Photoemission and DFT-calculations of CuPc: From molecules to solids

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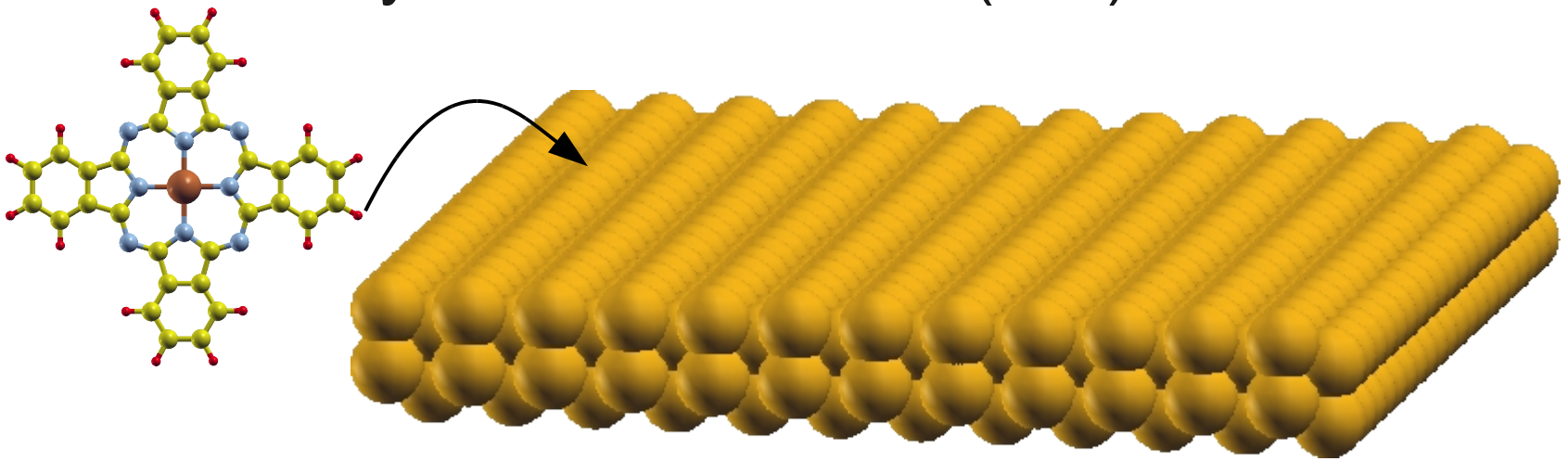
Topic

monolayers of CuPc on Au(110)



1) structural properties

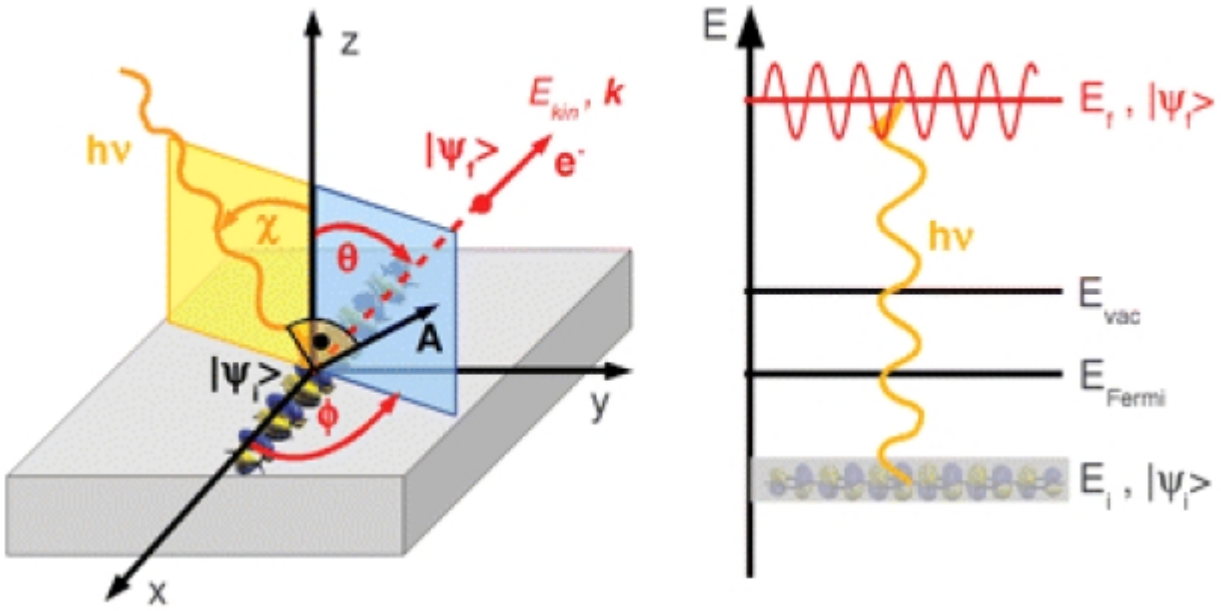
orientation of the molecules on the surface

How much can photoemission tell us

2) electronic properties

from molecules to solids

Introduction



DFT

LDA, GGA-PBE, HSE06-PBE, using pseudopotentials, PAWs,...

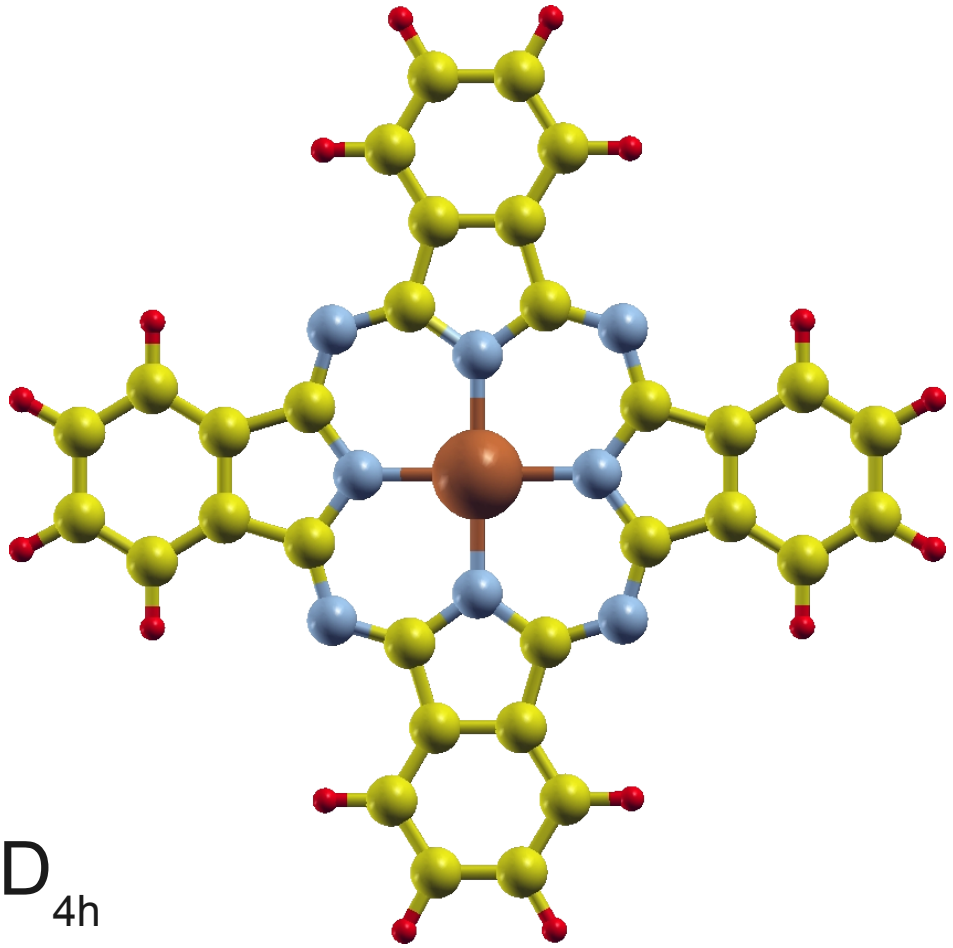
Photoemission

$$I(\theta,\phi;E_{kin}) \propto \sum_i \left|\left\langle \Psi_f(\theta,\phi;E_{kin}) \left|\mathbf{A}\cdot\mathbf{p}\right| \Psi_i \right\rangle\right|^2 \delta(E_i + \Phi + E_{kin} - \hbar\omega)$$

