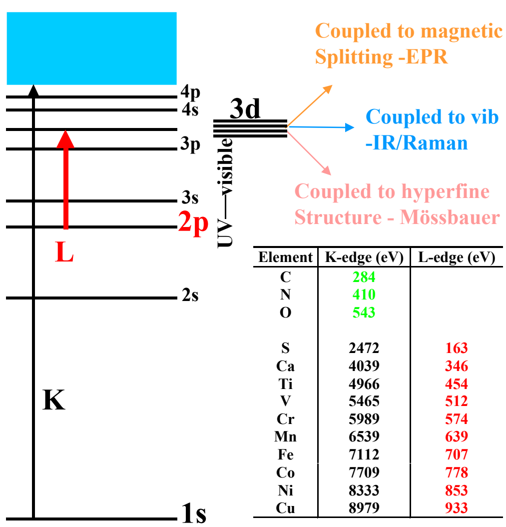
Soft X-ray Absorption Spectroscopy of Transition Metal Sites

Hongxin Wang
University of California at Davis

Berkeley, California
July 11, 2001

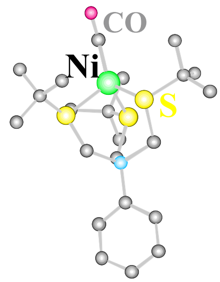
Spectroscopic Transitions

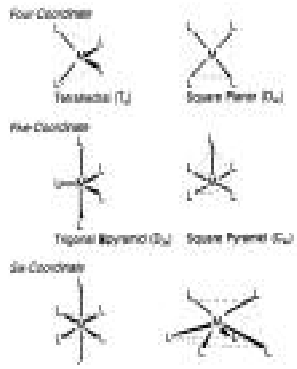


Element	K-edge (eV)	L-edge (eV)
C	284	
N	410	
O	543	
S	2472	163
Ca	4039	346
Ti	4966	454
V	5465	512
Cr	5989	574
Mn	6539	639
Fe	7112	707
Co	7709	778
Ni	8333	853
Cu	8979	933

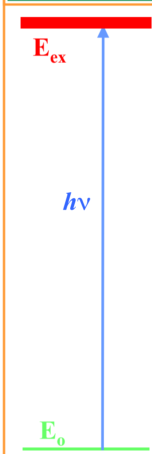
Coordination Geometries

$[P_hT_t]^{tBu}N_i^{I}CO$





Electronic Structures



Oxidation States of First Row Transition Metals

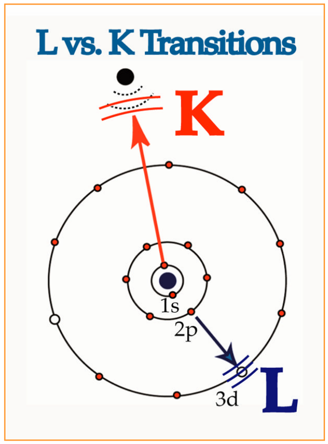
VB	VIB	VIIB	VIIIB			IB
V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
+1	+1	+1		+1	+1	+1
+2	+2	**+2**	+2	**+2**	**+2**	**+2**
+3	**+3**	+3	**+3**	+3	+3	+3
+4	+4	+4	+4	+4	+4	
+5	+5	+5	+5			
	+6	+6	+6			
		+7				

Octahedral Complexes

d^n	Examples	HS	LS	d^n	Examples	HS	LS
d^1	Ti^{3+}	S=1/2	—	d^6	Fe^{2+}, Co^{3+}	S=2	S=0
d^2	Ti^{2+}, V^{3+}	S=1	—	d^7	Co^{2+}	S=3/2	S=1/2
d^3	V^{2+}, Cr^{3+}	S=3/2	—	d^8	Ni^{2+}, Pt^{2+}	S=1	—
d^4	Mn^{3+}	S=2	S=1	d^9	Cu^{2+}	S=1/2	—
d^5	Mn^{2+}, Fe^{3+}	S=5/2	S=1/2	d^{10}	Zn^{2+}, Ag^{2+}	S=0	—

