X-ray Spectroscopy

A Critical Look at the Past
Accomplishments and Future Prospects

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Room 243
Monday – Wednesday 3-5 PM and by appointment
http://www.chem.usyd.edu.au/~penner_j/index.htm

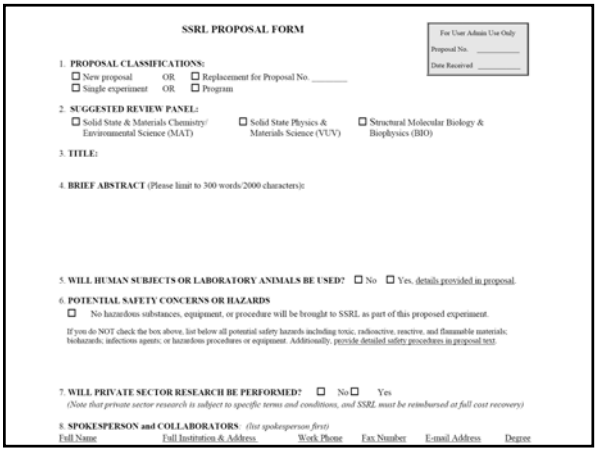
Lecture plan

1. Basic Physical Principles
2. Practical aspects of x-ray absorption
3. Data analysis
4. Near edge structure
5. Spatially and temporally resolved methods
6. Exotic x-ray spectroscopies

Grading

- Participation – 20%
- Draft research proposal – 30%
- Final research proposal – 50%
  - •Original
  - •Feasible
  - •Well presented

Proposal forms and guidelines at
http://www-ssrl.slac.stanford.edu/users/user_admin/xray_vuv_proposal_guide.html



SSRL PROPOSAL FORM

For User Admin Use Only
Proposal No. _____
Date Received _____

1. **PROPOSAL CLASSIFICATIONS:**
☐ New proposal OR ☐ Replacement for Proposal No. _____
☐ Single experiment OR ☐ Program

2. **SUGGESTED REVIEW PANEL:**
☐ Solid State & Materials Chemistry/ Environmental Science (MAT) ☐ Solid State Physics & Materials Science (VUV) ☐ Structural Molecular Biology & Biophysics (BIO)

3. **TITLE:**

4. **BRIEF ABSTRACT** (Please limit to 300 words/2000 characters):

5. **WILL HUMAN SUBJECTS OR LABORATORY ANIMALS BE USED?** ☐ No ☐ Yes, details provided in proposal.

6. **POTENTIAL SAFETY CONCERNS OR HAZARDS**
☐ No hazardous substances, equipment, or procedure will be brought to SSRL as part of this proposed experiment.
If you do NOT check the box above, list below all potential safety hazards including toxic, radioactive, reactive, and flammable materials; biohazards; infectious agents; or hazardous procedures or equipment. Additionally, provide detailed safety procedures in proposal text.

7. **WILL PRIVATE SECTOR RESEARCH BE PERFORMED?** ☐ No ☐ Yes
(Note that private sector research is subject to specific terms and conditions, and SSRL must be reimbursed at full cost recovery)

8. **SPOKESPERSON and COLLABORATORS** *(list spokesperson first)*
Full Name | Full Institution & Address | Work Phone | Fax Number | E-mail Address | Degree

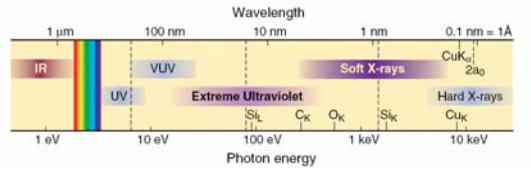
Proposal body – not more than 5 pages

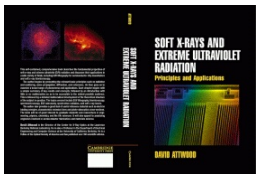
A. DESCRIPTION OF EXPERIMENT
   I. Background
   II. Previous results
   III. Proposed Experiments
   IV. Literature cited
B. PREVIOUS EXPERIENCE WITH THE TECHNIQUES AND FACILITY
C. DETAILED SAFETY CONCERNS
D. EQUIPMENT DEVELOPMENT SCHEDULE
E. RESOURCES FOR PROGRAM PROJECT