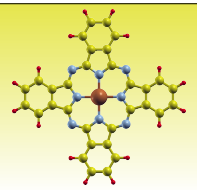
Final state - PW photon KS-state

Molecular tomography & geometry

CuPc

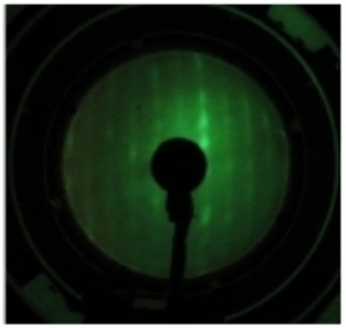


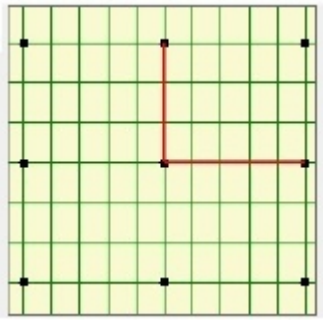
Point group: D_{4h}



Experimental unit cell

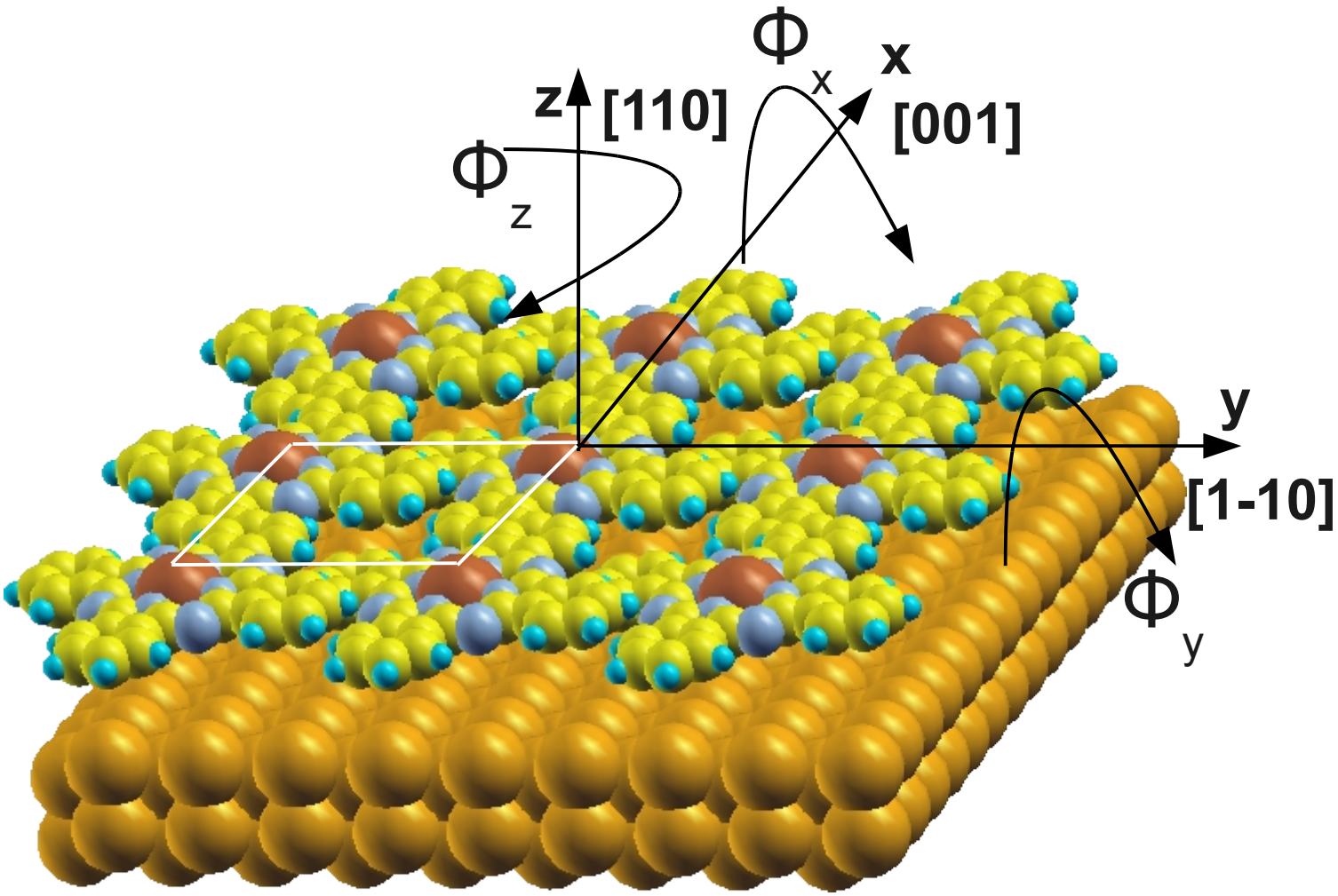
LEED experiment





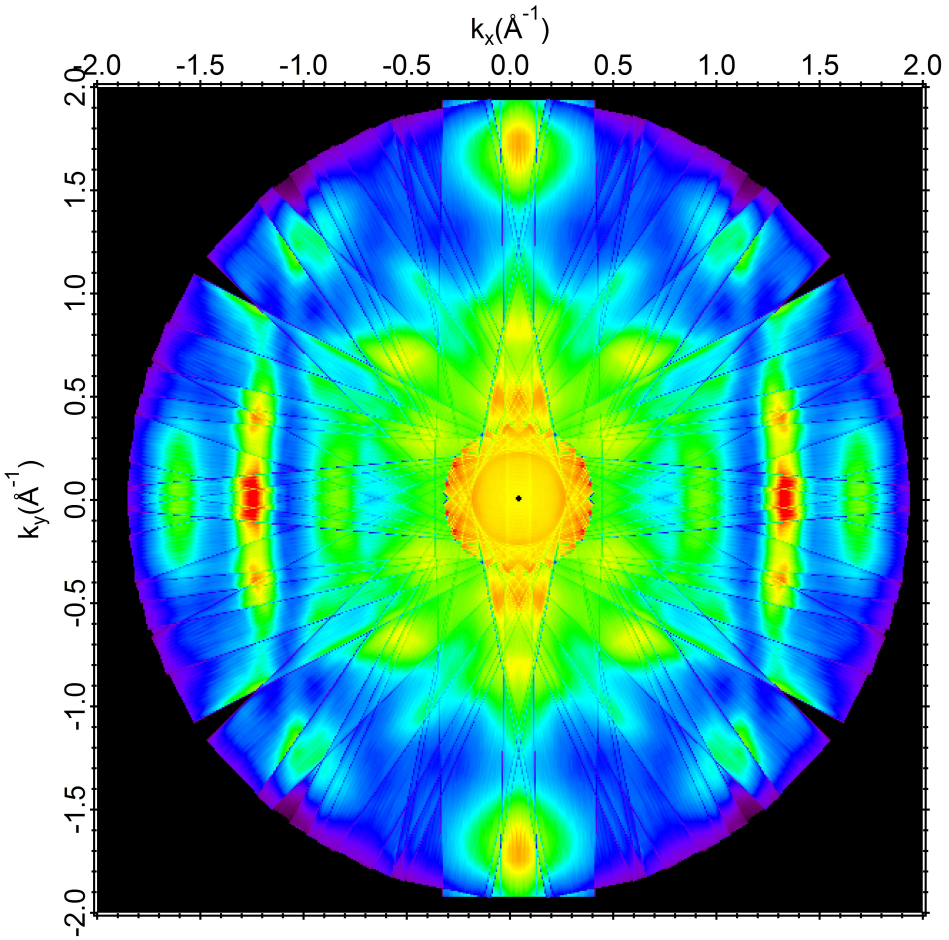
12.4 Å

14.4 Å

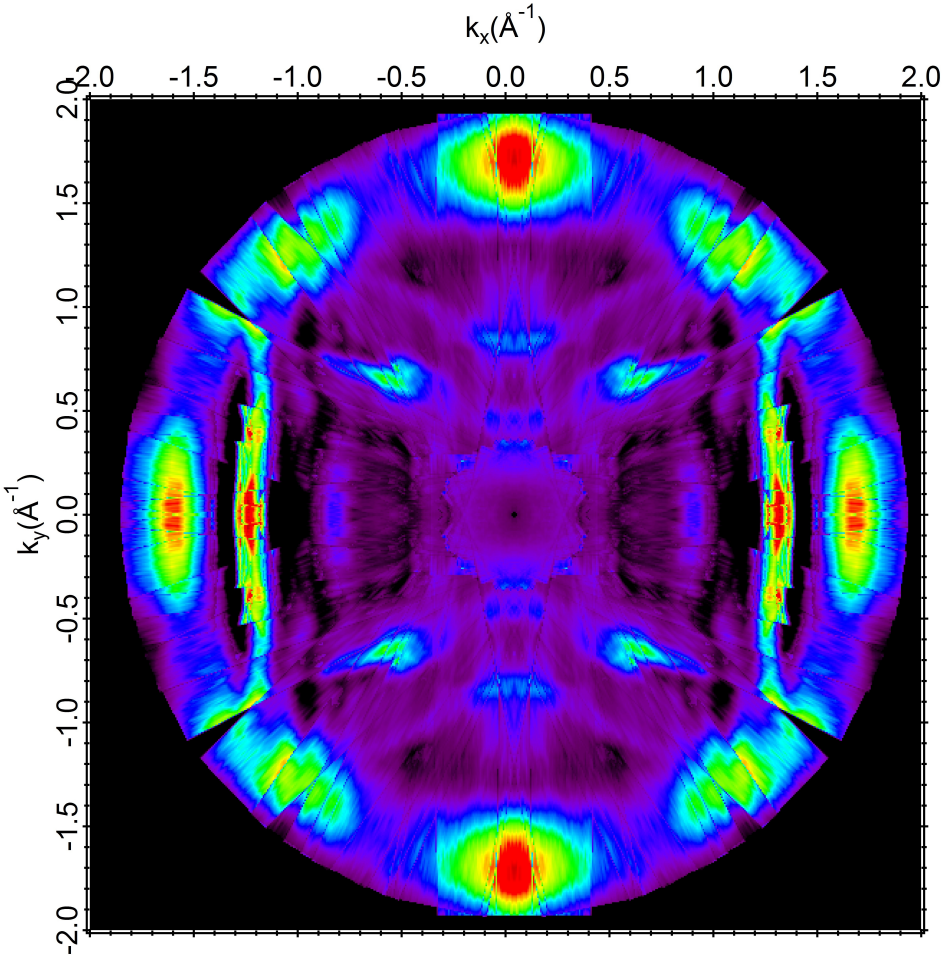


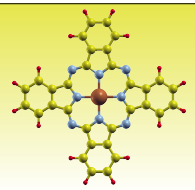
CuPc – HOMO measurements

raw data



