Radiopharmaceutical Studies @ MR-CAT

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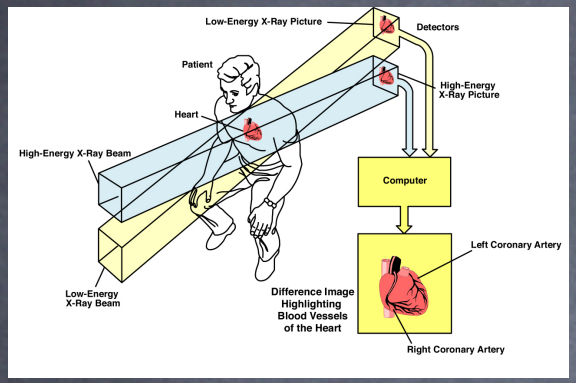
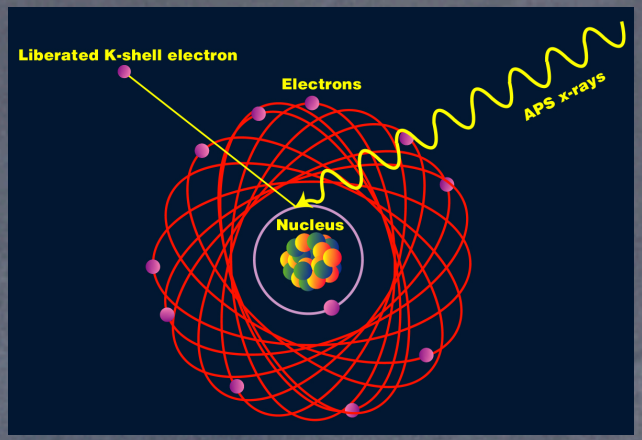
Introduction

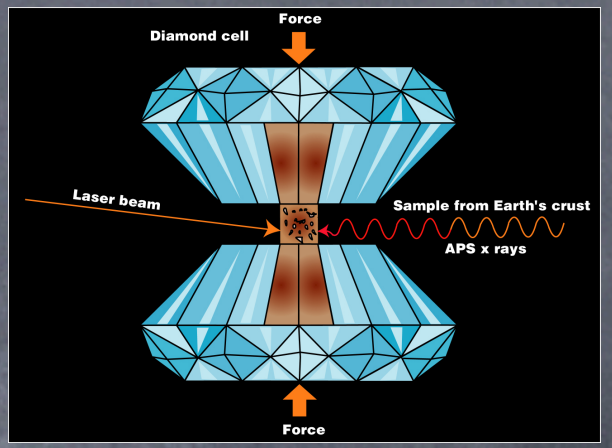
- Radiopharmaceuticals
  - ^{99m}Tc Compounds Widely Used
  - Chemistry Not Widely Understood
  - Low Concentrations
  - Difficulty in Crystalizing Compounds

