Recent Advances in Ambient Pressure XPS

Bongjin Simon Mun
Department of Physics and Photon Science
Gwangju Inst. of Science & Technology

ESCA

Gwangju Institute of Science and Technology

Outline

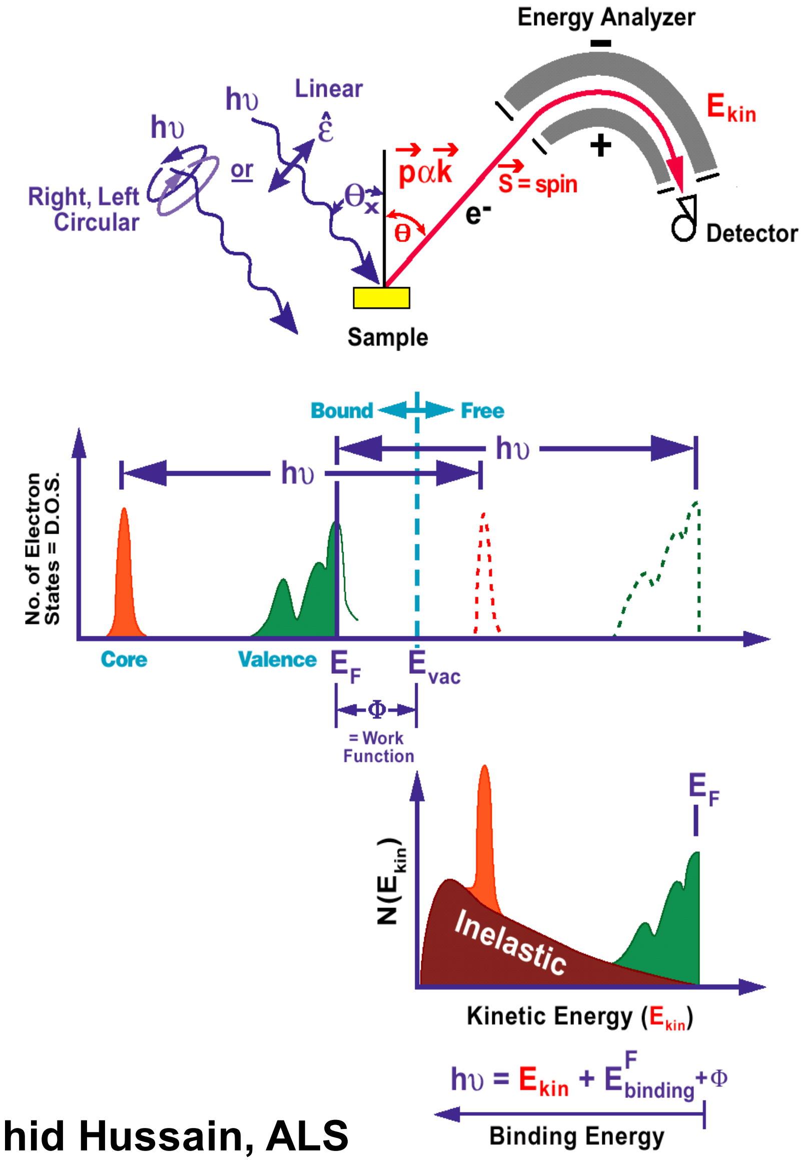
1. The basic concept of AP-XPS

2. Recent Development/Applications of AP-XPS

3. Case study: Hard X-ray AP-XPS with X-ray Scattering

4. Summary

X-ray Photoelectron Spectroscopy (XPS)



Zahid Hussain, ALS

Photoelectric Effect : Einstein (1905)

E(K.E.) = E(hv) – E(B.E.) – Work function

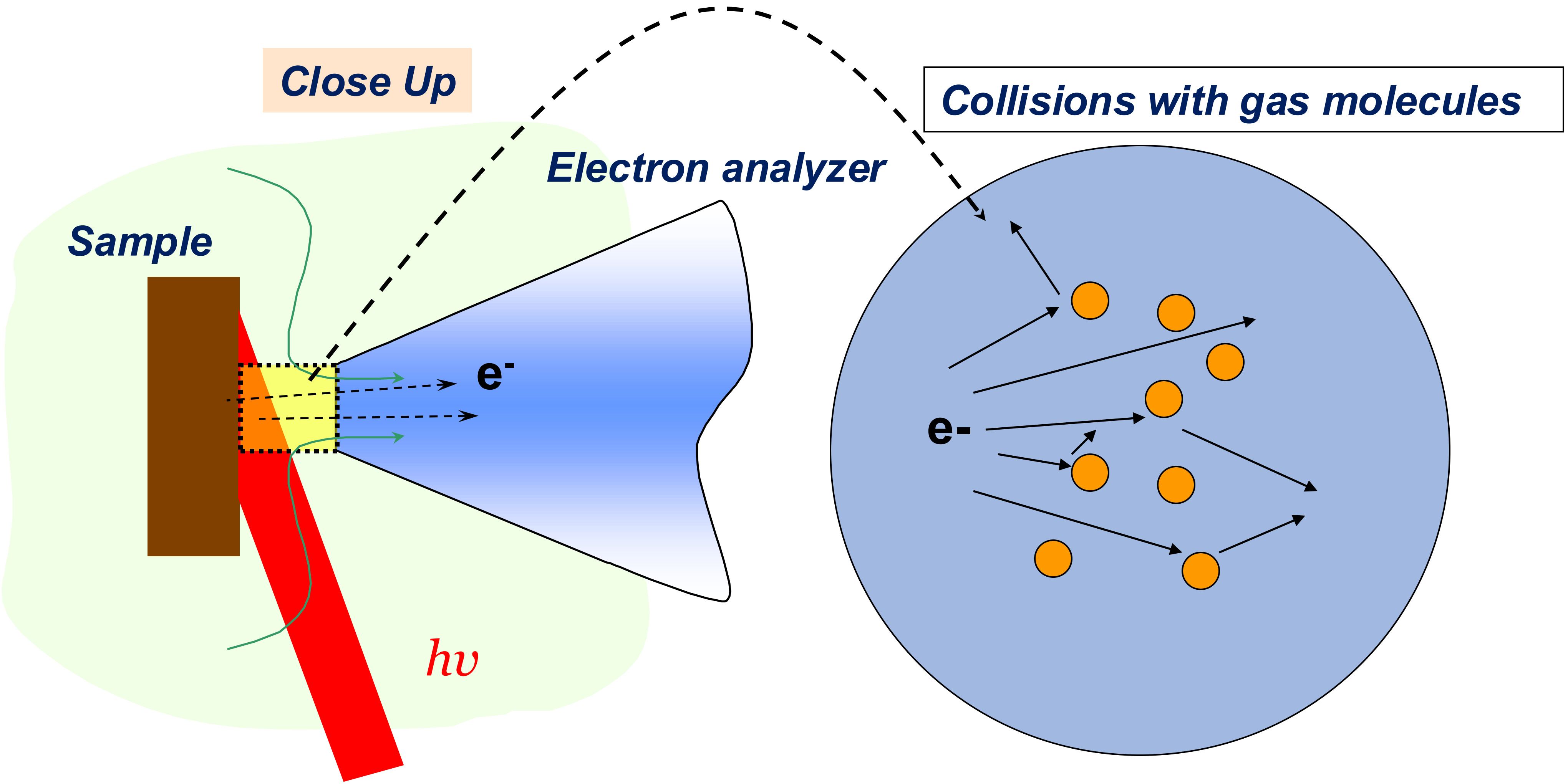
$$I \propto \sum_{f,i} |< f \mid p \cdot A \mid i >|^2 \, \delta(E_k^0 - E_m^0 - \hbar\omega)$$

f = final states
i = initial states
p = momentum of photoelectron
A = vector potential of photon
(Electric fields)

Nobel Prize (1981) K. Siegbahn (Sweden)

Limitation of XPS :

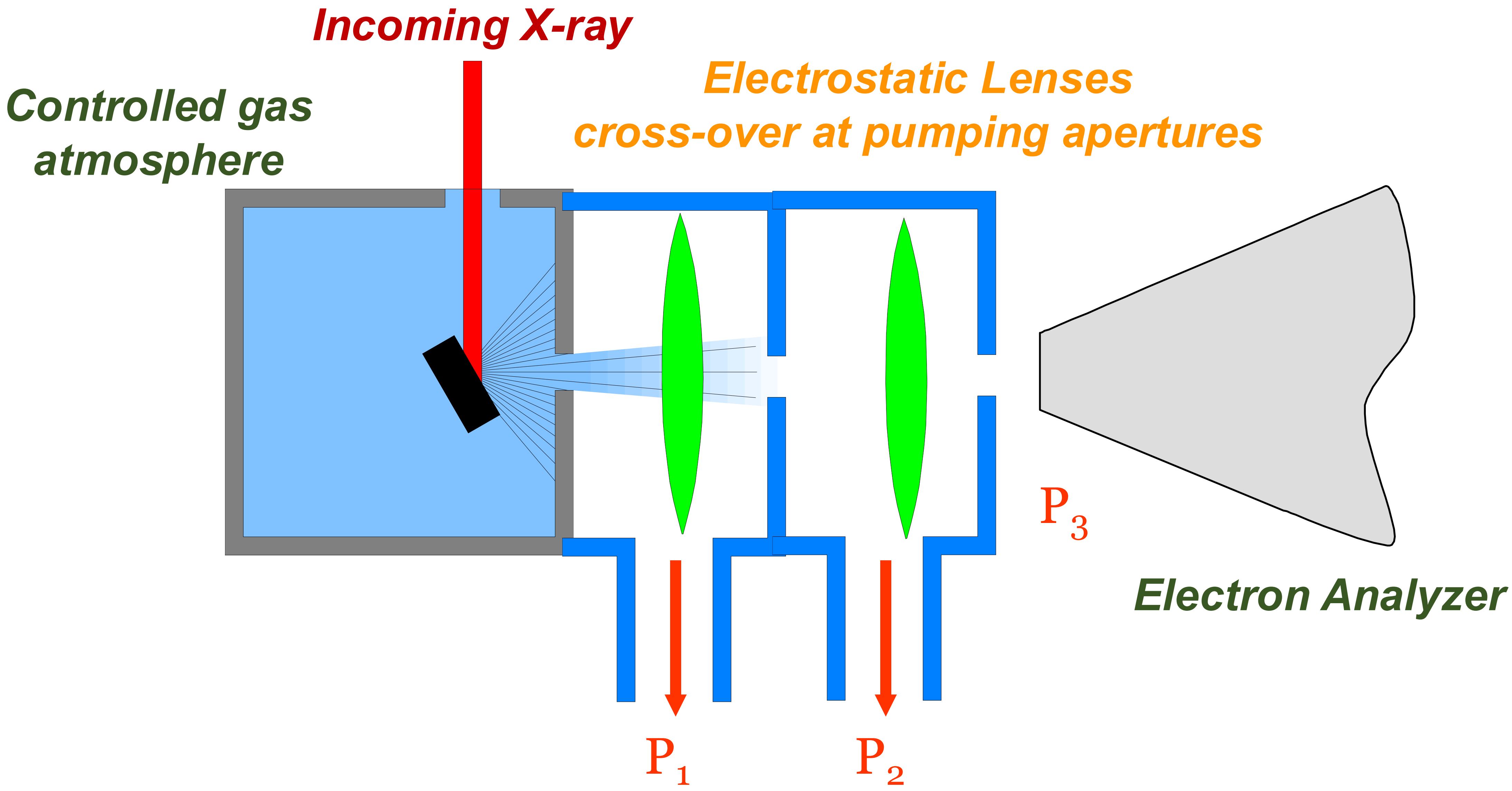
Inelastic scattering with gas molecules in the air



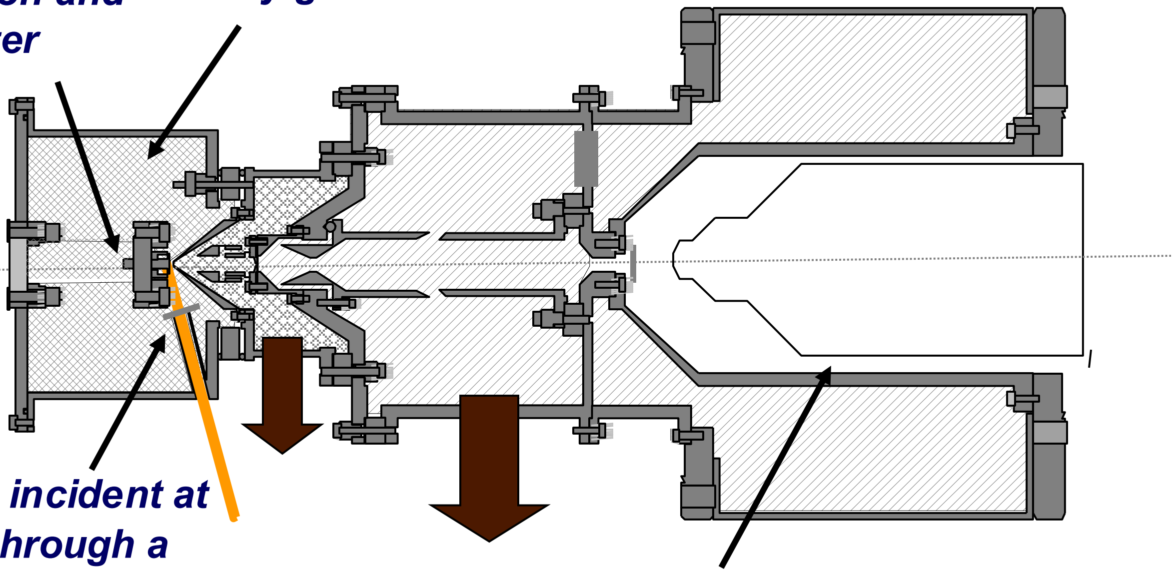
It requires UHV chamber system for quality work

= Impossible to work on liquid/solid interface system

Ambient pressure soft x-ray spectroscopy:
Differentially pumped electron transport



First Ambient Pressure XPS :
Differential Pumping and Electrostatic Lens



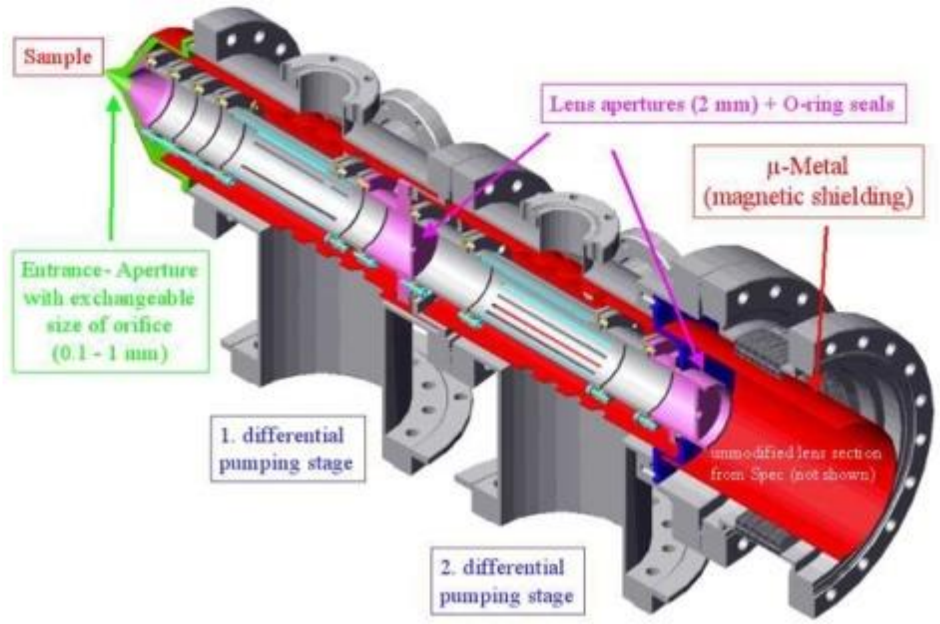
P_{max} = ~ 10 Torr

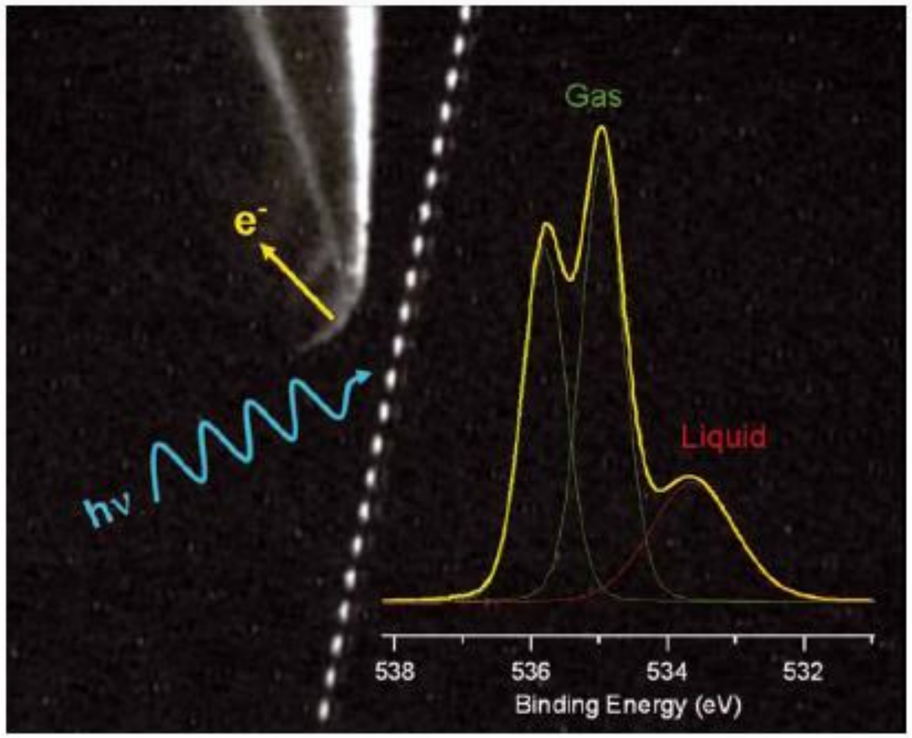
D. Ogletree, H. Bluhm, G. Lebedev, Z. Hussain, C. Fadley, M. Salmeron,
Rev. Sci. Inst. 73(2002) 3872

