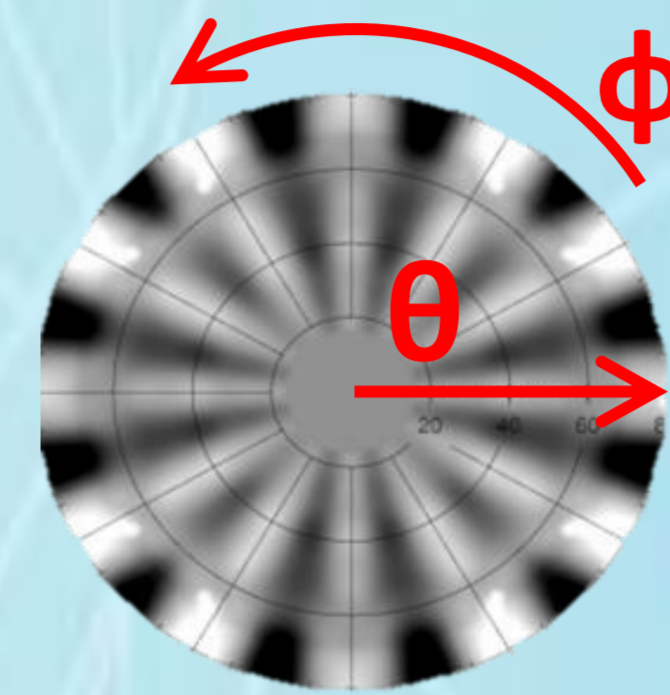
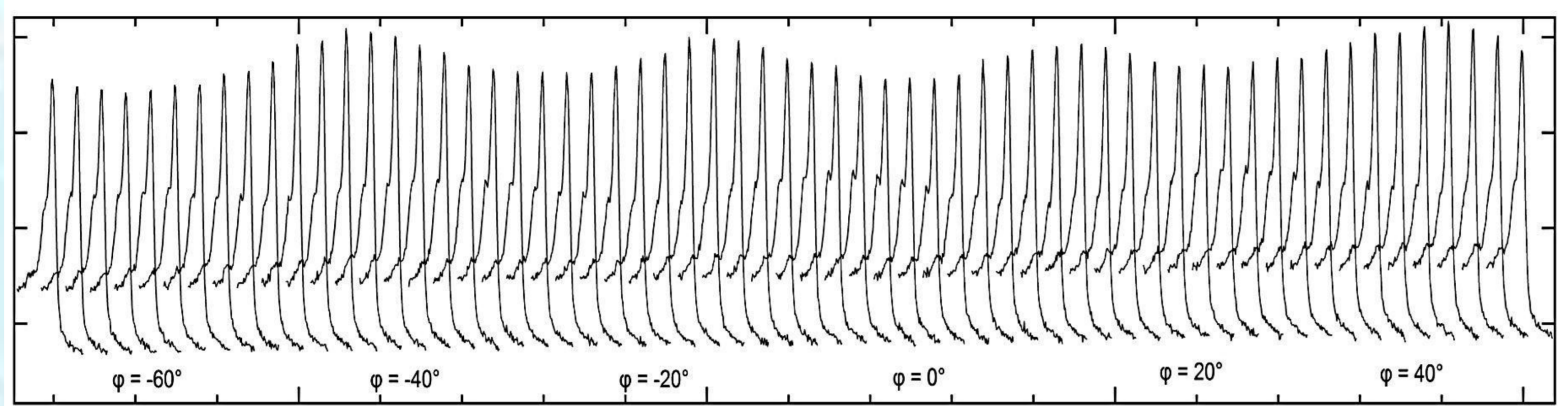
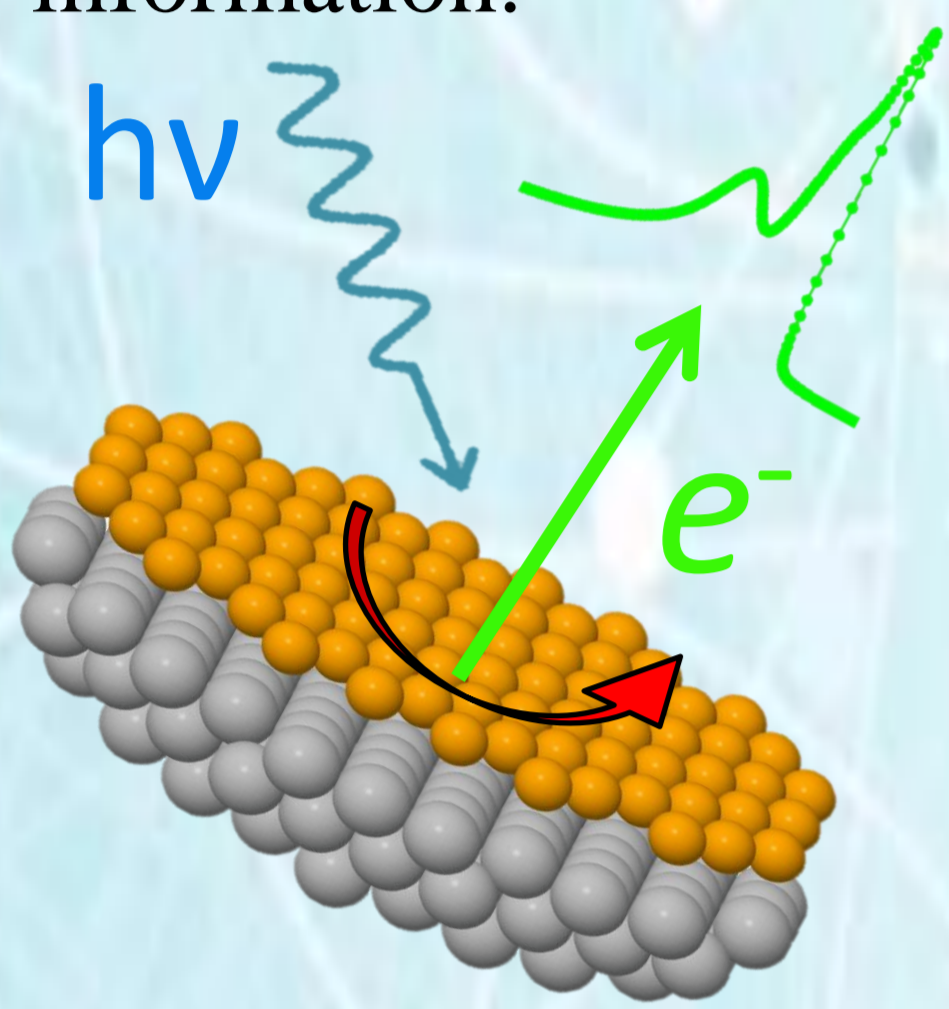


