Operando X-ray Absorption Spectroscopy for the study of charge transfer in electrodes for photo-electrochemical water oxidation

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Layout

- Energy Sources
- Photo Electrochemical Water Splitting
- XAS
- Operando XAS experiments

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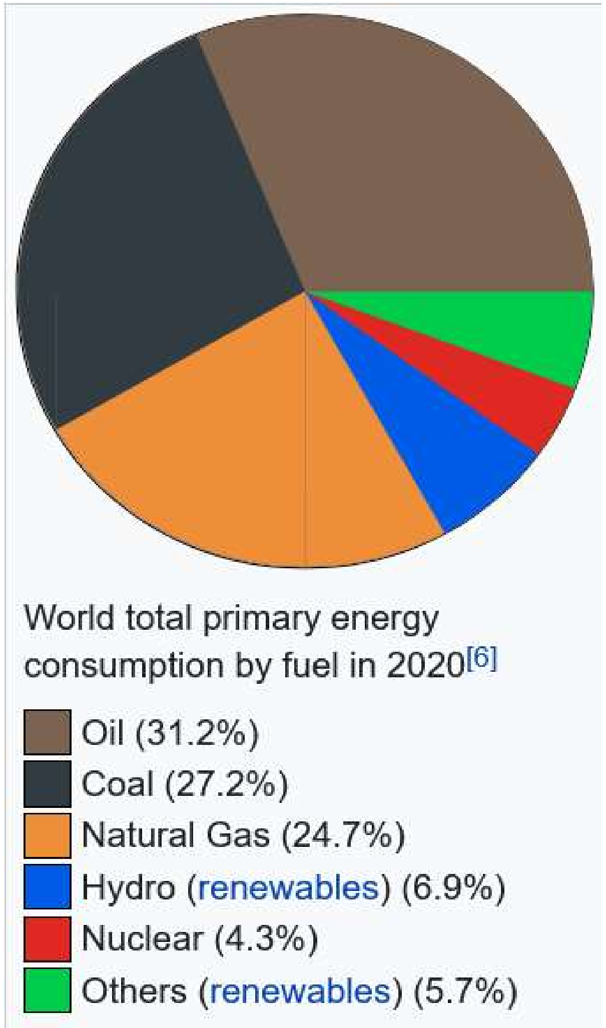
Energy sources

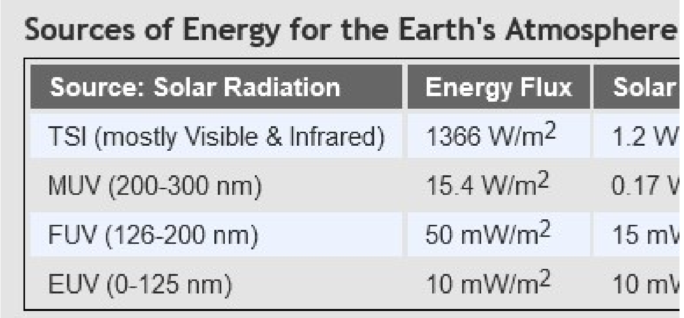
Energy production

- Up to now based mainly on (hydro)carbon(s)
- Environmental issues
    - CO_2 production -> greenhouse gas
        - (US-2009: 1GTon/y coal -> 3GTon/y CO_2)
    - Pollutants production
        - (US-2009: 1GTon/y coal -> 92 MTon/y ashes, www.epri.com)
    - Transport risks
        - Amoco-Cadiz, Exxon-Valdez, ...
- Geopolitical issues
    - Dependence upon (sometimes embarrassing) producers
- Limited amount


World total primary energy consumption by fuel in 2020[6]

Source Wikipedia/BP

Renewable energies



Sources of Energy for the Earth's Atmosphere

Source: Solar Radiation	Energy Flux	Solar
TSI (mostly Visible & Infrared)	1366 W/m^2	1.2 W
MUV (200-300 nm)	15.4 W/m^2	0.17 V
FUV (126-200 nm)	50 mW/m^2	15 mV
EUV (0-125 nm)	10 mW/m^2	10 mV

Solar Irradiance, Nasa.gov

- Mainly Solar-based
- Limited power (≈1kW/m^2 at ground level)
- Daytime, geographic position and seasonal variations
- Need of storing the excess energy produced
  - Electrical, mechanical forms
  - Chemicals (H_2)

H_2 as energy source

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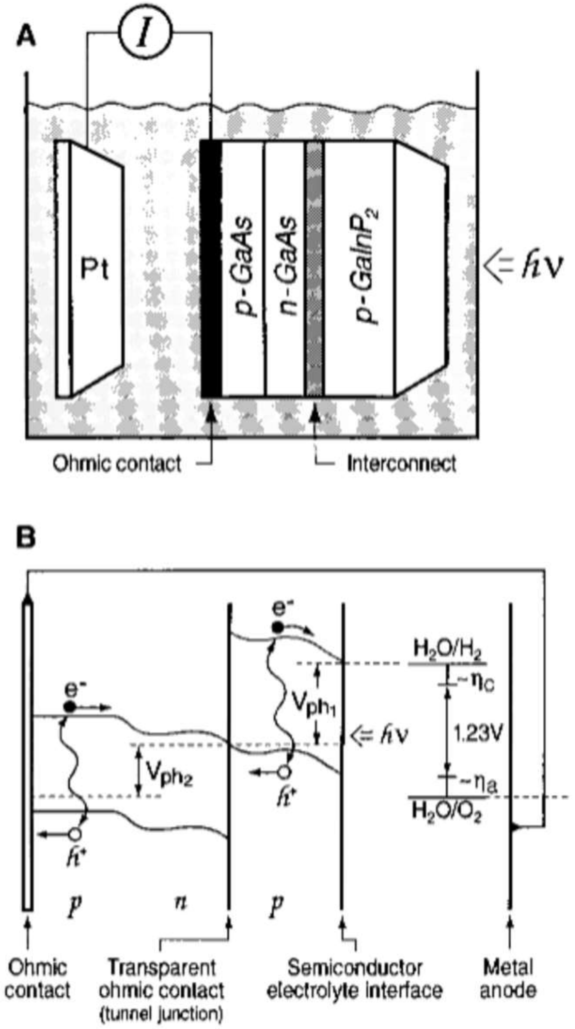
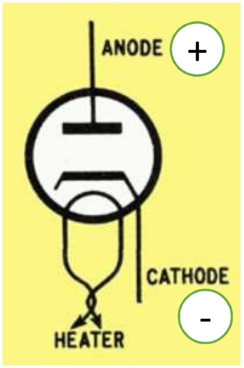
- Energy content 33kWh/kg
  - same as 1 Diesel Gallon Equivalent. Source afdc.energy.gov
- Easily stocked
  - though… density 63g/L @ 700 Bar, RT
- Useable in combustion engines and fuel cells.
- No Greenhouse gas production.
- Obtained from a widely abundant source
  - Water

Water photo-hydrolysis

- Semiconductor based
- Min. potential: 1.23 V ↔ $\lambda=1\ \mu m$
- Multi-junction stacks
- p-doped semiconductor
  - Cathode, emits e^-
  - Reduction process
  - $2e^- + 2H^+ \rightarrow H_2$
- n-doped semiconductor
  - Anode, grabs e^-
  - Oxidation process
  - $2h^+ + H_2O \rightarrow \frac{1}{2} O_2 + 2 H^+$

