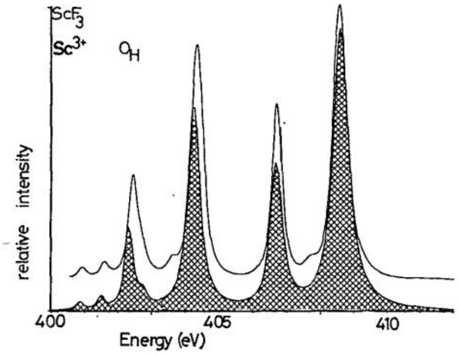
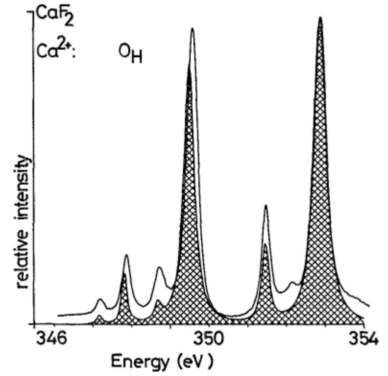
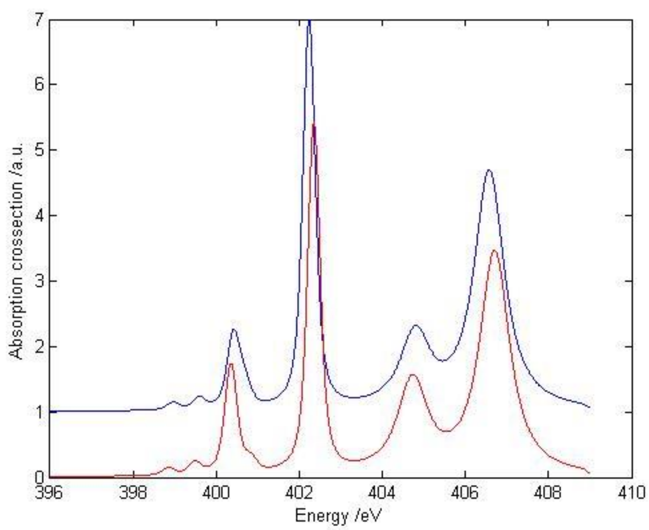
CTM4XAS: Discussion of tutorial exercises

Exercise crystal-1: The crystal field multiplet spectrum of ScF_3 and CaF_2





a) Calculate the 2p XAS spectrum of ScF_3. The symmetry is octahedral (Oh); optimise the value of 10Dq.



The blue spectrum has 10Dq = 1.5.
The red spectrum has 10Dq = 1.8.

To increase the correspondence with experiment the spectrum is split at 403 eV and the broadenings have been set to 0.1 Gaussian + 0.1 Lorentzian (0.4 Lorentzian above 403 eV).

>> to make a detailed simulation it is necessary to plot the experiment and theory on top of each other. (this will be improved in the next version of the exercises).

b) How many peaks do you observe in the experiment and the calculation?
7 peaks in the calculation; in experiment 2 extra peaks are visible at 403 and 408 eV (these are due to surface peaks because the experiment was measured with electron yield)

c) Reduce the Fdd Slater integral from 1.0 to 0.0. What is the effect on the spectrum? Explain.
There is no effect on the experiment. The ground state is 3d0 and has no 3d electrons filled, hence there are no 3d3d interactions.

d) Reduce the Fpd and Gpd Slater integrals from 1.0 to 0.5. What is the effect on the spectrum? Explain.