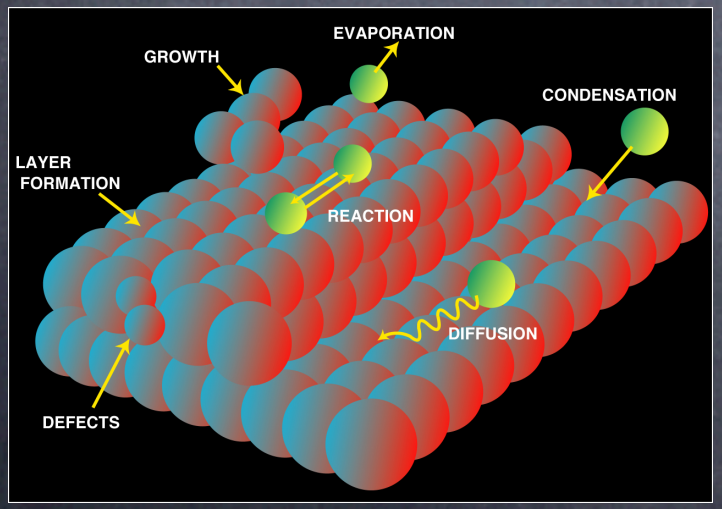
Advanced Photon Source

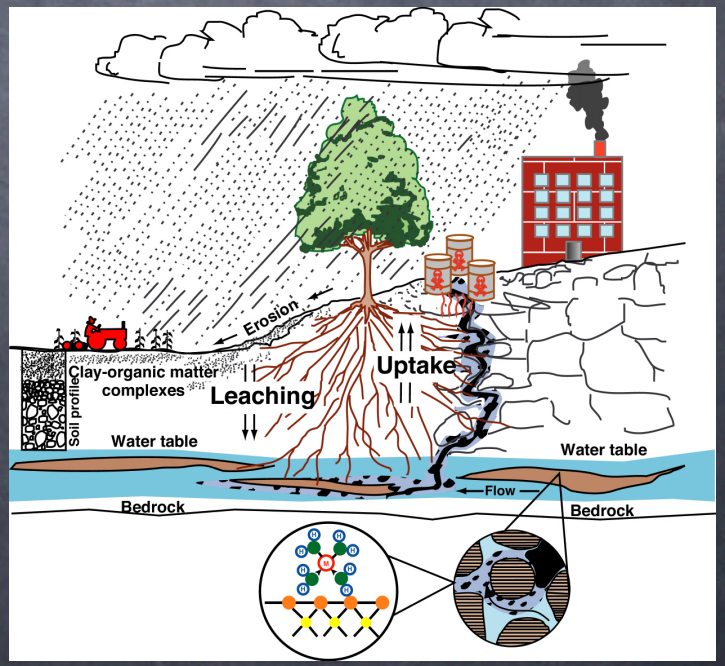
Synchrotron Science







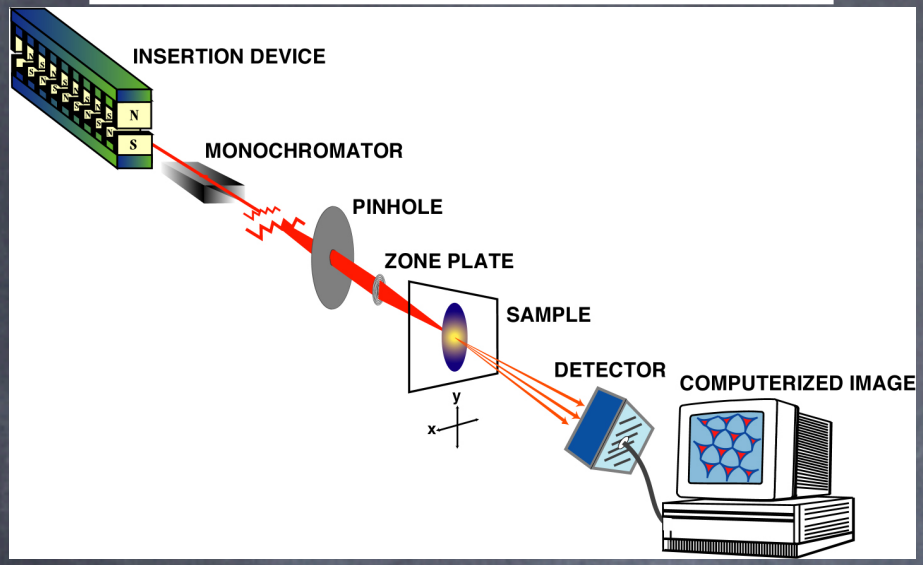


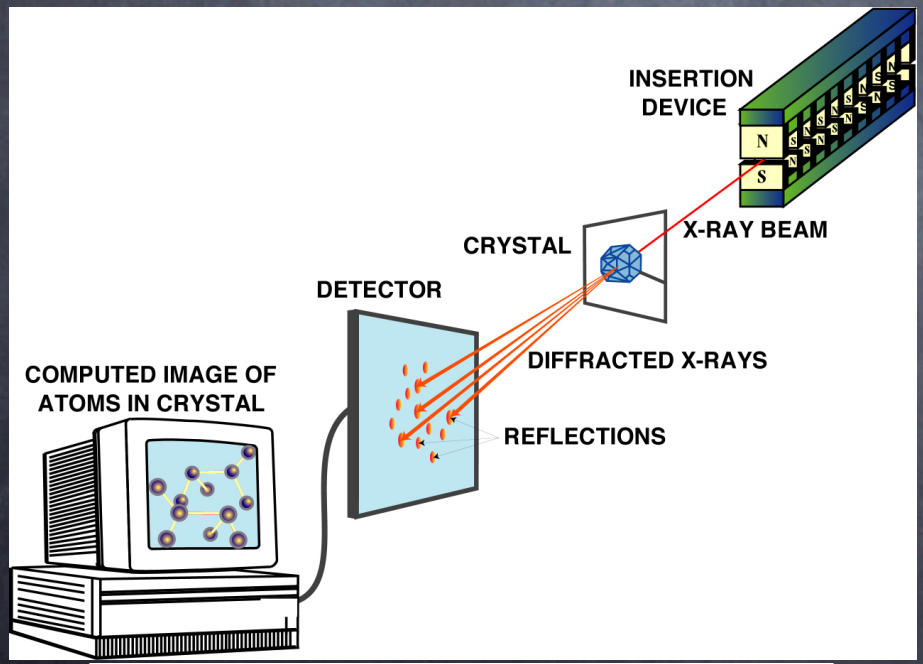


MR-CAT

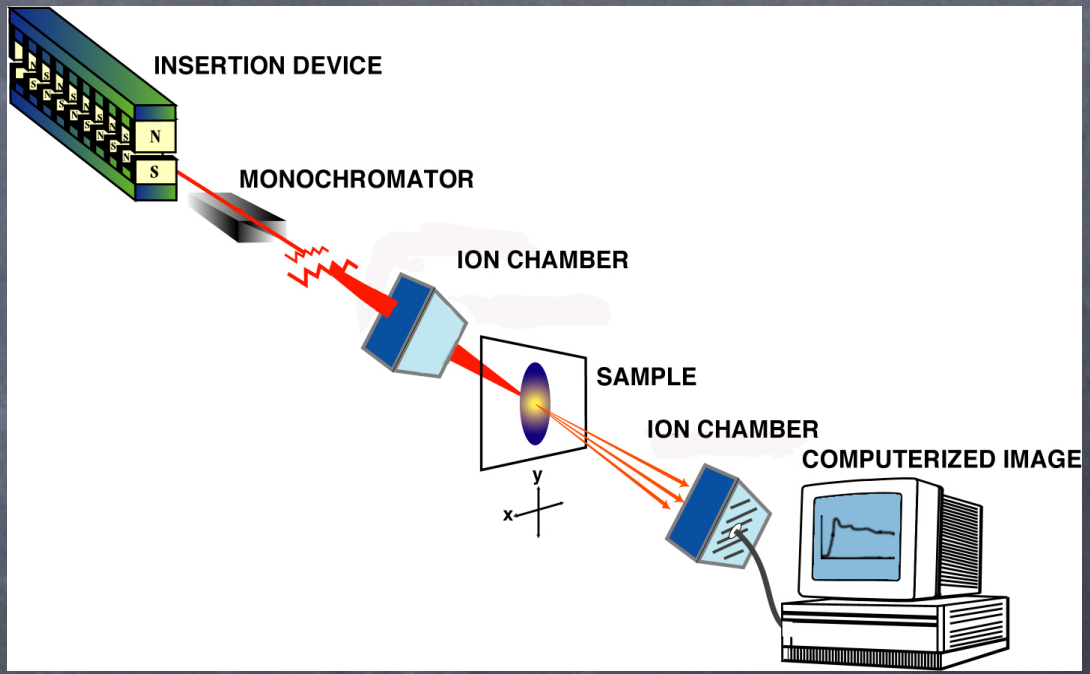
Materials Research

X-ray Microfocus





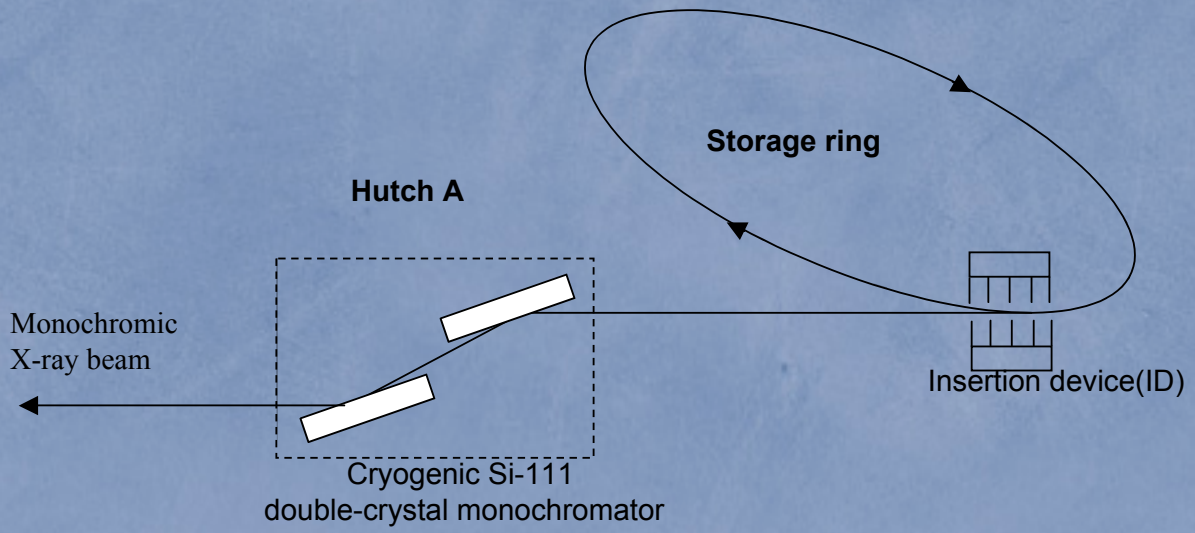
X-ray Scattering

