From traditional photoemission to laser photoemission: disclosing novel phenomena in the time domain at surfaces and interfaces

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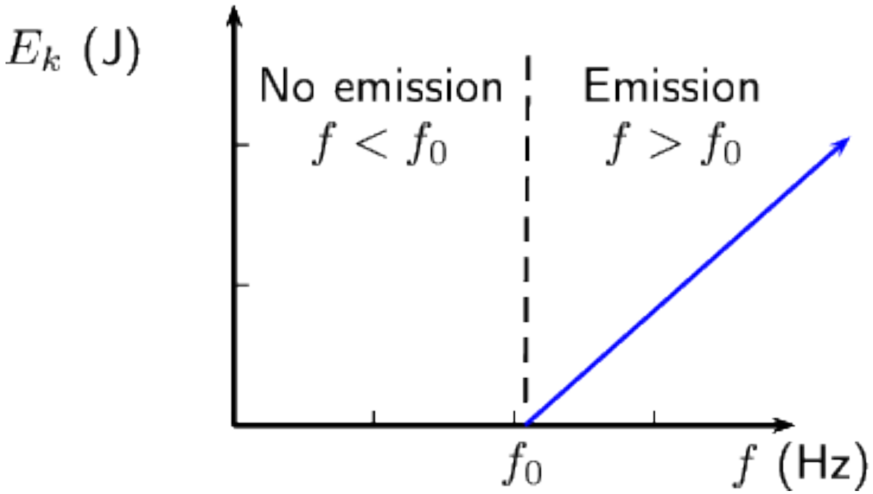
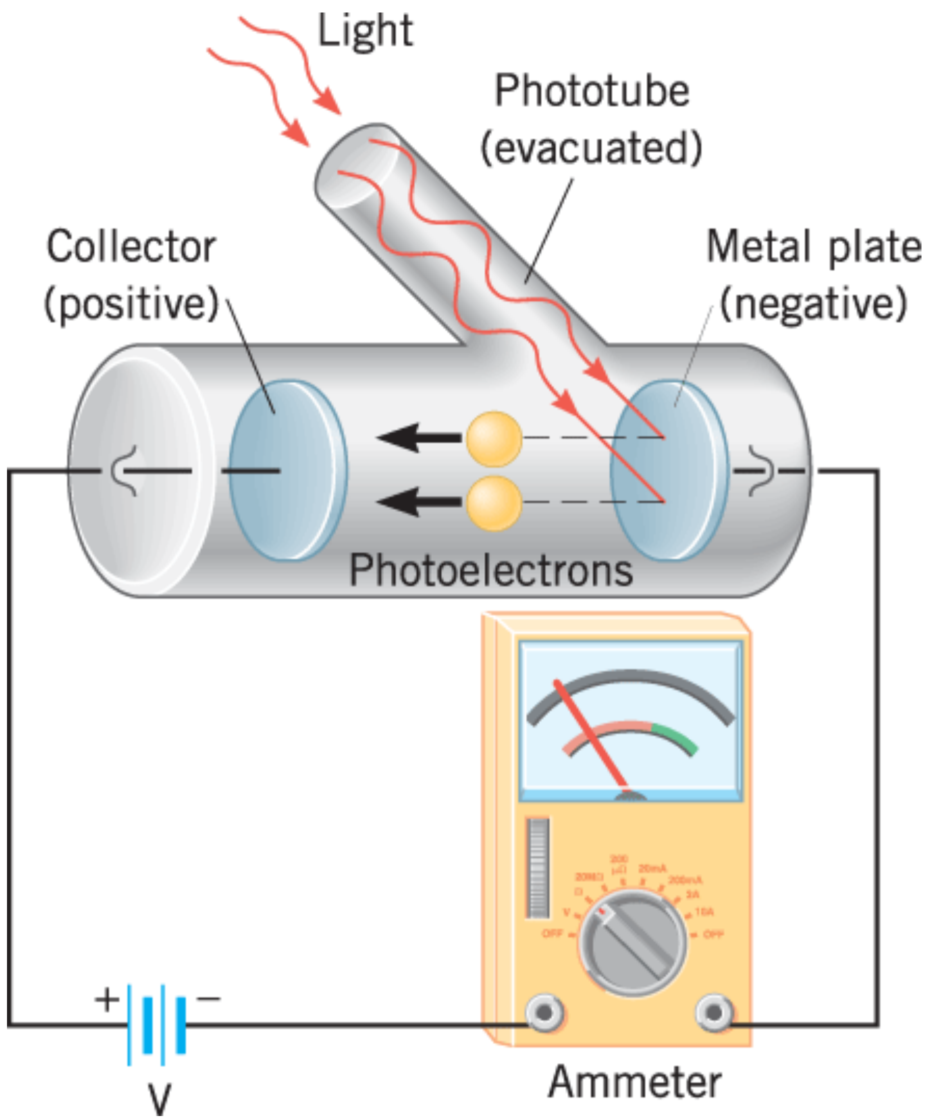
Interdisciplinary Laboratories for Advanced Materials Physics (i-Lamp)

December, 2017

Hertz 1887


E_k (J)
No emission
$f < f_0$
Emission
$f > f_0$
f_0
f (Hz)


Light
Phototube
(evacuated)
Collector
(positive)
Metal plate
(negative)
Photoelectrons
Ammeter
+
−
V

A. Einstein

$$E_{kin} = h\nu - \Phi$$

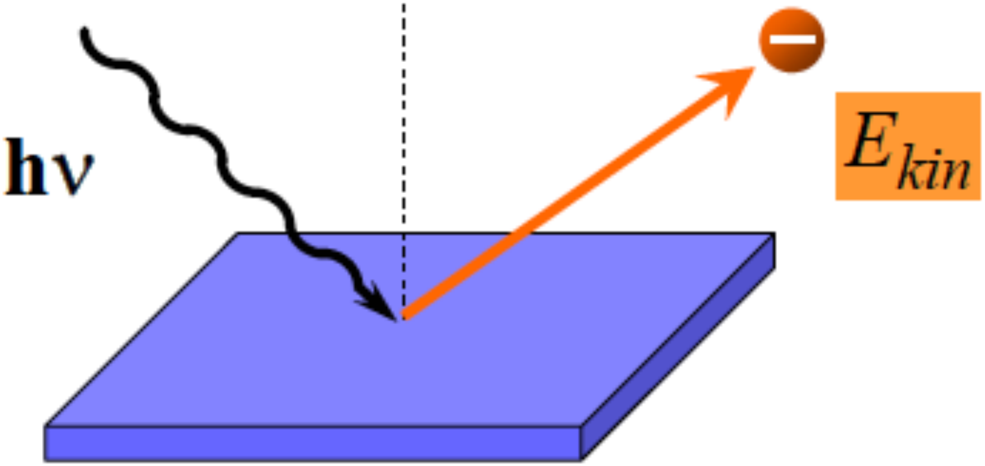
Theoretical explanation by A. Einstein (1905):

QUANTIZATION OF LIGHT

Ann. d. Phys. 17, 132 (1905):

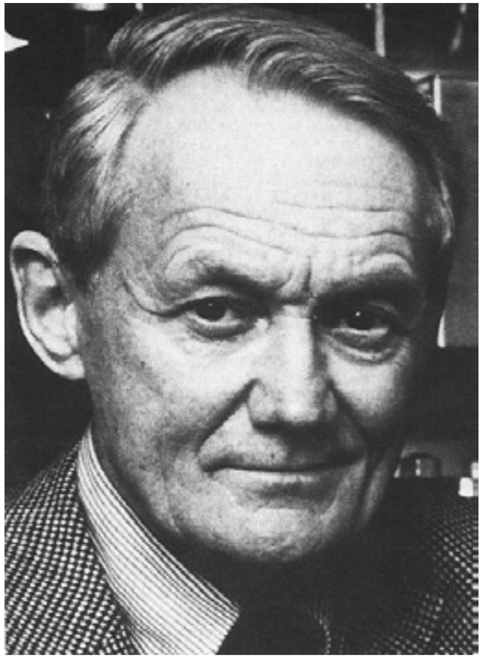
Die kinetische Energie solcher Elektronen ist

$$\frac{R}{N}\beta\nu - P.$$



Photoelectric effect

Einstein, Nobel Prize 1921



K.M. Siegbahn

Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

WE have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method

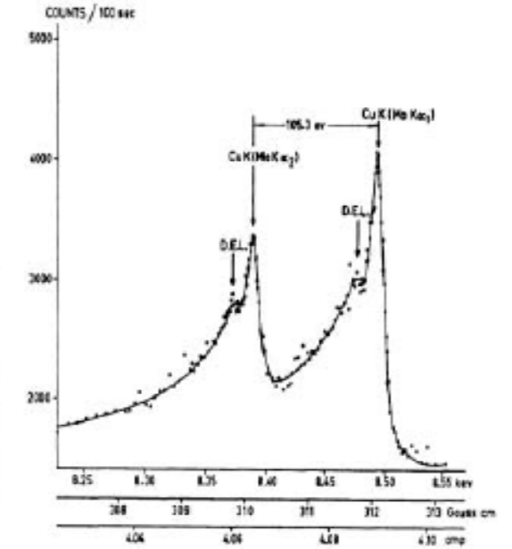
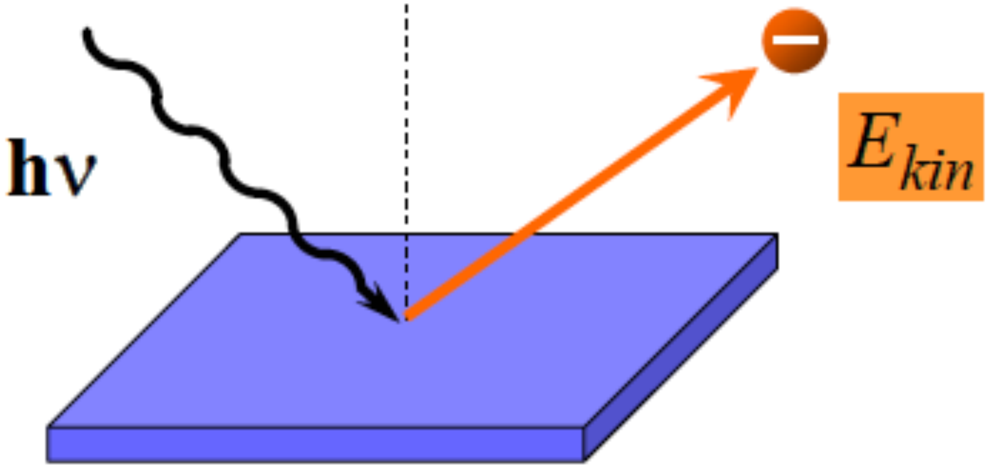


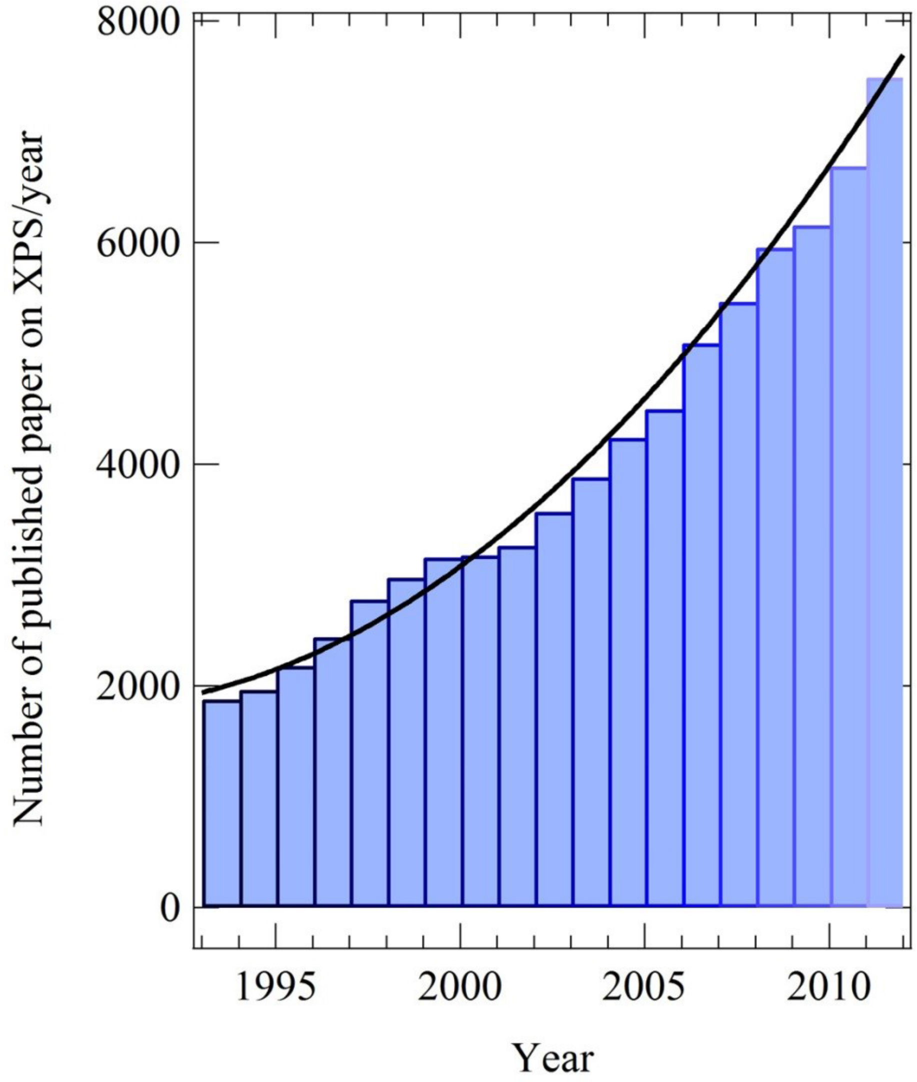
FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

Photoemission as an analytical tool
Kai Siegbahn, Nobel Prize 1981



Photoemission is one of the most widely employed experimental techniques

Number of papers published in the last twenty years in peer-review international
scientific journals on X-ray Photoelectron Spectroscopy,
according to the
Thomson Reuters ISI Web of KnowledgeR .



After thirty years

Home > Review of Scientific Instruments > Volume 59, Issue 9 > 10.1063/1.1140055

Published Online: June 1998 Accepted: May 1988

Novel system for picosecond photoemission spectroscopy

Review of Scientific Instruments **59**, 1941 (1988); https://doi.org/10.1063/1.1140055

R. Haight, J. A. Silberman, *and* M. I. Lilie

Femtosecond Laser Interaction with Metallic Tungsten and Nonequilibrium Electron and Lattice Temperatures

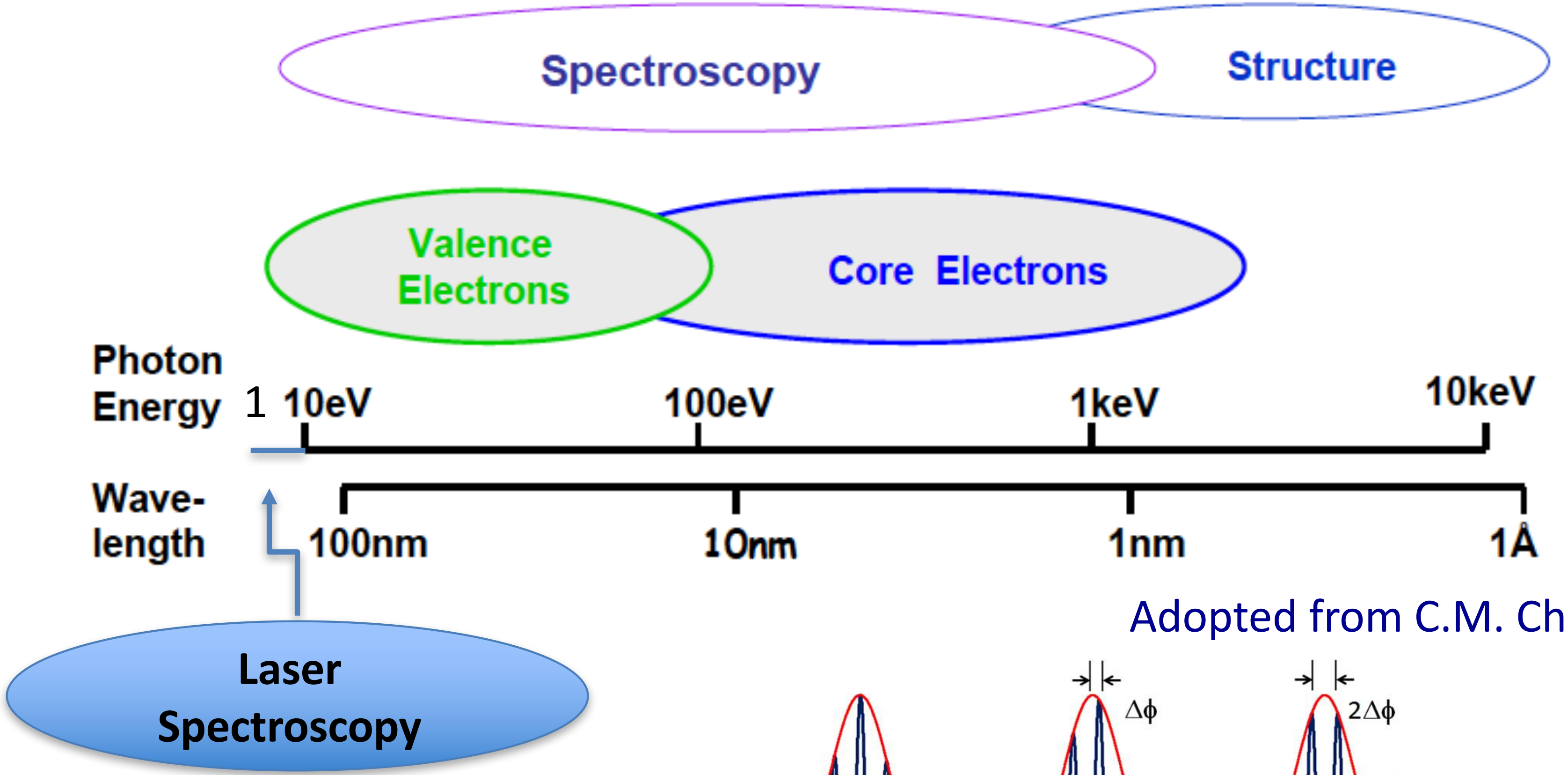
J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen
Phys. Rev. Lett. **53**, 1837 – Published 5 November 1984

Time-Resolved Coherent Photoelectron Spectroscopy of Quantized Electronic States on Metal Surfaces

U. Höfer*, I. L. Shumay, Ch. Reuß, U. Thomann, W. Wallauer, Th. Fauster

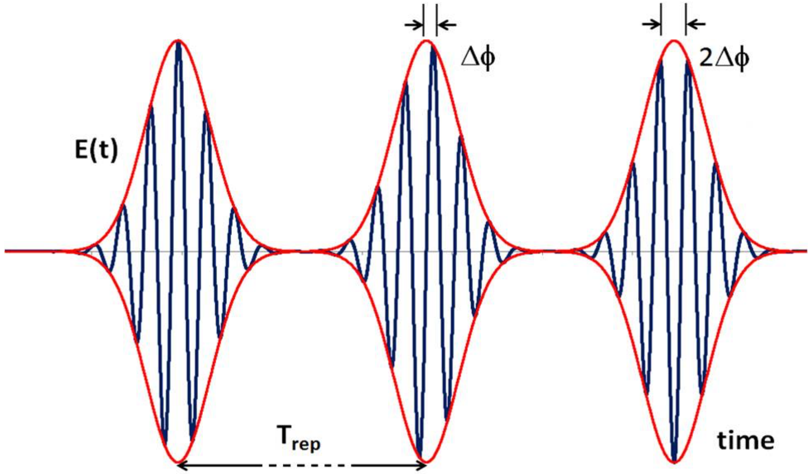
December, 2017

Science with Light Sources

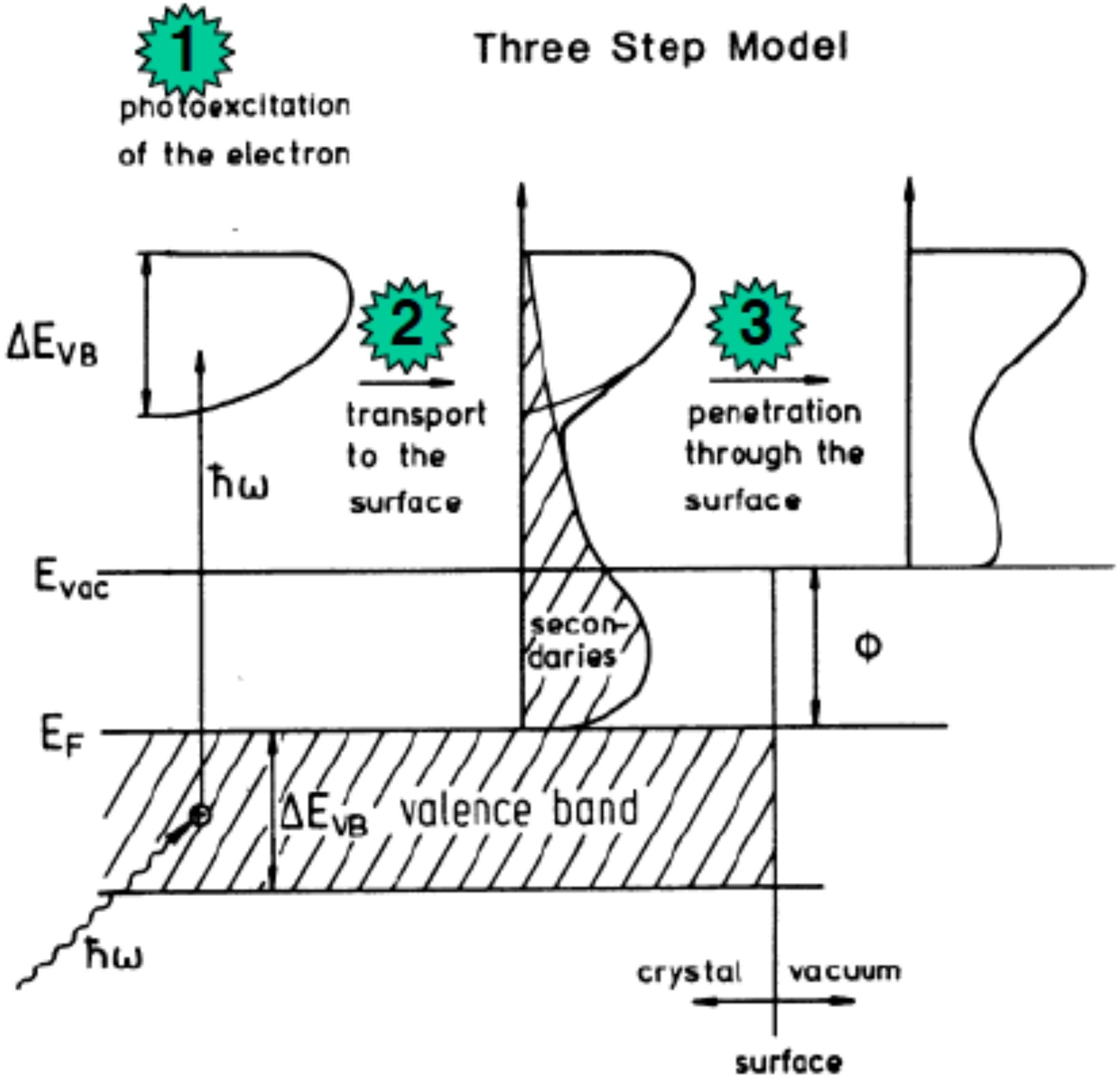


Adopted from C.M. Cheng

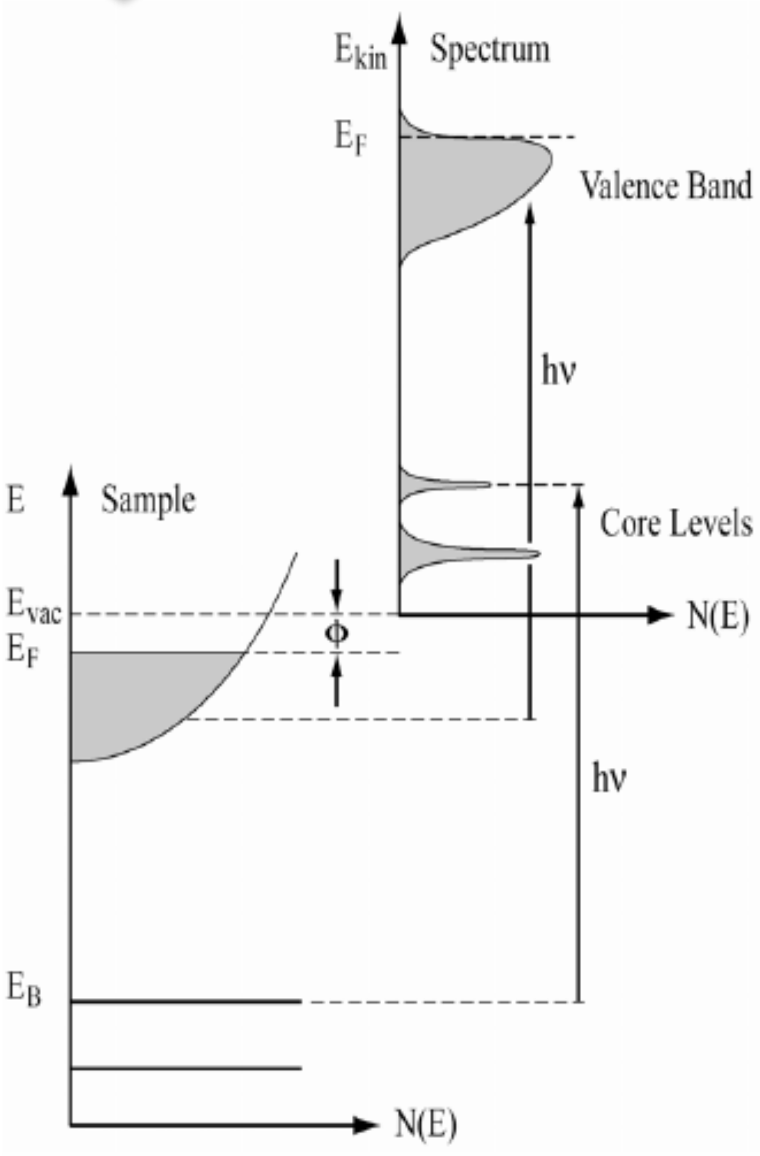
Laser photon energy
Laser timewidth
Laser Rep. Rate
Laser fluence



Three Step Model



1 Photoexcitation processess



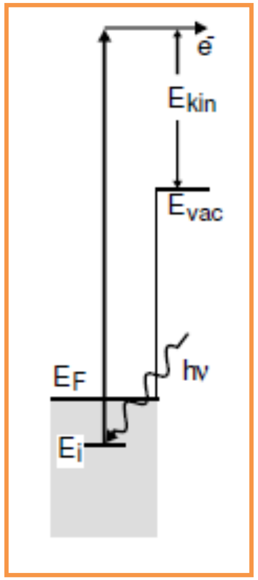
Energy Conservation

$$E_{kin} = \hbar\omega - \Phi - |E_B|$$

- E_{kin}: Measured Kinetic Energy
- $\hbar\omega$: Measureed Photon Energy
- Φ: Measured Work Function
- $|E_B|$: Electron Binding Energy

LINEAR PHOTOEMISSION

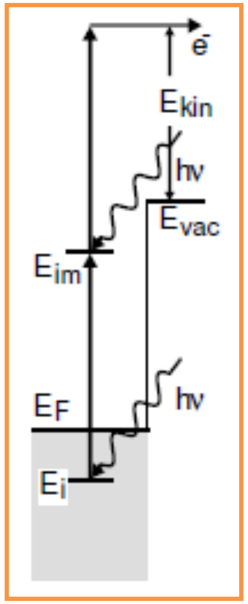
(hν > Φ)



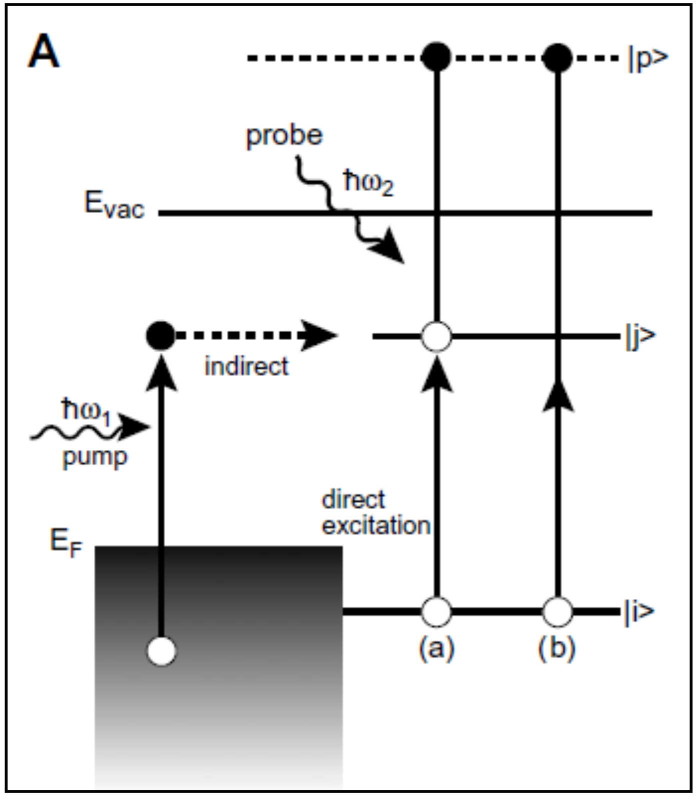
OCCUPIED STATES

NON- LINEAR PHOTOEMISSION

(hν < Φ)



OCCUPIED AND UNOCCUPIED STATES

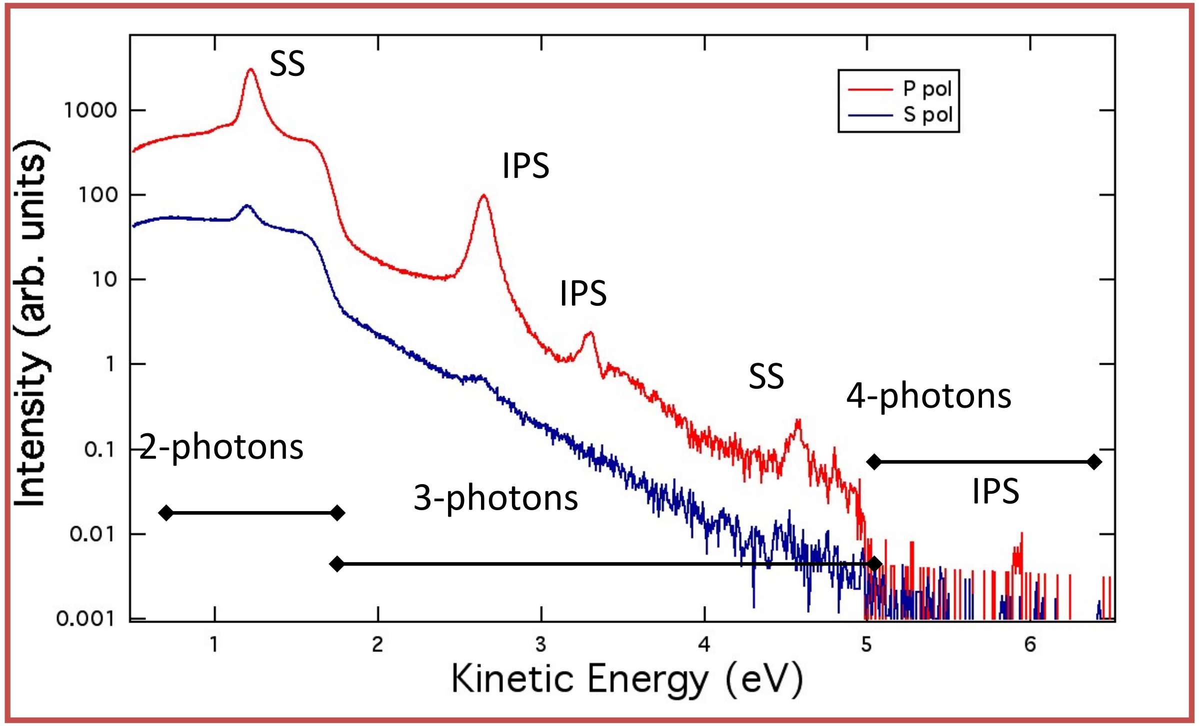


T. Fauster, Electromagnetic Waves: Recent Developments in Research 2, 347 (1995).

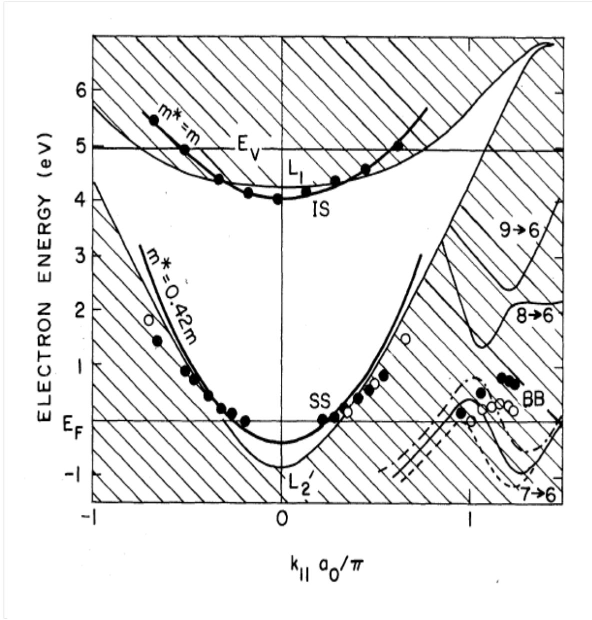
(a) Step-by-step one-photon process (direct or indirect excitation);

(b) Coherent two-photon or more processes;

Non-linear photoemission on Cu (111)



