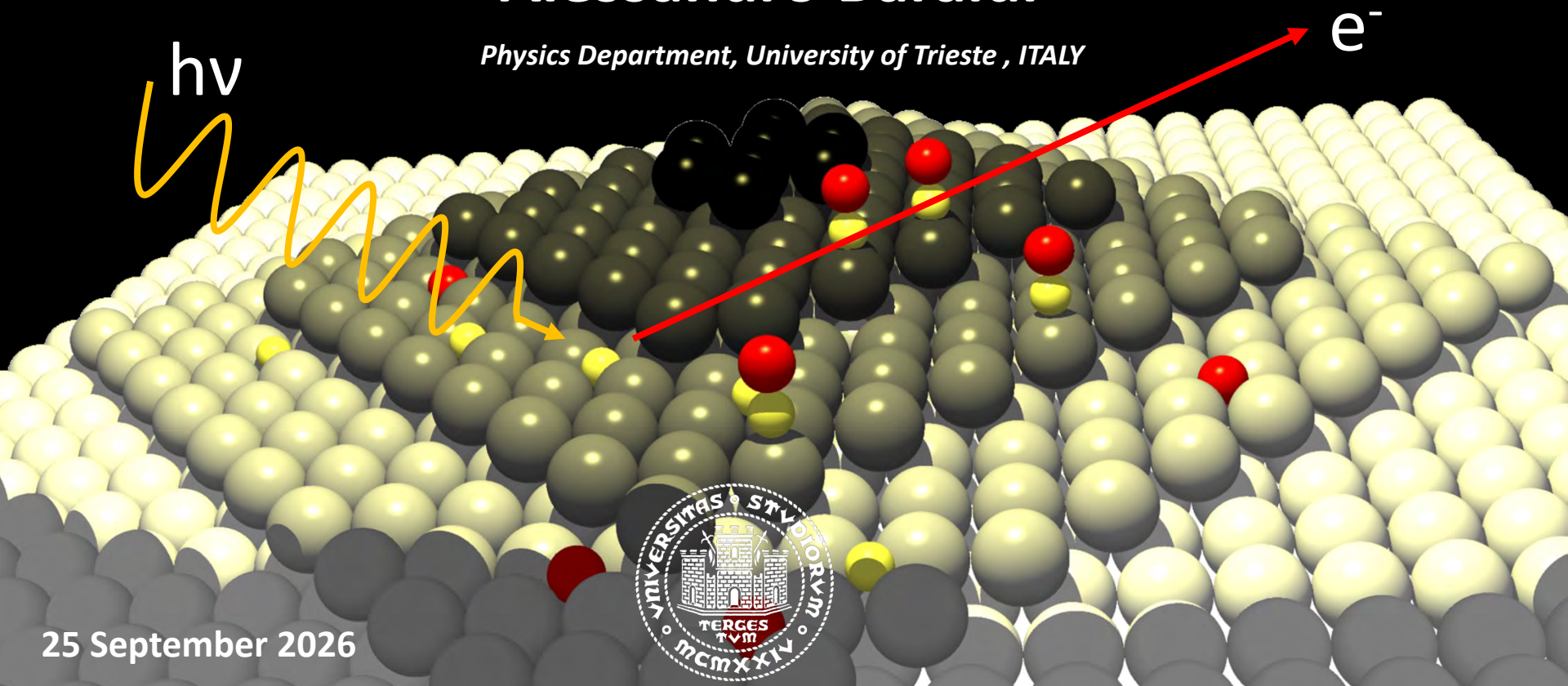




High-resolution x-ray photoelectron spectroscopy

Alessandro Baraldi

Physics Department, University of Trieste, ITALY

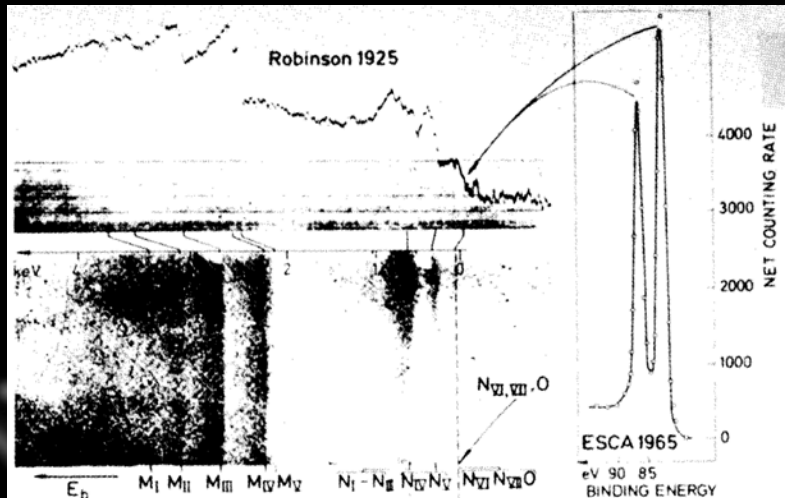


More than 120 years after Albert Einstein

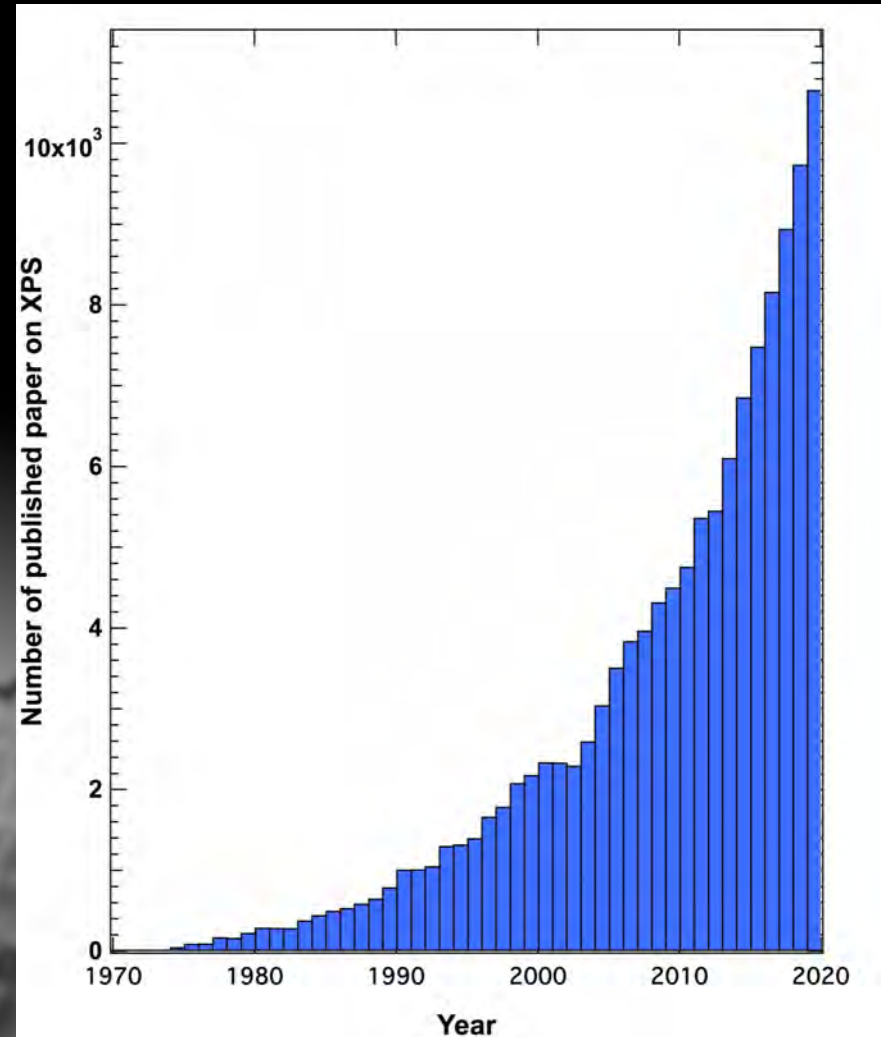


«1905, Annus mirabilis»

The interpretation of the photoelectric effect

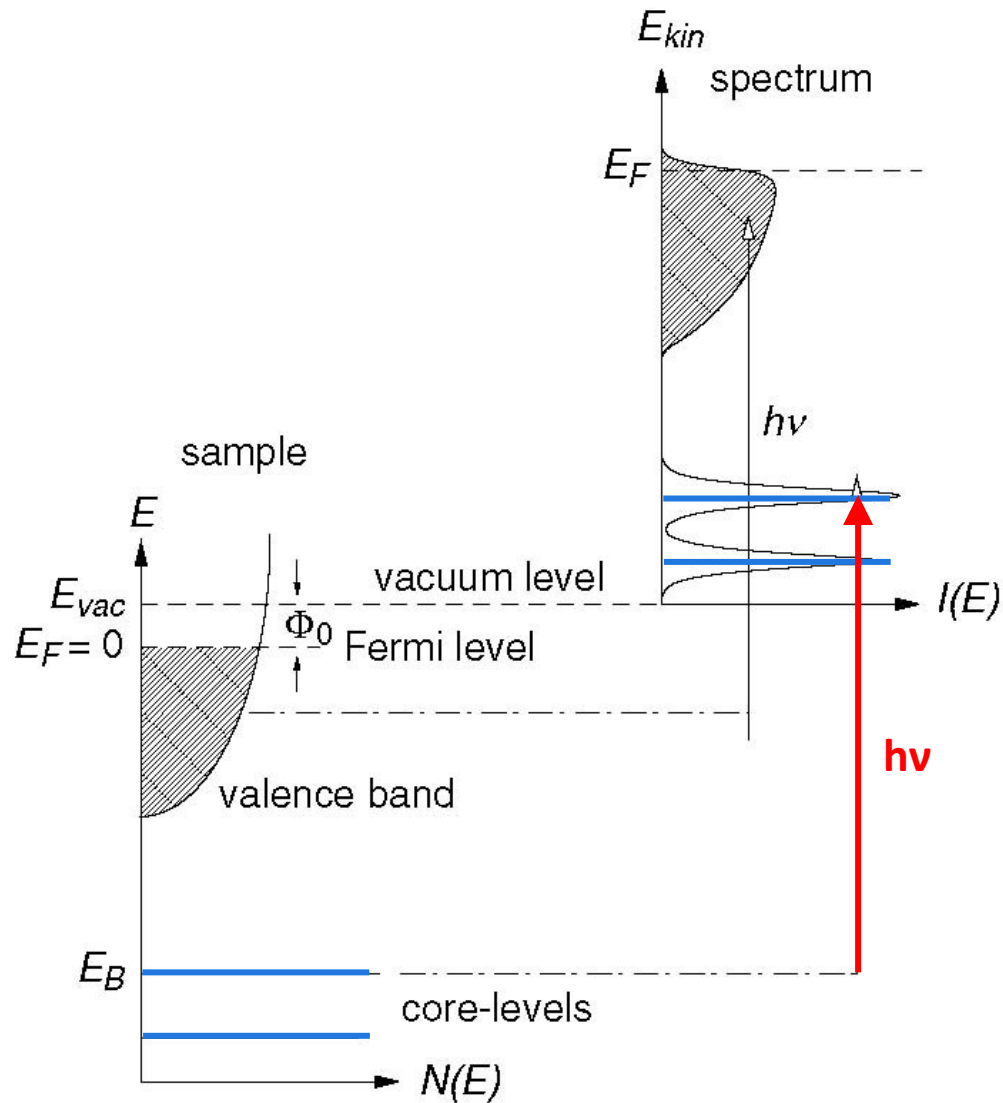


Comparison between Robinson (1925) and Siegbahn (1965)



Number of papers published in the period 1970-2020 in peer-review International Scientific Journals on XPS (Scopus).