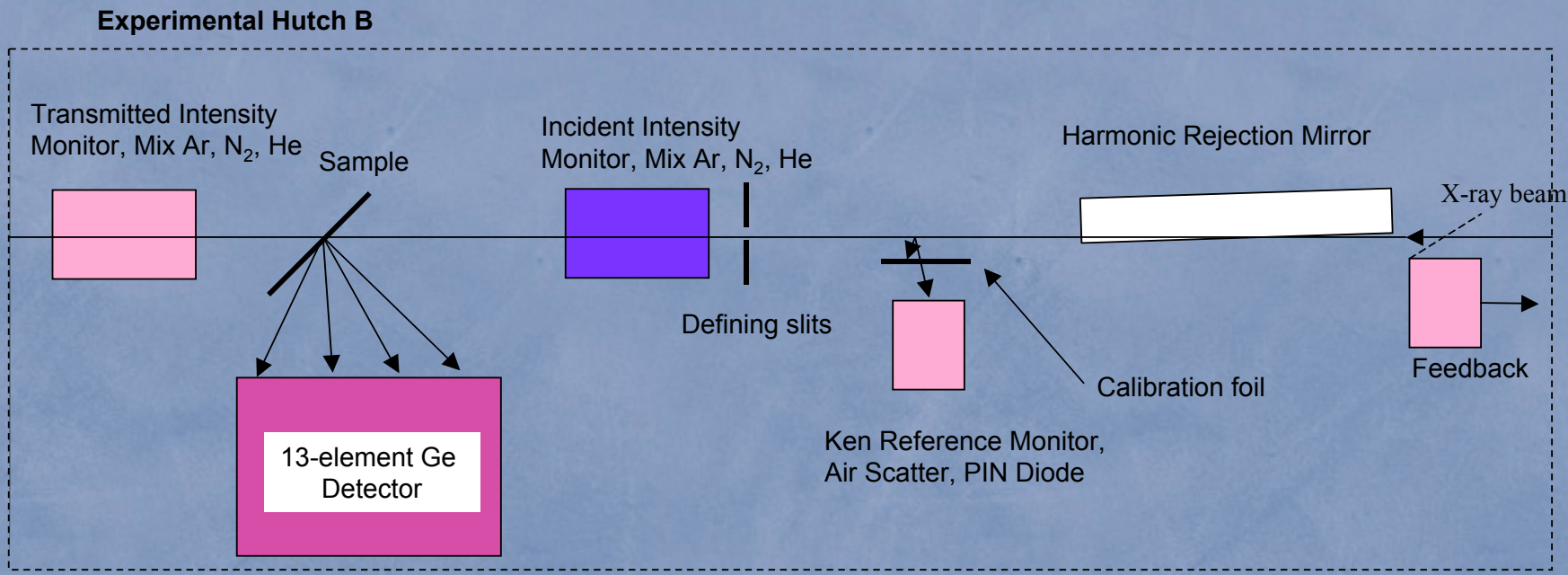


X-ray Absorption

XAS Experimental

MRCAT Beamline, Sector 10ID-B, Advanced Photon Source



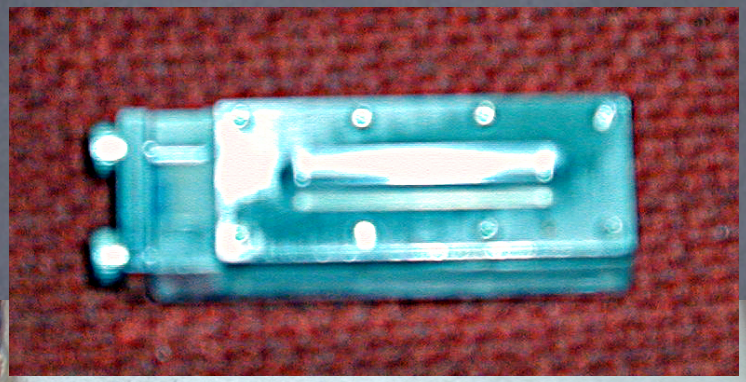


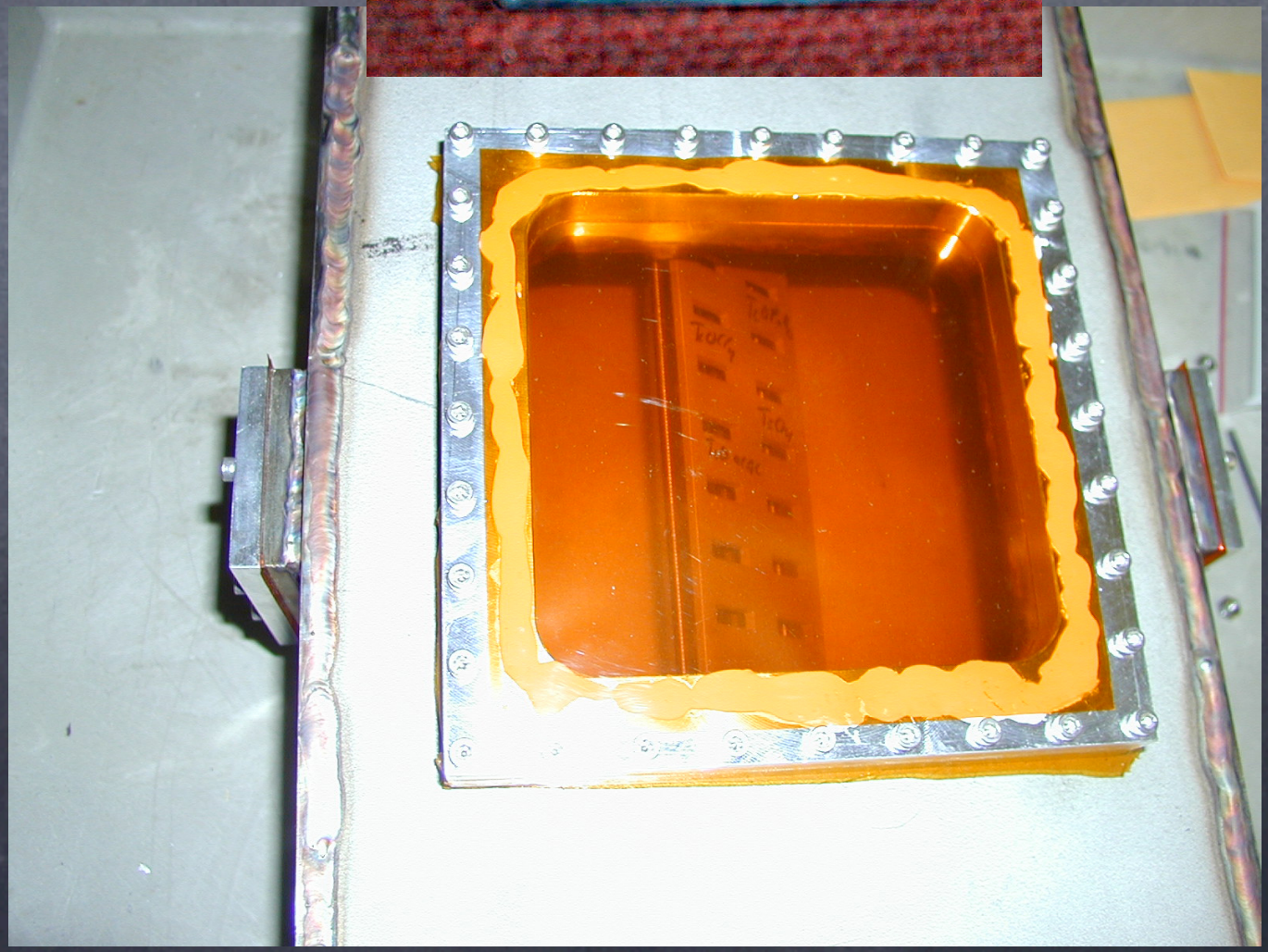
EXAFS Equation

$$\chi(k) = \sum_j \frac{N_j f_j(k)}{r_j^2} e^{\frac{-2r_j}{\lambda(k)}} e^{-2k^2\sigma_j^2} \sin(2kr_j + 2\delta_e + \delta_j)$$