Techniques for studying metal sites in proteins

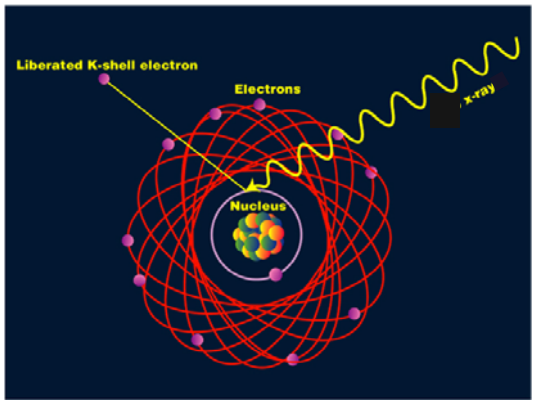
- UV-visible spectroscopy
- EPR spectroscopy — Require open d shell
- Magnetic susceptibility — Require open d shell
- MCD — Require open d shell
- NMR spectroscopy — Requires I=1/2 nucleus
- X-ray crystallography — Requires crystals

- X-ray spectroscopy

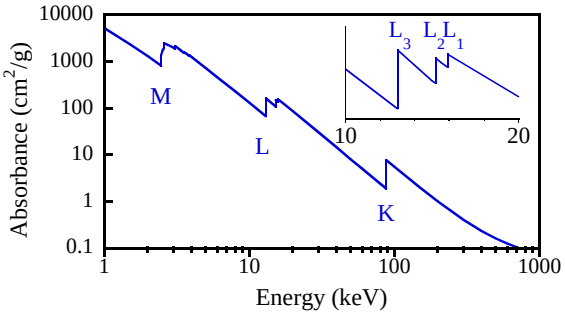




http://www.coe.berkeley.edu/AST/sxreuv



Absorption of x-rays by Pb



Electron binding energies of the elements

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$
1 H	13.6								
2 He	24.6[a]								
3 Li	54.7[a]								
4 Be	111.5[a]								
5 B	188[a]								
6 C	284.2[a]								
7 N	409.9[a]	37.3[a]							
8 O	543.1[a]	41.6[a]							
9 F	696.7[a]								
10 Ne	870.2[a]	48.5[a]	21.7[a]	21.6[a]					
11 Na	1070.8[f]	63.5[f]	30.4[f]	30.5[a]					
12 Mg	1303.0[f]	88.6[a]	49.6[f]	49.2[f]					
13 Al	1559.6	117.8[a]	72.9[a]	72.5[a]					
14 Si	1838.9	149.7[a]	99.8[a]	99.2[a]					
15 P	2145.5	189[a]	136[a]	135[a]					
16 S	2472	230.9[a]	163.6[a]	162.5[a]					
17 Cl	2822.4	270.2[a]	202[a]	200[a]					
18 Ar	3205.9[a]	326.3[a]	250.6[a]	248.4[a]	29.3[a]	15.9[a]	15.7[a]		
19 K	3608.4[a]	378.6[a]	297.3[a]	294.6[a]	34.8[a]	18.3[a]	18.3[a]		
20 Ca	4038.5[a]	438.4[f]	349.7[a]	346.2[f]	44.3[a]	25.4[f]	25.4[f]		
21 Sc	4492.8	498.0[a]	403.6[a]	398.7[a]	51.1[a]	28.3[a]	28.3[a]		
22 Ti	4966.4	560.9[f]	461.2[f]	453.8[f]	58.7[a]	32.6[f]	32.6[f]		
23 V	5465.1	626.7[f]	519.8[f]	512.1[f]	66.3[a]	37.2[f]	37.2[f]		
24 Cr	5989.2	695.7[f]	583.8[f]	574.1[f]	74.1[f]	42.2[f]	42.2[f]		
25 Mn	6539.0	769.1[f]	649.9[f]	638.7[f]	82.3[f]	47.2[f]	47.2[f]		
26 Fe	7112.0	844.6[f]	719.9[f]	706.8[f]	91.3[f]	52.7[f]	52.7[f]		
27 Co	7708.9	925.1[f]	793.3[f]	778.1[f]	101.0[f]	58.9[f]	58.9[f]		
28 Ni	8332.8	1008.6[f]	870.0[f]	852.7[f]	110.8[f]	68.0[f]	66.2[f]		
29 Cu	8978.9	1096.7[f]	952.3[f]	932.5[f]	122.5[f]	77.3[f]	75.1[f]		
30 Zn	9658.6	1196.2[a]	1044.9[a]	1021.8[a]	139.8[a]	91.4[a]	88.6[a]	10.2[a]	10.1[a]

