Operando characterization of materials by X-ray Absorption spectroscopy: Quick-EXAFS and Multivariate Analysis.

Valérie Briois

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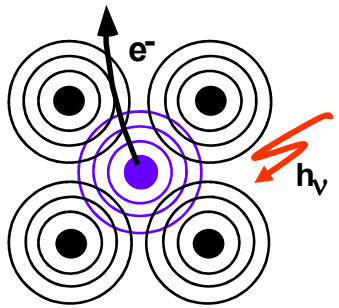
Outline

1) Introduction
2) Time Resolution at the ROCK beamline
3) How to handle a so huge amount of data
4) Applications in heterogeneous Catalysis
5) Conclusion

X –Ray Absorption Spectroscopy

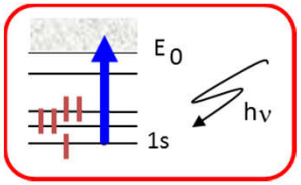
$\mu x = \mathrm{Ln}\, I_0 / I$



XANES

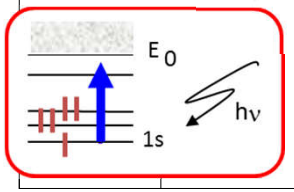
hυ

Nano-CoO at the Co K edge



Edge

EXAFS

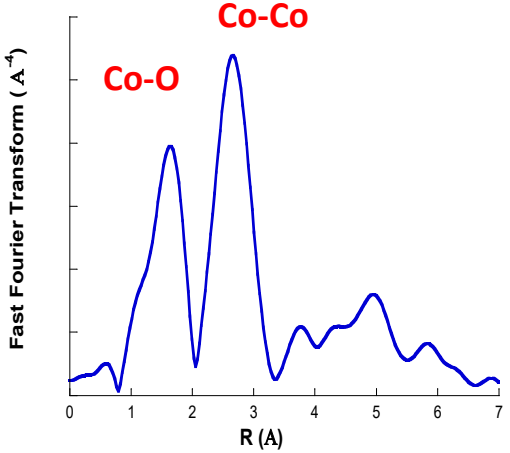


Log (I_0/I)

Photon Energy (eV)

7600 7700 7800 7900 8000 8100 8200 8300 8400

XAFS oscillations = Interferences between Outgoing wave and Backscattered waves

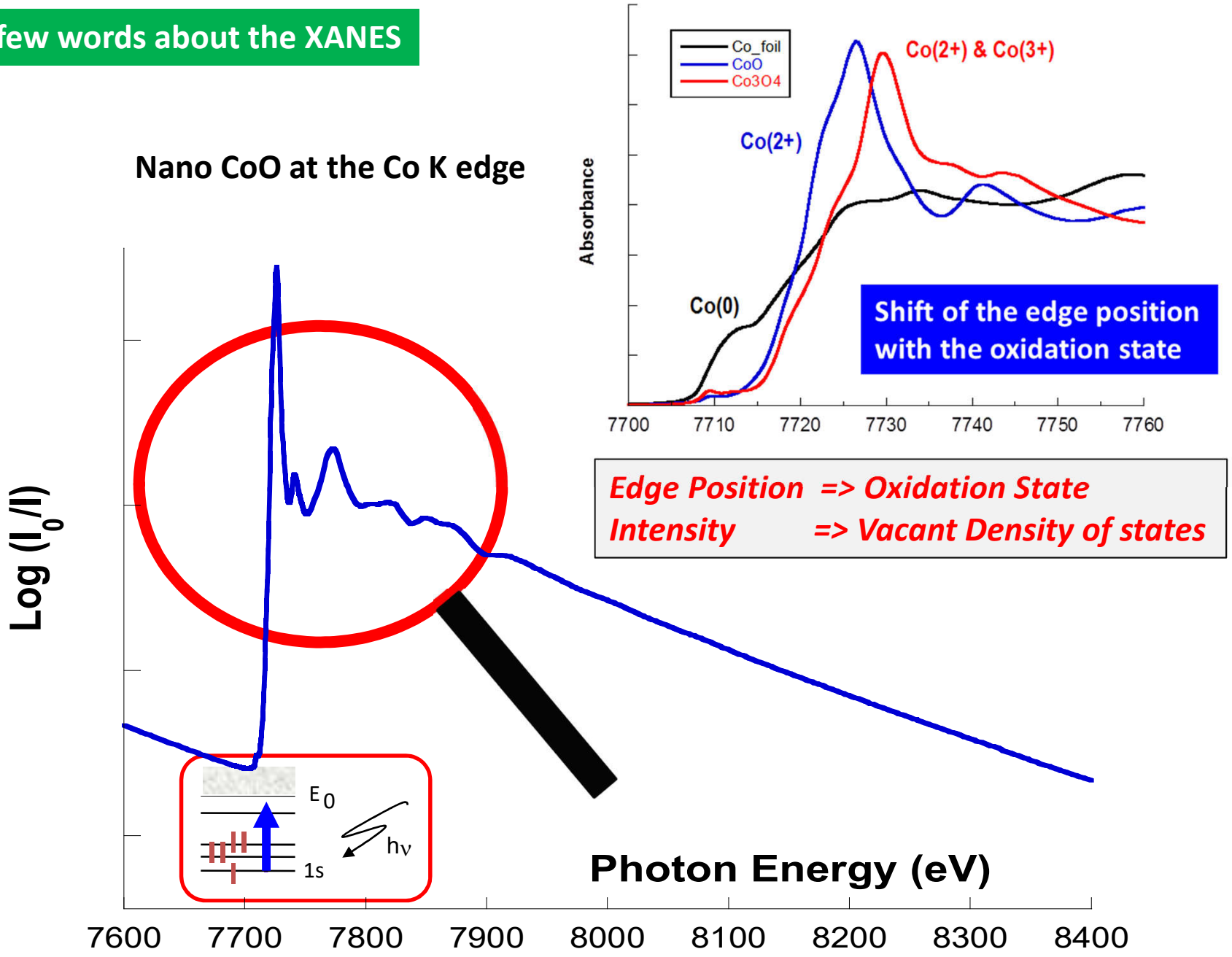


Fourier Transform

XANES : X-ray Absorption Near Edge Structure

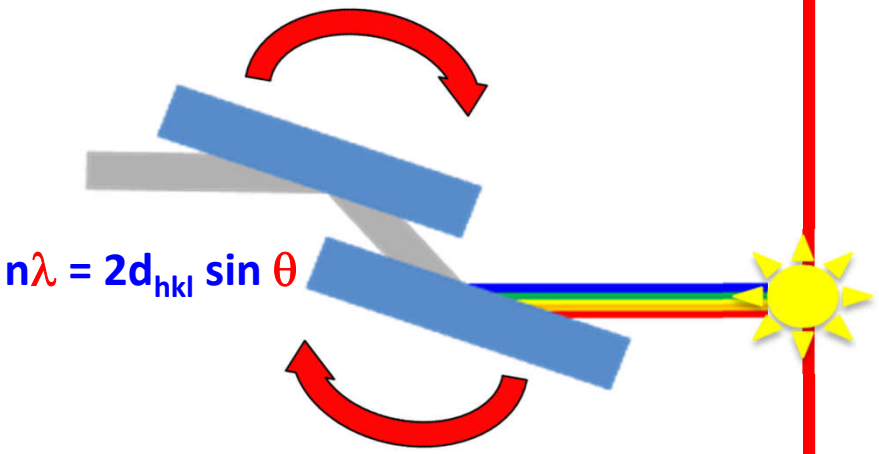
EXAFS: Extended X-ray Absorption Fine Structures

A few words about the XANES



Getting faster in the collection of X ray Absorption Data

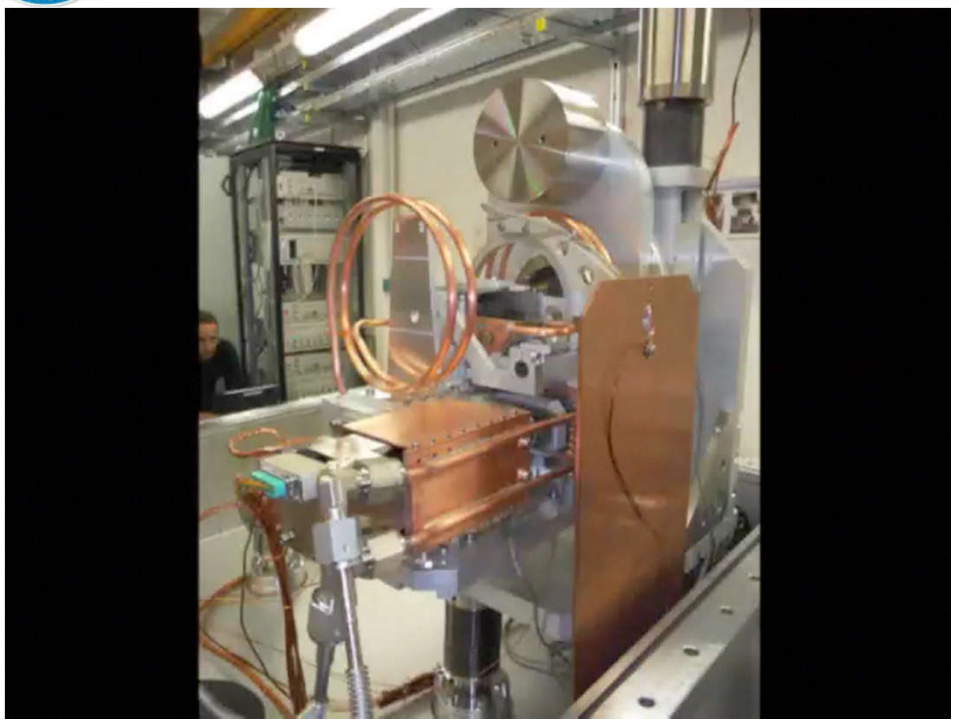
Two crystal scanning
Monochromateur : Quick-EXAFS



Fast s to ms
(limited by the speed of continuous monochromator movement attainable)

Variable Beam size

Large energy range
Transmission to Fluorescence



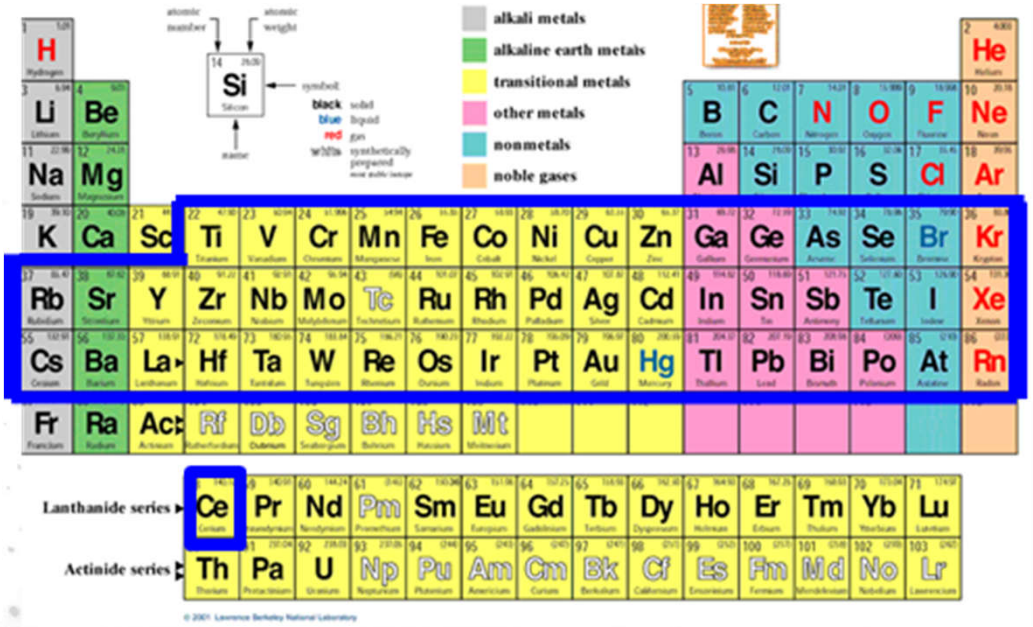
Oscillations frequency : 0.1 Hz to 30 Hz
for one spectrum => 16 ms to 5s