Exploiting the structures of ultra-thin films and adsorbates on graphene using X-ray Photoelectron Diffraction

Why Ultra-thin Layers? During the recent years researches have revealed interesting properties of ultra-thin metal and oxide films that make these materials particularly suitable for the application in nano-electronics, gas sensing and magnetic data storage devices [1]. Their physical and chemical properties are strictly related to the peculiar atomic arrangement in the outer surface layers. However, their structural determination is still a challenging issue because of the complex lateral arrangement and mismatch at the metal-oxide interface. Among the available surface science techniques, X-ray Photoelectron Diffraction have the great advantage of being sensitive to chemically non-equivalent atomic species sitting in the first atomic layers. Since the long-range order is not required, this approach can be applied to determine the local atomic arrangement of complicated specimens such as ultra-thin oxide films and adsorbates on epitaxial graphene.

X-ray Photoelectron Diffraction (XPD) is used to reveal the local atomic geometry (crystal symmetry, interatomic distances, bond lengths and angles) of the system under investigation. Long-range order is not required. High energy-resolution photoemission with synchrotron radiation allows us to combine chemical sensitivity to non-equivalent atomic species and structural information.



Stereographic projection of a XPD pattern

XPD data Analysis:

- Theoretical calculations provide us the XPD pattern expected from a trial structure.
- Reliability factor

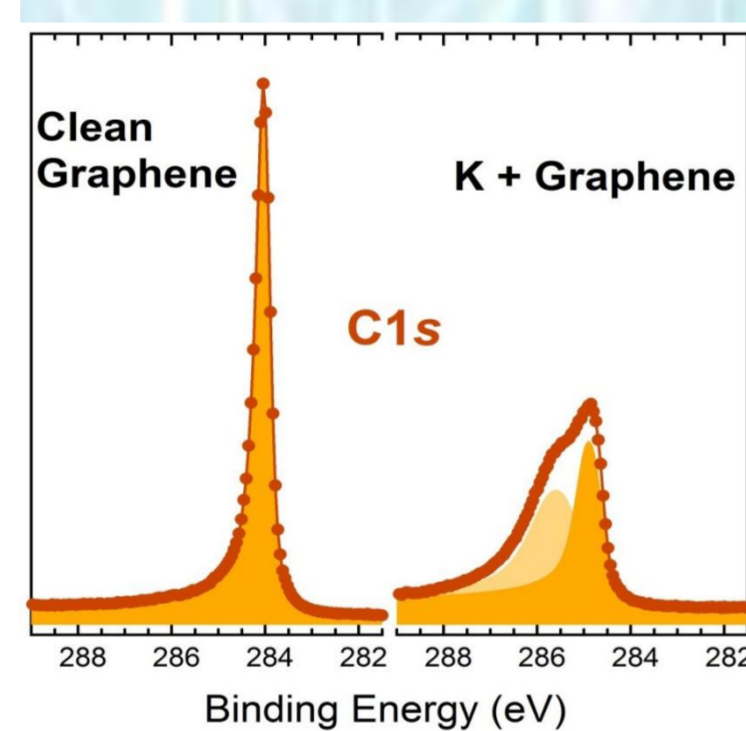
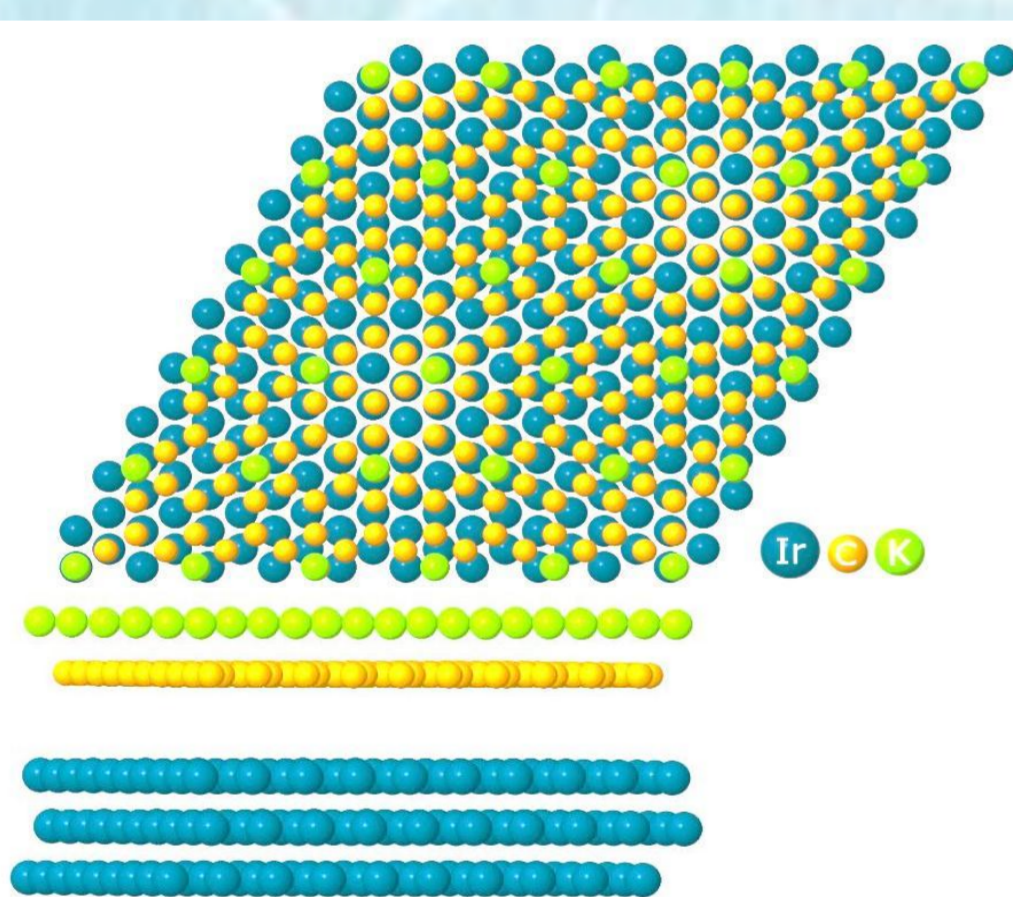
$$R\text{-factor} = \sum_i \frac{(\chi_{exp,i} - \chi_{th,i})^2}{(\chi_{exp,i}^2 + \chi_{th,i}^2)}$$
- Iterative methods by implementation of R-factor minimization algorithms (Steepest Descent, Genetic algorithm) are applied to search for the best final structure with the lowest R-factor.

