Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Local environment of arsenic in sulfide minerals: insights from high-resolution X-Ray spectroscopies, and first-principle calculations at the As K-edge.

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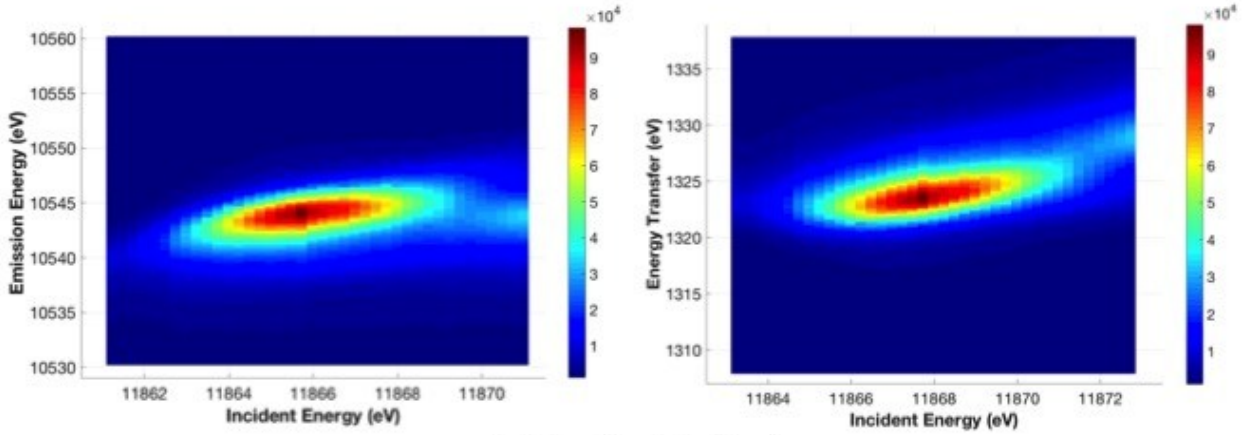
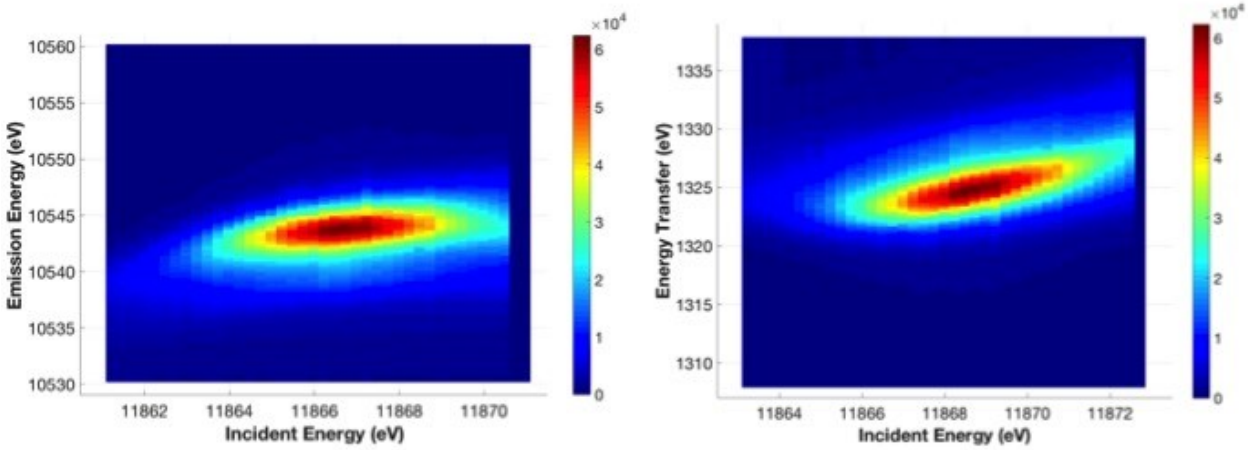
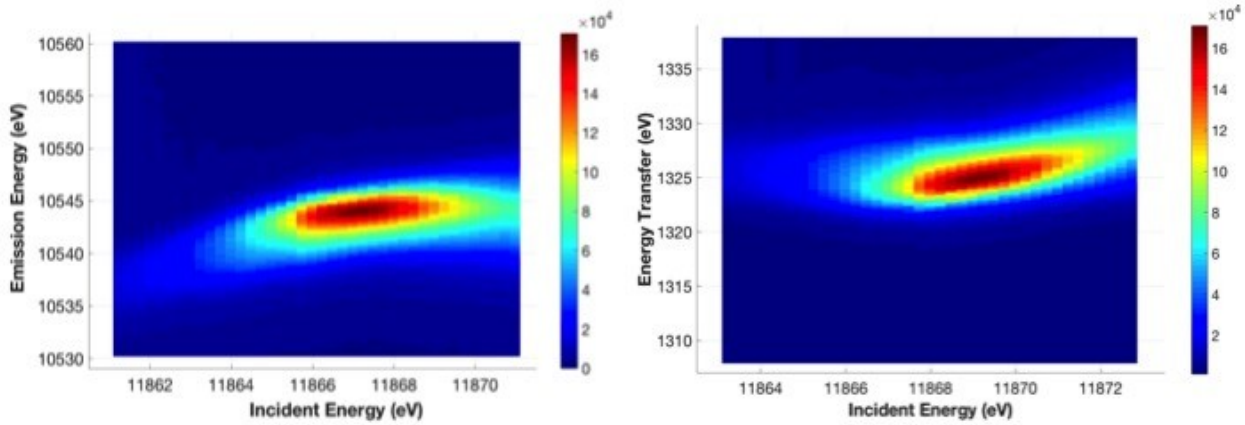
Arsenopyrite (FeAsS)