Oscillation amplitude range: 0.3 to 3.9°
- at least 1000 eV spectra (EXAFS)

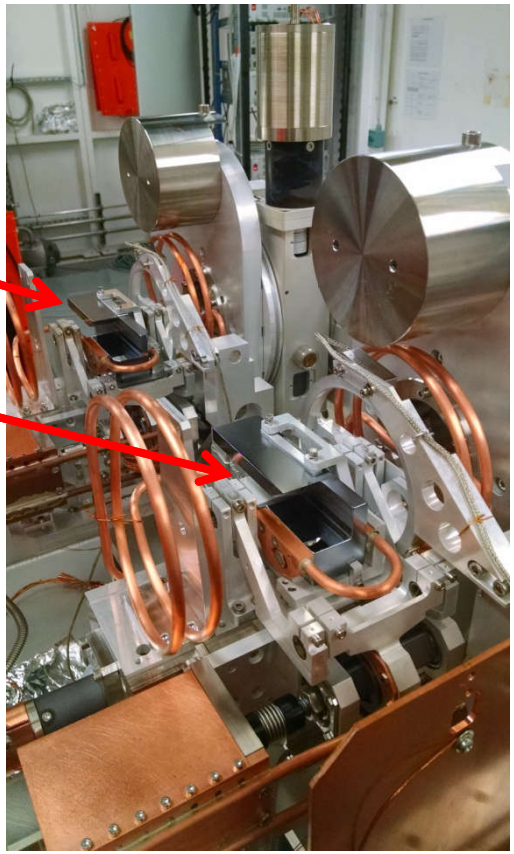
Briois et al., J. Phys.: Conf. Ser. 712 (2016) 012149

Characteristics of the ROCK Quick-EXAFS Beamline

Energy Range: 4 – 42 keV
Flux @ 8.5 keV: Si(111) : 1.7 10^{12} ph/s
Flux @ 20 keV: Si(220) : 3 10^{11} ph/s
Time resolution in the ms range



2 monochromators



4-42 keV energy range

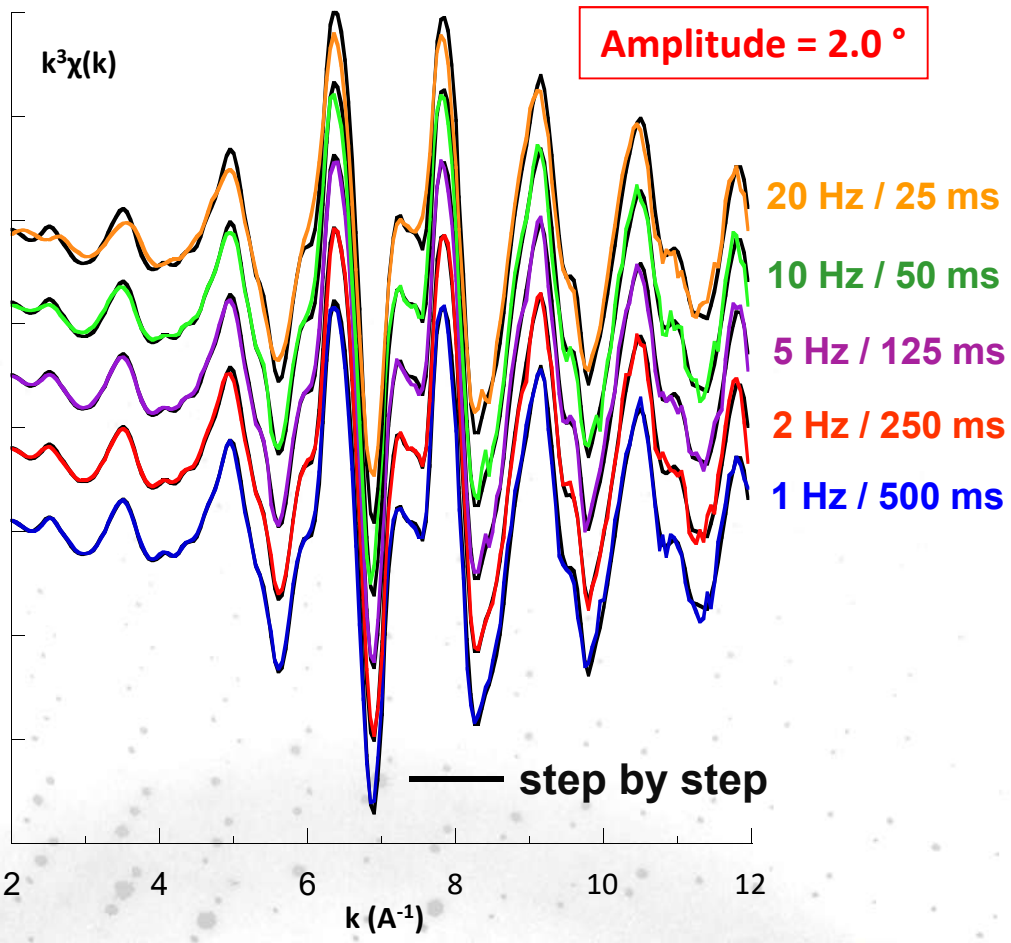
52 elements can be measured at the ROCK beamline…

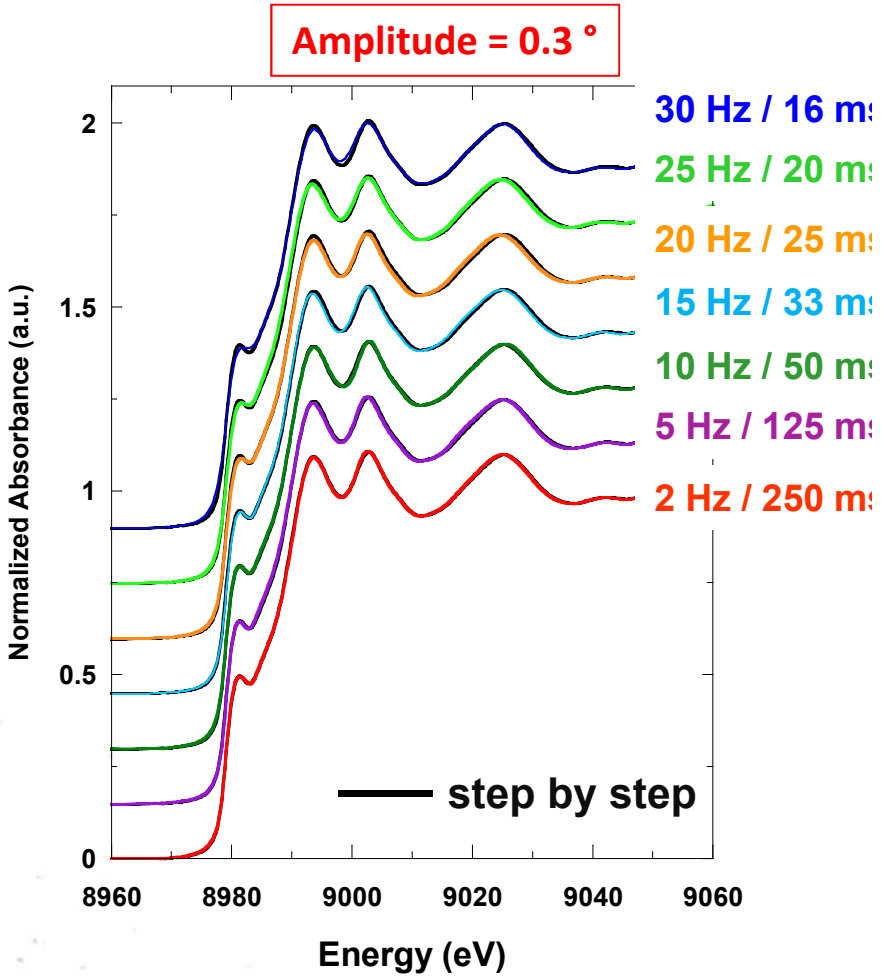
Briois et al., J. Phys.: Conf. Ser. 712 (2016) 012149

Time resolution

example of a Cu foil

Si(111) – average over 5 spectra

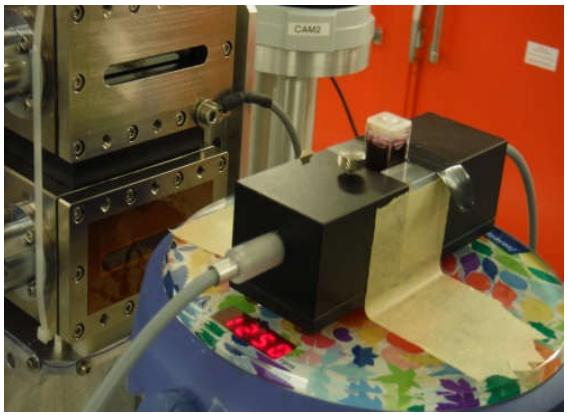




Briois et al., J. Phys.: Conf. Ser. 712 (2016) 012149

Quick-EXAFS : a lot of XAS data to analyze

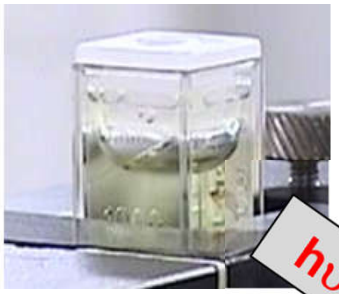
Radiolytic Preparation of Gold Nanoparticles

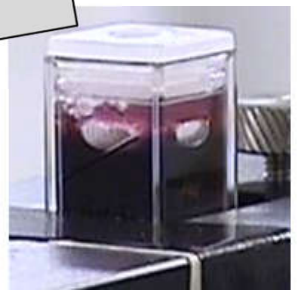


Precursors Solutions :

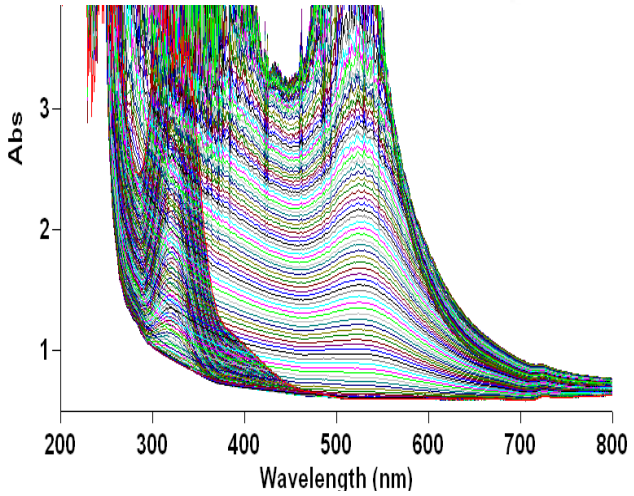
$HAuCl_4$ prepared with RT Imidazolium IL $C_{16}H_{31}N_2X$ with X= Cl, Br

