Understanding the Electronic Structure of Matter in Liquid Form Using Soft X-Ray XANES and RIXS

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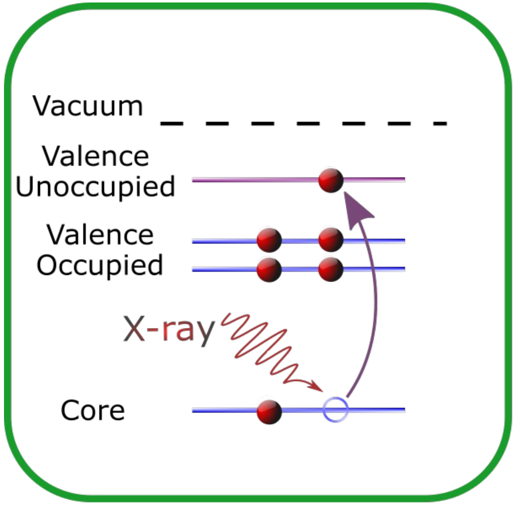
HESEB Webinar, 20 October 2020

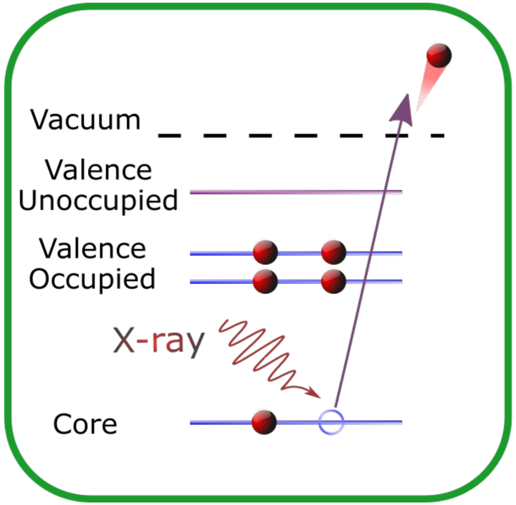
Outline

- Soft **X**-ray **A**bsorption **N**ear **E**dge **S**pectroscopy and **R**esonant **I**nelastic **X**-Ray **S**cattering:
  - Theory
  - Methodology
- Various Applications

Core-level absorption

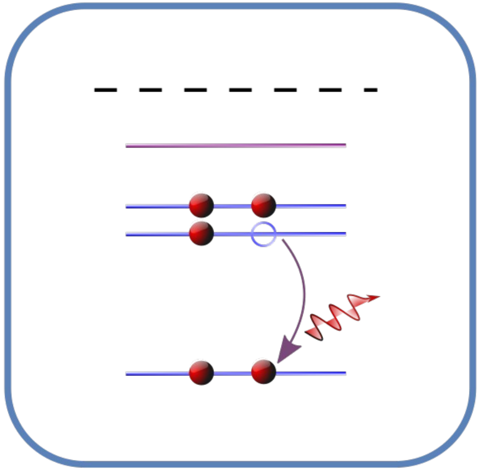


Resonant X-ray absorption (XAS/XANES)

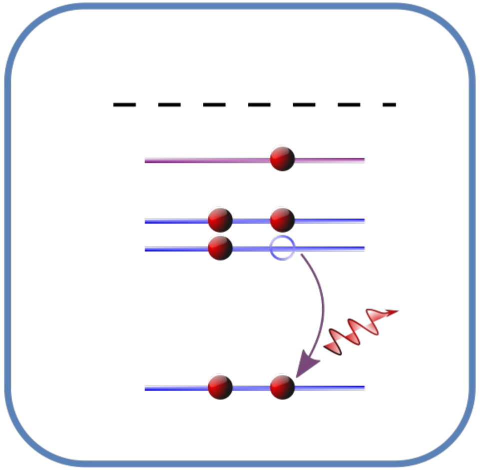


Core-level photoemission

Radiative decay

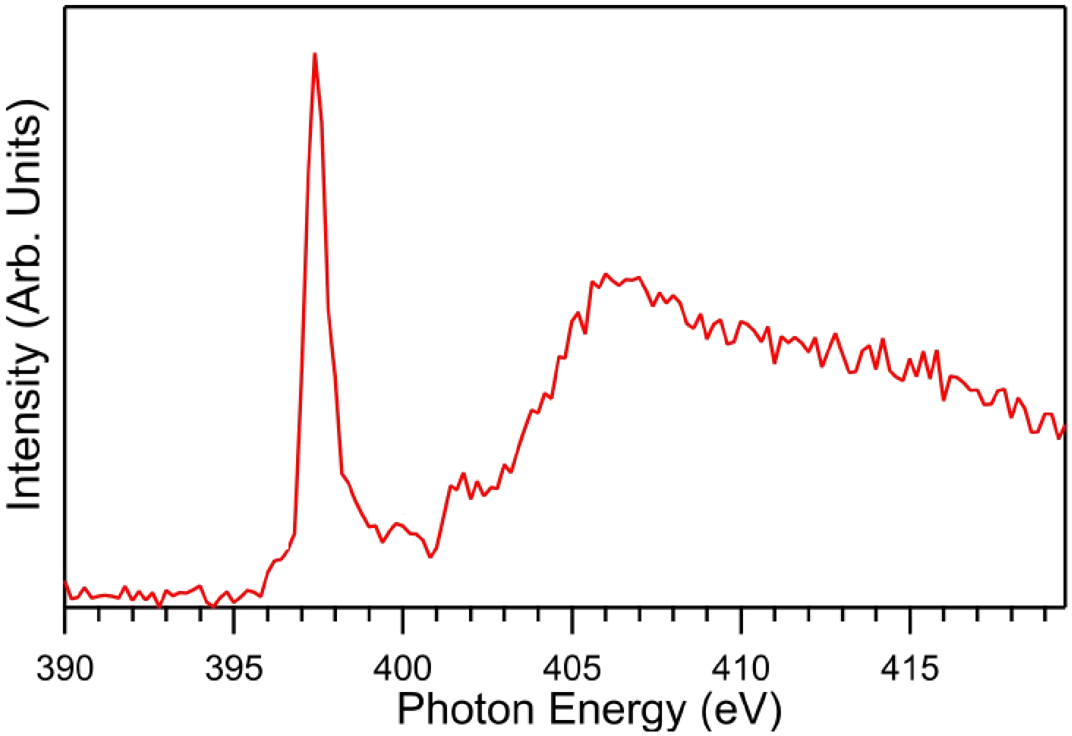


Non-resonant X-ray emission
(XES)



Resonant inelastic X-ray scattering
(RIXS)

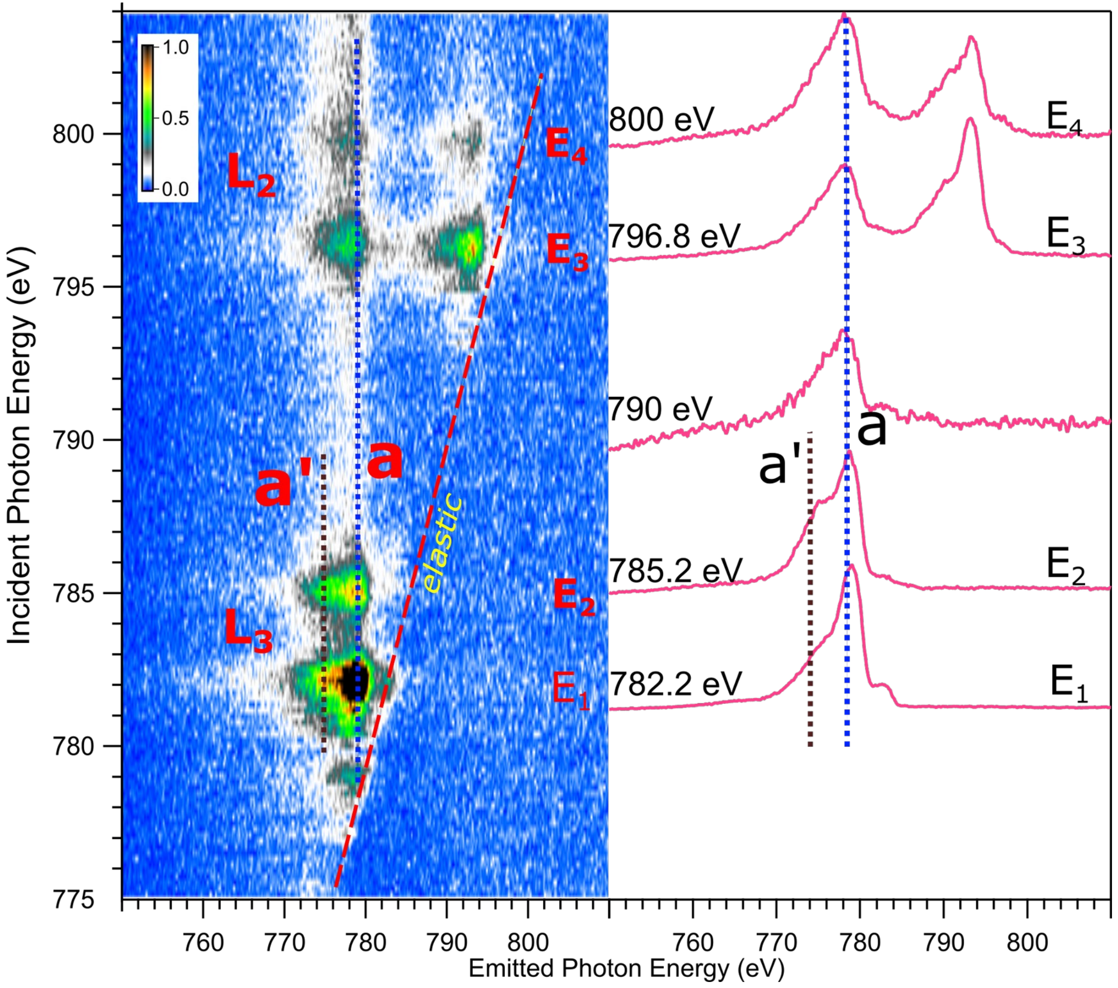
A typical XANES spectrum



- photon-in photon-out
- near-edge features and chemical shifts provide information
- various measurement modes: transmission, TFY, PFY