Center for Synchrotron Radiation Research and Instrumentation

http://www.csrri.iit.edu/

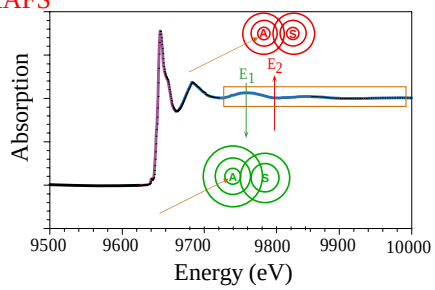
Synchrotron Radiation Related Links

- A list of Web sites of interest to the synchrotron radiation community.
- The International XAFS Society XAFS Database.
- Look up McMaster X-ray data.
- Look up McMaster X-ray data. (Alternate interface using HTML 3.0 tables.)
- X-Ray WWW Server (Uppsala, Sweden).
- Feff home page (Seattle, Washington).
- UWXAFS Project (Seattle, Washington).
- Rigaku Miniflex Data Conversion Program.

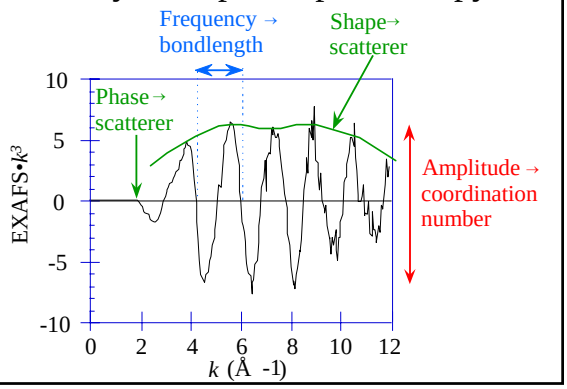
X-ray absorption spectroscopy

XAS
XAFS
NEXAFS

XANES EXAFS



X-ray absorption spectroscopy



Information Content of EXAFS

- Bond length ± 0.02 Å (accuracy)
- Bond length ±0.005 Å (precision)
- Coordination number (lower limit) ± 1
- Ligation type (Z) ± 10

R_{max} < ~ 4 Å

Scott, R. A. "Measurement of Metal-Ligand Distances by EXAFS" *Methods Enzymol.* **1985**, *117*, 414-459.

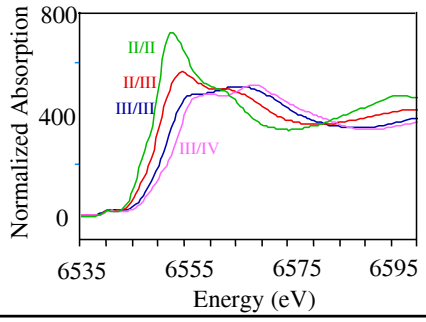
Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, **1986**.

Scott, R.A., "X-Ray Absorption Spectroscopy" in *Physical Methods in Bioinorganic Chemistry*, Que, L. (Ed)., **2000**, University Science Books.