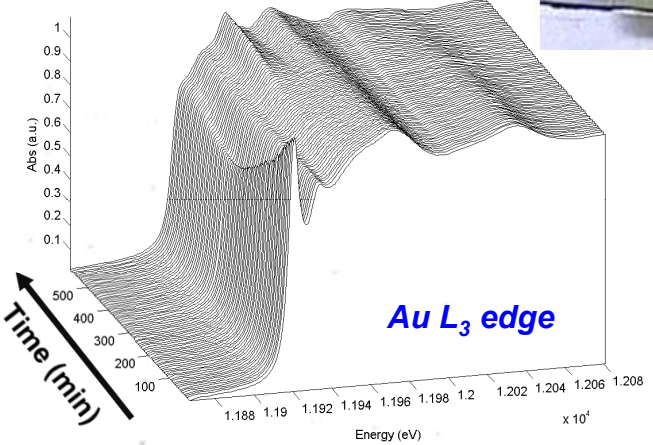
Au(III) solution





Au(0) solution



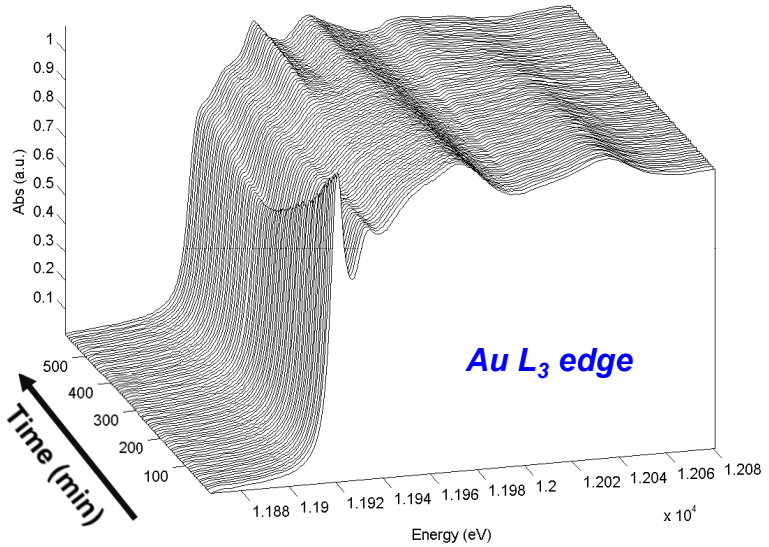


Monitoring by UV-Vis and Quick-XAS of Gold Formation upon X-rays irradiation

F. Meneau (LNLS, Brazil), A. F. Suzana (IQ_UNESP, LNLS, SOLEIL)
S. Blanchandin, V. Briois (SOLEIL)

Quick-EXAFS : a lot of XAS data to analyze

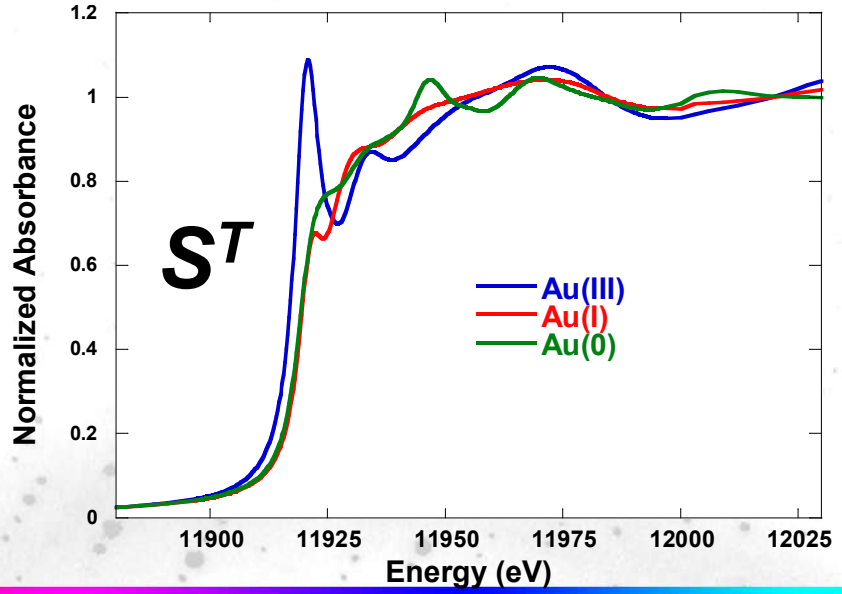
Multivariate Curve Resolution
Alternating Least Squares Fitting

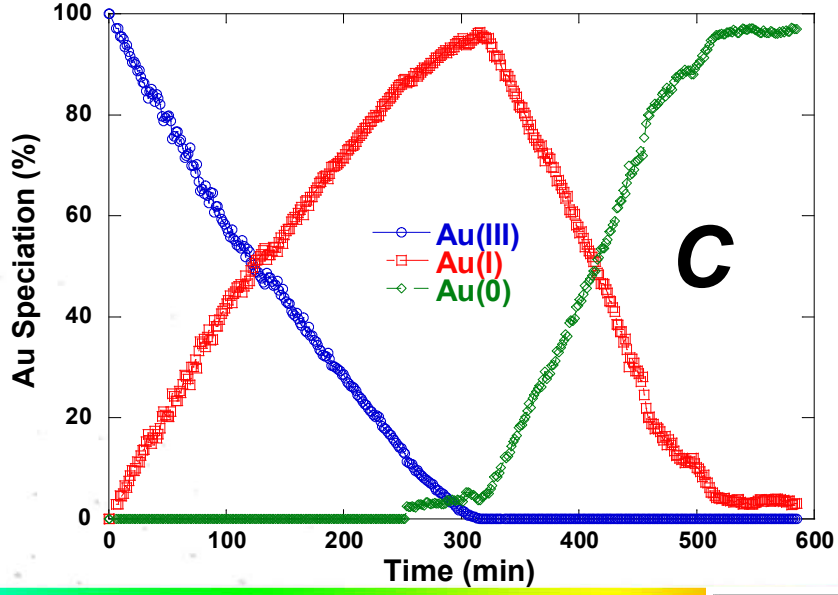


Bilinear Decomposition is fully verified for XAS
(Beer-Lambert Law Abs = Σ C Absi)

$$D = CS^T + E$$

MCR-ALS





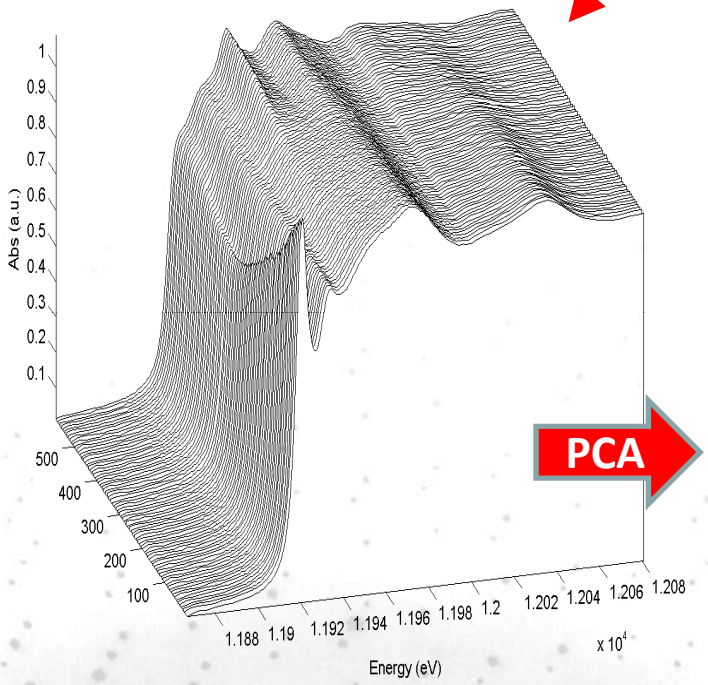
Multivariate Curve Resolution with Alternating Least Squares Fitting

MCR-ALS : How does it work ?

$$D = CS^T + E$$

Initial estimate of S^T

i.e. Guess of 3 spectra



PCA

Estimation of number of Components e.g. 3 components

ALS minimization

$$\min ||D - CS^T||^2$$

Determination of concentration matrix C which is used as a new guess for the minimization

Iteration is stopped when convergence is achieved.

Multivariate Curve Resolution with Alternating Least Squares Fitting

CONSTRAINTS to help CONVERGENCE of ALS fitting

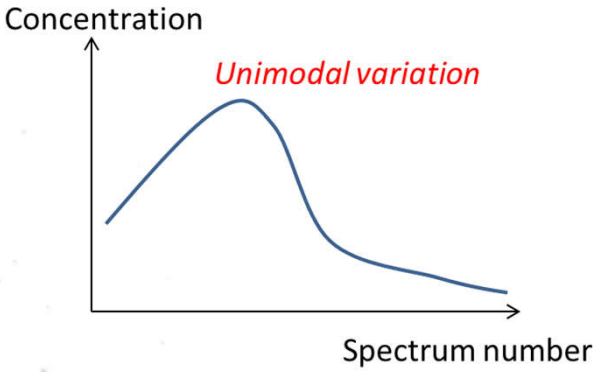
In the case of XANES, several constraints can be always applied:

- **Non-negativity of C and of spectra S**

- **Closure relation for the concentration of the n components:**

$$\sum_{i=1}^{n} C_i = 100\ \%$$

Additionnal ones can be the unimodality of concentration matrix (a single maximum for the profiles of concentration of each speies)

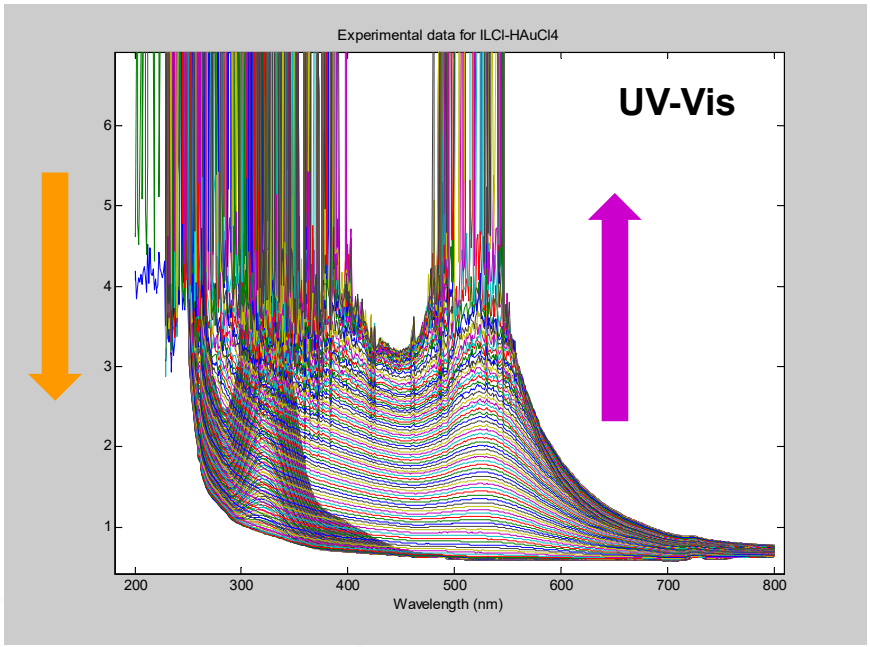


Matlab toolbox
R. Tauler et al. Chemom. Intell.Lab. Syst. (2015) 140, 1

Applications for XAS:
Catalysis Today (2014) 229, 114-122
Compte Rendus Chimie (2016) 19, 1337-1351
J. Phys. Chem. C (2017) 121, 18544-18556
J. Mater. Chem. A (2017) 5, 9998-10009