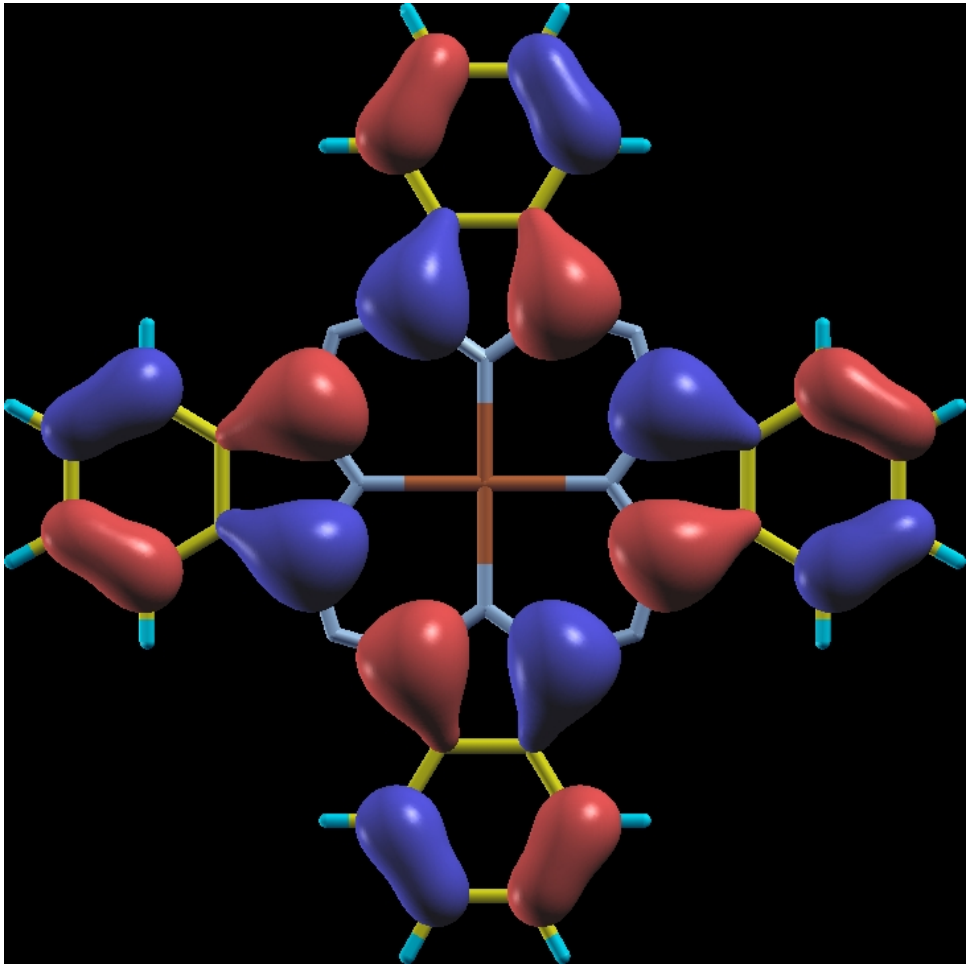
Gauss fit

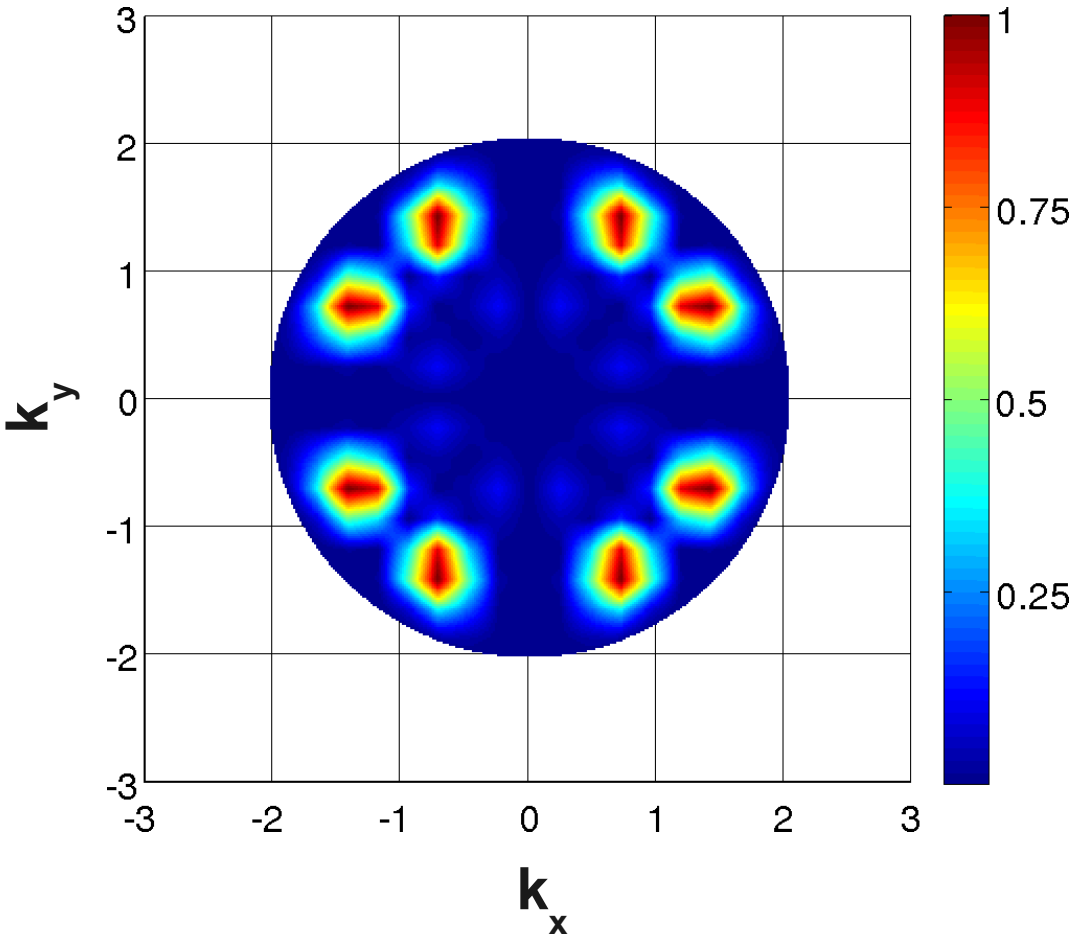


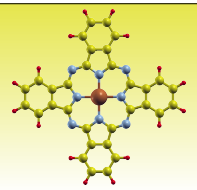


HOMO

π, a_{1u}

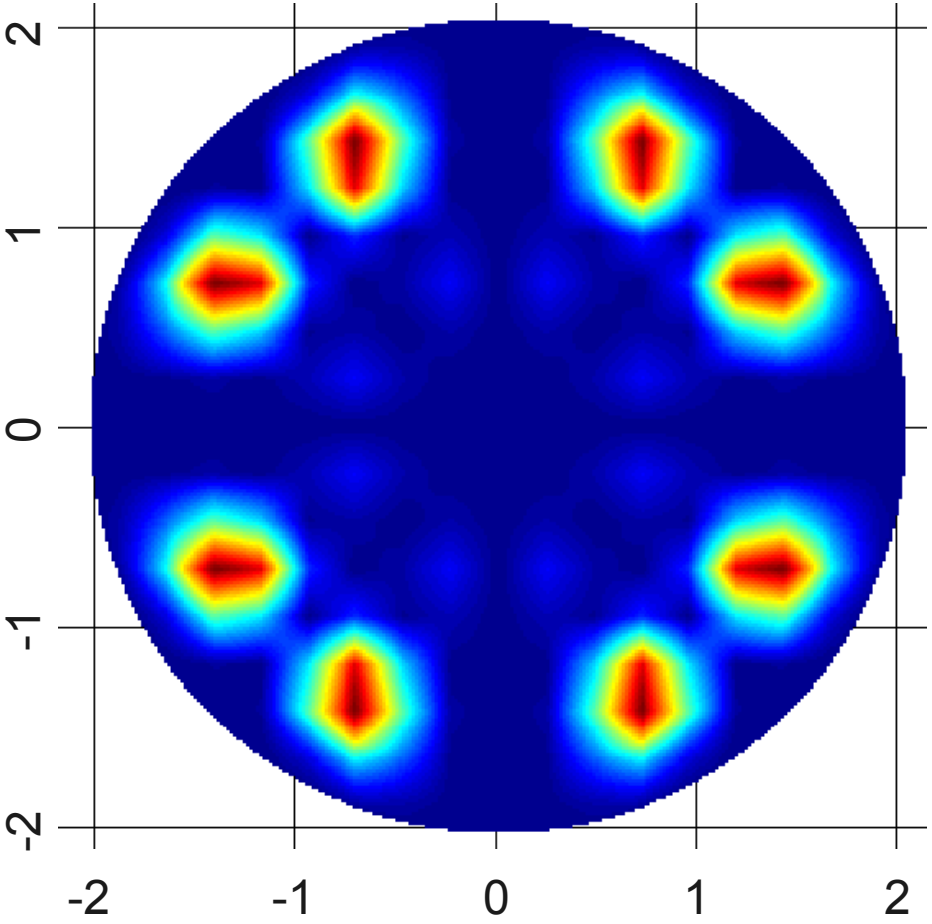




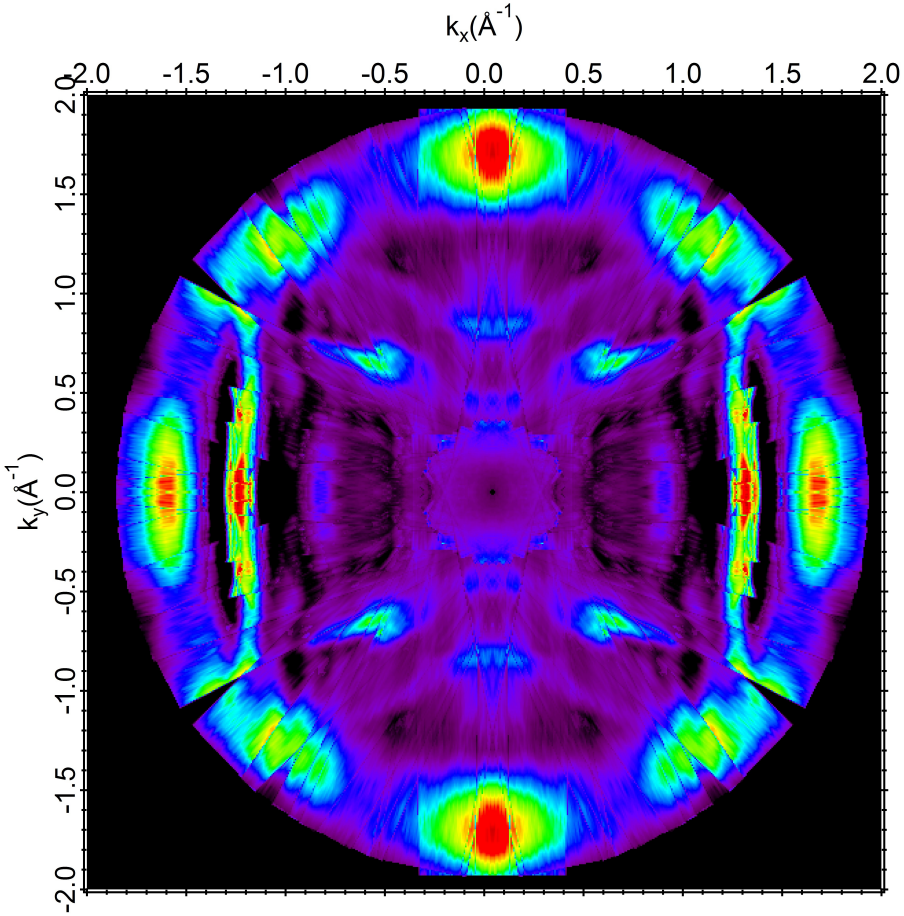


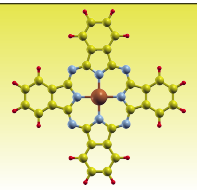
CuPc - HOMO

theory



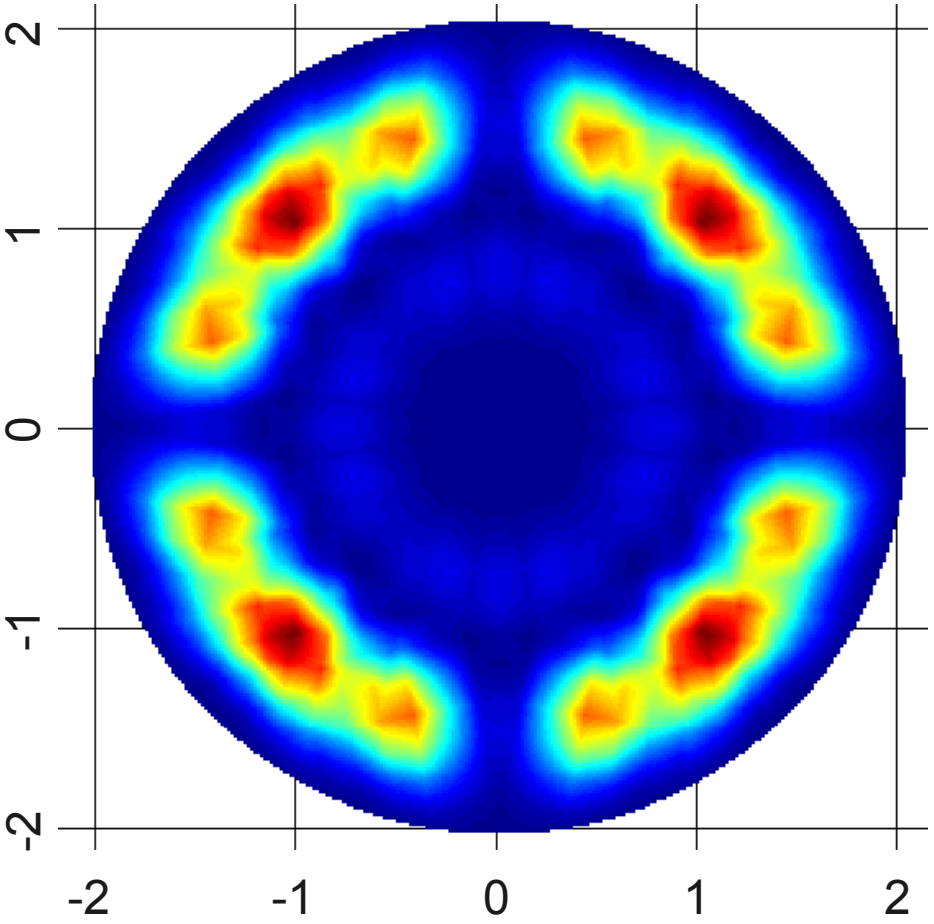
experiment

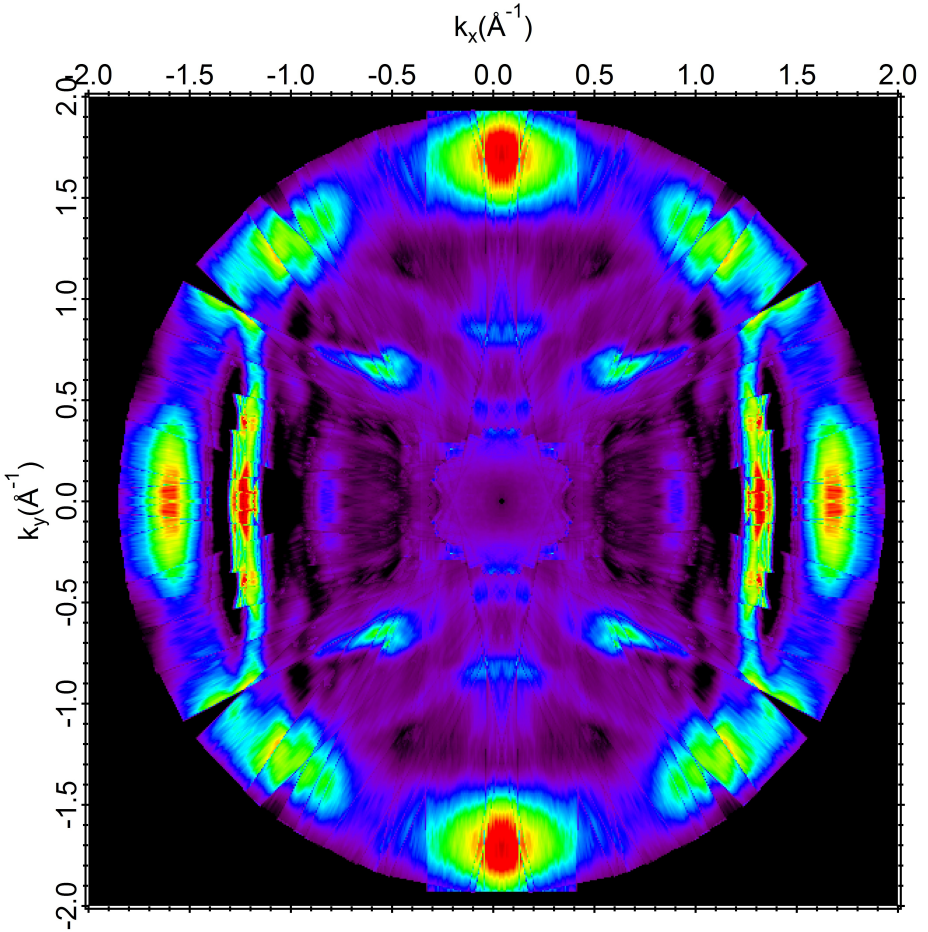


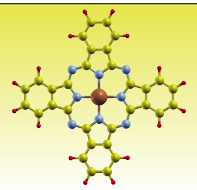


Orientation on the surface

Φ_z: 10°,-10°