ALS

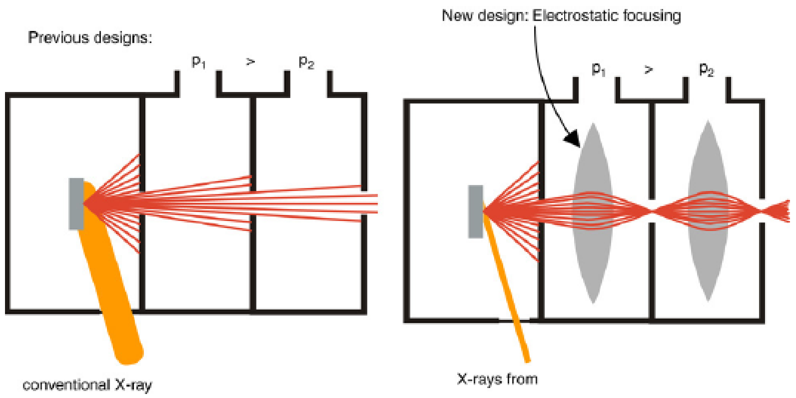
Specs (2004)

(NAP-XPS :Near Ambient Pressure XPS)



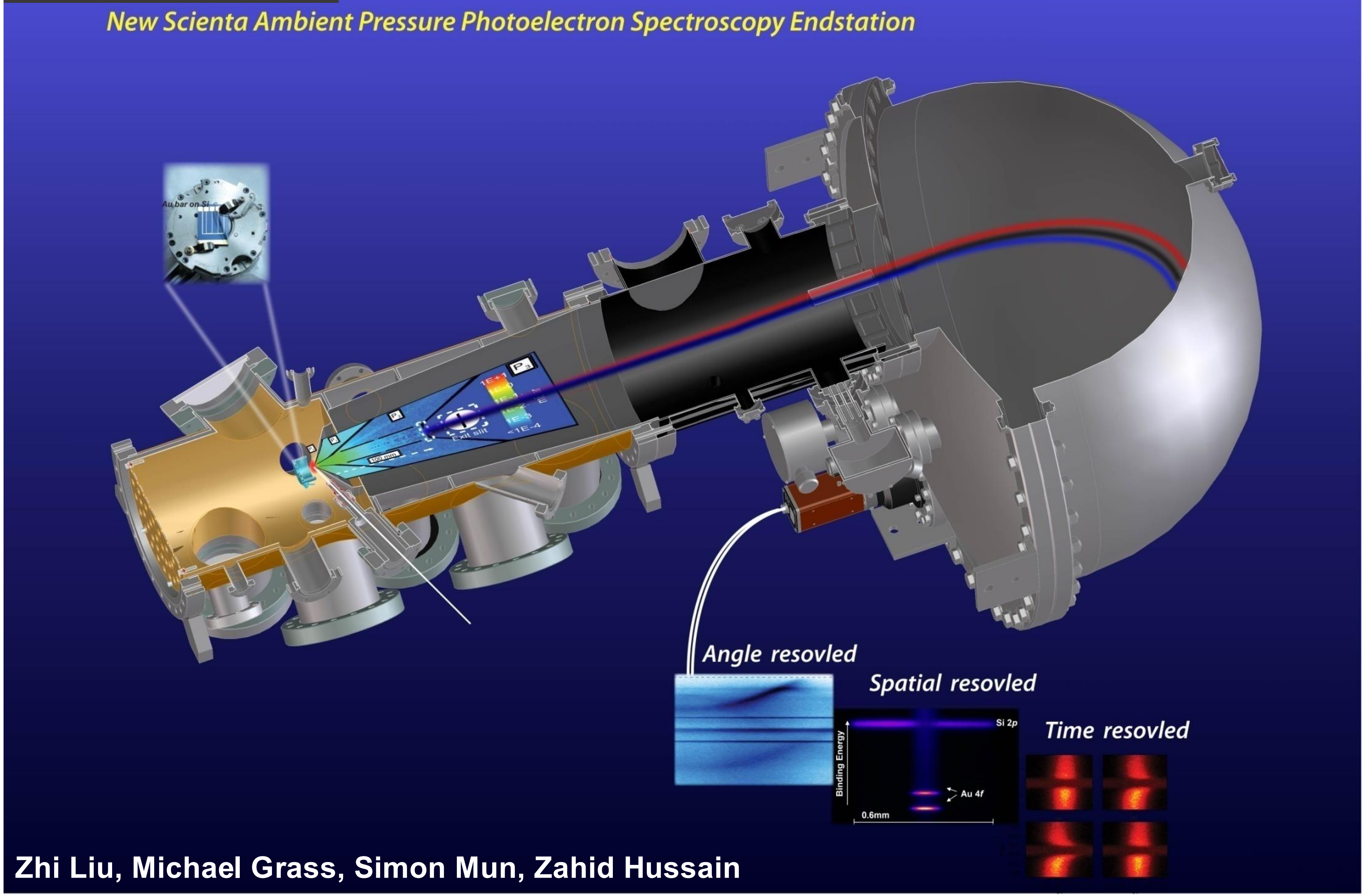


Stroboscopic photograph of a droplet jet prepared from a 40% ethanol solution in front of the entrance aperture (diameter 0.3 mm) of the differentially pumped lens system. The O 1s XP spectrum of the methanol solution droplets is recorded with incident photon energy of 938 eV. Both gas phase and liquid phase photoemission peaks are visible in the spectrum. Data courtesy of David E. Starr et al., published in Phys. Chem. Chem. Phys. 2008.

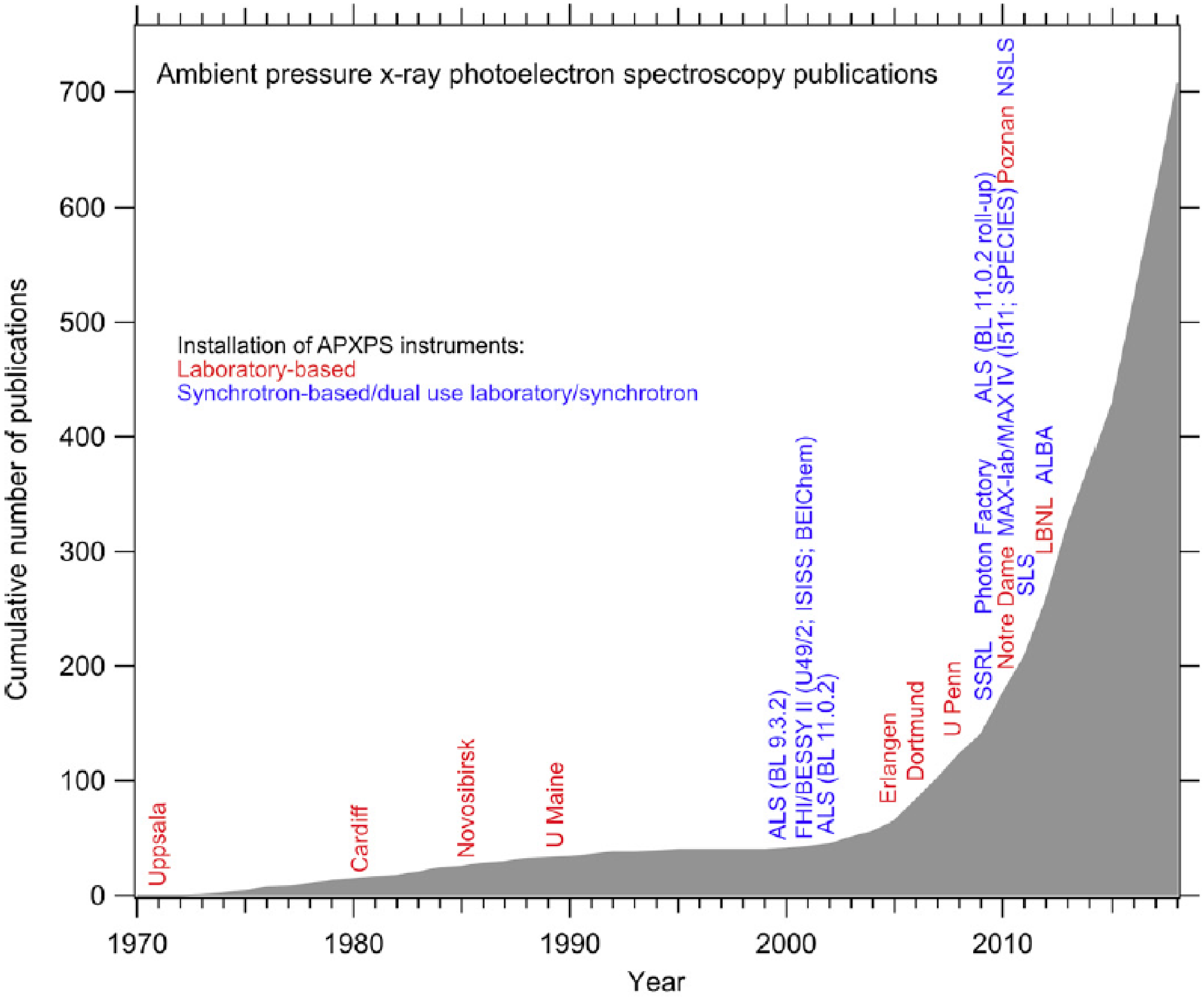


David Starr, Hendrik Bluhm

Scienta (2008)



AP-XPS around the world (2020)



2013:
SOLEIL/UPMC
MPI Düsseldorf
Singapore
FHI/BESSY II (ISISS)
Pune

2014:
SPring-8 (BL07LSU)
Daejon
Manchester
Diamond
Shanghai
U Delaware

2015:
Synfuels Technology
Shenzhen
Prague
Imperial College

2019-:
HZB/Institute for Solar Fuels
Lehigh
EPFL
Gwangju
Wien
Ohio State
Paderborn
ARCNL
KAUST
Fraunhofer-Gesellschaft München
NIMS
Innsbruck
Fuzhou
Hefei
Tsinghua U
PSI
Peking U
Rostock

2016:
U Illinois
Warsaw
MPG/BESSY II (Cat@EMIL)
SSRF
SPring-8 (BL36XU)
Brookhaven
Zhengzhou
Eindhoven
ALS (BL 9.3.1)
BESSY II (SOL^{3}PES)

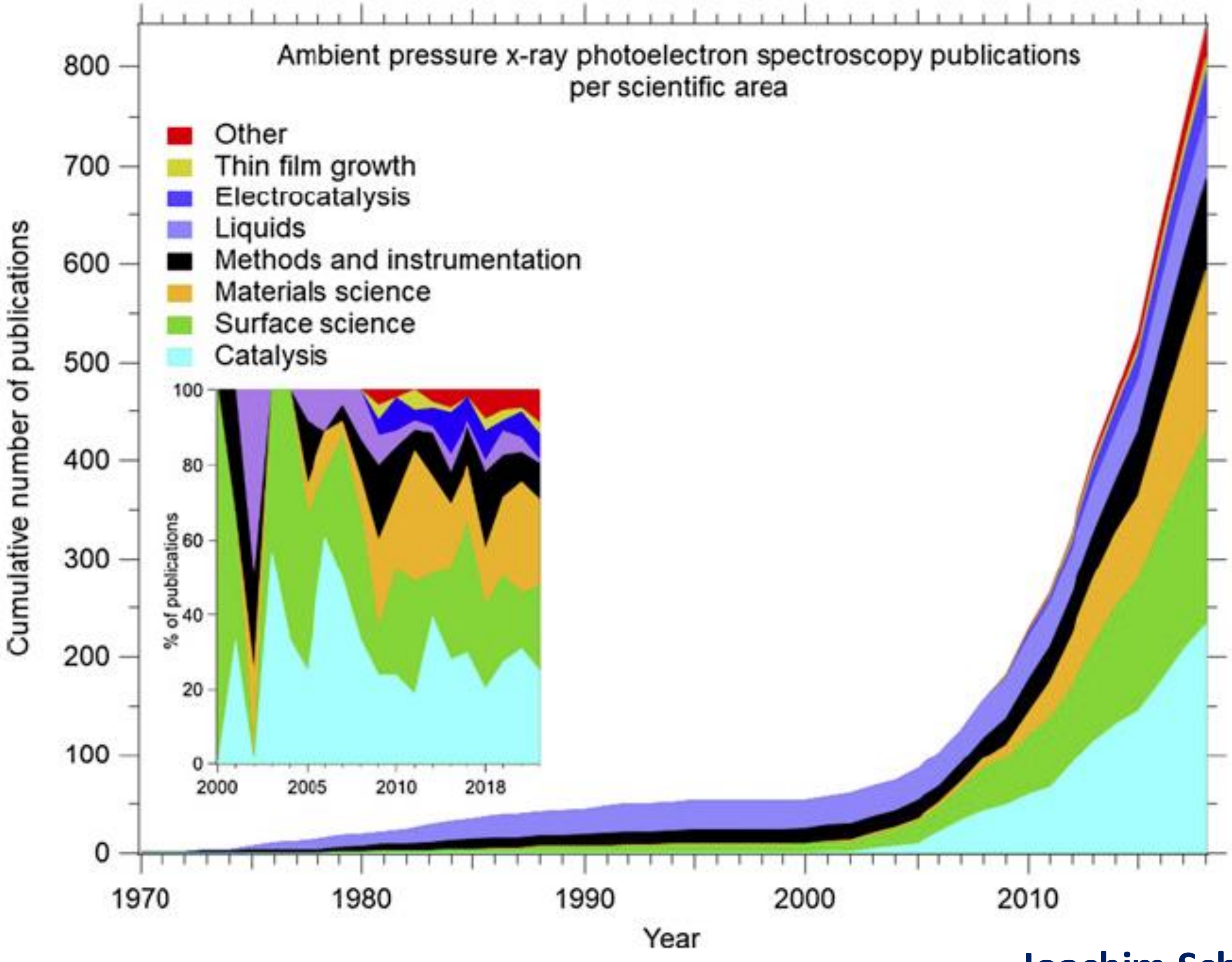
2017:
MAX IV (HIPPIE)
Irvine
Bochum
Medellin
Oregon State U
ShanghaiTech
SINANO
Mühlheim
NSRRC
Barcelona
Nottingham
Dalian
Alcon/Novartis Batam
FHI (LJ-PES)
Stockholm/DESY

2018:
Xiamen
Brookhaven
Cambridge
ECBC
IMDEA
Jülich
Daejon
Leeds
Golden, Colorado

Joachim Schnadt, Lund Univ./ MAX IV

J. Phys.: Condens. Matter **32** (2020) 413003 (29pp)

Various areas of APXPS applications (2020)



Joachim Schnadt, Lund Univ./ MAX IV

J. Phys.: Condens. Matter **32** (2020) 413003 (29pp)

Review Articles

1. Salmeron, M.; Schlögl, R,
   Surf. Sci. Rep. 2008, 63, 169

2. Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H.,
   Chem. Soc. Rev. 2013, *42*, 5833– 5857

3. Nguyen, L.; Tao, F. F.; Tang, Y.; Dou, J.; Bao,
   Chem. Rev. 2019, *119*, 6822– 6905

4. Han, Y.; Zhang H.,; Yu, Y.; Liu, Z, (Electrochemistry application)
   ACS Catal. 2021, 11, 3, 1464-1484

5. Dupuy, R.; Richter, C.;, Winter, B.; Meijer, G.; Schlögl, R.; Bluhm, H.;
   J. Chem. Phys. 2021, 154, 060901

Outline

1. The basic concept of AP-XPS

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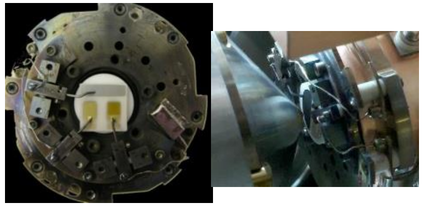
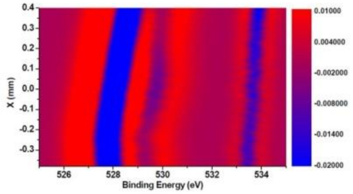
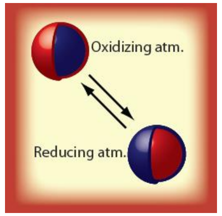
Fields of Science with AP-XPS :

Energy and Environment

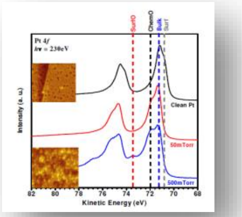


Batteries & Fuel cell

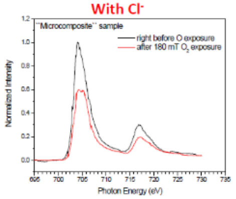


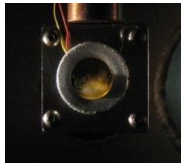


Catalysis

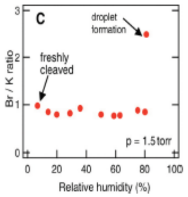


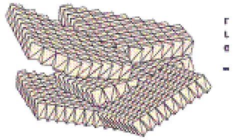
Corrosion



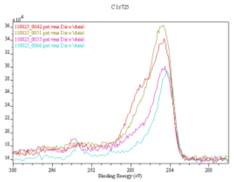


Water





CO_2 conversion



Courtesy of Prof. Zhi Liu (Shanghai Tech.)