$h\nu$=3.14 eV < Φ



For Coherent two or more photon processes, the energy conservation:

$$E_K = n\, h\nu - |E_B| - \Phi$$

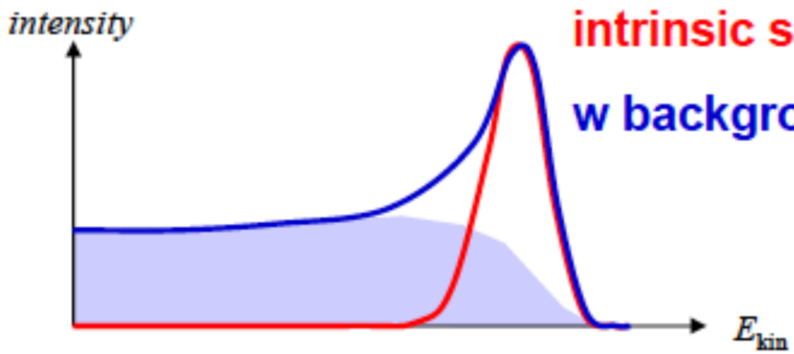
Pagliara et al. Surf. Science 2008
Pagliara et al. Surf. Science 2006
Ferrini, ..Pagliara,..PRL 2004
Banfi,…Pagliara,…PRL 2005

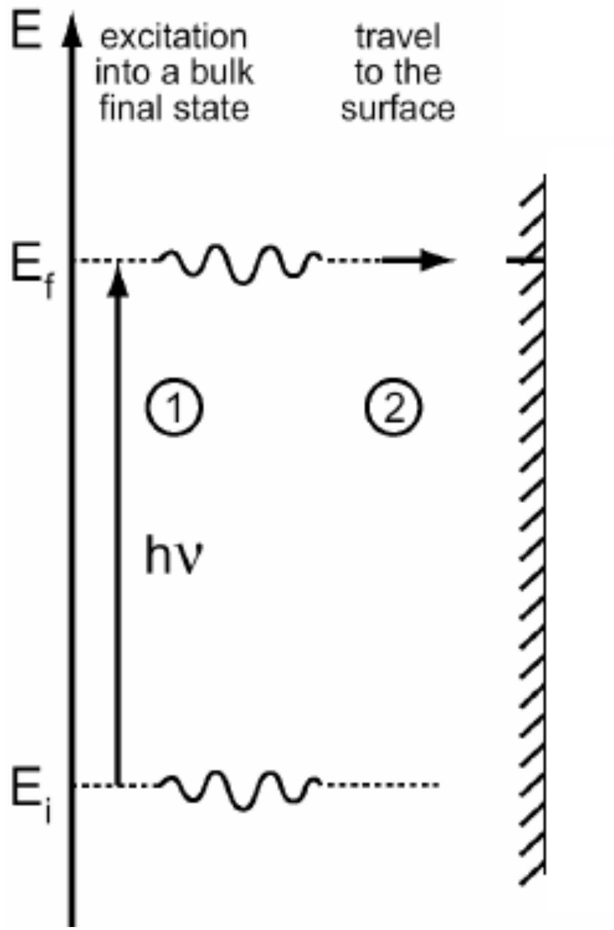
2 Transport to the surface

Inelastic scattering of the excited electrons with:

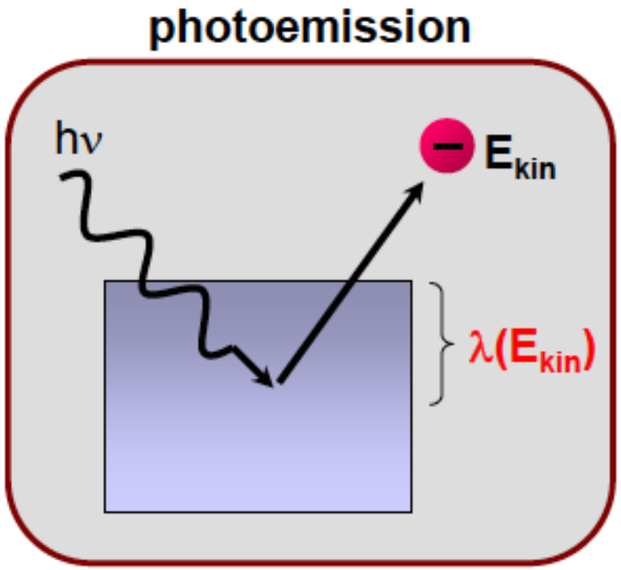
- Other electrons
- Phonons

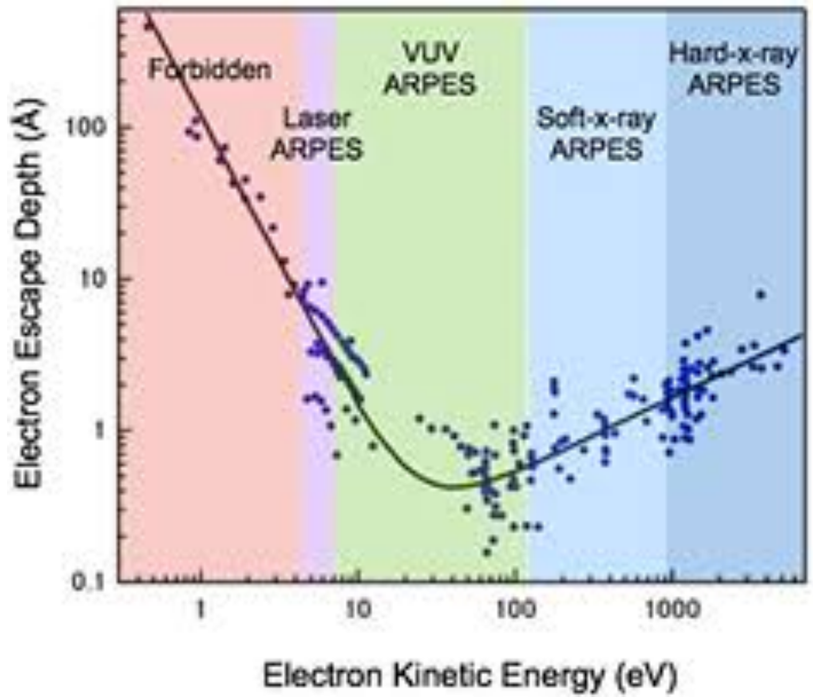
GENERATION OF SECONDARY ELECTRONS





Mean free path and photoemission probing depth



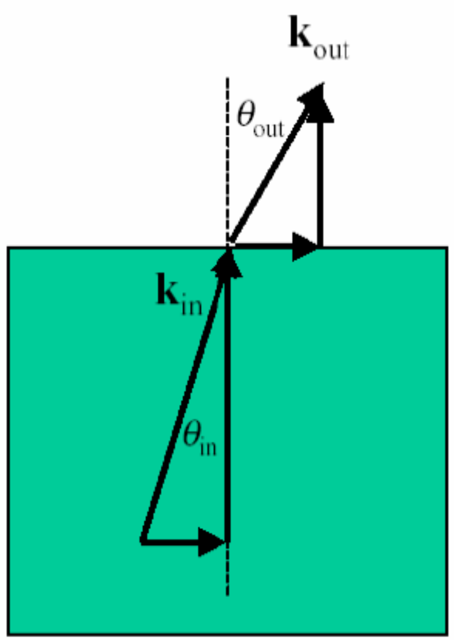


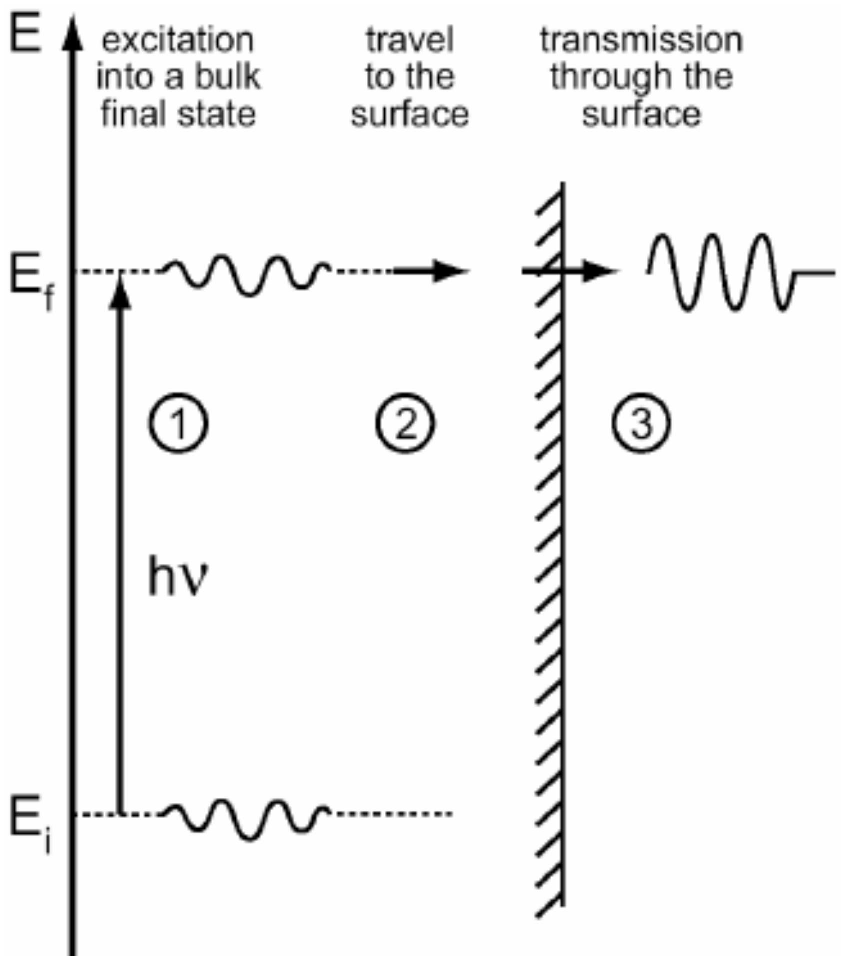
- Extreme surface sensitive
- Clean surface and UHV required
- Laser photoemission is more

Penetration through the surface

- k-parallel momentum remains conserved

$$\hbar k_{\|}(inside) = \hbar k_{\|}(outside)$$



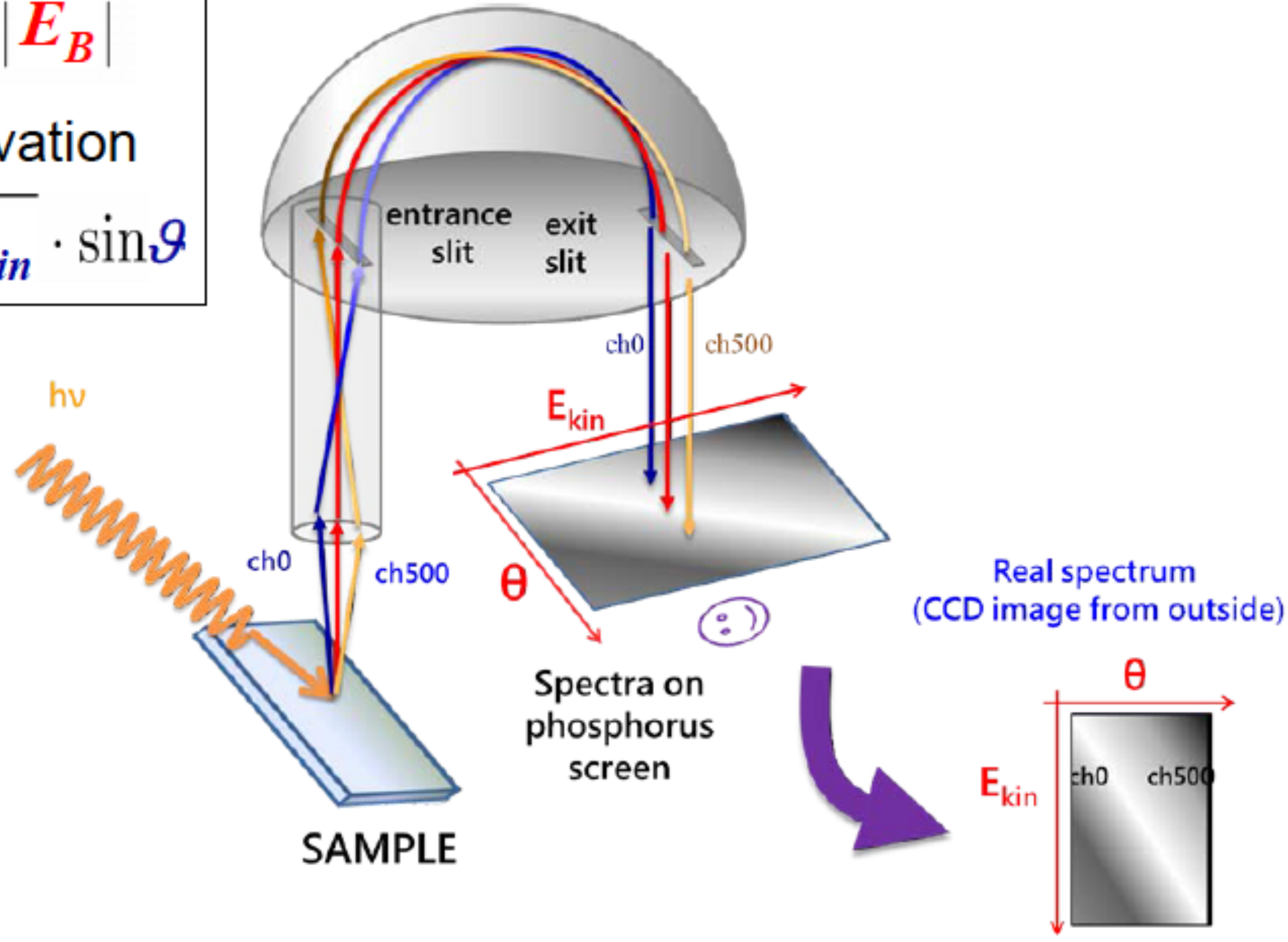


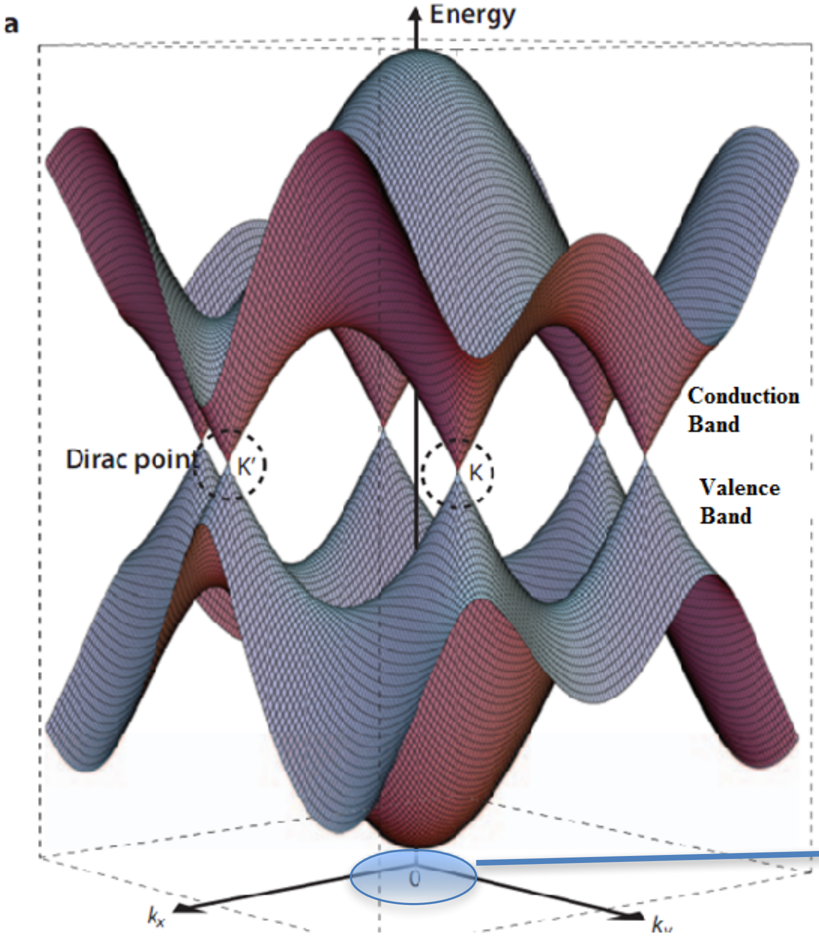
Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

Momentum Conservation

$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$





Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

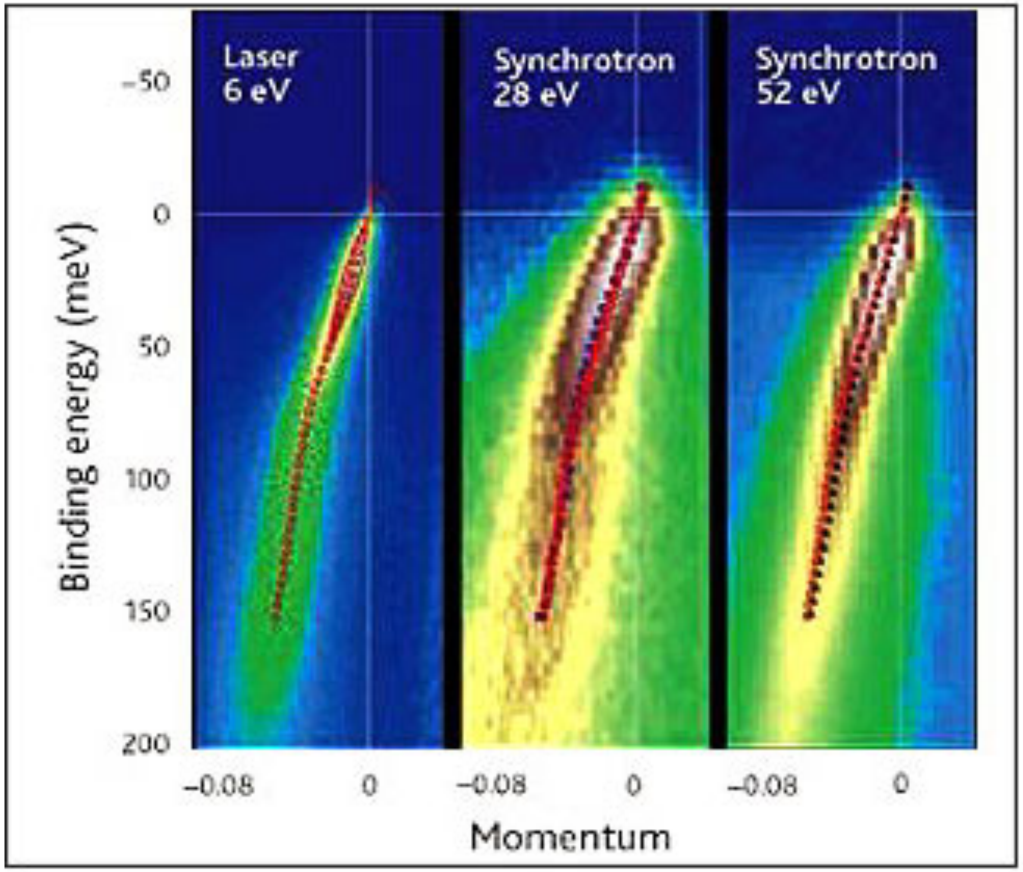
Momentum Conservation

$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

A shrinking of momentum space with Laser Photoemission.

Laser ARPES

Comparison of Bi2212 spectra at different photon energies

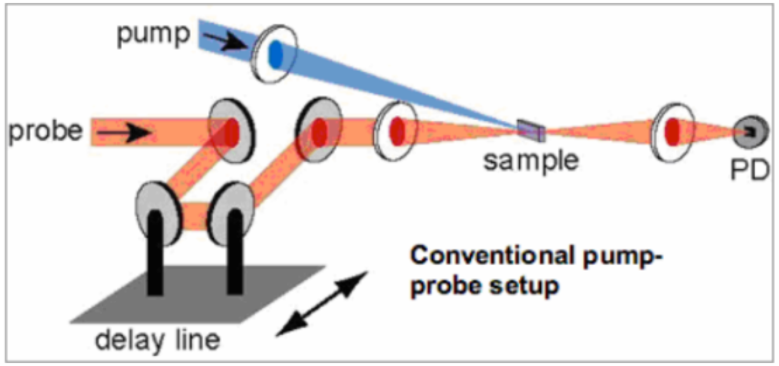


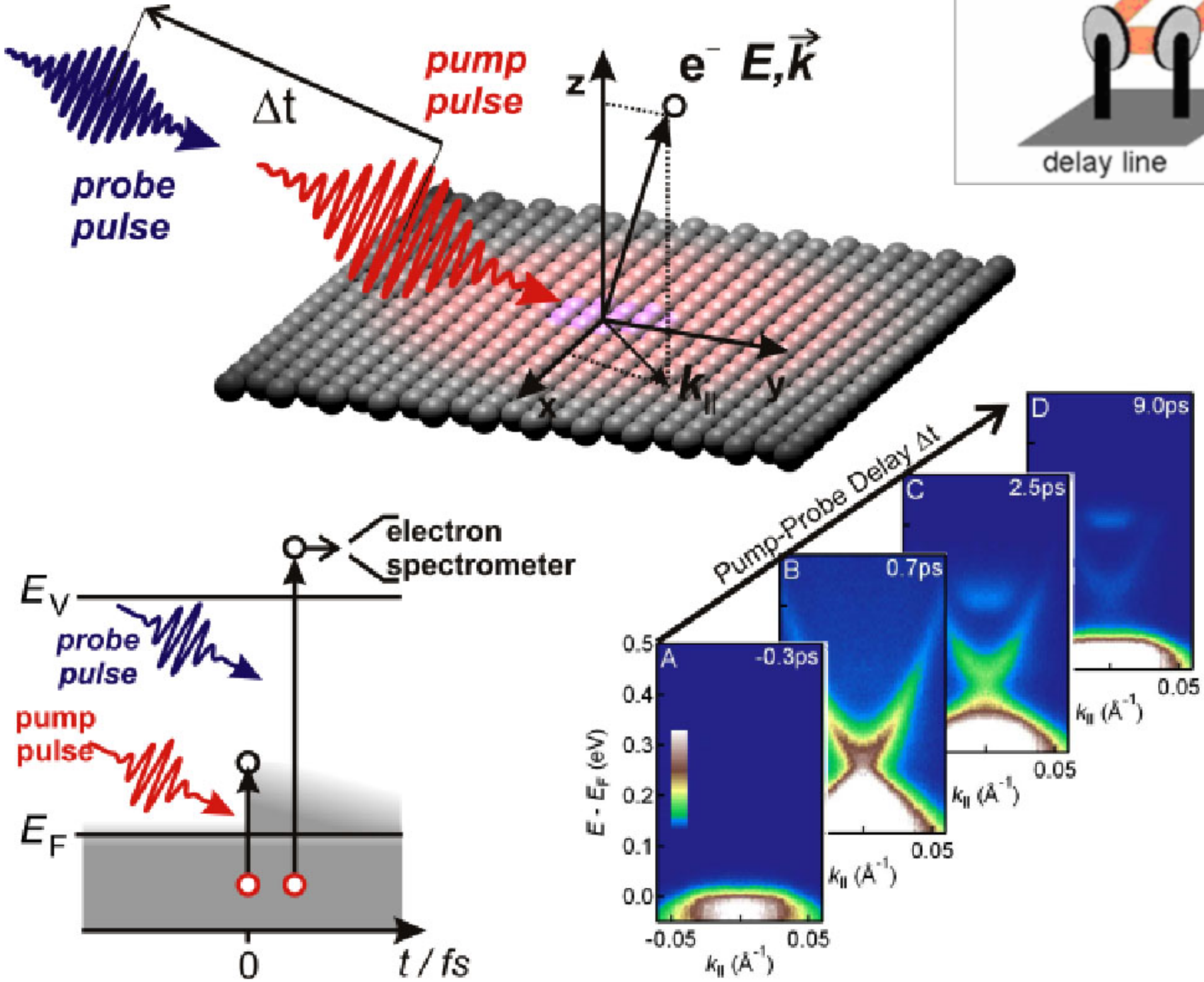
With Laser

- Superior Momentum Resolution
- Finer Energy Resolution
- Higher quality data in a shorter amount of time

From Dessau Group, Science **310**, 1271 (2005)

Time-resolved Laser Photoemission



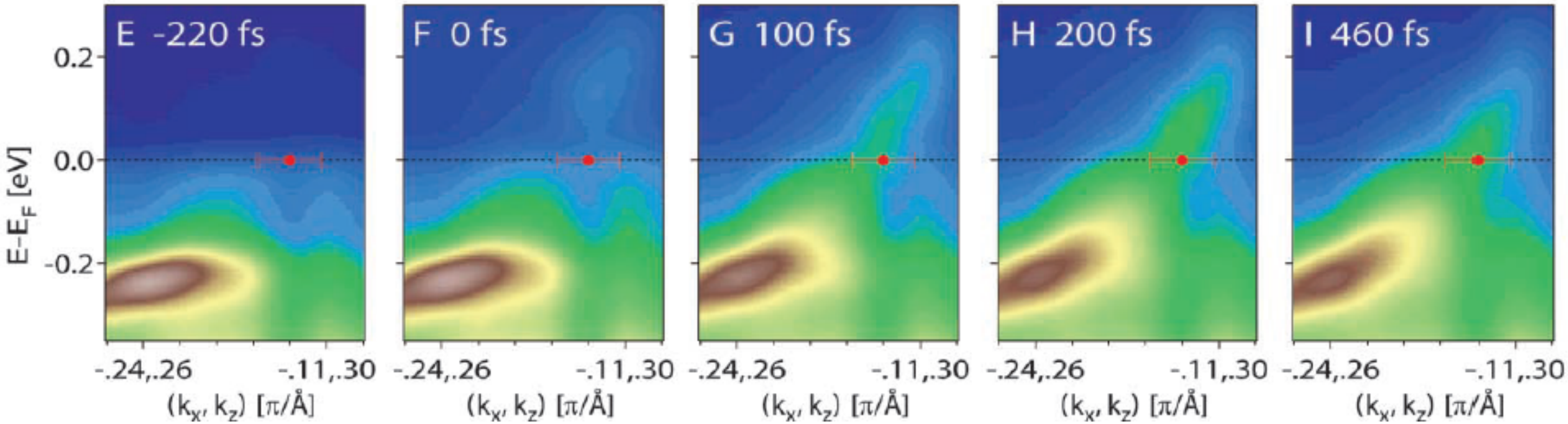


From a Wolf-Shen collaboration

Time Resolved Laser ARPES

ARPES from a laser excited sample

F. Schmitt et al., Science 321, 1649 (2008)



The pump $h\nu < \Phi$ (1.5 eV - 50fs)

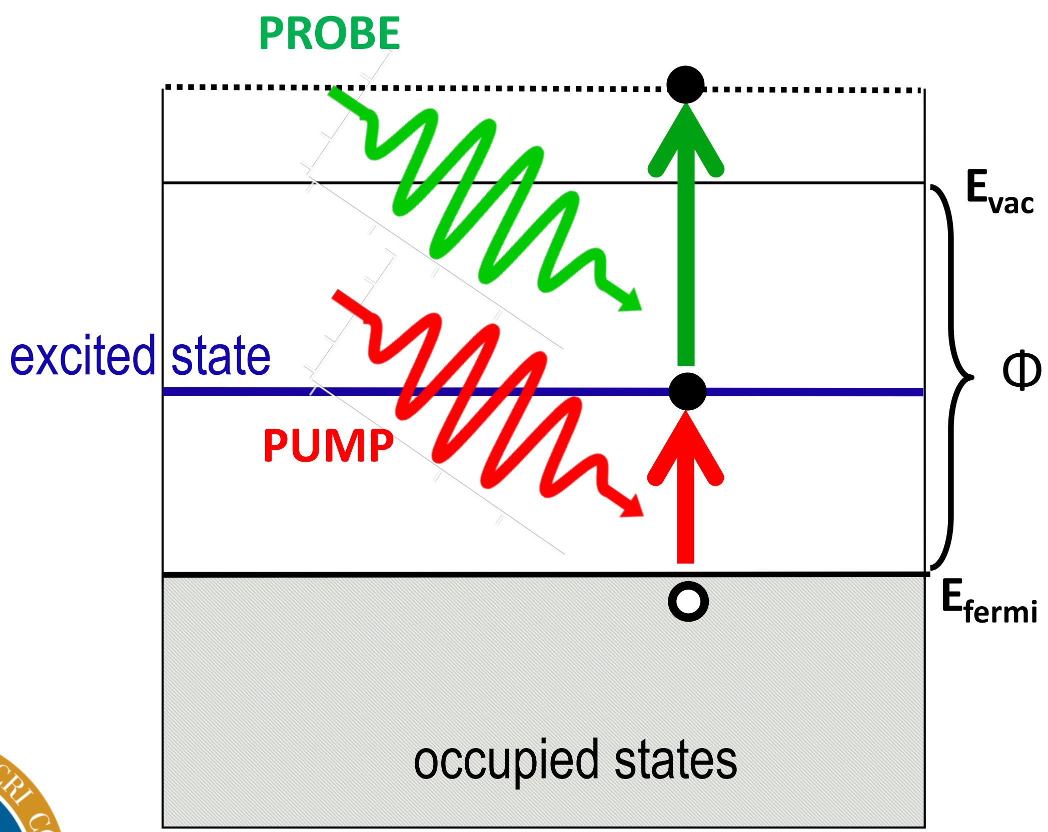
The probe $h\nu > \Phi$ (6 eV - 90 fs)

Time Resolved NonLinear Photoemission (TR-NLPE):

$h\nu_{PUMP} < \Phi$

$h\nu_{PROBE} < \Phi$

- fs relaxation time of excited states;
- charge transfer processes.



pump

$t = 0$

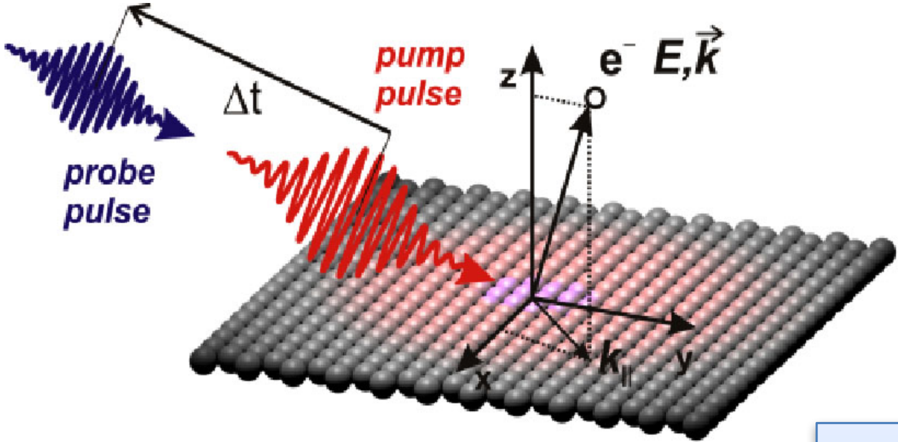
probe

$t = \Delta t$

Laser ARPES
Momentum Resolution
Energy Resolution
Higher quality data

NonLinear Photoemission
Occupied and
Unoccupied States
Interface States

LASER Photoemission



Time resolved laser ARPES
Topological Insulators
High Tc Superconductors

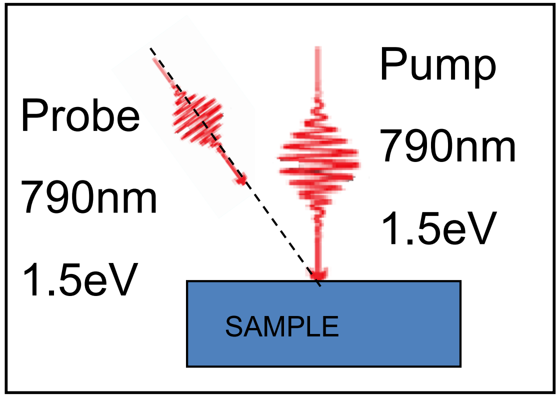
Time resolved NL Photoemission
Metal surfaces
Interfaces: Graphene/Metal
Molecules/Metal
Topological Insulators

Amplified Ti-Sa laser source

Tunability of the pump (0.8 eV to 6.1eV)

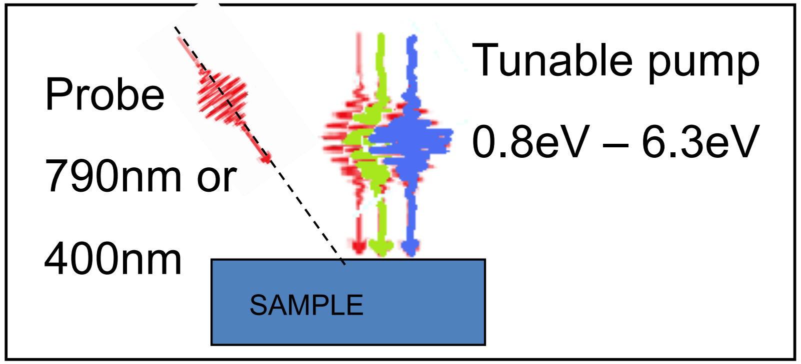
Amplified Ti:sapphire laser system

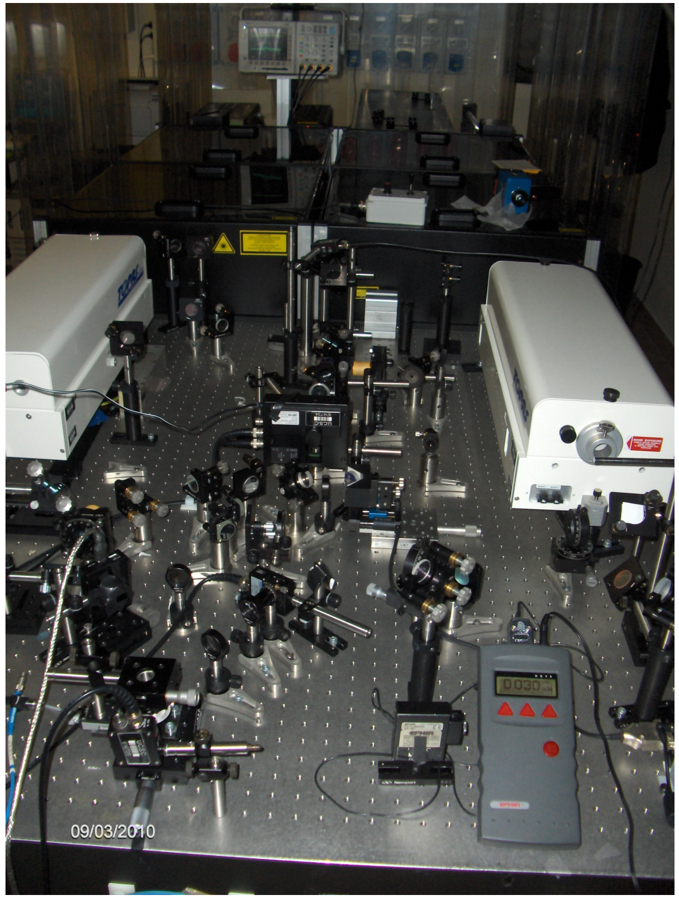
- 790 nm wavelength
- 130 fs pulse duration
- 1 kHz rep. rate, 0.5 W output power