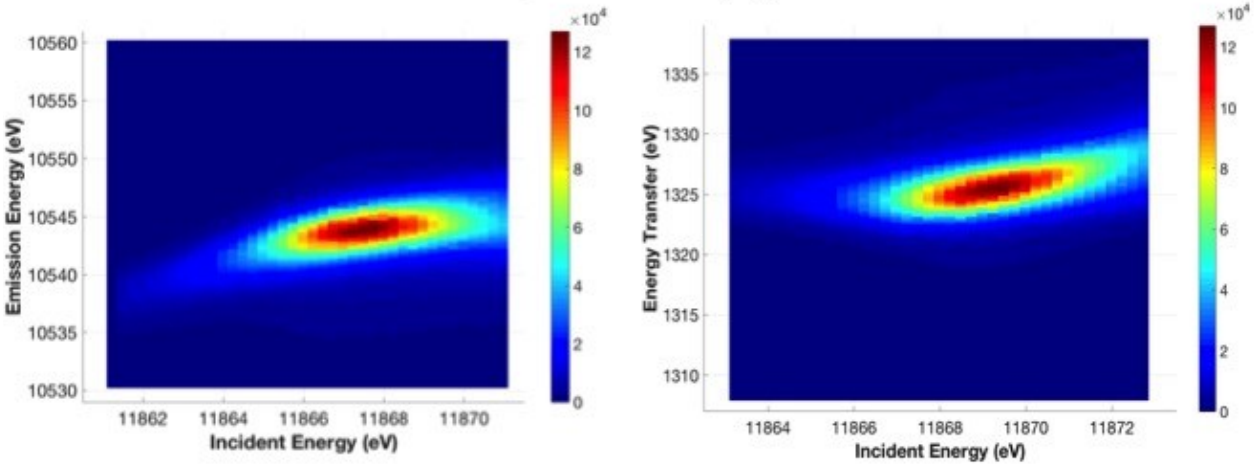
Lollingite ($FeAs_2$)



