

The chemical sensitivity of X-ray spectroscopy: High energy resolution XANES versus Valence-to-core X-ray emission of substituted ferrocenes

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Supporting Information

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1 Relativistic Calculation of XAS and XES

Figure 1: Calculated pre-edge XAS spectra of (a)–(e) obtained non-relativistically (left) and obtained by considering scalar relativistic effects within the ZORA approximation (right). Results are shown for the BP86 and the B3LYP exchange–correlation functionals. See main text for further computational details.

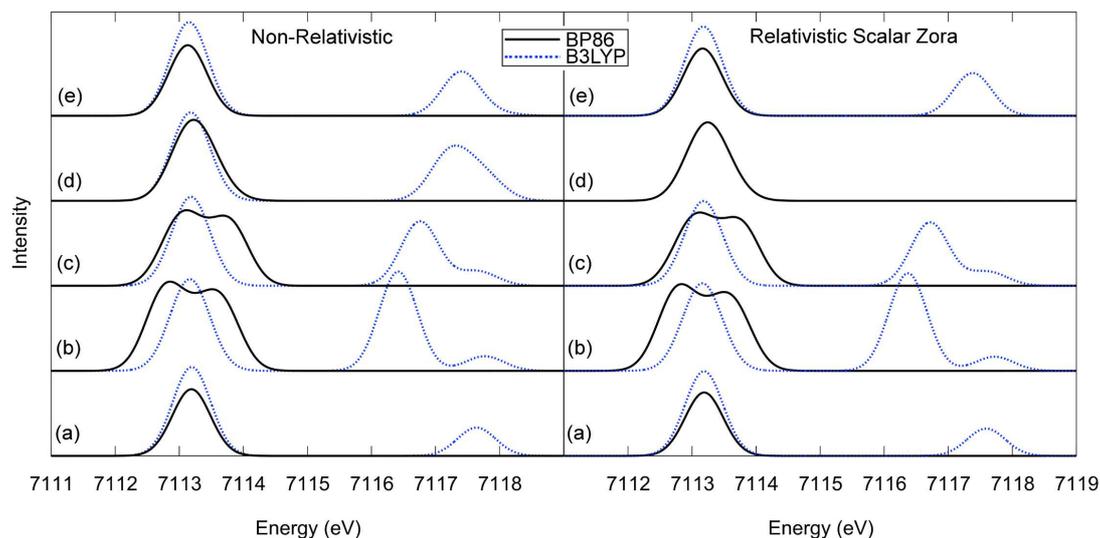


Figure 2: Calculated V2C-XES spectra of (a)–(e) obtained non-relativistically (left) and obtained by considering scalar relativistic effects within the ZORA approximation (right). Results are shown for the BP86 and the B3LYP exchange–correlation functionals. See main text for further computational details.

