Ground State Electronic Structures

from

Multi-Edge Analysis

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SMB XAS
SUMMER SCHOOL 2010

Program

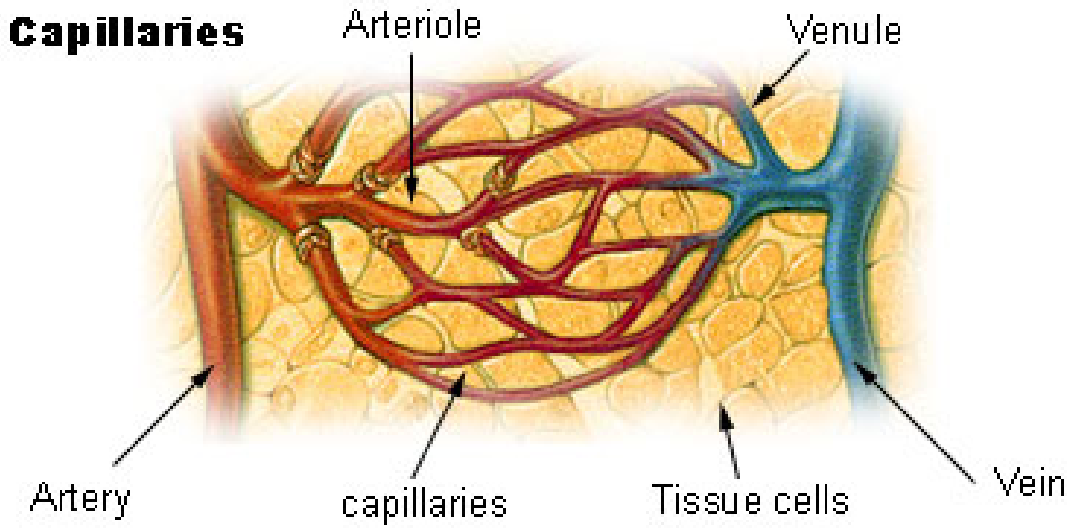
TUESDAY, JULY 20, 2010		
Building 48, Redwood Rooms		
9:00 AM	Welcome and Refreshments	
Morning Session: Introduction to the Syncrotron Radiation and S K-edge XAS at SSRL		
9:30 AM	**Development of S K-edge XAS at SSRL**	Britt Hedman
10:15 AM	**Beam Line Optics with Focus on Soft X-ray**	Tom Rabedeau
11:00 AM	**S K-edge XAS: Theory, Advantages, Pitfalls and Examples**	Ritimukta Sarangi
11:45 AM	**Introduction to Imaging: Instrumentation and Special Considerations**	Sam Webb
12:30 PM	Lunch Break	
Afternoon Session: S K-edge XAS and Fluorescence Mapping-Applications		
1:30 PM	**Ground State Electronic Structures from Multi-Edge Analysis**	Robert K. Szilagyi

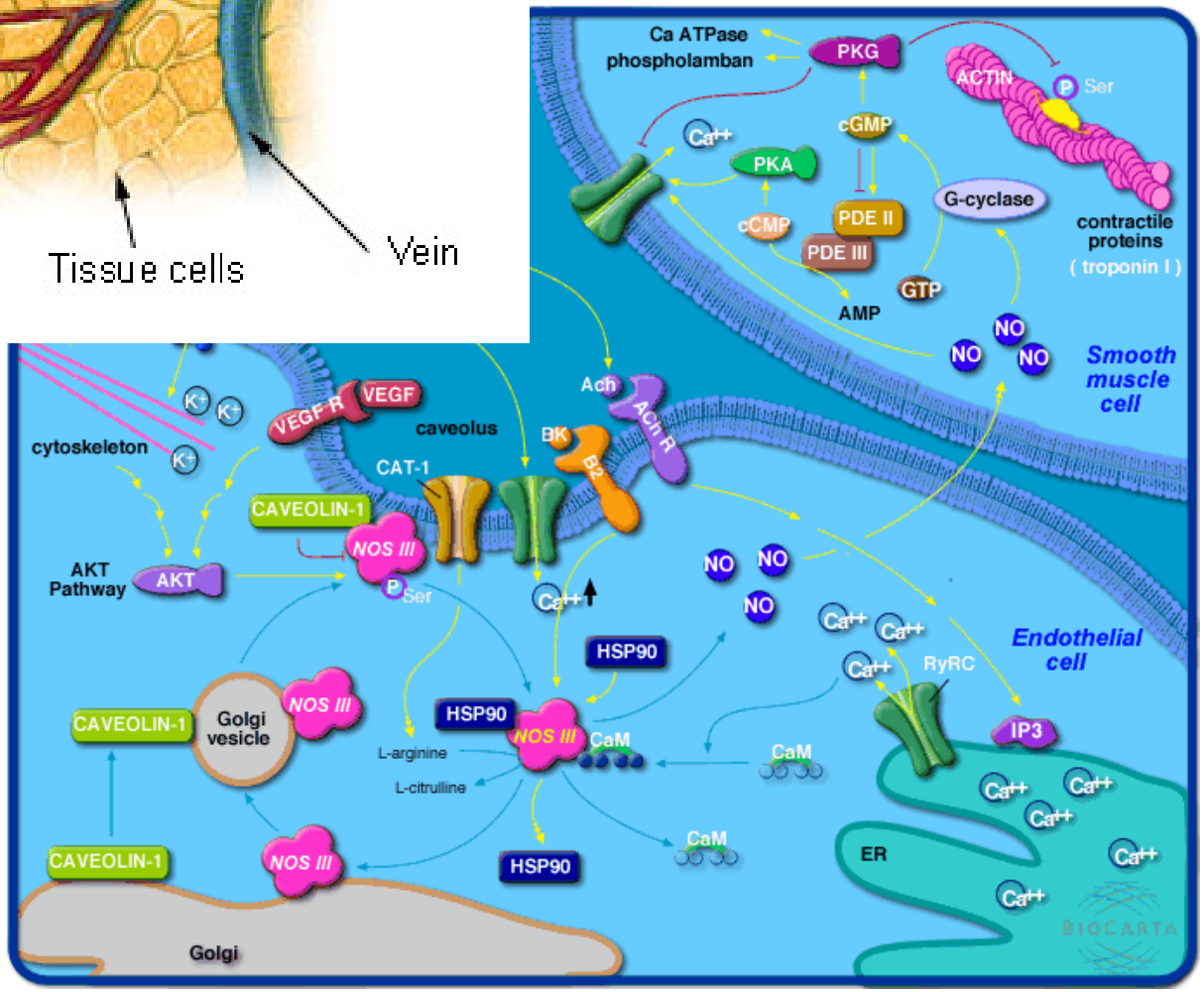
Reminders: unique research opportunities (no other spectroscopic technique for S and Cl)

facilities (beamlines, instrumentation, sample prep. expertise)

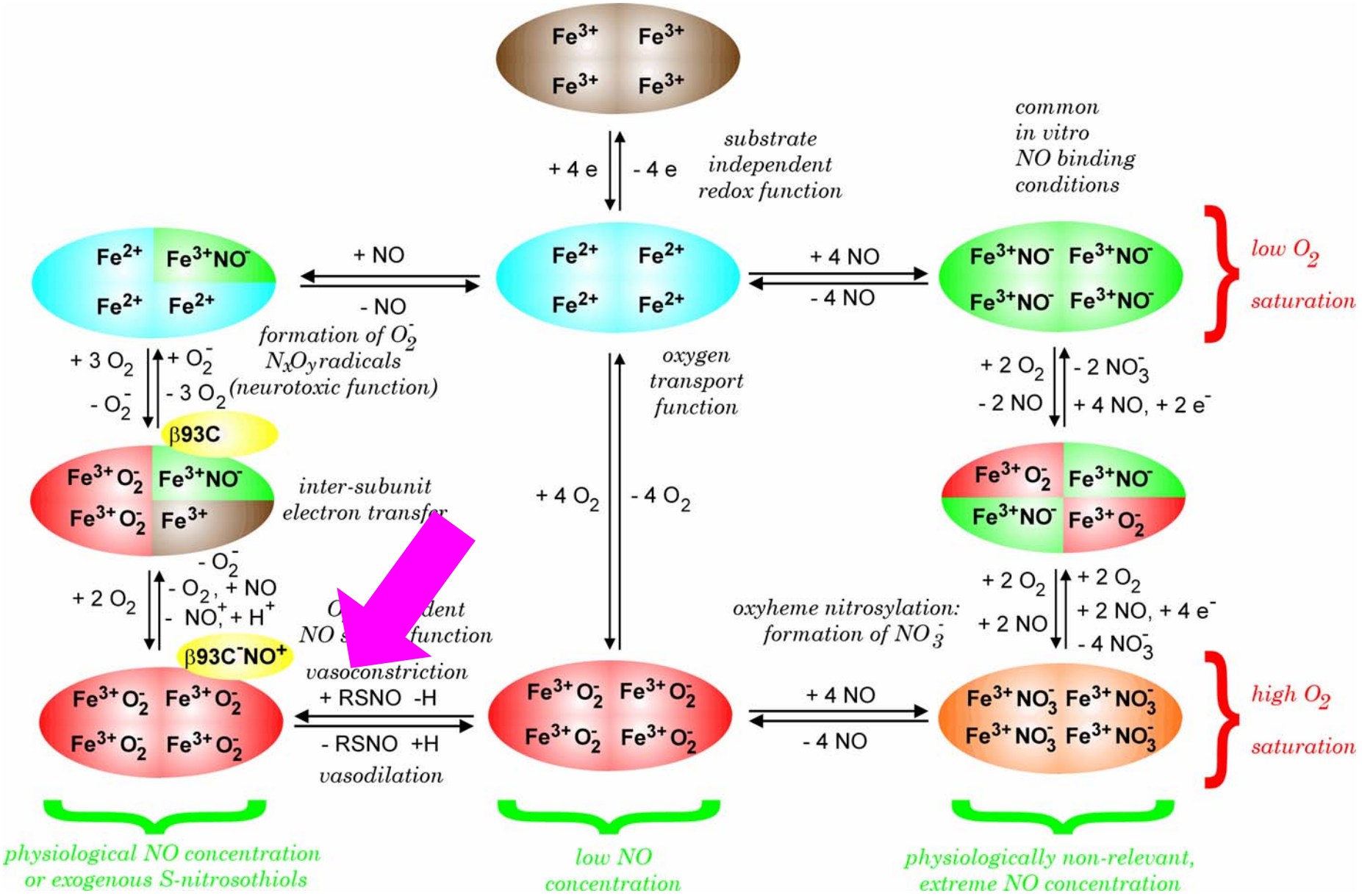
semi-empirical theory (effective nuclear charge, transition dipole, covalency

On a gloomy and snowy November afternoon …

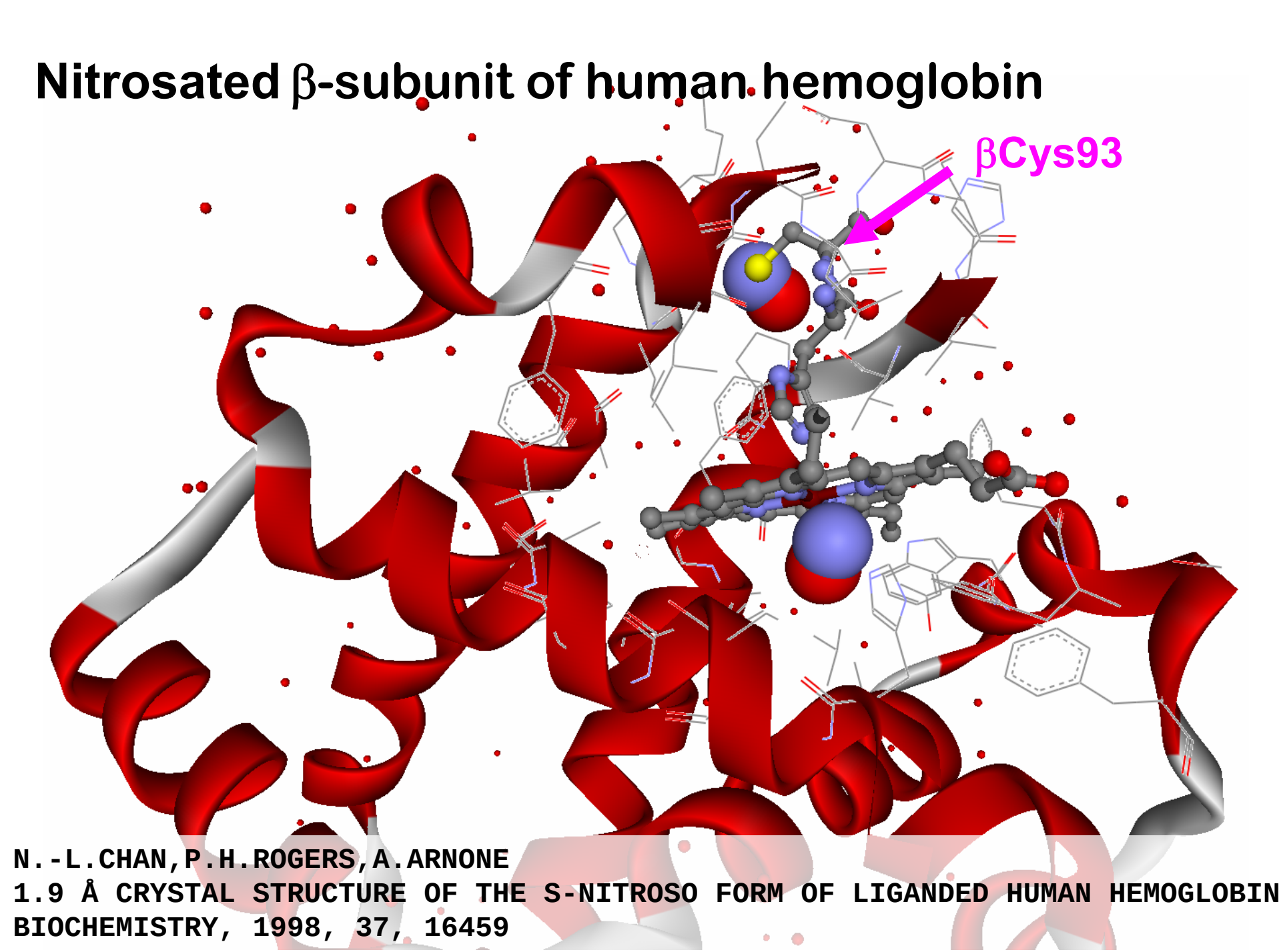




On a gloomy and snowy November afternoon …



Nitrosated β-subunit of human hemoglobin



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)

Search Overview

Search:	search1
Date/Time done:	Mon Oct 27 08:57:00 2003
Database(s):	CSD version 5.24 (November 2002)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	7

Single query used. Search found structures that:

match

Query 1

Page 1

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 1

APENTN01

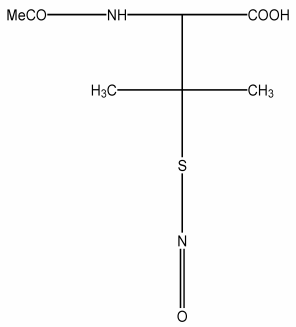
Reference: L.Field, R.V.Dilts, R.Ravichandran, P.G.Lenhert, G.E.Carnahan (1978) *Chem.Commun.*,249

Formula: $C_7 H_{12} N_2 O_4 S_1$

Compound Name: 2-(Acetylamino)-2-carboxy-1,1-dimethylethyl-thionitrite

Space Group:	P21/c	***Cell:***	***a***	7.001(2)	***b***	12.724(3)	***c*** 12.378(2)
Space Group No.:	14	***(Å,°)***	α	90.00	β	107.82(2)	γ 90.00

R-Factor (%): 4.60 ***Temperature(K):*** 295 ***Density(g/cm³):*** 1.394



Page 2

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 2

APENTN02

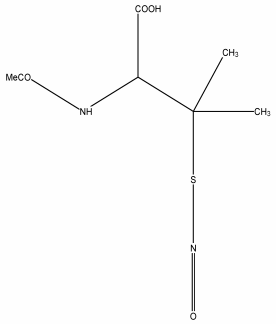
Reference: N.Arulsamy, D.S.Bohle, J.A.Butt, G.J.Irvine, P.A.Jordan, E.Sagan (1999) *J.Am.Chem.Soc.*,**121**,7115

Formula: $C_7 H_{12} N_2 O_4 S_1$

Compound Name: S-Nitrosoacetyl-DL-penicillamine

Space Group:	P21212	***Cell:***	***a***	12.173(2)	***b***	13.548(2)	***c*** 6.494(1)
Space Group No.:	18	***(Å,°)***	α	90.00	β	90.00	γ 90.00

R-Factor (%): 2.56 ***Temperature(K):*** 173 ***Density(g/cm³):*** 1.366



Page 3

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 3

APENTN20

Reference: G.E.Carnahan, P.G.Lenhert, R.Ravichandran (1978) *Acta Crystallogr.,Sect.B:Struct.Crystallogr.Cryst.Chem.*,**34**,2645

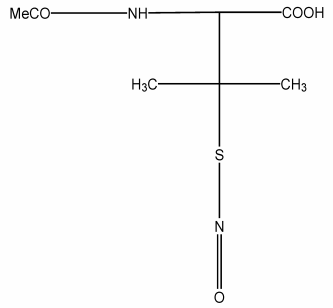
Formula: $C_7 H_{12} N_2 O_4 S_1$

Compound Name: S-Nitroso-N-acetyl-DL-penicillamine

Synonym: 2-Acetamido-3-methyl-3-thionitroso-butanoic acid

Space Group:	P21/c	***Cell:***	***a***	6.984(1)	***b***	12.698(2)	***c*** 12.353(2)
Space Group No.:	14	***(Å,°)***	α	90.00	β	107.80(1)	γ 90.00

R-Factor (%): 4.40 ***Temperature(K):*** 295 ***Density(g/cm³):*** 1.403



Page 4

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 4

CIYFEV

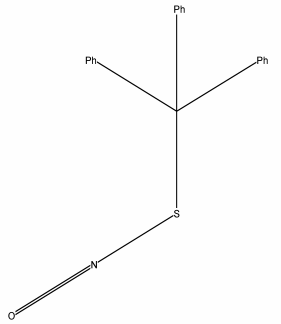
Reference: N.Arulsamy, D.S.Bohle, J.A.Butt, G.J.Irvine, P.A.Jordan, E.Sagan (1999) *J.Am.Chem.Soc.*,**121**,7115

Formula: $C_{19} H_{15} N_1 O_1 S_1$

Compound Name: S-Nitrosotriphenylmethanethiol

Space Group:	Pna21	***Cell:***	***a***	7.407(0)	***b***	28.165(3)	***c*** 7.579(1)
Space Group No.:	33	***(Å,°)***	α	90.00	β	90.00	γ 90.00

R-Factor (%): 4.15 ***Temperature(K):*** 295 ***Density(g/cm³):*** 1.283



Page 5

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 5

OCEZIF

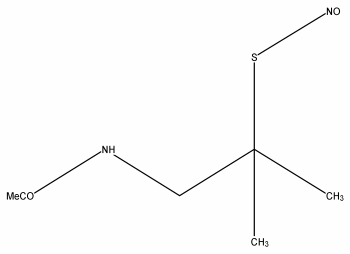
Reference: Jonghyuk Lee, Geun-Bae Yi, D.R.Powell, M.A.Khan, G.B.Richter-Addo (2001) *Can.J.Chem.*,**79**,830