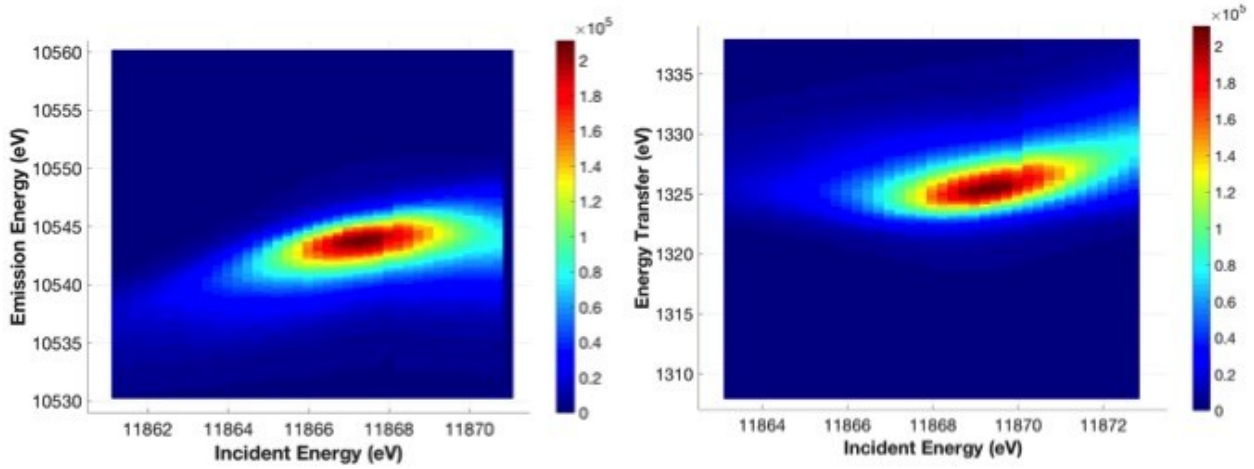
Realgar (AsS)



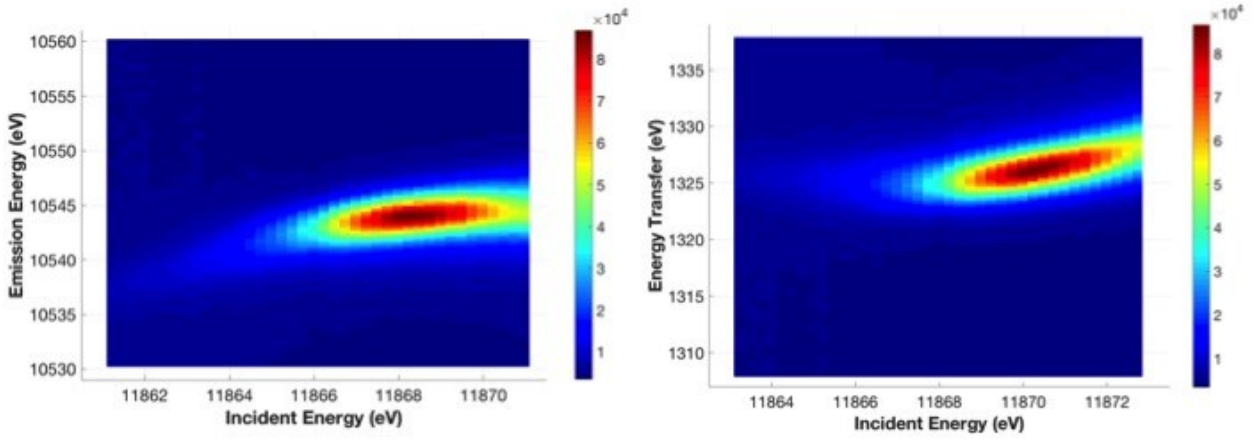
Orpiment (As_2S_3)



Amorphous orpiment (am_As_2S_3)



As(III)-gluthatione (As_Glu3)



