Fundamental and applied RIXS studies of transition metal oxides

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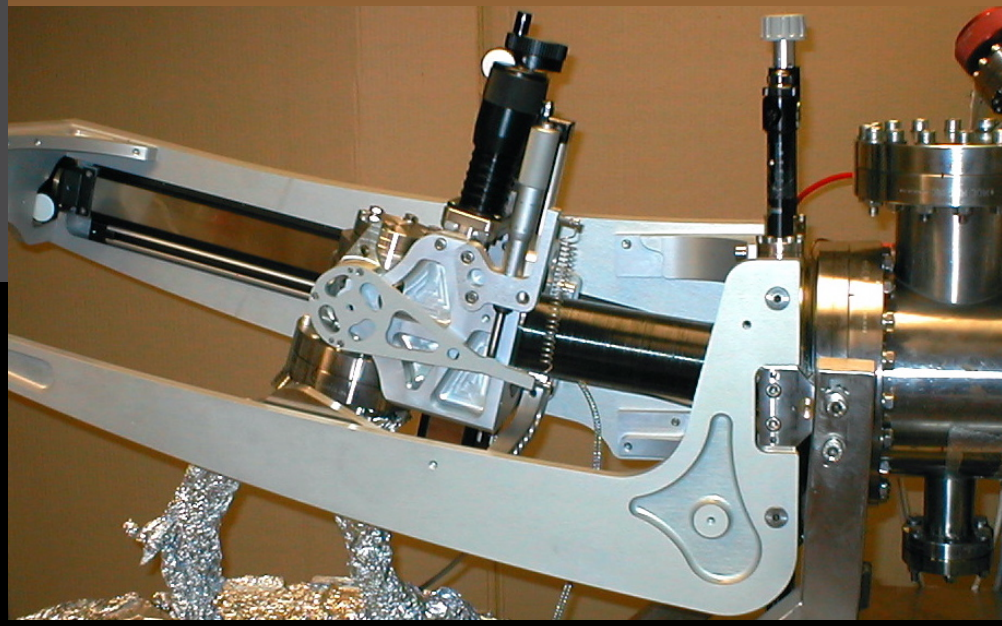
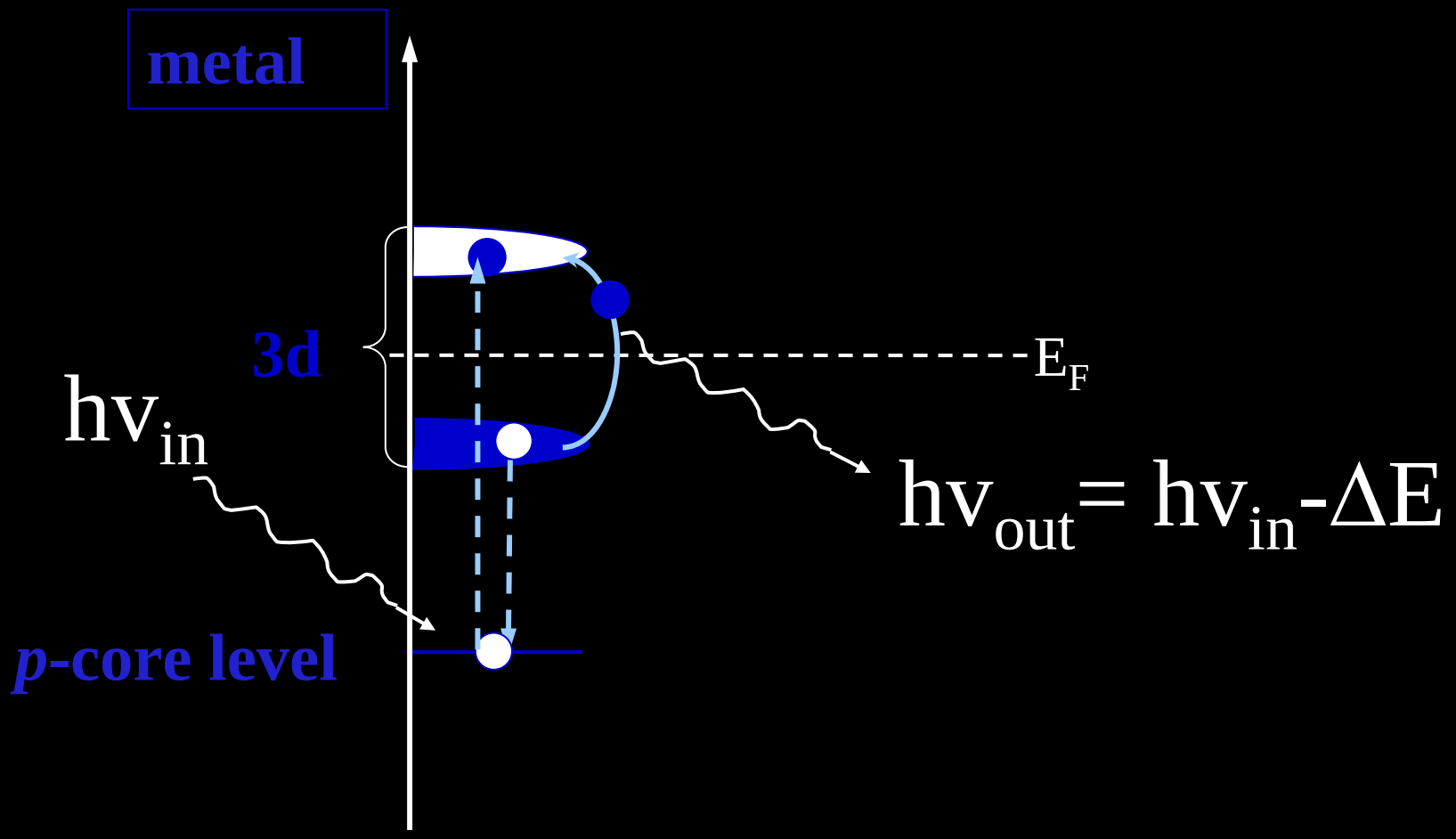
- NiO Ni *M*-RIXS and O *K*-RIXS
- *In situ* atmospheric corrosion in environmental cell: **First results**

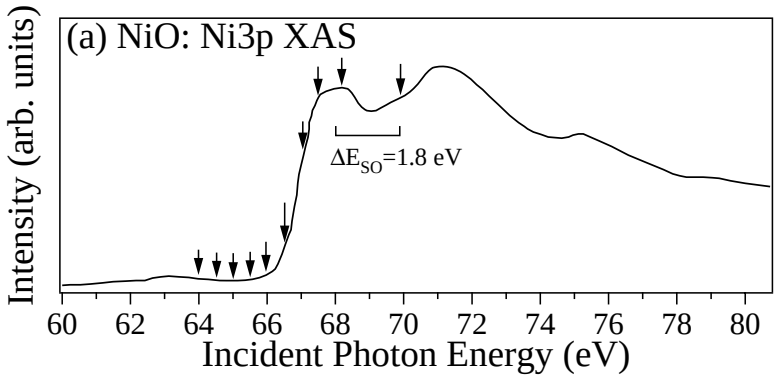
Uppsala spectrometer ”Grace”