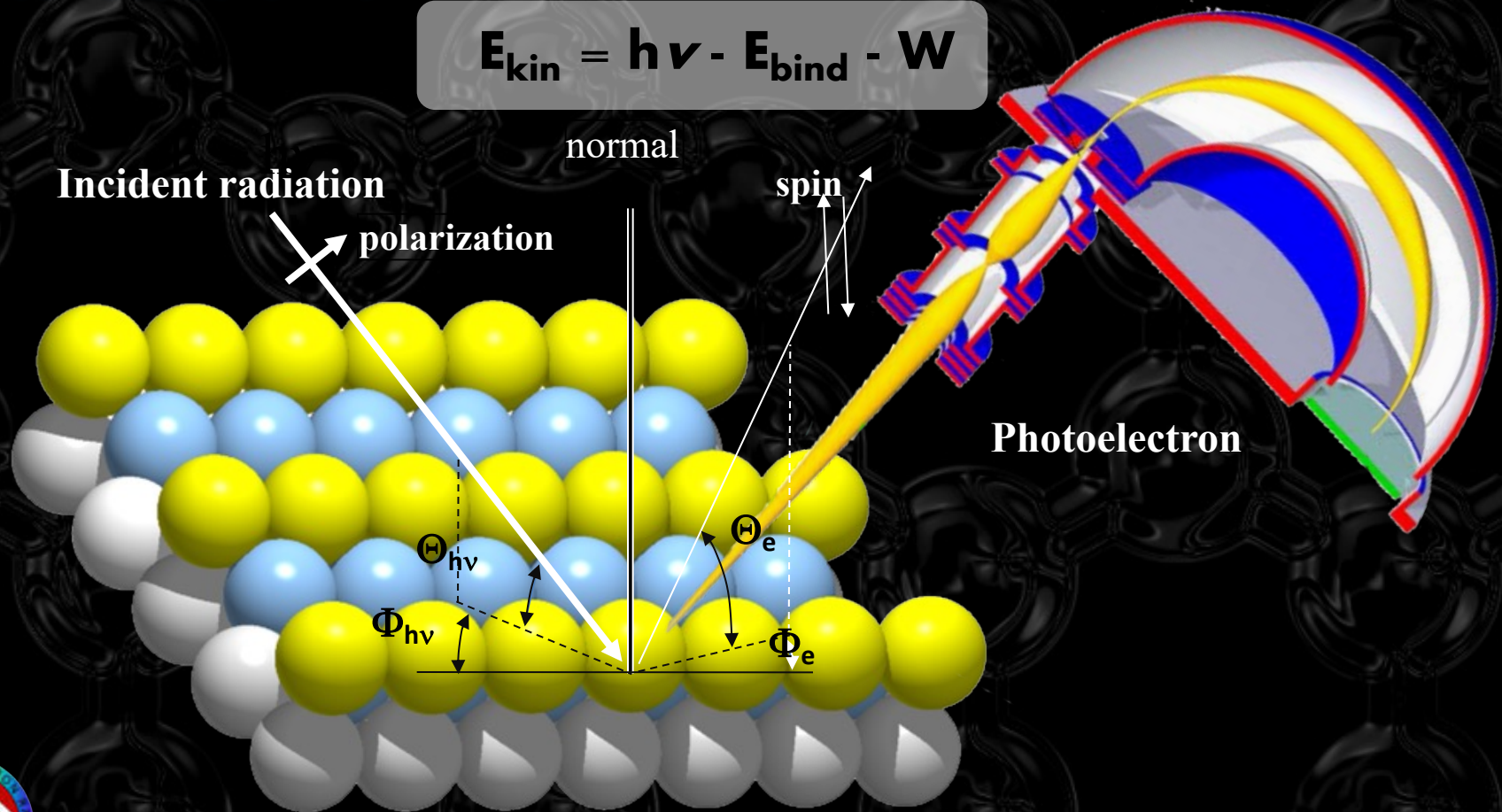
Photoelectron spectroscopy from a solid



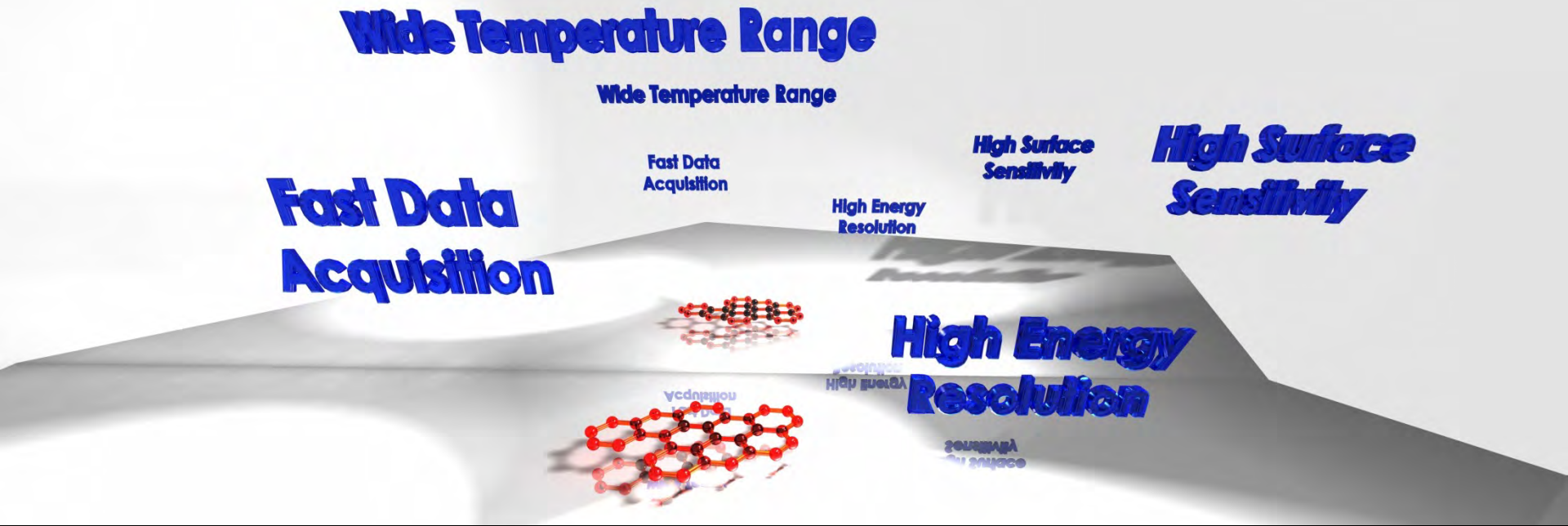
Photoelectron spectroscopy from a solid

- element specific and quantitative
- sensitive to chemical and structural environments
- surface sensitive

$$E_{\text{kin}} = h\nu - E_{\text{bind}} - W$$



The main advantages of core level spectroscopy with synchrotron radiation



- Down to the 100 ms time-scale
 - ΔE in the range 40-100 meV
 - Coverage < 0.1% of ML
 - Temperature 20÷1300 K

Lorentzian distribution

arising from the finite core-hole lifetime.

A convolution of a Doniach-Šunjić function and a **Gaussian**, which account for the vibration/phonon and the contribution of the instrumental resolution.

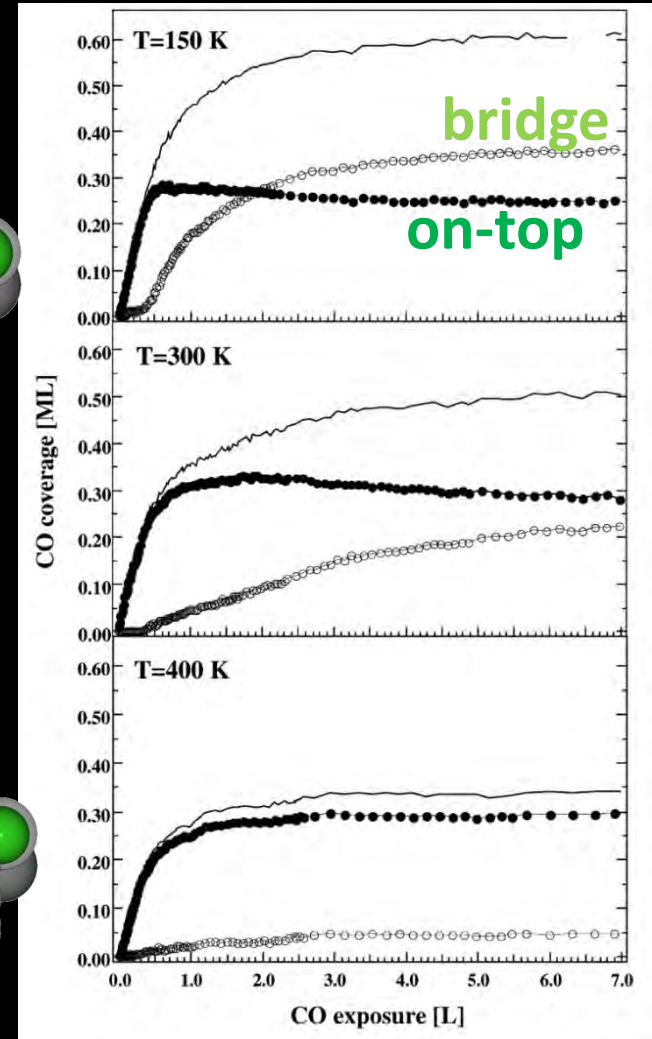
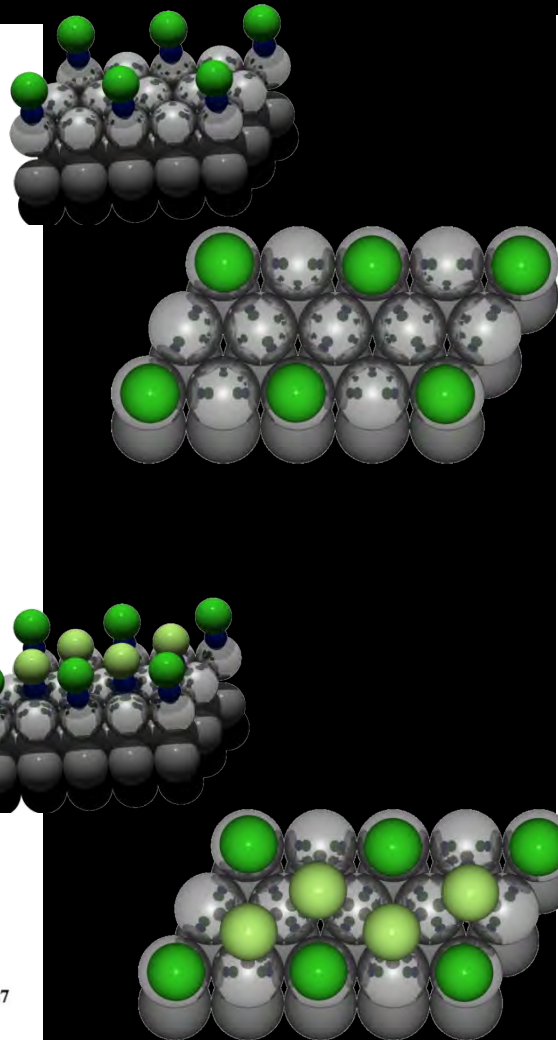
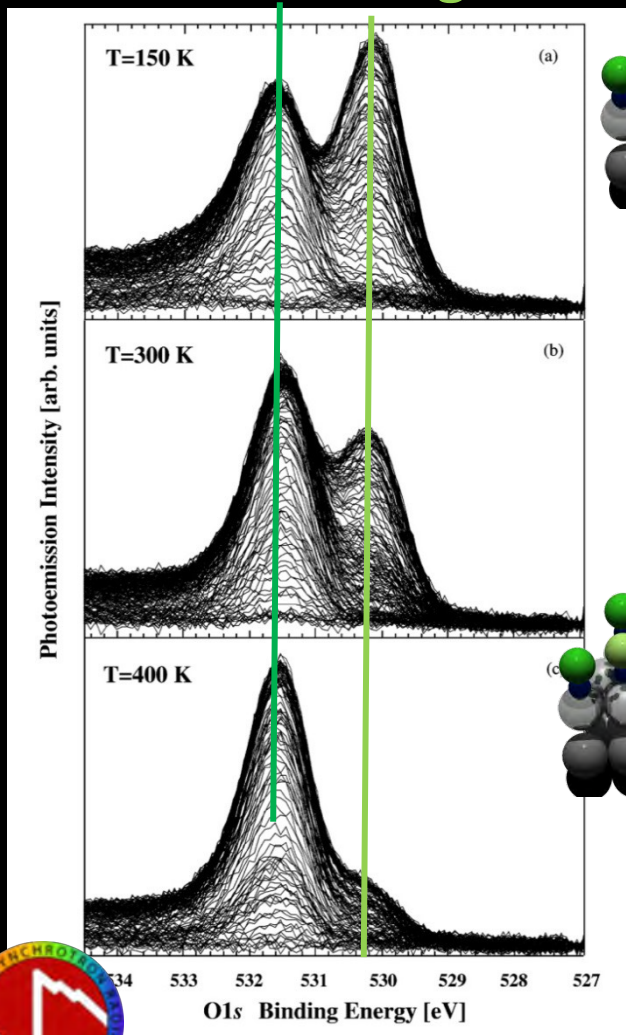
Asymmetry parameter, describing the contribution of electron-hole pairs excitation.

MOVIE

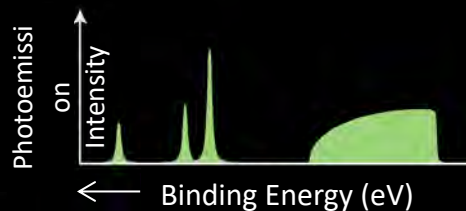
Adsorbates on solid surfaces

Carbon Monoxide adsorption on Rh(111)