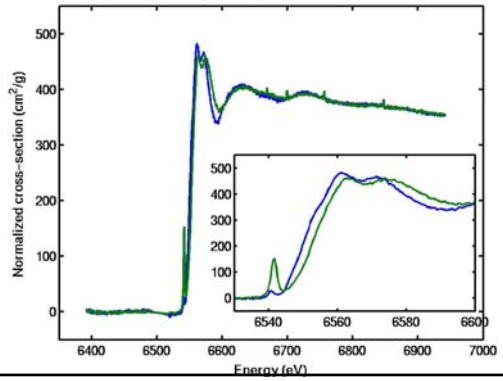
Penner-Hahn, J.E., "X-Ray Absorption Spectroscopy", in Comp. Coord. Chem. II, Vol. 2, **2004**.

Levina A, Armstrong R.S., Lay P.A., "Three-dimensional structure determination using multiple-scattering analysis of XAFS: applications to metalloproteins and coordination chemistry" *Coord. Chem. Rev.* **2005**, *249*, 141-160.

Dependence of XANES on Oxidation State



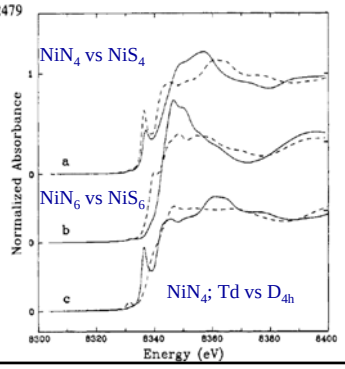
Mn(V)=O has intense pre-edge transition, not seen in Mn(III) analog



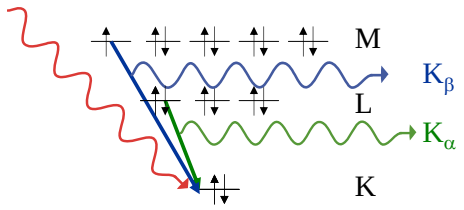
X-ray Absorption Spectroscopic Evidence for a Unique Nickel Site in *Clostridium thermoaceticum* Carbon Monoxide Dehydrogenase

Stephen P. Cramer,*[1a,b] Marly K. Eidsness,[1c,d] W.-H. Pan,[1a] Thomas A. Morton,[1e] Steve W. Ragsdale,[1e,f] Daniel V. DerVartanian,[1e] Lars G. Ljungdahl,[1e] and Robert A. Scott*[1g]

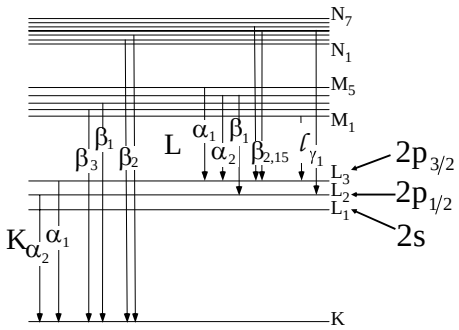
Inorg. Chem. **1987**, *26*, 2477–2479



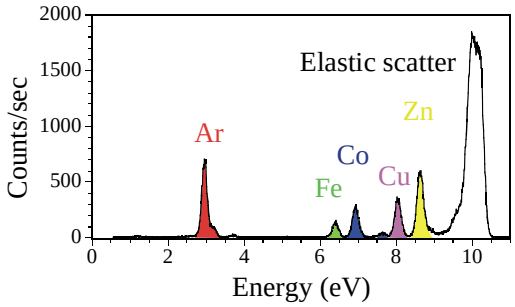
X-ray Fluorescence



X-ray fluorescence lines



X-ray fluorescence spectra give element sensitivity



Advantages of XAFS

Direct structural determination for:

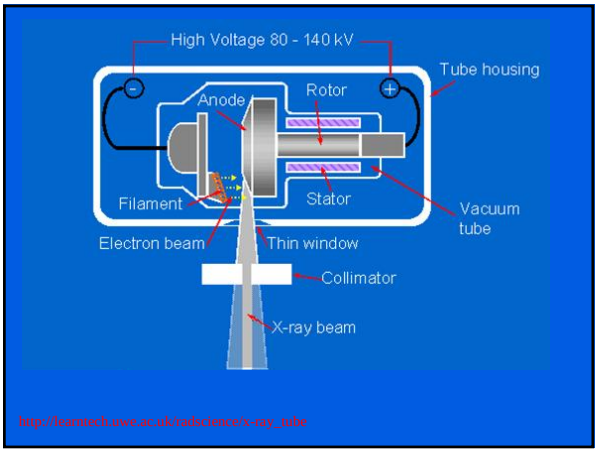
- Any form of matter
- Any isotope
- Any spin state

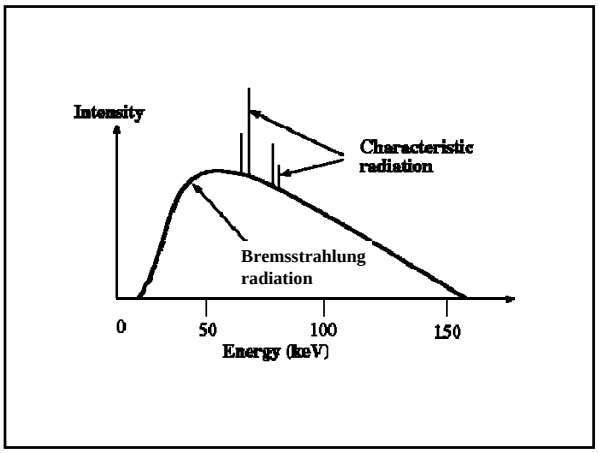
Direct determination of oxidation state

Disadvantages of XAFS

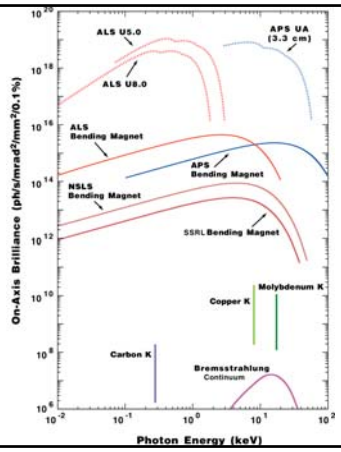
- Bulk spectroscopy (average structure)
- Little angular information
- Gives only *local* structural information
- Limited sensitivity