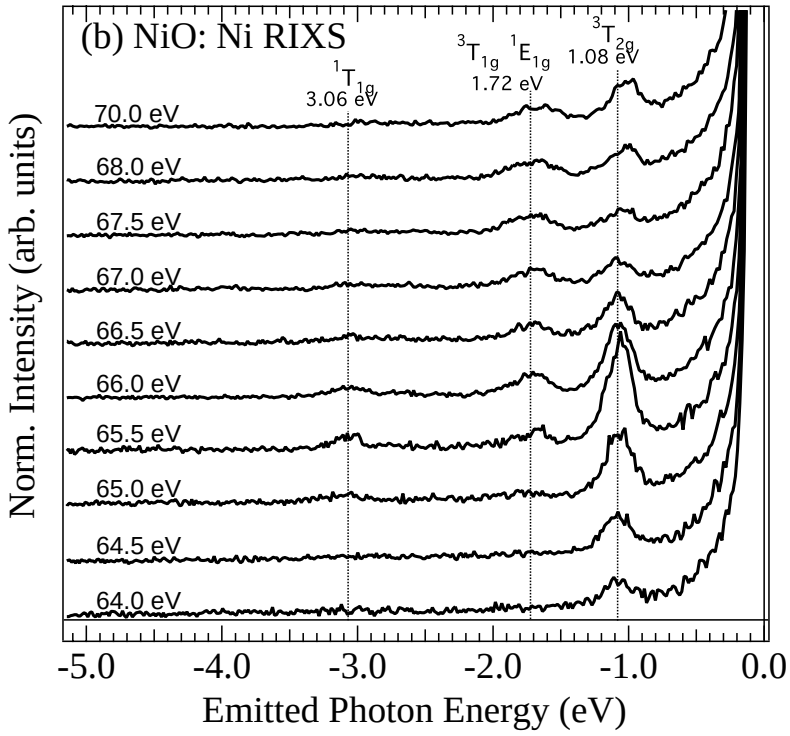


RIXS from *p*-resonances



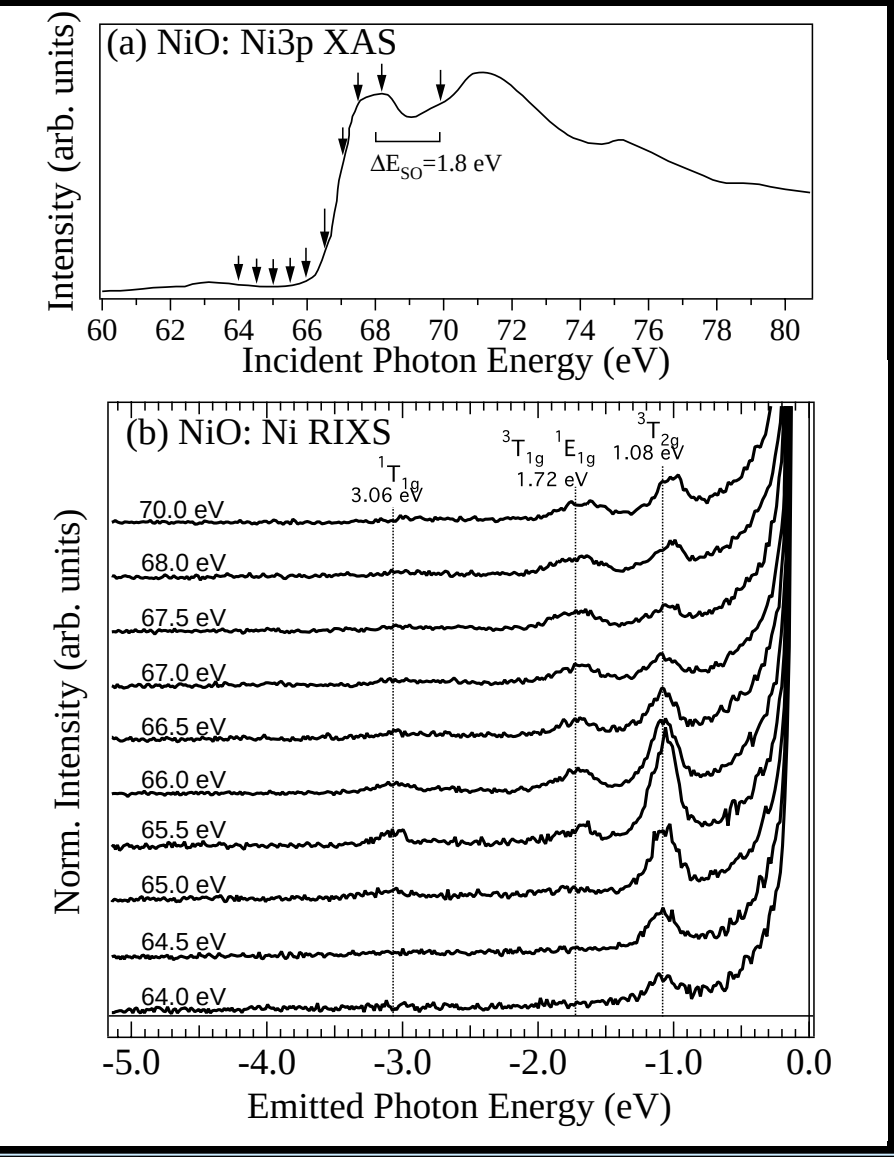
NiO: Ni *M*-RIXS



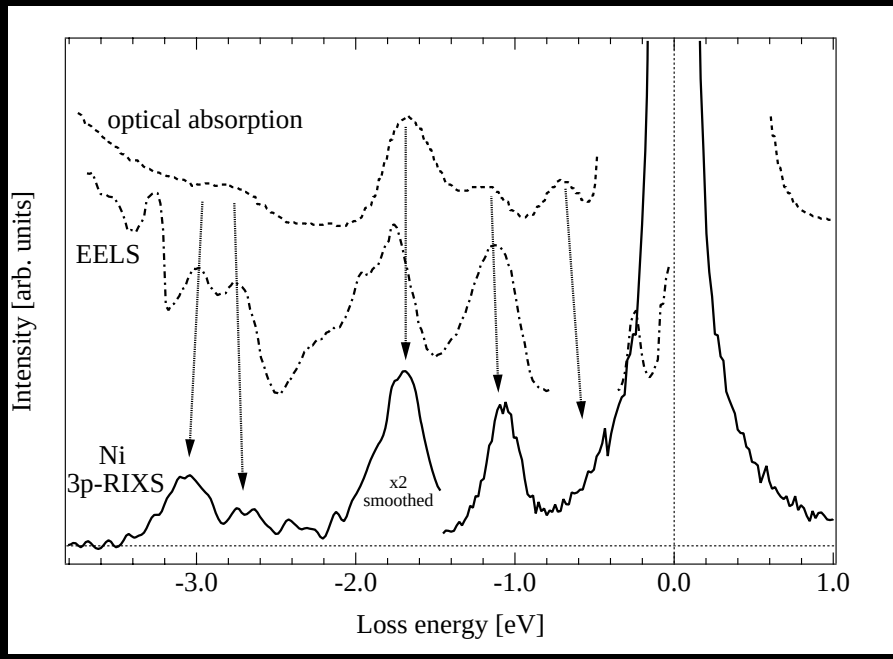


Highly resolved dd-excitations

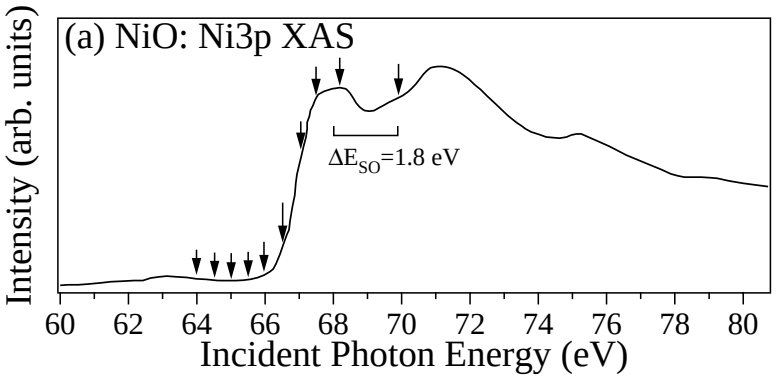
NiO: Ni *M*-RIXS

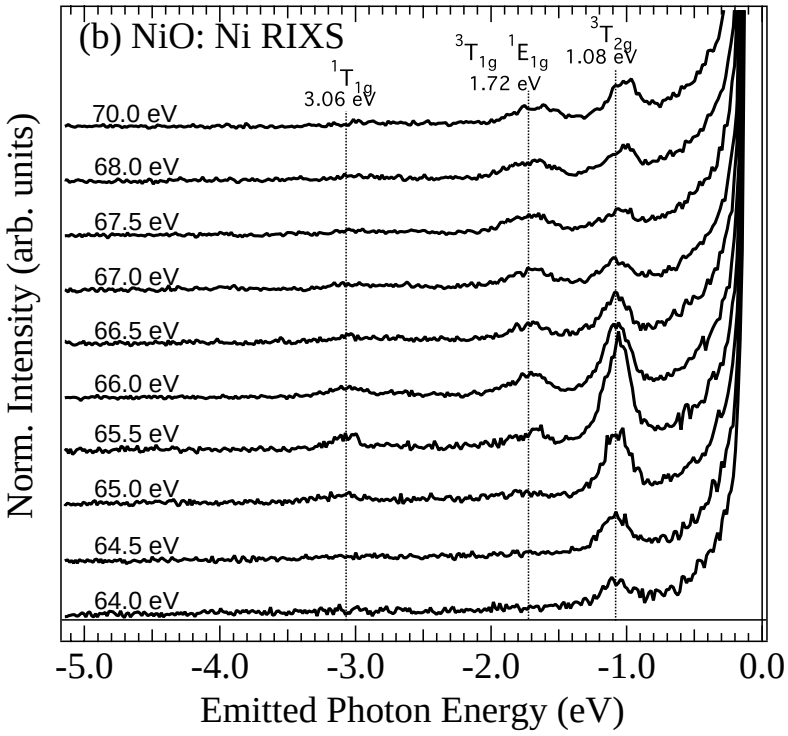


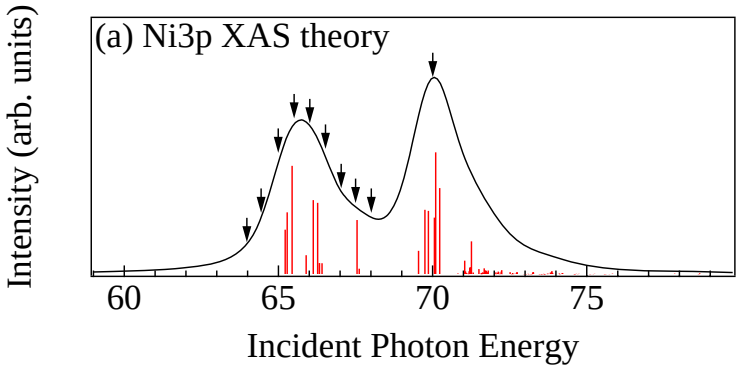
Comparison to other techniques

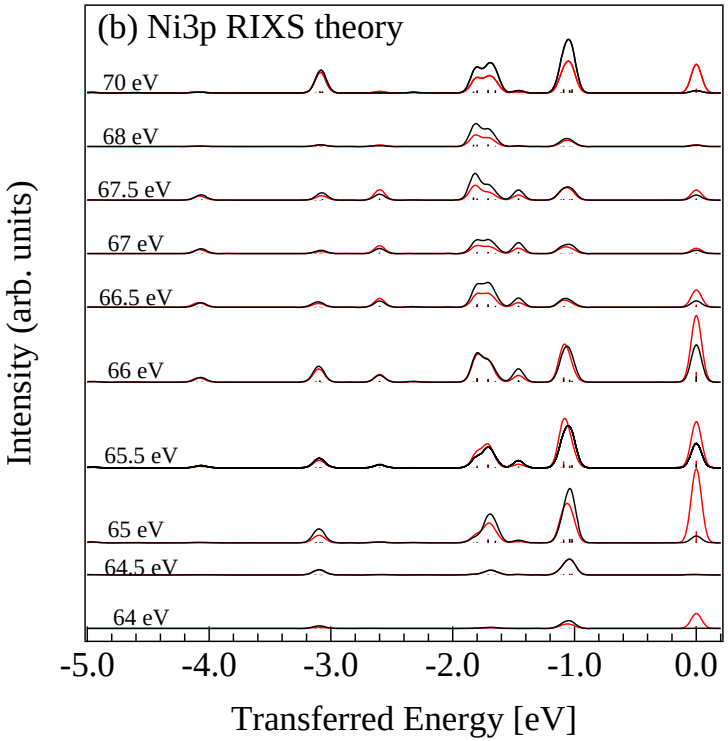


NiO: Ni *M*-RIXS


(a) NiO: Ni3p XAS
ΔE_{SO}=1.8 eV
Intensity (arb. units)
60 62 64 66 68 70 72 74 76 78 80
Incident Photon Energy (eV)


(b) NiO: Ni RIXS
$^1T_{1g}$ 3.06 eV
$^3T_{1g}$ $^1E_{1g}$ 1.72 eV
$^3T_{2g}$ 1.08 eV
70.0 eV
68.0 eV
67.5 eV
67.0 eV
66.5 eV
66.0 eV
65.5 eV
65.0 eV
64.5 eV
64.0 eV
Norm. Intensity (arb. units)
-5.0 -4.0 -3.0 -2.0 -1.0 0.0
Emitted Photon Energy (eV)


(a) Ni3p XAS theory
Intensity (arb. units)
60 65 70 75
Incident Photon Energy

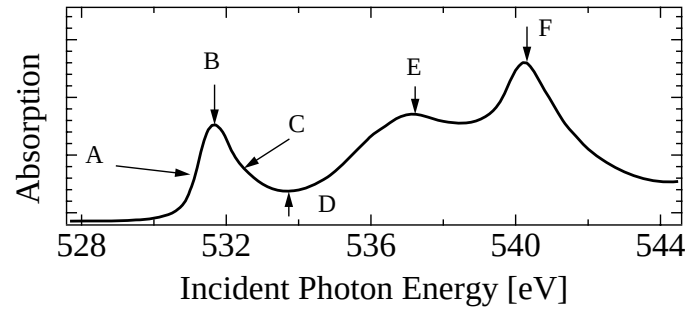

(b) Ni3p RIXS theory
70 eV
68 eV
67.5 eV
67 eV
66.5 eV
66 eV
65.5 eV
65 eV
64.5 eV
64 eV
Intensity (arb. units)
-5.0 -4.0 -3.0 -2.0 -1.0 0.0
Transferred Energy [eV]

NiO: O *K*-RIXS

- 2*p*-XPS line shape theory: ”*non-local* screening plays major role”
- O *K*-emission only analyzed according to band theory
- Ground state: $\alpha\, d^8 + \beta\, \underline{L} d^9 + \gamma\, \underline{L}^2 d^{10}$
- O *K*-RIXS: projects d^9 intermediate states
- Expected final states in O *K*-RIXS:
  - ✓ $d^9\underline{L}$, $d^{10}\underline{L}^2$ (CT)
  - ✓ d^8 (*dd*-exc.)
  - ✓ $| d^8 ; d^9\underline{L} >$ (NLCT)
  - ✓ spin-excitations ?

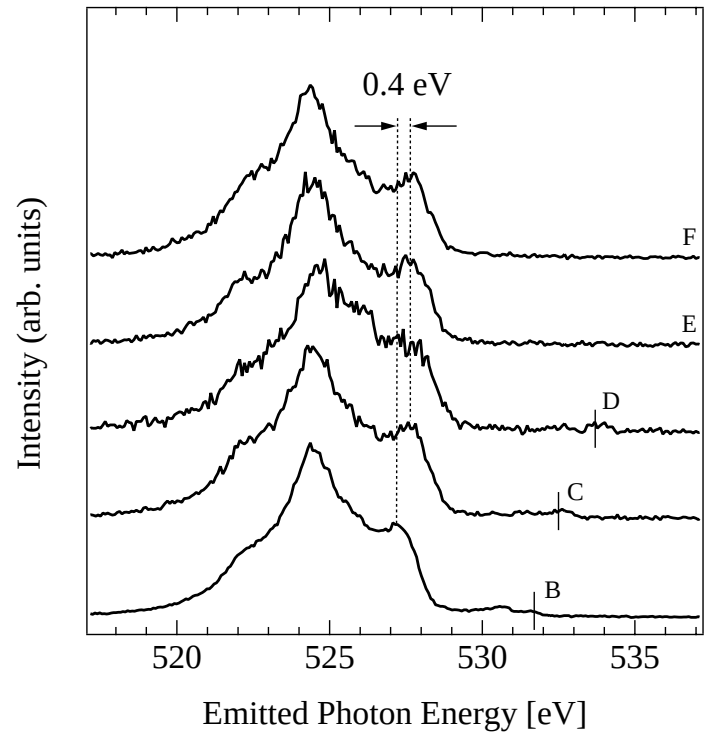
NiO: O *K*-RIXS

O *K*-absorption



O *K*-RIXS

energy dependence

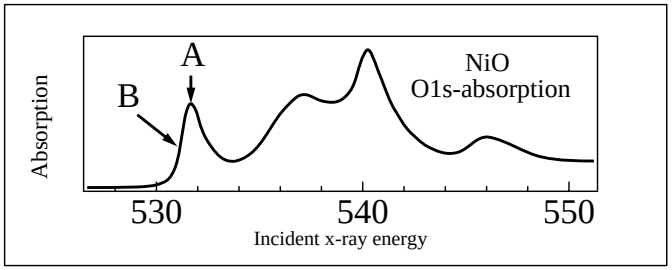


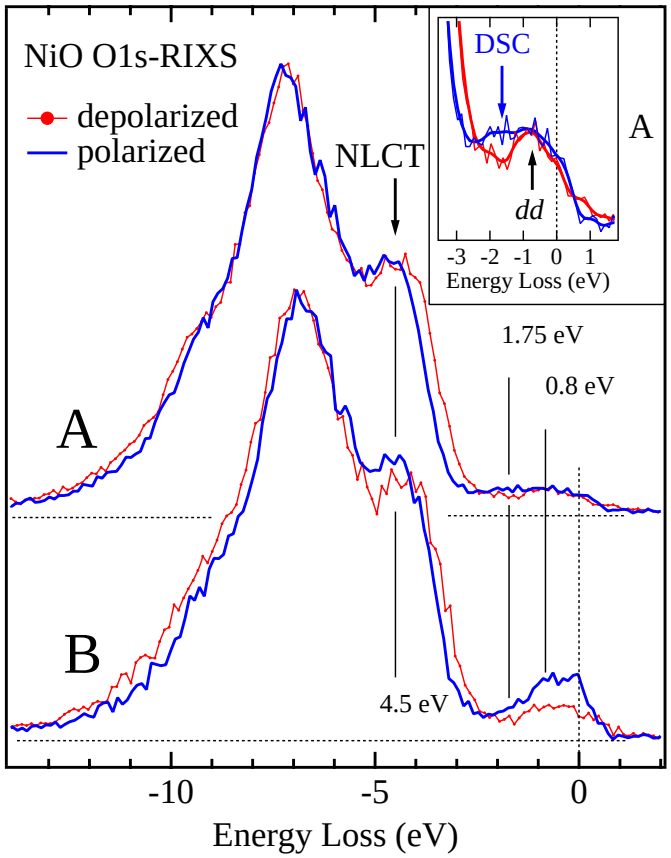
High-energy shoulder moves:

Band mapping effect?

Change of final state?

NiO: O *K*-RIXS

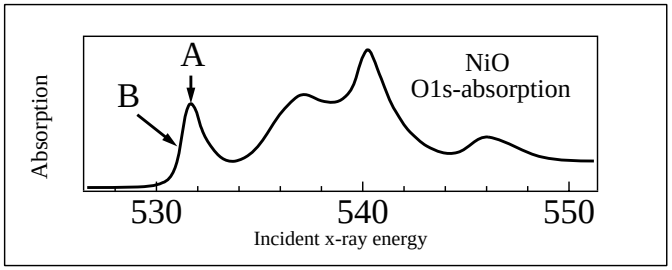


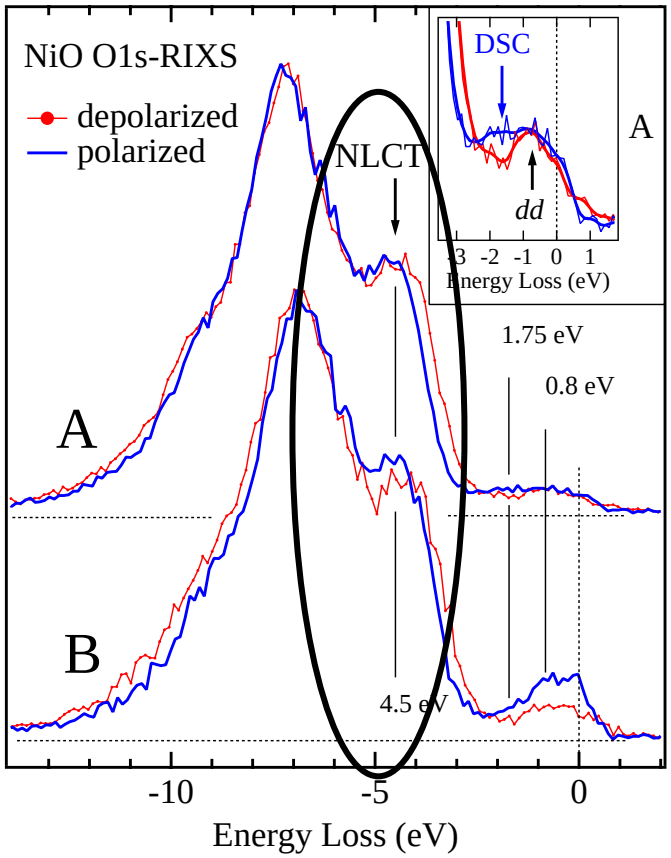


O *K*-RIXS

- Excitation on first peak
- Polarization dependent RIXS
- First time observation of low-energy structure

NiO: O *K*-RIXS

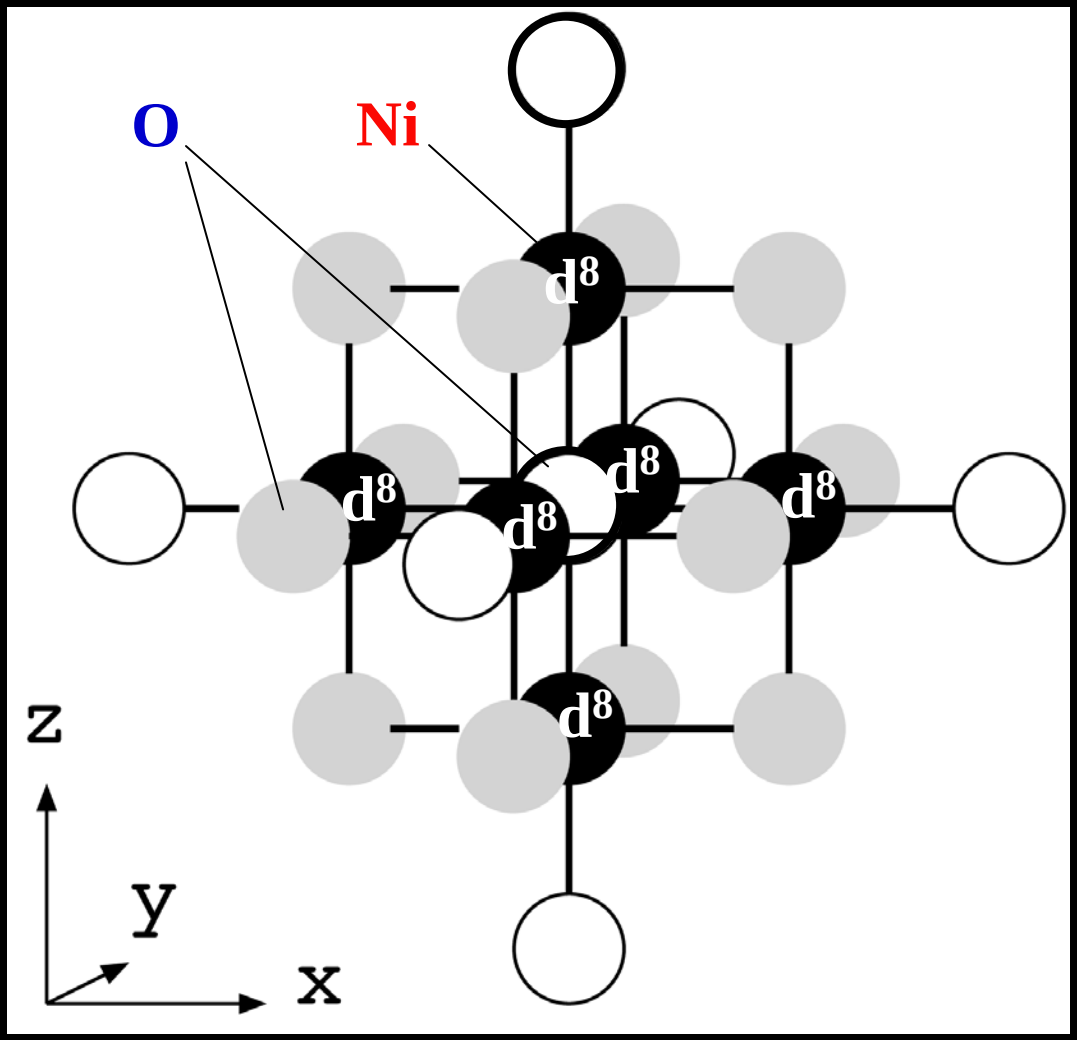




Nonlocal charge transfer edge (NLCT):

