High-resolution x-ray photoelectron spectroscopy

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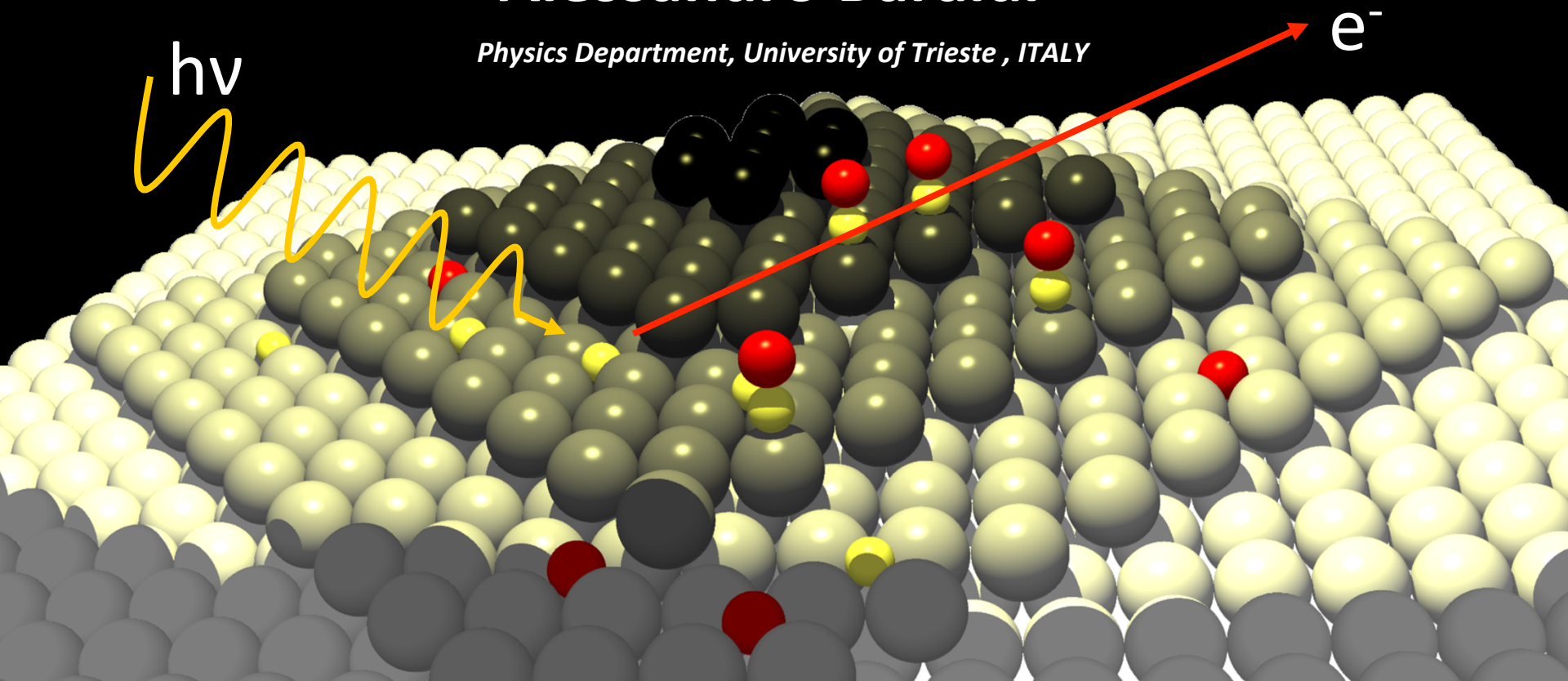
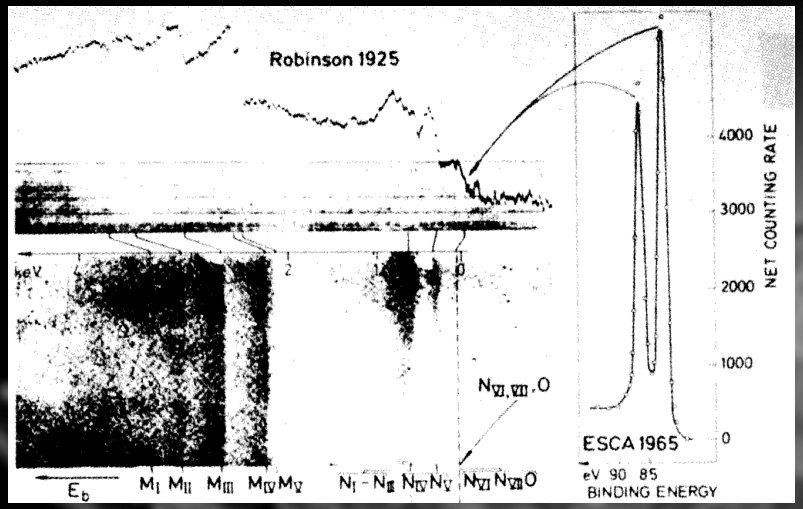


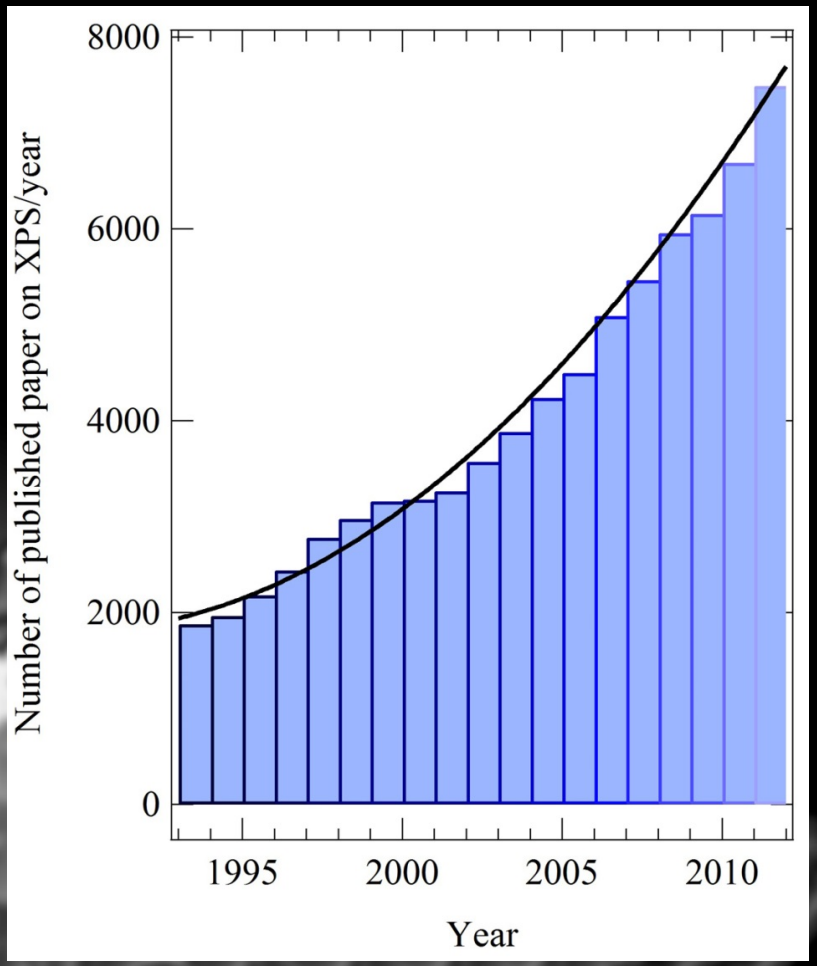
More than 100 years after Einstein

«1905, Annus mirabilis»

The interpretation of the photoelectric effect

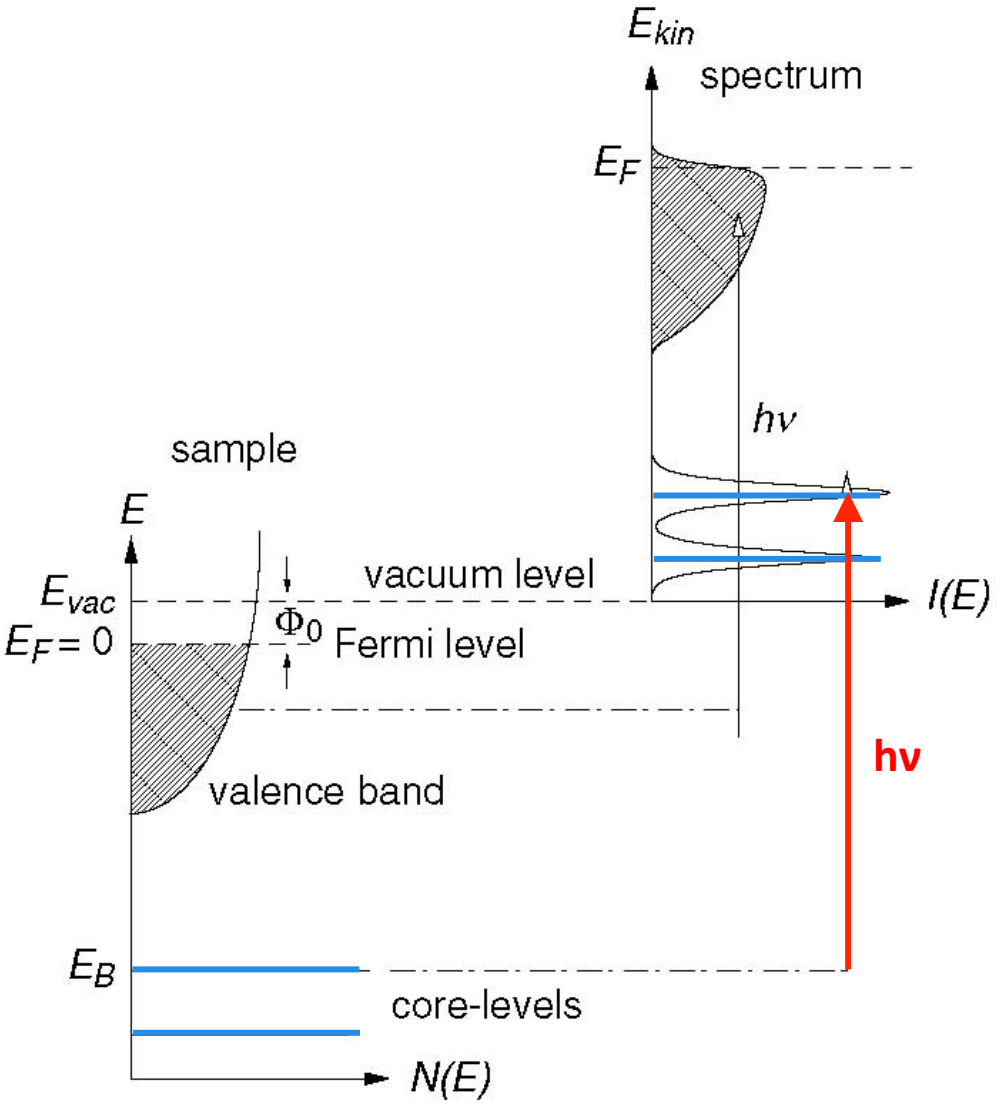


Comparison between Robinson (1925) and Siegbahn (1965)



Number of papers published in the period 1992-2012 in peer-review international scientific journals on X-ray Photoelectron Spectroscopy (Clarivate – Web of Science).