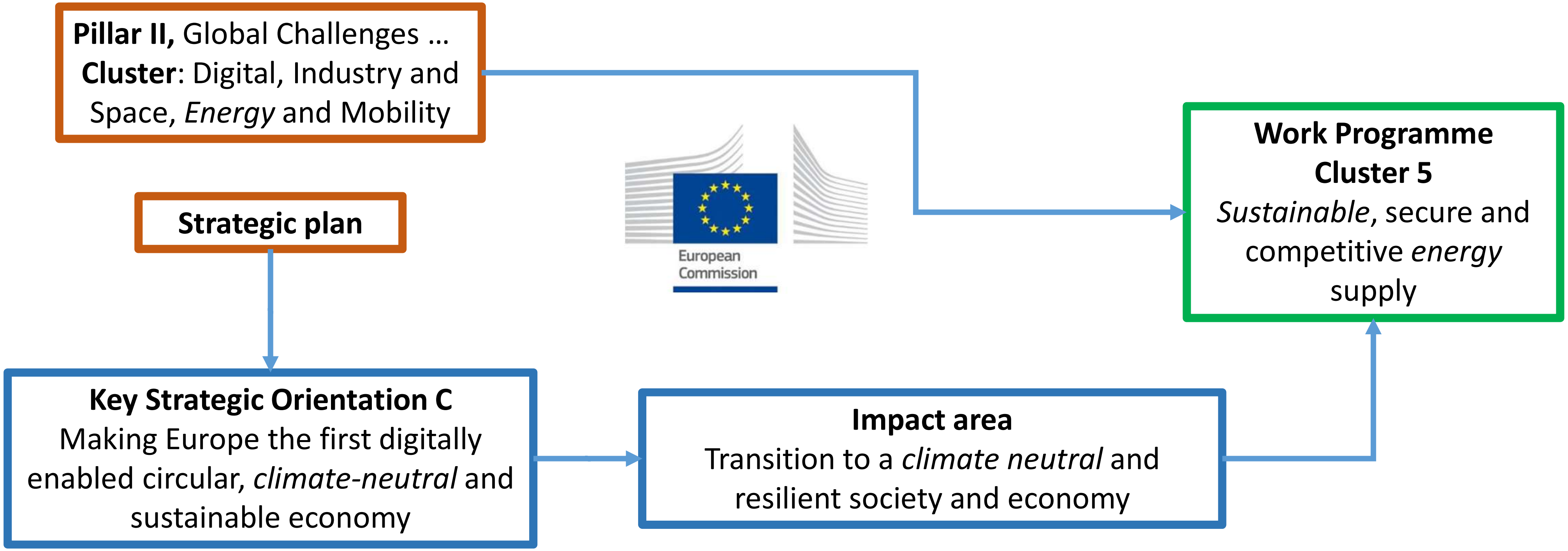


O. Khaselev, J. A. Turner, Science **280**, (1998), 425.



http://www.r-type.org

Horizon Europe Program



Pillar II, Global Challenges …
Cluster: Digital, Industry and Space, *Energy* and Mobility

Strategic plan

Key Strategic Orientation C
Making Europe the first digitally enabled circular, *climate-neutral* and sustainable economy

Impact area
Transition to a *climate neutral* and resilient society and economy

Work Programme Cluster 5
Sustainable, secure and competitive *energy* supply

Research on renewables is a key topic for Europe

X-ray Absorption Spectroscopy

Matter-radiation interaction

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$$\mu(\omega) = \frac{2\hbar}{\epsilon_0 \omega A_0^2} n W_{if}$$

Absorption coefficient

$$W_{if} = \frac{2\pi}{\hbar} |\langle f | \hat{H}_{Int} | i \rangle|^2 \rho(E_f)$$

Transition probabilities

$$\hat{H}_{Int} = i\hbar \vec{A}(\vec{r}) \cdot \vec{p}$$

Electron – photon
interaction Hamiltonian

Matter-radiation interaction

$$\vec{A} = |A_0|\vec{\epsilon}e^{i\vec{k}\cdot\vec{r}} \approx |A_0|\vec{\epsilon}\left(1 + i\vec{k}\cdot\vec{r} - \ldots\right) \approx |A_0|\vec{\epsilon}(1)$$

Dipole approximation == kr << 1

$$\vec{p} = -i\hbar\vec{\nabla} \quad \vec{\nabla} = \frac{m\omega}{\hbar}\vec{r}$$

From QM identities

$$W_{if} = \frac{\pi\hbar e^2}{m^2}|A_0|^2\sum_f |\langle f|\vec{\epsilon}\cdot\vec{r_j}|i\rangle|^2\delta\left(E_f - E_i - \hbar\omega\right)$$

Dependence on the photon polarization

Matter-radiation interaction

Angular part Radial part

$$\langle f|\hat{H}_{Int}|i\rangle = \left(\int_{\Omega} \ldots \partial\Omega\right) \int_{\vec{r}} f\hat{H}_{Int} i\partial\vec{r}$$

$$|i\rangle$$

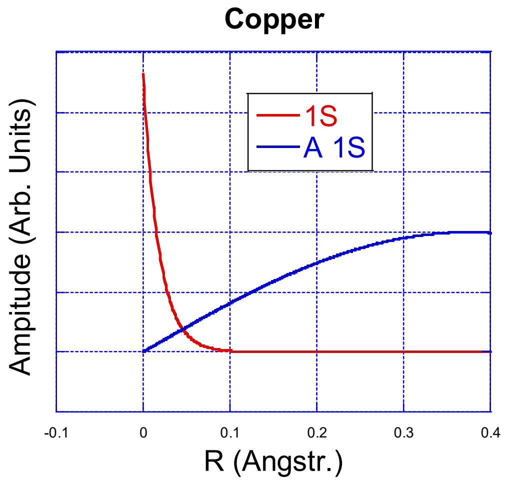
1s, 2s 2p states

(K, L_I, $L_{II,\ III}$ edges)

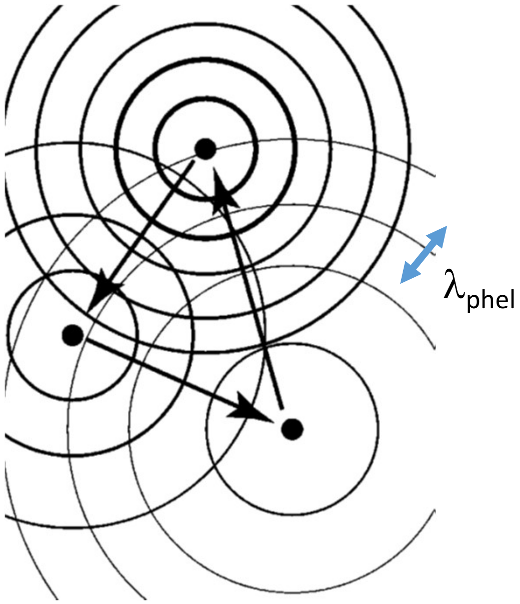
Nonzero only in a restricted region around the nucleus

Valid dipole approx.

More marked interference effect



Matter-radiation interaction



Rehr, RMP 2000

$$\langle f |$$

Outgoing spherical wave in case of isolated atom

Sum of partially reflected waves in condensed systems

Photoelectron wavevector k

$$k = \sqrt{\frac{2mE_{phel}}{\hbar}}$$

Typ. Values

E_{phel} ~ 15 – 800 eV

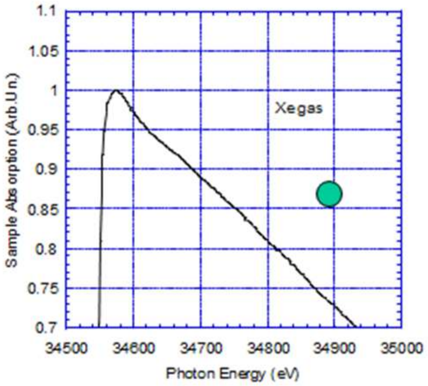
k ~ 2-15 $Å^{-1}$

Photoelectron wavelength

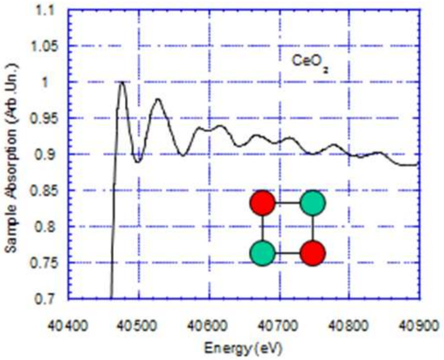
λ_{phel} = ~ 3 – 0.4 Å

- Being |i> nonzero only in a restricted region the integral <f|H|i> depends on the amplitude of <f| on the absorbing atom.
- Interference with other (phase coherent) scattered waves
- The maxima and minima in <f| determine the oscillations above the edge.