Formula: $C_6 H_{12} N_2 O_2 S_1$

Compound Name: 3-(Acetylamino)-2-methyl-2-propylthionitrite

Space Group:	P21/c	***Cell:***	***a***	9.814(0)	***b***	9.825(0)	***c*** 9.765(0)
Space Group No.:	14	***(Å,°)***	α	90.00	β	104.60(0)	γ 90.00

R-Factor (%): 4.41 ***Temperature(K):*** 133 ***Density(g/cm³):*** 1.285



Page 6

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 6

VIQDUU

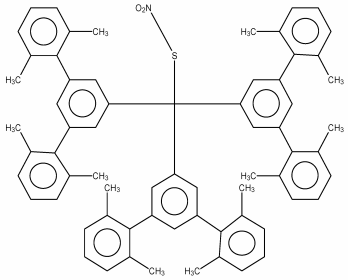
Reference: K.Goto, Y.Hino, T.Kawashima, M.Kaminaga, E.Yano, G.Yamamoto, N.Takagi, S.Nagase (2000) *Tetrahedron Lett.*,**41**,8479

Formula: $C_{67} H_{63} N_1 O_2 S_1$

Compound Name: tris(2,2',6,6'-Tetramethyl-m-terphenyl-5'-yl)methyl-S-nitrothiol

Space Group:	P21/c	***Cell:***	***a***	12.446(2)	***b***	23.327(3)	***c*** 20.063(2)
Space Group No.:	14	***(Å,°)***	α	90.00	β	105.69(0)	γ 90.00

R-Factor (%): 7.60 ***Temperature(K):*** 296 ***Density(g/cm³):*** 1.121



Page 7

Search: search1 (Mon Oct 27 08:57:00 2003): Hit 7

VIQFAC

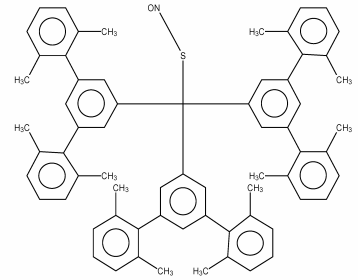
Reference: K.Goto, Y.Hino, T.Kawashima, M.Kaminaga, E.Yano, G.Yamamoto, N.Takagi, S.Nagase (2000) *Tetrahedron Lett.*,**41**,8479

Formula: $C_{67} H_{63} N_1 O_1 S_1$

Compound Name: tris(2,2',6,6'-Tetramethyl-m-terphenyl-5'-yl)methyl-S-nitrosothiol

Space Group:	P21/c	***Cell:***	***a***	12.484(2)	***b***	23.290(3)	***c*** 20.090(1)
Space Group No.:	14	***(Å,°)***	α	90.00	β	105.44(0)	γ 90.00

R-Factor (%): 6.90 ***Temperature(K):*** 296 ***Density(g/cm³):*** 1.097



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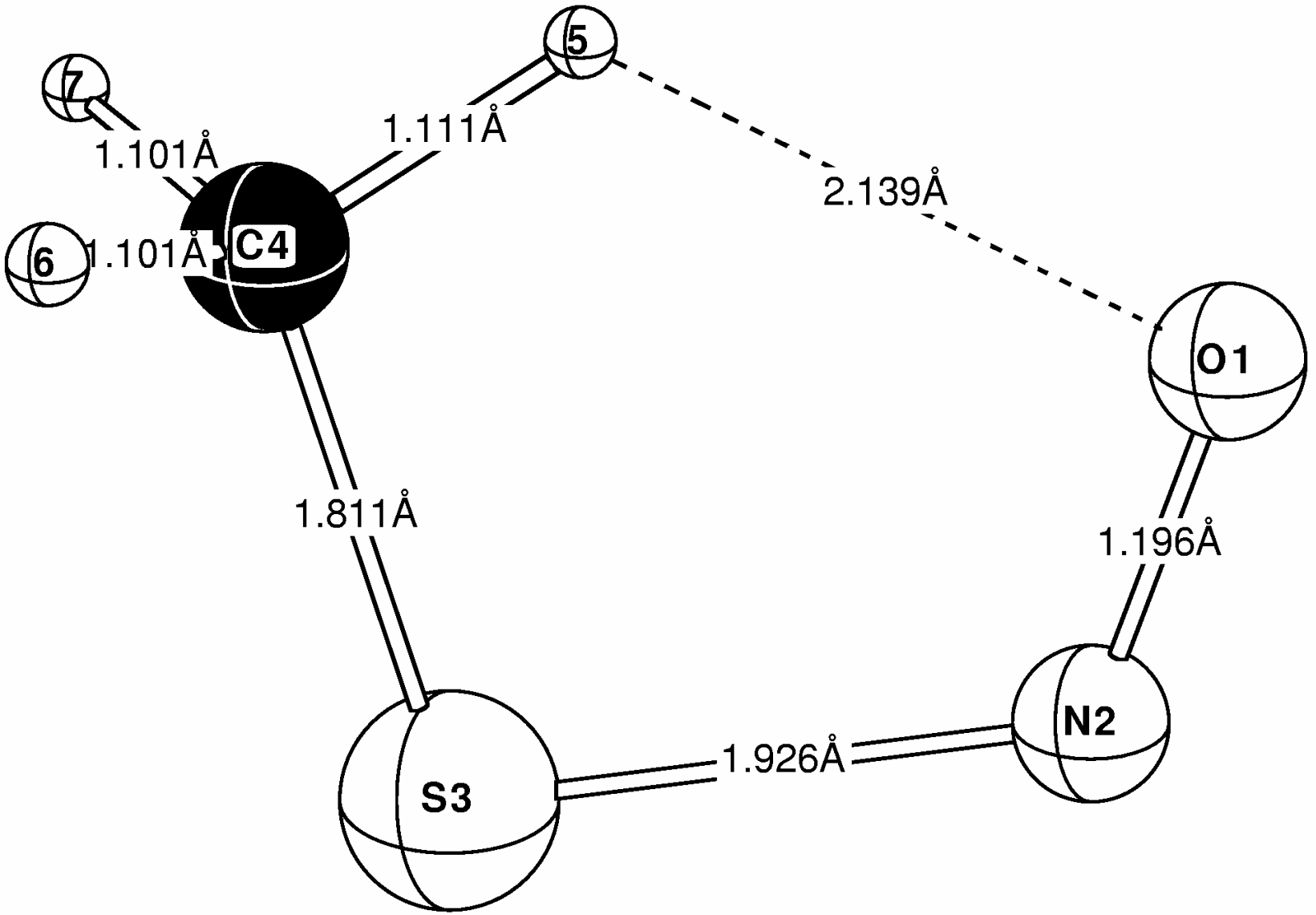
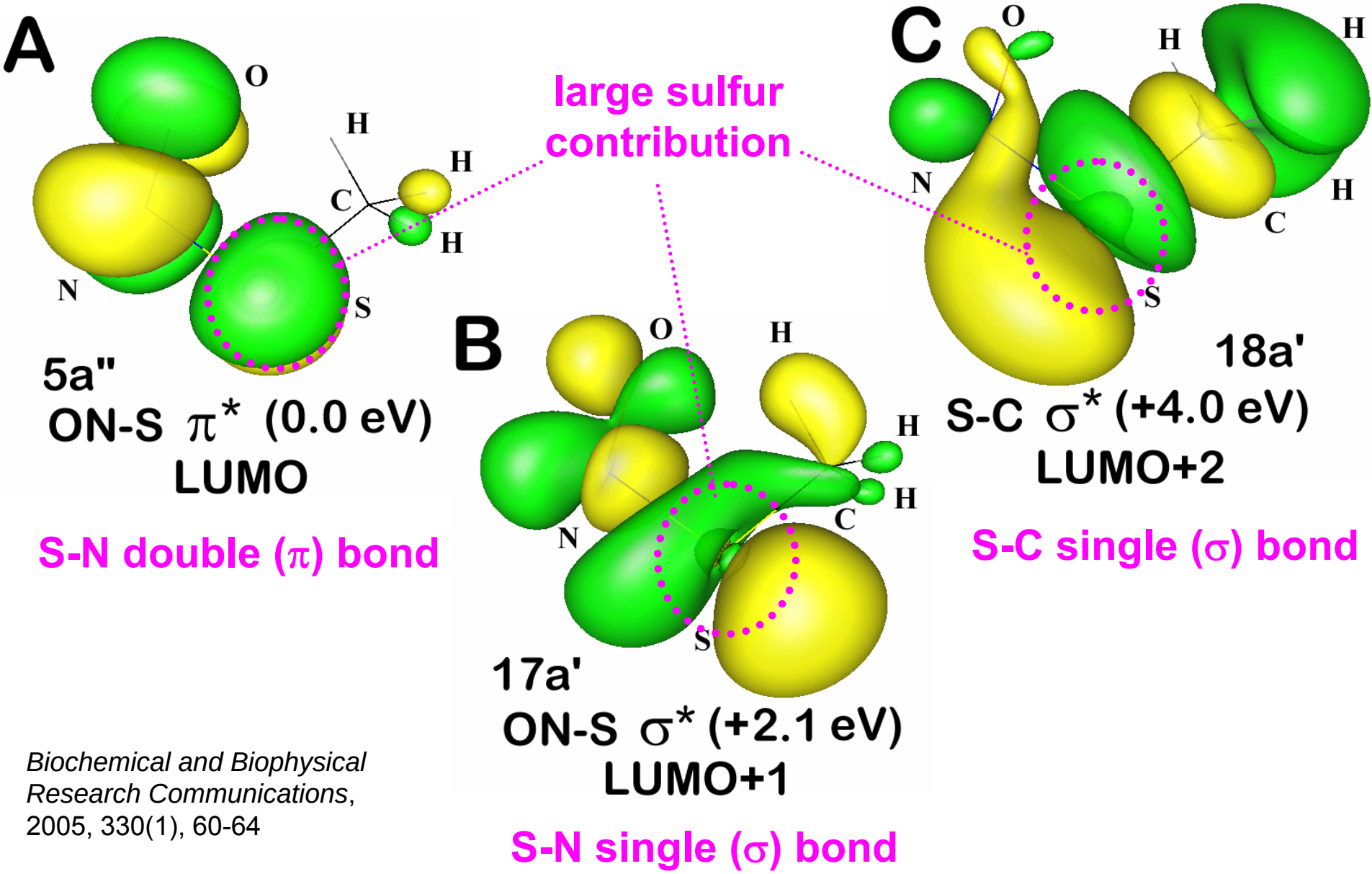
RSNO compounds: geometric structure

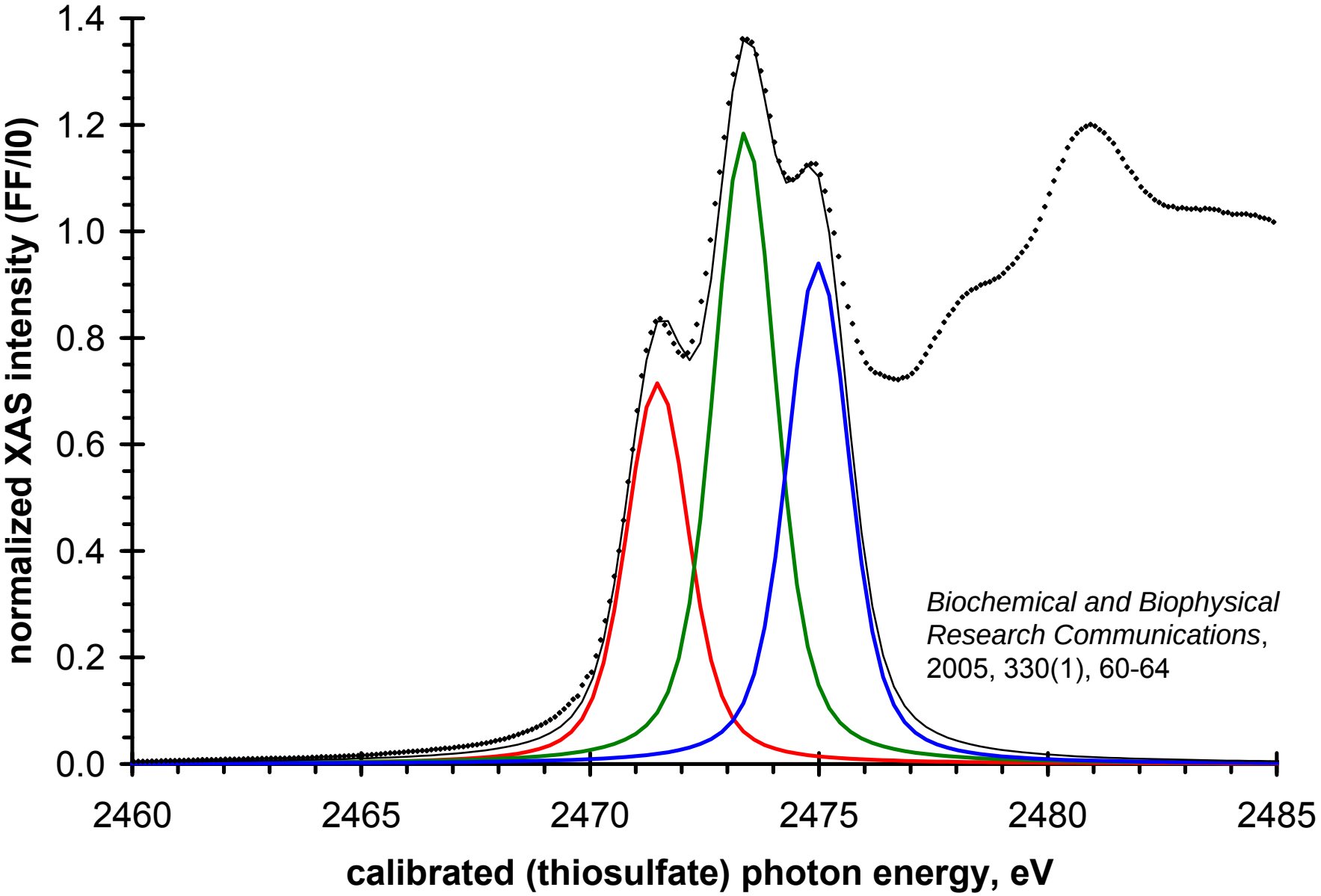


RSNO compounds: electronic structure

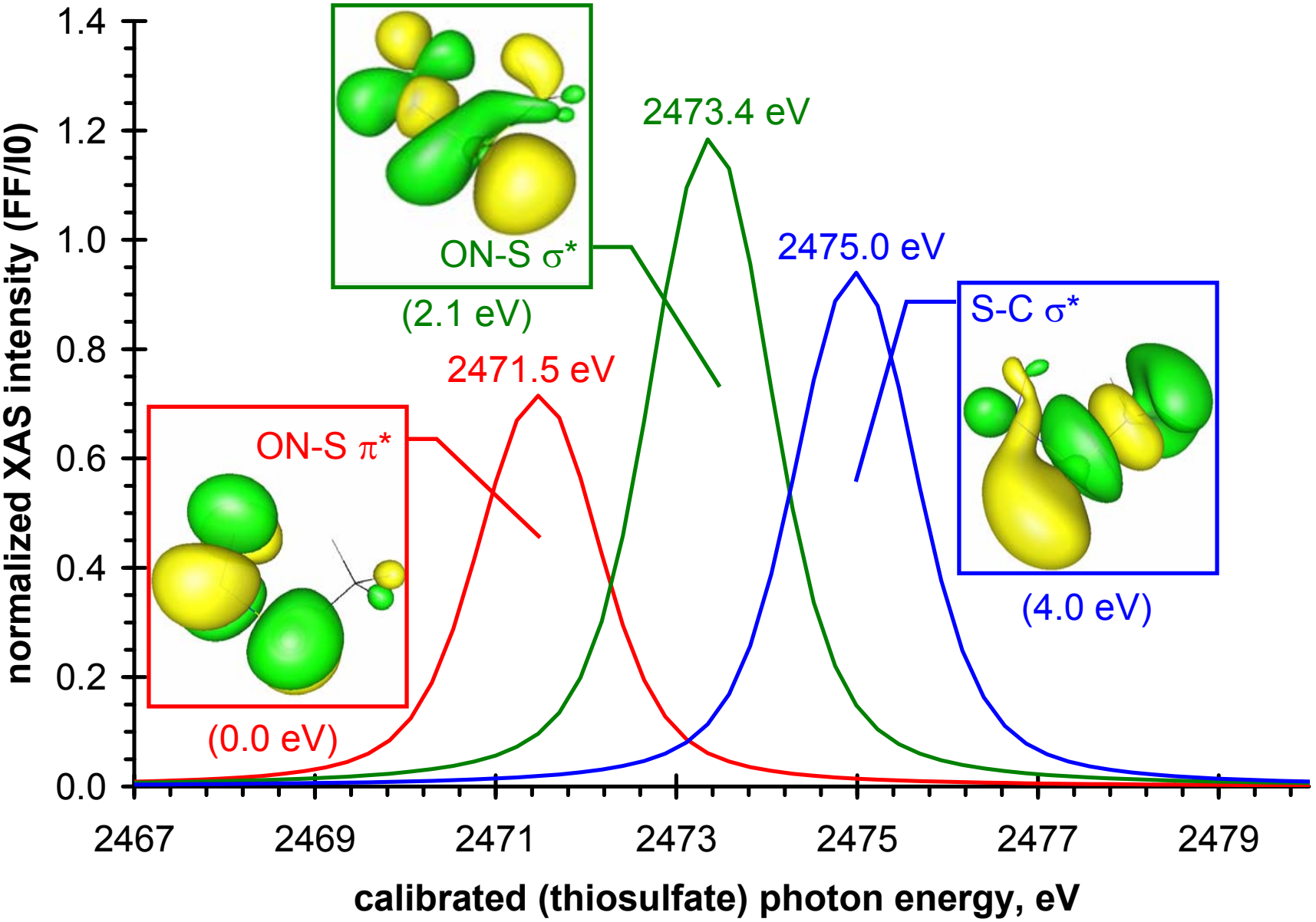


Biochemical and Biophysical Research Communications, 2005, 330(1), 60-64

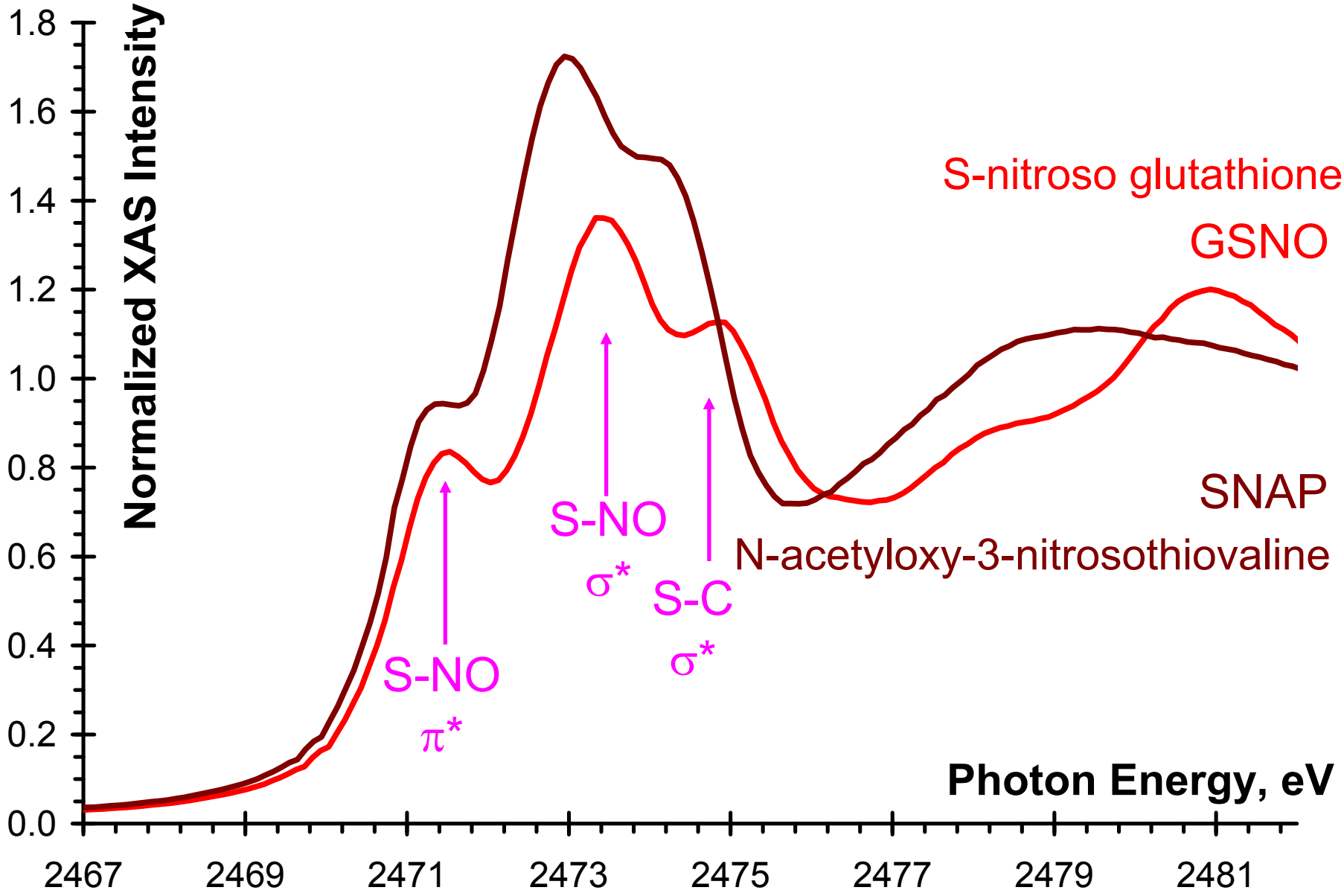
S K-edge XAS of S-nitrosated glutathione (GSNO)