on-top bridge

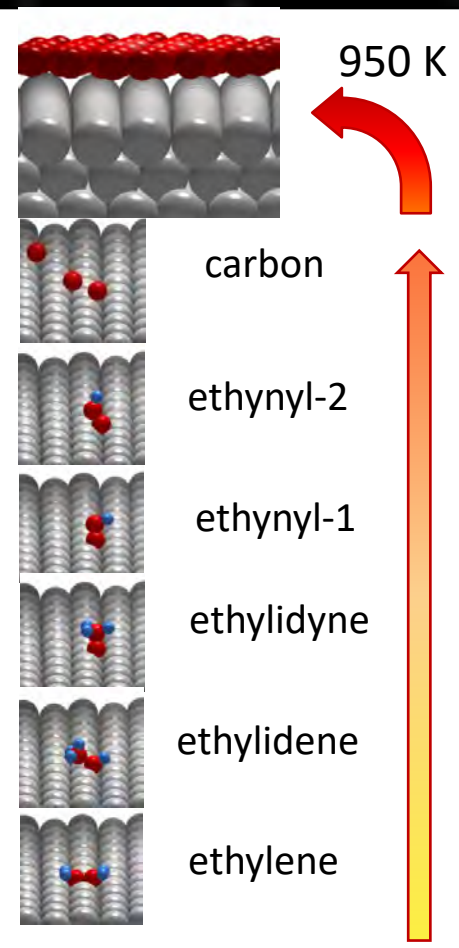
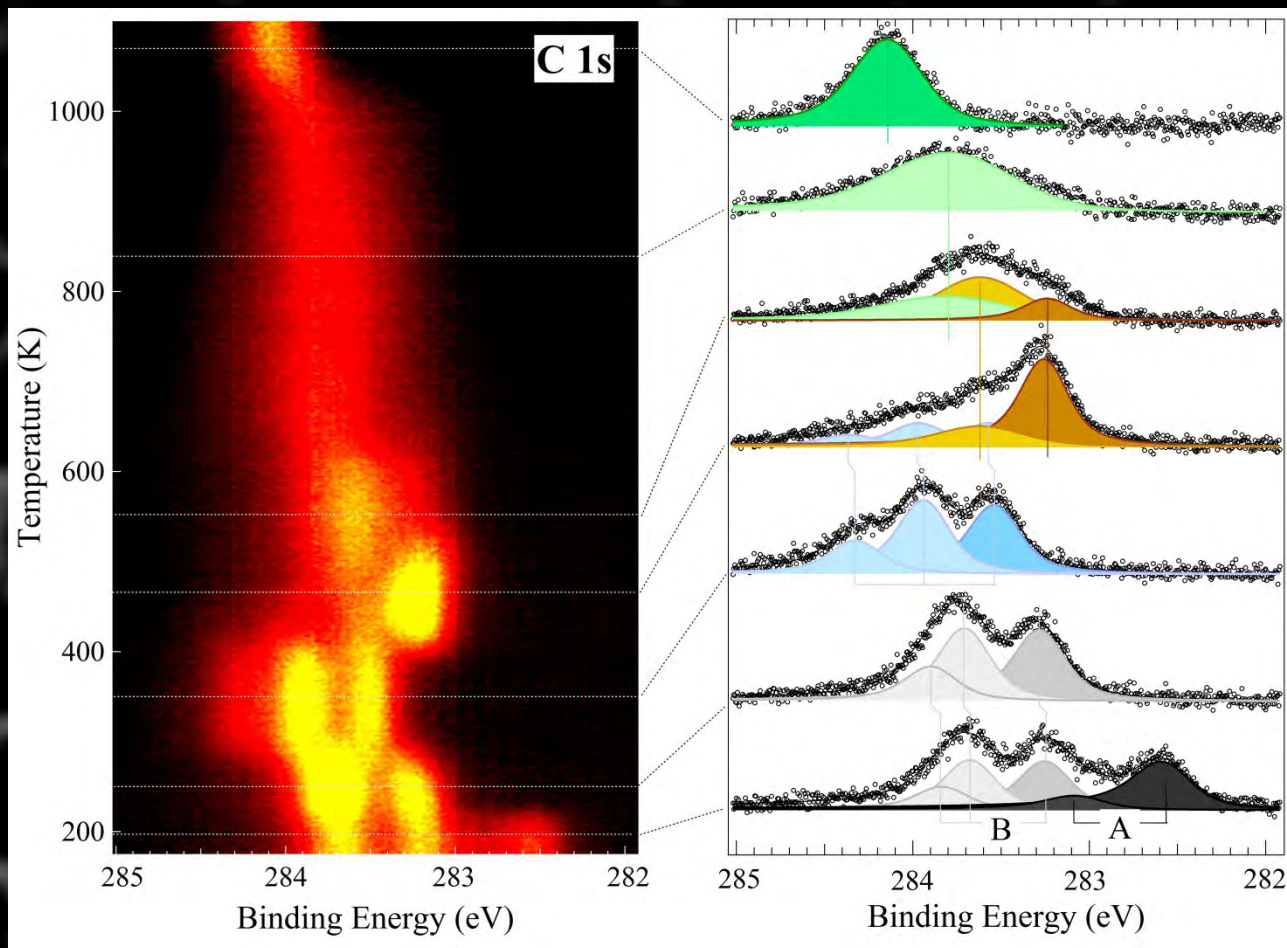


From simple molecules to graphene



$\Delta E = 50 \text{ meV}$
 $\Delta t = 100 \div 500 \text{ ms}$

From ethylene to
graphene formation

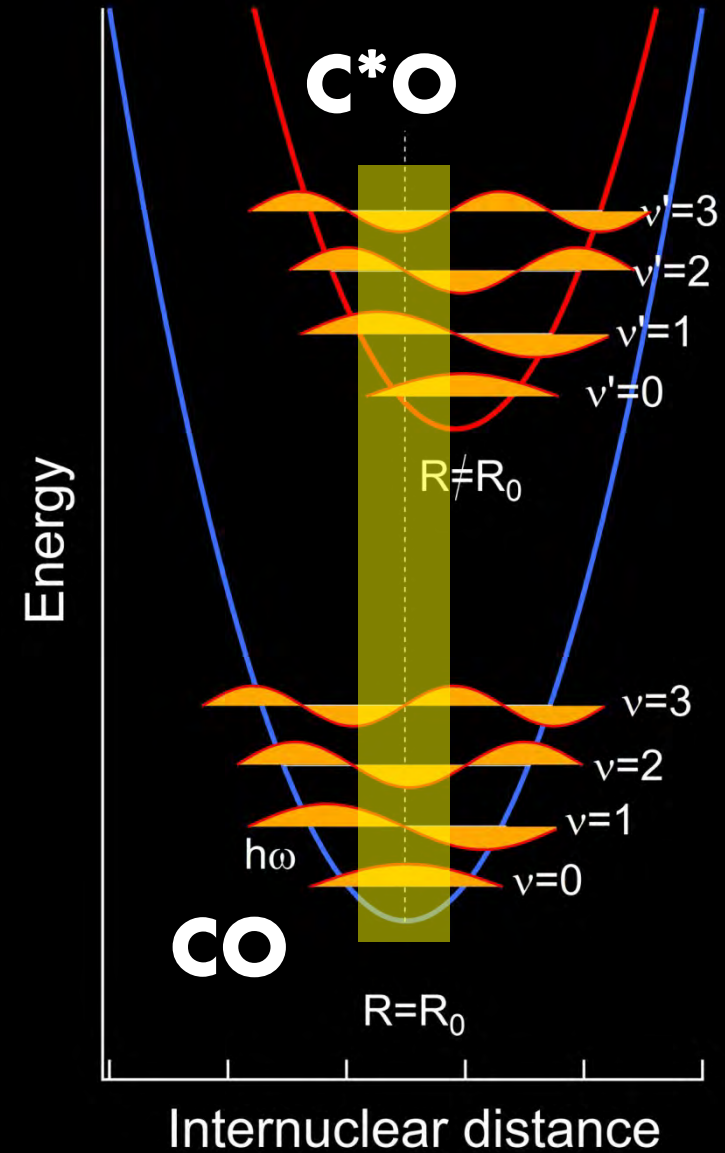
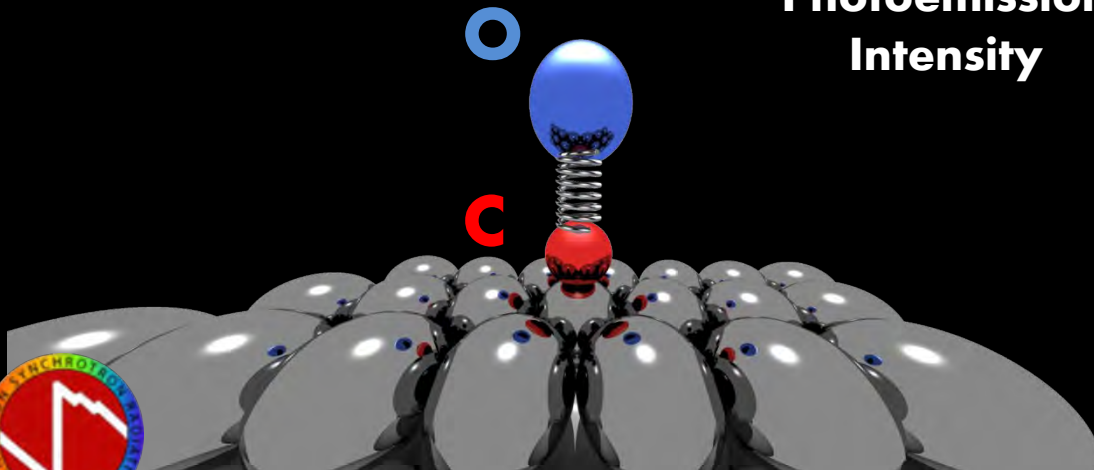


Harmonic approximation

$$V = \frac{1}{2} k(R - R_e)^2$$

**Probing the vibration of
C*O excited molecules**

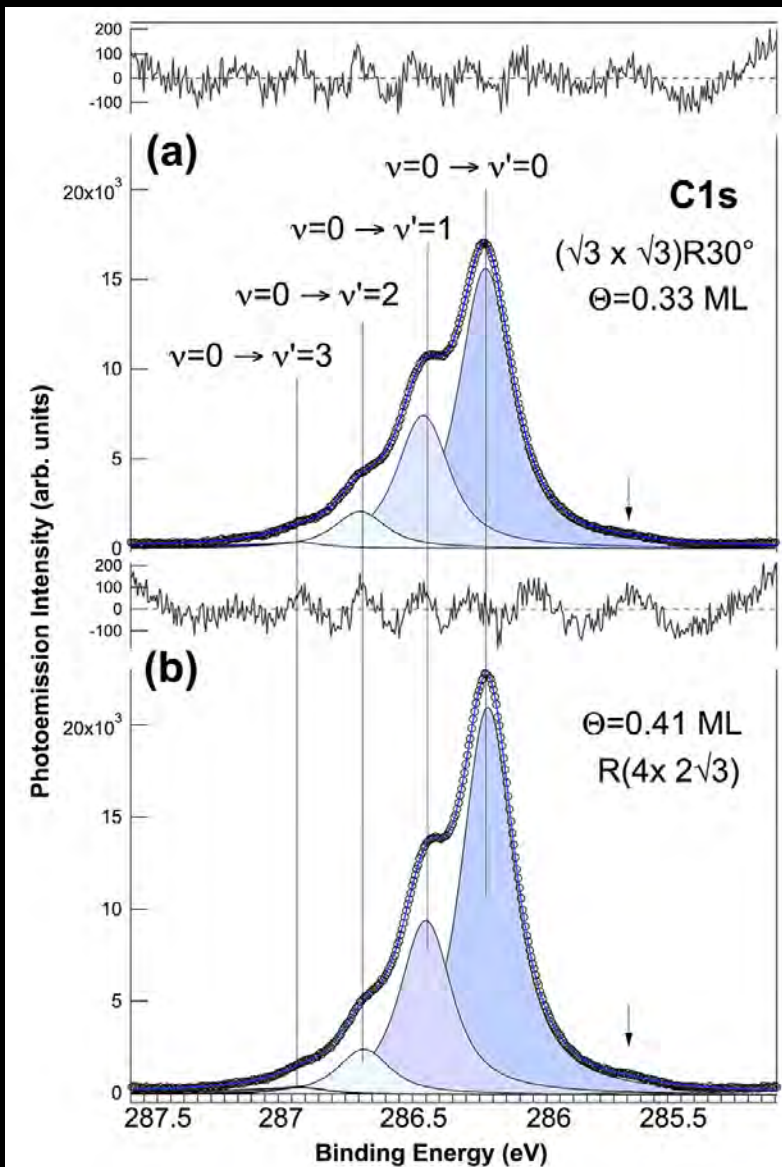
**Photoemission
Intensity**



CO on Ir(111)

$$\Delta E = 233.4 \pm 0.5 \text{ meV}$$

$$\Delta E = 231.4 \pm 0.4 \text{ meV}$$



to be compared with

301 ± 1

CO in gas phase

K.J. Randall *et al.*, *Phys. Rev. Lett.* **71**, 1156 (1993).

217.8 ± 1.2

on-top CO on Ni(100)

A. Föhlisch *et al.*, *Phys. Rev. Lett.* **81**, 1730 (1998).

CO on Ir(111)

256 meV - low coverage

258 meV - high coverage

J. Lauterbach *et al.*,
Surf. Sci. **350**, 32 (1996)

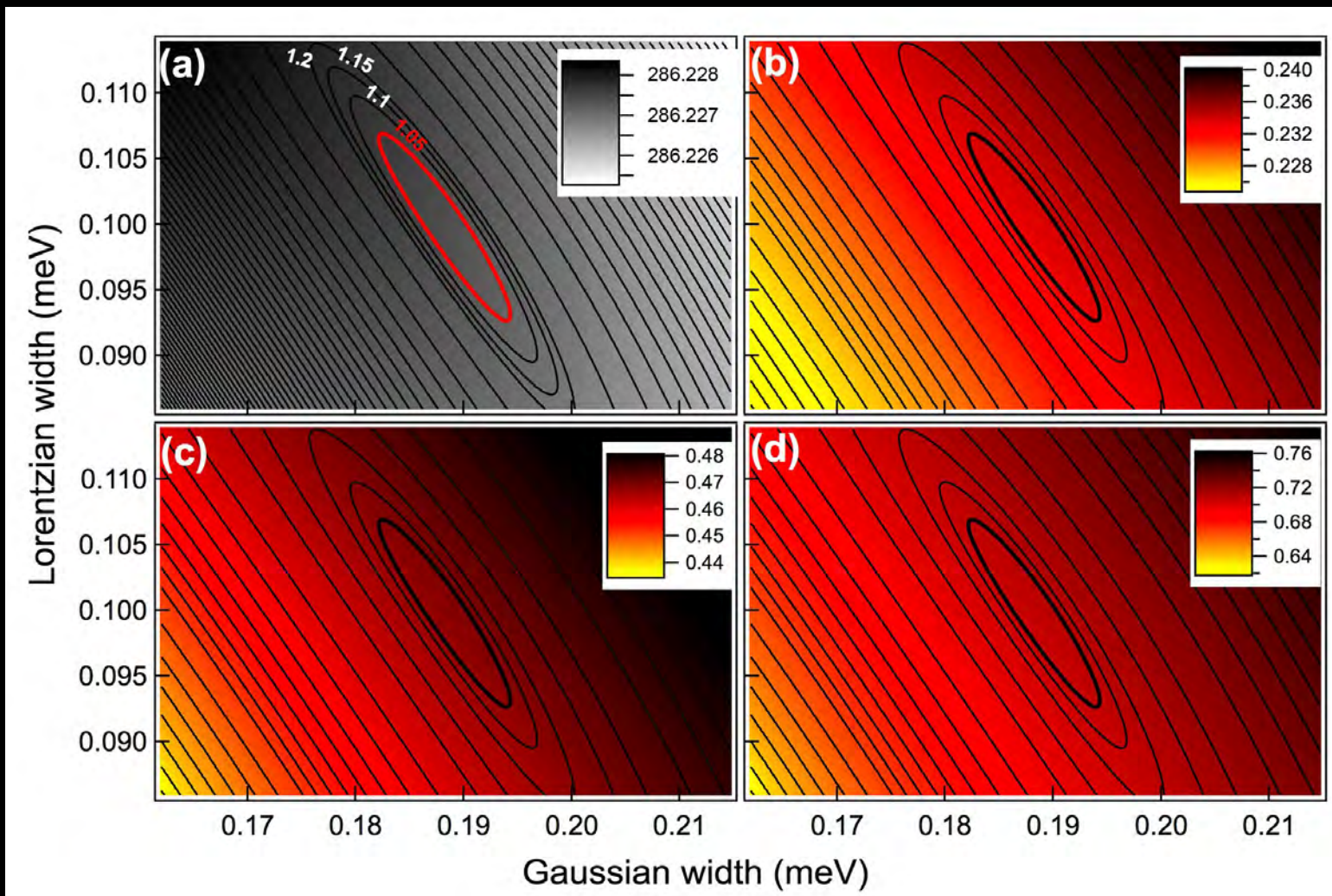
NO on Ir(111)