References:

- N. Nilius, *Surf. Sci. Rep.* **64**, 595 (2009).
- M. Bianchi, M. Pozzo, D. Alfé, R. Zhan, E. Vesselli, A. Baraldi, R. Larciprete, P. Lacovig, S. Lizzit, in prep.
- In collaboration with Z. Surnev, F. Netzer, in prep.
- Rong Rong Zhan, Erik Vesselli, Alessandro Baraldi, Silvano Lizzit and Giovanni Comelli *J. Chem. Phys.* **133**, 214701 (2010).

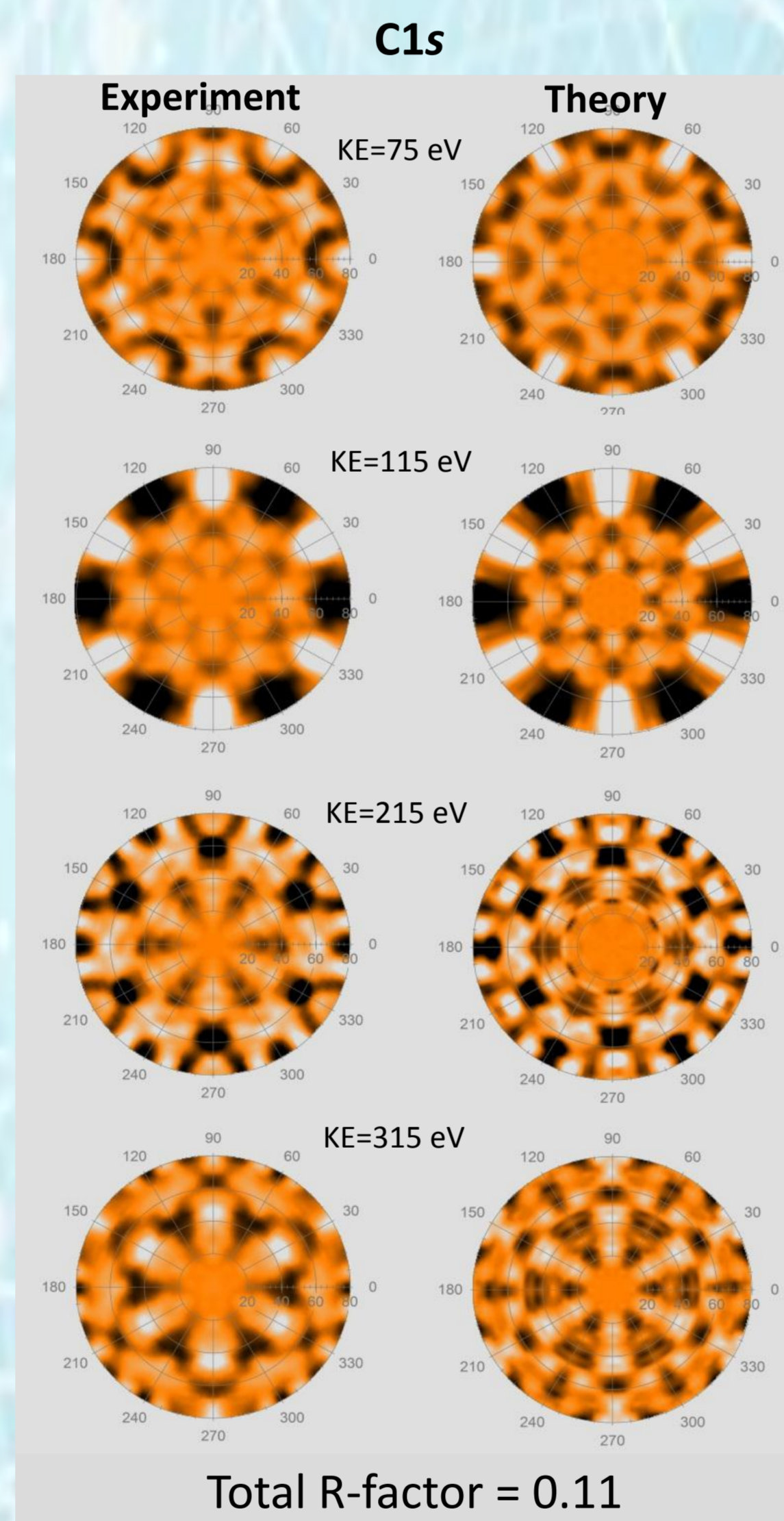
$p(2 \times 2)$ -K/graphene/Ir(111)

Potassium doped graphene represents a model system describing the interaction between alkali atoms and the structurally and electronically anisotropic single carbon layer. It handles extremely fascinating issues such as the effects of the electron charge transfer and redistribution on both the conduction properties of graphene, and the interaction strength between graphene and substrate. XPD investigations proved the quite large distance of K layer from the supported graphene as predicted by DFT calculations [2].



