LA-UR-14-20496
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Title: Chemical Bonding in Molecules with Valence 5f-electrons

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Intended for: SESTEC 2014 International Conference, 2014-02-25/2014-02-28 (Mumbai, India)

Issued: 2014-01-28 (Draft)

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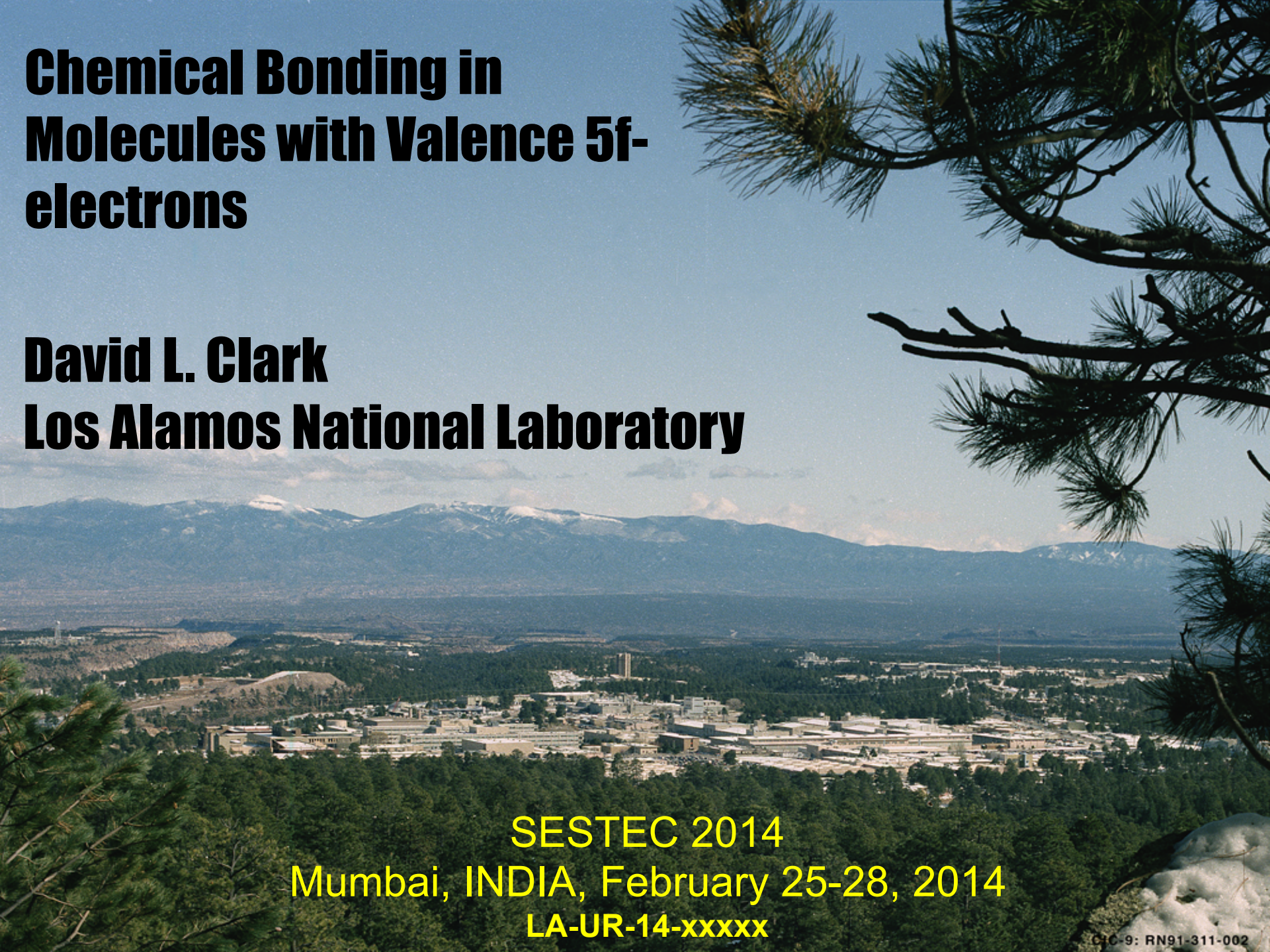
Chemical Bonding in Molecules with Valence 5f-electrons

David L. Clark
Los Alamos National Laboratory

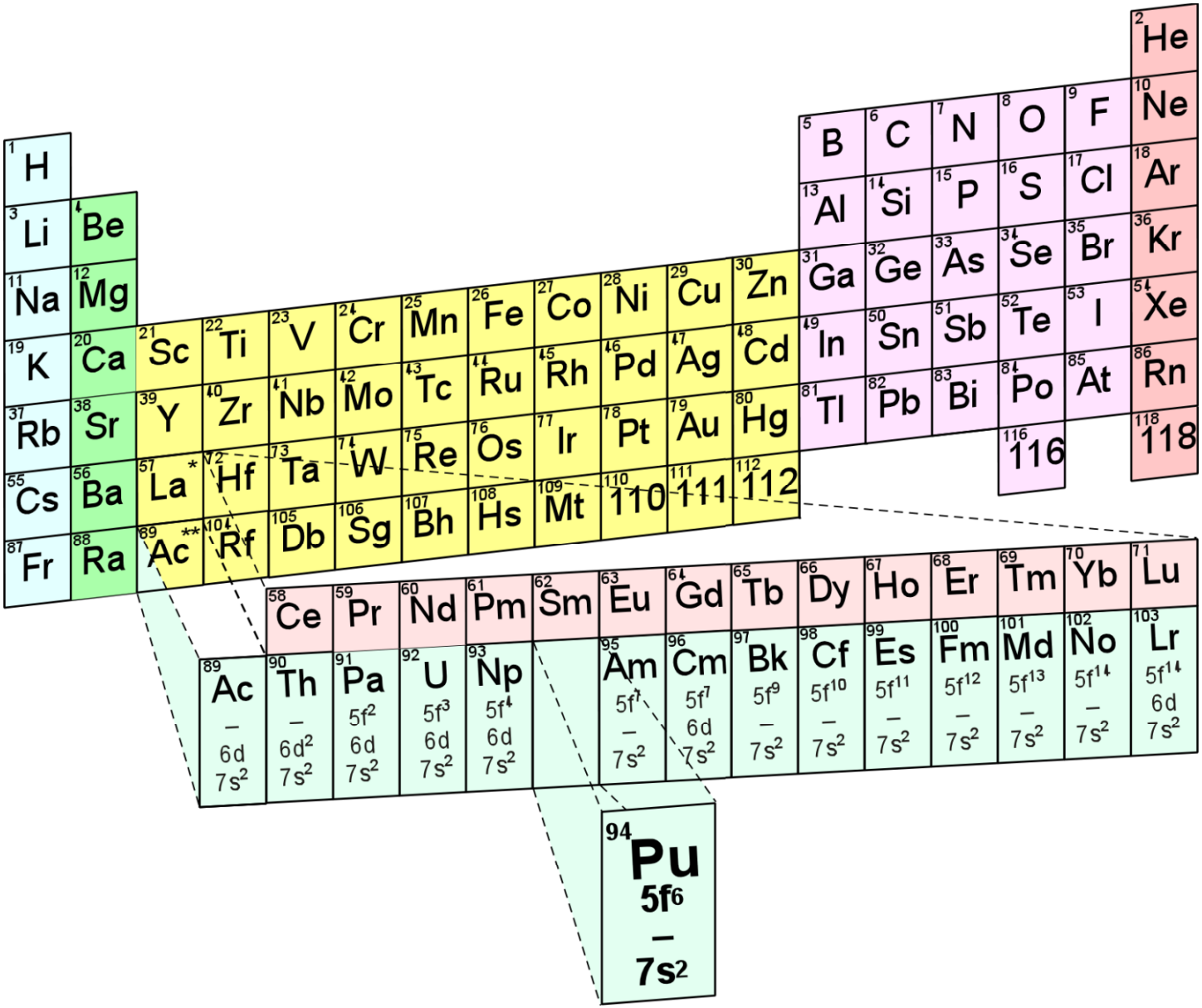


SESTEC 2014

Mumbai, INDIA, February 25-28, 2014

LA-UR-14-xxxxx

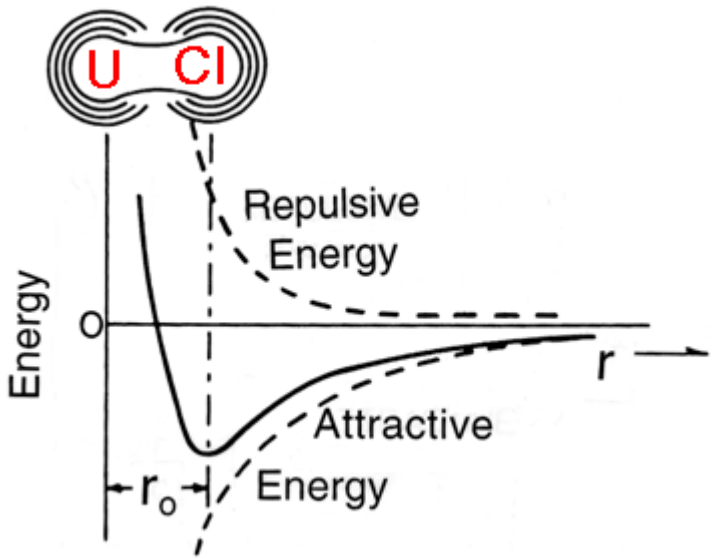
Chemists' Periodic Table

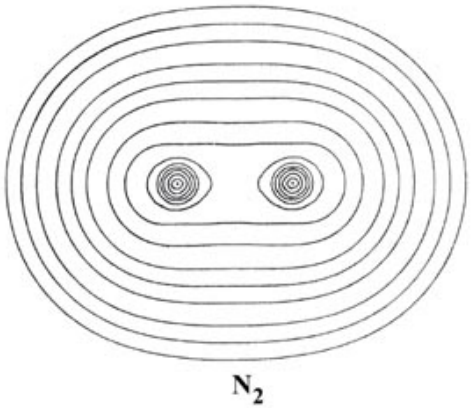


Chemical Bonding

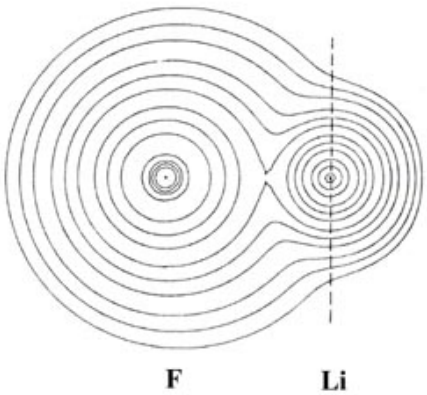
"There is nothing more fundamental to chemistry than the chemical bond….but it's not a simple concept."

Roald Hoffmann
C&EN, January 29, 2007





covalent



polar covalent

Covalency: sharing of a pair of electrons by two bonded atoms

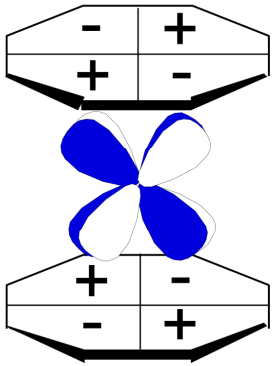
Irving Langmuir, *J. Am. Chem. Soc., (***1919***), 41, 869*

Linus Pauling, *Nature of the Chemical Bond,* **1960**

MO theory: mixing of atomic orbitals $\Psi = N(\phi_M + \lambda\phi_L)$

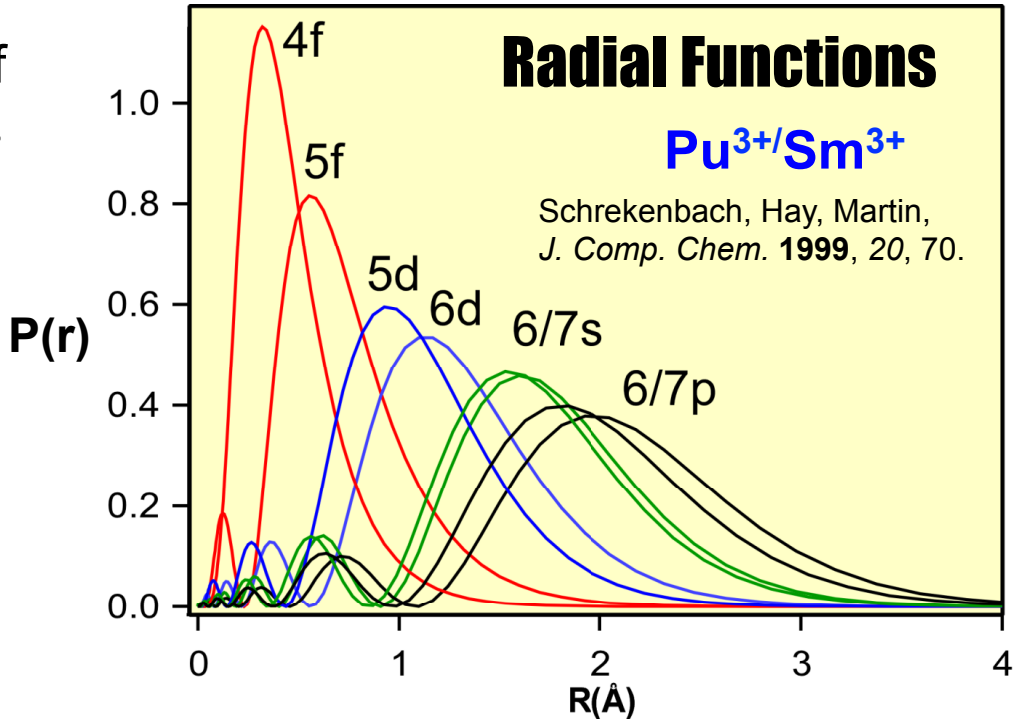
Covalency in f-element Compounds

- Focus on 5f orbital covalency has led to much debate and established dogma
- Diamond, Street, Seaborg, suggested hybridized 5f bonding in 1954
- Uranocene predicted in 1963 based on nodal properties of 5f-orbitals, synthesized in 1968



fδ

- Notion of greater covalency in 5f elements with soft donor ligands has been explored for An(III)/ Ln(III) separations
- Early focus centered on the greater radial extension of 5f vs 4f orbitals



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R. Hoffman, *Inorg. Chem.* **1980**, *19*, 2656
R. Denning, *Struct. Bonding*, **1992**, *79*, 215

Covalency in f-element Compounds

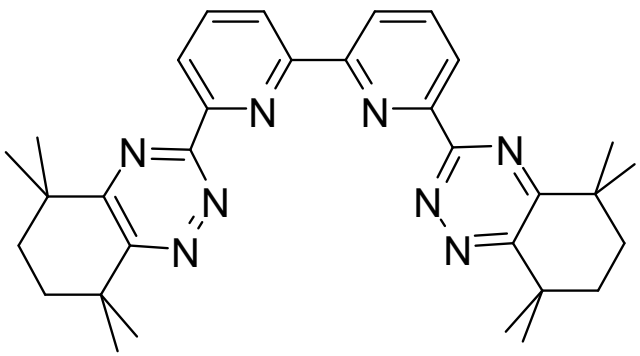
An Ion-exchange Study of Possible Hybridized 5f Bonding in the Actinides[1]

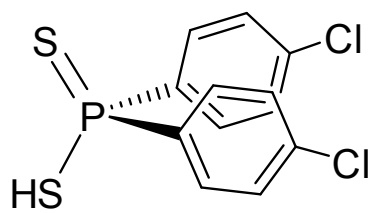
By R. M. Diamond,[2] K. Street, Jr., and G. T. Seaborg

Received October 1, 1953

A study has been made of the elution behavior of curium(III), americium(III), plutonium(III), actinium(III), plutonium(IV), neptunium(IV), uranium(IV), thorium(IV), neptunium(V), plutonium(VI), uranium(VI), lanthanum(III), cerium(III), europium(III), ytterbium(III), yttrium(III), strontium(II), barium(II), radium(II), cesium(I) with 3.2, 6.2, 9.3 and 12.2 *M* HCl solutions from Dowex-50 cation-exchange resin columns. These elutions indicate that in high concentrations of hydrochloric acid the actinides may form complex ions with chloride ion to a greater extent than the lanthanides. In order to explain these results, a partial covalent character may be ascribed to the bonding in the transuranium complex ions. It is shown that a reasonable structure for such covalent bonding involves hybridization of the 5f-orbitals in the actinide elements.