223 meV - low coverage

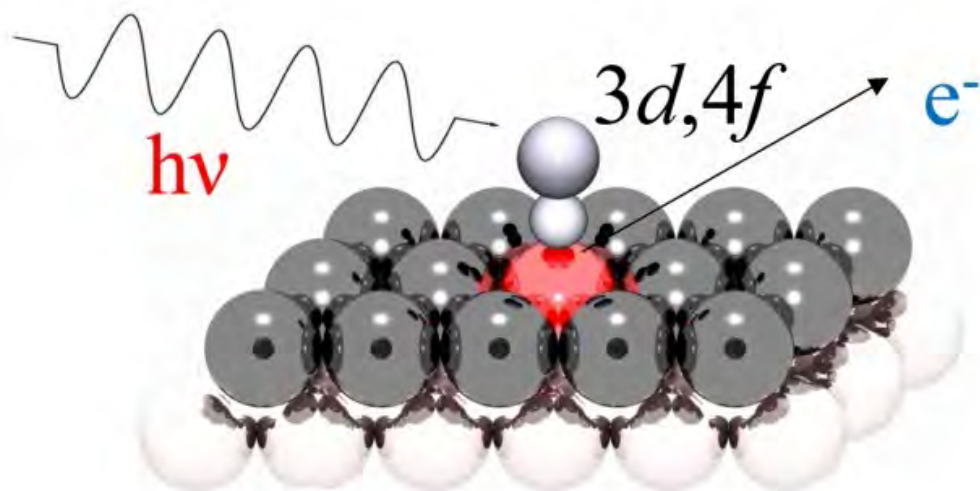
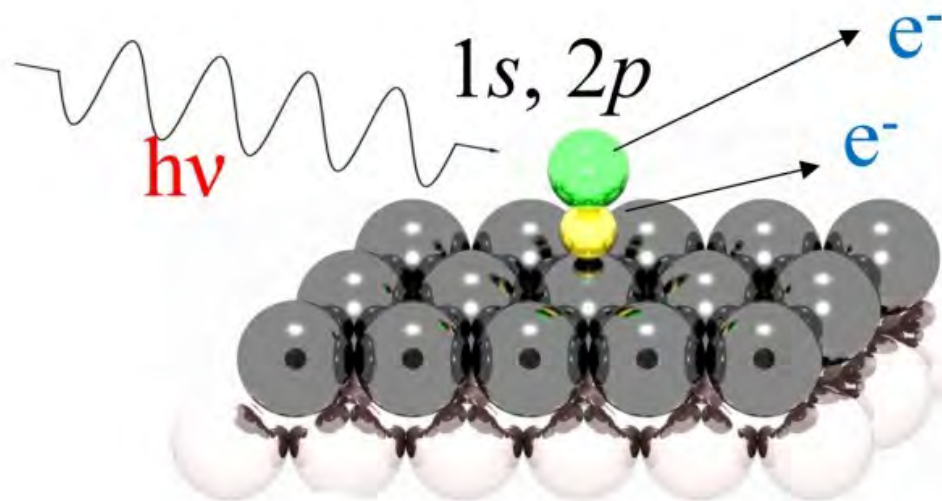
225 meV - high coverage

M. Matsumoto *et al.*,
Surf. Sci. **606**, 1489 (2012).

the data analysis

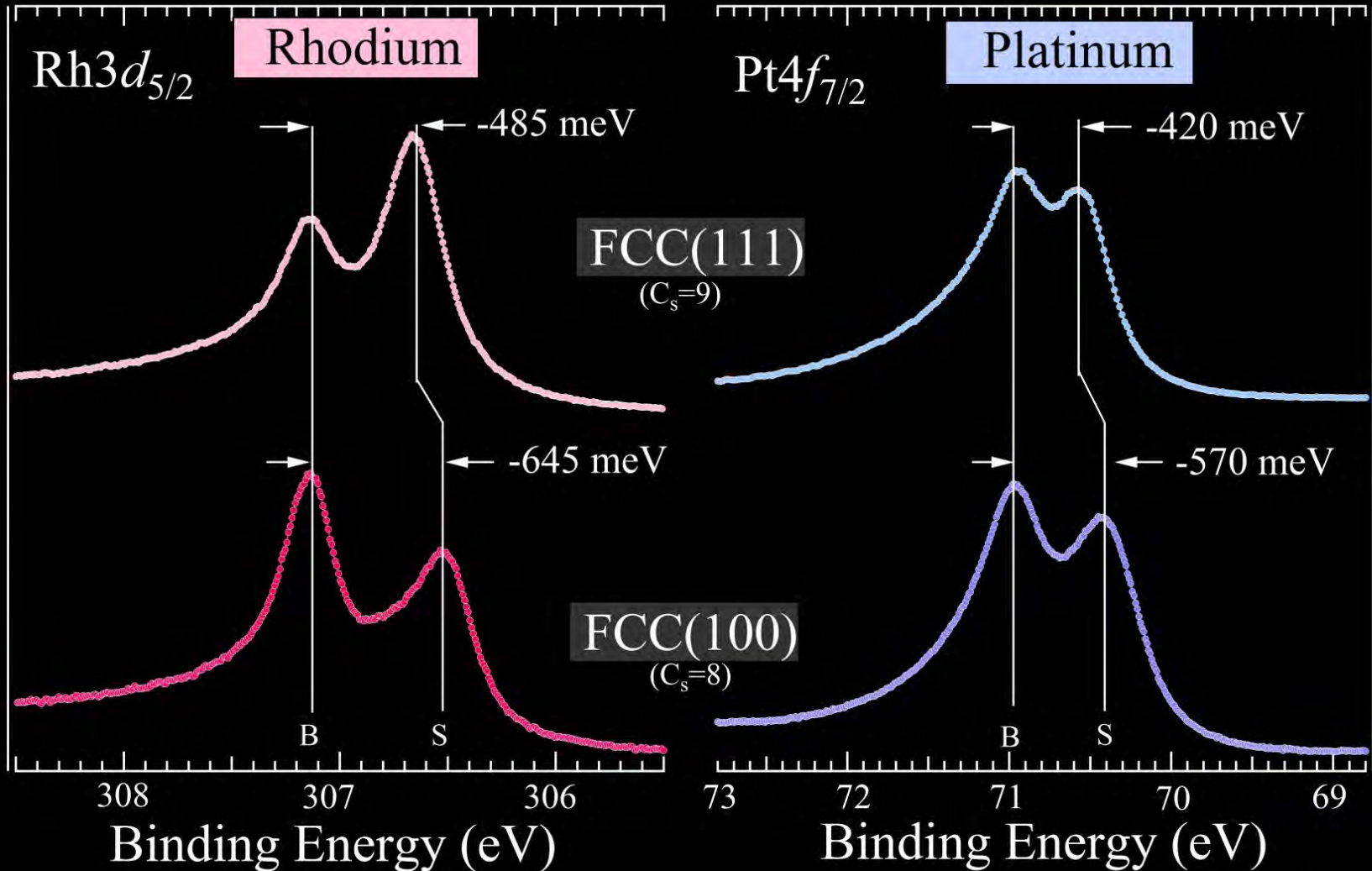


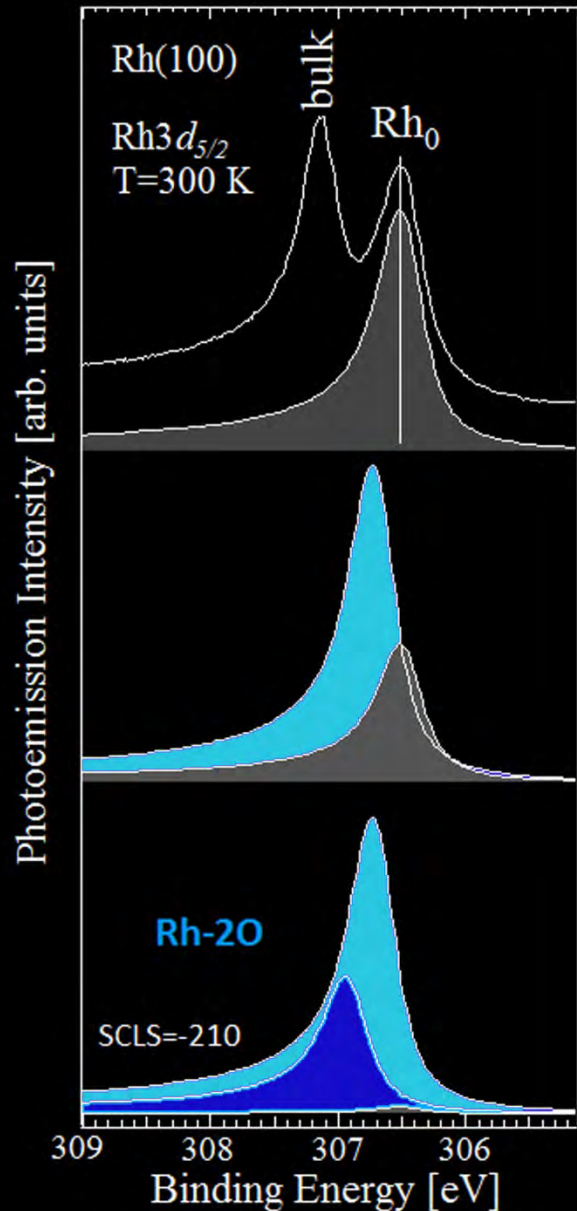
Different perspectives



The core levels from substrate atoms

Photoemission Intensity



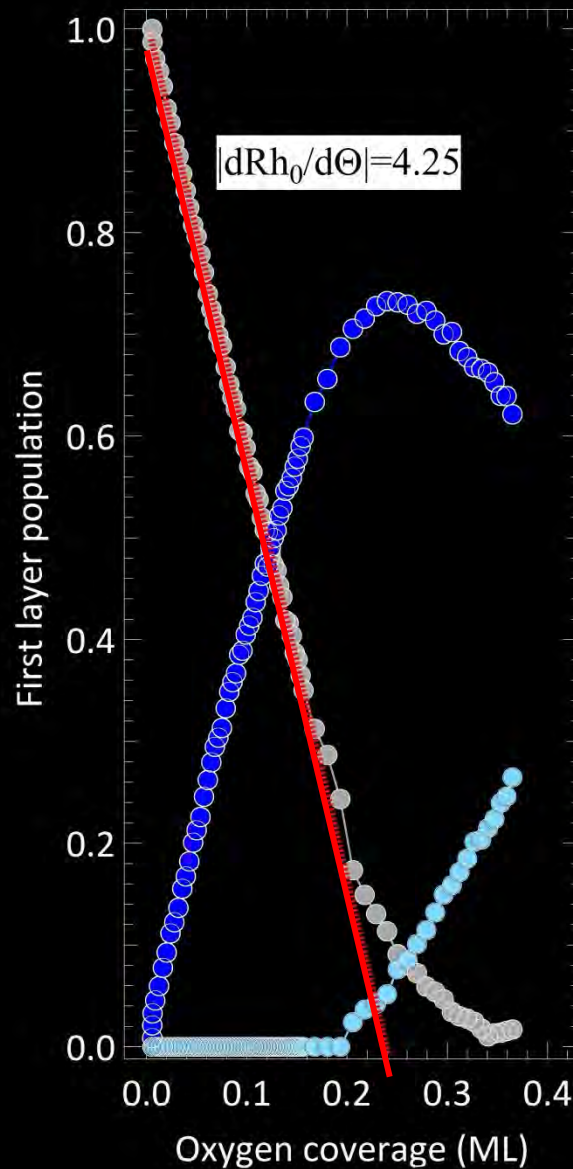
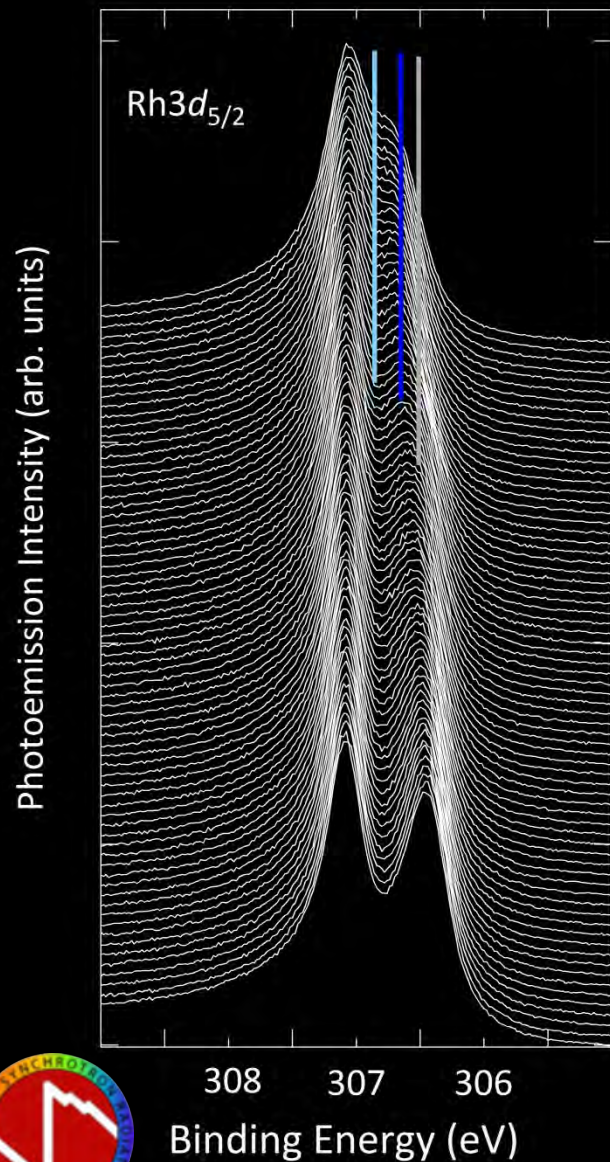