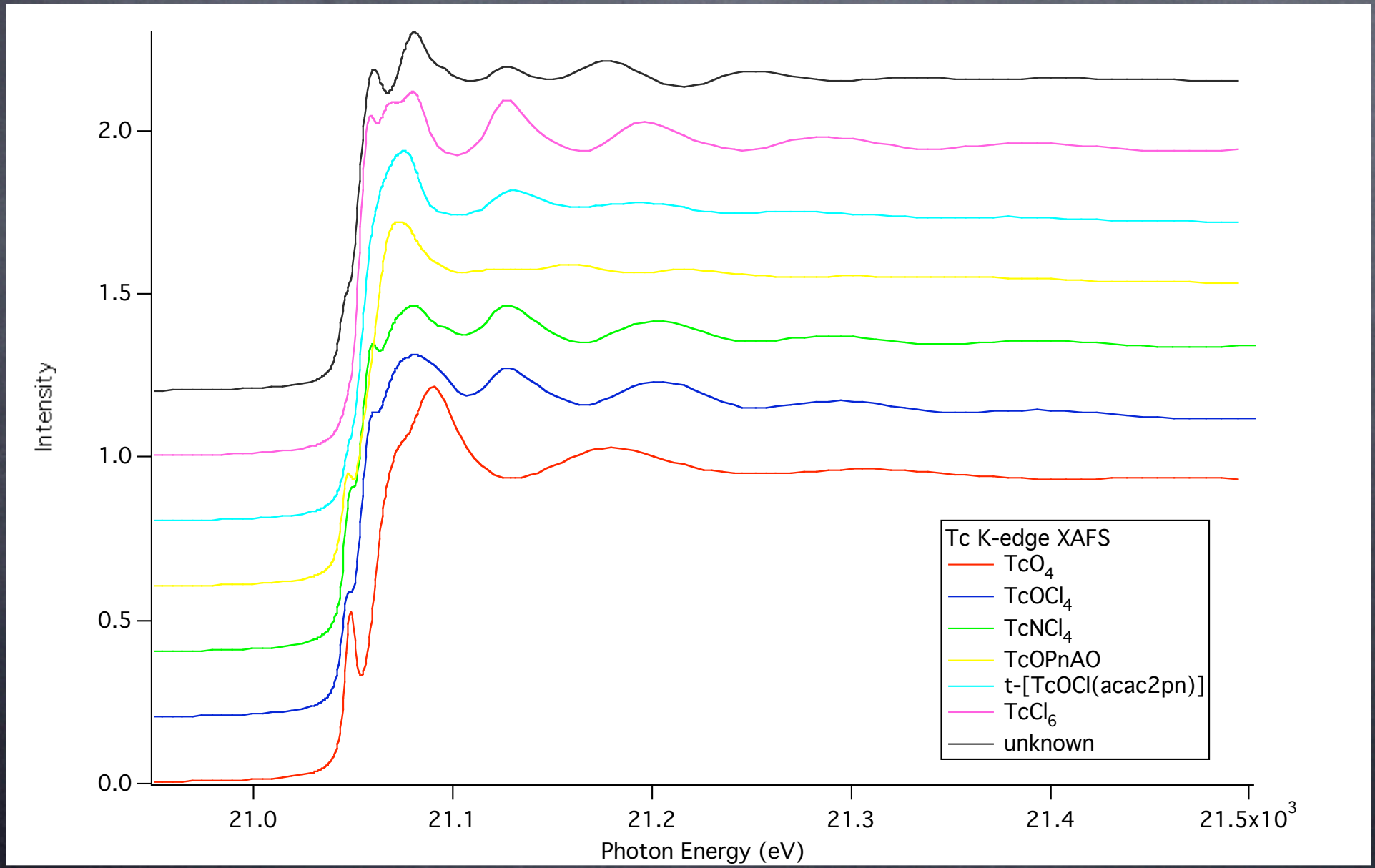
XAS Experimental

- Handling Radioactive Material

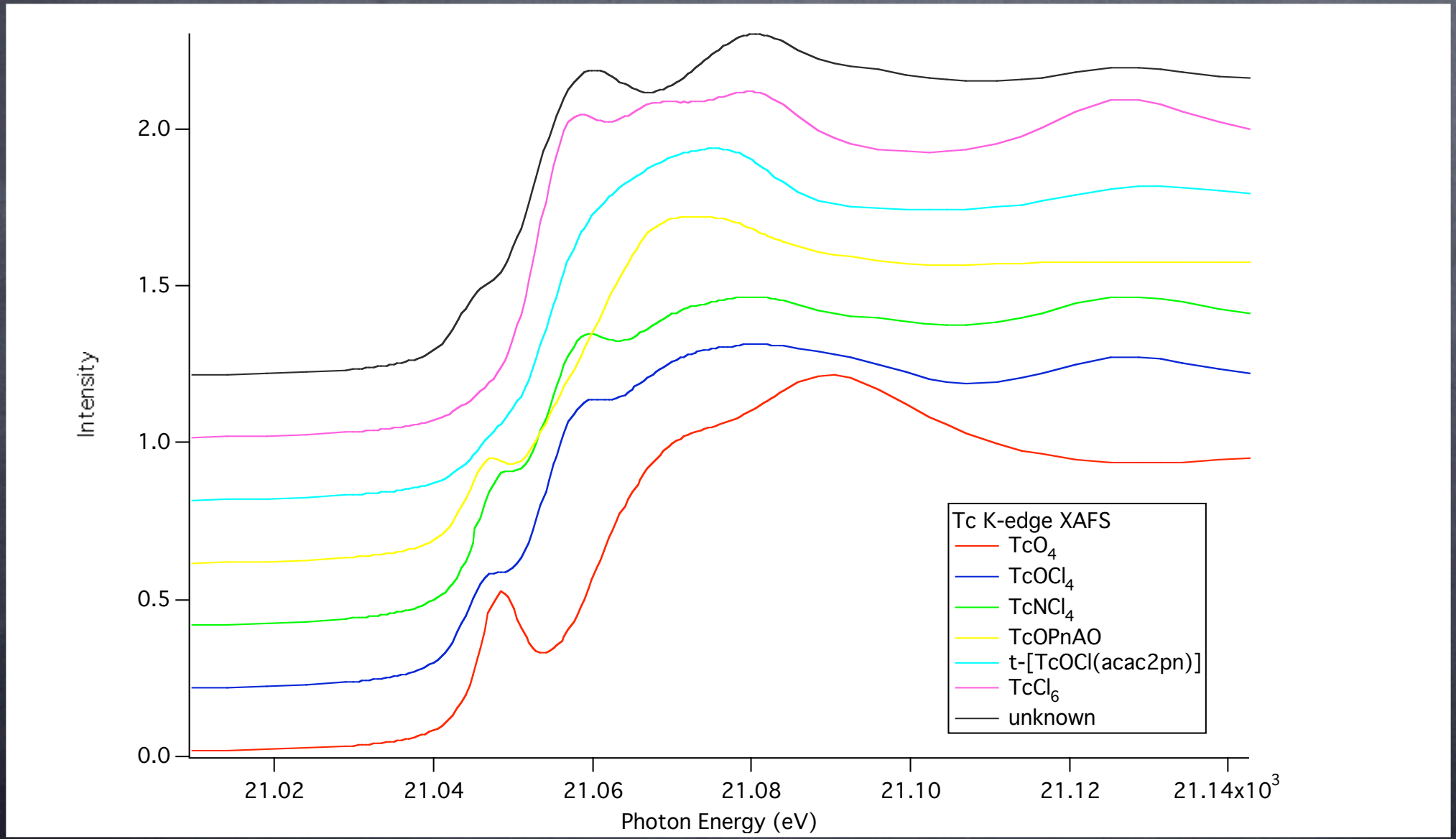




XAS


Intensity
2.0
1.5
1.0
0.5
0.0
21.0
21.1
21.2
21.3
21.4
21.5x10^3
Photon Energy (eV)
Tc K-edge XAFS
TcO4
TcOCl4
TcNCl4
TcOPnAO
t-[TcOCl(acac2pn)]
TcCl6
unknown

Near Edge


Intensity
2.0
1.5
1.0
0.5
0.0
21.02
21.04
21.06
21.08
21.10
21.12
21.14x10^3
Photon Energy (eV)
Tc K-edge XAFS
TcO4
TcOCl4
TcNCl4
TcOPnAO
t-[TcOCl(acac2pn)]
TcCl6
unknown