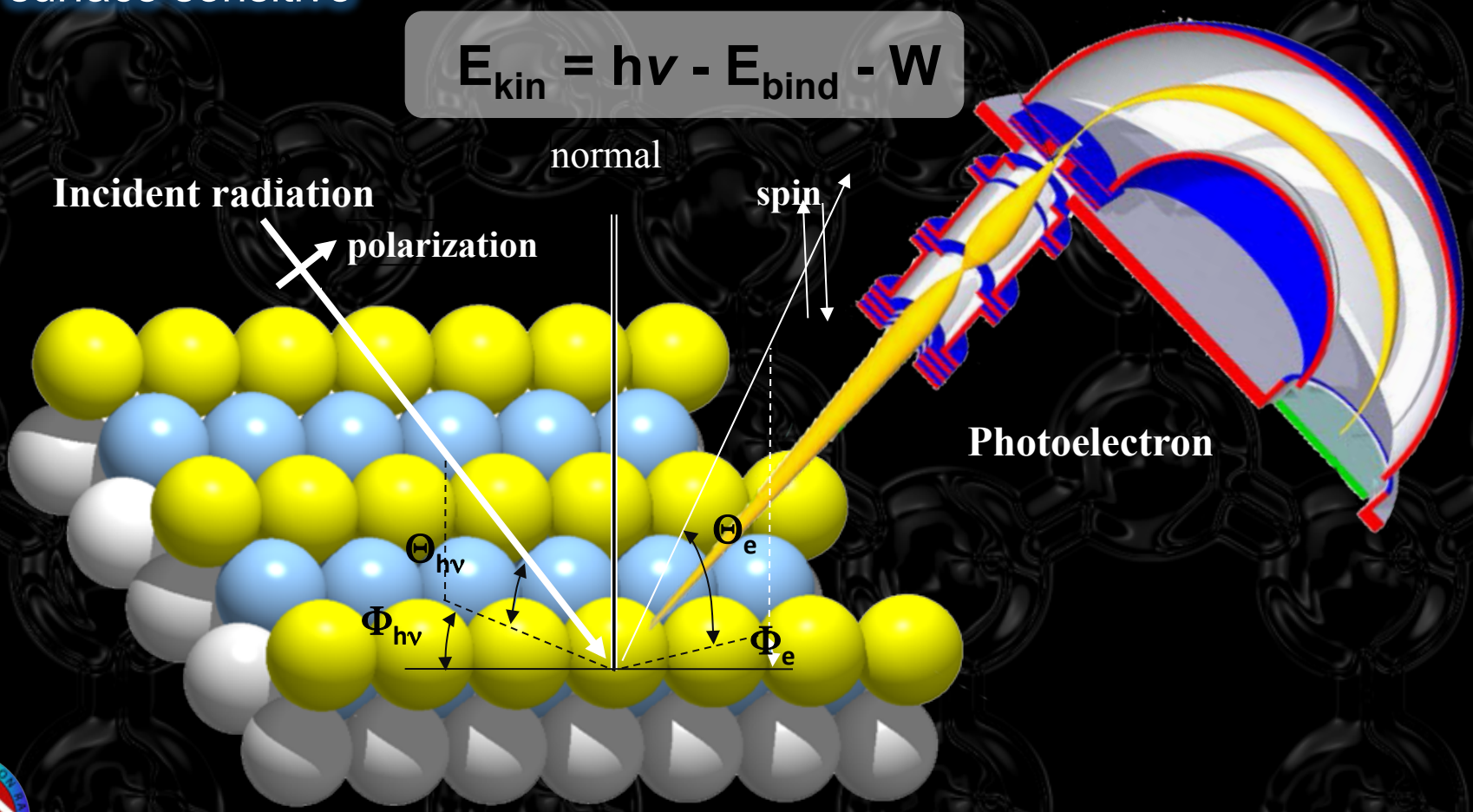
Photoelectron spectroscopy from a solid



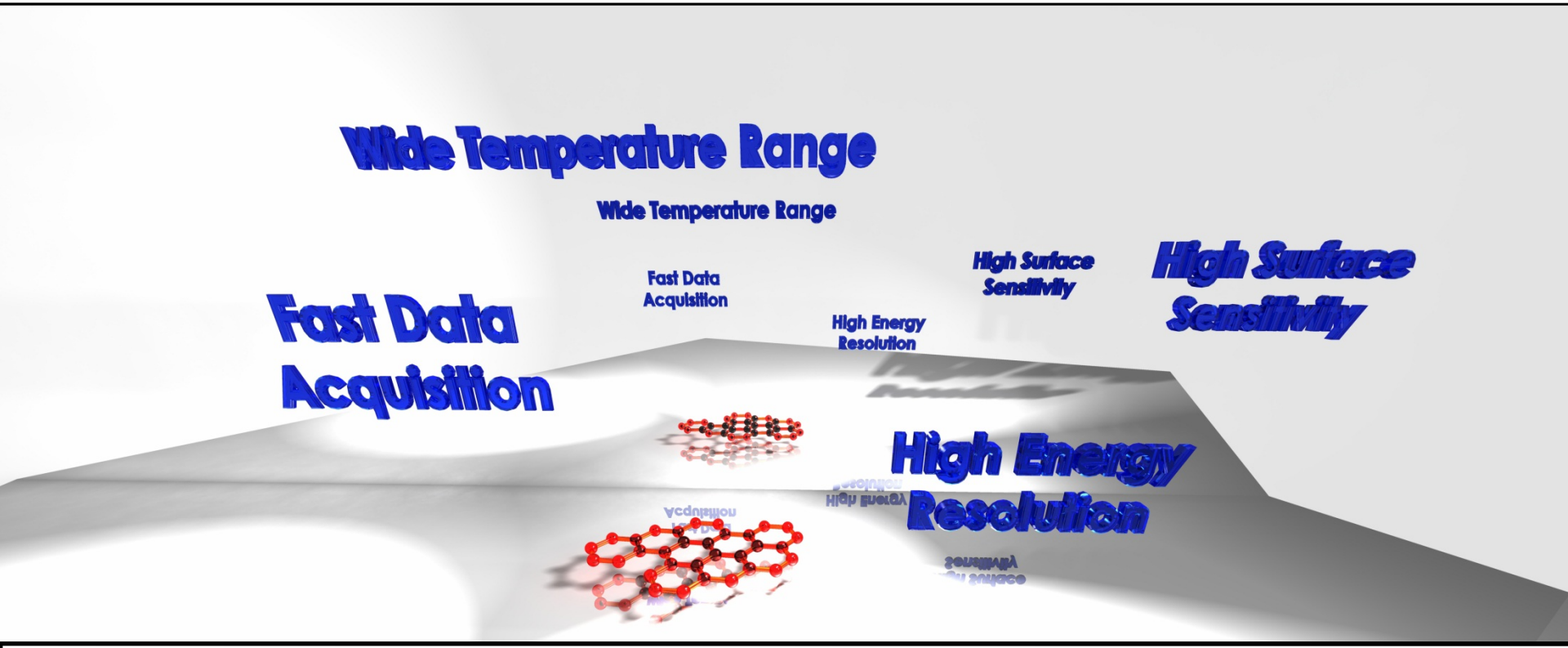
Photoelectron spectroscopy from a solid

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

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



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

Many-body effects in Doniach-Šùnjić

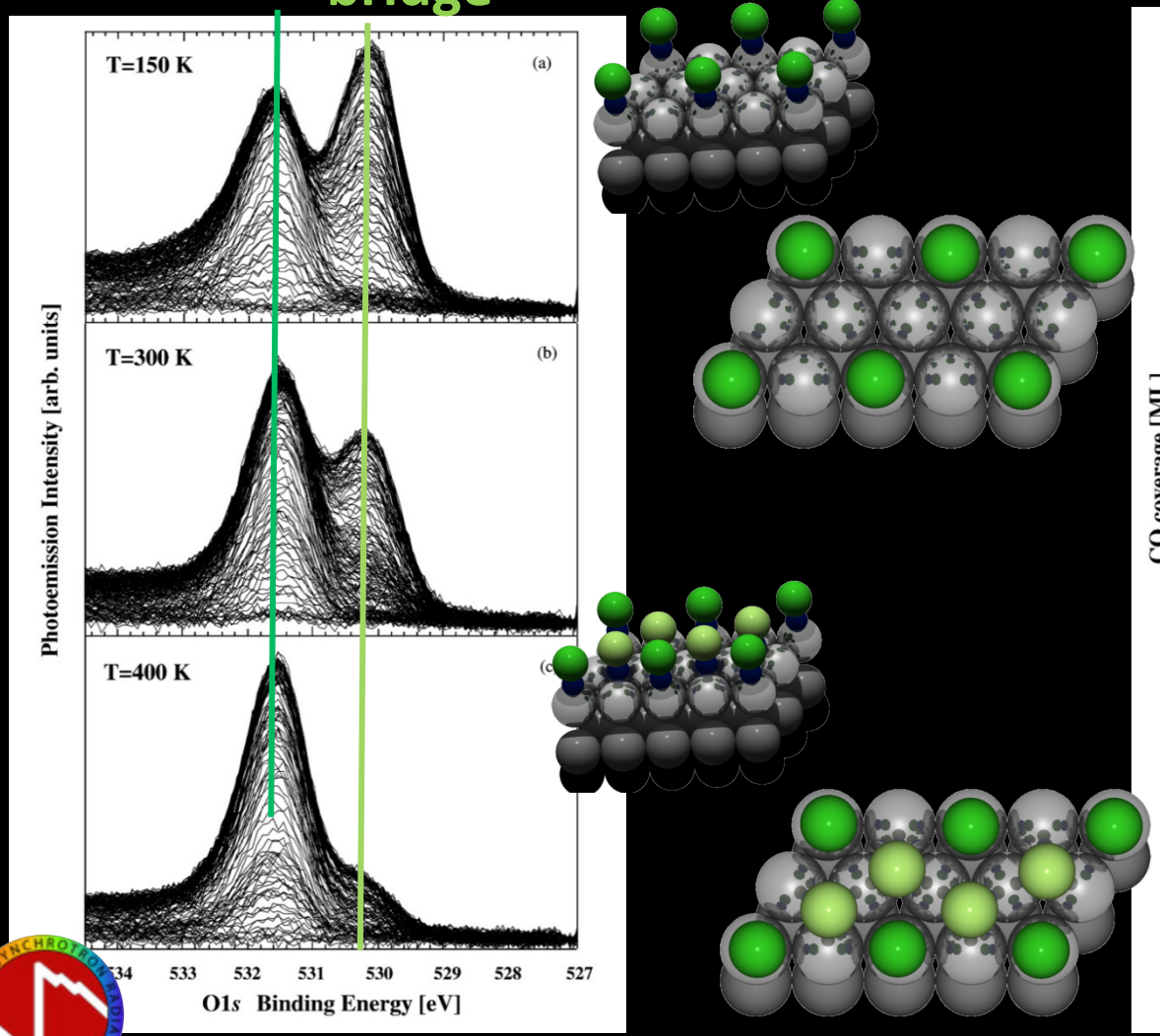
Lorentzian distribution arising from the finite core-hole lifetime.

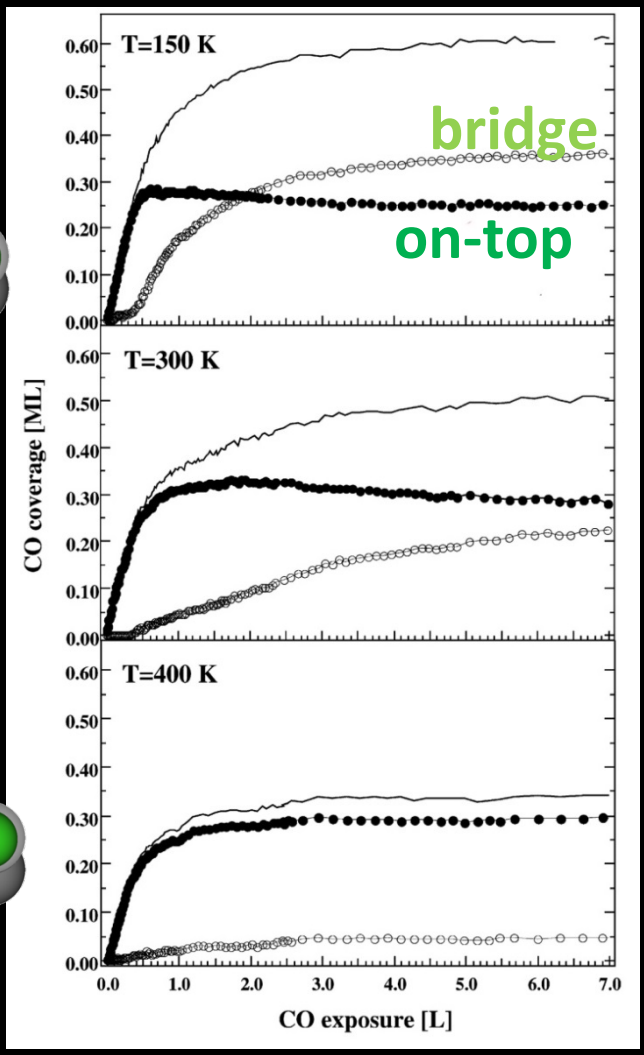
A convolution of a Doniach-Šùnjić function and a **Gaussian**, which account for the vibration/phonon and the contribution of the instrumental resolution.

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

Adsorbates on solid surfaces

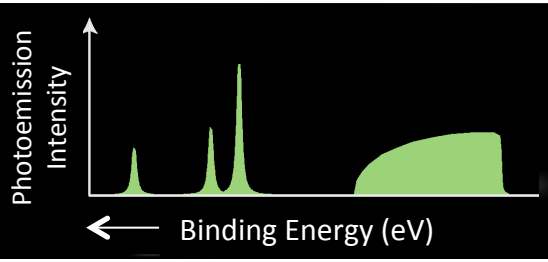
Carbon Monoxide adsorption on Rh(111)





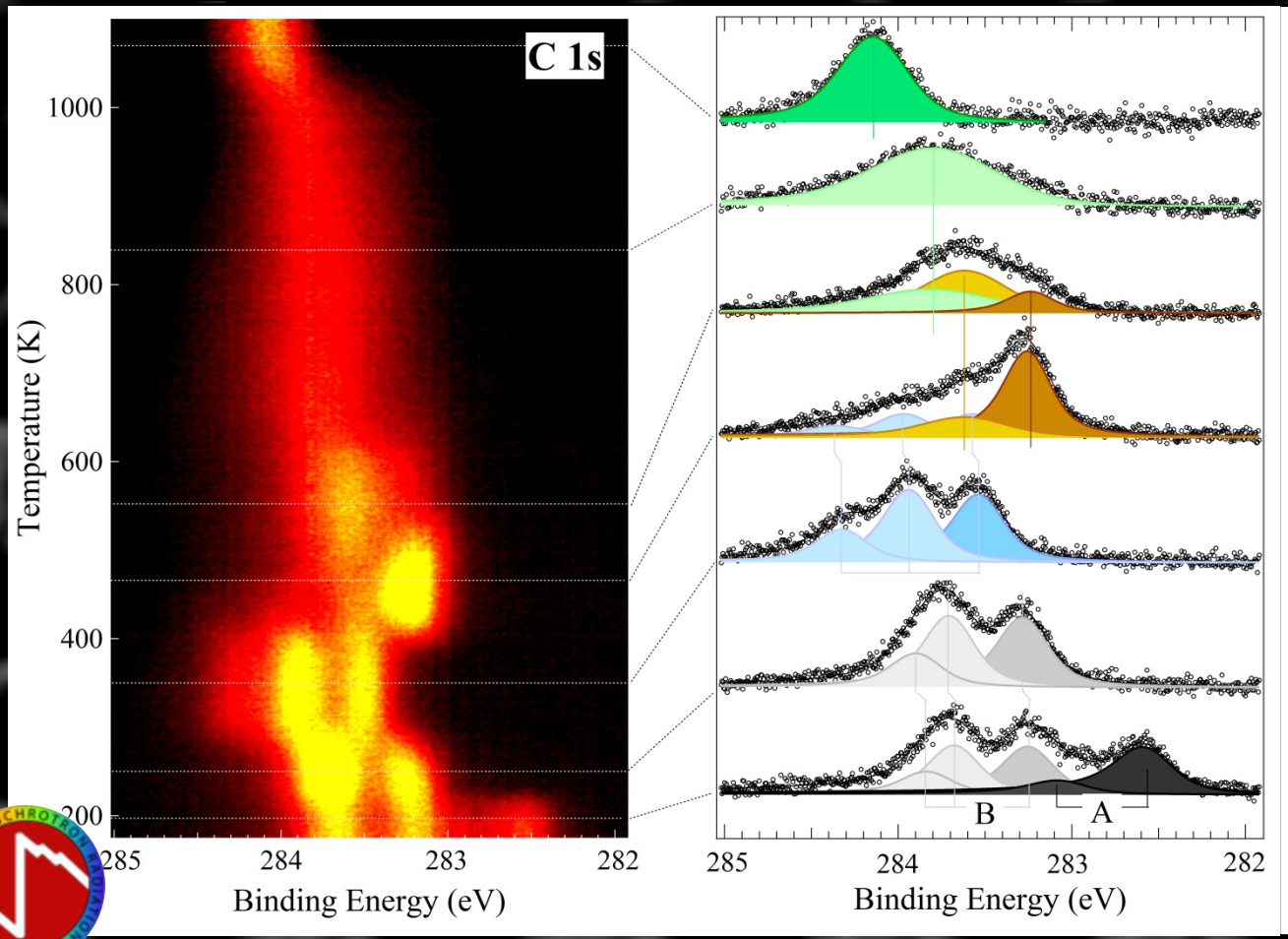
A. Baraldi *et al.*, Surf. Sci. Rep. **49**, 169 (2003).