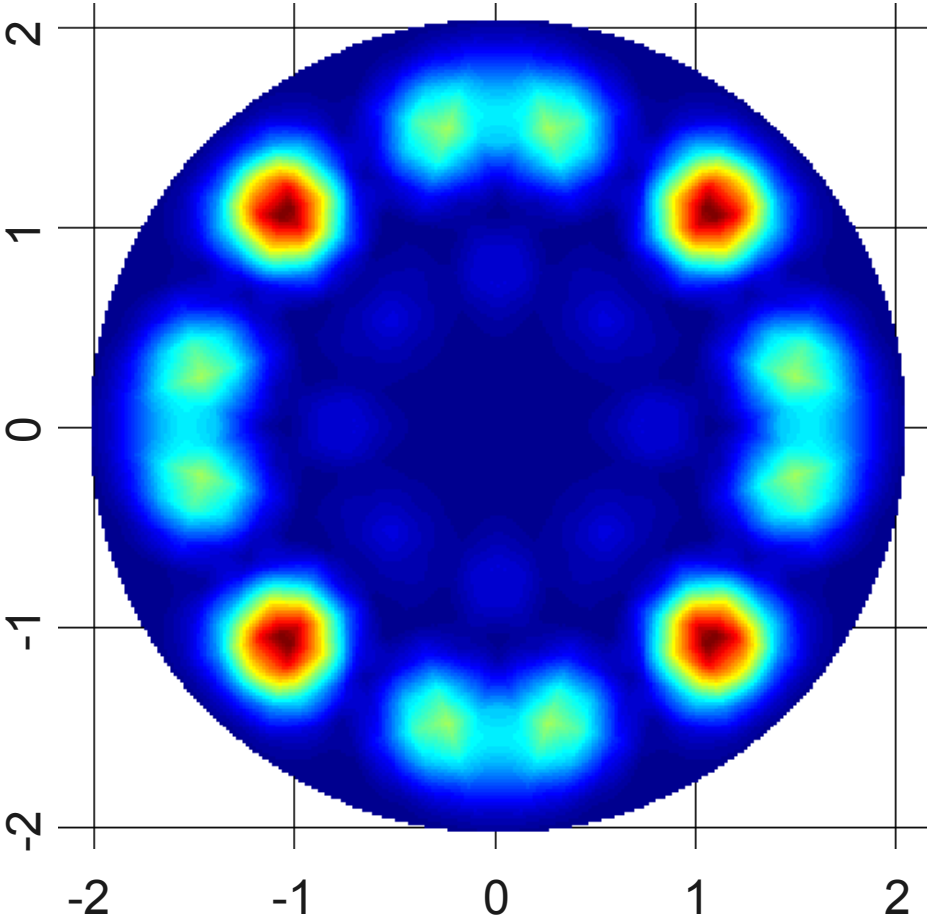


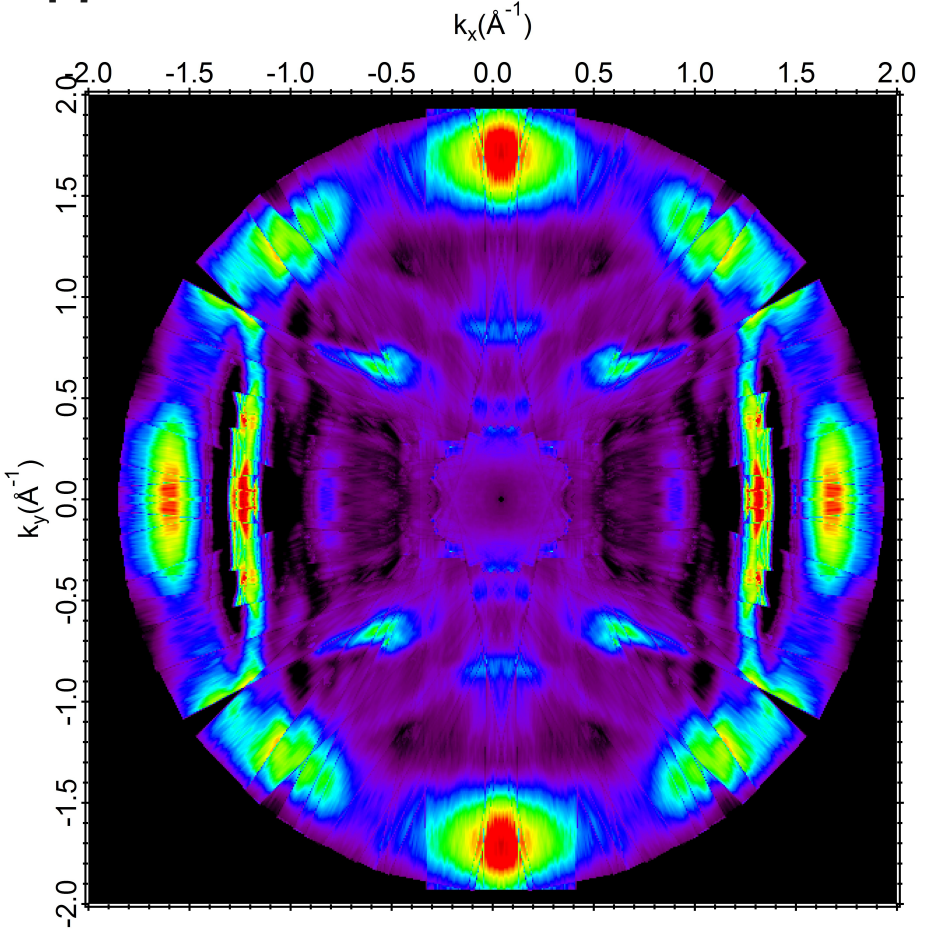


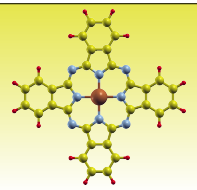


Orientation on the surface

Φ_z: 17°,-17°

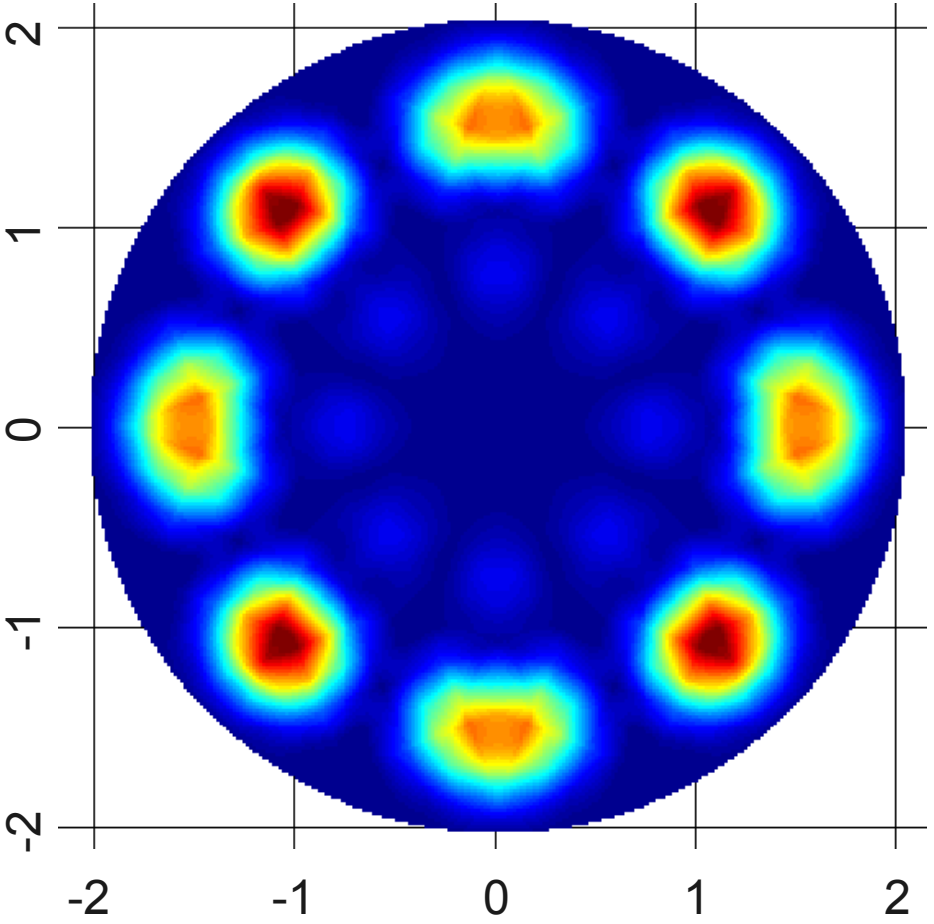


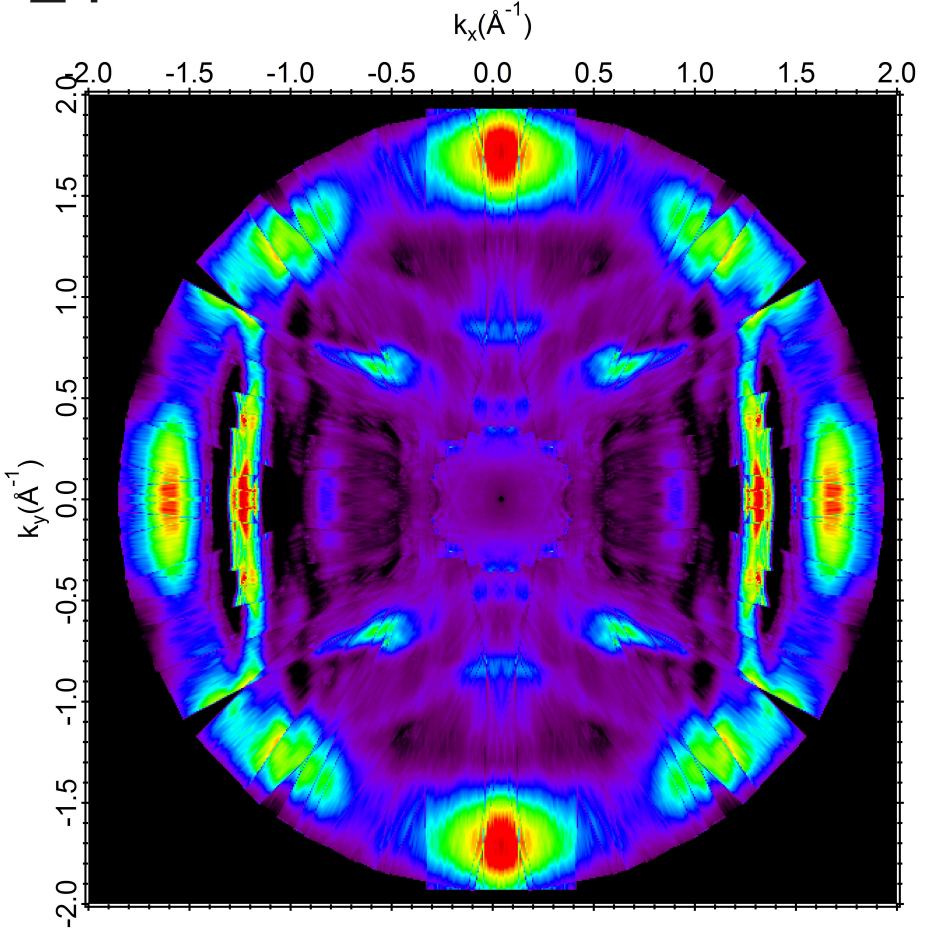


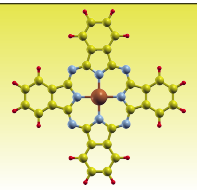


Orientation on the surface

Φ_z: 21°,-21°

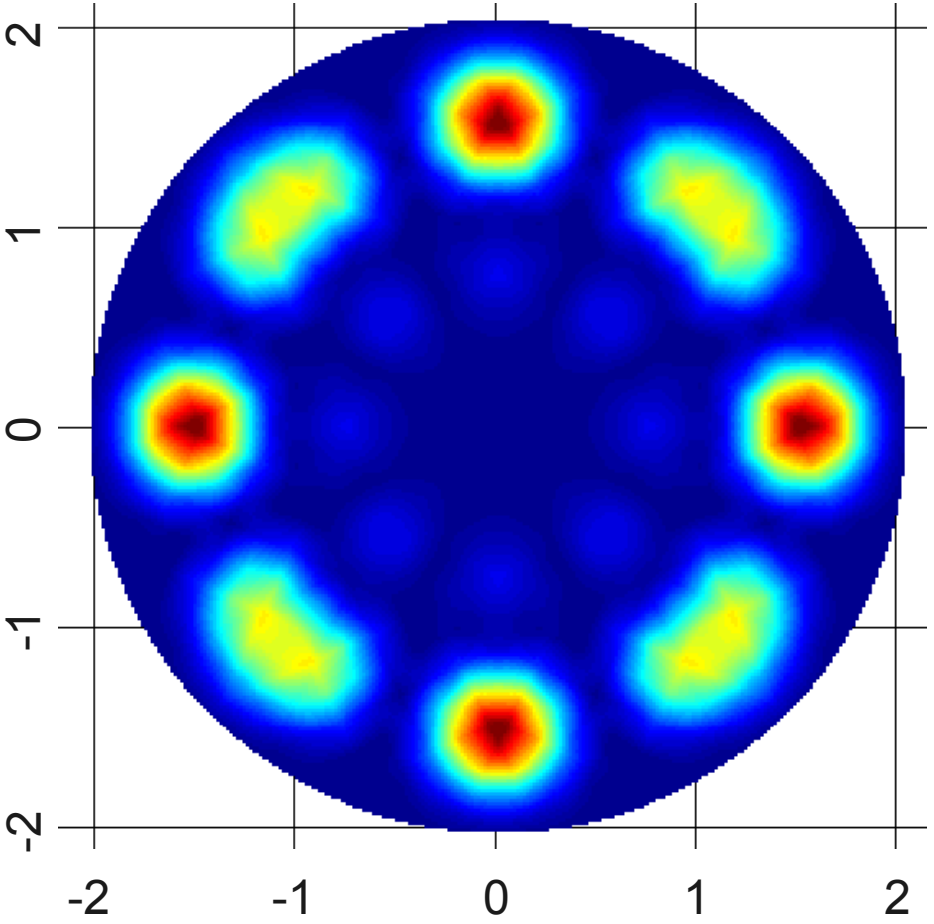


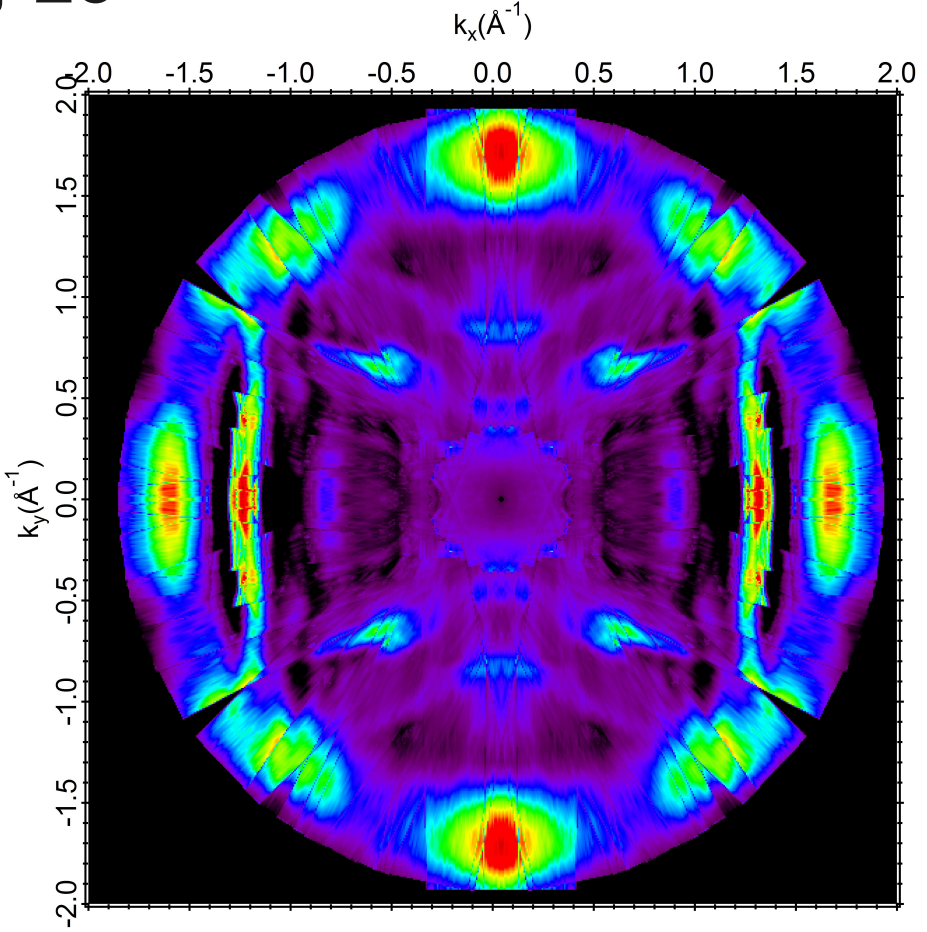


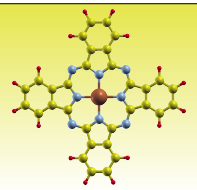