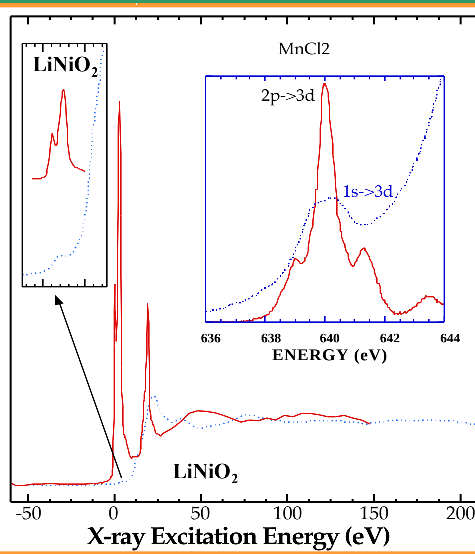
Electronic Configuration
→ Absorption Spectral Multiplet

L vs. K-edge Transitions



L-edge advantages over K-edges: 1) a spectral multiplet which is sensitive to electronic structures (due to the strong 2p-3d interaction); 2) a dipole allowed transition; 3) a better energy resolution and 4) a bigger XMCD effect.

L vs. K Spectroscopy



Hamiltonian

Ground State Hamiltonian:

$$H_{ls} + H_{mu} + H_{3d}$$

Final State Hamiltonian:

$$H_{ls} + H_{mu} + H_{c.3d} + H_{3d} + H_{c} + H_{c.ls}$$

$H_{c.ls}$ - core hole spin-orbital coupling, 5-20 eV

H_{c} - chemical shift, 1-2 eV / oxi st.

H_{3d} - energy of the 3d states, ~ 5 eV*

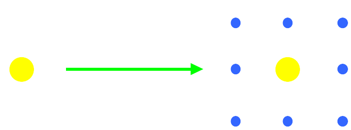
$H_{c.3d}$ - Coulomb/Exchange Interactions, 0-2 eV*