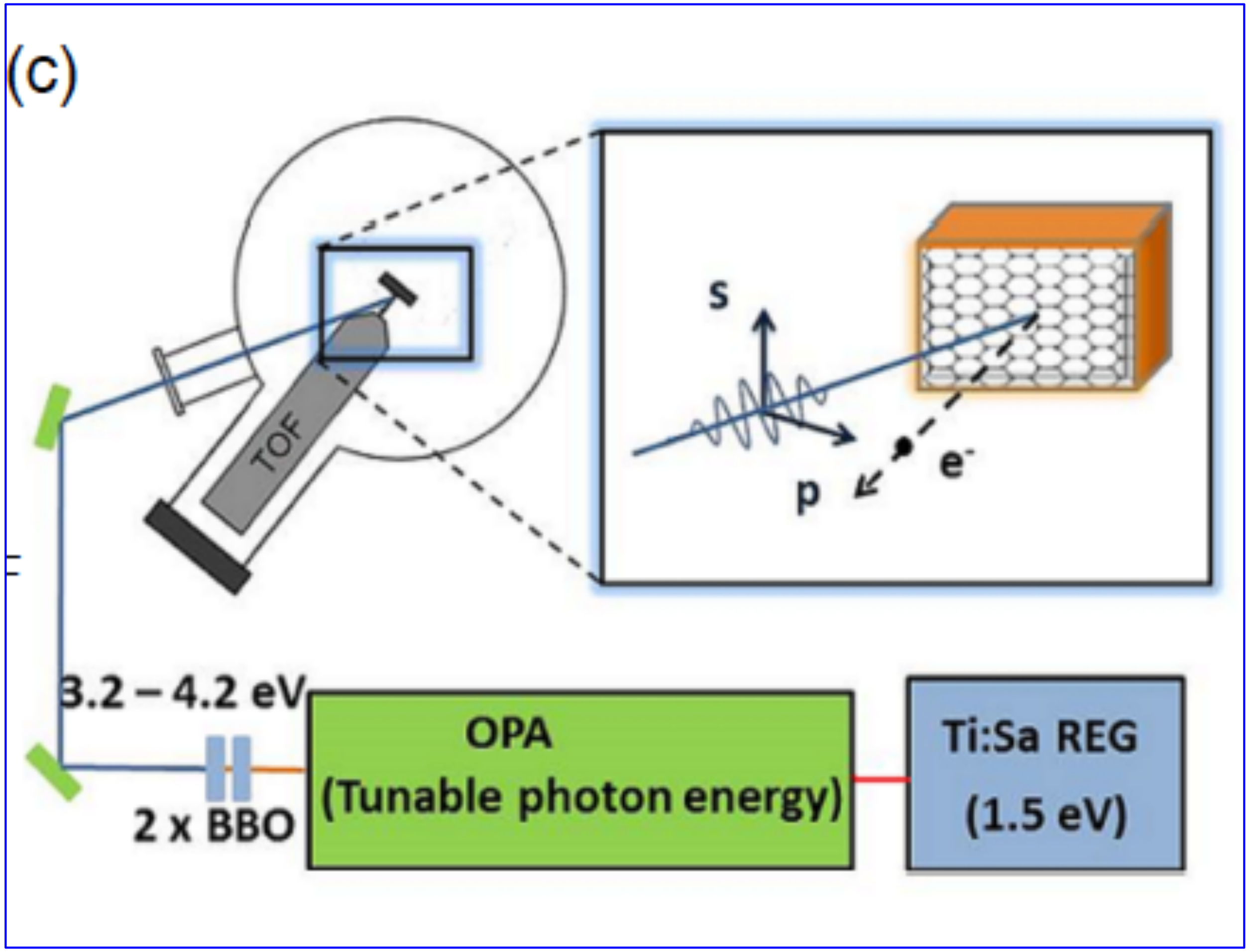
Two Optical Parametric Amplifiers

OPA – NOPA





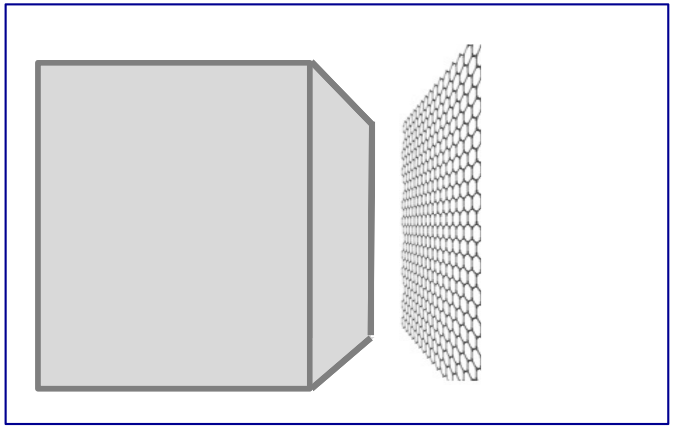
TIME-RESOLVED NON-LINEAR PHOTOEMISSION



TOF PARAMETERS : Acceptance Angle : $\pm 0.83°$ **ΔE** = 30meV @ 2eV

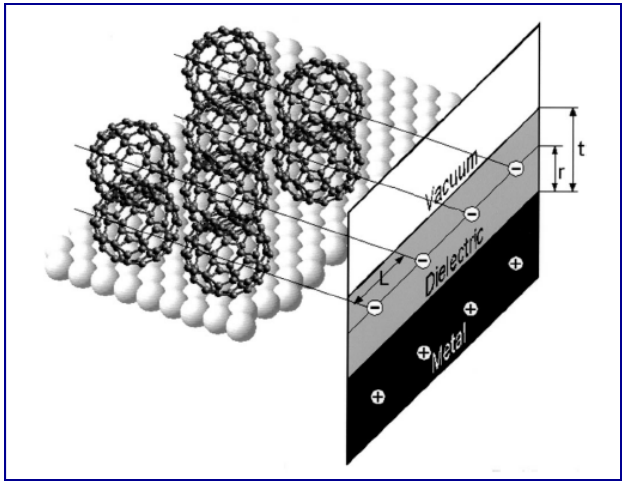
Our Aims: Investigation of electronic structure and electron dynamics **at the interfaces**

Graphene /metal interface



- Gr/Cu(111);
- Gr/Ir(111);
- Gr/Ni(111).

Molecules /metal interface



- C60/Ag(100);
- TPP/Ag(100) e TPP/Ag(111) ;
- C60/Tpp/Ag(100).

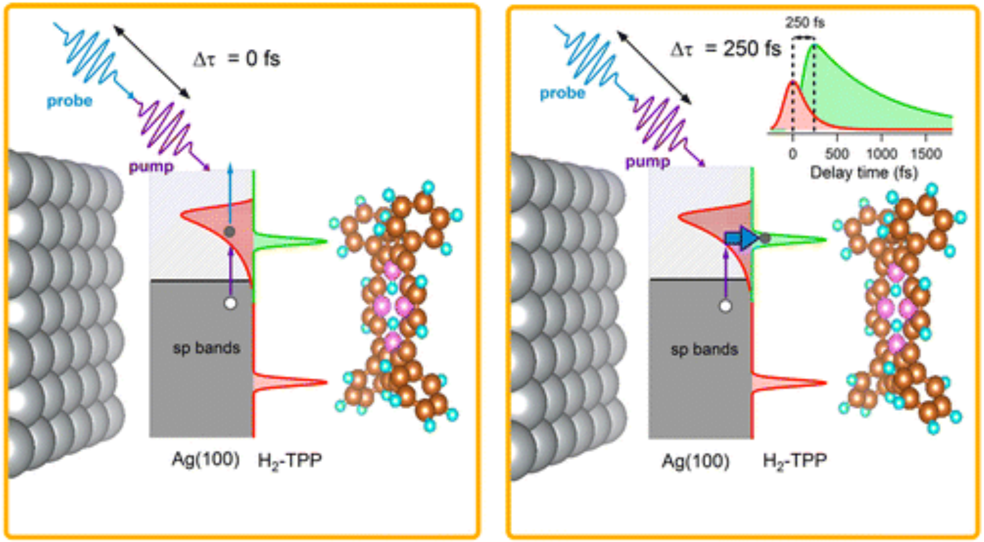
Role of the Substrate Orientation in the Photoinduced Electron Dynamics at the Porphyrin/Ag Interface

Silvia Tognolini†, Stefano Ponzoni†, Francesco Sedona‡, Mauro Sambi‡, and Stefania Pagliara*†
† I-LAMP and Dipartimento di Matematica e Fisica, Università Cattolica, 25121 Brescia, Italy
‡ Dipartimento di Scienze Chimiche, Università di Padova and Consorzio INSTM, Via Marzolo 1, 35131 Padova, Italy

J. Phys. Chem. Lett., **2015**, *6* (18), pp 3632–3638
DOI: 10.1021/acs.jpclett.5b01528
Publication Date (Web): August 31, 2015

*E-mail: stefania.pagliara@unicatt.it.

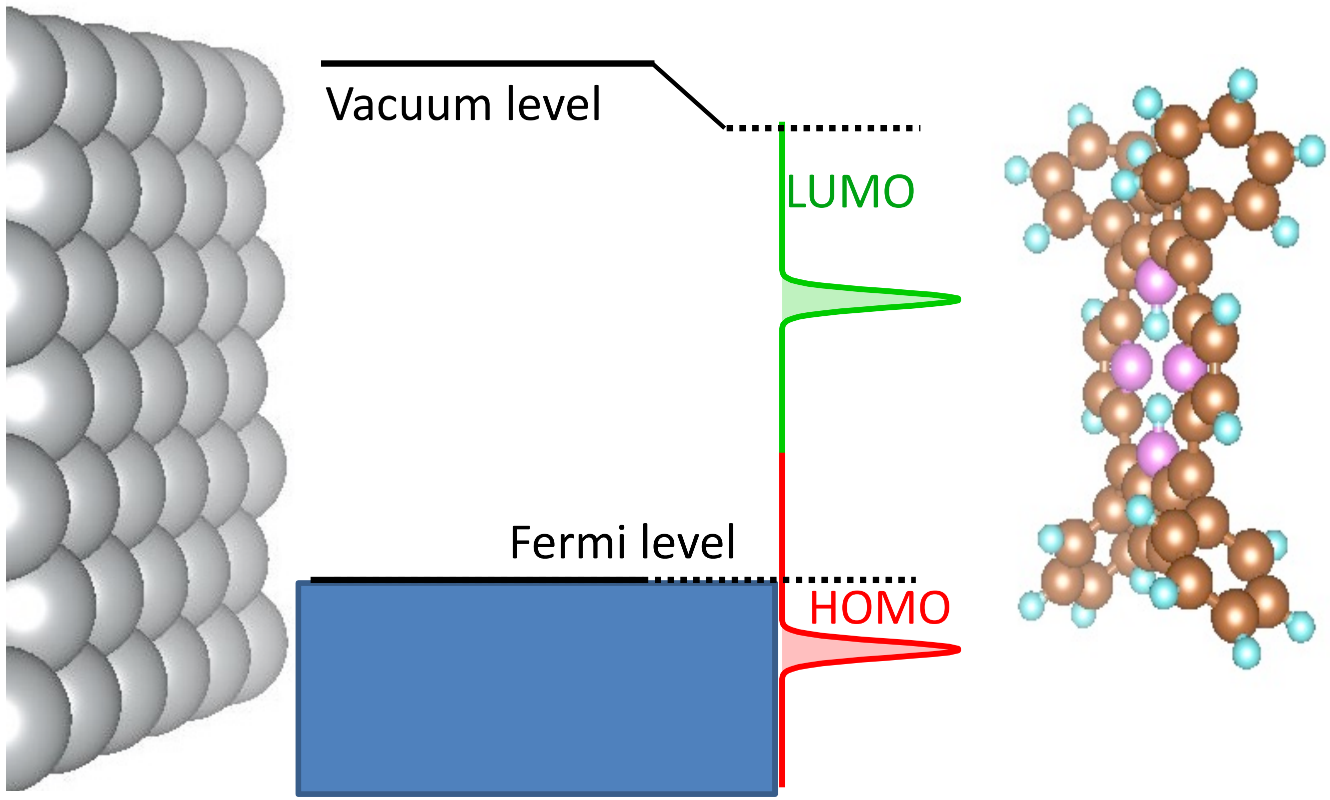
Abstract



The interaction of molecules with metal substrate is the crucial element in charge injection devices:

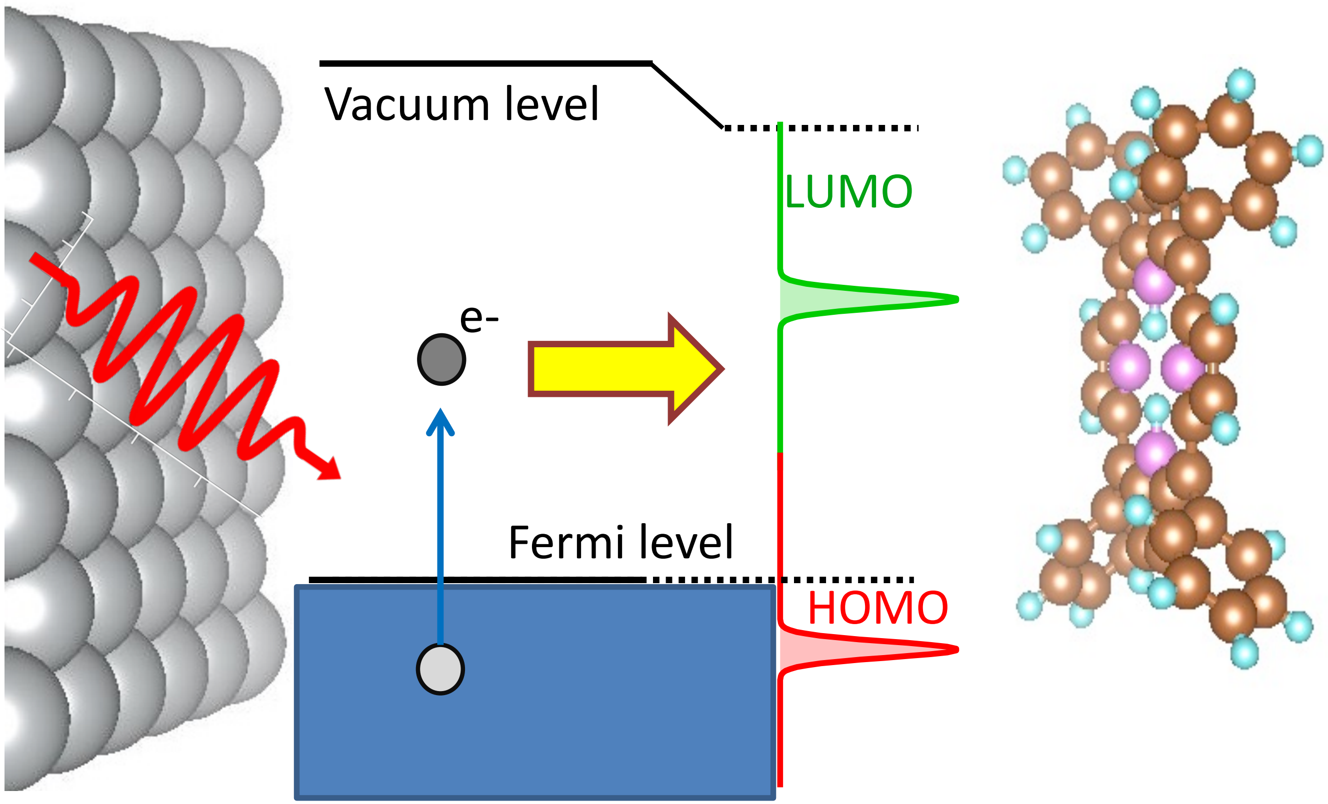
1. **Molecular electronic energy levels alignment;**

Clean Metal **Porphyrins**



The interaction of molecules with metal substrate is the crucial element in charge injection devices:

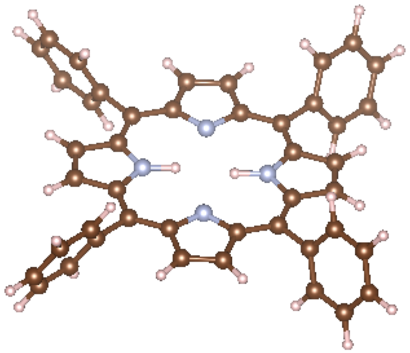
1. **Molecular electronic energy levels alignment;**
2. **Electron transfer processes at the interface.**



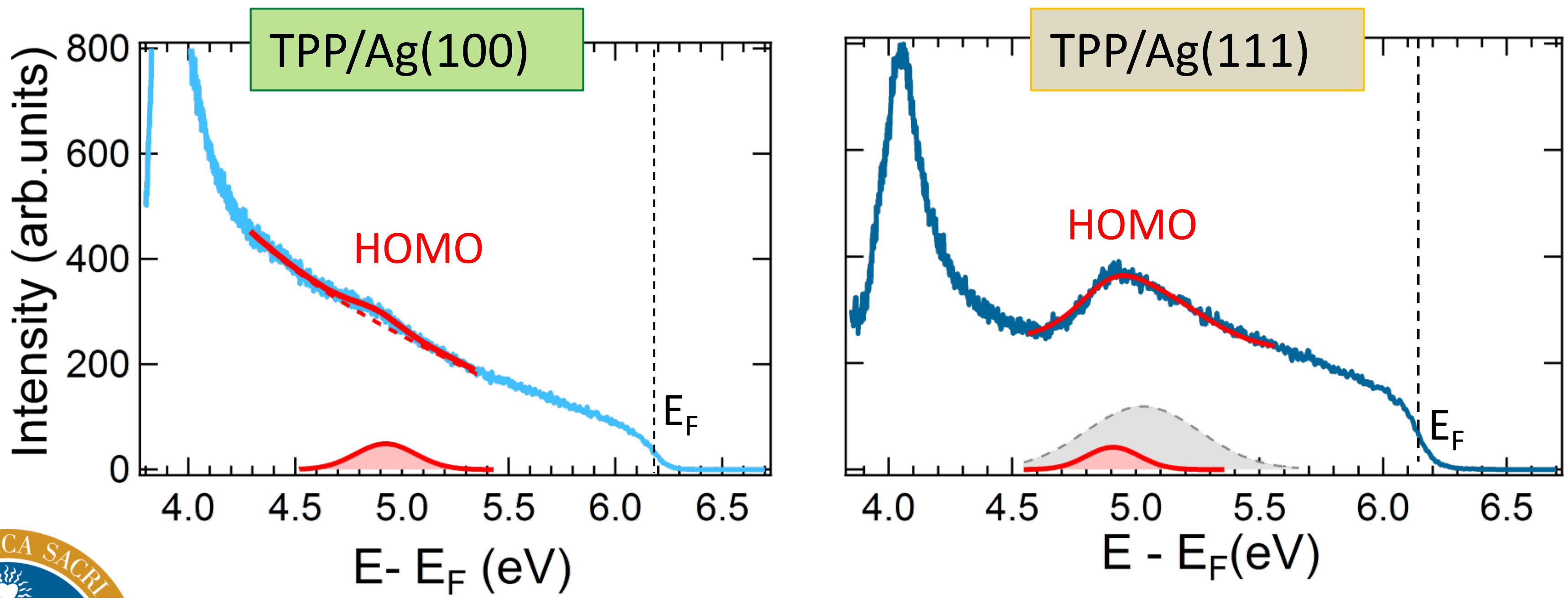
Clean Metal **Porphyrins**

Tetraphenylporphyrin (TPP) / Silver interfaces:

Energy levels alignment



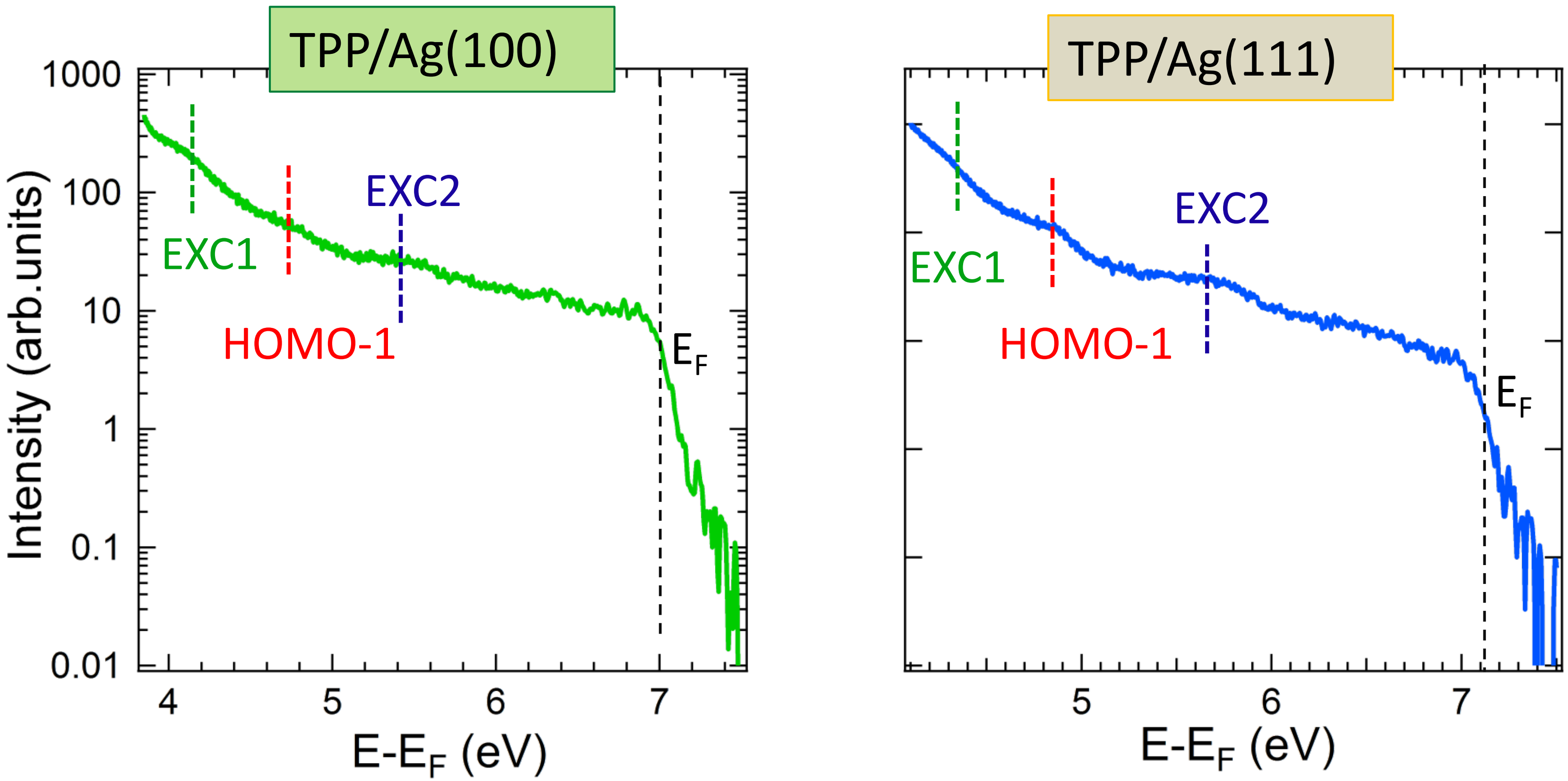
Linear photoemission ($h\nu$ = 6.25 eV> Φ @ $k_{//}$=0) at TPP/Ag interfaces



HOMO: Highest Occupied Molecular Orbital (@1.3 eV below Fermi level)

Molecules/metal interface

NonLinear photoemission (hν = 3.54 eV< Φ @ $k_{//}$=0) at TPP/Ag interfaces

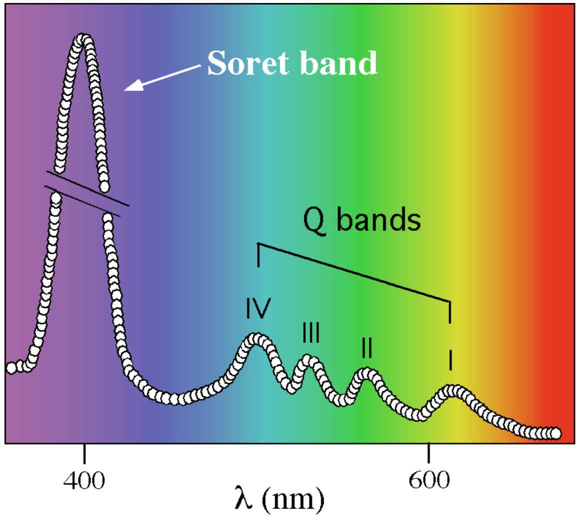


HOMO-1 @ 2.3 eV below Fermi level

EXC1: 1° excited state (@ 0.6 eV above the Fermi level)

EXC2: 2° excited state (@ 2.1 eV above the Fermi level)

TPP UV-VIS absorption spectrum



Soret (or B band) at 400 nm

$a_1u \rightarrow e_g$ transition

Q band at 550 nm

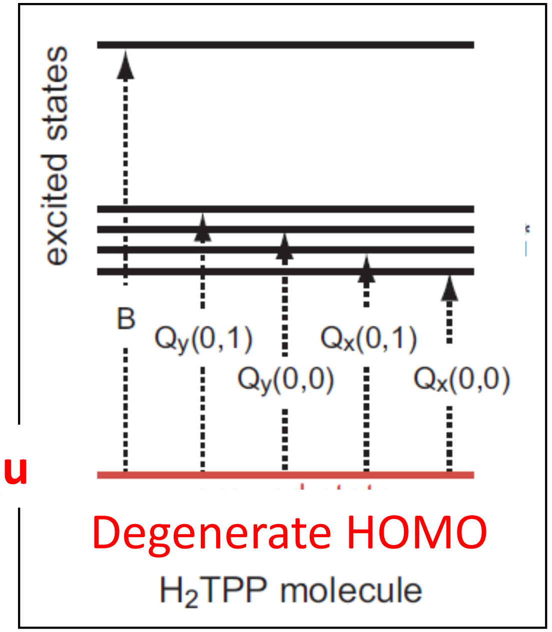
$a_2u \rightarrow e_g$ transition

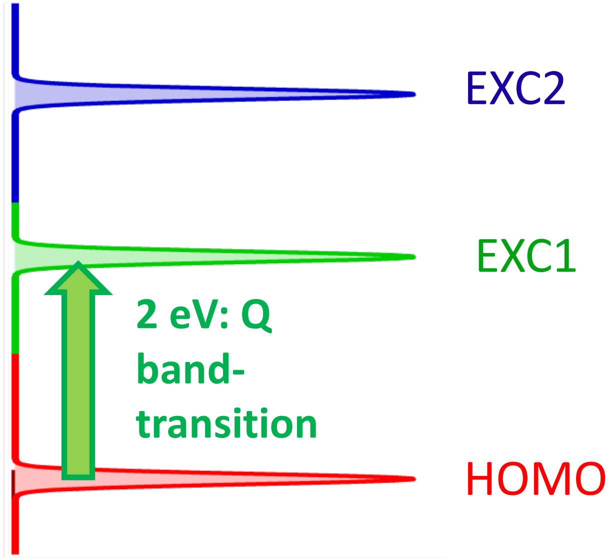
e_g

Degenerate LUMO

e_g

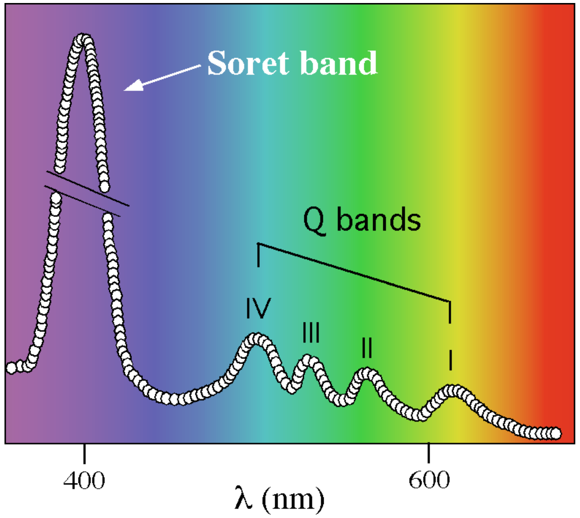
a_1u, a_2u





Molecules/metal interface

TPP UV-VIS absorption spectrum



Soret (or B band) at 400 nm

$a_1u \rightarrow e_g$ transition

Q band at 550 nm

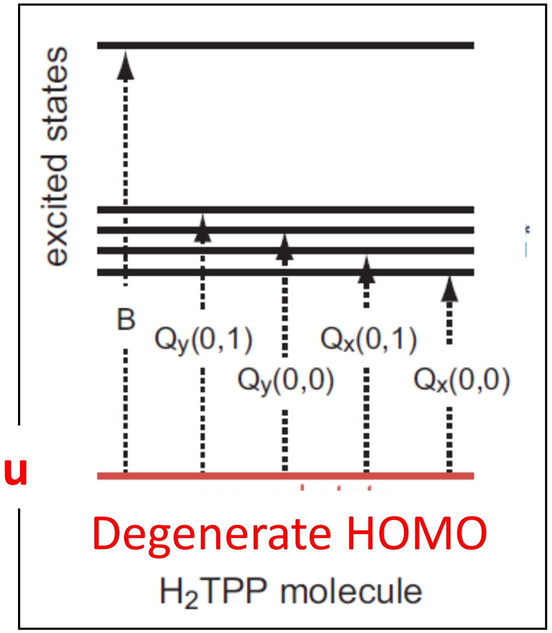
$a_2u \rightarrow e_g$ transition

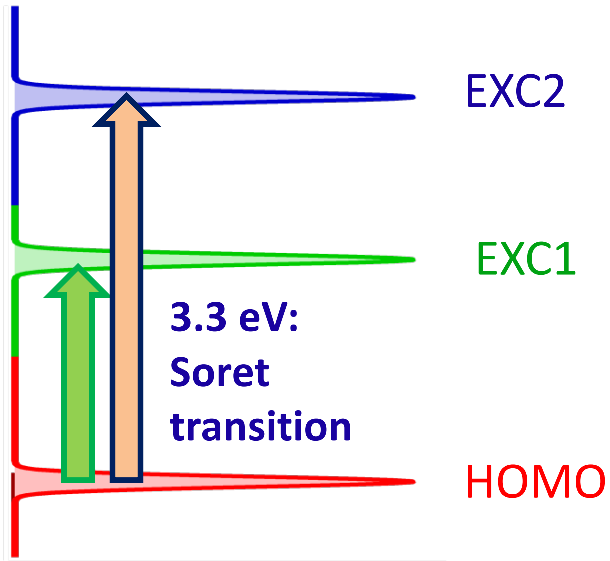
Degenerate LUMO

e_g

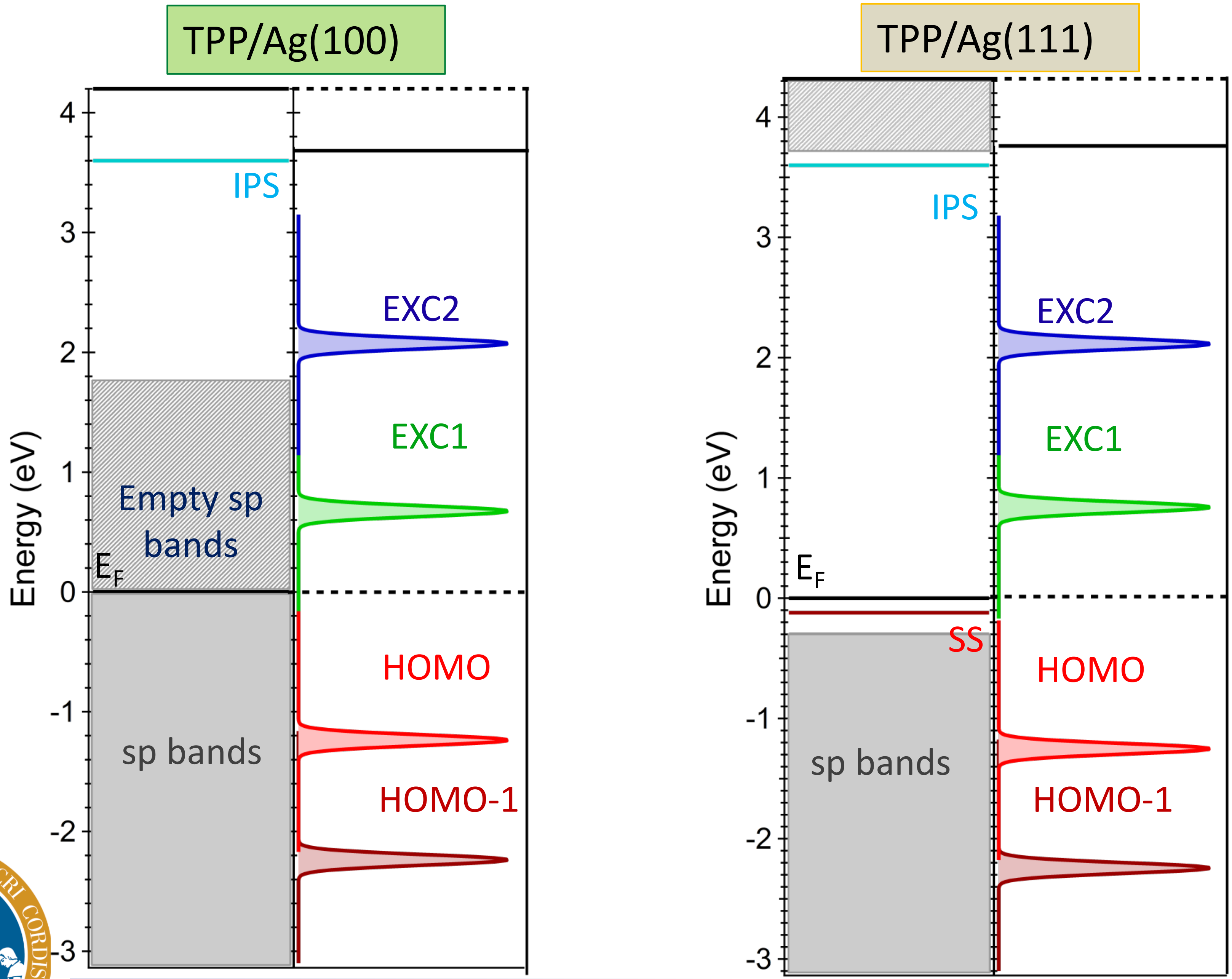
e_g

a_1u, a_2u



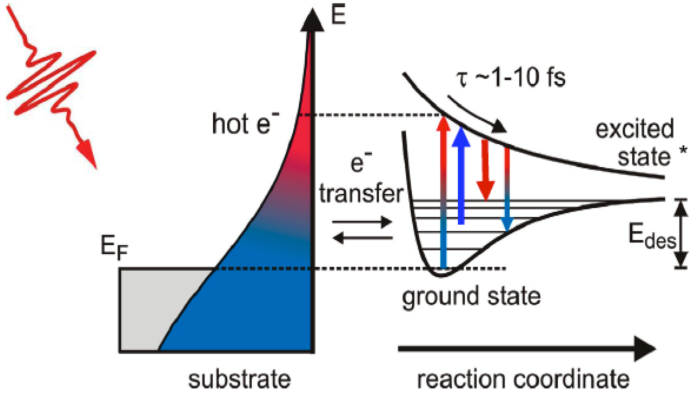


Molecules/metal interface

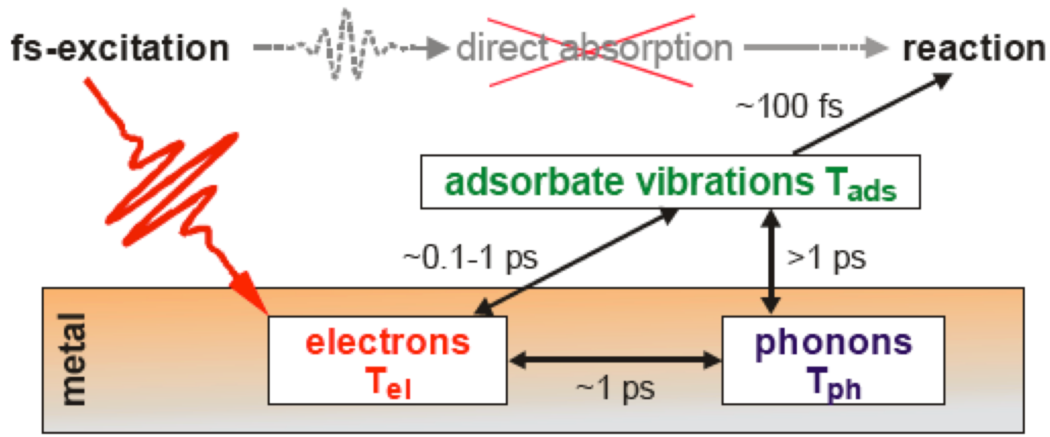


December, 2017

The role of the hot electrons is crucial in the indirect charge transfer across the organic - metal /semiconductor interface