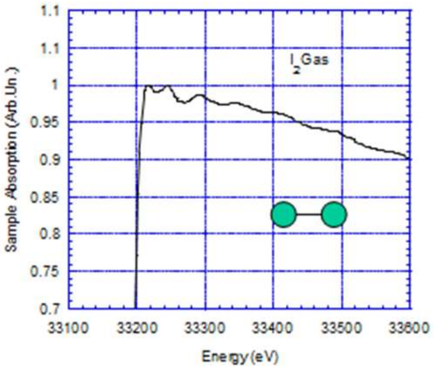
Matter-radiation interaction



A monoatomic gas



A crystalline system:
Cerium Oxyde



A molecular system:
Iodine

$$\langle f| = \frac{e^{i\vec{k}\cdot\vec{r}}}{\vec{k}\cdot\vec{r}} Y_{l,m}$$

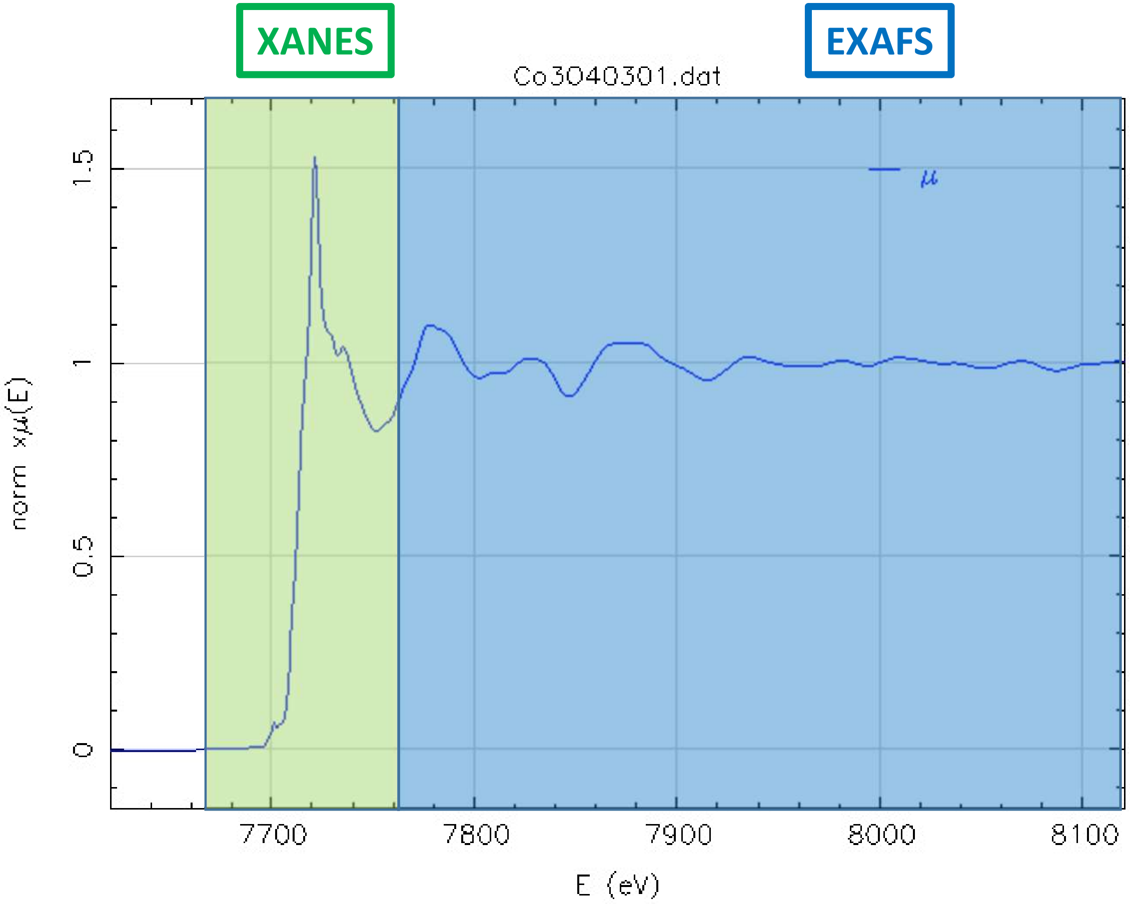
<f| = ?

<f| = ?

<f| must obey the selection rules ΔL = ± 1
In practice we have s —> p and p—> d transitions

XANES & EXAFS

XANES
Low E photoelectrons
$\lambda_{phel} > R_{interatomic}$
Symmetry
Valence state
Semi-quantitative



EXAFS
High E photoelectrons
$\lambda_{phel} < R_{interatomic}$
Local structure
R @ 1%
N@ 10%

Formulas

$$\chi(k) = \sum_{j=shells} S_0^2 \frac{N_j}{kR_j{}^2} f_j^{eff}(k) e^{\frac{-2R_j}{\lambda}} sin(2kR_j + \phi_j^{tot}(k)) e^{-2k^2\sigma_j^2}$$

High Photoelectron energy
(~ 100 – 2000 eV)

- MS approach
- == EXAFS region

$$\mu(E) \propto \lim_{\eta \to 0+} \Im \left(\langle i|\vec{\epsilon} \cdot \vec{r} \frac{1}{E - H - i\eta} \vec{\epsilon} \cdot \vec{r}|i\rangle \right)$$

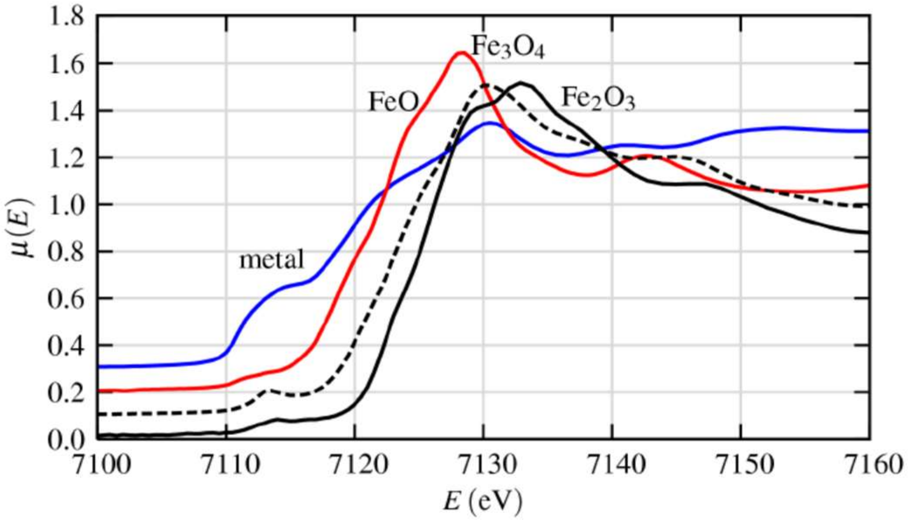
Low photoelectron energy (~ 0-100 eV)

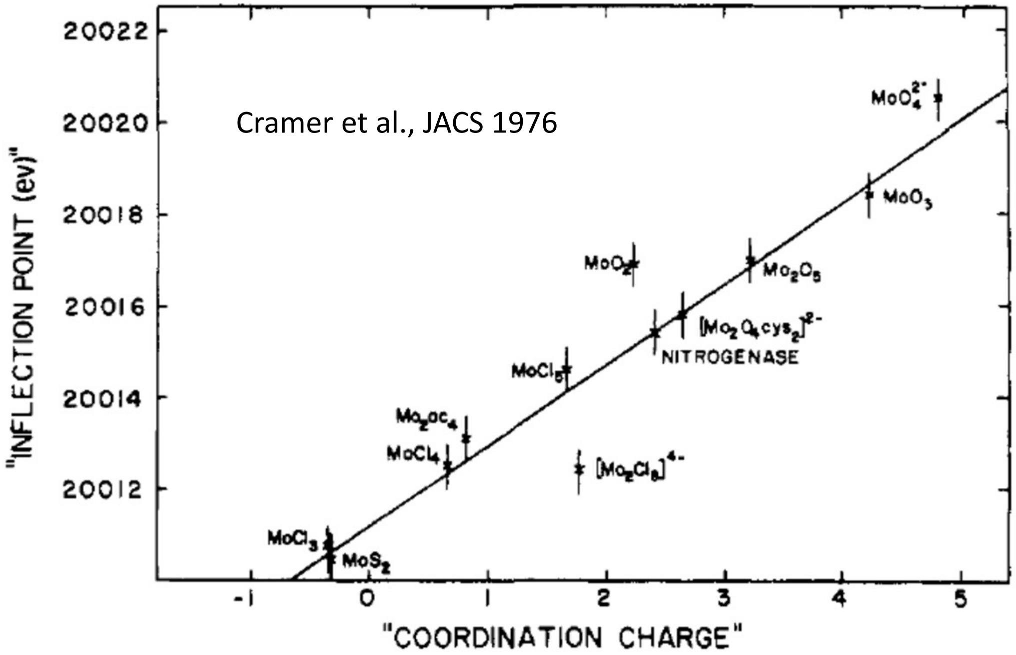
- FMS approach
- == XANES region

Valence state from XANES

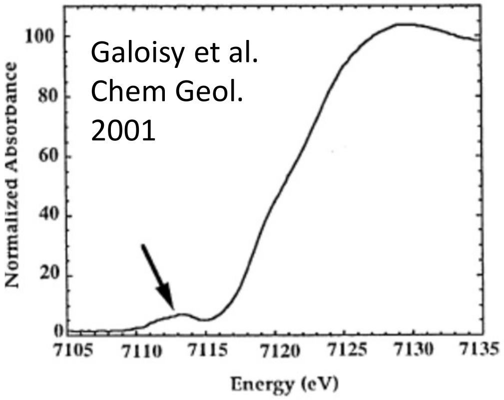
The valence state can be estimated from the edge position

M Newille “*Fundamentals of XAFS*”




