

# SIMULATION OF ANGLE-RESOLVED PHOTOEMISSION CROSS-SECTIONS FOR ORGANIC/METAL INTERFACES



Dario Knebl, Daniel Lüftner, Bernd Kollmann, and Peter Puschnig

Institute of physics, Karl-Franzens-University Graz, Universitätsplatz 5, A-8010 Graz, Austria

## Abstract

Several combined experimental / theoretical investigations have demonstrated a close relation between the angle-resolved photoemission (ARPES) intensity of oriented organic molecular films and the Fourier transform of the molecular orbital [1, 2, 3]. So far, experimental ARPES data has been accounted for by neglecting the interaction of molecule with the underlying metal substrates. The remaining small differences have been tentatively attributed to modifications of the molecular states due to molecule-substrate hybridization [4, 5], though alternative explanations, e.g., light polarization effects or the failure of the simple plane-wave final state approximation could not be excluded. Here we calculate ARPES intensity maps for the prototypical PTCDA/Ag(110) interface by explicitly considering molecule-substrate interactions within ab-initio density functional calculations. We perform careful convergence studies with respect to the number of metallic layers and the number of k-points, and compare our results to ARPES measurements.

## PTCDA / Ag(110) geometries

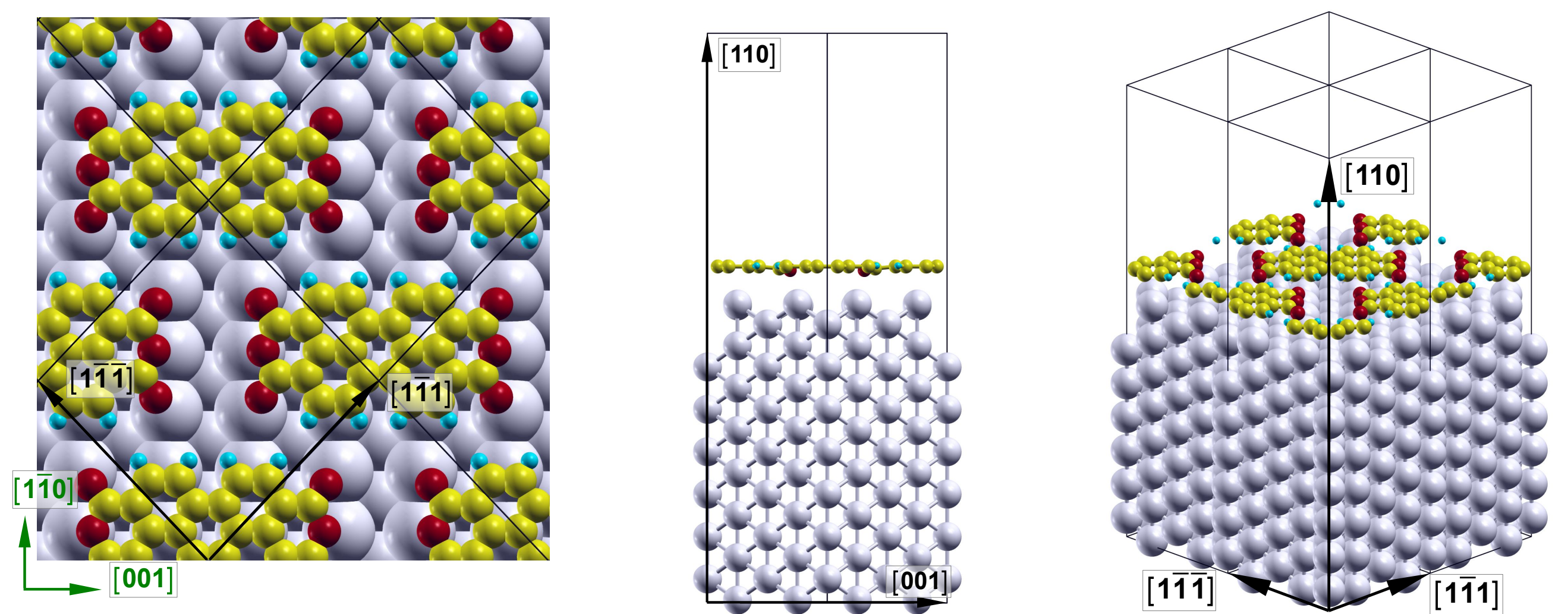


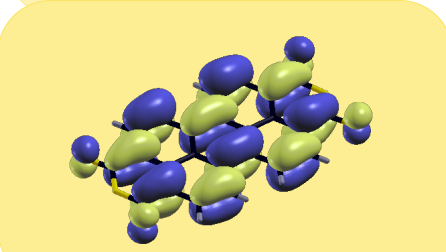
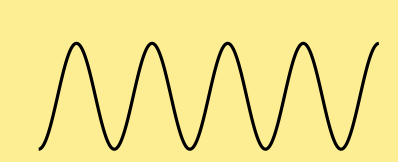
Fig. 6: From left to right: Top view, side view, and diagonal view of a PTCDA ML on 15 layers Ag(110).

