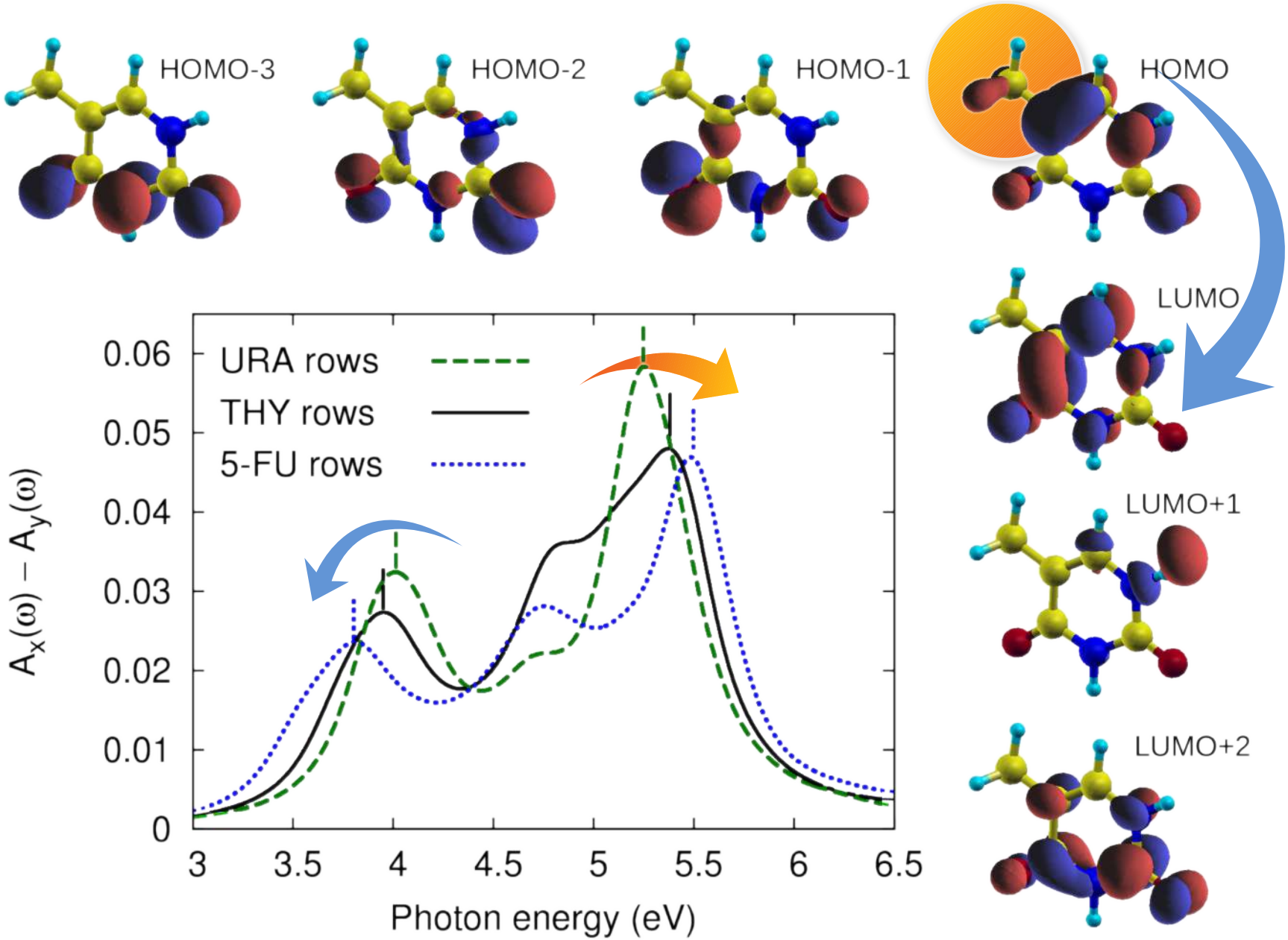
Molecule/substrate contributions to the RAS



Understanding chemical sensitivity



Understanding chemical sensitivity



Understanding chemical sensitivity