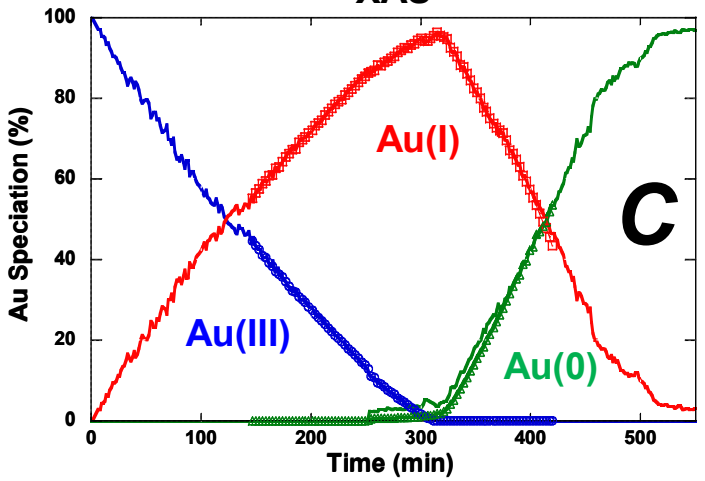
SOLEIL SYNCHROTRON

Radiolytic Preparation of Gold Nanoparticles from $HAuCl_4$ -ILCl

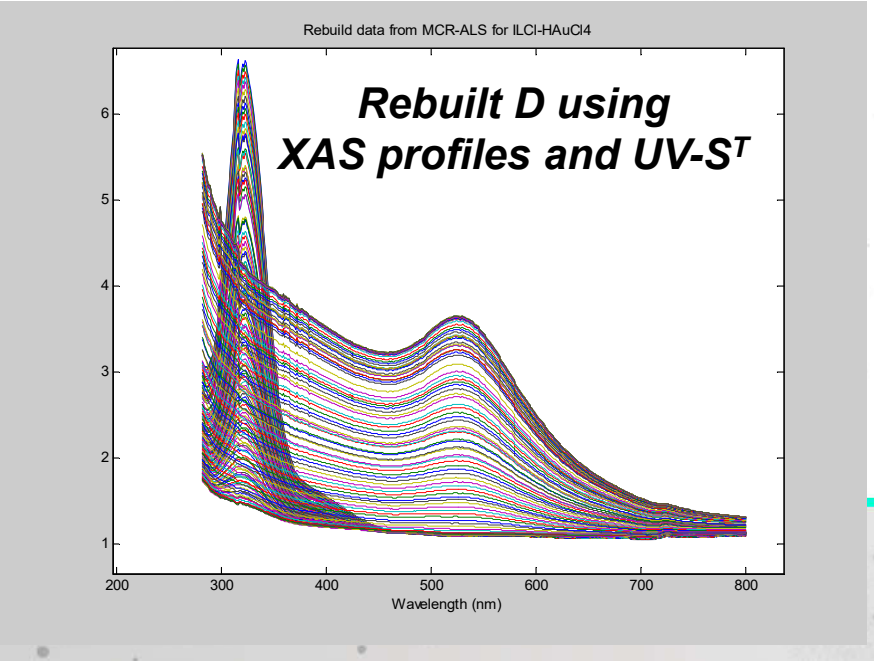


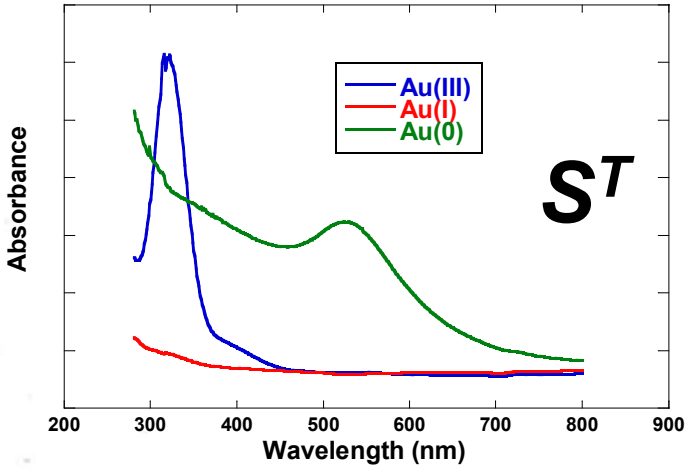
o UV-Vis

—XAS



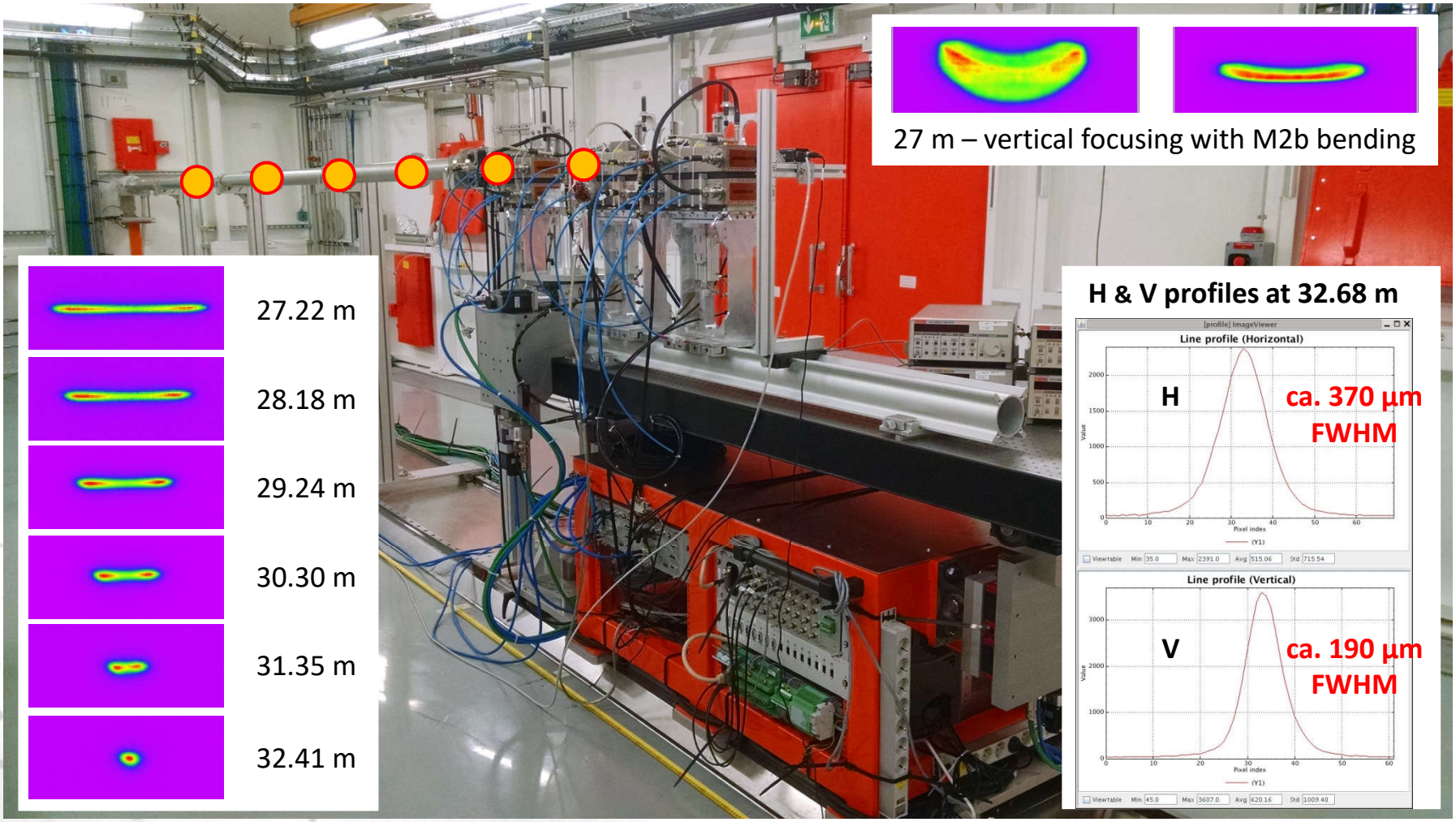
$$D = CS^T + E$$





Versatile beam size

… depending on the position along the X-ray beam and on the M2b curvature



27 m – vertical focusing with M2b bending

27.22 m

28.18 m

29.24 m

30.30 m

31.35 m

32.41 m

H & V profiles at 32.68 m

Briois et al., J. Phys.: Conf. Ser. 712 (2016) 012149

Spectroscopie d'Absorption X pour l'étude Operando de catalyseurs

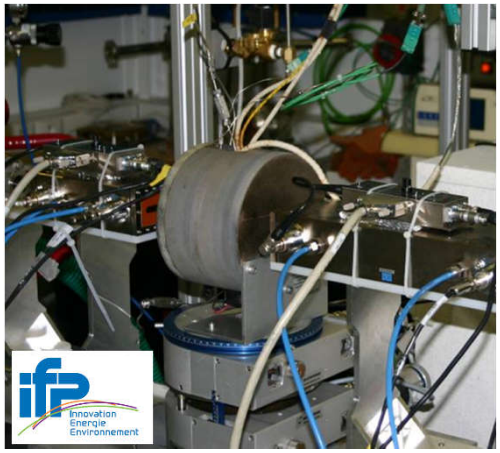
OPERANDO studies in Heterogeneous Catalysis

Catalytic Cells
Gas Distribution
Products analysis
Combination with other Techniques

Dedicated sample environments for heterogeneous catalysis

Lytle-type cells *(Lytle et al., J. Chem. Phys. 70 (1979) 4849-4855)*

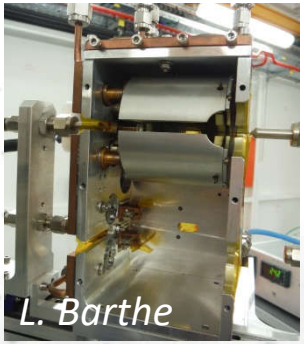
1 bar, RT – 600°C



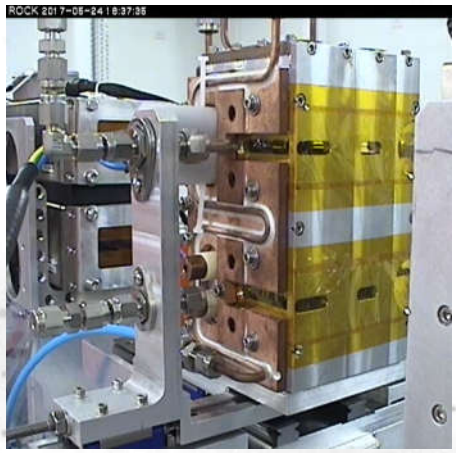
20 bar, RT – 600°C

La Fontaine et al., Catal. Today 205 (2013) 148-158

Capillary cells



3 bar – RT – 1000°C



30 bar, RT – 400°C

Gas delivery system and analysis

- *6 Mass Flow Controllers*
- *1-200 amu. MS (Cirrus, MKS)*

- *Raman spectrometer*
- *Raman gas probe (532 nm laser, 175-4350 cm^{-1})*

Cobalt-based supported catalysts for Ethanol Steam Reforming Reaction

Passos A. R., La Fontaine C., Martins L, Pulcinelli S. H., Santilli C. V., Briois V.

