Ground State Electronic Structures
from
Multi-Edge Analysis

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Program

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00 AM</td>
<td>Welcome and Refreshments</td>
<td></td>
</tr>
<tr>
<td>9:30 AM</td>
<td><strong>Morning Session: Introduction to the Syncrotron Radiation and S K-edge XAS at SSRL</strong></td>
<td>Britt Hedman</td>
</tr>
<tr>
<td>10:15 AM</td>
<td>Beam Line Optics with Focus on Soft X-ray</td>
<td>Tom Rabedeau</td>
</tr>
<tr>
<td>11:00 AM</td>
<td><strong>S K-edge XAS: Theory, Advantages, Pitfalls and Examples</strong></td>
<td>Ritimukta Sarangi</td>
</tr>
<tr>
<td>11:45 AM</td>
<td><strong>Introduction to Imaging: Instrumentation and Special Considerations</strong></td>
<td>Sam Webb</td>
</tr>
<tr>
<td>12:30 PM</td>
<td>Lunch Break</td>
<td></td>
</tr>
<tr>
<td>1:30 PM</td>
<td><strong>Afternoon Session: S K-edge XAS and Fluorescence Mapping-Applications</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Ground State Electronic Structures from Multi-Edge Analysis</strong></td>
<td>Robert K. Szilagyi</td>
</tr>
</tbody>
</table>

Reminders: unique research opportunities (no other spectroscopic technique for S and Cl) facilities (beamlines, instrumentation, sample prep. expertise) semi-empirical theory (effective nuclear charge, transition dipole, covalency)
On a gloomy and snowy November afternoon …
On a gloomy and snowy November afternoon ...

\[
\begin{align*}
\text{Fe}^{2+} & \quad \text{Fe}^{3+} \quad \text{Fe}^{3+} \\
\text{Fe}^{2+} & \quad \text{Fe}^{3+} \quad \text{Fe}^{3+}
\end{align*}
\]

\[
\begin{align*}
+ 4 \text{e} & \quad - 4 \text{e} \\
\text{substrate independent redox function}
\end{align*}
\]

\[
\begin{align*}
\text{common in vitro NO binding conditions}
\end{align*}
\]

\[
\begin{align*}
\text{formation of } \text{O}_2^* \quad \text{N}_2\text{O}_5\text{ radicals} \\
(\text{neurotoxic function})
\end{align*}
\]

\[
\begin{align*}
\text{+ NO} & \quad - \text{NO} \\
\text{inter-subunit electron transfer} & \quad \beta\text{93C}
\end{align*}
\]

\[
\begin{align*}
\text{Oxyheme nitrosylation: formation of NO}_3^- \\
\text{physiologically non-relevant, extreme NO concentration}
\end{align*}
\]

\[
\begin{align*}
\text{physiological NO concentration} & \quad \text{low NO concentration} \\
\text{or exogenous S-nitrosothiols} & \quad \text{vasodilation}
\end{align*}
\]

\[
\begin{align*}
\text{low } \text{O}_2 & \quad \text{saturation} \\
\text{high } \text{O}_2 & \quad \text{saturation}
\end{align*}
\]
Nitrosated β-subunit of human hemoglobin

βCys93

N.-L. Chan, P. H. Rogers, A. Arnone
1.9 Å CRYSTAL STRUCTURE OF THE S-NITROSO FORM OF LIGANDED HUMAN HEMOGLOBIN
BIOCHEMISTRY, 1998, 37, 16459
RSNO compounds (CCDB)
RSNO compounds: geometric structure
RSNO compounds: electronic structure

A

5a''
ON-S $\pi^*$ (0.0 eV)
LUMO

S-N double ($\pi$) bond

B

17a'
ON-S $\sigma^*$ (+2.1 eV)
LUMO+1

S-N single ($\sigma$) bond

C

18a'
S-C $\sigma^*$ (+4.0 eV)
LUMO+2

S-C single ($\sigma$) bond

large sulfur contribution

Biochemical and Biophysical Research Communications, 2005, 330(1), 60-64
S K-edge XAS of S-nitrosated glutathione (GSNO)

Biochemical and Biophysical Research Communications, 2005, 330(1), 60-64
S K-edge XAS of S-nitrosated glutathione (GSNO)