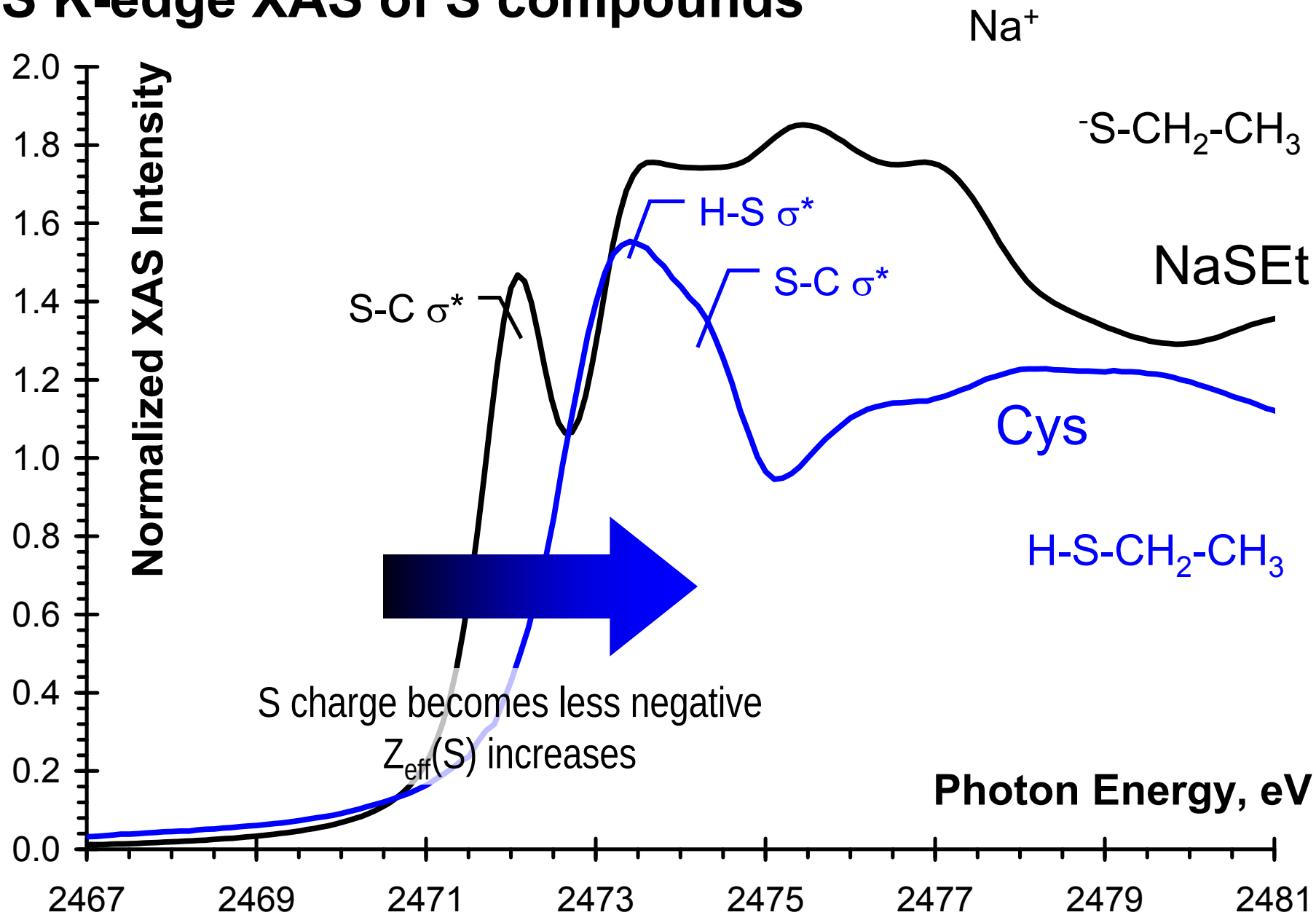
S K-edge XAS of S-nitrosated glutathione (GSNO)



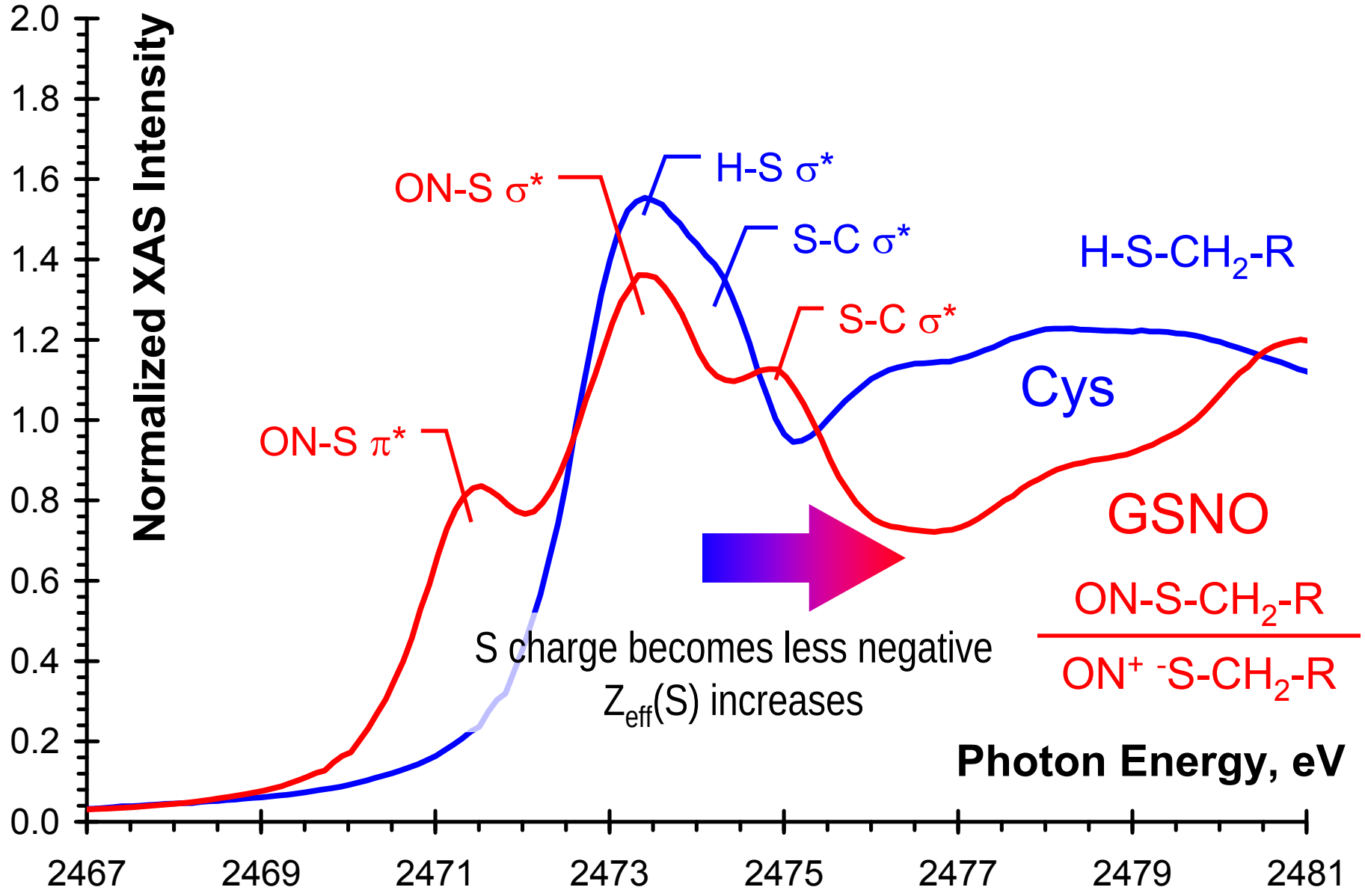
S K-edge XAS of SNO compounds



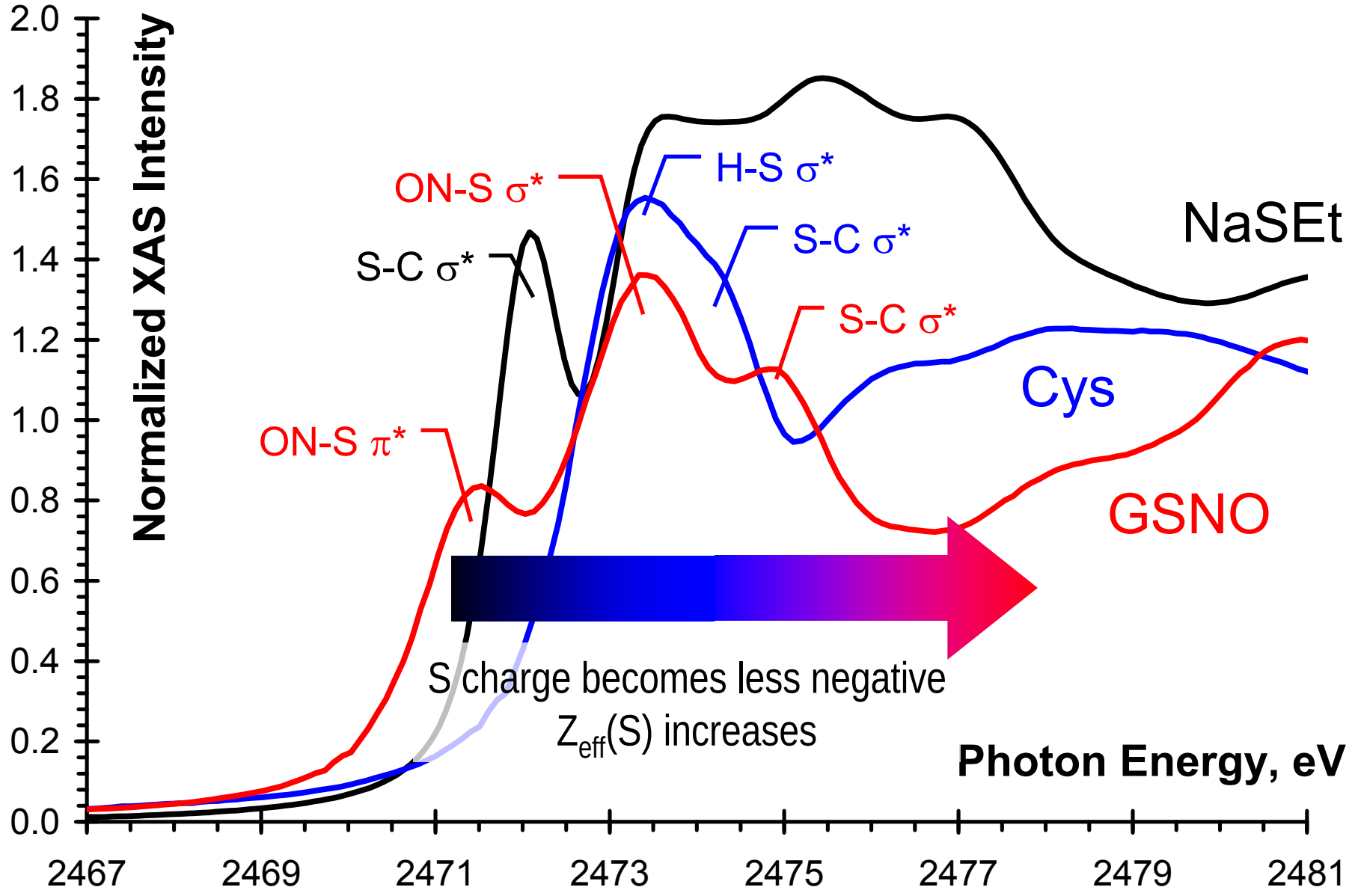
S K-edge XAS of S compounds



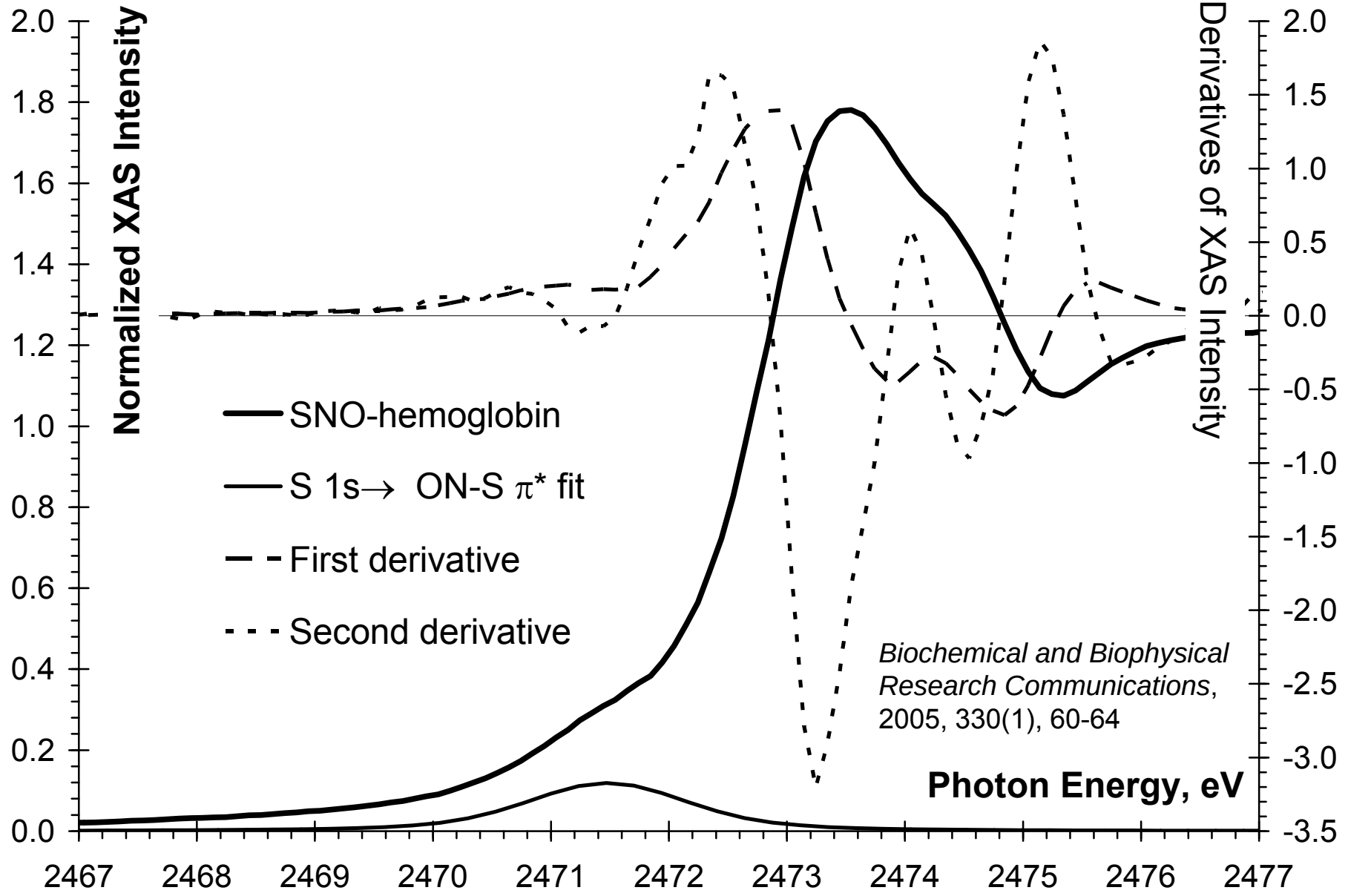
S K-edge XAS of S compounds



S K-edge XAS of S compounds



S K-edge XAS as detection method for SNO



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: $\varphi^* = \Sigma\, c_i\, \phi_i$

for a 'simple' M-S bond: $\varphi^* = c_{M,d}\, \phi_M(n\mathrm{d}) + c_{M,s}\, \phi_M(n{+}1\ \mathrm{s}) + c_{M,p}\, \phi_M(n{+}1\ \mathrm{p})$

$- c_{S,s}\, \phi_S(3\mathrm{s}) + c_{S,p}\, \phi_S(3\mathrm{p}) + c_{S,d}\, \phi_S(3\mathrm{d})$

Multi-edge XAS

for a ‘simple’ M-S bond:

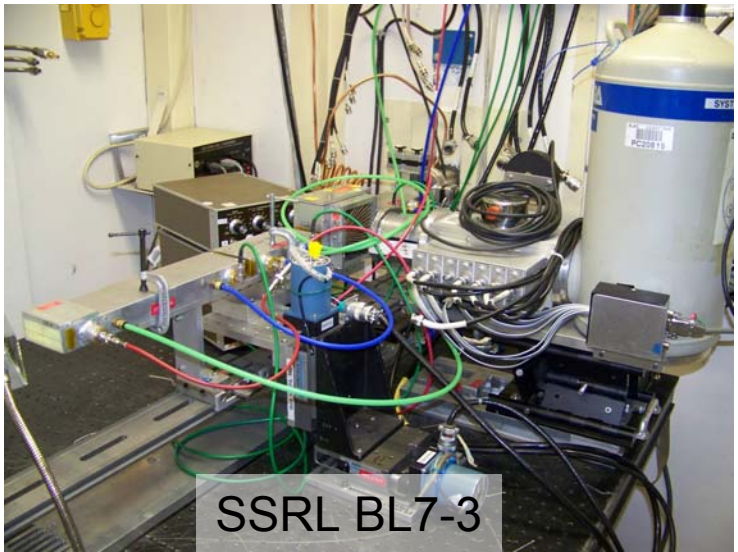
$$\varphi^* = c_{M,d}\,\phi_M(nd) + c_{M,s}\,\phi_M(n{+}1\ s) + c_{M,p}\,\phi_M(n{+}1\ p) - c_{S,s}\,\phi_S(3s) + c_{S,p}\,\phi_S(3p) + c_{S,d}\,\phi_S(3d)$$