Orientation on the surface

Φ_z: 25°,-25°

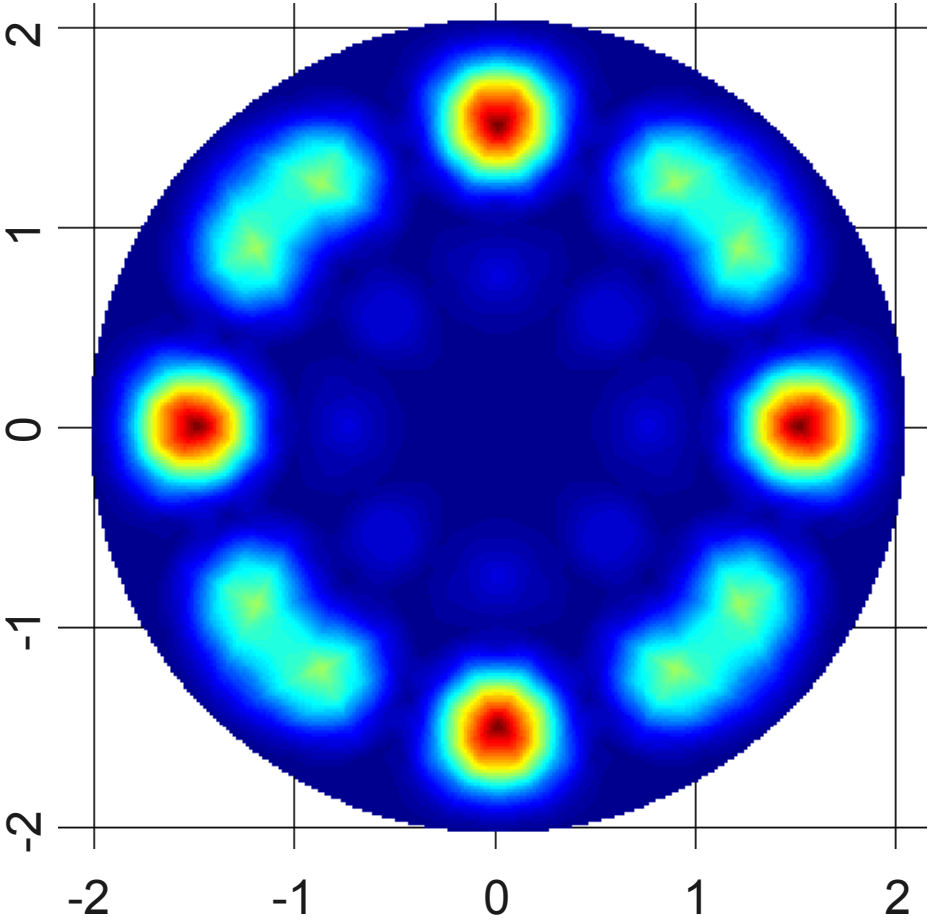


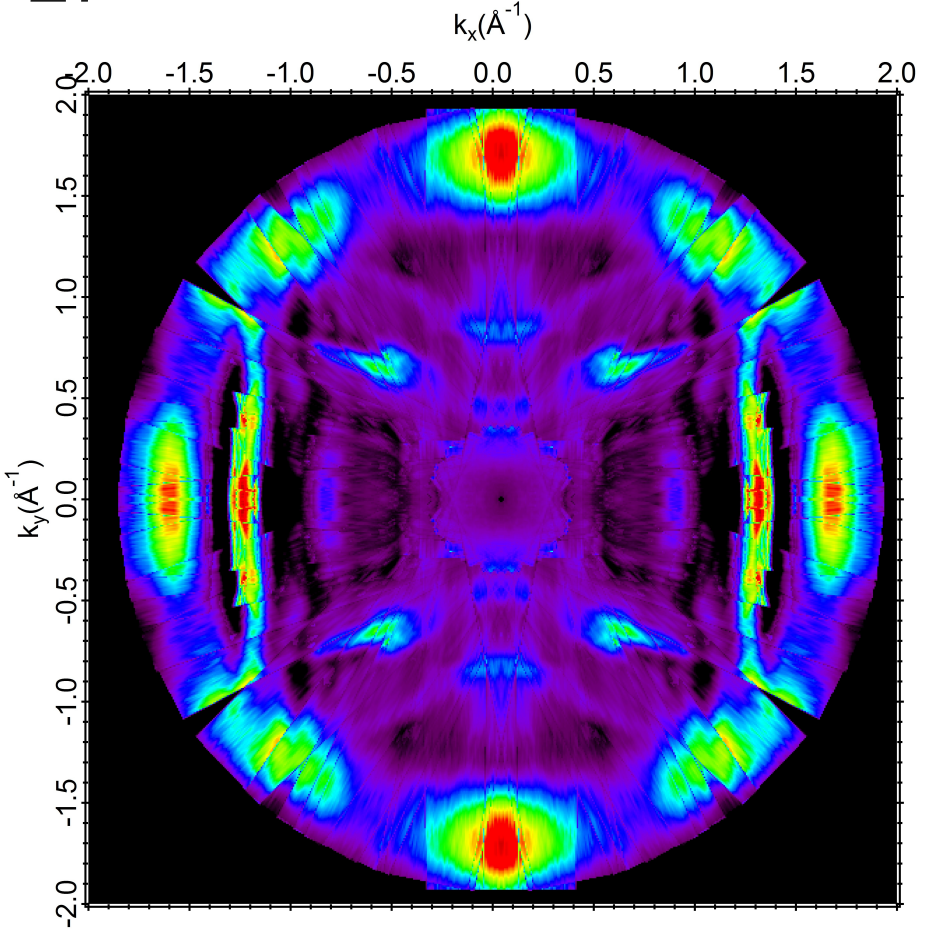


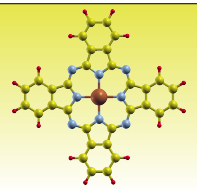


Orientation on the surface

Φ_z: 27°,-27°

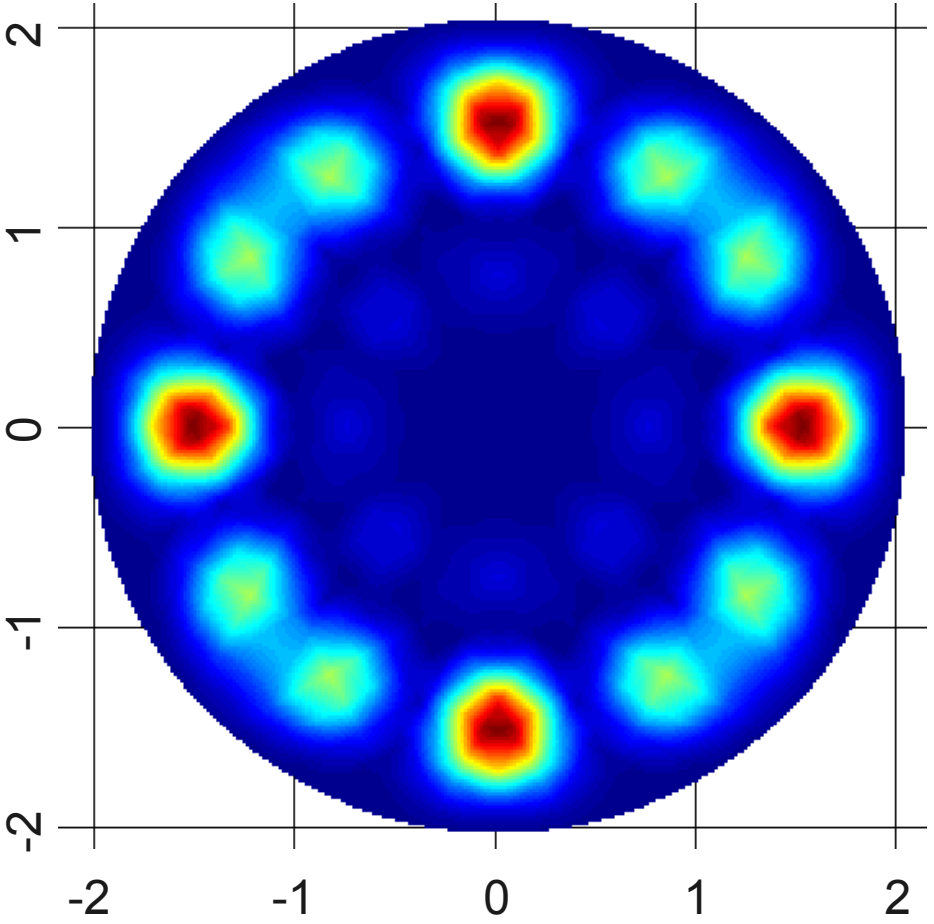


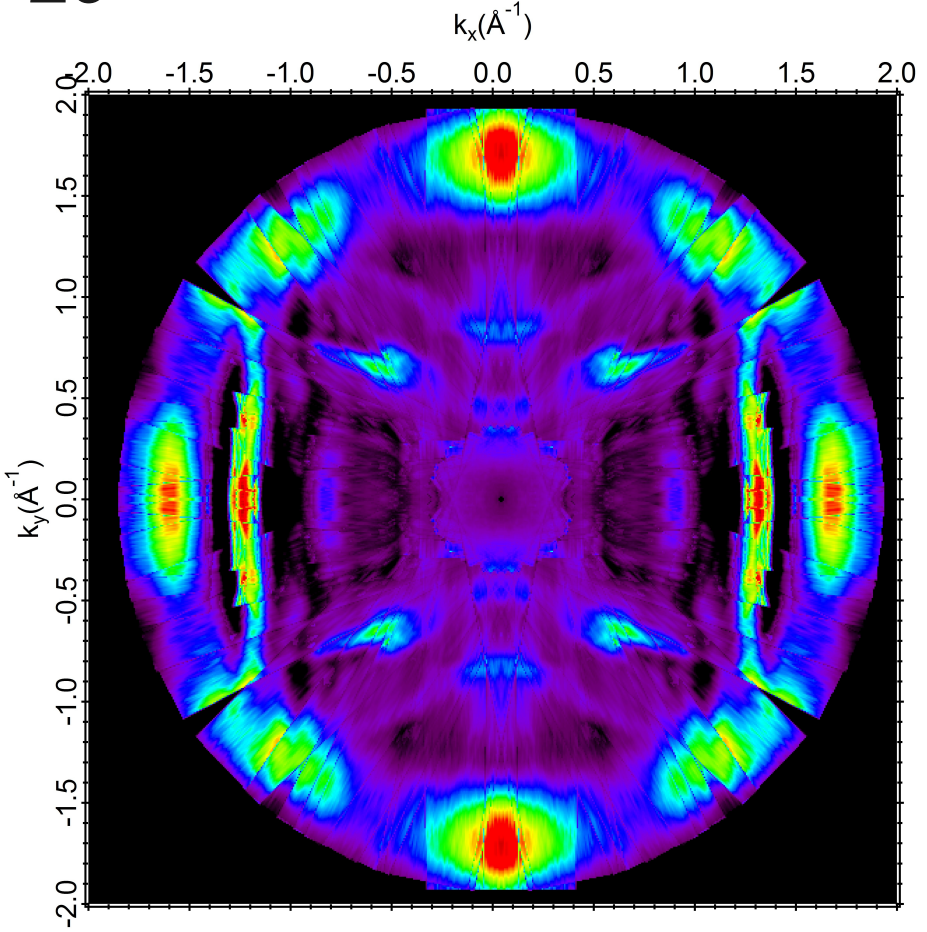




Orientation on the surface

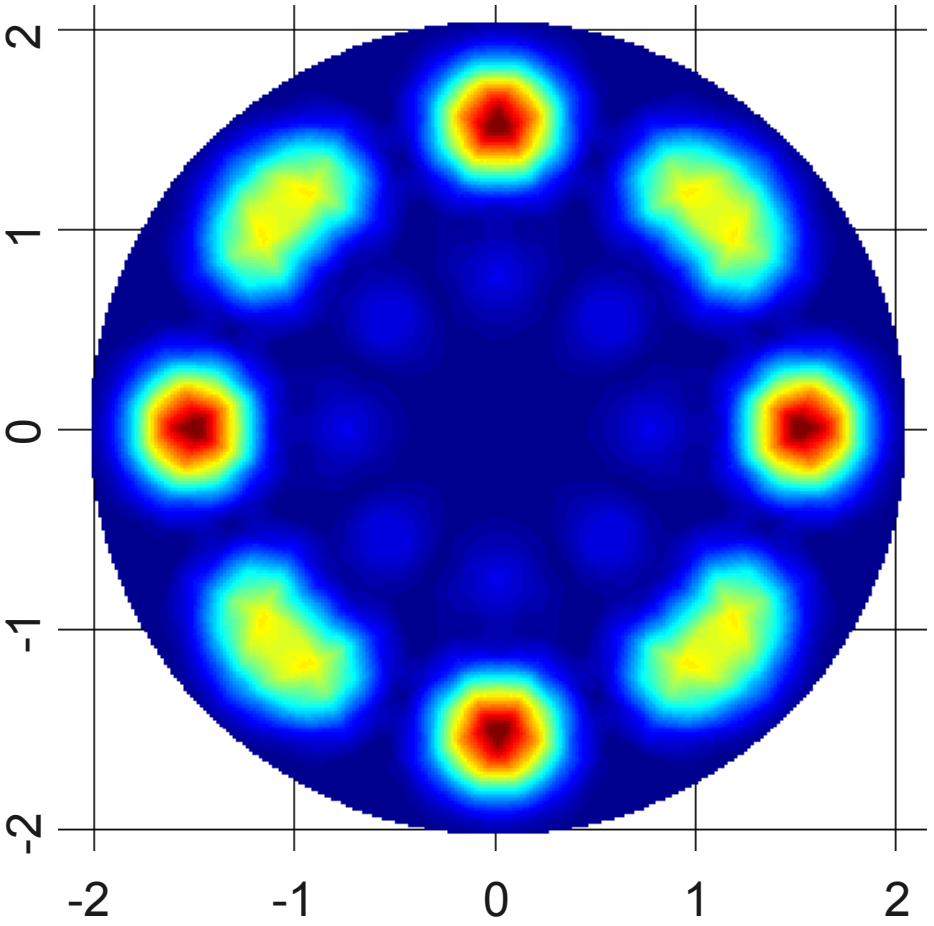
Φ_z: 29°,-29°

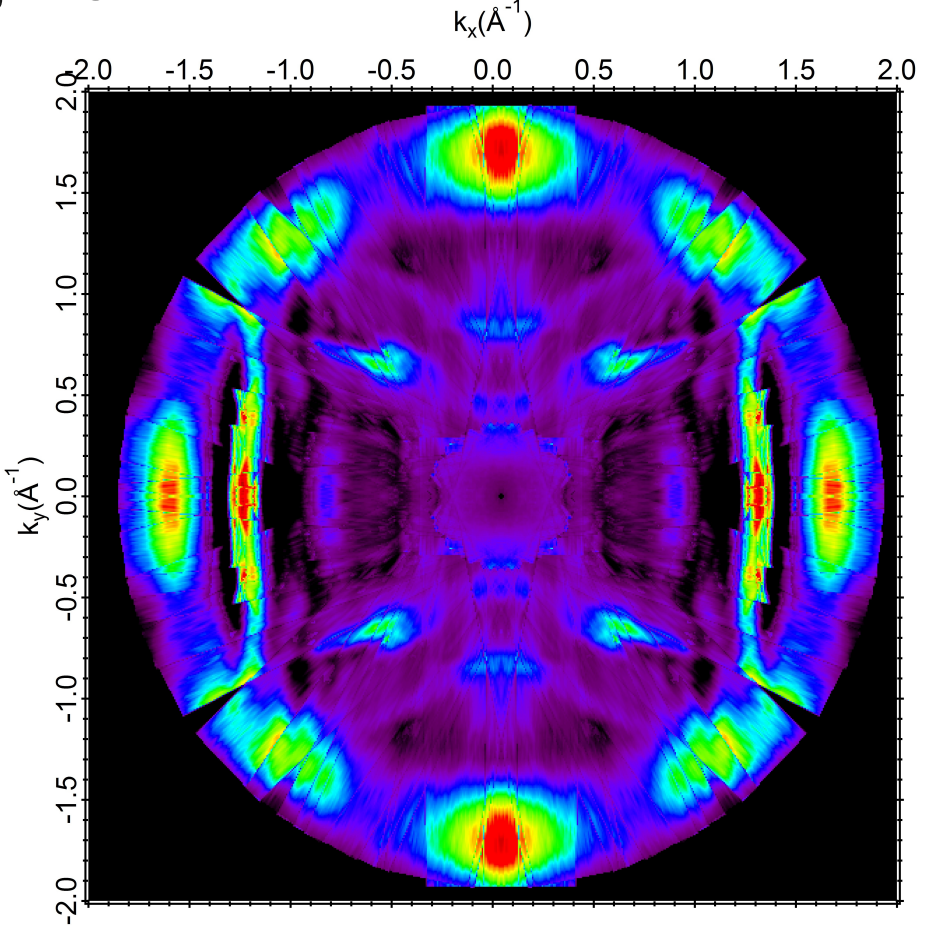




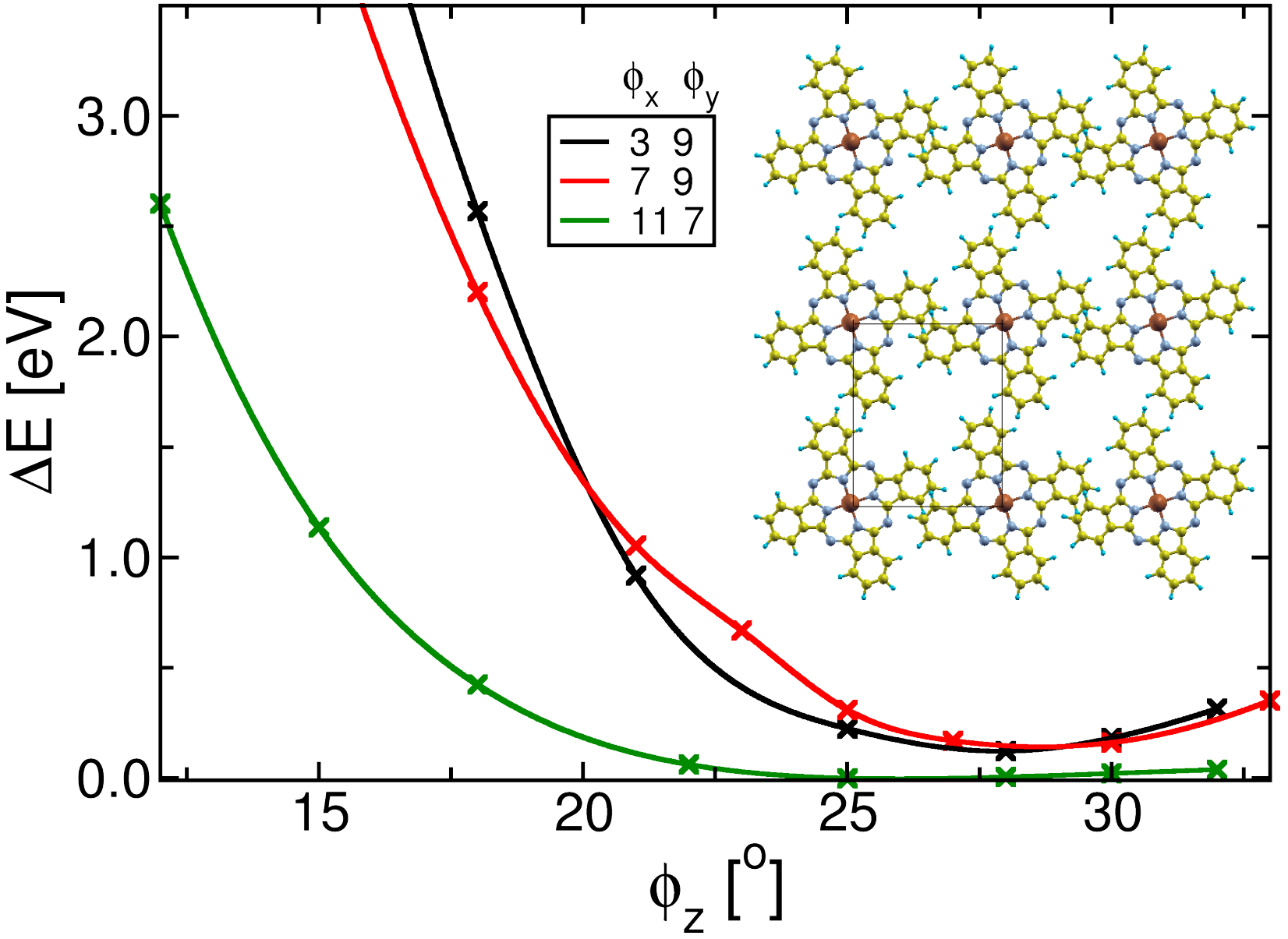
Orientation on the surface