Inorganic Chemistry, 2019, Vol 58, pages 4731-4740

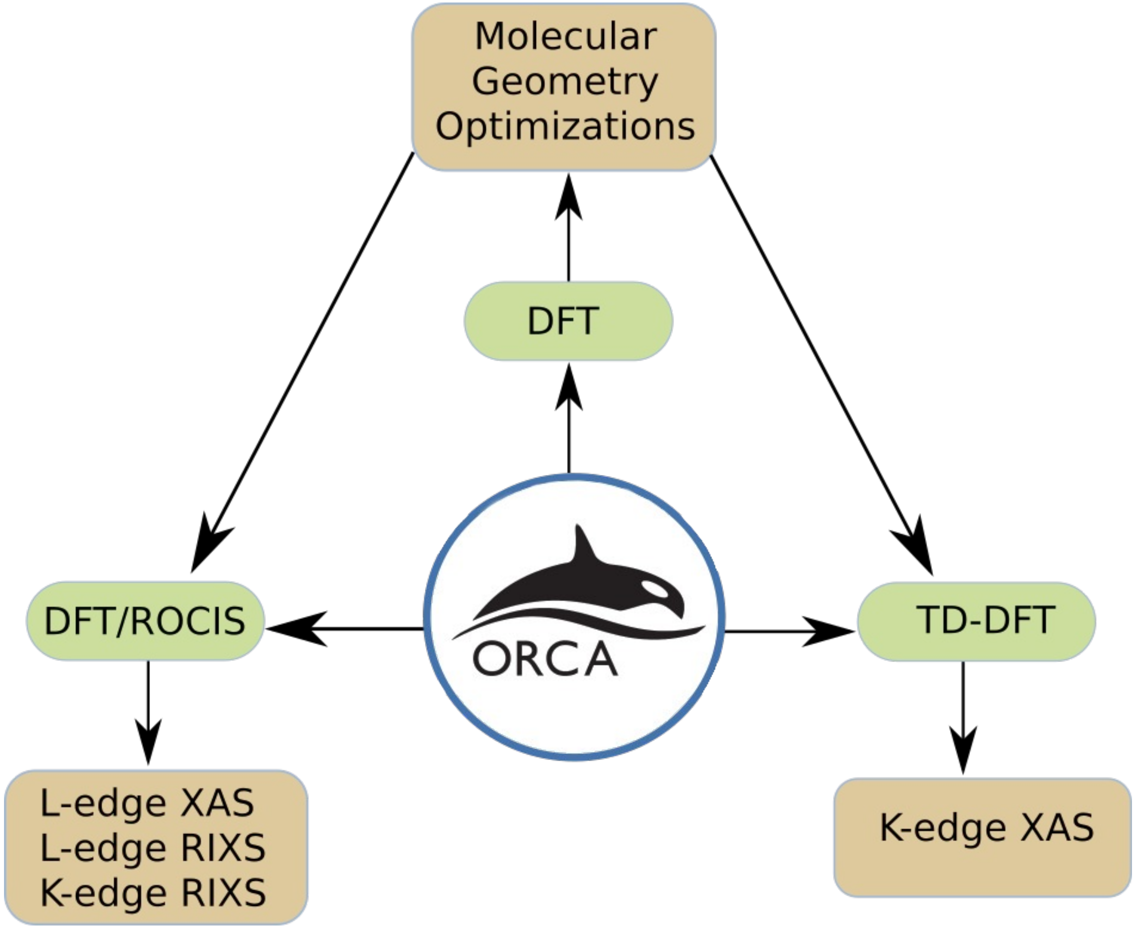
A typical RIXS spectrum



Scientific Reports, 2017, Vol 7, page 40811

- Raman vs. Fluorescence features
- Emission pattern dependent on excitation energy
- Resonance occurs where absorption is strong

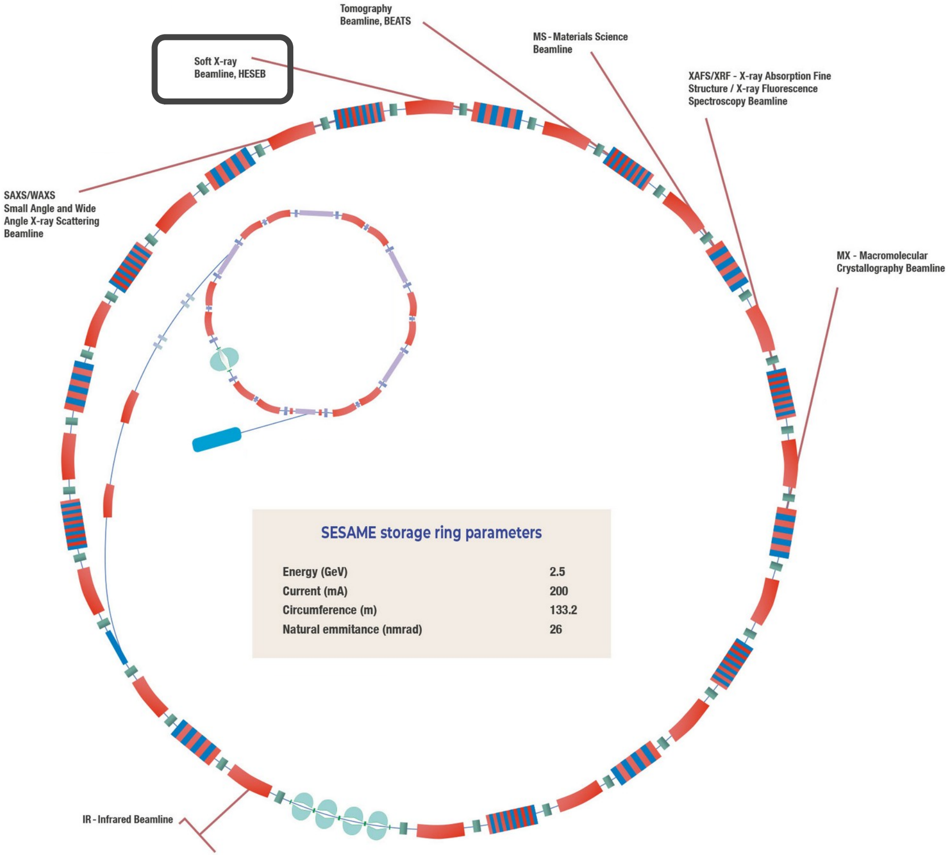
First principles computational methods



WIREs Comput Mol Sci, 2018, Vol 8, 1759

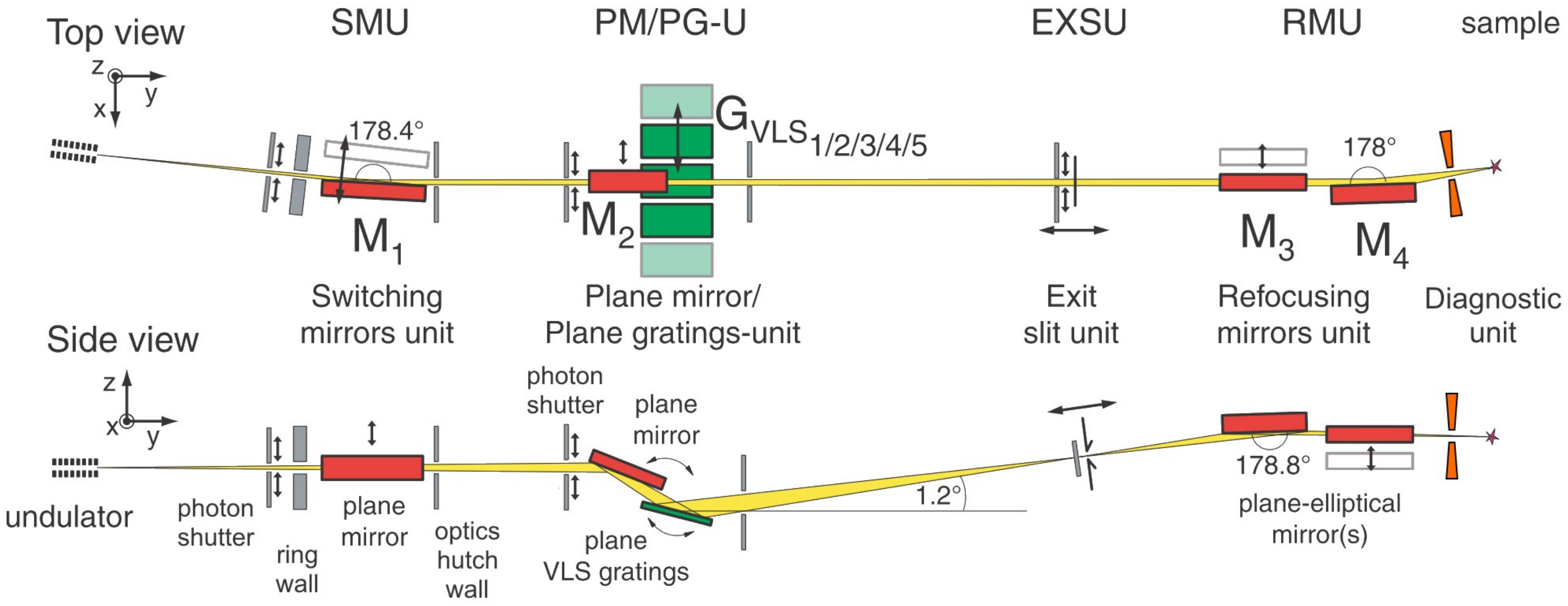
S.S.N.Lalithambika, http://dx.doi.org/10.17169/refubium-2725

A third generation synchrotron and a soft X-ray beamline

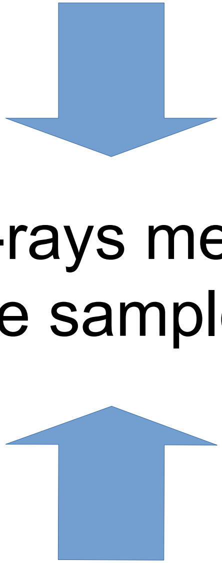


https://www.sesame.org.jo/sites/default/files/2017-11/machine2.jpg

Layout of a soft X-ray beamline (P04 - Petra III)