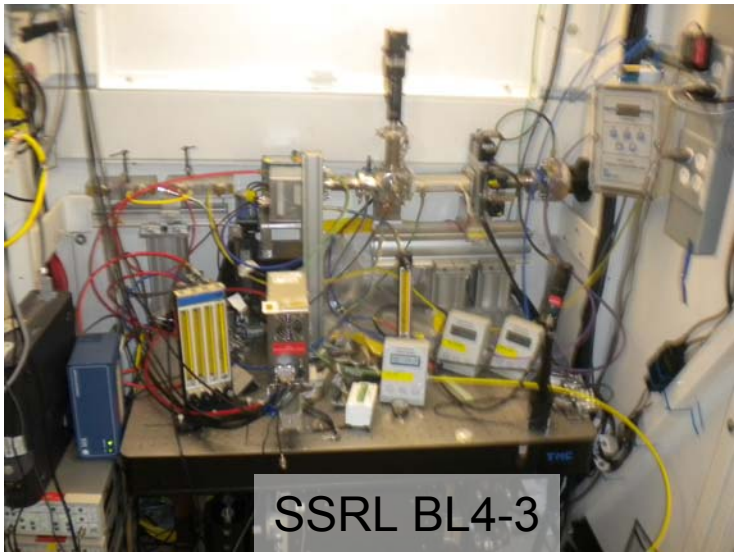
metal contribution/character

ligand character/covalency

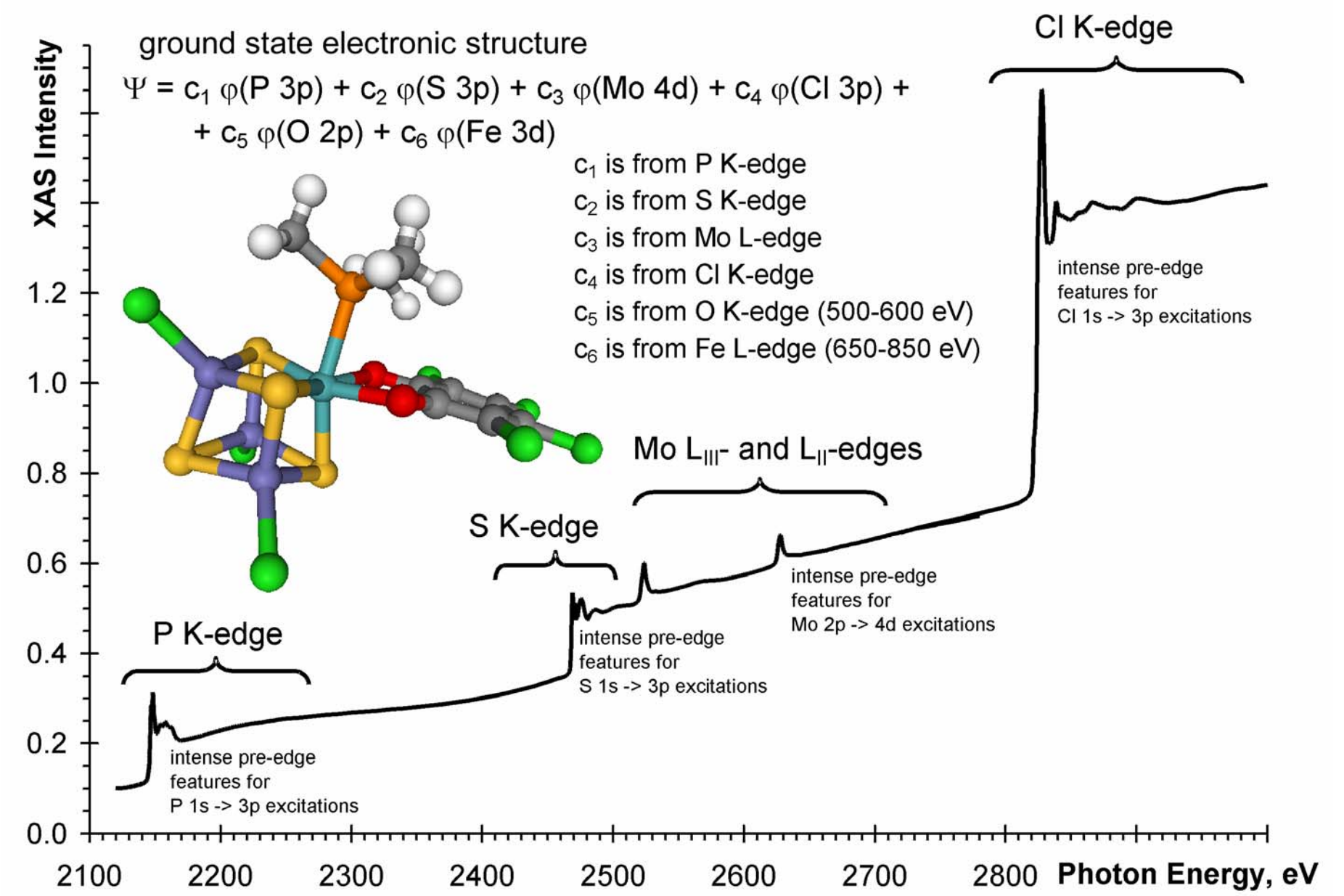
for intense spectral features in absorption spectroscopy – $\Delta l = 1$

M 2p	M 1s	L 1s	L 2p
metal L-edge XAS	metal K-edge XAS	ligand K-edge	L-edge
SSRL BL10-1/8-2	BL7-3/9-3/4-1/4-3	BL6-2/4-3	BL10-1/8-2

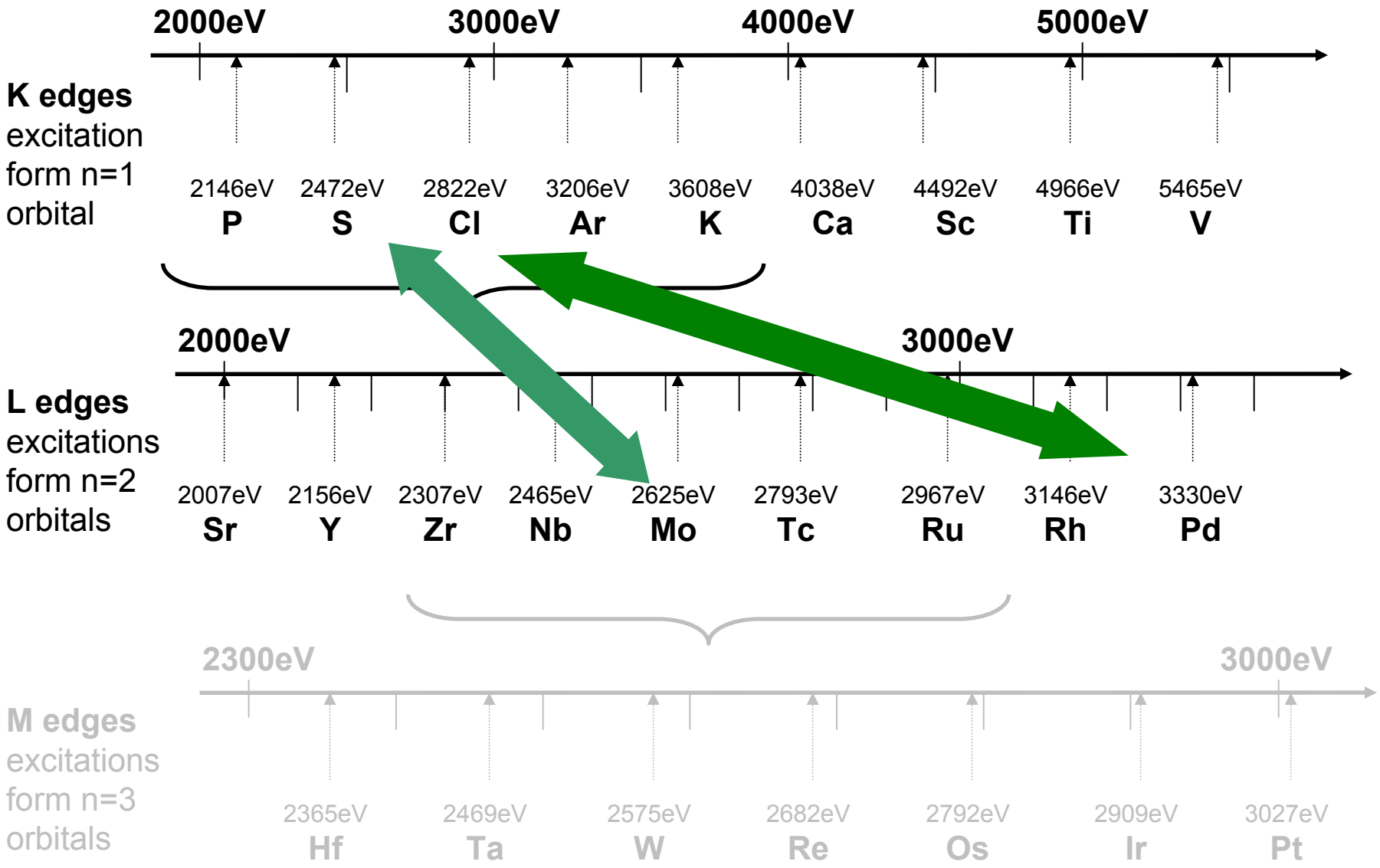




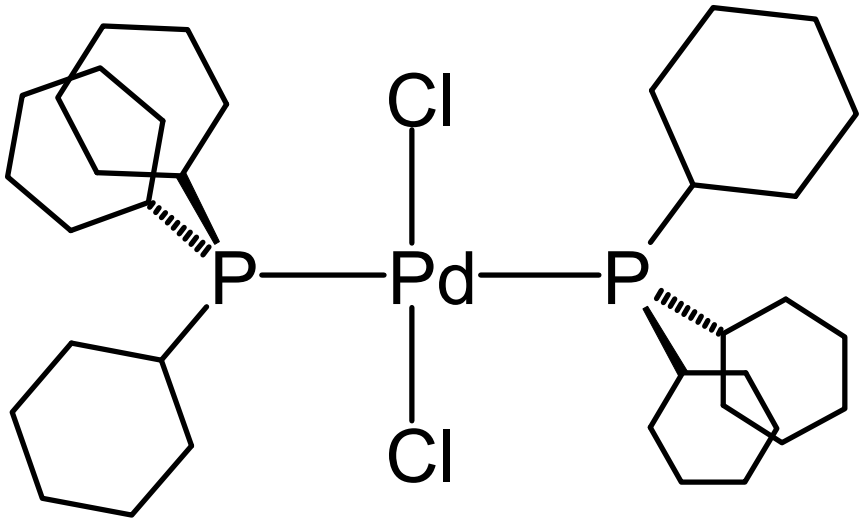
Multi-edge XAS

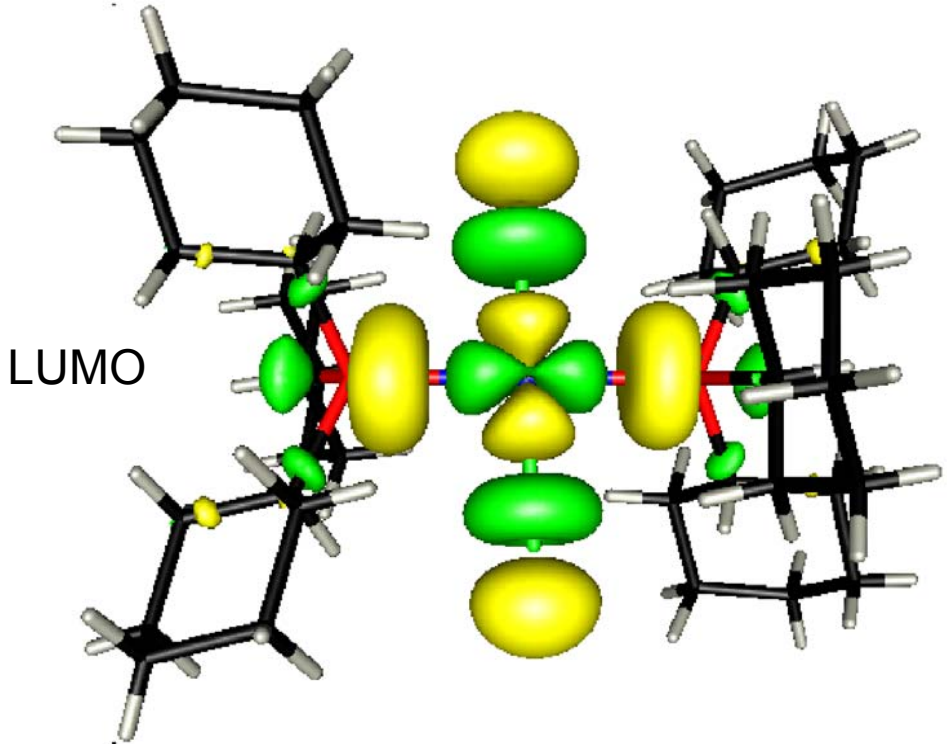


Multi-edge XAS at SSRL BL6-2/4-3



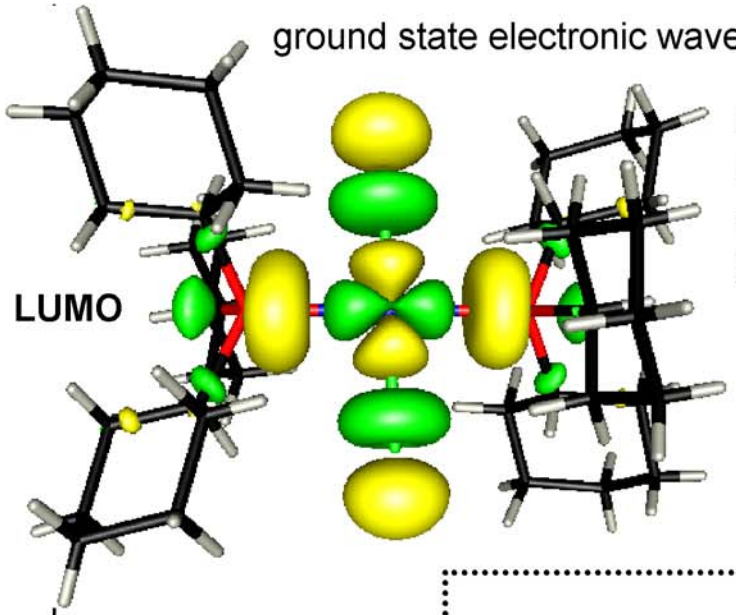
Multi-edge XAS: A non-biological, but simple example





Inorganica Chimica Acta,
2008, 361(4), 1047-1058

Multi-edge XAS: A non-biological, but simple example



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

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

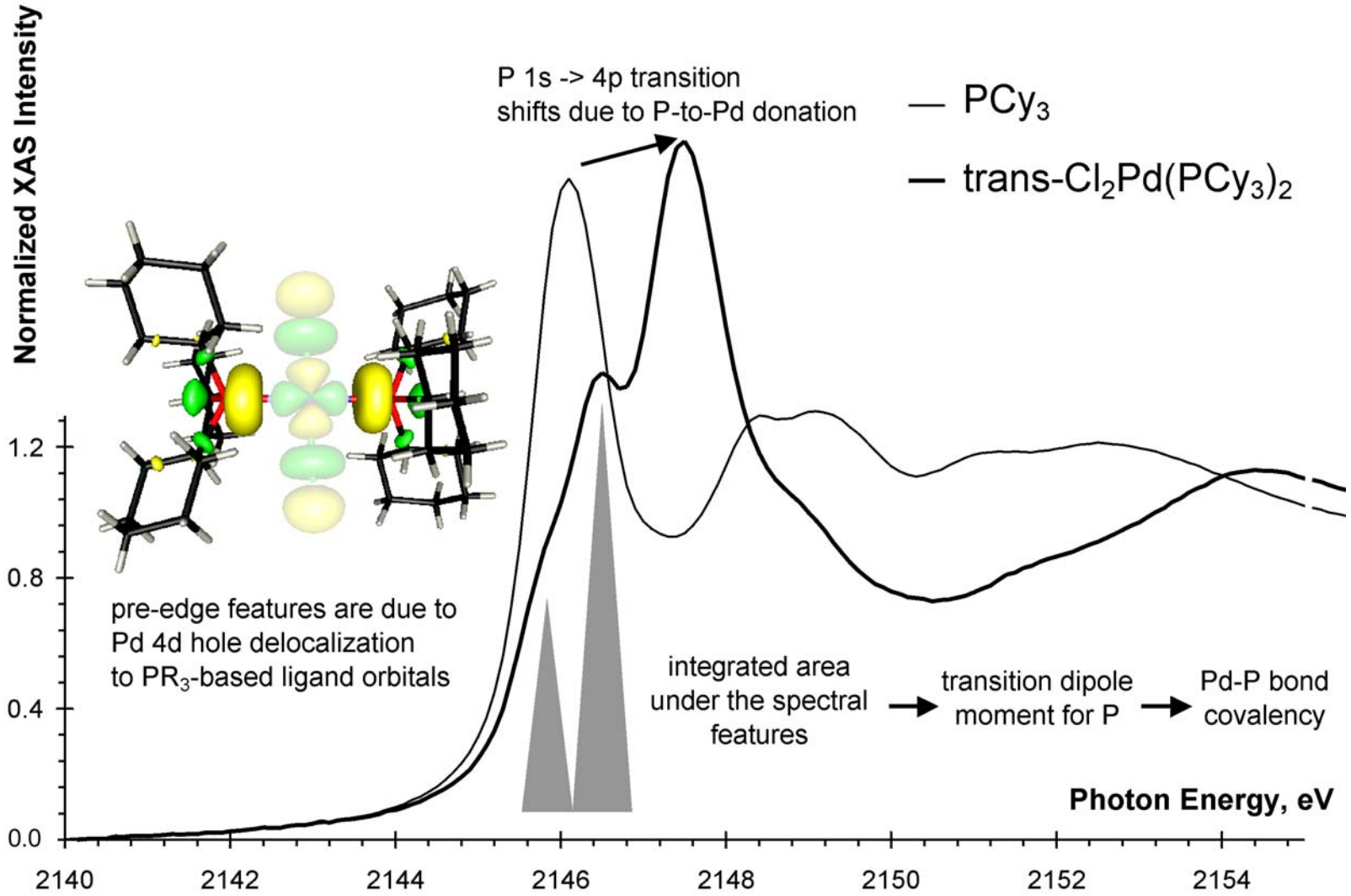
Pd L_3-edge intense pre-edge features for Pd 2p -> 4d excitations