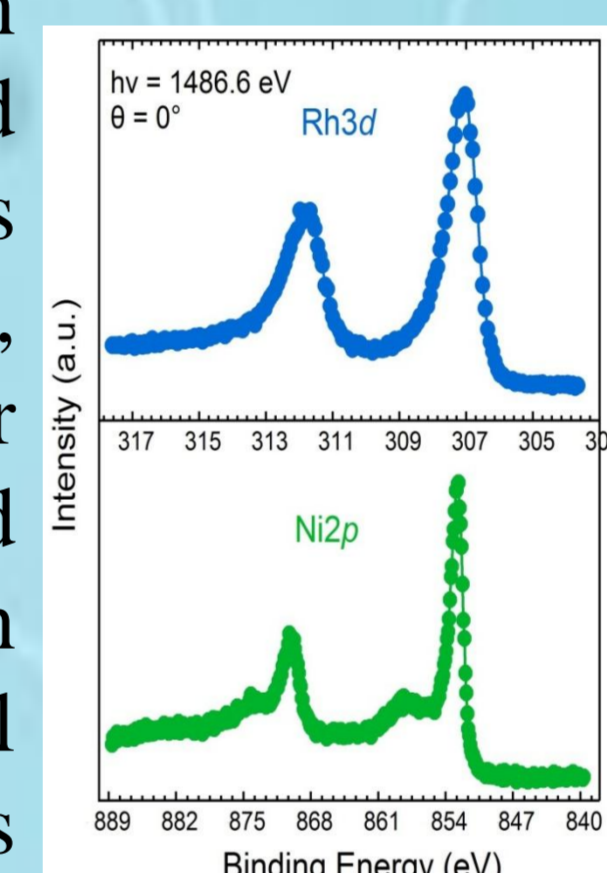
C1s XPS Spectra before (left) and after (right) K doping: an intense satellite structure is arisen due to charge redistribution at the interface.

Structure of the close-packed (2×2) phase formed by potassium (green atoms) adsorption on epitaxial graphene (orange atoms).

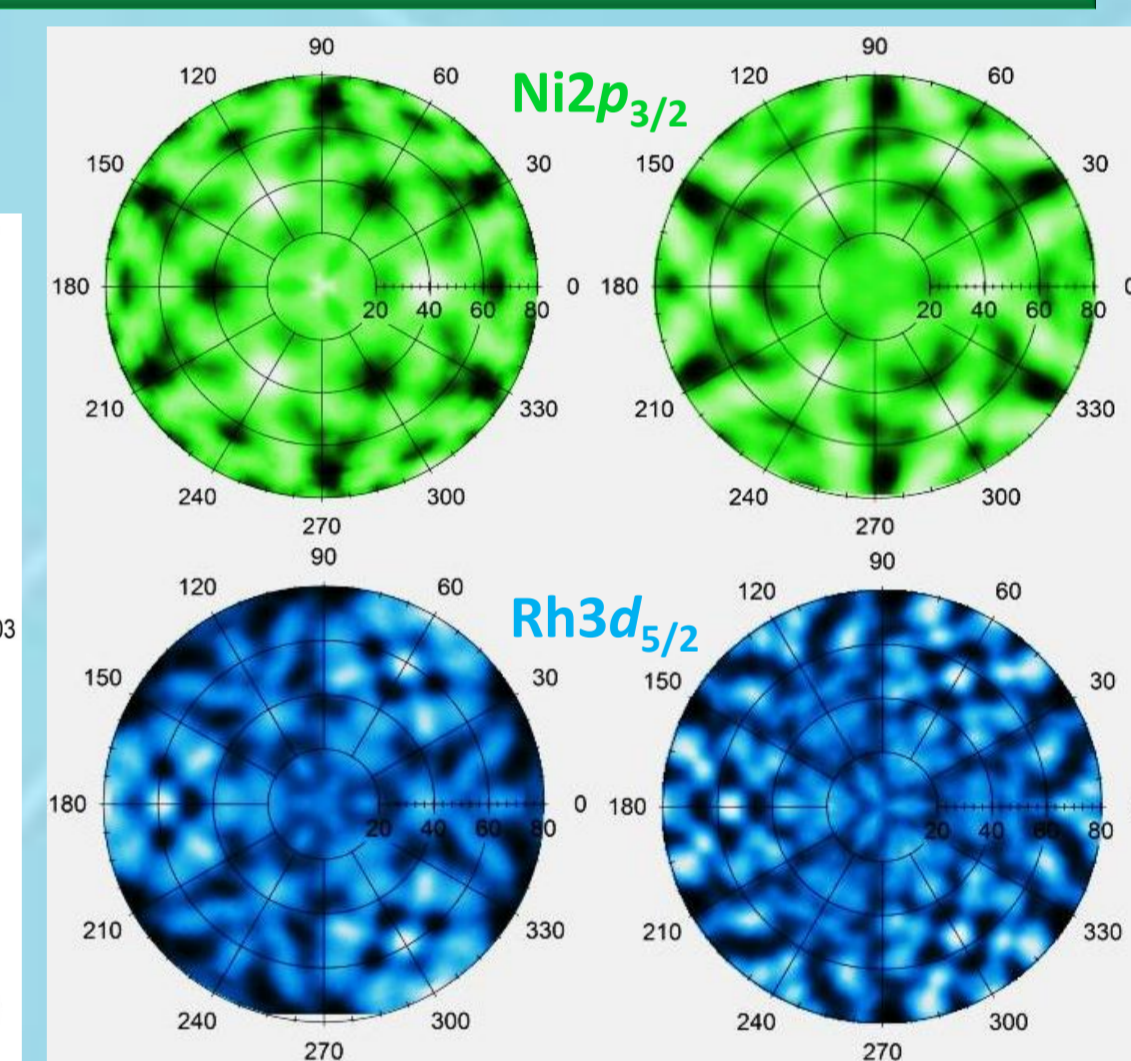


Strain relaxation in epitaxial Ni/Rh(111)

