

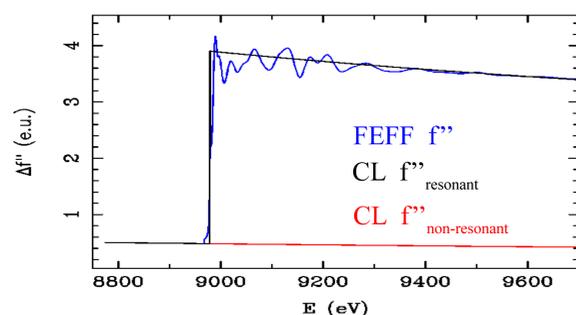
Including solid state effects in f' and f'' using *ab initio* calculations of x-ray absorption spectra

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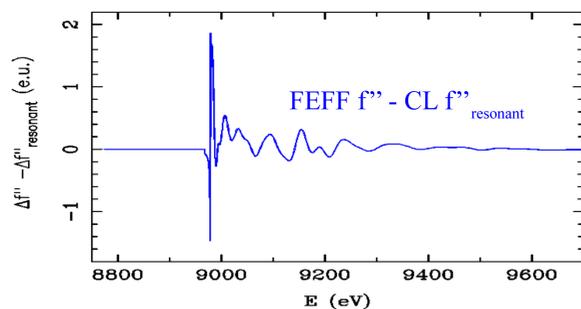
Because of the close mathematical relationship between the absorption cross-section μ and the resonant elastic scattering amplitude f'' , the theoretical calculations of x-ray absorption fine-structure, such as those from FEFF[1], can be applied to modeling resonant diffraction.

The Difference Kramers-Kronig Transform

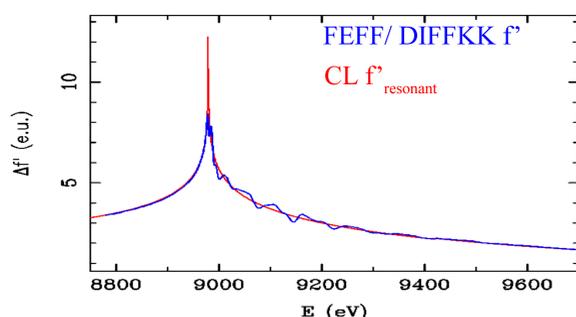
Step 1: Match FEFF $\mu(E)$ to Cromer-Liberman $f''(E)$ away from resonance. Take difference.



Step 2: Take Kramers-Kronig transform of difference of FEFF $f'' - CL f''_{resonant}$ to get the fine-structure on f'

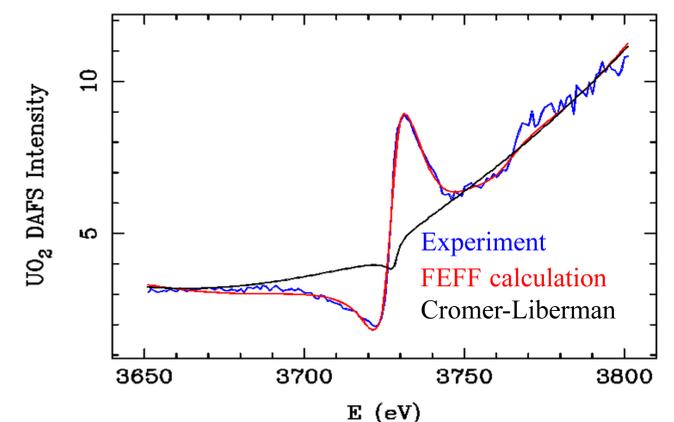
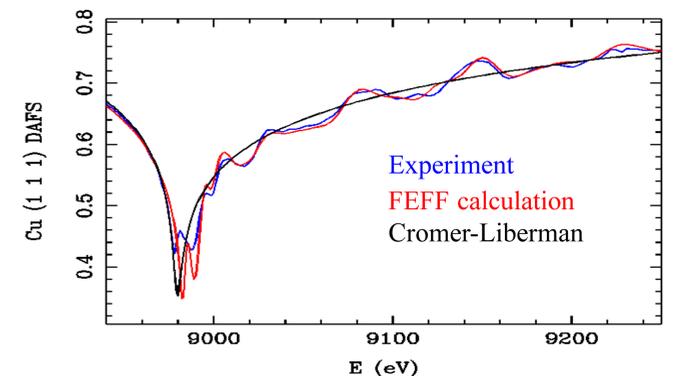


Step 3: Add this fine-structure in $f'(E)$ to the smooth f' from Cromer-Liberman, to get XAFS-like $f'(E)$.