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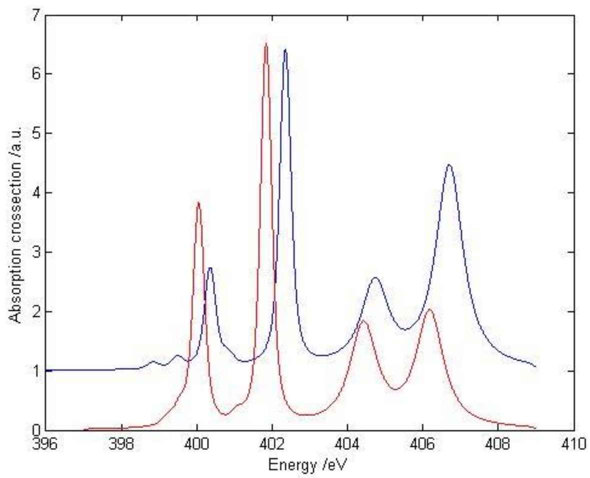
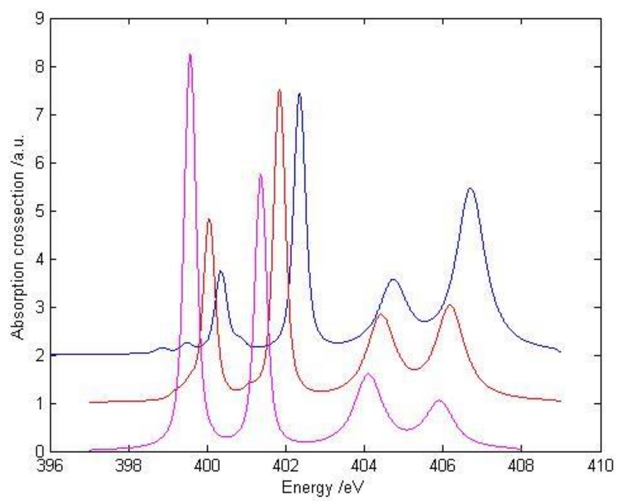


The blue spectrum is atomic.

The red spectrum has the Fpd and Gpd Slater integrals reduced to 50%.

The pre-peaks merge with the other peaks and the multiplet states come closer together and the spectrum starts to look like a single particle result.

e) Reduce the Fpd and Gpd Slater integrals to 0.0. What is the effect on the spectrum? Explain.



The bottom spectrum has all Slater integrals set to zero.

This is the single-particle spectrum with 4 peaks.

- The ratio between L3 and L2 is 4:2 following the degeneracy of the 2p3/2 and 2p1/2 states
- The ratio between the t2g and eg peaks is 3:2 following the number of states.
- This yields 4 peaks with relative intensities 6:4:3:2.

f) How many peaks are now visible? Explain the symmetry of all peaks. (see above) First peak is related to the t2g states of the L3 edge. Then follow eg-L3, t2g-L2 and eg-L2

g) Explain the number of peaks using atomic theory and the branching rules.
Atomic: 3d0 > 2p53d1. Ground state is 1S0. Final state has 1P, 1D, 1F, 3P, 3D and 3F term symbols.
The number of term symbols with J=0 is equal to 1. There are 3 states with J=1, 4 states with J=2, 3 states with J=3 and 1 state with J=4. [Check that 1*(2*0+1) + 3*3 + 4*5 + 3*7 + 1*9 = 1 + 9 + 20 + 21 + 9 = 60, equal to the total number of states of a 2p and a 3d electron (i.e. 6*10=60)]
The atomic spectrum has 3 peaks (due to the selection rules the final state must have J=1)
Applying the branching rules (see reader), there will be 7 states in Oh symmetry.

h) Calculate the 2p XAS spectrum of CaF_2. (Check first [on the web] the crystal structure of CaF_2 and the consequences for the local symmetry of Ca^{2+})
CaF2 is cubic, i.e. the Ca2+ ion has 8 F- neighbours. This implies that the t2g and eg states are inverted with respect to octahedral symmetry. This can be simulated with a negative 10Dq value. 10Dq=-0.9 gives a good spectrum.

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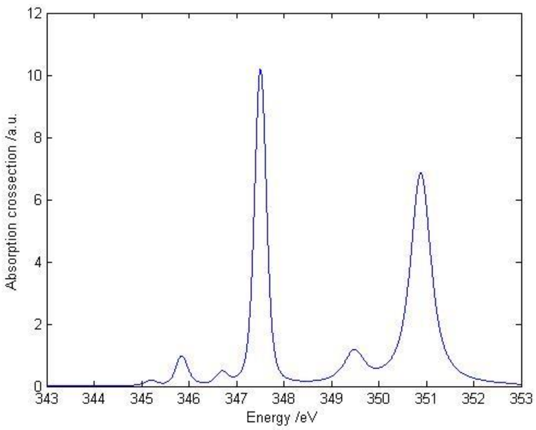

The spectrum is split at 348 eV and the broadenings are 0.1 for Gaussian and 0.05 respectively 0.2 for Lorentzian.