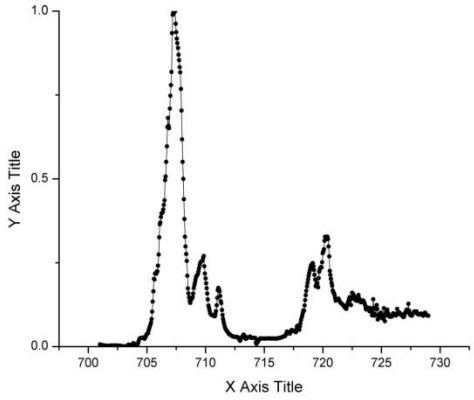
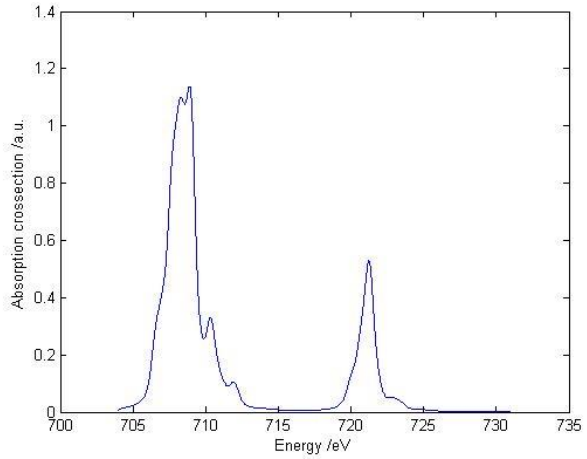
CTM4XAS: Discussion of tutorial exercises

Exercise 4: atomic multiplet spectrum of Fe2+



An iron atom has the atomic configuration ([Ar]$4s^2$ $3d^6$), which can be simulated from an iron 2+ ion with the configuration $3d^6$

a) Calculate the atomic multiplet spectrum of Fe2+, with the name fe2. Plot the file fe2.xy with plotting software.



The atomic multiplet spectrum of Fe2+ with all atomic values set to 1.0

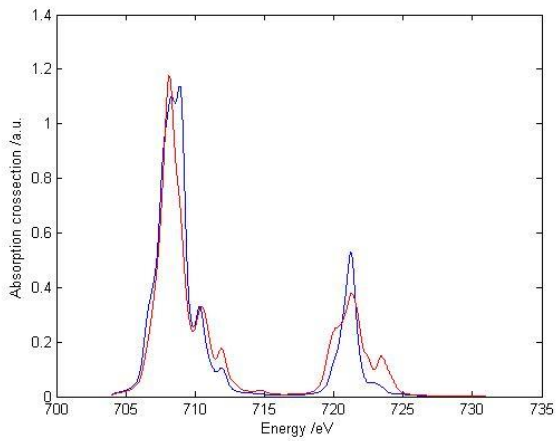
b) The experimental spectrum of an iron atom is given in the file fe2at.DAT. Plot the file with plotting software in the same panel. The theoretical spectrum can be normalised to 1.0 to compare better with the experiment. Does the calculated spectrum look like the experimental spectrum?

The normalisation is allowed because the experimental spectrum is measured in arbitrary units.
The theoretical spectrum is always calculated with its energy scale (up to) a few eV wrong; in fact in the CTM4XAS interface the theoretical binding energy is replaced by an empirical binding energy that is a few eV different, but still can be a little off. Shift the calculation to get the best alignment with theory.
See the figure at the end of this file.

Conclusion: It looks a bit like the experiment, but some peaks have too high or too low intensity, for example the peak at 818 eV.

c) Set the 3d spin-orbit coupling to zero and compare again with the experimental spectrum. Use a different name, for example fe2n.

CTM4XAS: Discussion of tutorial exercises



[NOTE: Due to a rounding error in the calculations, you should set the temperature to 1 K to include all ground states]

The red spectrum is without 3d spin-orbit coupling. This looks better if compared with experiment.

The experiment is sharper; this can be corrected for the calculations to use a smaller Gaussian broadening.

d) What is the conclusion? The 3d spin-orbit coupling seems quenched.

e) Look into the file fe2n.ora. Search for the ground state energies. They are given separately for each symmetry. Count all states with an energy within 0.3 eV from the lowest energy. What is the degeneracy of the ground state?