Cramer et al., JACS 1976

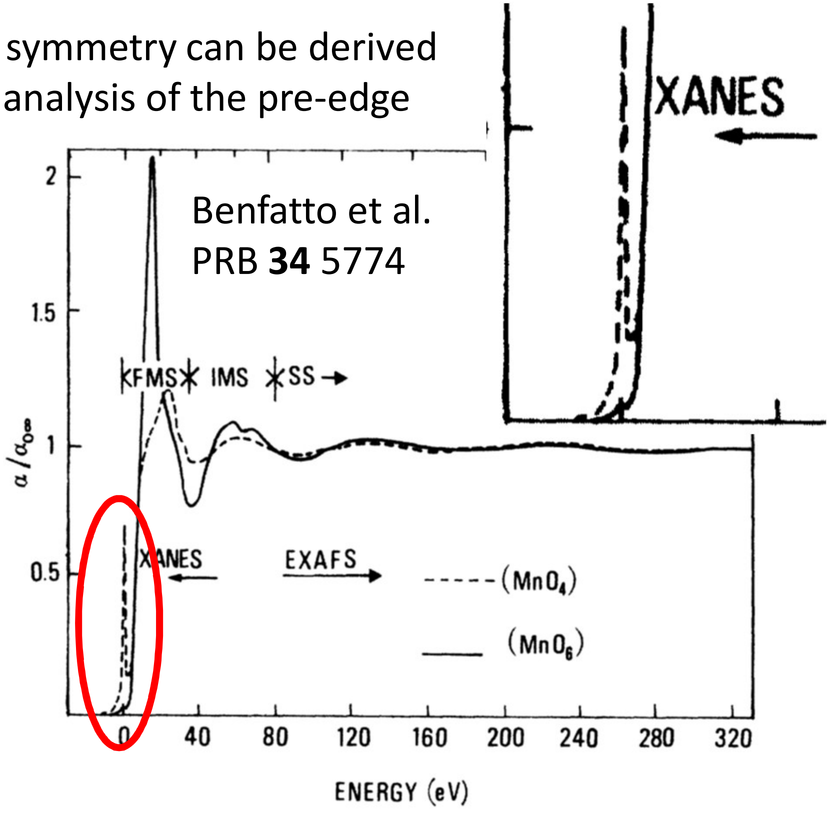
Local symmetry from XANES



Galoisy et al.
Chem Geol.
2001

- Appear on the K edge of 3d metals
- Due to 1s-3d (semi-forbidden) transitions
- Well visible in non-centrosymmetric environments

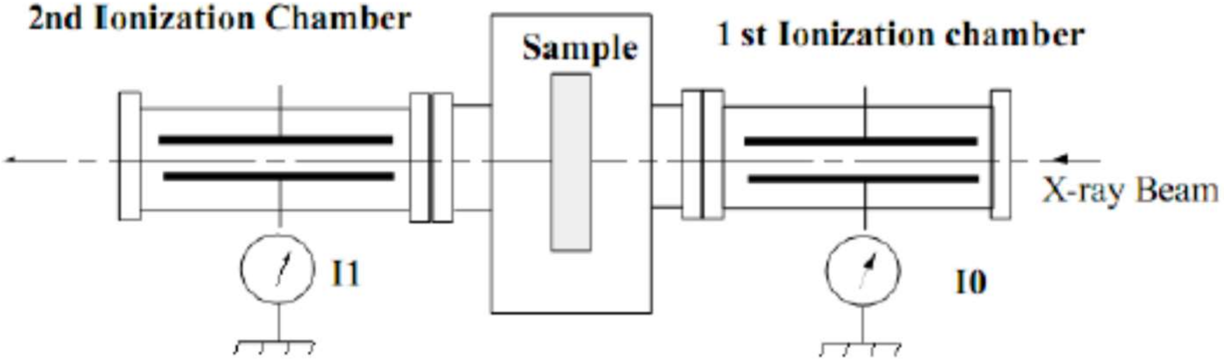
The local symmetry can be derived from the analysis of the pre-edge peaks