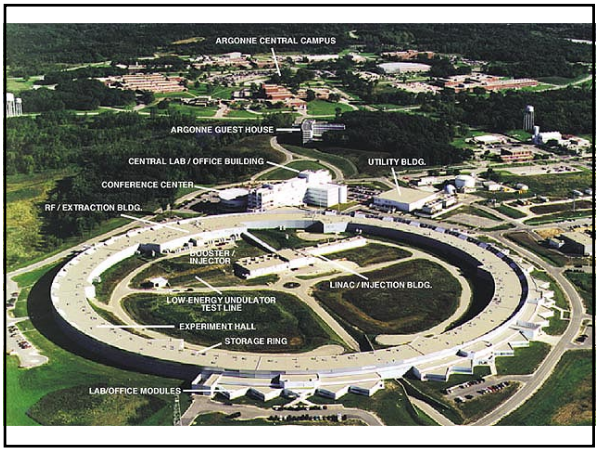
- Requires synchrotron x-ray source

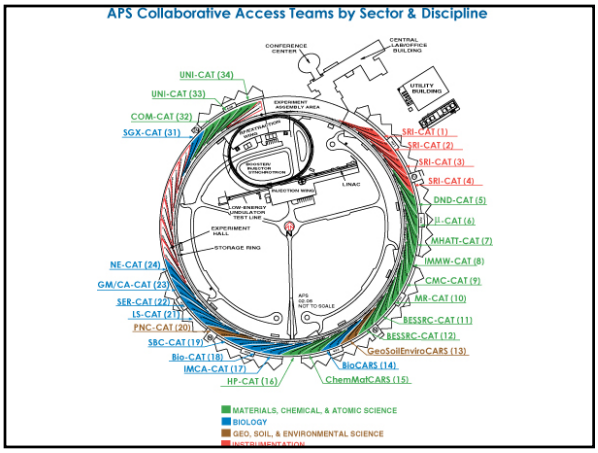


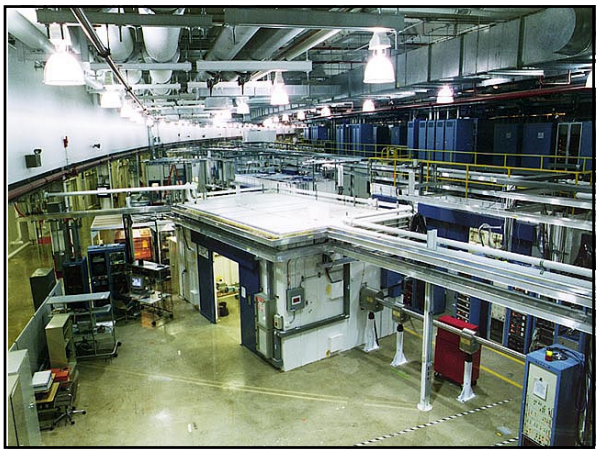


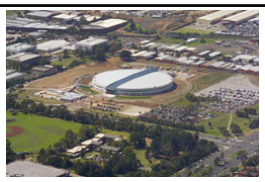
Synchrotrons produce intense, tunable x-ray beams









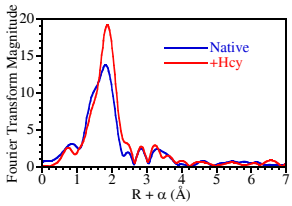


http://www.synchrotron.vic.gov.au

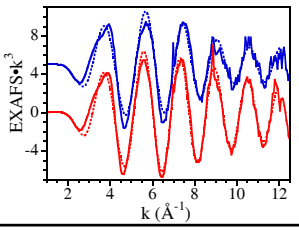
MetE (cobalamin independent MetSyn) contains Zn

Zn is tightly bound
Zn is required for activity
Is Zn involved in reaction, or does it play a structural role?

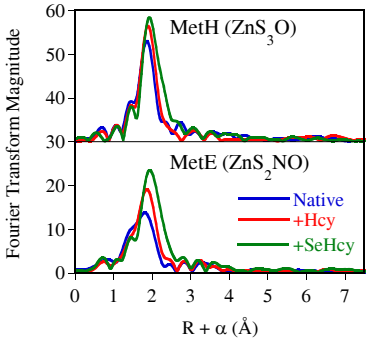
The Zn site in MetE has $ZnS_2(O/N)_2$ ligation.



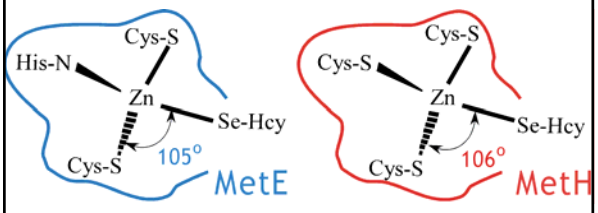
Addition of homocysteine changes ligation to $ZnS_3(O/N)$.



Changes in ligation are due to homocysteine binding to Zn



Combination of Zn + Se EXAFS consistent with only a small distortion from tetrahedral geometry in substrate-bound enzyme



J. Am. Chem. Soc., **112** (10) 1990

p. 4031-4032

"Higher Order" Cyanocuprates $R_2Cu(CN)Li_2$: Discrete Reagents or "Lower Order" LiCN-Modified Gilman Cuprates?

Bruce H. Lipshutz,* Sunaina Sharma, and Edmund L. Ellsworth†

as R_2CuLi·LiCN. We now describe, using spectroscopic studies, prima facie evidence in support of HO cyanocuprates.