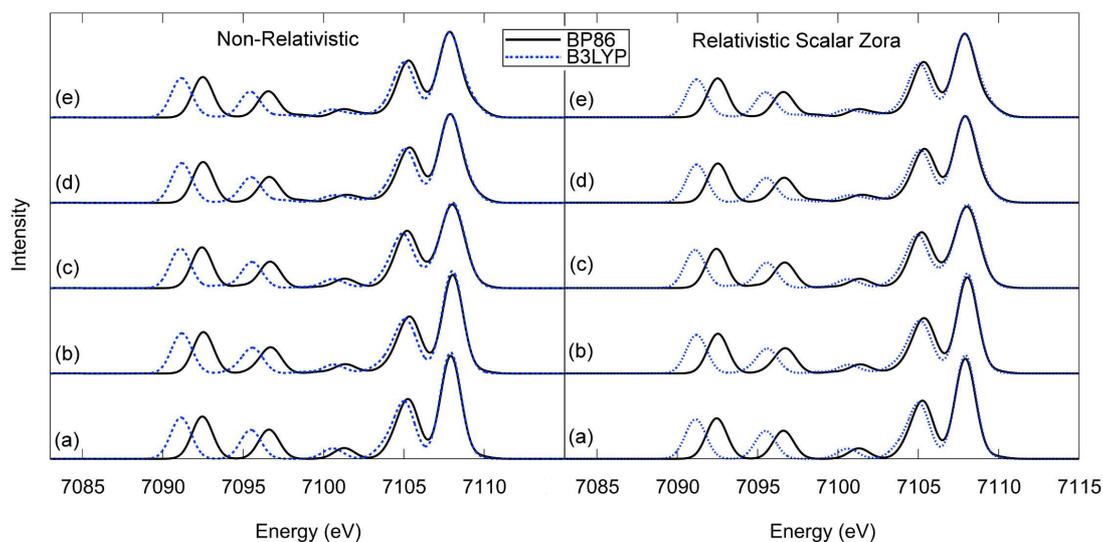


Table I: Energies (E_{rel} , in eV), intensities (Rel. Int.), and full width at half maximum (FWHM, in eV) extracted from the deconvolution of the experimental spectra compared to the energies and intensities predicted with DFT calculations using the BP86 and B3LYP exchange-correlation functionals and **including scalar relativistic effects with the ZORA approximation**. All energies are given as shifts relative to the highest energy peak in ferrocene at 7107.94 eV, and intensities are normalized to the one of this peak.

Complex	Experimental			DFT/ZORA/BP86		DFT/ZORA/B3LYP	
	E_{rel}	Rel. Int.	FWHM	E_{rel}	Rel. Int.	E_{rel}	Rel. Int.
(a) Fe(Cp) ₂	0.00	1.00	2.87	0.00	1.00	0.00	1.00
	-3.05	0.63	3.45	-2.67	0.64	-2.90	0.62
	-7.44	0.29	4.83	-6.62	0.10	-7.32	0.10
	-12.54	0.34	4.60	-11.32	0.27	-12.43	0.26
	-16.96	0.51	5.90	-15.47	0.39	-16.78	0.37
(b) Fe(Cp)(CpAc)	0.20	0.91	2.78	0.13	0.96	0.12	0.97
	-2.86	0.58	3.42	-2.57	0.66	-2.82	0.64
	-7.25	0.22	4.56	-6.54	0.11	-7.26	0.10
	-12.42	0.28	4.52	-11.21	0.27	-12.33	0.26
	-16.91	0.44	5.91	-15.39	0.39	-16.72	0.37
(c) Fe(Cp)(CpVinyl)	0.17	0.84	3.02	0.10	1.02	0.12	1.02
	-2.99	0.57	3.62	-2.71	0.61	-2.98	0.59
	-7.22	0.25	5.01	-6.58	0.11	-7.28	0.10
	-12.51	0.35	5.19	-11.24	0.28	-12.36	0.27
	-16.95	0.42	5.55	-15.49	0.38	-16.81	0.36
(d) Fe(CpPPh ₂) ₂	-0.01	1.03	2.96	0.00	0.98	0.00	0.98
	-2.88	0.55	3.11	-2.54	0.63	-2.79	0.61
	-6.48	0.30	5.76	-6.42	0.10	-7.13	0.10
	-12.76	0.41	5.70	-11.27	0.26	-12.39	0.25
	-17.35	0.46	6.01	-15.40	0.38	-16.71	0.36
(e) Fe(CpP ⁱ Pr ₂) ₂	0.09	0.94	3.08	-0.03	0.99	-0.04	0.99
	-2.90	0.61	3.48	-2.59	0.61	-2.85	0.59
	-7.27	0.27	5.14	-6.58	0.11	-7.31	0.11
	-12.55	0.33	4.74	-11.32	0.25	-12.44	0.24
	-16.96	0.40	5.31	-15.41	0.38	-16.72	0.36

2 Experimental and Calculated Difference Spectra

Figure 3: Experimental V2C-XES spectra of (a)–(e) (left) and corresponding difference spectra compared to ferrocene (a) (right),