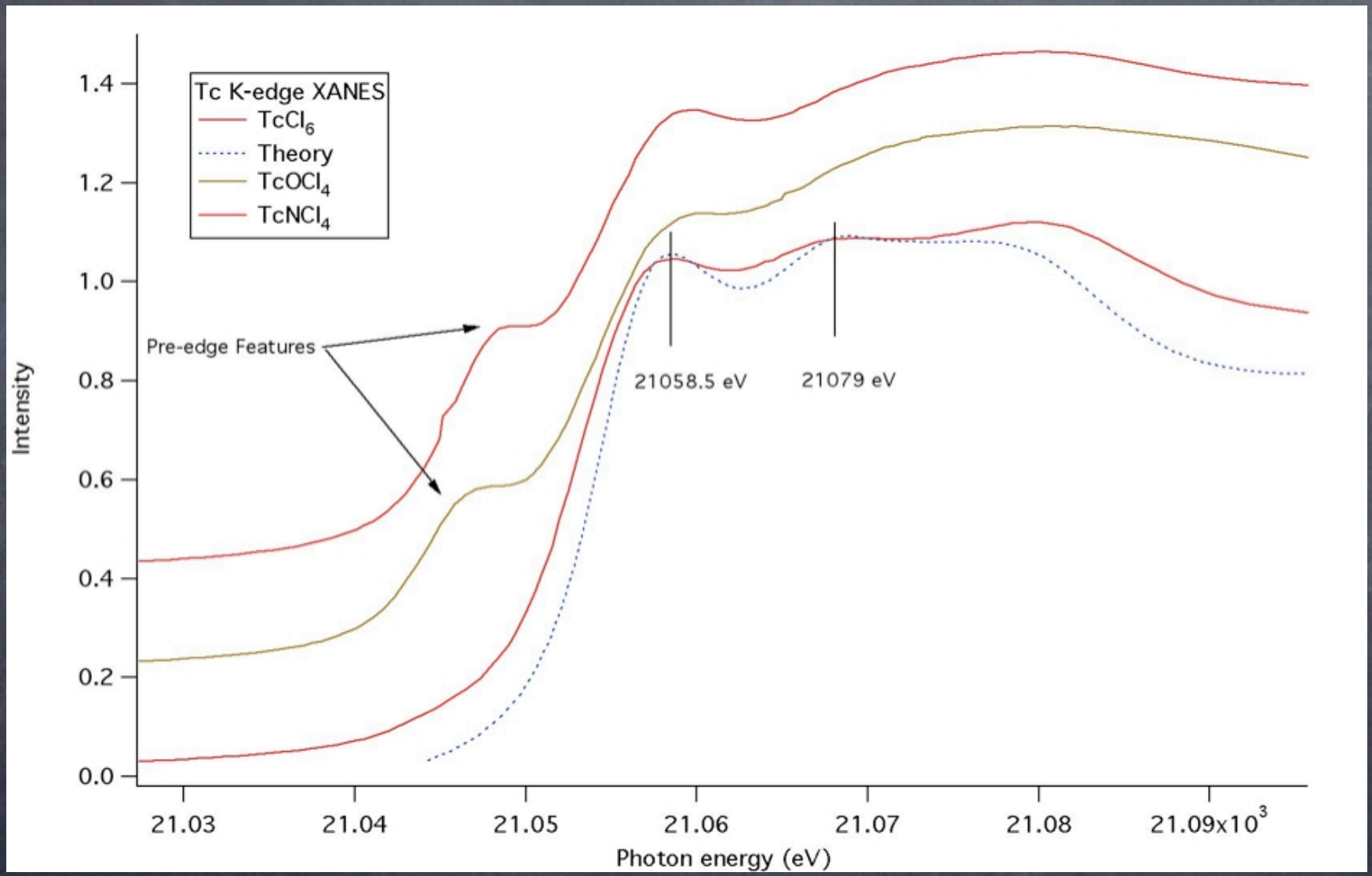
Cluster Feff Calculations

- Feff 8.2 is a program designed to calculate the X-ray absorption spectrum of a system from 1st principles.
- It uses the Local Density Approximation method of Density Functional Theory to calculate self-consistent potentials that it uses to model electron scattering in a material.

Feff Calculations

- We must make assumptions about our system in order to model it with Feff
- One assumption that we must make is the position of the counterion. We do not know the exact locations of the atoms in the big organic counterions used in these materials.
  - We essentially have to perform multiple calculations with various counterion positions.
    - Very time consuming.

$TcCl_6$ XANES/Theory



- $Tc(IV)Cl_6^{2-}$ (No Pre-edge), $Tc(V)OCl_4^-$ (Pre-edge), and $Tc(VI)NCl_4^-$ (Pre-edge)

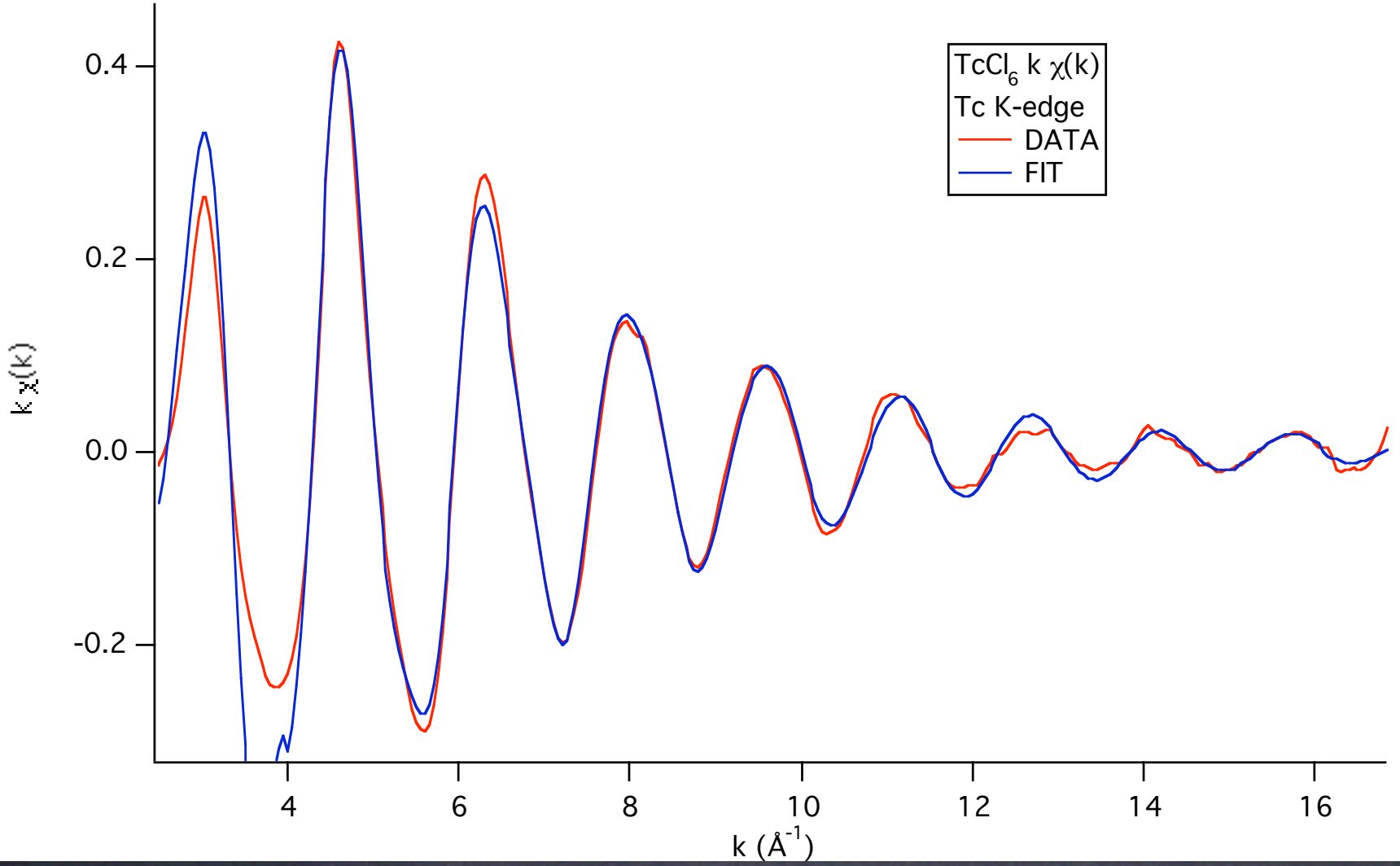
Oxidation State

- The Tc K-edge positions did not correlate with oxidation state.
- Strong final state effects were observed.
  - Major rearrangement of e-'s due to the creation of the photoelectron.
- Theoretical modeling of the observed XAS spectra is necessary to determine speciation.

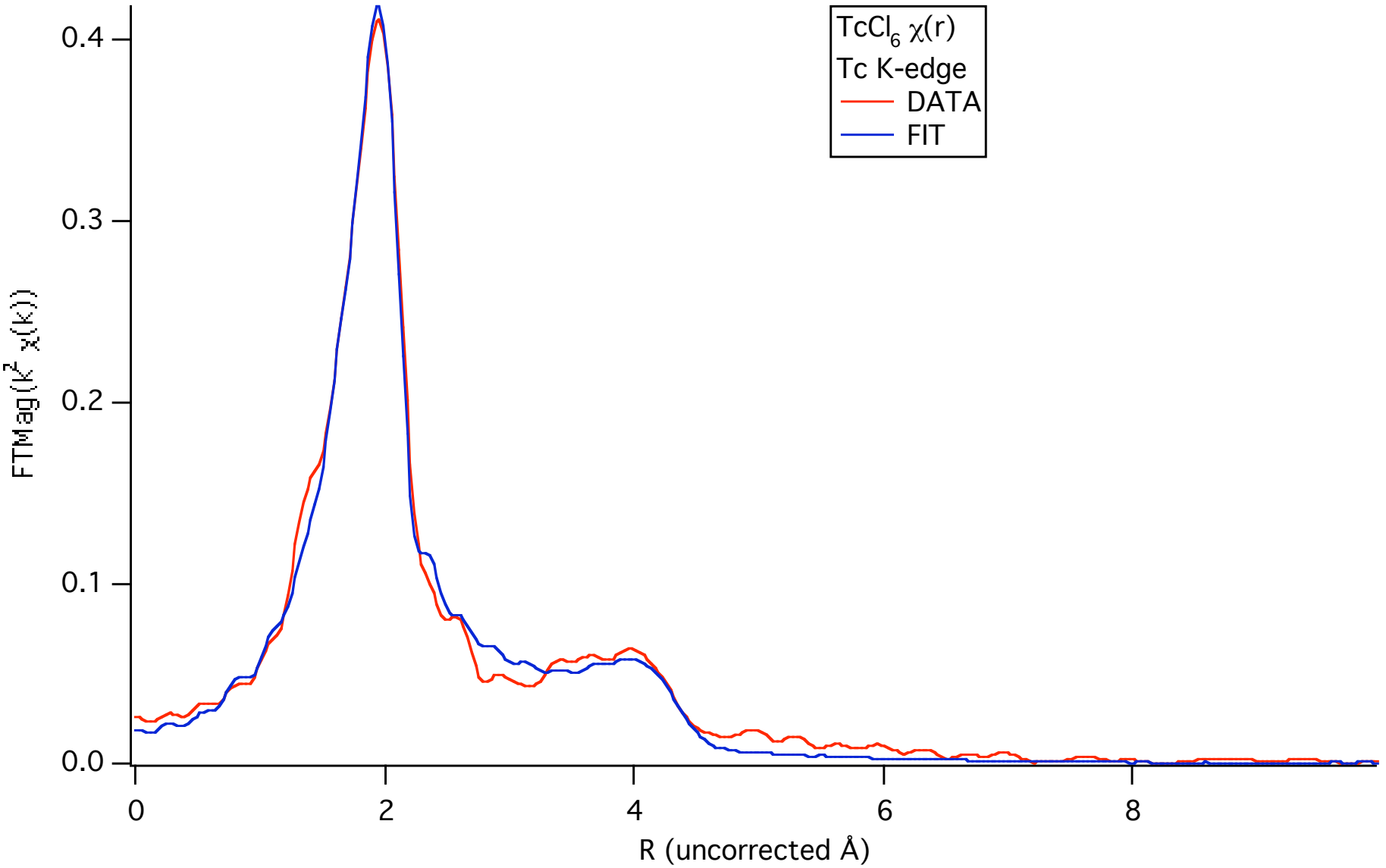
Unfamiliarity

- We needed to prove that EXAFS works with Tc.
  - Plenty of literature examples
  - Government three letter agencies, Oh Well