## ARPES-Intensity

Using the one-step model (depicted in Fig. 1) the intensity of the emitted electron current is given by a Fermi golden-rule-like formula

$$I(\vartheta, \varphi; E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\vartheta, \varphi; E_{kin}) | \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{kin} - \hbar\omega) \quad (1)$$

where  $|\psi_i\rangle$  is the  $i$ -th molecule orbital of the sample and  $|\psi_f\rangle$  describes the outgoing electron by a (damped) plane wave.



The tuple  $(\vartheta, \varphi, E_{kin})$  is just another representation of the wavevector  $\mathbf{k}$  of the emitted electron

$$\begin{aligned} k_x &= \sqrt{2m_e E_{kin} / \hbar^2} \sin \vartheta \cos \varphi \\ k_y &= \sqrt{2m_e E_{kin} / \hbar^2} \sin \vartheta \sin \varphi \\ k_z &= \sqrt{2m_e E_{kin} / \hbar^2} \cos \vartheta \end{aligned} \quad (2)$$

Within this work the electric dipole approximation is applied

$$[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \cdot \mathbf{A} \approx 0 \quad (3)$$

which simplifies the term

$$\frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) \approx \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \quad (4)$$

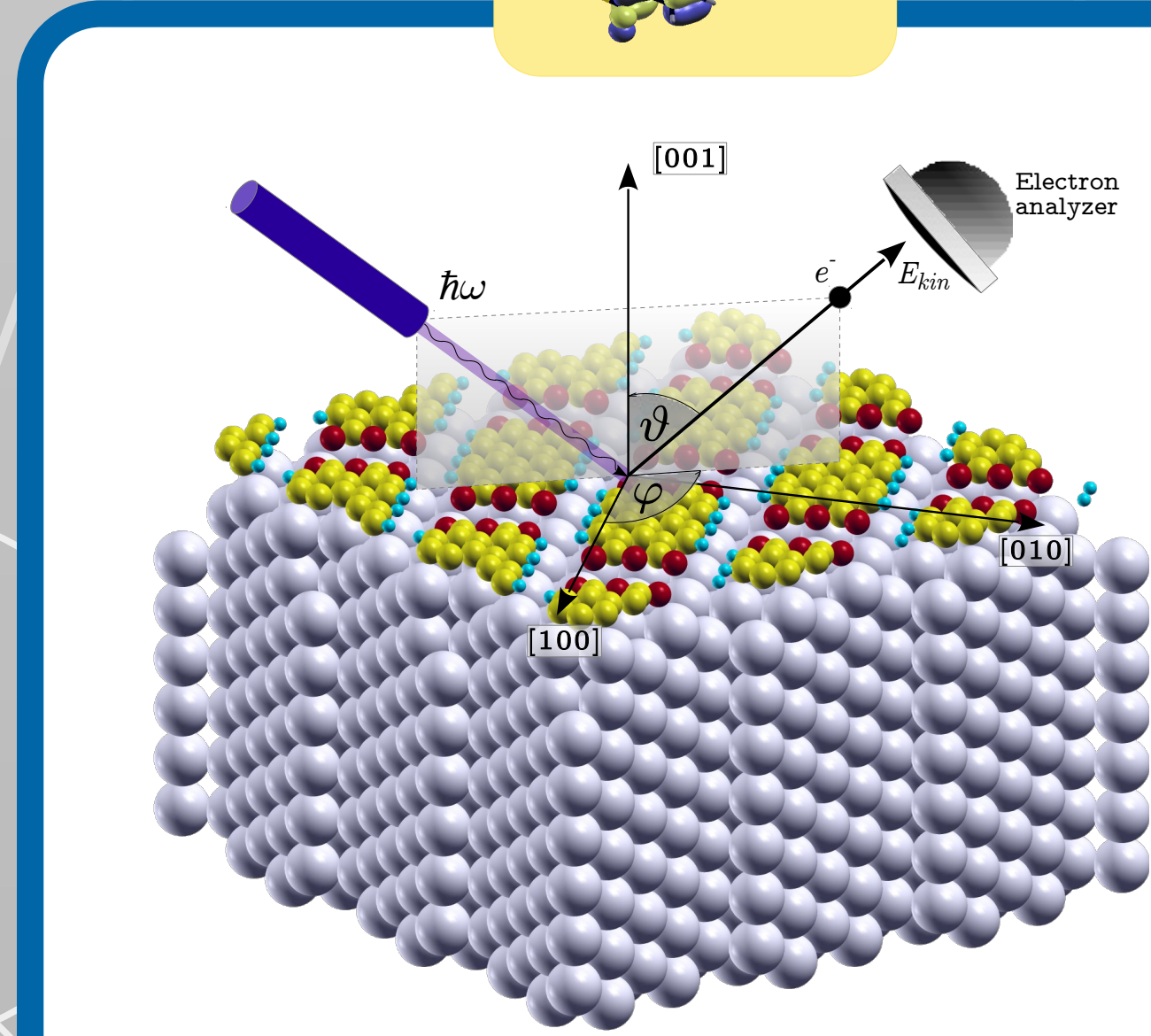


Fig. 1: A simple illustration of ARPES.

## Experiment vs. Theory

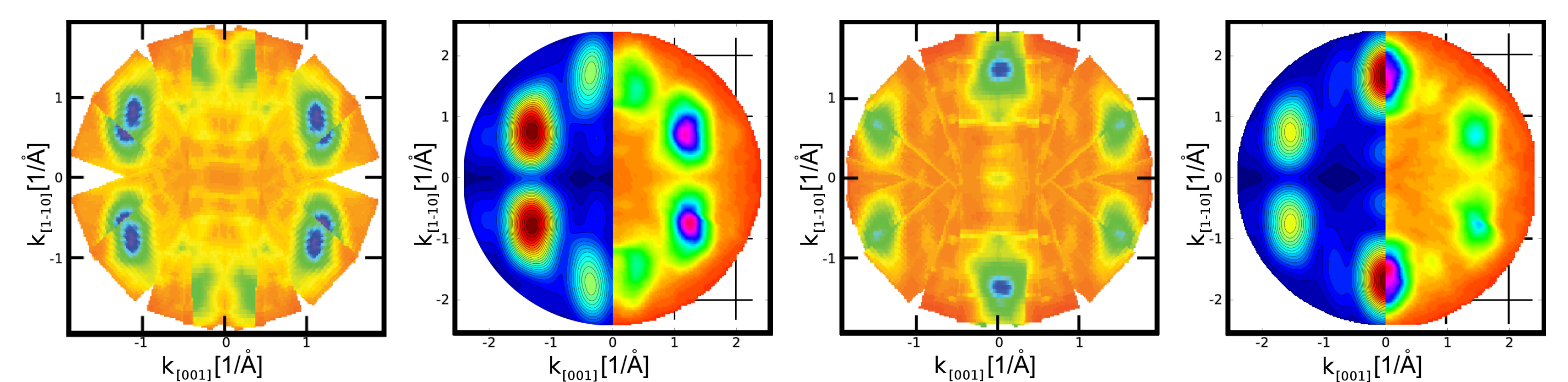


Fig. 7: **Numeration from left to right:** (1) Experimental HOMO and (3) FLUMO maps of PTCDA/Ag(110) sample [4]. (2) HOMO and (4) LUMO map of a free PTCDA ML (left semi-circle: simulation, right semi-circle: experiment [2])