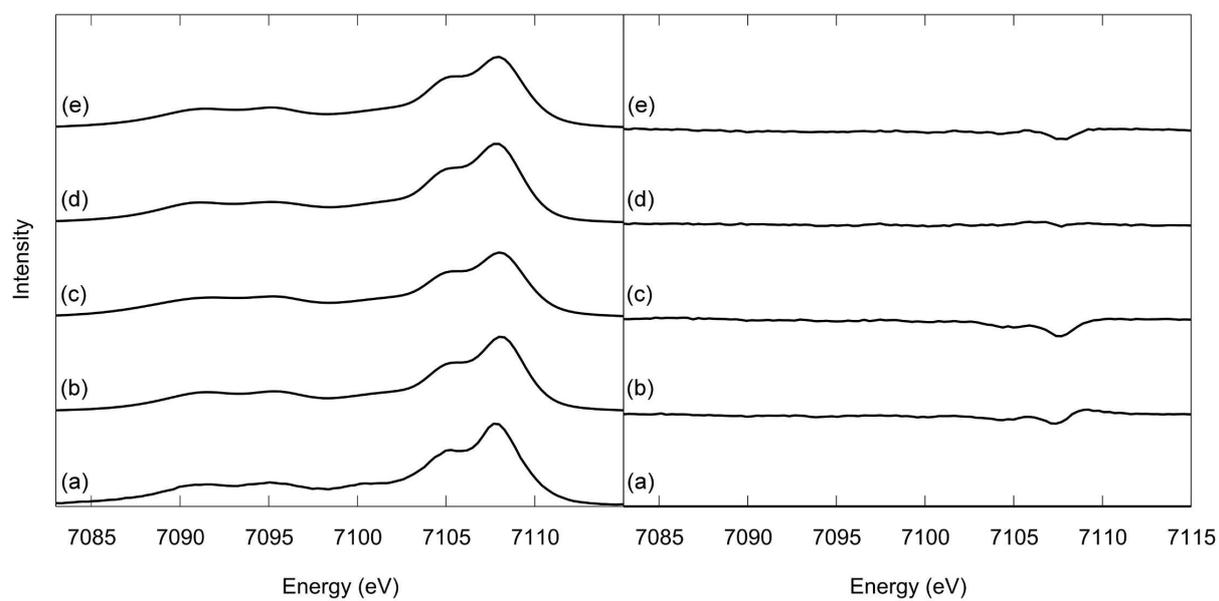


Figure 4: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 3.0 eV** (left) and corresponding calculated difference spectra compared to ferrocene (right).

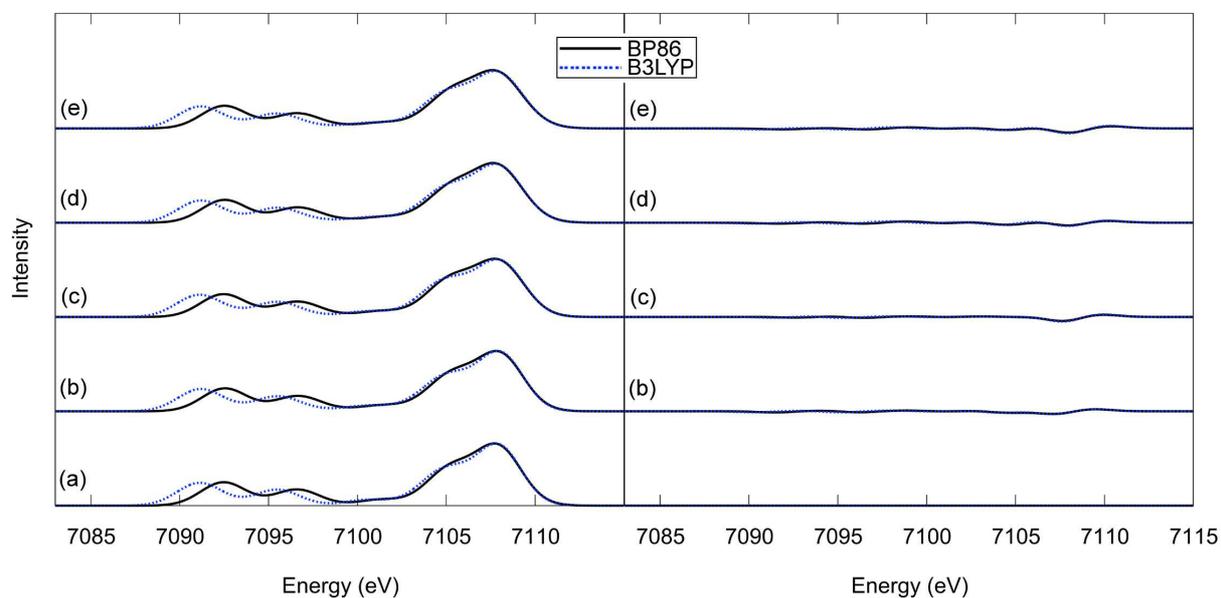


Figure 5: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 2.5 eV** (left) and corresponding calculated difference spectra compared to ferrocene (right).