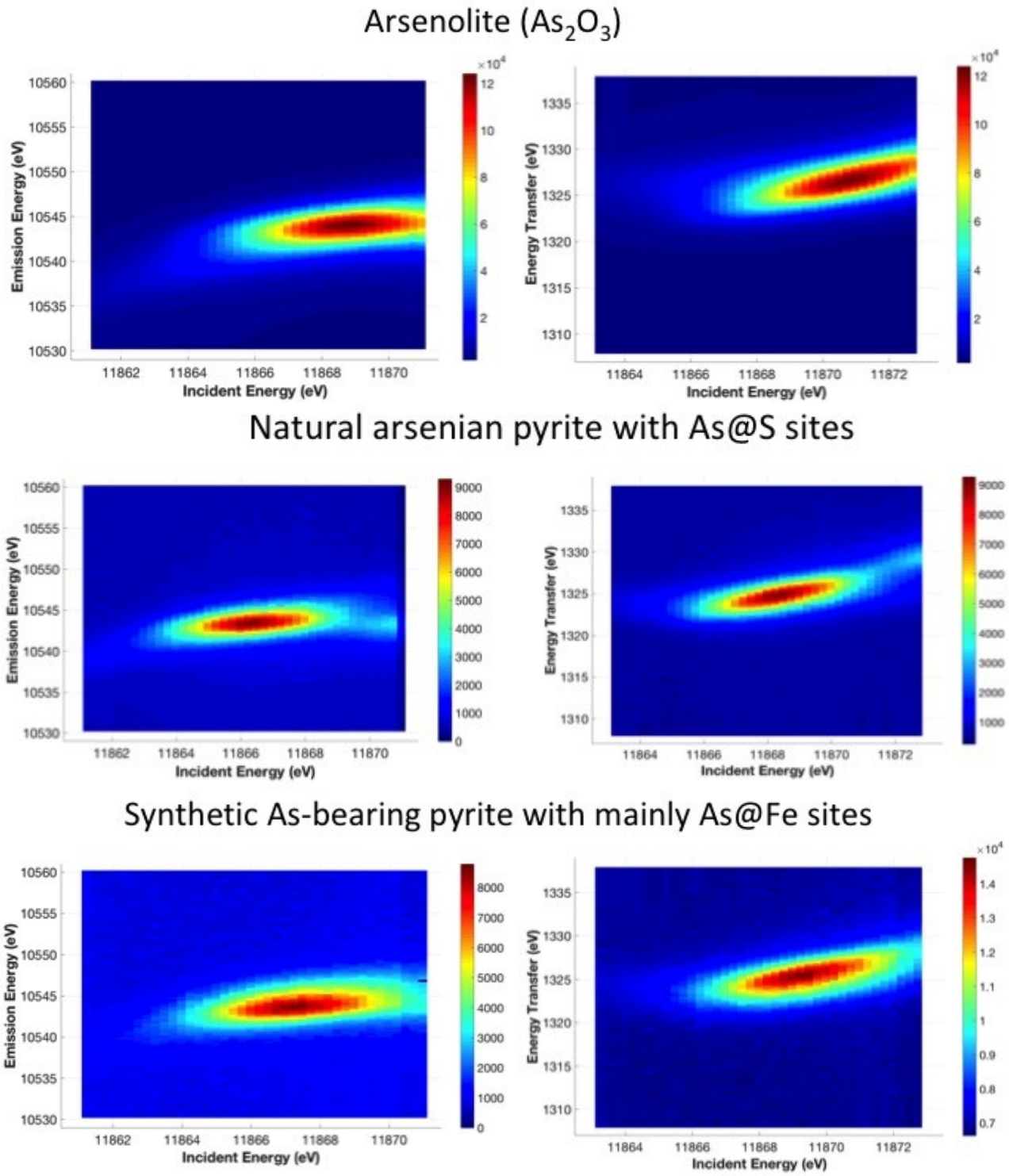


Figure S1. RIXS maps obtained for the As-bearing samples of the As-S-Fe system considered in this study and analyzed at the GALAXIES beamline. The position of the maximum value on the RIXS plane for each sample is reported in Fig. 6. RIXS maps are plotted as Emission Energy over Incident Energy and Energy transfer over Incident energy.