$| d^8 ; d^9\underline{L} >$

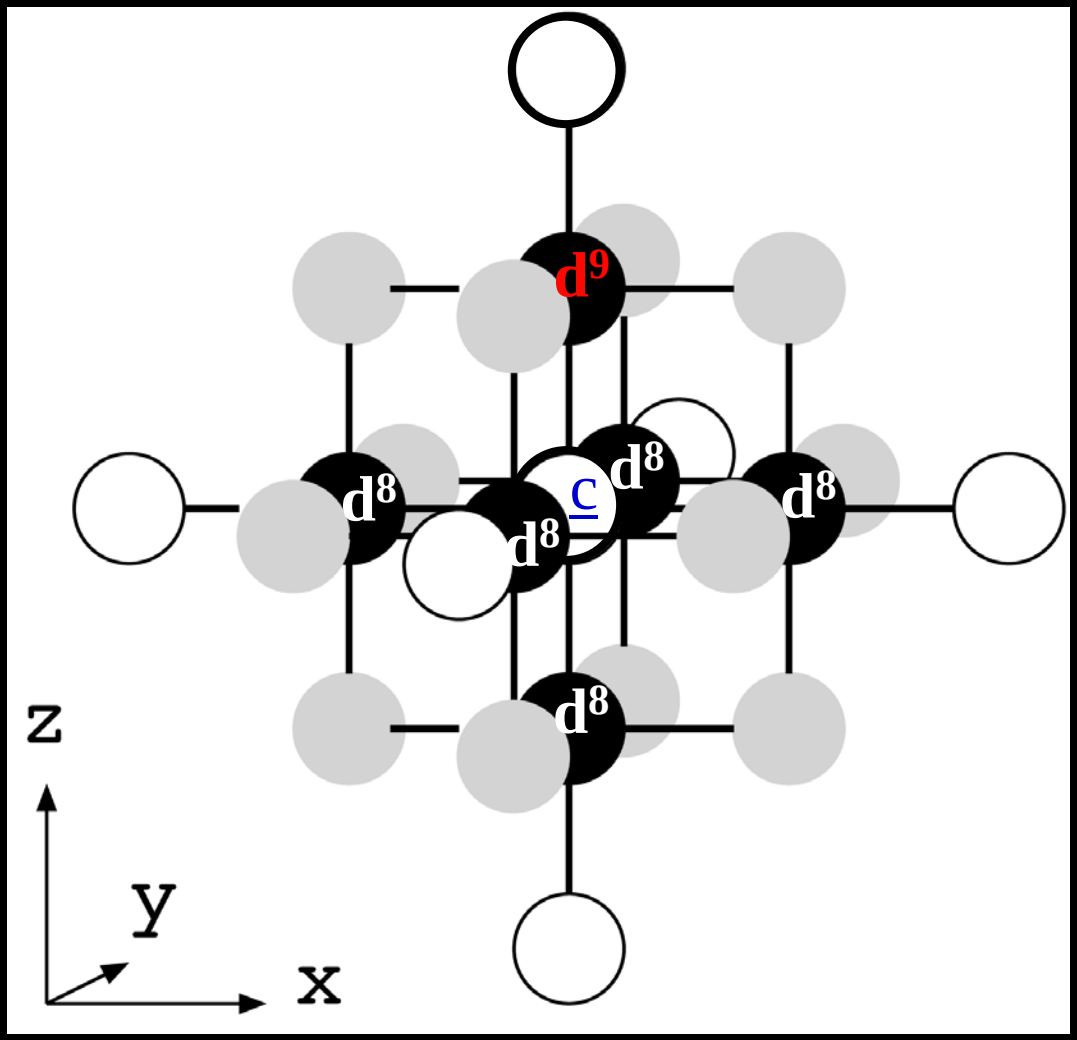
NiO: Non-local charge transfer (NLCT) edge



Ground state:

$|d^8;d^8>$

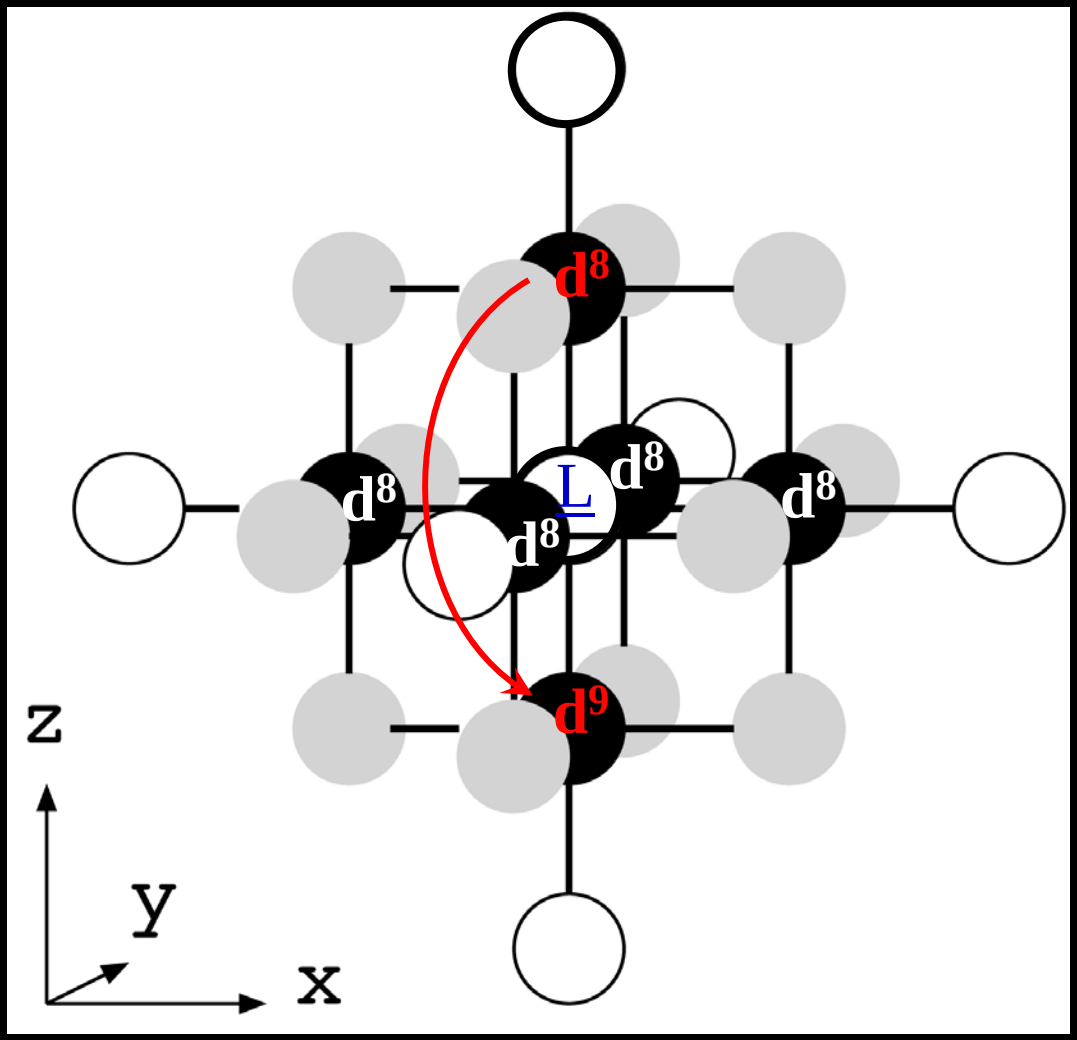
NiO: Non-local charge transfer (NLCT) edge



Intermediate state:

$| d^9\underline{cL} ; d^8 >$

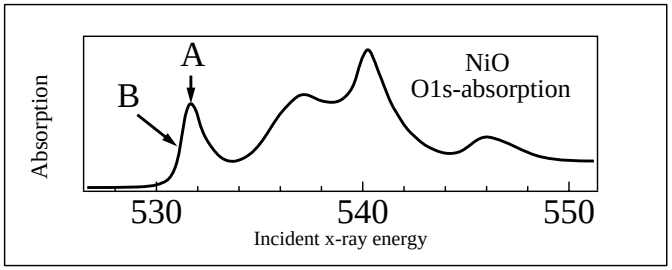
NiO: Non-local charge transfer (NLCT) edge

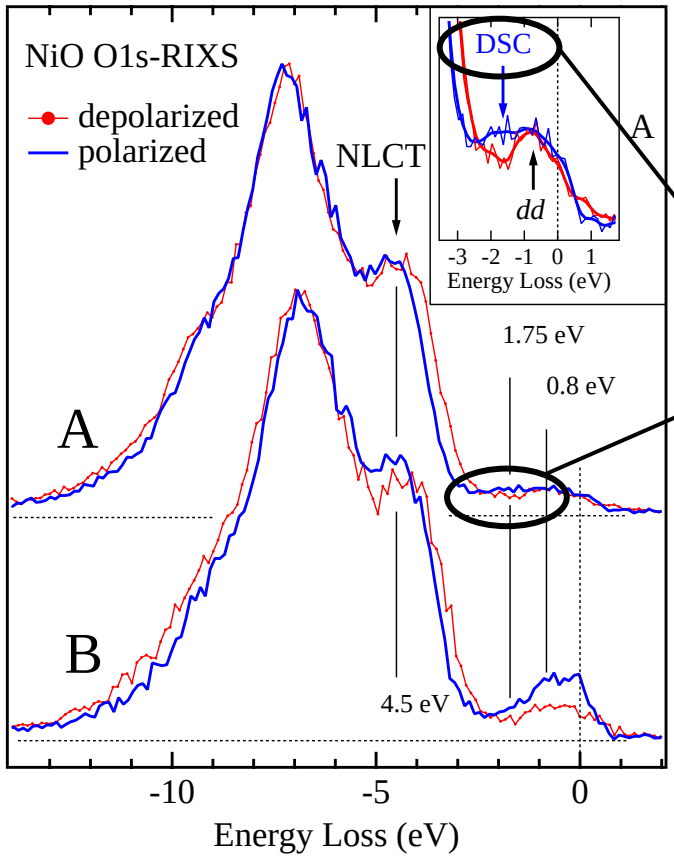


Final state:

$| d^8 ; d^9\underline{L} >$

NiO: O *K*-RIXS

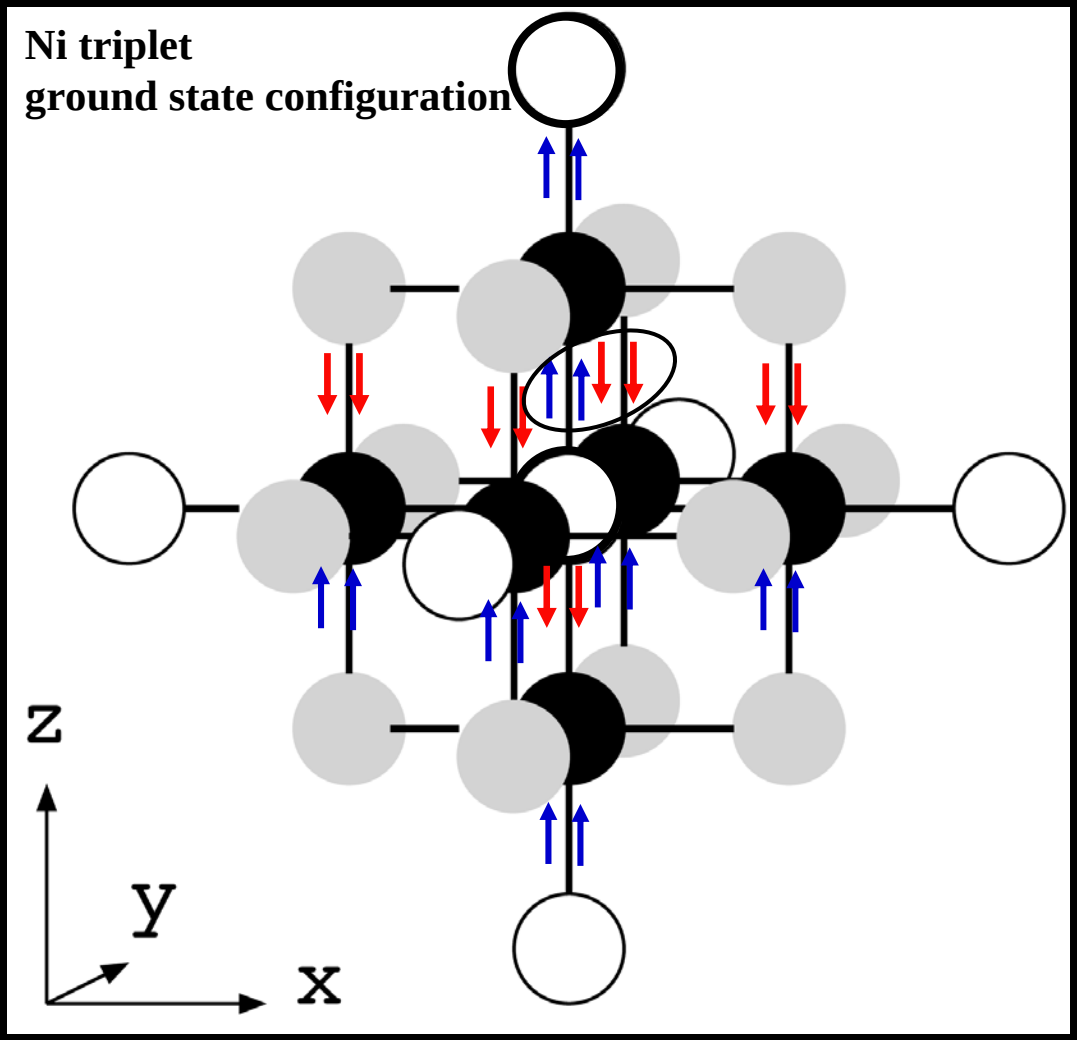




O *K*-RIXS

Double spin creation (DSC) peak

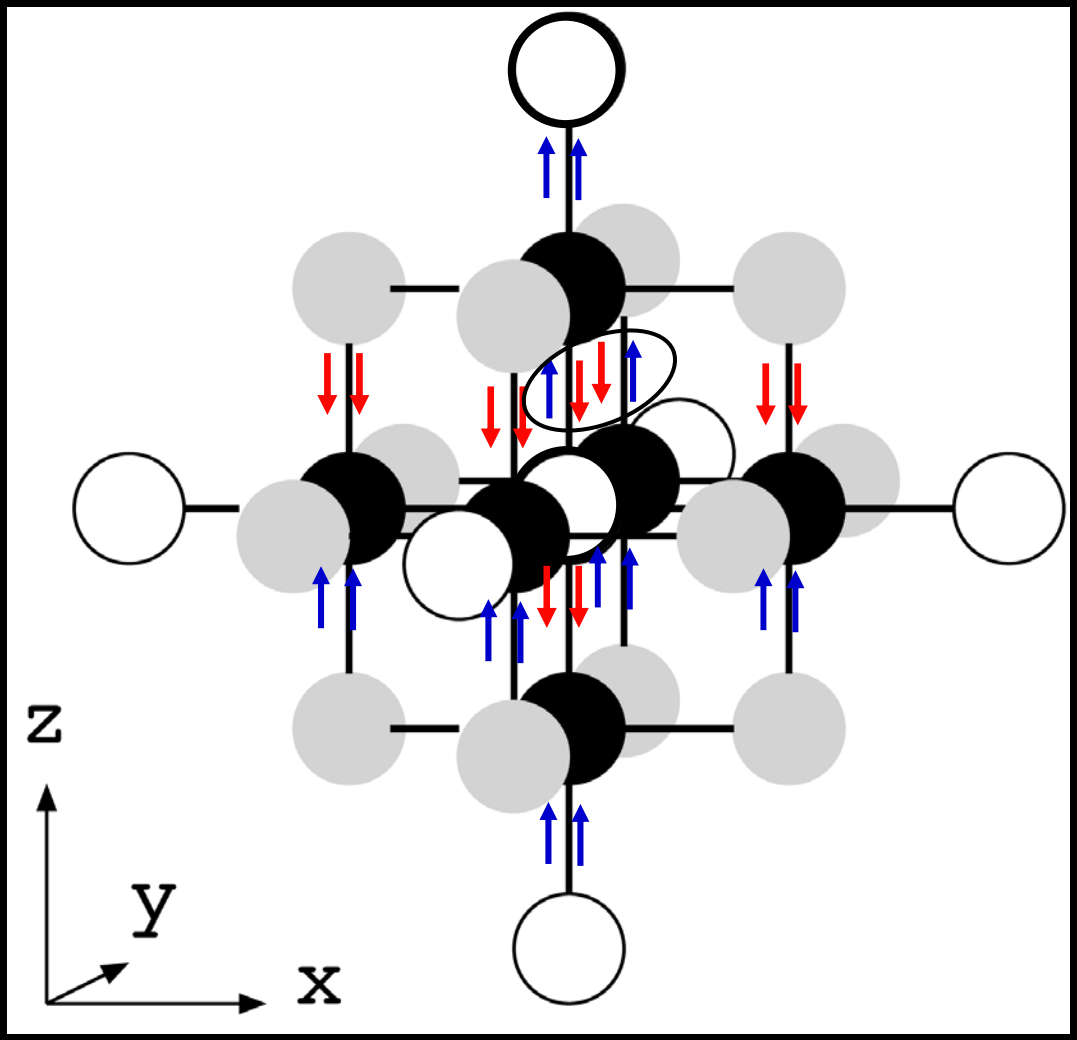
NiO: Double spin creation (DSC) peak



Ground state:

$|\downarrow\downarrow;\uparrow\uparrow>$

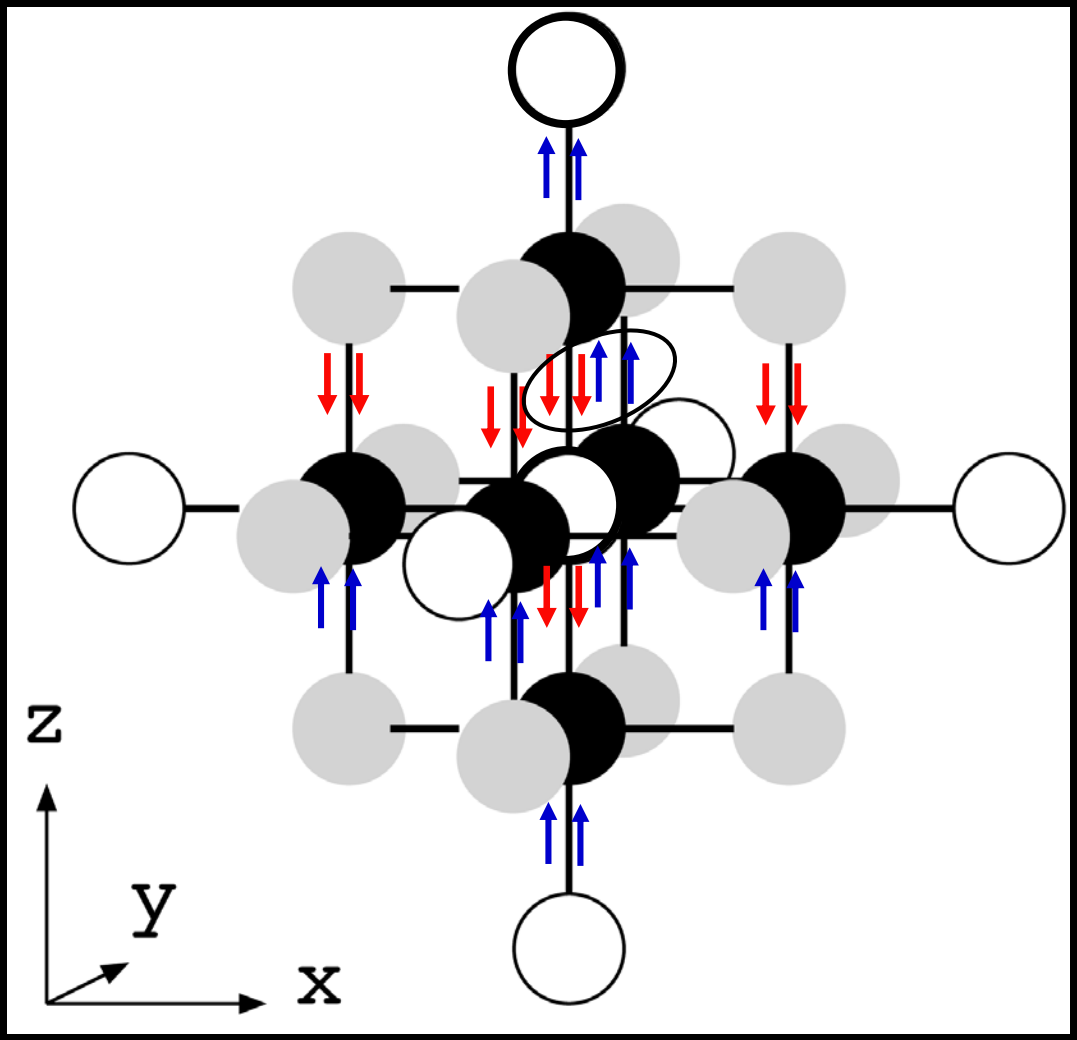
NiO: Double spin creation (DSC) peak



Intermediate state:

$|\downarrow\uparrow;\downarrow\uparrow>$

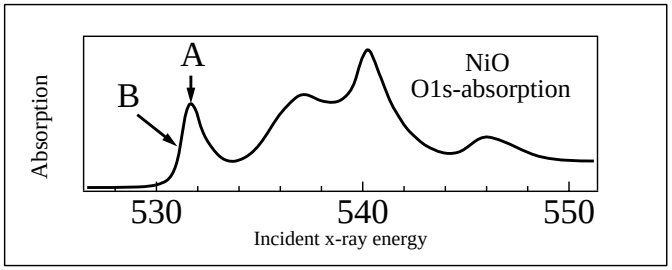
NiO: Double spin creation (DSC) peak

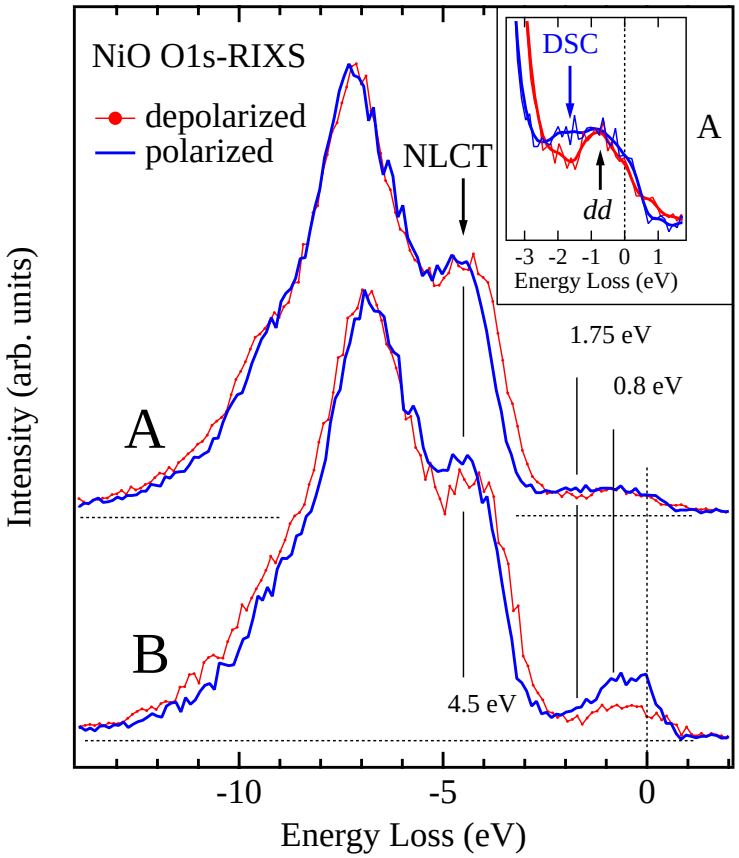


Final state:

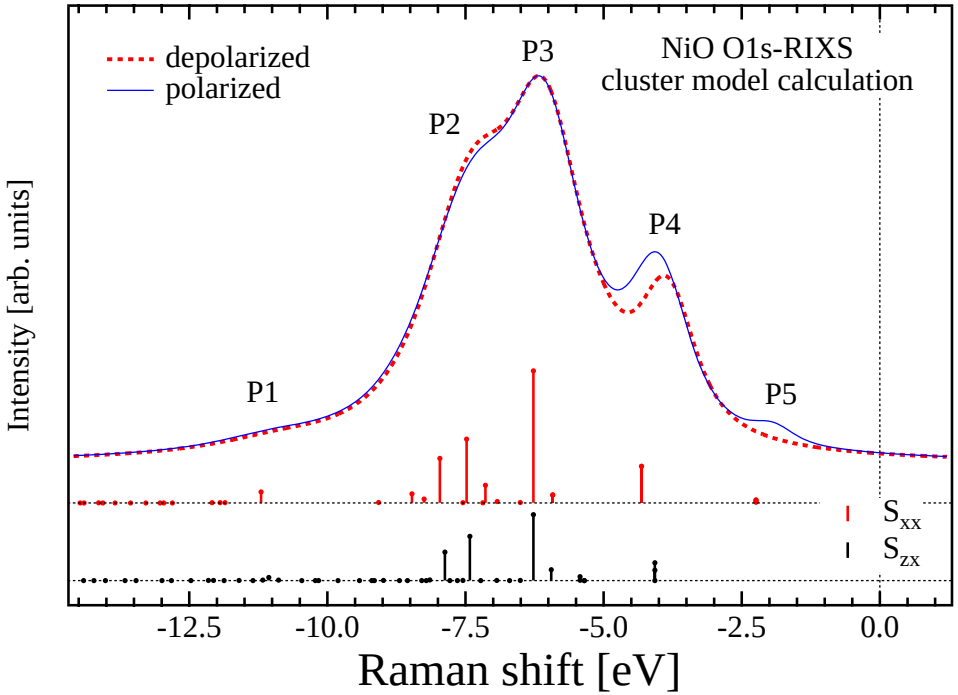
$|\uparrow\uparrow;\downarrow\downarrow>$

NiO: O *K*-RIXS



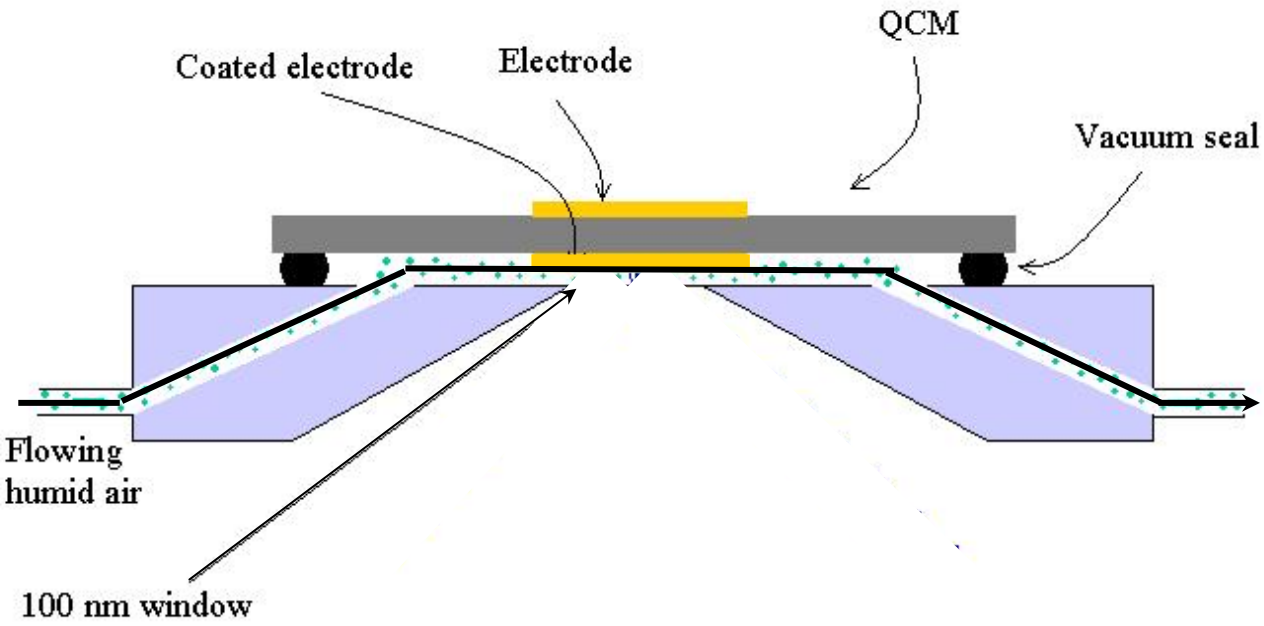


Comparison to multi-cluster model calculation

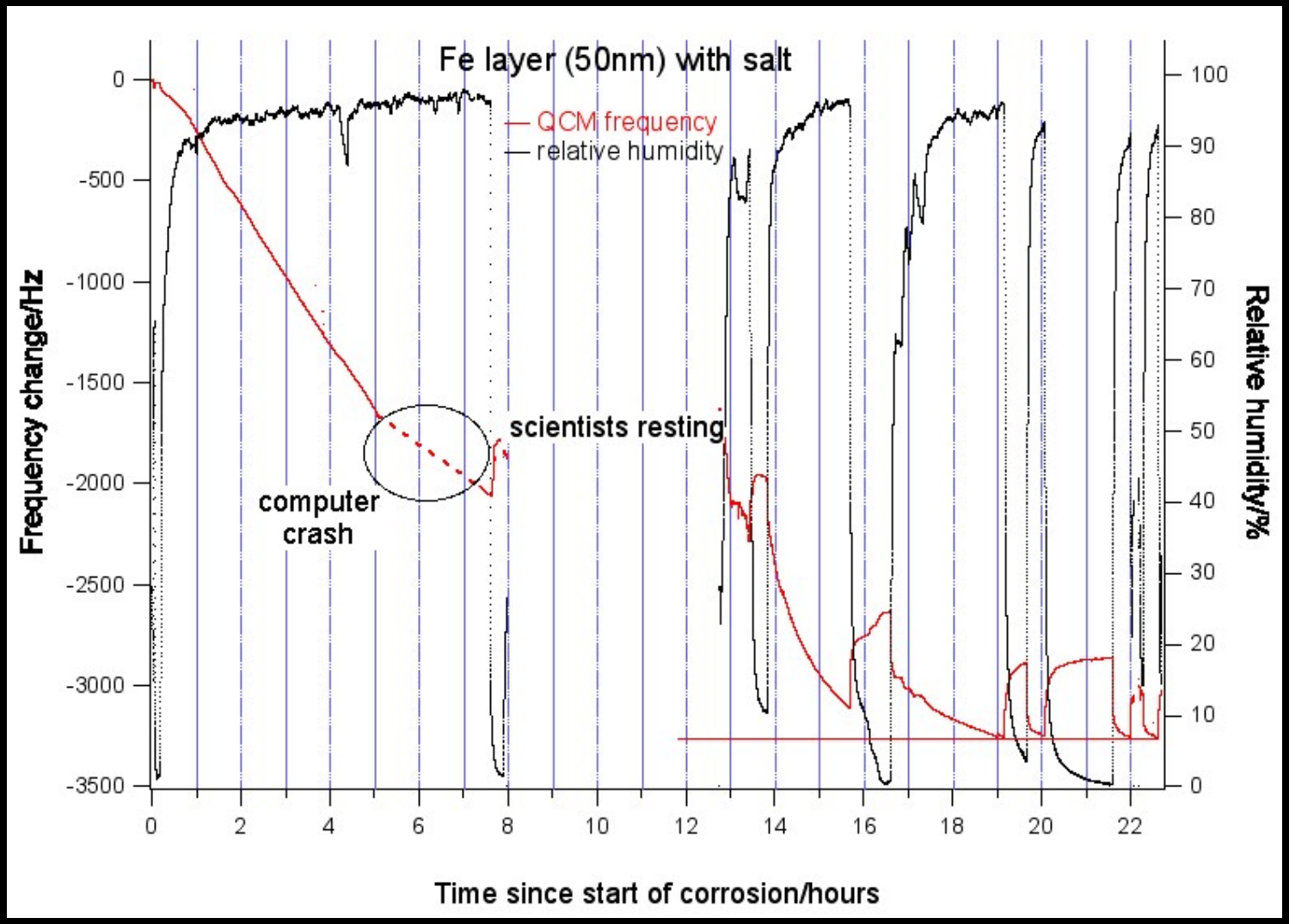


Environmental cell principle drawing

- QCM adlayer thickness control
- *in situ* electronic structure studies with RIXS