$TcCl_6$ EXAFS

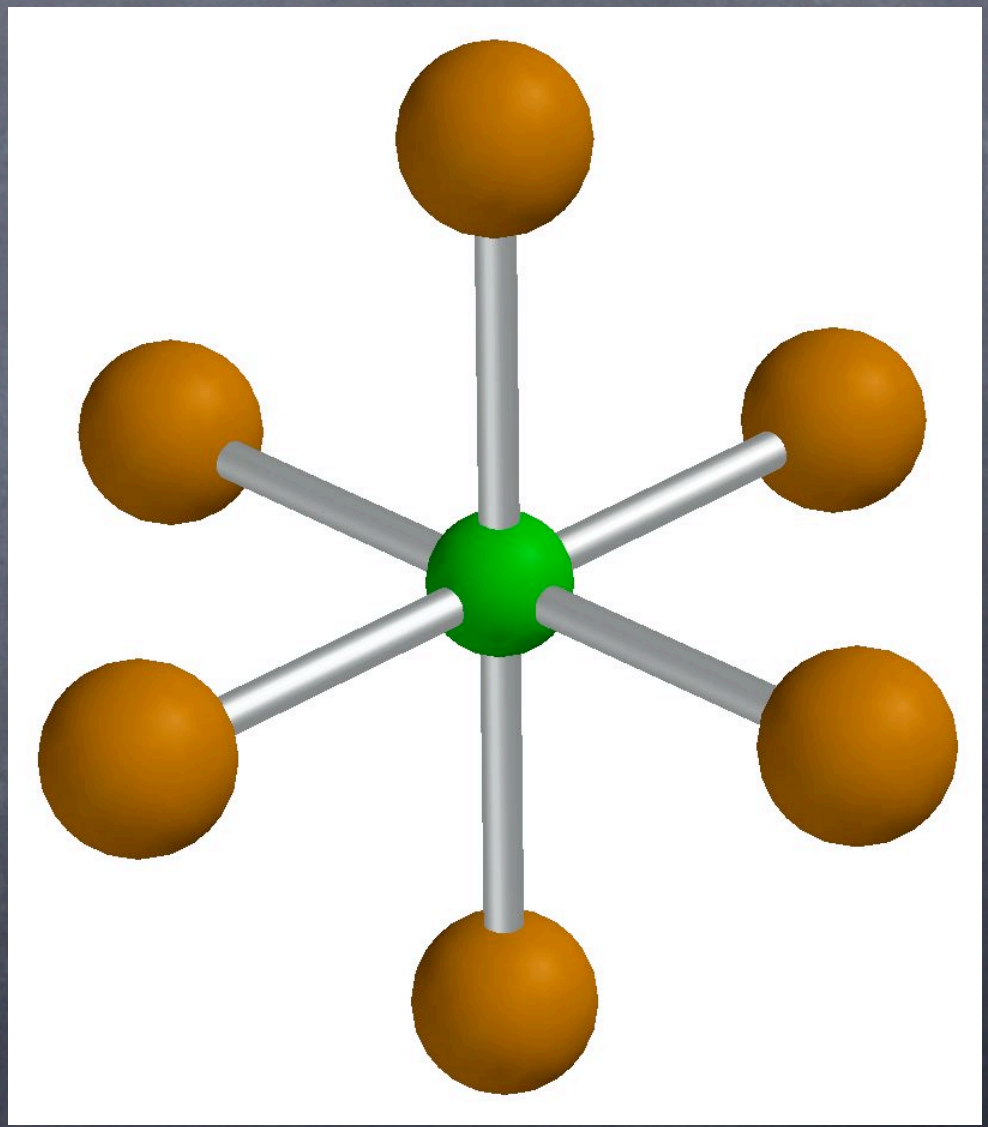


$TcCl_6$ EXAFS

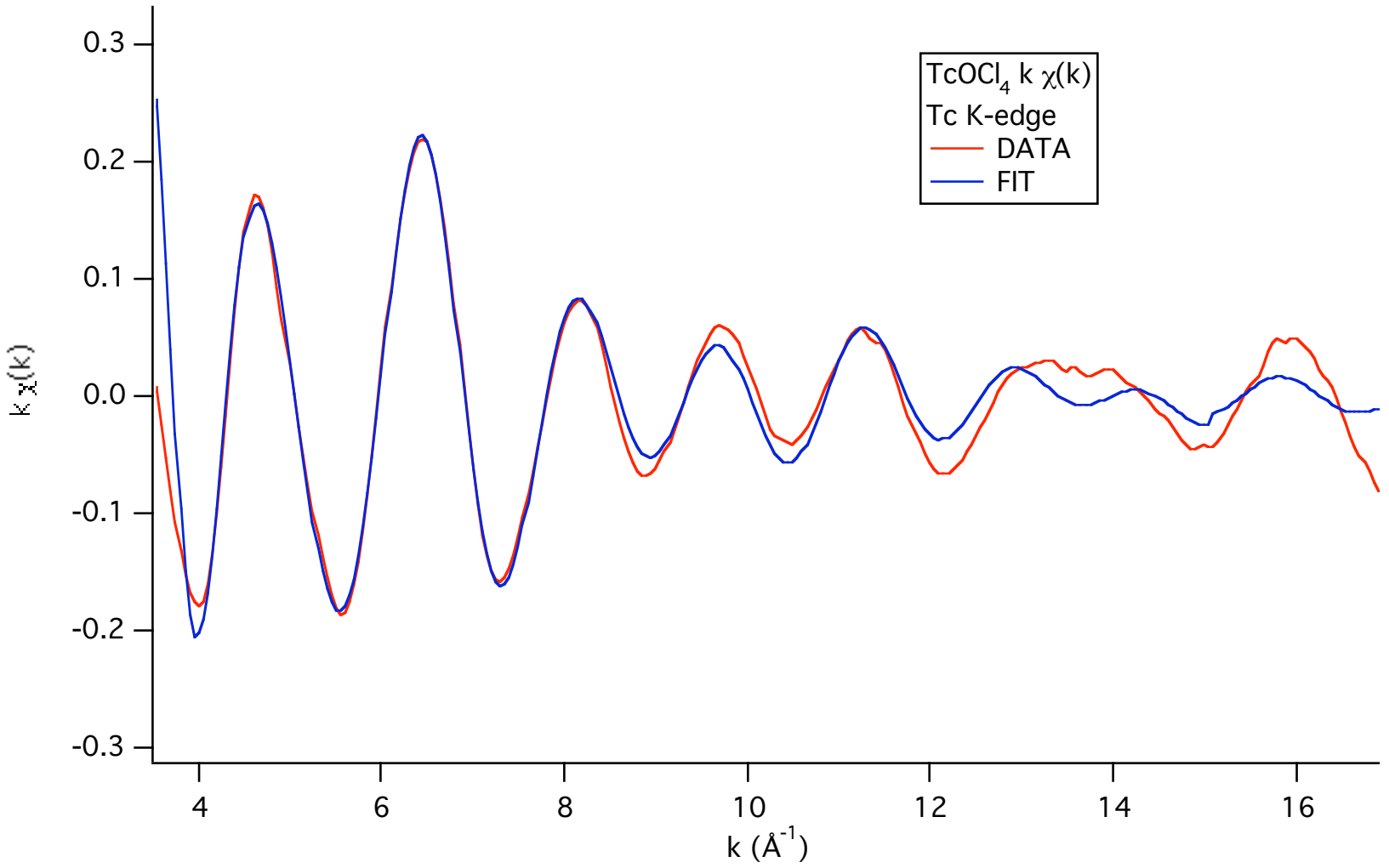

TcCl6 χ(r)
Tc K-edge
DATA
FIT
FTMag(k² χ(k))
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
R (uncorrected Å)

$TcCl_6$ EXAFS

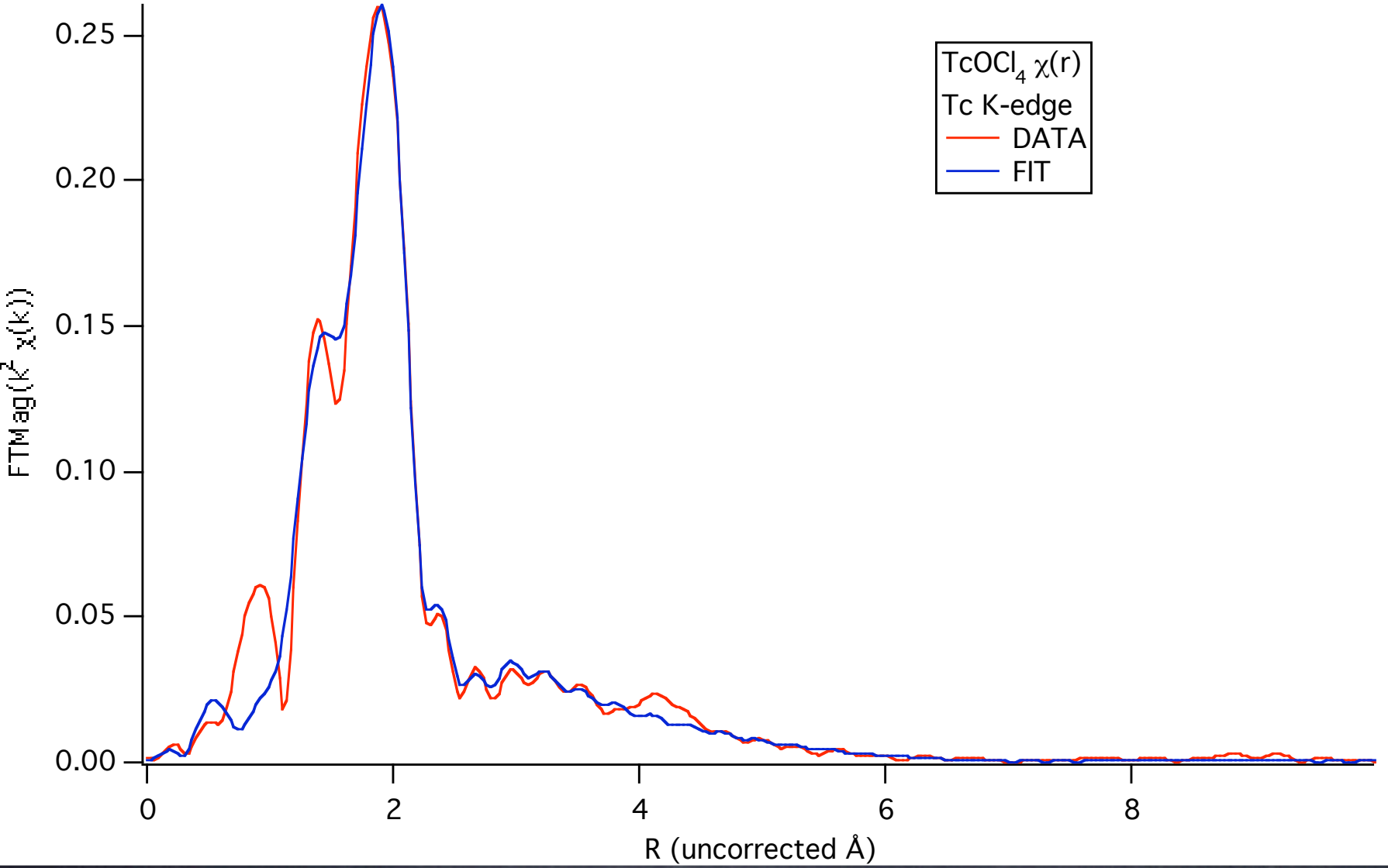
- The Tc-Cl bond distance was determined to be 2.36 ± 0.02 Å.
- The Coordination # was determined to be 6 ± 1 atom.