Normalized XAS intensity (FF/I0) vs. calibrated (thiosulfate) photon energy, eV

- ON-S $\sigma^*$ at 2473.4 eV
- ON-S $\pi^*$ at 2471.5 eV
- S-C $\sigma^*$ at 2475.0 eV

Energy levels:
- 0.0 eV
- 2.1 eV
- 4.0 eV
S K-edge XAS of SNO compounds

Normalized XAS Intensity

Photon Energy, eV

GSNO
SNAP
S-nitroso glutathione
N-acetyloxy-3-nitrosothiovaline

S-NO
π*
S-NO
σ*
S-C
σ*

2467 2469 2471 2473 2475 2477 2479 2481
S K-edge XAS of S compounds

Normalized XAS Intensity

Photon Energy, eV

-\( S-\text{CH}_2-\text{CH}_3 \)
-\( \text{NaSEt} \)
-\( \text{Cys} \)
-\( \text{H-S-CH}_2-\text{CH}_3 \)

\( \text{Na}^+ \)

S charge becomes less negative
\( Z_{\text{eff}}(S) \) increases
S K-edge XAS of S compounds

Normalized XAS Intensity

PHOTON ENERGY, eV

ON-S σ*
ON-S π*
H-S σ*
S-C σ*
S-C σ*

GSNO
Cys
ON-S-CH₂-R
ON⁺-S-CH₂-R

S charge becomes less negative
Z_{eff}(S) increases
S K-edge XAS of S compounds

S charge becomes less negative
$Z_{\text{eff}}(S)$ increases

Photon Energy, eV

Normalized XAS Intensity

ON-S $\pi^*$

ON-S $\sigma^*$

S-C $\sigma^*$

H-S $\sigma^*$

S-C $\sigma^*$

NaSEt

Cys

GSNO
S K-edge XAS as detection method for SNO

Phon Energy, eV

Normalized XAS Intensity

- SNO-hemoglobin
- S 1s $\rightarrow$ ON-S $\pi^*$ fit
- First derivative
- Second derivative

Biochemical and Biophysical Research Communications, 2005, 330(1), 60-64
Multi-edge XAS

Conceptually NOT an original idea!

Conscious exploitation of complementary ground state electronic structure information from multiple absorbers

Molecular Orbital Theory:

Experimentally probing the excitation of an absorber core electron (1s for K) to a unoccupied/virtual molecular orbital with some absorber contribution.

Donor orbital:  S 1s (localized on S, in MO picture as s.a.l.c.)

Acceptor orbital:  \( \phi^* = \sum c_i \phi_i \)

for a ‘simple’ M-S bond:  
\[
\phi^* = c_{M,d} \phi_M(nd) + c_{M,s} \phi_M(n+1\ s) + c_{M,p} \phi_M(n+1\ p) \\
- c_{S,s} \phi_S(3s) + c_{S,p} \phi_S(3p) + c_{S,d} \phi_S(3d)
\]
Multi-edge XAS

for a ‘simple’ M-S bond:

\[ \phi^* = c_{M,d} \phi_M(nd) + c_{M,s} \phi_M(n+1s) + c_{M,p} \phi_M(n+1p) - c_{S,s} \phi_S(3s) + c_{S,p} \phi_S(3p) + c_{S,d} \phi_S(3d) \]

for intense spectral features in absorption spectroscopy – \( \Delta l = 1 \)

SSRL BL10-1/8-2  BL7-3/9-3/4-1/4-3  BL6-2/4-3  BL10-1/8-2
Multi-edge XAS

\[ \Psi = c_1 \varphi(P\ 3p) + c_2 \varphi(S\ 3p) + c_3 \varphi(Mo\ 4d) + c_4 \varphi(Cl\ 3p) + c_5 \varphi(O\ 2p) + c_6 \varphi(Fe\ 3d) \]

- \( c_1 \) is from P K-edge
- \( c_2 \) is from S K-edge
- \( c_3 \) is from Mo L-edge
- \( c_4 \) is from Cl K-edge
- \( c_5 \) is from O K-edge (500-600 eV)
- \( c_6 \) is from Fe L-edge (650-850 eV)

Intensity features:
- Intense pre-edge features for Cl 1s \( \rightarrow \) 3p excitations
- Intense pre-edge features for Mo 2p \( \rightarrow \) 4d excitations
- Intense pre-edge features for S 1s \( \rightarrow \) 3p excitations
- Intense pre-edge features for P 1s \( \rightarrow \) 3p excitations