MOVIE

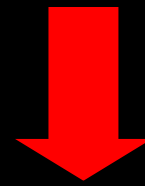
MOVIE

Rh-10

Rh-20



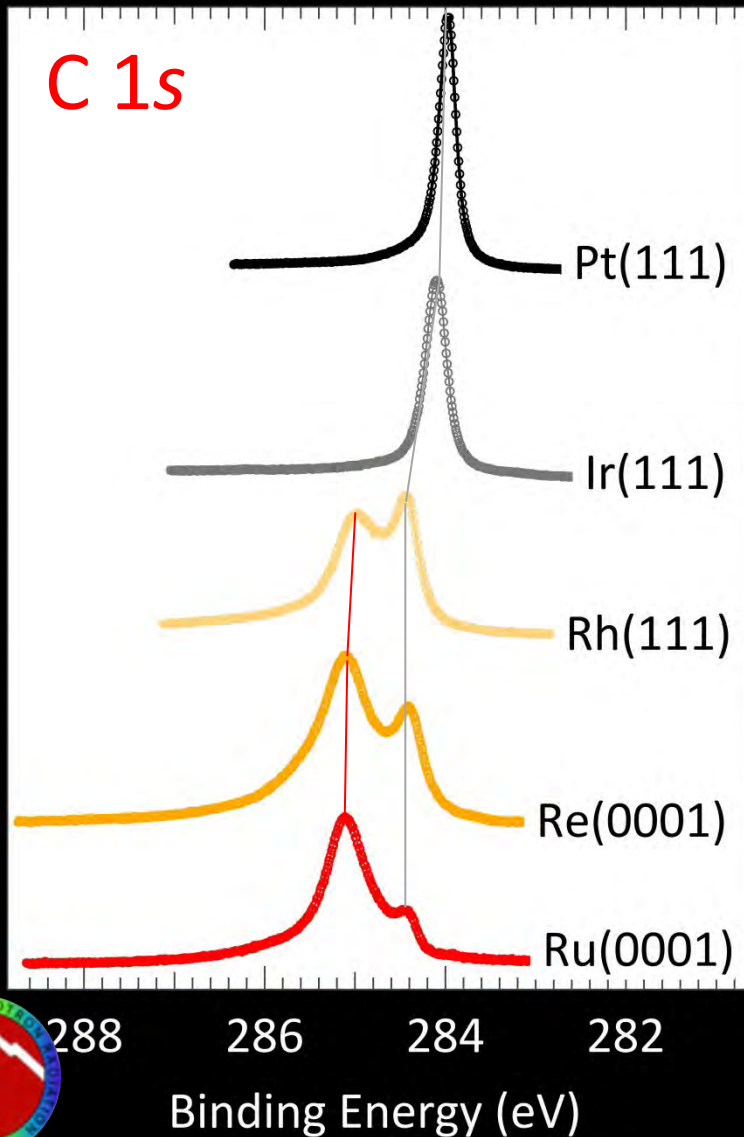
$$\frac{dRh_0}{d\Theta} = -4$$



four-fold hollow
adsorption site

C1s core level shifts of epitaxial graphene

Photoemission Intensity



weak interaction

Strong chemical bond

A correlation between
graphene-substrate bond strength
and
graphene corrugation

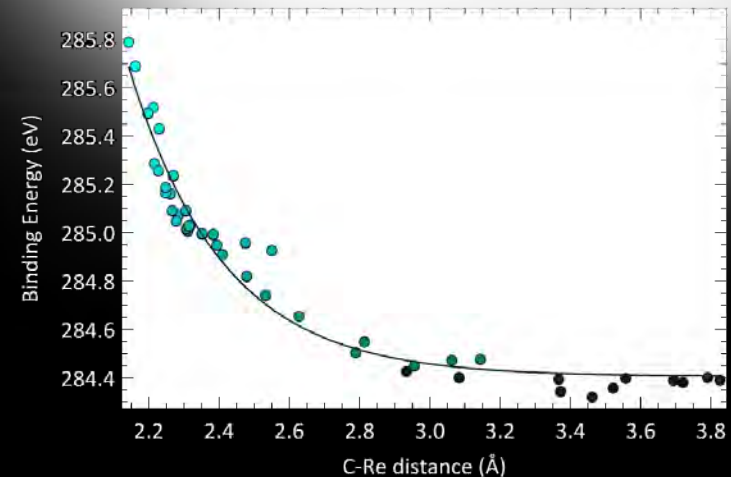
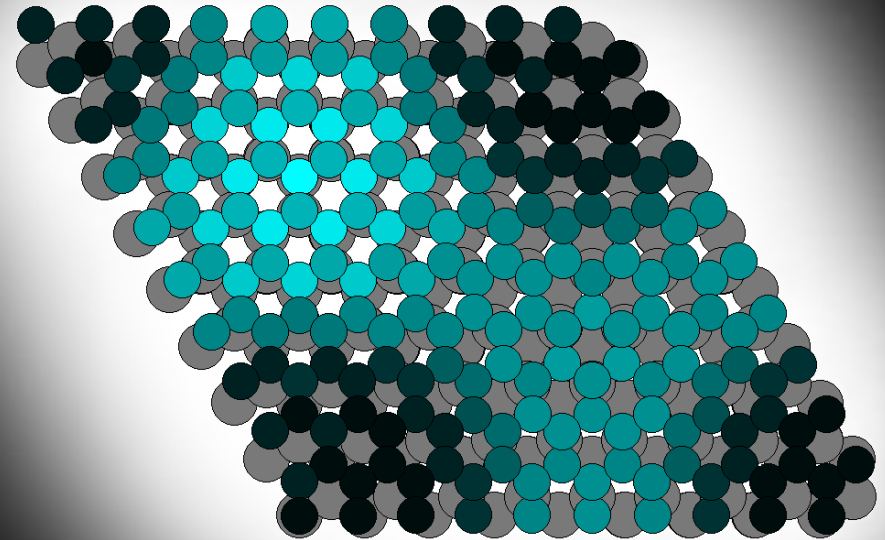
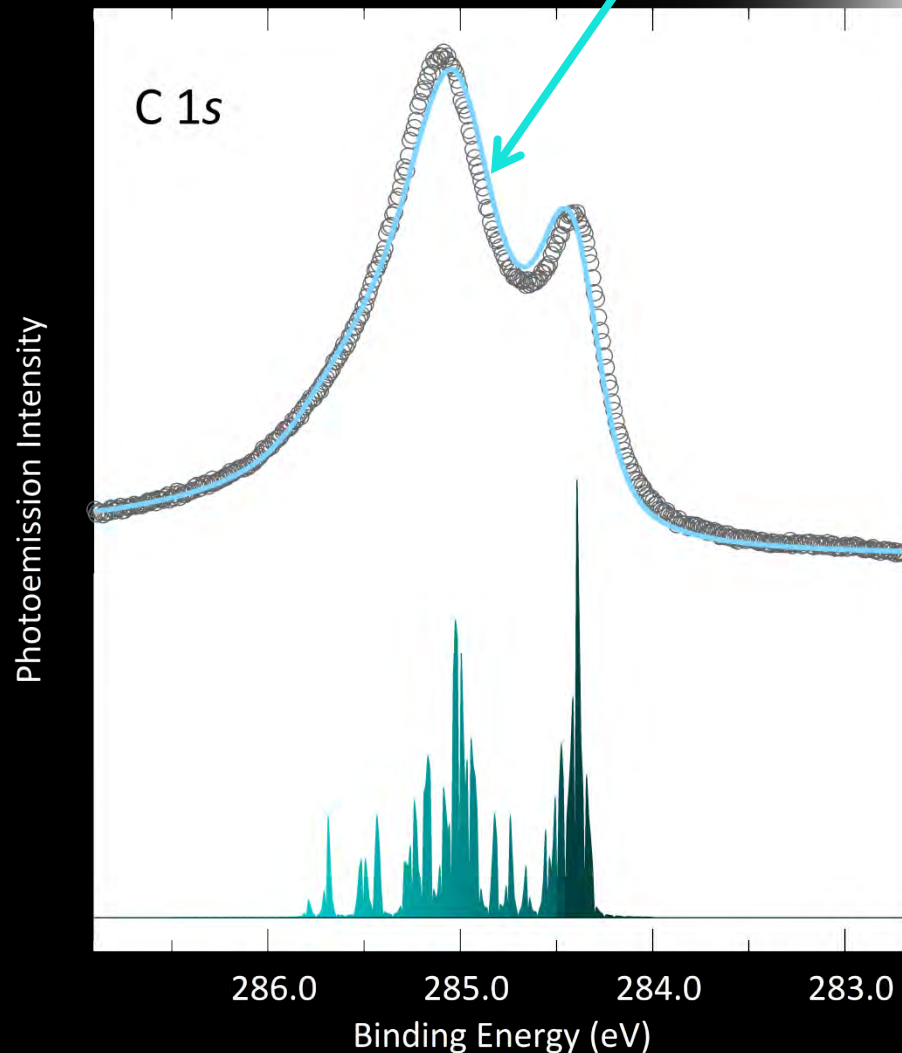
0.2 Å

1.5 Å

Why just two components?

Corrugation vs C1s binding energies

Simulated spectrum Gr/Re(0001)





A narrow window for graphene growth on Re(0001)



Formation of a high-quality single-layer of graphene is strongly opposed by two competing processes, namely **surface carbide formation** and **carbon bulk dissolution**.

Time-lapsed
spectral sequence
of C_{1s} spectra
taken during
ethylene exposure
and surface
annealing to high
temperature.

MOVIE





Growth mechanism on transition metals

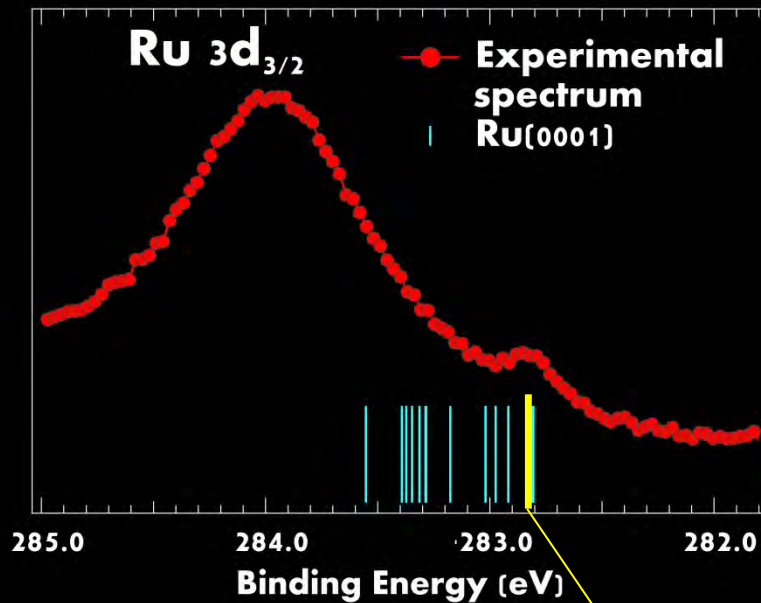
Fast-data acquisition allows to monitor the C_{1s} spectral evolution while dosing ethylene at high temperature.