Early studies with AP-XPS at ALS

Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles

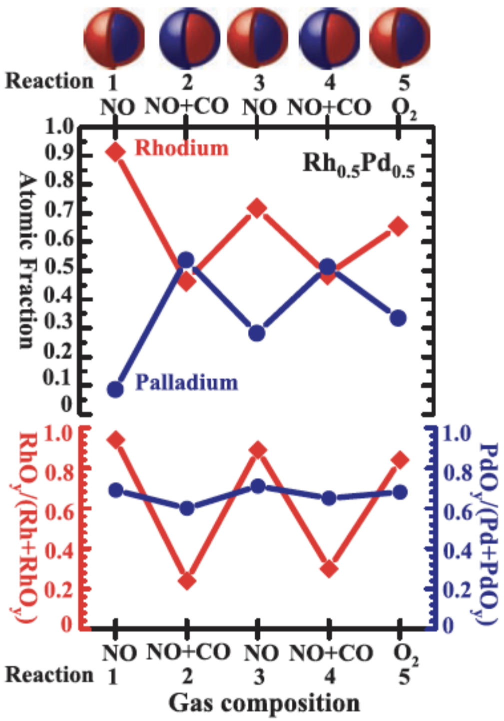
Feng Tao,[1,2] Michael E. Grass,[1,2] Yawen Zhang,[1,2,5] Derek R. Butcher,[1,2] James R. Renzas,[1,2] Zhi Liu,[1,3] Jen Y. Chung,[3] Bongjin S. Mun,[3] Miquel Salmeron,[1,4*] Gabor A. Somorjai[1,2*]

In Situ Oxidation Study of Pt(110) and Its Interaction with CO

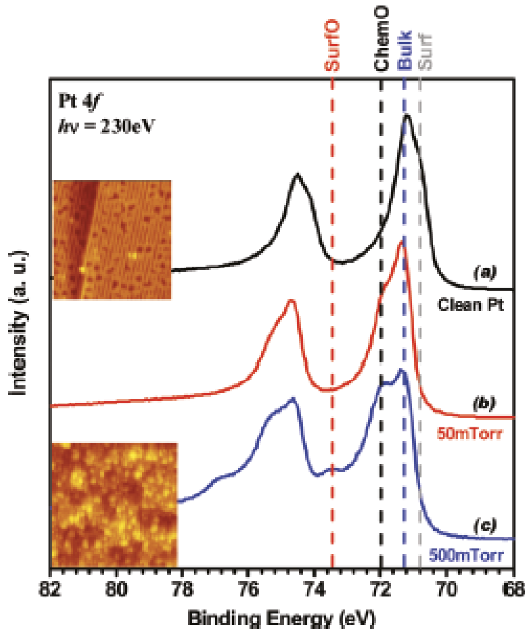
Derek R. Butcher,[†,#,$] Michael E. Grass,[†,‡,#] Zhenhua Zeng,[§] Funda Aksoy,[†,∥] Hendrik Bluhm,[†] Wei-Xue Li, Bongjin S. Mun,[*,‡] Gabor A. Somorjai,[†,⊥] and Zhi Liu[*,†]

Electron Spectroscopy of Aqueous Solution Interfaces Reveals Surface Enhancement of Halides

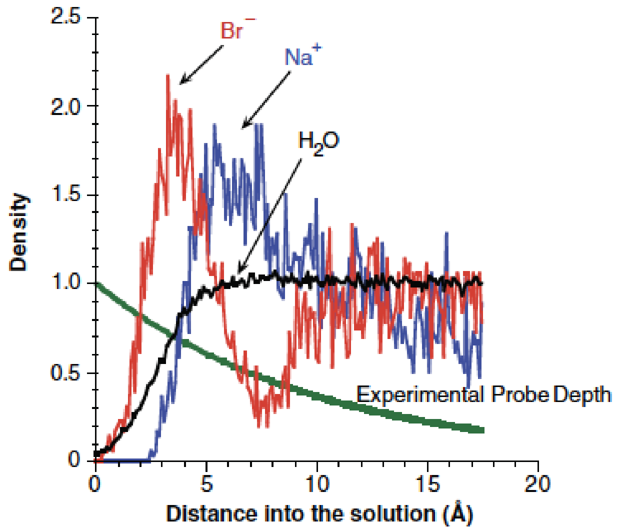
Sutapa Ghosal,[1,2] John C. Hemminger,[1*] Hendrik Bluhm,[3] Bongjin Simon Mun,[4] Eleonore L. D. Hebenstreit,[2] Guido Ketteler,[2] D. Frank Ogletree,[2] Felix G. Requejo,[2,5] Miquel Salmeron[2]



Nanoparticle under Reaction conditions



Surface reaction under Reaction conditions



Liquid-Solid Interface

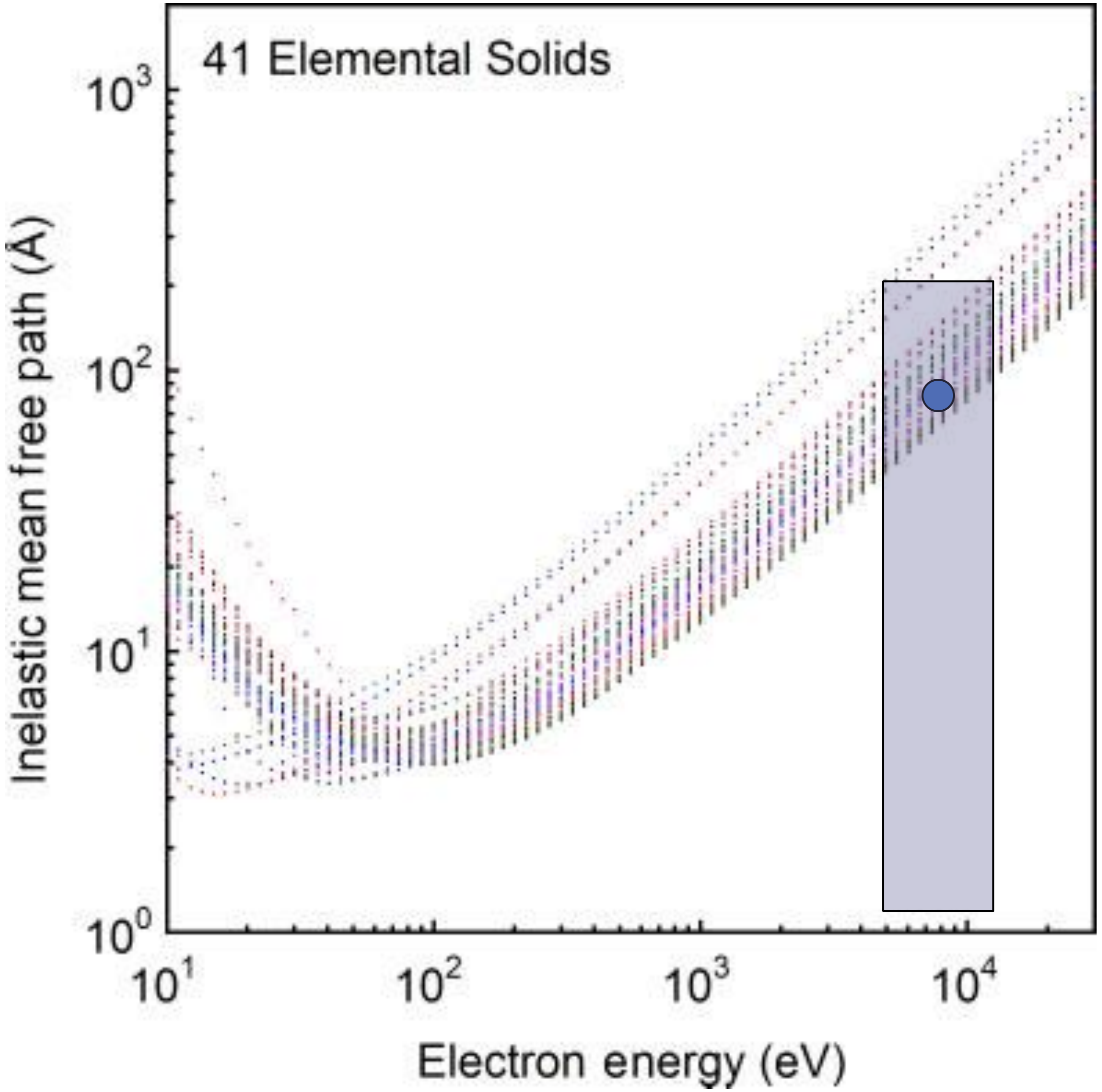
Challenges of AP-XPS

a. Pressure Gap: What’s really happening at 1 Bar?

b. Liquid/Solid Interface or Liquid Phase:
Can we monitor/control the liquid surface at equilibrium ?

c. Time-resolved surface reaction dynamics under reaction condition

Hard X-ray : Increasing Inelastic Mean Free Path (~ 9 KeV)



Ratio = $e^{-d/\lambda}$

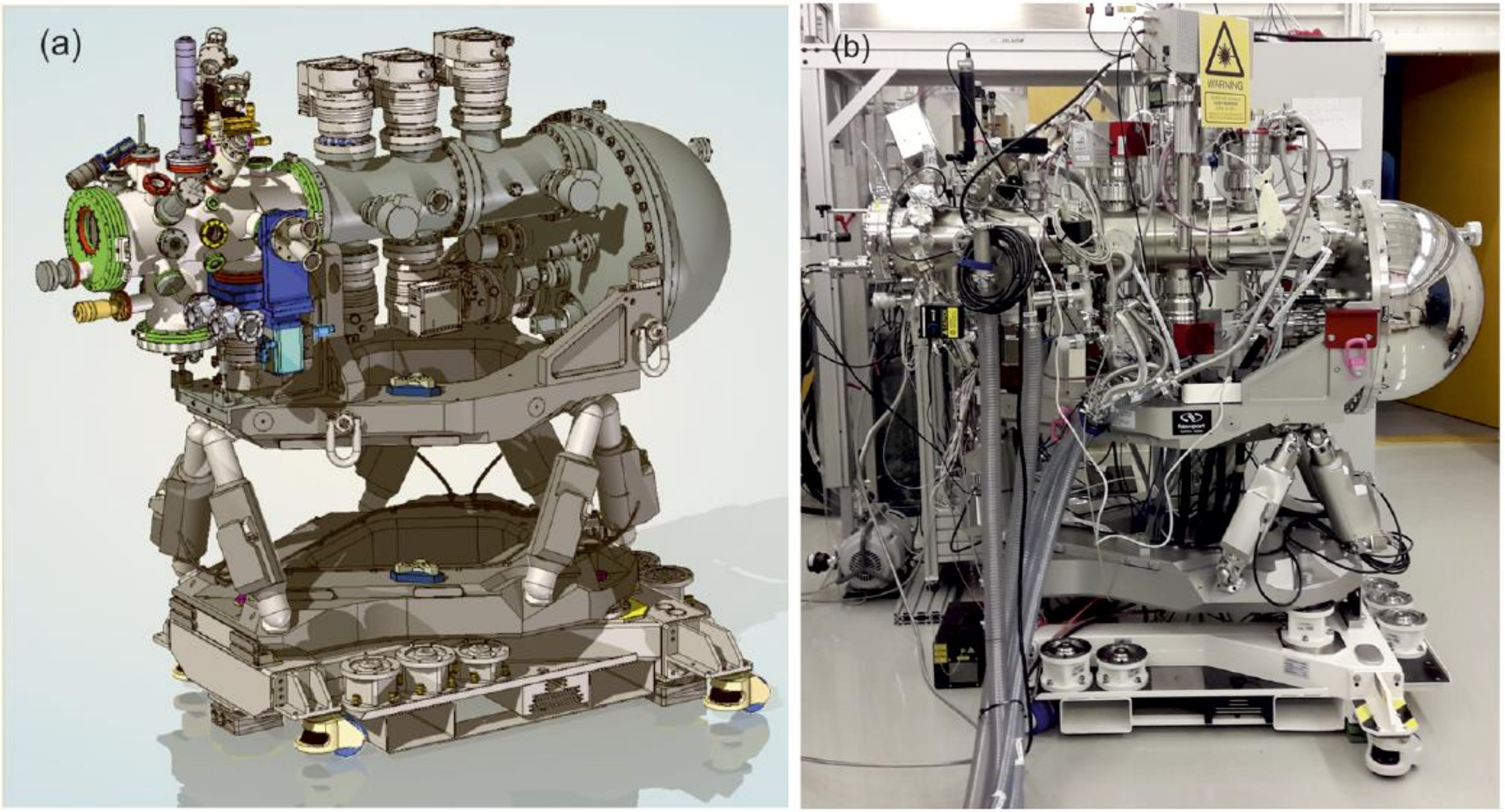
$\lambda \sim 10 \pm 1$ nm

Clearly we can get to information of buried interface of 10nm under, maybe even 20nm…

S. Tanuma, C. Powell, and D. R. Penn Surf. Interface Anal., 43,689(2010)

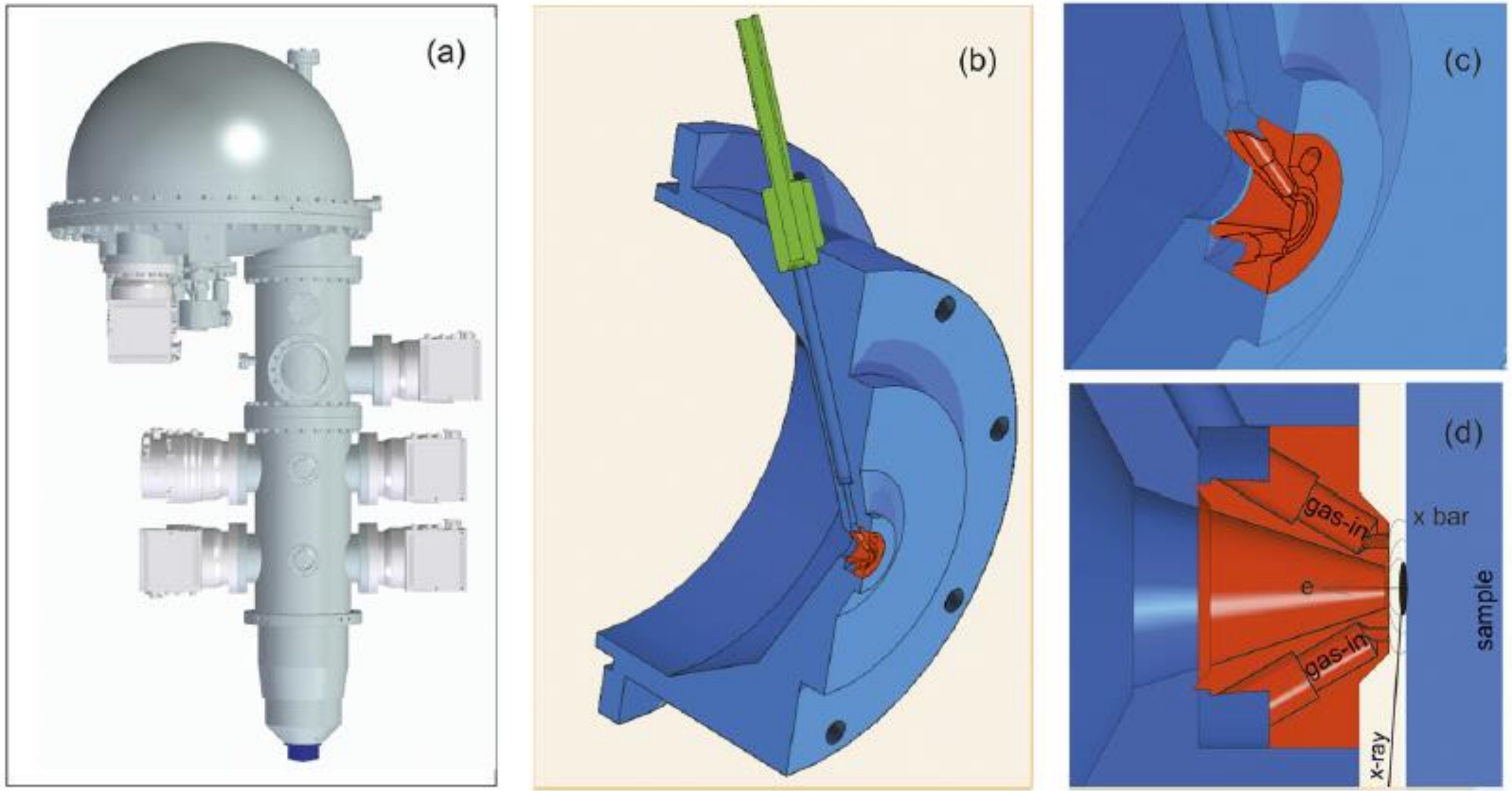
Pressure Gap

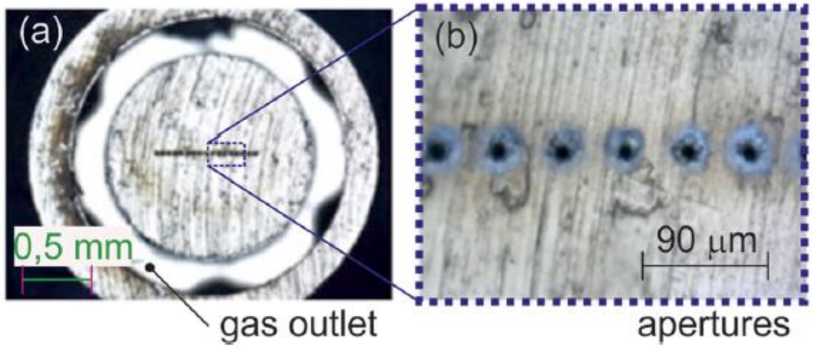
Tender X-ray AP-XPS at 2Bar pressure at DESY (2019)



Rev. Sci. Instrum. **90**, 103102 (2019); https://doi.org/10.1063/1.5109321

Tender X-ray AP-XPS at 2Bar pressure at DESY (2019)