Ground state electronic structure:

\[ \psi = \sum_{n} \varphi_{n} \alpha_{n} \]

Photon Energy, eV
Multi-edge XAS at SSRL BL6-2/4-3
Multi-edge XAS: A non-biological, but simple example

Inorganica Chimica Acta, 2008, 361(4), 1047-1058
Multi-edge XAS: A non-biological, but simple example

ground state electronic wave function: \( \Psi^* = c_1 \varphi(\text{Pd} 4d) - (1-c_1)^{1/2}(c_2 \varphi(\text{Cl} 3p) + c_3 \varphi(\text{P} 3p)) \)

- \( c_1 \) is from Pd L-edge;
- \( c_2 \) is from Cl ligand K-edge;
- \( c_3 \) is from P ligand K-edge

**XANES analyses**

- **P K-edge**
  - Intense pre-edge features for P 1s -> 3p excitations

- **S K-edge**
  - Intense pre-edge features for S 1s -> 3p excitations

- **Cl K-edge**
  - Intense pre-edge features for Cl 1s -> 3p excitations

- **Pd L_2-edge**
  - Intense pre-edge features for Pd 2p -> 4d excitations

- **Pd L_3-edge**
  - Intense pre-edge features for Pd 2p -> 4d excitations

**Photon Energy, eV**

2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500
Phosphorous 3p character of the palladium-phosphorous bonds is determined from phosphorous K-edge XAS
Chlorine 3p character of the palladium-chlorine bonds is determined from chlorine K-edge XAS.
Multi-edge XAS: palladium L-edge

Metal 4d character of the palladium-ligand bonds is determined from palladium L-edge XAS (only L_{III} edge is shown)
Multi-edge XANES: chloropalladium(II/IV)

$K_2\text{Pd}^{\text{II}}\text{Cl}_4$
closed shell $d^8$

$K_2\text{Pd}^{\text{IV}}\text{Cl}_6$
closed shell $d^6$
Chlorine K-edge XANES:

\[ \varphi^* = \sqrt{1 - \alpha^2} \text{Cu } 3d_{x^2-y^2} - \alpha \text{Cl } 3p_{\text{sal}} \]

\[ \text{Cu } 3d_{x^2-y^2} \quad \text{Cl } 3p_{\text{sal}} \]

\[ \text{Cl } 1s \]

\[ \text{NaCl} \]

\[ \text{Cs}_2\text{ZnCl}_4 \quad T_d \]

\[ \text{Cs}_2\text{CuCl}_4 \quad D_{4h} \]
Multi-edge XANES: Cl

[PdCl₄]²⁻
PdCl₂
[PdCl₆]²⁻
Cs₂ZnCl₄

Pd(II) is the hydrogen atom of organometallic chemistry

Normalized XAS Intensity

Photon Energy (eV)

Normalized XAS Intensity

Photon Energy (eV)

Inorganica Chimica Acta, 2008, 361(4), 1047-1058
Multi-edge XANES: Pd

[\text{PdCl}_4]^{2-}

PdCl$_2$

[\text{PdCl}_6]^{2-}

Pd powder

Inorganica Chimica Acta, 2008, 361(4), 1047-1058
Experimental M-L covalency

acceptor orbital \[ \Psi_a = \sqrt{1 - \alpha^2} \phi_M - \alpha \phi_L \]

\[ \phi_L = \sum \sum c_{l,o} \phi_{l,o} \]

donor orbital \[ \Psi_d = \sum \sum_{l,d} c_{l,d} \phi_{l,d} \] (donor is 1s for K-edge excitations)

electric dipole allowed transition/Fermi golden rule: \[ I \propto |<\Psi_a | r | \Psi_d>|^2 \]

\[ I \propto \left(1 - \alpha^2\right) \sum_{l,d} c_{l,d} <\phi_M | r | \phi_{l,d}> - \alpha \sum_{l} \sum_{l,o} \sum_{l,d} c_{l,d} c_{l,o} <\phi_{l,o} | r | \phi_{l,d}> \]

ligand core/metal overlap \( \approx 0 \)

ligand core/ligand core overlap \( \approx 0 \)

for 1s \( \rightarrow \) np excitation \[ |<\Psi_a | r | \Psi_d>| - \alpha \sum_{l} c_{l,1s} c_{l,np} \frac{1}{\sqrt{3}} <\text{Rad}(\Psi_{l,np}) | r | \text{Rad}(\Psi_{l,1s})> \]

\[ <\mathcal{R}> \text{ dipole integral} \]

\[ I = |<\Psi_{M-L(3p)} | r | \Psi_{L(1s)}>|^2 = \frac{1}{3} \alpha^2 <\mathcal{R}> \]