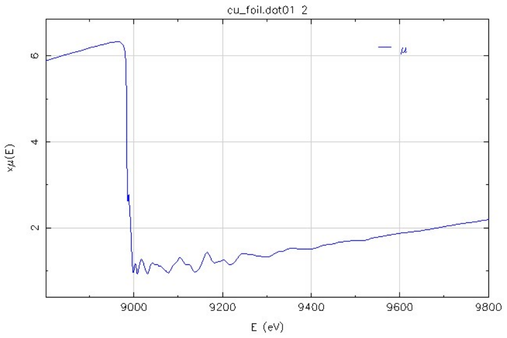


Benfatto et al.
PRB **34** 5774

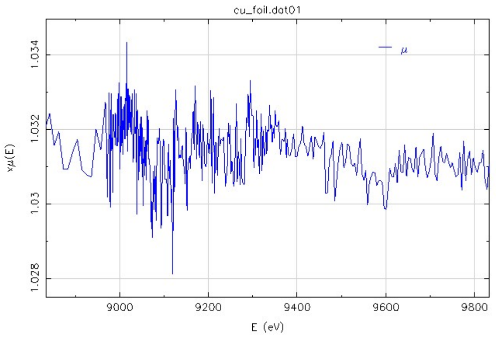
Data collection modes

Measuring μ direct method



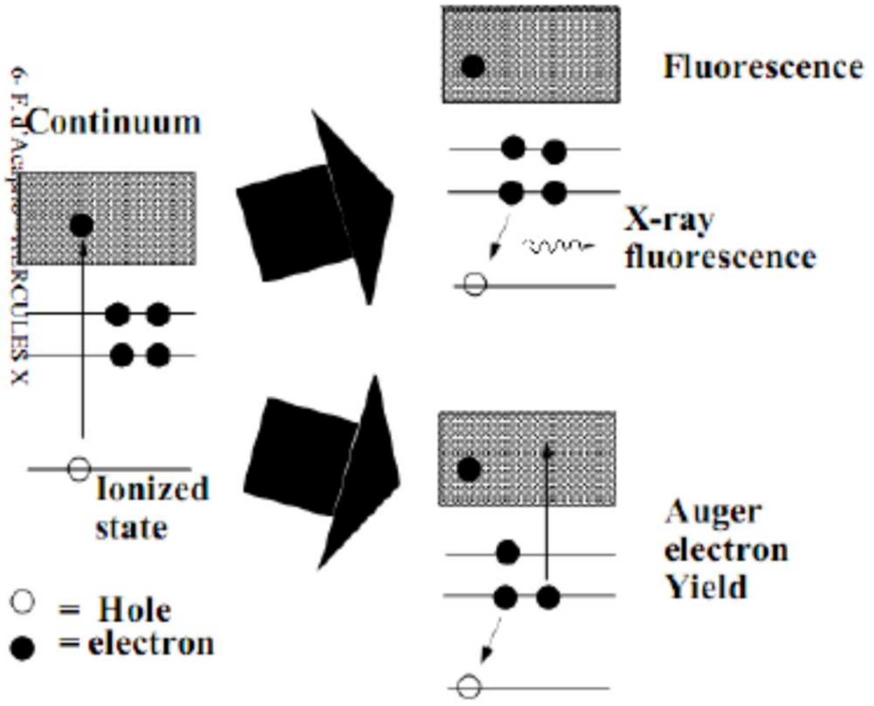


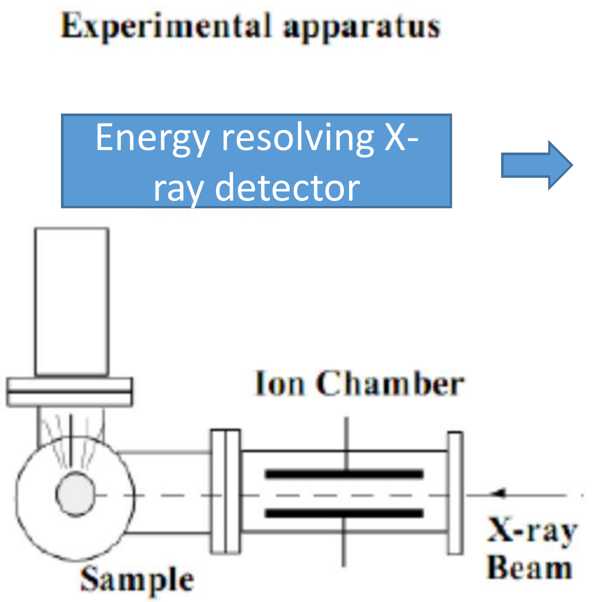
$$\mu = -\ln (I1/I0)$$



OK for concentrated samples

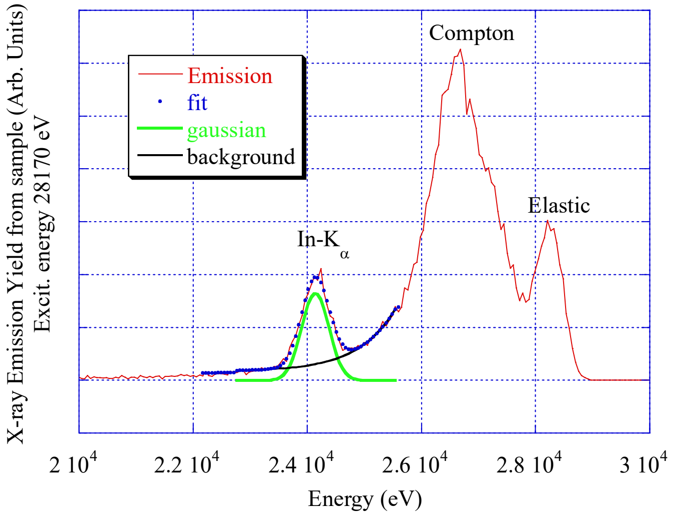
Indirect mode





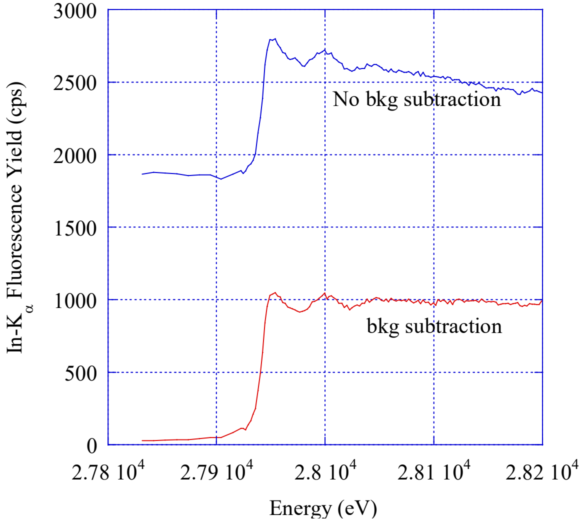
Energy resolving X-ray detector

OK for diluted samples



Integration of only the region relative to the absorber emission

Plotting the integral vs energy the spectrum is recovered



10^{13} In/cm^2 implanted Si

F. d'Acapito et al APL **88** 212102

Pump and Probe

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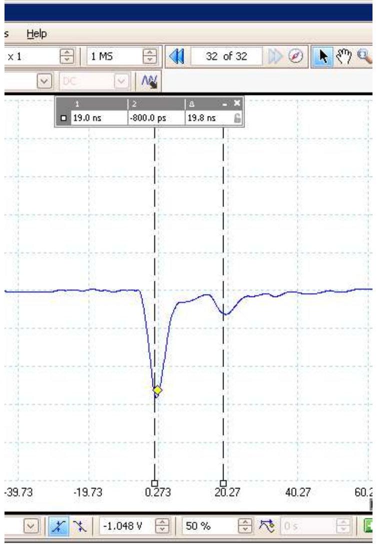
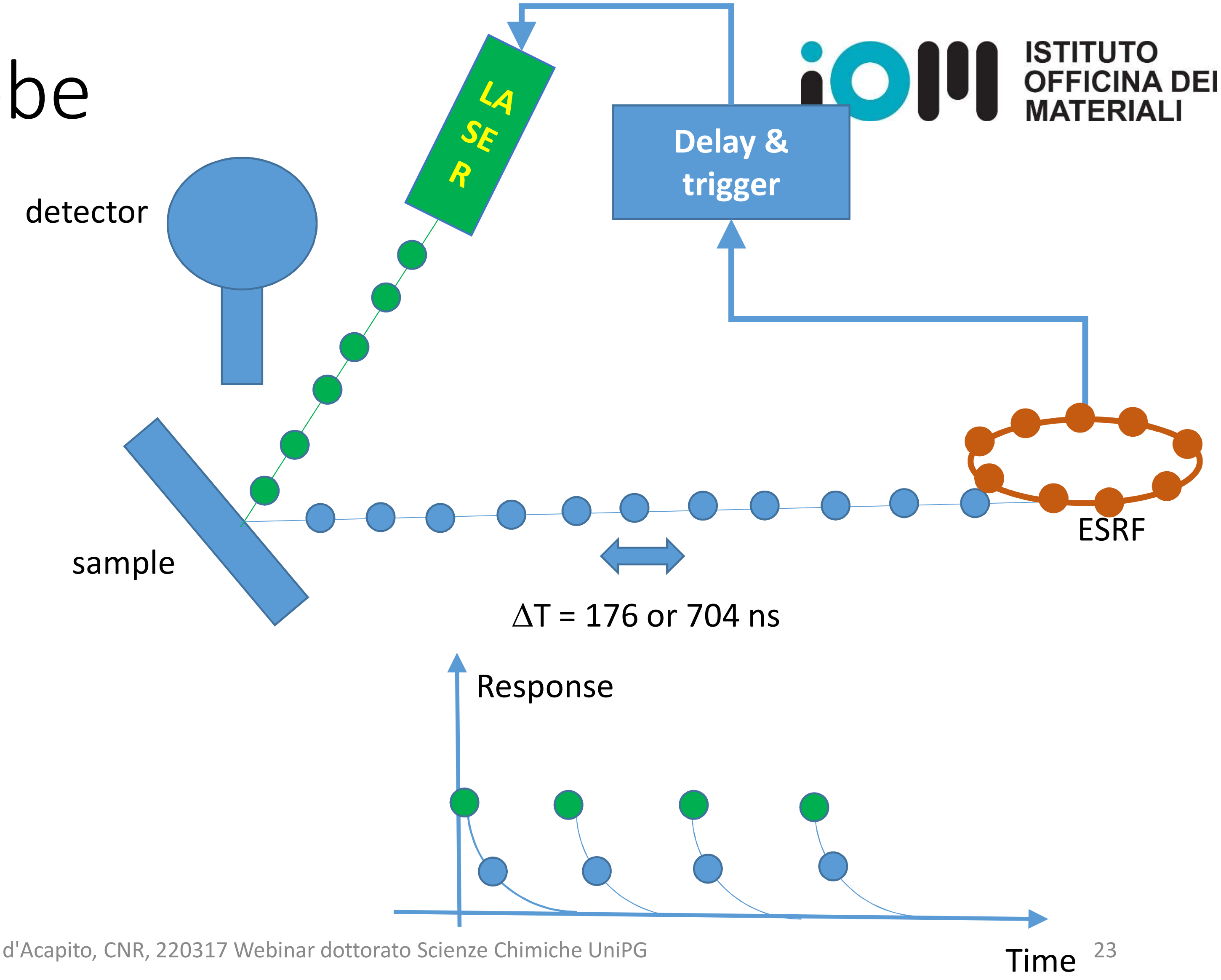
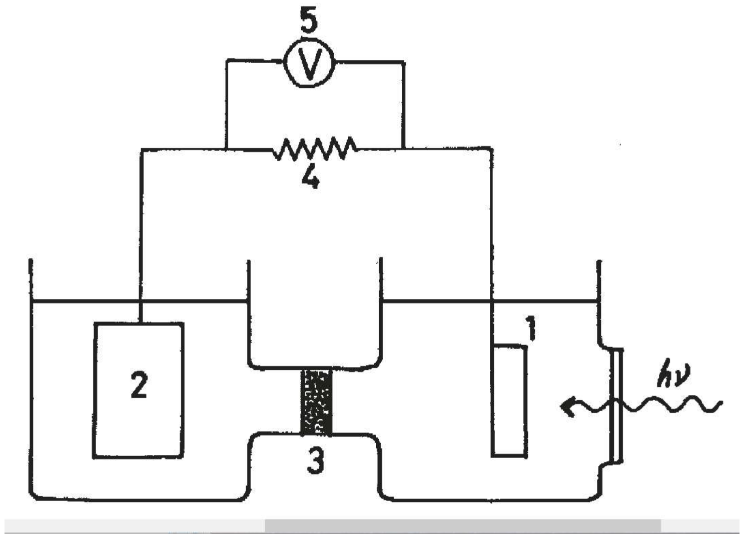


1	2	Δ
19.0 ns	-800.0 ps	19.8 ns



ΔT = 176 or 704 ns

Experimental Examples



A. Fujishima, K. Honda Nature 238 (1972), 37

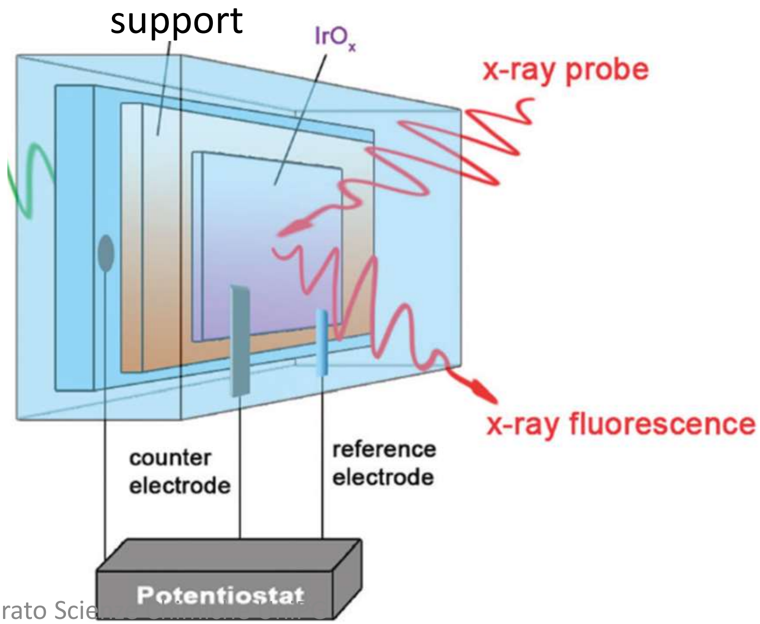
analytical chemistry
Letter
pubs.acs.org/ac
dx.doi.org/10.1021/ac401414v | *Anal. Chem.* 2013, 85, 7009–7013