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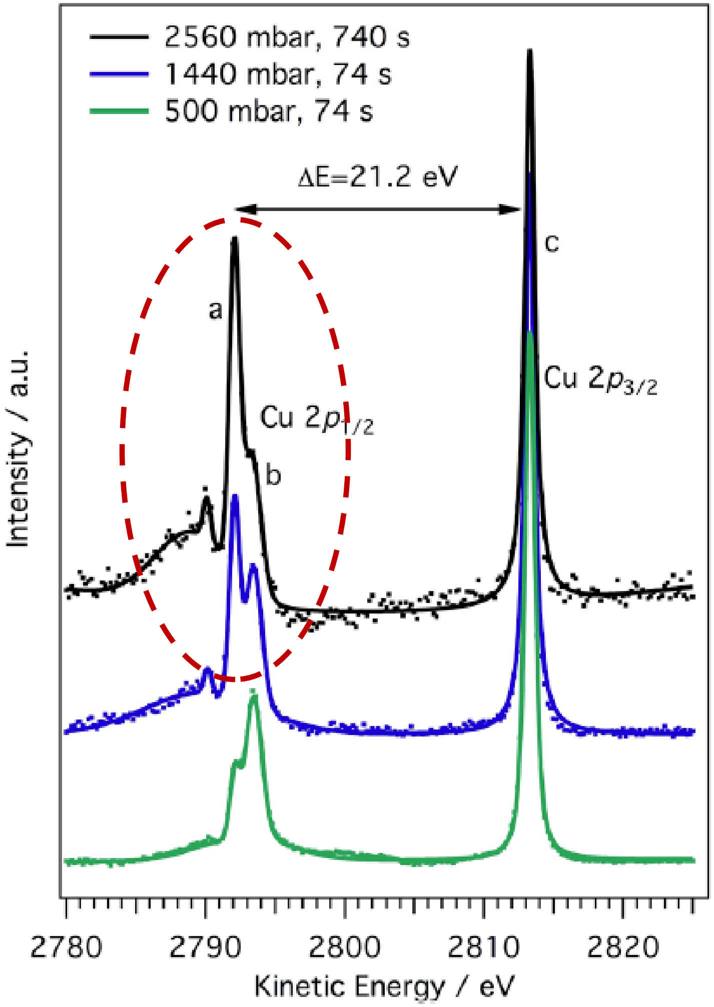
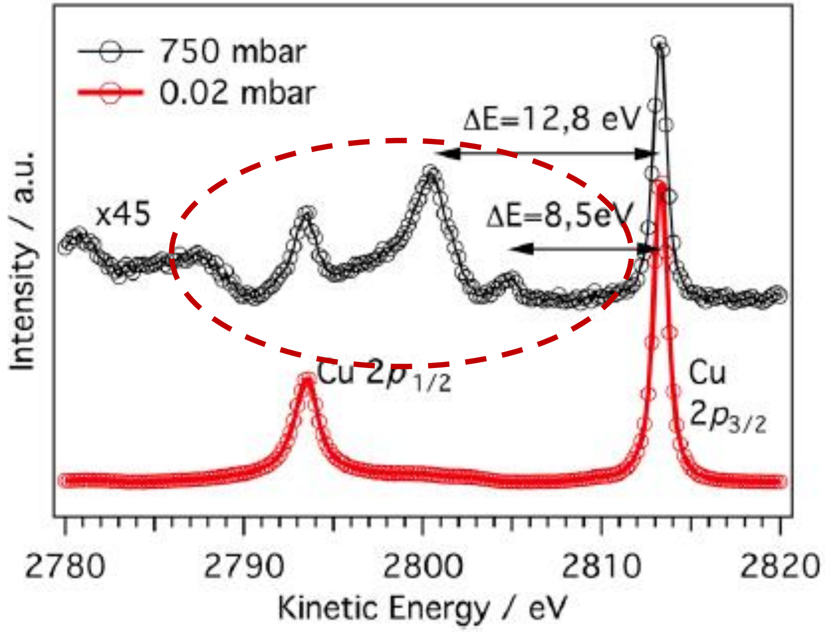


Photon Energy = 3750 eV

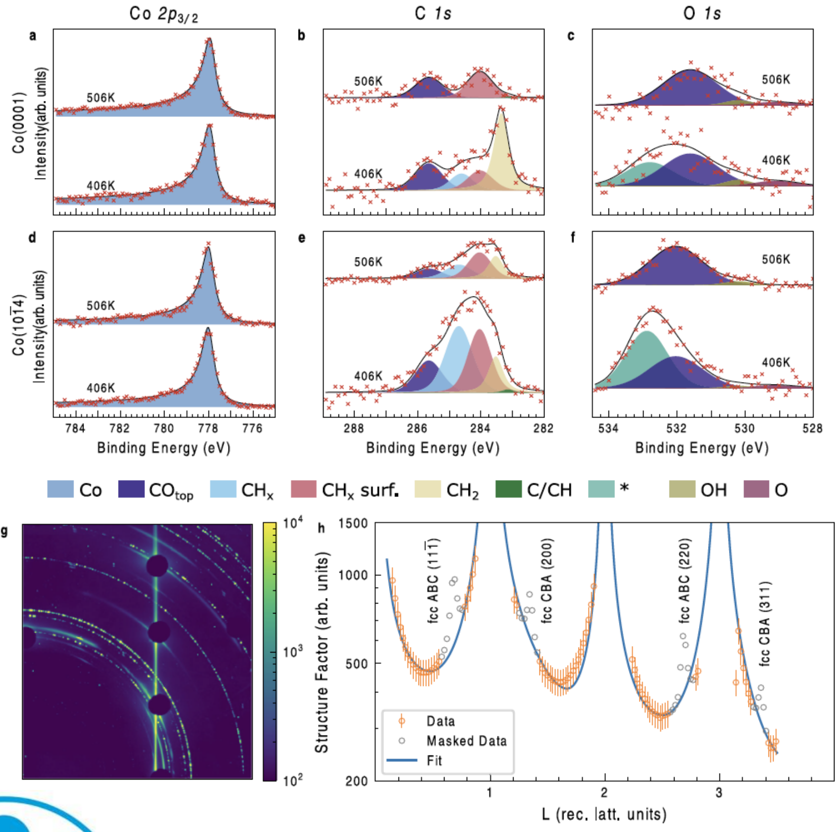


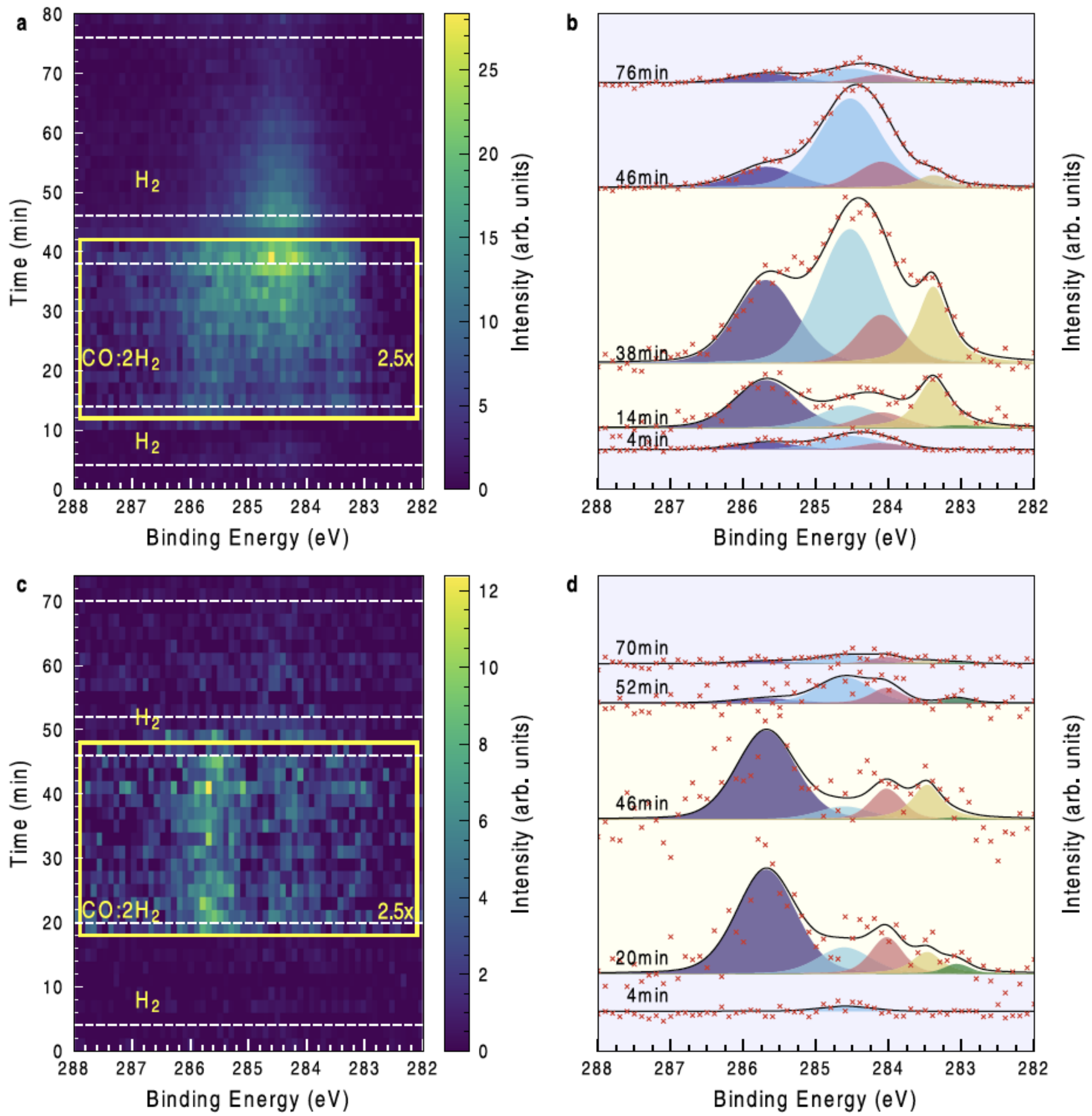
Electron Energy Loss due to He gas

https://doi.org/10.1038/s41467-025-56082-8

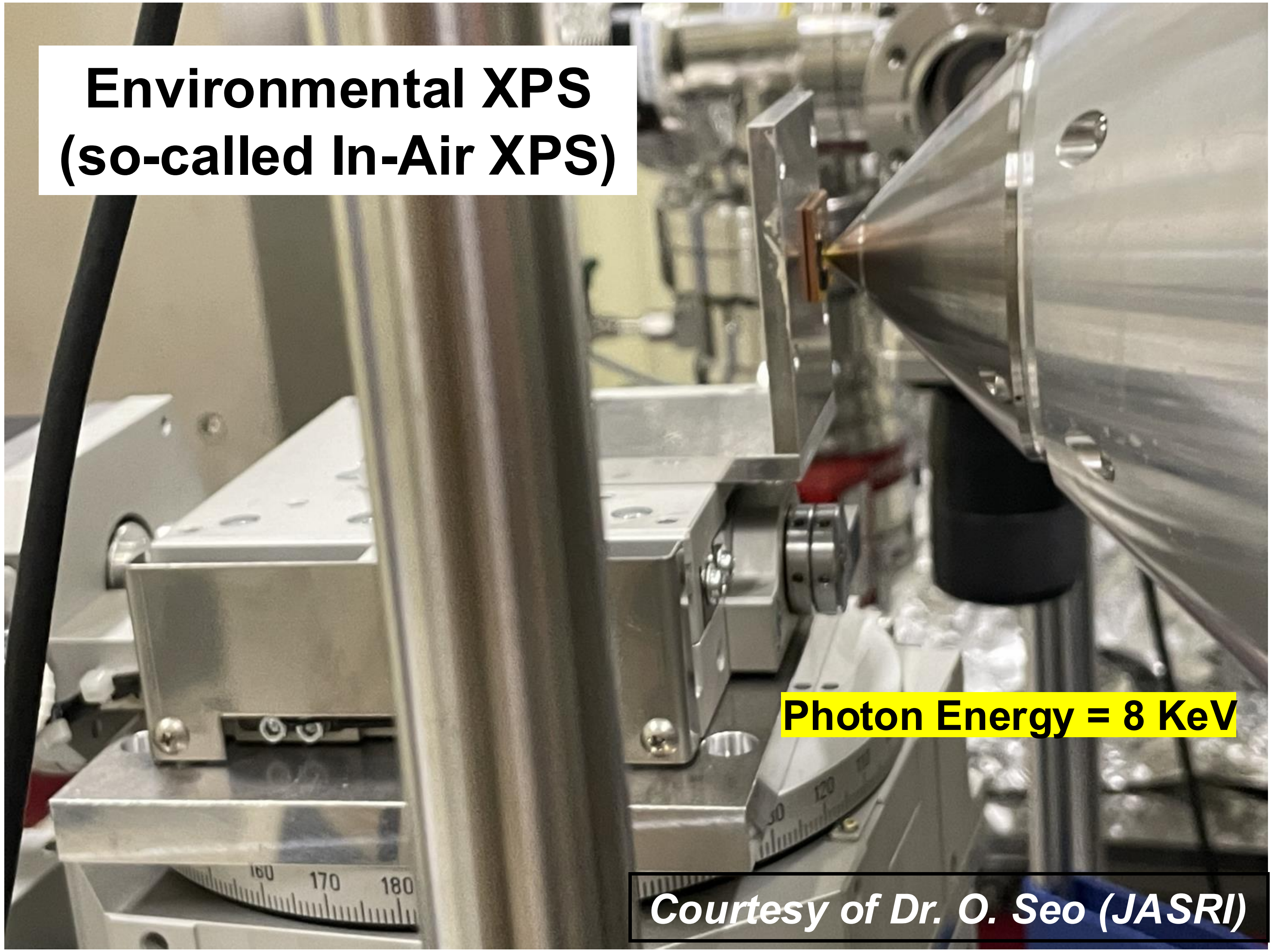
In-situ probing of the Fischer-Tropsch reaction on Co single crystal surfaces up to 1 bar

Nature Communications | (2025)16:1005





Hard X-ray AP-XPS Endstation at Spring-8, Japan (2023)



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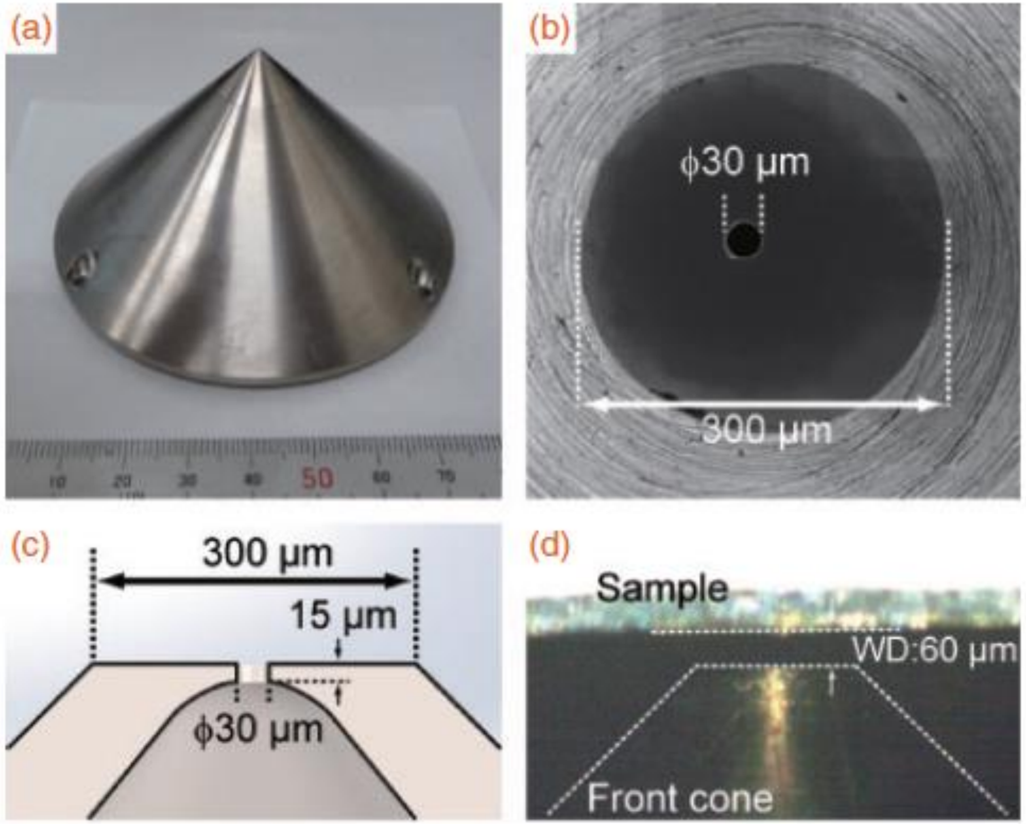
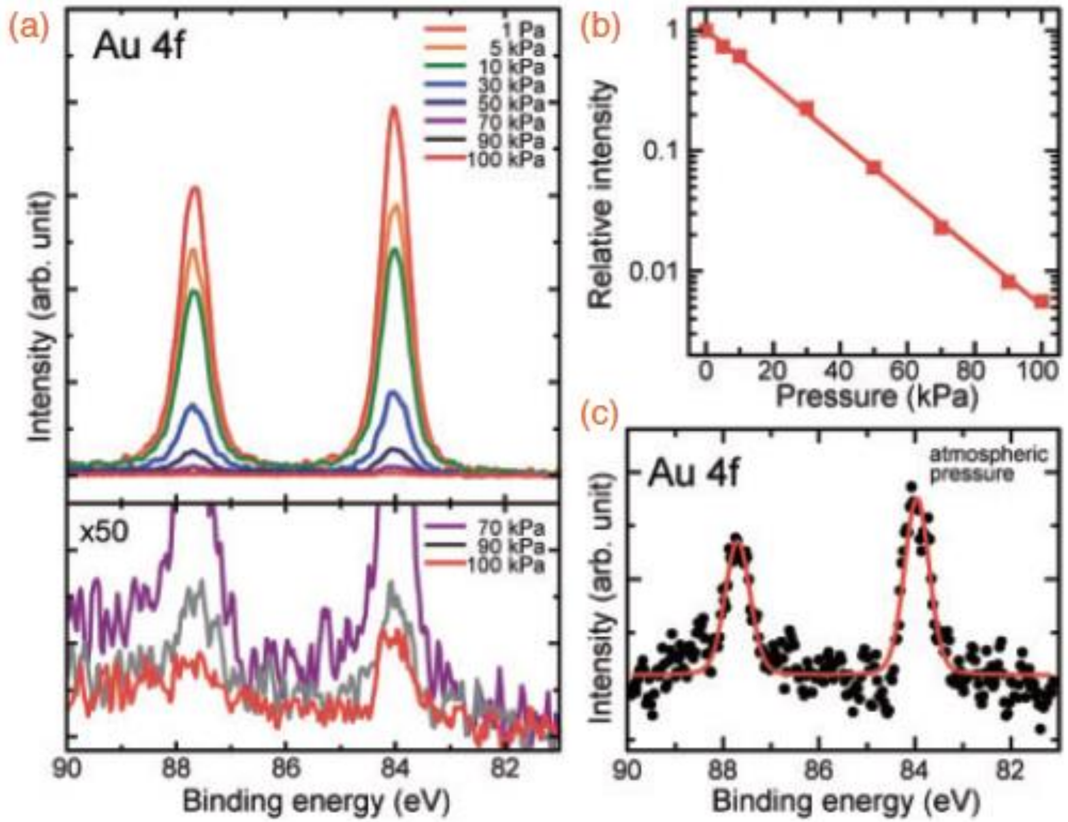