*JACS*, 1992, 112(4), 1643-1645
Multi-edge XANES: chloropalladium(II/IV)

using $I(\text{Cl}^{-}) = 21.0$ eV $\rightarrow$ ~50% Cl covalency in both $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ and $[\text{Pd}^{\text{IV}}\text{Cl}_6]^{2-}$

from complementarity this corresponds to ~50% Pd covalency in each molecular orbital probed by XAS

from area under pre-edge features at Pd L-edges we get

$I(\text{Pd}^{\text{II}}) = 20.8$ (SSRL) $16.9$ (ALS) eV
$I(\text{Pd}^{\text{IV}}) = 14.1$ (SSRL) $11.9$ (ALS) eV

to test the transferability we used $I(\text{Pd}^{\text{II}})$ to determine the covalency of Pd-Cl bonds in PdCl$_2$ to be ~50% with a new transition dipole integral for $I(\text{Cl}^{-}_b)16.4$ (SSRL) $14.5$ (ALS)

Pd-Cl bond in organometallic chemistry is the Fe-S bond in coordination chemistry
Multi-edge XANES: non-innocent ligands

A) Crystal structure of $[\text{Ph}_2\text{BP}^\text{Bu}_2]\text{Cu}^{\text{III}}(\text{NTol}_2)$
B) Structural overlay of reduced and oxidized forms
C) Ligand based redox chemistry

JACS, 2009, 131(11), 3878-3881
Multi-edge XANES: non-innocent ligands

Cu K-edge

First electric dipole allowed Cu 1s → 4p transition

Photon Energy, eV

Normalized Intensity

8984.5 eV
8982.5 eV
8982.2 eV
8987.4 eV

Cu^I Cl

{[Ph_2BP^tBu_2]Cu^I(NTol_2)}

{[Ph_2BP^tBu_2]Cu^II(NTol_2)}
anhydrous Cu^II Cl_2
Multi-edge XANES: non-innocent ligands

**P K-edge**

- **P 1s → P-C σ**
- **P 1s → P 4p**

2146.5 eV

2147.9 eV

2147.9 eV

2145.3 eV

2171.1 eV

**PPh₃**

**{[Ph₂BPᵗBu₂]Cu^{II}(NTol₂))}**

**{[Ph₂BPᵗBu₂]Cu^{I}(NTol₂)}**

P 1s → P 3p/4p based electric dipole allowed transitions
Multi-edge XANES: non-innocent ligands

Cu L_{III}-edge

Cu 2p → 3d transition

Cu → L backdonation transition envelopes

Normalized intensity

Photon Energy, eV

Cu_{II}Cl

[[Ph_{2}BP^{tBu}_{2}]Cu^{II}(NTol_{2})]

[[Ph_{2}BP^{tBu}_{2}]Cu^{I}(NTol_{2})]

anhydrous Cu^{II}Cl_{2}

Cu^{I}Cl

930.4 eV

931.9 eV
Multi-edge XANES: quantitative treatment

Photon Energy, eV

Normalized intensity

930.4 eV

 Cu L_{III}-edge

What is the Cu contribution to the redox active orbital?

What is the % Cu character the blue vs. green areas correspond to?