Fixed Energy X-ray Absorption Voltammetry

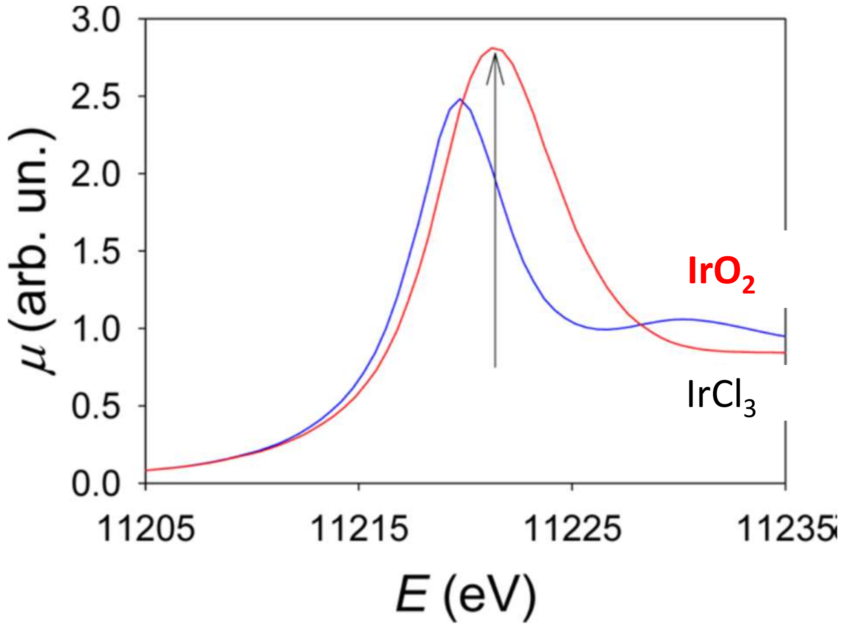
Alessandro Minguzzi,*[,†] Ottavio Lugaresi,[†] Cristina Locatelli,[†] Sandra Rondinini,[†] Francesco D'Acapito,[‡] Elisabetta Achilli,[§] and Paolo Ghigna[§]

Site – selective voltammetry

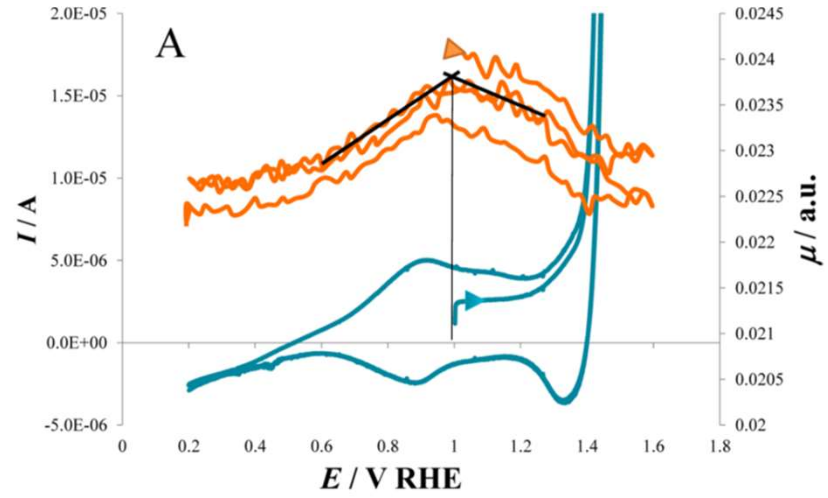
XAS-based
IrO_x films in an Electrochemical cell
Ir-L_3 edge



Fixed Energy X-ray Absorption Voltammetry

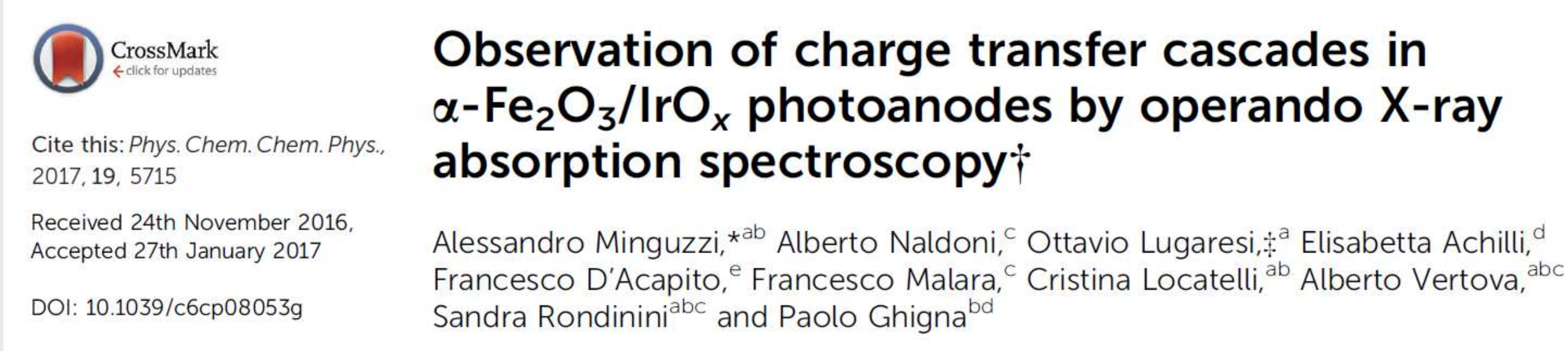


Different XANES spectra for Ir^{3+} and Ir^{4+}



Blue: standard voltammetry
Orange: “Ir voltammetry”

With XAS we see the contribution of an element to the total voltammetric response



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Observation of charge transfer cascades in α-Fe_2O_3/IrO_x photoanodes by operando X-ray absorption spectroscopy†

Alessandro Minguzzi,*[ab] Alberto Naldoni,[c] Ottavio Lugaresi,‡[a] Elisabetta Achilli,[d] Francesco D'Acapito,[e] Francesco Malara,[c] Cristina Locatelli,[ab] Alberto Vertova,[abc] Sandra Rondinini[abc] and Paolo Ghigna[bd]