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

Photon Energy, eV

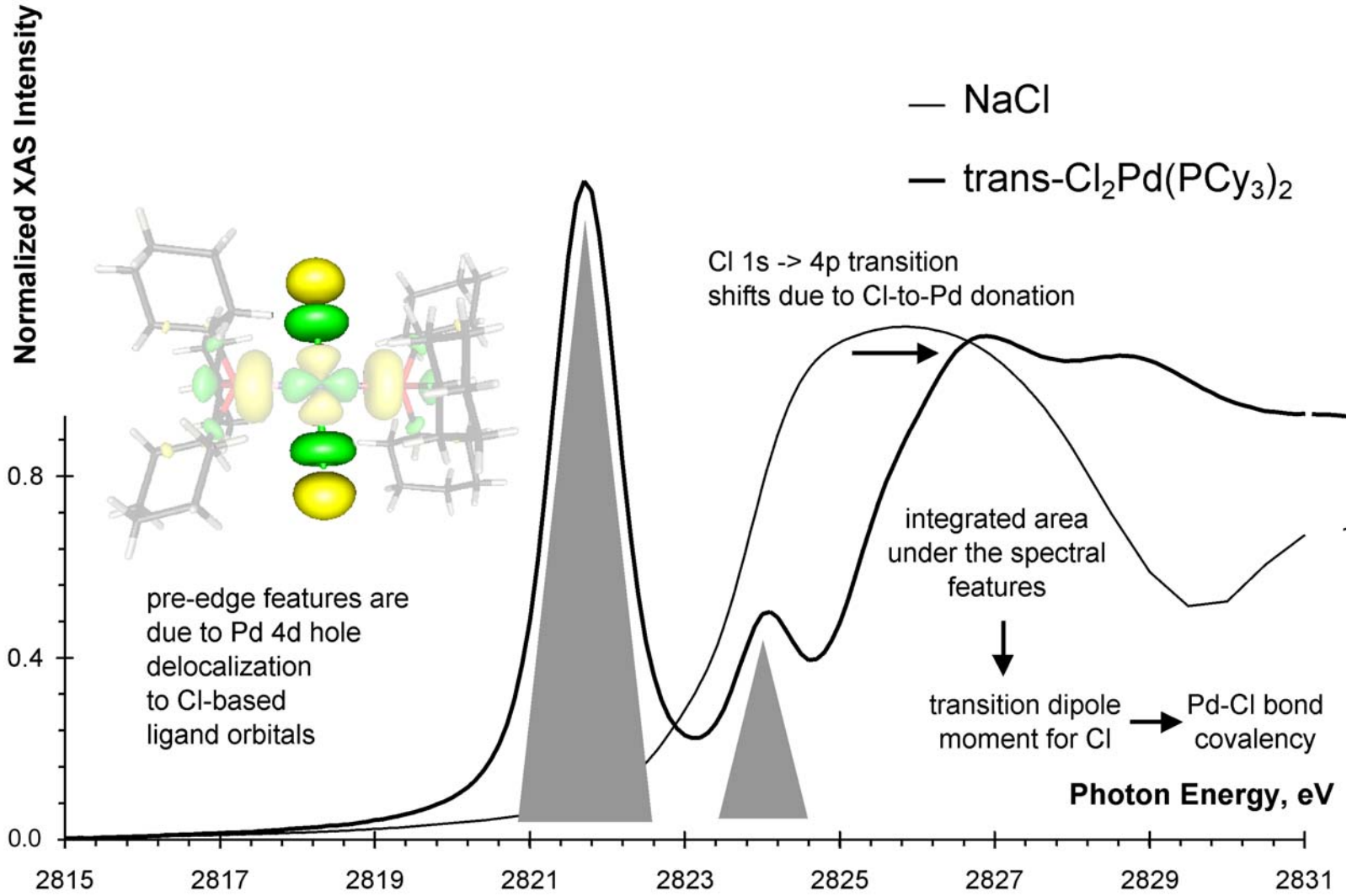
2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500

Multi-edge XAS: phosphorous K-edge



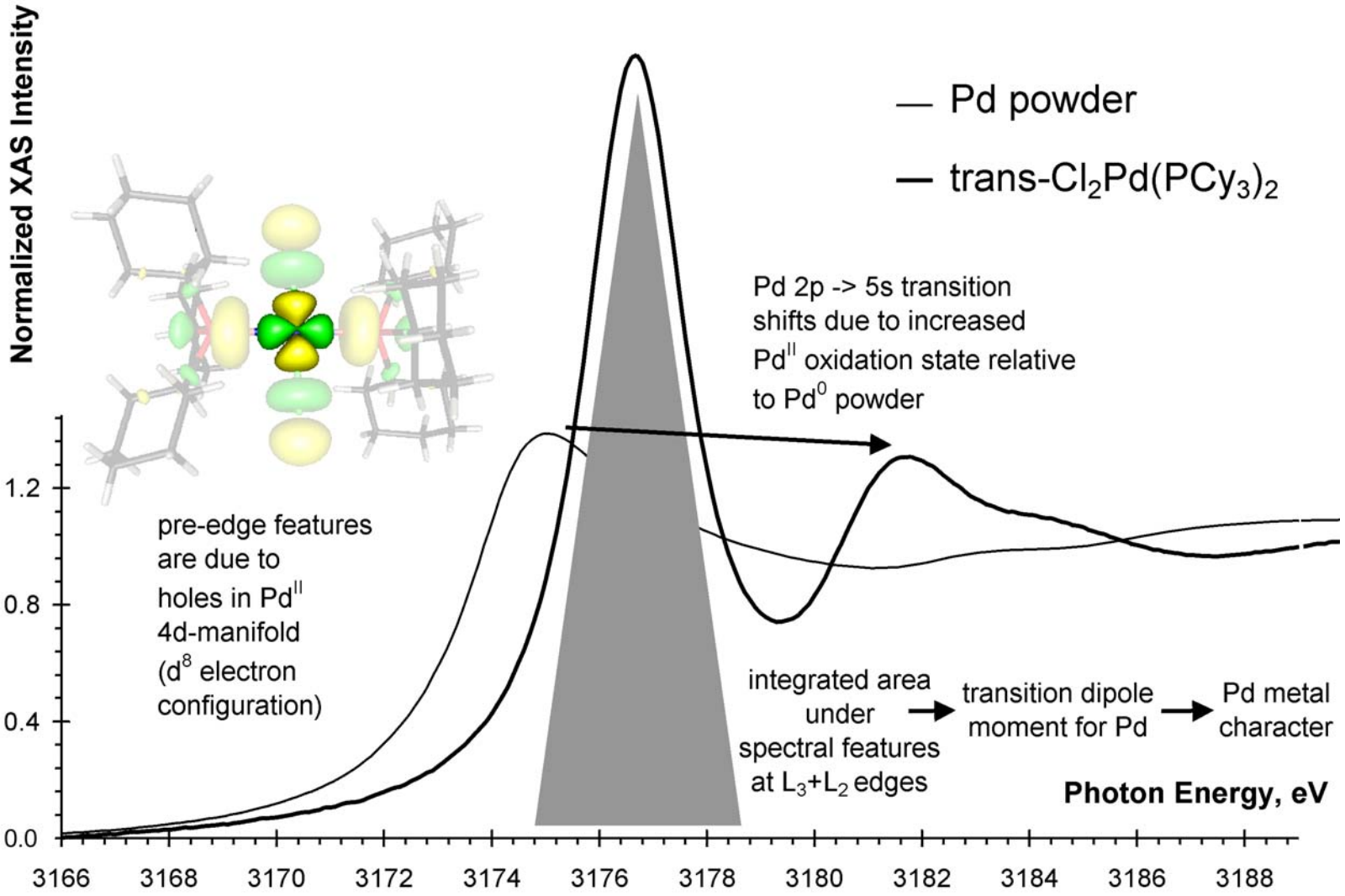
Phosphorous 3p character of the palladium-phosphorous bonds is determined from phosphorous K-edge XAS

Multi-edge XAS: chlorine K-edge



Chlorine 3p character of the palladium-chlorine bonds is determined from chlorine K-edge XAS

Multi-edge XAS: palladium L-edge

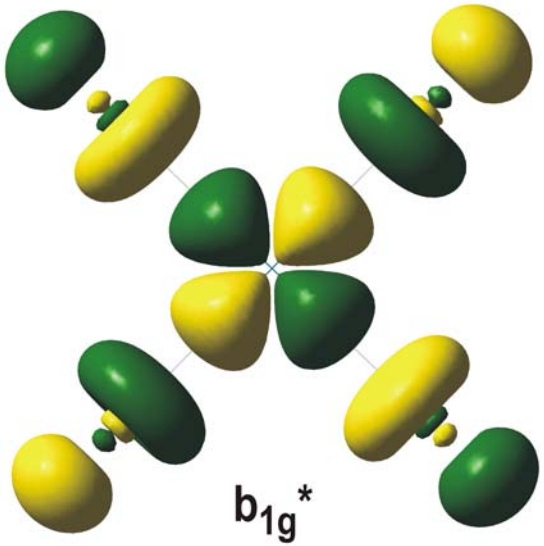


Metal 4d character of the palladium-ligand bonds is determined from palladium L-edge XAS (only L_{III} edge is shown)

Multi-edge XANES: chloropalladium(II/IV)

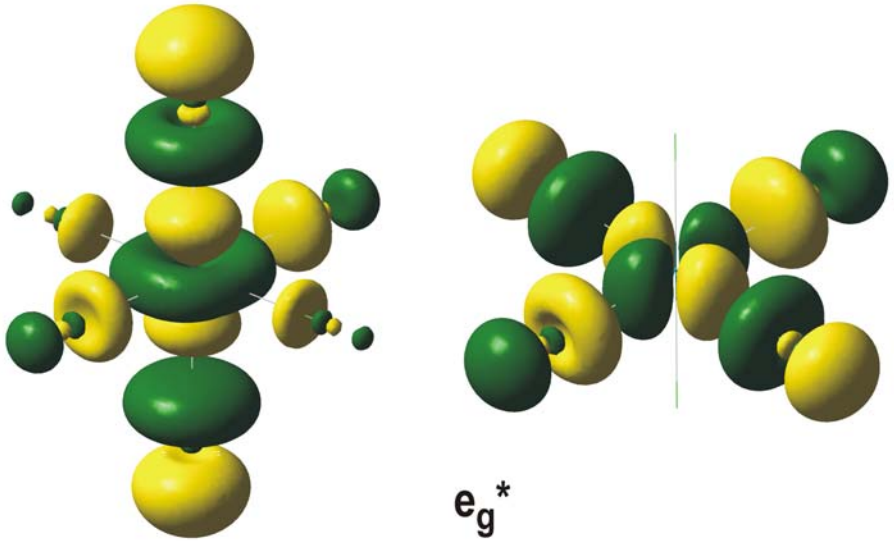
$K_2Pd^{II}Cl_4$

closed shell d^8



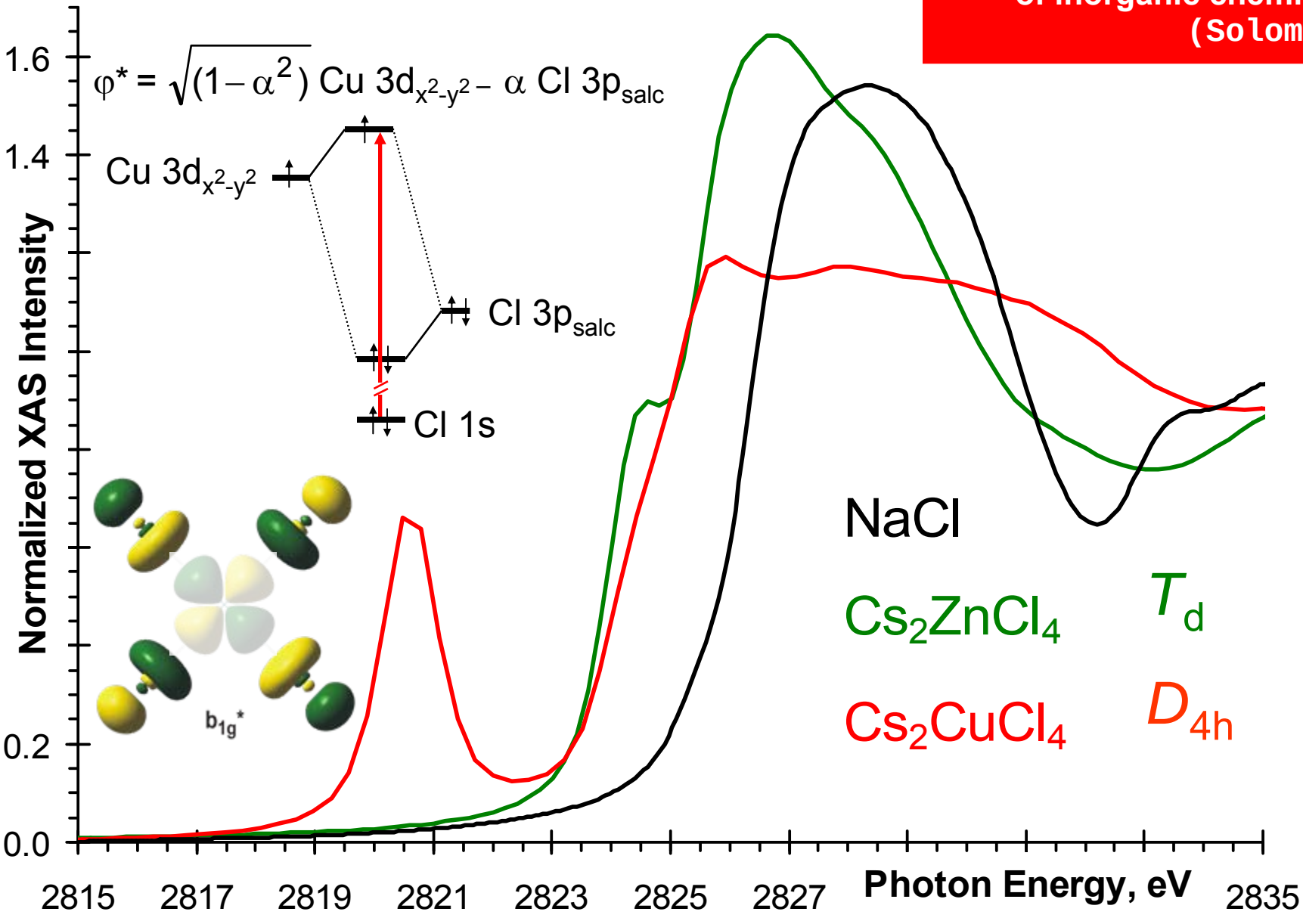
$K_2Pd^{IV}Cl_6$

closed shell d^6



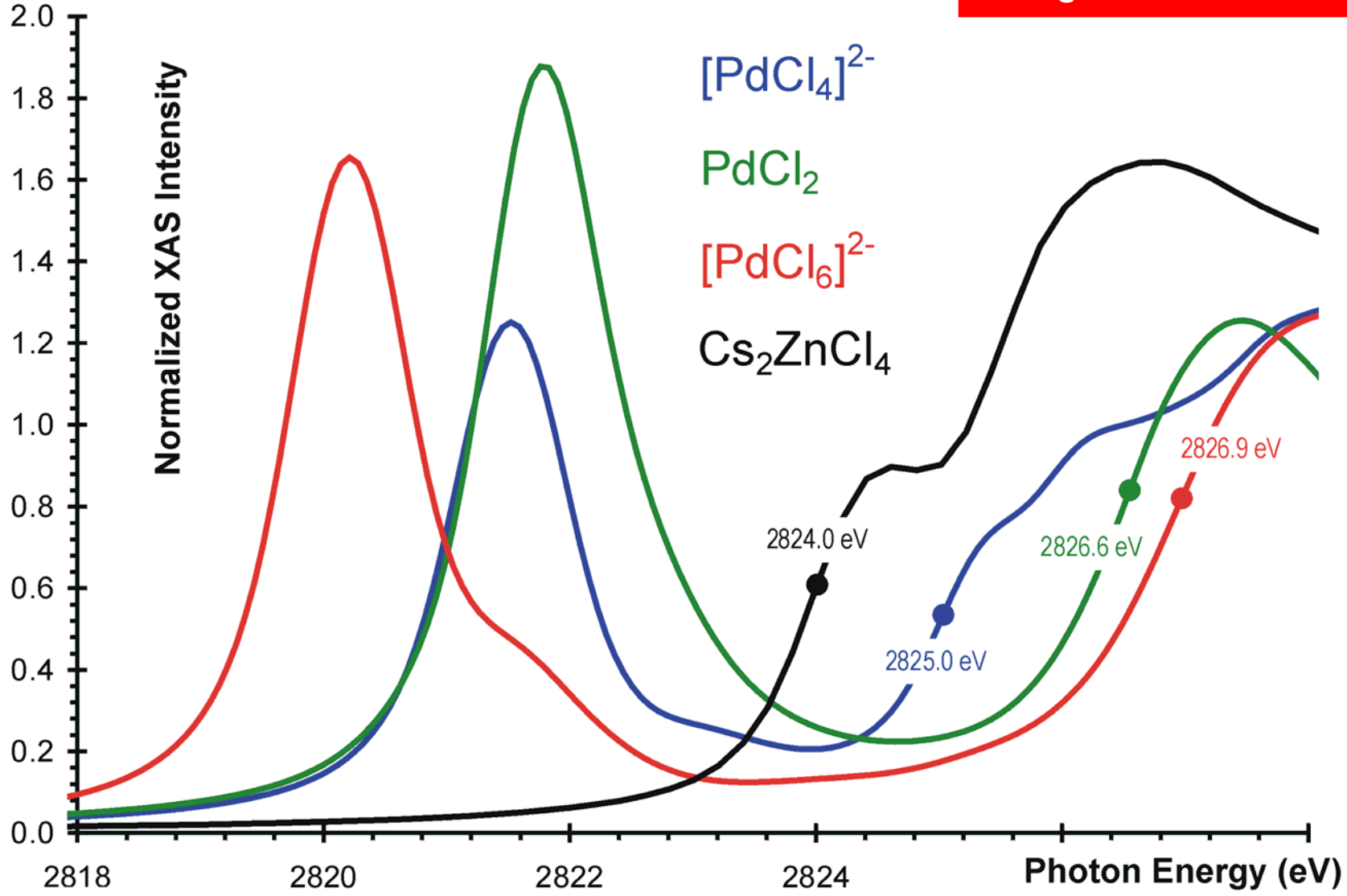
Chlorine K-edge XANES:

Cu(II) is the hydrogen atom of inorganic chemistry (Solomon)