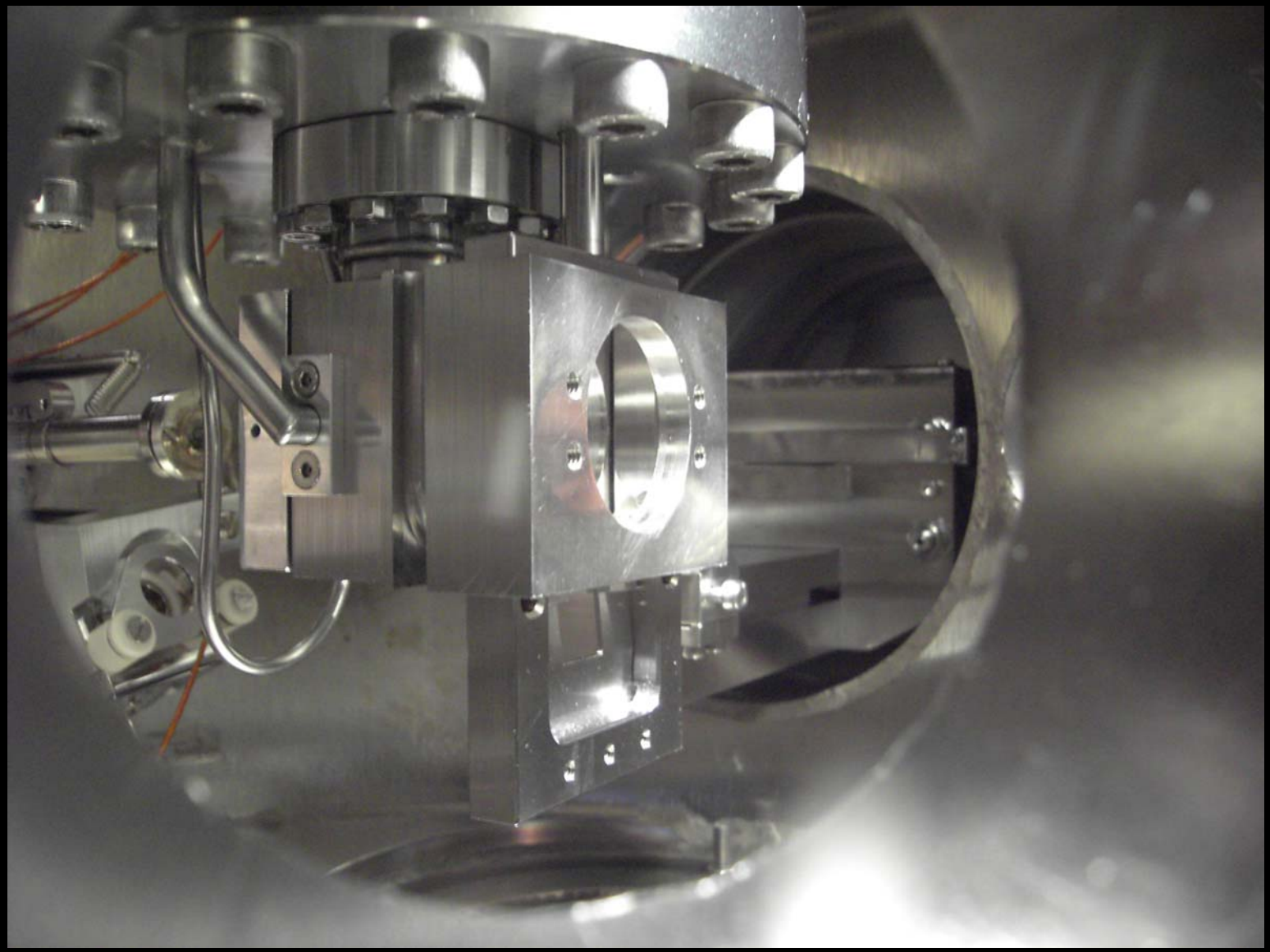


Humidity dependent QCM frequency changes

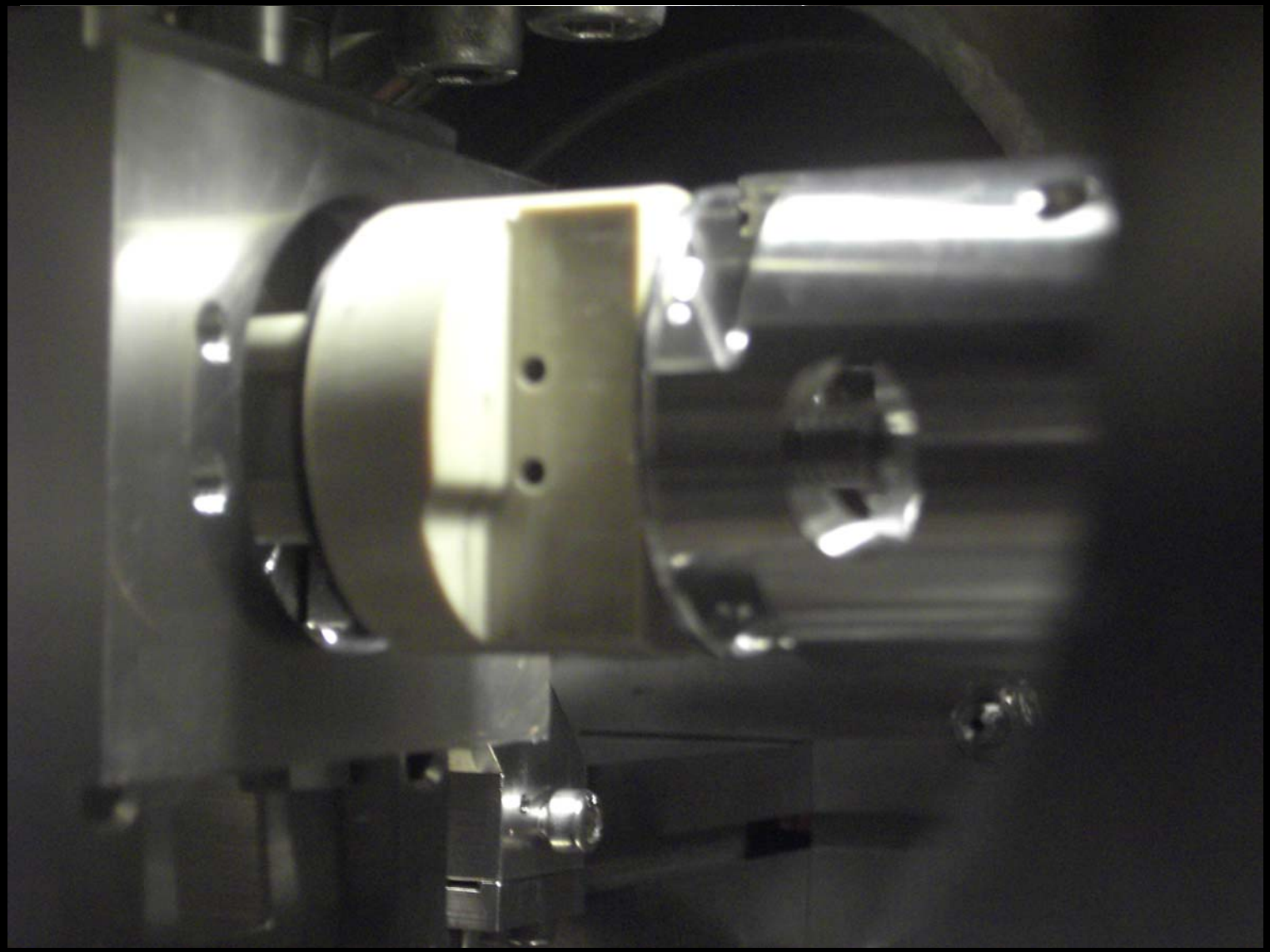


Removable sample holder piece with QCM

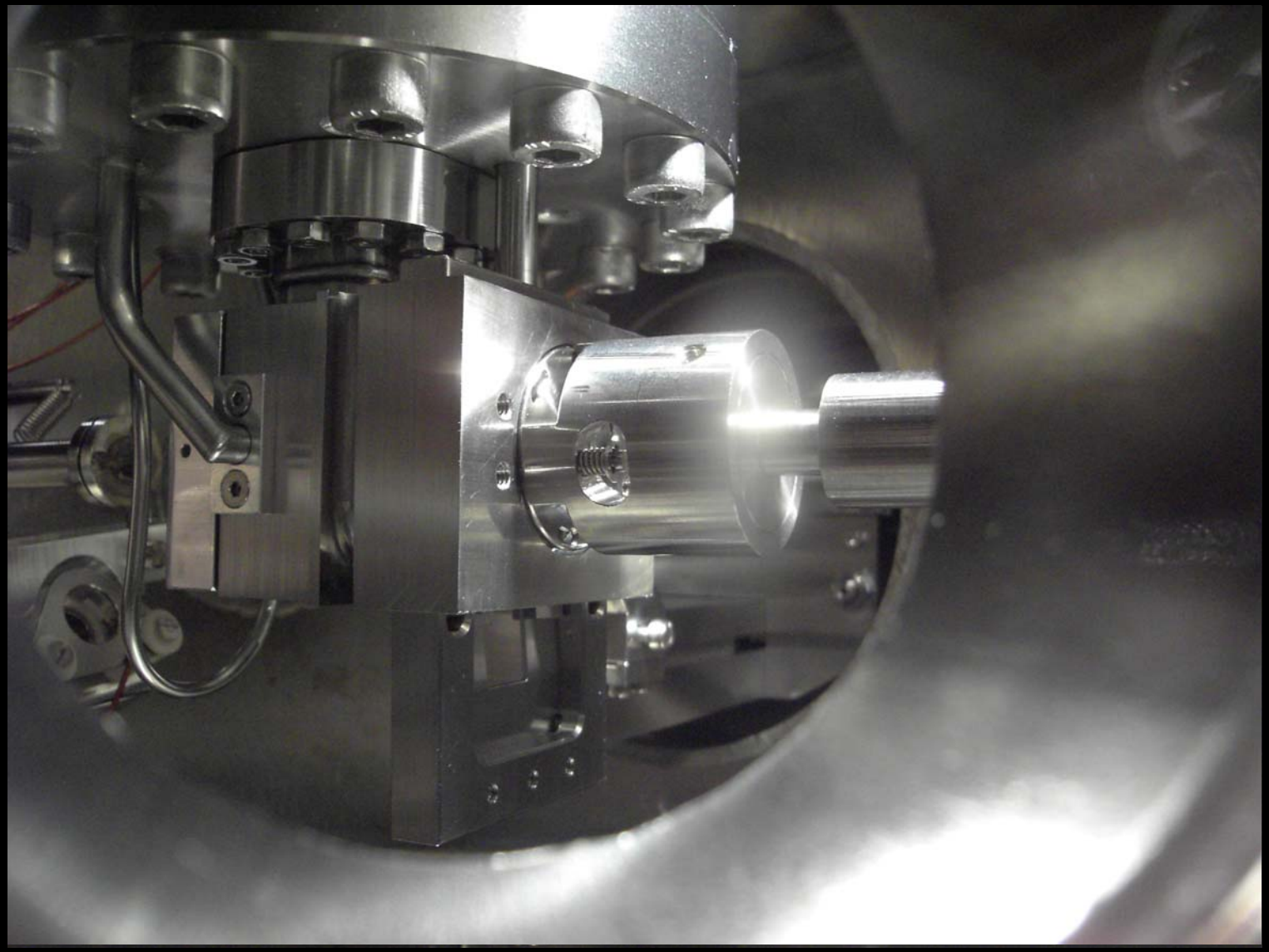
Environmental cell in vacuum chamber



Environmental cell in vacuum chamber

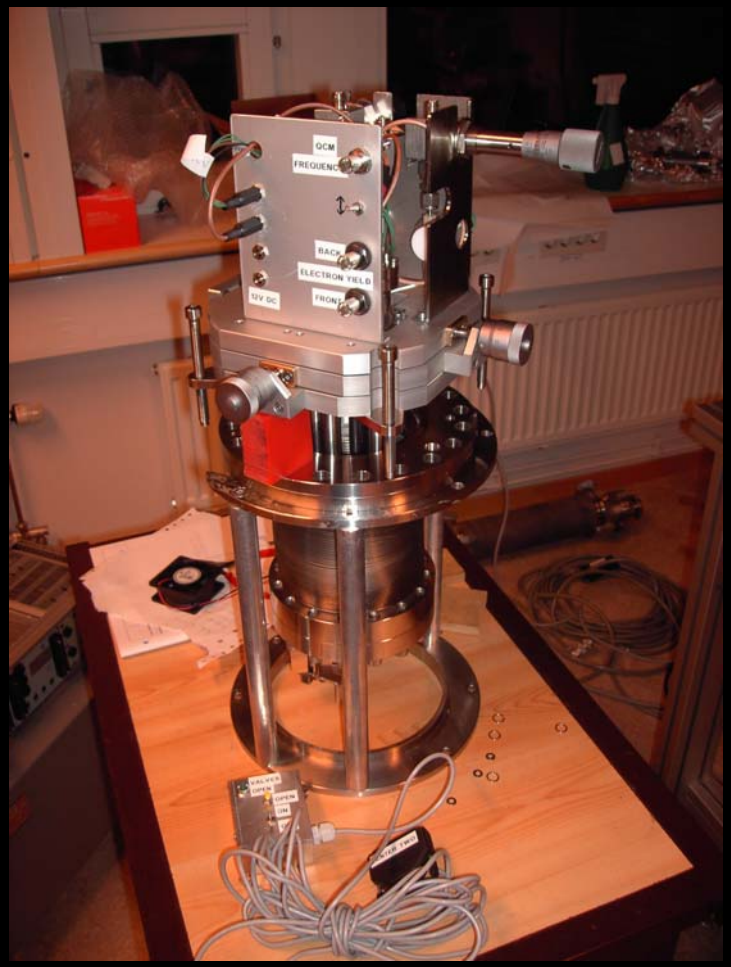


Environmental cell in vacuum chamber

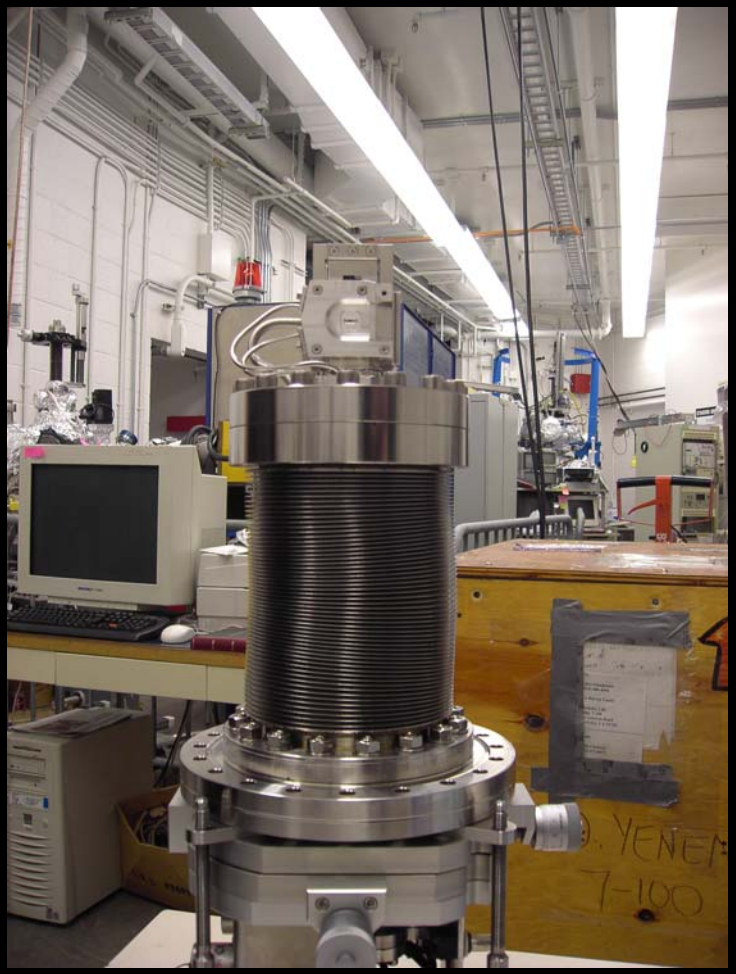


Environmental cell prior to mounting…

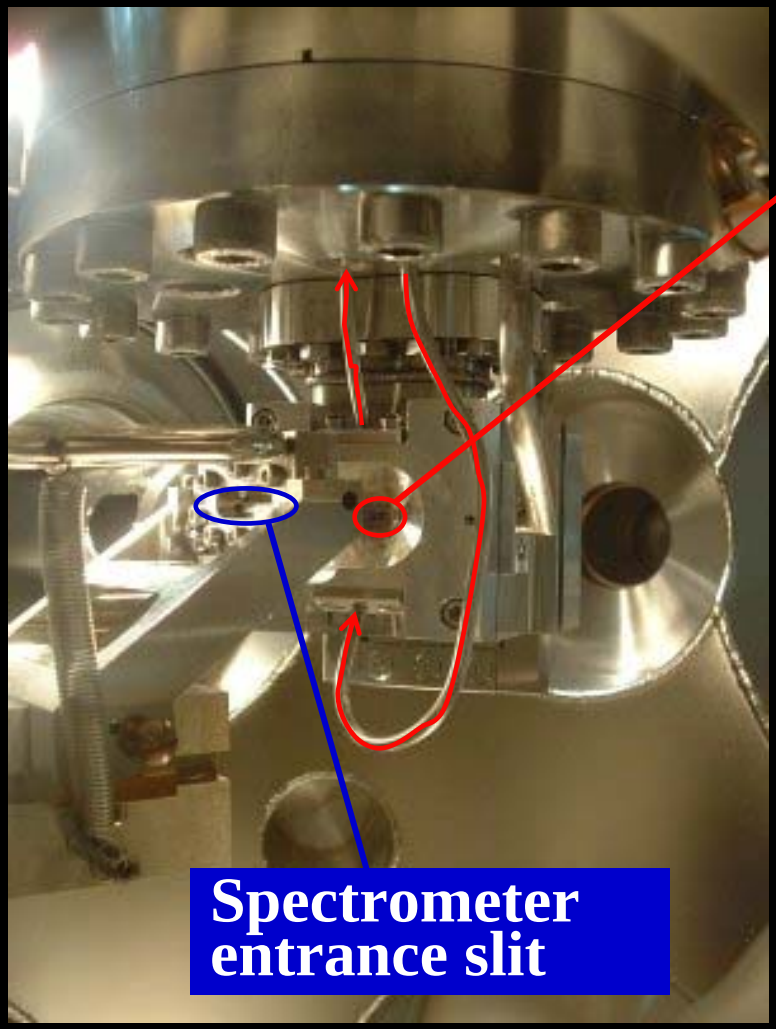
At home lab