Look into the file fe2n.ora and search these lines:

```
CALCULATIONS for ACTOR:HAMILTONIAN     GROUND

        CALCULATING MATRIX for TRIAD  1   (  0+   0+   0+ )  (56*56)
[..]
      EIGVAL  -3.38686  -3.38686  -3.38686  -3.38686  -3.38686  -3.38686  -3.38686

        CALCULATING MATRIX for TRIAD  8   (  1+   0+   1+ )  (50*50)
  [..]
      EIGVAL -3.386858 -3.386858 -3.386858 -3.386858 -3.386858 -3.386858

    CALCULATING MATRIX for TRIAD 15   ( -1+   0+  -1+ )  (50*50)
      EIGVAL -3.386858 -3.386858 -3.386858 -3.386858 -3.386858 -3.386858

  [..]

        CALCULATING MATRIX for TRIAD 22   (  2+   0+   2+ )  (54*54)
      EIGVAL -3.386858 -3.386858 -3.386858 -3.386858 -3.386858 -3.386858
```

The ground state has an energy -3.386858.

[You also see the numerical error as the first matrix is rounded to -3.38686].

The ground state is 25 fold degenerate.

f) What is the term symbol of the ground state?

Fe^{2+} is $3d^6$. Following Hunds rules (max S, Max L, max J), the five spin-up states are filled. One spin-down state is filled with M_L=+2. This yields L=2. The total spin S= 5/2 – 1/2 =2. The LS ground state is then ^5D. With spin-orbit coupling the ground state is $^5D_4$. Note that the 25-fold degenerate ground state as found in question e) is correct for a ^5D ground state.

g) Now look into the file fe2.ora. Search for the ground state energies. They are given separately for each symmetry. Count all states with an energy within 0.3 eV from the lowest energy. What is the degeneracy of the ground state?

CTM4XAS: Discussion of tutorial exercises

- -3.44286 -3.44286 -3.44286 -3.38906 -3.35125 -3.32693 -3.31500
- -3.442864 -3.442864 -3.389057 -3.389057 -3.351252 -3.326928
- -3.442864 -3.442864 -3.389057 -3.389057 -3.351252 -3.326928
- -3.442864 -3.442864 -3.389057 -3.389057 -3.351252 -3.351252

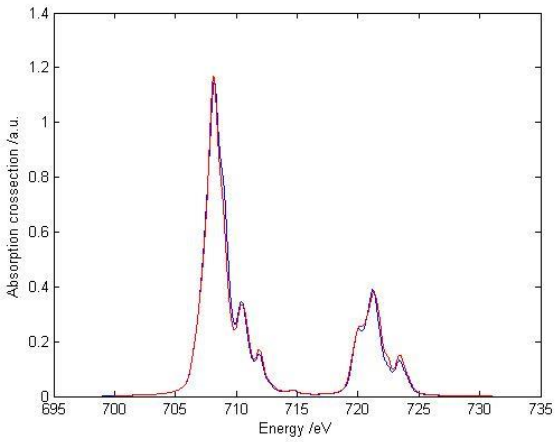
This are the 25 states within the first 0.3 eV. The state at -3.44 eV is 9 fold degenerate, next come -3.38 (7), -3.35 (5), -3.32 (3) and -3.31 (1), i.e. respectively the 5D4, 5D3, 5D2, 5D1 and 5D0 states with their 2J+1 degeneracies.

h) What is the term symbol of the ground state? 5D4

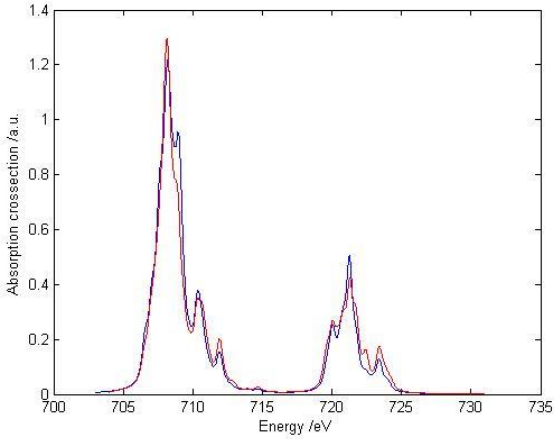
i) What is the effect of the 3d spin-orbit coupling? It splits the 5D0 ground state into 5 sub-states.

j) Plot the spectrum of the fe2 calculation with a temperature of 3000 K and compare with experiment. (The experiment has been performed at 1700 K). Try also 1700 K. If the 3000 K spectrum appears better than the 1700 K spectrum, what could be the reason?

CTM4XAS: Discussion of tutorial exercises



At 3000 Kelvin the spectra with and without 3d spin-orbit coupling are almost the same.
This means that there is an almost statistical distribution over the spin-orbit split states.
The excited state are found (cf answer g) at ~60 meV, 90 meV, 120 meV and 130 meV. 100 meV corresponds to approx. 1000 Kelvin.



At 1000 Kelvin (and a Gaussian of 0.1 eV) the red spectrum looks very much like experiment.

[The question is misleading/incorrect as the conclusion is that the 1000 K spectrum gives the best result; a possible reason is that the 3d spin-orbit coupling is calculated not exactly correct]