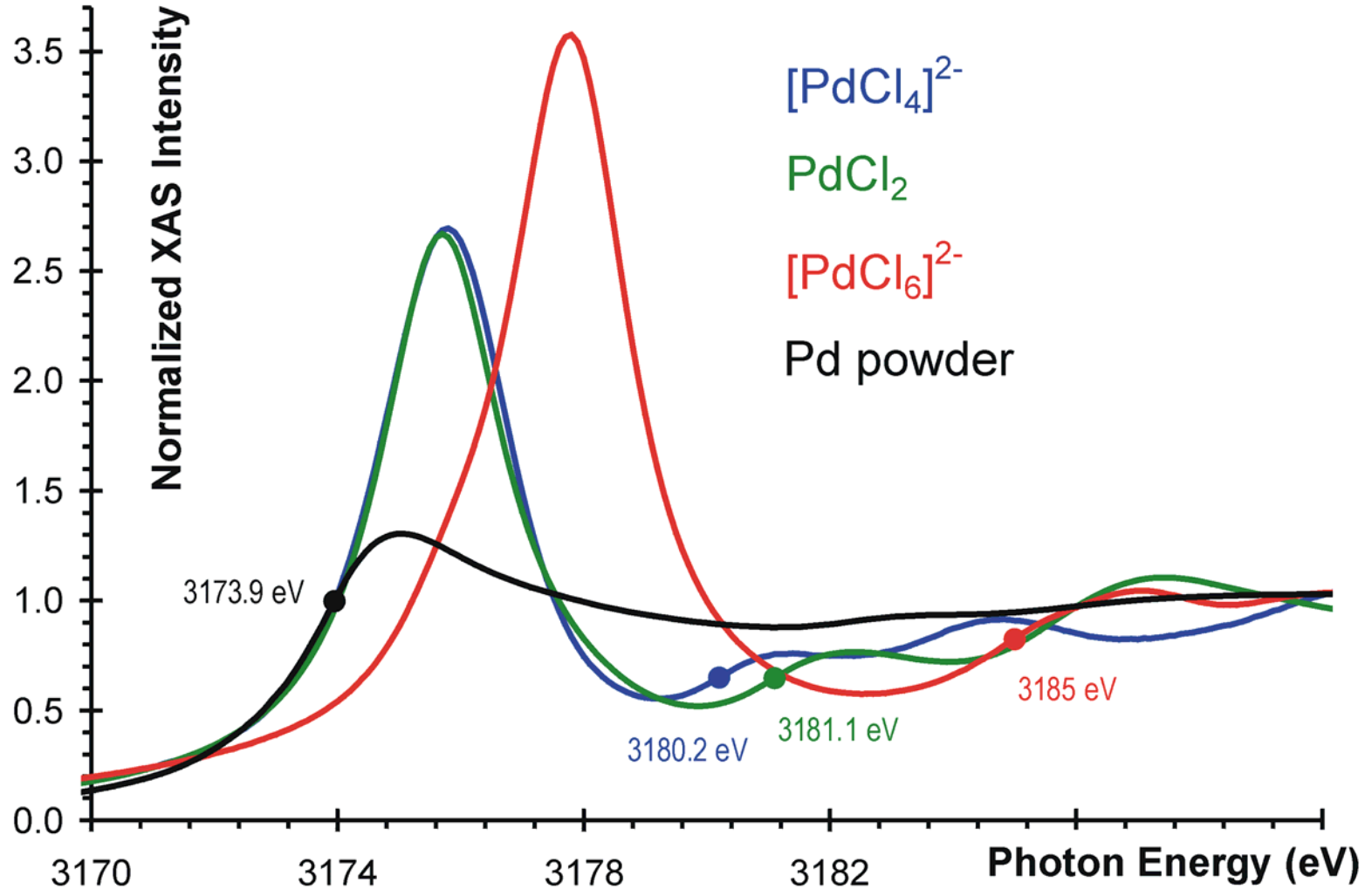
Multi-edge XANES: Cl

Pd(II) is the hydrogen atom of organometallic chemistry



Inorganica Chimica Acta, 2008, 361(4), 1047-1058

Multi-edge XANES: Pd



Inorganica Chimica Acta, 2008, 361(4), 1047-1058

Experimental M-L covalency

acceptor orbital $\Psi_a = \sqrt{(1-\alpha^2)}\phi_M - \alpha\,\phi_L$ $\qquad \phi_L = \sum_{\text{ligands}} \sum_{\text{orbitals}} c_{l,o}\phi_{l,o}$

donor orbital $\Psi_d = \sum_{\text{ligands}} c_{l,d}\phi_{l,d}$ (donor is 1s for K-edge excitations)

electric dipole allowed transition/Fermi golden rule: $I \propto \left| <\Psi_a \,|\, \boldsymbol{r} \,|\, \Psi_d> \right|^2$

$$I \propto \left(\sqrt{(1-\alpha^2)} \sum_{\text{ligands}} c_{l,d} <\phi_M \,|\, \boldsymbol{r} \,|\, \phi_{l,d}> - \alpha \sum_{\text{ligands}} \sum_{\text{ligands}} \sum_{\text{orbitals}} c_{l,d}c_{l,o} <\phi_{l,o} \,|\, \boldsymbol{r} \,|\, \phi_{l,d}> \right)^2$$

ligand core/metal overlap ≈ 0 ligand core/ligand core overlap ≈ 0

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

$<\mathscr{R}>$ dipole integral

$$I = \left| <\Psi_{M-L(3p)} \,|\, \boldsymbol{r} \,|\, \Psi_{L(1s)}> \right|^2 = \frac{1}{3}\alpha^2 <\mathscr{R}>$$

JACS, 1992, 112(4), 1643-1645

Multi-edge XANES: chloropalladium(II/IV)

using $I(Cl^-_t)$ = 21.0 eV → ~50% Cl covalency in both $[Pd^{II}Cl_4]^{2-}$ and $[Pd^{IV}Cl_6]^{2-}$

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

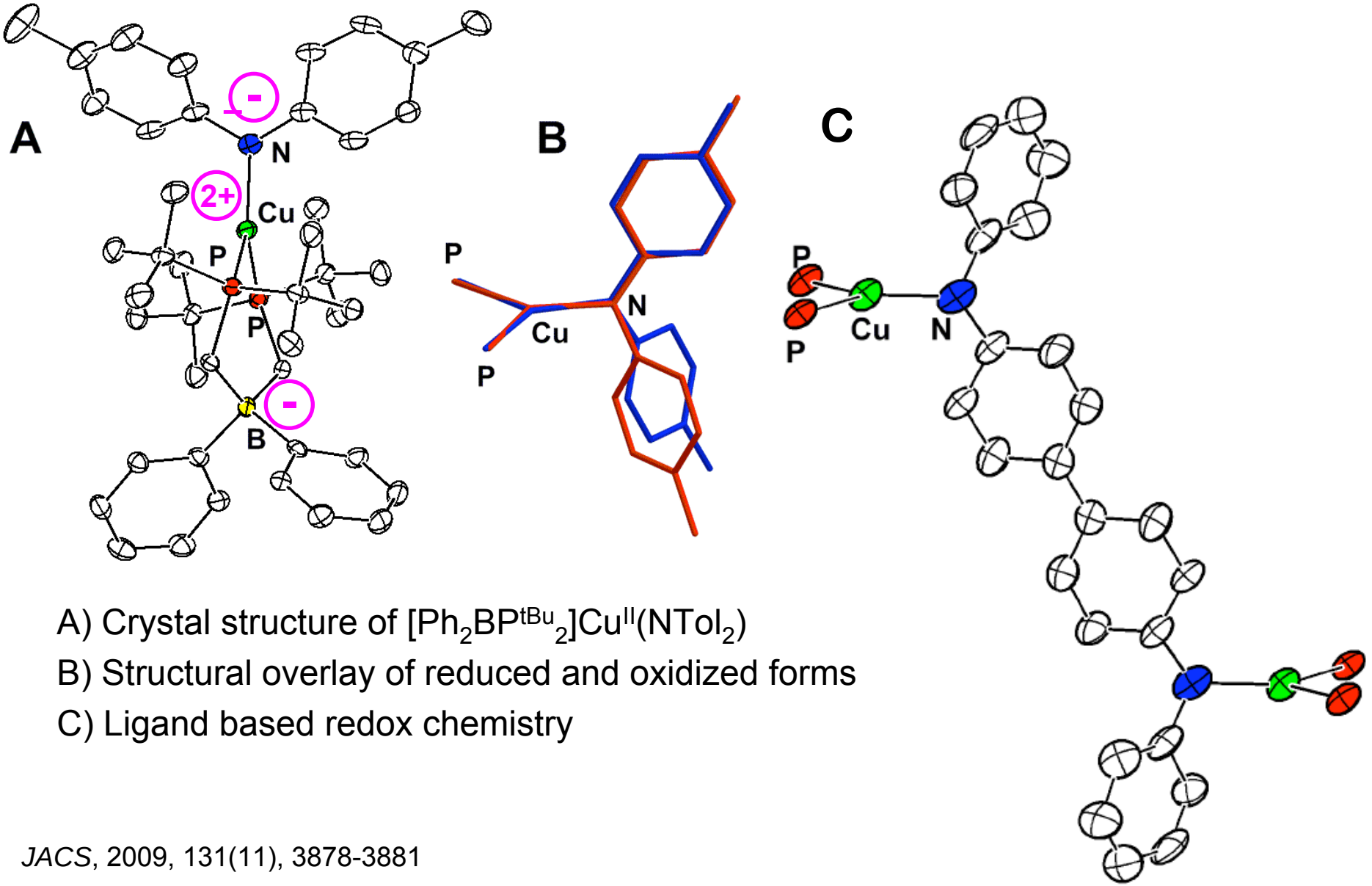
$I(Pd^{II})$ = 20.8 (SSRL) 16.9 (ALS) eV

$I(Pd^{IV})$ = 14.1 (SSRL) 11.9 (ALS) eV

to test the transferability we used $I(Pd^{II})$ to determine the covalency of Pd-Cl bonds in $PdCl_2$ to be ~50% with a new transition dipole integral for $I(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



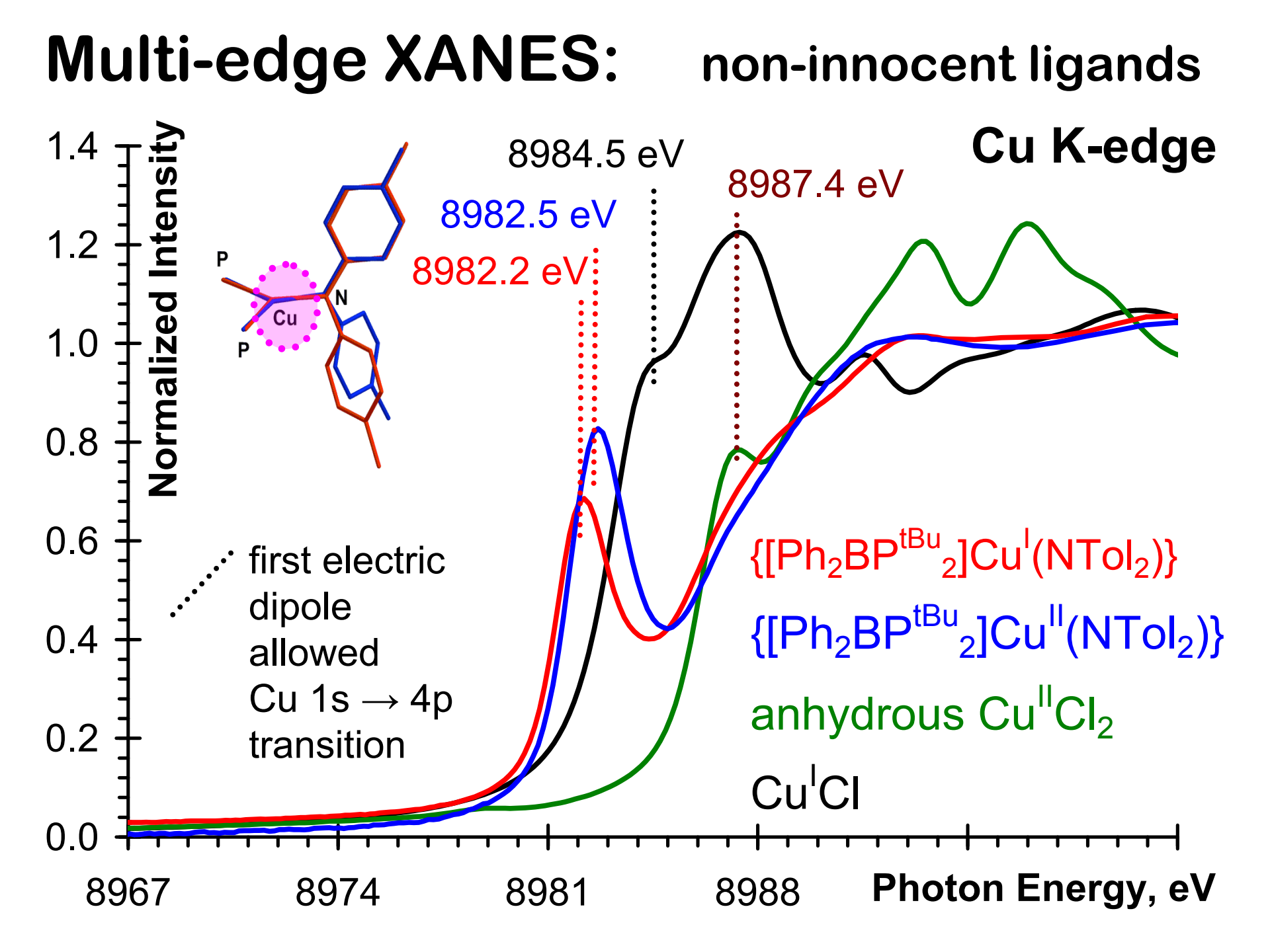
A) Crystal structure of $[Ph_2BP^{tBu}_2]Cu^{II}(NTol_2)$