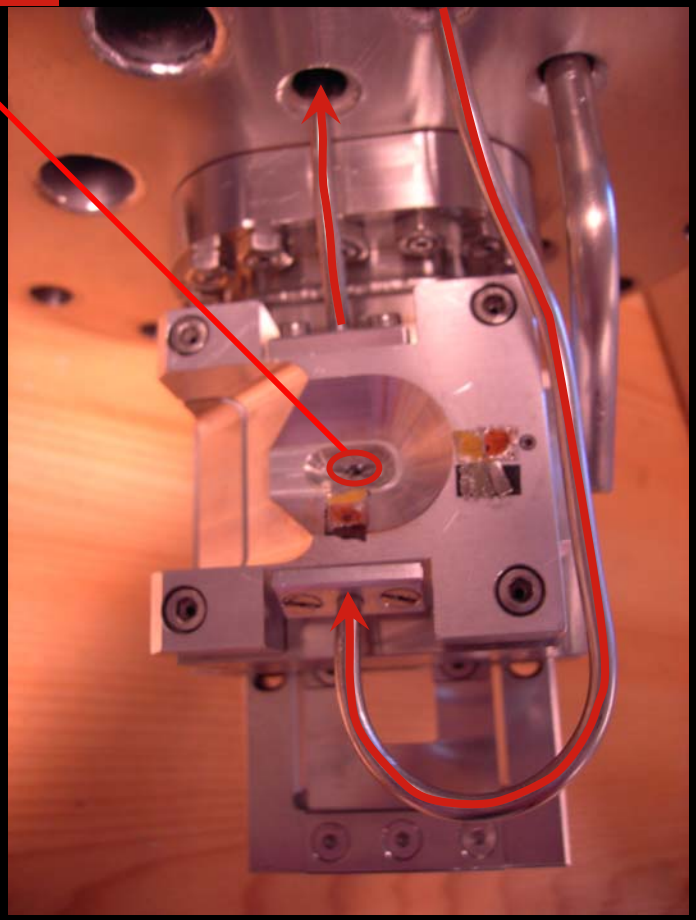


After shipping to ALS…



Environmental cell in the vacuum chamber

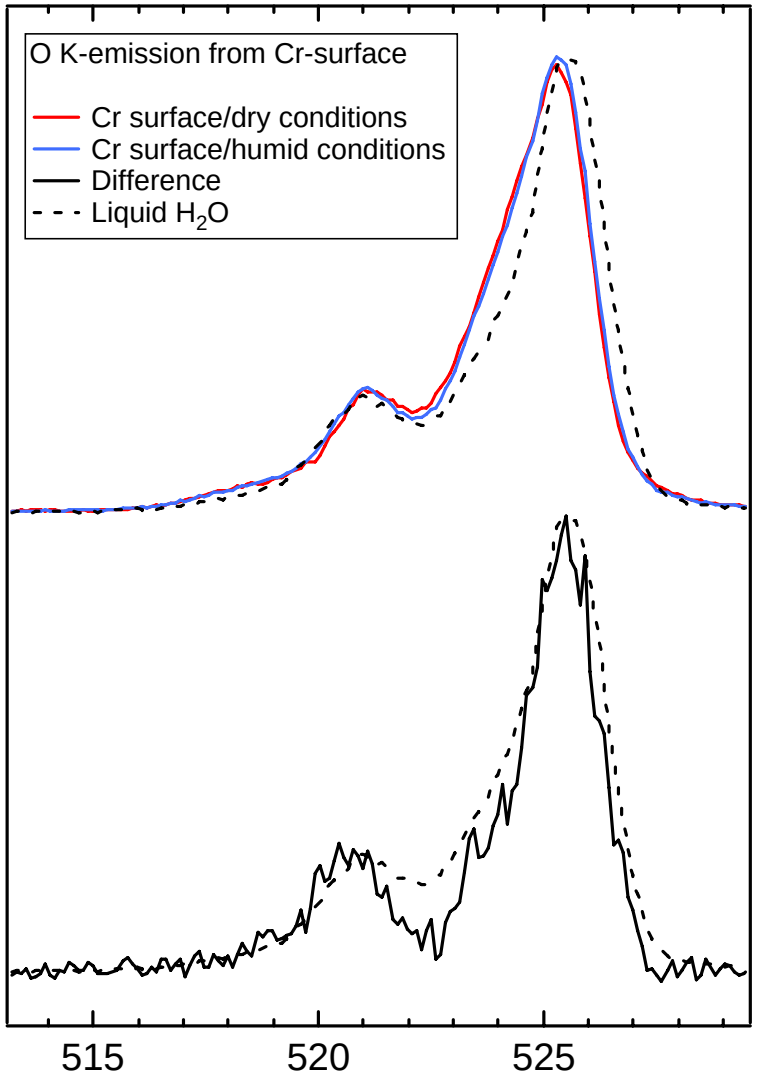




Environmental cell in the chamber…

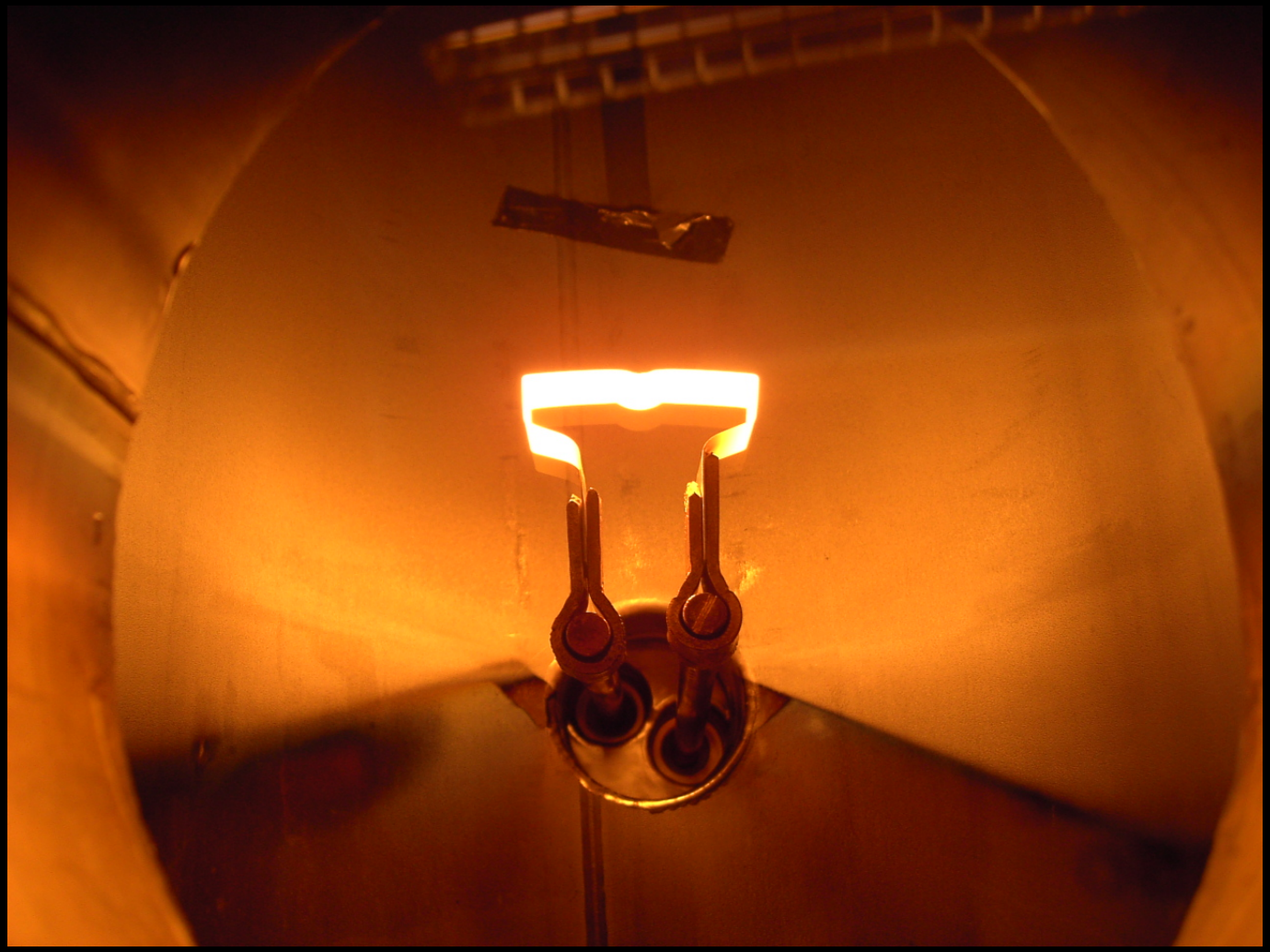
The beam is on…

Water layers on surface at atmospheric pressure



O *K*-emission from Cr-film (oxidized) with and without humid nitrogen present.

Evaporating thin metal films onto QCM

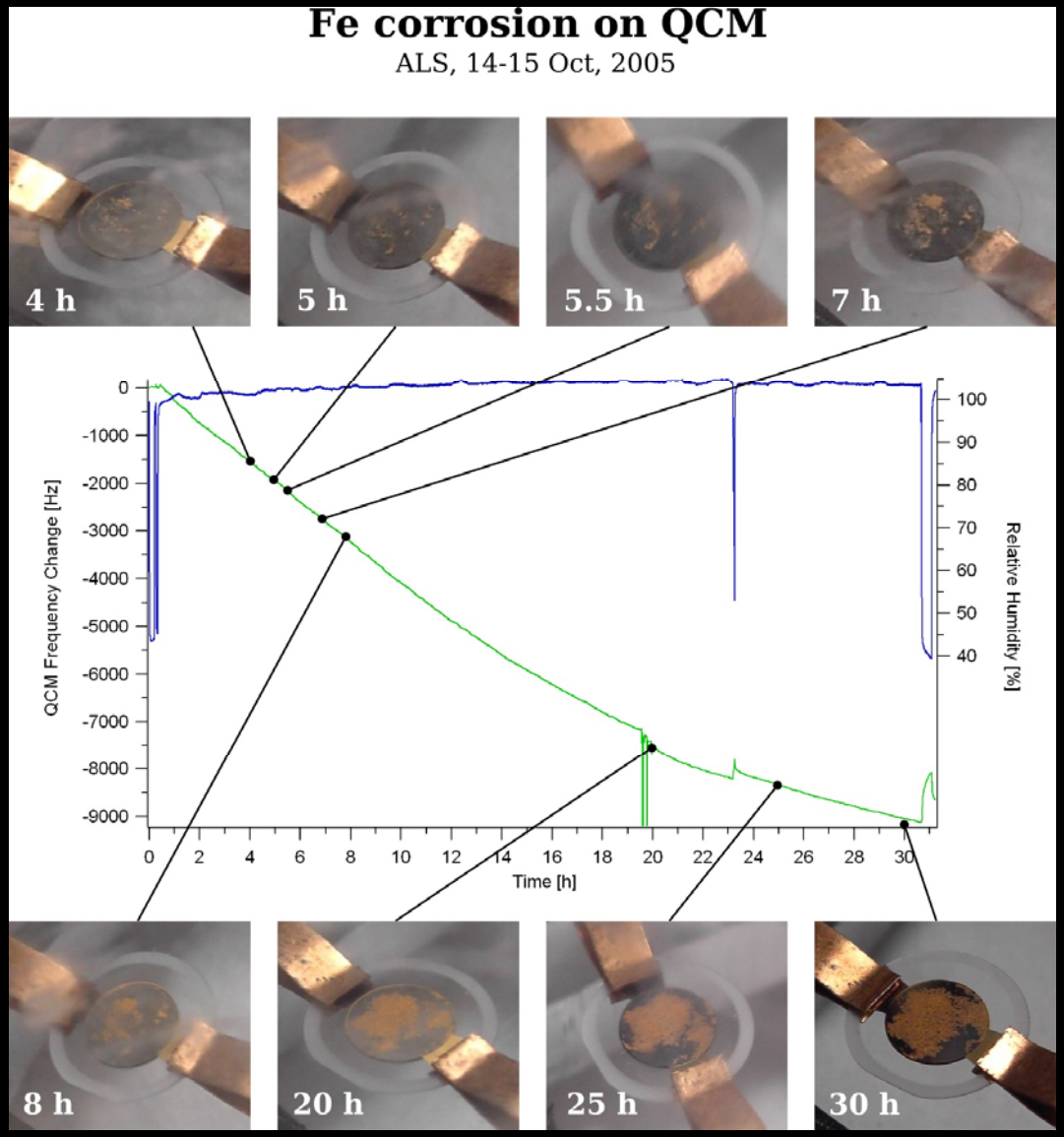


How quickly does iron turn into rust?