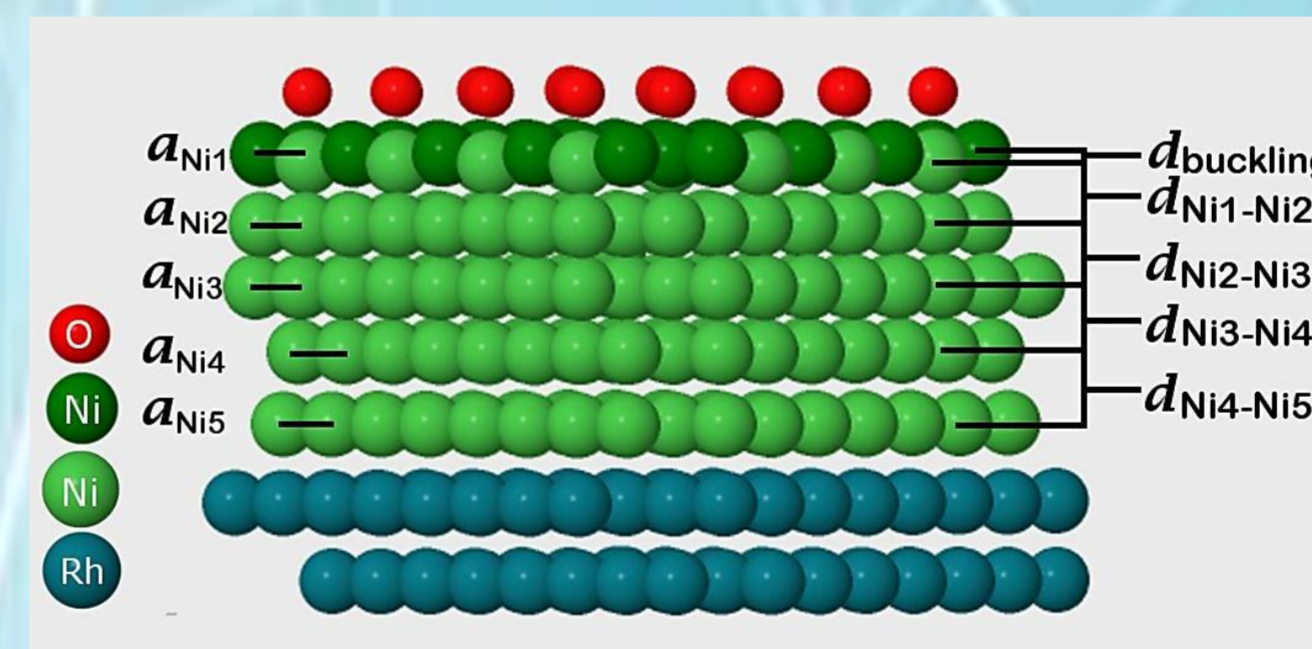
Nickel nano-islands are epitaxially grown on Rh(111). The large lattice mismatch between Ni and Rh (8%) introduces significant tensile stress in the Ni overlayers. This is released when the thickness of Ni islands reaches to 5 ML. At this Ni coverage, a $p(2 \times 2)$ -O phase is formed under oxygen chemisorption. We evaluated the Ni layers strain relaxation behavior. We found an exponential contraction of the lattice parameters from Rh-like to bulk Ni-like with increasing distance of the layer from the Rh substrate[3].



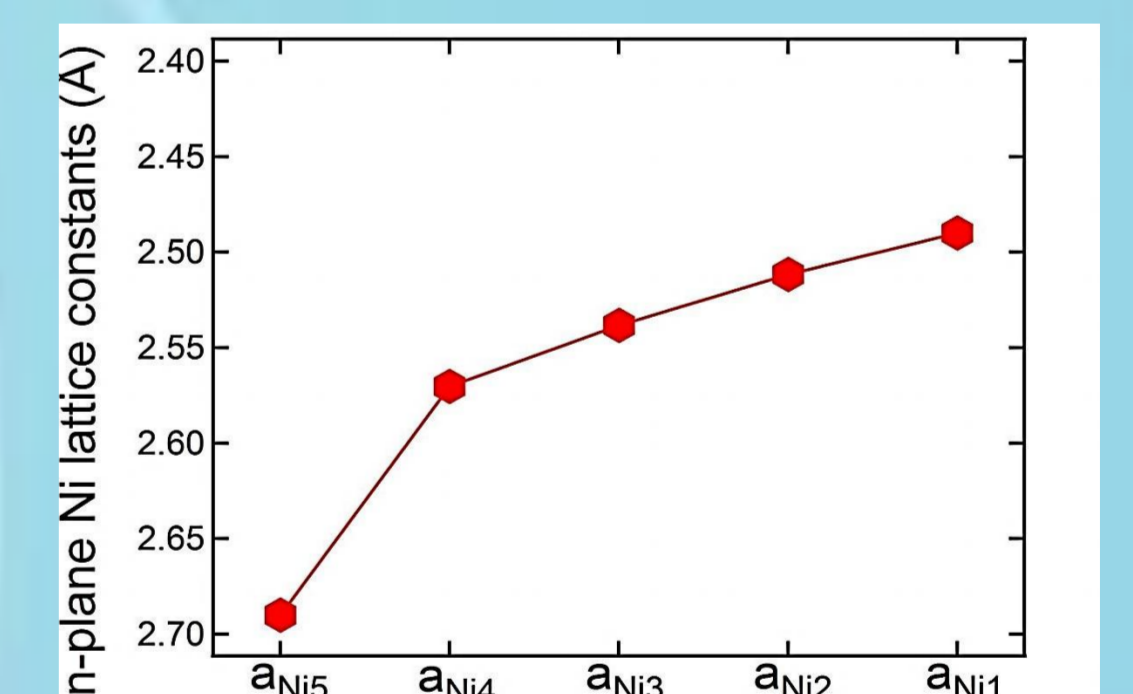
Photoemission spectra of Ni2p and Rh3d core levels.