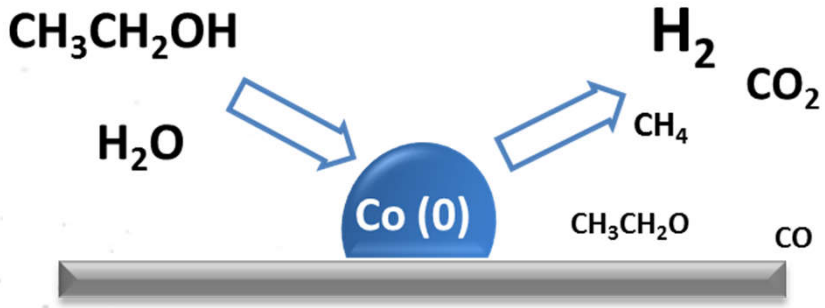
$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2$$

Zero-emission hydrogen-powered train built by Alstom in France

Catalyst: Noble metals: Pd, Pt, Ru, Rh Non-noble metals: Co, Ni

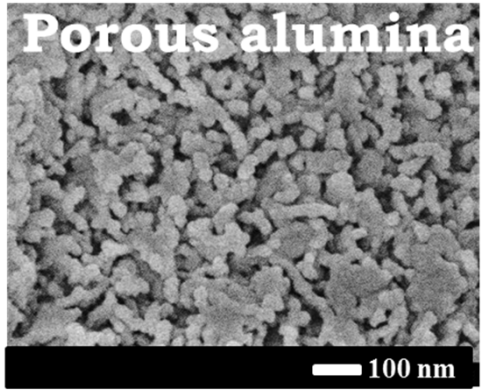
Cobalt has a high activity for the cleavage of C-H and C-C bonds

Catalyst Life → Activation, Reaction, Deactivation, Regeneration

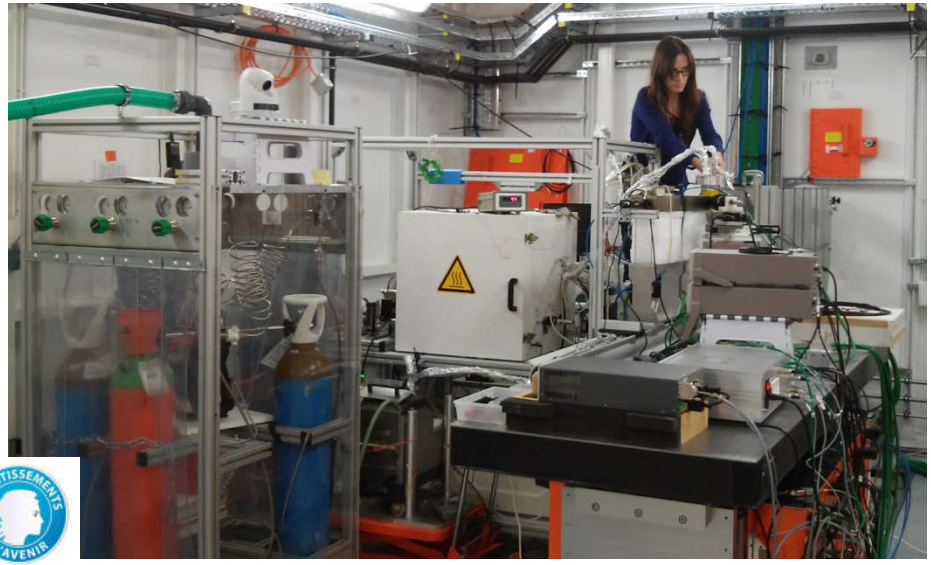


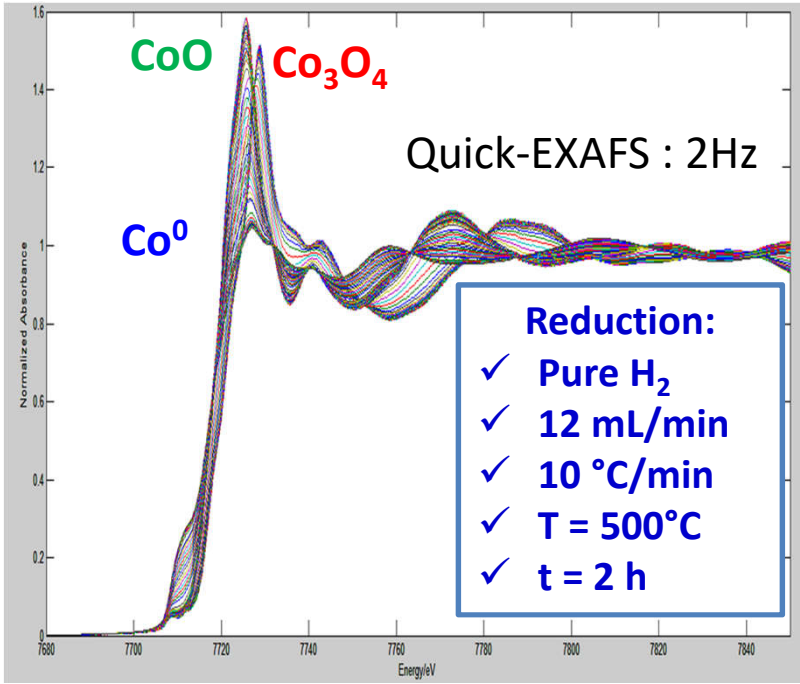
Cobalt-based supported catalysts for Ethanol Steam Reforming Reaction

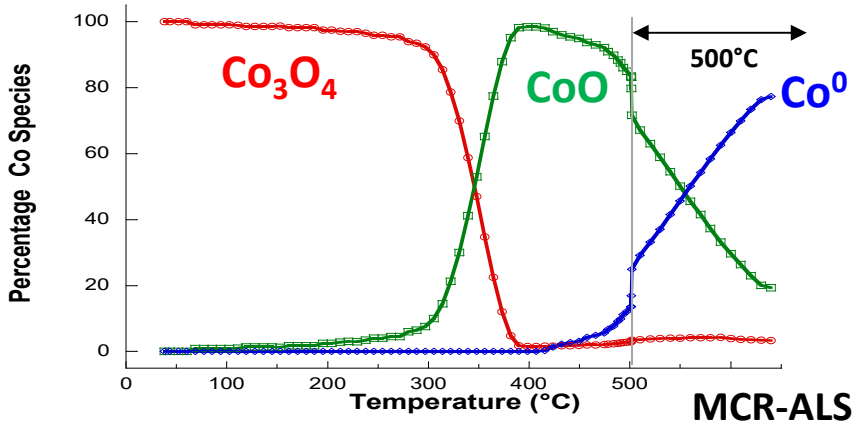
1/ Activation of Co_3O_4 supported on Porous Alumina



Formation of the active Co(0) supported nanoparticles

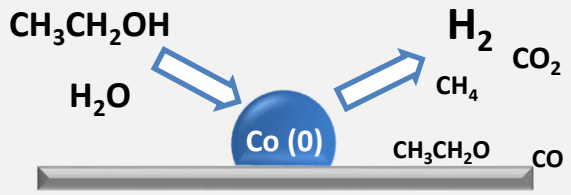






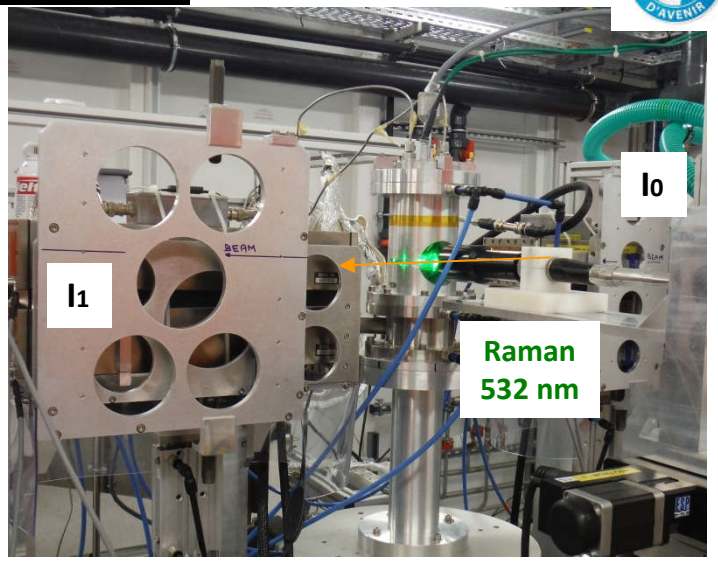
MCR-ALS

2/ Reaction and …. Deactivation



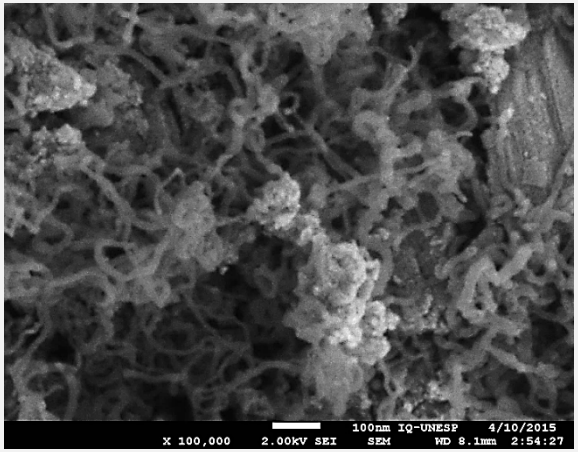
Reaction:

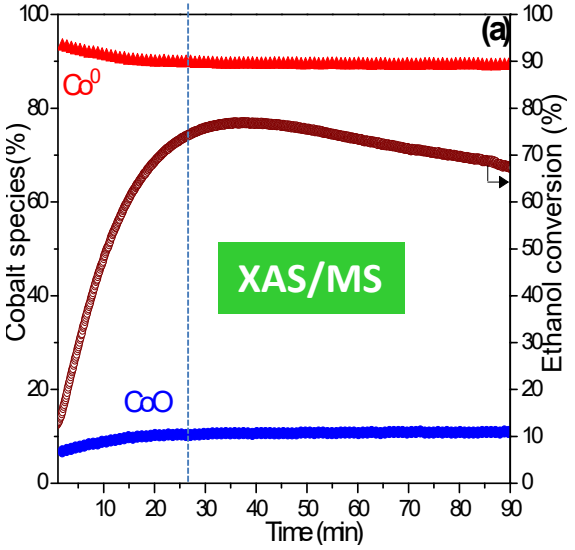
- ✓ $EtOH/H_2O = 1:6$
- ✓ $He = 40\ mL/min$
- ✓ $T = 500\ °C$