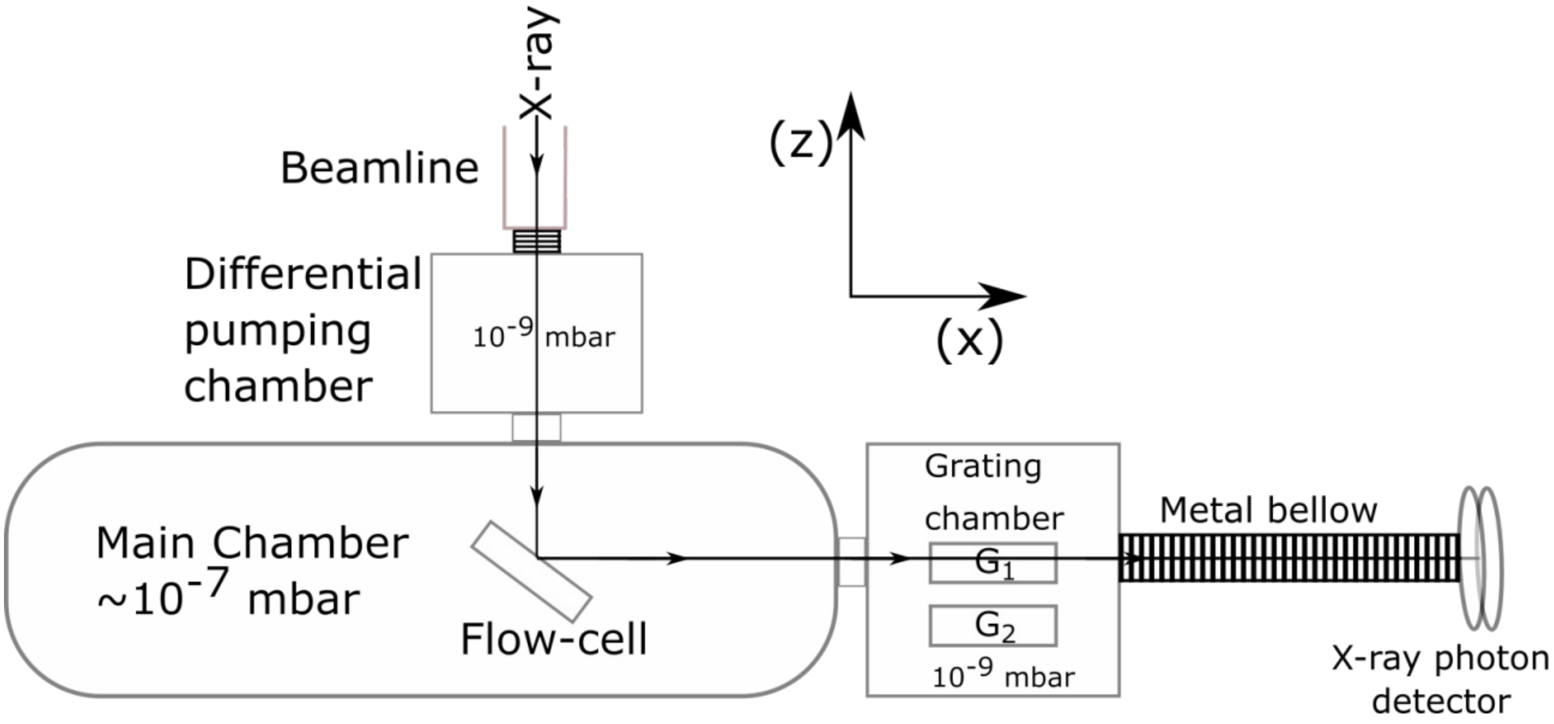


X-rays meet the sample



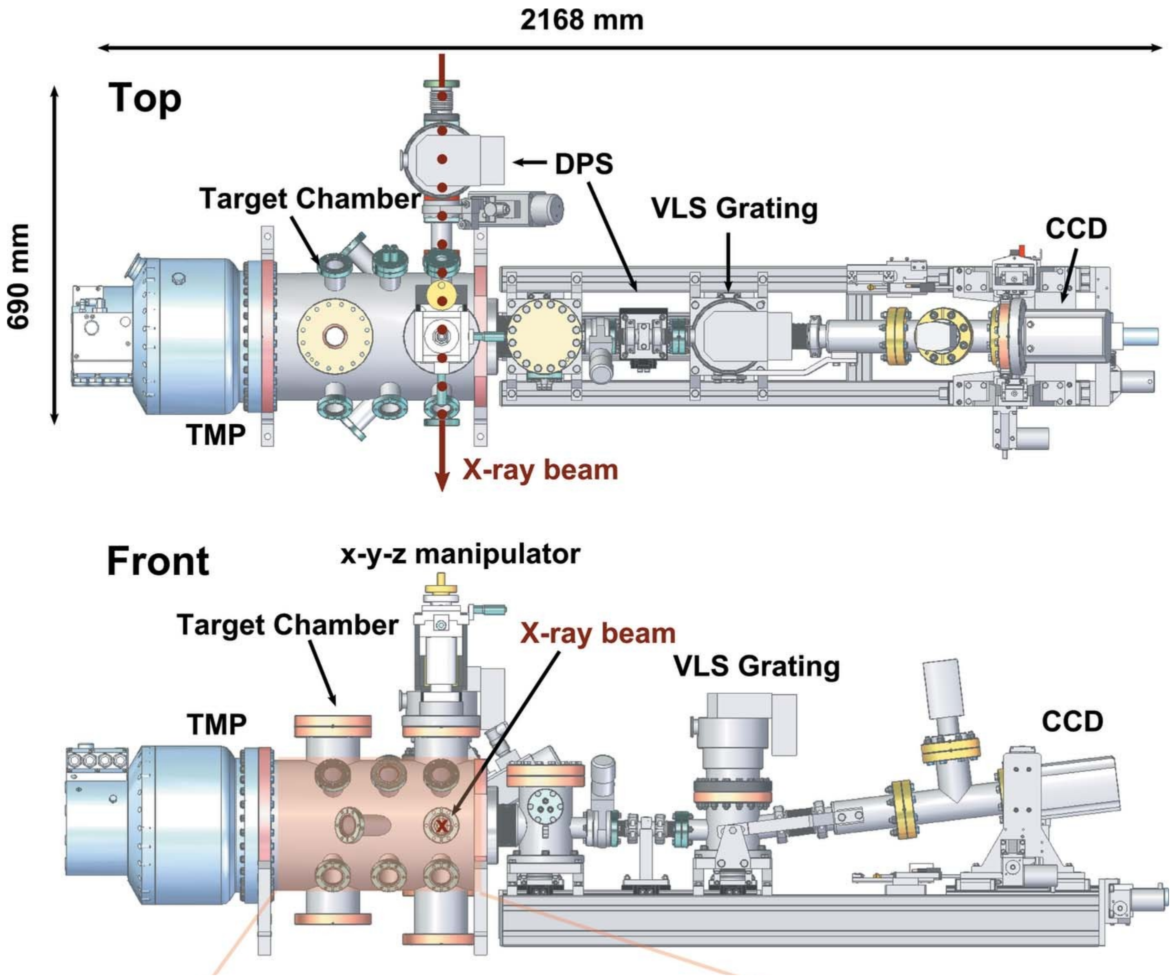
https://photon-science.desy.de/facilities/petra_iii/beamlines/p04_xuv_beamline/beamline_layout/index_eng.html

A typical endstation capable of XANES/RIXS applied to liquids



S.S.N.Lalithambika, http://dx.doi.org/10.17169/refubium-2725

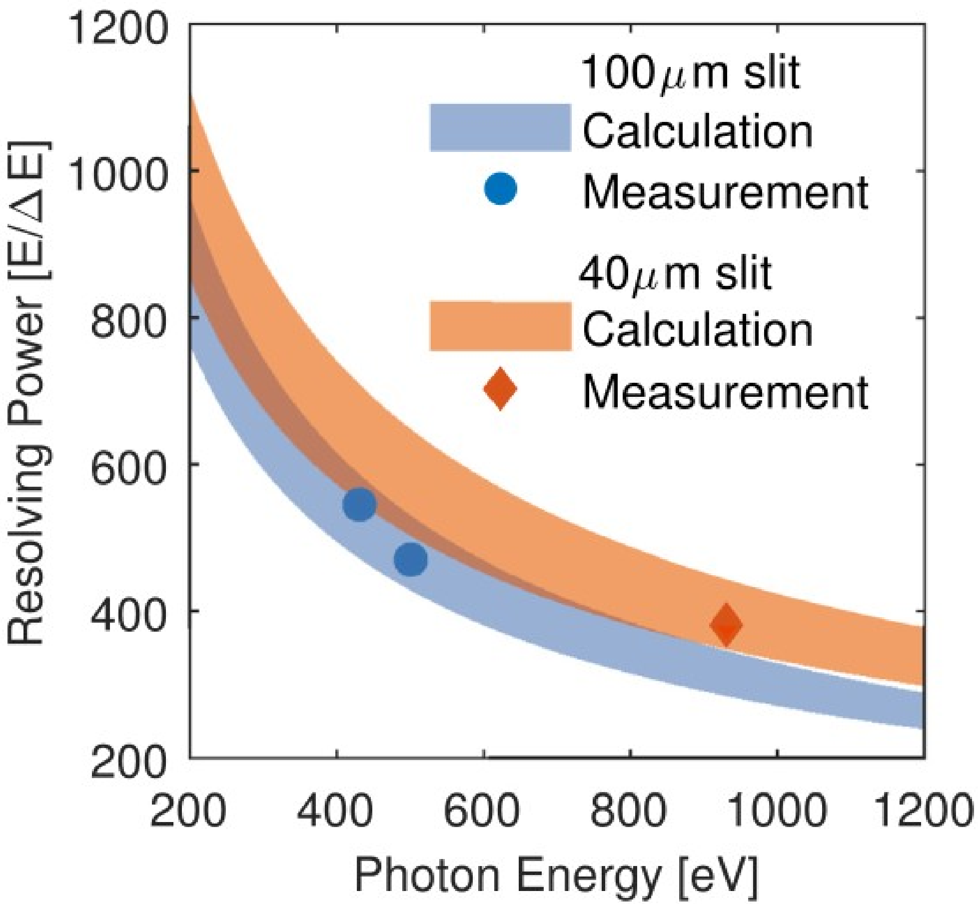
ChemRIXS



- Compact and mobile
- Low cost (~300k)
- Acceptable resolution

J. Synchrotron Rad. (2017), 24, 302–306

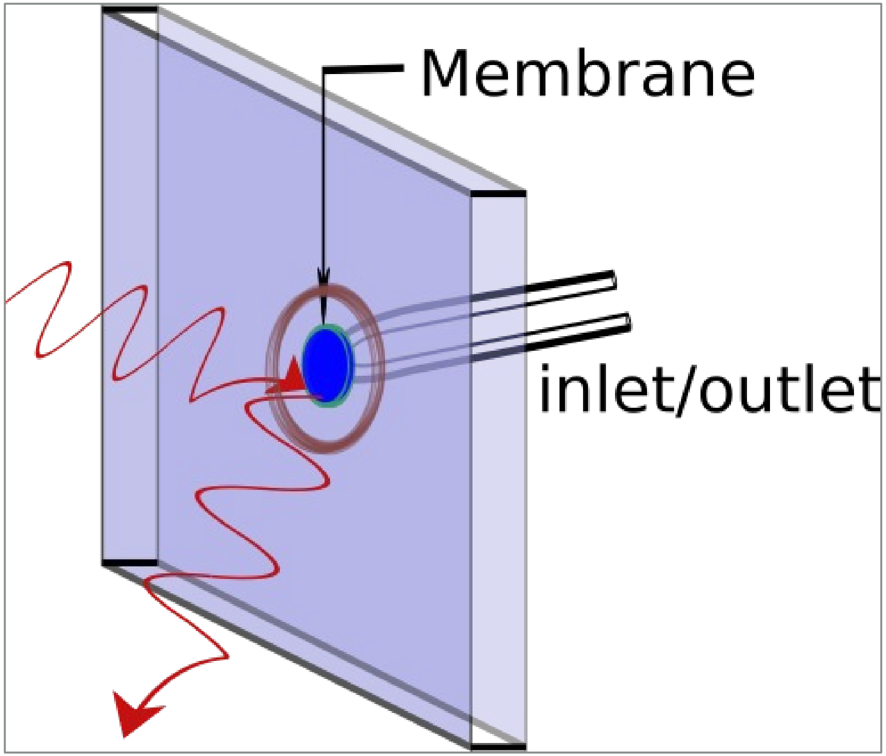
Resolution



- proportional to detector arm length
- inversely proportional to grating line width and camera pixel size