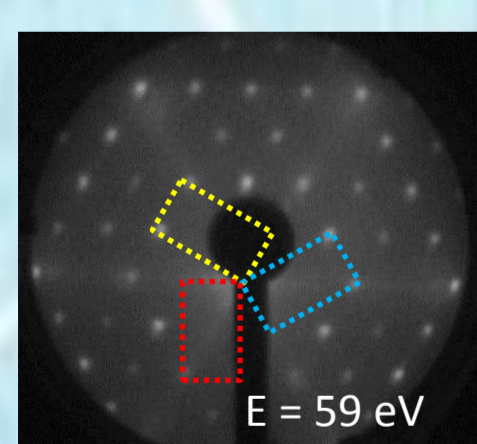
Experimental (left) and best simulated (right) XPD patterns of the core levels shown in graph on left.



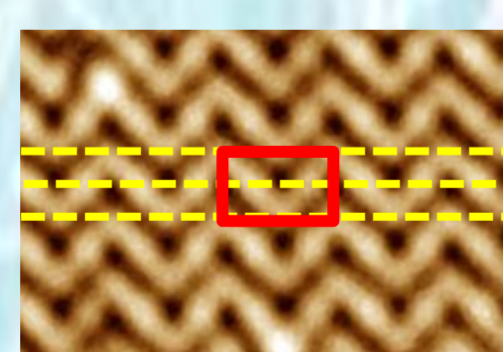
Left: a model for the $p(2 \times 2)$ -O phase on 5 ML high Ni-island/Rh(111). The interlayer distance variation and the first Ni layer buckling are visible. Right: exponential attenuation of Ni lattice constant with increasing distance from the interface layer.



Ni₃O₄ / Rh(111)

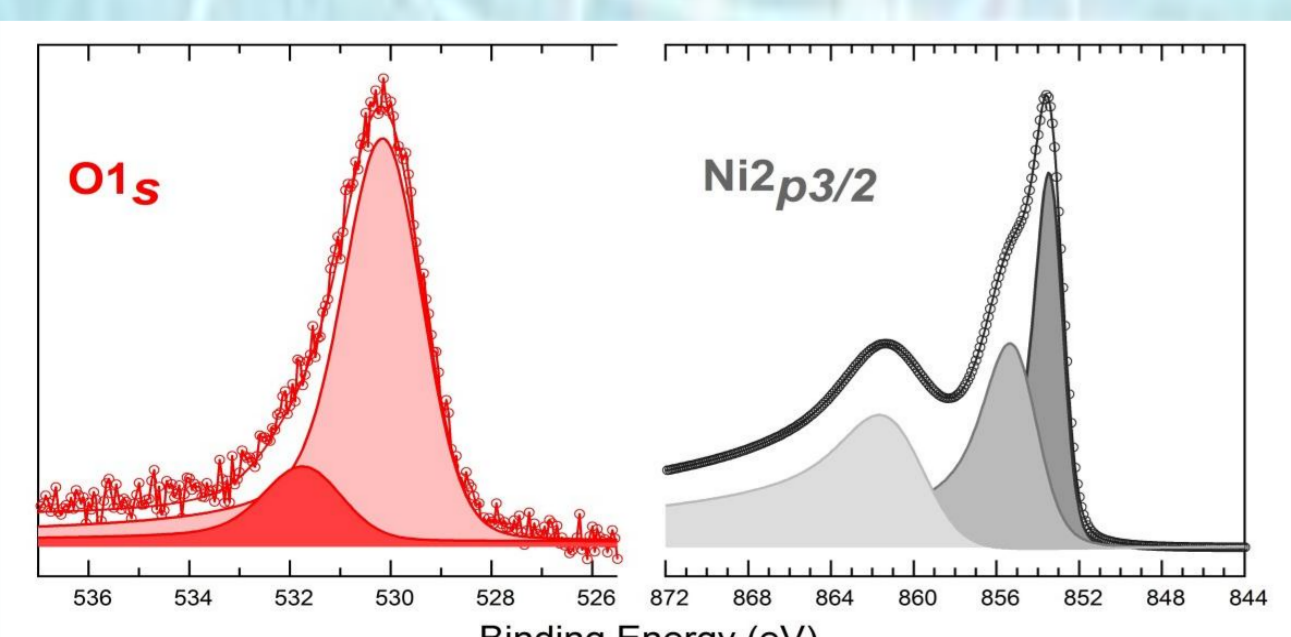


LEED image: the 3 Rotational domains of the rectangular $c(4 \times 2)$ unit cell are shown

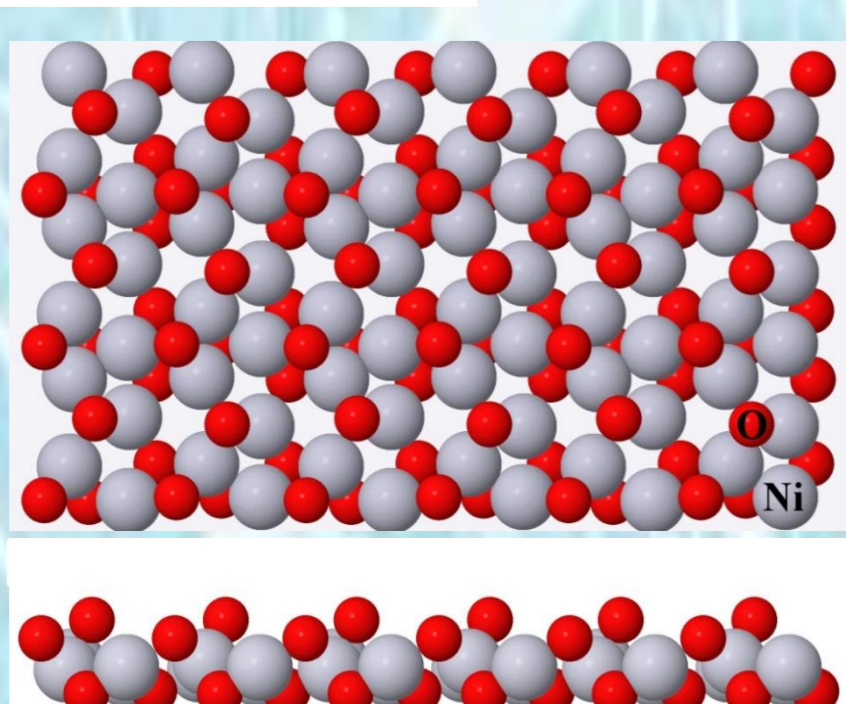


STM image
 $U = 300\text{mV}$,
 $I = 0.1\text{nA}$ [3]