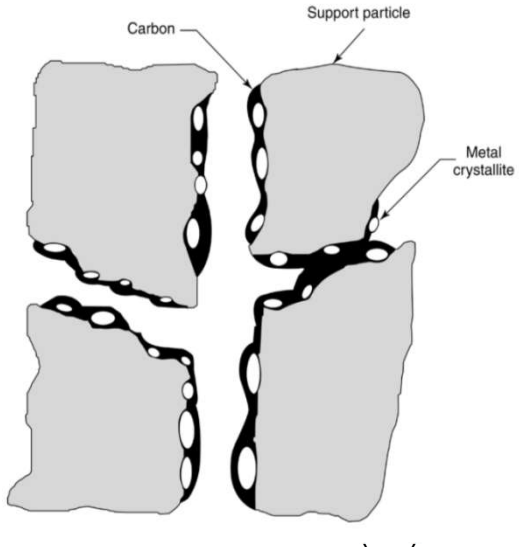


$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2$$

Upon reaction formation of coke







Monitoring of the coke formation *vs* Co speciation

⇒ **Slight reoxidation (4%)**

⇒ **Deactivation mainly due to the non-accessibility of active sites**

3/ Regeneration of Cobalt active sites with O_2 pulses

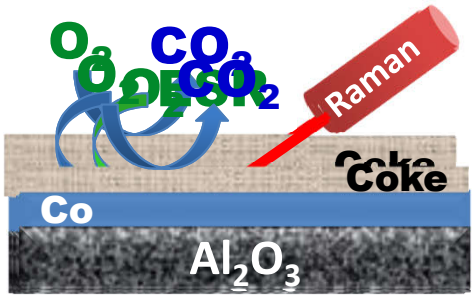
⇒ **Monitoring of the coke combustion vs Co speciation**

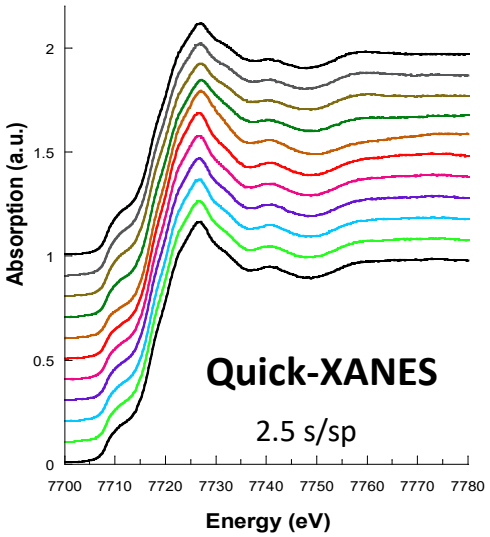
Regeneration

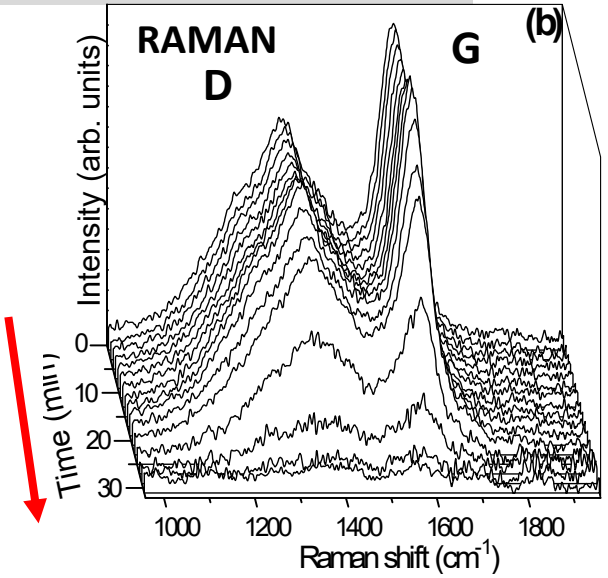
ESR Condition
- ✓ $EtOH/H_2O$
- ✓ He = 40 mL/mim

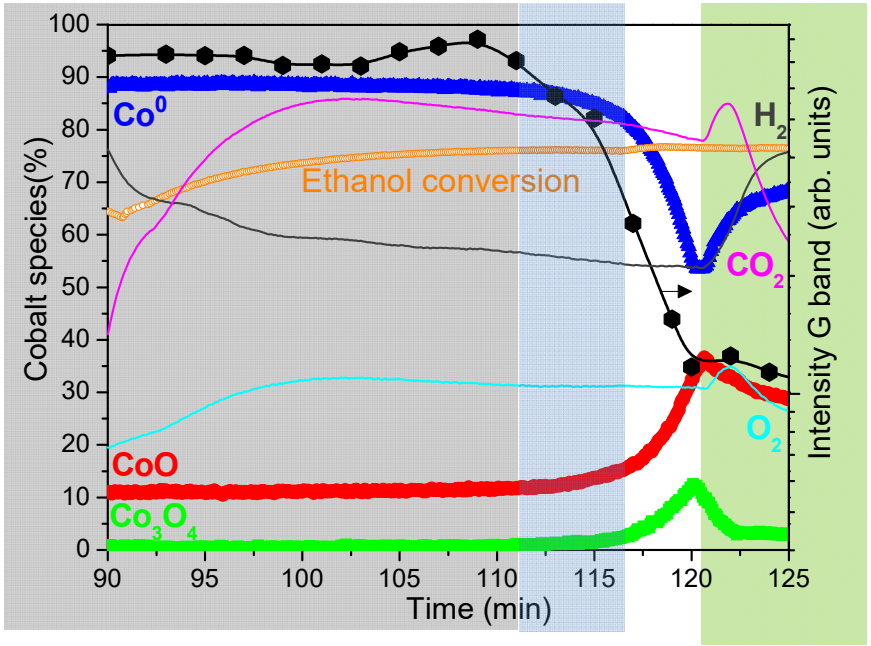
+

Oxidative treatment:
- ✓ 5% O_2 /He = 5 mL/min
- ✓ 30 min

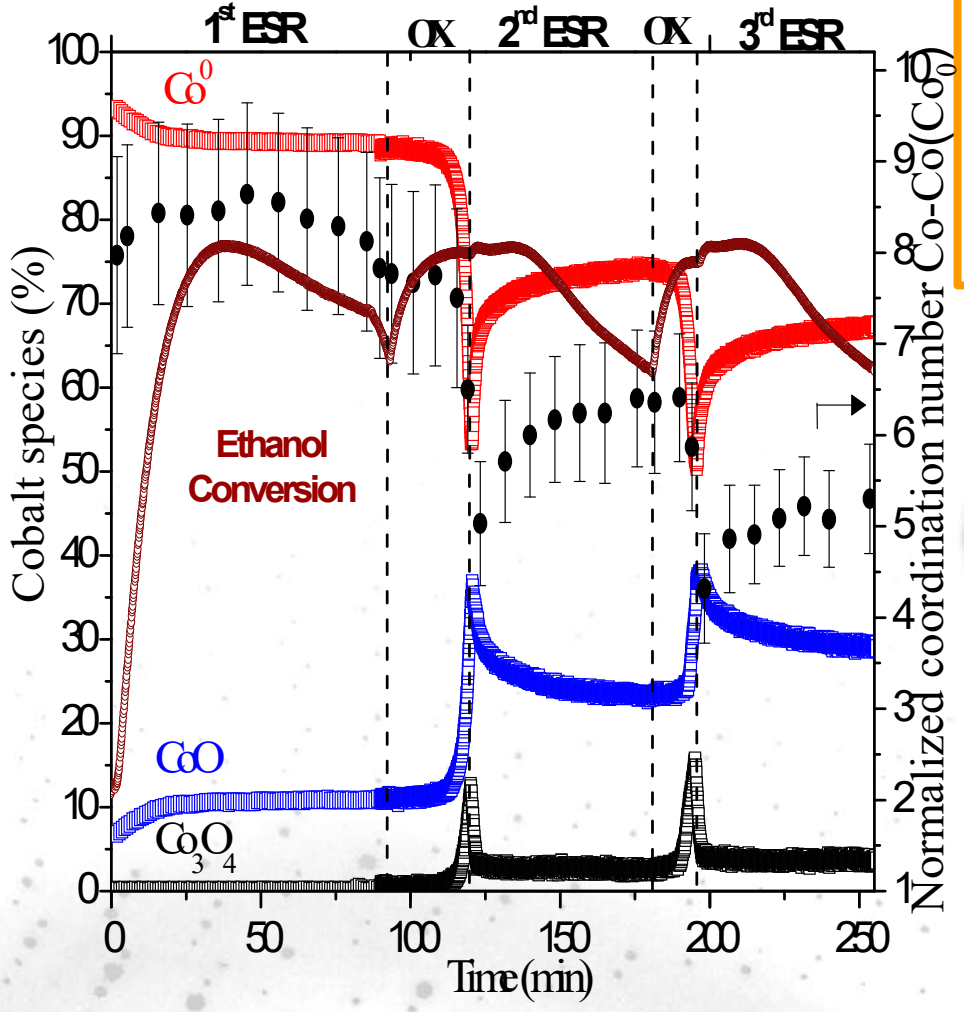






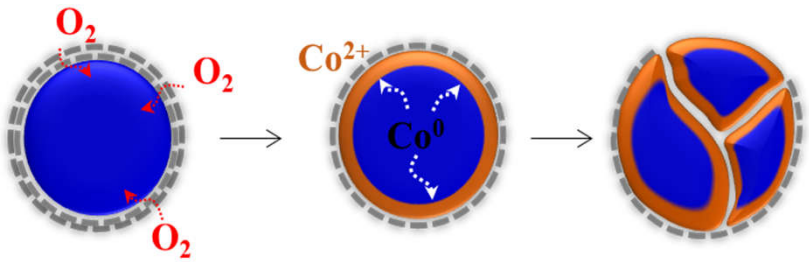


3/ Regeneration of Cobalt active sites with O_2 pulses… and successive reactions



- ✓ similar EtOH conversion after regeneration
- ✓ BUT ↓ % of Co^0 phase

How is it possible ?