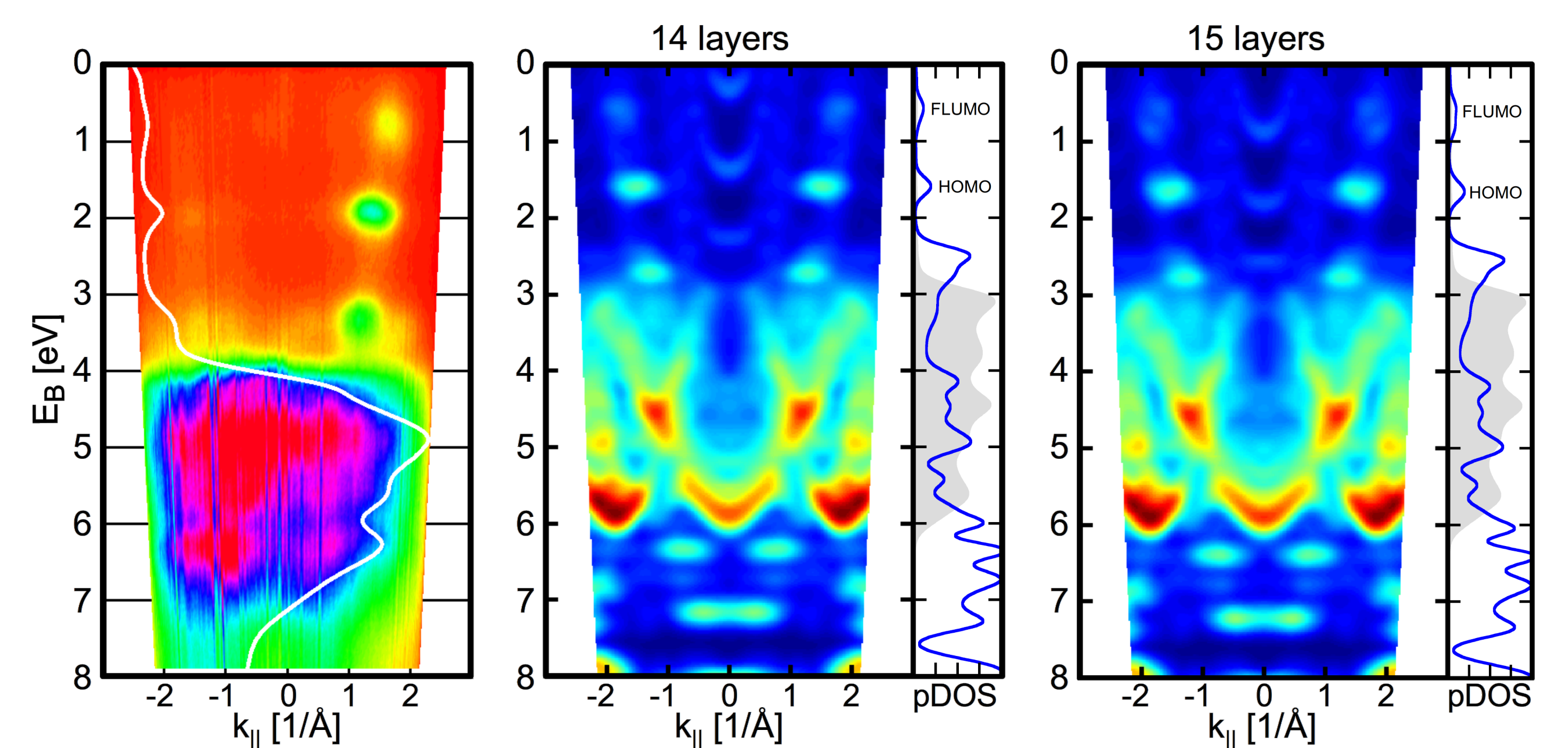


Fig. 8: **From left to right:** (1) Experimental energy-momentum map [2] of PTCDA on Ag(110) along the  $32^\circ$ -rotated  $k_{\parallel}$ -axis, compared to simulated band maps of PTCDA ML on (2) 14-layer Ag(110) and (3) on 15-layer Ag(110).

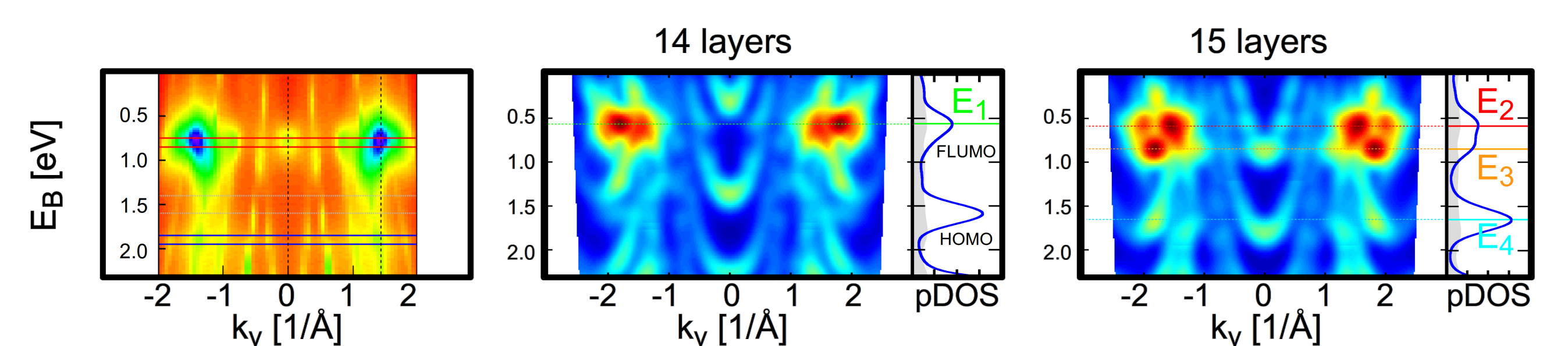


Fig. 9: **From left to right:** (1) Experimental energy-momentum map [2] of PTCDA on Ag(110) along the  $k_{\parallel}$ -axis, compared to simulated band maps of PTCDA ML on (2) 14-layer Ag(110) and (3) on 15-layer Ag(110).