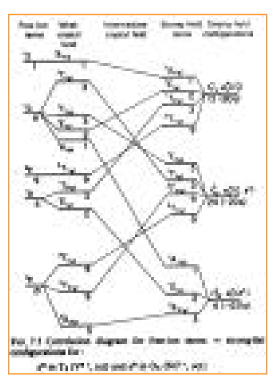
H_{mu} - all 2-electron integrals

H_{ls} - 3d spin-orbital coupling

* The crystal filed strength is roughly ~ 1-5 eV

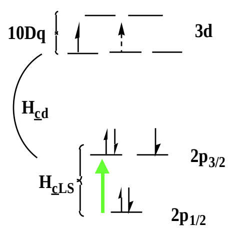
Ligand Field Approach

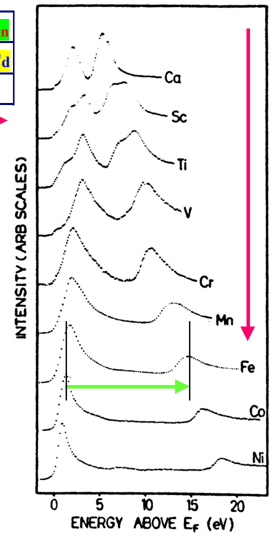




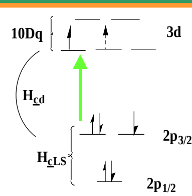
Core Hole S-O Splitting

V		Mn	Fe	Co	Ni	Cu	Zn
	Mo						Cd
	W						



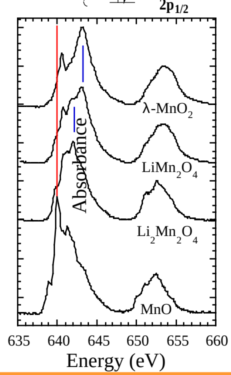


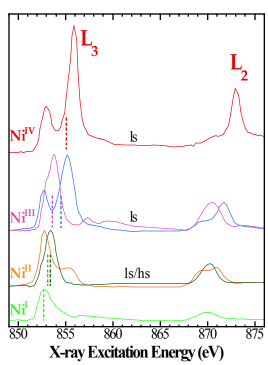
Mn/Ni Chemical Shifts



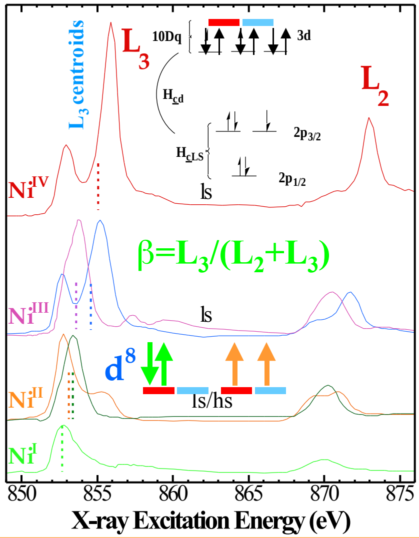
Mn: 2 eV/ oxi st.

Ni: 1 eV/ oxi st.