Gr/Ru(0001) using C₂H₄

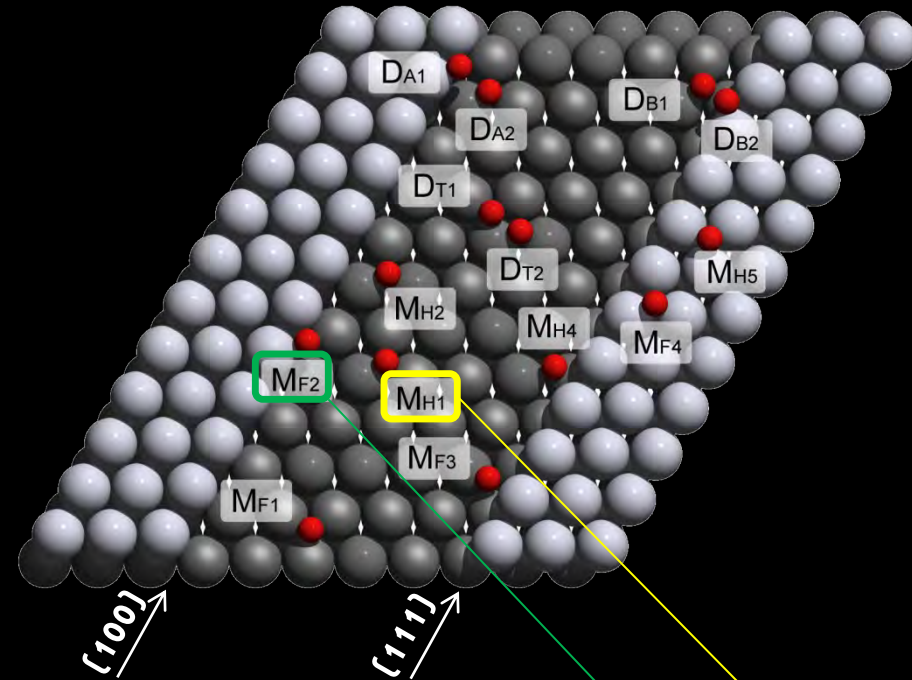
MOVIE



The carbon lattice-gas: precursor to graphene formation



	E _b (eV)	C 1s(eV)		E _b (eV)	C 1s(eV)
M _{H2}	7.53	283.02	M _{H1}	7.67	282.82
M _{F2}	7.78	283.55	D _{A1}	15.78	283.14
M _{H4}	7.31	282.97	D _{A2}		283.35
M _{F3}	7.45	283.37	D _{T1}	14.73	283.28
M _{H5}	7.38	282.89	D _{T2}		283.39
M _{F4}	7.15	282.92	D _{B1}	15.52	283.29
M _{F1}	6.98	282.89	D _{B2}		283.17

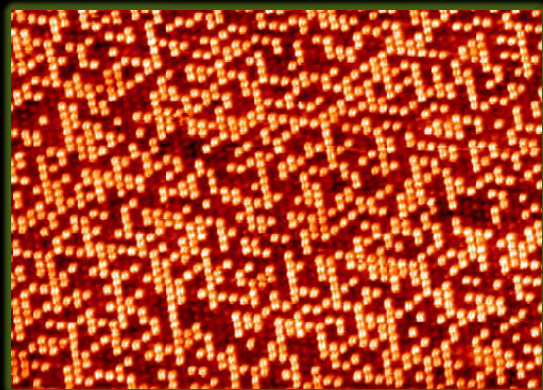
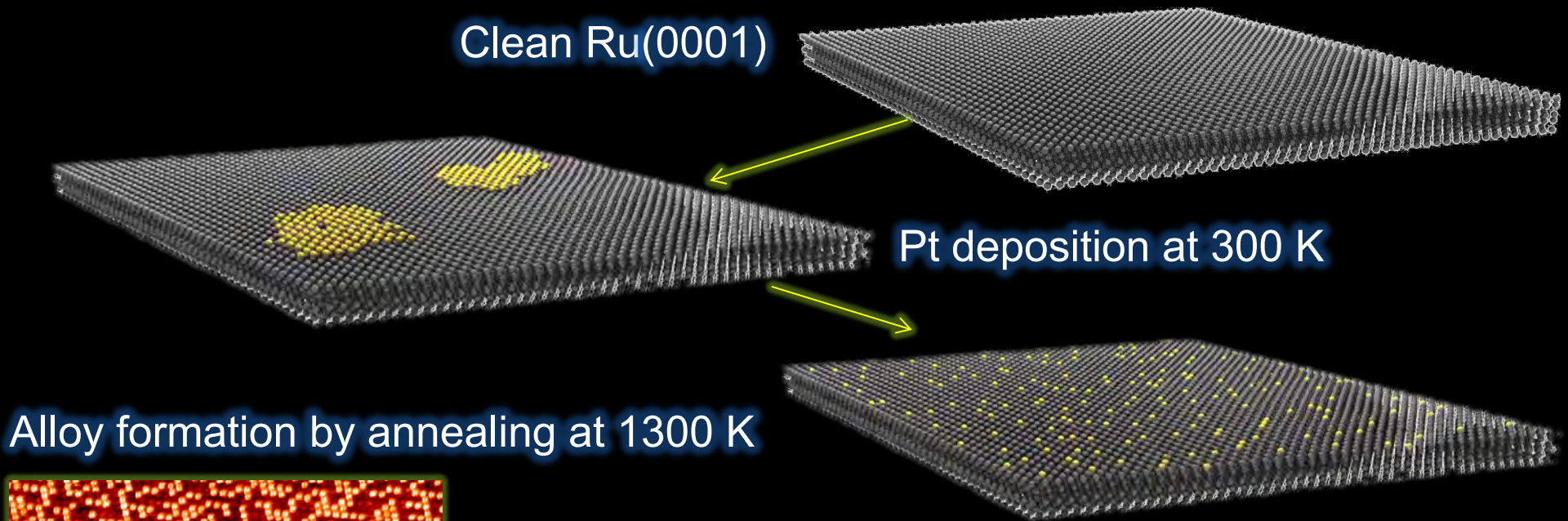


Three-fold hcp site on the terraces (**M_{H1}**) and the C monomer at the steps (**M_{F2}**) have very similar adsorption energies.

Monomers form a 2D lattice gas which supplies C atoms for GR growth

Fine-tuning of graphene-metal adhesion

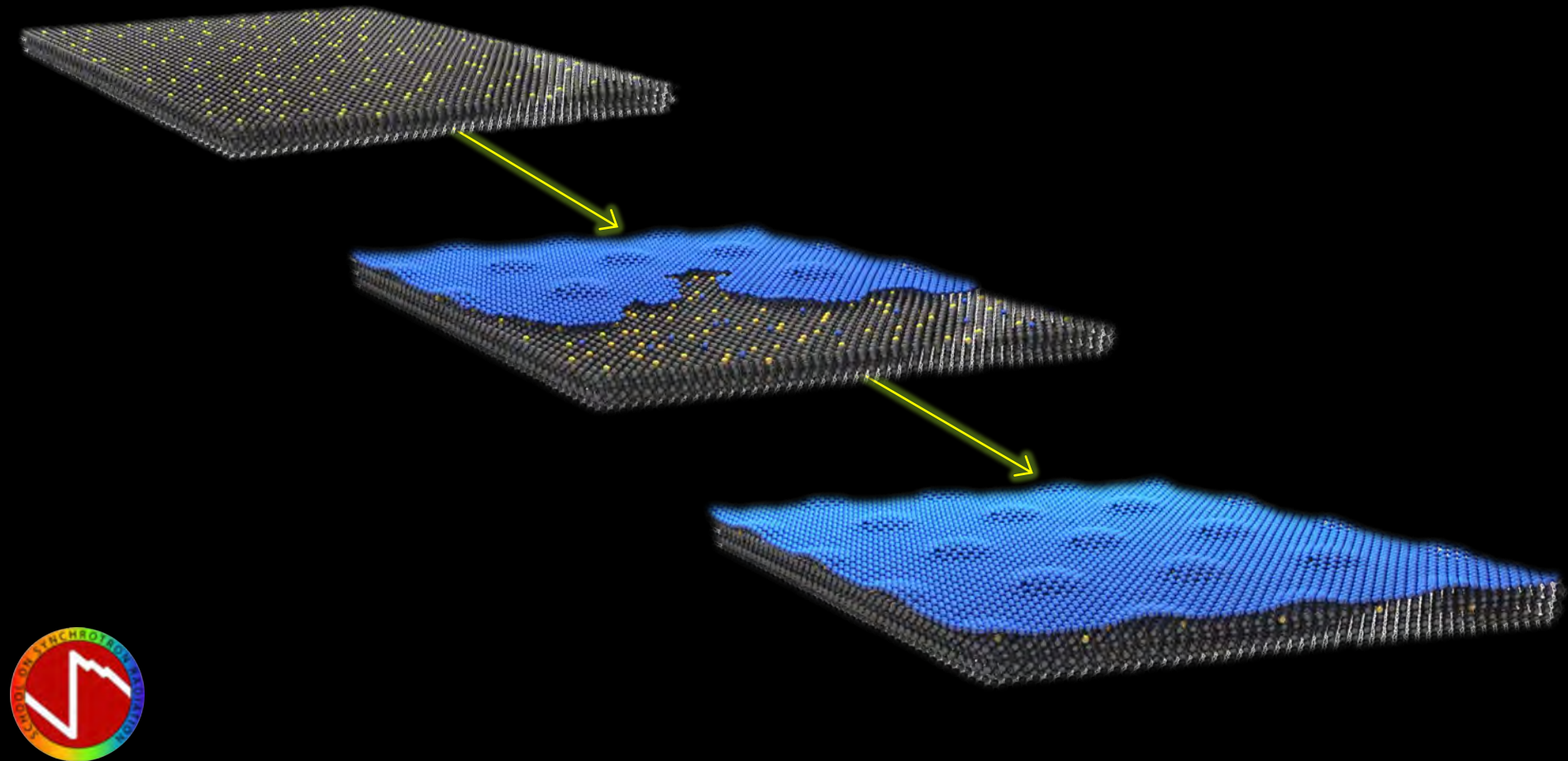
Graphene on PtRu/Ru(0001) bimetallic surface alloys



Previous STM studies: Pt atoms confined in the first layer and randomly distributed.

[H.E. Hoster *et al.*, Phys. Chem. Chem. Phys. 10, 3812 (2008)]

Epitaxial GR growth on the PtRu surface alloy by C_2H_4 CVD at 1050 K.



Comparison with DFT simulations

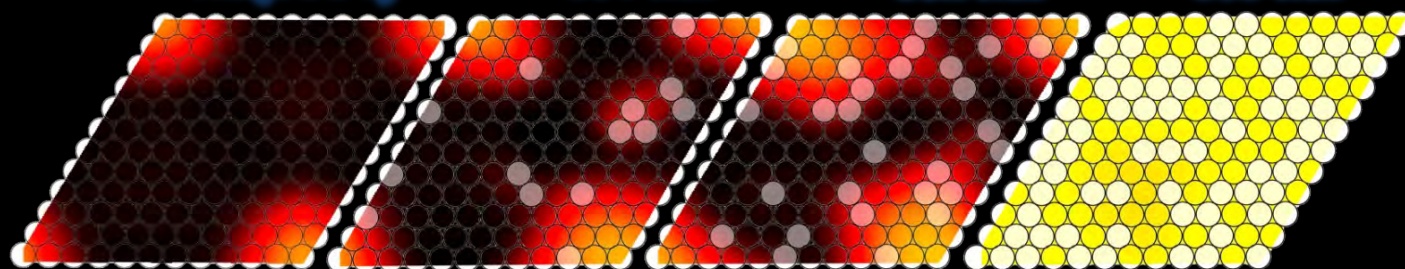
C-substrate
distance

Ru(0001)

0.1 ML

0.2 ML

0.5 ML

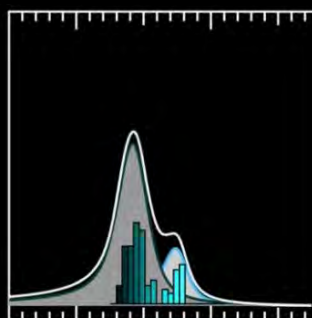


Pt concentration

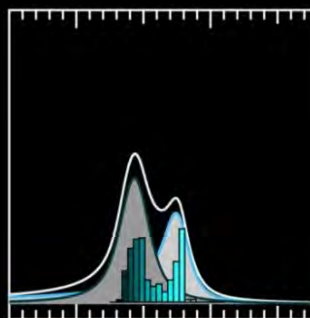
C-substrate distance

GR corrugation

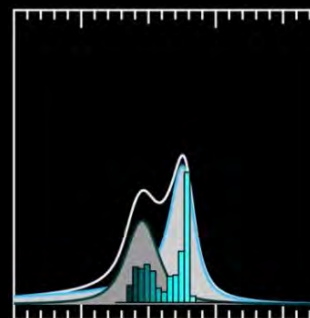
Simulated
C1s spectra



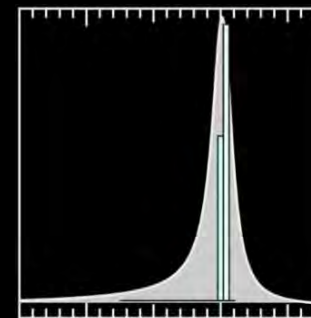
286 284
Binding Energy (eV)



286 284
Binding Energy (eV)