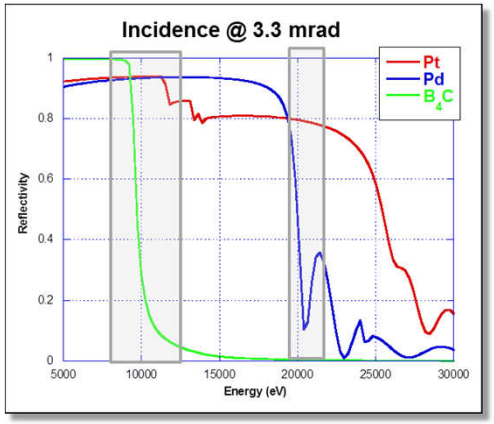
Kirkendal voids during reoxydation on a confined nanoparticle => decrease of the particle size

“Edge jumping” performances

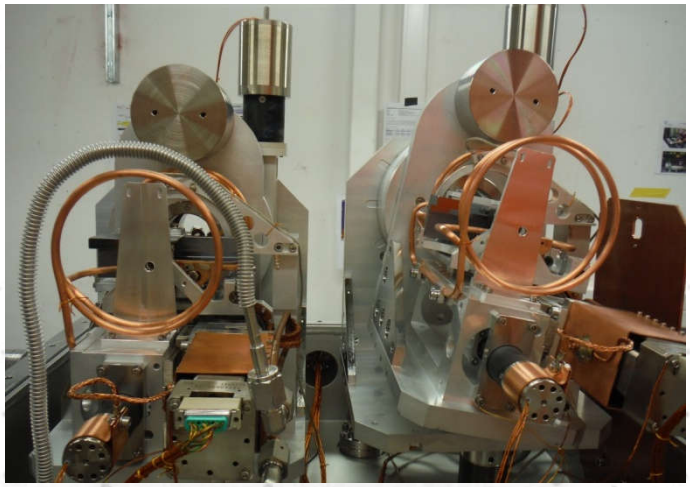
Full automation of the beamline changes and acquisition procedure

3 different coating strips on the harmonic rejection mirrors

Pd | B_4C | Pt

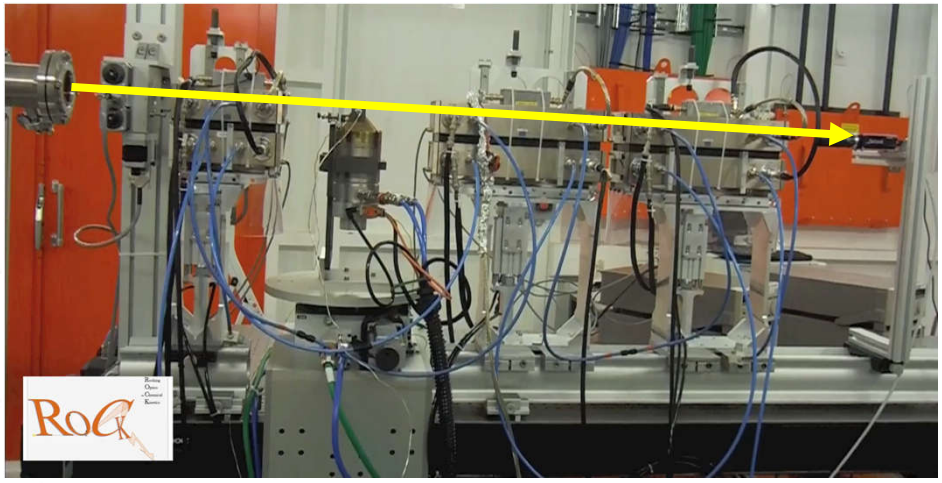


2 monochromators



Si(220) Si(111)

2 set of ionization chambers



< 1 min for complete optimization

Activation of HDS Catalysts

HDS Reaction :
Removal of Sulfur
From naphta, gasoline…

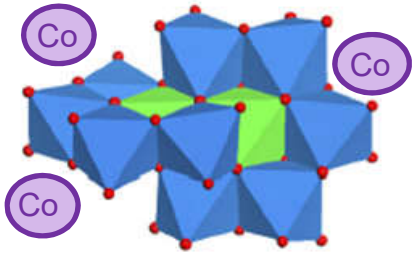
Clean Fuels

Prevent poisoning catalysts used in reforming plants

Understanding of the formation of the active CoMoS species is of prime importance for improving the catalytic activity

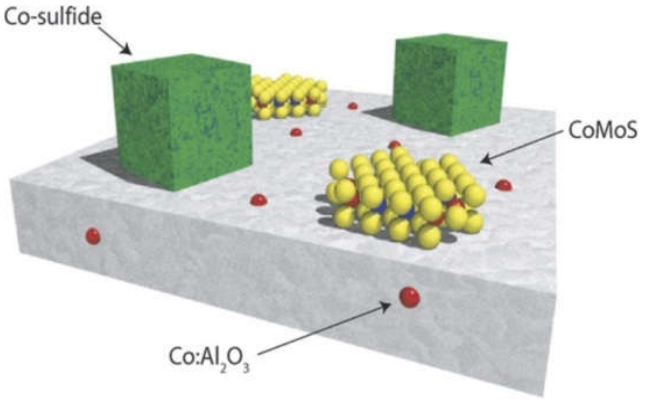
Dimeric Anderson HPA

$Co_3Co_2Mo_{10}O_{38}H_6$

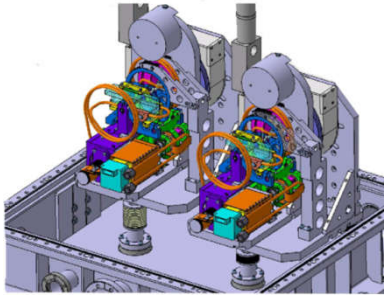


Sulfidation

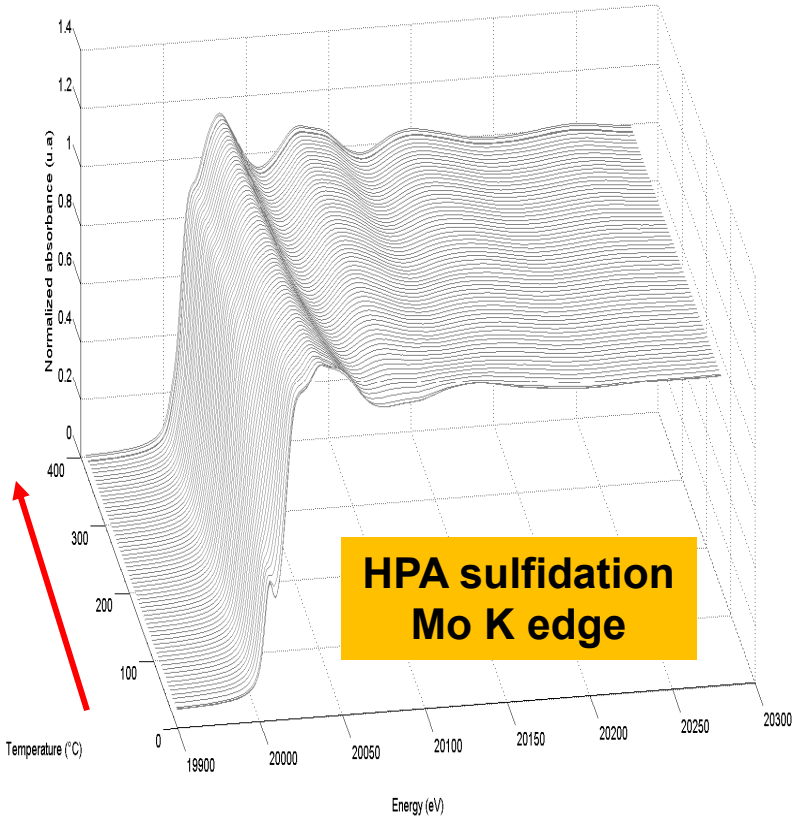
RT -> 400°C
under H_2/H_2S

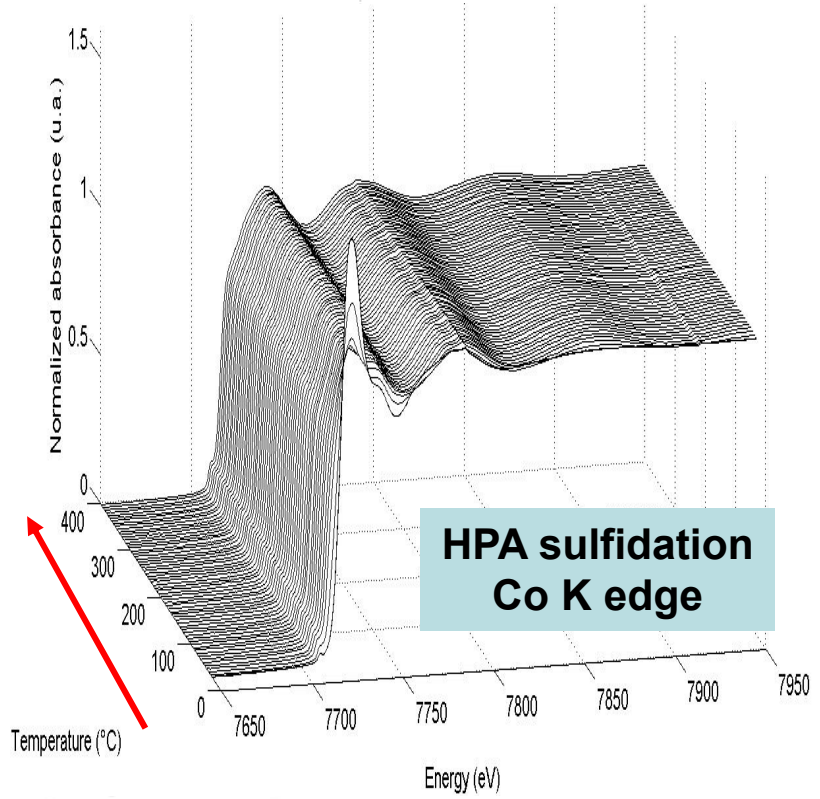


“Edge jumping” Mode between Mo and Ni K edges

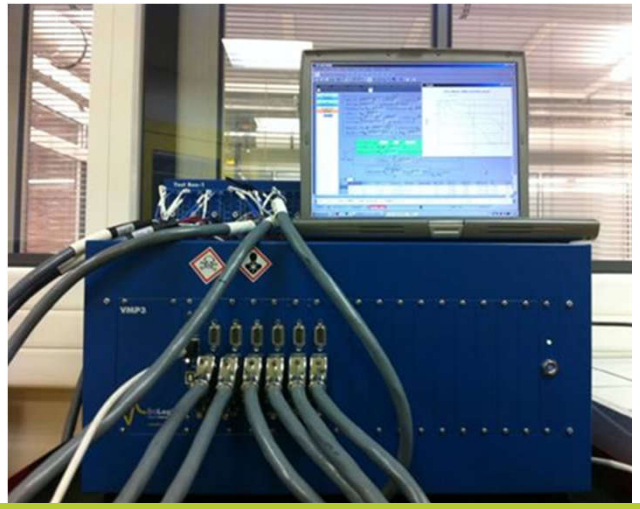


T	T + 3°C	T + 6°C	T + 9°C
Co 27s	35s → Mo 27	35s → Co 27s	35s → Mo 27
t	t + 62s	t + 124 s	t + 186 s



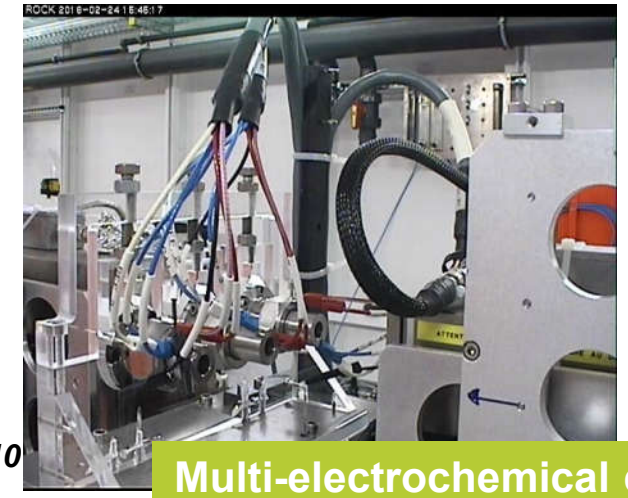


Dedicated environments for *operando* study of energy storage



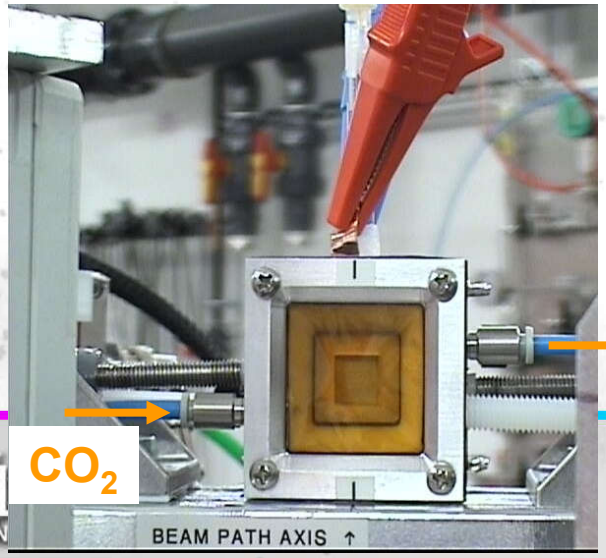
VMP3 Bio-Logic multi-channel potentiostat