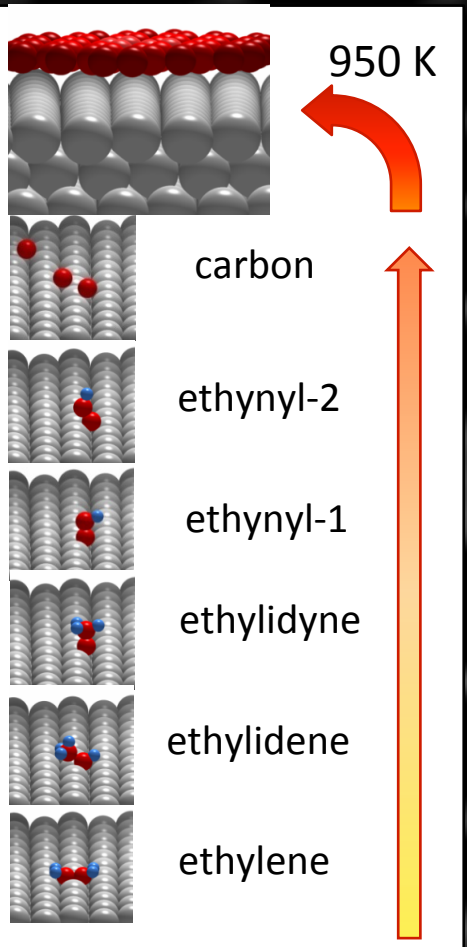
From simple molecules to graphene



ΔE=50 meV
Δt=100÷500 ms

From ethylene to graphene formation



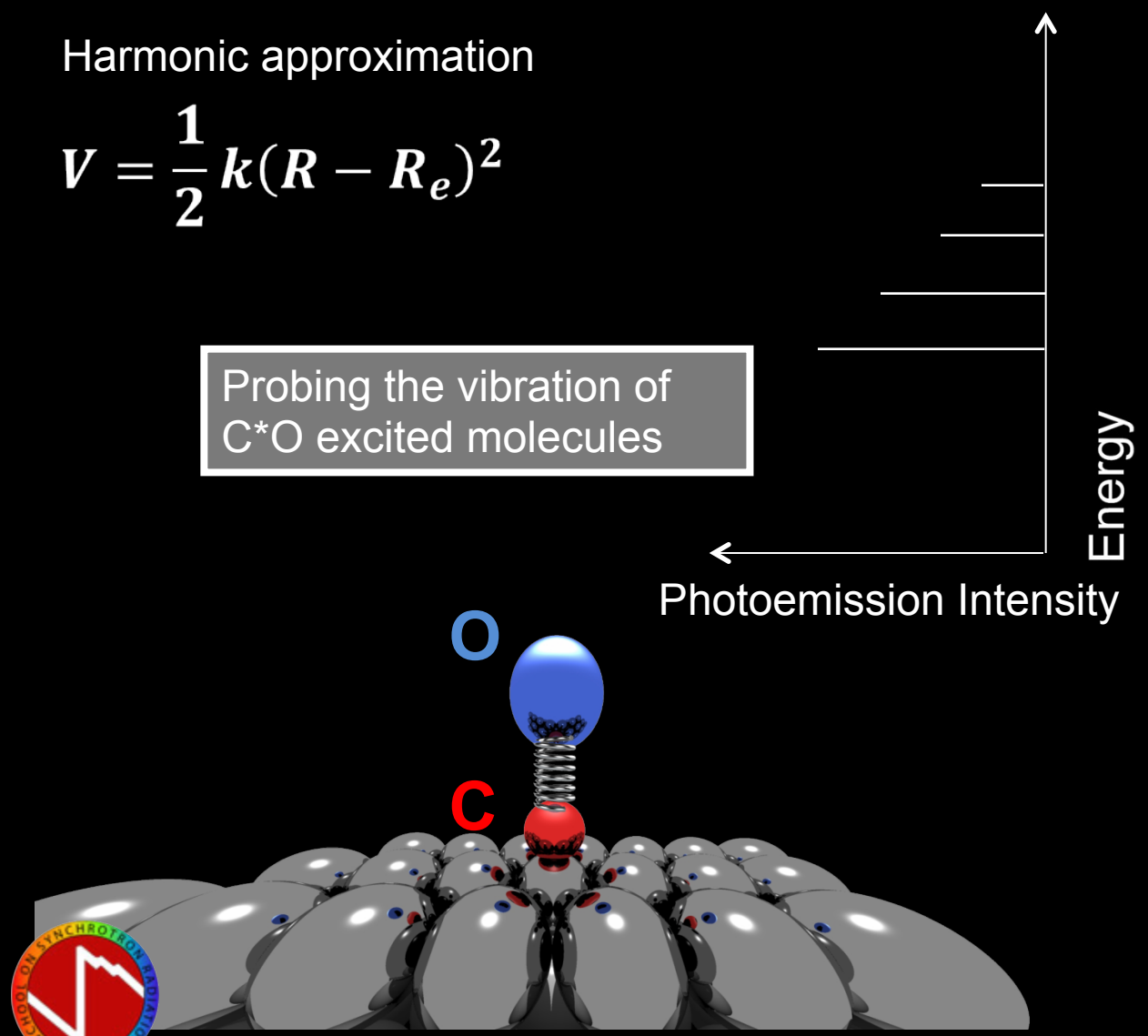


Localized vibrations of adsorbed molecules

Harmonic approximation

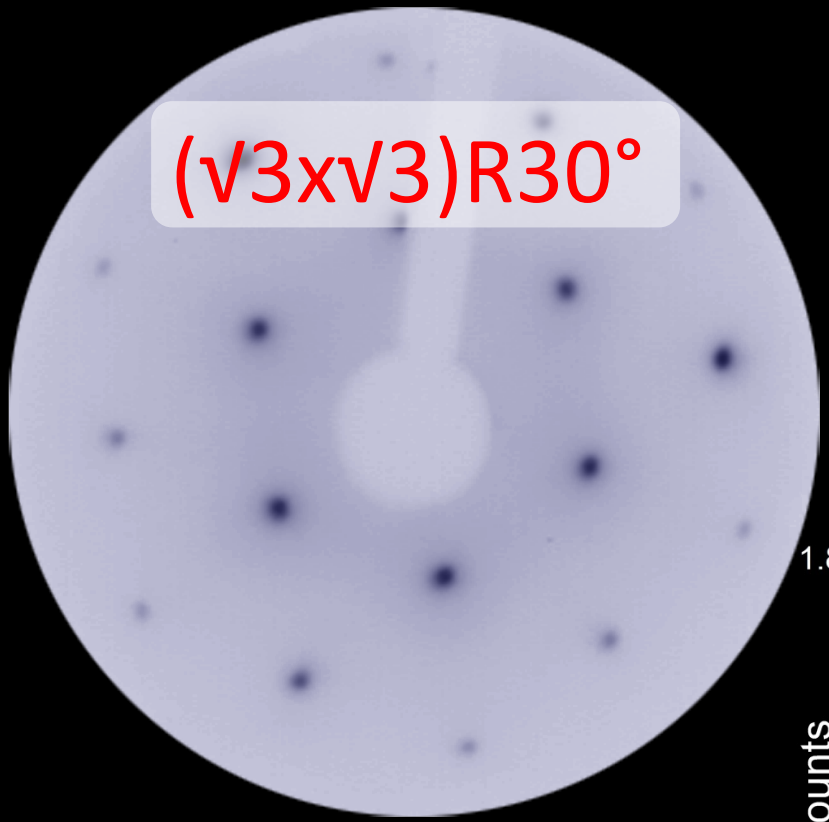
$$V = \frac{1}{2}k(R - R_e)^2$$

Probing the vibration of C*O excited molecules



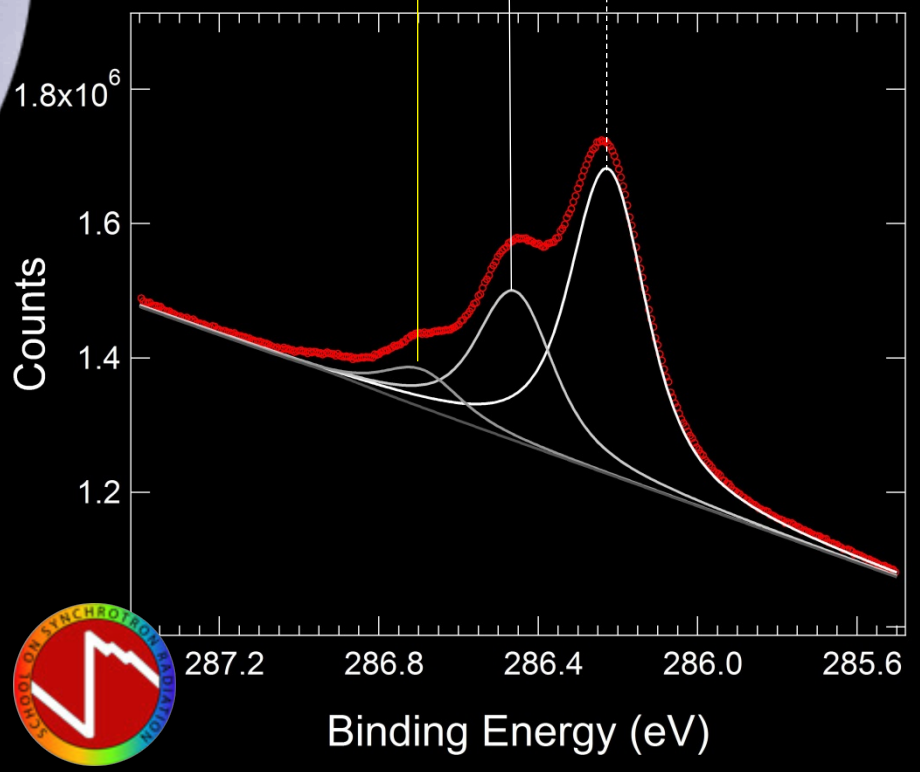
C1*s* core-level spectrum of adsorbed CO

CO on Ir(111)

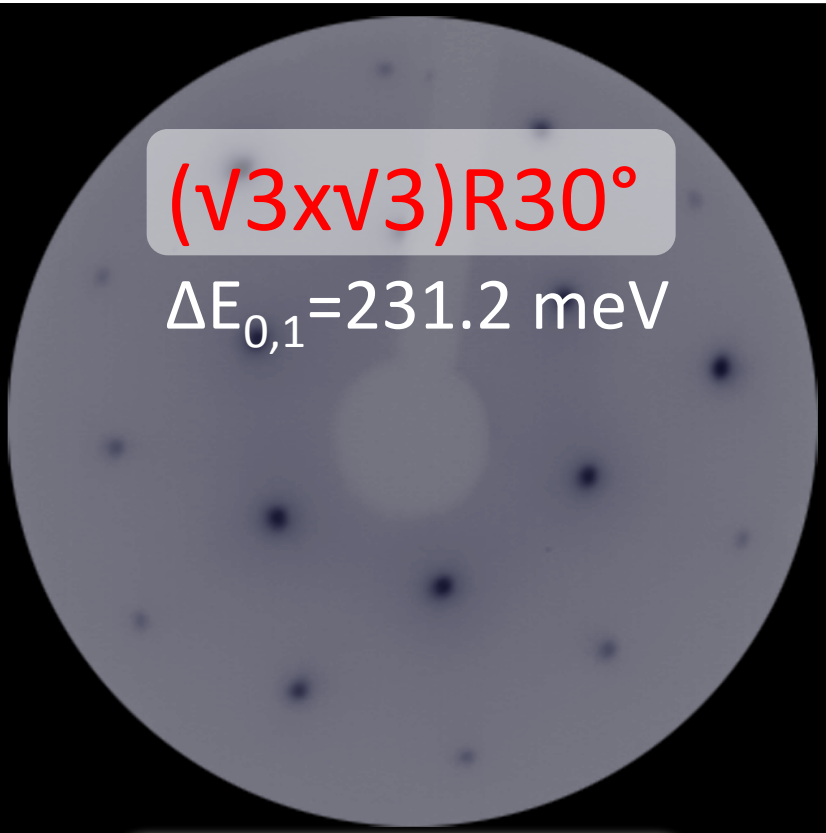


$\Delta E_{0,1}$=231.2 meV

$\Delta E_{0,2}$=461.7 meV



C1*s* core-level spectrum of CO on Ir(111)



(√3x√3)R30°

$\Delta E_{0,1}$=231.2 meV

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).

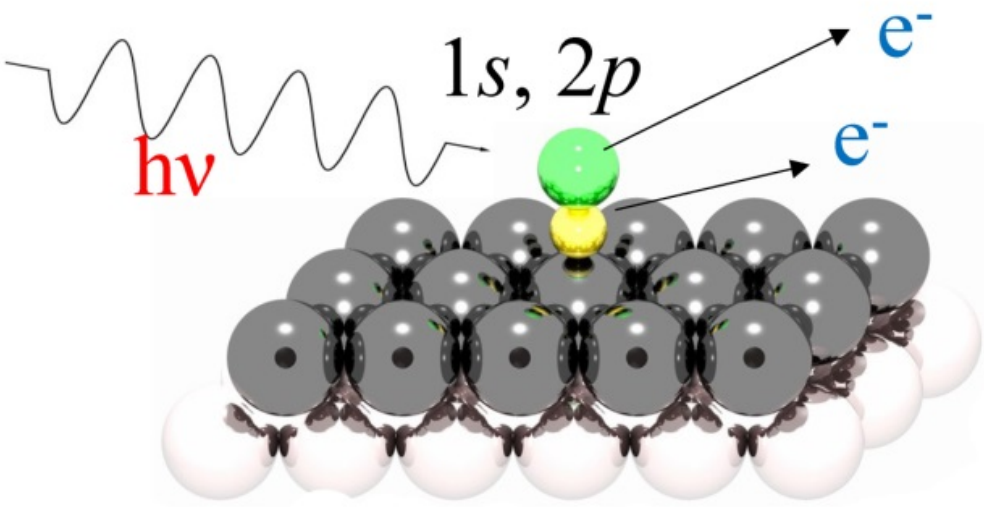
CO on Ir(111)
256 meV - low coverage
258 meV - high coverage

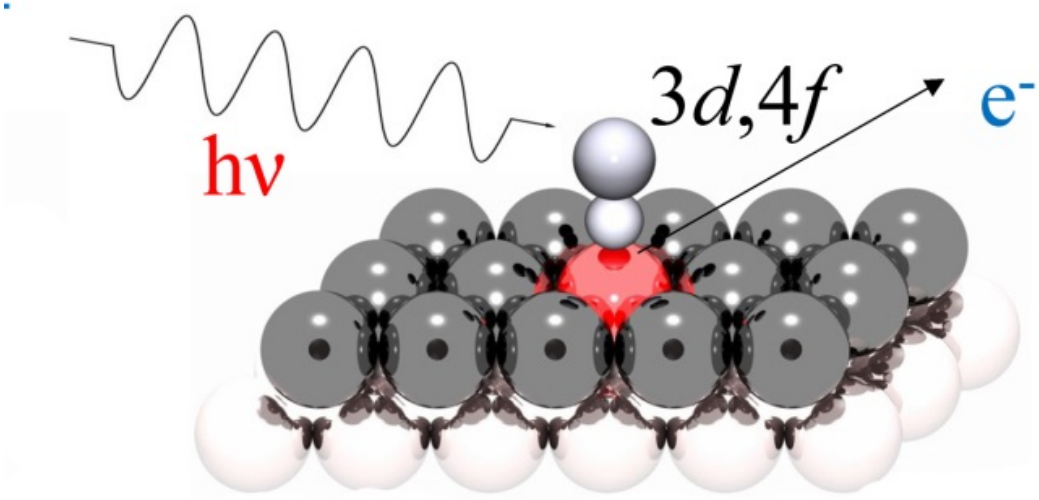
J. Lauterbach *et al.*,
Surf. Sci. **350**, 32 (1996)