- Focus on 5f orbital covalency has led to much established dogma
- Notion of greater covalency in 5f elements with soft donor ligands has been explored for An(III)/Ln(III) separations





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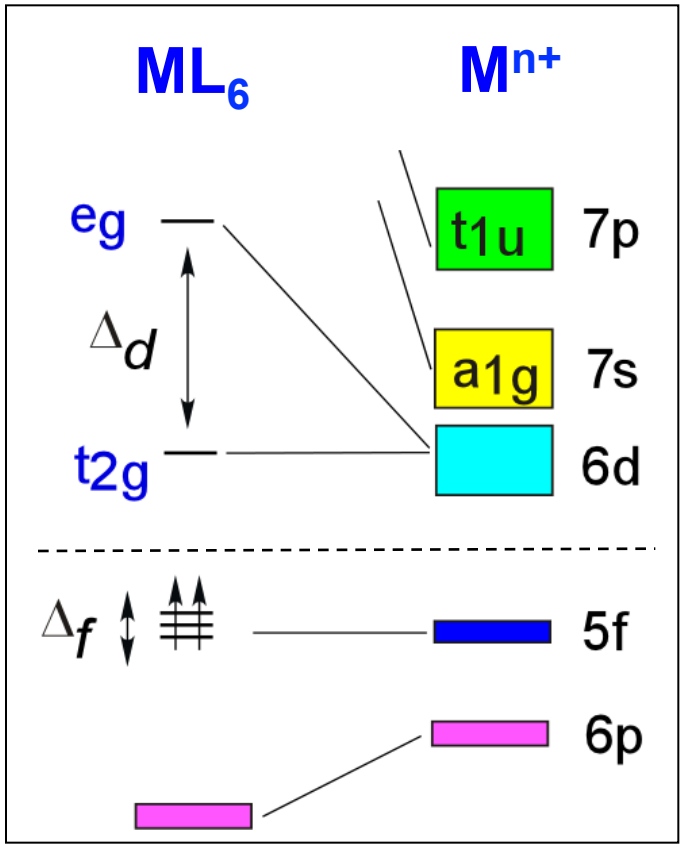
N. Kaltsoyannis, *Dalton Trans*, **2011**, *40*, 124

Two Decades of Electronic Structure Theory

Actinide Elements



Burns, Bursten, *Comm. Inorg. Chem.* **1989**, *9*, 61

N. Kaltsoyannis, et al. *Chem. Act. & Transact. Elmnts*, **2006**, 1893

Clark, Hecker, Jarvinen, Neu, *Chem. Act. & Transact. Elmnts*, **2006,** 813

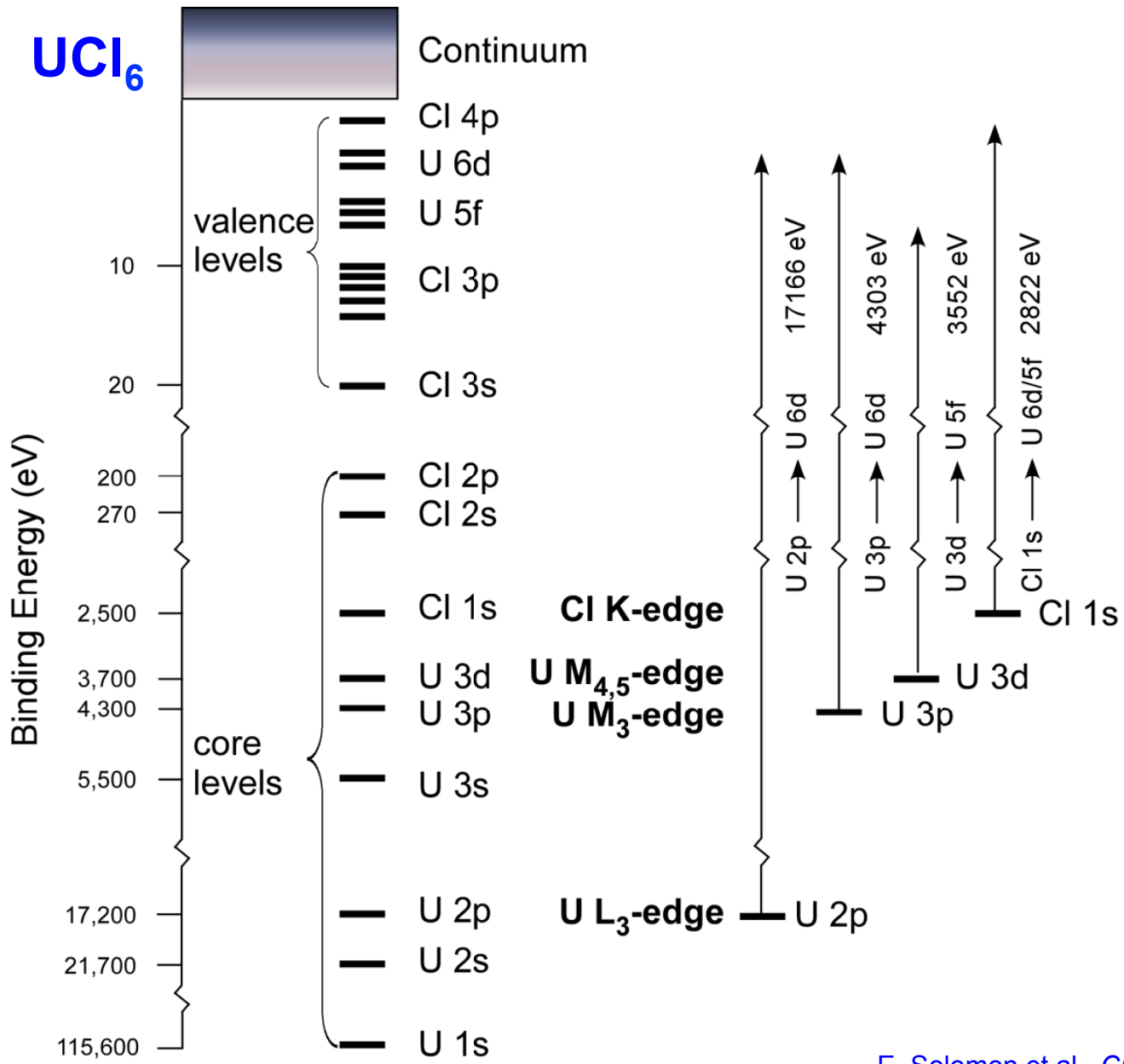
- 6*d*-orbital interactions dominate M-L bonding
  - Strong ligand fields, delocalized electrons (*covalent bonding*)
- 5*f* orbitals essentially uninvolved, and accomodate the valence electrons
  - Weak ligand fields, localized electrons (*ionic bonding*)
  - Yet – recent calculations are showing significant 5*f* orbital mixing
- **X-ray absorption spectroscopy (XAS) can provide information on empty 5f and 6*d* orbitals**

- Ligand K-edge XAS well-developed

E. Solomon et al., *Coord. Chem. Rev.* **2005**, 249, 97

Goal: develop new information on the relative roles of 5*f* and 6*d* orbitals

X-ray Absorption Spectroscopy to Measure Covalency



6d final states

U L_3 XANES

U $2p_{3/2} \rightarrow 6d$

U M_3 XANES

U $3p_{3/2} \rightarrow 6d$

5f final states

U $M_{4/5}$ XANES

U $3d_{3/2} \rightarrow 5f$

5f/6d final states

Cl K XANES

Cl 1s $\rightarrow \psi^*$

E. Solomon et al., *Curr. Opinion Chem. Bio.* **2001**, 176-187

Covalent Mixing: Ligand K-edge XAS

- If metal forms covalent bonds with L 3*p* orbitals, then ψ^* has L 3*p* character

$$\psi^* = c^*_M \phi_M - c^*_L \phi_L$$

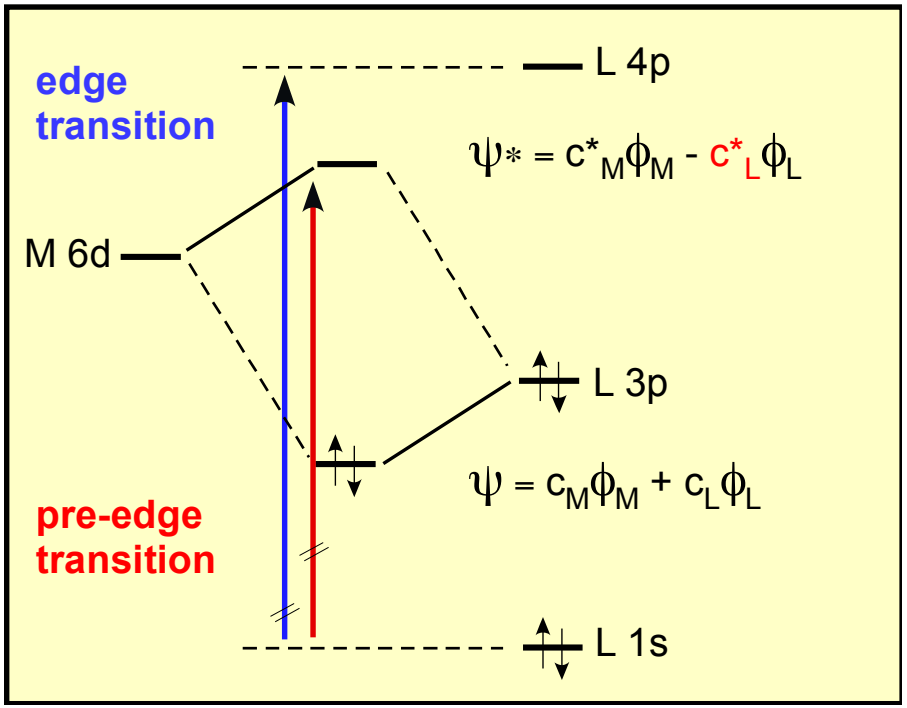
- Pre-edge transition may be described as L 1*s* -> ψ^*, where intensity is gained from L 3*p* character in ψ^*

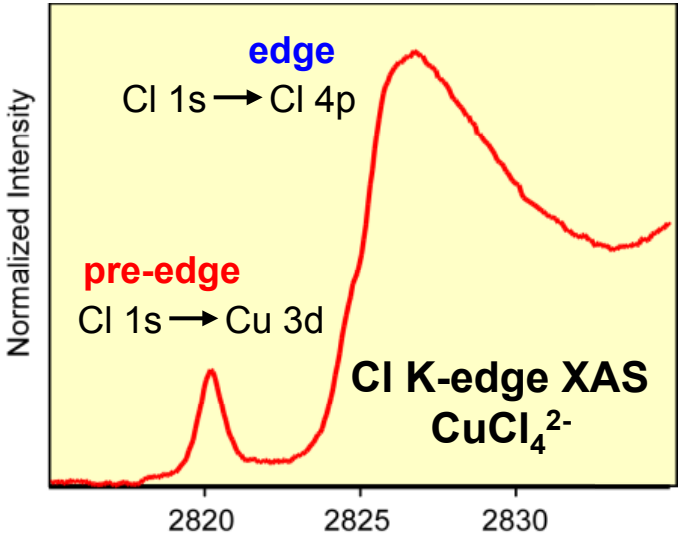
$$I\ L_{1s \rightarrow \psi^*} = |\langle L_{1s} | \boldsymbol{r} | \psi^* \rangle|^2$$

$$= c^{*2}_L\ k|\langle L_{1s} | \boldsymbol{r} | L_{3p} \rangle|^2$$

- Pre-edge transition intensity derived from L-centered 1*s*->3*p* transition, weighted by c^{*2}_L, the covalent character of L 3*p* orbitals in Ψ^*

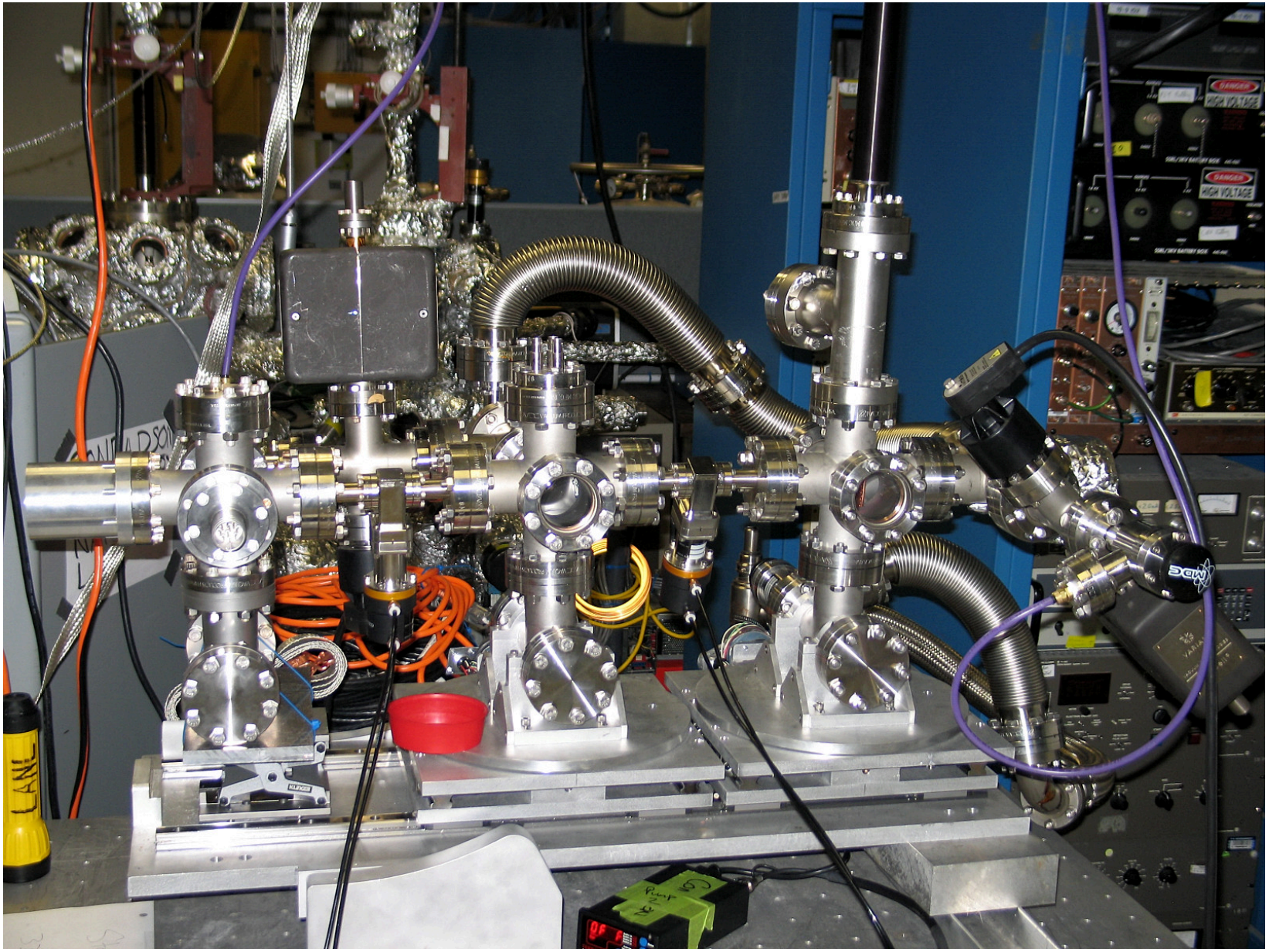
Ligand K-edge XAS is a direct, quantitative probe of covalency in M-L bond





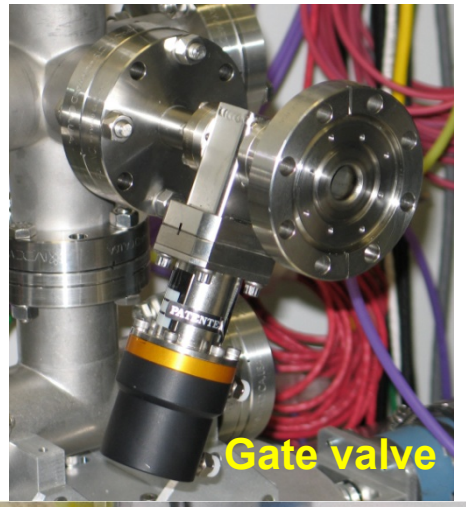
E. Solomon et al., *Coord. Chem. Rev.* **2005**, 249, 97

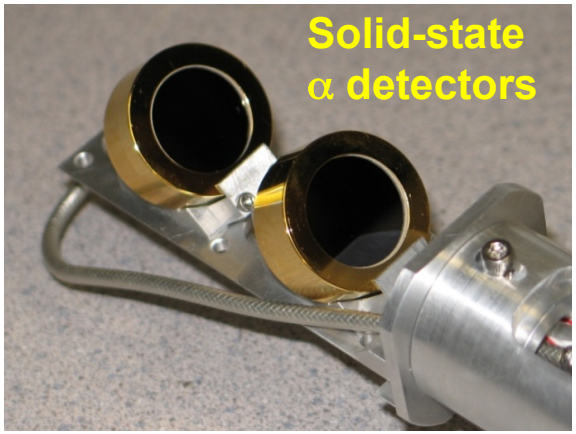
UHV Experimental Setup: 200 – 5000 keV

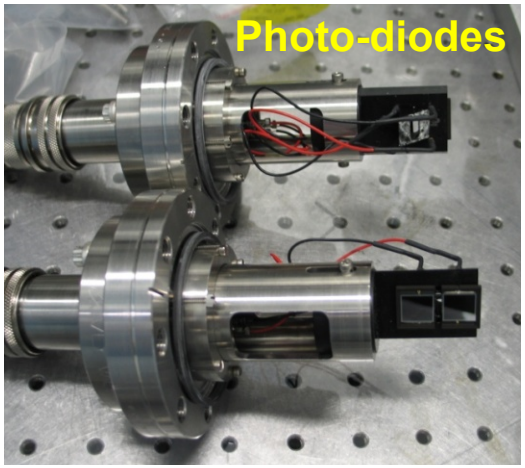


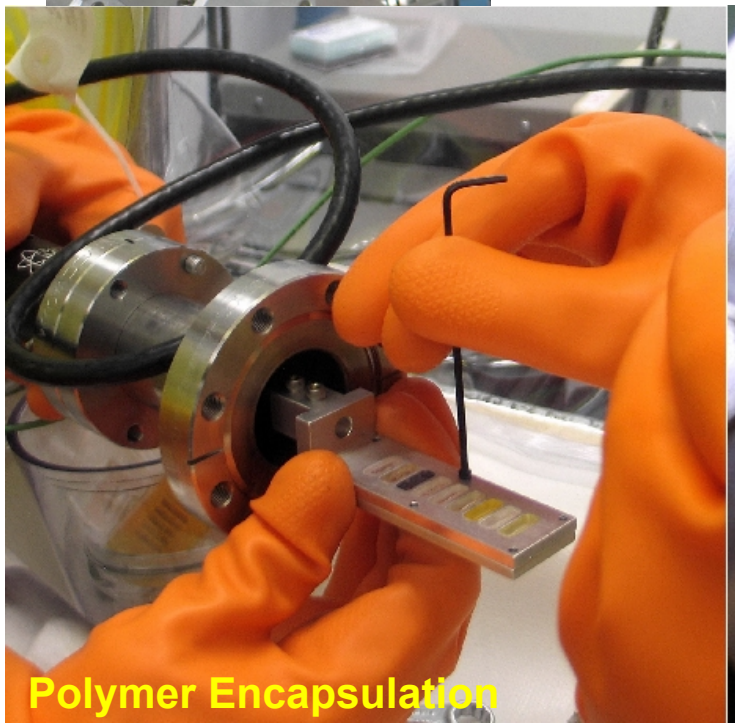
"how's the plumbing?"