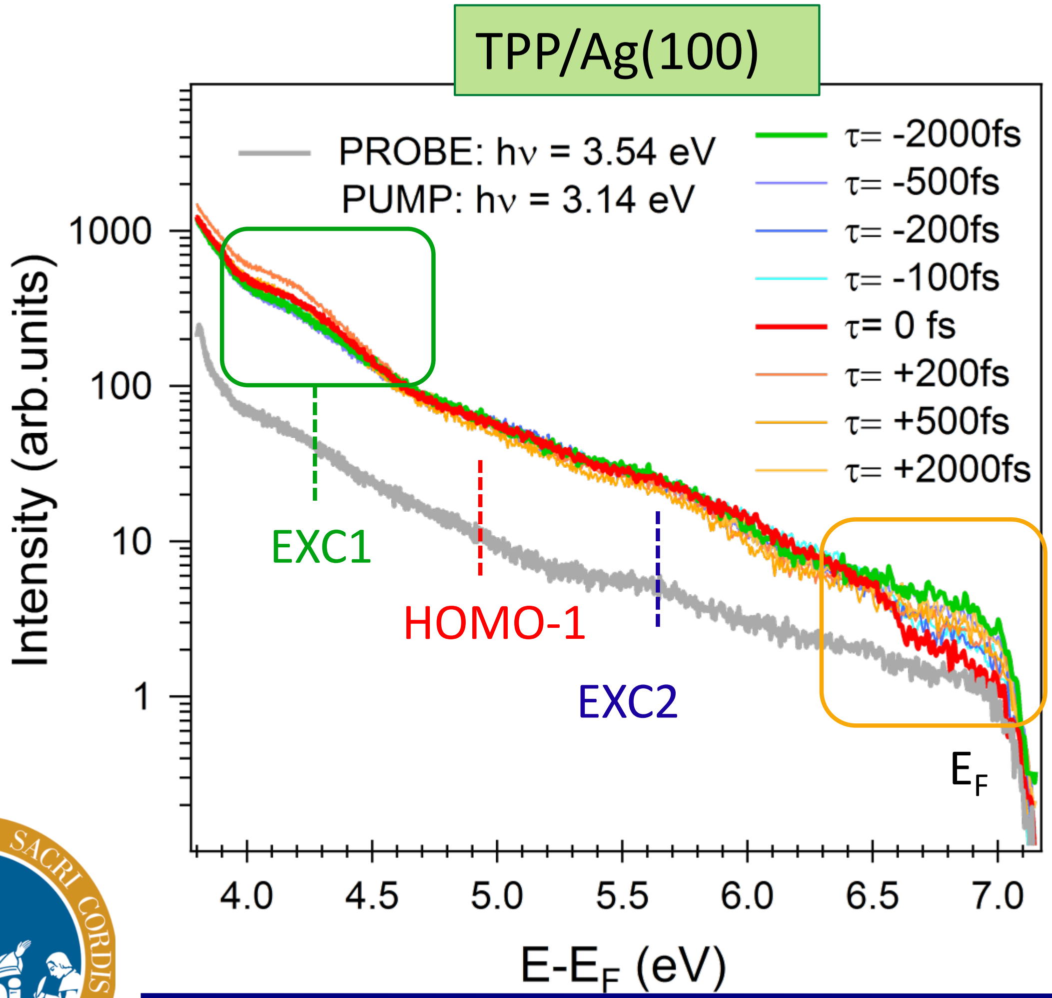
- -- *hot electron mediated femtochemistry*
- -- *electron injection in dye sensitized solar cells*
- -- *charge injection in organic light emitting diodes*



C. Frishkorn and M. Wolf, Chem. Rev. 2006

Time Resolved Non Linear Photoemission on TPP/Ag(100)

PUMP: hν = 3.14 eV, PROBE: hν = 3.54 eV @ $k_{//}=0$

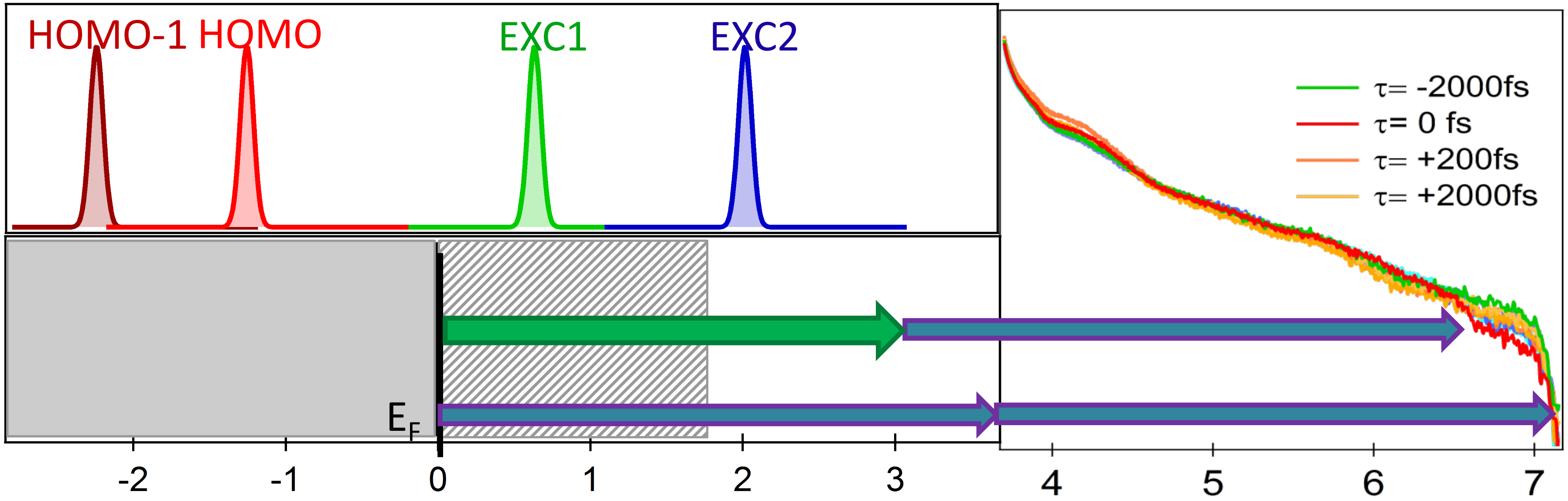


Photoemission intensity is maximum out of temporal coincidence.

Photoemission intensity decreases when the pump and the probe are in temporal coincidence (τ=0).

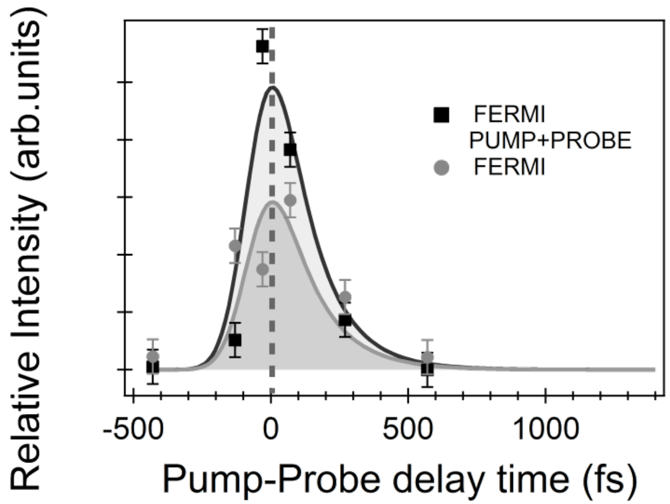
Molecules/metal interface

Time-Resolved NL-PES (PUMP: hν = 3.14 eV, PROBE: hν = 3.54 eV @ $k_{//}$=0) at TPP/Ag(100) interface

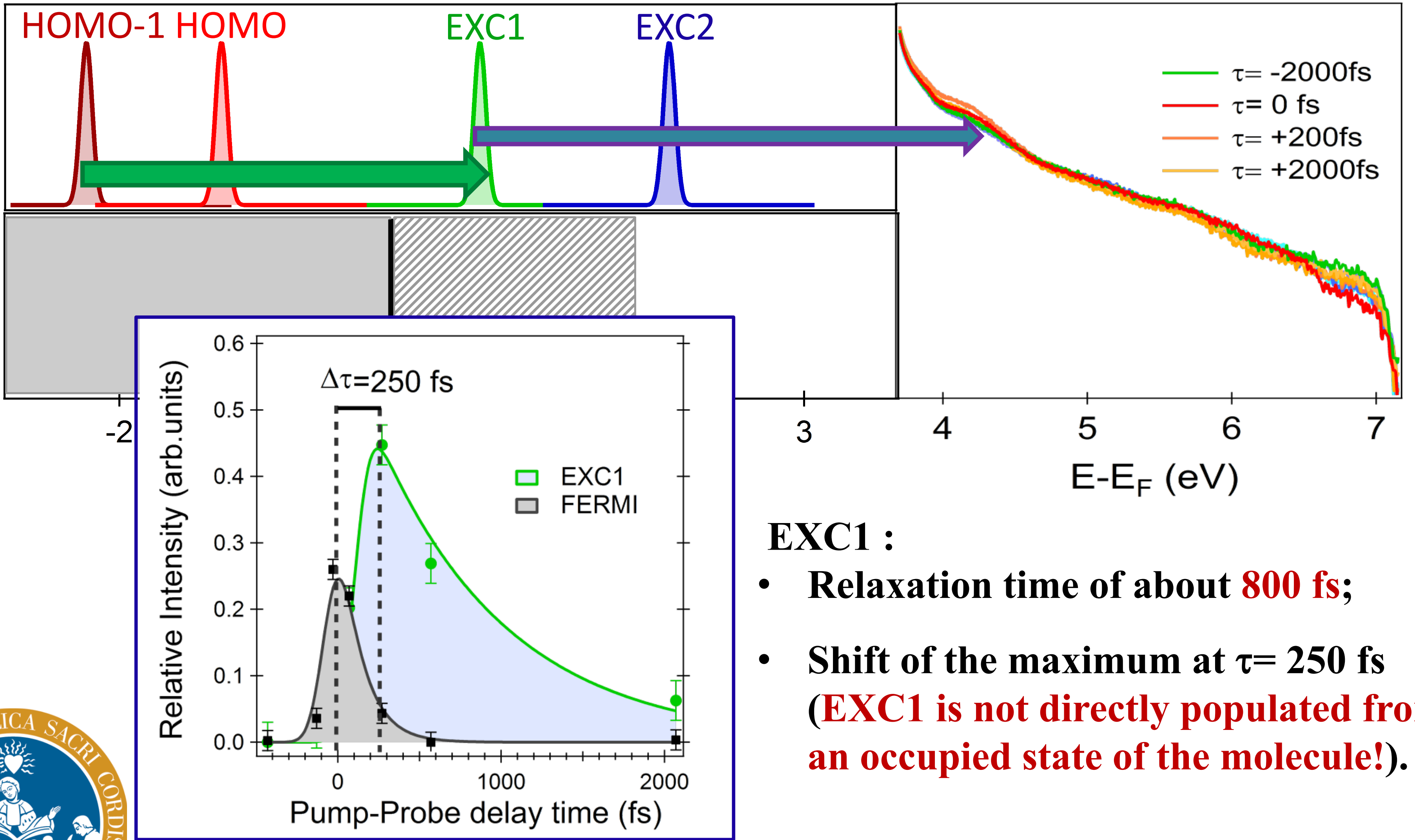


Two competitive processes:

- **E_F coherently photoemitted by 3.14eV+3.54 eV photons;**
- **E_F coherently photoemitted by 3.54 eV+3.54 eV photons;**



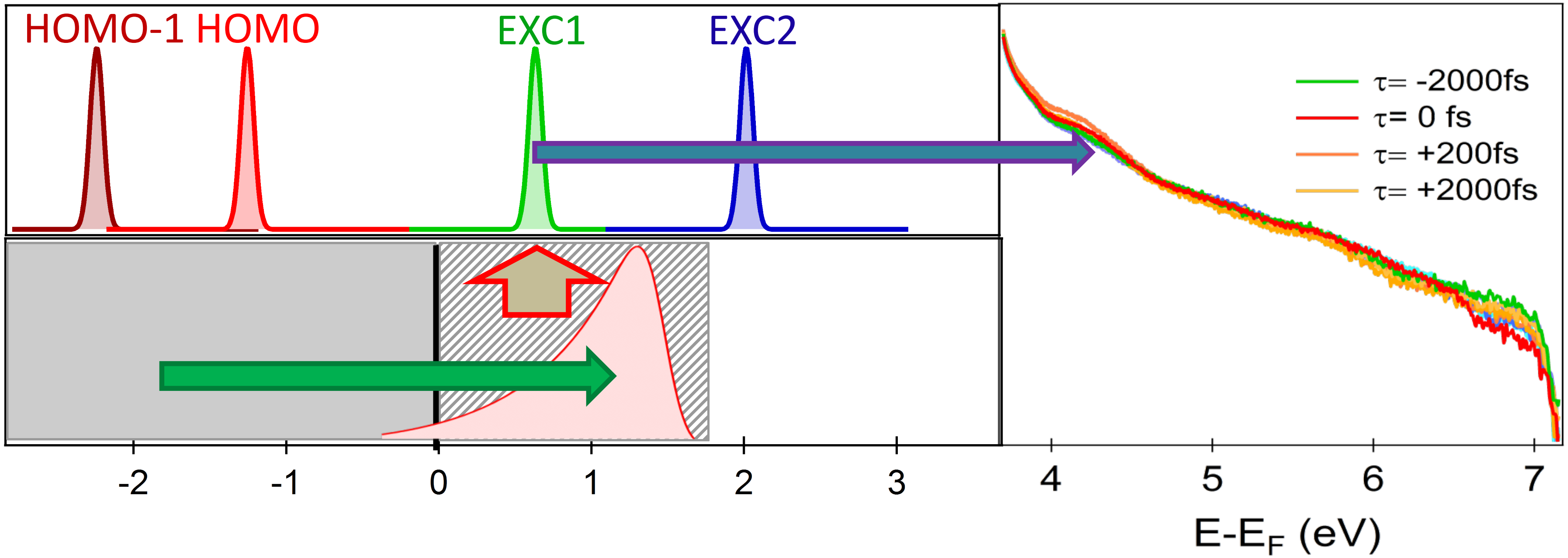
Time-Resolved NL-PES (PUMP: hν = 3.14 eV, PROBE: hν = 3.54 eV @ $k_{//}$=0) at TPP/Ag interfaces



EXC1 :

- **Relaxation time of about 800 fs;**
- **Shift of the maximum at τ= 250 fs (EXC1 is not directly populated from an occupied state of the molecule!).**

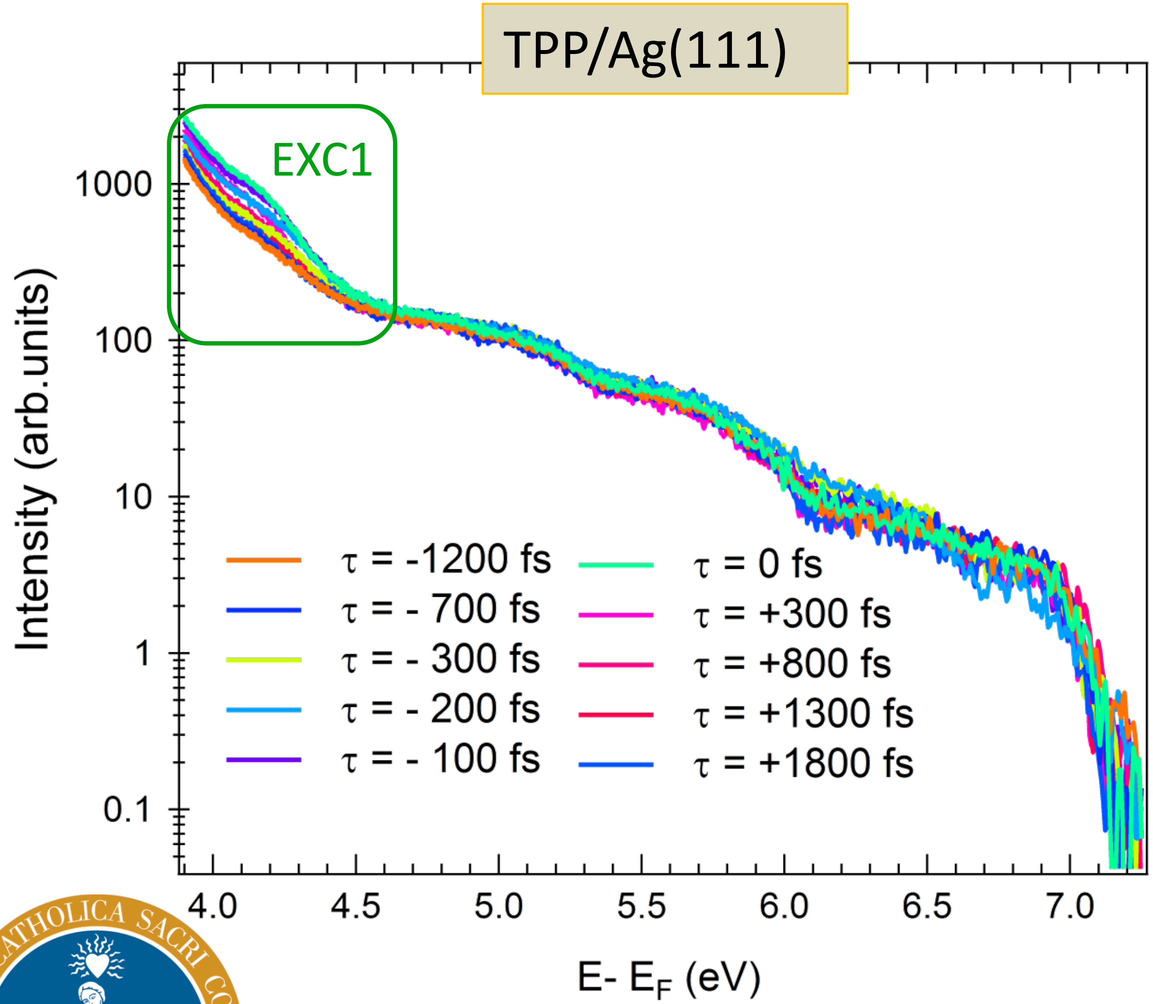
Time-Resolved NL-PES (PUMP: hν = 3.14 eV, PROBE: hν = 3.54 eV @ $k_{//}$=0) at TPP/Ag interfaces

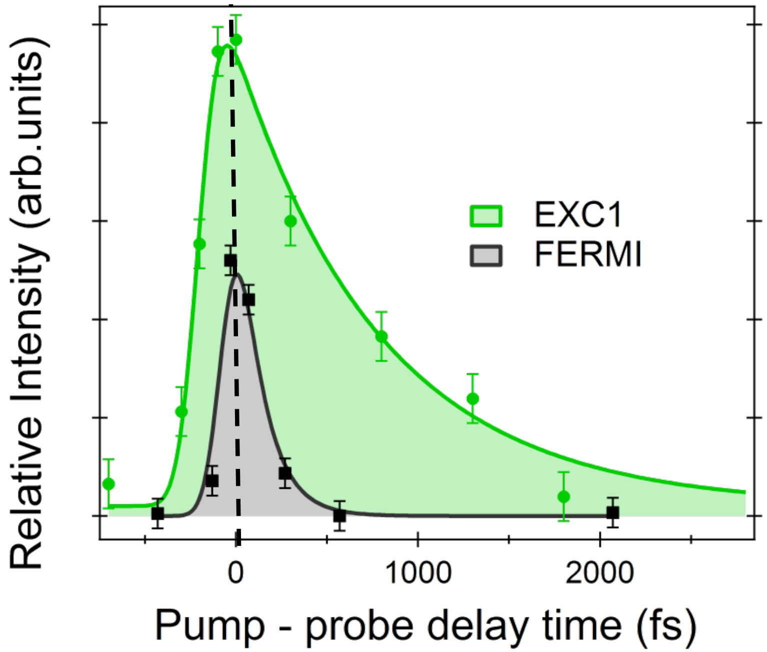


- **The pump pulse excites a hot electrons population in the empty Ag(100) sp-bands;**

- **The electrons excited in a state of higher energy relax in the EXC1 in a time of 250 fs and finally they are photoemitted by the probe pulse.**

Time-Resolved NL-PES (PUMP: hν = 3.14 eV, PROBE: hν = 3.54 eV @ $k_{//}$=0) at TPP/Ag interfaces



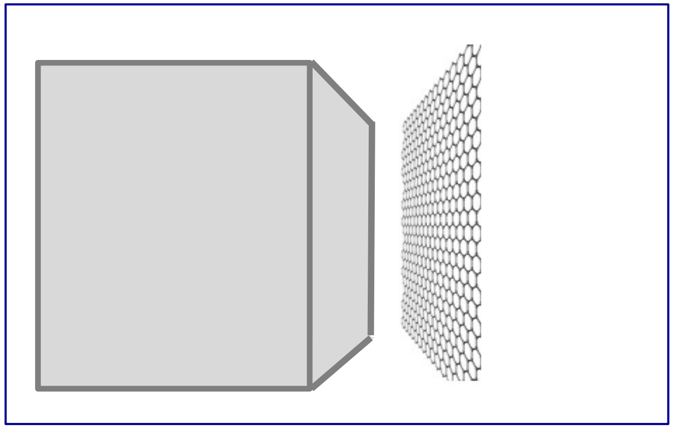


EXC1 :

- **Relaxation time of about 800 fs;**
- **Maximum at τ=0 fs (EXC1 is directly populated from an occupied state of the molecule!!).**

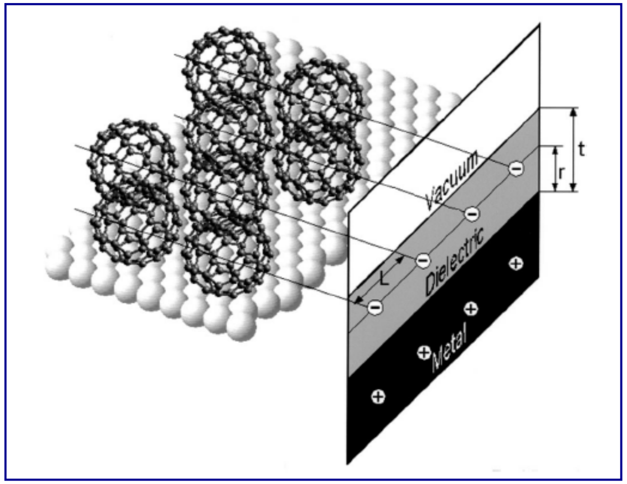
Our Aims: Investigation of electronic structure and electron dynamics **at the interfaces**

Graphene /metal interface



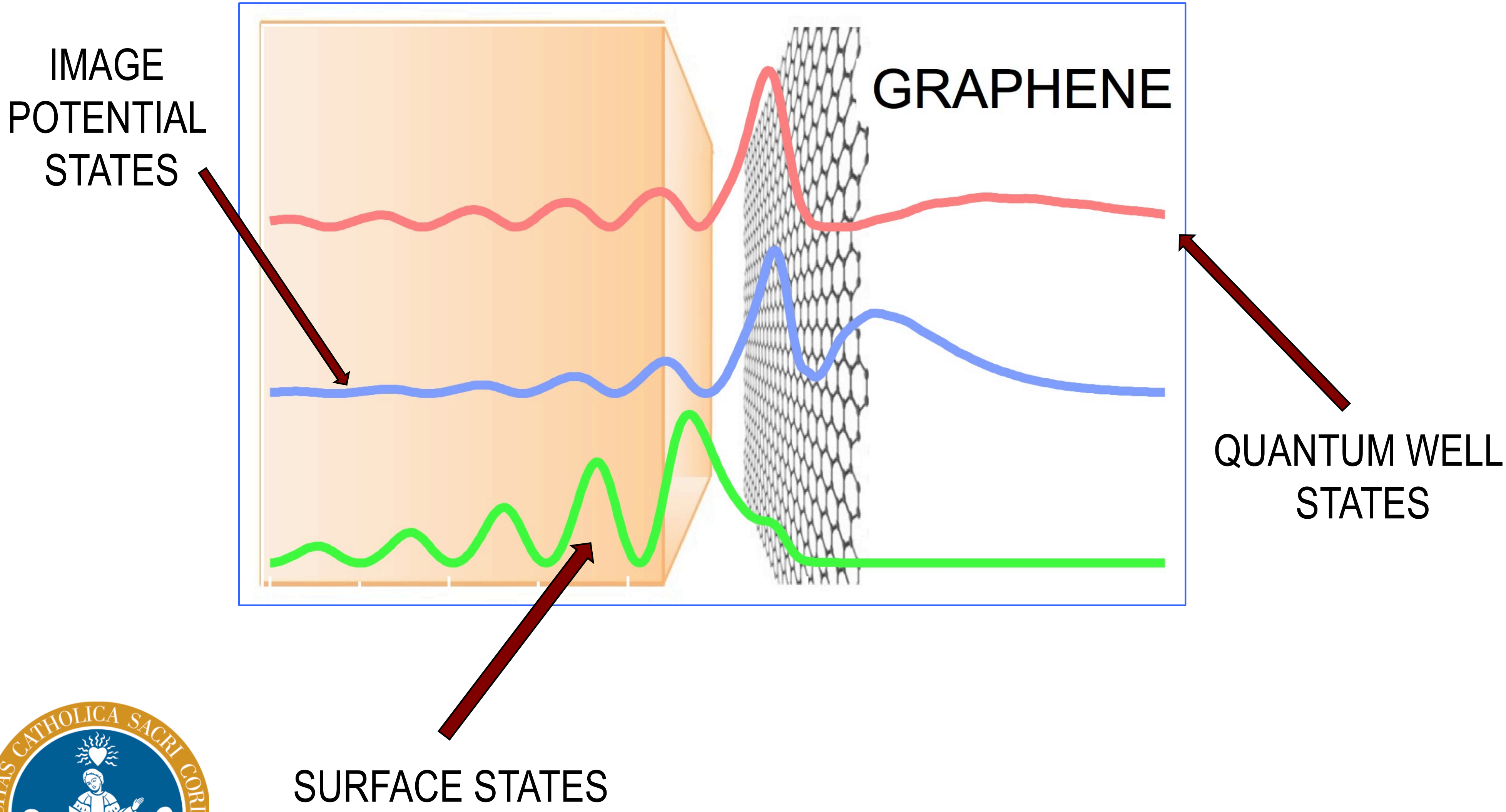
- Gr/Cu(111);
- Gr/Ir(111);
- Gr/Ni(111).

Molecules /metal interface



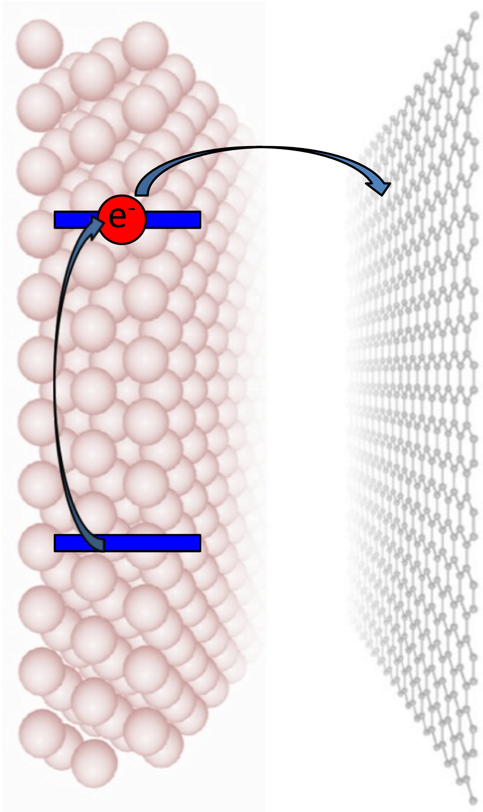
- C60/Ag(100);
- TPP/Ag(100) e TPP/Ag(111) ;
- C60/Tpp/Ag(100).

What are Interface States?

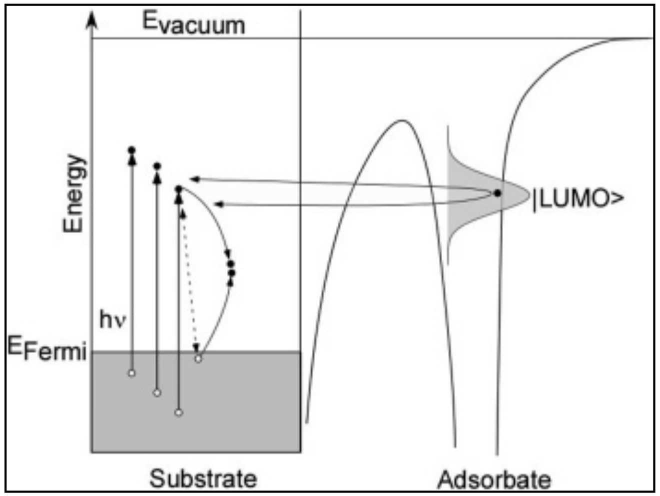


Graphene/metal interface

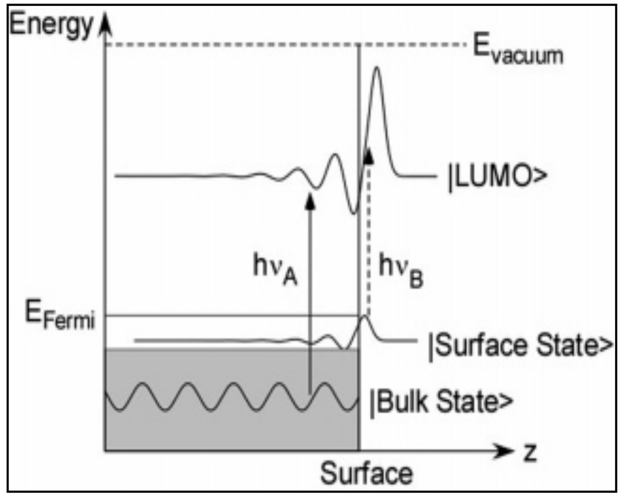
…. surface states play a key role in the photo-induced charge transfer processes at the interface



Indirect electron transfer



Direct electron transfer



C. Frishkorn and M. Wolf, Chem. Rev. 2006

Why to study Interface and Image Potential States?