Photon Energy = 8.0 keV

SPring-8

Applied Physics Express **10**, 076603 (2017)

https://doi.org/10.7567/APEX.10.076603

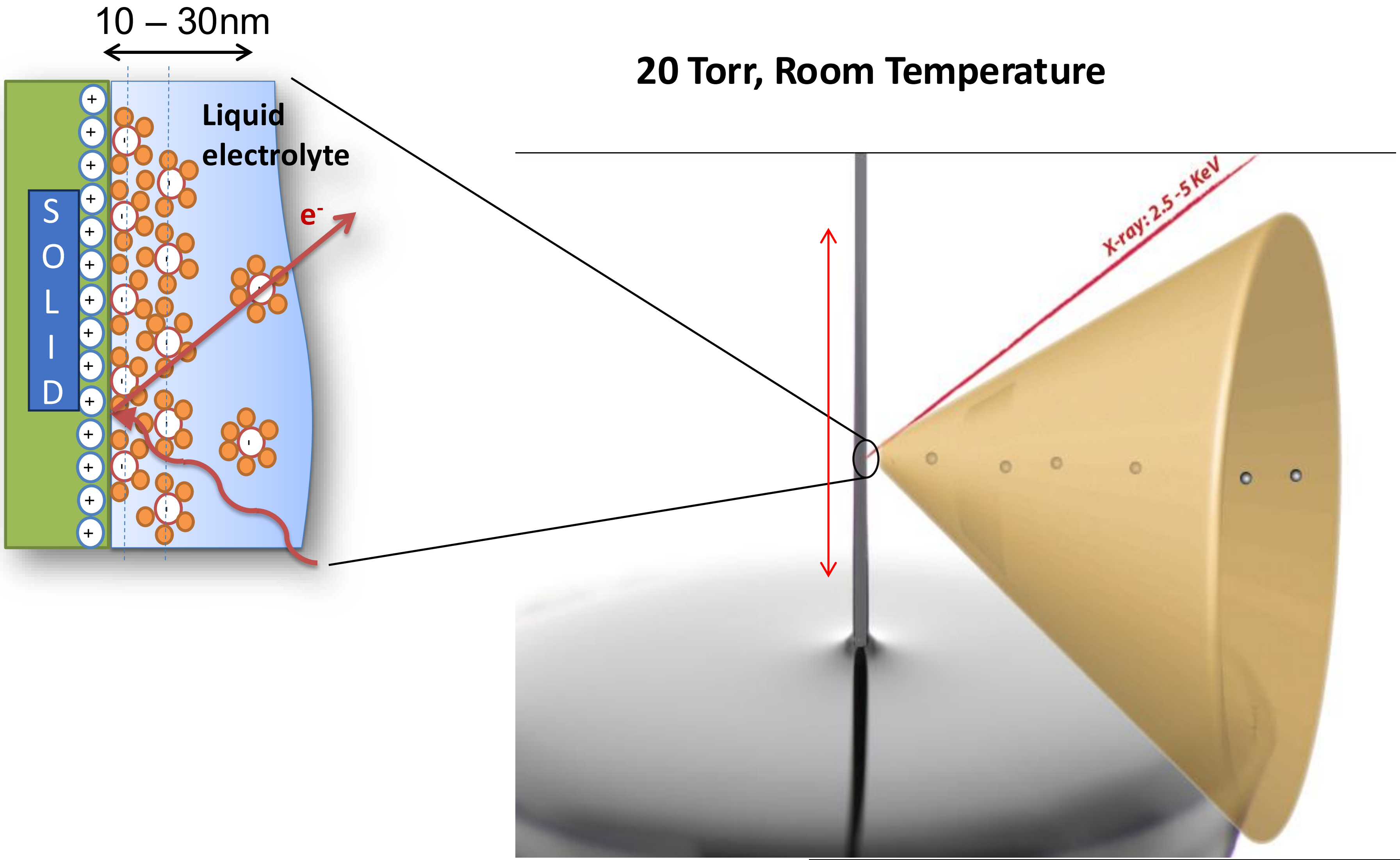
Challenges of AP-XPS

a. Pressure Gap: What's really happening at 1 Bar?

b. Liquid/Solid Interface or Liquid phase:
Can we monitor/control the liquid surface at equilibrium ?

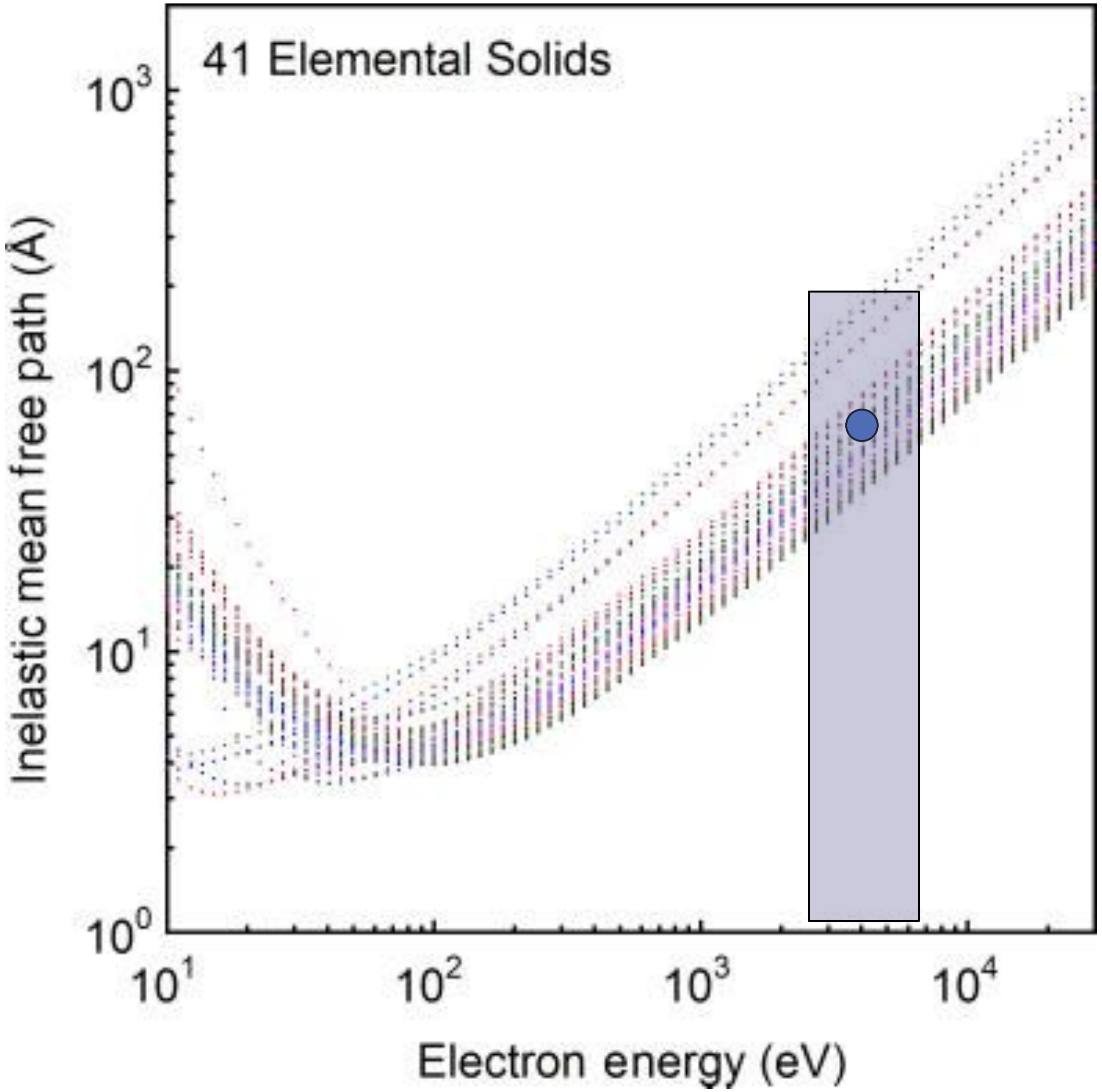
c. Time-resolved surface reaction dynamics under reaction condition

Electrochemistry : Can we observe electrochemical double layer ?



Courtesy of Prof. Zhi Liu (Shanghai Tech.)

Tender X-ray : Increasing Inelastic Mean Free Path (3~5 KeV)



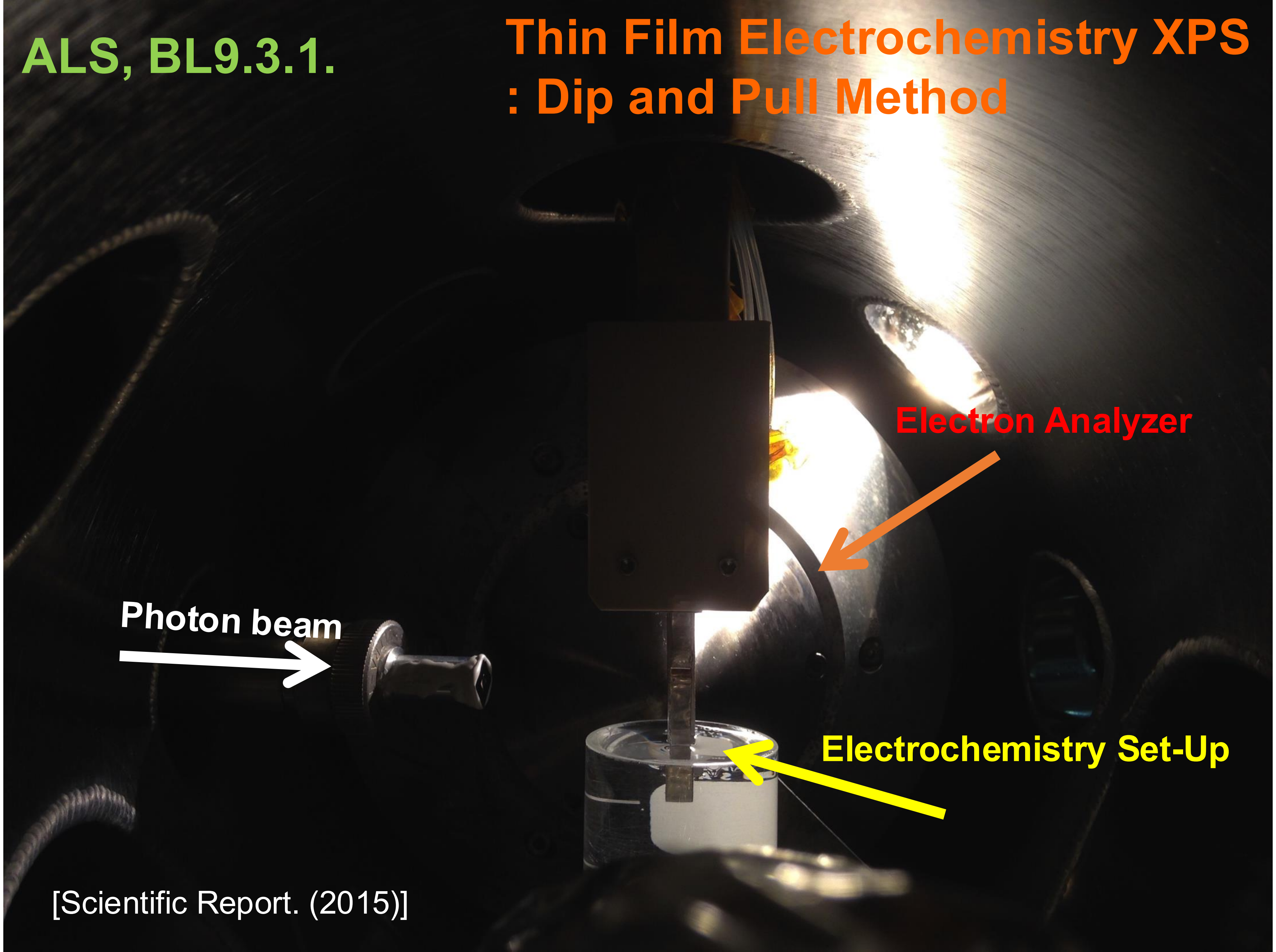
Ratio = $e^{-d/\lambda}$

$\lambda = 5.9 \pm 1$ nm

Clearly we can get to information of buried interface of 10nm under, maybe even 20nm…

Study of Liquid/Solid Interface is possible.

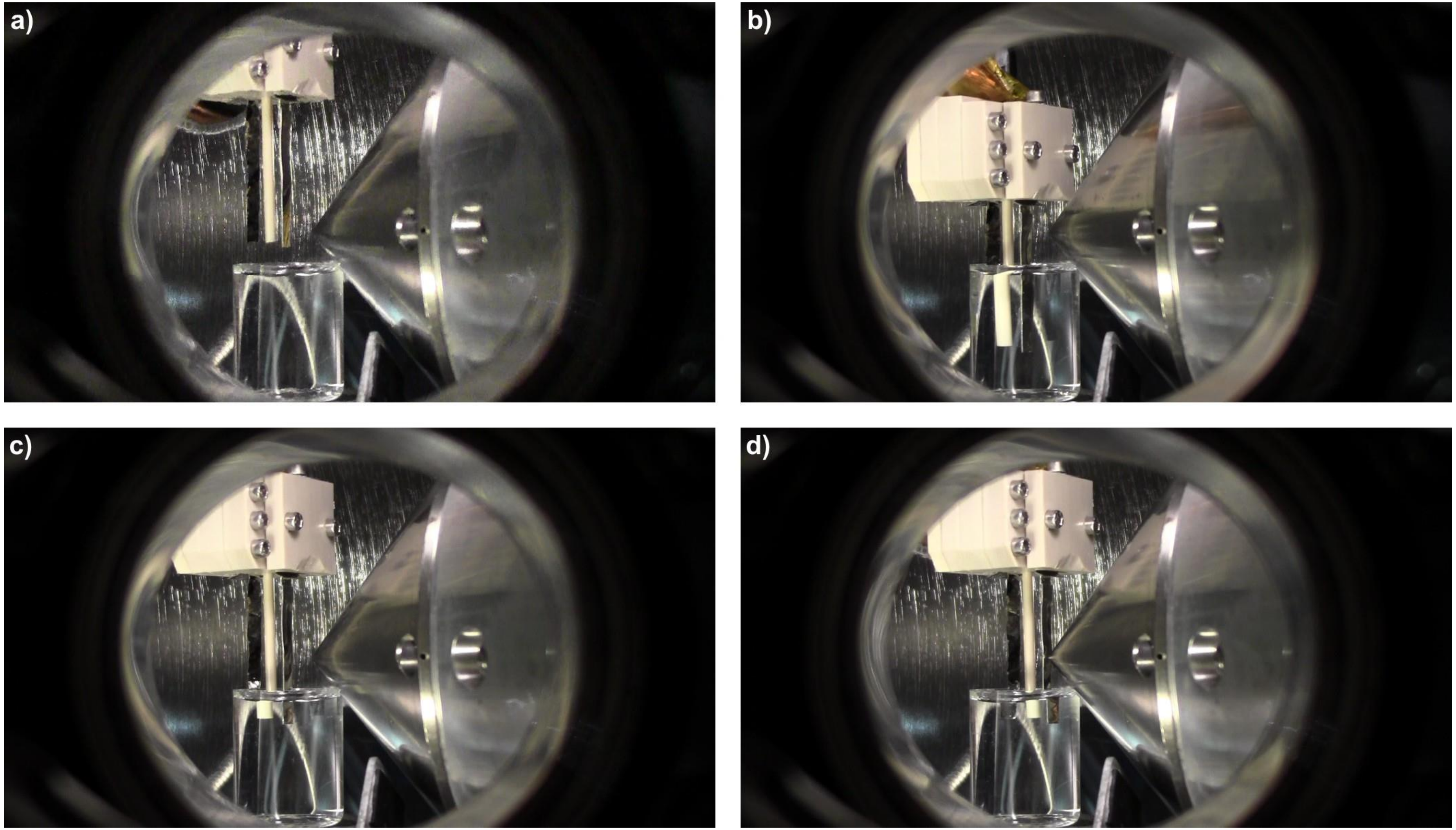
S. Tanuma, C. Powell, and D. R. Penn Surf. Interface Anal., 43,689(2010)


ALS, BL9.3.1.
Thin Film Electrochemistry XPS
: Dip and Pull Method
Electron Analyzer
Photon beam
Electrochemistry Set-Up
[Scientific Report. (2015)]

Liquid-Solid interface (Electrochemistry)