…add salt and it can take as little as about ***12 h*** for a 50nm Fe-film to oxidize.

On right: ***time lapse series*** of a Fe-layer (100nm) subjected to 100% humid air…

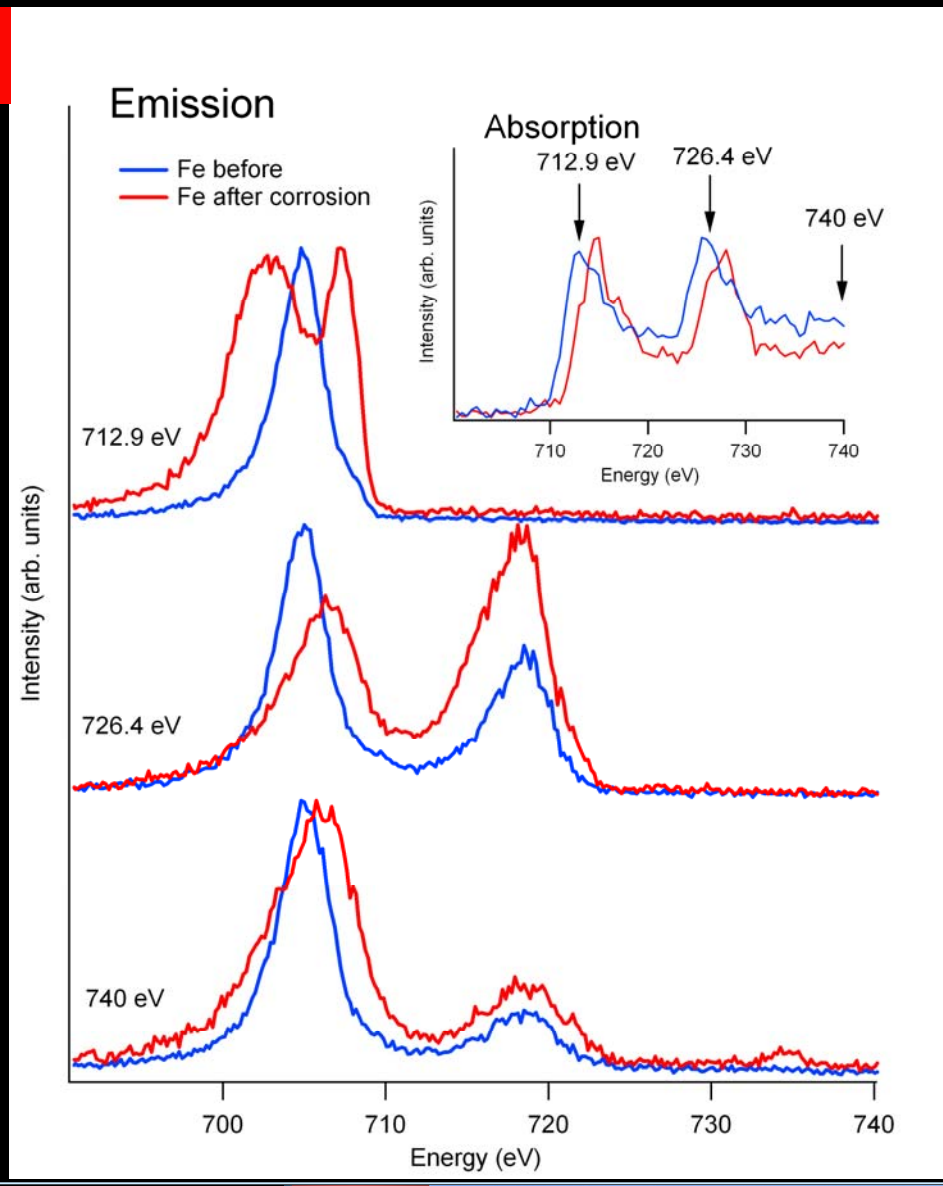
… and QCM frequency changes.



What is the spectroscopic fingerprint of rust ?

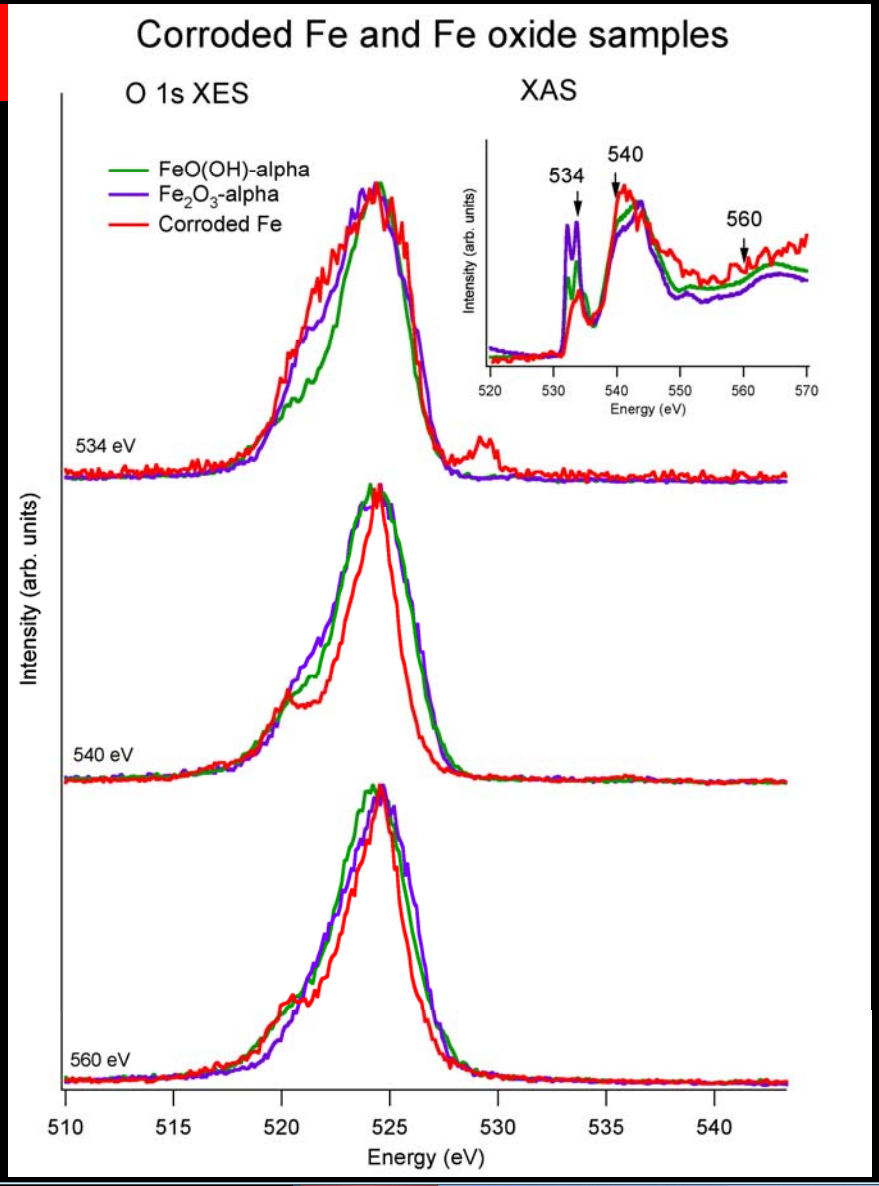
Fe *L*-edge

An *iron film* that has corroded in humid air is expected to resemble FeOOH…



Check with reference samples…

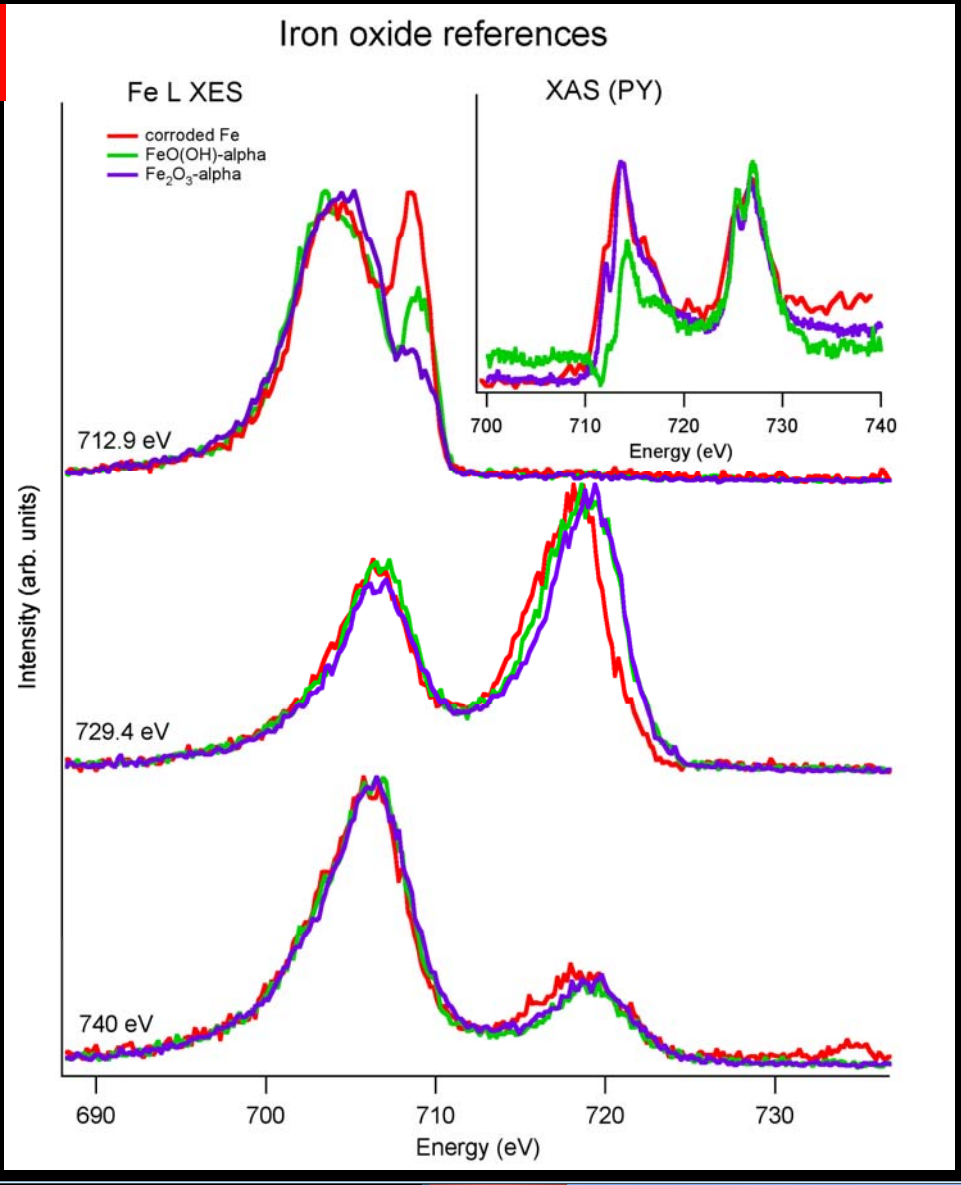
O *K*-edge



Corrosion product is somewhat different from both Fe_2O_3 and FeOOH.