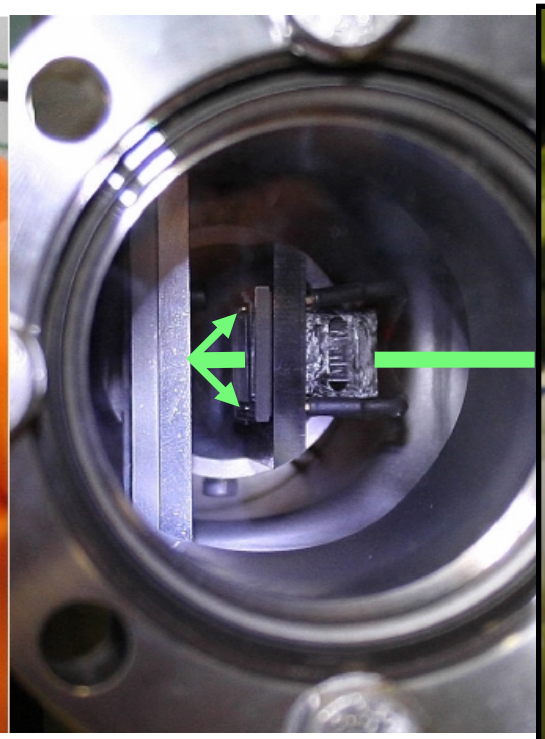
Air Sensitive, Radioactive, Soft X-ray UHV Setup

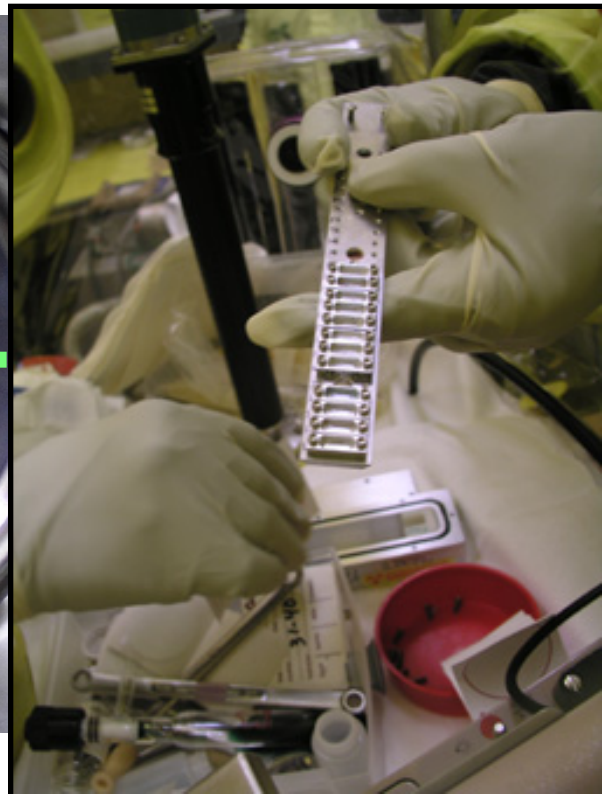




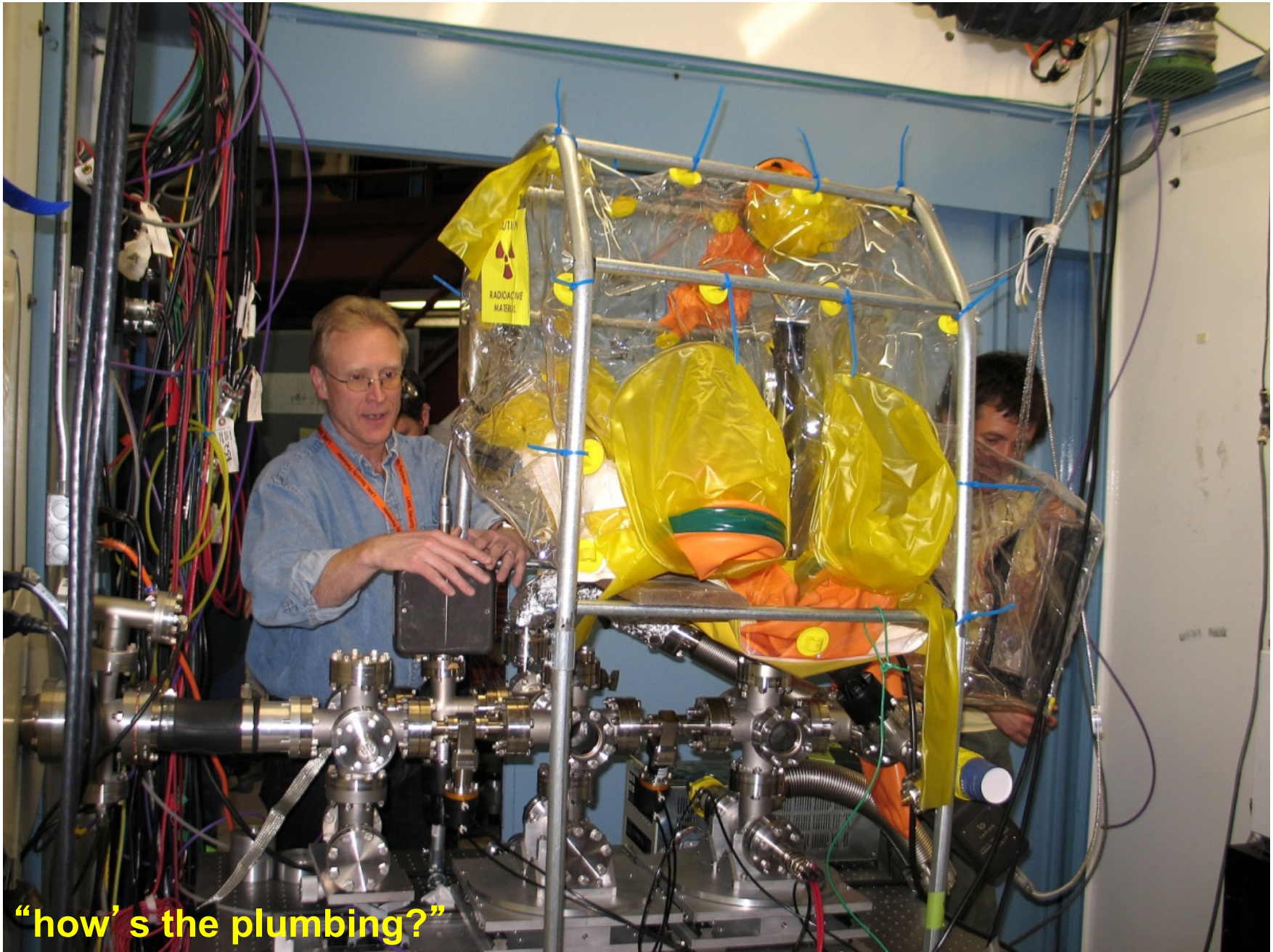






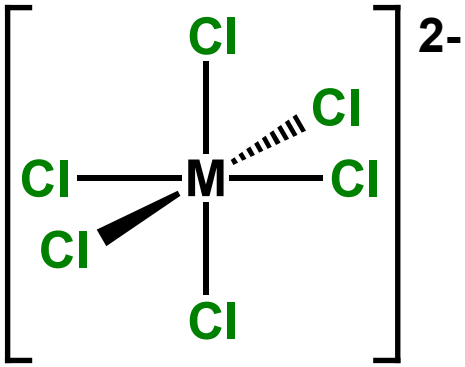


Radioactive and air-sensitive sample loading

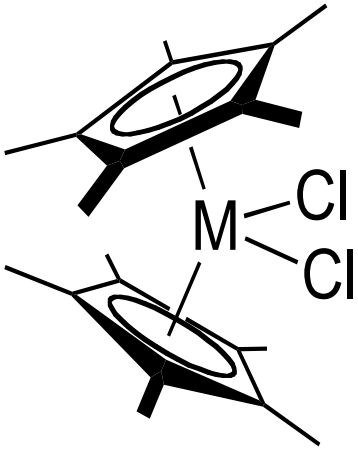


Benchmark molecules for Ligand K-edge XAS

Chlorine K-edge XAS

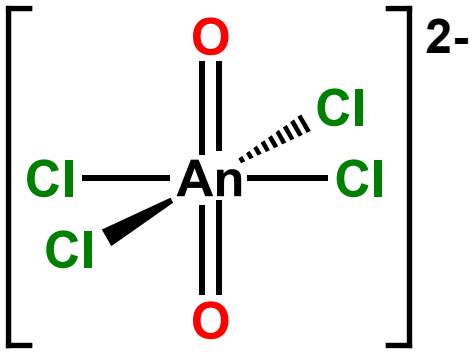


M = Ti, Zr, Hf, Th, U, Np, Pu

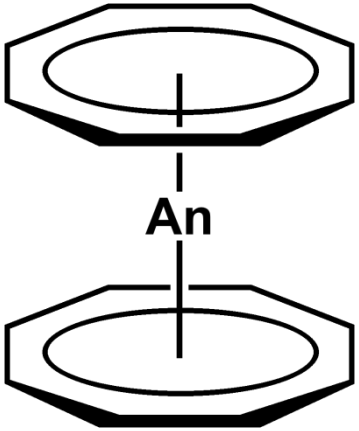


M = Ti, Zr, Hf, Th, U

C or O K-edge XAS



An = U, Np, Pu



An = Th, U, Np, Pu

Electronic Structure Model for Octahedral UCl_6^{n-}

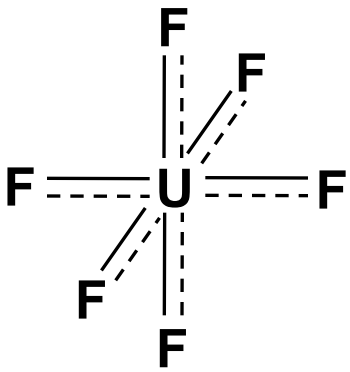
Ligand SALCS for MCl_6

$\Gamma_{p\sigma} = A_{1g} + E_g + T_{1u}$

$\Gamma_{p\pi} = T_{1g} + T_{1u} + T_{2g} + T_{2u}$

WCl_6	UCl_6
T_{1u} σ (6*p*)	T_{1u} $\sigma+\pi$ (7*p*)
A_{1g} σ (6*s*)	A_{1g} σ (7*s*)
E_g σ (5*d*)	E_g σ (6*d*)
T_{2g} π (5*d*)	T_{2g} π (6*d*)
	T_{2u} π (5*f*)
	T_{1u} $\sigma+\pi$ (5*f*)

UF_6



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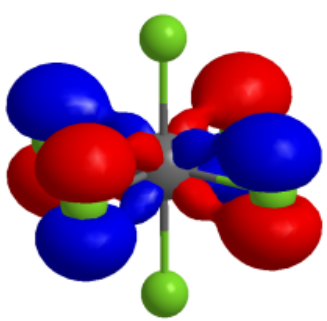
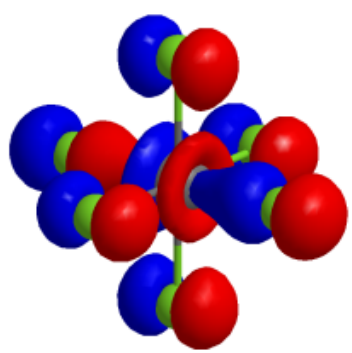
bonding (occupied) orbitals for UCl_6

T_{2u} π

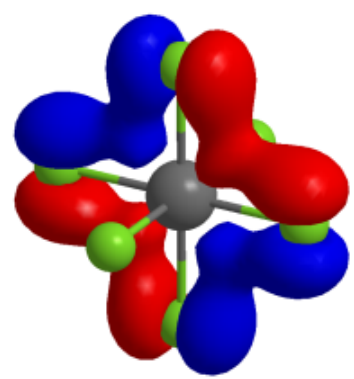


T_{1u} $\sigma+\pi$

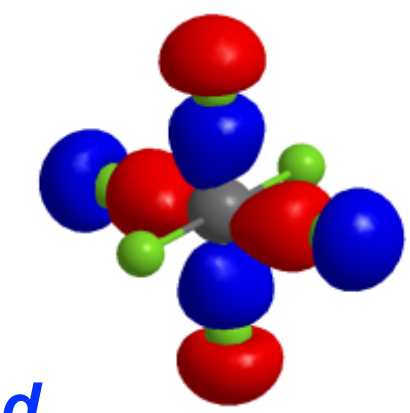


5f

T_{2g} π



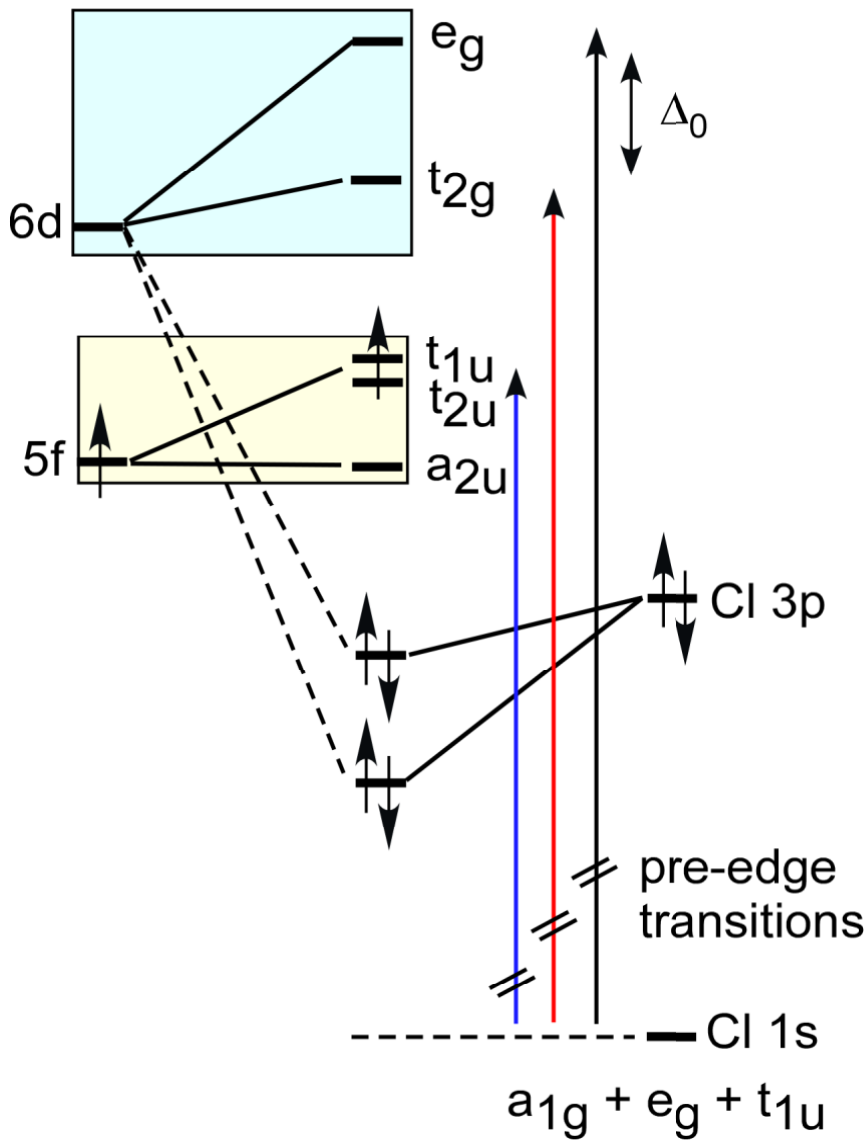
E_g σ



6d

DFT (B3LYP)

Electronic Structure Model for Octahedral MCl_6^{n-}



From elementary group theory:

Can expect two kinds of Cl K-edge transitions for MCl_6^{n-}

Transition metals: two transitions

nd : t_{2g} ($d\pi^*$) and e_g ($d\sigma^*$)

Actinides: four transitions

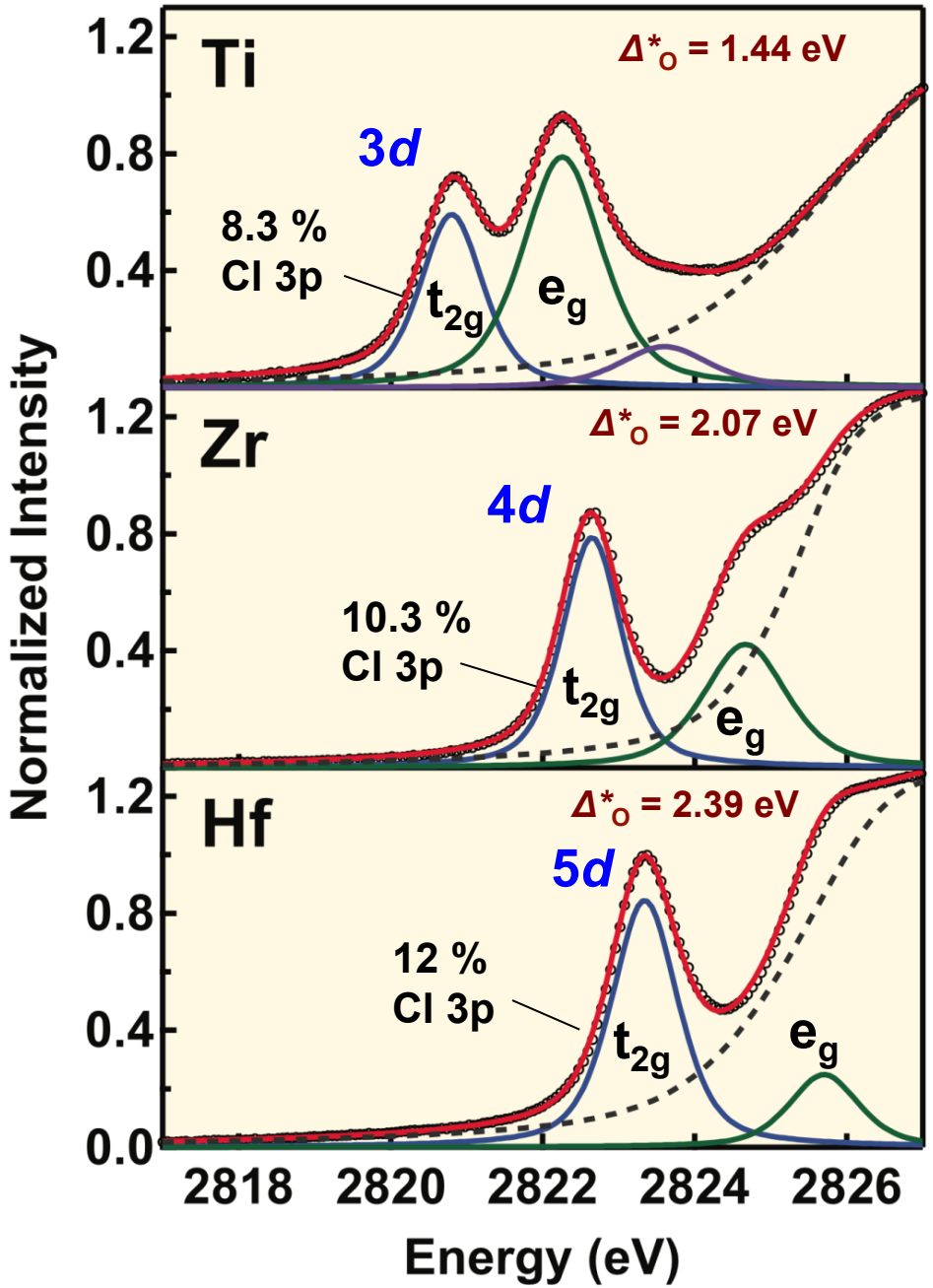
6d : t_{2g} ($d\pi^*$) and e_g ($d\sigma^*$)