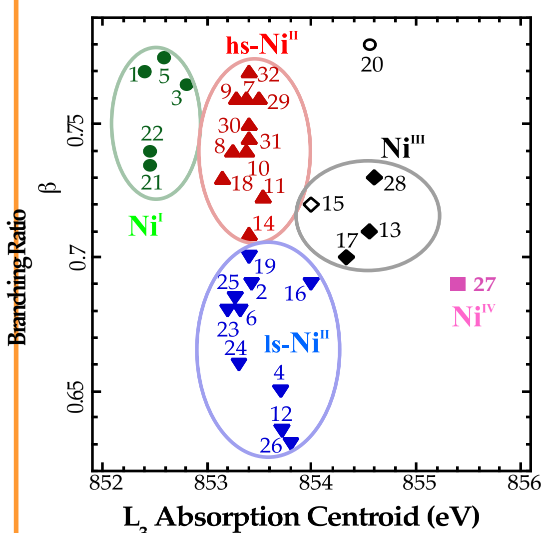




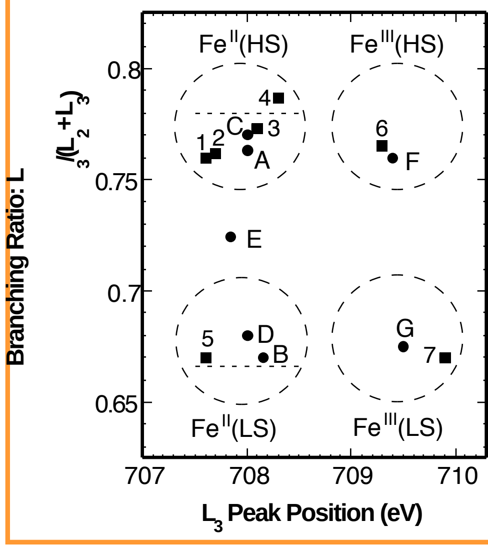
Branching Ratios



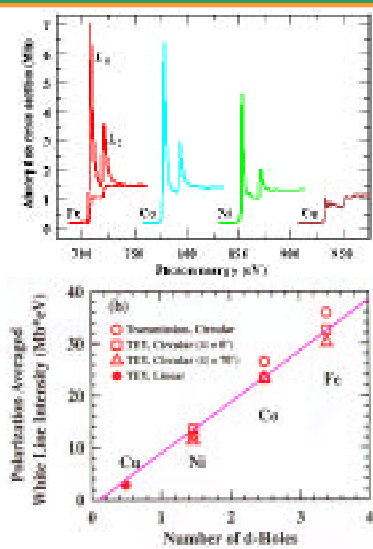
Ni L$_3$-β Diagram



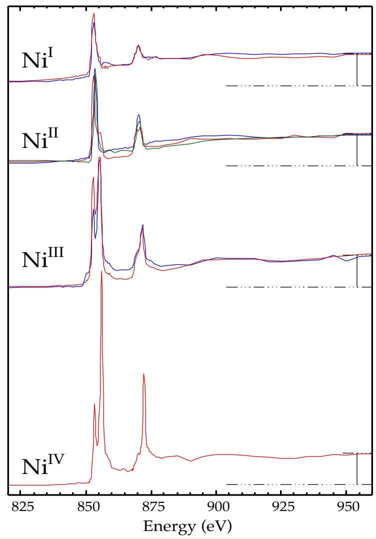
Fe L_3-β Diagram



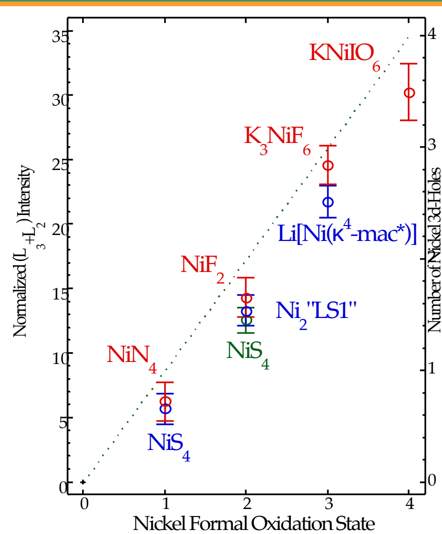
Sum Rule Analysis



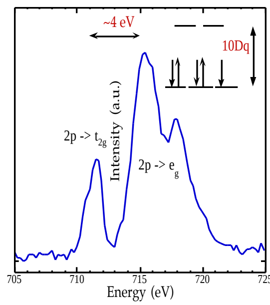
Ni Sum Rule Analysis

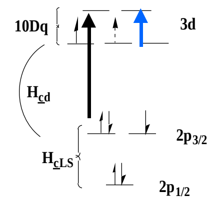


Ni Sum Rule Analysis

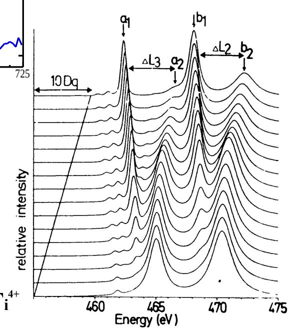


Ligand Field Effect



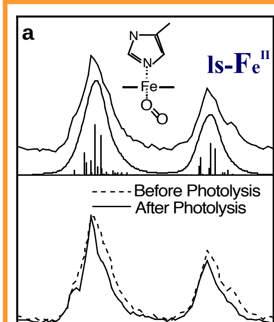


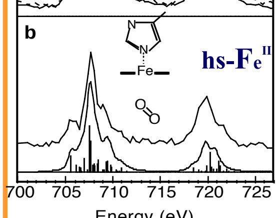
Above: Observed L-edges for $K_3[Fe(CN)_6]$