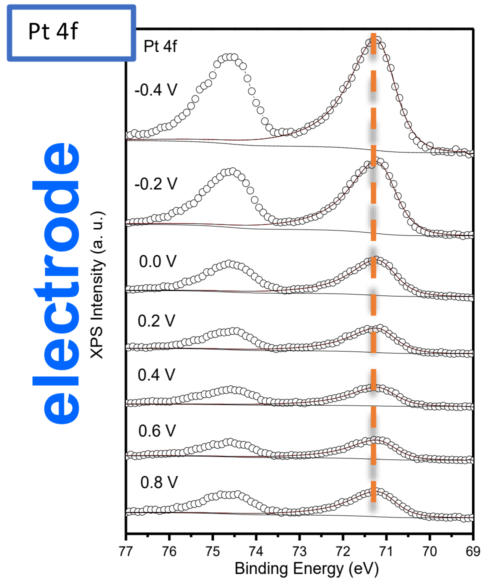
Three Electrode Dipping Stick

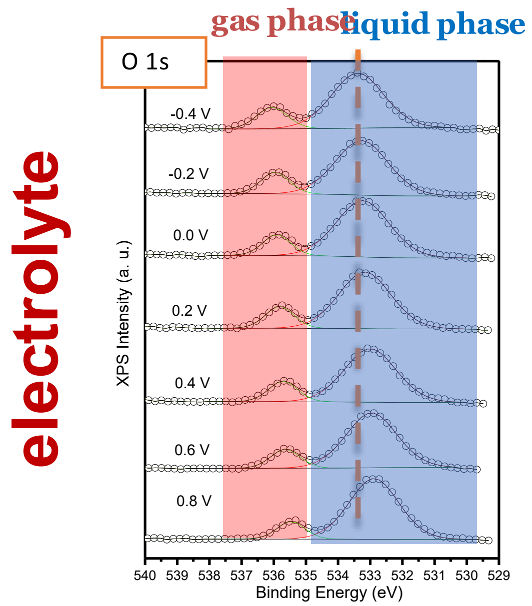
"Dip & Pull" to create thin meniscus

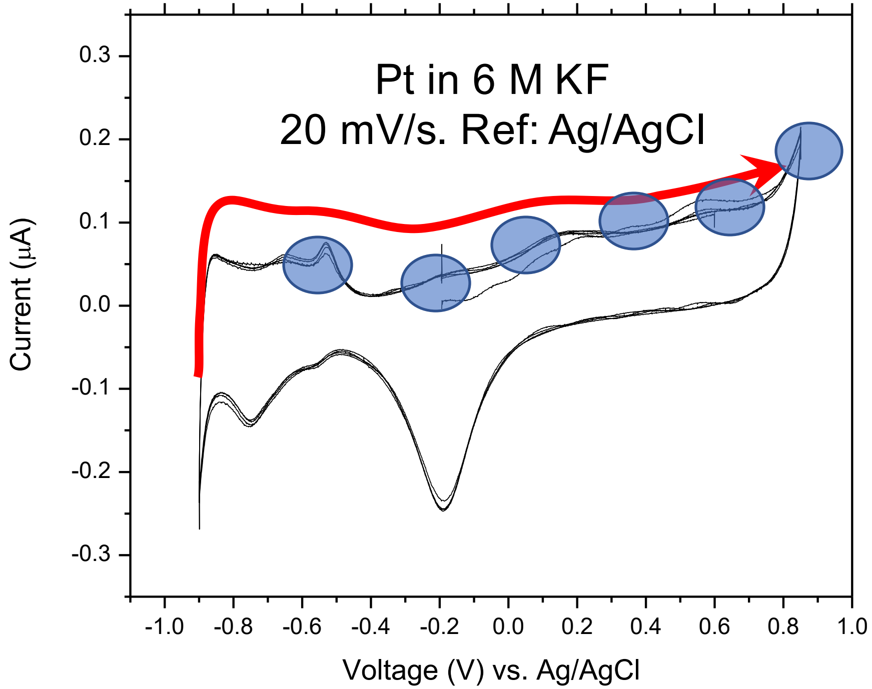


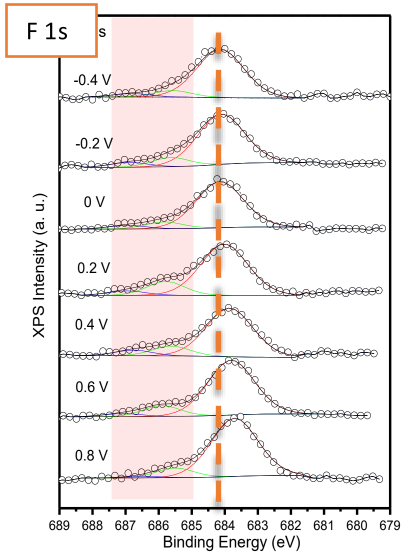
Courtesy of Prof. Zhi Liu (Shanghai Tech.)

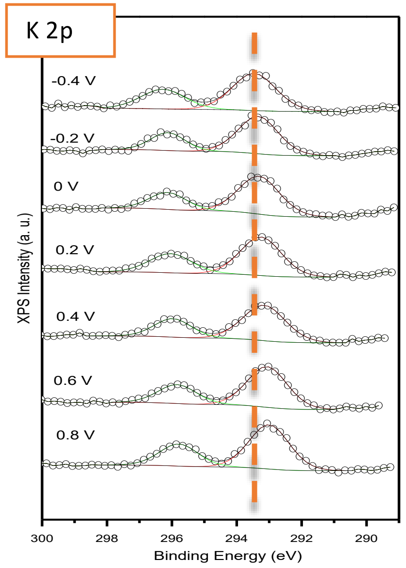
Electrode-electrolyte interface characterization using APXPS under in-situ EC treatment

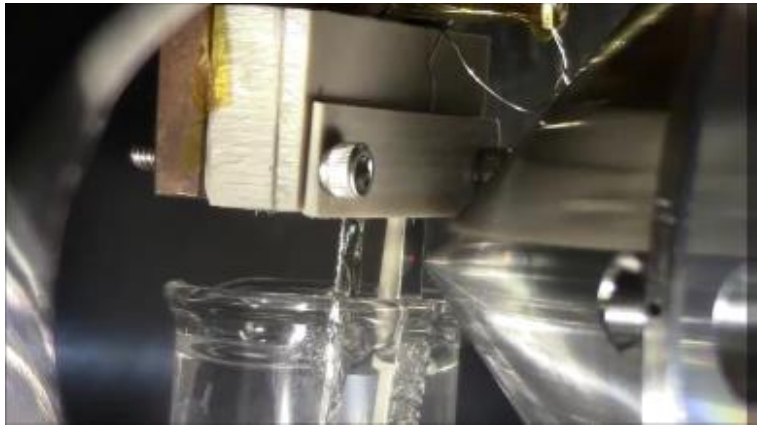








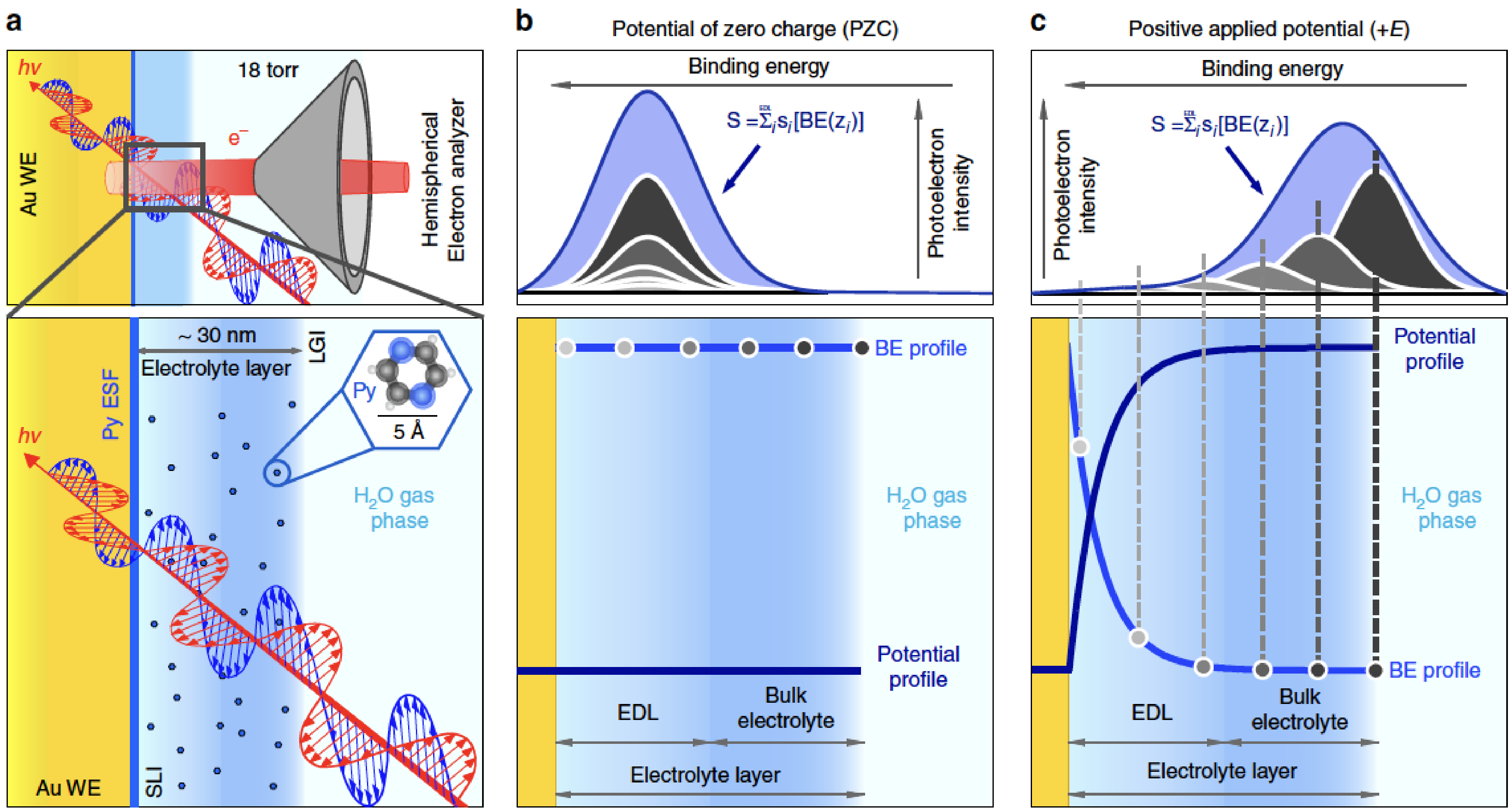




ALS

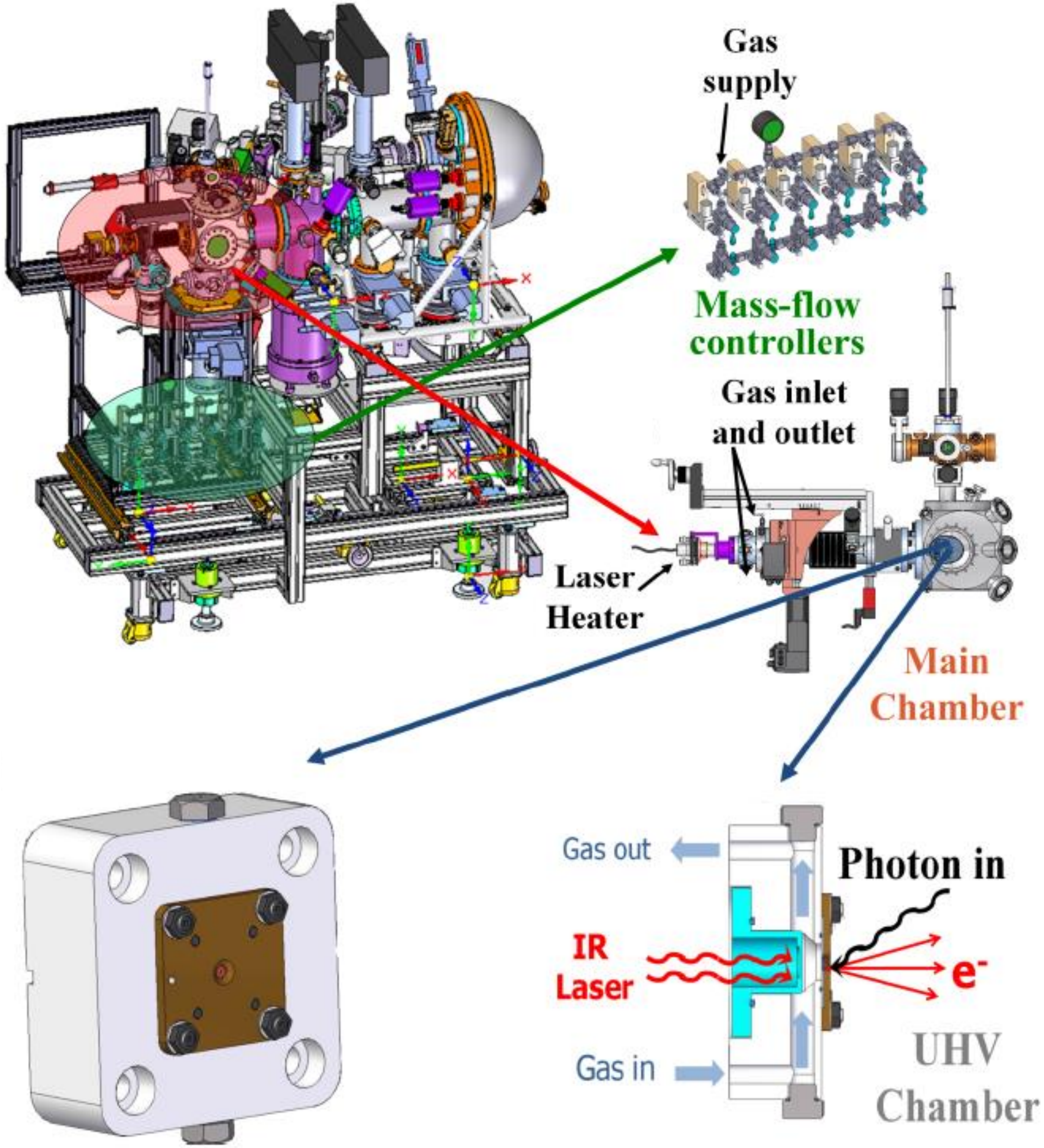
S. Axnanda, E. Crumlin, R. Chang, B. H. Mao, S. Rani, P. Ross, Z. Hussain, Z. Liu. Scientific Report. (2015)

Electrochemistry : Can we observe electrochemical double layer ?

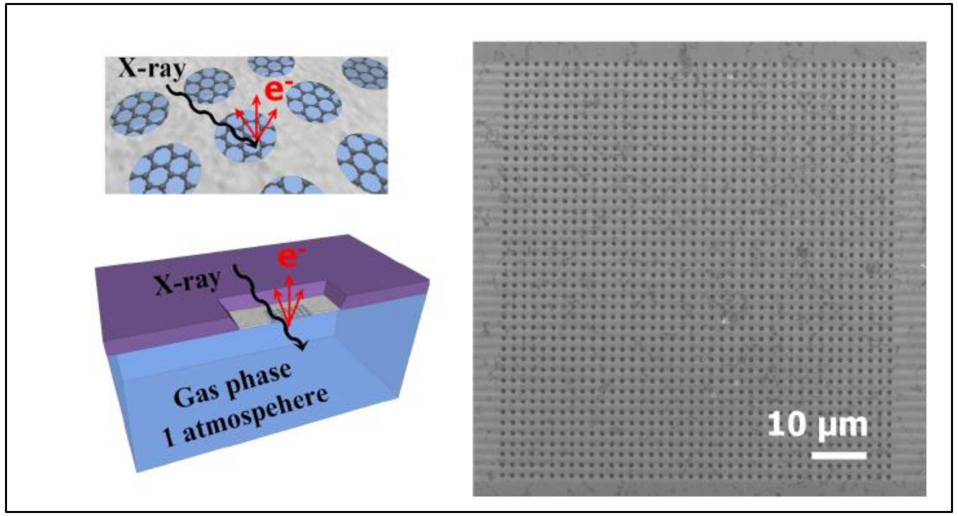


M. Favaro, Z. Liu, E. Crumlin, Nat. Commun. 2016, 7, 12695.

Micro-Cell with AP-XPS



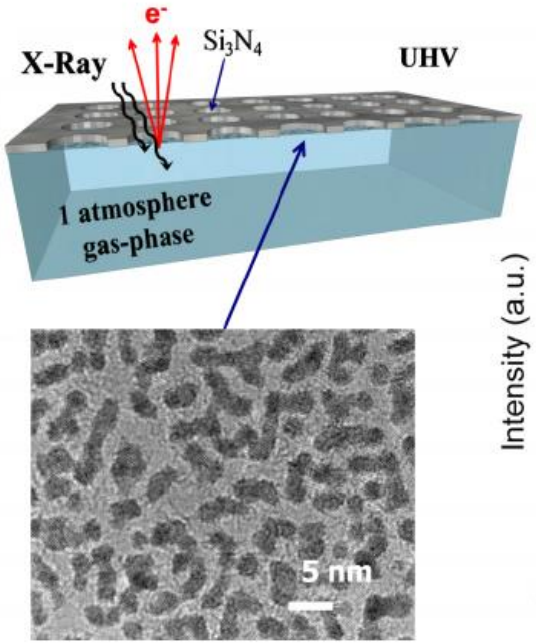
X-ray Absorption Spectroscopy

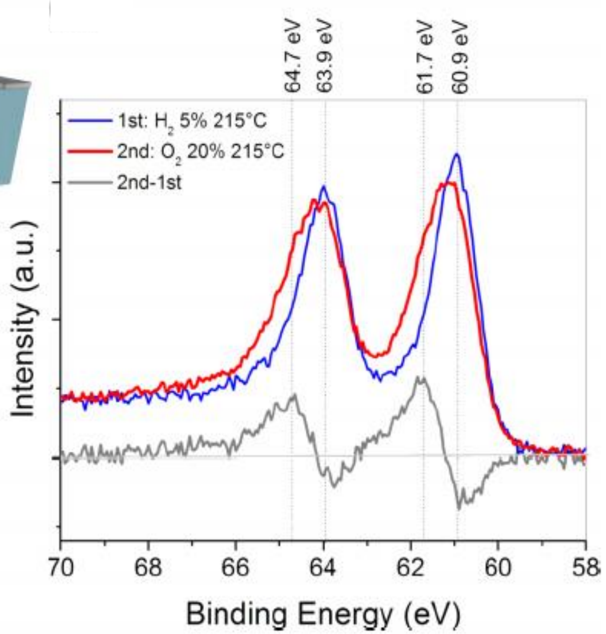


Axel Knop-Gericke
Robert Schlögl
FHI-MPI, BESSY, Helmholtz Germany

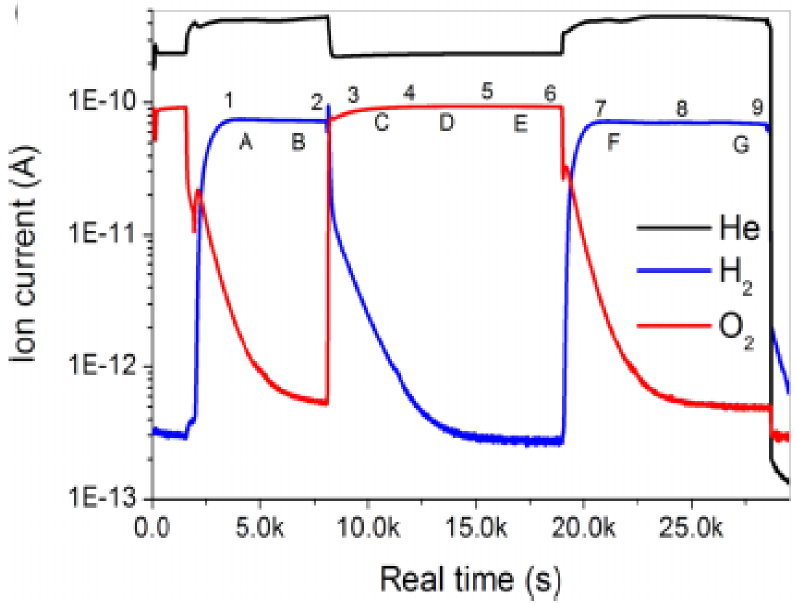
Rev. Sci. Instrum. 87, 053121 (2016)