5f : t_{2u} ($f\pi^*$), t_{1u} ($f\sigma^*+\pi^*$)

•***5f*** transitions will be observed if and only if there is covalent mixing

•Ignore spin-orbit & muliplet effects – ***for now***

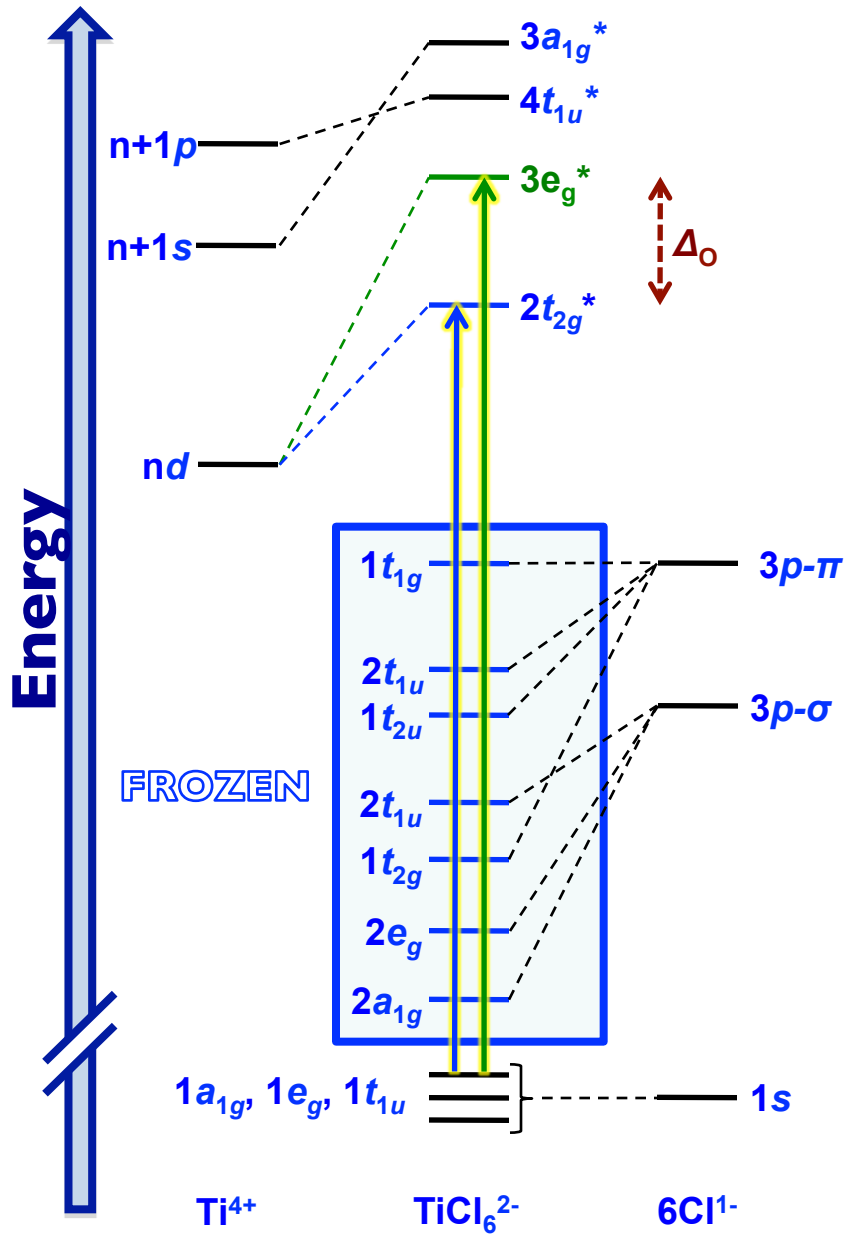
Cl K-edge XAS for octahedral Group IV MCl_6^{2-}

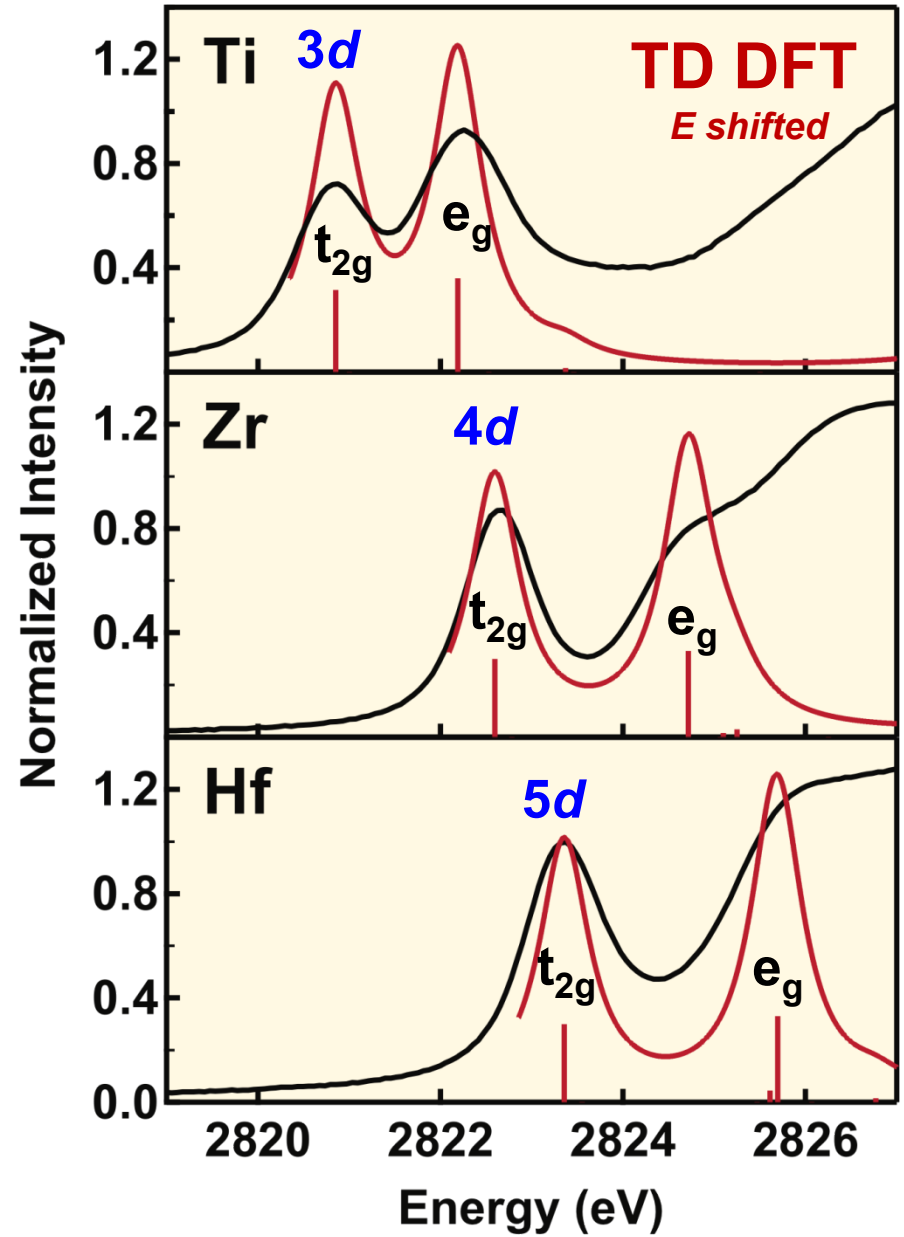


- All MCl_6^{2-} analyses on single crystals (XRD)
- **Pre-edge features confirm <u>covalent mixing</u>**
- Two-peaks consistent w expectations for d elements
- d orbitals move to higher energy with increasing Z_{eff}
- Curve fits give % Cl 3p character in metal t_{2g} orbital
- Electronic structure calculations give similar trends and % Cl 3p **mixing**

Minasian, J. Am. Chem. Soc., **2012** p. 5586

Simulated spectra confirm peak assignments for MCl_6^{2-}





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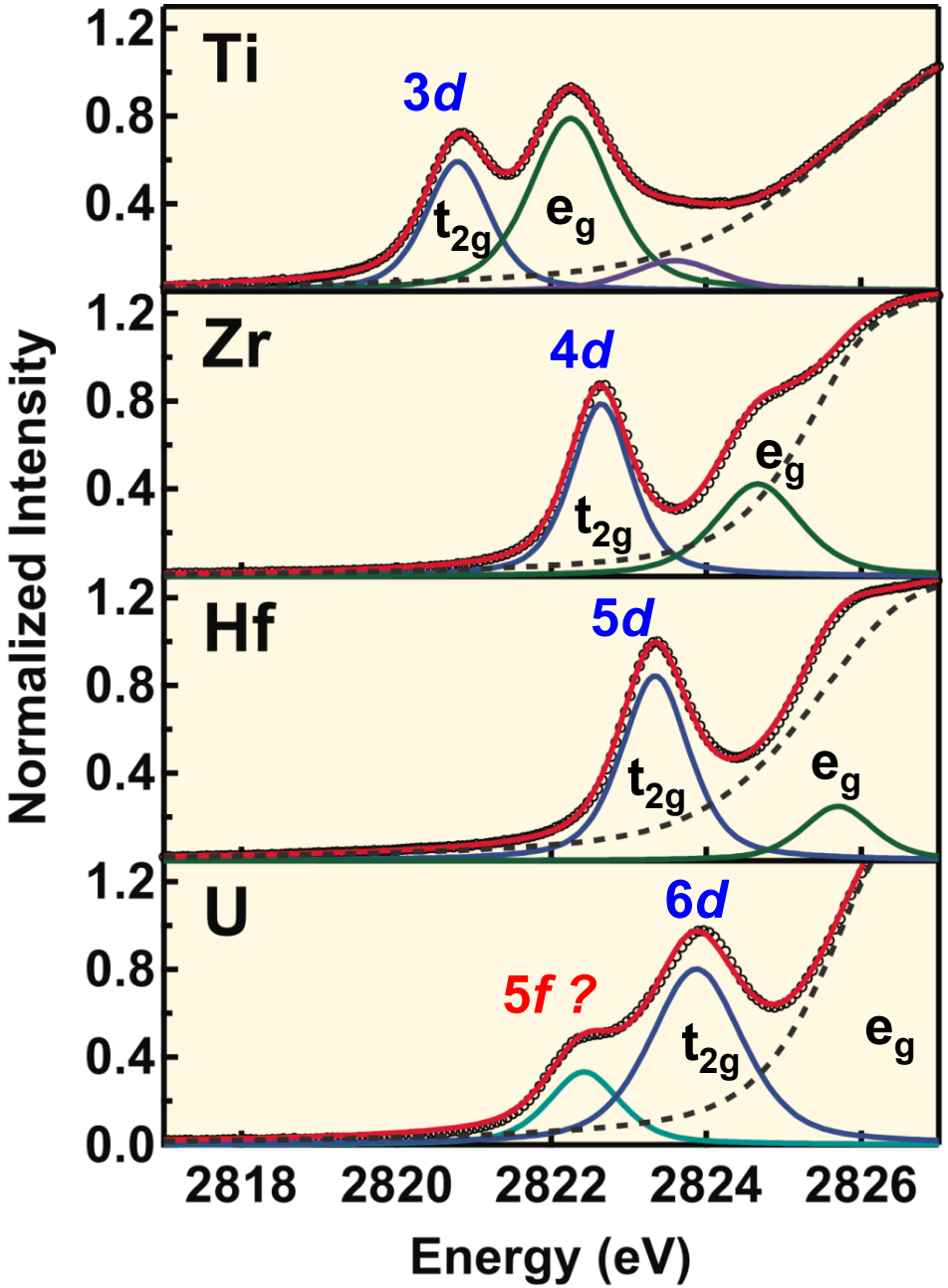
Cl K-edge XAS for octahedral Group MCl_6^{2-}

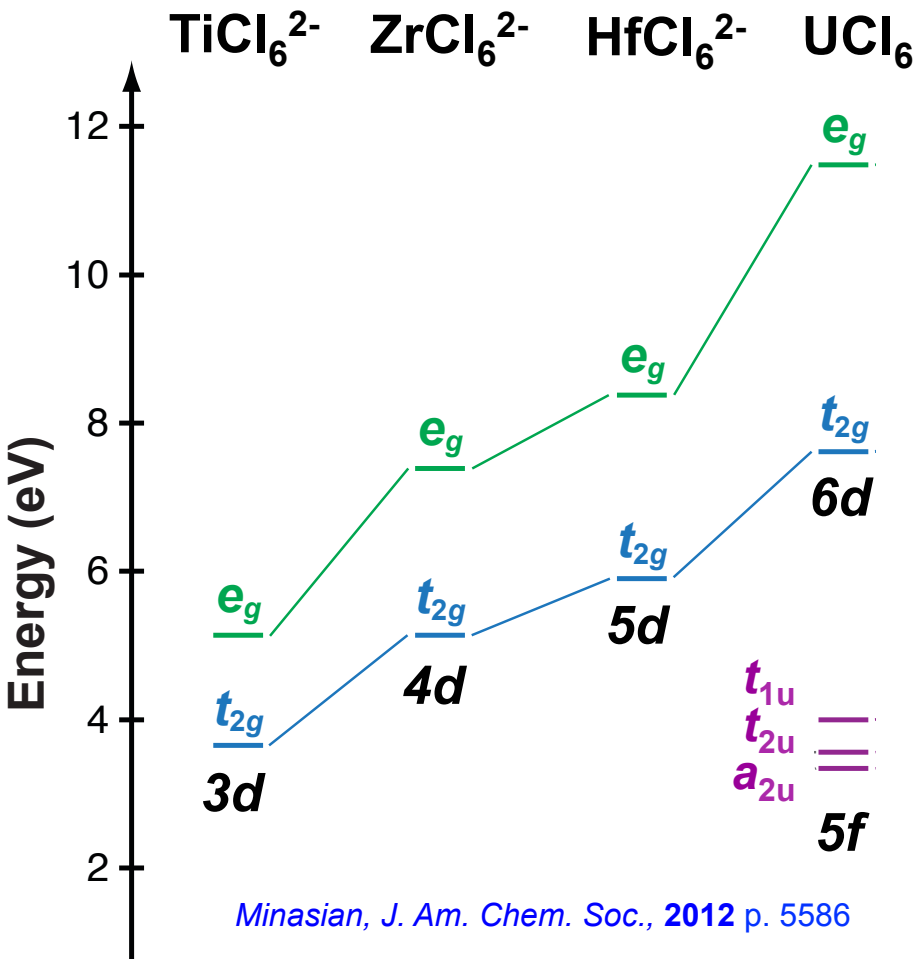


- **Pre-edge features confirm <u>covalent mixing</u> in MCl_6^{2-}**
- Transitions into d orbitals move to higher energy with increasing Z_{eff}
- Transitions to e_g move under white line with increasing Z_{eff}
- New peak in UCl_6^{2-} could be evidence for 5*f* mixing with Cl 3*p*

Minasian, J. Am. Chem. Soc., **2012** p. 5586

Cl K-edge XAS and Electronic Structure Theory for MCl_6^{2-}

- Experiments at the Cl K-edge demonstrate both 5f- and 6d-orbital involvement in bonding.
- Trends in bonding can vary significantly depending on ligand, geometry, oxidation state.