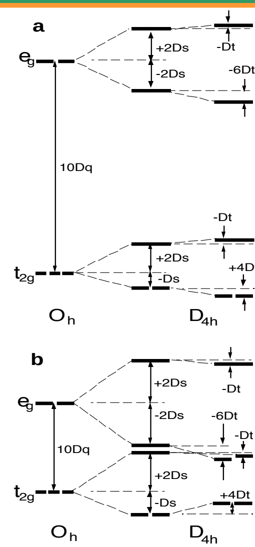


Right: Calculated L-edges for Ti^{4+}

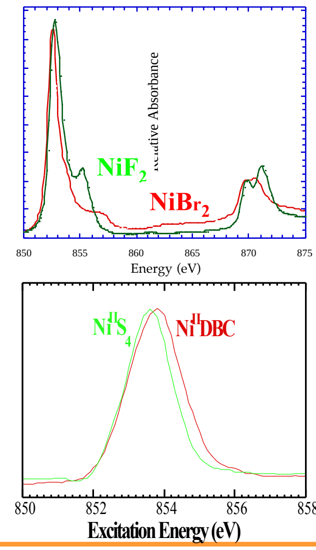
Ligand Field Effect



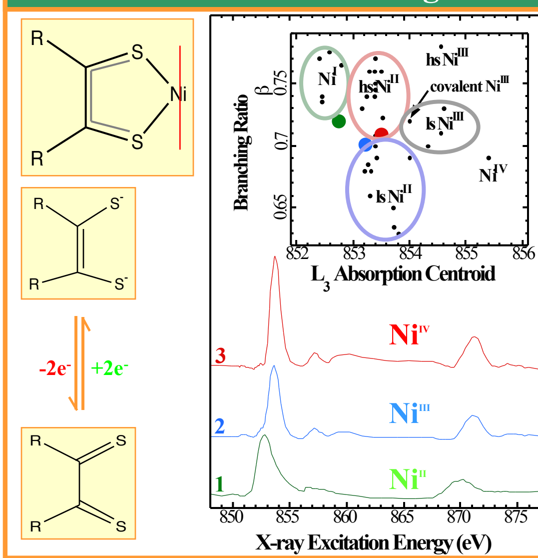




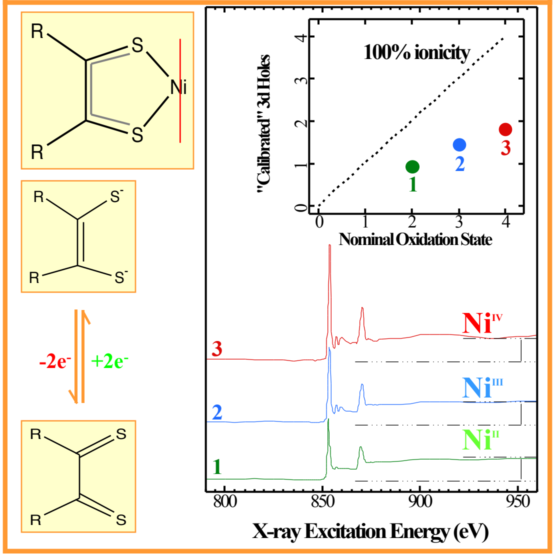
Ionic vs. Covalent Ni



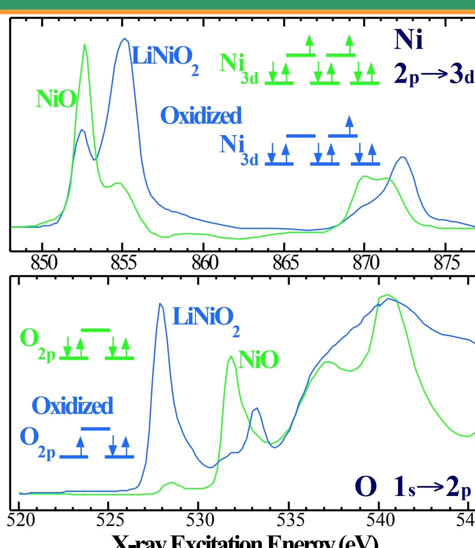
Ni Dithiolene L-edges