NO on Ir(111)
223 meV - low coverage
225 meV - high coverage

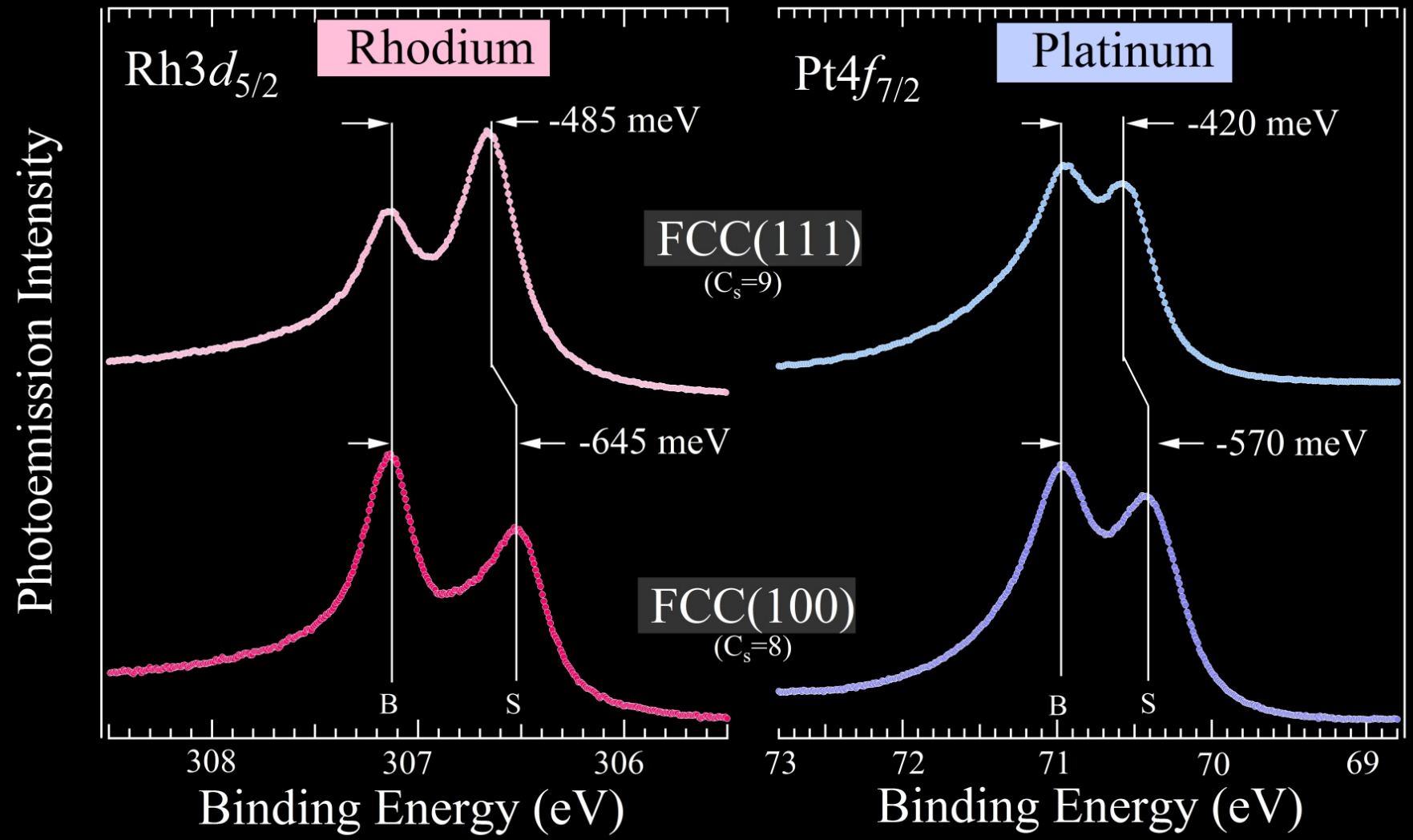
M. Matsumoto *et al.*,
Surf. Sci. **606**, 1489 (2012).

Different perspectives

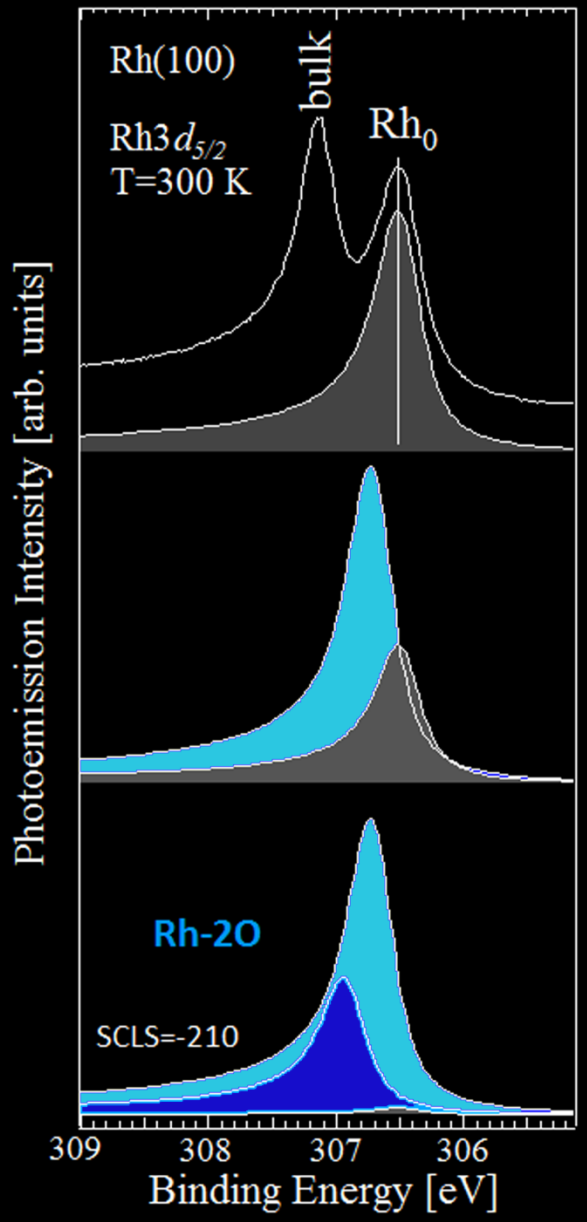




The core levels from substrate atoms



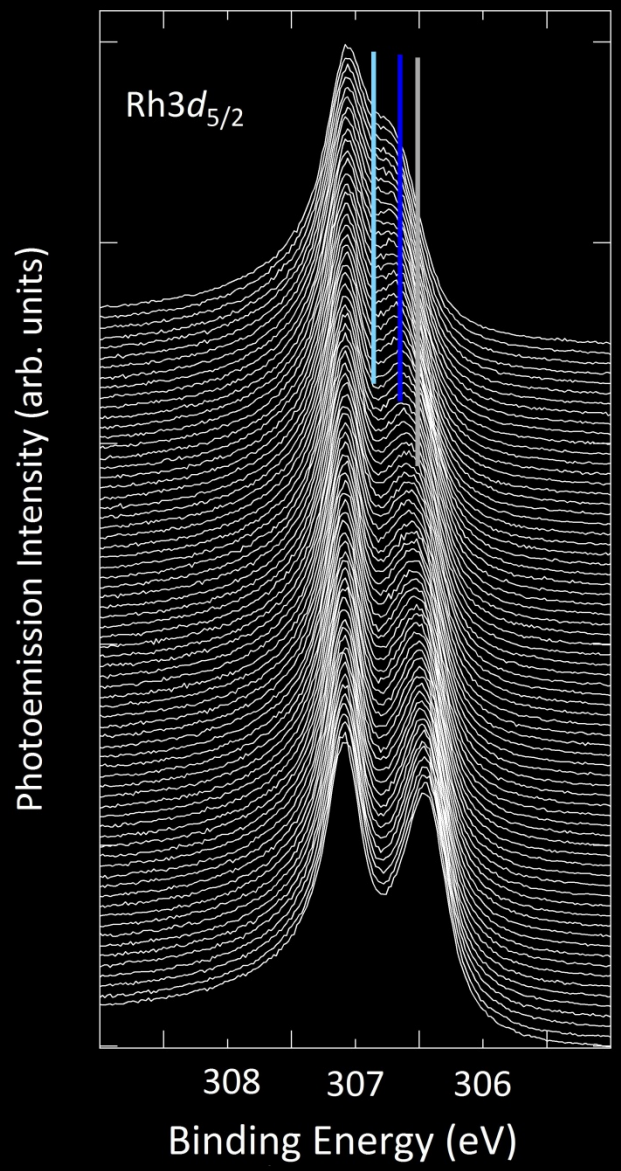
Oxygen adsorption and dissociation on Rh(100)

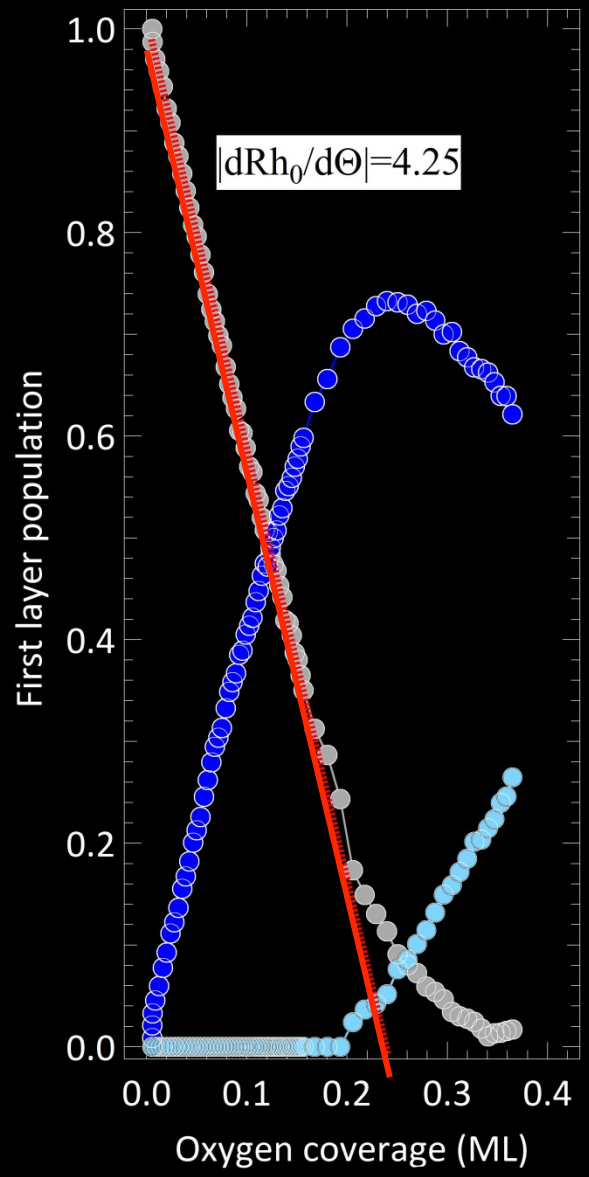


Rh-1O

Rh-2O

Atomic adsorption site determination





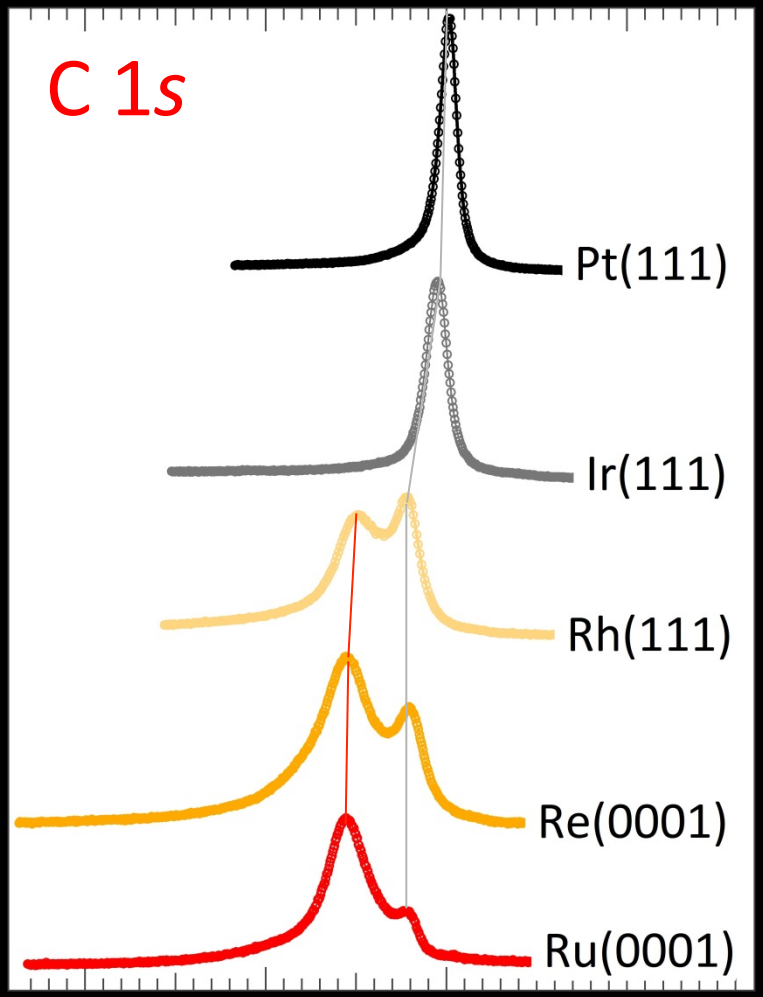
$$\frac{dRh_0}{d\Theta} = -4$$

four-fold hollow adsorption site

A. Baraldi *et al.,* Phys. Rev. Lett. **93**, 046101 (2004).

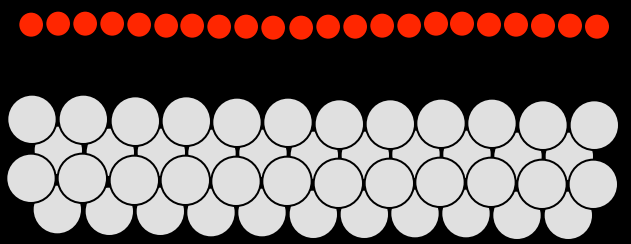
C1s core level shifts of epitaxial graphene