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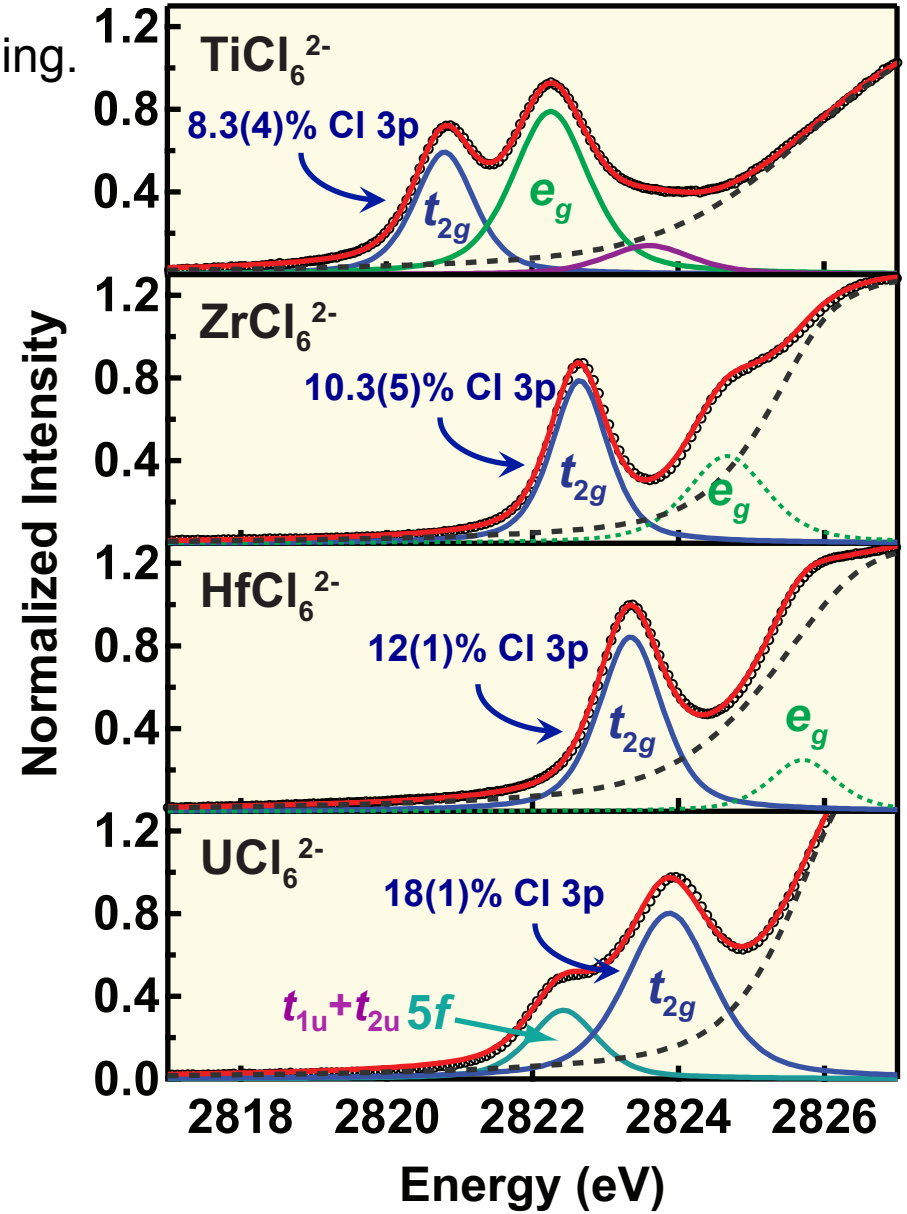
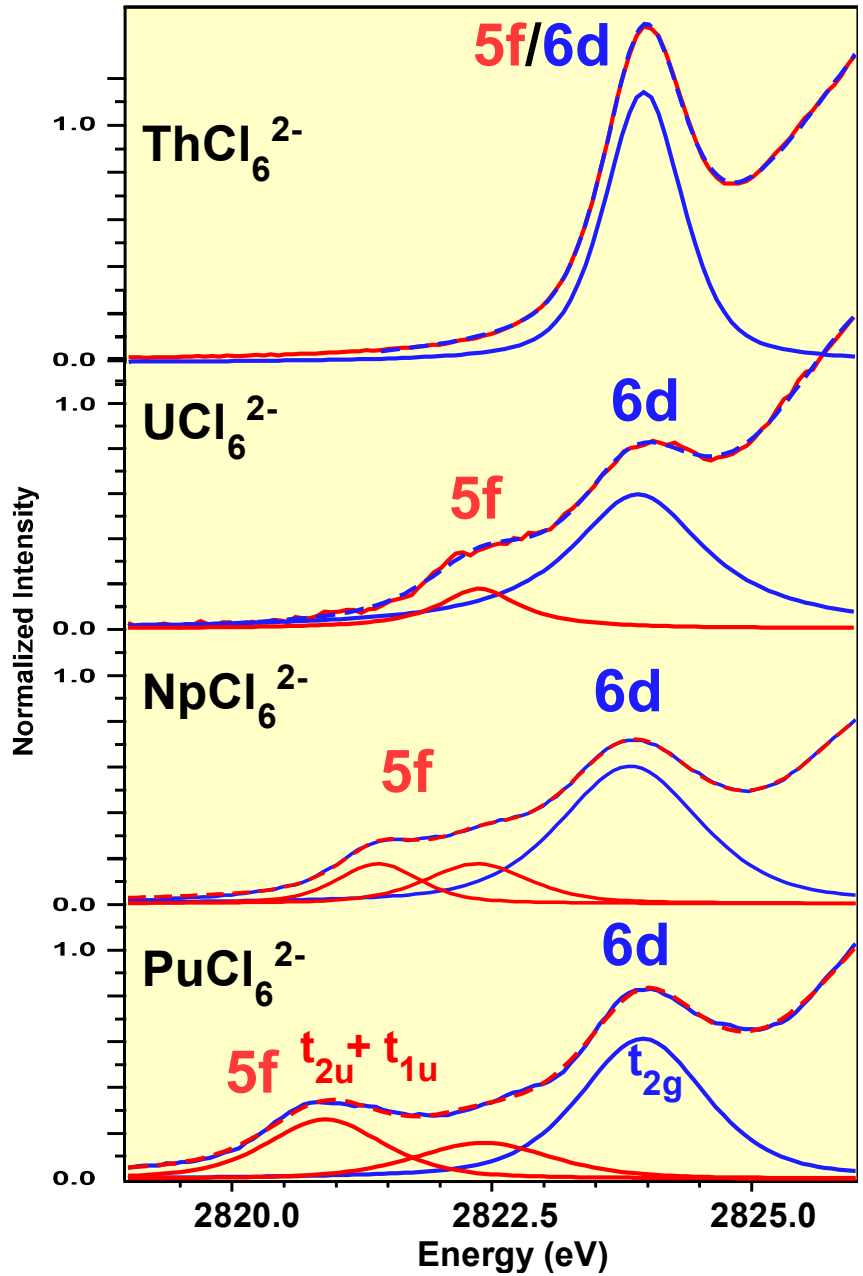


Extension to Transuranic $AnCl_6^{2-}$ systems



Curve fits

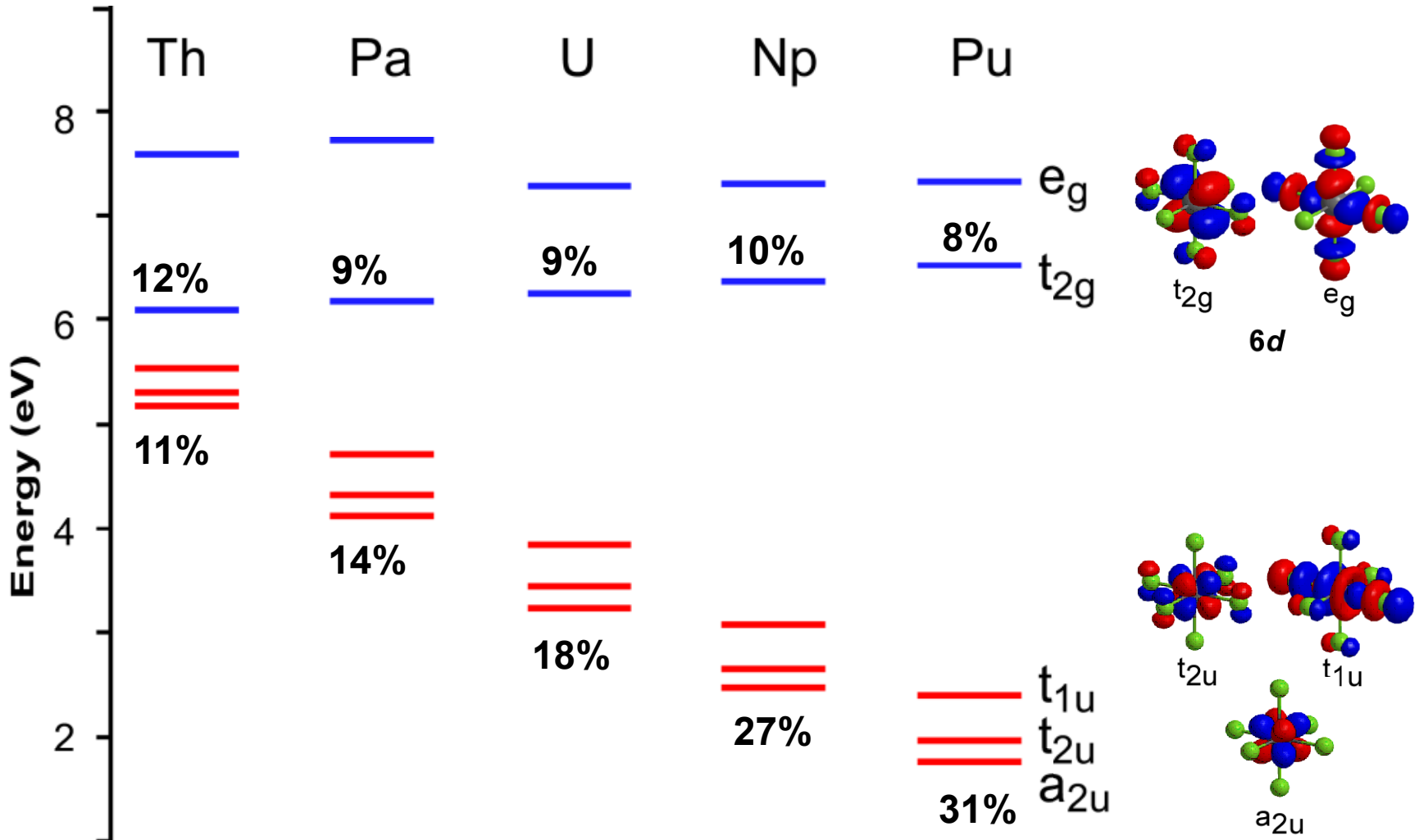
	% Cl 3*p* (tot)	% Cl 3*p* (5f)	% Cl 3*p* (6d)
Th-Cl	18(1)	--	--
U-Cl	22(1)	5	18
Np-Cl	23(1)	7	16
Pu-Cl	24(1)	8	16

- ***"Unexpected" increase in 5f orbital mixing with increasing Z_{eff}***

Theoretical Predictions by

- B. Bursten for $AnCp_3$
  J. Am. Chem Soc **1991**,*113*, 552
- R. Martin in AnO_2
  PRB Condens. Matter Mater. Phys. **2007**, 76, 033101
- N. Kaltsoyannis for $AnCp_4$, $AnCp_3$, and $An[N(EPH_2)_2]_3$
  Dalton Trans., ***2011***, *40, 124;* **2010**, *39*, 671,
  Inorg Chem., **2008**, *47*, 7824

Calculated Energy Levels for $AnCl_6^{2-}$ systems

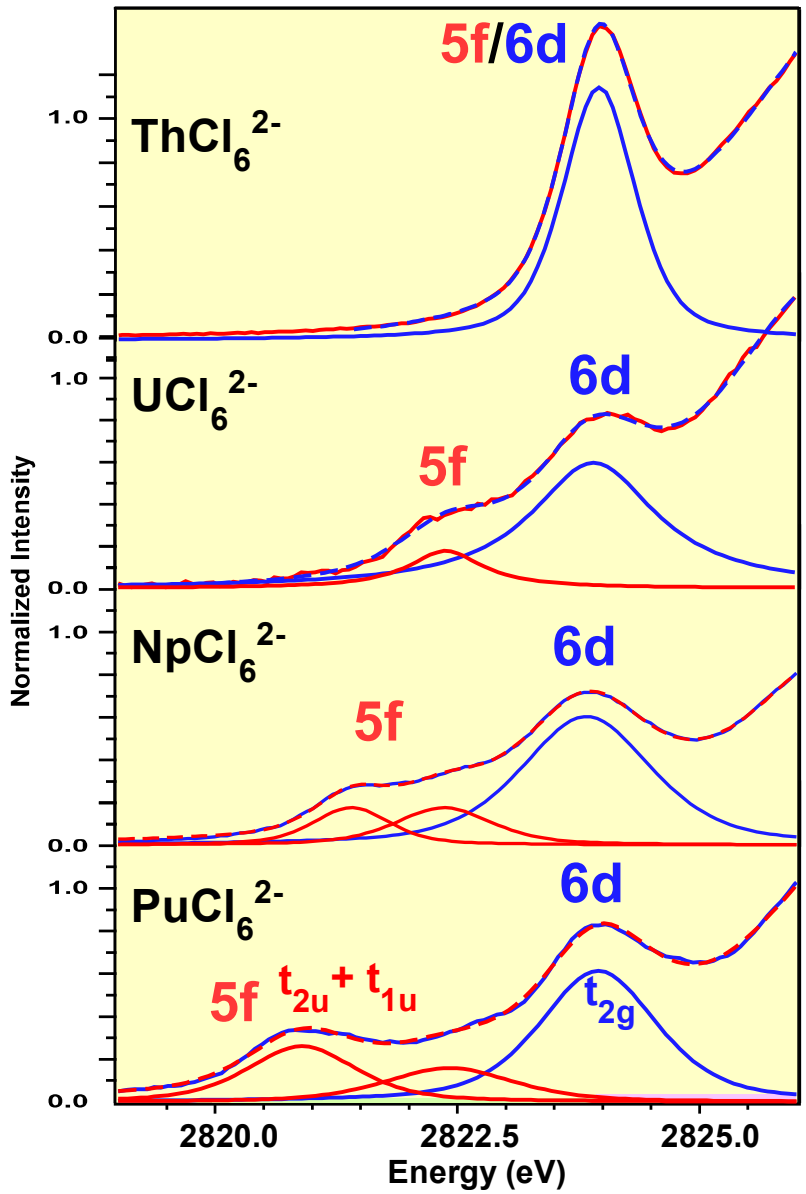


Calculated % Cl 3p character reveals unexpected increase in covalent mixing in 5f orbitals with Z_{eff} - ***Neglects multiplets and spin-orbit coupling***

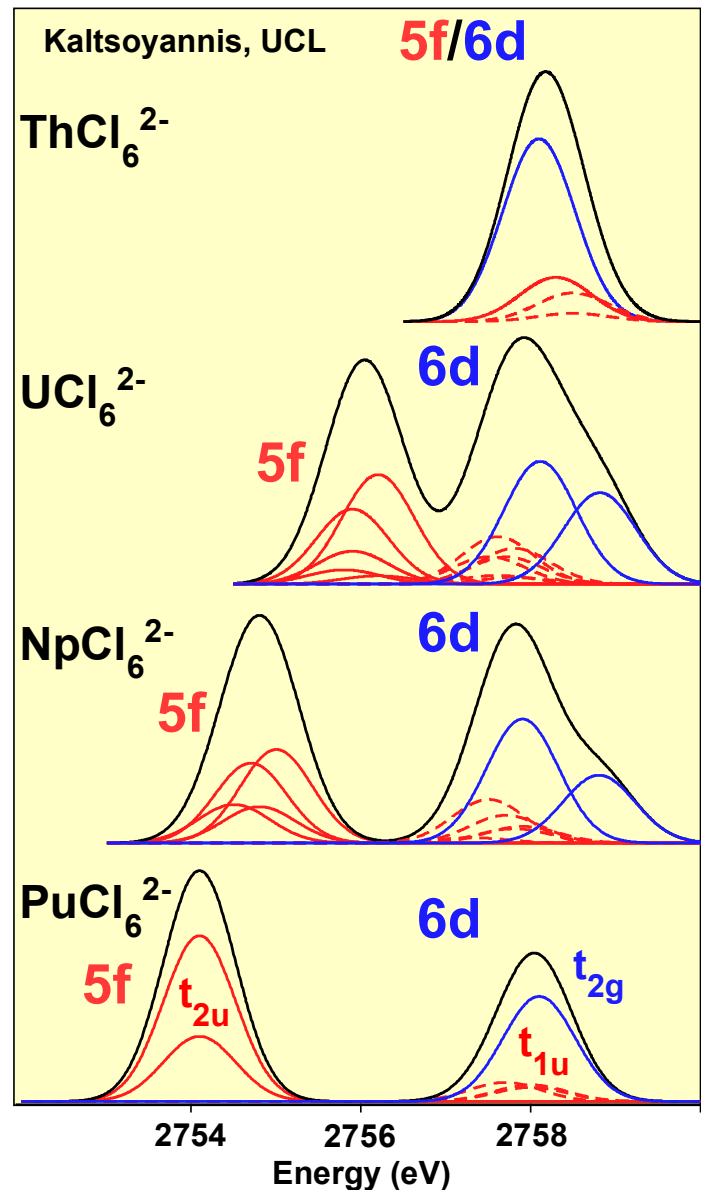
Kaltsoyannis, Tassell, UCL

Electronic Structure Calculations aid Assignments

Cl K-edge XAS

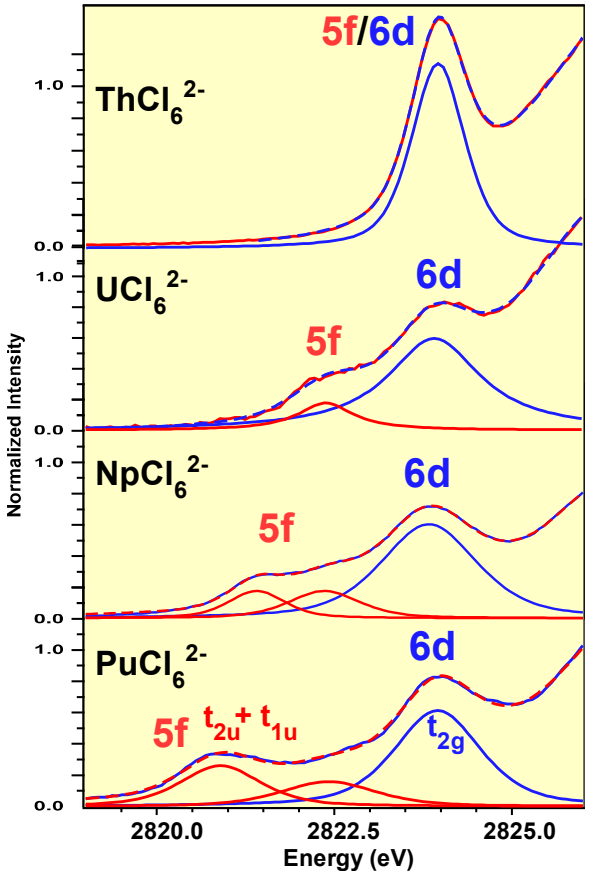


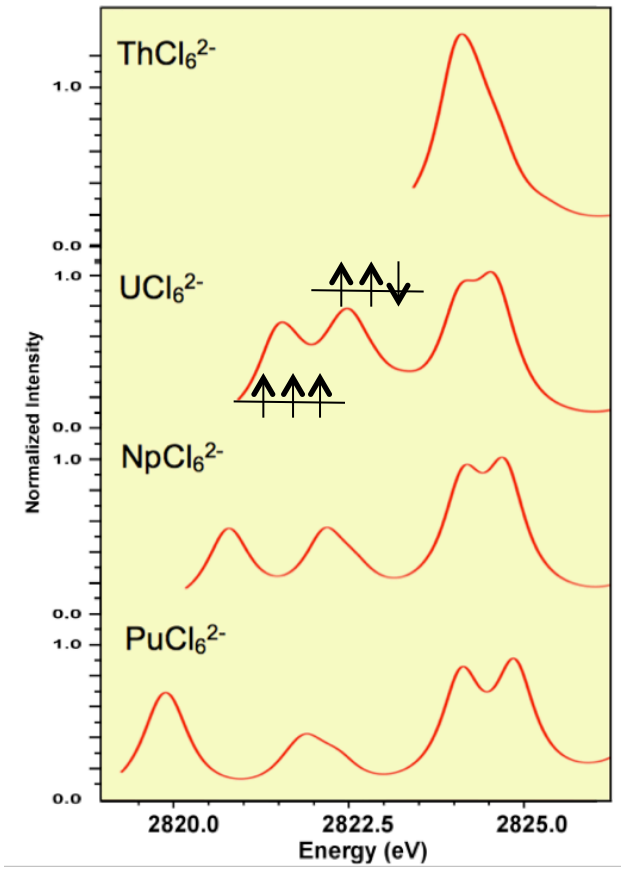
TD-DFT Simulation

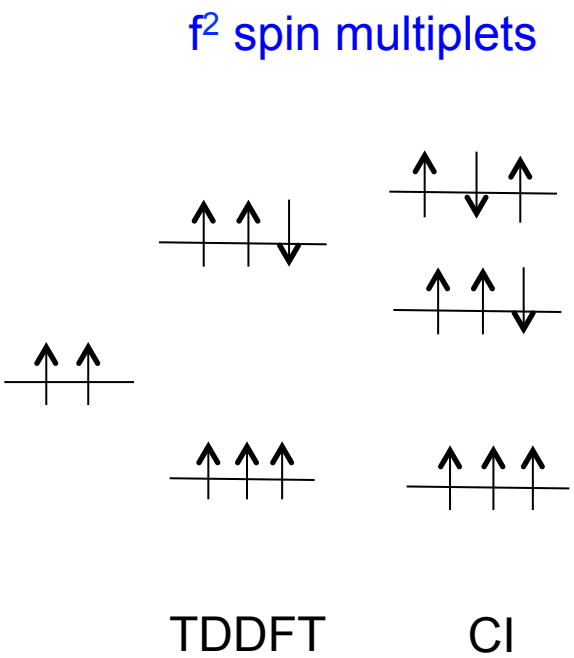


Multiplet Effects Dominated by Spin Couplings

- TDDFT multiplet structure for UCl_6^{2-} dominated by spin couplings / exchange interaction
- In agreement with all-electron, intermediate coupling CAS calculations by P. S. Bagus wfn. techniques have difficulty placing f and 6d on equal footing.