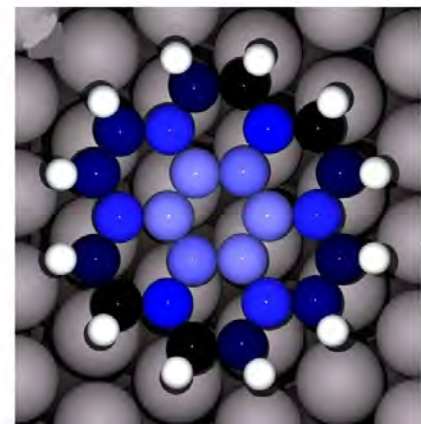
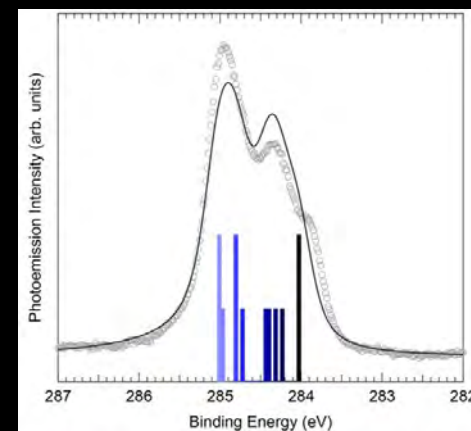
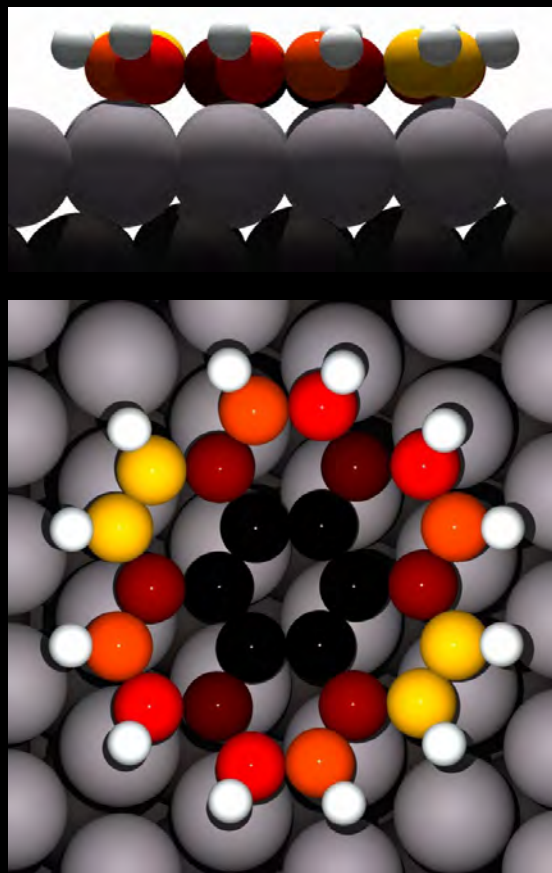
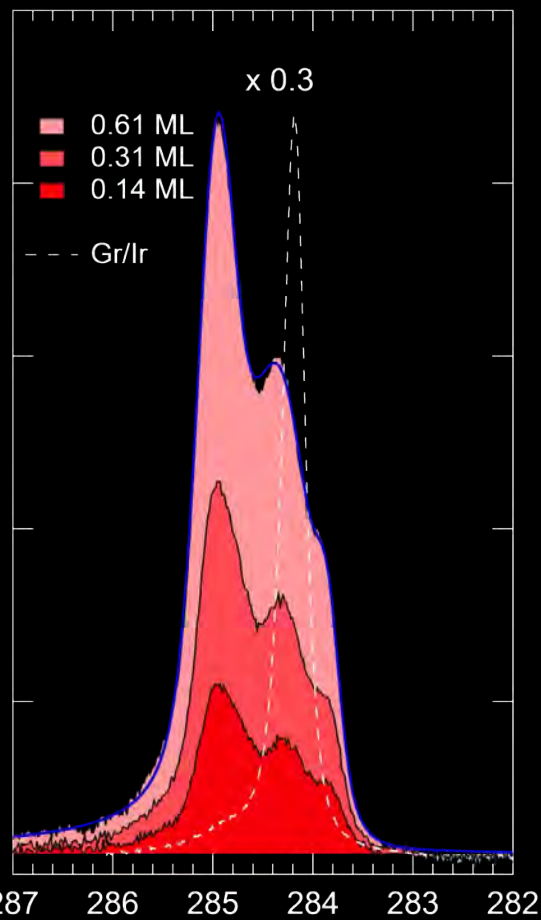
286 284
Binding Energy (eV)



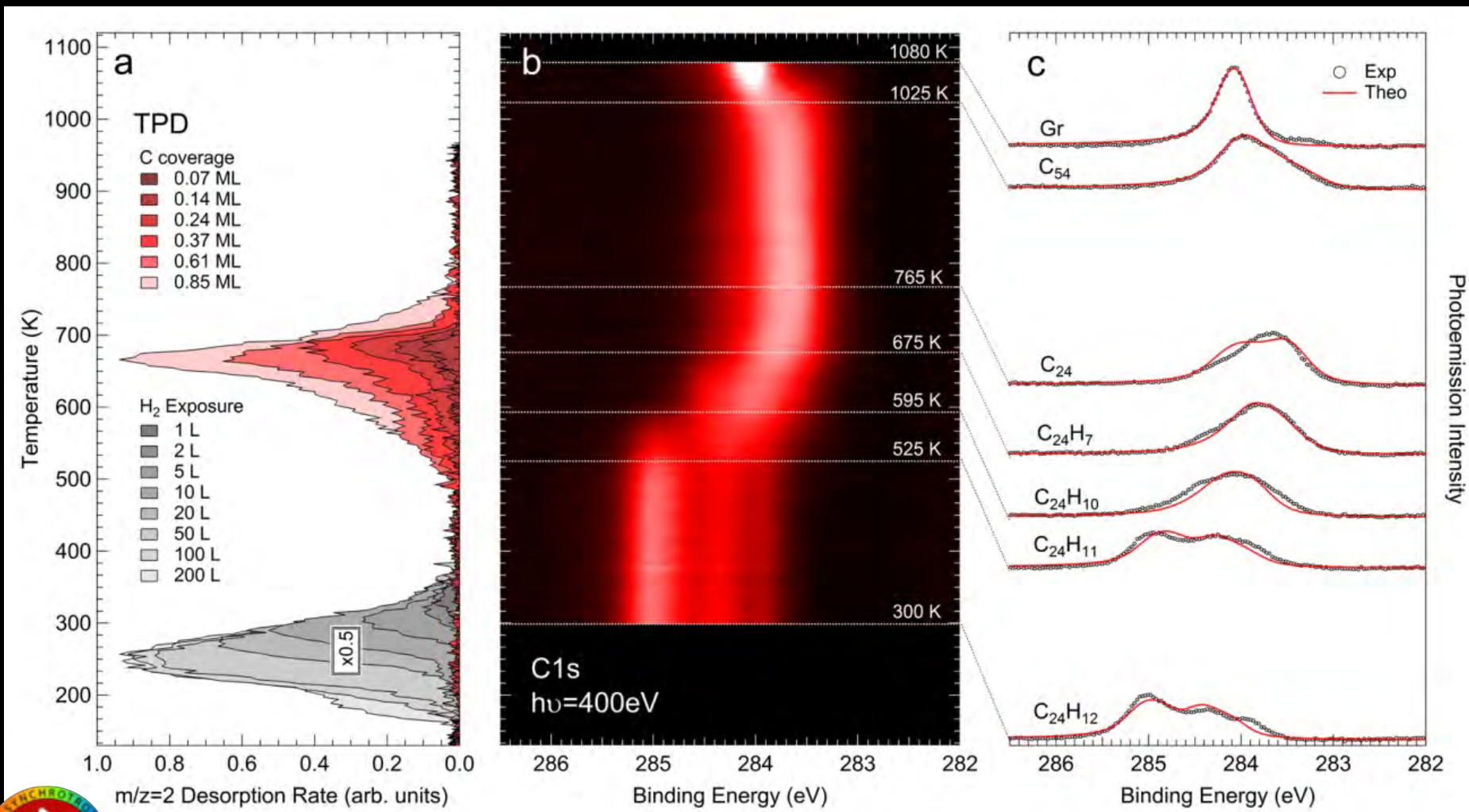
286 284
Binding Energy (eV)

Graphene formation via polycyclic hydrocarbon dehydrogenation

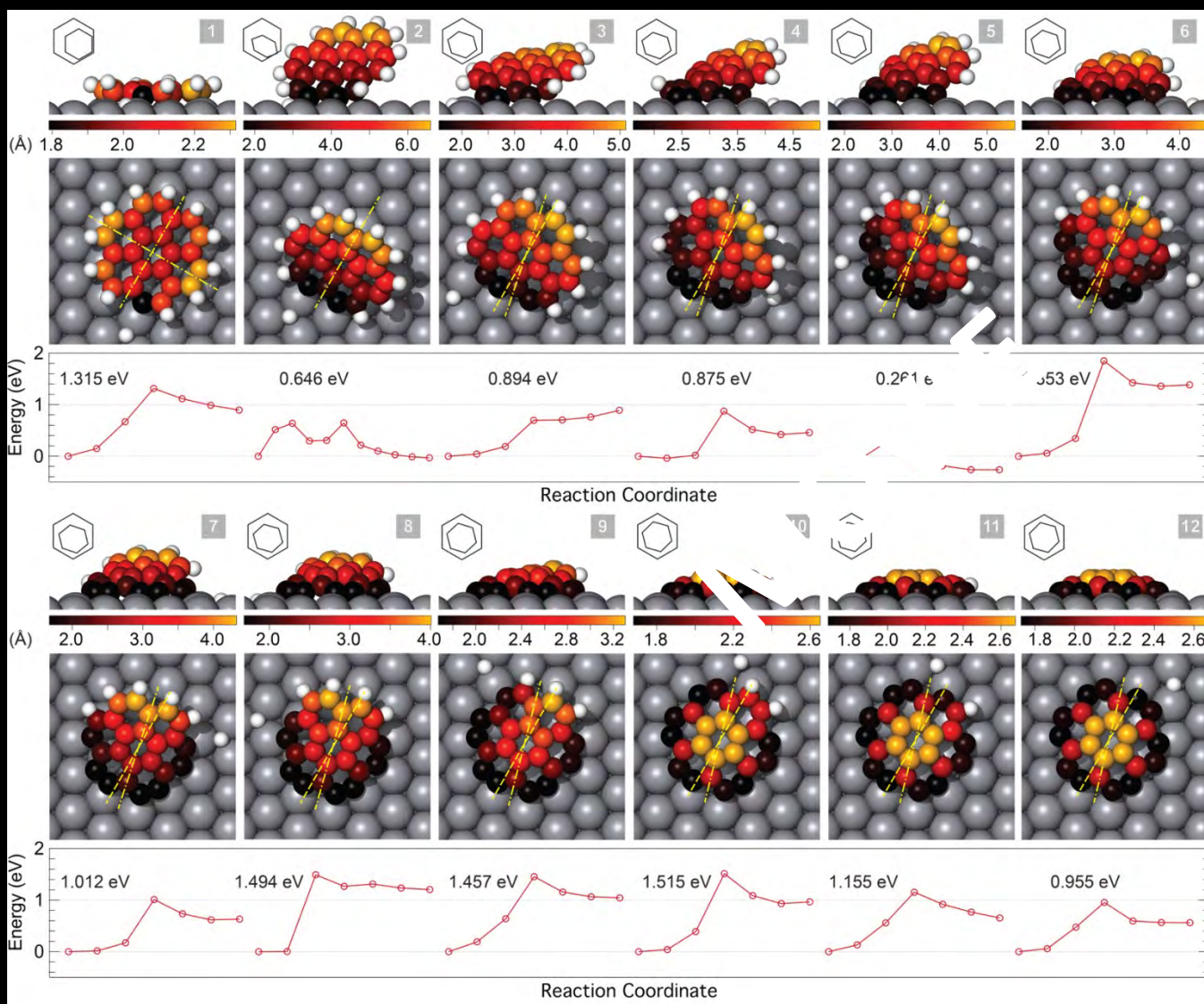
C_{1s} core level of adsorbed coronene on Ir(111)



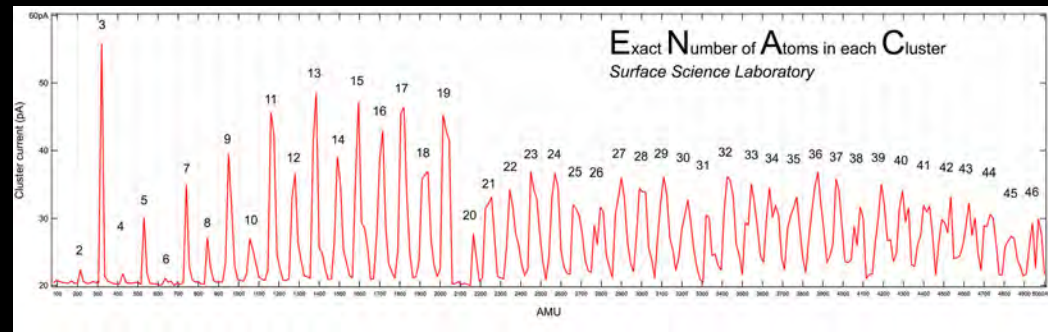
Graphene formation via polycyclic hydrocarbon dehydrogenation



Graphene formation via polycyclic hydrocarbon dehydrogenation



At the nanoscale a very small cluster of atoms can drastically change its properties by adding or removing just a single atom.



The goal of our research team will be to understand how structural, electronic and chemical properties evolve atom by atom, from the monomer to the bulk.