Elettra Sincrotrone Trieste

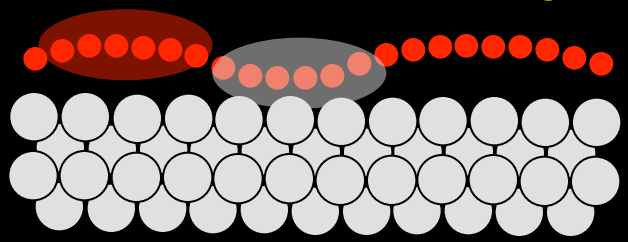


A correlation between
graphene-substrate bond strength
and
graphene corrugation

weak interaction



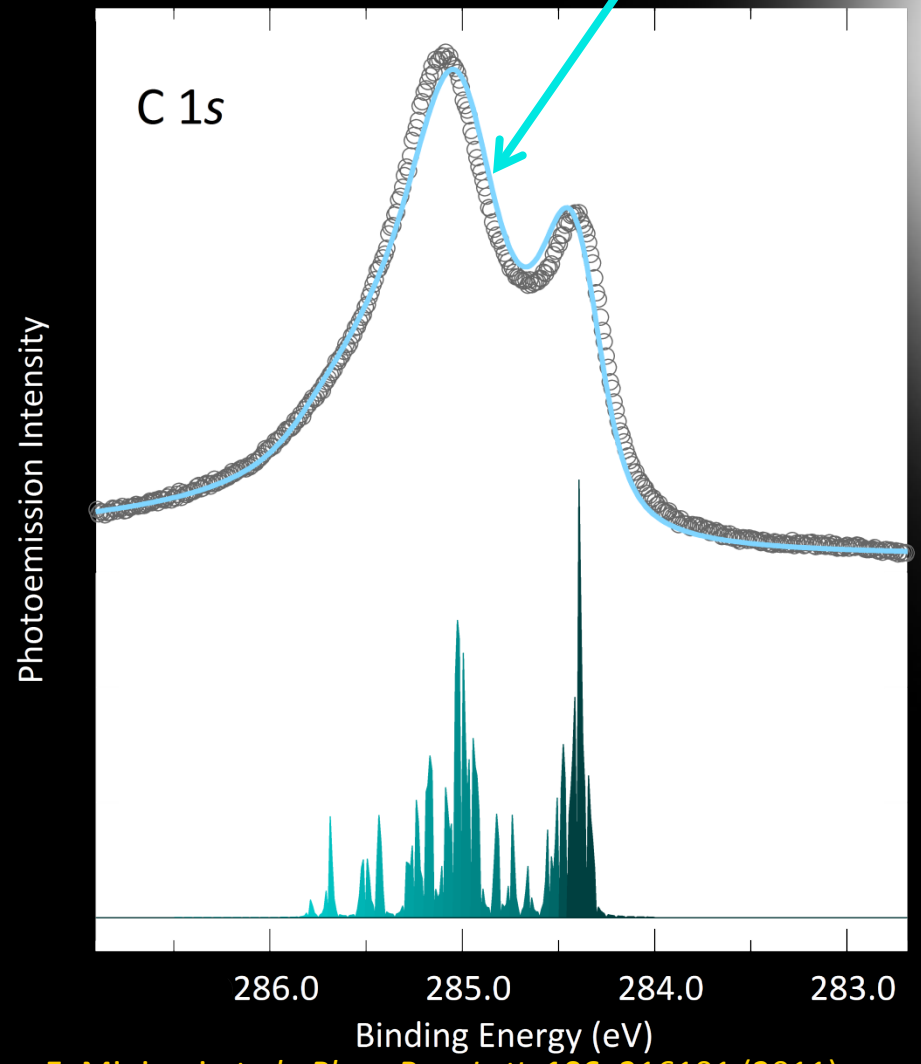
Strong chemical bond

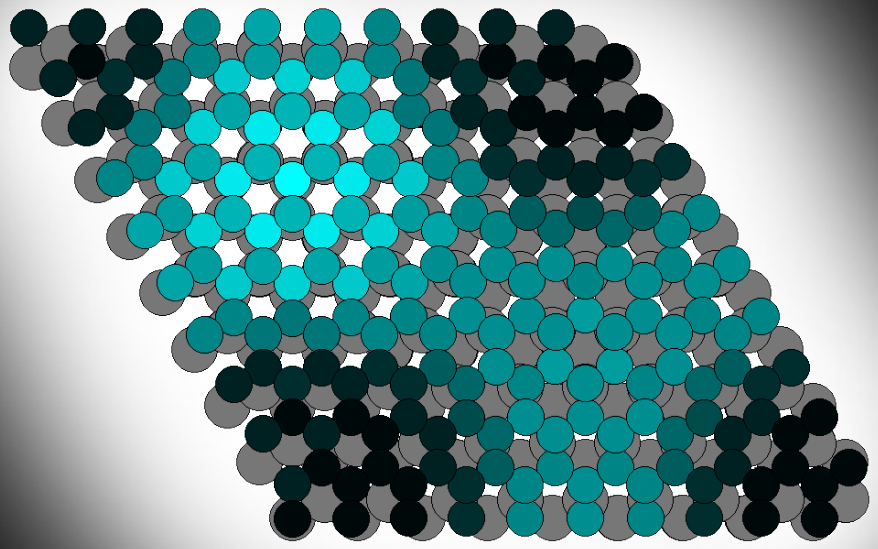


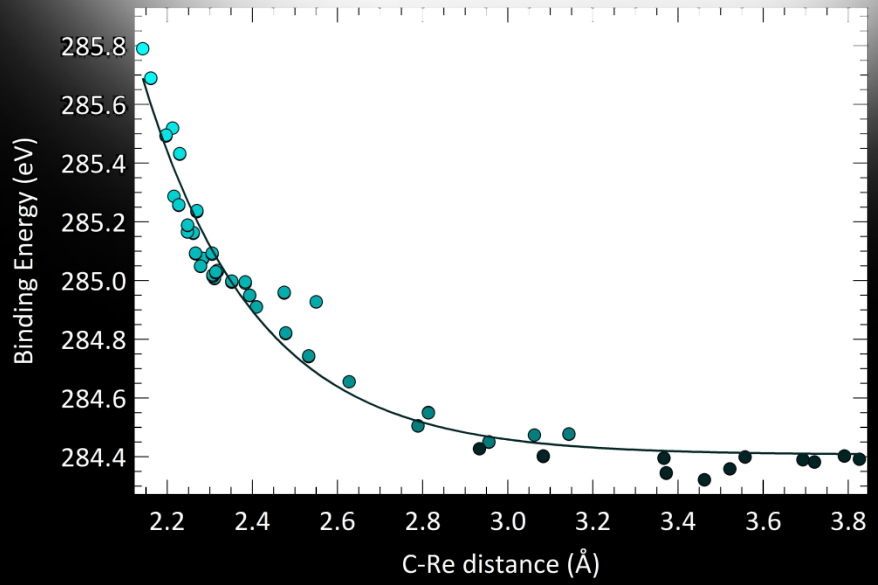
Why just two components?

Corrugation vs C1s binding energies

Simulated spectrum Gr/Re(0001)





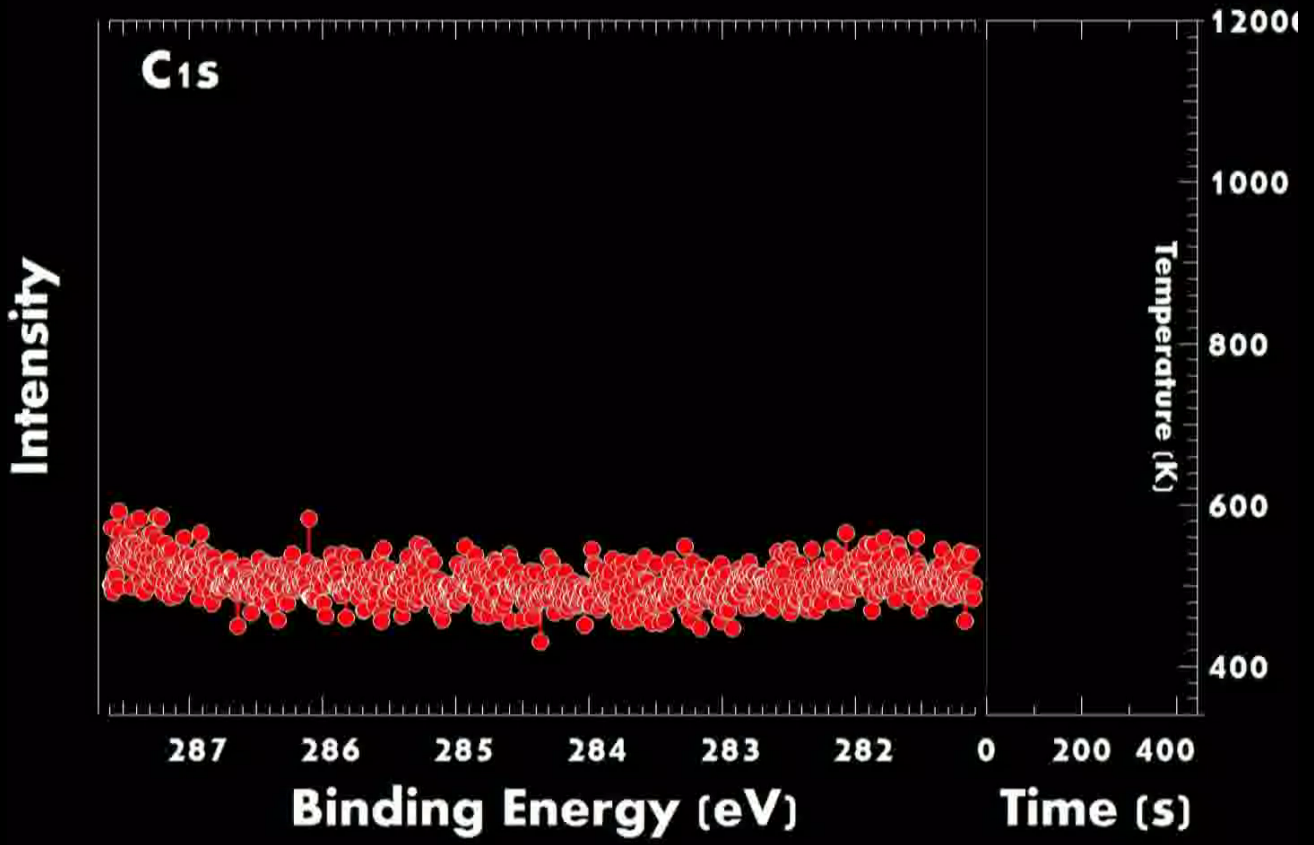


E. Miniussi *et al., Phys. Rev. Lett.* **106**, 216101 (2011).

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 C1s spectra taken during ethylene exposure and surface annealing to high temperature.

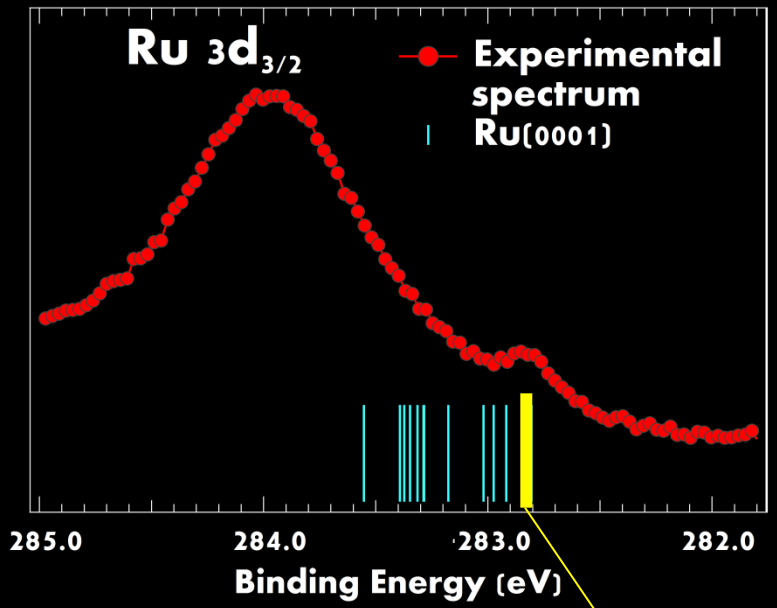


Growth mechanism on transition metals

Fast-data acquisition allows to monitor the C1s spectral evolution while dosing ethylene at high temperature.