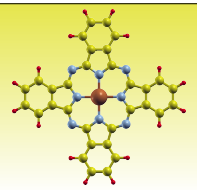
theory Φ_z: 25°,-25° experiment



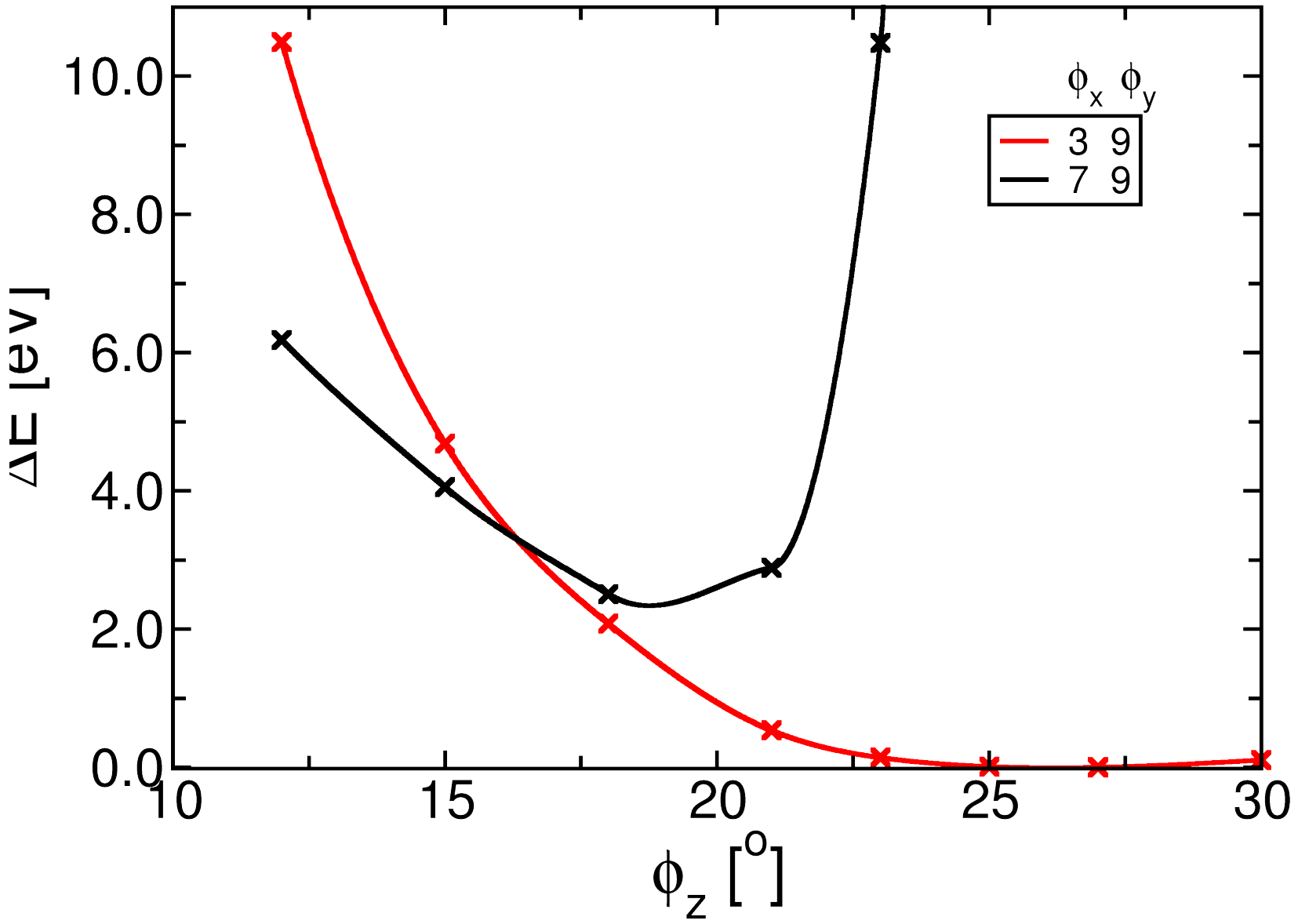


Molecular array without substrate

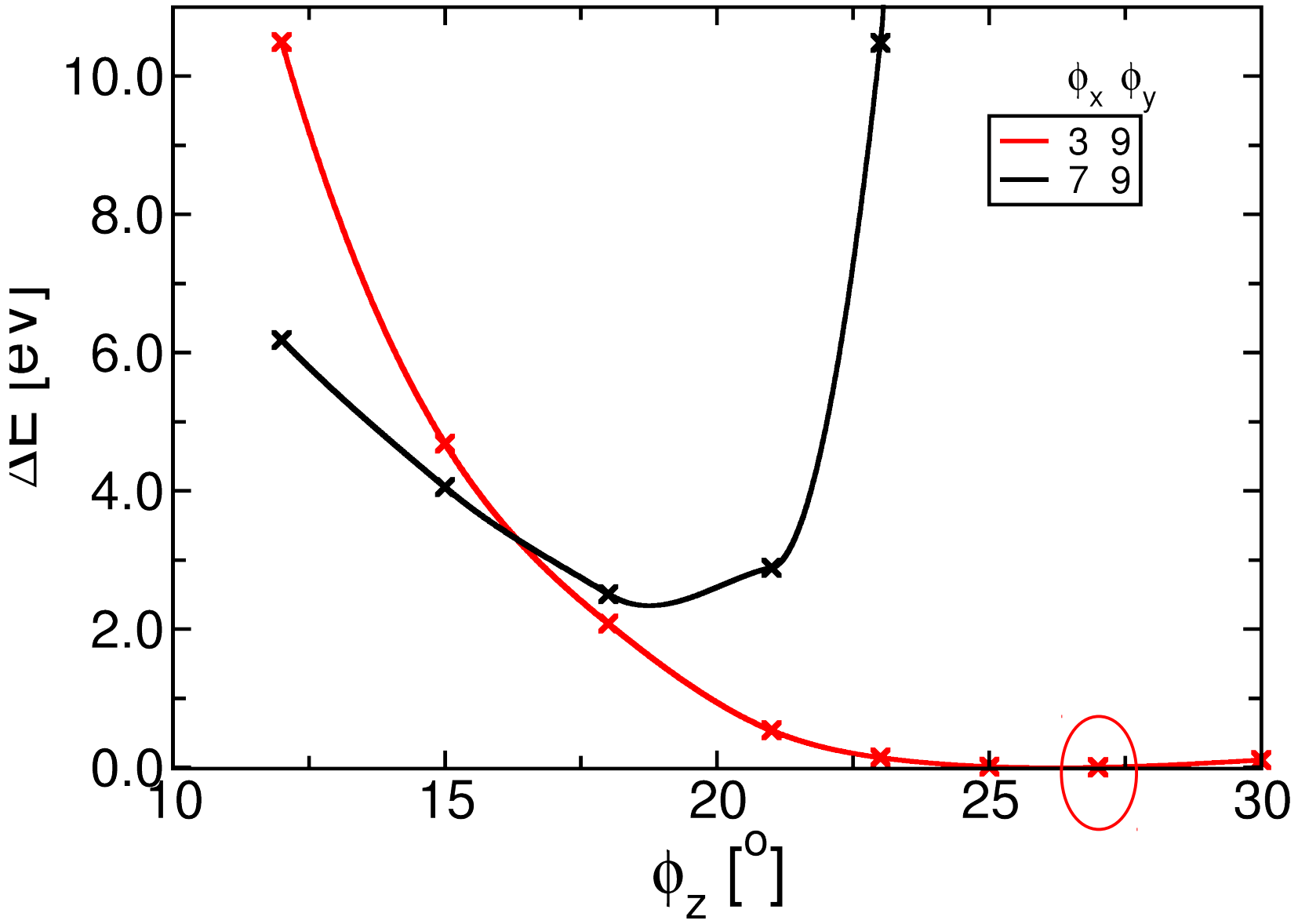




Molecular array with substrate

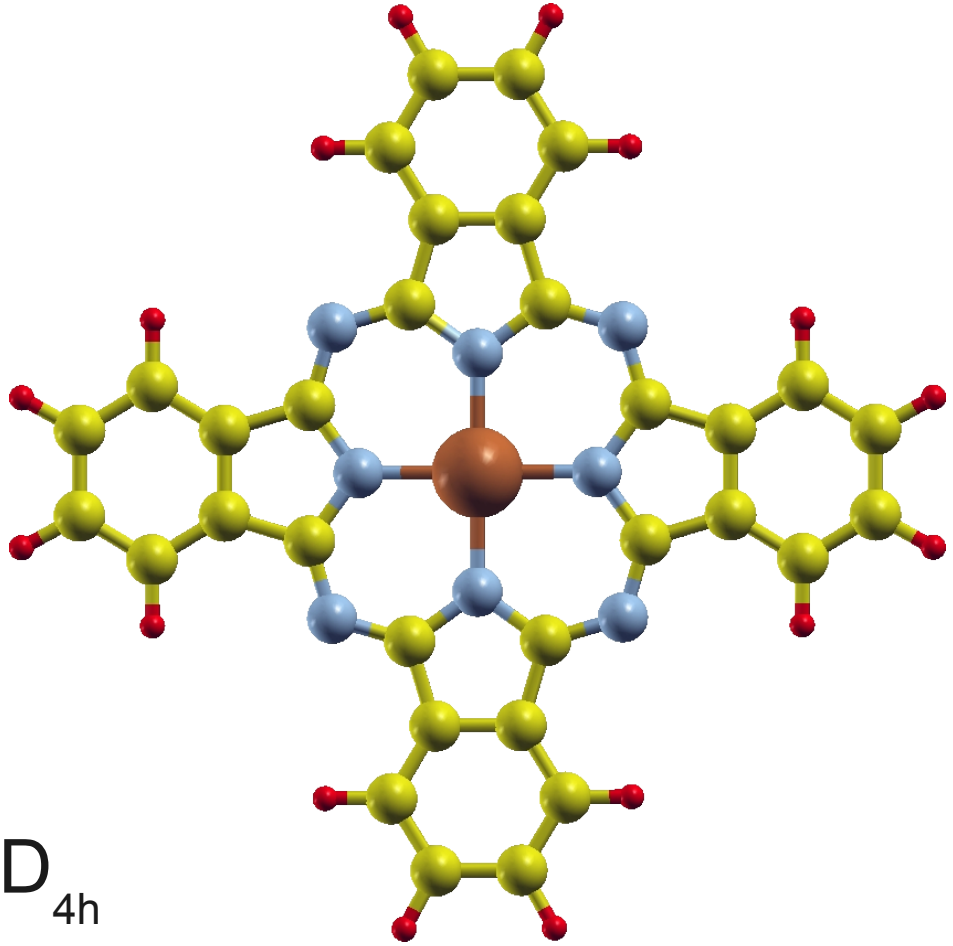


Molecular array with substrate



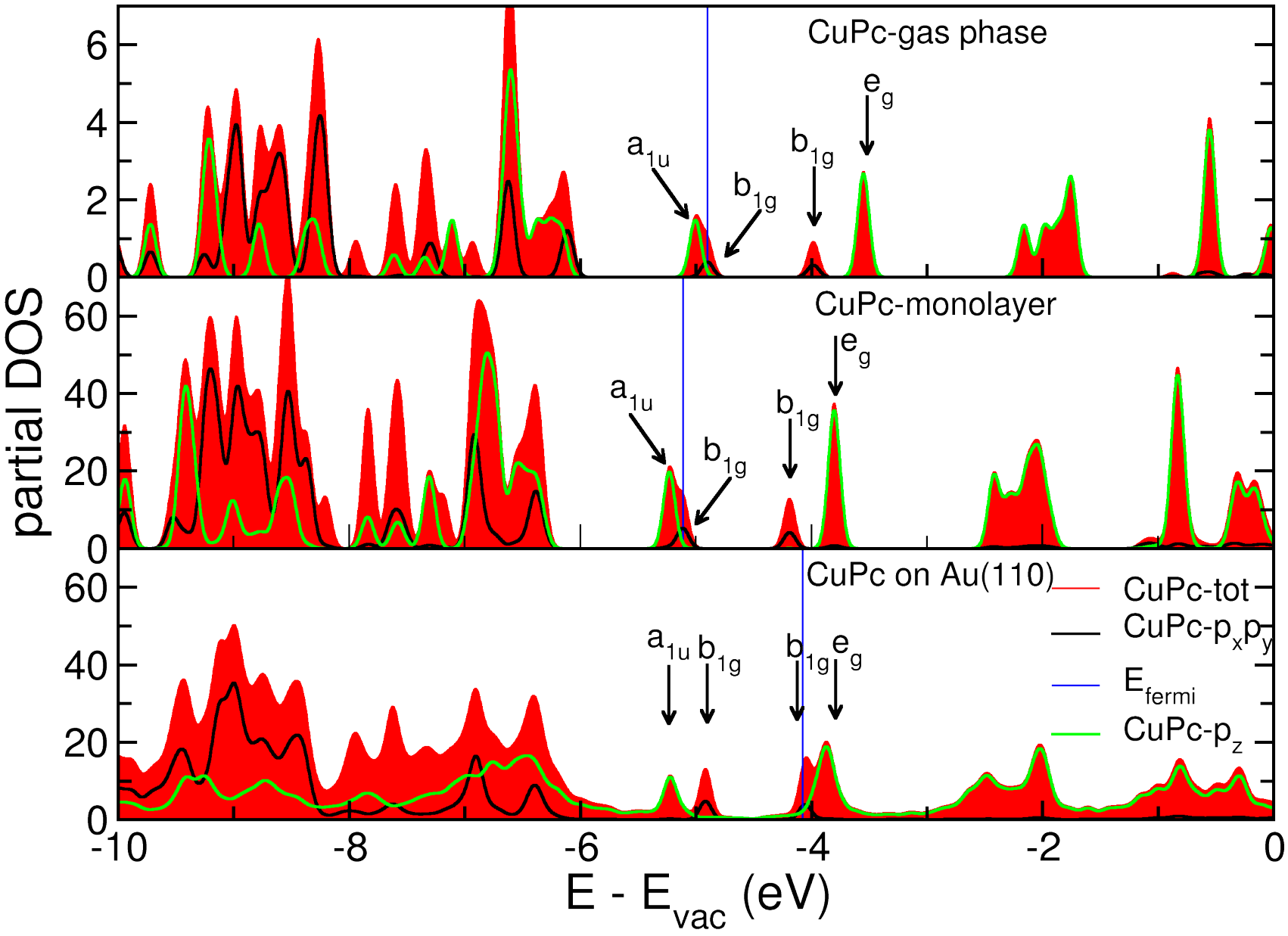
Electronic properties

CuPc

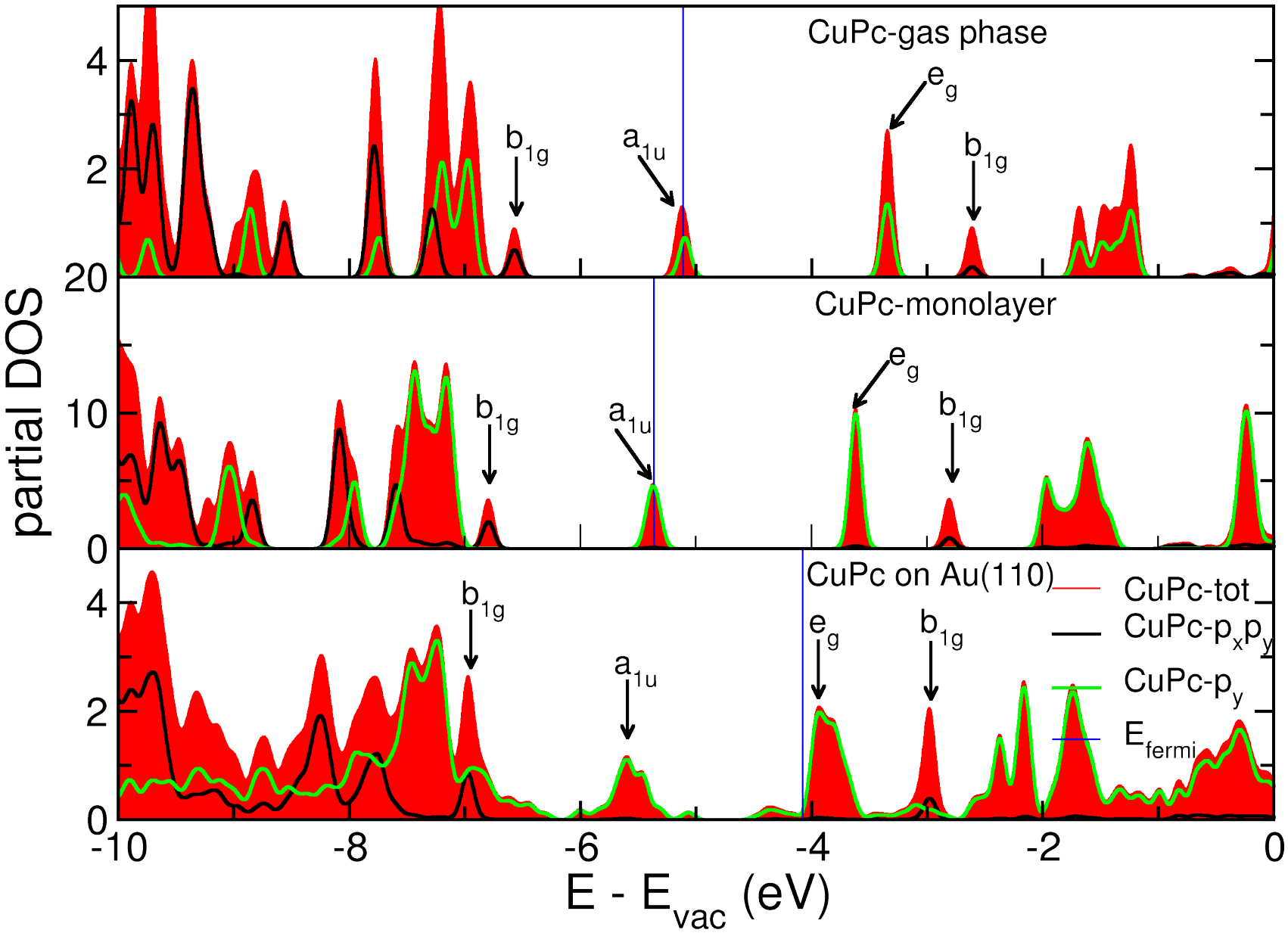


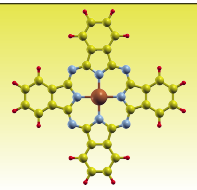
