10.1071/CH11484_AC

Australian Journal of Chemistry 2012, 65(3), 241–253.

X-Ray Spectroscopy and Structure Elucidation of Reactive Electrogenerated Triiron Carbonyl Sulfide Clusters

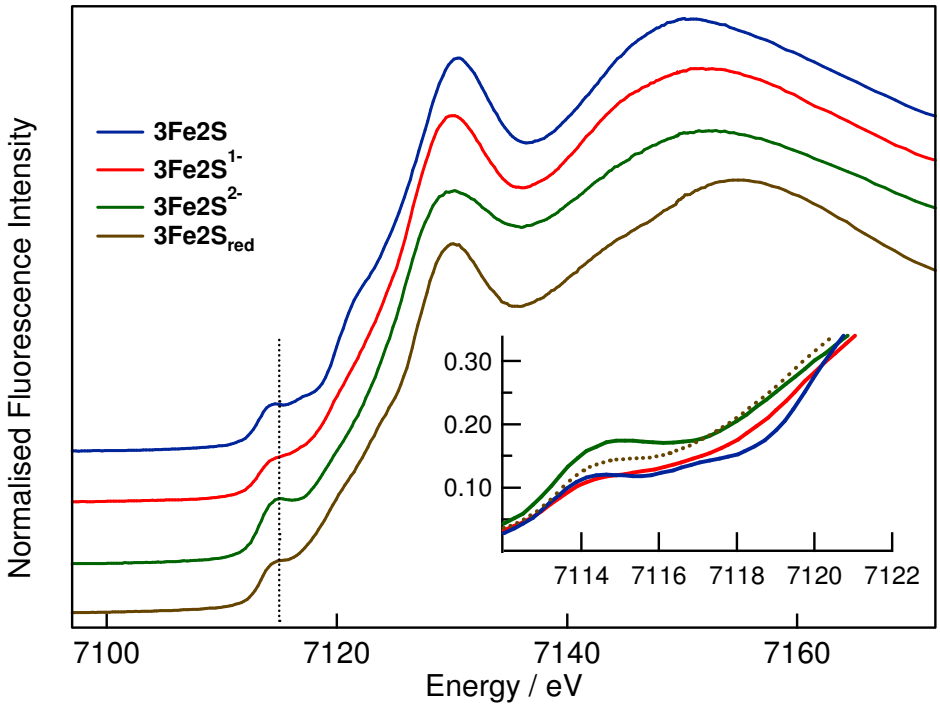
Joey Yeo, Mun Hon Cheah, Mark I. Bondin, and Stephen P. Best*

School of Chemistry University of Melbourne , Victoria 3010, Australia.

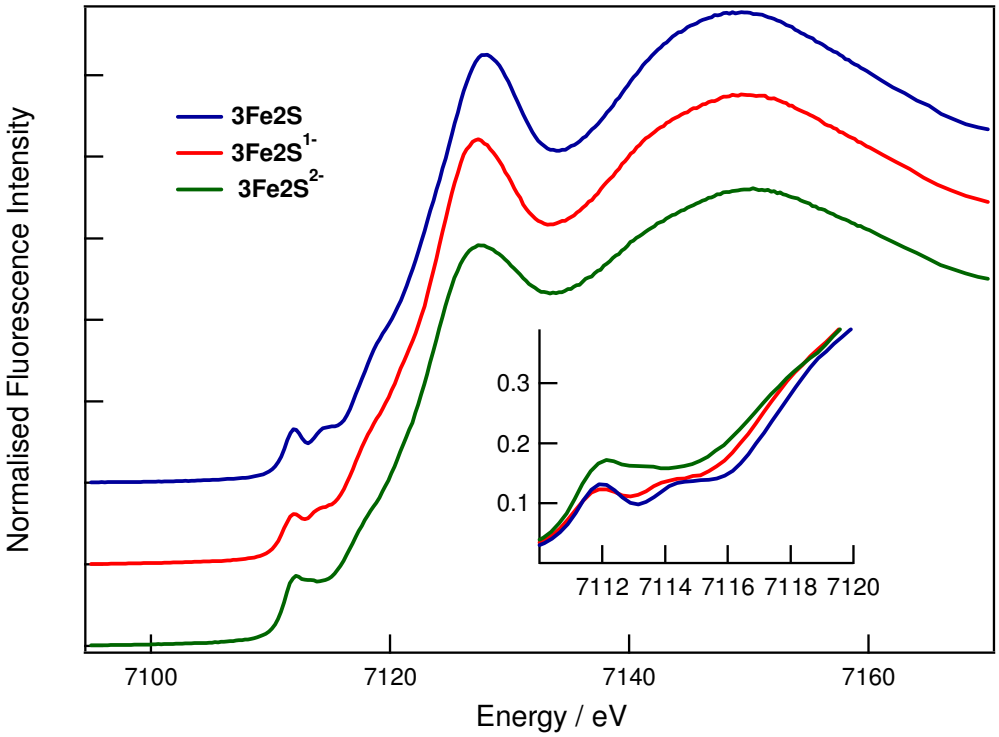
Supplementary Material

1. Comparison of XANES spectra for the $[Fe_3S_2(CO)_9]^{0/1-/2-}$ redox series obtained using the CFES cell (ANBF) and the FQXES cell (XAS, AS).
2. Comparison between the calculated and experimental IR spectra of $[Fe_3S(CO)_9]^{2-}$ in the ν(CO) region.
3. XAFS analysis of a solid-state sample of $PPN_2[Fe_3S(CO)_9]$.