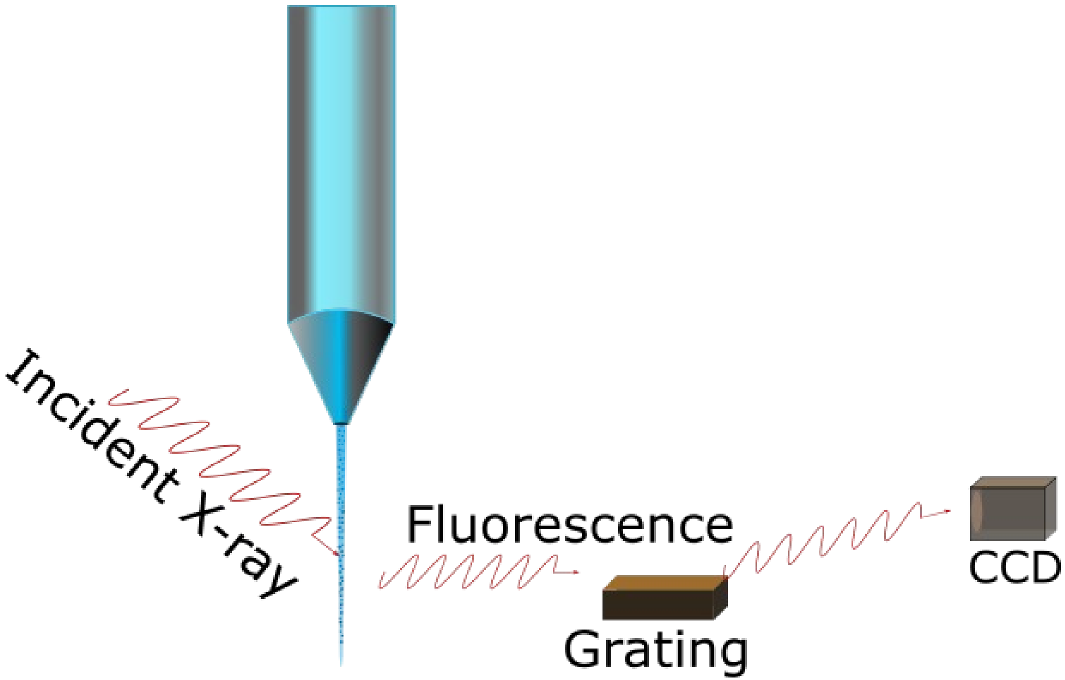
Nuclear Inst. and Methods in Physics Research, A 922 (2019) 114–118

The liquid flow-cell technique



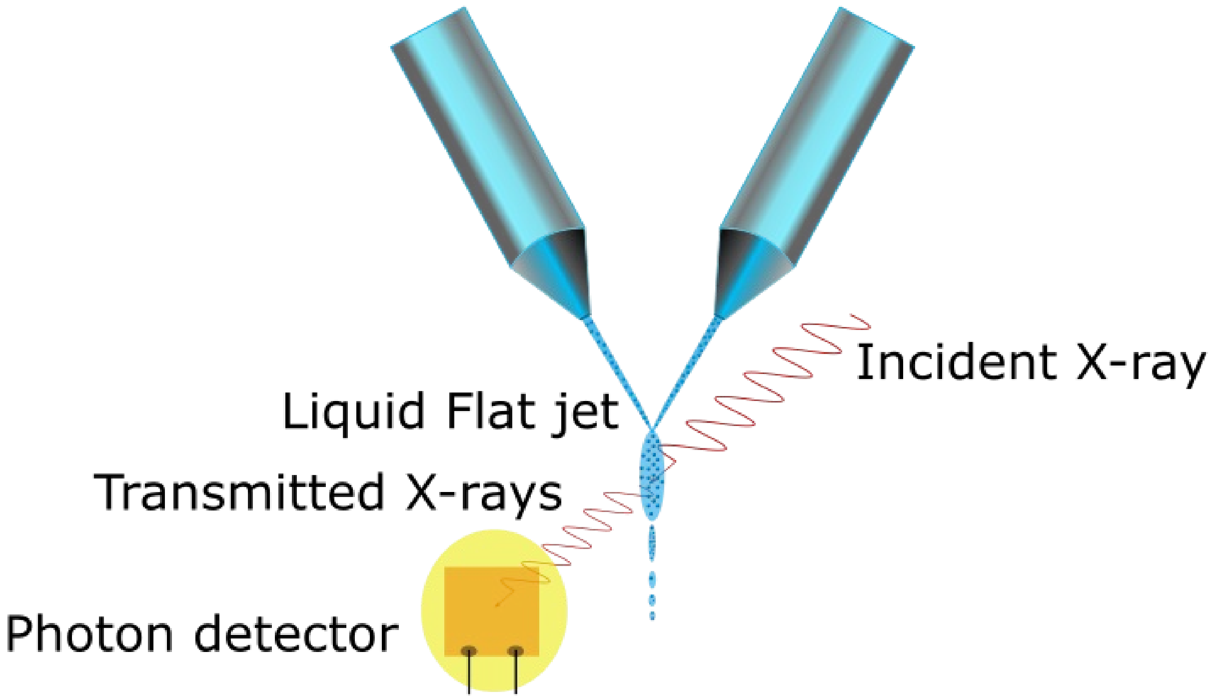
- allows for absorption measurements using fluorescence yields
- fresh sample is flown minimizing sample damage
- suitable for samples in small amounts

The liquid micro jet technique



- allows for absorption measurements using fluorescence yields
- lack of membranes resolve sample-membrane interaction issues
- fresh sample is flown effectively nullifying sample damage
- suitable for samples in larger amounts

The flat jet



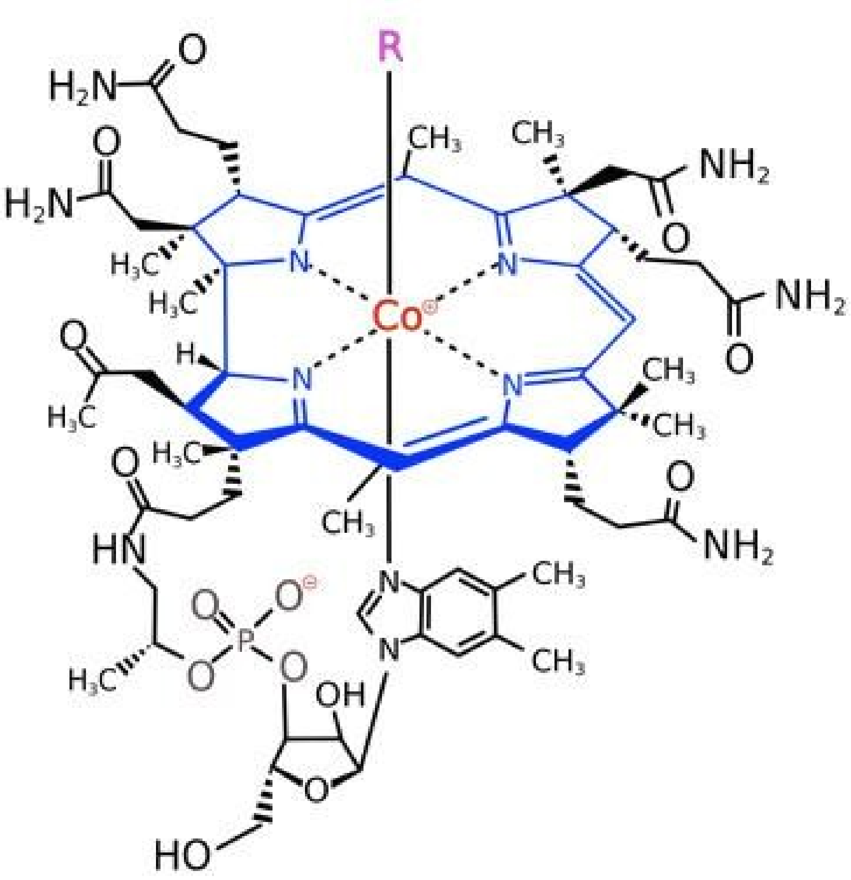
- allows for a “true” absorption measurement in the transmission mode
- resolves the issues arising from the deviations between fluorescence and transmission mode absorption

What type of questions can liquid state XANES/RIXS address?

We have an active site in a functional molecule, it has a central atom (such as a TM):

- What type of bonding does it exhibit? (pi, sigma,...)
- What is its coordination with neighboring atoms?
- What is its oxidation state?
- What is its spin state?
- Does the surrounding liquid have a chemical effect?
- How about electronic transitions such as d-d or charge transfer?
- ...

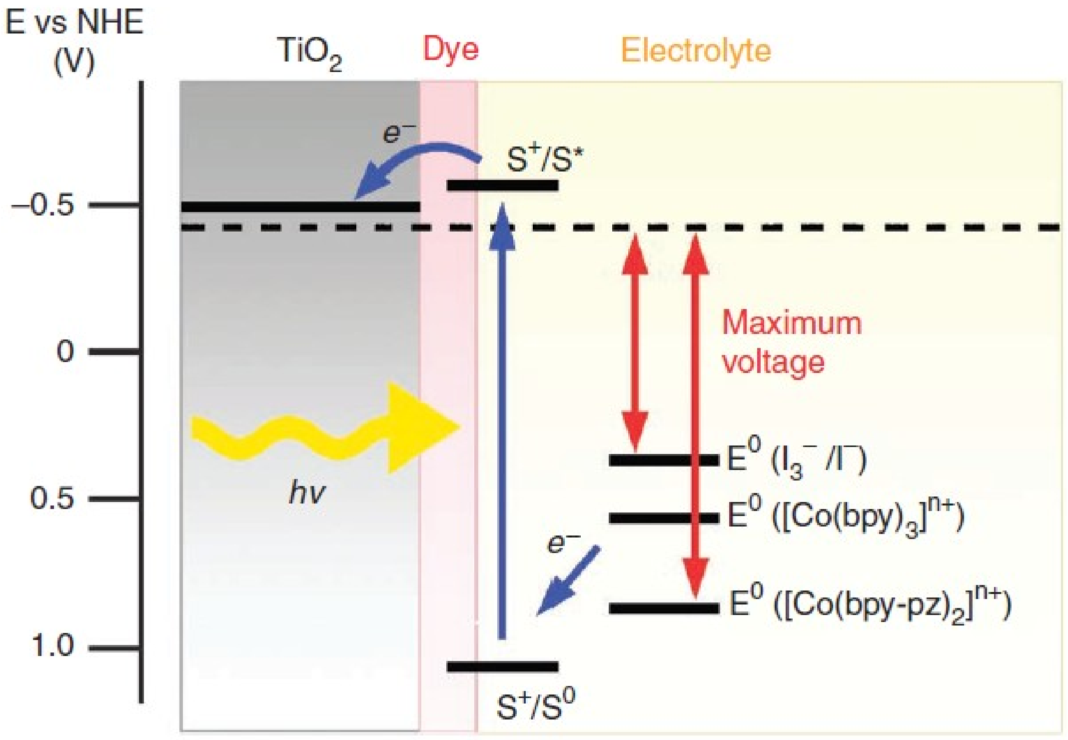
A biologically relevant Co TM-complex: Cobalamin (B12)