Point group: D_{4h}

Electronic structure from PBE



Electronic structure from HSE06

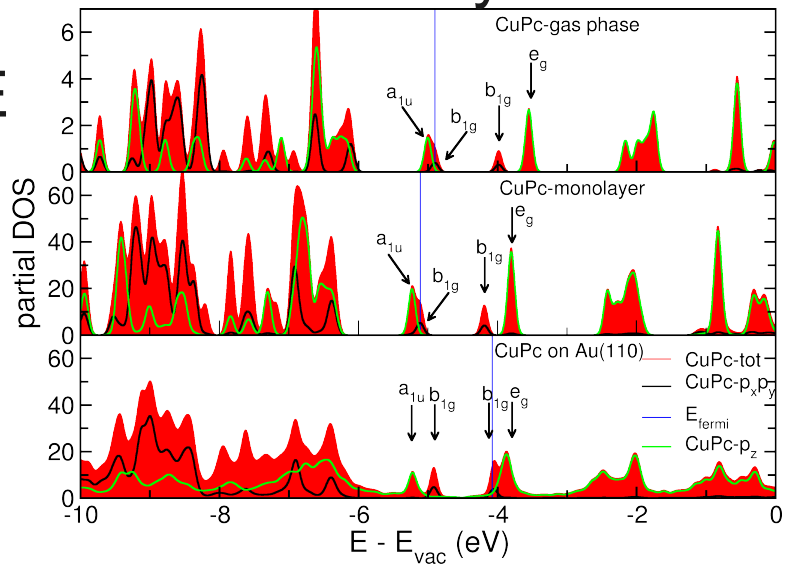




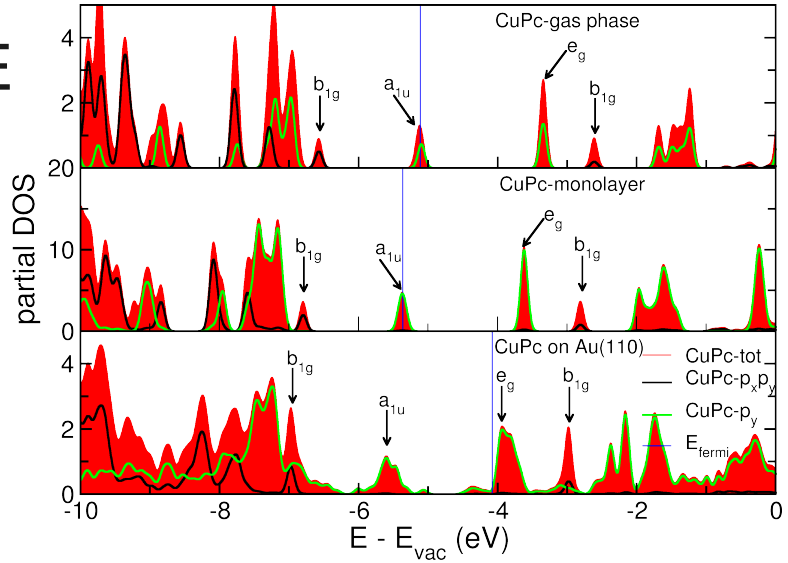
Comparison to experiment

Theory

PBE

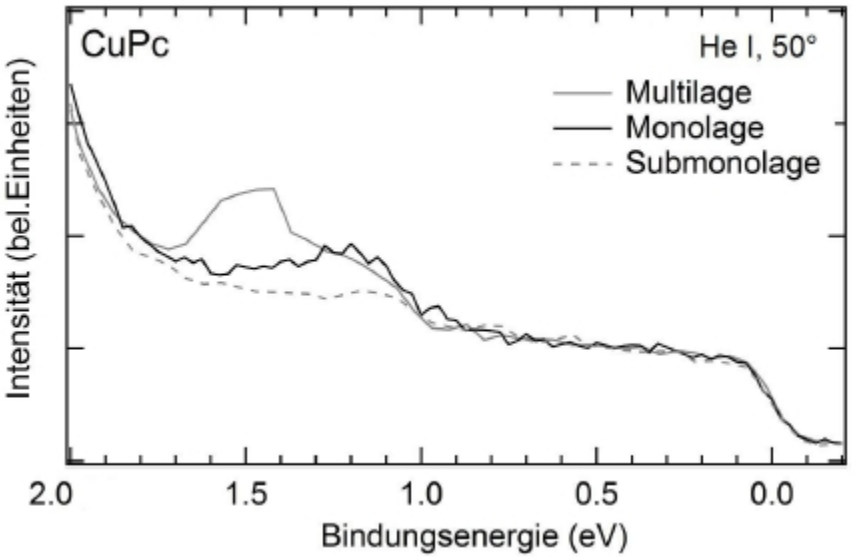


HSE

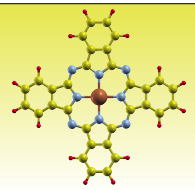


Experiment

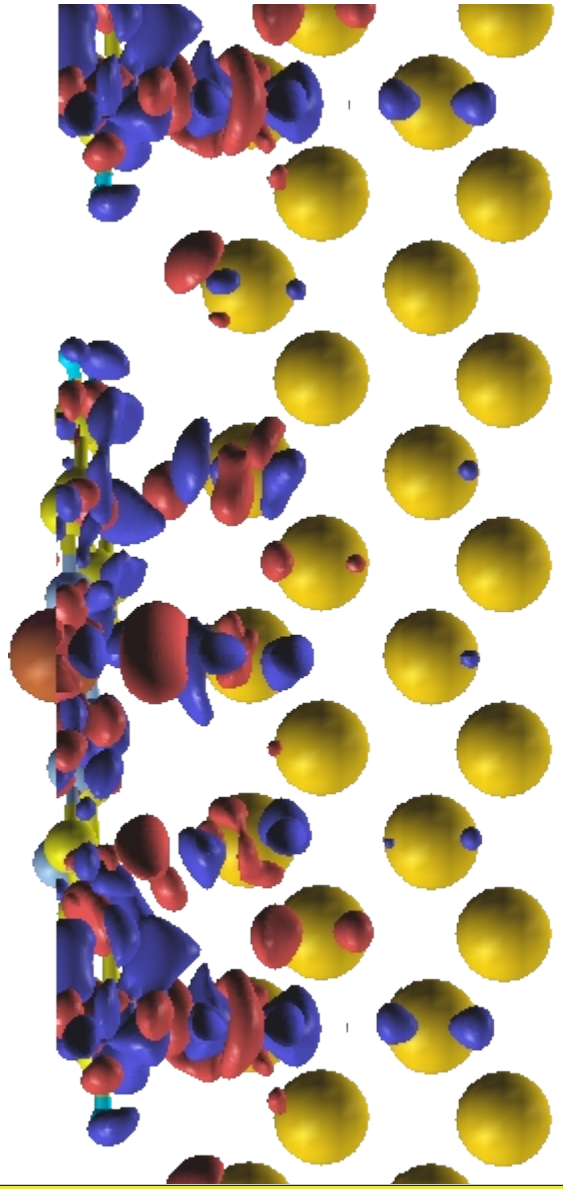
E_b = 1.2 eV



E_b = 1.3 eV

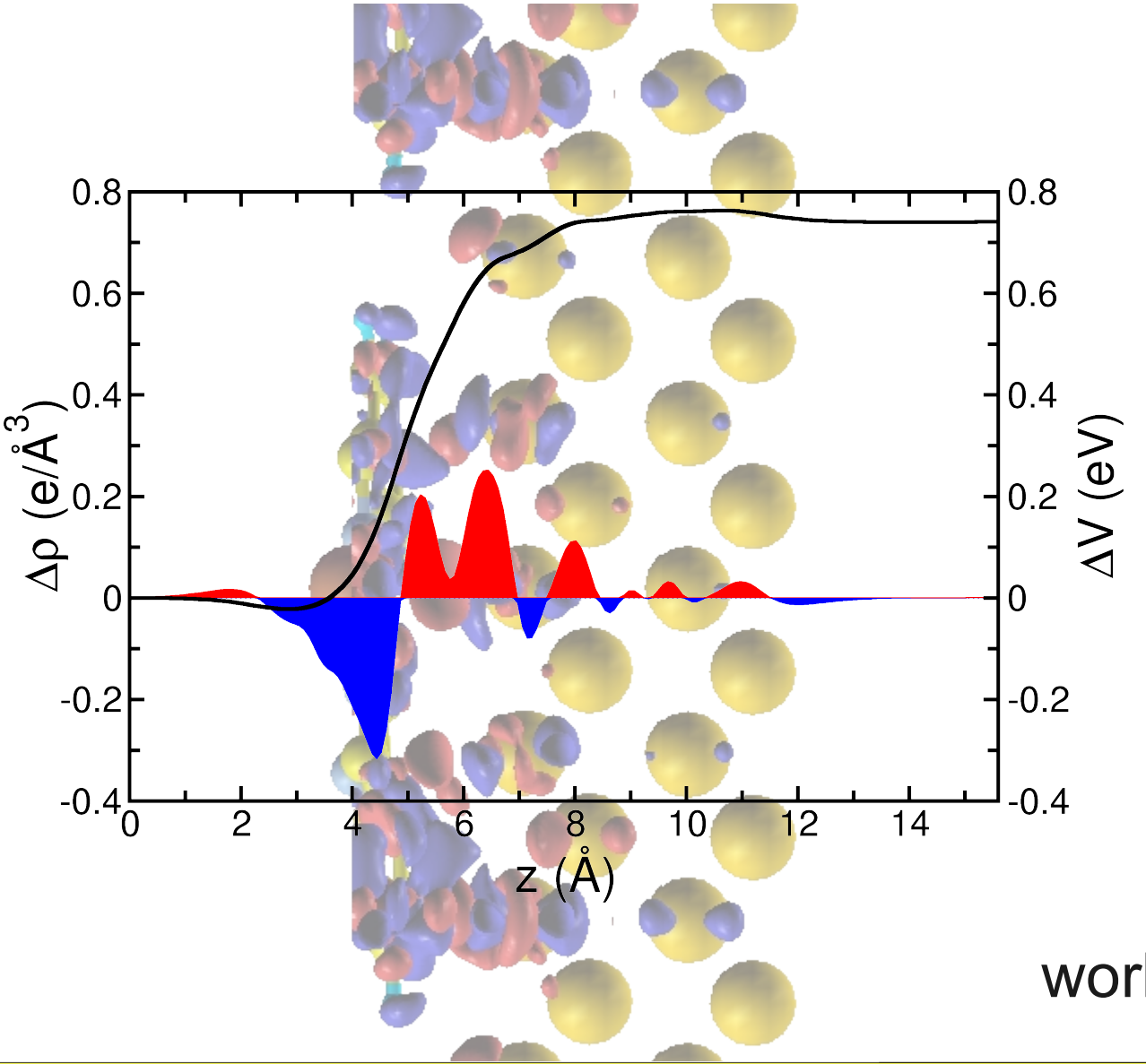


Charge transfer



Differential charge density
isovalue 0.01

Charge transfer



Charge transferred
0.318 e
from the molecule

Potential jump
0.7 eV
work function decrease

Conclusions

· ARPES and LEED in combination with DFT can provide full information about the structure of an overlayer

· There is a light interaction between the molecule and the surface, practically no charge transfer and slight change of the work function

· The description of CuPc`s electronic structure is sensitive to the basis set used and to the level of theory used