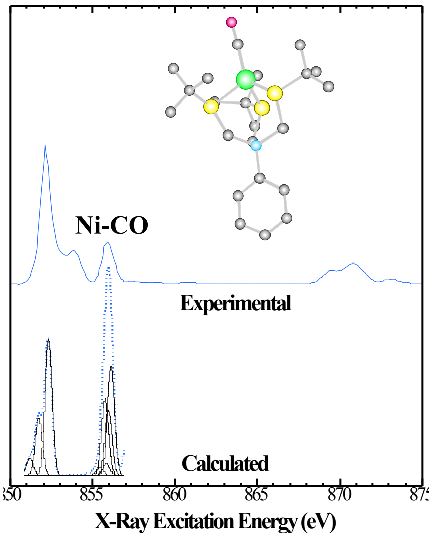
Ni Dithiolene L-edges



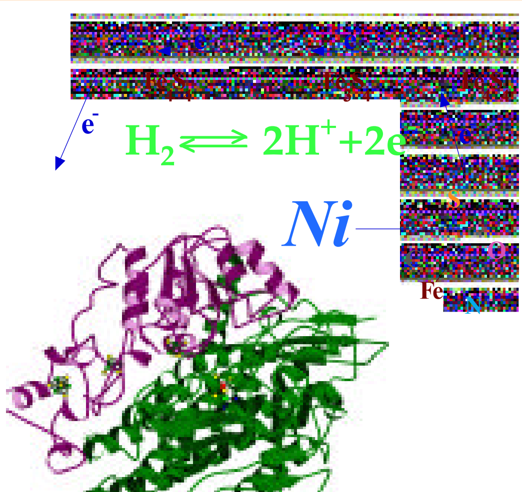
Oxidation of Both Ni and O



Transition to Mixed Orbital

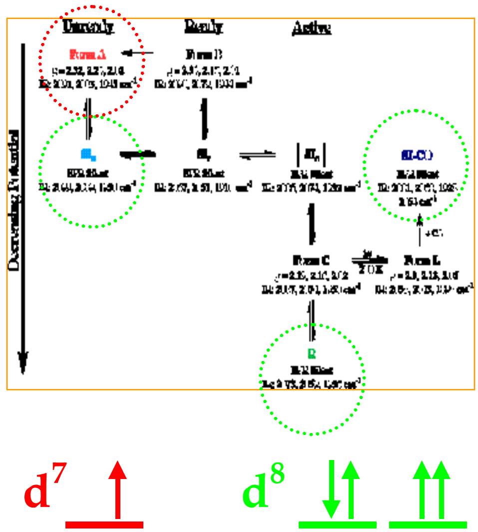


Ni Site in Hydrogenases

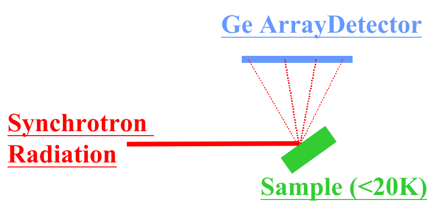


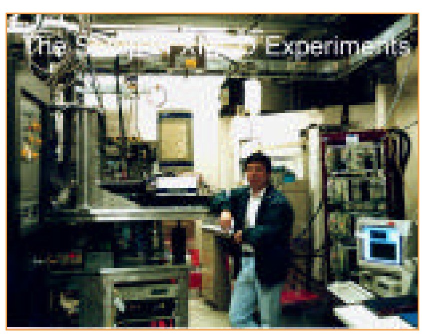
Volbeda *et al.*, *Nature*, 373, 580 (1995)