$\{[\text{Ph}_2\text{BP}^{t\text{Bu}}_2]\text{Cu}^{\text{II}}(\text{NTol}_2)\}$

anhydrous Cu^{\text{II}}\text{Cl}_2

931.9 eV
Multi-edge XANES: quantitative treatment

Cl K-edge

 photons Energy, eV

Renormalized Intensity

4 Cl absorbers

Cs$_2$Cu$^{II}$Cl$_4$

2 Cl absorbers

anhydrous Cu$^{II}$Cl$_2$
Multi-edge XANES: quantitative treatment

Cl K-edge

$\text{Cs}_2\text{Cu}^{\text{II}}\text{Cl}_4$

anhydrous $\text{Cu}^{\text{II}}\text{Cl}_2$

$\text{D}_2\text{d} \text{Cs}_2\text{CuCl}_4$
pre-edge
area = 0.521 eV
$\sim$ 30% Cl 3p

anhydrous CuCl$_2$
pre-edge
area = 0.616 eV
$\sim$ 35% Cl 3p

4 Cl absorbers

2 Cl absorbers

Renormalized XAS Intensity
Photon Energy, eV
Multi-edge XANES: quantitative treatment

Cu L$_{III}$-edge

$[[\text{Ph}_2\text{BP}^{t\text{Bu}_2}]\text{Cu}^{\text{II}}(\text{NTol}_2)]$

anhydrous Cu$^{\text{II}}$Cl$_2$

35% Cl 3p character with limited 4s mixing
Cu 3d character is ~ 65%
pre-edge area = 4.114 eV

930.4 eV

pre-edge area 0.910 eV
Cu 3d character ~14%

931.9 eV

Normalized intensity

Photon Energy, eV
Calculated spin densities for $[\text{Ph}_2\text{BP}^{t\text{Bu}}_2]\text{Cu}^{\text{I}}(\text{NTol}_2)$:

- $\text{BPh}_2$: 2%
- $\text{PtBuPh}_2$: 15%
- $\text{Cu}$: 13%
- N: 49%
- (p-tol)$_2$: 20%

*JACS*, 2009, 131(11), 3878-3881
State-of-the-Art S K-edge Data

galactose oxidase

fungus *Dactylium dendroides*

1GOG

*fungus Dactylium dendroides*
State-of-the-Art S K-edge Data

galactose oxidase

\[
\text{Cu}^{2+}/\cdot\text{O(Tyr-Cys)} \\
\downarrow 400 \text{ mV} \\
\text{Cu}^{2+}/\text{O(Tyr-Cys)} \\
\downarrow 150 \text{ mV} \\
\text{Cu}^{+}/\text{O(Tyr-Cys)}
\]
State-of-the-Art S K-edge Data

GO samples:
93% Cu-loaded
150 μL
0.633 mM
In phosphate buffer
w/2M urea, pH=7
50-fold excess of
K$_3$Fe(CN)$_6$
37±3% oxidation

BL6-2 only!
LHe cryojet only!

19 absorbers:
13 Met 4 Cys-Cys thioether crosslink

galactose oxidase

JACS, 2010, submitted
State-of-the-Art S K-edge Data

- Ferricyanide oxidized
- As isolated/semi reduced
- Dithionite reduced

Normalized XAS Intensity vs. Photon Energy, eV

- TyrCys\(^{1-}\) (Met\(_{13}\)Cys\(_{5}\))
- TyrCys\(^{1-}\) (Met\(_{13}\)Cys\(_{5}\))

*Buffer contamination
State-of-the-Art S K-edge Data

- ferricyanide oxidized
- as isolated/semi reduced
- dithionite reduced

presence of Tyr-Cys• in Met_{13}Cys_{5} background

renormalized pre-edge
  hhlw = 0.40 eV
  A = 0.78
  thus D_0 = 0.31

oxidized-reduced XANES spectrum

TyrCys^{1-}
(Met_{13}Cys_{5})

* buffer contamination
State-of-the-Art S K-edge Data

Experimental area $D_0 = 0.016$ eV for $N_{abs} = 19$ and $n_{holes} = 1$.

S character ($\alpha^2$) is defined by the transition dipole expression

$$D_0 = \frac{1}{3} \frac{n_{holes}}{N_{absorber}} \alpha^2 (S \, 3p) \, I(S \, 1s \to 3p)$$

$I(S \, 1s \to 3p)$ for sulfide (formally $Z=-2$) $6.54$ eV
for thiolate (formally $Z=-1$) $8.47$ eV
for thioether (formally $Z=0$) $10.4$ eV

and with corrections for partial Cu loading and Tyr-Cys oxidation:

S character ($\alpha^2$) from XAS for oxidized holo GO is $24\pm11\%$
(calc.: $22\pm2\%$)

from EPR for oxidized apo GO is $20\pm3\%$
(calc: $15\pm1\%$)

JACS, 2010, submitted