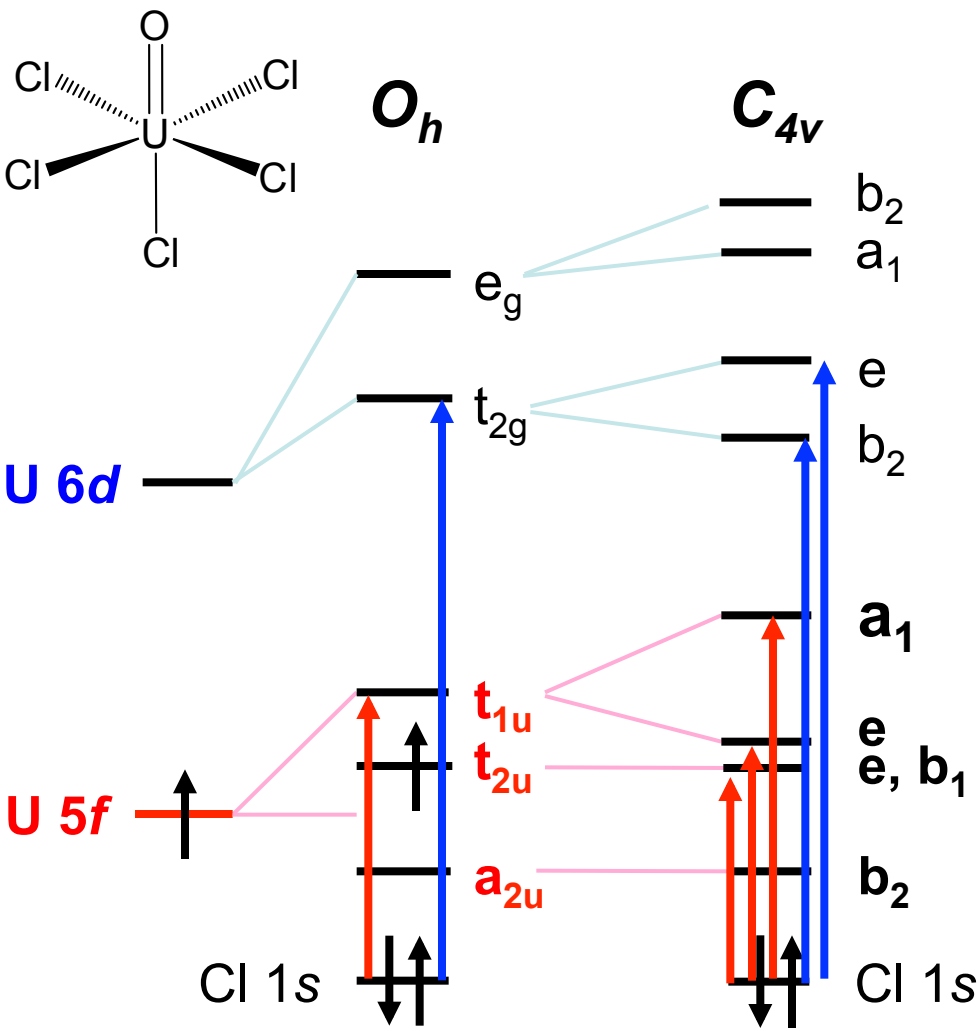


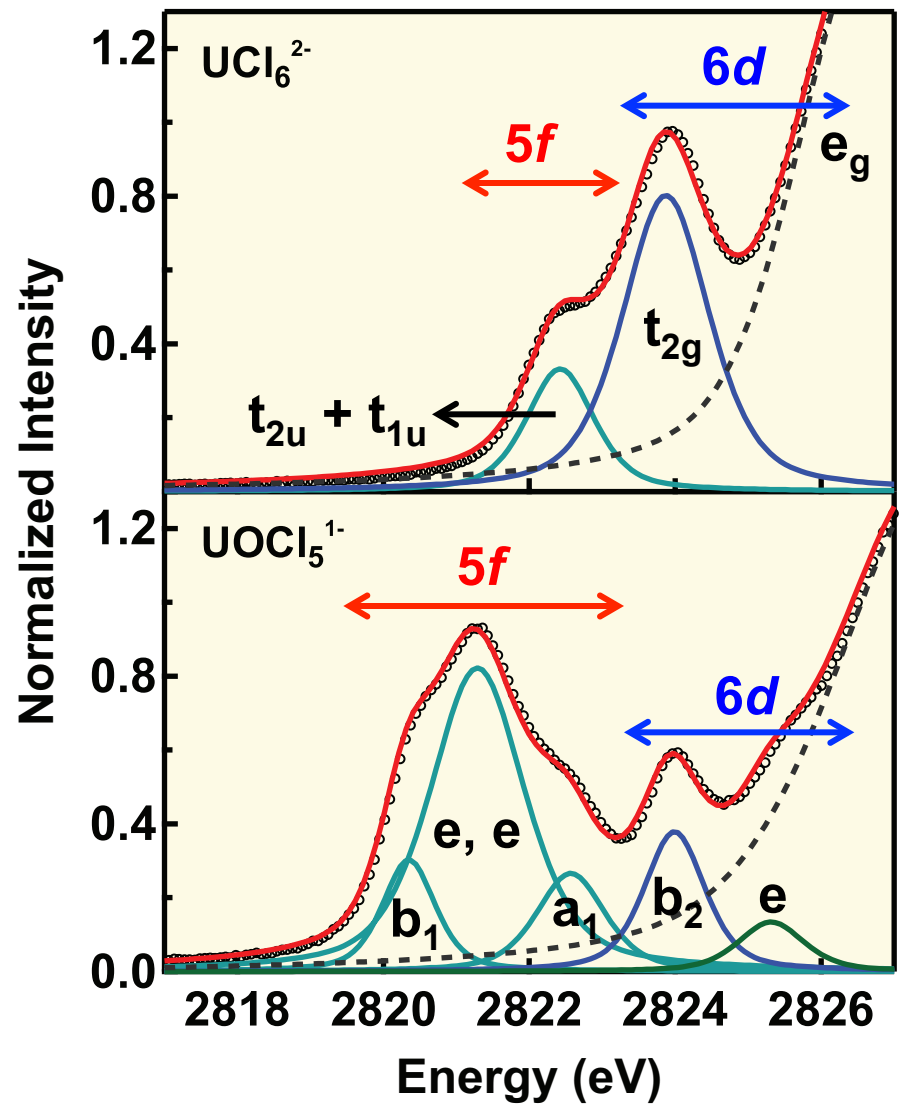




Symmetry reduction to $UOCl_5^-$

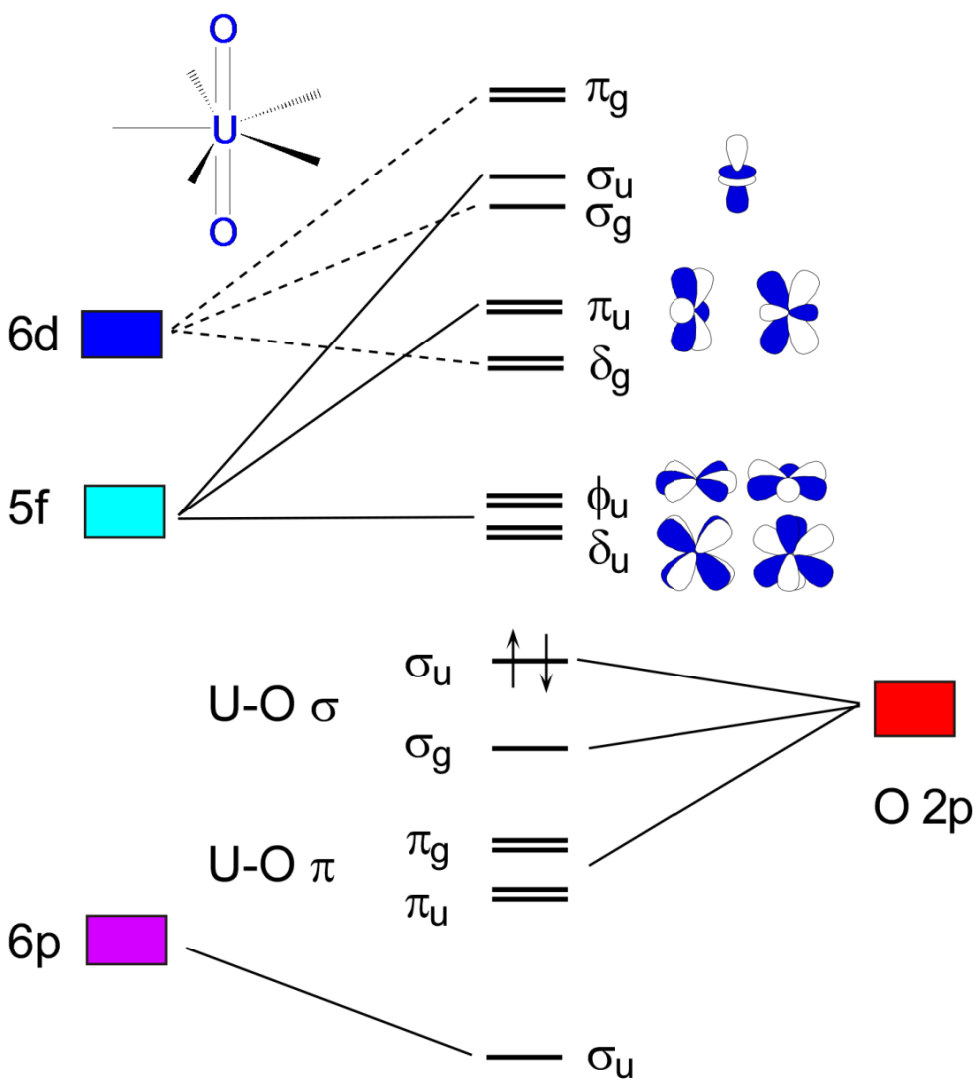
Cl K-edge XAS can be used to deconvolute 5f and 6d contributions to U–Cl bonding.





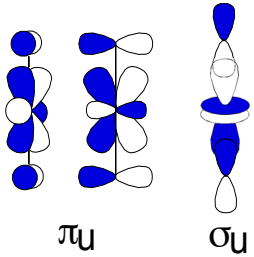
Minasian, J. Am. Chem. Soc., **2012** p. 5586

Bonding Description for Actinyl Ions



R. G. Denning, *J. Chem. Phys*, 2002, *117*, 8008

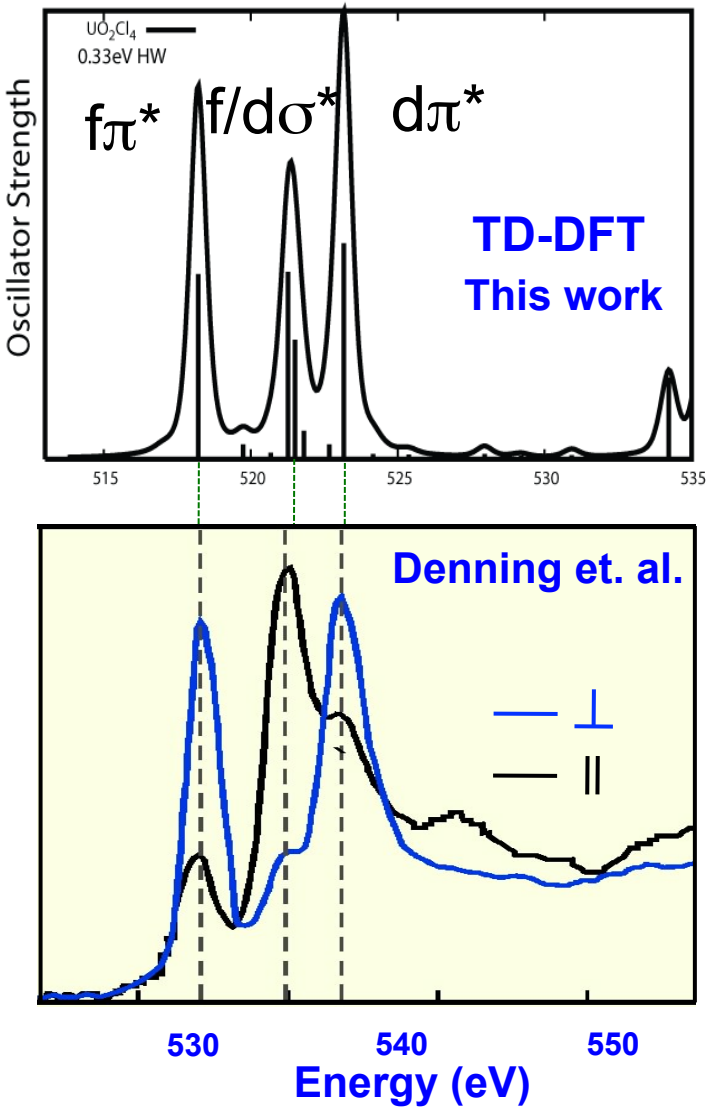
- M=O triple bond character in trans configuration

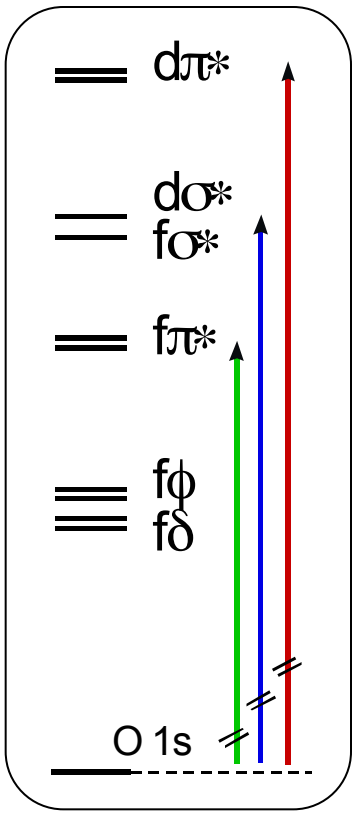


- trans configuration allows $5f_{z^3}$ and semi-core $6p_z$ mixing to form strong σ bonds
- 5f-6p σ bonding mode not available for transition elements
- Addition of 5f electrons to non-bonding δ_u or ϕ_u orbitals has little effect on An=O bonding – Np, Pu, Am all <u>trans</u>
- Strong axial (An=O) and weak equatorial (An-L) bonding

U=O Bonding Probed by O K-edge XAS

O K-edge XAS

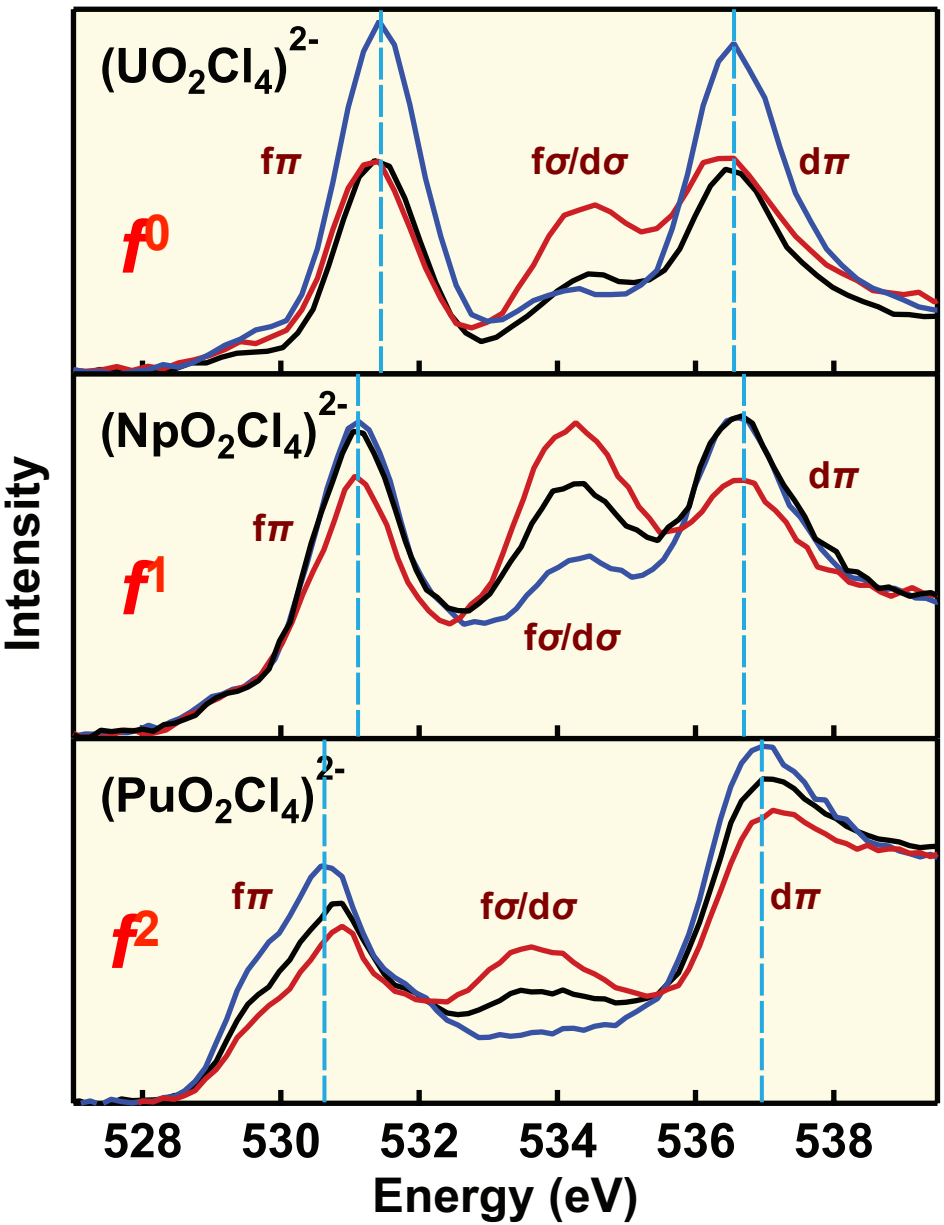




- Denning *et al*. reported seminal study on $Cs_2UO_2Cl_4$
- Large single crystal, x-ray self-absorption, Fluorescence Yield
- 3 pre-edge peaks observed by Denning *et al*.
  - fπ*, d/fσ*, dπ*
- TD-DFT simulation confirms assignments (this work)
- Peak areas should be quantitative measure of covalency