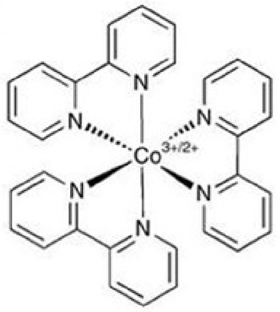
- The central Co^{3+} ion is vital for biological activity
- The alpha position (R) can bind to (CN^{-}, OH, CH_3, and 5-deoxyadenosyl) ligands

The Vitamins (Fifth Edition) Academic Press 2017

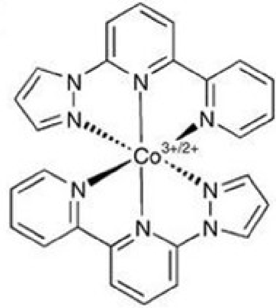
Cobalt TM-complexes in catalysis: electron mediators in a dye sensitized solar cell



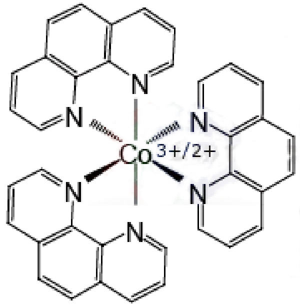
Nature Communications 3, 631 (2012)



$[Co(bpy)_3]^{2+/3+}$

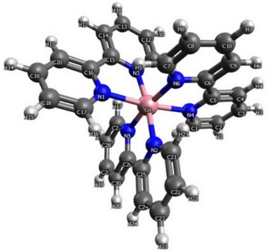


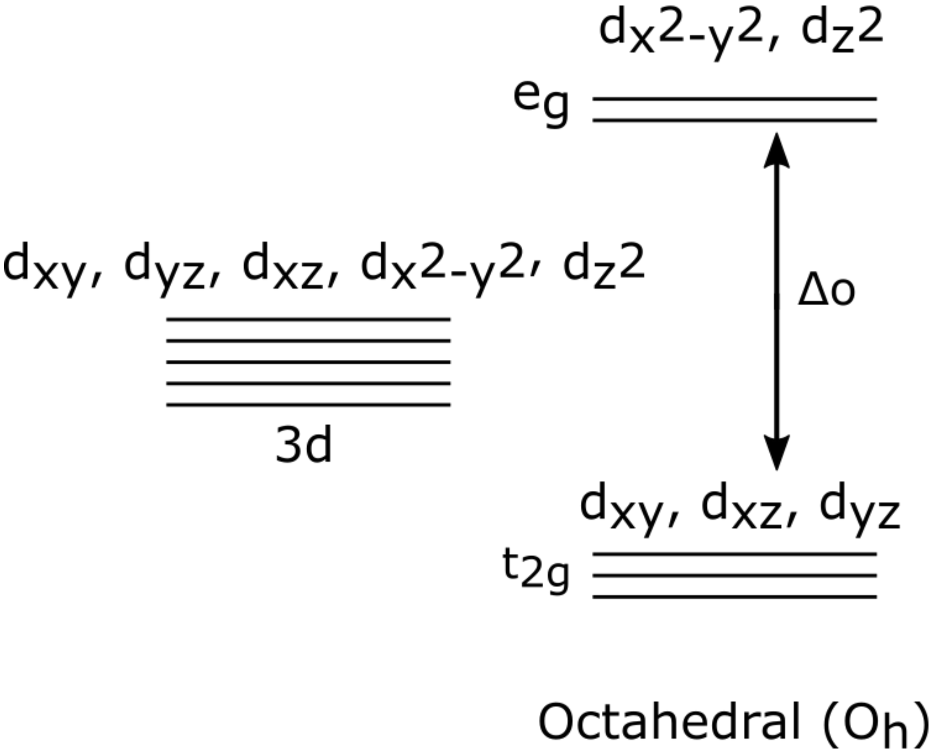
$[Co(bpy\text{-}pz)_3]^{2+/3+}$



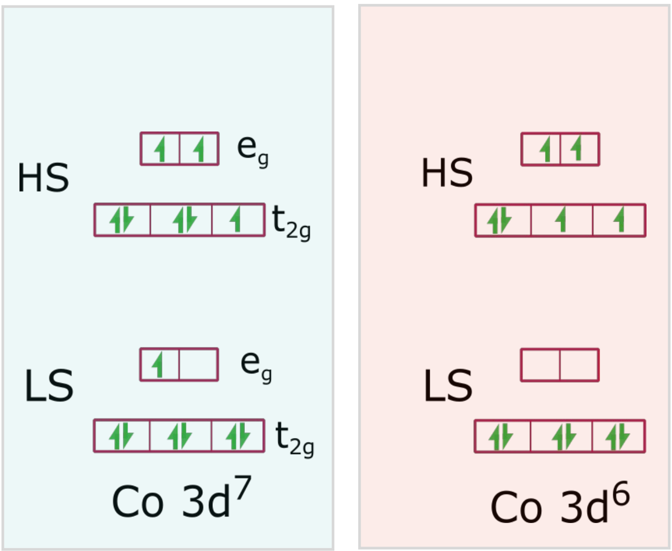
$[Co(phen)_3]^{2+/3+}$

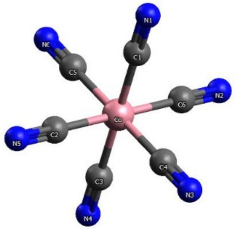
Octahedral splitting in strong ligand field