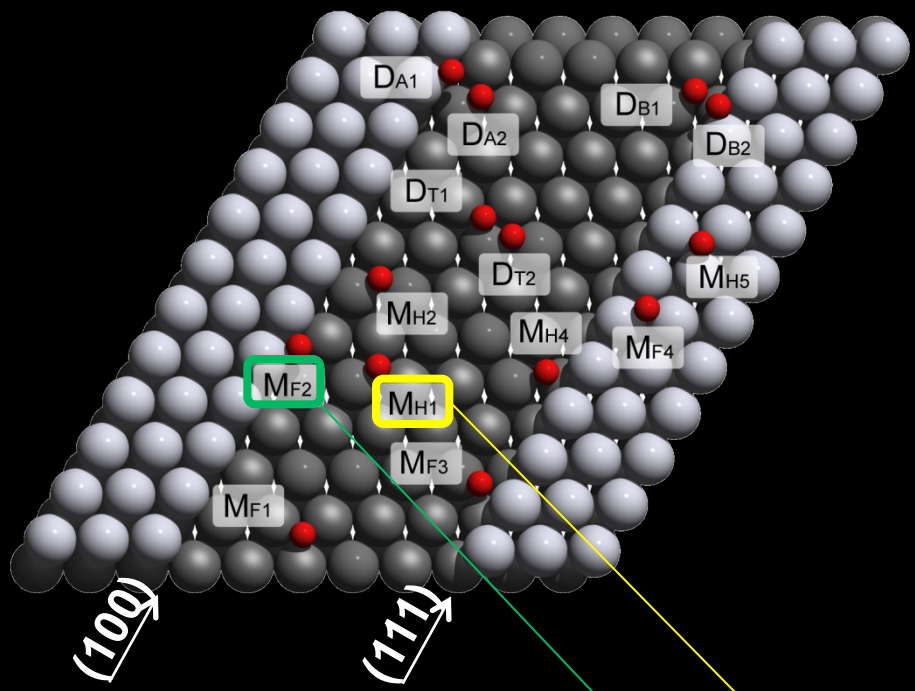
Gr/Ru(0001) using C_2H_4

The carbon lattice-gas: precursor to graphene formation



	E_b(eV)	C 1s(eV)
M_{H2}	7.53	283.02
M_{F2}	7.78	283.55
M_{H4}	7.31	282.97
M_{F3}	7.45	283.37
M_{H5}	7.38	282.89
M_{F4}	7.15	282.92
M_{F1}	6.98	282.89

	E_b(eV)	C 1s(eV)
M_{H1}	**7.67**	**282.82**
D_{A1}	15.78	283.14
D_{A2}		283.35
D_{T1}	14.73	283.28
D_{T2}		283.39
D_{B1}	15.52	283.29
D_{B2}		283.17



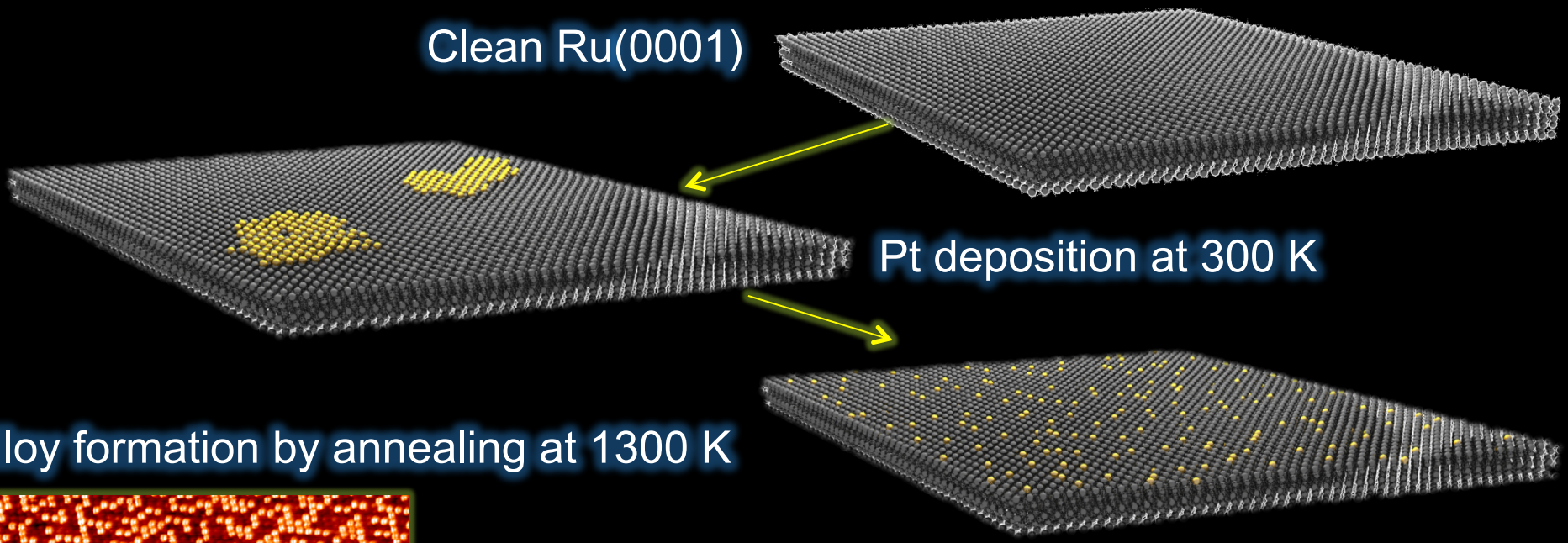
Three-fold hcp site on the terraces (MH1) and the C monomer at the steps (MF2) have very similar adsorption energies.

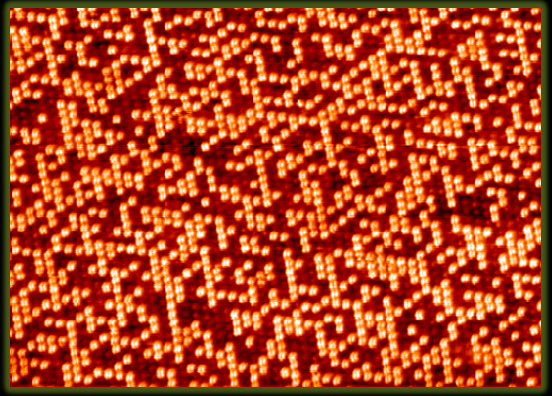
Monomers form a 2D lattice gas which supplies C atoms for GR growth

Fine-tuning of graphene-metal adhesion

Elettra Sincrotrone Trieste

Graphene on PtRu/Ru(0001) bimetallic surface alloys



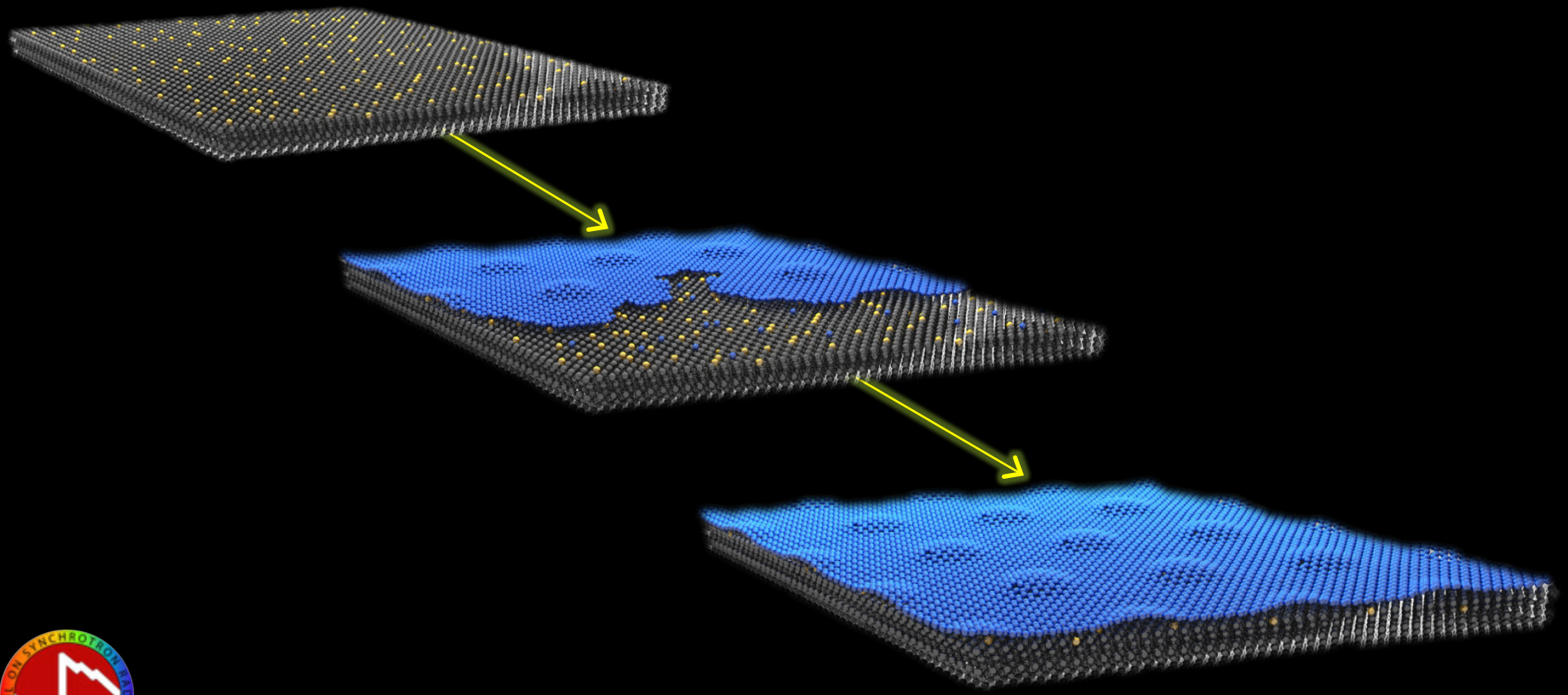


Previous STM studies: Pt atoms confined in the first layer and randomly distributed.