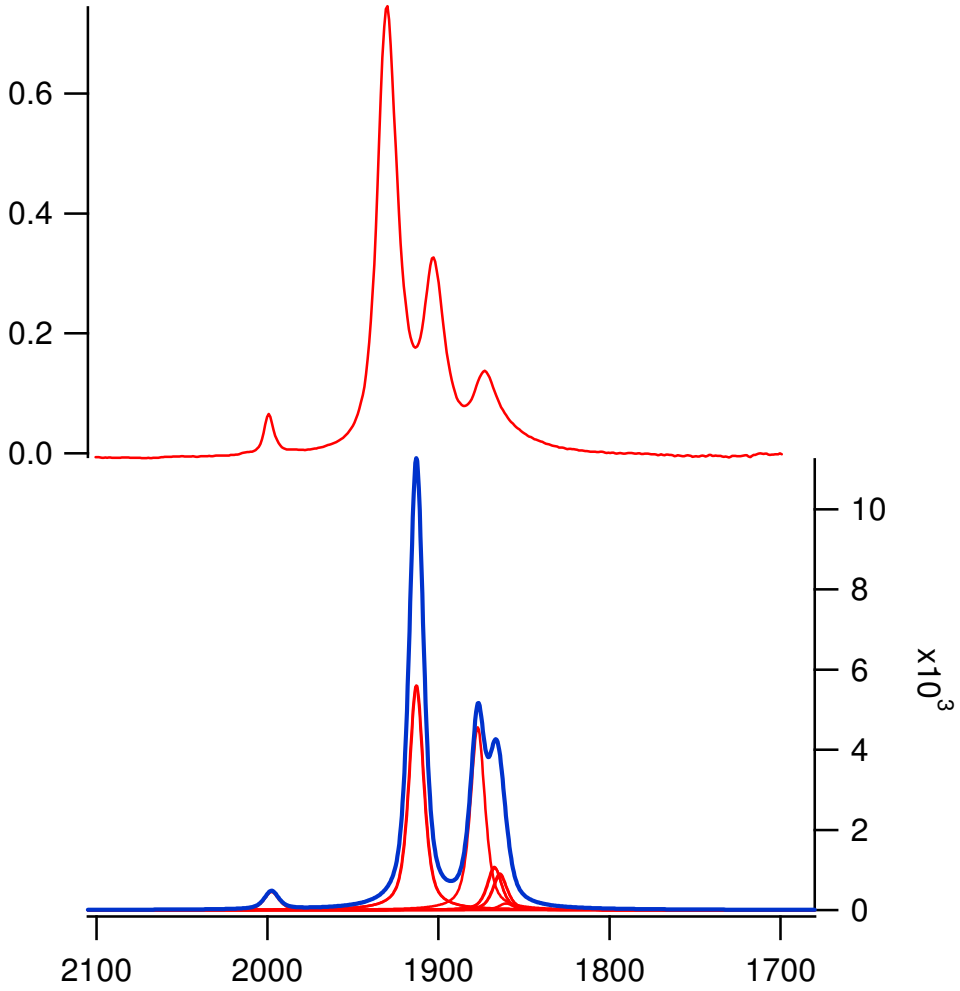
1. Comparison of XANES spectra for the $[Fe_3S_2(CO)_9]^{0/1-/2-}$ redox series obtained using the CFES cell (ANBF) and the FQXES cell (XAS, AS).



XANES from **Fe3S2** and reduced products obtained using the CFES cell (ANBF, above) and the FQXES cell (XAS, below).