B) Structural overlay of reduced and oxidized forms

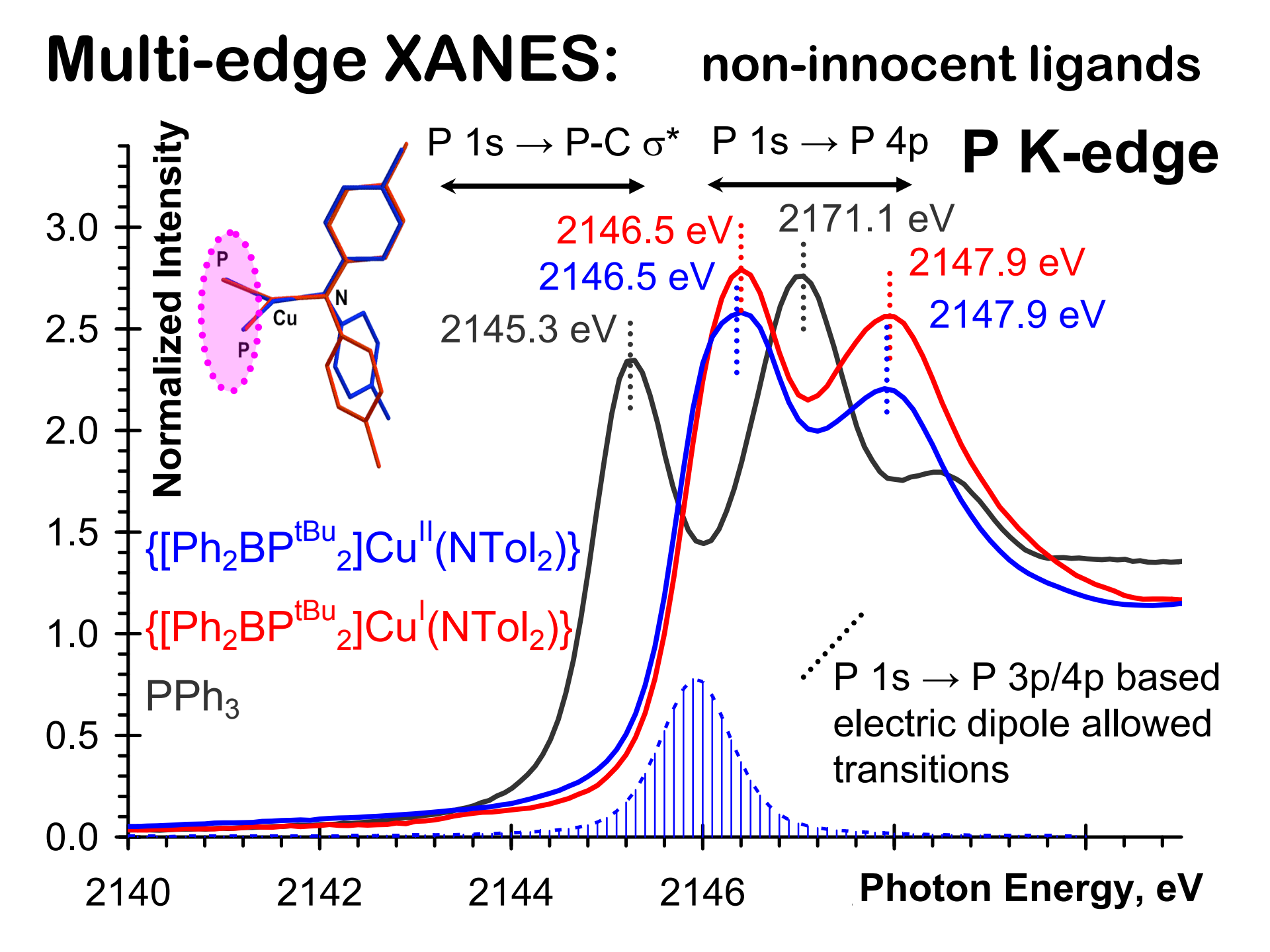
C) Ligand based redox chemistry

JACS, 2009, 131(11), 3878-3881

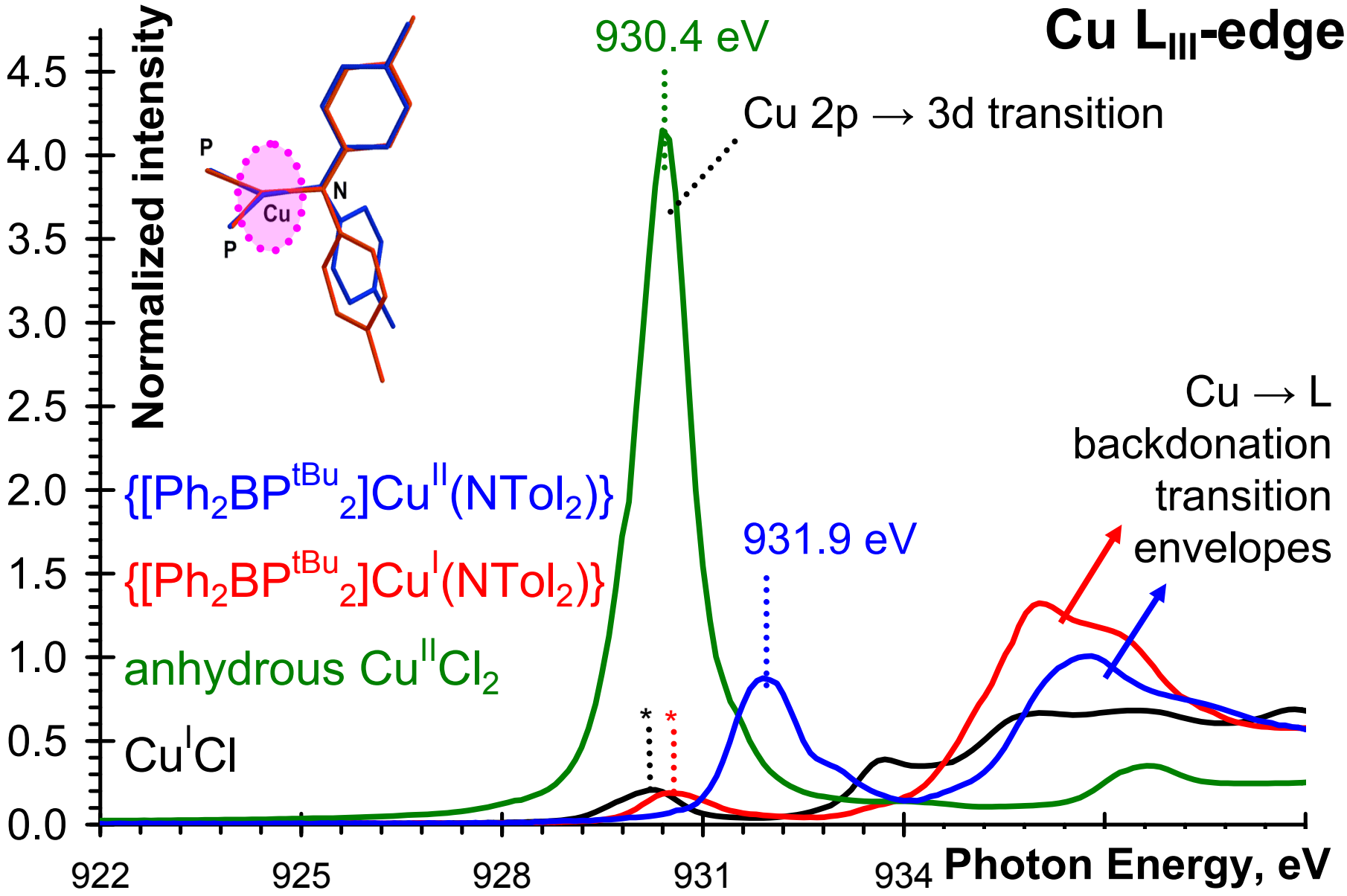
Multi-edge XANES: non-innocent ligands



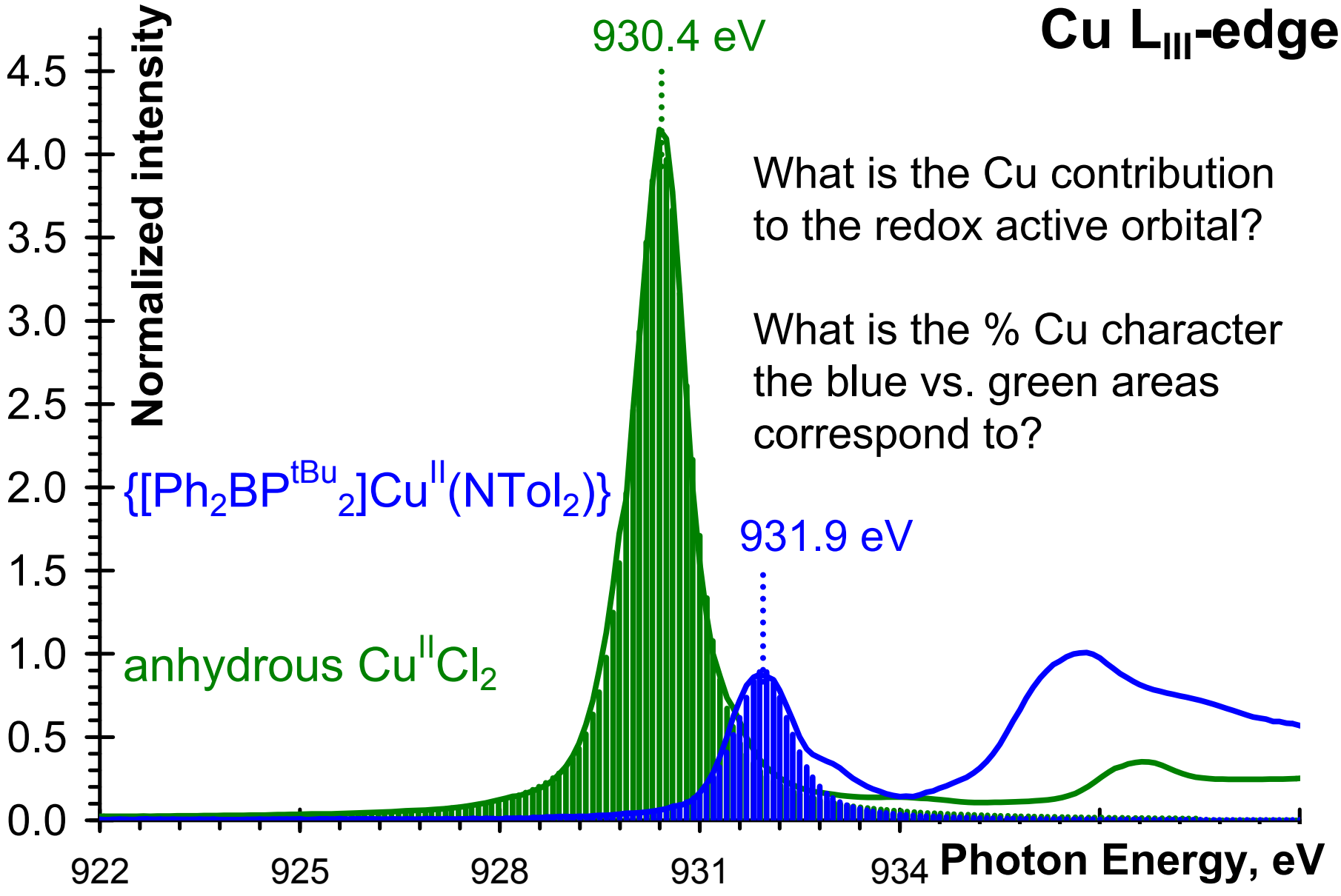
Multi-edge XANES: non-innocent ligands



Multi-edge XANES: non-innocent ligands

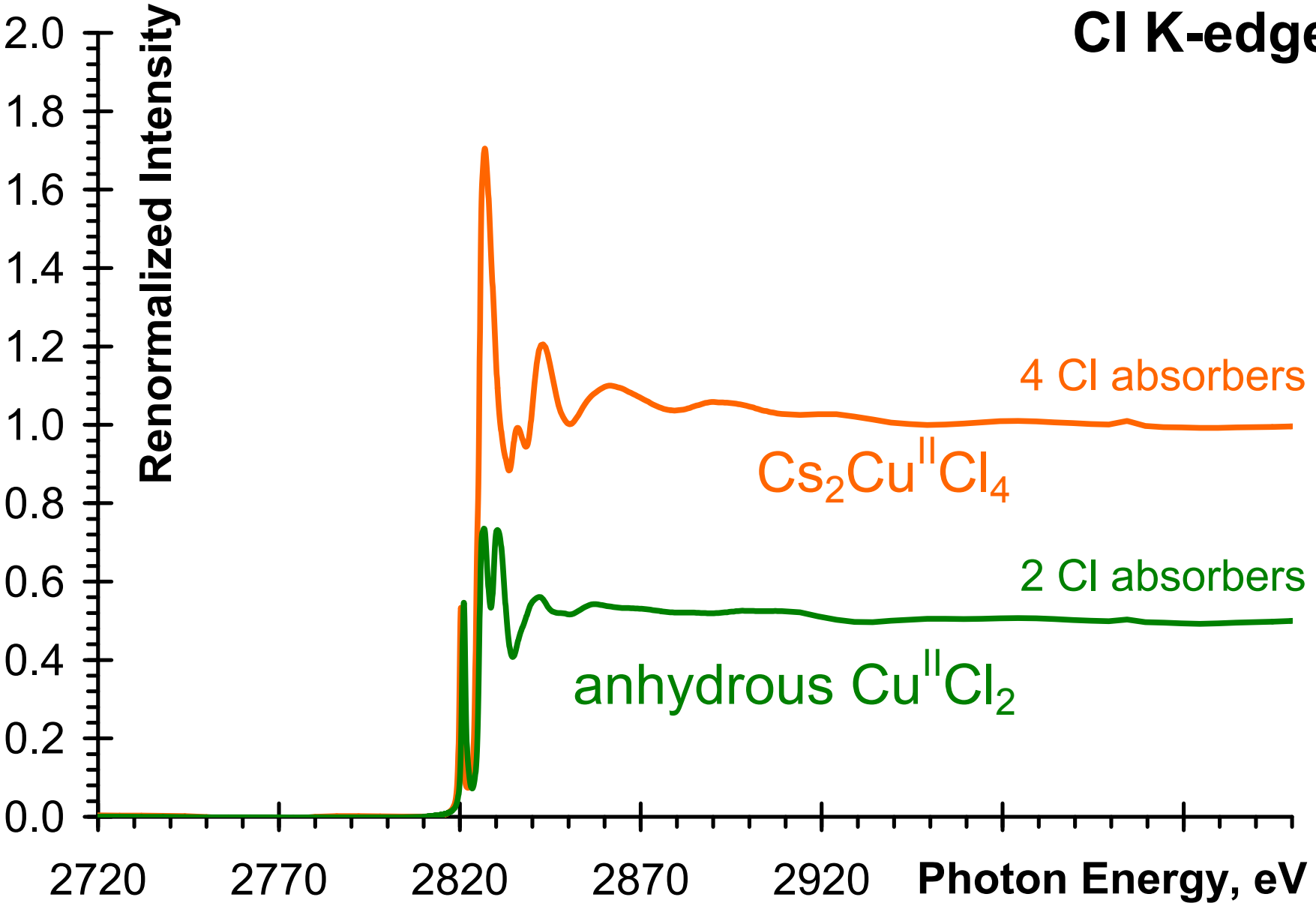


Multi-edge XANES: quantitative treatment

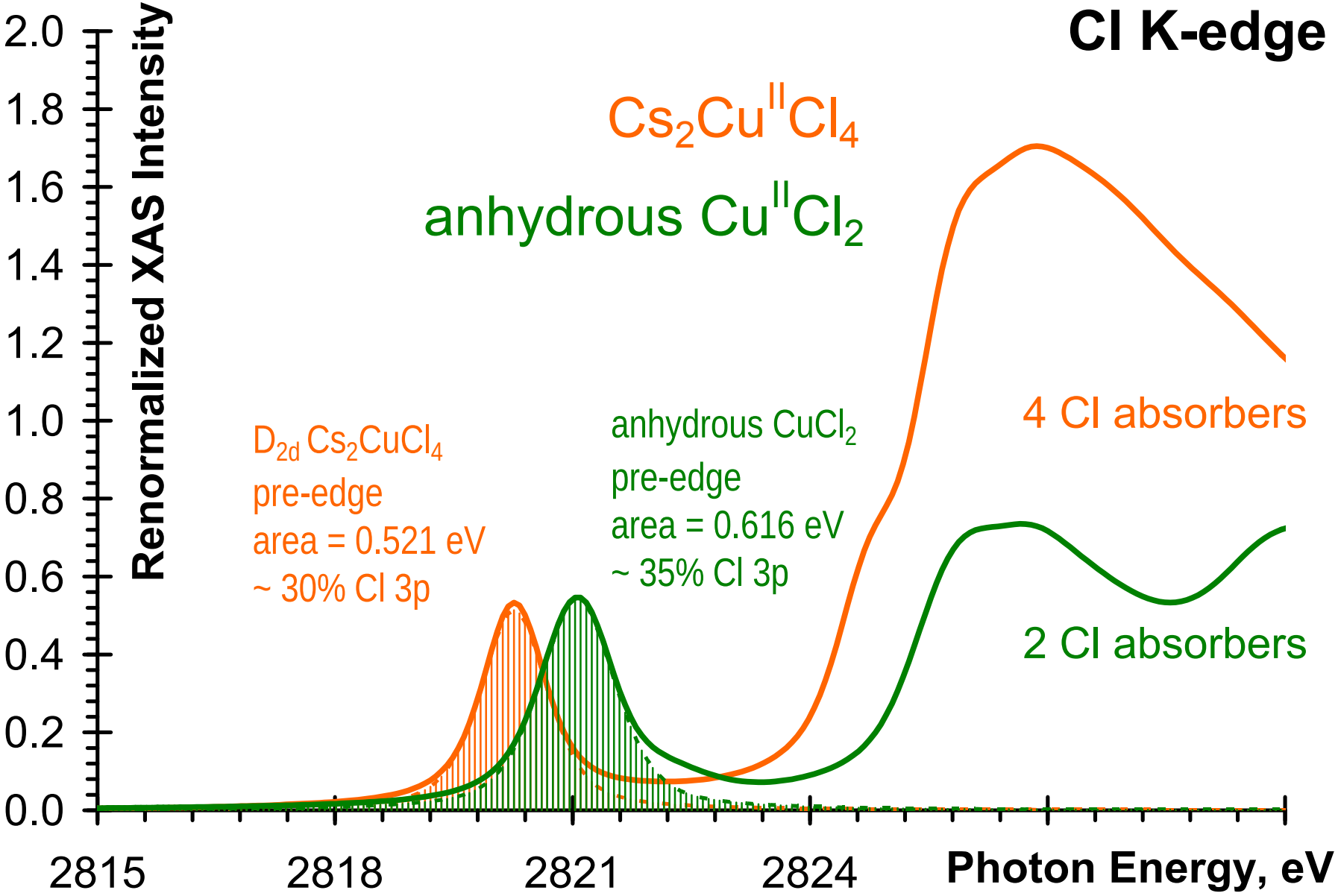


Multi-edge XANES: quantitative treatment

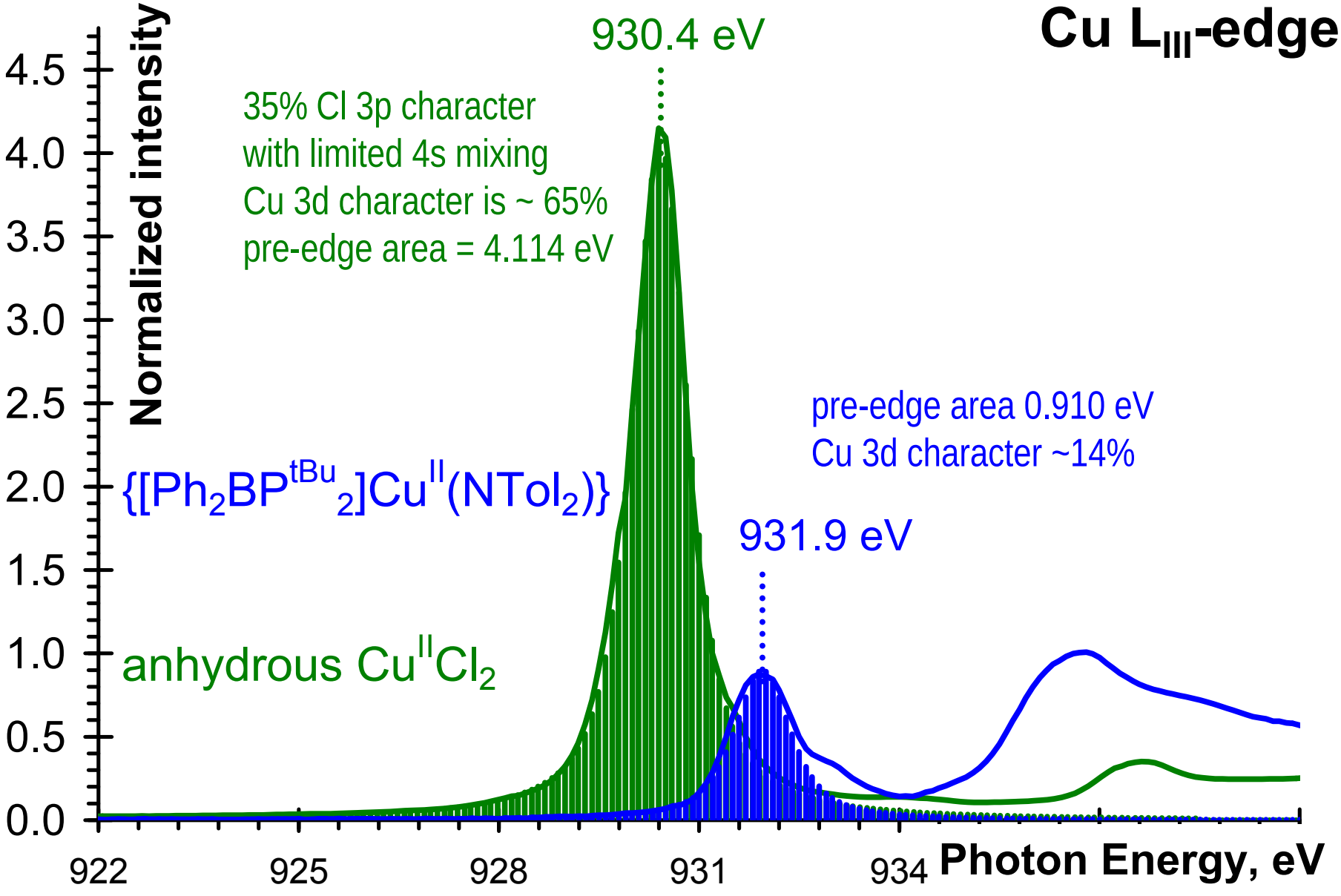
Cl K-edge



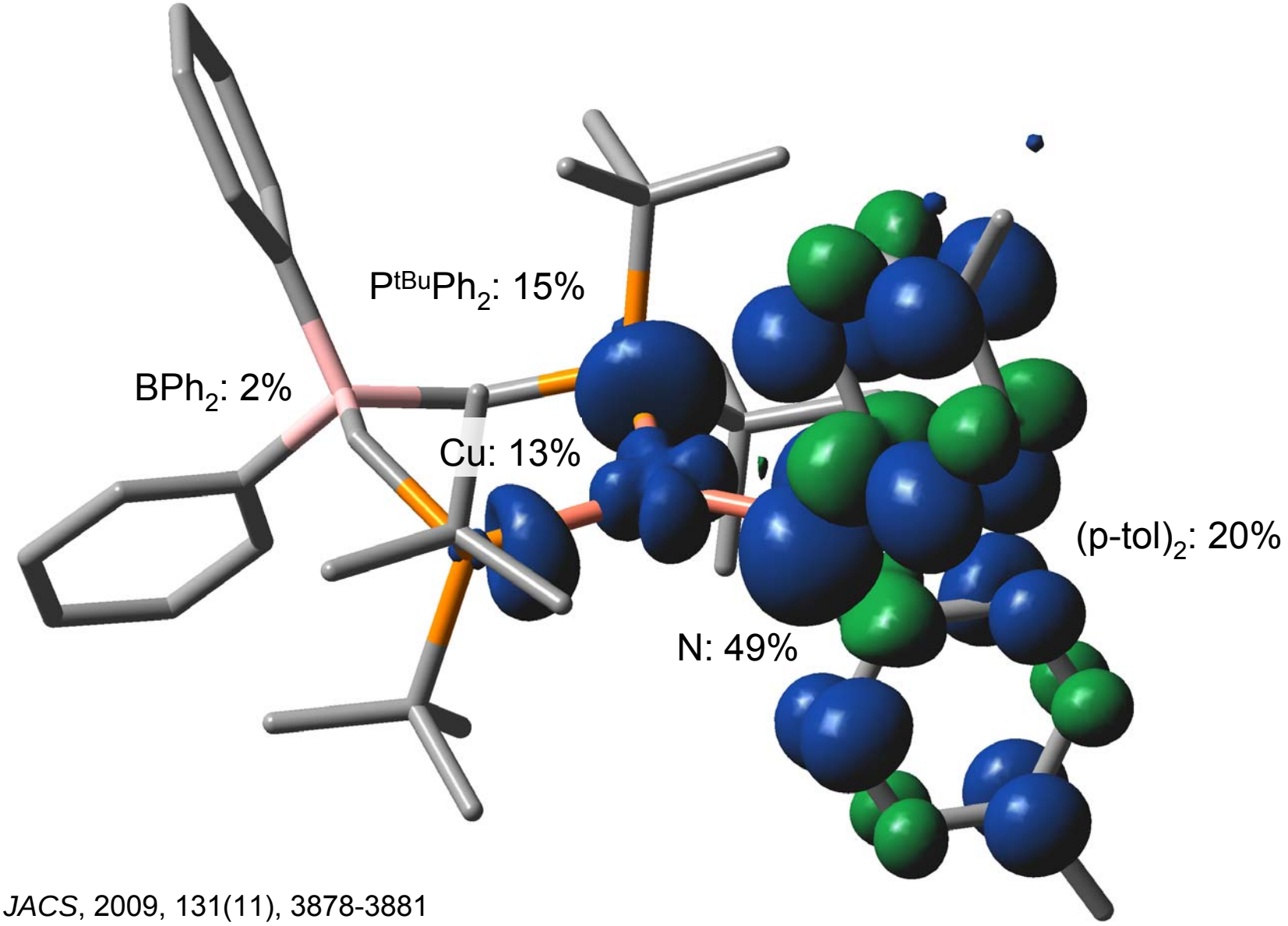
Multi-edge XANES: quantitative treatment