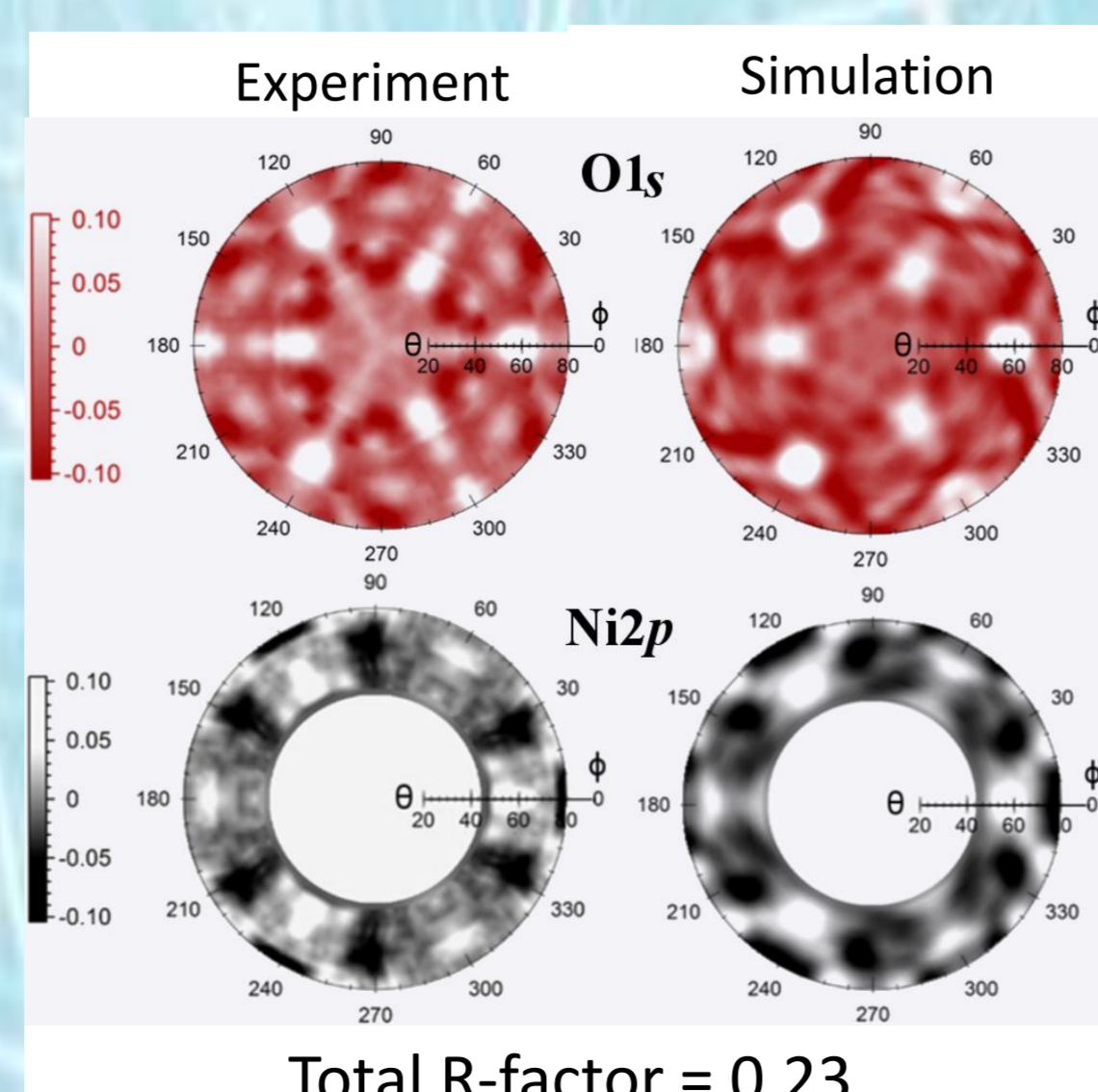
A quasi-2D nickel oxide is observed during oxidation of epitaxial Ni films. It presents strong local atomic rippling and lateral reconstruction. Conventional monochromatic X-ray source ($h\nu = 1486.6\text{ eV}$) is employed. In this way, forward scattering characterizes the main diffraction features.



The core level shifts for both O1s and Ni2p3/2 spectra.