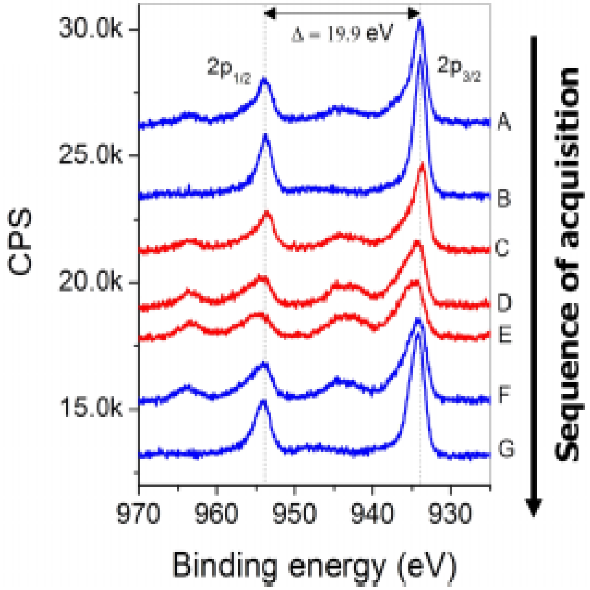
Micro-Cell with AP-XPS

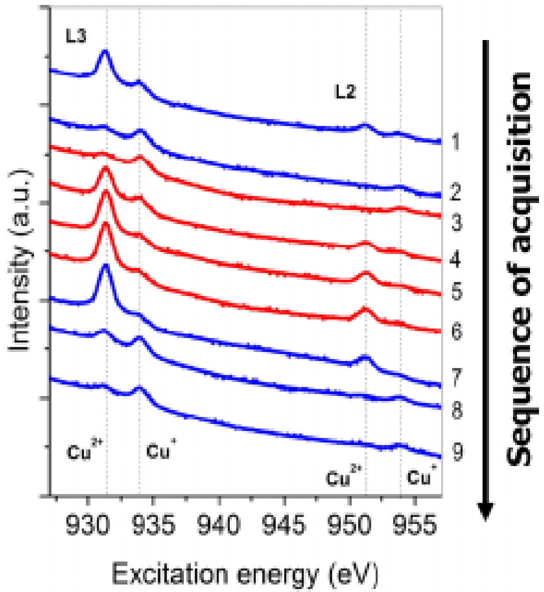




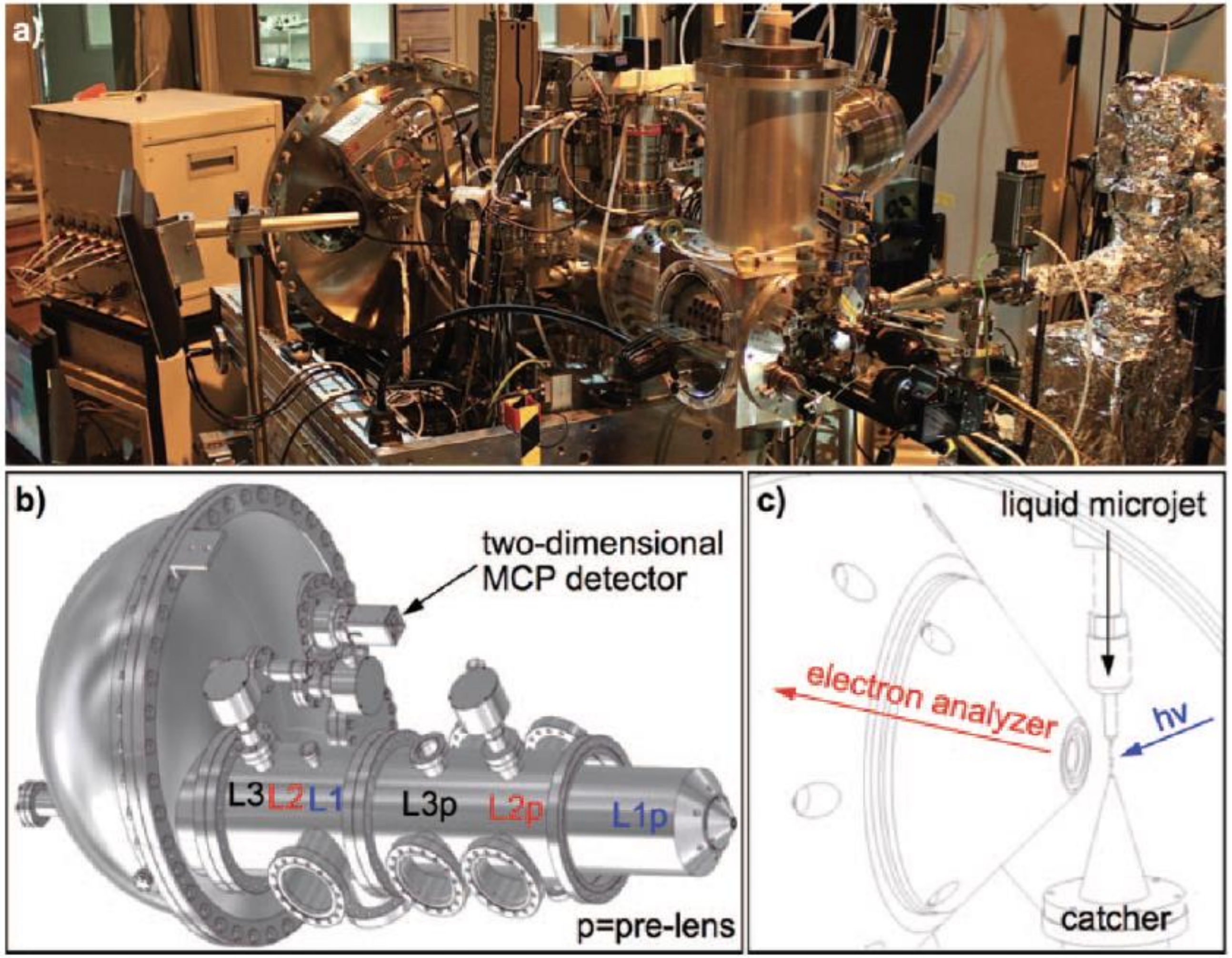
Rev. Sci. Instrum. **87**, 053121 (2016)

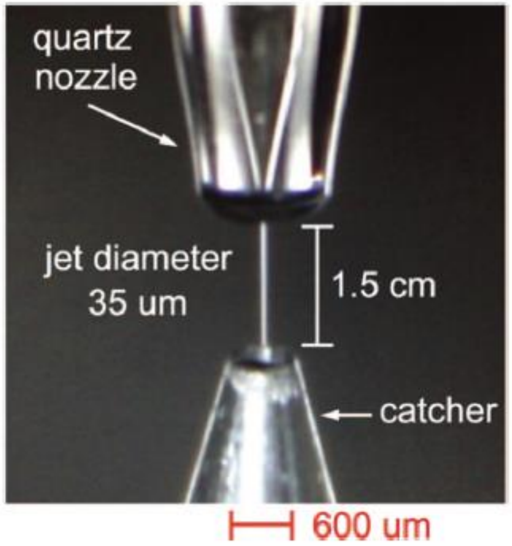






Liquid-Jet with AP-XPS



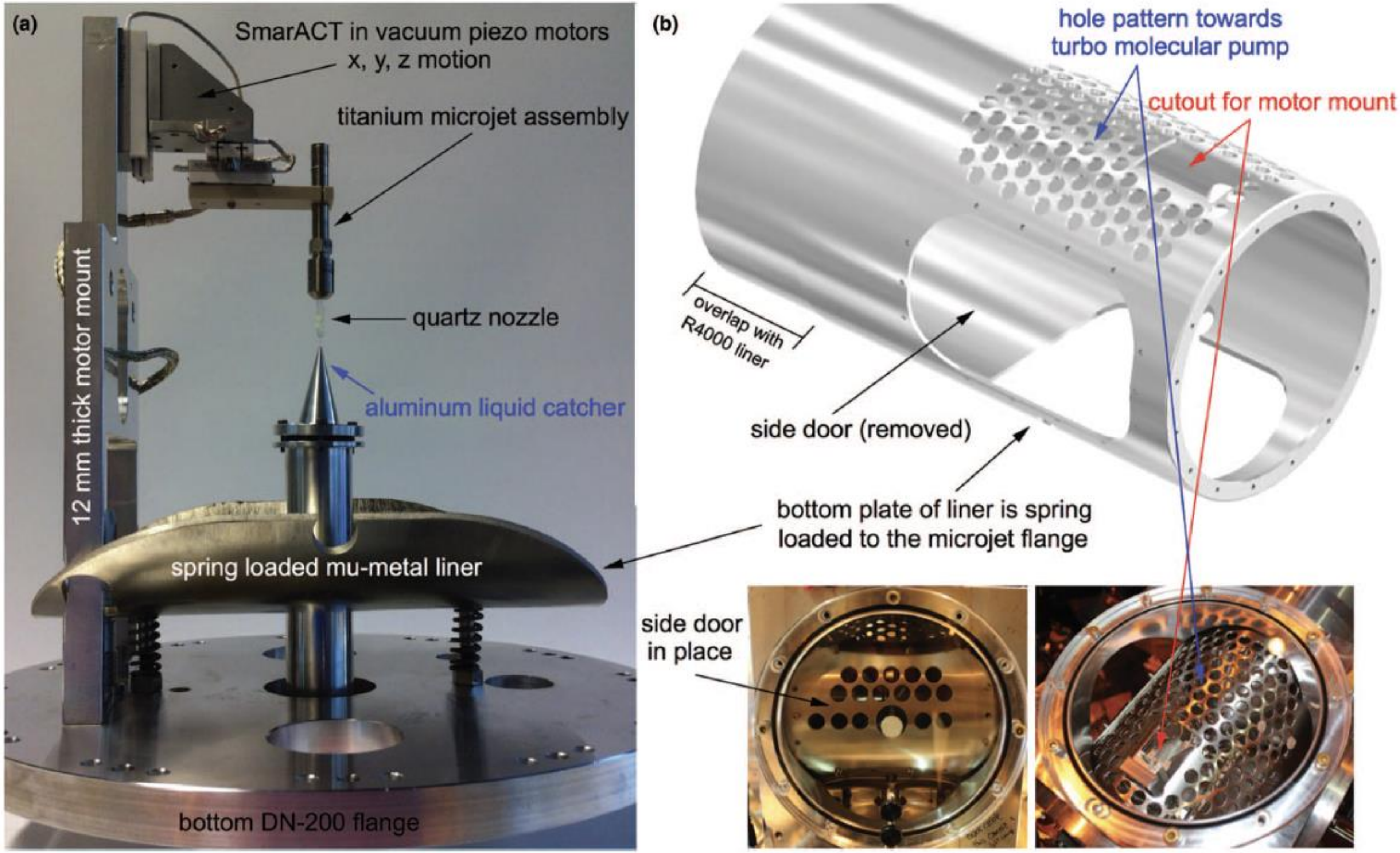


Matthew Brown

Rev. Sci. Instrum. **84**, 073904 (2013)

PSI, Switzerland

Liquid-Jet with AP-XPS



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Challenges of AP-XPS

a. Pressure Gap: What’s really happening at 1 Bar?

b. Liquid/Solid Interface or Liquid phase:
Can we monitor/control the liquid surface at equilibrium ?

c. Time-resolved surface reaction dynamics under reaction condition

Time-Resolved Study with AP-XPS

Time-resolved ambient pressure XPS setup: the simultaneous recording of the kinetic energy and the time stamp (tagging) of every electron relative to the trigger signal of the laser.

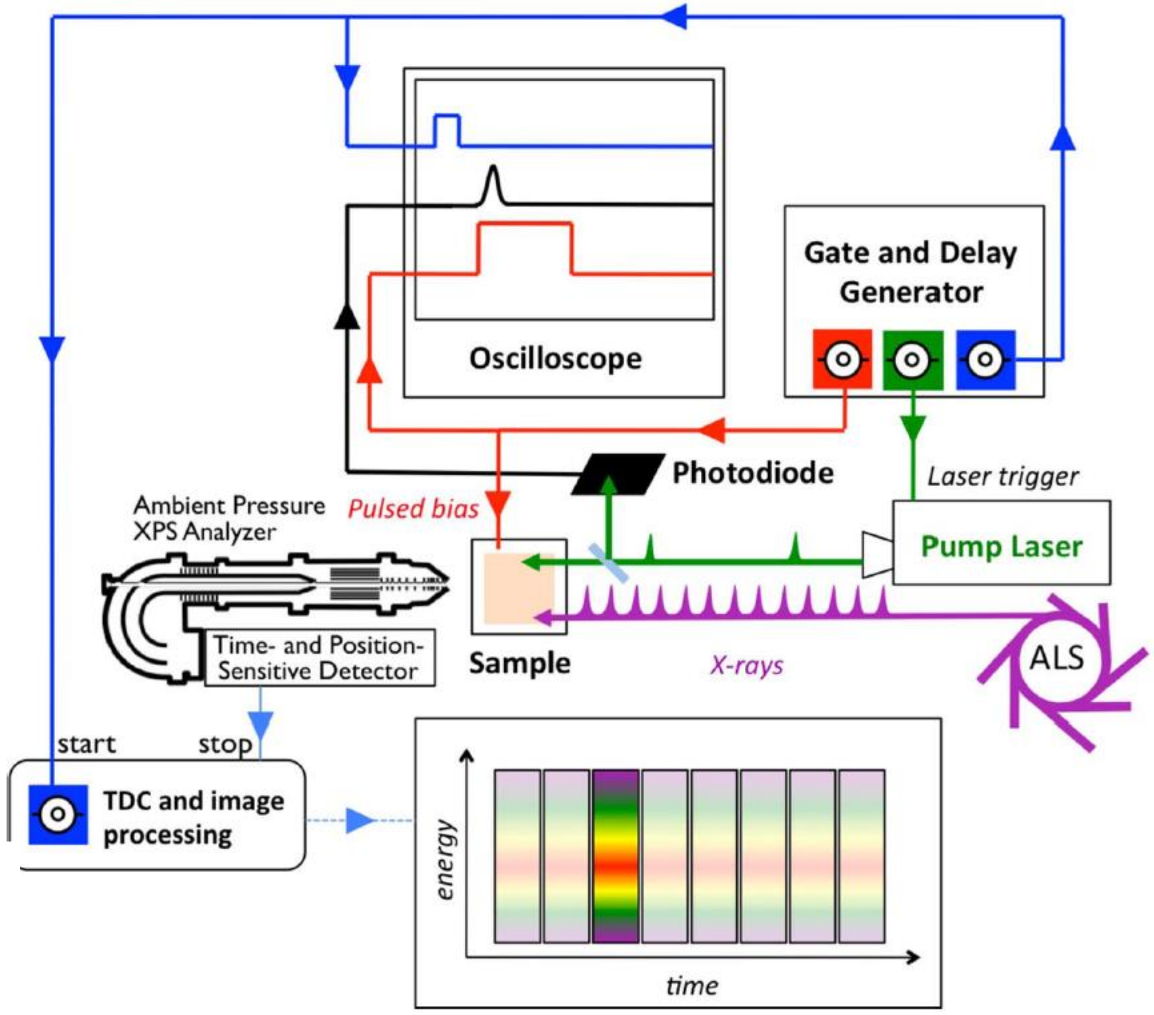
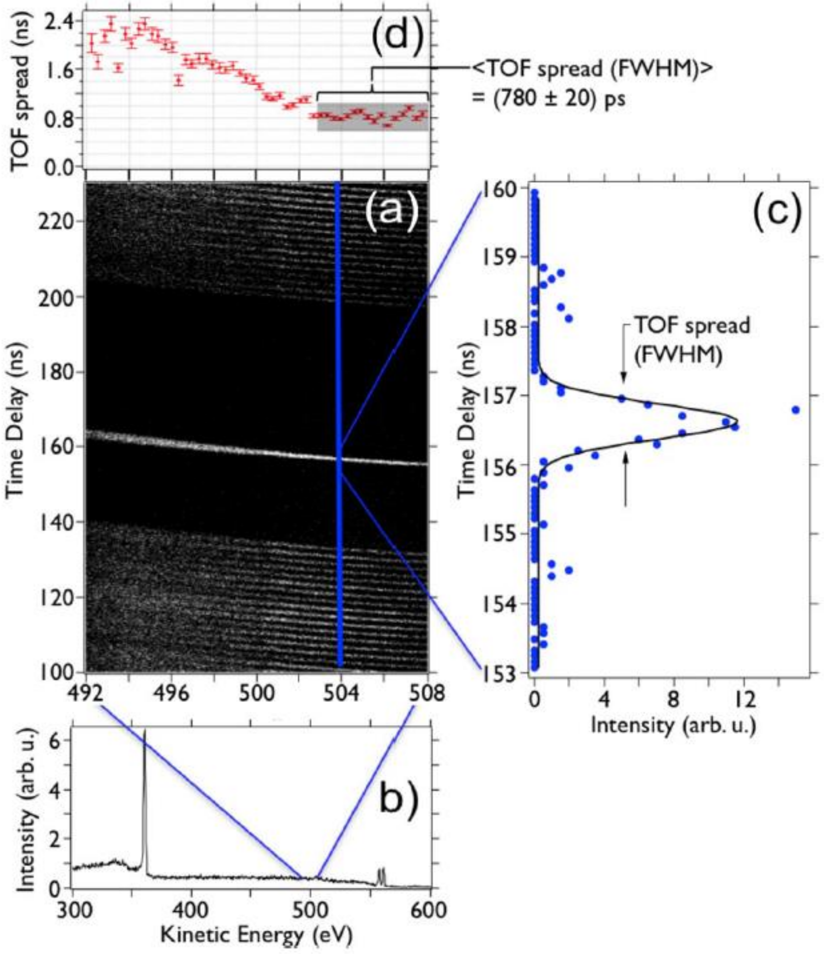


FIG. 1. Timing scheme of the tr-XPS apparatus. See text for details.