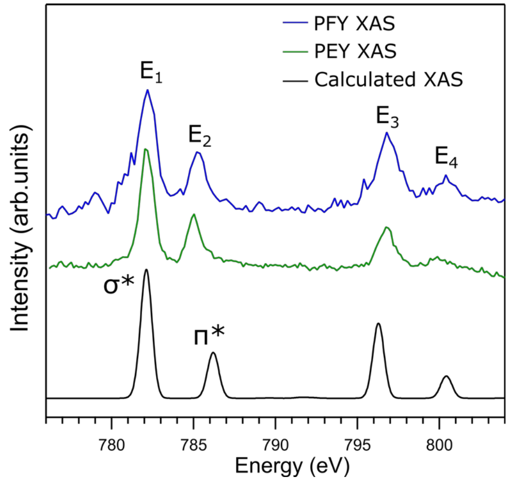
$[Co(bpy)_3]^{2+}$ $[Co(bpy)_3]^{3+}$

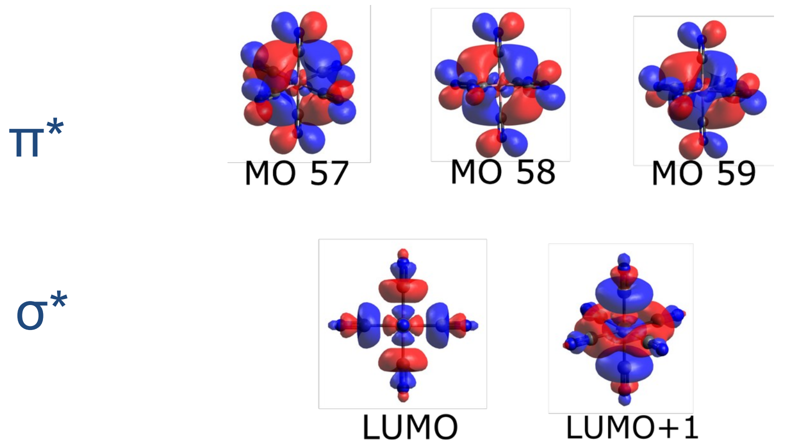


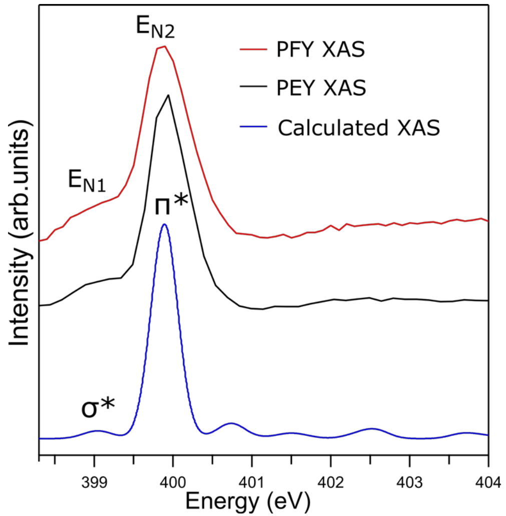


$[Co(CN)_6]^{3-}$

Aqueous $[Co(CN)_6]^{3-}$



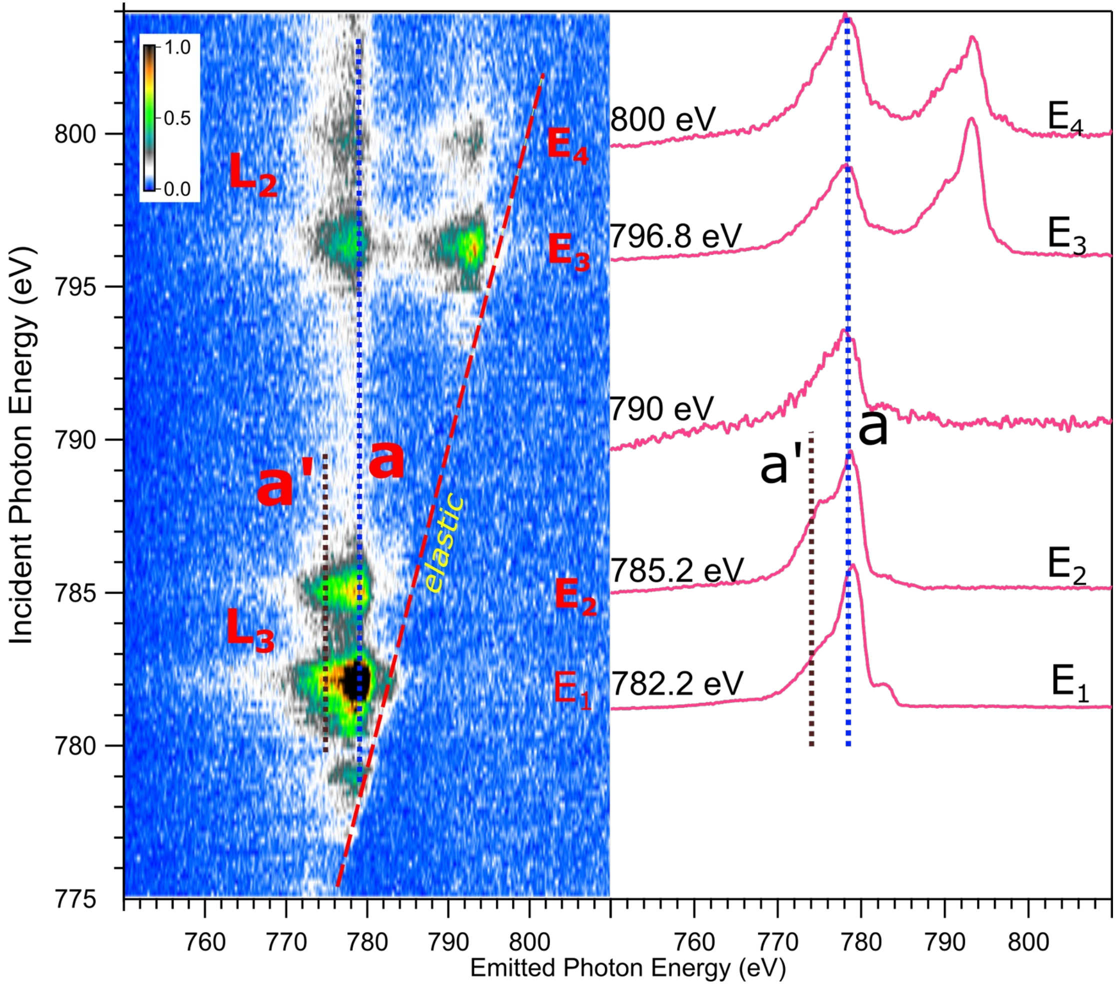




- The characteristic π* peak shows the mixing of Co 3d t_{2g} orbitals with 2π* orbitals of CN^-.
- The orbital characters are obtained by Löwdin population analysis.
- LUMO and LUMO+1 have 60% Co contribution, MOs #57-59 have 20% metal character.

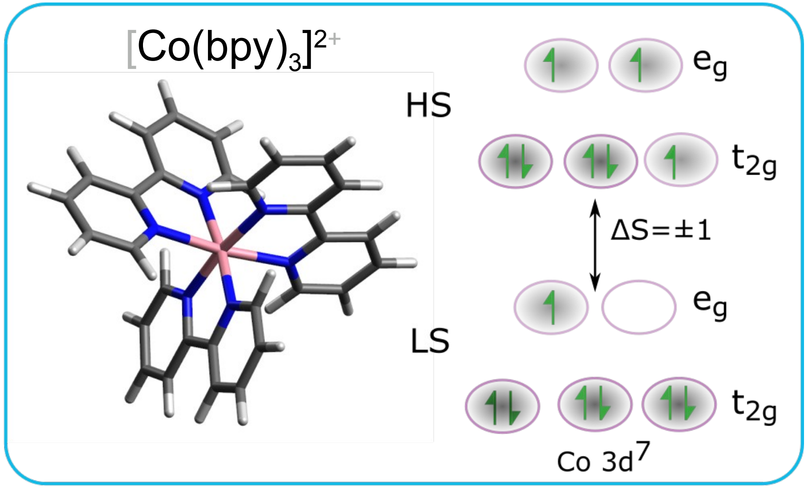
Scientific Reports, 2017, Vol 7, page 40811

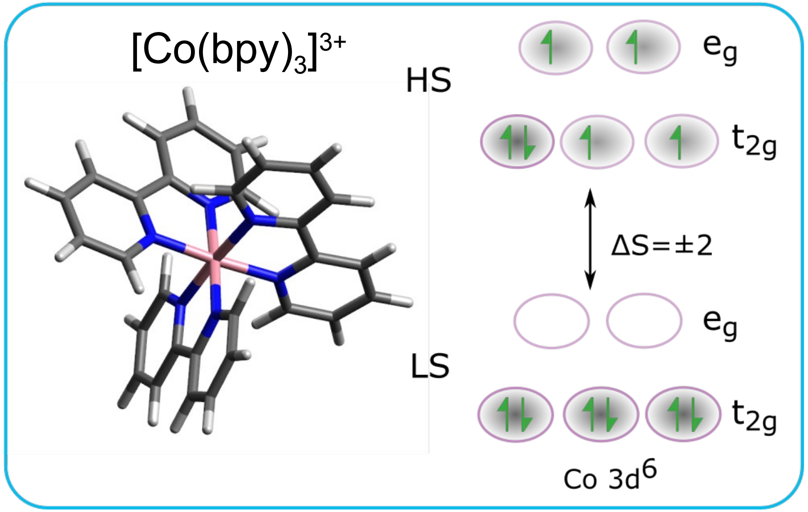
Aqueous $[Co(CN)_6]^{3-}$



- Emission channel **3d→2p**, fluorescence **a** and **a'**
- 3d t_{2g}^{6} closed shell nature of the nature.

Aqueous $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$





- $[Co(bpy)_3]^{2+}$ - two spin possibilities for the valence d^7 configuration. LS with $t_{2g}^{6}\,e_g^{1}$ and HS with $t_{2g}^{5}\,e_g^{2}$
- The uneven occupation in the e_g level causes strong Jahn-Teller distortions for LS case
- $[Co(bpy)_3]^{3+}$ - three different spin possibilities. LS with t_{2g}^{6} and e_g^{0} HS with t_{2g}^{4} and e_g^{2}

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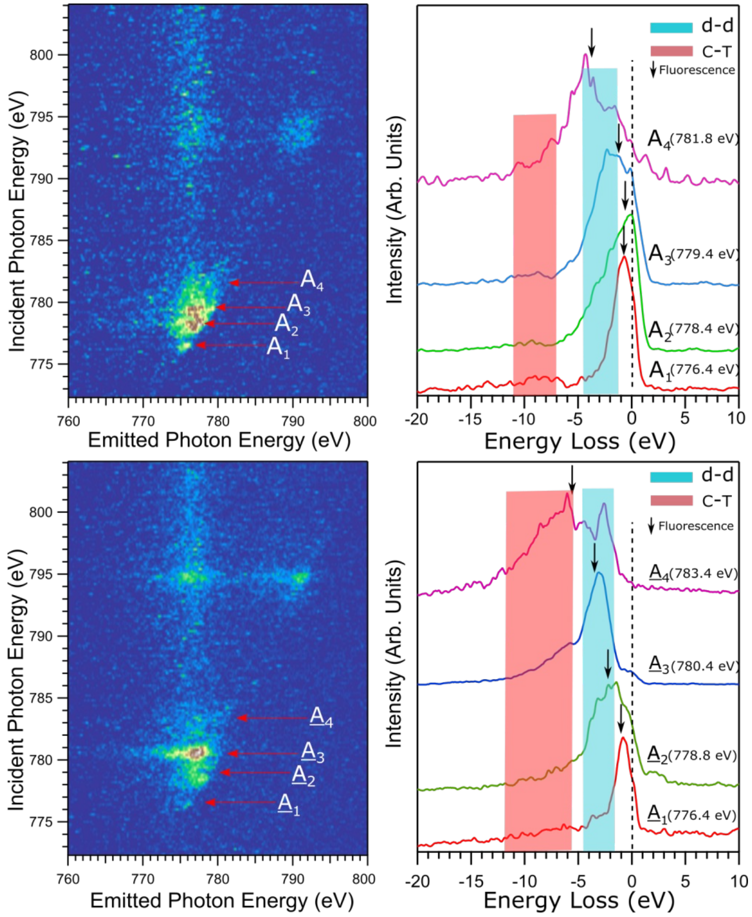
Co L-edge RIXS of $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$

$[Co(bpy)_3]^{2+}$

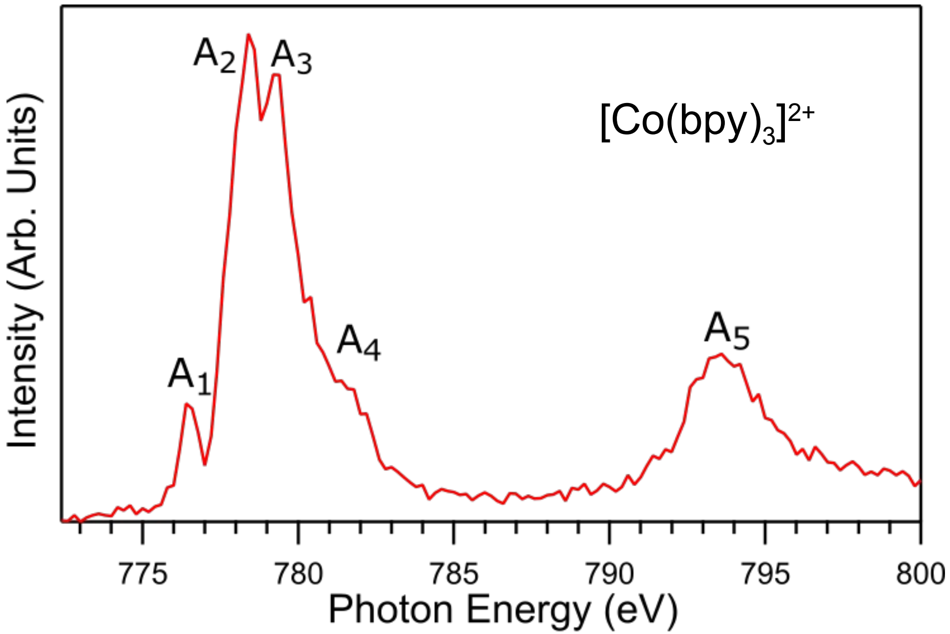
$[Co(bpy)_3]^{3+}$

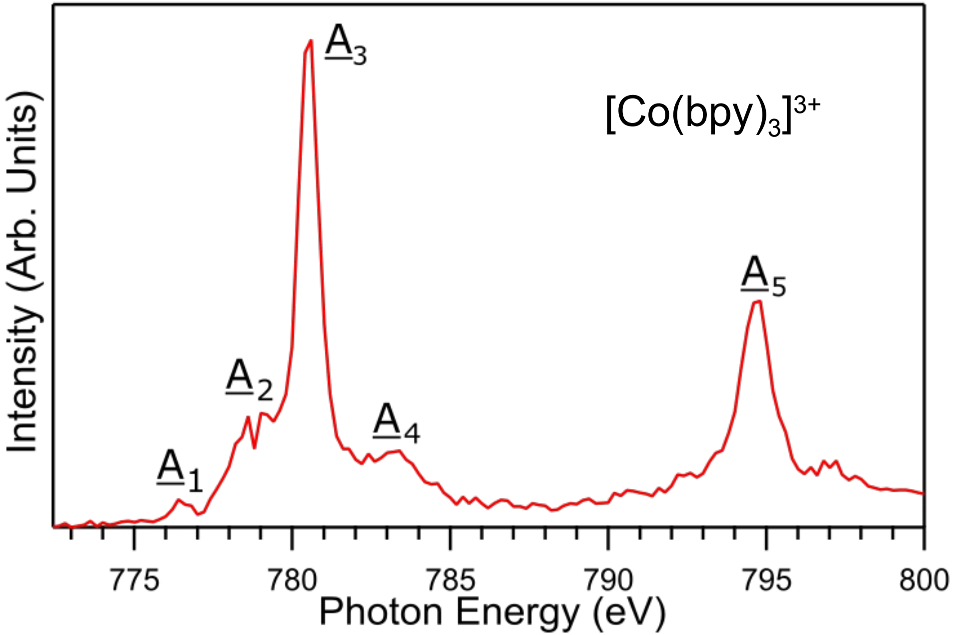


- Co L-edge RIXS maps showing dd and CT emission following a **2p→3d** excitation
- In the $[Co(bpy)_3]^{2+}$ case, both possible spin states are open shell
- The $[Co(bpy)_3]^{3+}$ case, spin state is not purely LS (zero spin), a HS component must be considered