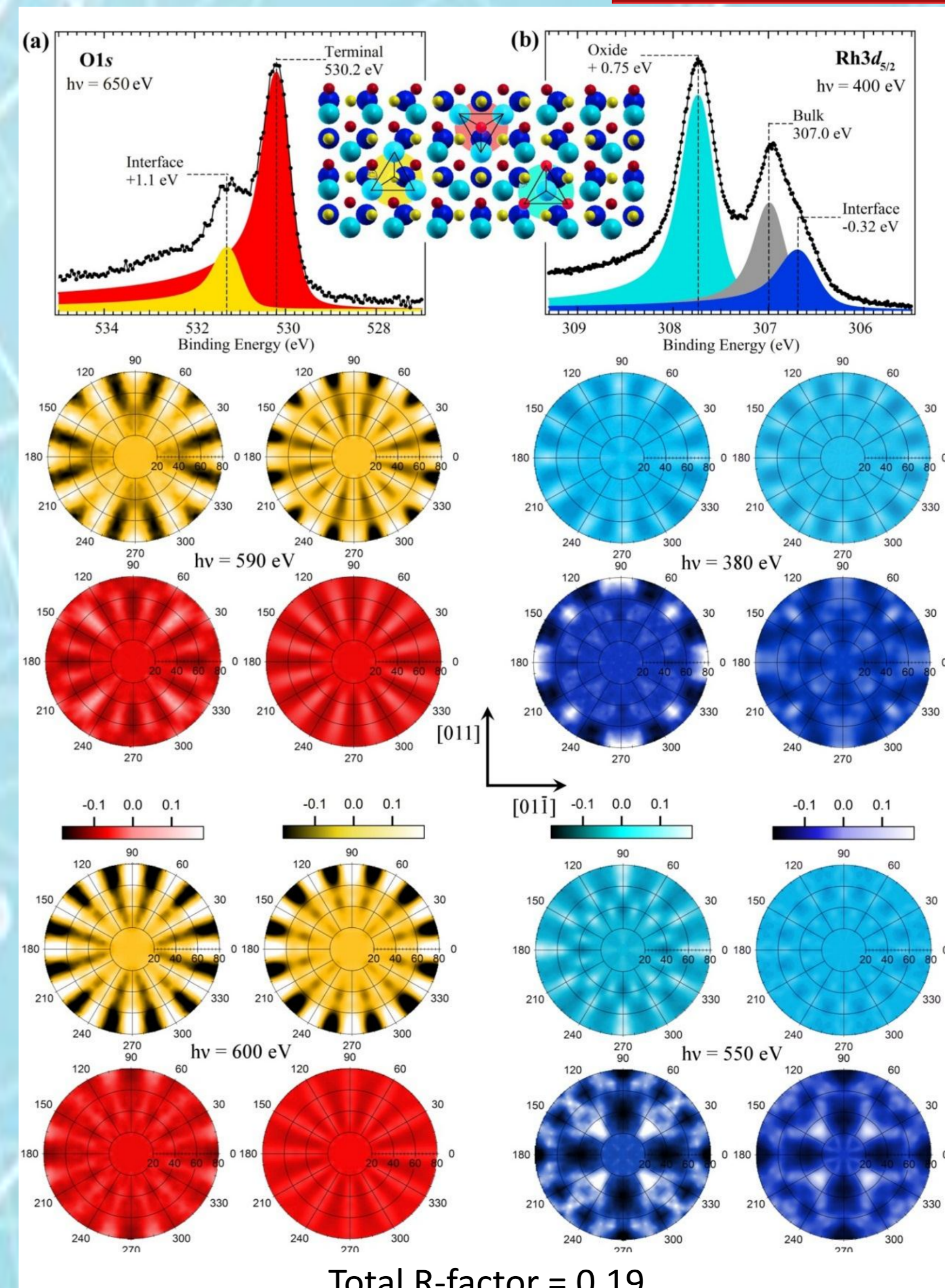
Top and site view of the best agreement structure.



Comparison between the experimental and best theoretical modulation patterns.

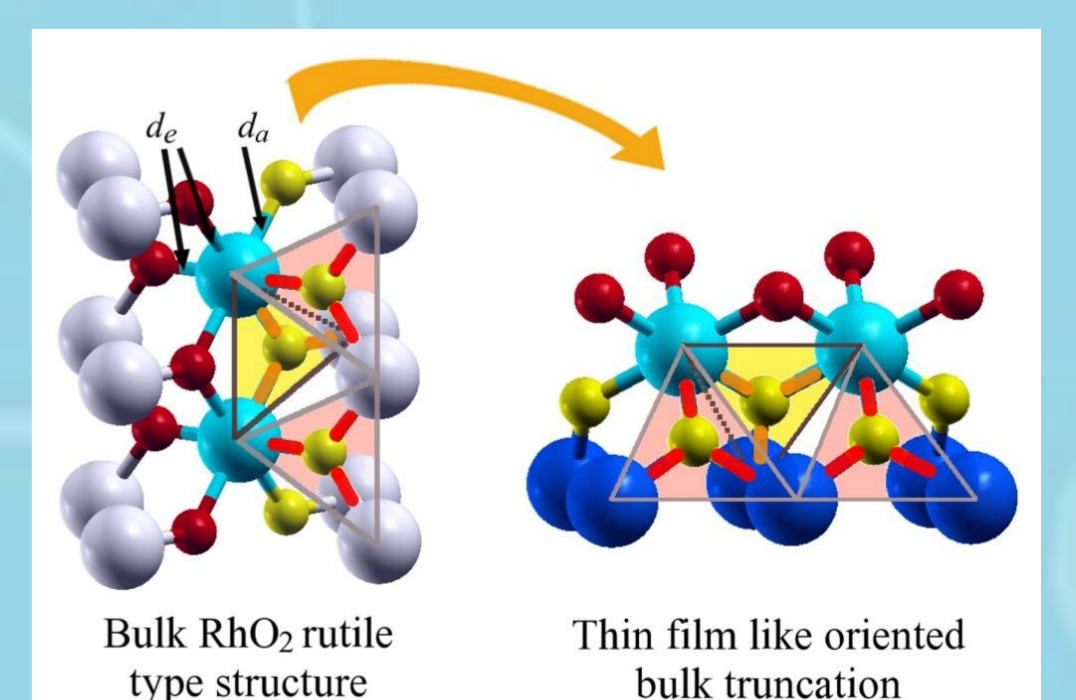
Ultra-thin oxide films

RhO₂ / Rh(100)



Total R-factor = 0.19

Formation of RhO₂ film can modify the reactivity of the Rh surface during CO oxidation. By means of XPD approach the theoretical O-Rh-O tri-layer model is confirmed [4]. Synchrotron radiation is used as excitation source, thus allowing us to work in electron backscattering regime.



As shown in the picture above, the oxide-to-substrate interface matching is forced to resemble the bulk oxide coordination.