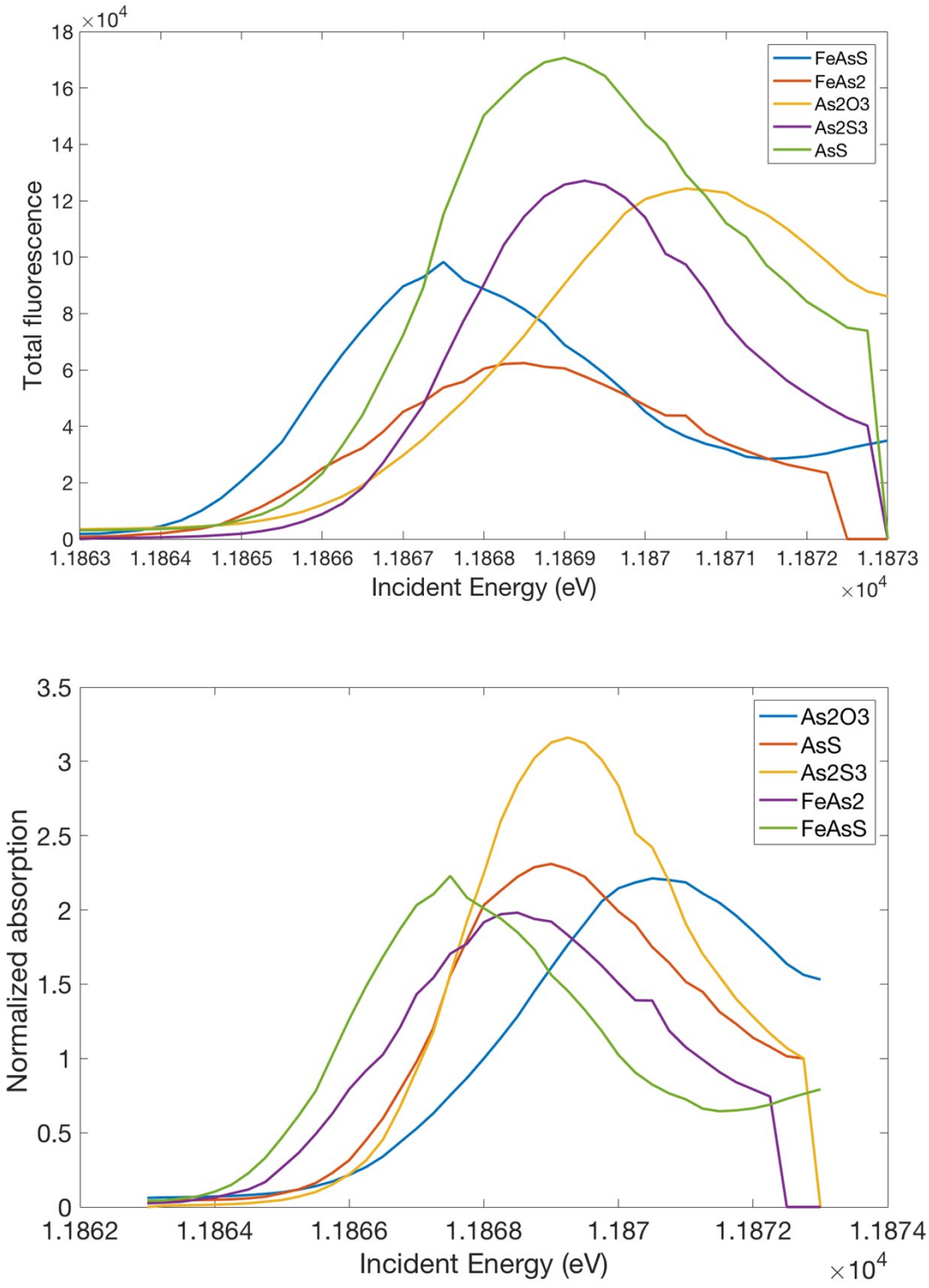


Figure S2. HERFD-XANES spectra for the reference compounds of the As-S-Fe system performed at the emission energy for wich the fluorescence is maximum in the RIXS plane. The spectra are presented not normalized (up) and as normalized (down) as a function of their standard XANES experimental counterparts.