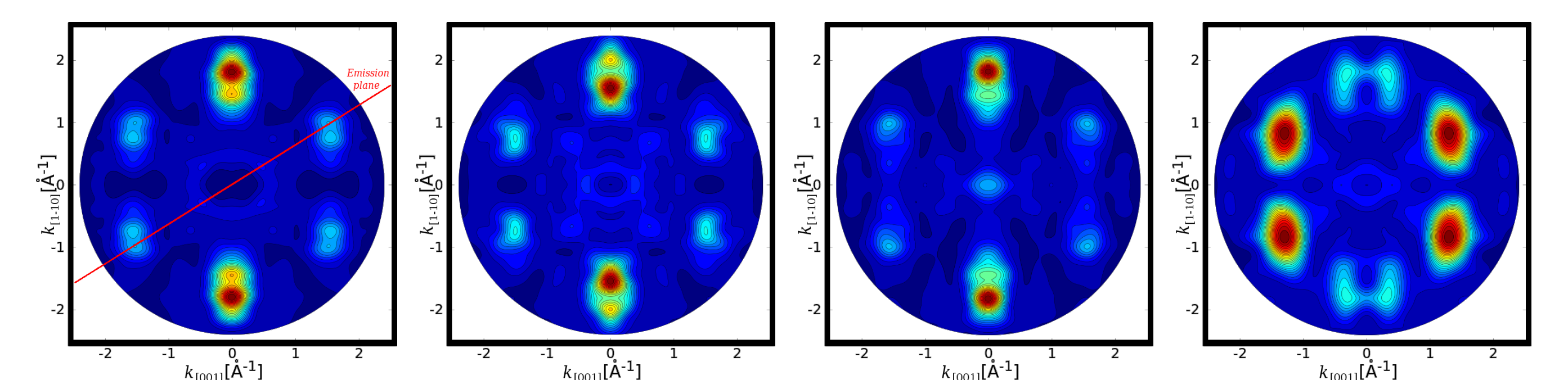


Fig. 10: **From left to right:** The corresponding simulated maps at the binding energies (**E1**) 0.56eV, (**E2**) 0.59eV, (**E3**) 0.85eV and (**E4**) 1.65eV defined in Fig. 9.

In Figs. 7-10 the number of k-points is  $6 \times 6 \times 1$ . The blue line represents the pDOS of the PTCDA ML while the gray filled curve represents the pDOS of the Ag(110).

## Density of States

Convergence studies with respect to the number of k-points in the Brillouin zone and convergence studies w. r. t. the number of Ag(110) layers are performed in order to obtain converged density of states (DOS) curves.