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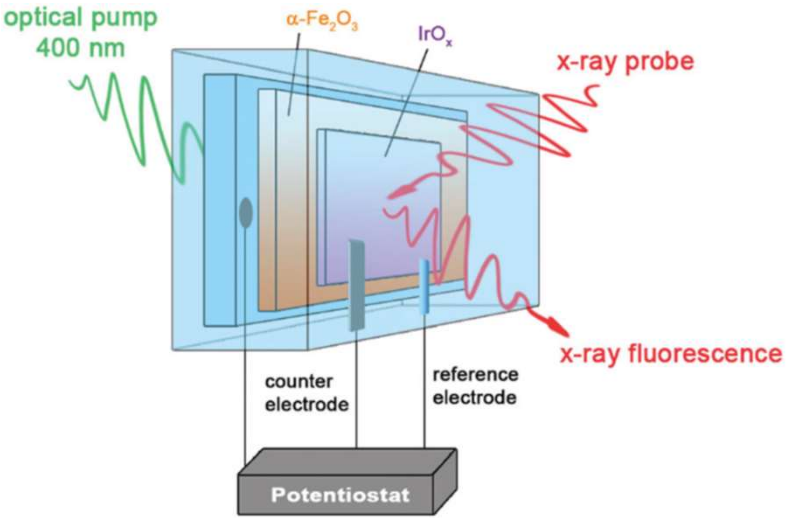
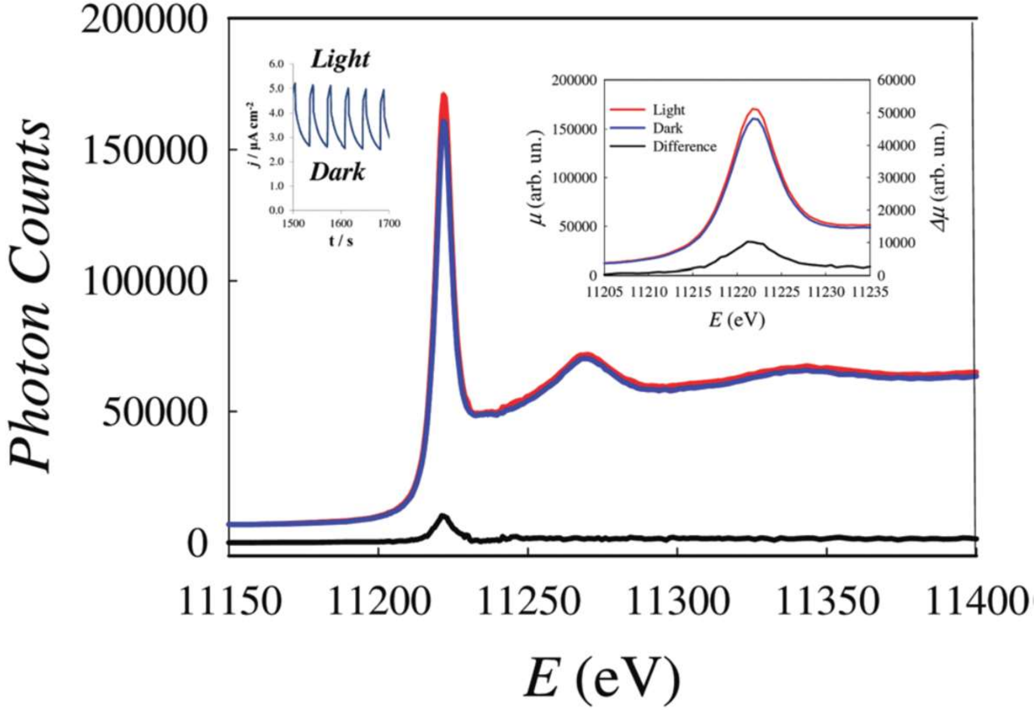
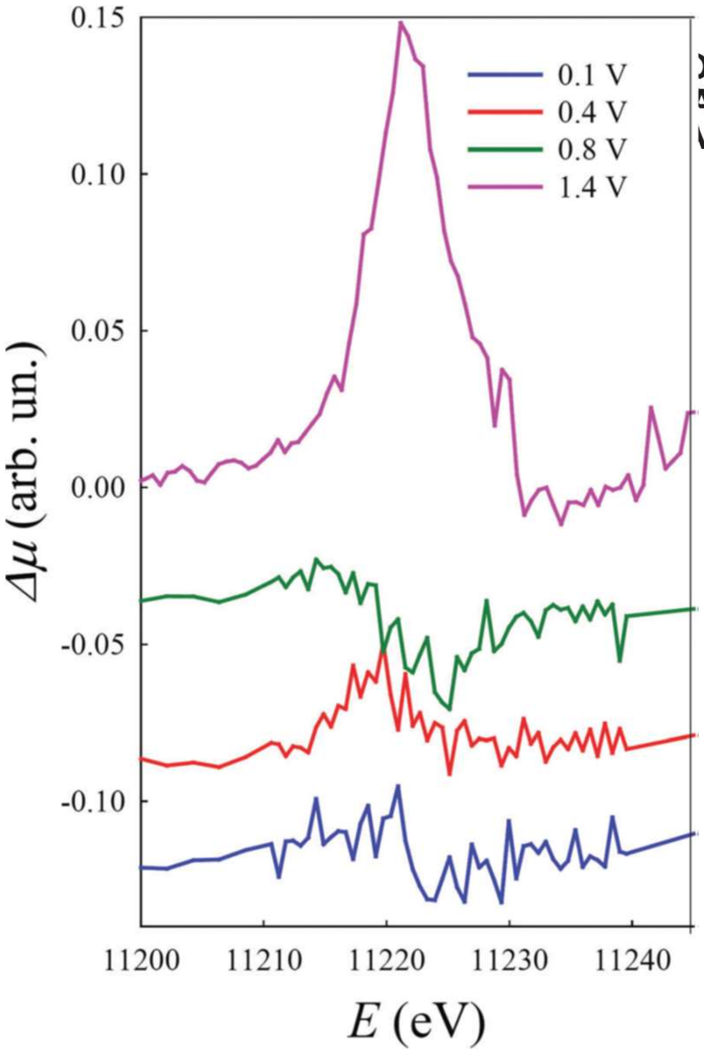
α-Fe_2O_3: photoanode
IrO_x: hole collector

Is Ir really an efficient hole collector ?

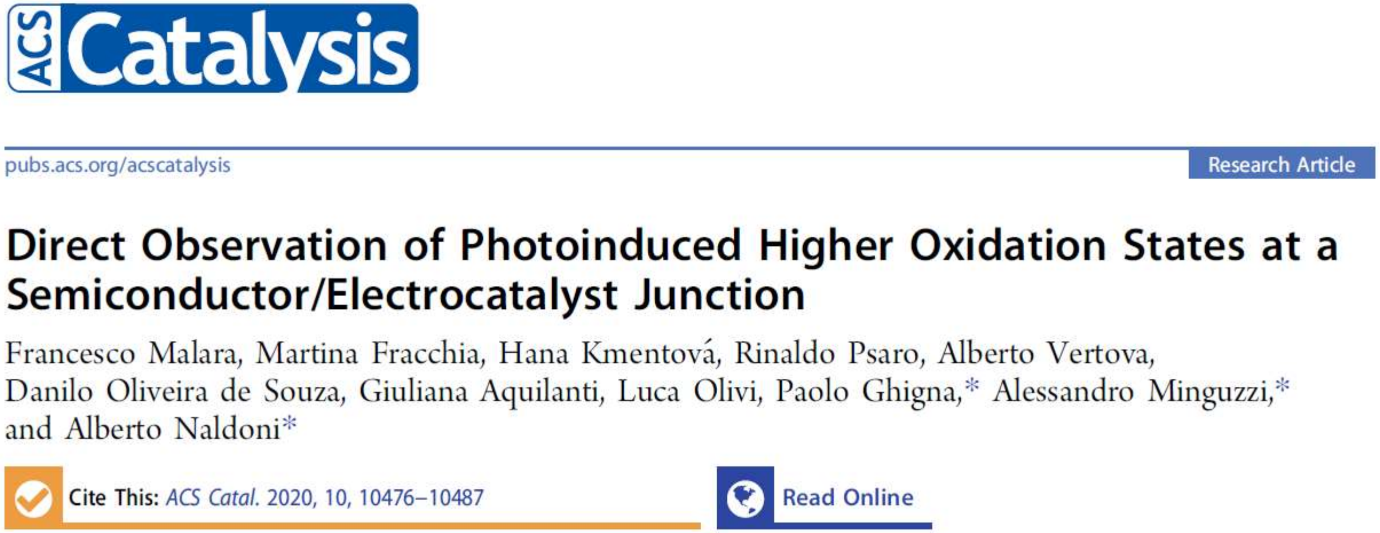






Difference of spectra Light-Dark
Nothing happens up to 0.8 V (remember: water splits at 1.23 V)
Big increase of the WL at 1.4 V

WL == holes in the 5d stats of Ir



ACS Catalysis

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Research Article

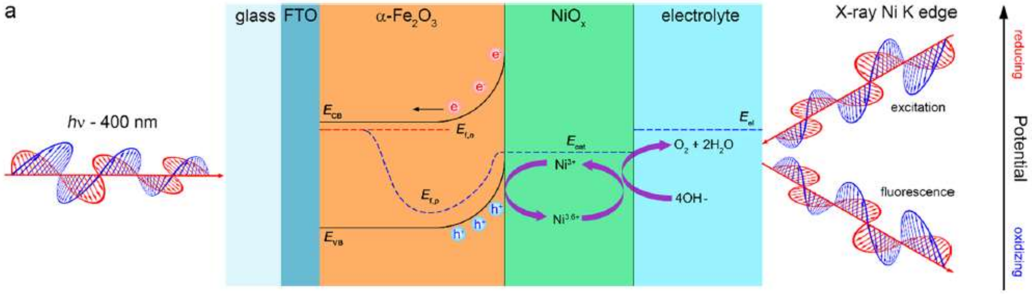
Direct Observation of Photoinduced Higher Oxidation States at a Semiconductor/Electrocatalyst Junction