The energy range of the resonant fine-structure is limited to ~ 1000 eV above the absorption edge energy, so a Kramers-Kronig transform of the *difference* between the XAFS-like f'' (as from FEFF) and the bare-atom f'' (as from Cromer-Liberman[2]) will give the fine-structure in f' that can be added to the bare-atom f' . [3]

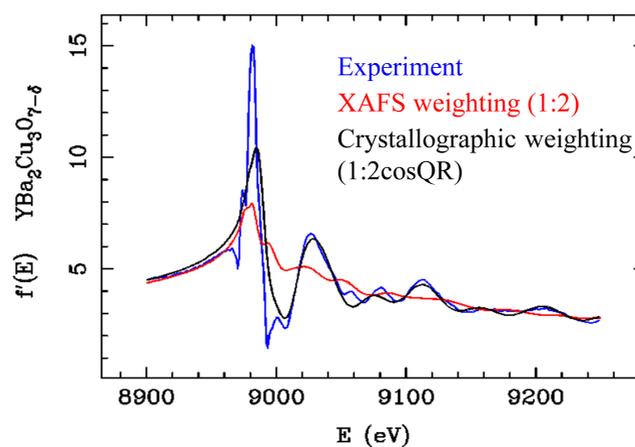
Calculations of Δf based on isolated atom models, such as the method of Cromer and Liberman, fail to reproduce the spectral features just above absorption edge energies due to the local environment of the resonant atoms. Shown here are the DAFS spectra for Cu (111) (top) and UO_2 (bottom).



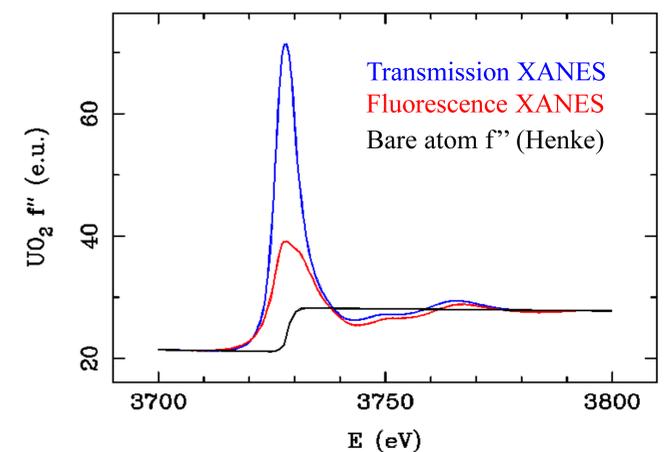
The origins of these fine-structure features are well understood from x-ray absorption spectroscopy (XAS), and extensive work has been done to develop a theoretical formalism which describes them in terms of the local environment of the resonant atoms. XAS calculations from FEFF are shown here.

Why not simply take the Kramers-Kronig Transform of XAFS data?

A. Near classically forbidden reflections in multi-site materials, the gross spectral features of f' and f'' add destructively, but the fine-structure does not cancel. In $YBa_2Cu_3O_{7-\delta}$, the two different Cu sites add destructively at the (001) reflection, but the fine-structure remains.



B. Self-absorption at a strong whiteline, such as the M_{IV} edge of UO_2 , can give errors as large as a factor of two for x-ray absorption cross-sections measured by fluorescence.



XAFS gives equal weight to all atoms in the unit cell, which is inappropriate for DAFS.

[1] S. I. Zabinsky, *et al*, Phys. Rev. B **52**, p2995 (1995).
 [2] D. T. Cromer and D. Liberman, J. Chem. Phys. **53**, p1891 (1970).
 [3] J. O. Cross, *et al*, Phys. Rev B in press (1998).

See <http://cars.uchicago.edu/~newville/dafs/diffkk/> for the DIFFKK program that automates these procedures.