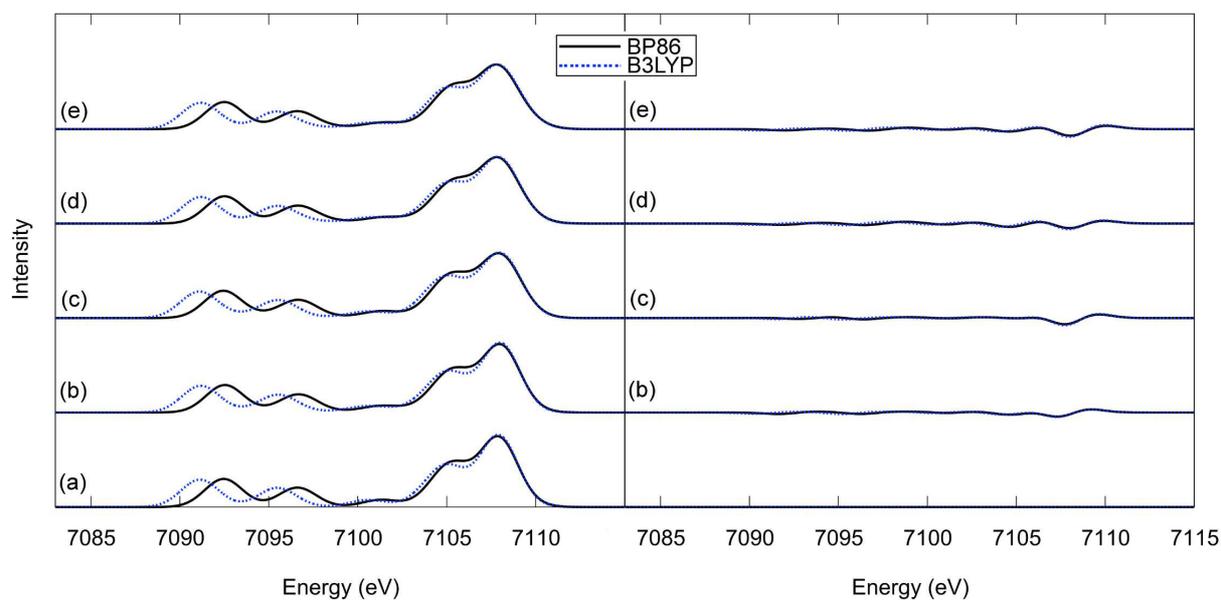


Figure 6: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 2.0 eV** (left) and corresponding calculated difference spectra compared to ferrocene (right).