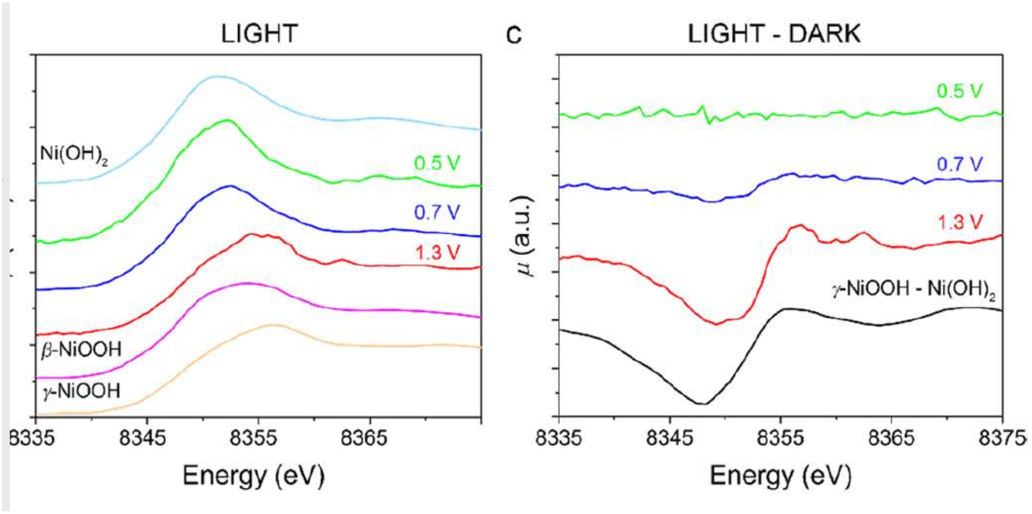
Francesco Malara, Martina Fracchia, Hana Kmentová, Rinaldo Psaro, Alberto Vertova,
Danilo Oliveira de Souza, Giuliana Aquilanti, Luca Olivi, Paolo Ghigna,* Alessandro Minguzzi,*
and Alberto Naldoni*

Cite This: *ACS Catal.* 2020, 10, 10476–10487

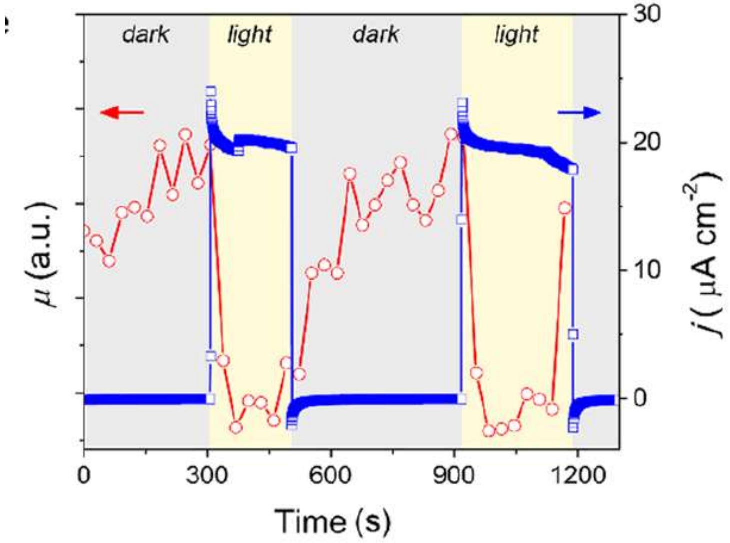
Read Online

Like the previous case
NiOx in place of IrOx



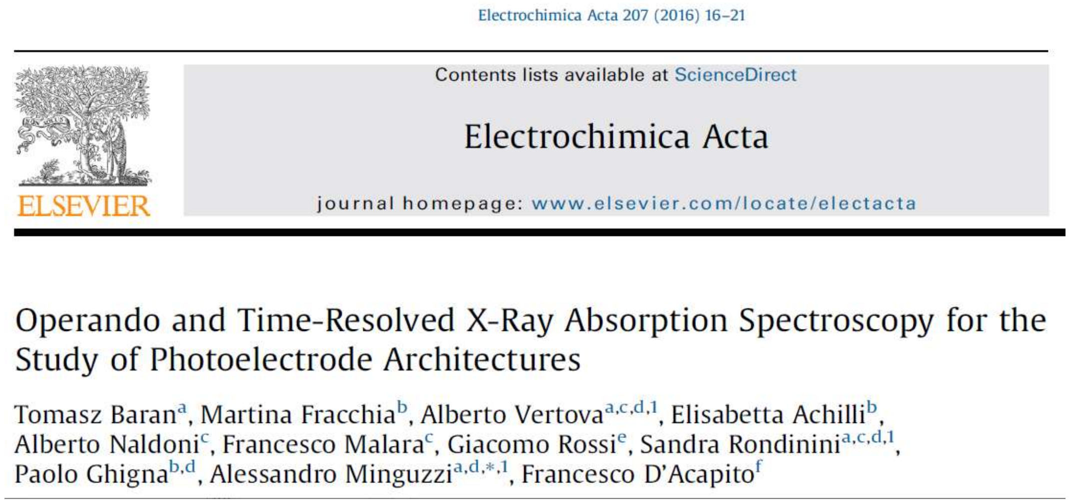


Difference spectra L-D in various potential conditions



FEXRAV L-D at constant potential

Also for Ni: observation of transfer of holes in the NiOx layer



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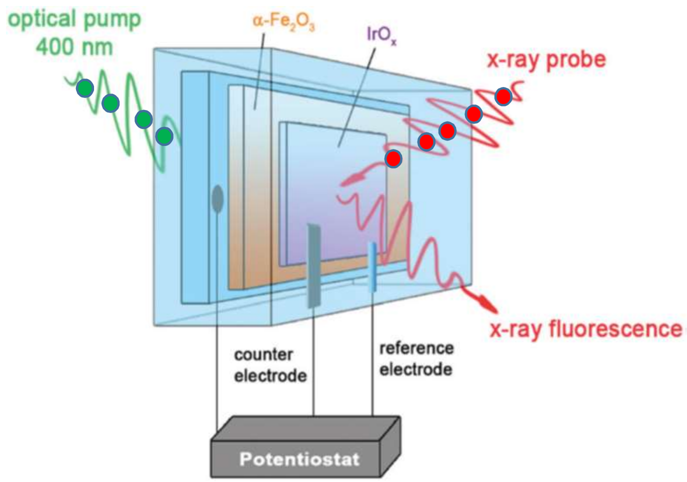
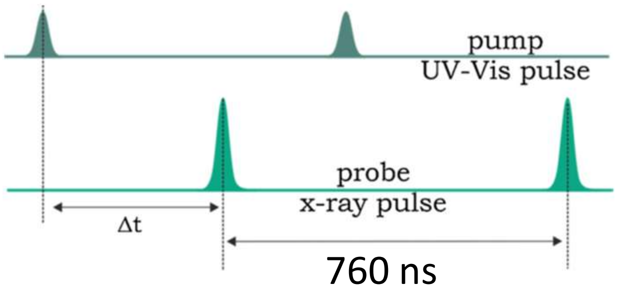
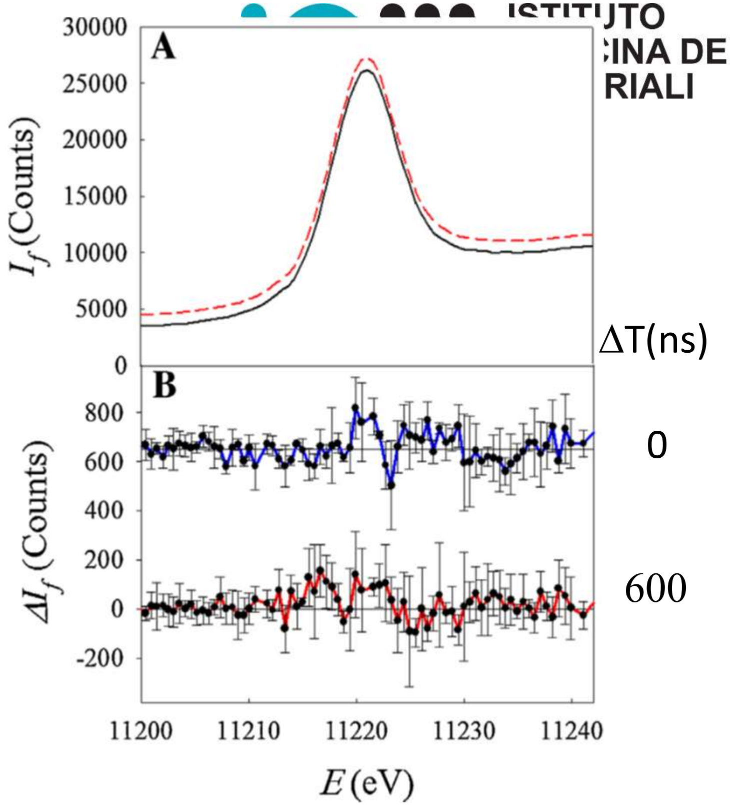
Operando and Time-Resolved X-Ray Absorption Spectroscopy for the Study of Photoelectrode Architectures

Tomasz Baran[a], Martina Fracchia[b], Alberto Vertova[a,c,d,1], Elisabetta Achilli[b], Alberto Naldoni[c], Francesco Malara[c], Giacomo Rossi[e], Sandra Rondinini[a,c,d,1], Paolo Ghigna[b,d], Alessandro Minguzzi[a,d,*,1], Francesco D'Acapito[f]







The charge transfer goes on for about 600 ns

Limited effect due to low laser power

Conclusion

- Need of understanding light-matter phenomena in order to develop renewable energy sources
- XAS is a technique that permits the speciation of elements also in time resolved mode
- Evidence of hole transfer from the semiconductor to the coating oxide.