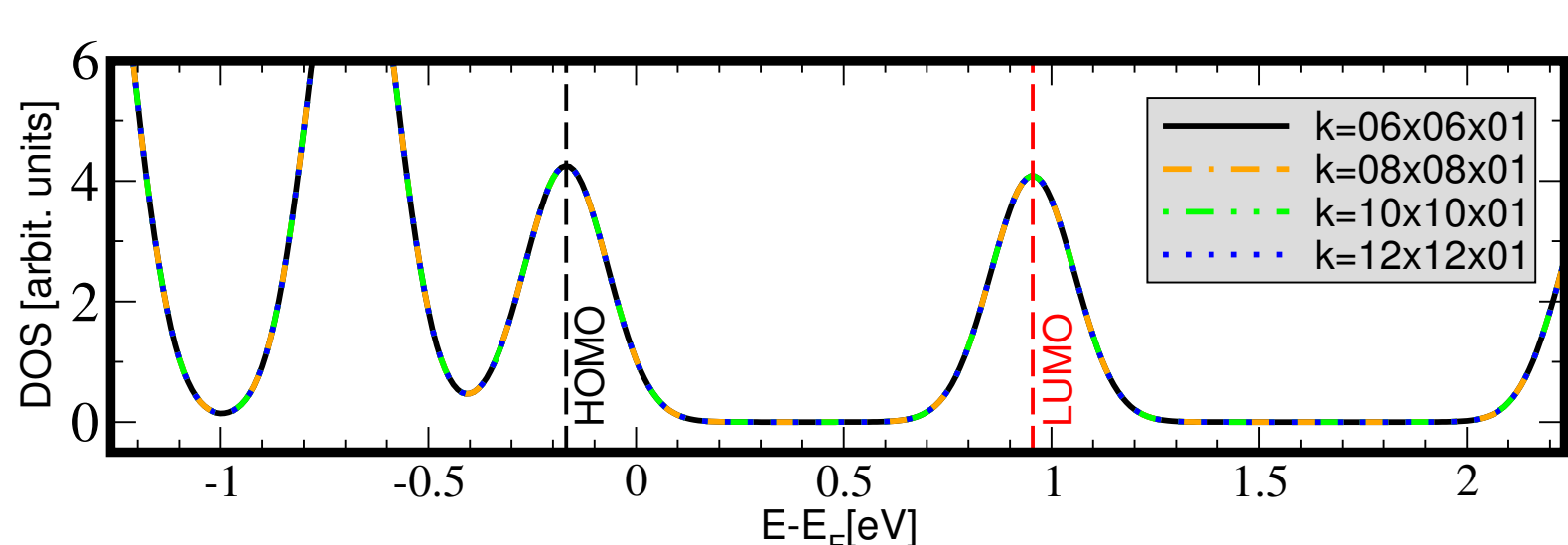


Fig. 2: DOS of a free standing PTCDA monolayer (ML).

The black dashed lines in Fig. 2-3 indicates the energy of the highest occupied molecule orbital (HOMO).

The red dashed lines indicates the energy of the lowest unoccupied molecule orbital (LUMO).

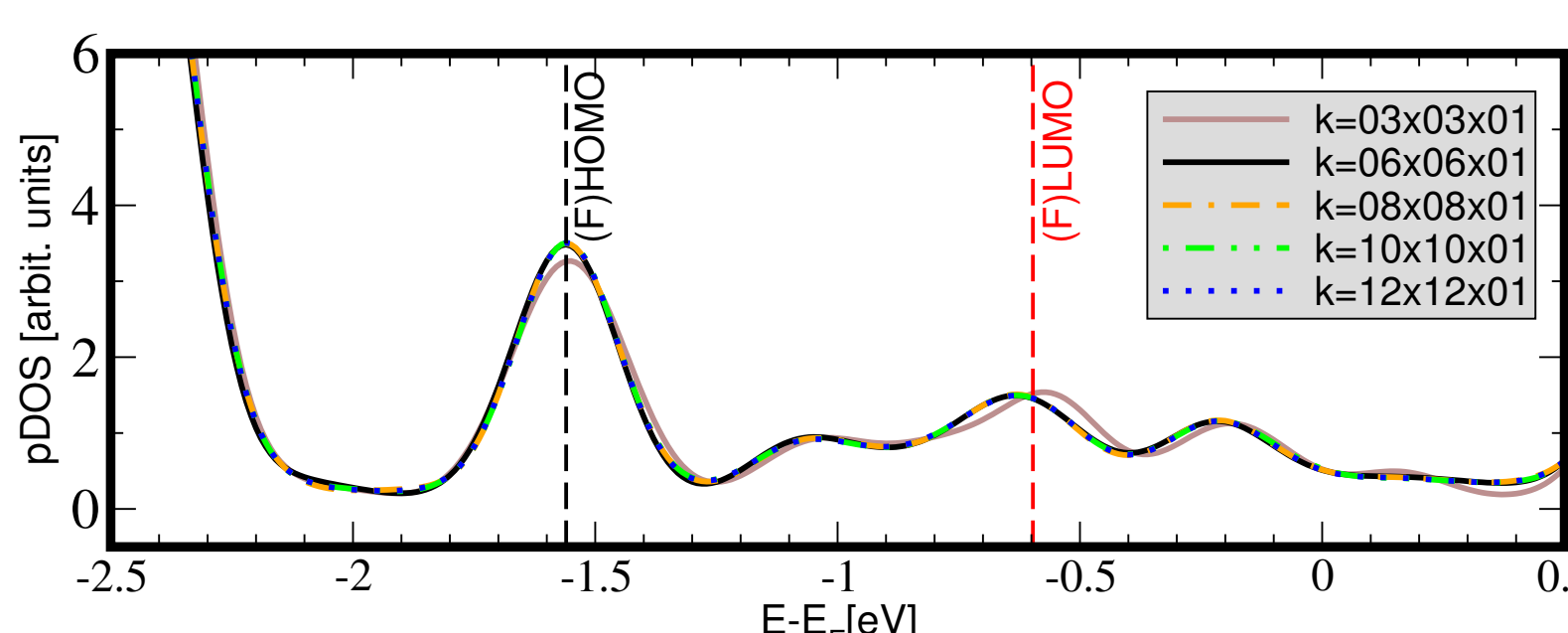


Fig. 3: pDOS of 5 layers Ag(110) covered with a PTCDA ML.