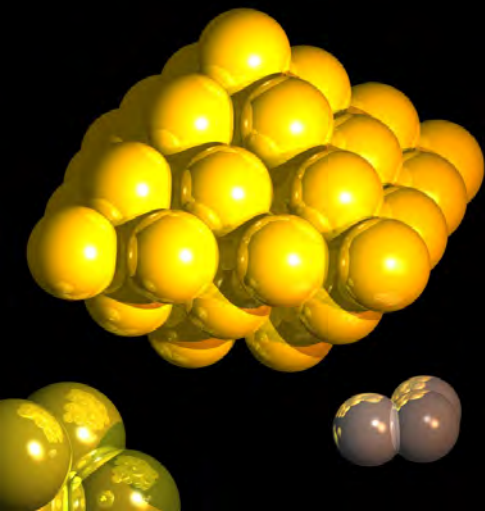
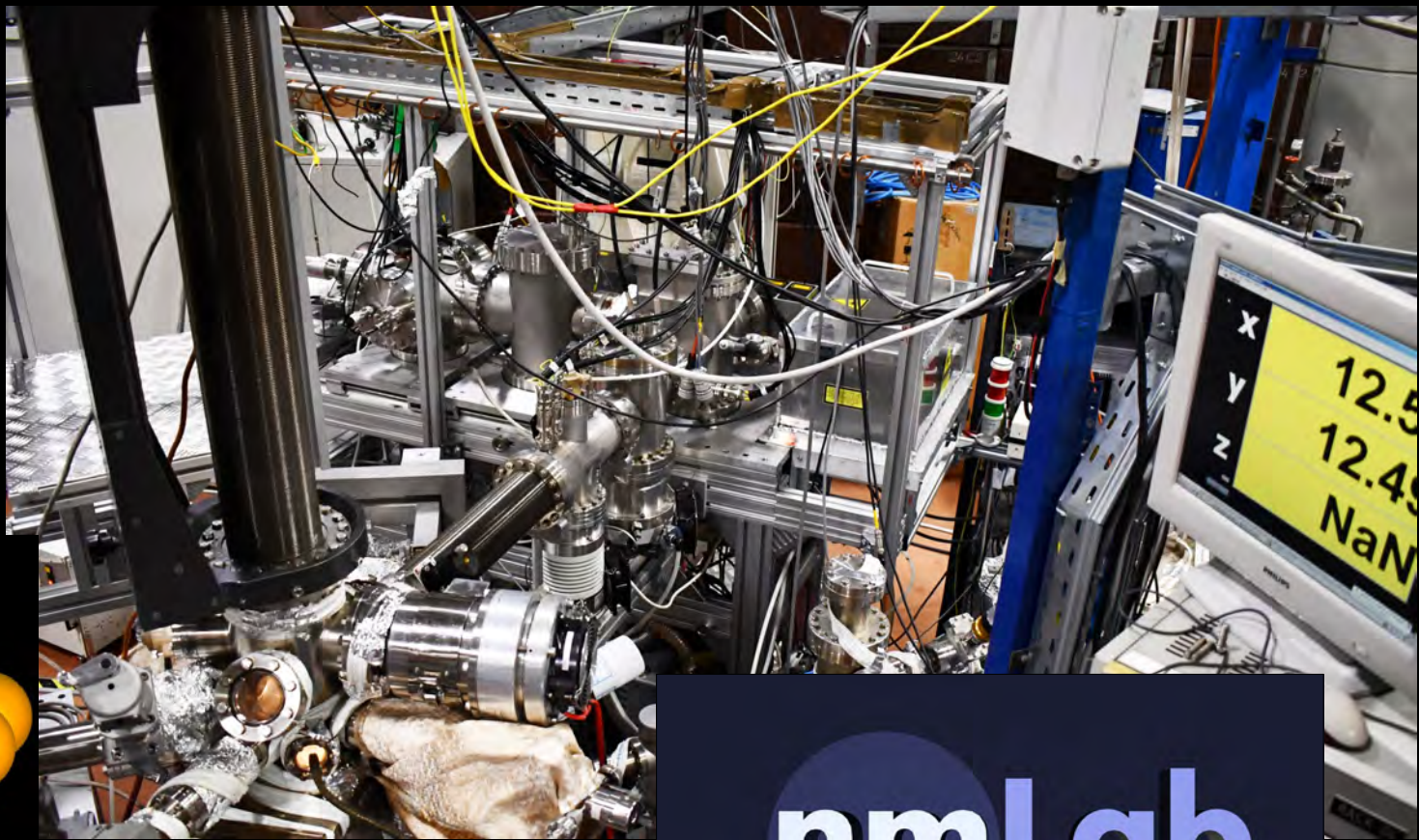
MOVIE



Size-selected cluster source

ENAC

Exact
Number of
Atoms in each
Cluster



nmLab
nanoscale materials Laboratory

Limitations in Determining Oxidation States in Condensed Matter at the Subnanometric Scale

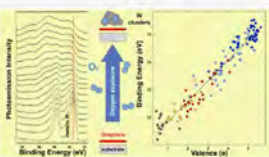
Deborah Perco, Monica Pozzo, Andrea Berti, Federico Loi, Paolo Lacovig, Silvano Lizzit, Aras Kartouzian, Ueli Heiz, Dario Alfè, and Alessandro Baraldi*

Cite This: *J. Am. Chem. Soc.* 2025, 147, 21501–21511

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The oxidation state is a fundamental chemical concept commonly employed to rationalize, classify, and predict the chemical reactivity of a variety of compounds. Understanding and defining the elemental oxidation state of solid materials at the atomic level becomes increasingly complex as their physical dimensions are reduced from tens of nanometers—where properties are still dominated by bulk or outer atomic crystal plane characteristics—to the subnanometric limit. In this work, we highlight the significant limitations in determining even a basic quantity, such as the oxidation state, when oxidized low-nuclearity mass-selected clusters are investigated by means of X-ray photoelectron spectroscopy (XPS), widely recognized as the selective approach to resolve different oxidation states. The lack of crystalline order in these nanoclusters, unlike that in periodic bulk systems and in solid surfaces, leads to a broad distribution of measured core levels, as shown in the case study of W nanoclusters. These cannot be unambiguously assigned to a valence state based solely on the knee emphasize the substantial rigorous and quantitative represent crucial knowledge.



Photon-Driven Cluster Fluxionality: Breaking the Bulk Stoichiometry Ceiling in Subnanometric Molybdenum Oxides

Yao Wei, Deborah Perco, Alejandro Santana-Bonilla, Federico Loi, Paolo Lacovig, Silvano Lizzit, Lev Kantorovich, and Alessandro Baraldi*

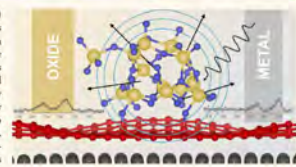
Cite This: *ACS Nano* 2026, 20, 25481–25491

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We investigate the low-temperature (40 K) oxidation behavior of size-selected molybdenum clusters supported on epitaxial graphene. By combining high-resolution X-ray photoelectron spectroscopy with first-principles density functional theory, we demonstrate that subnanometric clusters can break the stoichiometric ceiling of bulk transition-metal oxides. Quantitative agreement between experiment and theory is achieved only when the clusters accommodate an unusually high oxygen content, with metal-to-oxygen ratios reaching up to Mo:O = 1:5, far exceeding the 1:3 limit of bulk oxide MoO₃. This superstoichiometric regime is a consequence of coordination plasticity, where the molybdenum framework undergoes pronounced structural expansion to stable tetrahedral MoO₄ motifs that are energetically inaccessible in extended solids. We provide compelling evidence that this process is mediated by photon-driven structural fluxionality: with kinetic energies exceeding 10 eV, secondary electrons generated during photoemission represent the only source to provide the vibrational excitations necessary to overcome the thermal constraint for structural transformation, allowing the clusters to disrupt the atomic connectivity and reach low-energy isomer configurations characterized by large structural expansion. Furthermore, atomic valence, rather than formal oxidation state, provides a physically meaningful and transferable descriptor for interpreting the main trend in core electron binding energy shifts in nanoscale disordered systems. These findings reveal a fundamentally non-bulk oxidation mechanism governed by non-thermal energy-activated structural dynamics, outlining a strategy for engineering oxygen-rich reactive sites at the ultimate size limit.

KEYWORDS: fluxionality, nanoclusters, oxidation, molybdenum, oxygen activation, XPS, DFT



Ultra-Low Atomic Diffusion Barrier on Two-Dimensional Materials: The Case of Pt on Epitaxial Graphene

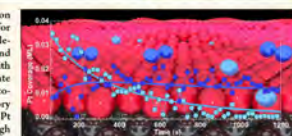
Andrea Berti, Ramón M. Bergua, Jose M. Mercero, Deborah Perco, Paolo Lacovig, Silvano Lizzit, Elisa Jimenez-Izal, and Alessandro Baraldi*

Cite This: *ACS Nano* 2025, 19, 35921–35932

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Understanding the energetics of atomic diffusion on graphene and two-dimensional (2D) materials is critical for advancing ultraminiaturized nanodevices, where even single-atom dynamics can significantly impact their functionality and performance, and for designing next-generation catalysts with superior activity and selectivity. In this work, we demonstrate that the combination of fast, high-resolution X-ray photoelectron spectroscopy (HR-XPS) and density functional theory (DFT) simulations provides a powerful approach to probe Pt atoms diffusion on epitaxial graphene. HR-XPS with its high chemical sensitivity and temporal resolution allows *in situ* tracking of Pt 4f_{7/2} spectral components associated with monomers, dimers, and larger clusters at low temperature. This capability enabled us to monitor the rapid decay of monomer coverage and the subsequent aggregation into larger clusters. By fitting the time evolution of the different Pt species using a kinetic model, we extracted a diffusion barrier of 128 ± 6 meV, in excellent agreement with the 130 meV value obtained by nudged elastic band (NEB) calculations. These findings establish fast HR-XPS as a noninvasive tool to study atomic dynamics and for guiding the design of surface nanodevices.



Room-Temperature Adsorption on Magnetite Induces Spontaneous Fragmentation of Early Transition-Metal Size-Selected Nanoclusters

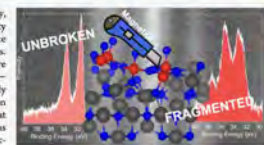
Gabriele Coltrilli, Deborah Perco, Luca Sementa, Marco Bianchi, Andrea Berti, Mikhail Bandurist, Paolo Lacovig, Silvano Lizzit, Aras Kartouzian, Ueli Heiz, Alessandro Fortunelli, and Alessandro Baraldi*

Cite This: <https://doi.org/10.1021/jacs.4c15419>

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The stability of supported metal nanoclusters, namely, their ability to preserve structure, composition, and catalytic activity over time, is a fundamental prerequisite for catalyst durability, resistance to deactivation, and long-term performance under operating conditions. Despite their often-exceptional intrinsic activity, nanoclusters are particularly susceptible to structural evolution driven by strong metal–support interactions. Here, we demonstrate that size-selected early transition-metal nanoclusters (W, Mo, and Ta) soft-landed on reconstructed Fe₃O₄(001) undergo spontaneous breakdown already at room temperature, in the absence of thermal activation or reactive gas environments. Combining high-energy resolution photoelectron spectroscopy and scanning tunneling microscopy with density functional theory, we show that strong metal–oxygen bonding, together with reconstruction-induced surface defects of the oxide support, provides the driving force required to overcome metal–metal cohesion within the clusters, leading to their dissociation. Upon further oxidation, an enhanced degree of atomization is produced, particularly for larger clusters, yielding highly dispersed metal species. The propensity for fragmentation, i.e., the partial or total breaking of metal–metal bonds in the cluster, follows the trend Ta > W > Mo, which correlates closely with metal oxophilicity, adsorption energies, and intrinsic metal–metal bond strengths. These findings establish adsorption-induced fragmentation of metal nanoclusters as an intrinsic manifestation of metal–support interactions for early transition metals on reducible oxides. More broadly, they reveal a spontaneous room temperature pathway to cluster destabilization and identify an innovative strategy for the controlled generation of high densities of single metal atoms from well-defined nanocluster precursors.



References:

A. Baraldi

"High-resolution Core Level Photoelectron Spectroscopy and Diffraction: Powerful Tools to Probe Physical and Chemical Properties of Solid Surfaces"

in *Synchrotron Radiation, Basics, Methods and Applications*, S. Mobilio, F. Boscherini and C. Meneghini Editors, Springer-Verlag Berlin Heidelberg (2015)

L. Bignardi, P. Lacovig, R. Larciprete, D. Alfè, S. Lizzit, A. Baraldi

"Exploring 2D Materials at Surfaces through Synchrotron-Based Core-Level Photoelectron Spectroscopy"
Surface Science Reports **78**, 100586 (2023)

For any question do not hesitate to contact me:

Prof. Alessandro Baraldi

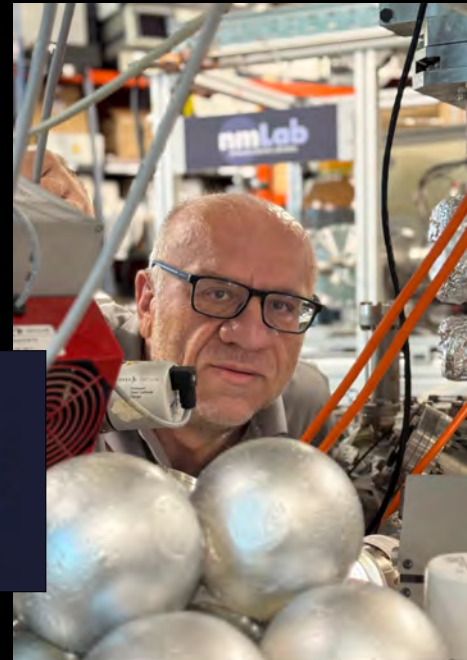
University of Trieste, Physics Department

e-mail: abaraldi@units.it

Head Nanoscale Materials Laboratory

Elettra-Sincrotrone Trieste

e-mail: alessandro.baraldi@elettra.eu





XVI School on Synchrotron Radiation: *Fundamentals, Methods and Applications*

Muggia, Italy / 19-30 September 2022



Società
Italiana
Luce di
Sincrotrone



Elettra Sincrotrone Trieste

Thank you !