New Journal of Physics
The open-access journal for physics

Image potential states as a quantum probe of graphene interfaces

Sangita Bose[1,9], Vyacheslav M Silkin[2,3,4], Robin Ohmann[1], Ivan Brihuega[1], Lucia Vitali[1], Christian H Michaelis[1], Pierre Mallet[5], Jean Yves Veuillen[5], M Alexander Schneider[6], Evgueni V Chulkov[2,3,7], Pedro M Echenique[2,3,7] and Klaus Kern[1,8]

Properties of Image Potential States:

- Localized in the z direction outside the substrate surface
- Electrons are quasi-free in the plane parallel to the sample surface
- Long lifetime
- Interactions may result in a modified IPS electron mass m*

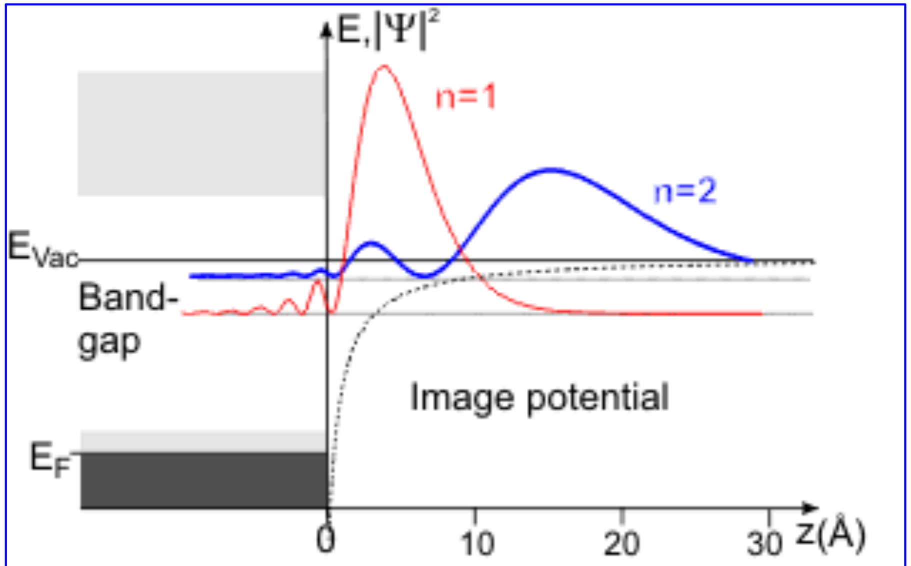


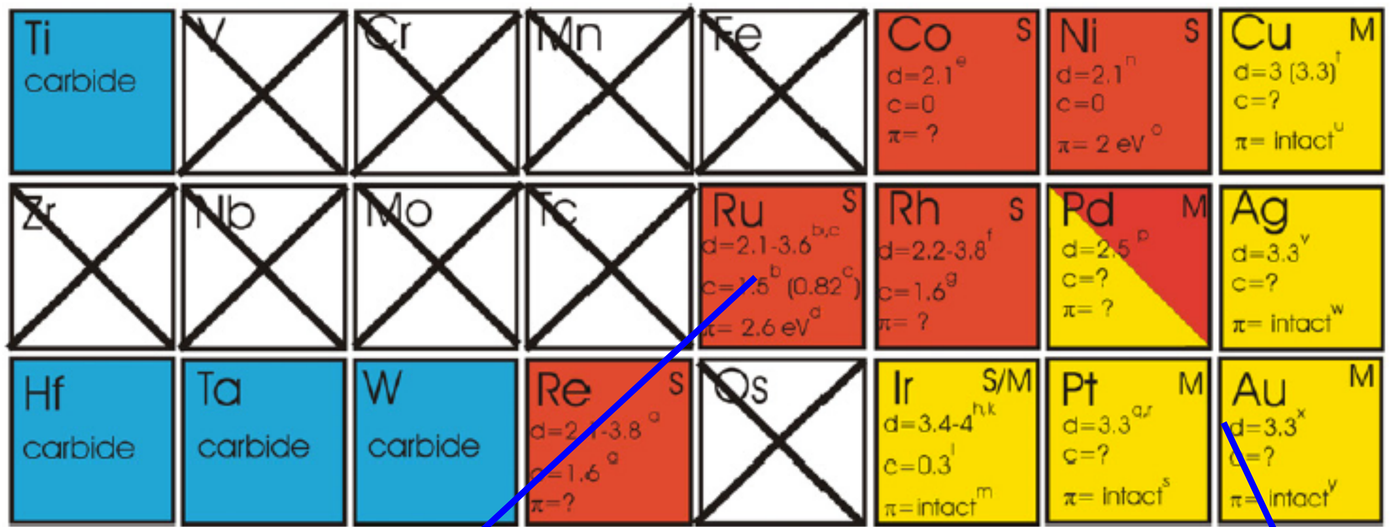
Fig. 2: Image potential and the corresponding image-potential states

$$E(k_{||}) = E_v - e_n + \hbar^2 k_{||}^2 / 2m \ ,$$
$$e_n = (1\ \mathrm{Ry})/16(n+a)^2, \quad n = 1,2,3,\ldots$$
$$a = (1 - \Phi_C/\pi)/2 \ .$$

Echenique et al., Surface Science Reports 2004

U. Höfer et al., Progresse in Surface Science 80, 49- 91, 2005

Graphene / Metal interface



Batzill *et al.*, Surf. Science Rep. **67,** 83 (2012).

- Strongly interacting system

Strong hybridization
π band – d level
(Ni, Ru)

- Weakly interacting system

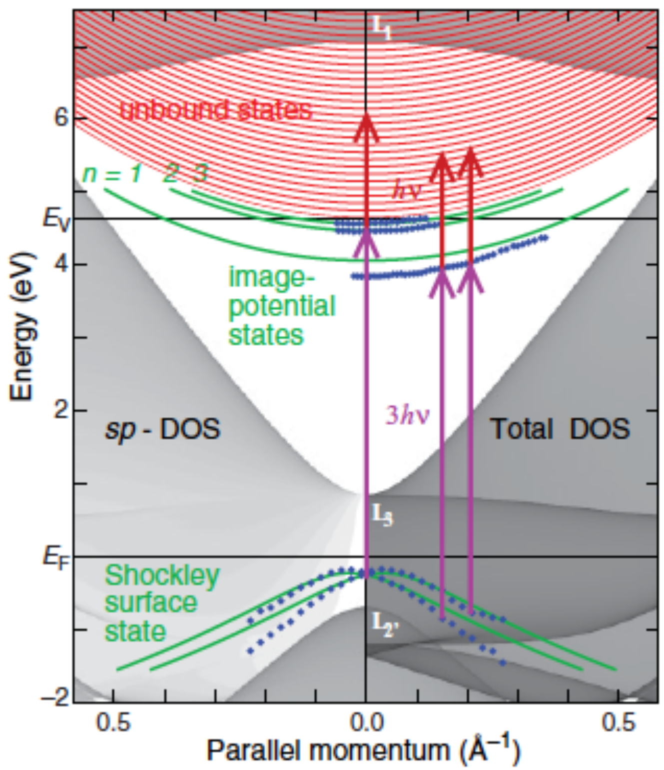
Unchanged π band
(Ir, Cu)

Graphene/metal interface

PHYSICAL REVIEW B 85, 081402(R) (2012)

Trapping surface electrons on graphene layers and islands

D. Niesner,[1] Th. Fauster,[1] J. I. Dadap,[2] N. Zaki,[2] K. R. Knox,[2] P.-C. Yeh,[2] R. Bhandari,[2] R. M. Osgood,[2]
M. Petrović,[3] and M. Kralj[3]



Graphene-Ir(111)
distance > 3 Å

- A Surface State
- Image Potential States

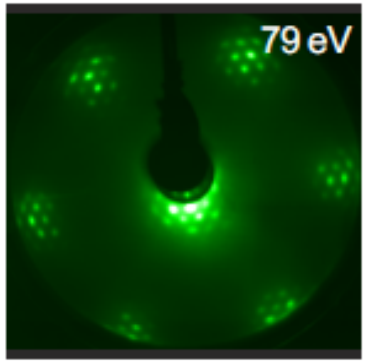


TABLE I. Experimental and calculated binding energies and lifetimes for image-potential states on graphene/Ir(111).

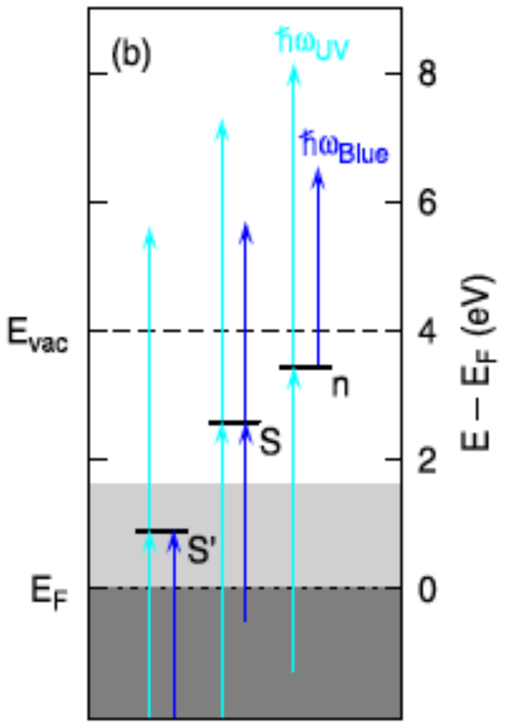
n	E_n^{exp} (eV)	E_n^{calc} (eV)	τ (fs)
1	0.83 ± 0.02	0.59	35 ± 3
2	0.19 ± 0.02	0.18	114 ± 6
3	0.09 ± 0.02	0.08	270 ± 12

Graphene/metal interface

PRL 108, 056801 (2012) PHYSICAL REVIEW LETTERS week ending 3 FEBRUARY 2012

Time-Resolved Two-Photon Photoemission of Unoccupied Electronic States of Periodically Rippled Graphene on Ru(0001)

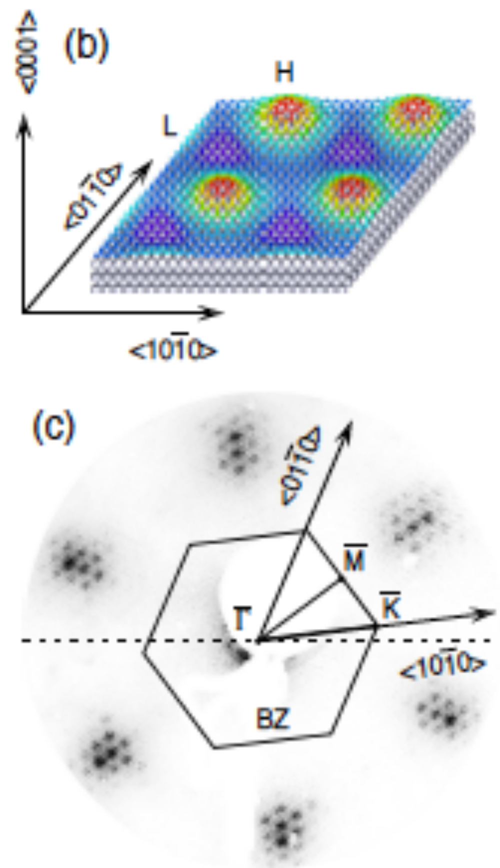
N. Armbrust,[1] J. Güdde,[1] P. Jakob,[1] and U. Höfer[1,2]

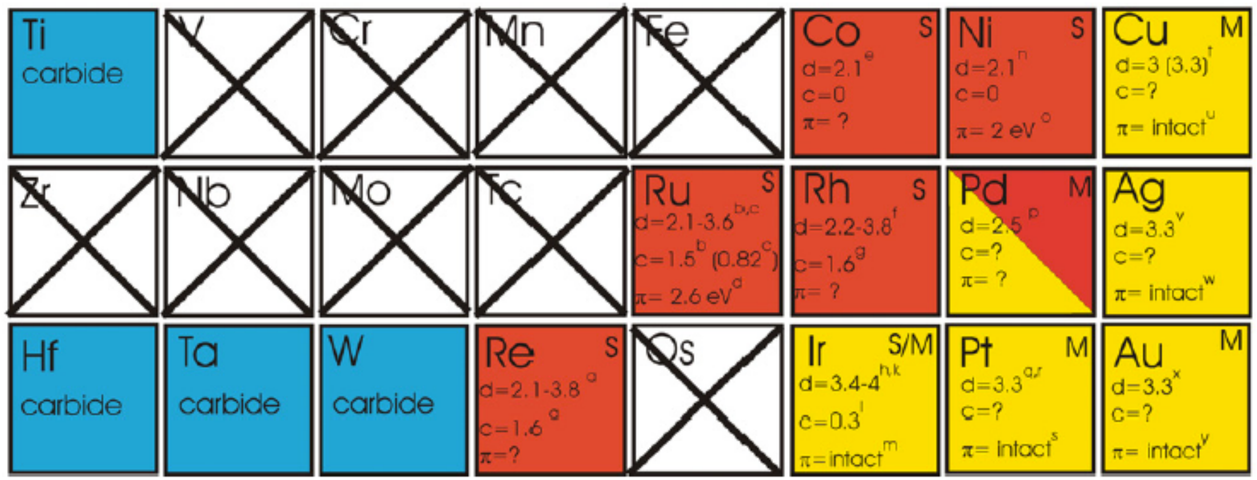


Graphene-Ru(0001) large corrugation

- Low interaction in H region
  Gr-Ru > 3 Å
- Strong interaction in L region
  Gr-Ru = 2.2 Å

- Two n=1 Image States
- Two Surface States



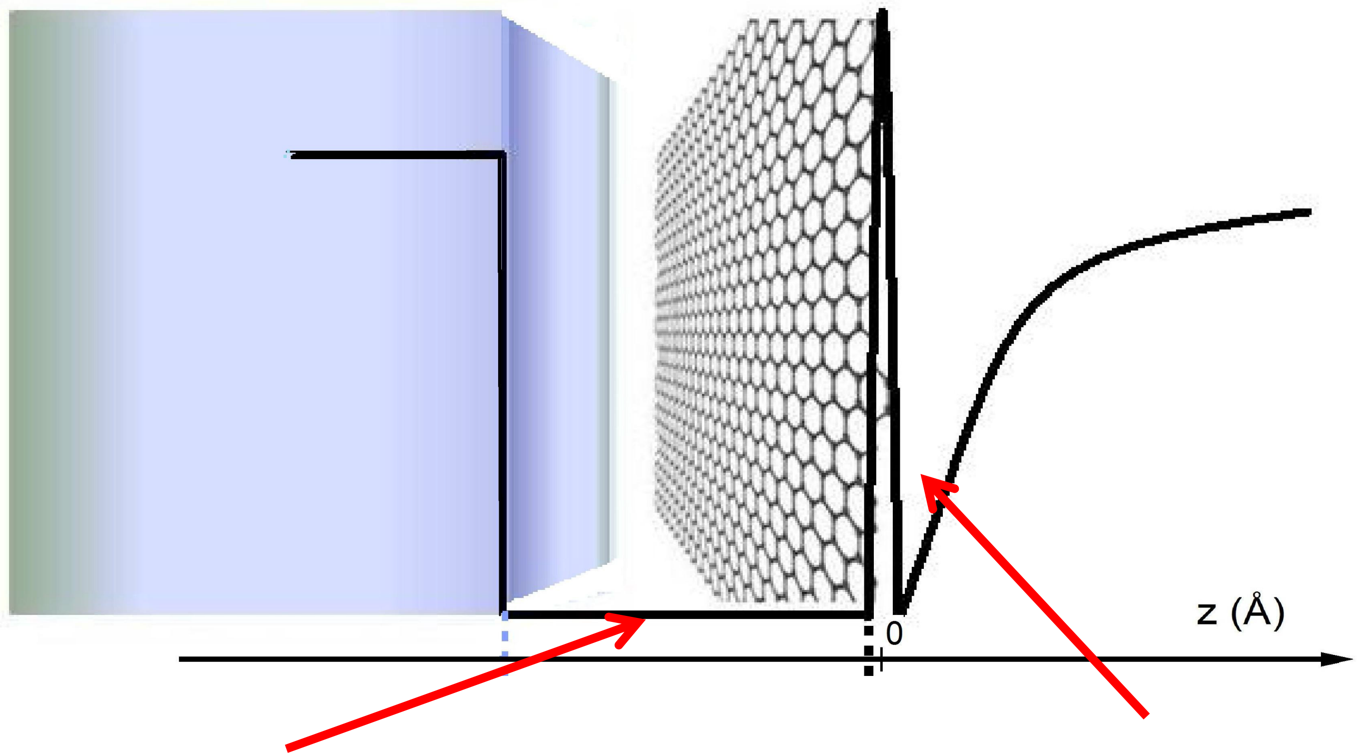


Gr/Cu(111)
Gr/Ir(111)
-
- Weakly interacting system

Gr/Ni(111)

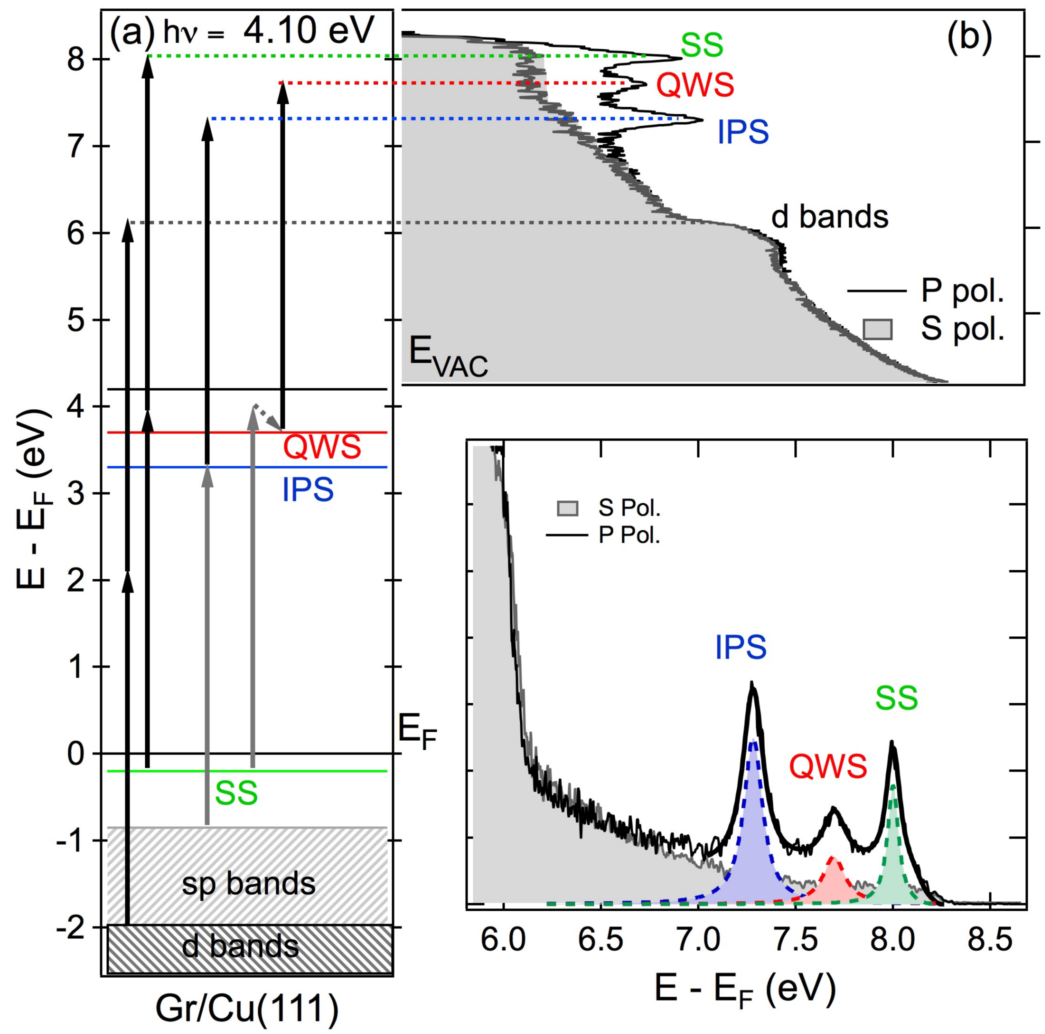
- Strongly interacting system

Two Potential Wells



- Quantum Well States
- Image Potential States

ARE EXPECTED !!



Gr/Cu(111)

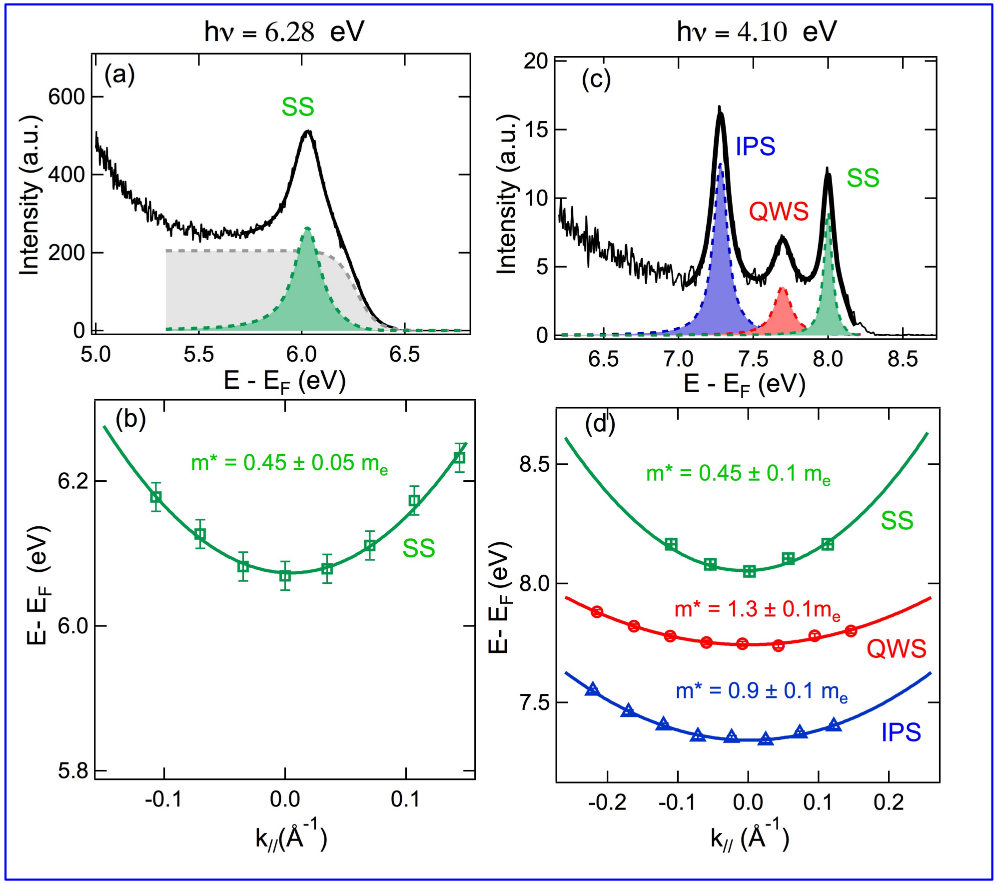
- An occupied Surface State: SS
- Two unoccupied States: QWS and IPS

In collaboration with

Fulvio Parmigiani
Petra Rudolf

S Pagliara, S Tognolini, L Bignardi, G Galimberti, S Achilli, MI Trioni, WF van Dorp, V Ocelík, P Rudolf, F. Parmigiani, Physical Review B 91 (19), 195440 (2015)

Graphene/metal interface

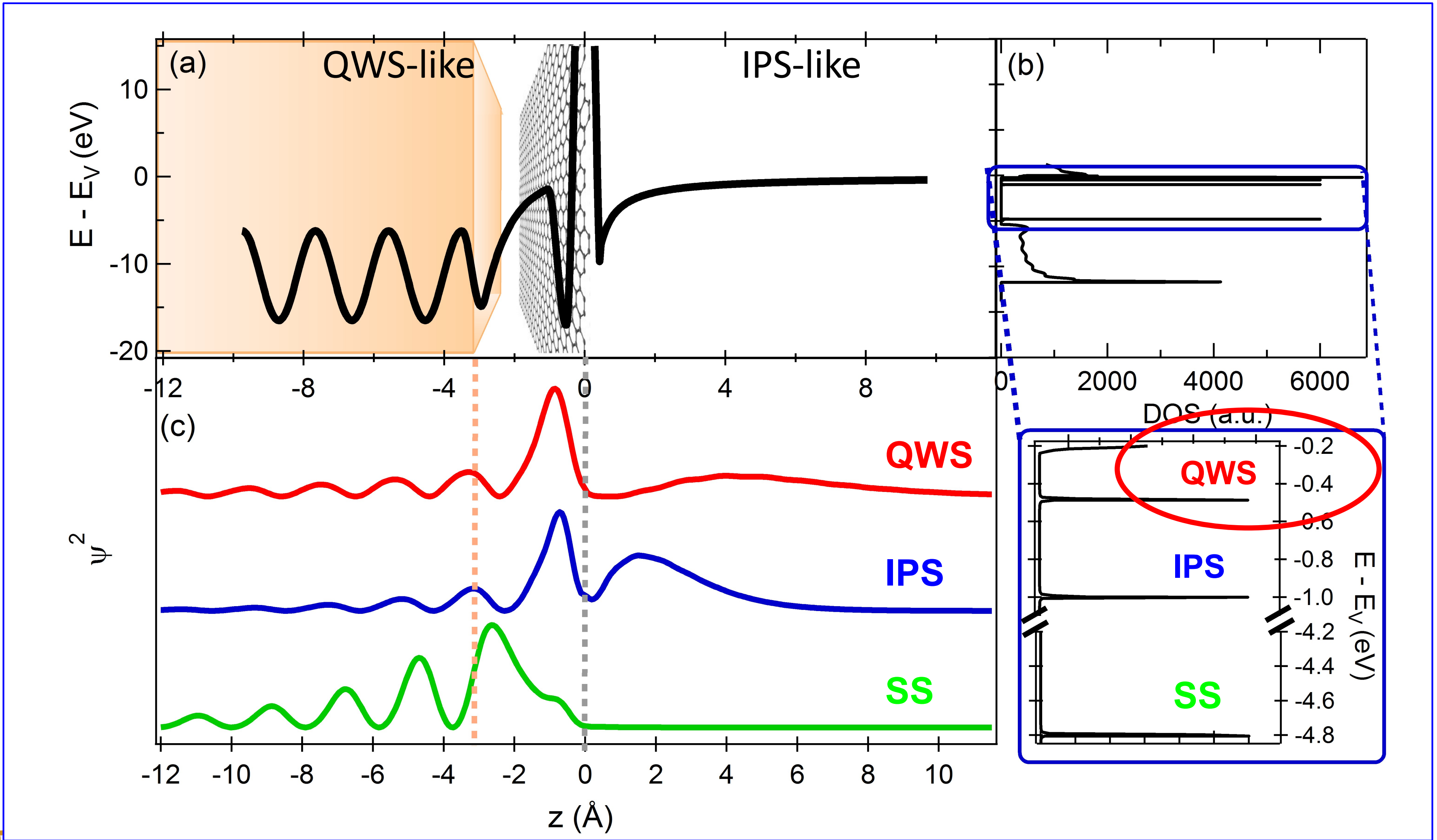


Gr/Cu(111)

- The SS results shifted of about 150 meV
- IPS state preserves the metal character

	SS	IPS (n=1)	QWS
Gr/Cu(111)	BE 0.24±0.05 eV m^*/m_e=0.47±0.04	BE= 0.90 ±0.05 eV m^*/m_e = 0.9±0.1	BE = 0.45±0.05 eV m^*/m_e = 1.3±0.1
Cu(111)	BE = 0.39 ±0.05 eV m^*/m_e=0.45±0.05	BE= 0.84 ±0.03 eV m^*/m_e = 1.26±0.07	

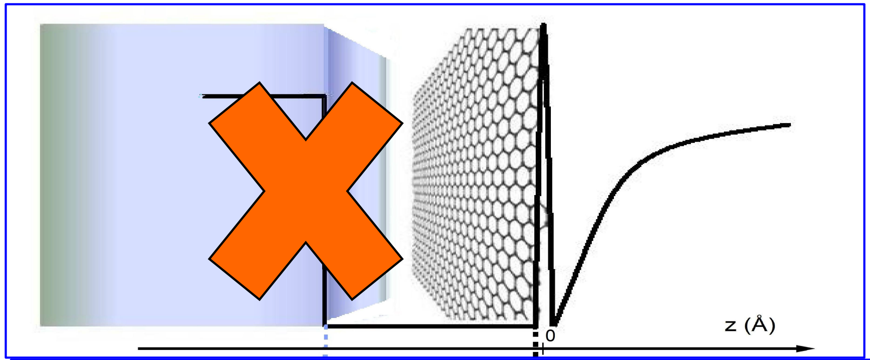
One potential model



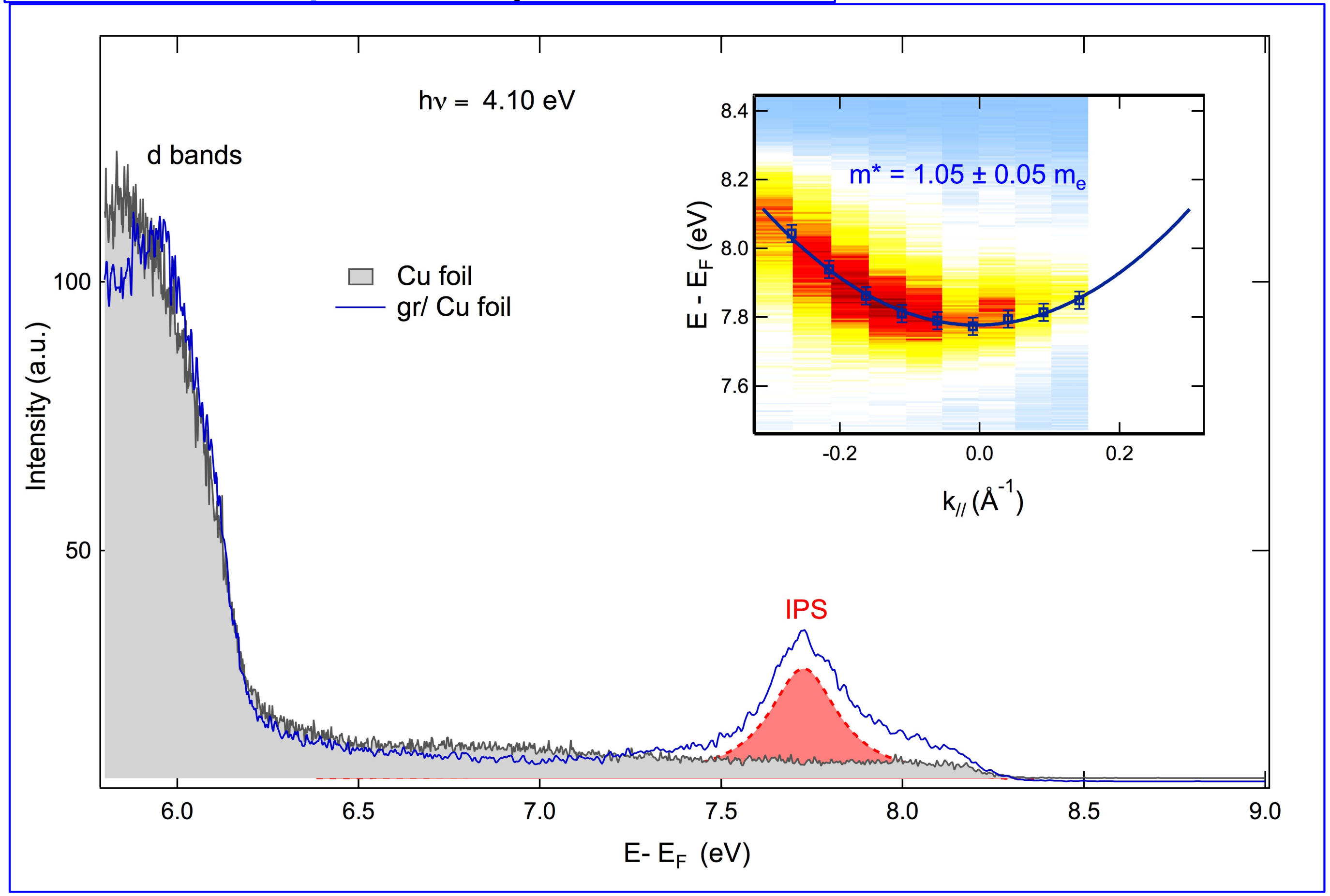
E. V. Chulkov et al., Surf. Sci. **437**, 330 (1999).