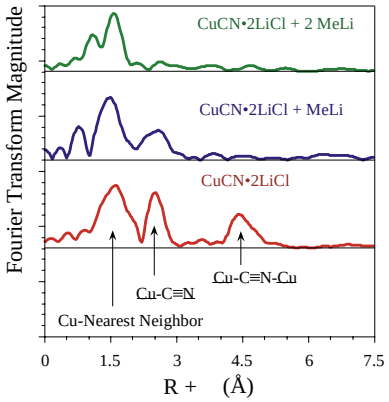
p. 4032-4034

"Higher-Order" Cyanocuprates: Are They Real?[1]

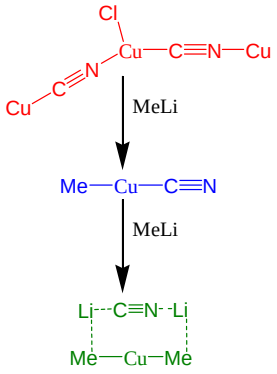
Steven H. Bertz

It can now be reported that the reagents prepared from 2 equiv of RLi (R = alkyl or aryl) and 1 equiv of CuCN may not be truly higher order *ate* complexes of Cu. ^{13}C NMR spectral evidence

EXAFS shows that CN^- does not remain bound



Structures of cyanocuprates in THF



Solution speciation of CuI+PhLi

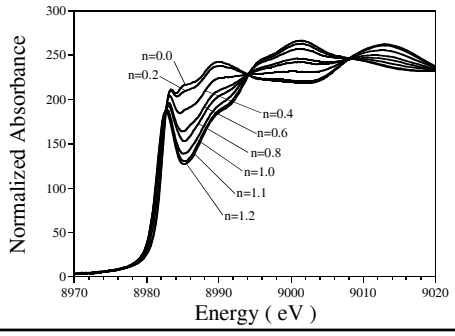
PhLi + CuI → "phenylcopper"

2PhLi+ CuI → "diphenylcuprate"

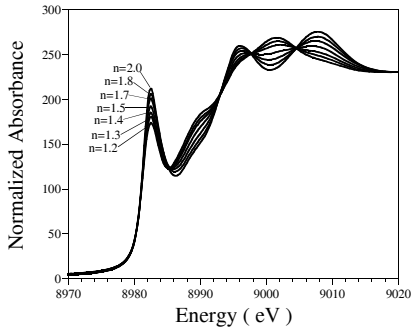
Crystalline phenyl:copper species

1:1	$Cu_4Ph_4(Me_2S)_2$	2:1	$[CuPh_2]^-$
	Cu_5Mes_5		$[CuPh_2Li]_2$
1.2:1	$[Cu_5Ph_6]^-$		$[Cu_3Li_2Ph_6]^-$
1.5:1	$[Cu_4LiPh_6]^-$		
	$[Cu_4MgPh_6]$		

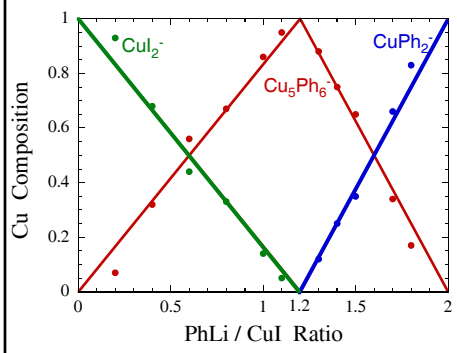
Titration of CuI+ *n* PhLi shows isosbestic behavior up to 1.2 equivalents



Titration of CuI+ *n* PhLi shows isosbestic behavior from 1.2-2.0 equivalents



EXAFS data support XANES speciation



$[CuI_2]^-$

$[Cu_5Ph_6]^-$

$[CuPh_2]^-$

Inorg. Chem. **1994**, *33*, 1249–1250

EXAFS Evidence That the $CuCl_4^{2-}$ Ion in (3-Chloroanilinium)$_2$($CuCl_4$)Cl_2 Has an Elongated Rather Than Compressed Tetragonal Geometry

Paul J. Ellis,[†] Hans C. Freeman,*[,†] Michael A. Hitchman,*[,‡] Dirk Reinen,[§] and Burghard Wagner[§]