Inorganic Chemistry, 2019, Vol 58, pages 4731-4740

Co L-edge PFY-XA spectra





✔ Partial fluorescence yield mode X-ray absorption (PFY- XA) spectra obtained by integrating the Co L-edge RIXS maps

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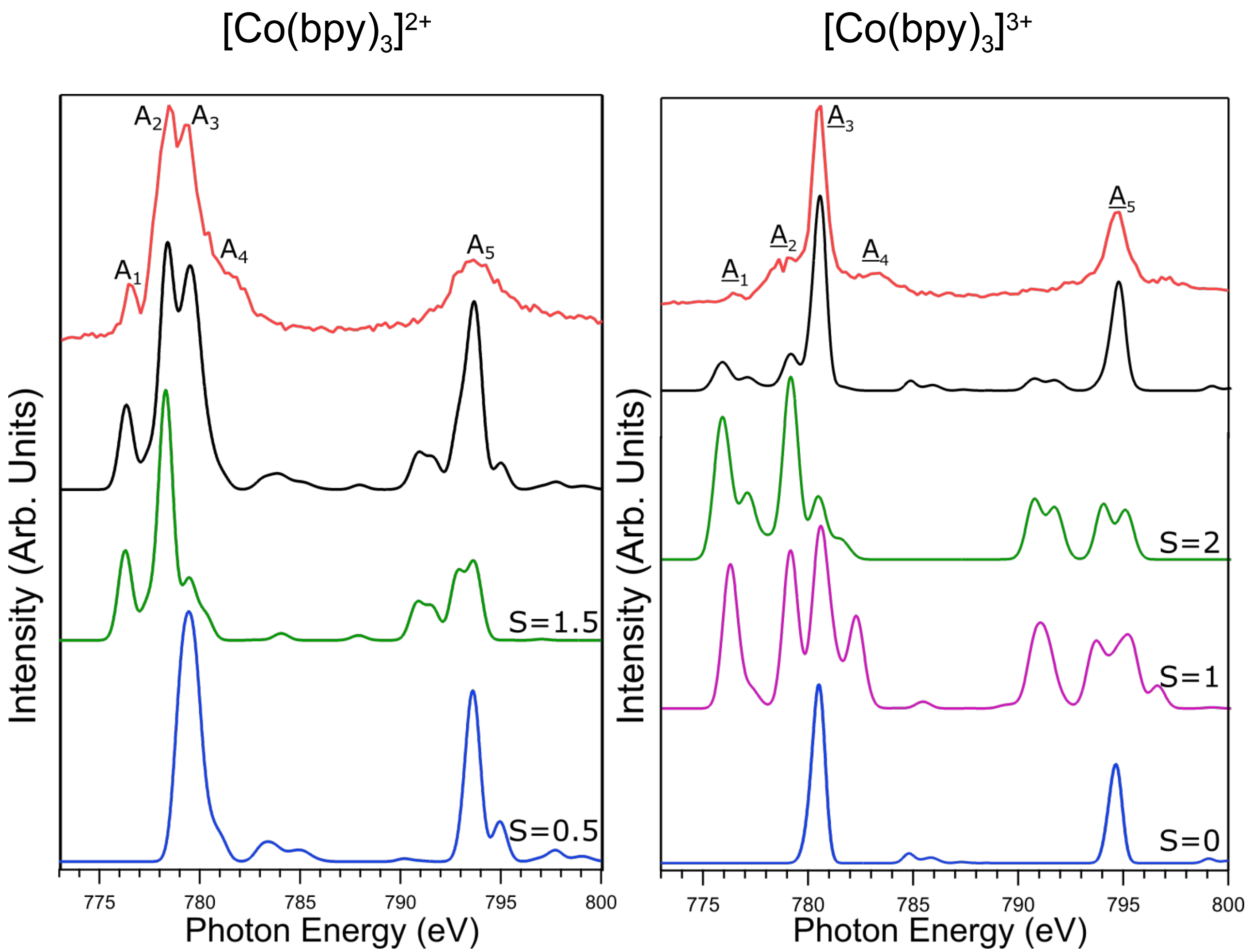
Co L-edge PFY-XA spectra comparison with theory



- DFT/ROCIS level theory suggests multiple spin states to consider for both $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$

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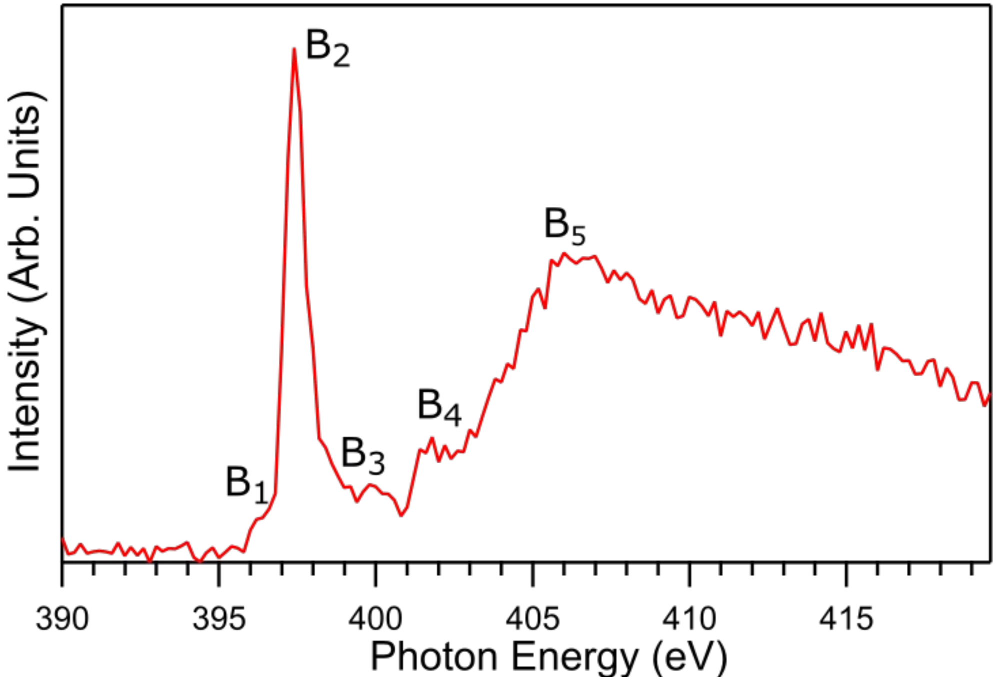
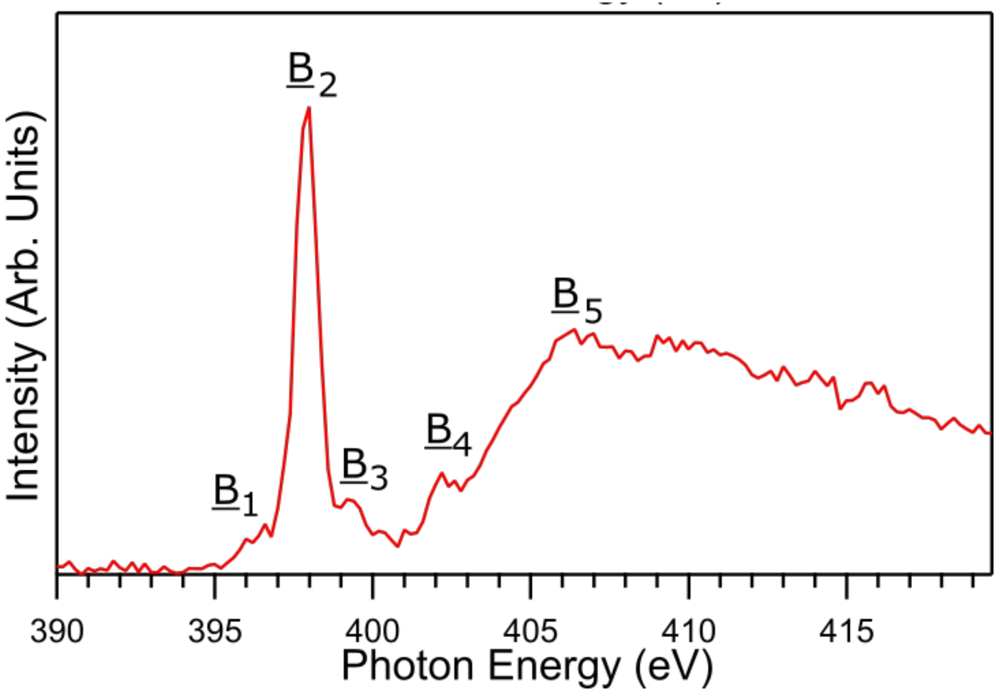
N K-edge PFY-XA spectra