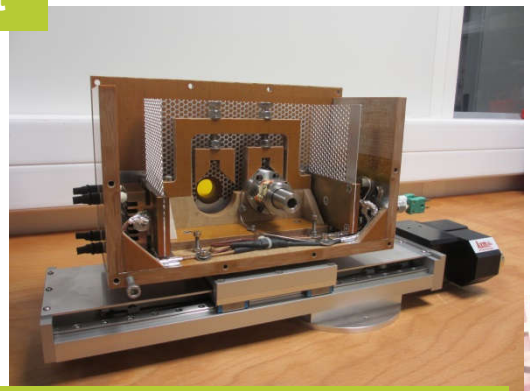
JES, 157, (2010) A606-A610



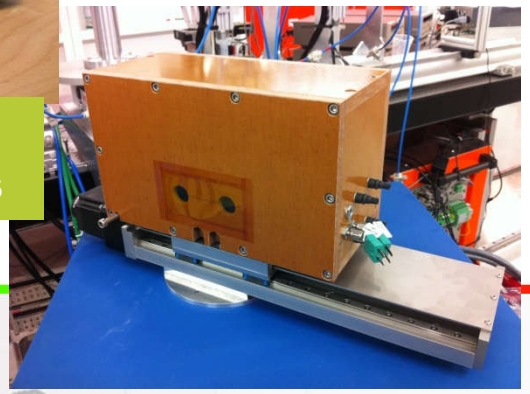
Multi-electrochemical cells

& of electro-catalysts



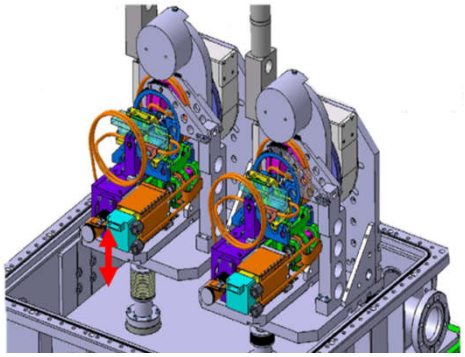


Thermostated box
for electrochemical cells



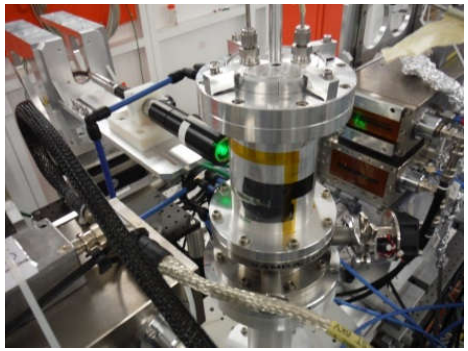
ROCK a beamline optimized for Operando characterizations

- ✓ **Time resolution ranging from 20 ms to 5s**
- ✓ **2 Quick-EXAFS monochromators for 4-42 keV energy range**
- ✓ **"Edge jumping" capability**

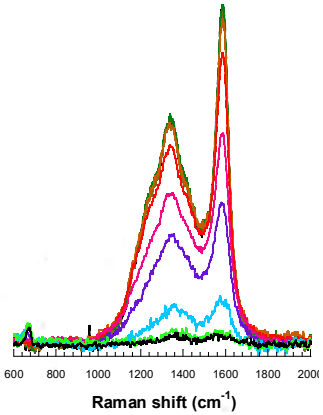


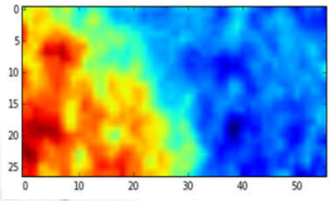
- ✓ **Dedicated sample environments for *operando* studies**

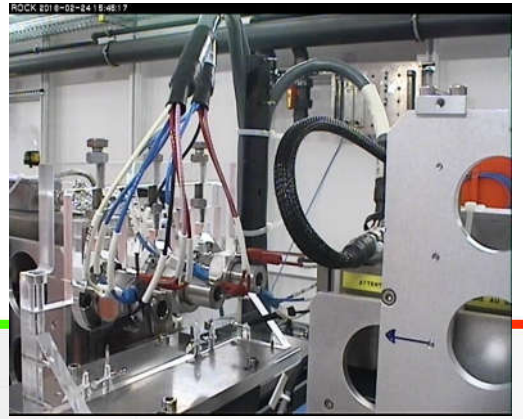
In heterogeneous catalysis, electrocatalysis, energy storage, nanoparticles nucleation/growth



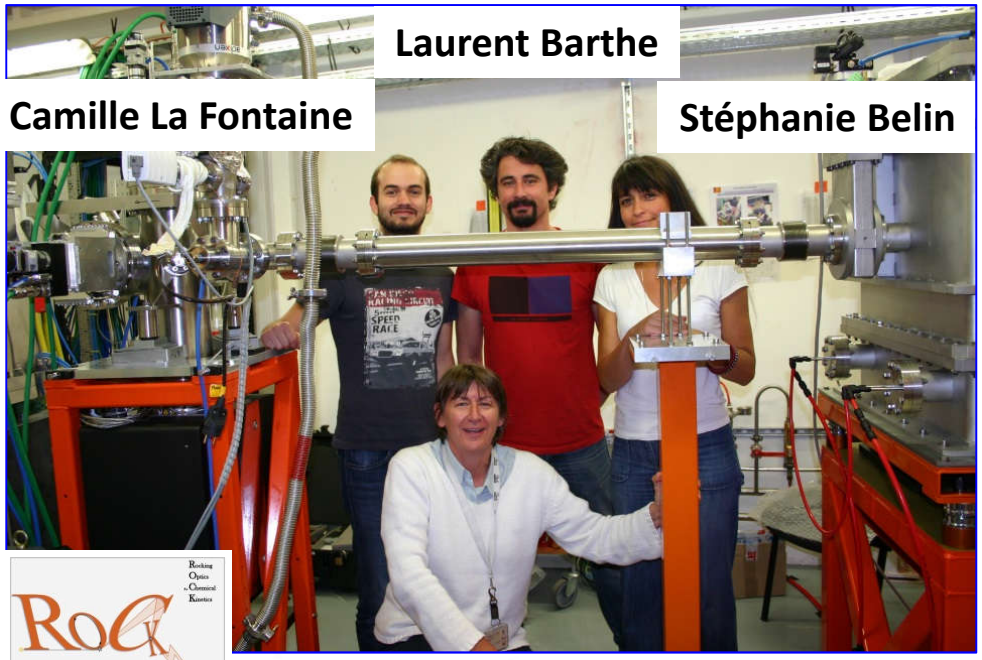
- ✓ **Combination of Techniques**
  - **Raman spectroscopy**
  - **UV-Vis spectroscopy**
  - **2D microscopy**
  - **X-ray diffraction**



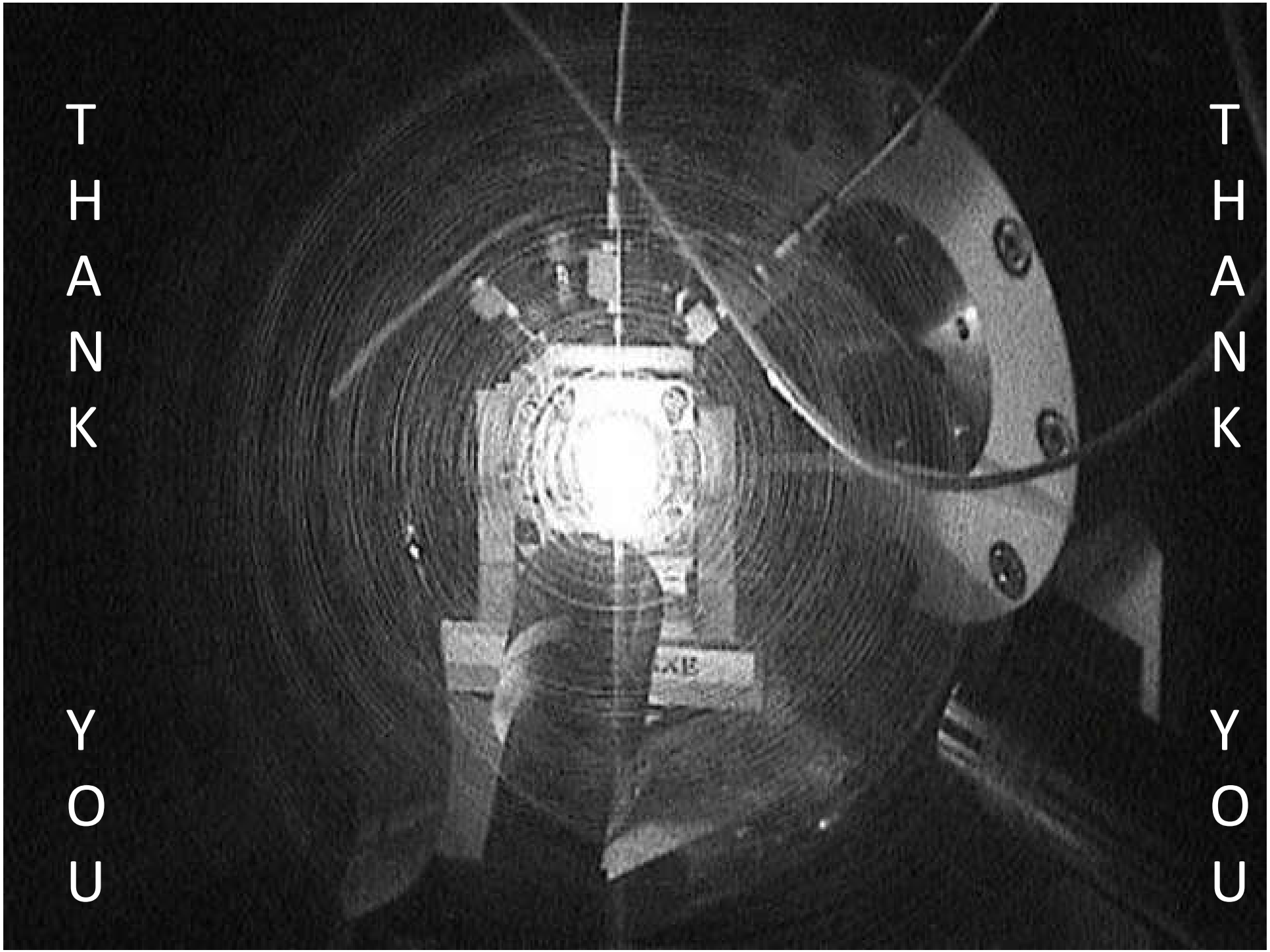




- ✓ $D = C S^T + E$



ANR-10-EQPX-45


THANK YOU
THANK YOU