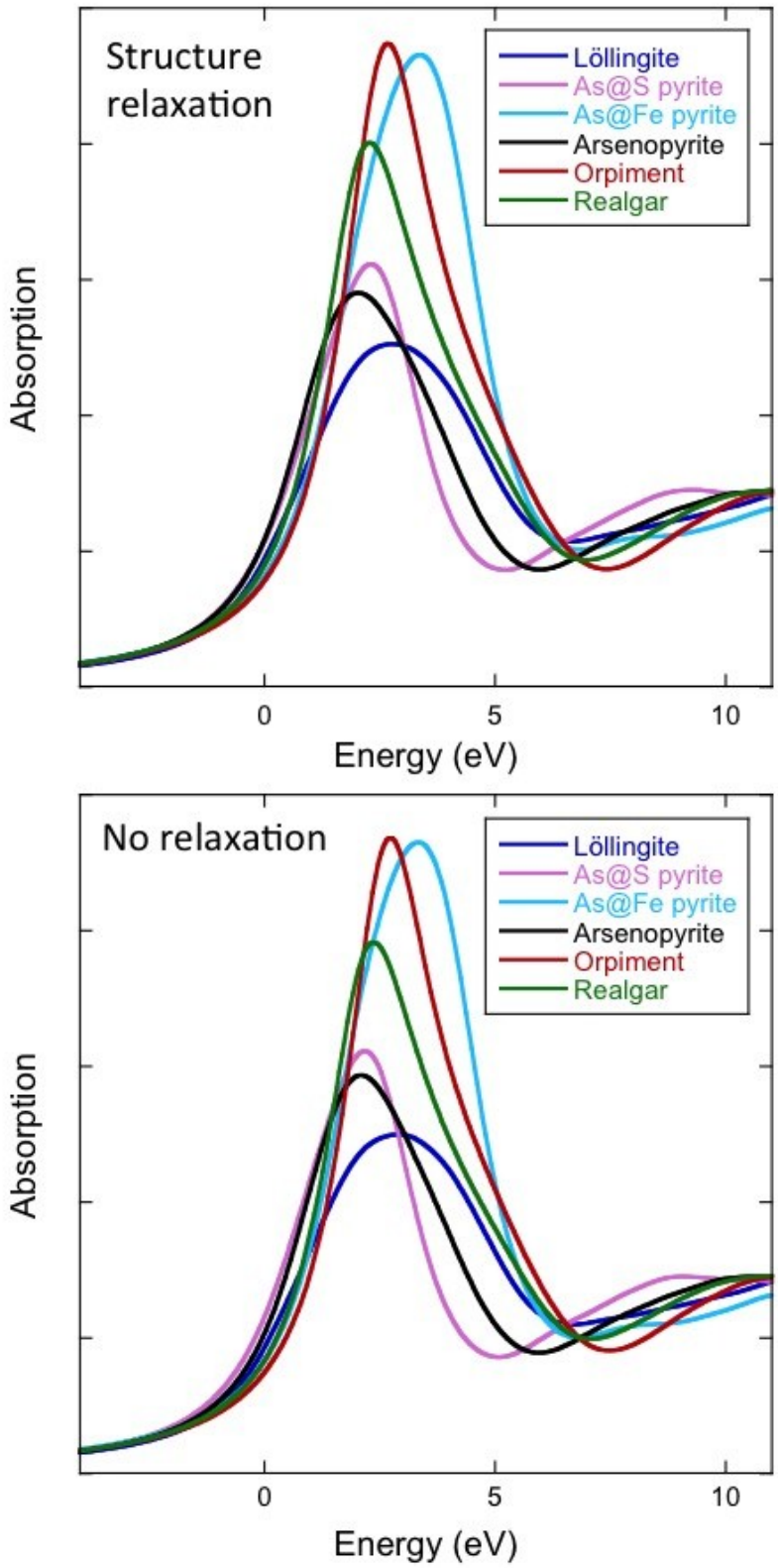


Figure S3. Calculated As *K*-edge XANES spectra from DFT-optimized structures (structure relaxation, top) or from experimental structures (no relaxation, bottom). In As-bearing pyrites, arsenic is a chemical impurity. Therefore atomic positions have been relaxed keeping the cell parameters fixed to the experimental values