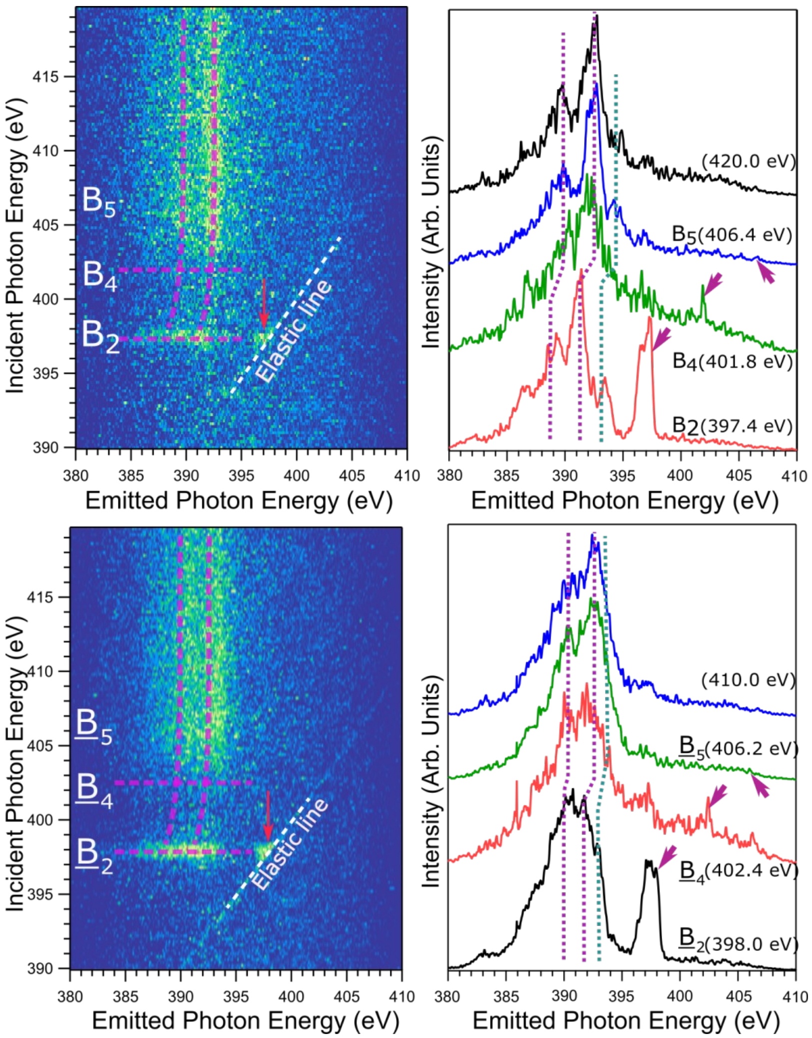


✔ PFY- XA spectra obtained by integrating the N K-edge RIXS maps

N K-edge RIXS of $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$

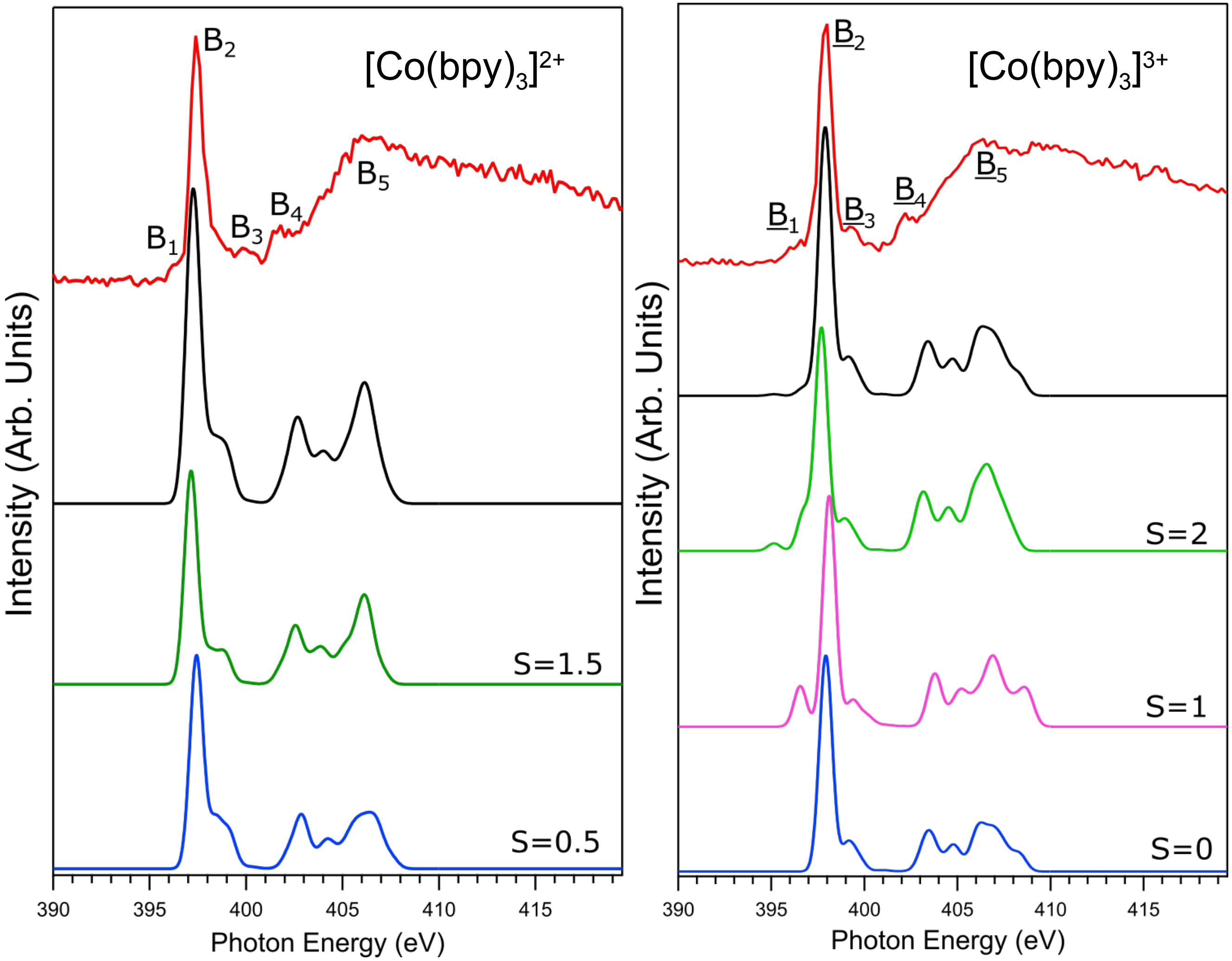
$[Co(bpy)_3]^{2+}$

$[Co(bpy)_3]^{3+}$



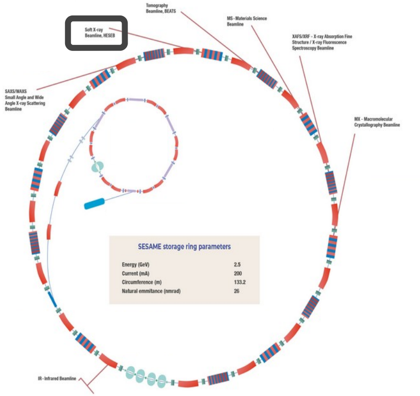
- RIXS/X-ray emission after ligand **1s→2p** excitation
- Main emission from **ligand 2p orbitals**
- A special feature is seen on the high energy emission side marked by dotted blue line
- Both systems exhibit fluorescence features above B_4 and $\underline{B}_4$

N K-edge PFY-XA spectra comparison with theory

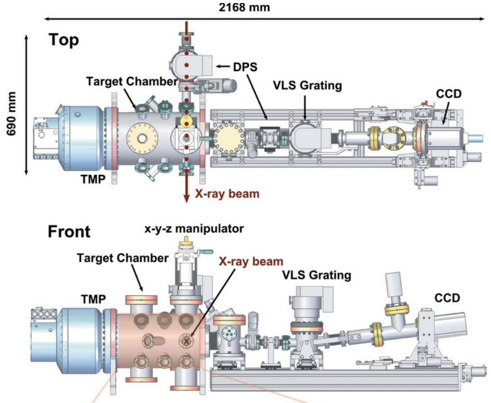


- Sensitivity towards metal spin state is minimum from the ligand side
- B_2 and <u>B</u>$_2$ – N 1s→π* characteristic C=N π* unoccupied orbitals
- B_5 and <u>B</u>$_5$ – σ* shape resonance

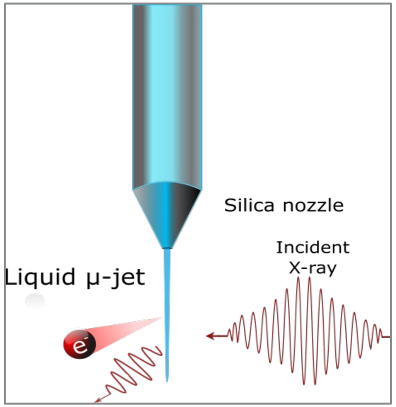
Summary



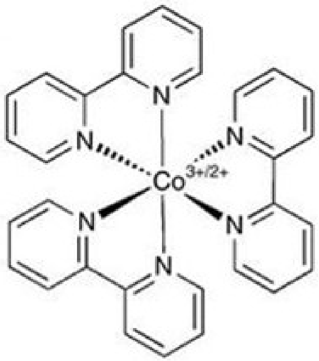
Tomography Beamline, BEATS
Soft X-ray Beamline, HESEB
MS - Materials Science Beamline
XAFS/XRF - X-ray Absorption Fine Structure / X-ray Fluorescence Spectroscopy Beamline
SAXS/WAXS Small Angle and Wide Angle X-ray Scattering Beamline
MX - Macromolecular Crystallography Beamline
IR - Infrared Beamline
SESAME storage ring parameters
Energy (GeV) 2.5
Current (mA) 200
Circumference (m) 133.2
Natural emmitance (nmrad) 26



2168 mm
690 mm
Top
DPS
Target Chamber
VLS Grating
CCD
TMP
X-ray beam
Front
x-y-z manipulator
Target Chamber
X-ray beam
VLS Grating
TMP
CCD



Silica nozzle
Incident X-ray
Liquid μ-jet
e-



N
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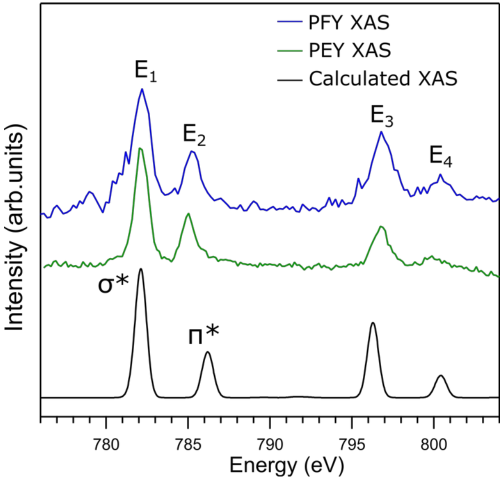
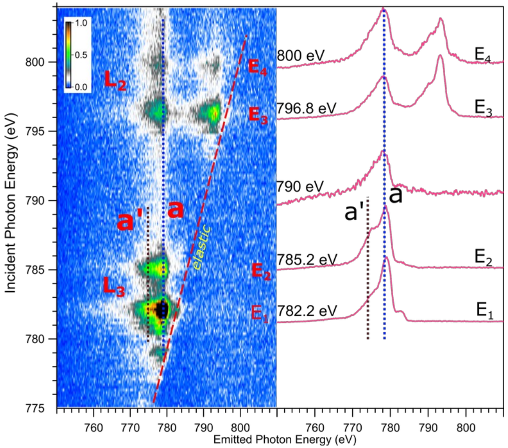
N
Co3+/2+



PFY XAS
PEY XAS
Calculated XAS
E1
E2
E3
E4
σ*
π*
Intensity (arb.units)
780
785
790
795
800
Energy (eV)



1.0
0.5
0.0
L2
L3
E4
E3
E2
E1
a'
a
elastic
800 eV
796.8 eV
790 eV
785.2 eV
782.2 eV
Incident Photon Energy (eV)
775
780
785
790
795
800
760
770
780
790
800
Emitted Photon Energy (eV)

Acknowledgements

Prof. Simone Techert
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Dr. Sreeju Sreekantan Nair Lalithambika
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