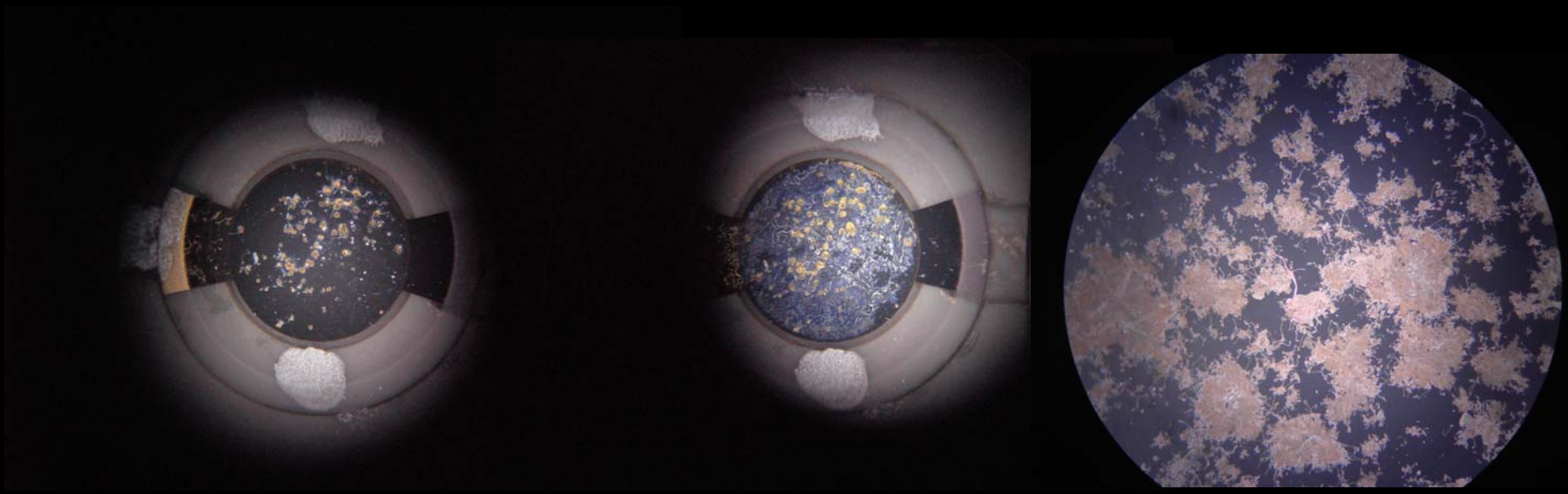
Check with reference samples…

Fe *L*-edge



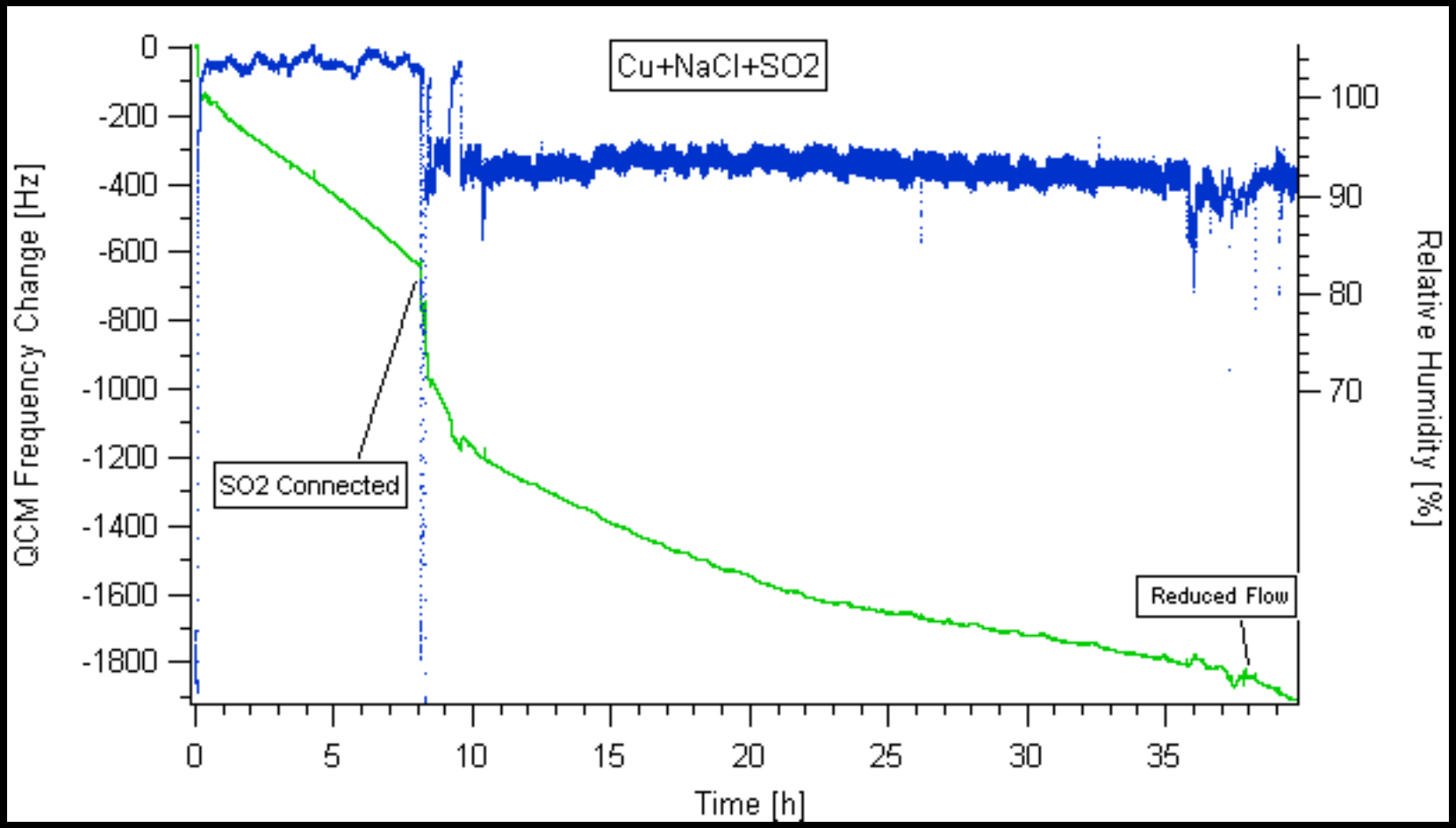
Environmental cell poject: Goals

- grow metal films *in situ* on QCM
- RIXS of surface degradation from a flow of corrosive artificially produced atmosphere: air, humidity, SO_2, O_3, NO_2
- simultaneous *in situ* monitoring of mass change and SXES
- *spatial* resolution: 2D, 3D?



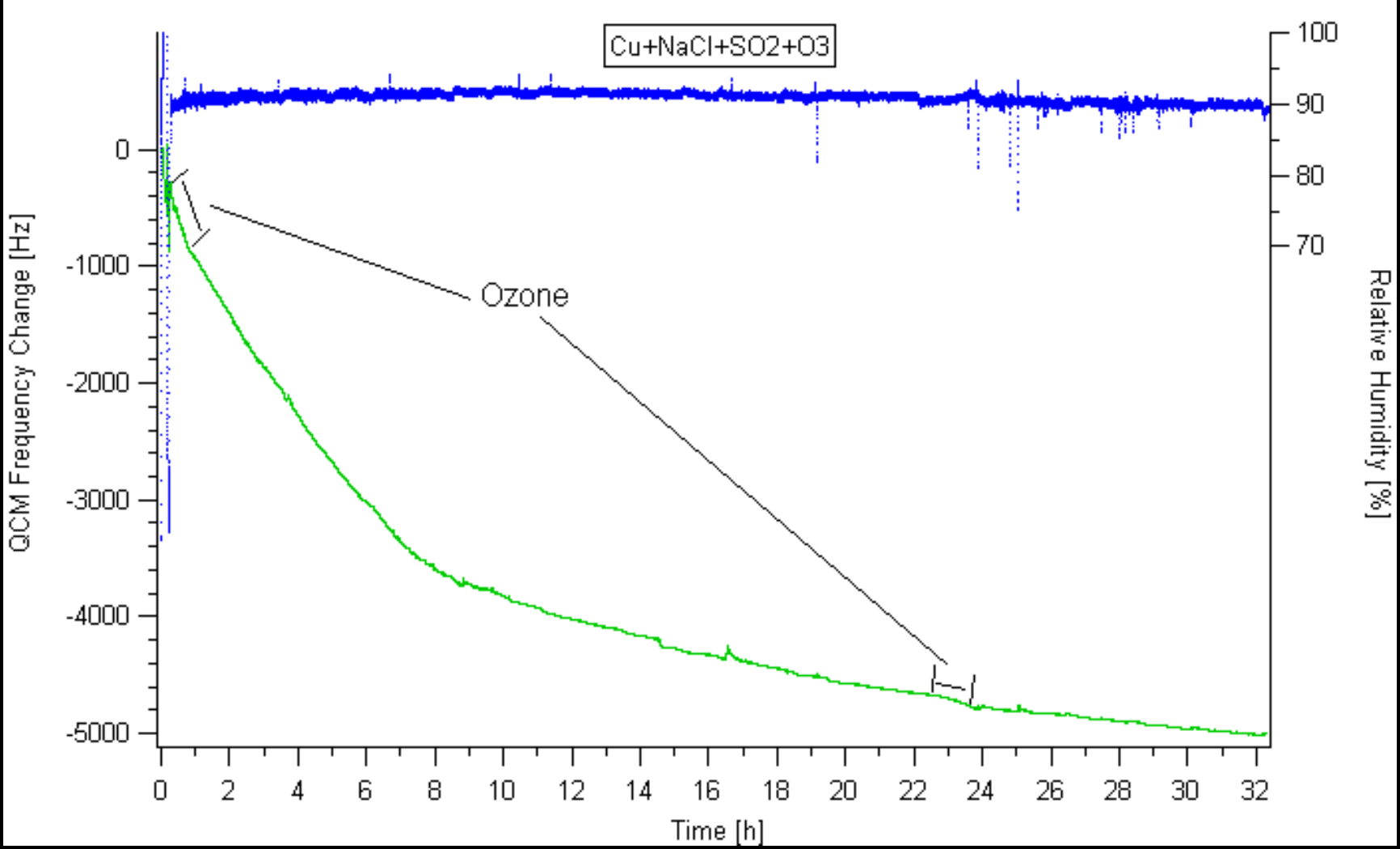
Pollutants accelerate corrosion of copper

Humid air + SO_2



Pollutants accelerate corrosion of copper

Humid air + SO_2 + O_3



Conclusions

- O *K*-RIXS rich source of information for NiO and other strongly correlated materials - higher resolution wanted!

- Environmental cell up and working!

- First *in situ* atmospheric corrosion spectra give ***fingerprints*** of reaction products

- Detailed **electronic structure** information about chemical process.

Thanks to…

Prof. J. Nordgren, head of USX group

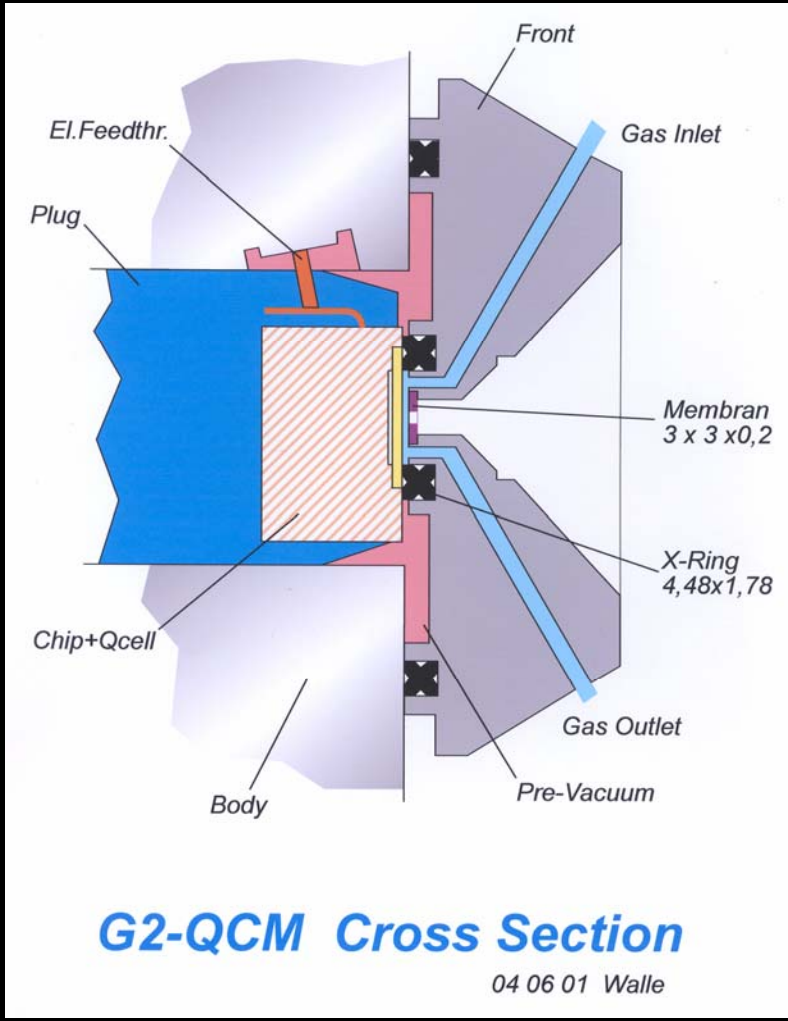
QCM Collaborations (exp.): Prof. C. Leygraf, Dr. T. Aastrup, Prof. U. Karlsson

SCM Collaborations (theor.): Prof. K. Okada, A. Kotani, Dr. M. Matsubara

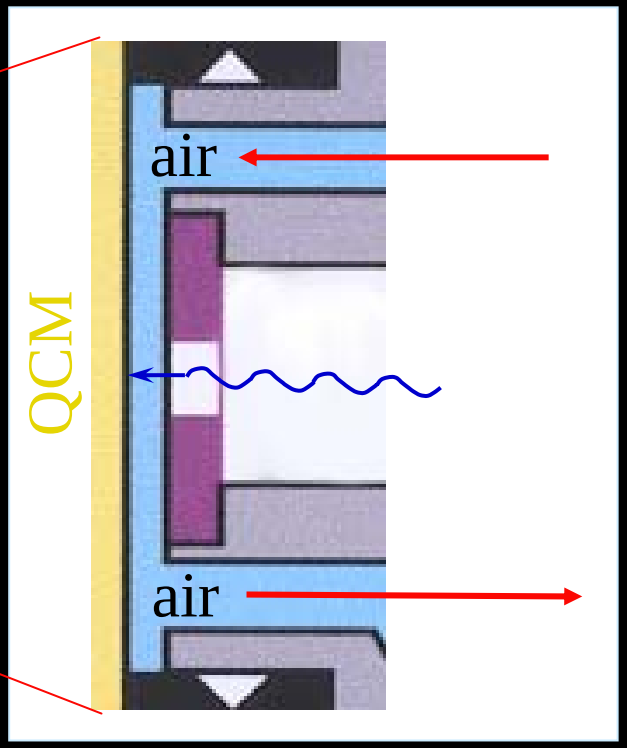
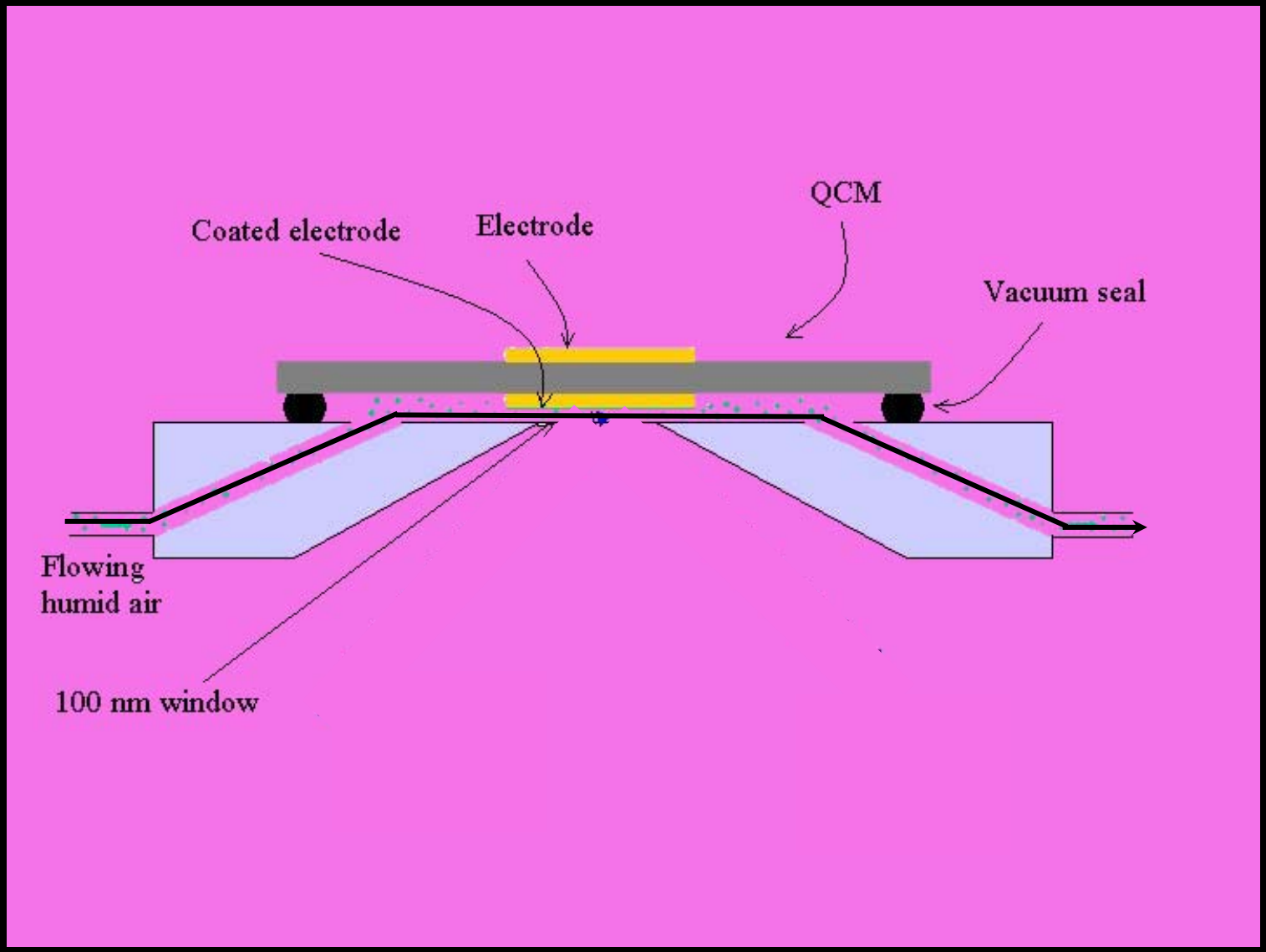
PhD students: J. Forsberg, A. Olsson

ALS beamline assistance/collaboration: Dr. J. Guo, Dr. T. Schmitt, Dr. T. Käämbre, P.-A. Glans, T. Learmonth, A. Guy, Dr. D. Kilcoyne, Dr. J. Bozek, Dr. S. Canton

Schematic view of the *environmental cell*



Schematic view of the *environmental cell*



Environmental cell principle drawing