$TcOCl_4$ EXAFS

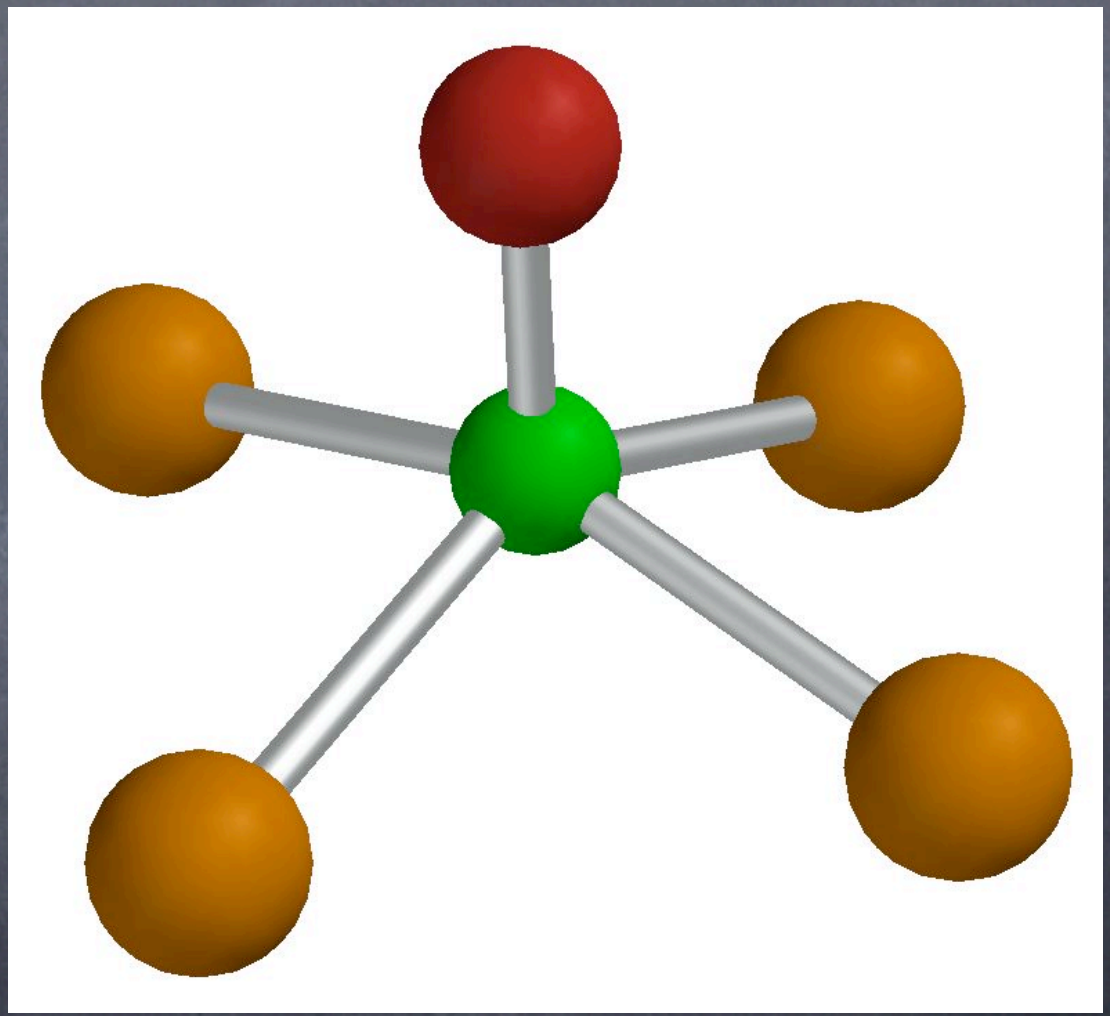


$TcOCl_4$ EXAFS

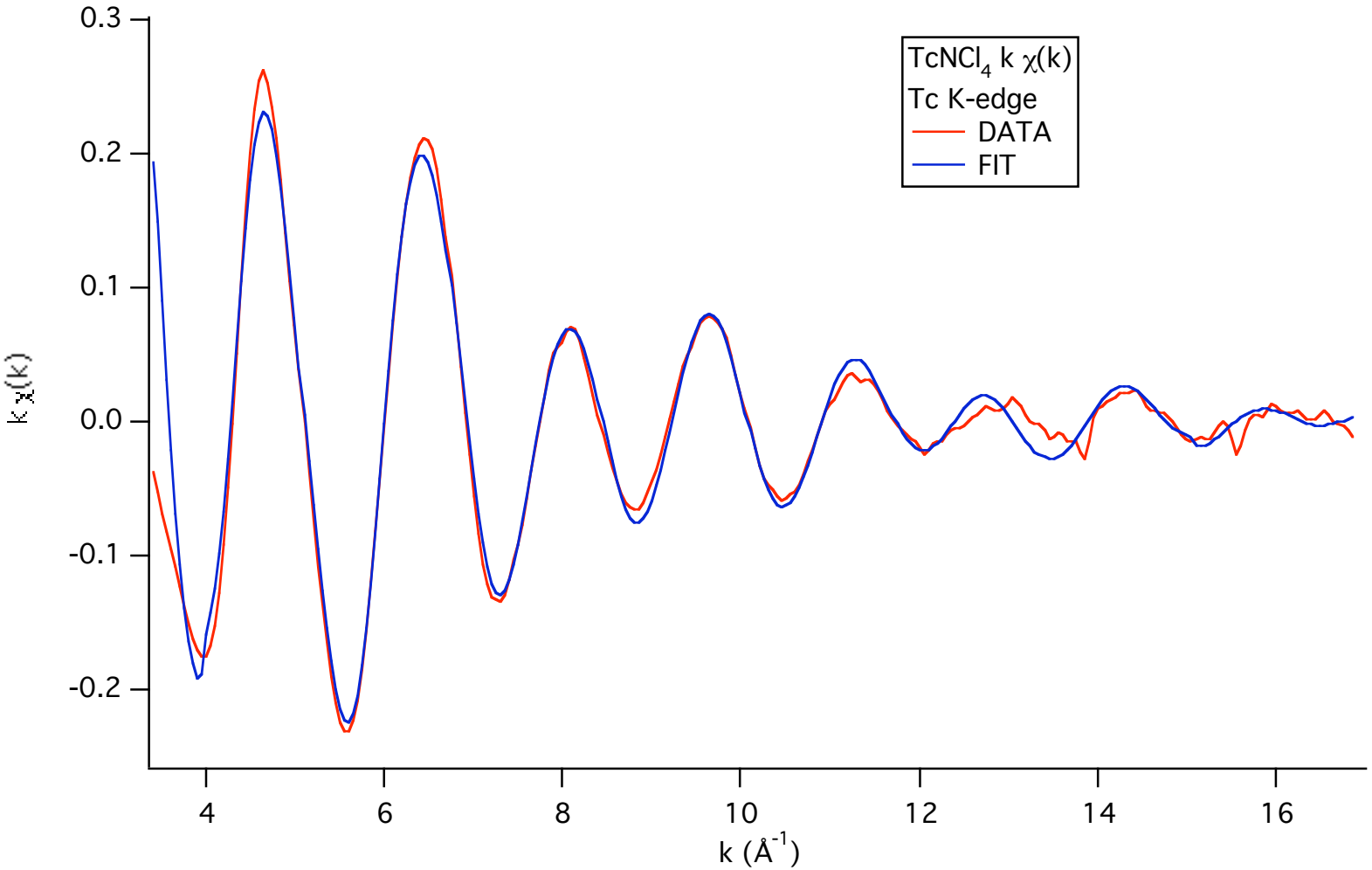


$TcOCl_4$ EXAFS

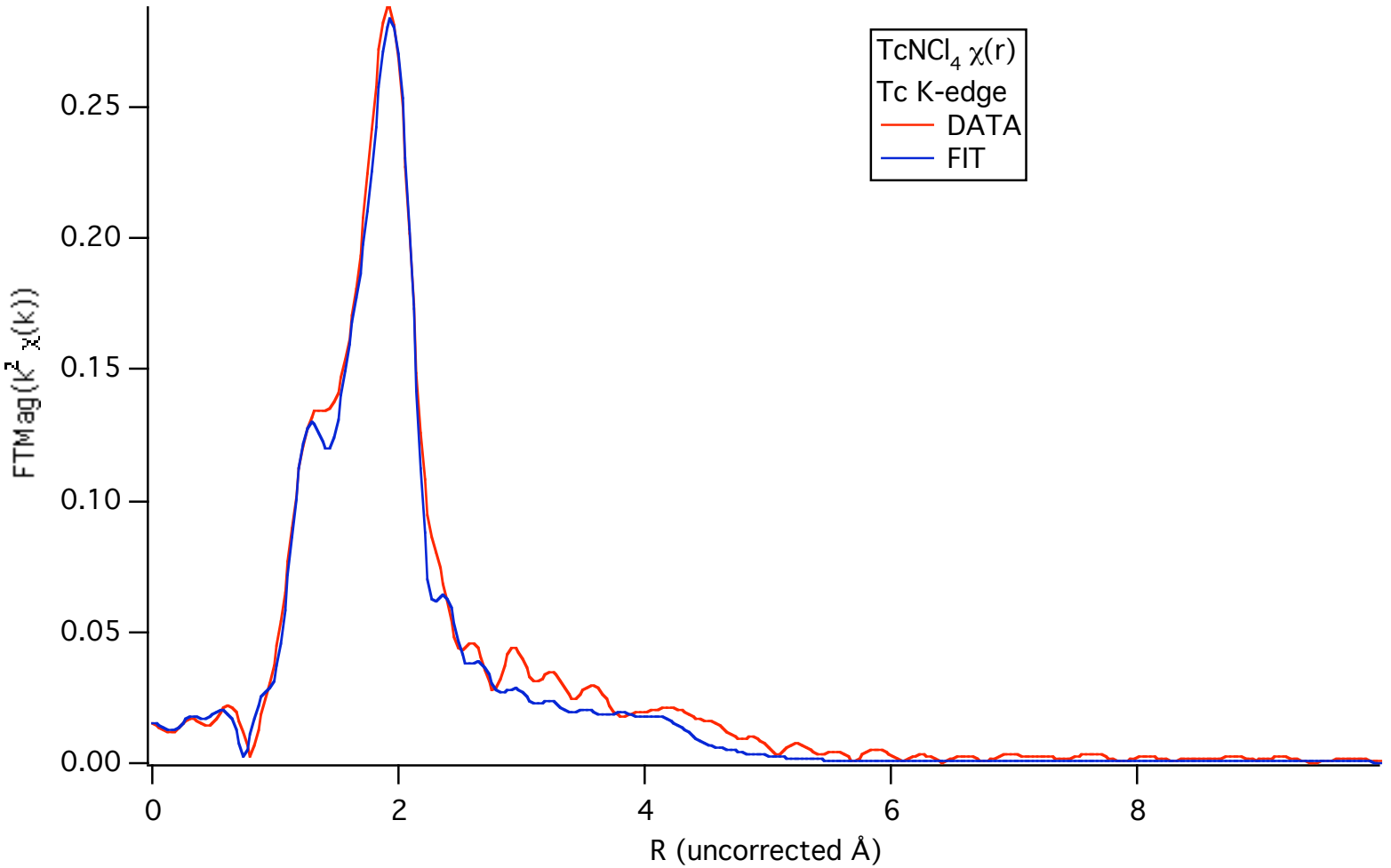
- The Tc-Cl bond distance was 2.33 ± 0.02 Å.
- The Tc-O bond distance was 1.65 ± 0.02 Å.
- The Coordination was determined to be 1 ± 0.5 O atoms and 3.7 ± 1 Cl Atoms.



$TcNCl_4$ EXAFS

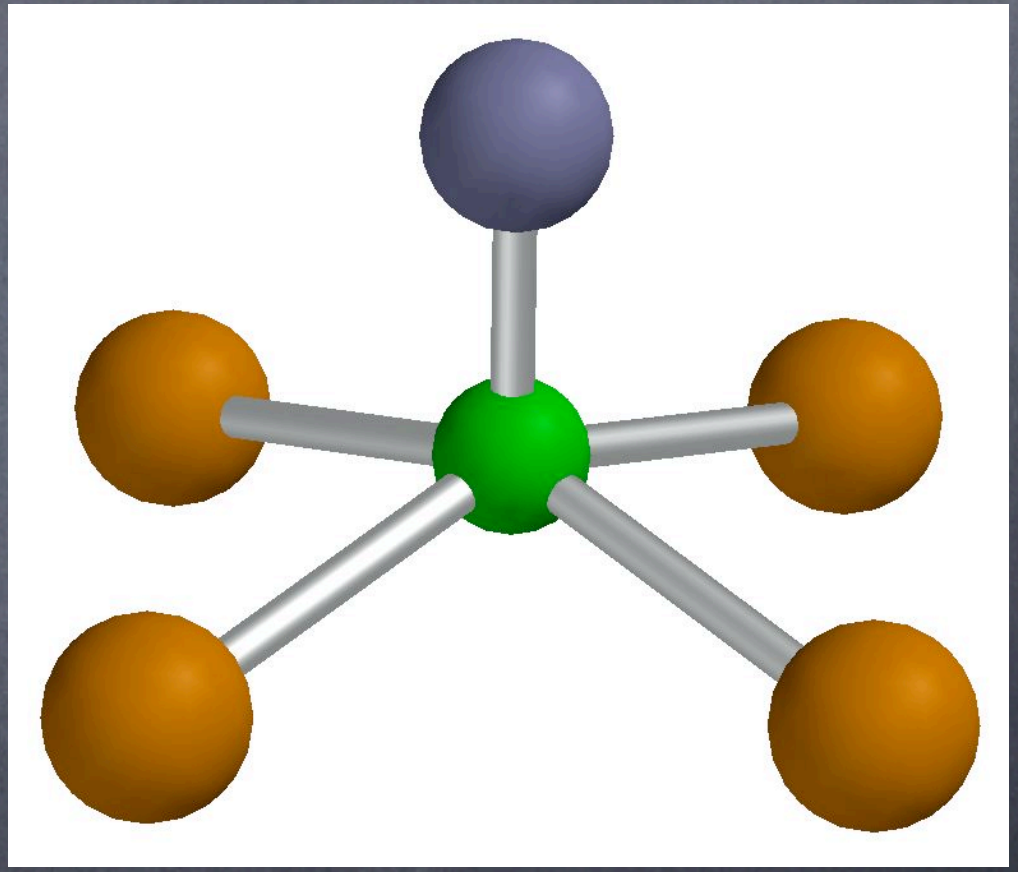


$TcNCl_4$ EXAFS



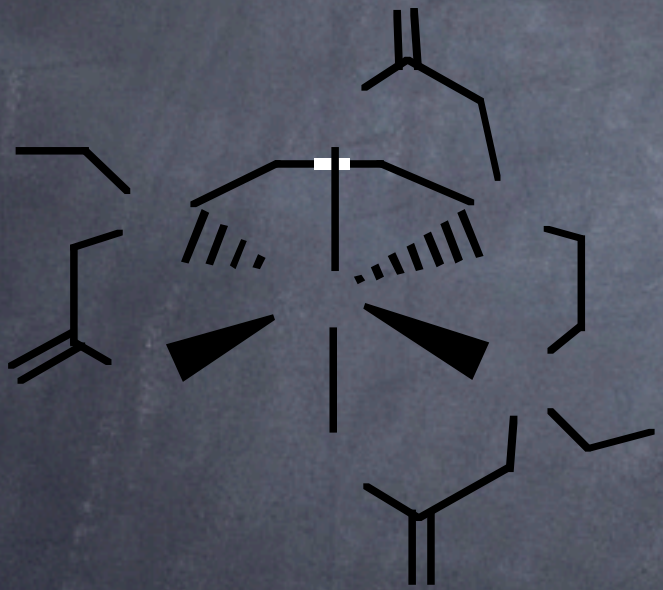
$TcNCl_4$ EXAFS

- The Tc-Cl bond distance was 2.35 ± 0.02 Å.
- The Tc-N bond distance was 1.59 ± 0.02 Å.
- The Coordination was determined to be 0.9 ± 0.5 O atoms and 3.8 ± 1 Cl Atoms.