H. G. Zhang, J. Phys.: Condens. Matter **22**, 399802 (2010).

Graphene/metal interface

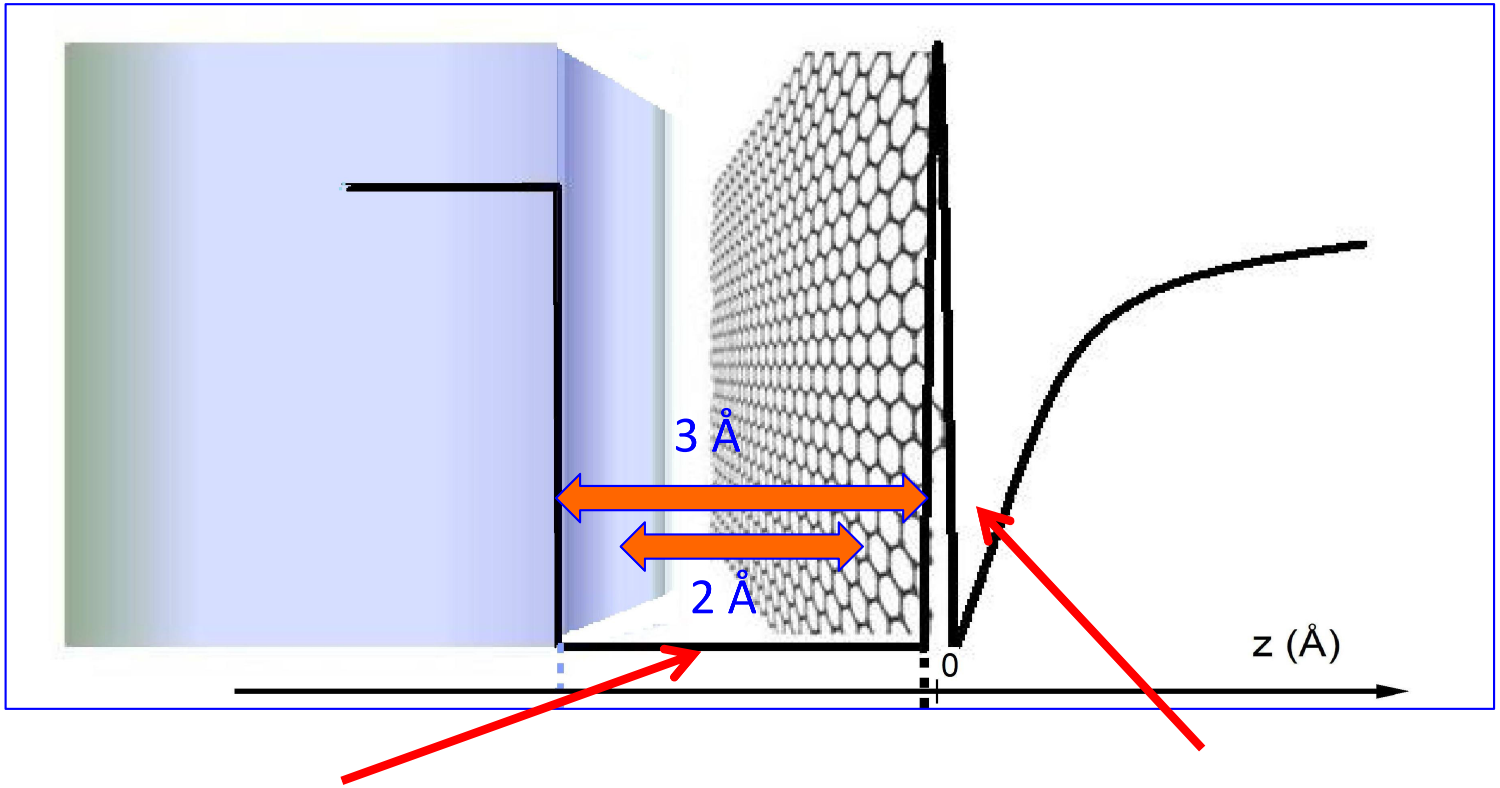


Graphene on Cu polycristalline foil



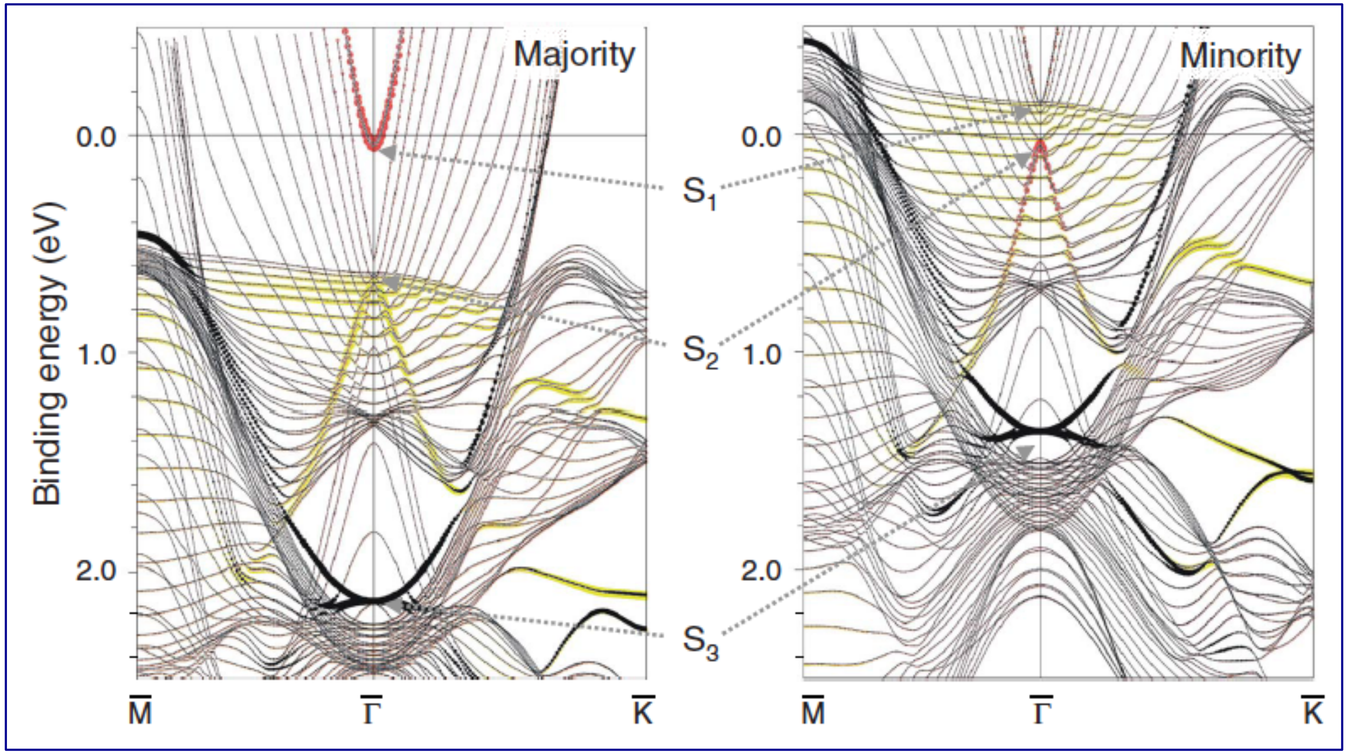
Graphene/metal interface

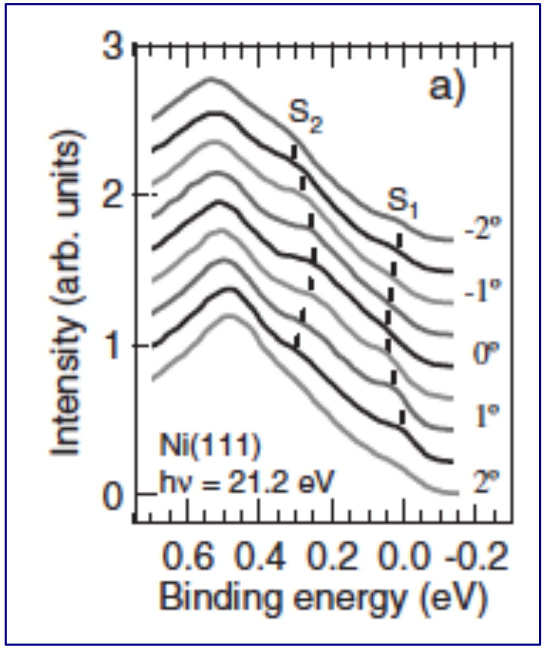
Gr/Ni(111)



- Quantum Well States
- Image Potential States

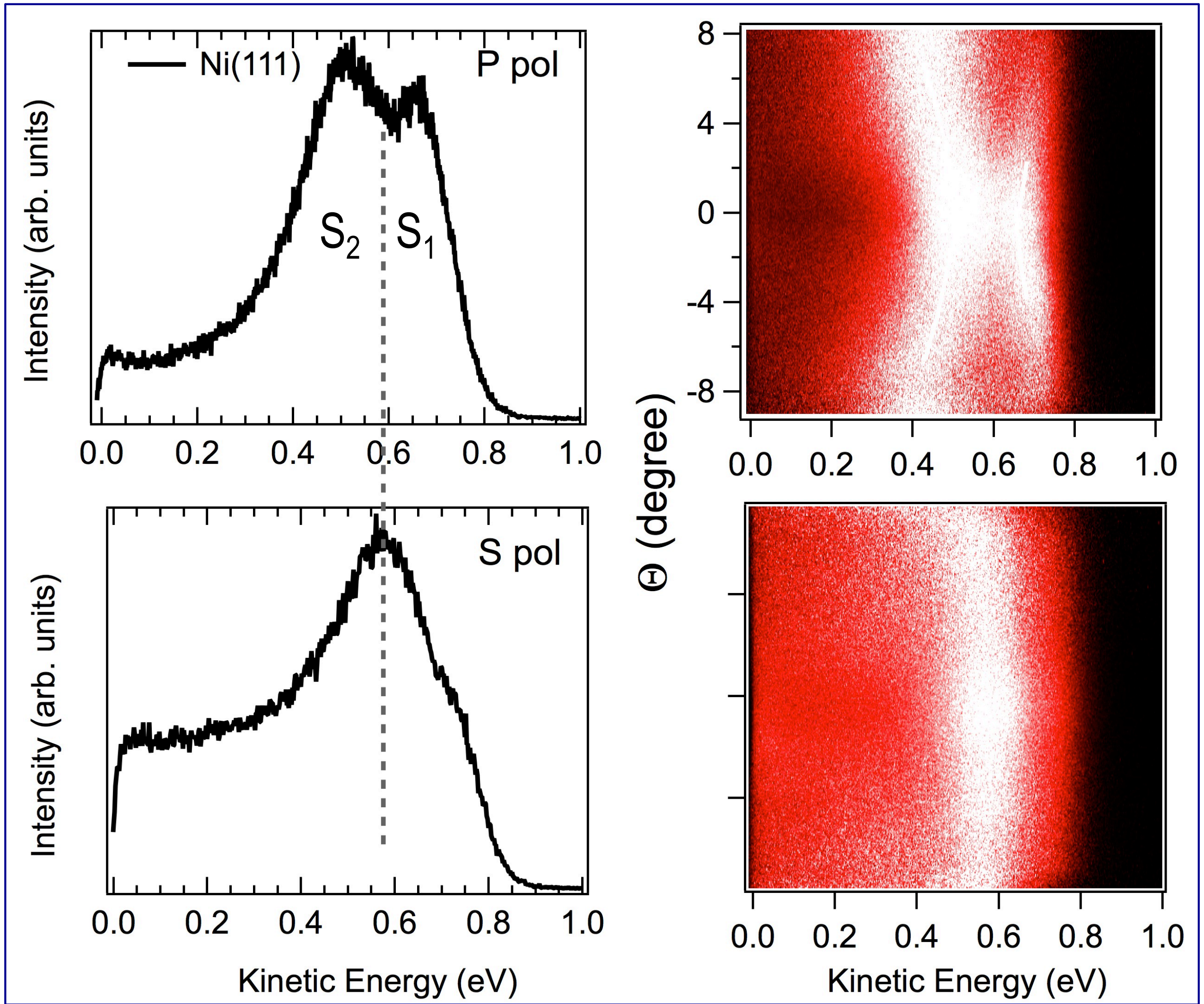
Surface State on Ni(111)



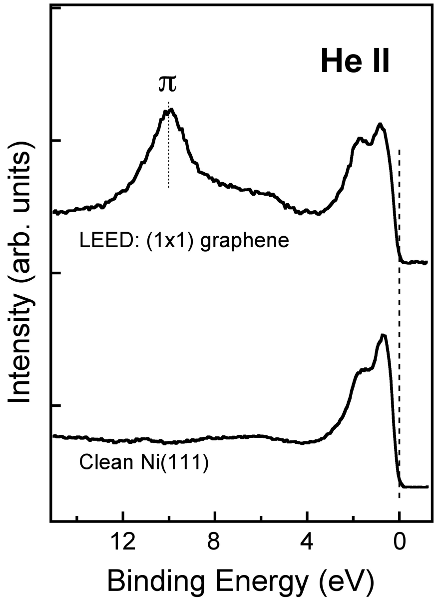


J. Lobo-Checa et al. PRB 77, 075415 (2008)

Graphene/metal interface

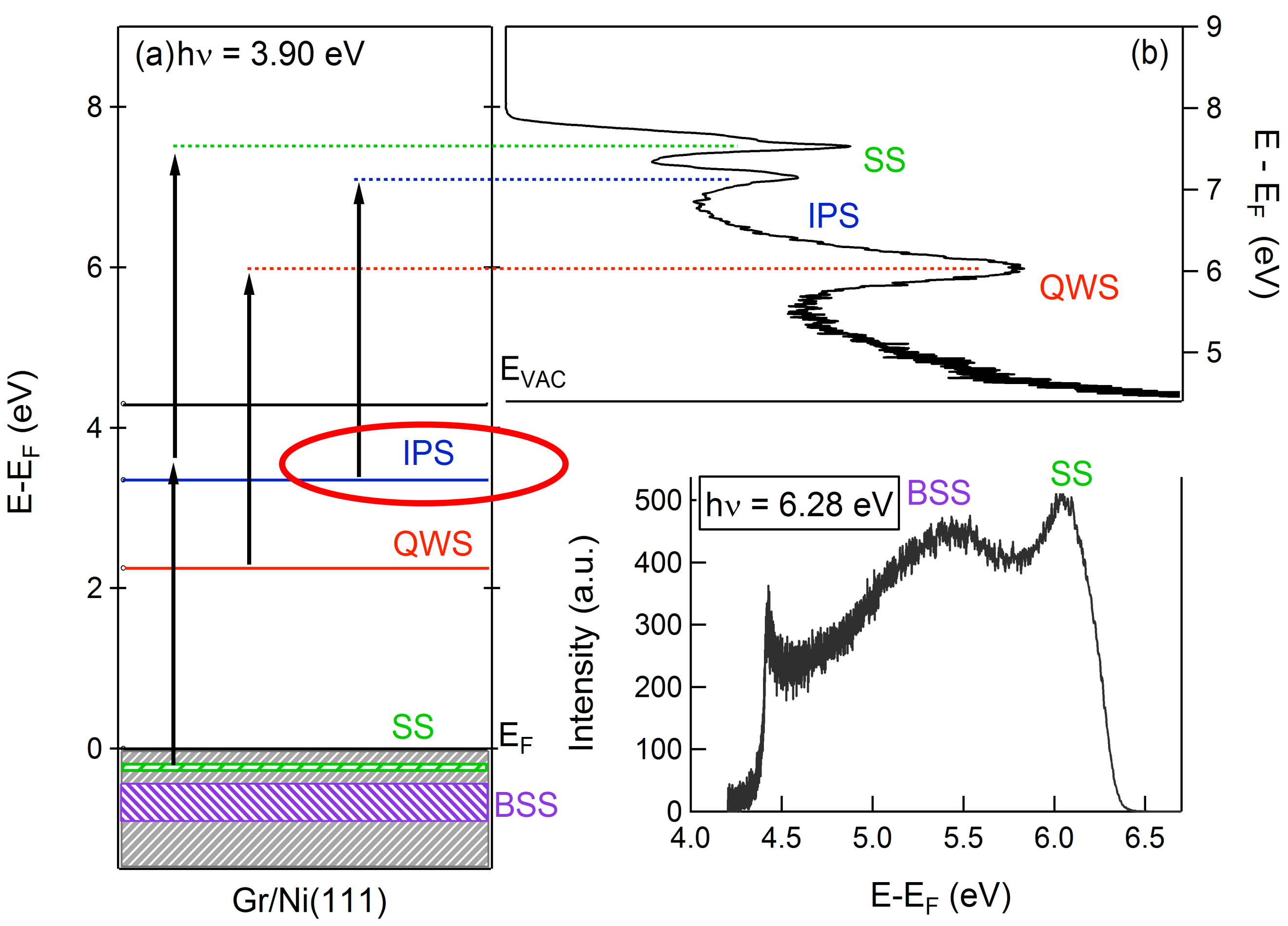


Linear Photoemission
hν=6.3 eV



	S_1	S_2
Ni(111)	BE = 0.08 ±0.05 eV m^*/m_e = 0.4±0.05	BE= 0.25 ±0.05 eV m^*/m_e = -0.3±0.05

Graphene/metal interface



Gr/Ni(111)

- An occupied Surface State: SS
- Two unoccupied States: QWS and IPS

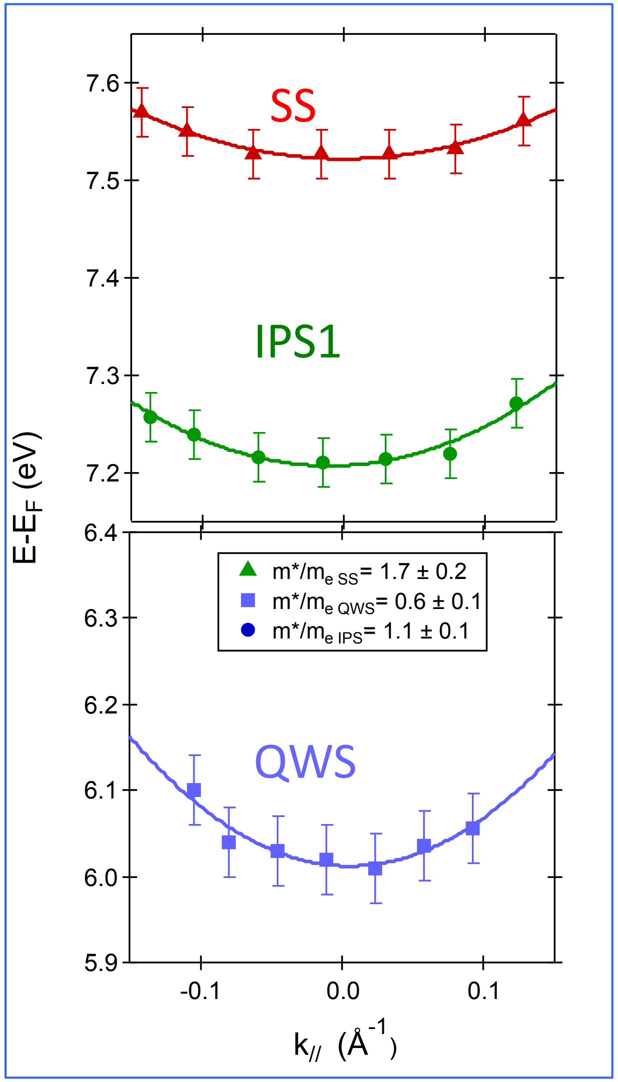
In collaboration with

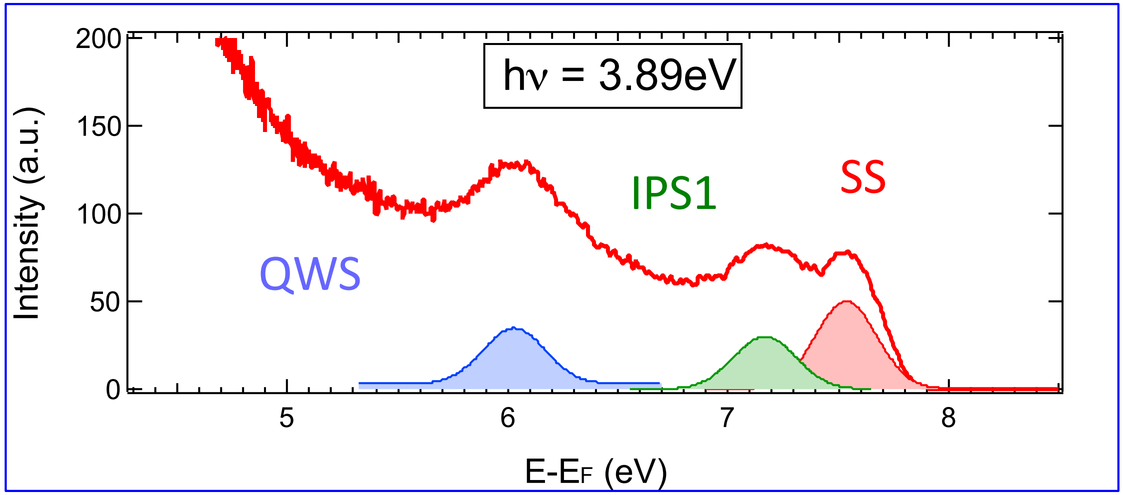
Cinzia Cepek
Cristina Africh

Unpublished data

December, 2017

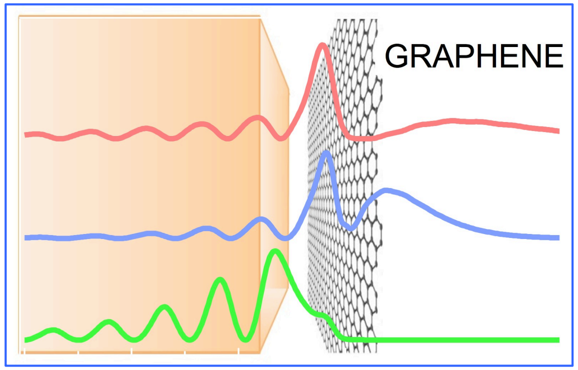
Graphene/metal interface



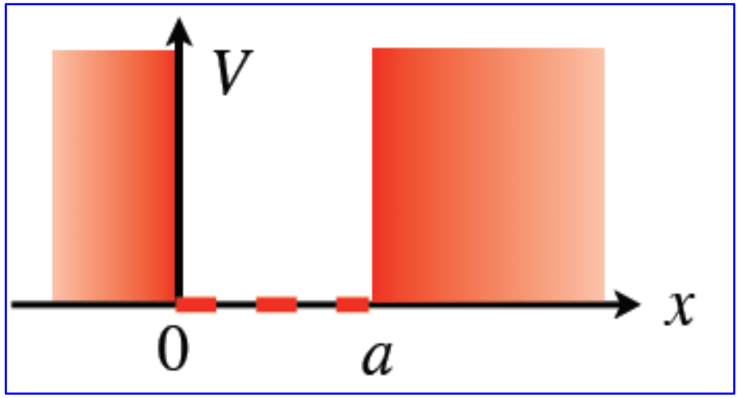


	SS	IPS (n=1)	QWS
Gr/Ni(111)	BE 0.25±0.05 eV m^*/m_e= 1.7±0.2	BE= 0.95 ±0.05 eV m^*/m_e = 1.1±0.1	BE = 2.05±0.05 eV m^*/m_e = 0.6±0.1
Ni(111)		BE= 0.80 ±0.03 eV [6] m^*/m_e = 1.12±0.06[6]	

[6] Lobo-Checa et al., Phys. Rev. B 77,(2008).
[7] S.Schuppler et al., Phys. Rev. B 42,(1990).



As in the classical "particle in a box" problem !!!

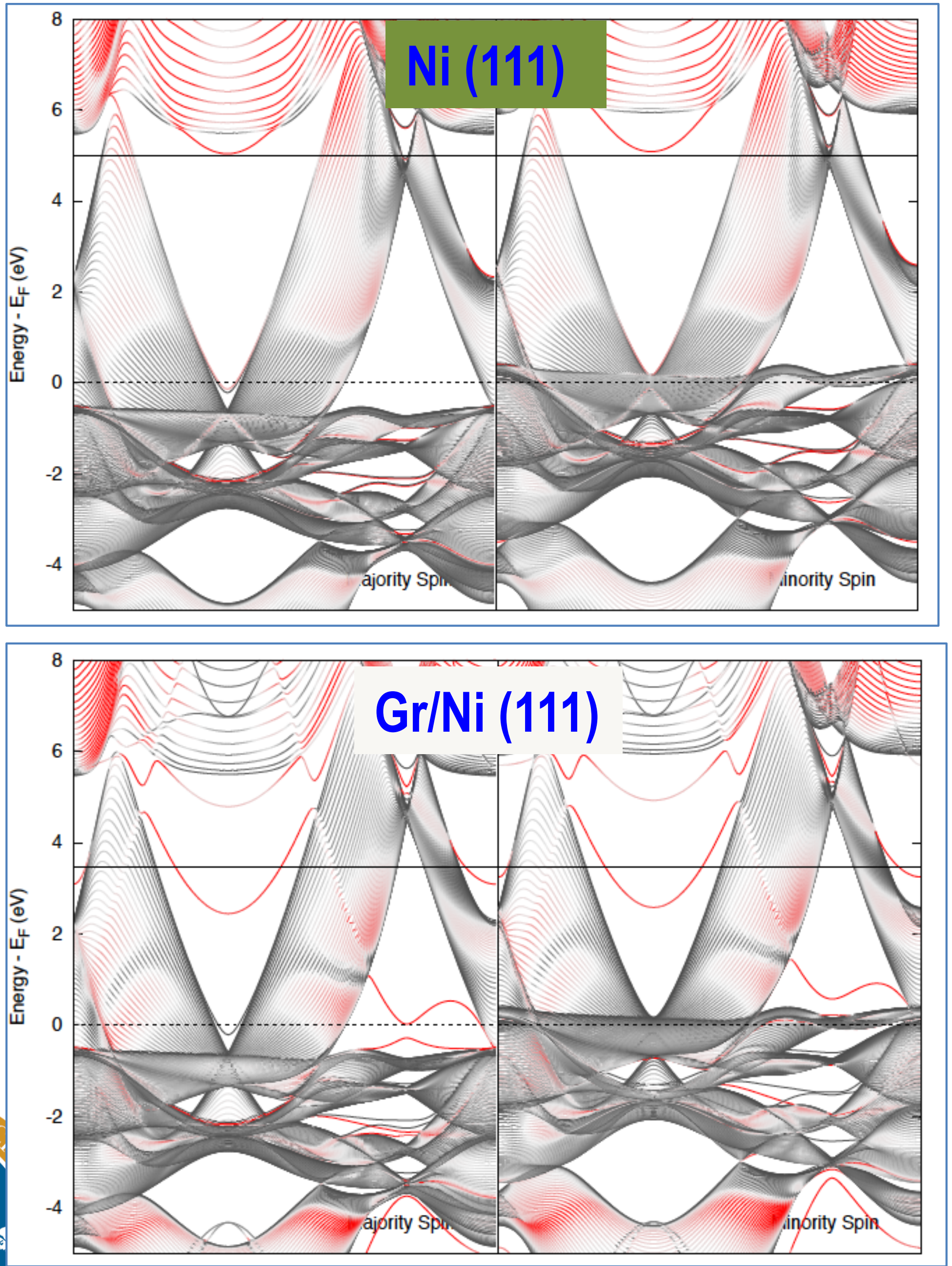


$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Gr/Cu(111) a ≈ 3Å
E_{QWS}= 0.5 ± 0.05 eV
m^*= 1.3 ± 0.1 m_e

Gr/Ni(111) a ≈ 2Å
E_{QWS}= 2.0 ± 0.1 eV
m^*= 0.5 ± 0.1 m_e

Graphene/metal interface

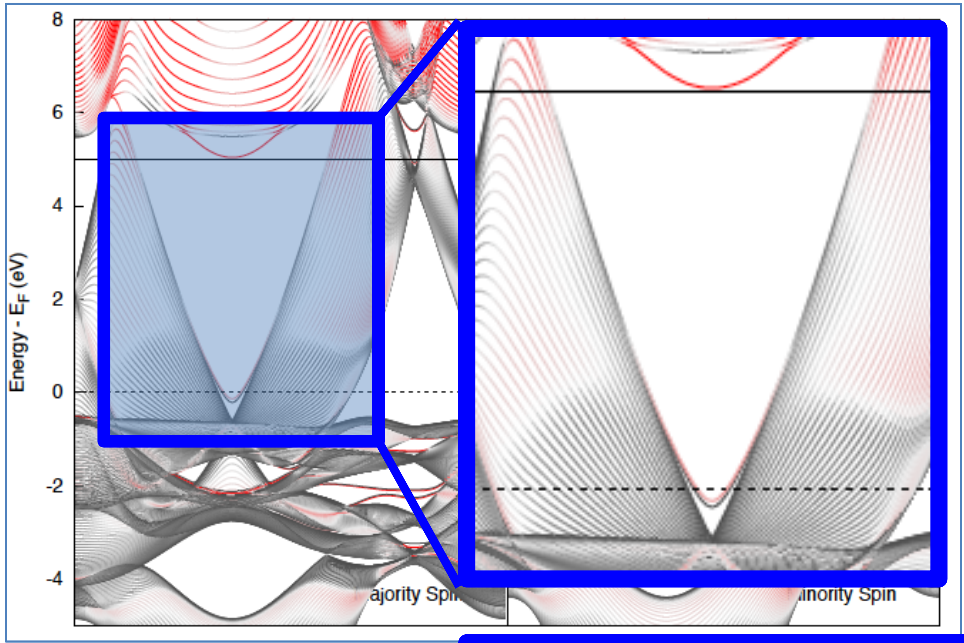


Ab initio calculations

Density functional theory (DFT) as implemented in the SIESTA package.
To model the Ni(111) surface we used a supercell approach with a thick nickel slab (52 layers).

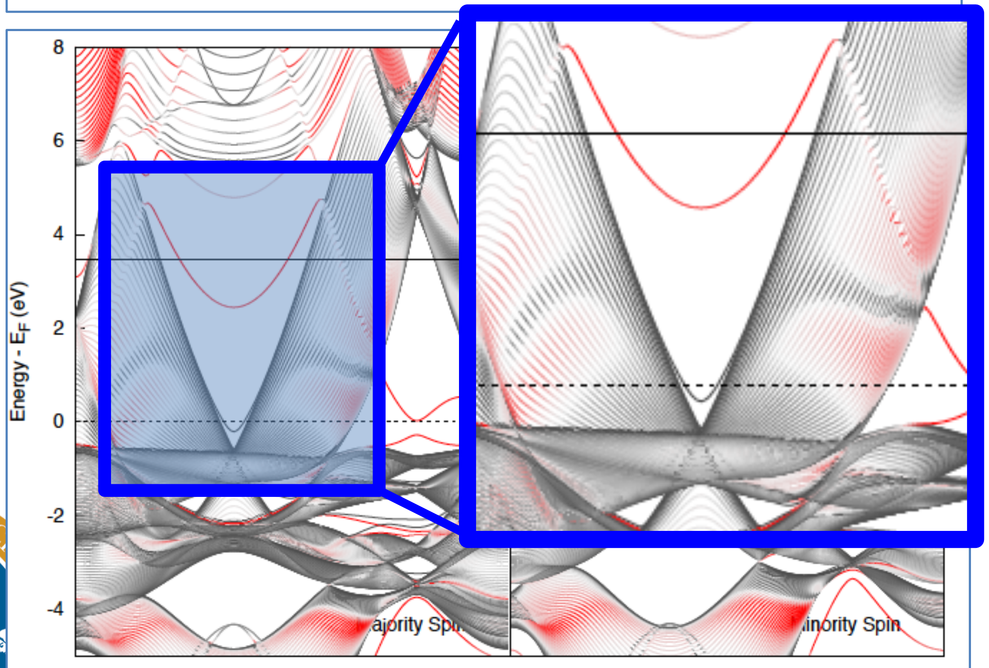
In the model the image potential is not present.
The electronic structure has been projected on the Ni atoms at the surface.

Graphene/metal interface



Ni (111)

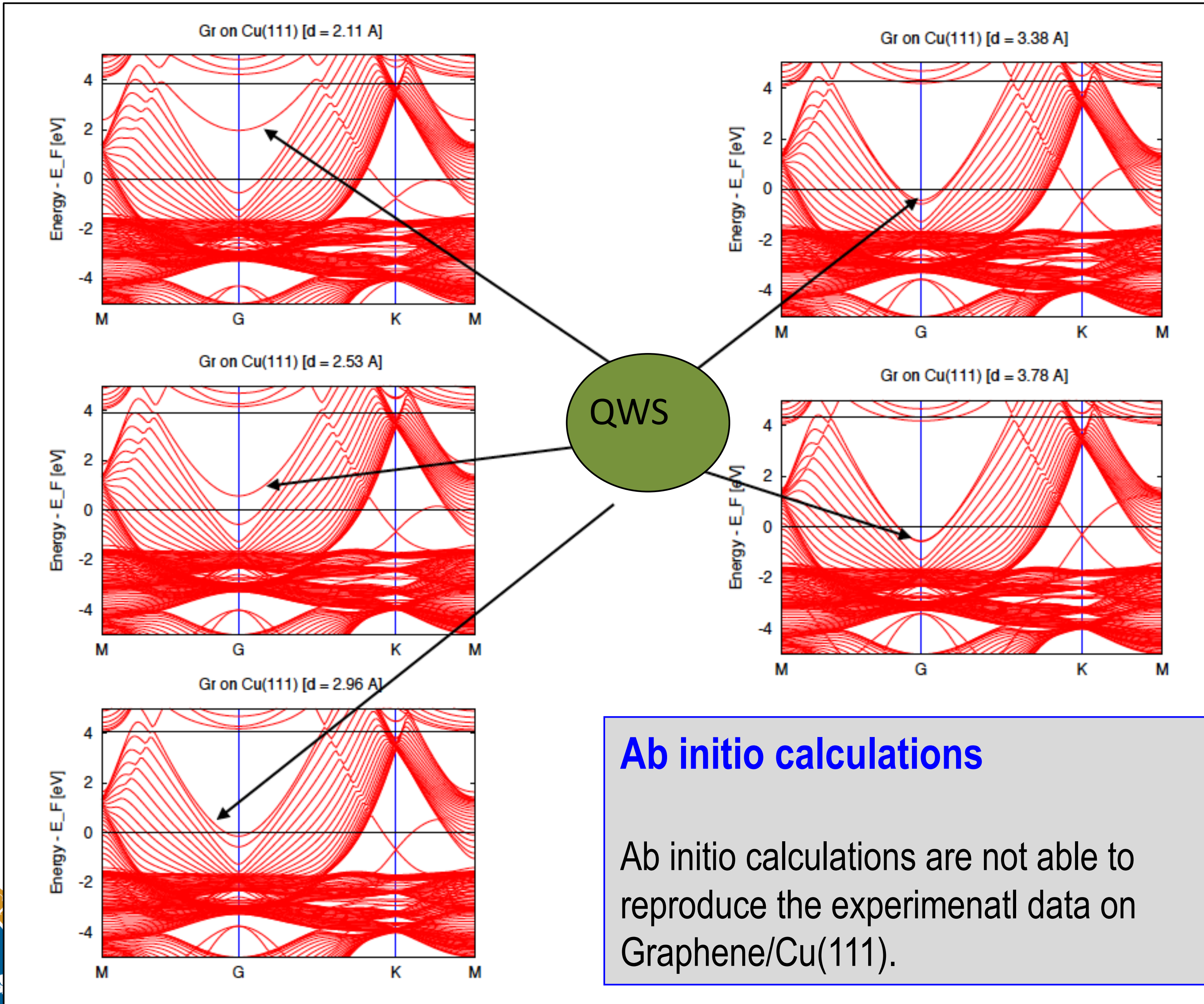
- IPS
- No QWS in the gap
- Two Occupied Surface States



Gr/Ni (111)

- IPS
- A QWS in the gap
- One Occupied Surface State

Graphene/metal interface



Ab initio calculations

Ab initio calculations are not able to reproduce the experimenatl data on Graphene/Cu(111).