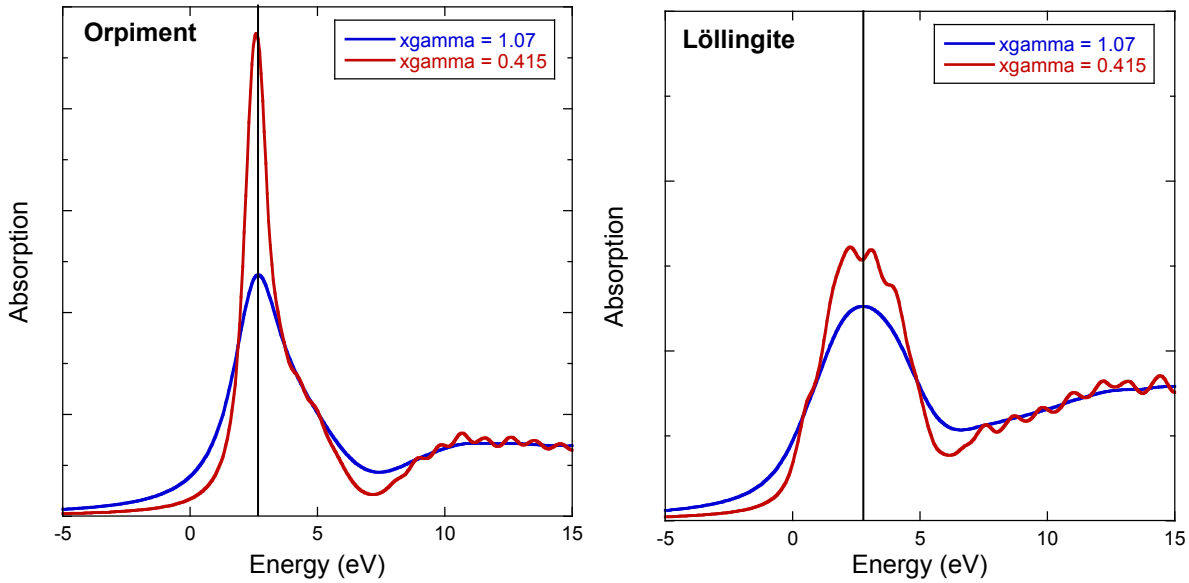


Figure S4. Comparison of the DFT calculation of XANES spectra for orpiment (As_2S_3) and löllingite ($FeAs_2$) when changing the lifetime broadening from 2.14 eV to 0.83 eV. Such a change would be representative of the resolution gained between standard and HERFD-XANES.

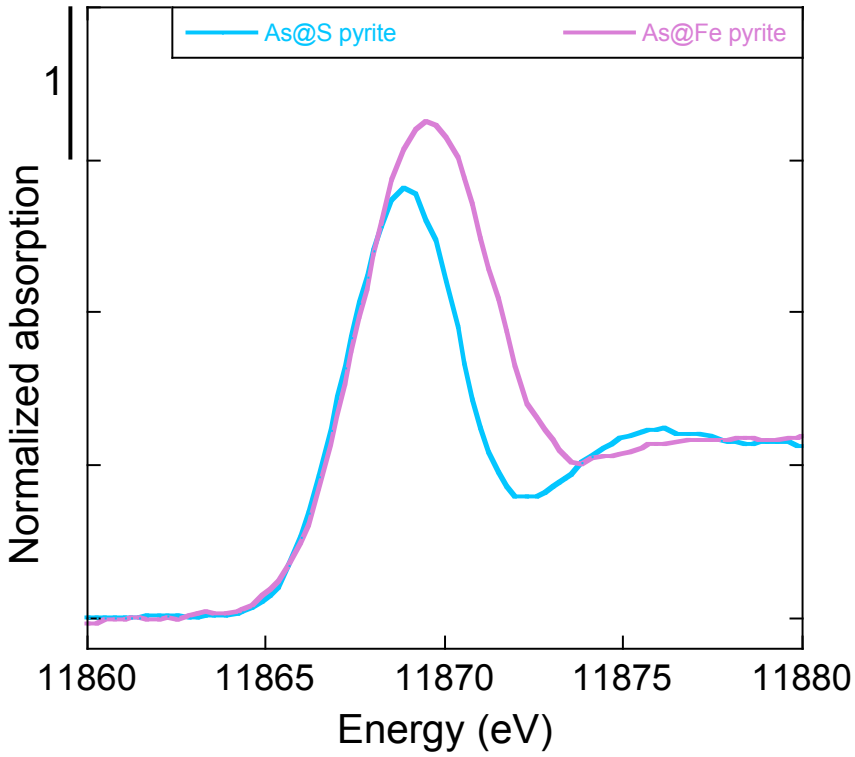


Figure S4. HERFD-XANES measured at the As K-edge for As@S and As@Fe pyrite at an emission energy of 10543.3 eV.