Multi-edge XANES: quantitative treatment



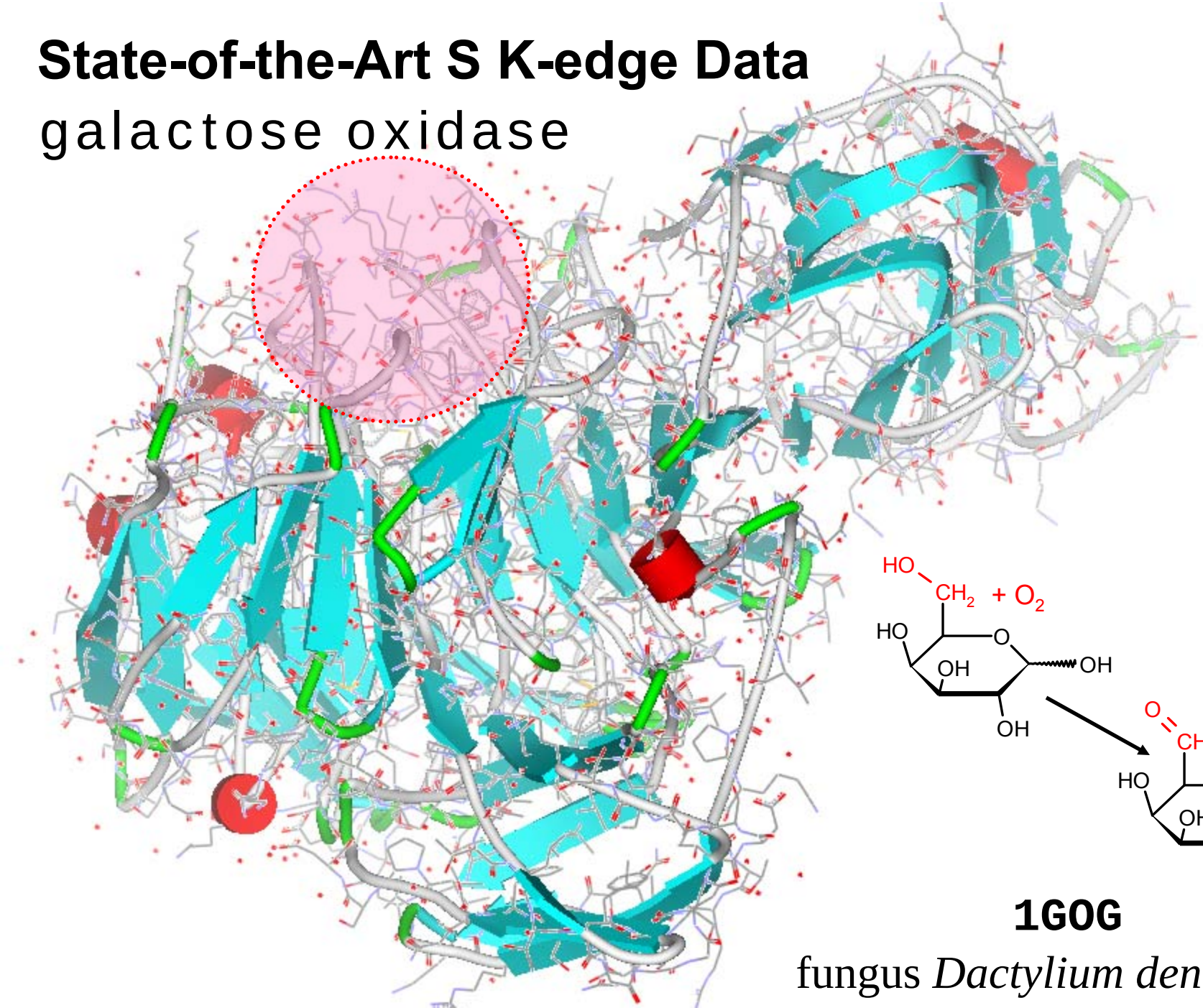
Calculated spin densities for $[Ph_2BP^{tBu}{}_2]Cu^{II}(NTol_2)$



JACS, 2009, 131(11), 3878-3881

State-of-the-Art S K-edge Data

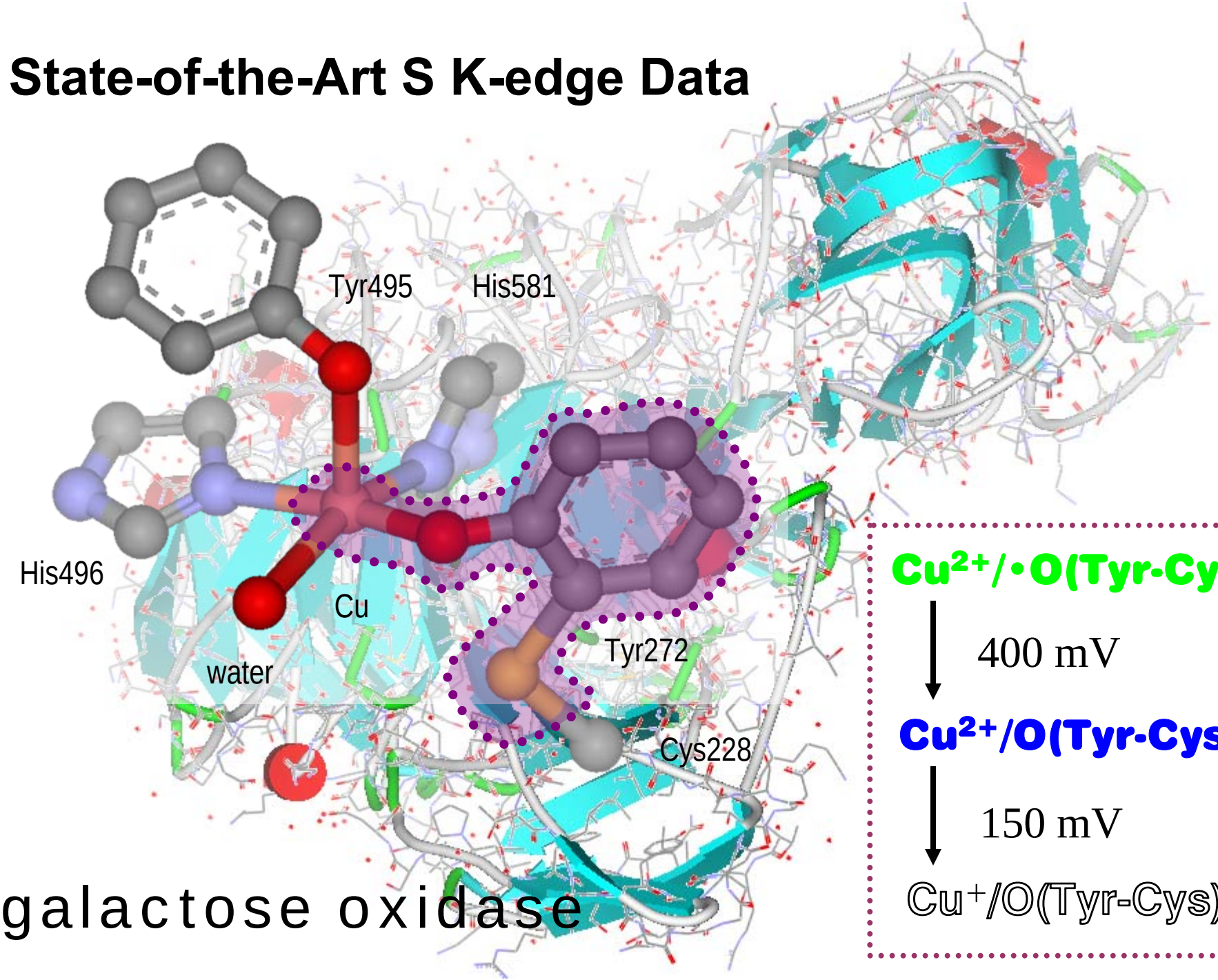
galactose oxidase



1GOG

fungus *Dactylium dendroides*

State-of-the-Art S K-edge Data



galactose oxidase

$Cu^{2+}/\bullet O(Tyr\text{-}Cys)$

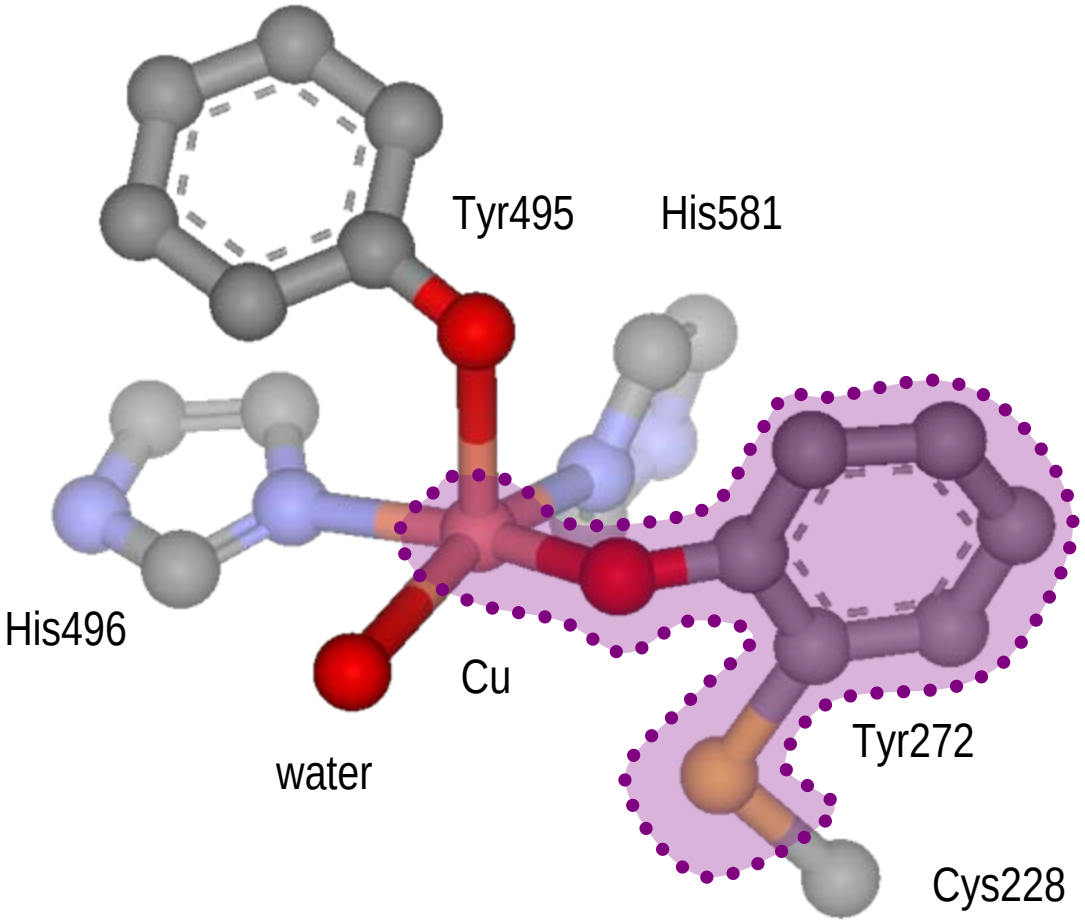
↓ 400 mV

$Cu^{2+}/O(Tyr\text{-}Cys)$

↓ 150 mV

$Cu^{+}/O(Tyr\text{-}Cys)$

State-of-the-Art S K-edge Data



galactose oxidase

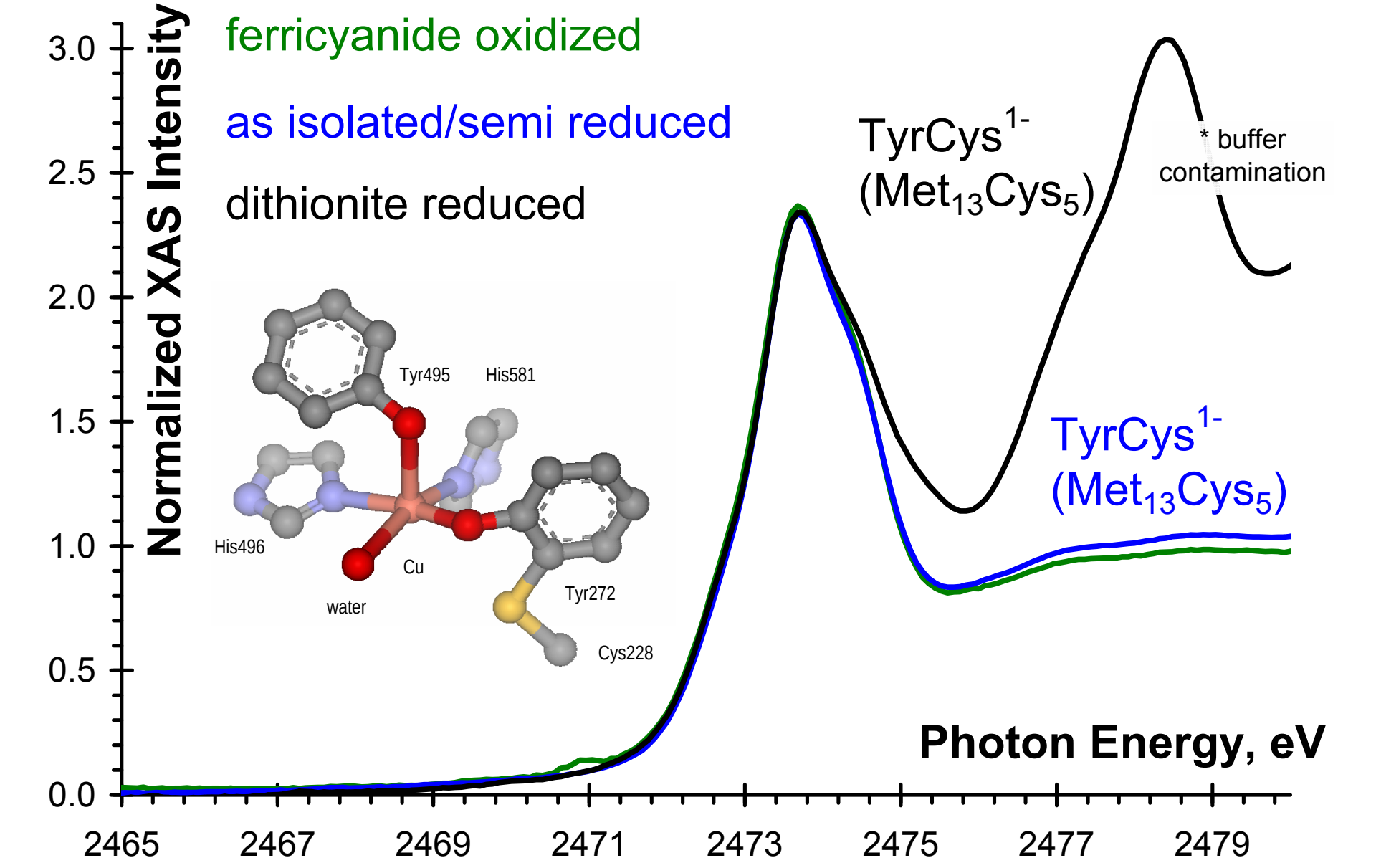
JACS, 2010, submitted

GO samples:
93% Cu-loaded
150 μL
0.633 mM
In phosphate buffer
w/2M urea, pH=7
50-fold excess of $K_3Fe(CN)_6$
37±3% oxidation

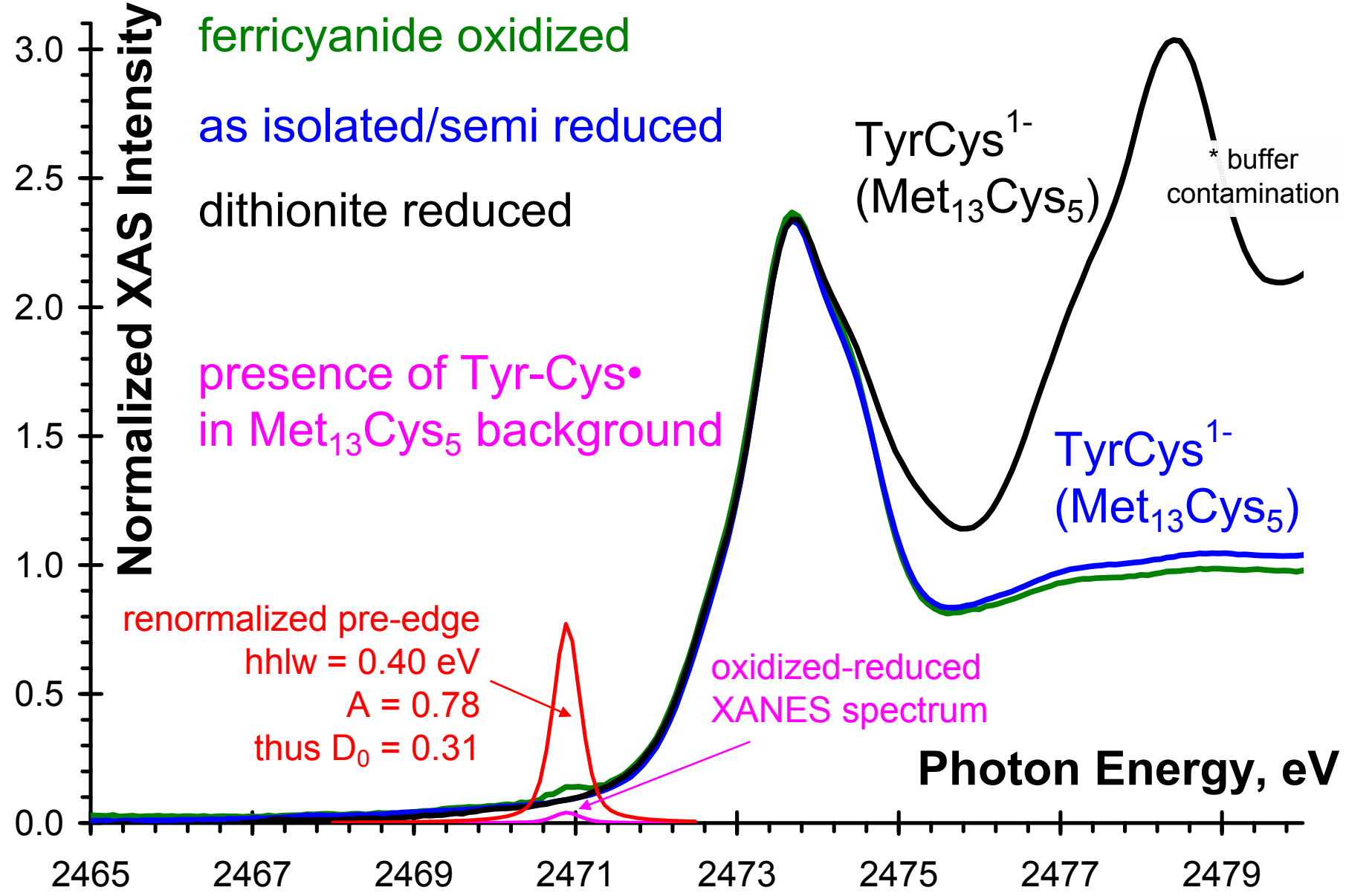
BL6-2 only!
LHe cryojet only!

19 absorbers:
13 Met 4 Cys-Cys thioether crosslink

State-of-the-Art S K-edge Data



State-of-the-Art S K-edge Data



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 (α^2) is defined by the transition dipole expression

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

I(S 1s→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 (α^2) from XAS for oxidized holo GO is 24±11%
(calc.: 22±2%)

from EPR for oxidized apo GO is 20±3%
(calc: 15±1%)

JACS, 2010, submitted