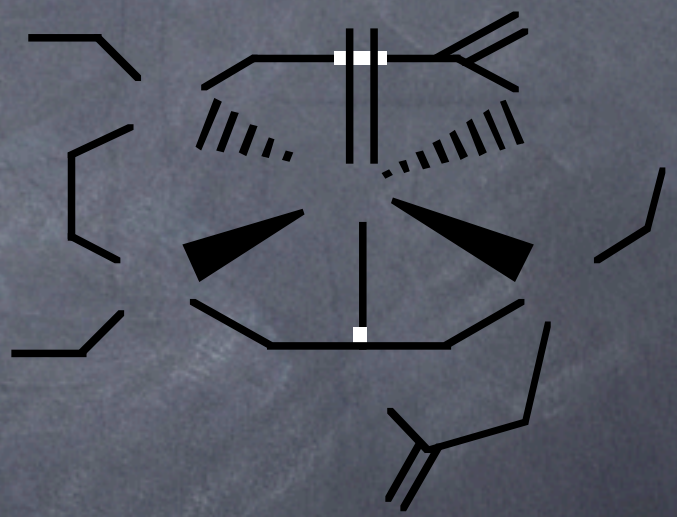


Tc DTPA

Diethylenetriaminepentaacetic acid



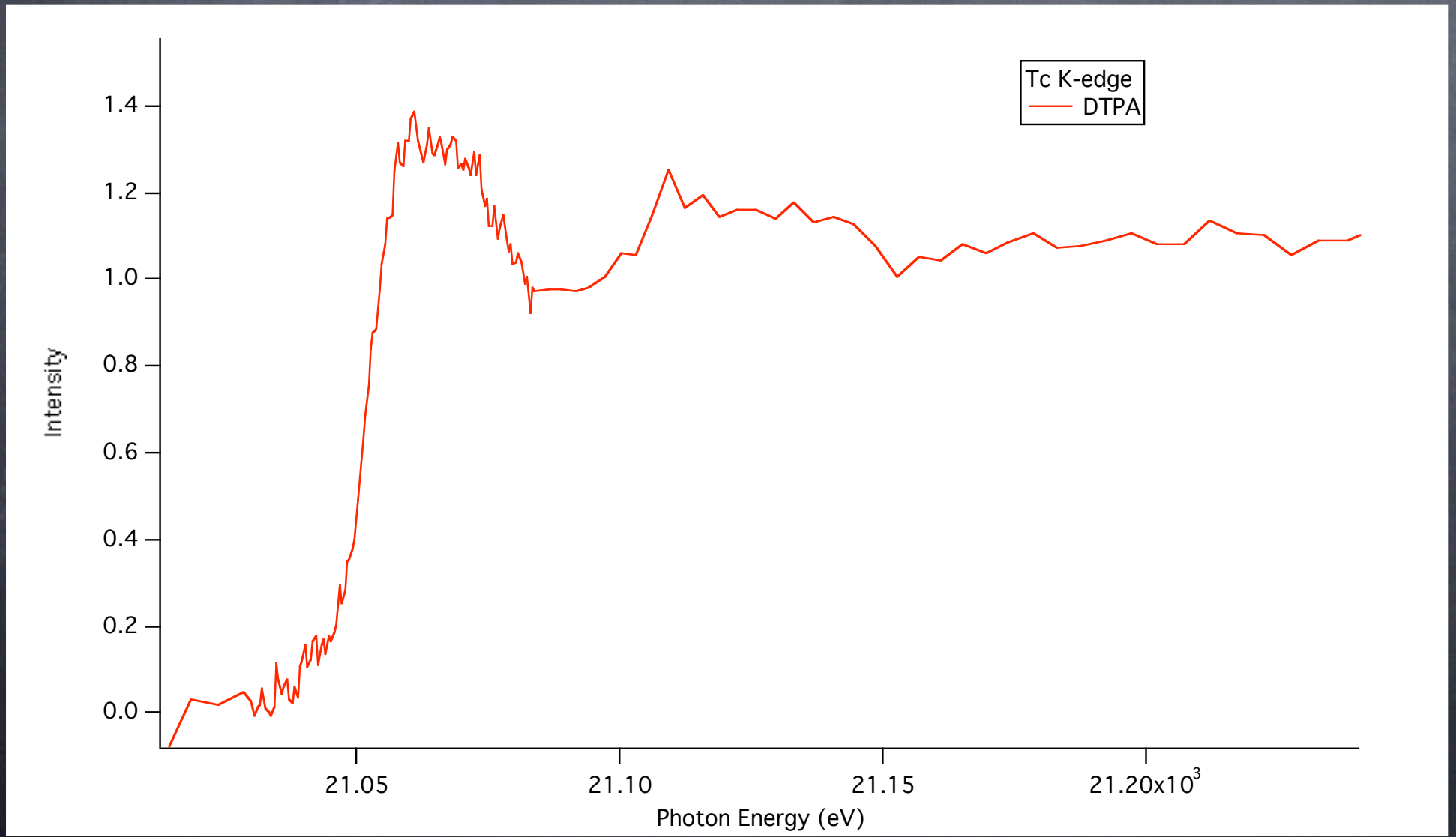
renal agent



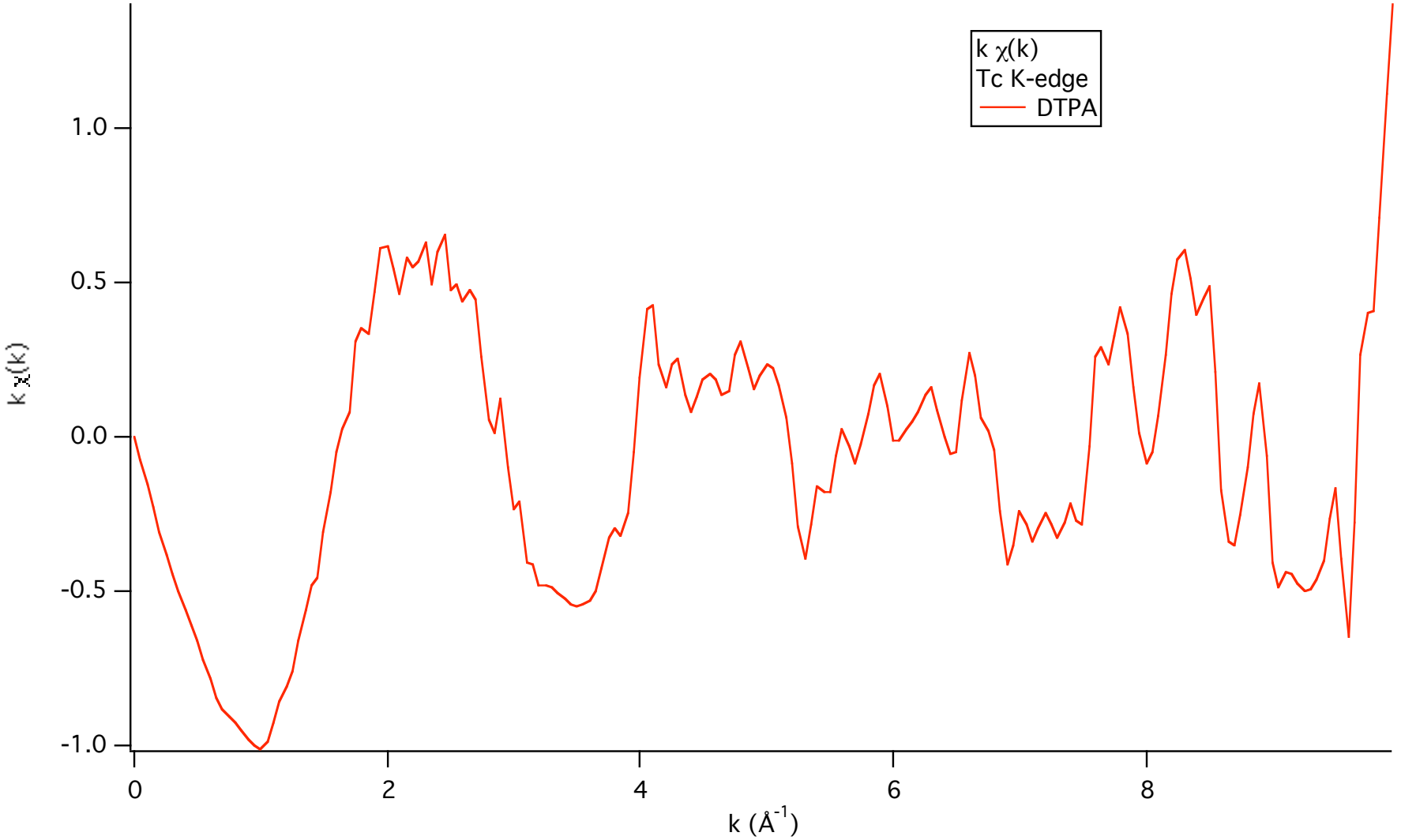
Structure 1

Structure 2

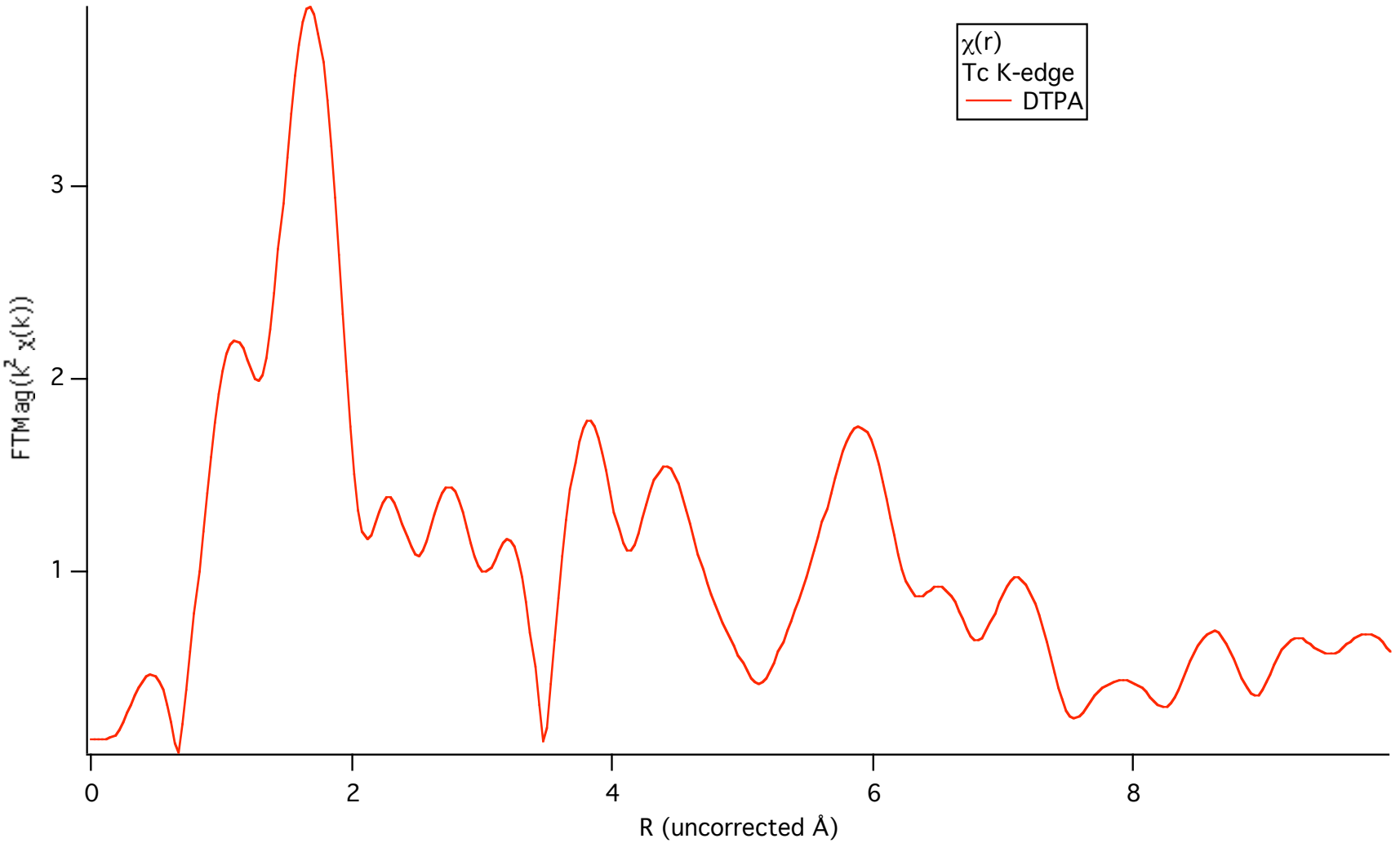
TcDTPA EXAFS
77 ng



TcDTPA EXAFS



TcDTPA EXAFS



Small Quantities

- Measured XAS Signal from 80 ng of TcDTPA.
- The Tc was eluted from a standard kit.
- We will be able to determine local structure from this quantity of material.

Conclusions

- Readily Handle Radioactive Materials
- Determine Tc Local Structures
- Need Theory to Understand Speciation
- Need Only ~50 ng of Material For Analysis

Collaborators

- Soma Chattopadhyay - IIT
- Beth Grzenia - IIT
- Sylivia Jurisson -U Missouri Columbia
- J. David Robertson - U Missouri Columbia
- Dioni Papagiannopoulou - U Missouri Columbia
- Joe Kyger - U Missouri Columbia

Acknowledgements

- MR-CAT is funded by the Department of Energy, Office of Energy Research under grant number DEFG0200ER45811.
- The APS is funded by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract number W-31-109-Eng-38.
- $^{99}Mo/^{99m}Tc$ generator was a gift from Tyco, Mallinckrodt, St. Louis MO.