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

Fine-tuning of graphene-metal adhesion

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



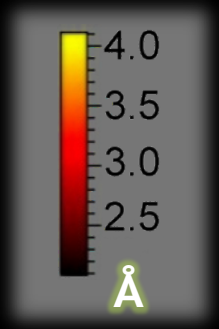
Fine-tuning of graphene-metal adhesion

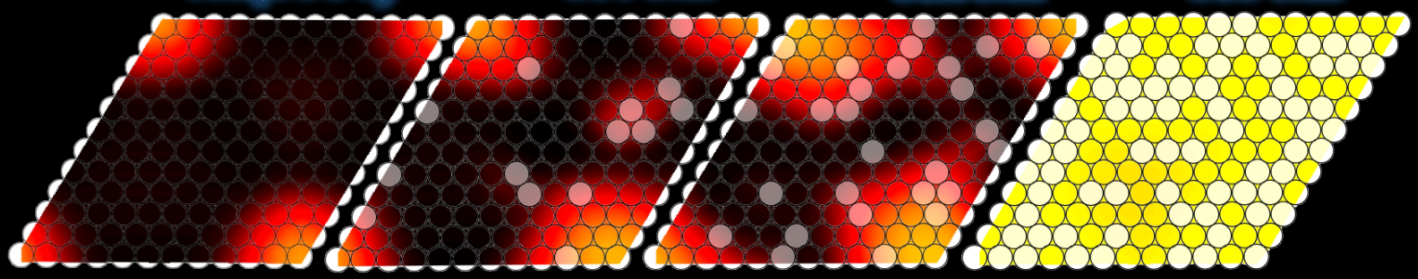
Elettra Sincrotrone Trieste

Comparison with DFT simulations

Ru(0001) 0.1 ML 0.2 ML 0.5 ML

C-substrate distance



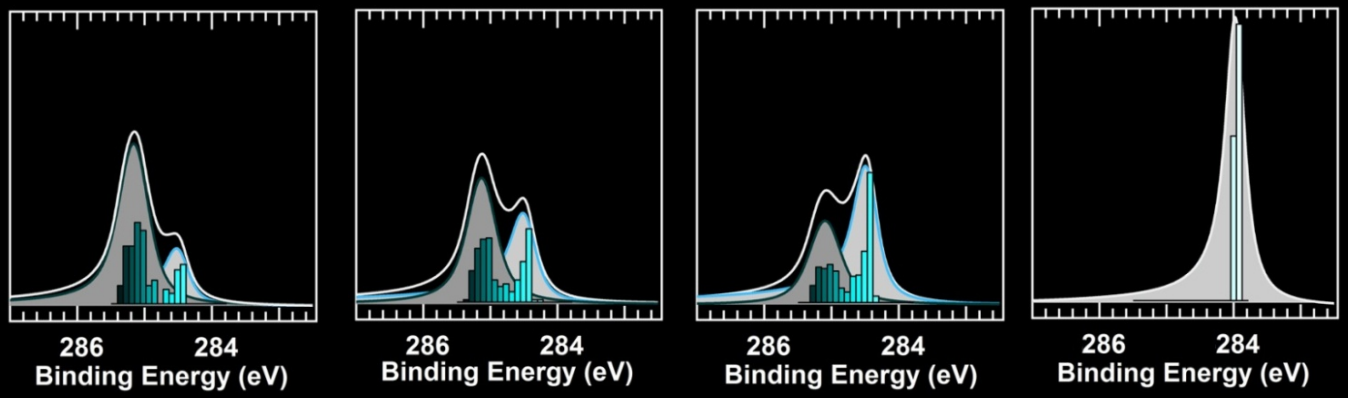


Pt concentration

C-substrate distance

GR corrugation

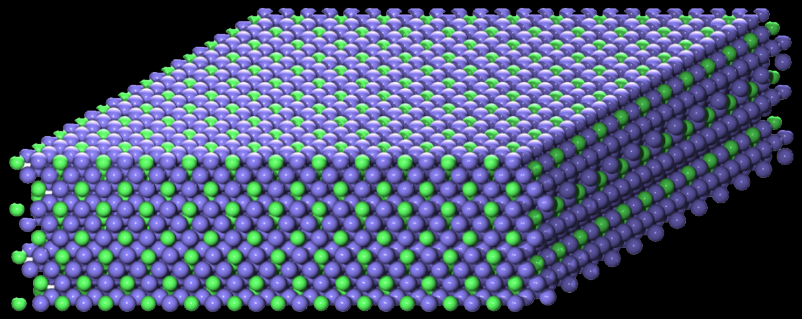
Simulated C1s spectra



Graphene on dielectrics

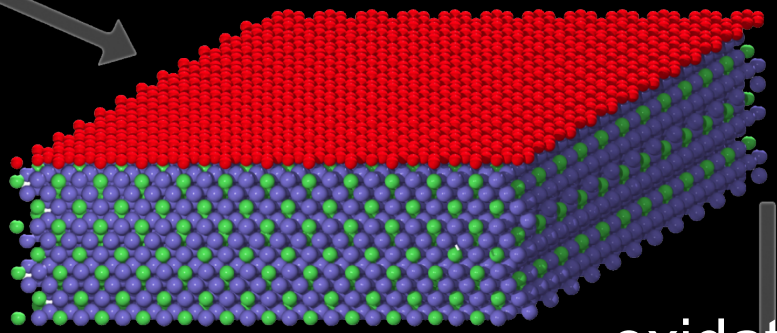
Elettra Sincrotrone Trieste

$Ni_3Al(111)$



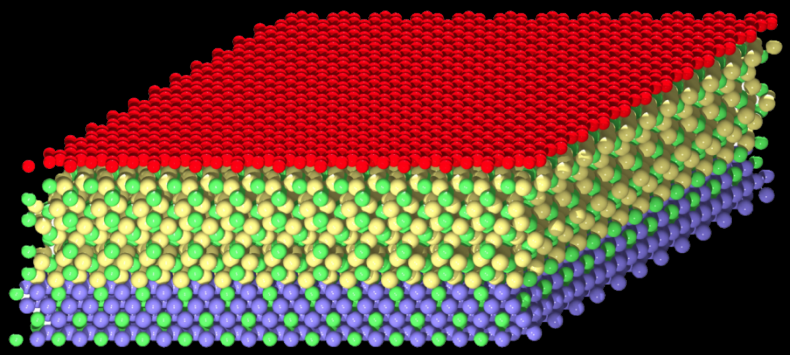
CVD

$GR\text{-}Ni_3Al(111)$



oxidation

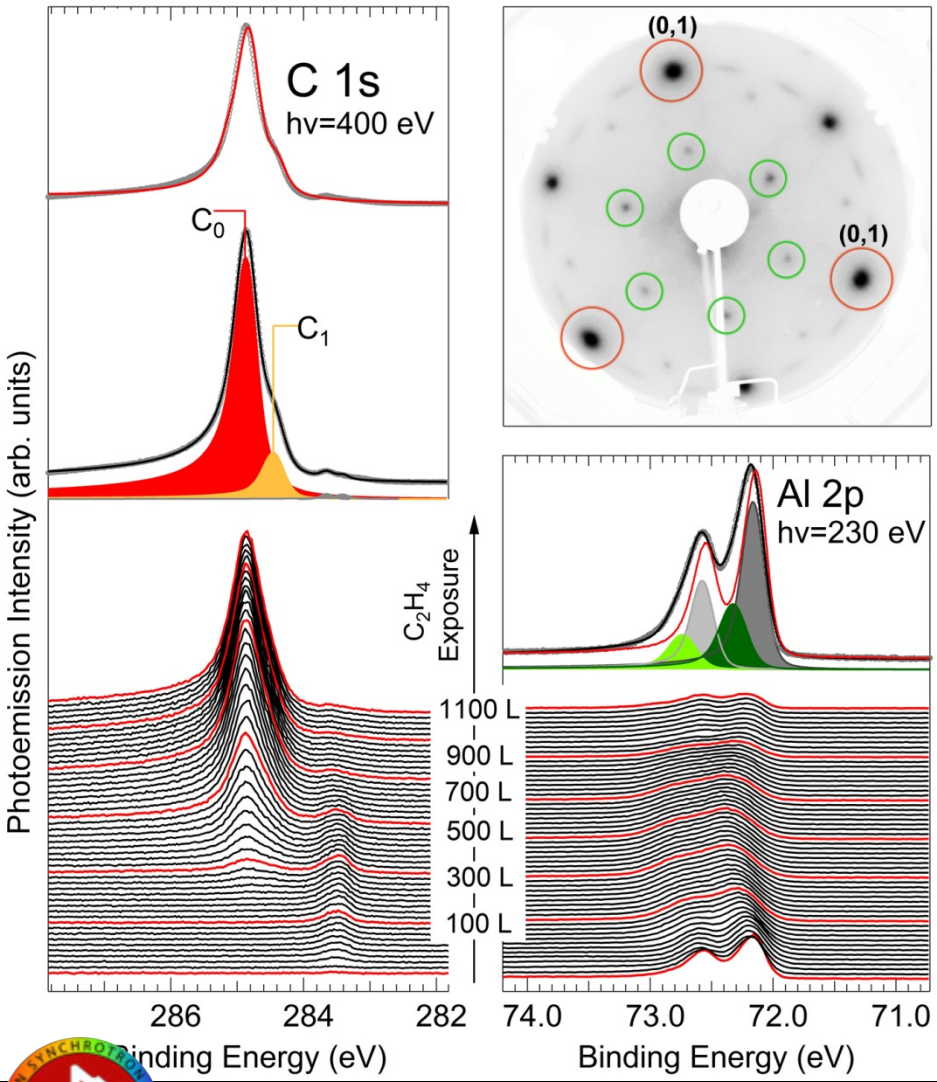
GR/Al_2O_3

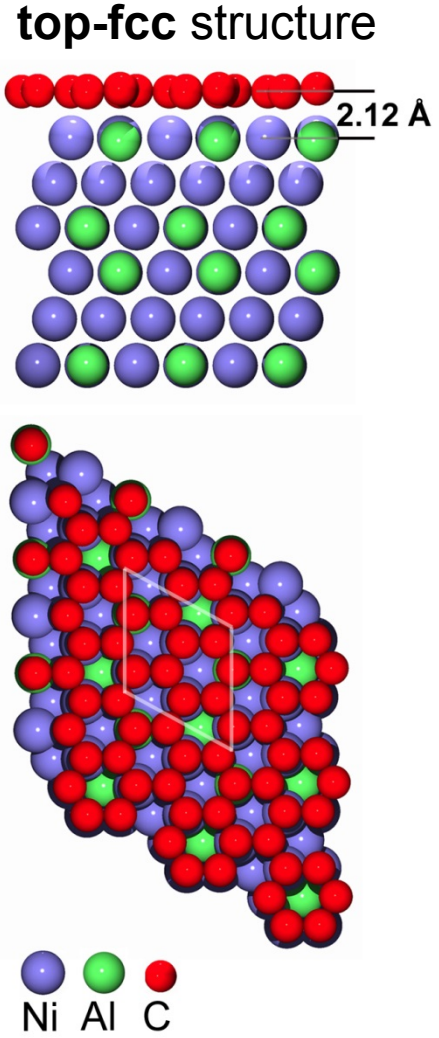


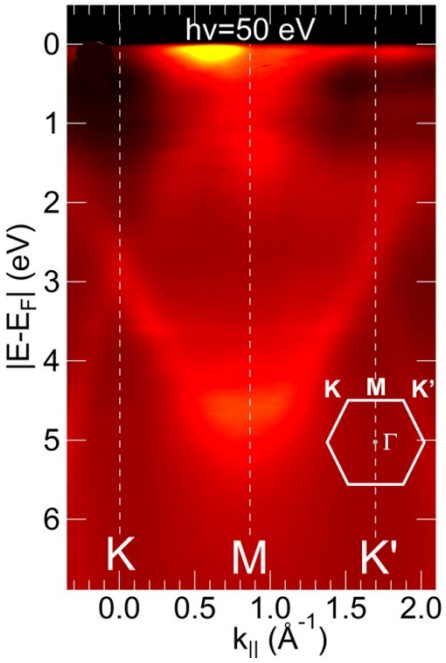
- Nickel
- Aluminum
- Carbon
- Oxygen

Selective oxidation of the Al atoms and in the formation of a 1.5 nm thick alumina nanosheet underneath graphene.

Graphene on $Ni_3Al(111)$

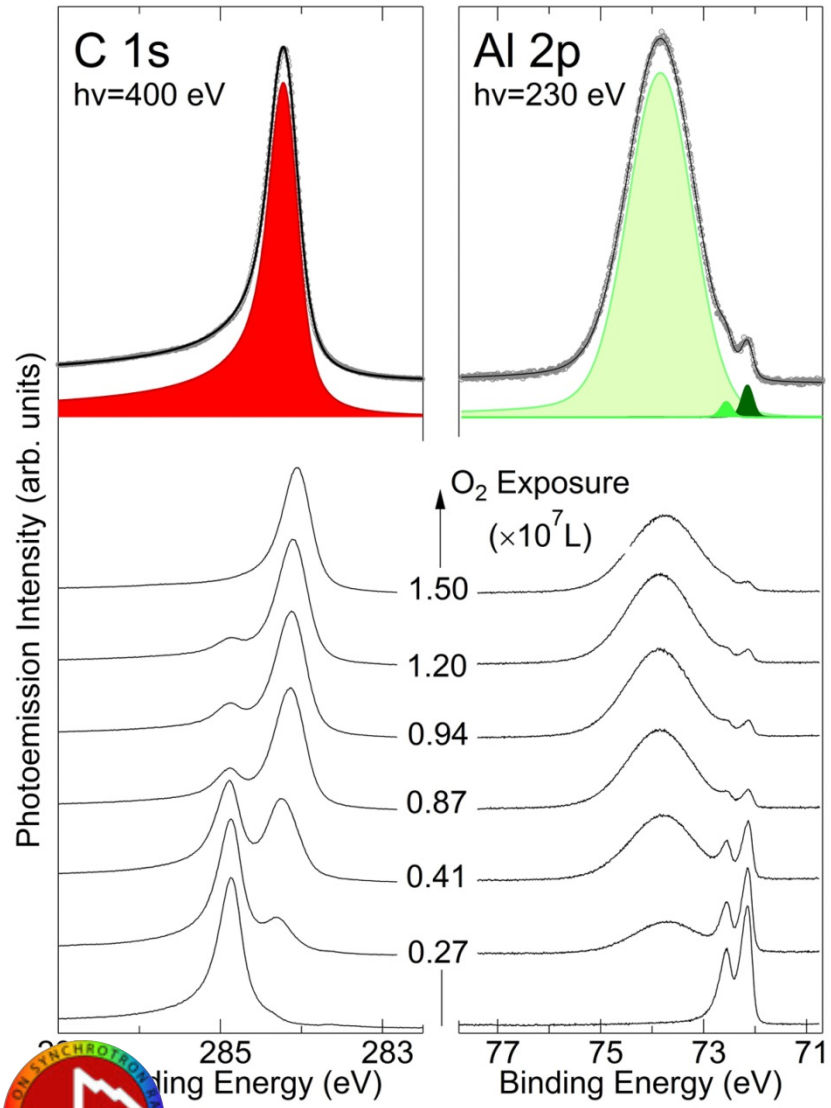


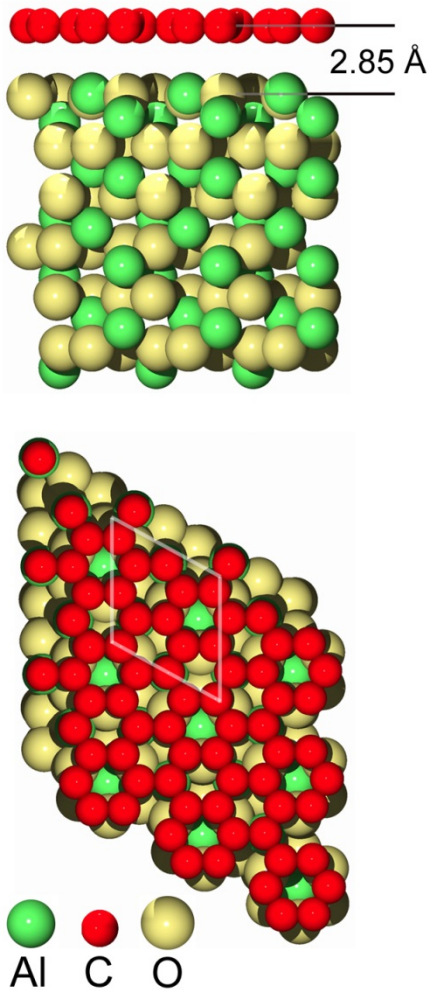


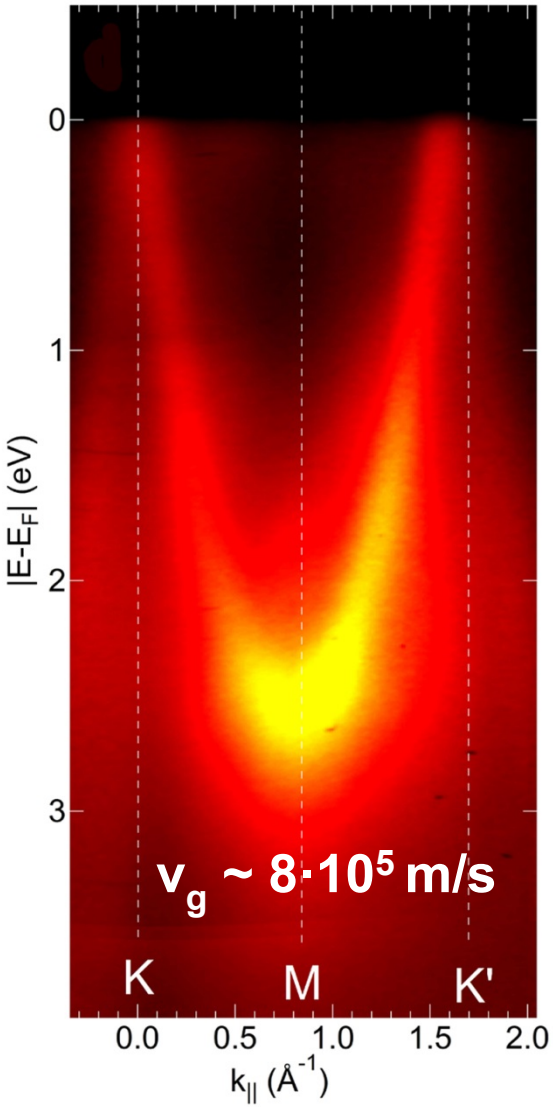


Due to the interaction with the substrate, the GR band dispersion is strongly modified

Graphene on ultra-thin alumina layer



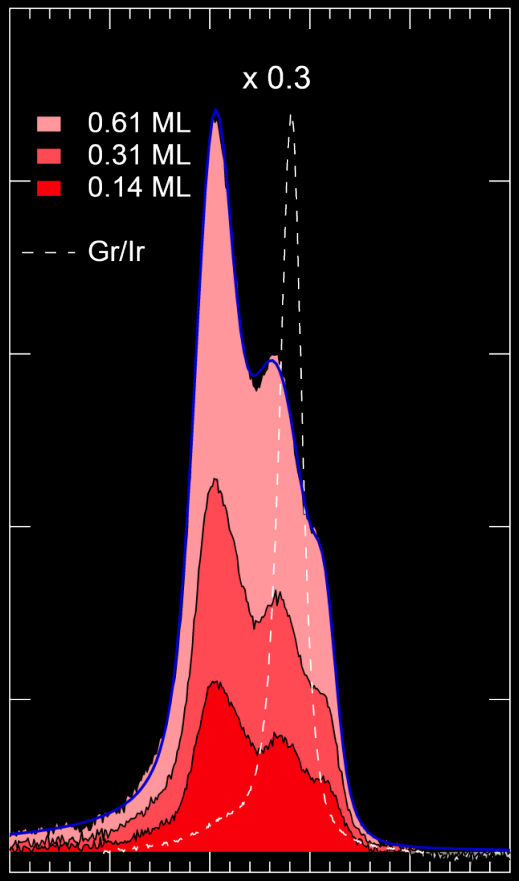


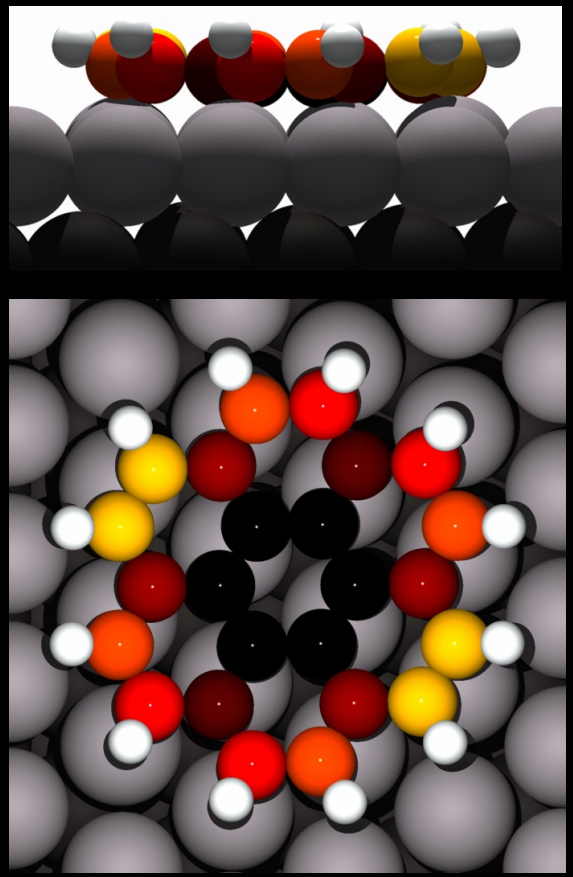


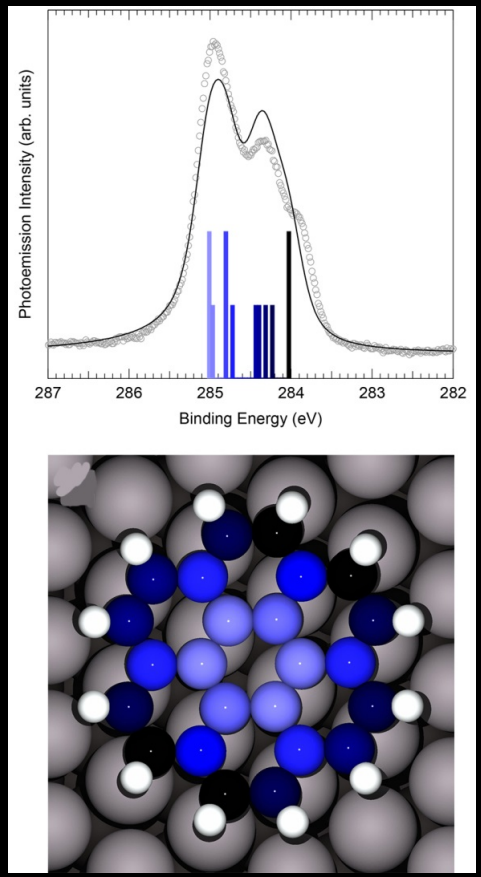
Graphene formation via polycyclic hydrocarbon dehydrogenation