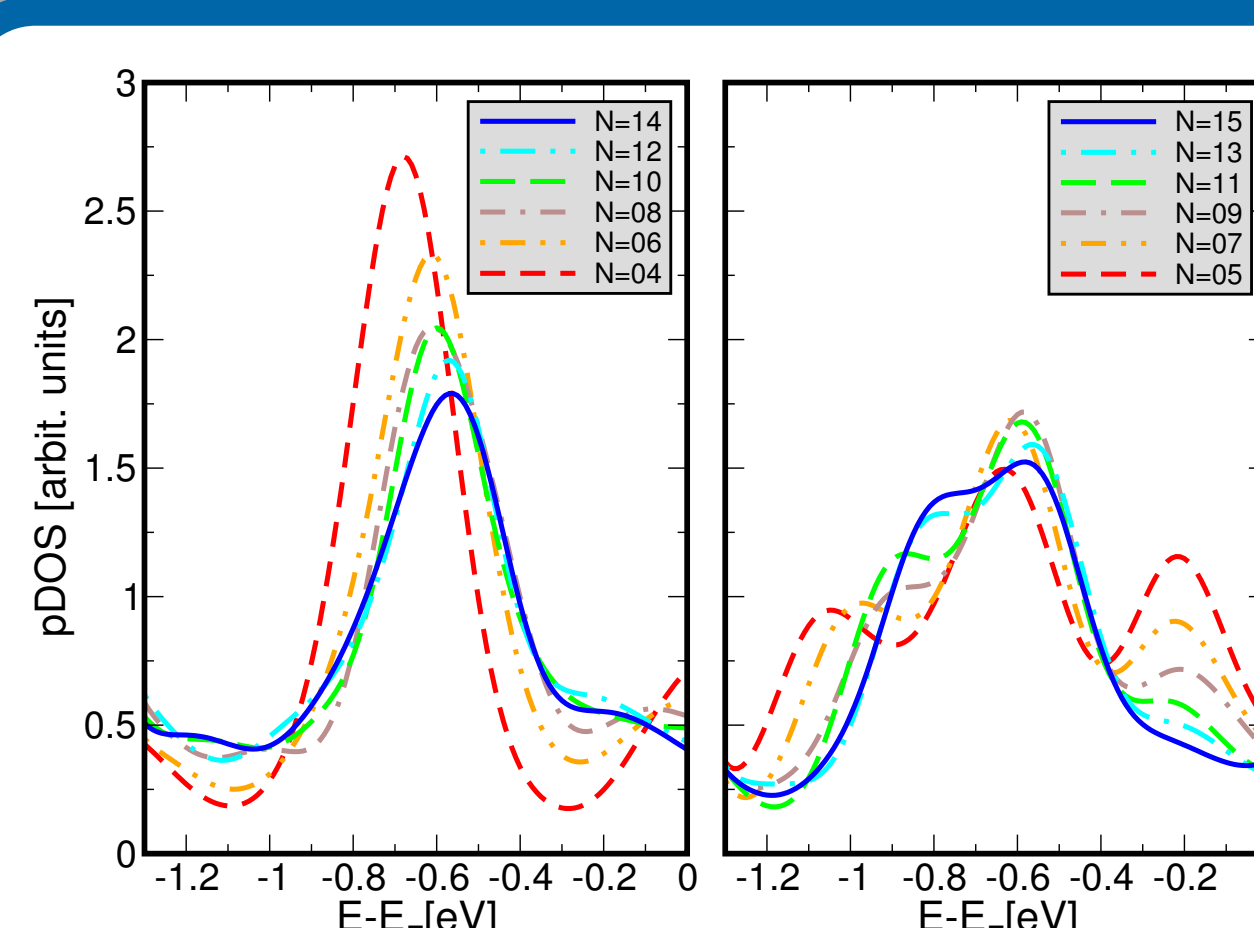


Fig. 4:  $N = 4, 5, 6, \dots, 15$ ;  $k$ -grid= $6 \times 6 \times 1$

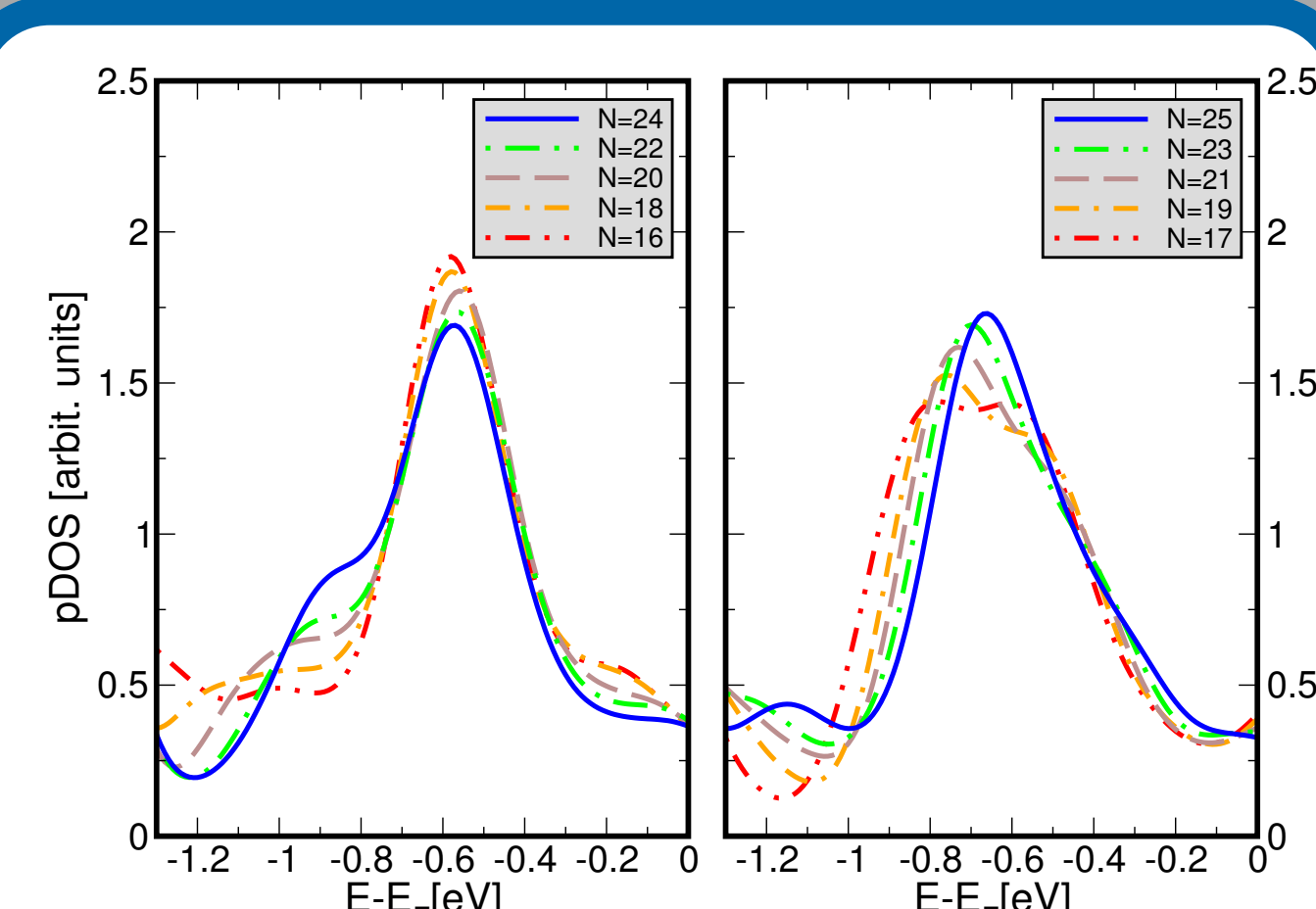


Fig. 5:  $N = 16, 17, \dots, 25$ ;  $k$ -grid= $3 \times 3 \times 1$

The convergence studies w. r. t. the number of Ag(110) layers highlight a parity dependence of the pDOS in the energy range of the (F)LUMO (Fig. 4 and Fig. 5).

## Methodology

The DFT (GGA) calculations of this work are performed by the Vienna Ab initio Simulation Package (VASP).

## Reference

- [1] Puschnig et. al. *Science*, 326:702-706, 2009.
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