Collaborations

- Graphene /Cu(111)
Petra Rudolph (Groningen University)
Fulvio Parmigiani (Università di Trieste)
Luca Bignardi (Trieste Elettra)

- Graphene/Ni(111)
Cinzia Cepek (CNR-IOM)
Cristina Africh (CNR-IOM)

- Graphene/Ir(111)
Carlo Mariani (La Sapienza)
Luca Longetti (La Sapienza)

- Theory group
Mario I. Trioni (ISTM-CNR)
Simona Achilli (ISTM-CNR)
Elisabetta del Castillo

- ELPHOS Group
Silvia Tognolini
Stefano Ponzoni
Eleonora Fava
Gianluca Galimberti
Gina Ambrosio

- Molecules /Ag
(Università di Padova)
Mauro Sambi
Francesco Sedona

Thanks for your attention

More details here:

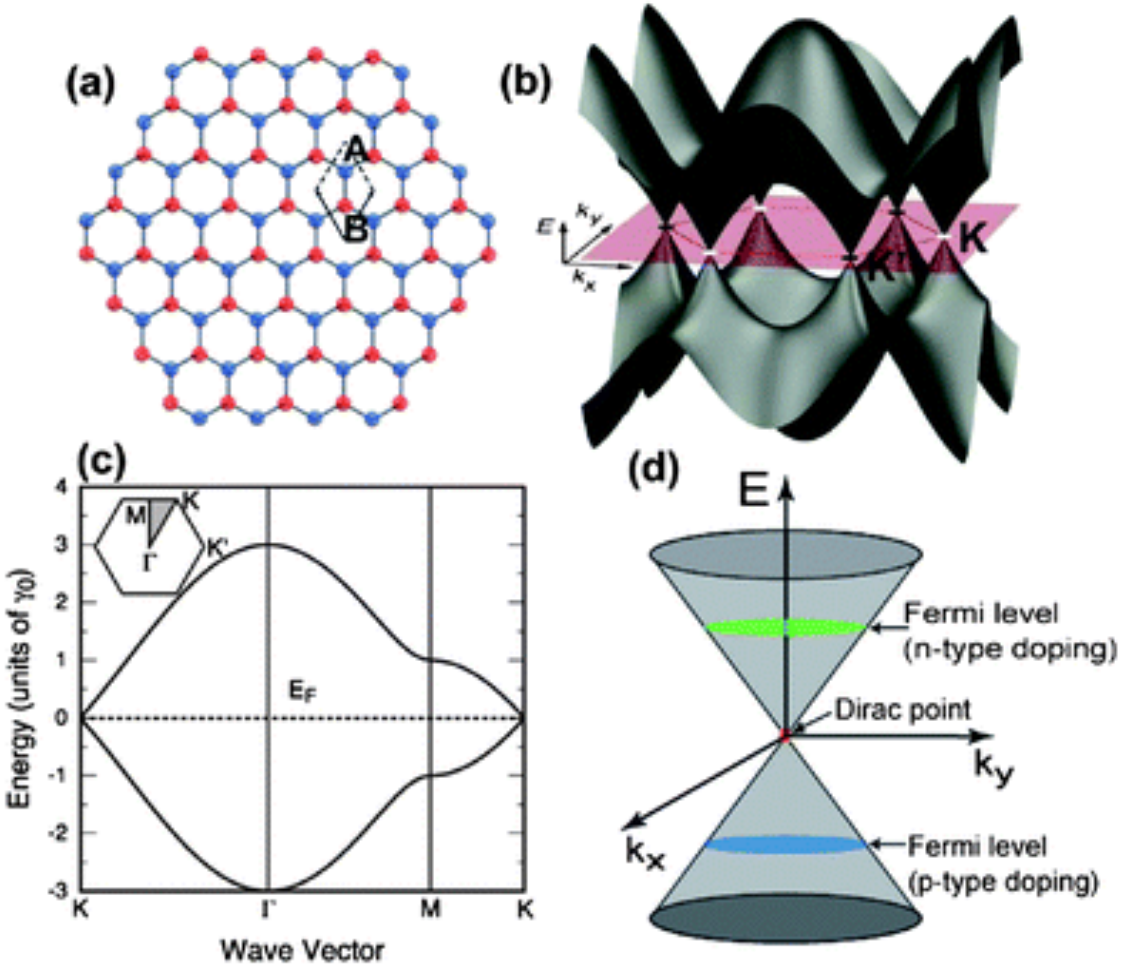
- S Tognolini, S Ponzoni, F Sedona, M Sambi, S Pagliara
  Role of the Substrate Orientation in the Photoinduced Electron Dynamics at the Porphyrin/Ag Interface
  The Journal of Physical Chemistry Letters 6 (18), 3632-3638 (2015)

- S Tognolini, S Achilli, L Longetti, E Fava, C Mariani, MI Trioni, S Pagliara
  Rashba Spin-Orbit Coupling in Image Potential States
  Physical Review Letters 115 (4), 046801 (2015)

- S Pagliara, S Tognolini, L Bignardi, G Galimberti, S Achilli, MI Trioni, WF van Dorp, V Ocelík, P Rudolf, F Parmigiani
  Nature of the surface states at the single-layer graphene/Cu (111) and graphene/polycrystalline-Cu interfaces
  Physical Review B 91 (19), 195440 (2015)

- S Tognolini, S Pagliara, L Bignardi, S Ponzoni, P Rudolf, F Parmigiani
  Surface states resonances at the single-layer graphene/Cu (111) interface
  Surface Science 643, 210-213 (2016)

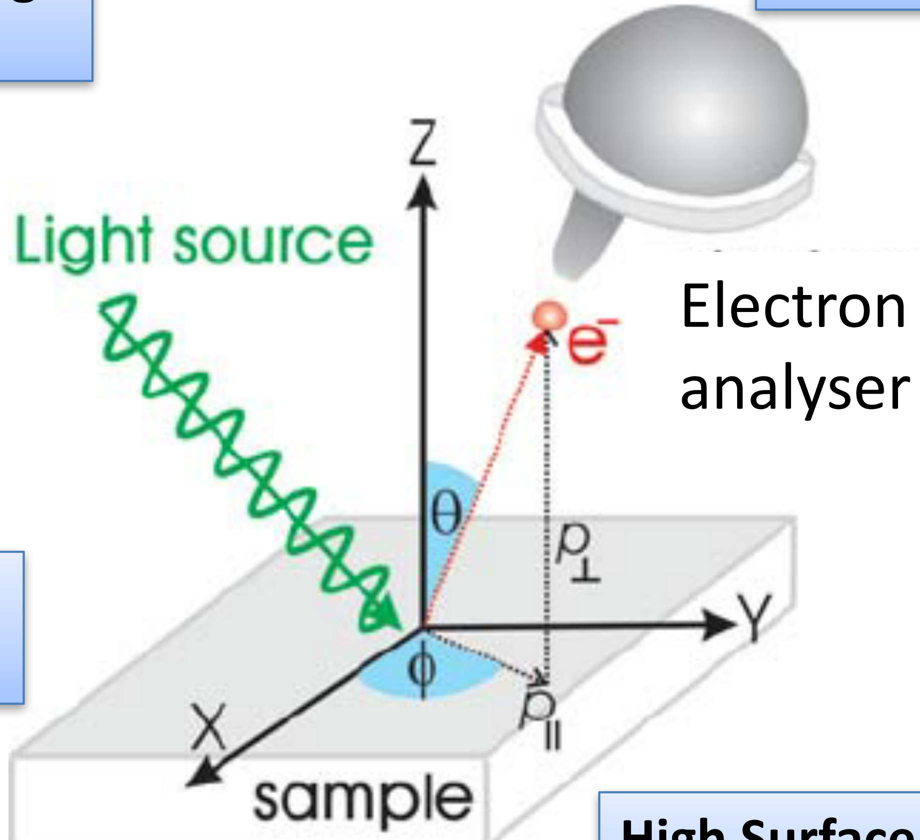
Thanks for your attention



(a)
A
B
(b)
E
k_y
k_x
K'
K
(c)
M
K
K'
Γ
Energy (units of γ_0)
4
3
2
1
0
-1
-2
-3
E_F
K
Γ
M
K
Wave Vector
(d)
E
Fermi level
(n-type doping)
Dirac point
k_y
k_x
Fermi level
(p-type doping)

Wide Temperature Range
From 20 K to 1300 K

Fast Data Acquisition
Down to 100 ms timescale

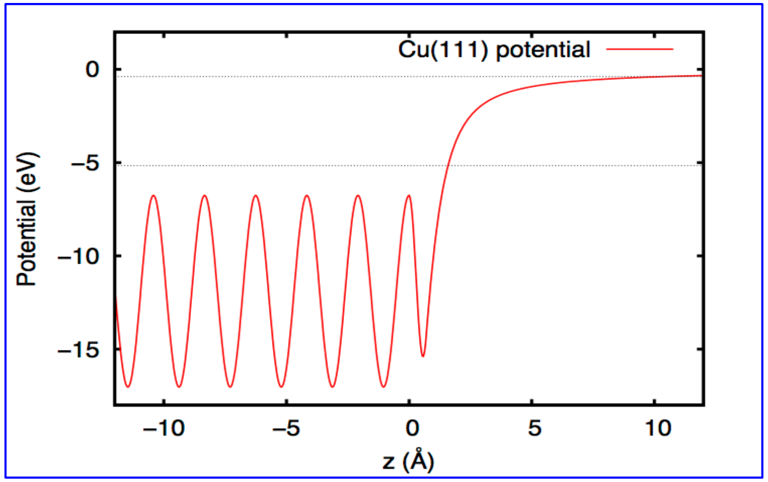


High Energy Resolution
In the range 40-100 meV

High Surface Sensitivity
0.5 of ML

One potential model

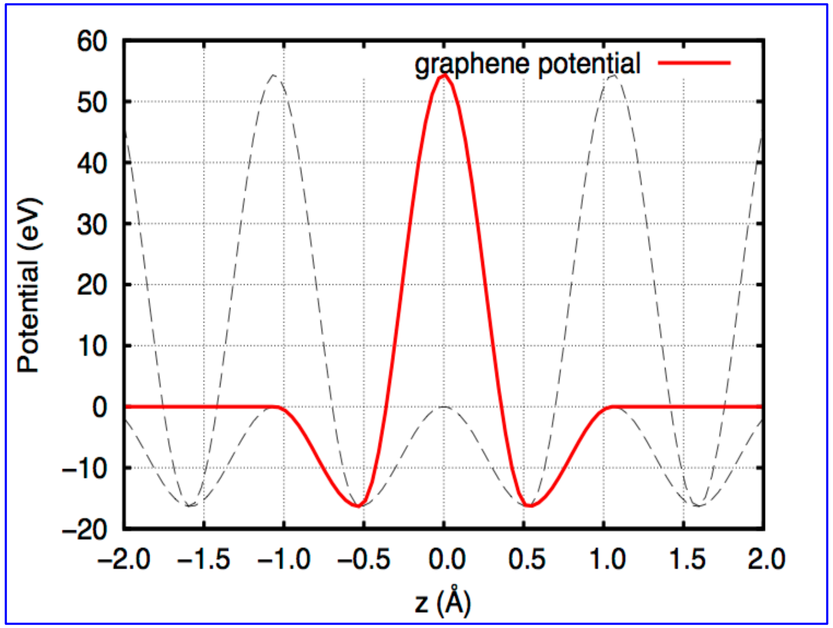
Cu(111) potential



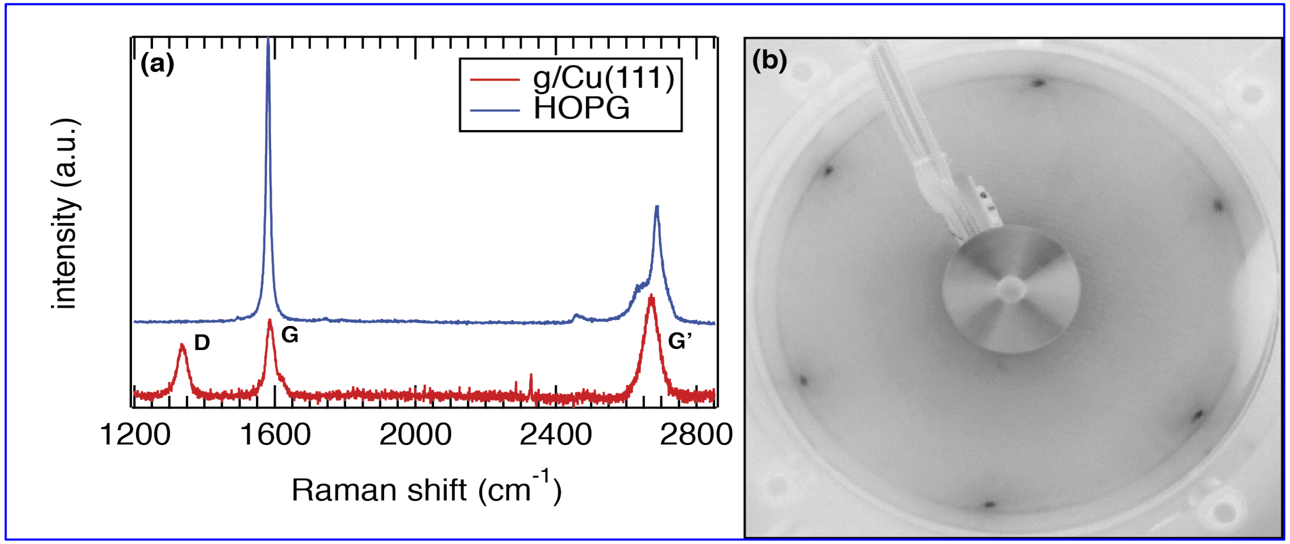
E. V. Chulkov et al., Surf. Sci. **437**, 330 (1999).

Graphene potential

$$v_{Gr}(z) = \begin{cases} 0 & \text{for } z < -2 \\ A_1\{\cos[(z-2)\pi] - 1\} & \text{for } -2 < z < -1 \\ A_2\{\cos[z\pi] + 1\} & \text{for } -1 < z < 1 \\ A_1\{\cos[(z-2)\pi] - 1\} & \text{for } 1 < z < 2 \\ 0 & \text{for } z > 2 \end{cases}$$



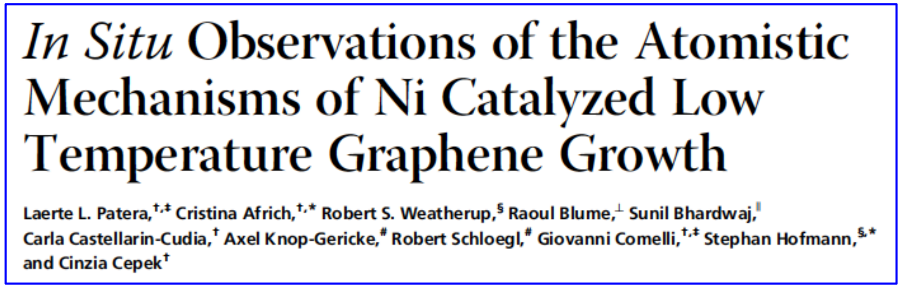
H. G. Zhang, J. Phys.: Condens. Matter **22**, 399802 (2010).



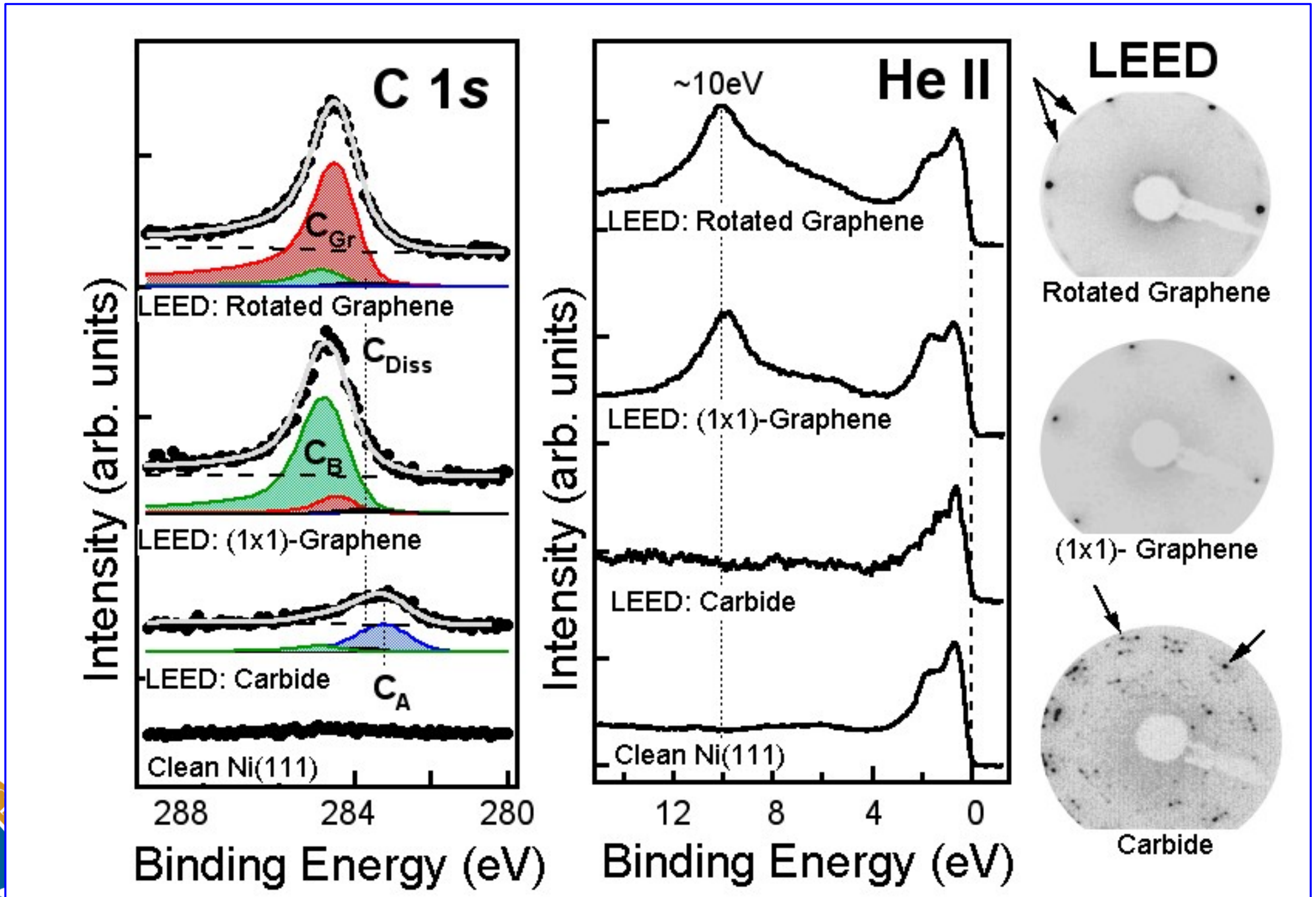
Graphene was grown on a Cu(111) single crystal (MaTeck GmbH) that was previously Ar-sputtered (1 keV) and annealed (650 K) in ultrahigh vacuum. The crystal was then transferred (through air) into a vacuum furnace (base pressure 10^{-5} mbar), where it was reduced in a mixture of 0.5 mbar of hydrogen (Messer, purity 5.0) and 0.1 mbar of argon (Linde, purity 5.0) for 4 h at a temperature of 1250 K before graphene was grown by exposure to a mixture of argon (0.1 mbar), hydrogen (0.5 mbar), and methane (0.5 mbar, Messer, purity 4.0) for two min at 1250 K. The sample was subsequently cooled to room temperature in an argon flow (0.09 mbar) at a rate of 15 K/min. The Cu foil (thickness 25 µm, 99.999% purity, ESPI Metals) was pre-etched in a 0.25 M solution of H_2SO_4 in water for 5 min, rinsed in water and ethanol, dried in an argon flow and transferred to the vacuum furnace. The foil was then reduced in H_2 and Ar for 1 hr. at the same temperature and pressure employed for Cu(111), while the growth of graphene followed the same protocol described above for the growth on Cu(111).

All the calculations of the electronic structures were carried out within the density functional theory (DFT) as implemented in the SIESTA package. Within this code, linear combinations of pseudo-atomic orbitals are used to solve the Kohn-Sham equations with 3D periodic boundary conditions. The exchange-correlation energy and electron-ion interaction were described by the Perdew-Burke-Ernzerhof generalized gradient approximation and norm-conserving pseudopotentials in the fully nonlocal form, respectively.

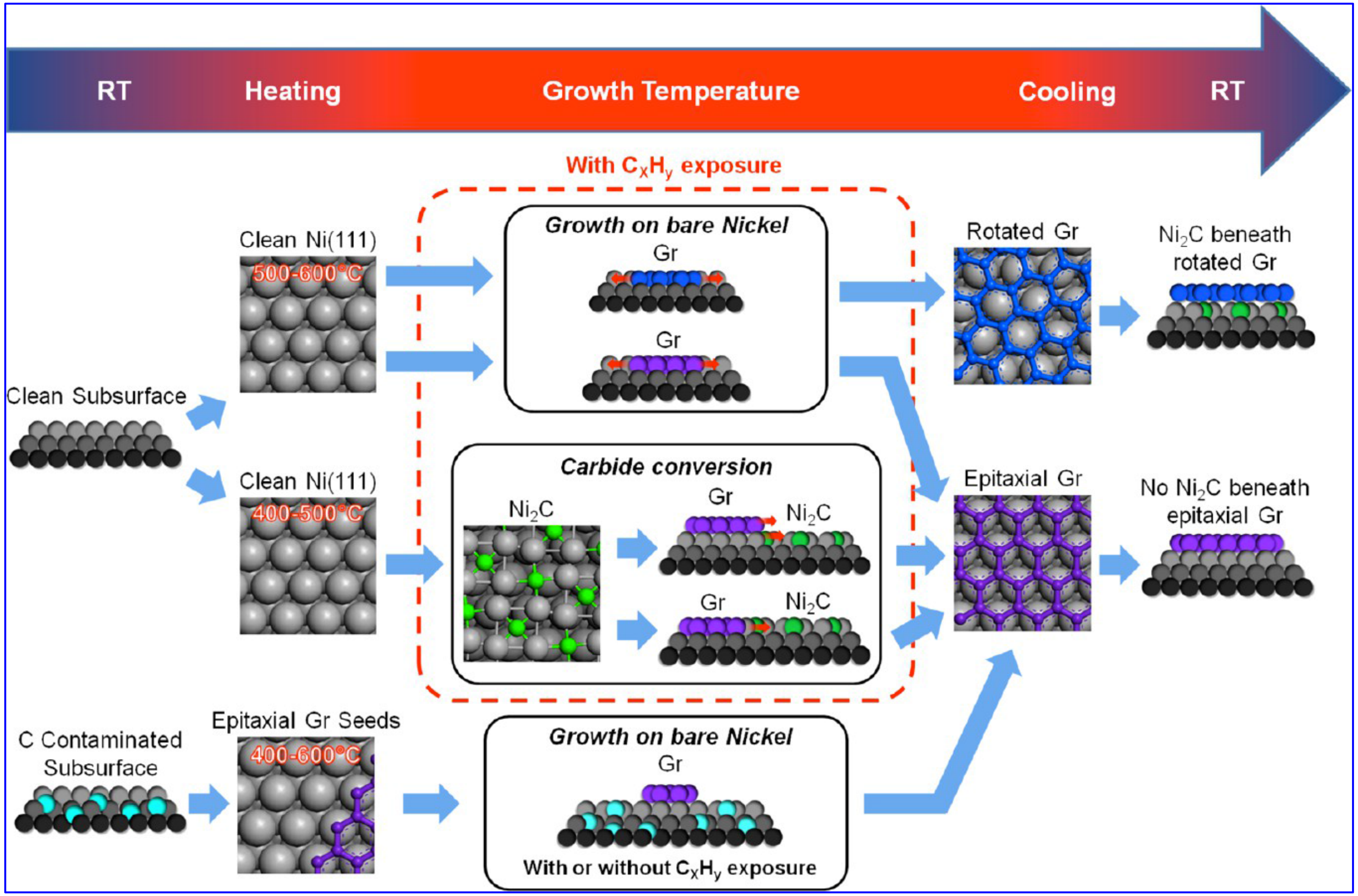
To test our computational setup (basis set, pseudopotential, etc.) we calculated the lattice constant of the Ni bulk and we obtained a value of 3.56 Ang, being the experimental one equal to 3.52 Ang.
To model the Ni(111) surface we used a supercell approach with a thick nickel slab (52 layers).
In order to avoid spurious interactions we separated periodic replicas of nickel slabs with an appropriate vacuum region.
The optimized geometry was obtained relaxing the two upper layers until the residual forces were smaller than 0.01~eV/Ang.



Epitaxial graphene on Ni(111) surface. No trace of carbide is present.



ACSNano, 9, 7901 (2013)



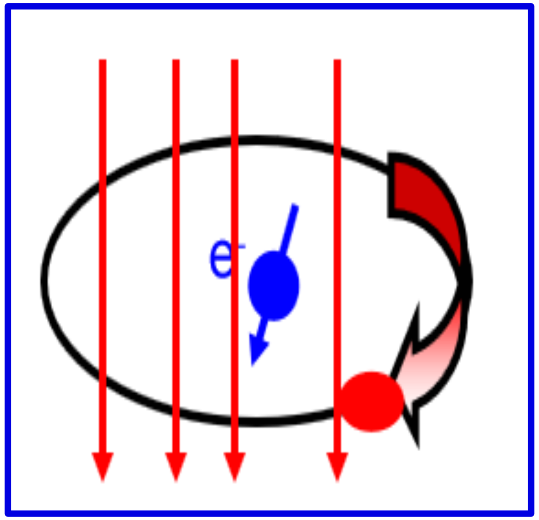
Gr/Ni(111)

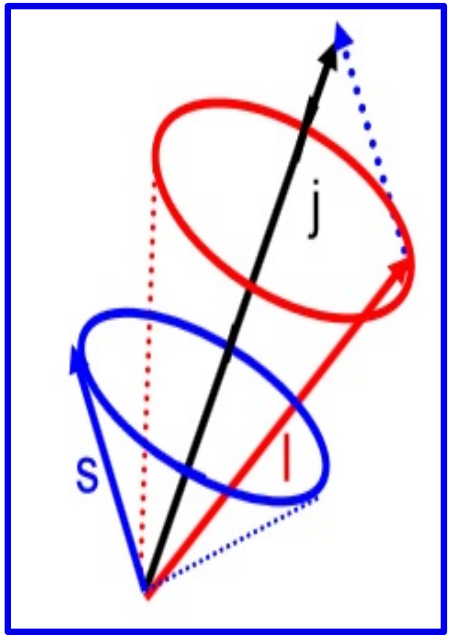
- Grown by CVD , hydrocarbon precursor, 400°C<T<500°C

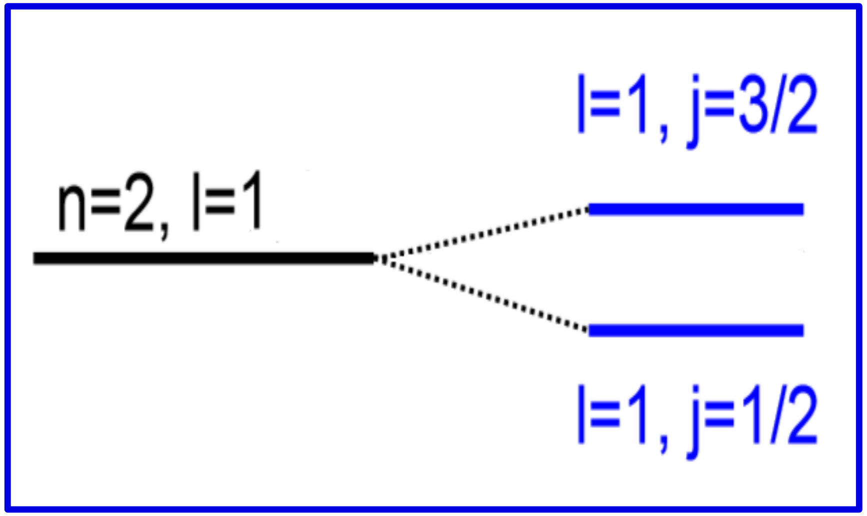
Spin-orbit interaction from solid state course

$$\Delta E = -\boldsymbol{\mu}_s \cdot \boldsymbol{B}_l$$

$$\Delta E = \frac{Ze^2\mu_0}{8\pi m_e^2}\langle r^{-3}\rangle \boldsymbol{l}\cdot\boldsymbol{s}$$

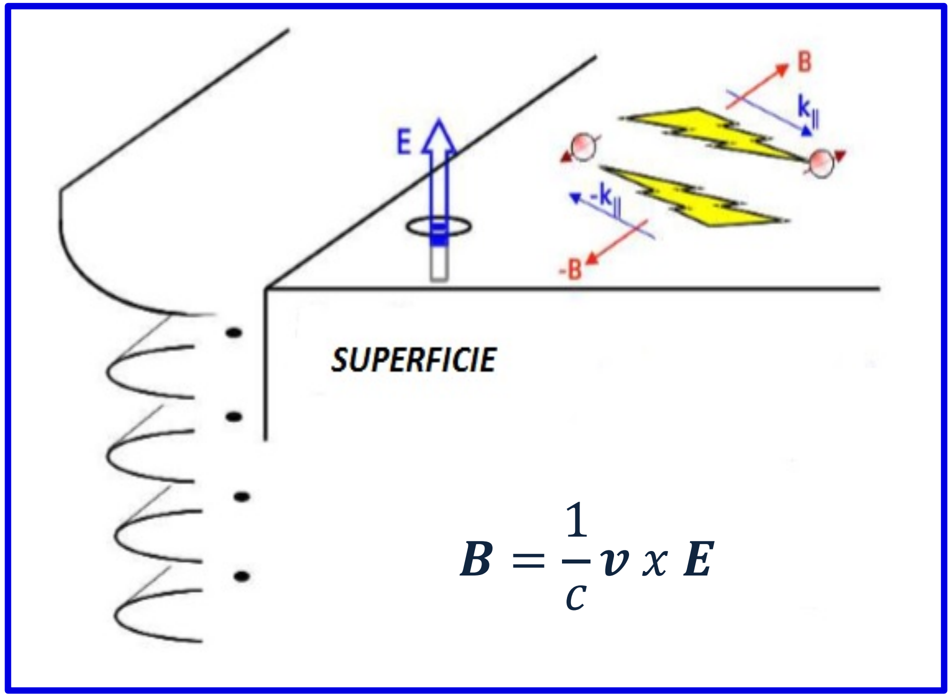




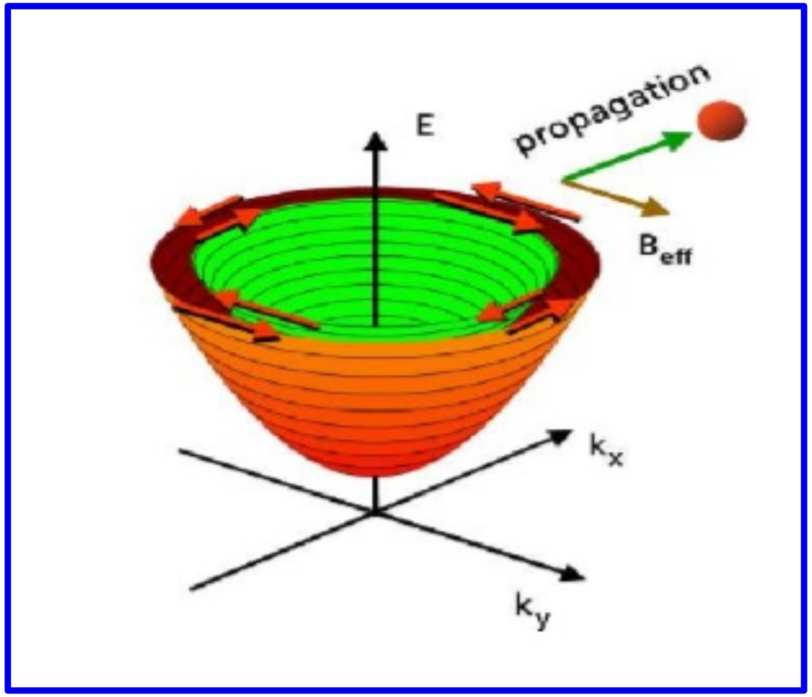


RASHBA EFFECT

The magnetic field is due to the electron moving in the electric field at the surface



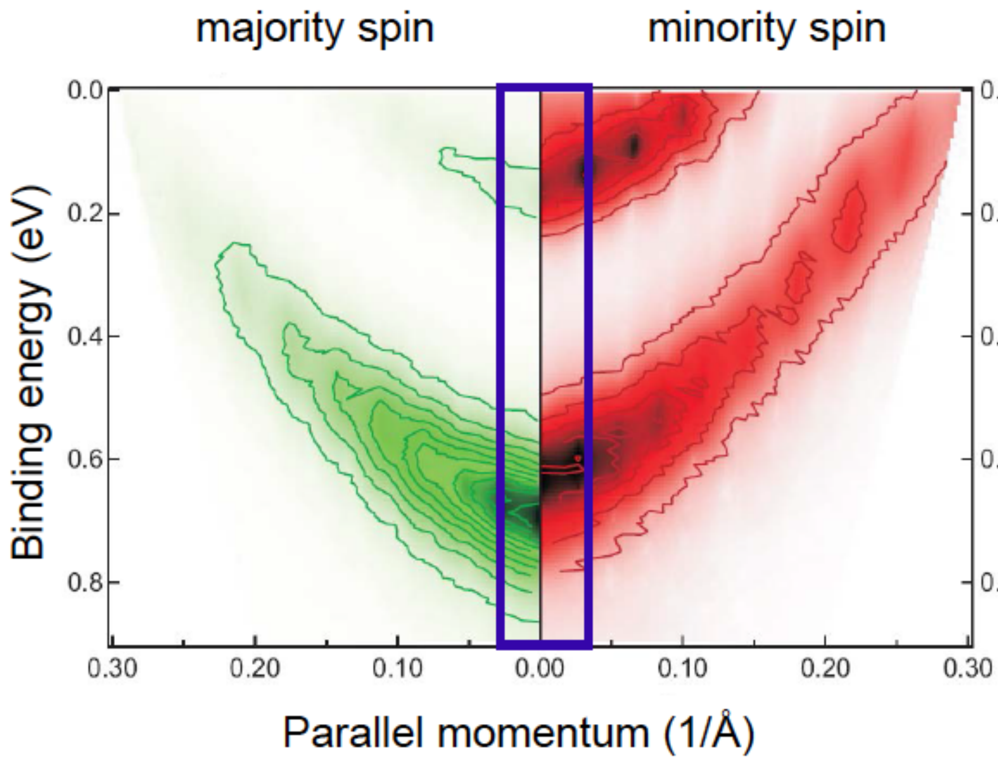
$$\boldsymbol{B} = \frac{1}{c}\boldsymbol{v}\, x\, \boldsymbol{E}$$



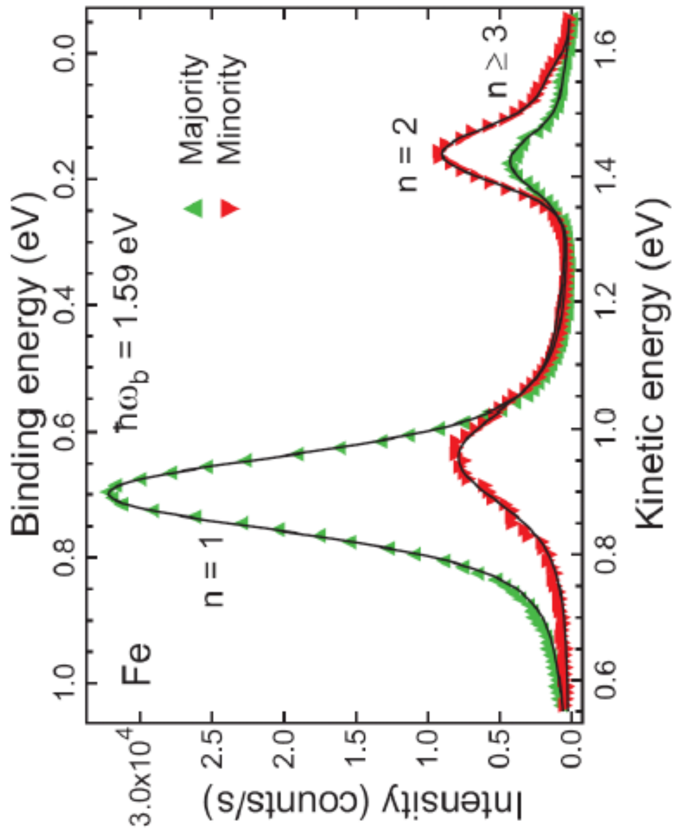
$$\Delta E = -\boldsymbol{\mu}_s \cdot \boldsymbol{B}_l$$

M. Weinelt & coworkers, PRL **95**, 107402 (2005)

Example: 3ML Fe film on Cu(100)



pronounced spin dependence !