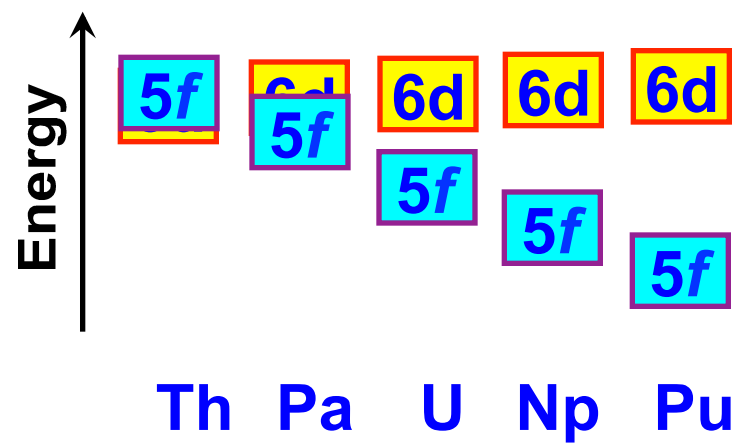
Denning *et al*. *J Chem Phys*. **2002**, *117*, 8008

STXM of $(AnO_2Cl_4)^{2-}$ (An = U, Np, Pu)



STXM provides horizontal, vertical, elliptical polarization

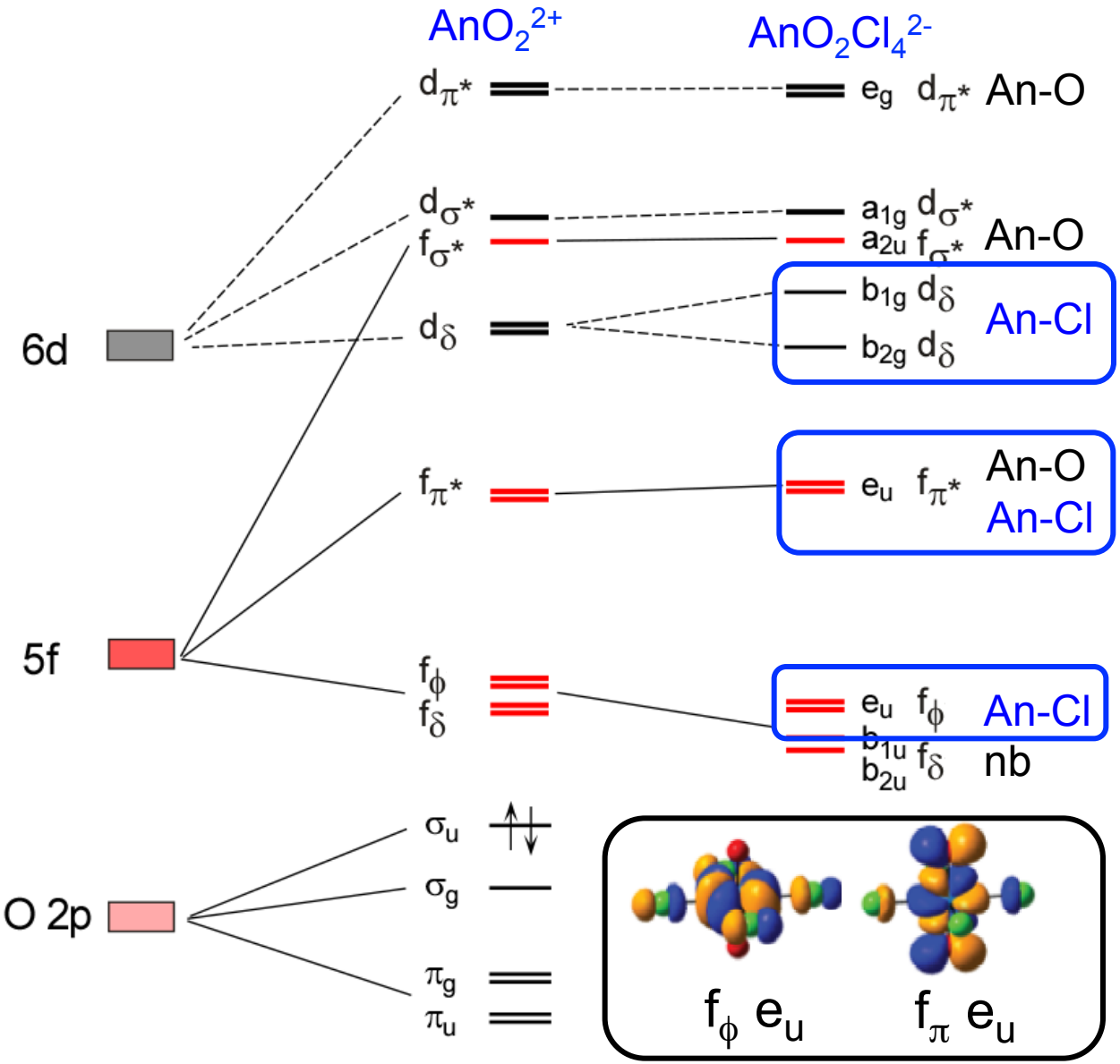
- Transitions involving *5f* final states move to lower energy with increasing Z.
- Consistent with $AnCl_6^{2-}$ Cl K-edge data (An = Th, U, Np, Pu)

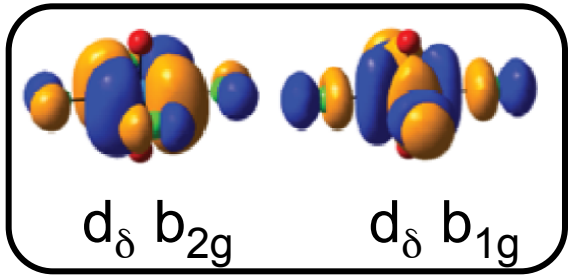


Pepper, Bursten, *Chem. Rev.* **1991** *91* 719

– Possible mutliplet effects

Actinyl Ions and Equatorial Ligands

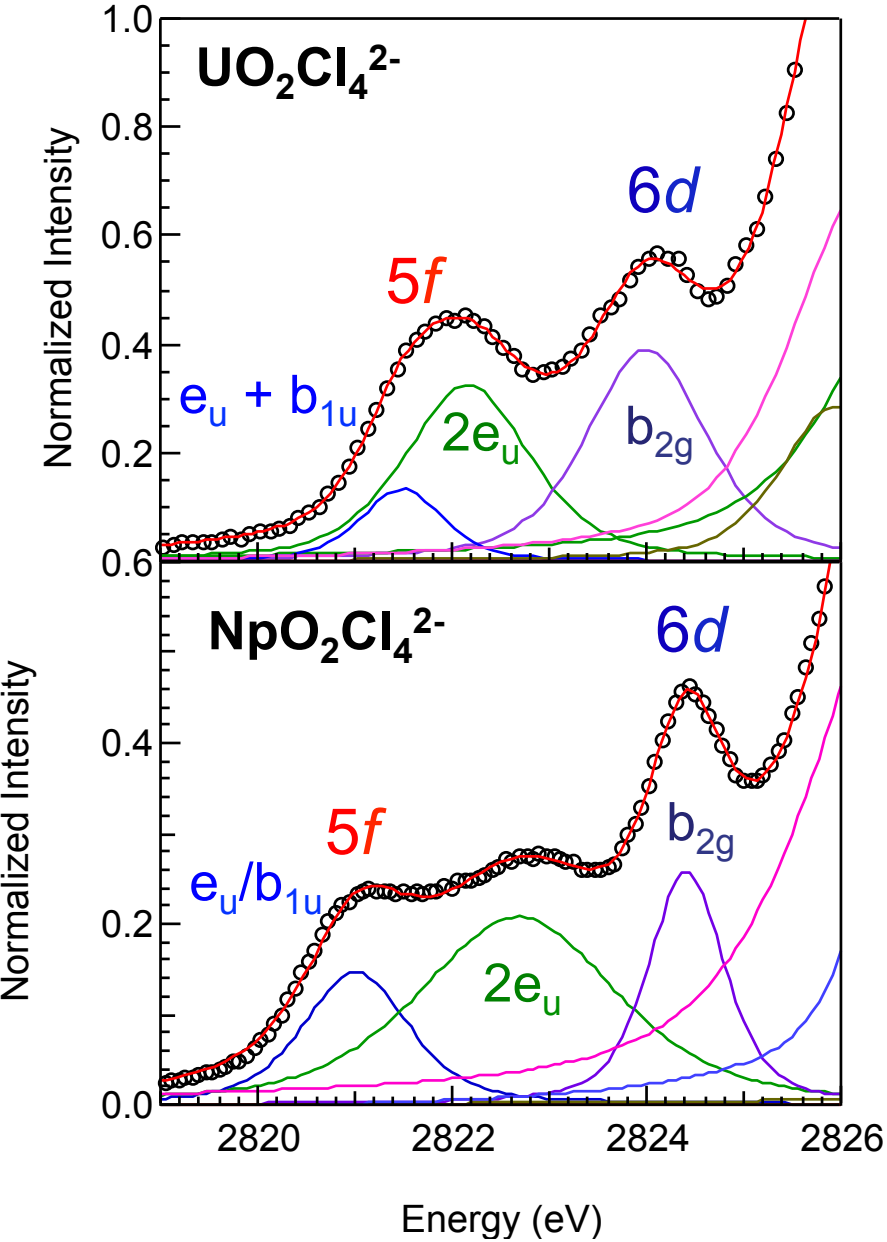


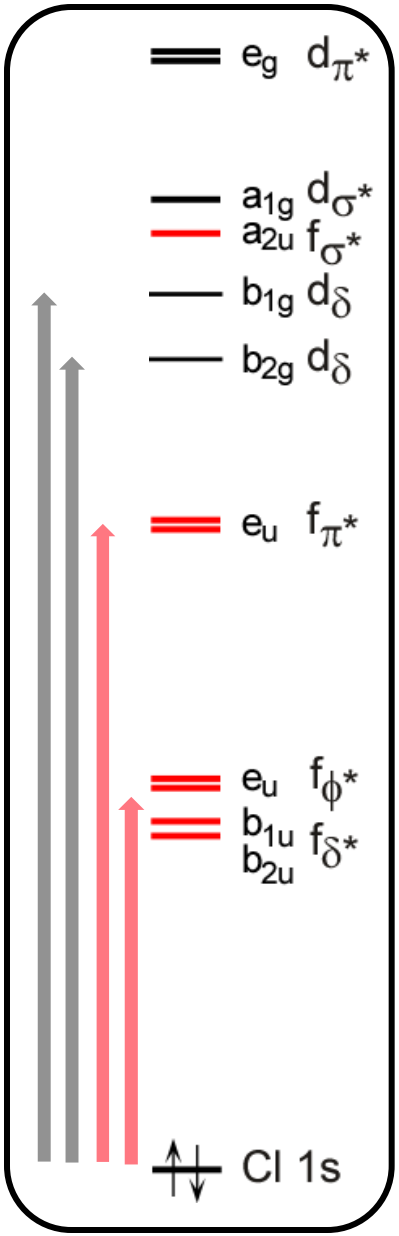


- An≡O triple bond character
- By symmetry, equatorial bonding derived from 6d (b_{1g} + b_{2g}) and 5f (e_u)
- The position of $6d_\delta$ orbitals that give rise to equatorial An-L bonds not well established
- Equatorial bonding is only a small perturbation to the An≡O bonding
- equatorial (An-L) bonding is weak (ionic)

R. G. Denning, *J. Chem. Phys. A*, 2007, *111*, 4125

Equatorial Bonding probed by Cl K-edge XAS



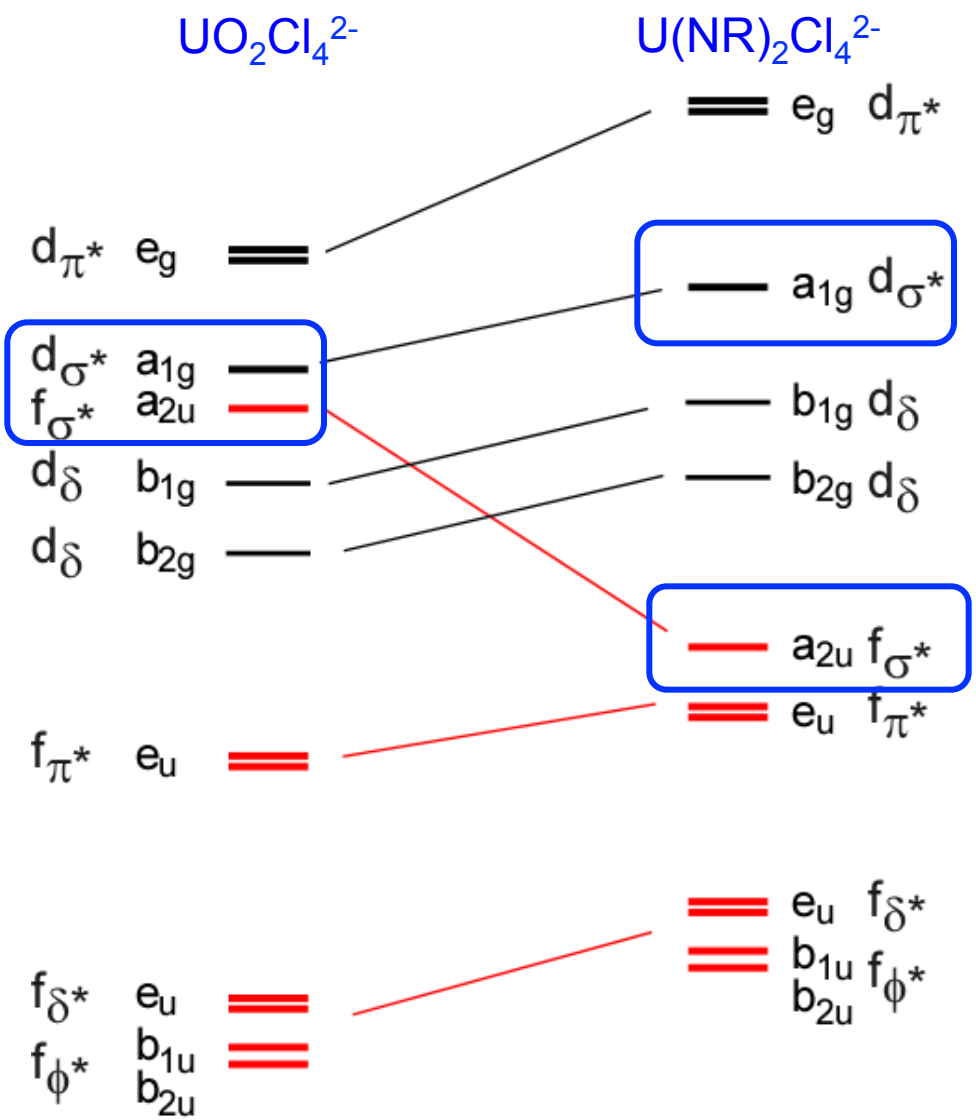


$AnO_2Cl_4^{2-}$

- Pre-edge peaks confirm some covalency in equatorial An-Cl bonds
- first band of 2 peaks is assigned as *5f* covalency
- Derived from f_{δ} + f_{ϕ} (t_{2u}) and f_{π^*} (t_{1u})
- second band is assigned as *6d* covalency derived from d_{δ}