Elettra Sincrotrone Trieste

C1s core level of adsorbed coronene on Ir(111)

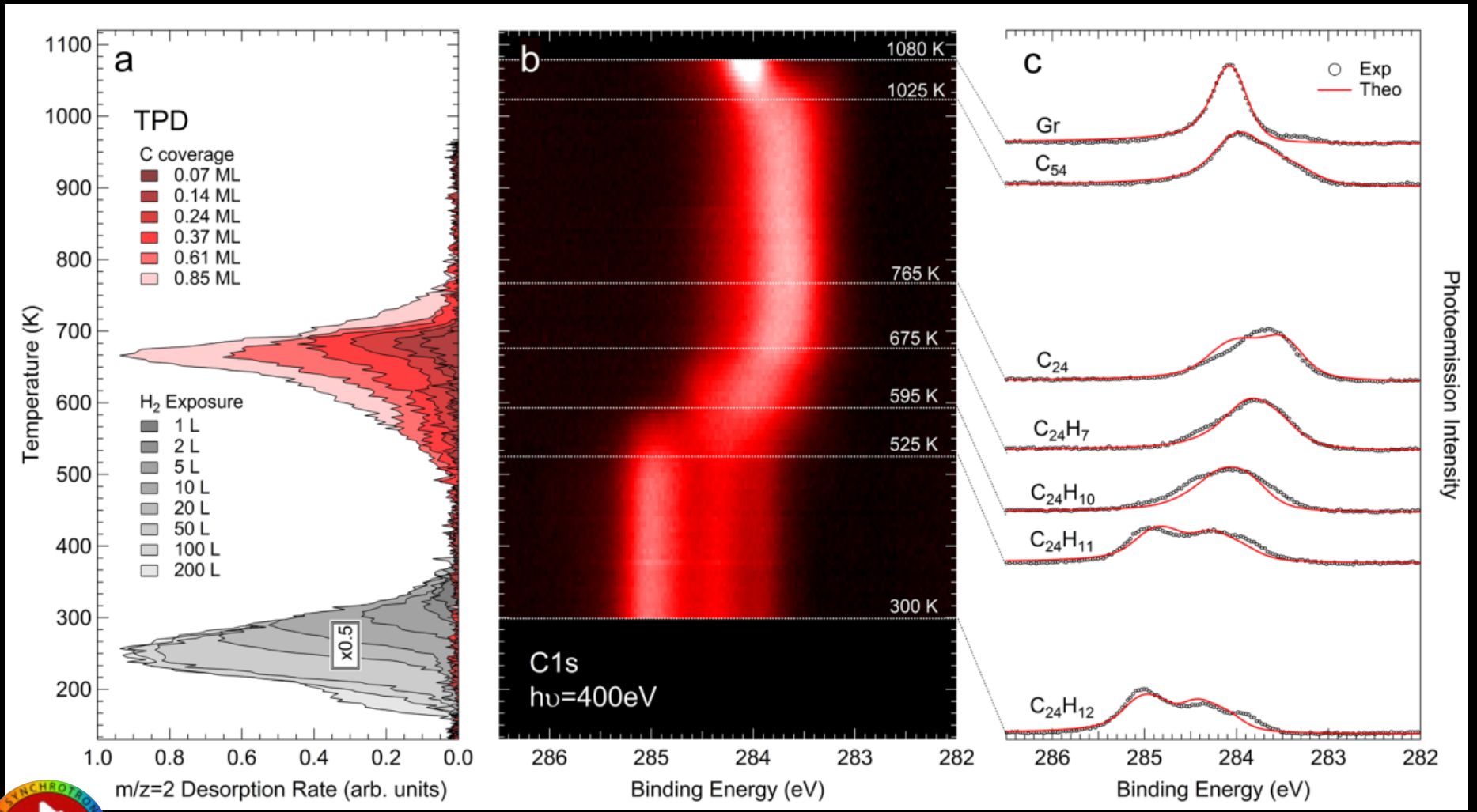






D. Curcio *et al.*, *JACS* **138**, 3395 (2016).

Graphene formation via polycyclic hydrocarbon dehydrogenation



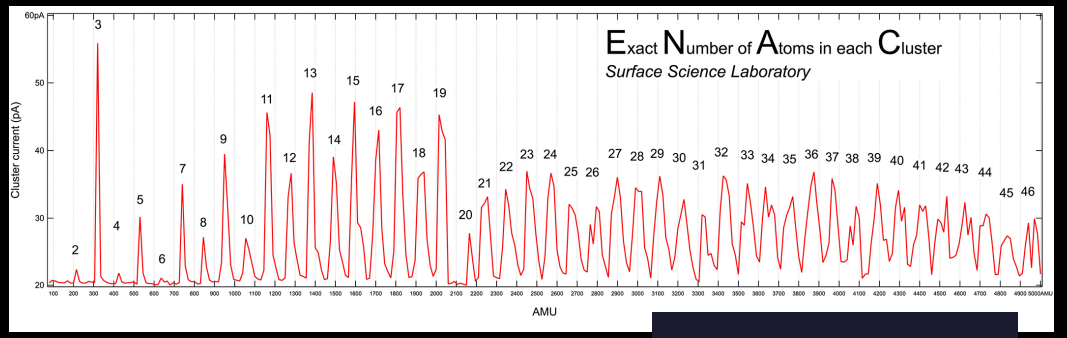
D. Curcio *et al.*, *JACS* **138**, 3395 (2016).

Graphene formation via polycyclic hydrocarbon dehydrogenation

D. Curcio *et al.*, *JACS* **138**, 3395 (2016).

A glimpse to the future

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



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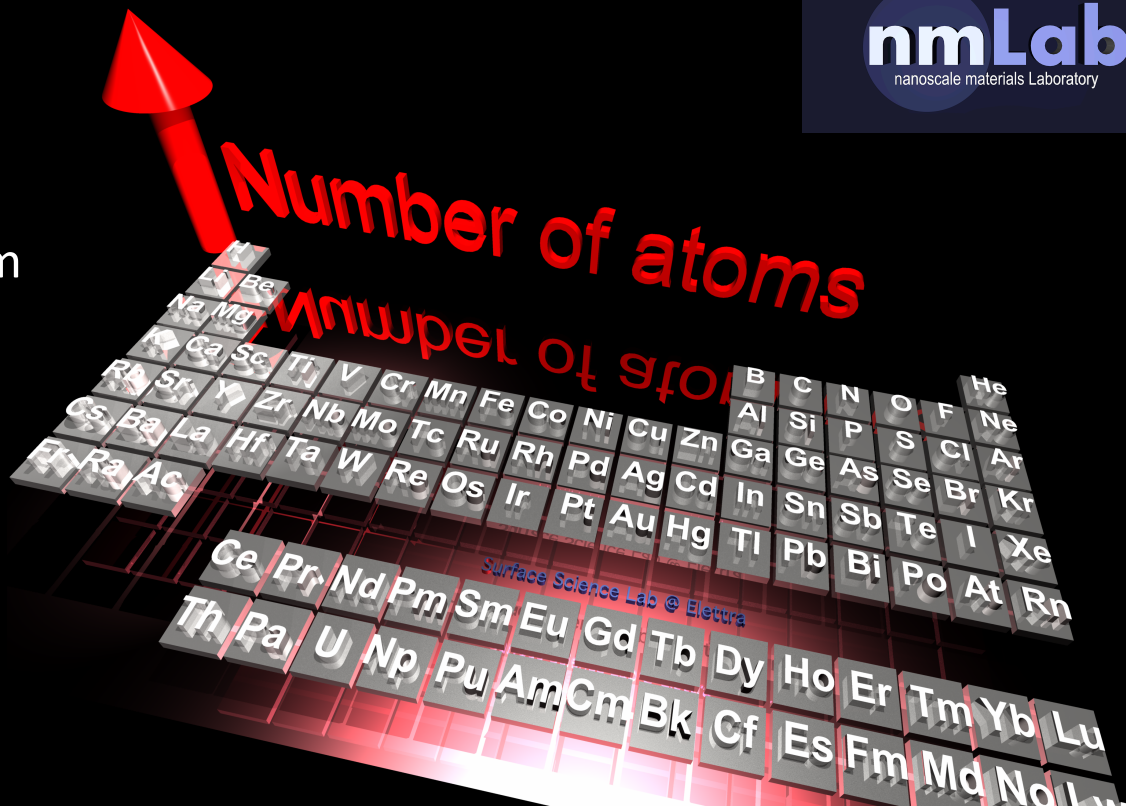
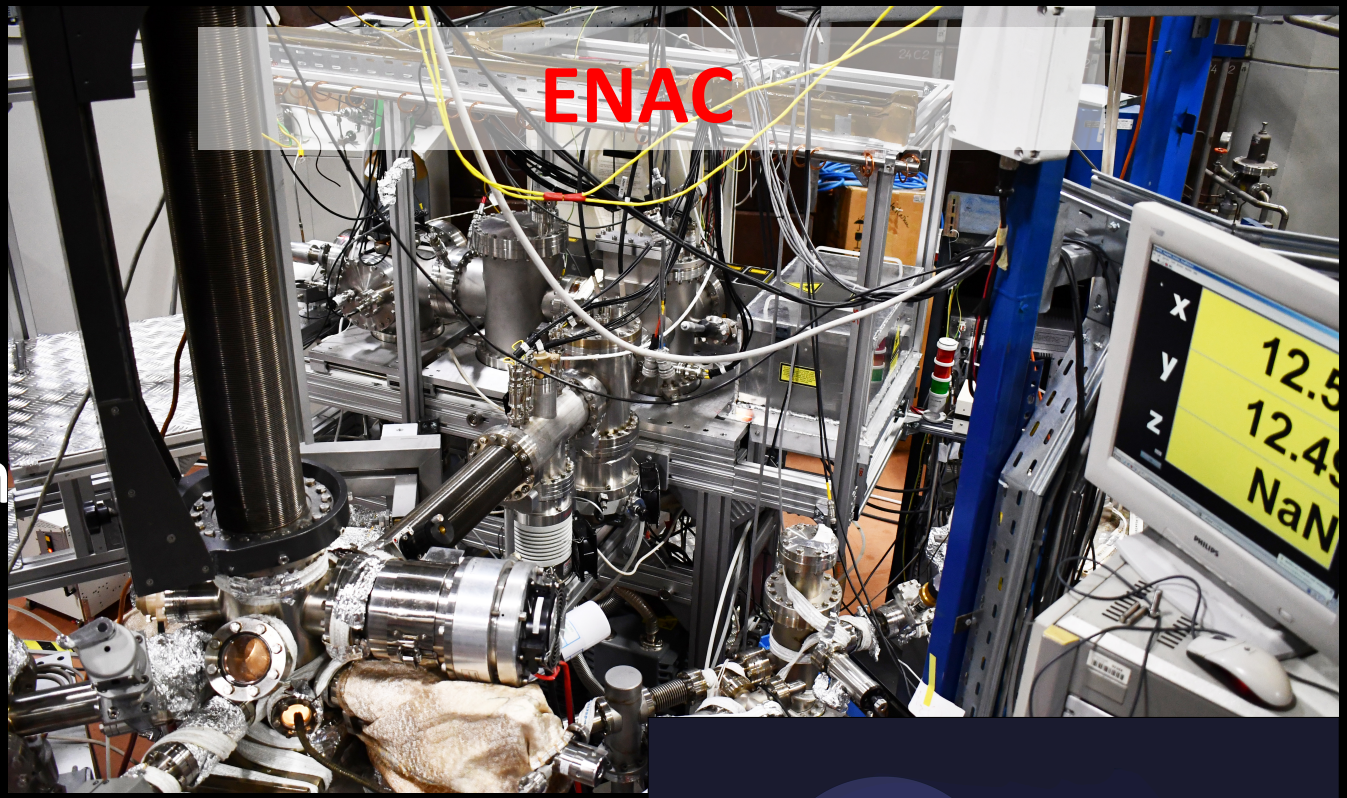
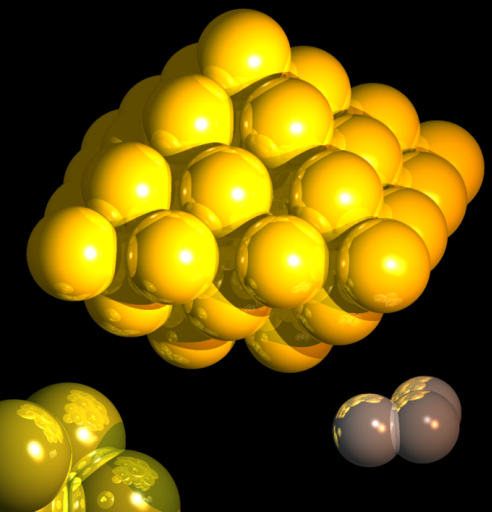
The goal of our research team will be to understand how structural, electronic and chemical properties evolve atom by atom, from the monomer to the bulk.



Size-selected cluster source

Exact
Number of
Atoms in each
Cluster





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For any question do not hestitate to contact me:

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