NiFe Hydrogenases States

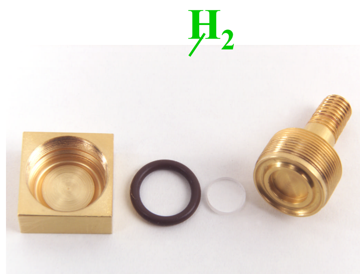


Experimental Setup

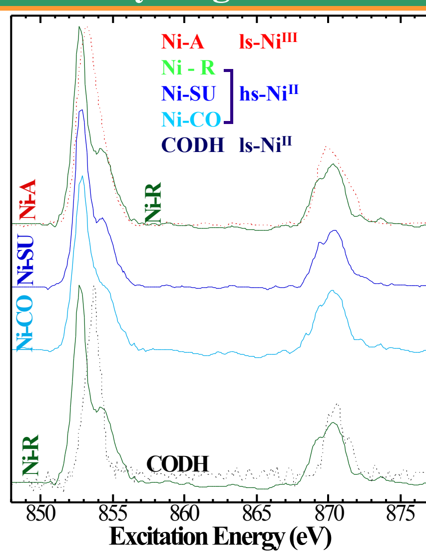


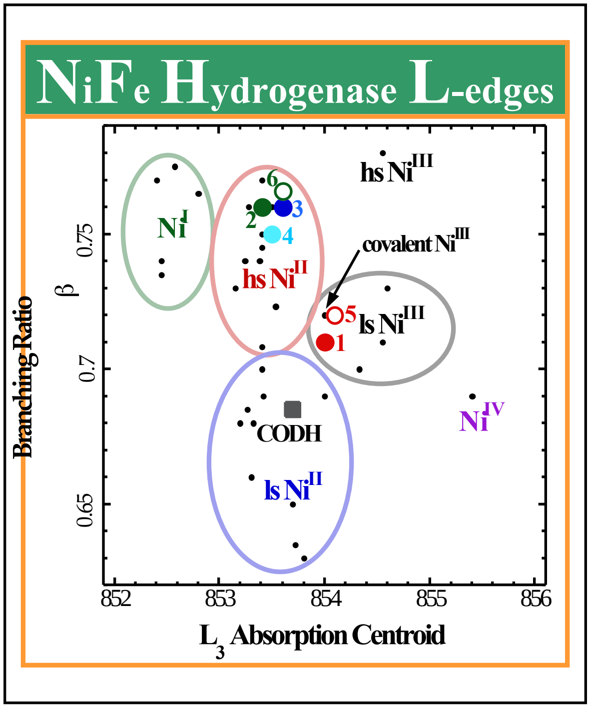


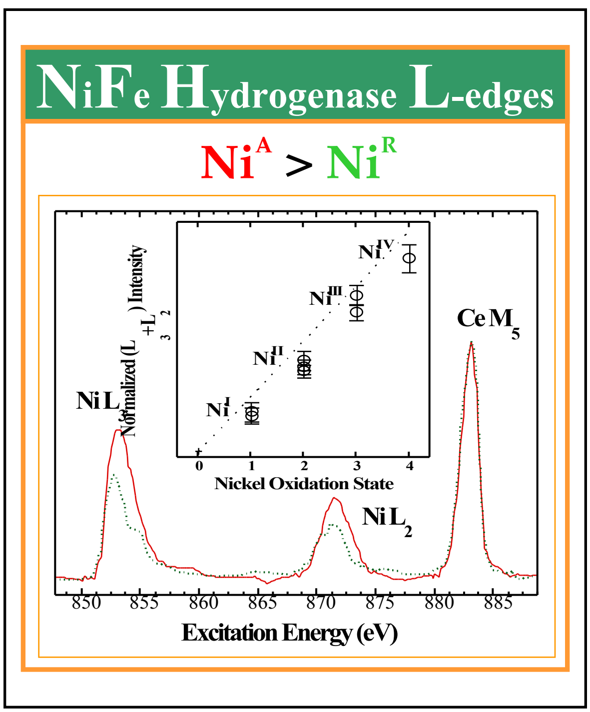
Samples in UHV



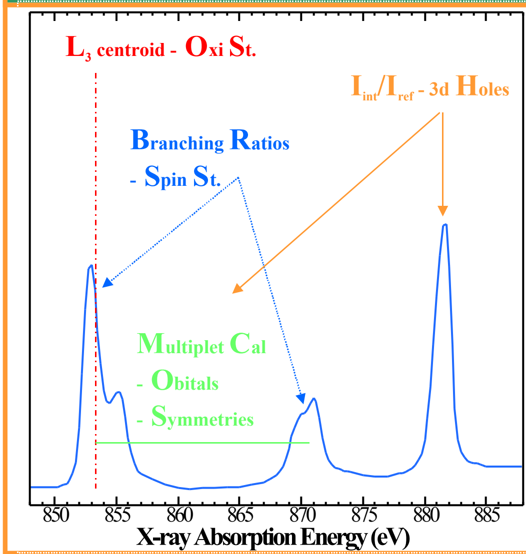
NiFe Hydrogenase L-edges




NiFe Hydrogenase L-edges
Branching Ratio
β
0.75
0.7
0.65
852
853
854
855
856
L3 Absorption Centroid
NiI
hs NiII
hs NiIII
covalent NiIII
ls NiIII
ls NiII
NiIV
CODH
1
2
3
4
5
6


NiFe Hydrogenase L-edges
NiA > NiR
Ni L3
Ni L2
Ce M5
850
855
860
865
870
875
880
885
Excitation Energy (eV)
Normalized (L3+L2) Intensity
Nickel Oxidation State
0
1
2
3
4
2
NiI
NiII
NiIII
NiIV

L-edge Summary



Further Reading

Soft X-rays and Synchrotron Radiation

Attwood, *Soft X-rays and Extreme Ultraviolet Radiation*, Cambridge Univ. Press (1999)

Soft X-ray Absorption Spectroscopy

Chen, *Surf. Sci. Rep*. 30, 5 (1997)

Cramer et al., *J. Electron Spectroscopy*, 86, 175 (1997)

Cramer et al., *ACS Series*, 692, 154 (1998)

de Groot, *J. Electron Spectroscopy*, 76, 529 (1994)

de Groot, *Chem. Rev.*, 101, 1779 (2001)

Bio-Applications of Soft XAS

Wang et al., *JACS*, 119, 4921 (1997)

Wang et al., *J. Electron Spectroscopy*, 114, 855 (2001)