Spencer, *J. Am. Chem. Soc.*, **2013**, 135(6), 2279

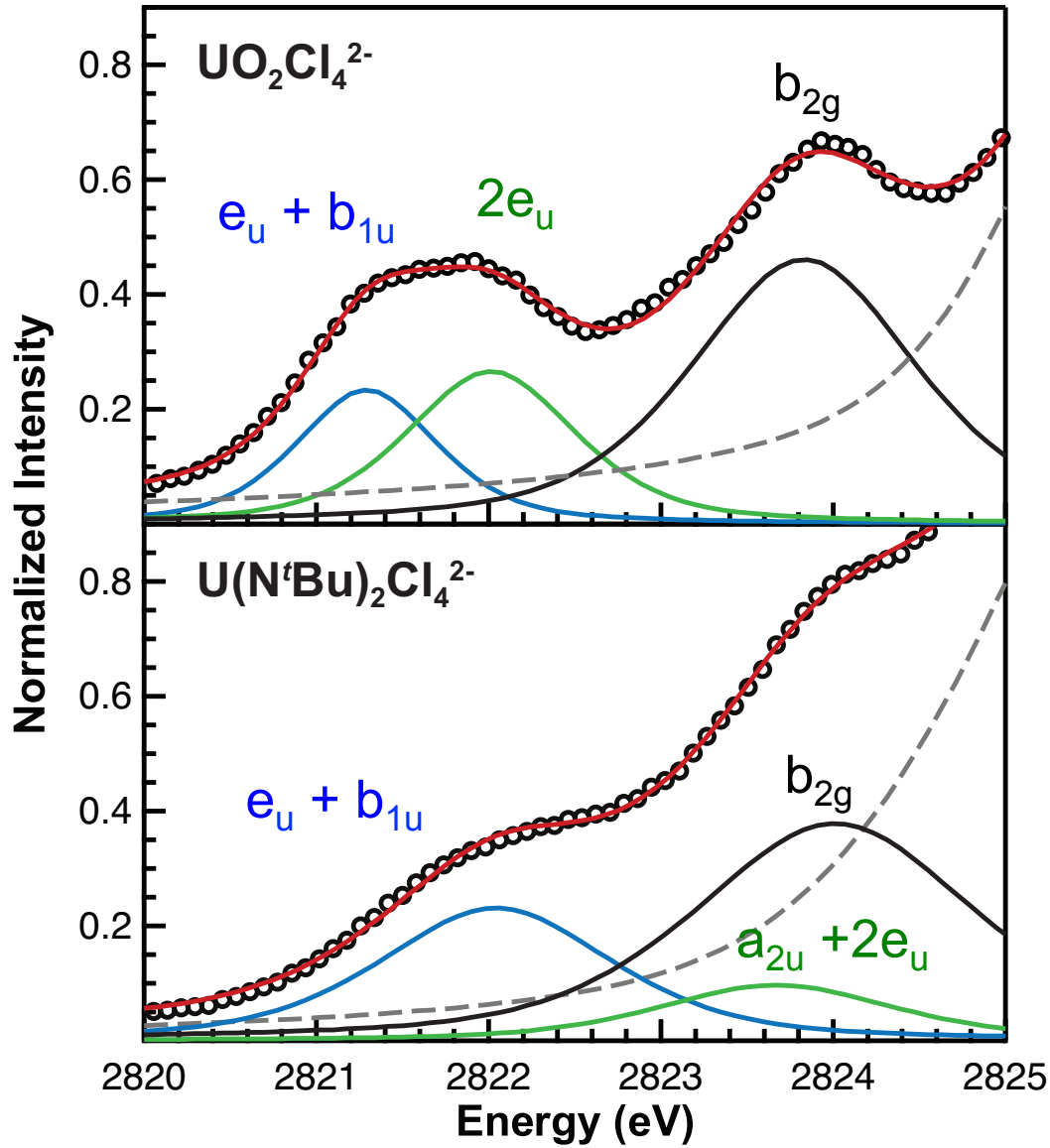
Effects of Axial Oxo versus Imido Ligands

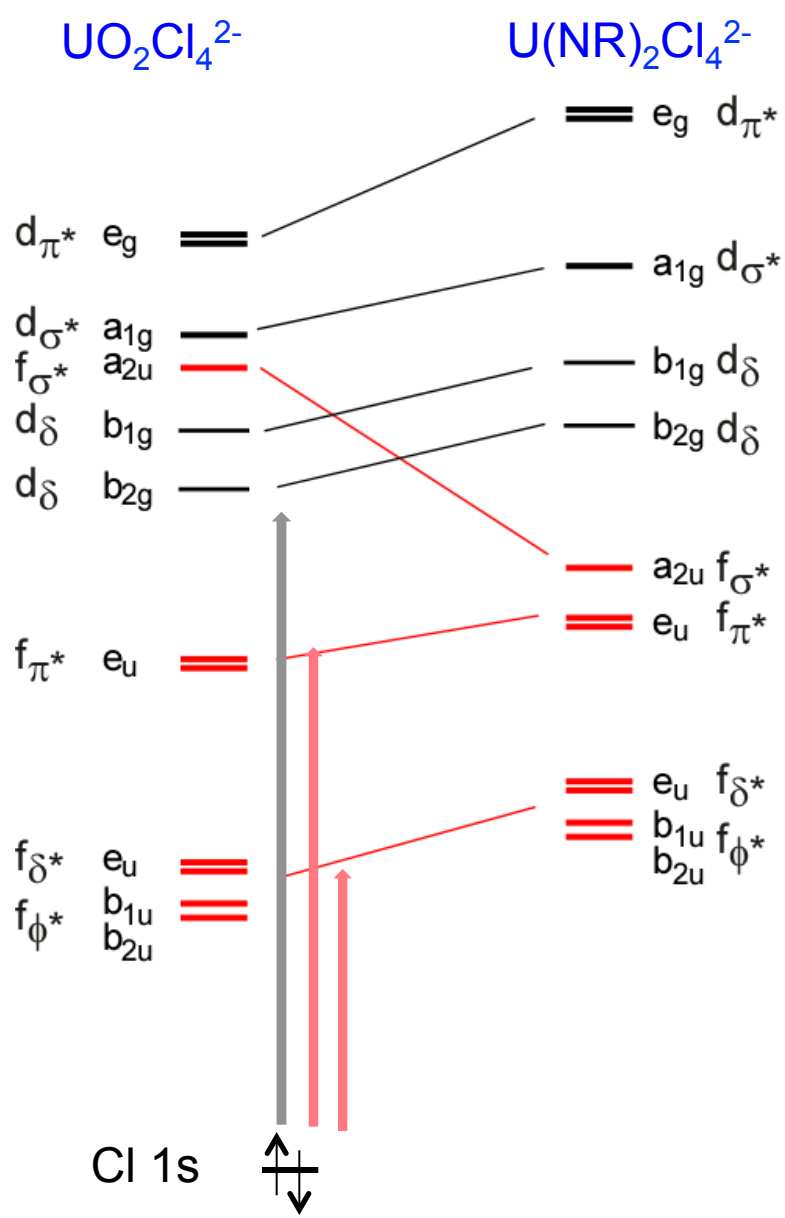


- All valence orbitals rise in presence of less electronegative imido (NR) ligand
- σ orbitals for imido (NR) ligand are heavily mixed with N-C and C-H character
- σ mixing stabilizes the axial σ type orbitals for U=N bonds
- U=N bonding is more covalent than U=O bonding
- For U=N occupied orbitals, σ is more stable than π

Spencer, *J. Am. Chem. Soc.*, **2013**, 135(6), 2279

Effect of Oxo and Imido Ligands on equatorial bonds

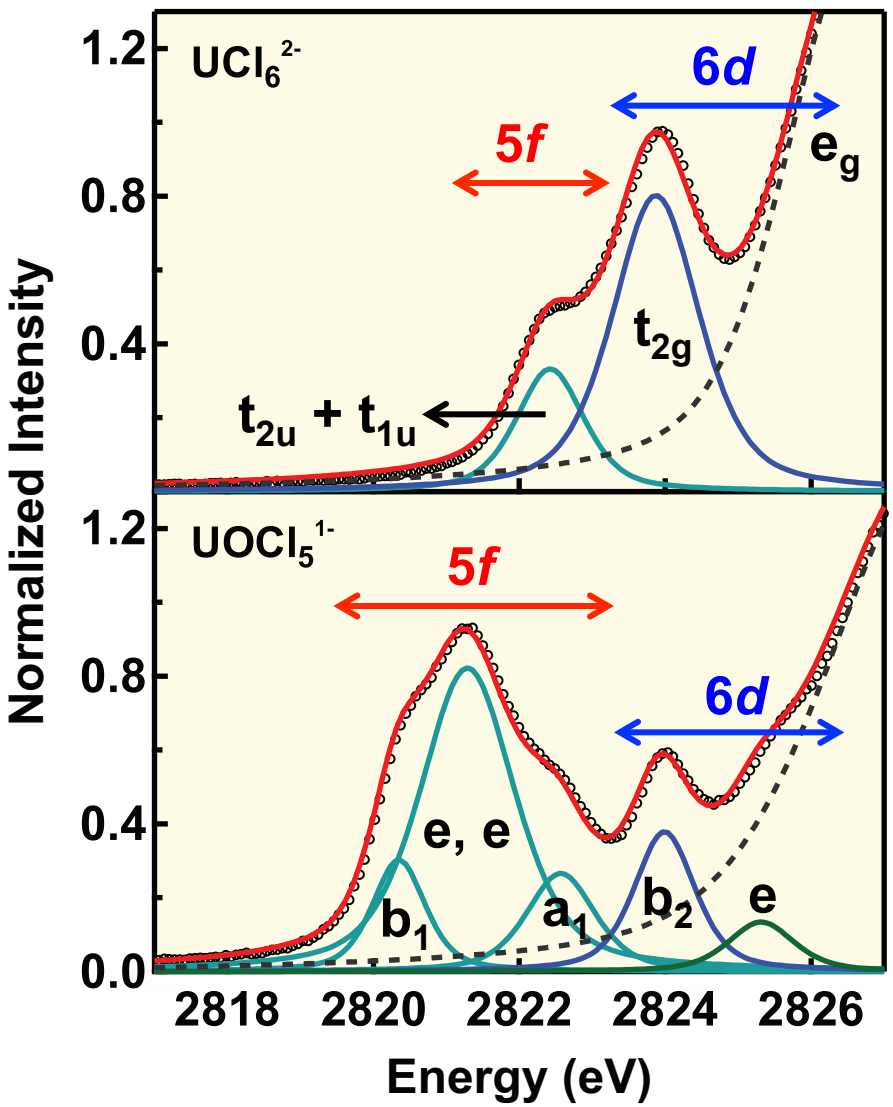




Spencer, *J. Am. Chem. Soc.*, **2013**, 135(6), 2279

Summary

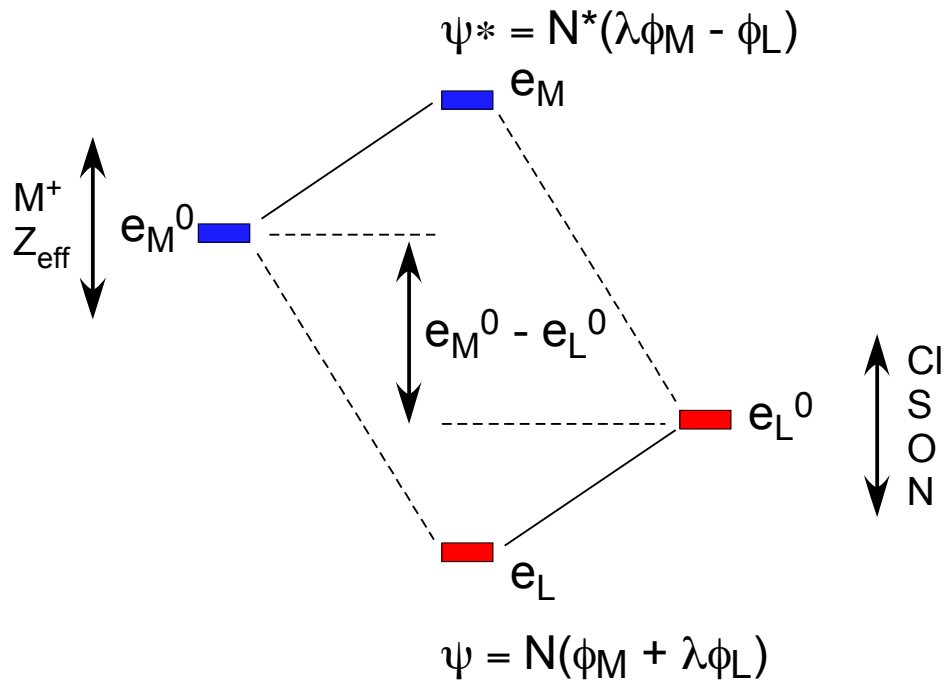
- O_h MCl_6^{n-} complexes of demonstrate ***indisputable evidence for covalency***
- Pre-edge XAS features can be grouped into ***f*** and ***d*** regions of spectra
- Electronic structure calculations are essential for interpretation
- For An ions, ***6d*** orbitals play dominant role, but ***5f*** orbitals show "unexpected" increase with Z_{eff}
- Covalency changes with M oxidation state, with Z_{eff}, and L orbital energetics (Cl vs S)



Minasian, J. Am. Chem. Soc., **2012** p. 5586

Covalency and M-L bonding for Actinides

- The versatility of ligand K-edge XAS shows that trends in actinide covalency are complex and can vary significantly with changes in metal, ligand, or oxidation state
- Covalency in M-L bonding has been extensively discussed using ***ligand field theory***
- Mixing coefficient $\lambda \sim -\mathbf{S} / \Delta\mathbf{E}$
- **Covalency** (LFT) – mixing of metal and ligand orbitals (ϕ_M , ϕ_L) as defined by non-zero values of λ
- A covalent interaction may be realized in two ways:
  - *A significant Overlap (S_{ML})*
  - *A vanishing denominator (ΔE)*
- Only overlap driven orbital mixing leads to stronger bonds.



$$\lambda \sim \frac{-S_{ML}}{e_M^0 - e_L^0}$$

Ballhausen, *Introduction to Ligand Field Theory*, **1962**
Albright, Burdett, Whangbo, *Orbital Interactions in Chemistry, **1985***
Neidig, Clark, Martin, Coord Chem Rev, **2013**, *257*, 394

Summary of MCl_6^{n-} and $MX_2Cl_4^{2-}$ systems

- XAS for O_h MCl_6^{n-} complexes of Ti, Zr, Hf, Th, U, Np, Pu, and Ce demonstrate ***indisputable evidence for covalent orbital mixing***
- Ligand pre-edge XAS features can be grouped into ***f*** and ***d*** regions of spectra that change in understandable ways upon varying the metal (Ti, Zr, Hf) (Ce, Th, U, Np, Pu) or the oxidation state (VI, V, IV, III)
- For An ions, ***6d*** orbitals play dominant role, but ***5f*** orbitals not insignificant at higher oxidation states
- Where quantitative data have been obtained, the covalent mixing of actinide 5f orbitals is small compared to 6d
- We find unexpected changes in 5f intensity with Z – **unexpected increase for Np/Pu**
- Multiplet effects are becoming important for heavy elements with large numbers of unpaired electrons f^3, f^4 (Np(IV), Pu(IV))

Acknowledgements

Los Alamos NATIONAL LABORATORY EST. 1943

Enrique R. Batista
Kevin S. Boland
Scott R. Daly
Steven D. Conradson
Jason M. Keith
Stosh A. Kozimor
Richard L. Martin
Stefan Minasian
Louis J. Vernon
Gregory L. Wagner
Marianne P. Wilkerson

BERKELEY LAB

Richard A. Andersen
Norman M. Edelstein
Wayne W. Lukens
David K. Shuh
Kenneth N. Raymond
Tolek T. Tyliszczak

SLAC NATIONAL ACCELERATOR LABORATORY

Dennis Nordlund
Dimosthenis Sokaras
Tsu-Chein Weng

LANL Seaborg Institute
& LBNL Seaborg Center
Postdoctoral Fellowships

3 OBES Synchrotrons:
SSRL, ALS, APS

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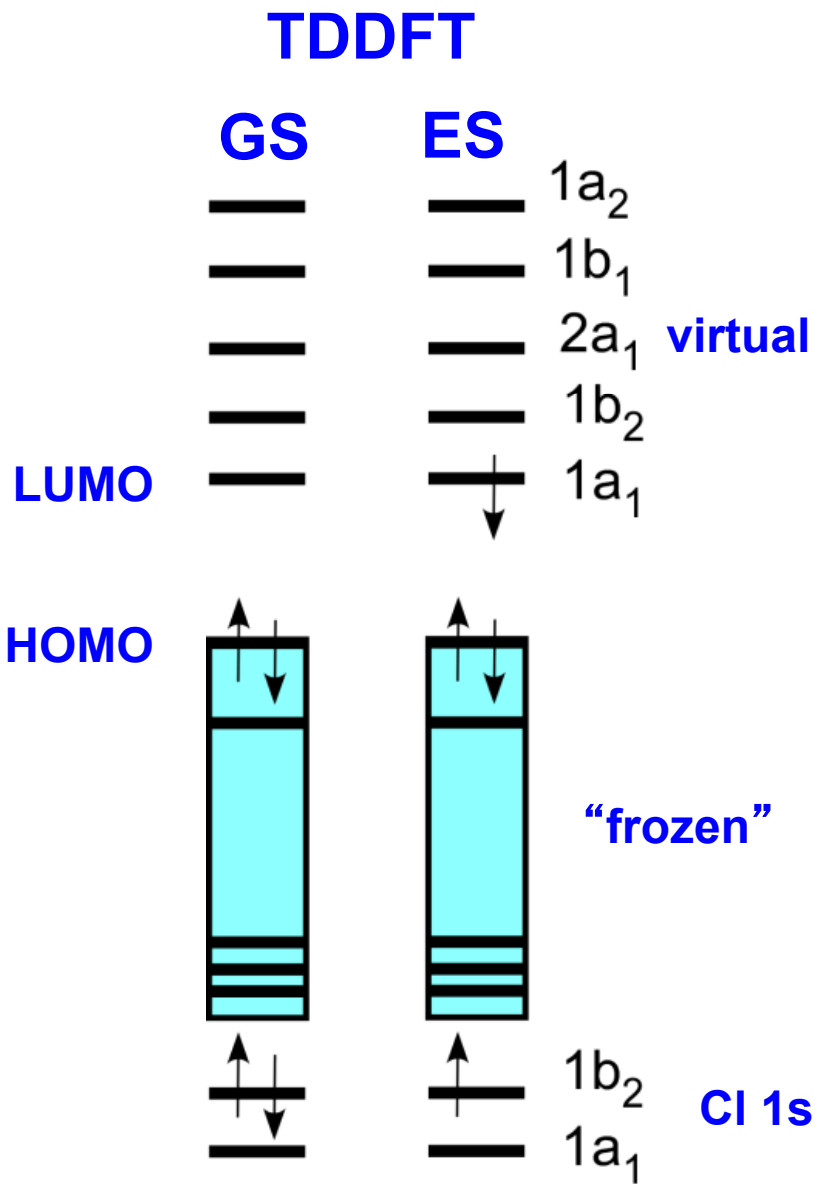
DFT Methodology

- Functionals: B3LYP (hybrid DFT)
- Uranium Basis:
  - Stuttgart RSC 1997 ECP (60 core e^-)
  - Outer core and valence: [8s/7p/6d/4f]
- Cl Basis:
  - (17s/10p/1d) → [5s/5p/1d]
- Ions embedded in dielectric cavity
- Three levels of theory
  - GS calculations & Mulliken populations (%Cl 3p, %M nd)
  - Orbital energies & dipole transition calculations
  - TDDFT for excited state and transition dipole strength calculation