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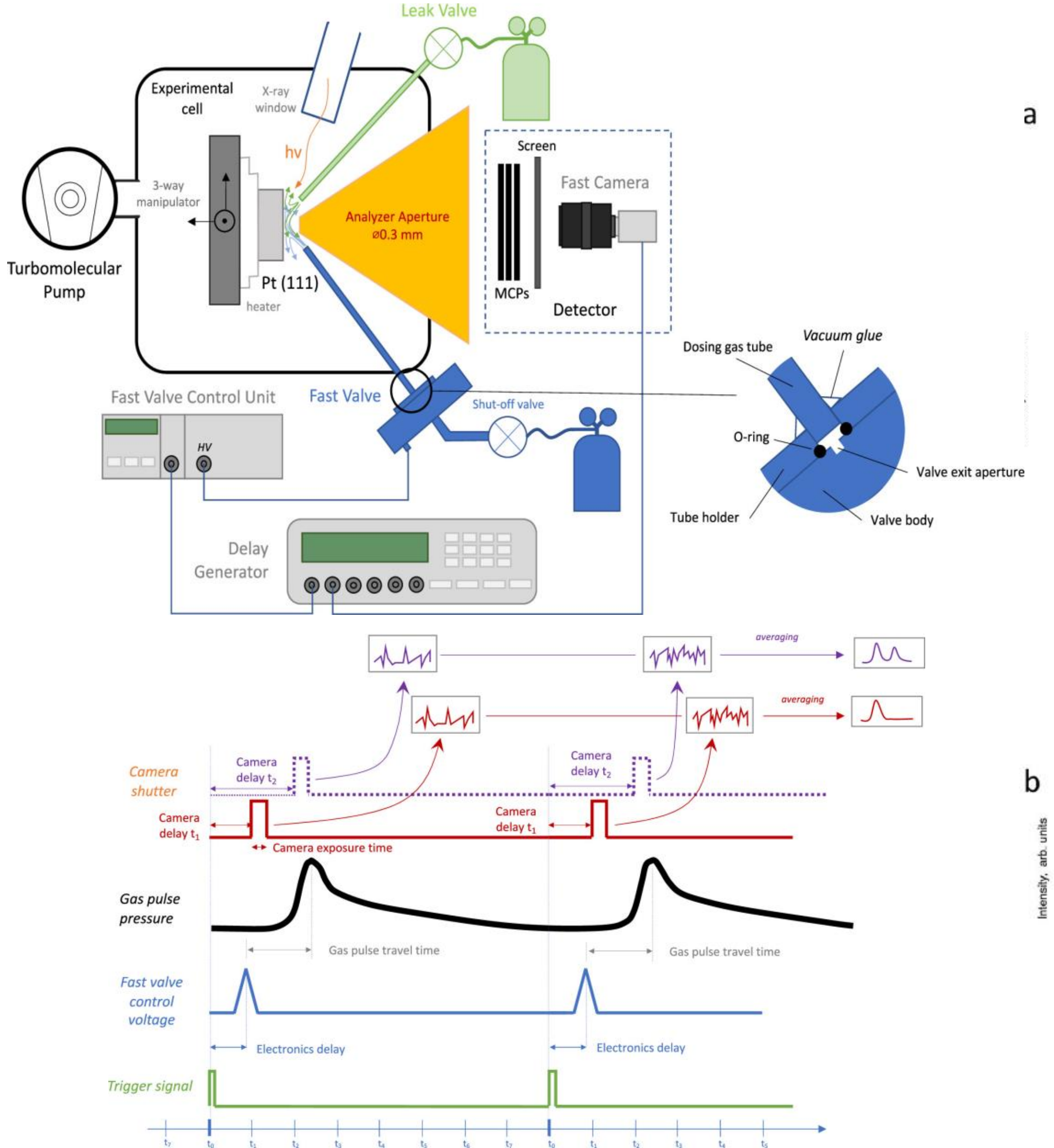
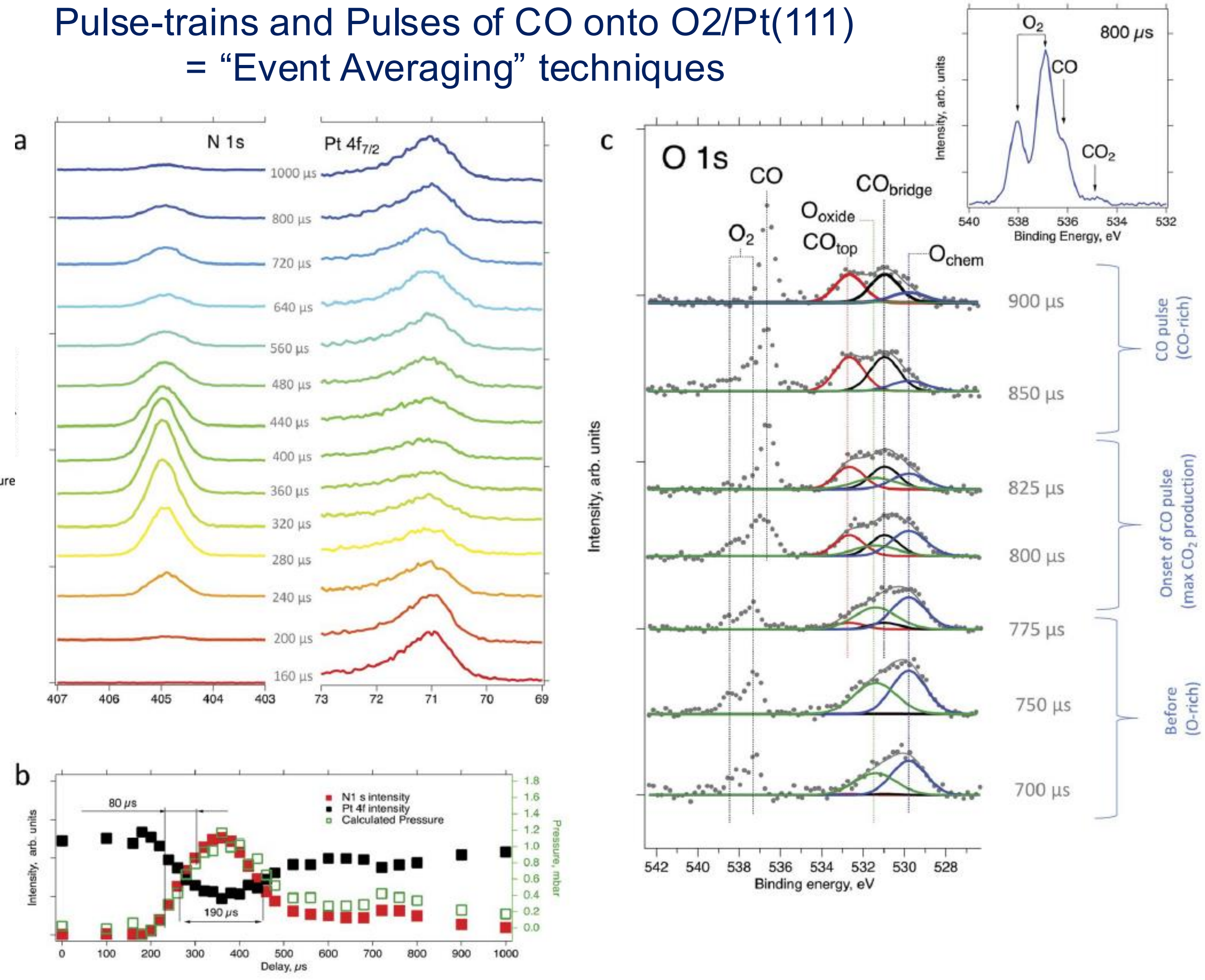
Time-Resolved Study with AP-XPS

Event Average with external source of spectroscopic probing
Time resolution : ~20 micro second



Pulse-trains and Pulses of CO onto O2/Pt(111)
= "Event Averaging" techniques

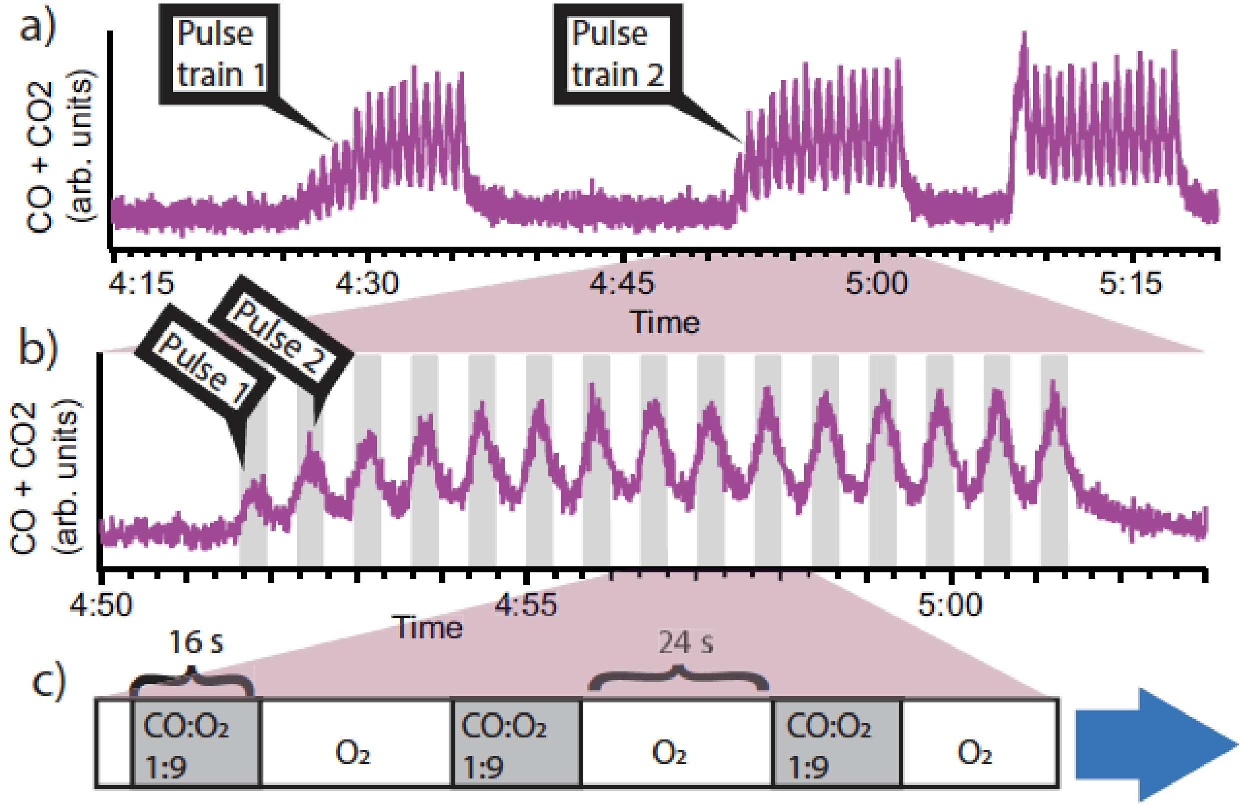


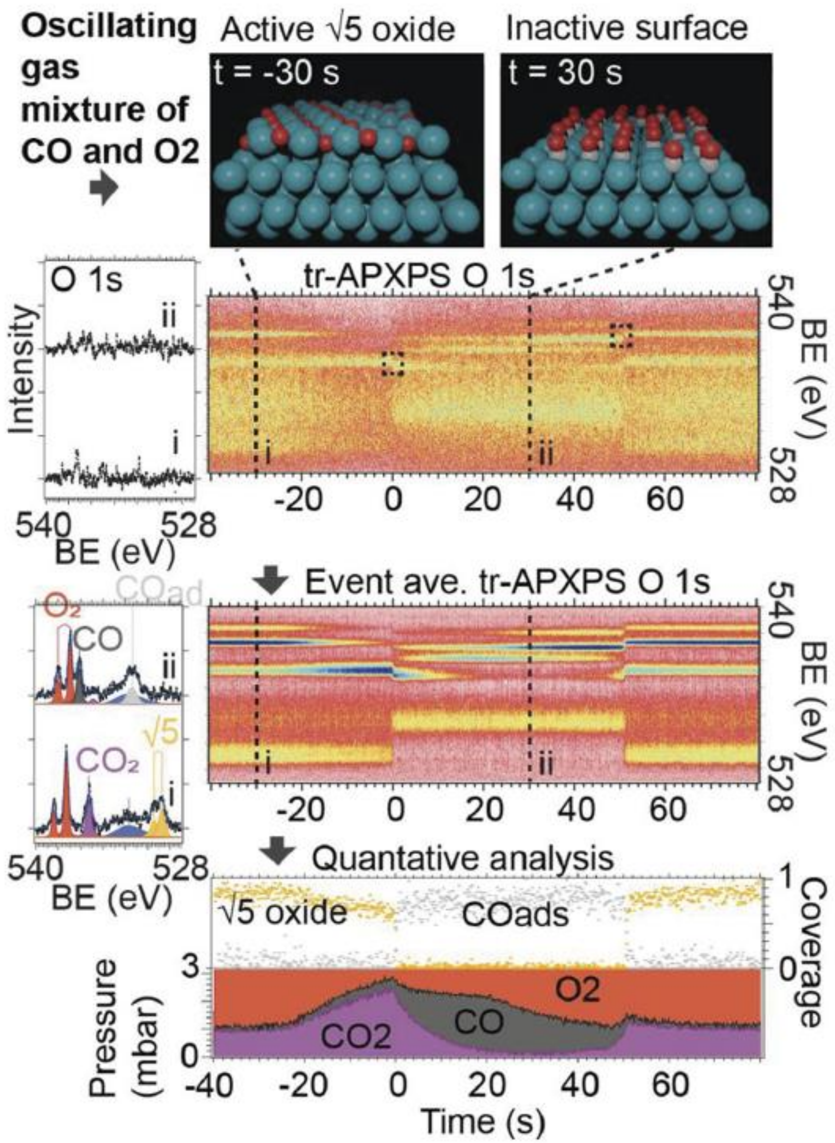
https://doi.org/10.1021/acsami.1c13590
ACS Appl. Mater. Interfaces 2021, 13, 47629–47641

Time-Resolved Study with AP-XPS

Event Average with internal source of spectroscopic probing
Time resolution : ~158 ms

Pulse-trains and Pulses of CO/O2 mixture and O2
= "Event Averaging" techniques





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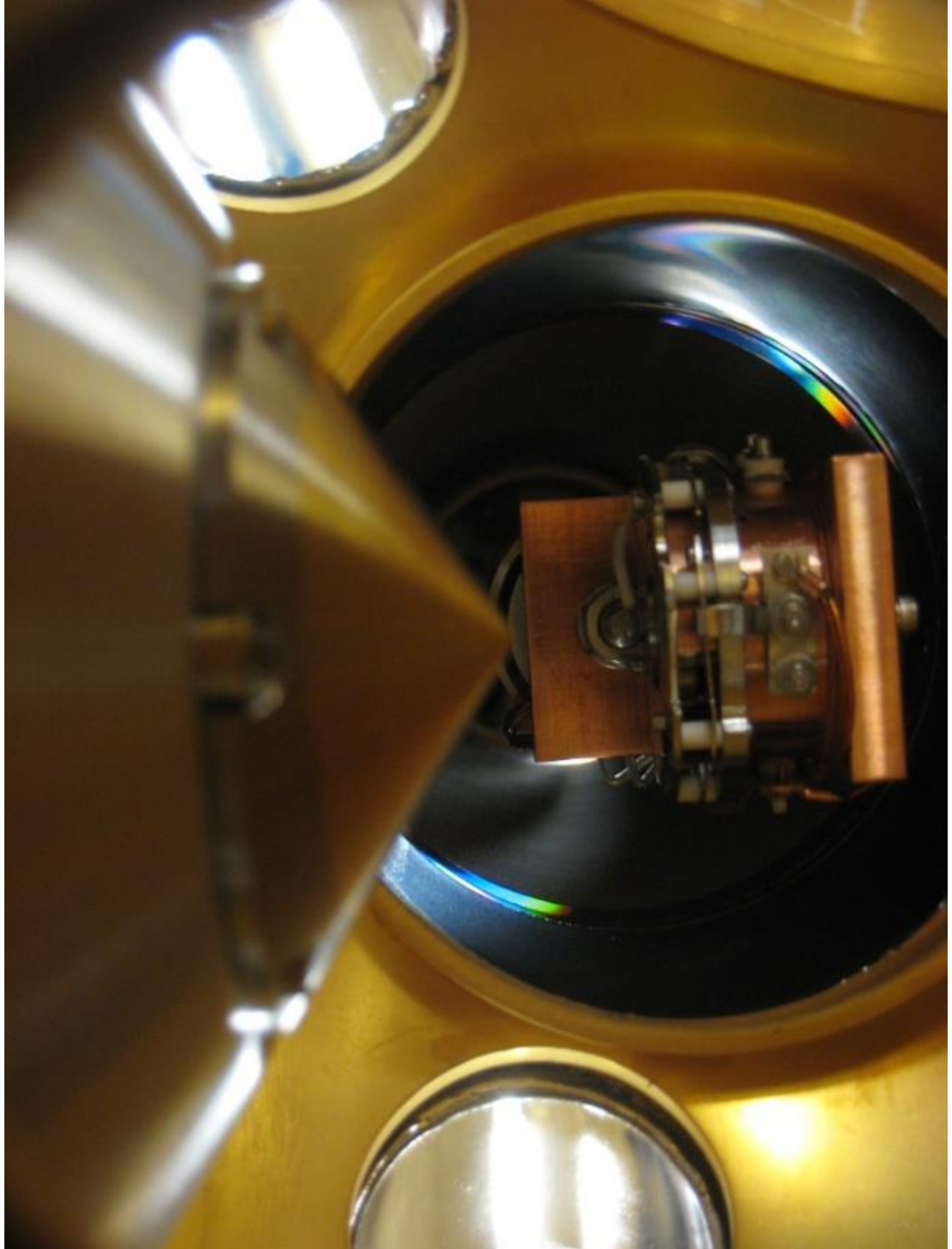

Thank you

Q & A