Thanks!!!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Relaxation dynamics in carbon-based materials for photovoltaic applications
Understanding the different steps of the exciton behavior such as formation, dissociation and charge transport in the fs timescale is mandatory to the development of high-efficiency solar cells
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Time-resolved angle-resolved non-linear photoemission is a powerfull tool to investigate electron dynamics at surface and at interface of carbon-based materials with metallic substrate.
see more ...
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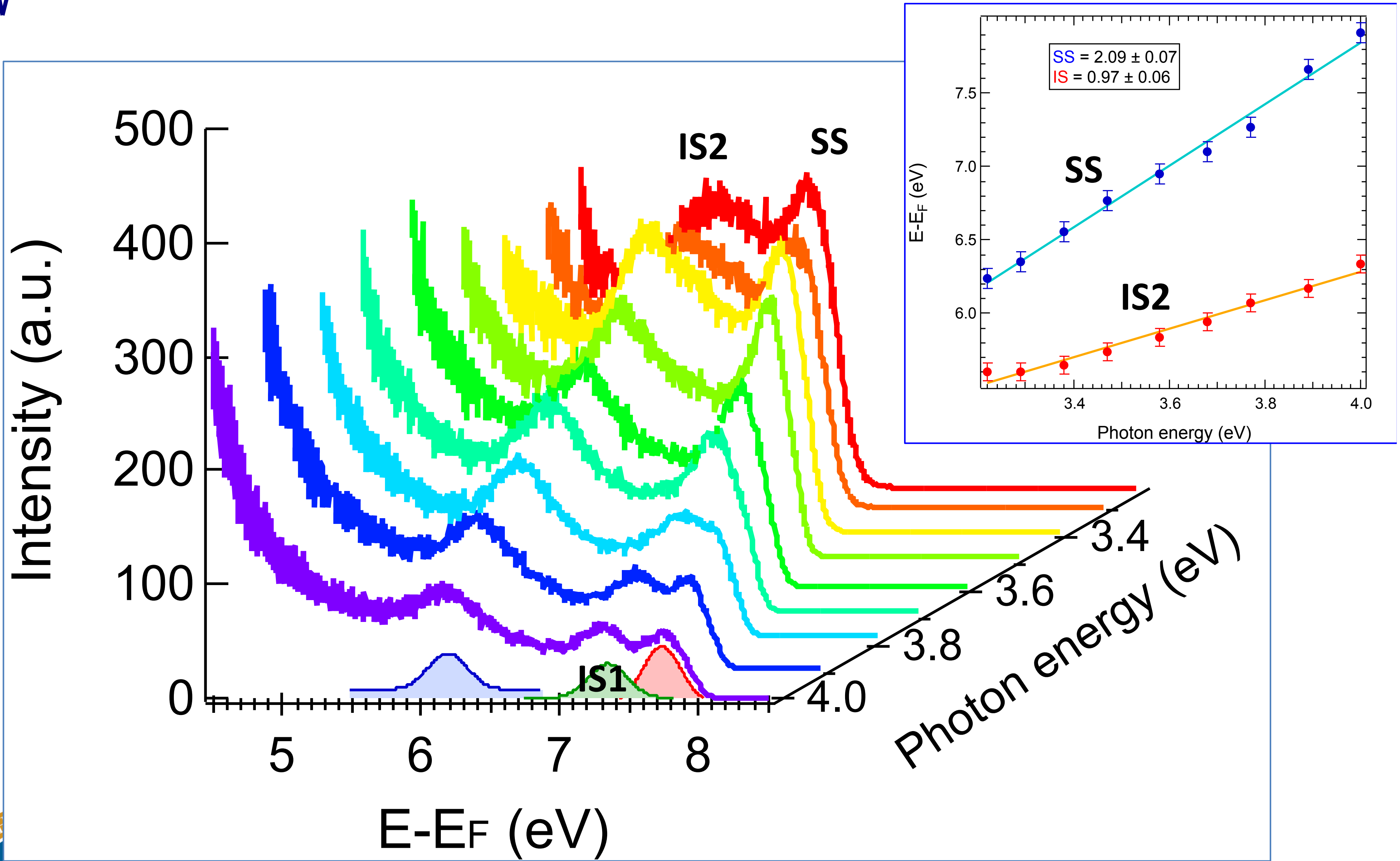
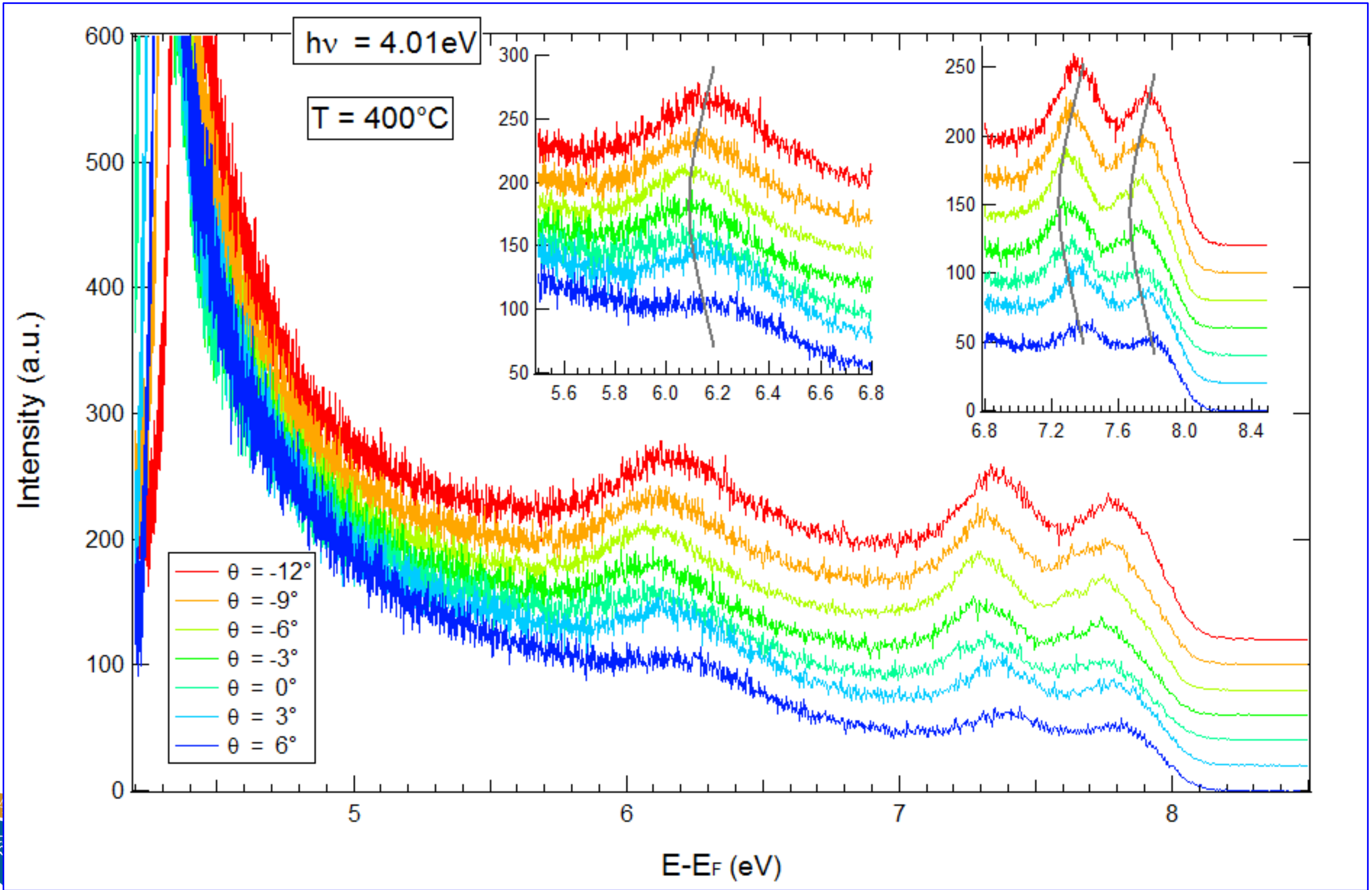
ON-LINE MATERIALS
Relaxation dynamics in carbon-based materials for photovoltaic applications
One of the key aspects underlying the application of novel materials in electro-optical devices is the understanding of the steps immediately following the hole-electron pair (exciton) photo-excitation: exciton transport, recombination and dissociation [12]. These processes occur on ultrafast timescales. Information on this timescale is difficult to access, and much of the current research into solar cell devices focuses on the time averaged properties. Such steady state measurements give little information about processes actually occurring on fast timescales. The goal of this research activity is to increase the performance of solar cell based on carbon nanotube (CNT) by understanding and optimizing the mechanisms, in the femtosecond domain, that enhance the solar light harvesting and the photon-to-electron conversion efficiency, by using time-resolved optical spectroscopies. Different architectures of CNT and CNT inorganic hybrids are the building blocks chosen for CNT-based efficient photovoltaic devices.



500
400
300
200
100
0
Intensity (a.u.)
IS2
SS
IS1
5
6
7
8
E-EF (eV)
3.4
3.6
3.8
4.0
Photon energy (eV)
SS = 2.09 ± 0.07
IS = 0.97 ± 0.06
SS
IS2
7.5
7.0
6.5
6.0
E-EF (eV)
3.4
3.6
3.8
4.0
Photon energy (eV)


hν = 4.01eV
T = 400°C
Intensity (a.u.)
E-EF (eV)
θ = -12°
θ = -9°
θ = -6°
θ = -3°
θ = 0°
θ = 3°
θ = 6°

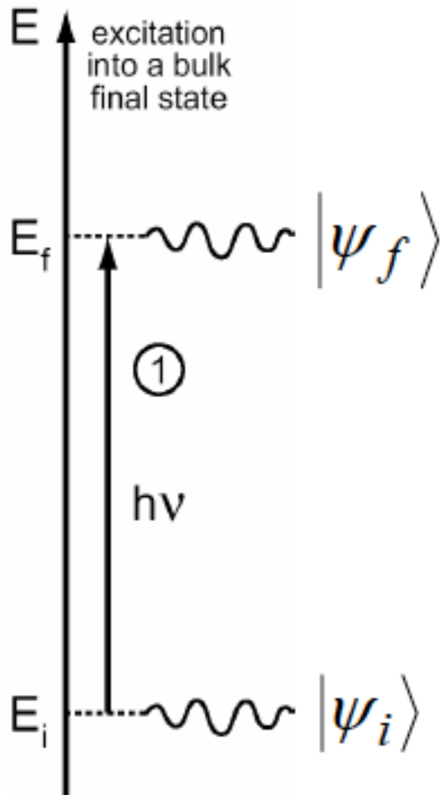
Photoemission intensity:

$$w_{i\to f} \propto \left|\langle \psi_f | \vec{A}\cdot\vec{p} | \psi_i \rangle\right|^2 \delta(E_f - E_i - h\nu)$$

Matrix element:

- k-conservation
- symmetry

Energy conservation



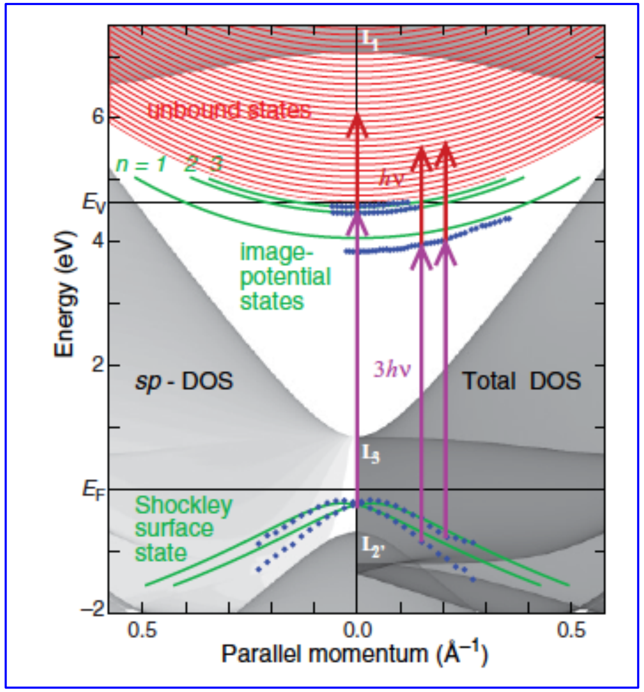
Only vertical transition:

momentum conservation:

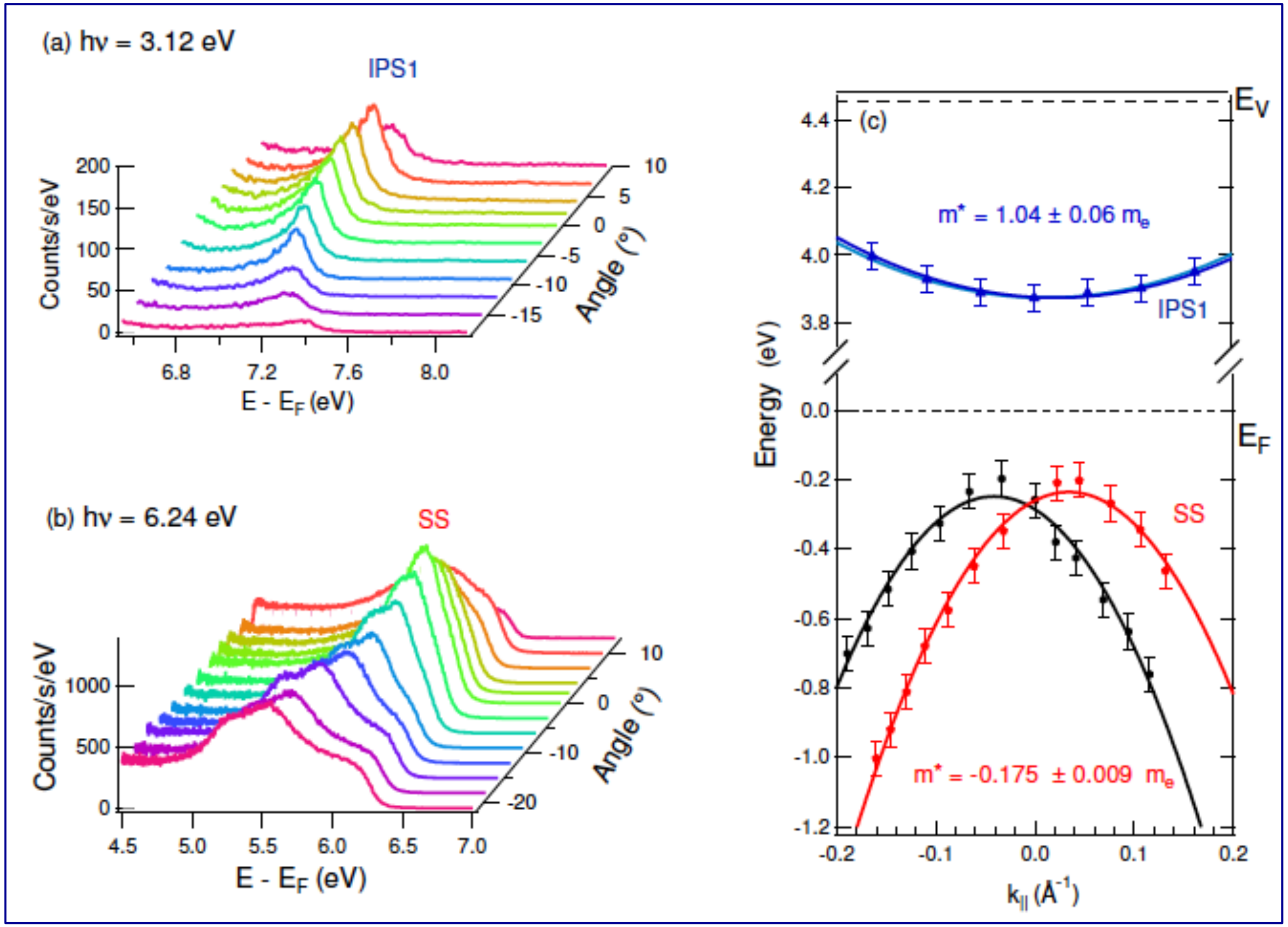
$\vec{k}_f = \vec{k}_i + \vec{G} +$ ~~$\vec{k}_{photon}$~~

Graphene/metal interface

Graphene-Ir(111) distance > 3 Å



PRB 85, 081402R (2012)

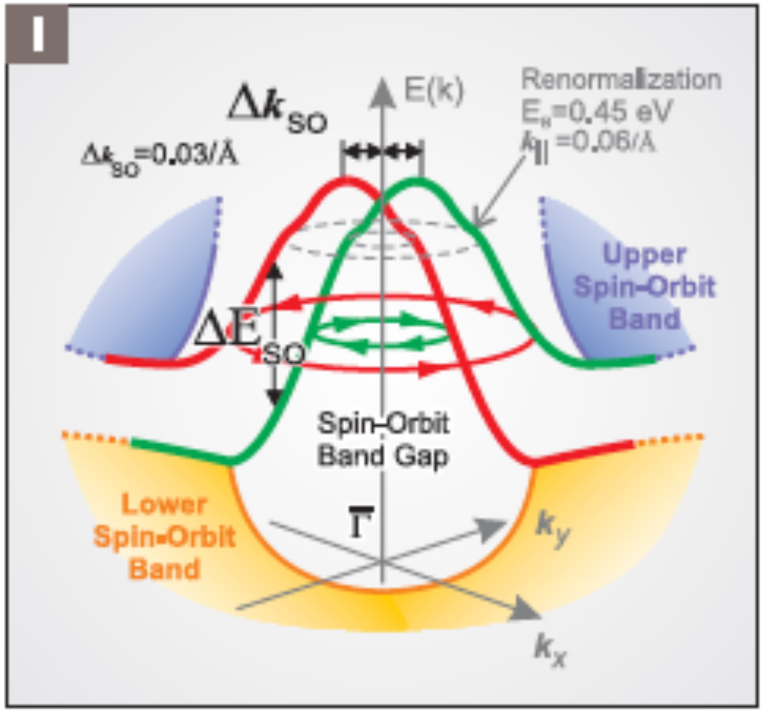


In collaboration with

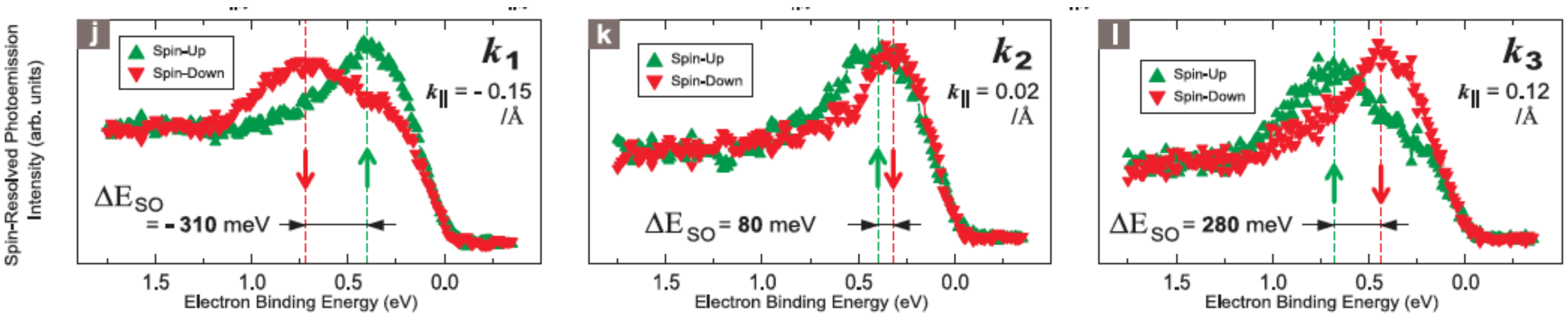
Carlo Mariani

Graphene/metal interface

Surface State with a giant Rashba splitting



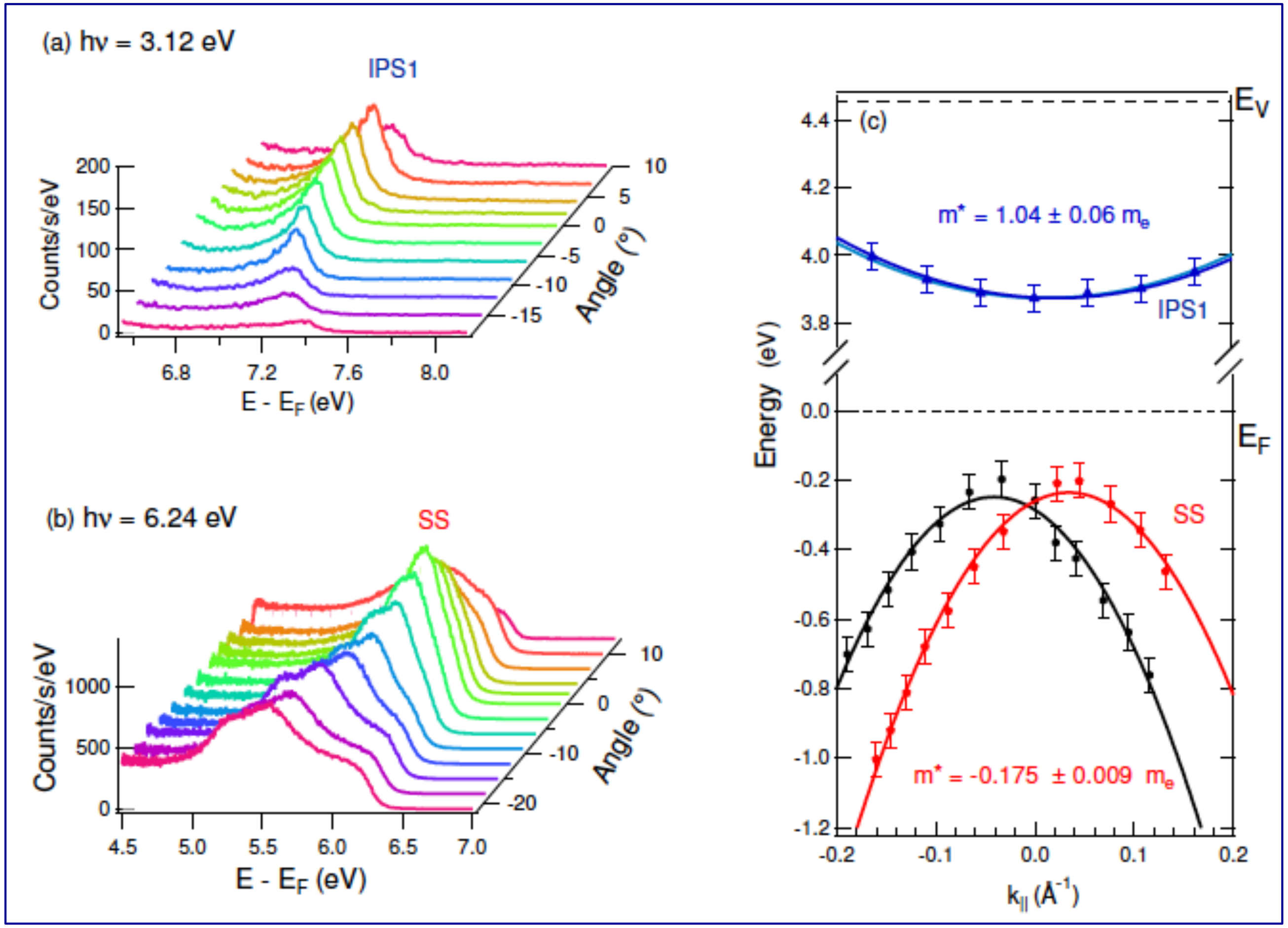
$$E_{\pm}(\mathbf{k}_{\|}) = \frac{\hbar^2 \mathbf{k}_{\|}{}^2}{2m^*} \pm \alpha_R |\mathbf{k}_{\|}|,$$



A. Varykhalov et al., Phys. Rev. Lett. 108, 066804 (2012).

Graphene/metal interface

Is the Image State Rashba splitted??



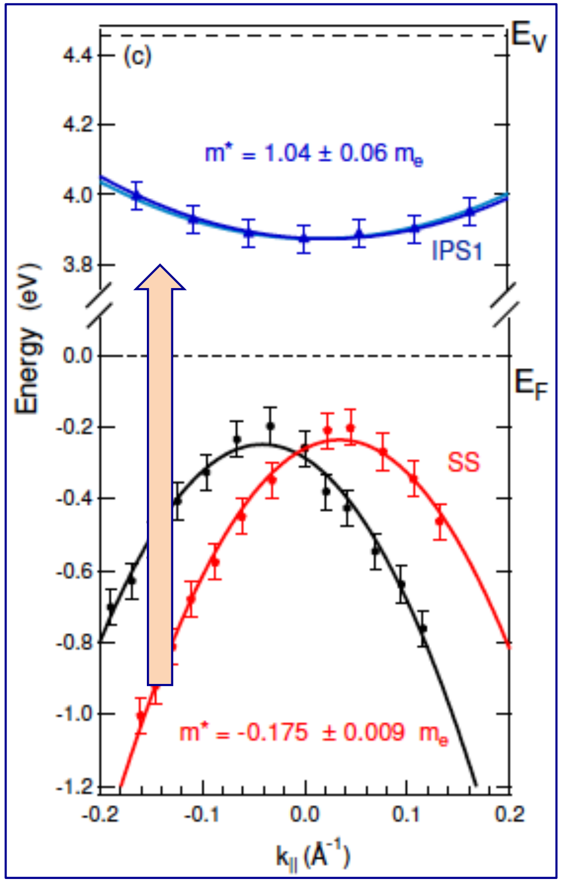
$$E_{\pm}(\mathbf{k}_{\|}) = \frac{\hbar^2 \mathbf{k}_{\|}{}^2}{2m^*} \pm \alpha_R |\mathbf{k}_{\|}|,$$

Two parabolas shifted at $k_{||}=0$ by $\Delta k_{||}=0.0377\pm0.0026$ Å^{-1}

$\alpha_R=1.64\pm0.18 \times 10^{-10}$ eVm

S. Tognolini, S. Achilli, L. Longetti, E. Fava, C. Mariani, M. I. Trioni, and S. Pagliara
Phys. Rev. Lett. 115, 046801 (2015)

Pump is circularly polarized
at hν=4.64 eV

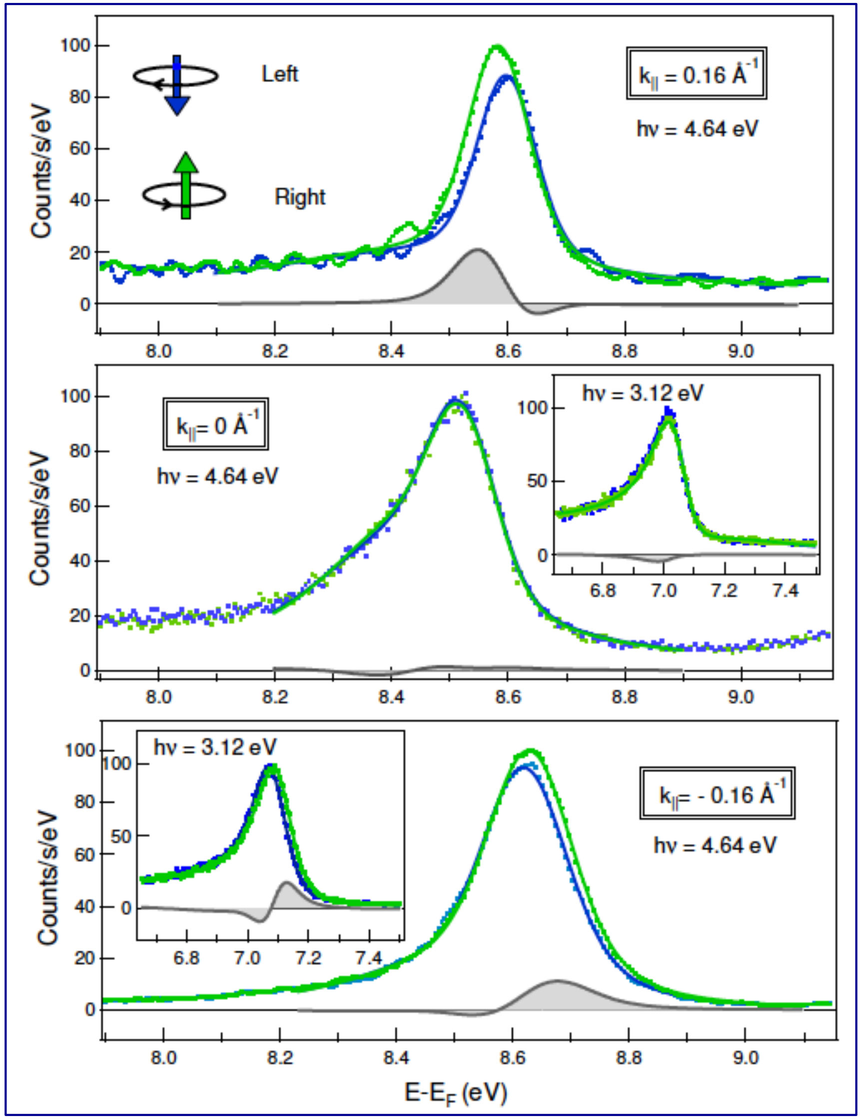


For SS
$\Delta k_{||}$=0.0377±0.0026 $Å^{-1}$

α_R=1.64±0.18 x 10^{-10} eVm

For IPS
$\Delta k_{||}$=0.005±0.001 $Å^{-1}$

α_R=3.6±0.6 x 10^{-12} eVm



Forty-five times smaller!!

Graphene/metal interface

WHY?

$$\alpha_R = 2/c^2 \int |\psi(z)|^2 \partial_z V dz,$$

Derivative of the atomic potential

Charge distribution of the surface state

The Rashba parameter depends on the amplitude of the wave function at the surface and on its decay into the substrate!

- J. R. McLaughlan, E. M. Llewellyn-Samuel, and S. Crampin, J. Phys. Condens. Matter 16, 6841 (2004)

- T. Nakazawa, N. Takagi, M. Kawai, H. Ishida, and R. Arafune, Phys. Rev. B 94, 115412 (2016).