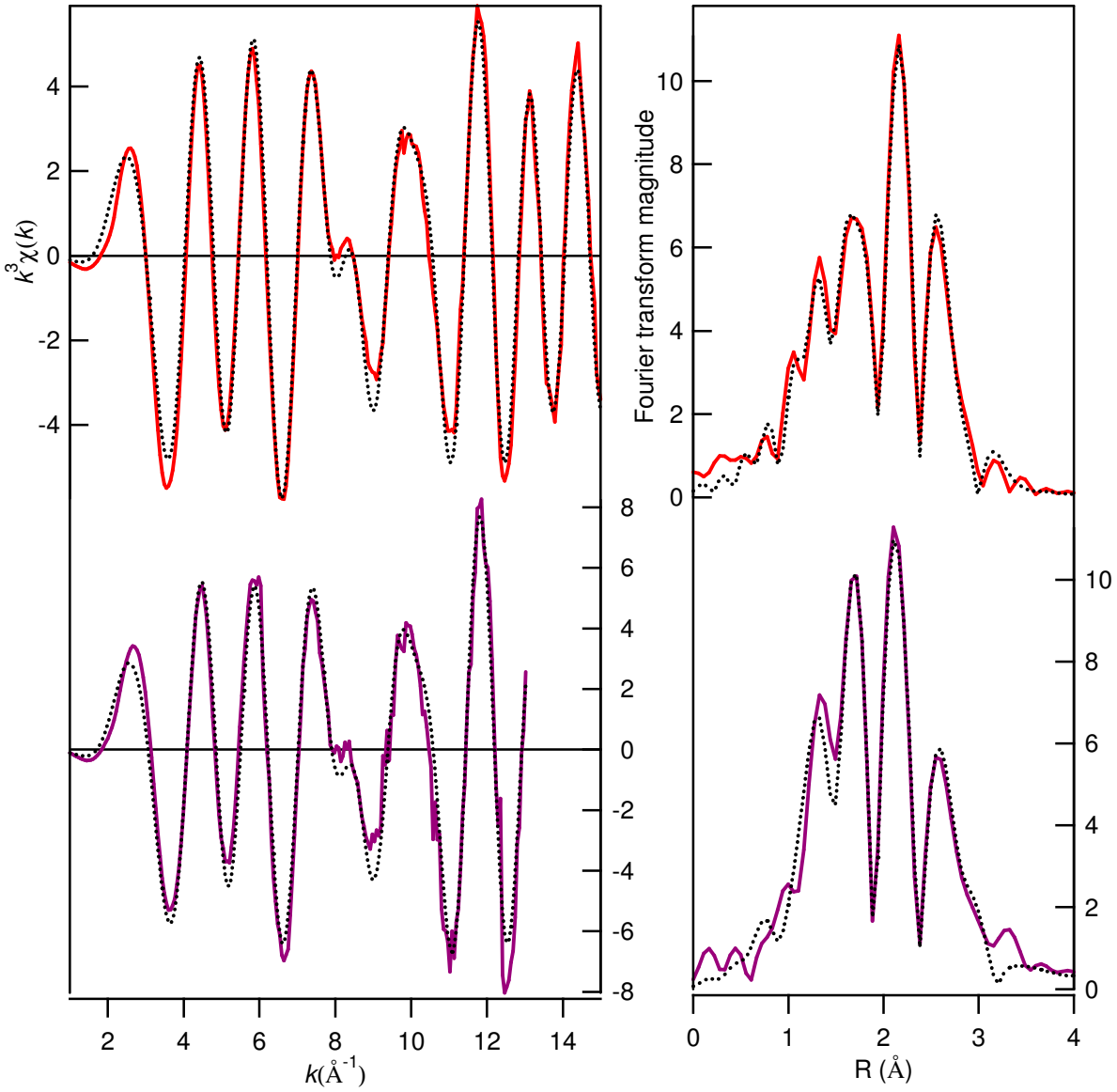


2. Comparison between the calculated and experimental IR spectra of $[Fe_3S(CO)_9]^{2-}$ in the ν(CO) region.



An offset of 30 cm^{-1} has been added to all the calculated band wavenumbers (so as to be consistent with the offset applied to the calculations for the **3Fe2S** compounds.

3. XAFS analysis of a solid-state sample of $PPN_2[Fe_3S(CO)_9]$.



The top trace gives the XAFS and non-phase corrected Fourier transform of a solid sample of $PPN_2[Fe_3S(CO)_9]$ analysed using model $\mathbf{M_{31}1}$. The bottom trace shows the solution data as included in Figure 6 of the manuscript.

EXAFS and DFT analysis of **3FeS^{2-}**.[#]

	Solid PPN_2 **3FeS^{2-}**	Solution **3FeS^{2-}**
*E*0/eV	-9.83	-8.15
*S*02	0.69	0.75
χ2 (*R*EXAFS / %)	2.09 (13.10)	5.16 (18.01)
N_{rp} (N_{idp})	10 (28.7)	10 (28.7)
Fe-Fe/Å σ^2 (Fe)	2.57 [2.596][a] {2.610}[b] (0.0023)	2.57 (0.0020)
Fe-S/Å σ^2 (S)	2.18 [2.201] {2.246} (0.0014)	2.17 (0.0013)
Fe-C/Å σ^2 (C)	1.75 [1.763] {1.747} (0.0020)	1.76 (0.0005)
C-O/Å σ^2 (O)	1.18 [1.158] {1.189} (0.0035)	1.17 (0.0031)

[#] EXAFS analysis conducted on solid data; k = 1-15 Å^{-1}, r = 1-4 Å and solution data; k = 1-13 Å^{-1}, r = 1-4 Å, using Model A with Rmax = 4 Å. *a* X-ray distances from the compound [TS][PPN]2.70 *b* Bond length obtained from DFT geometry optimisation.56