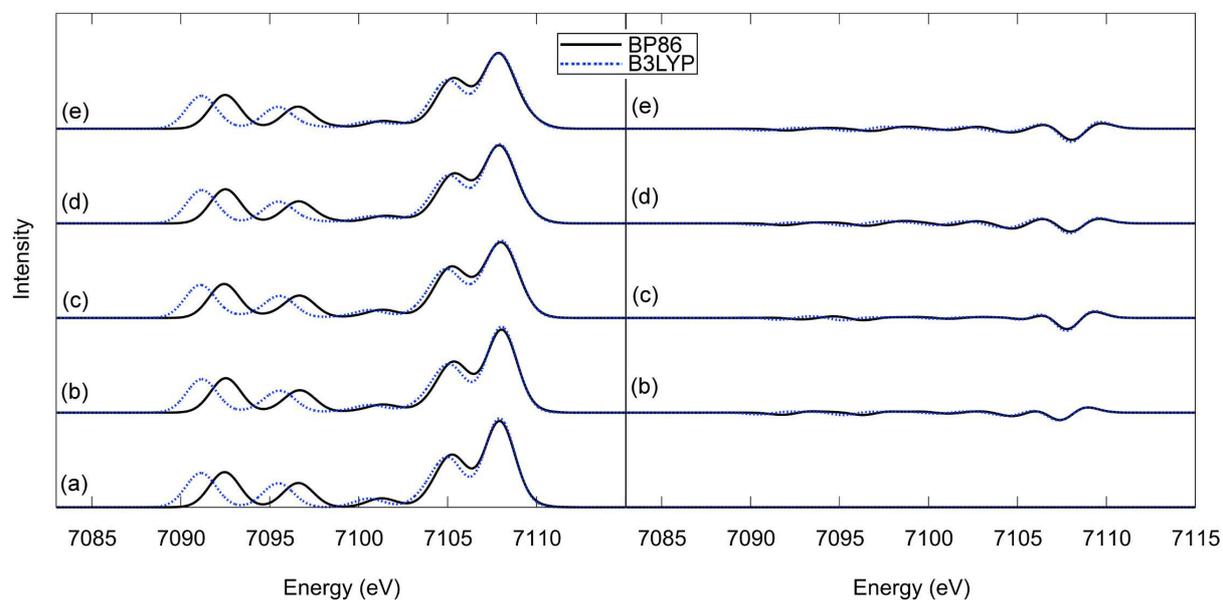


Figure 7: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 1.5 eV** (left) and corresponding calculated difference spectra compared to ferrocene (a) (right).

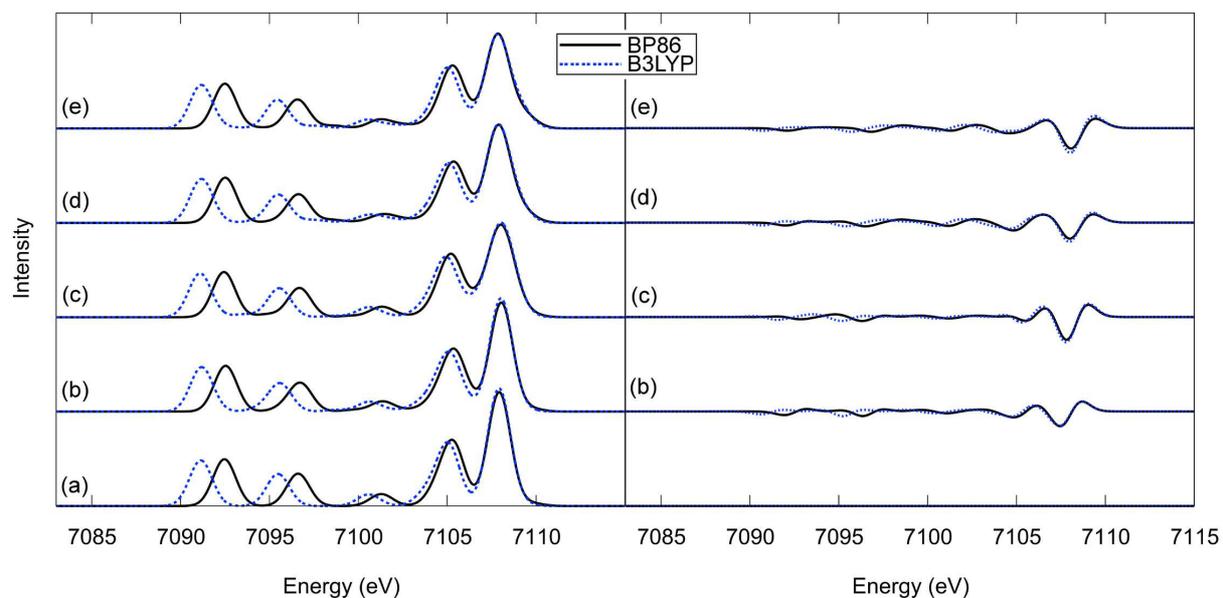


Figure 8: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 1.0 eV** (left) and corresponding calculated difference spectra compared to ferrocene (a) (right).

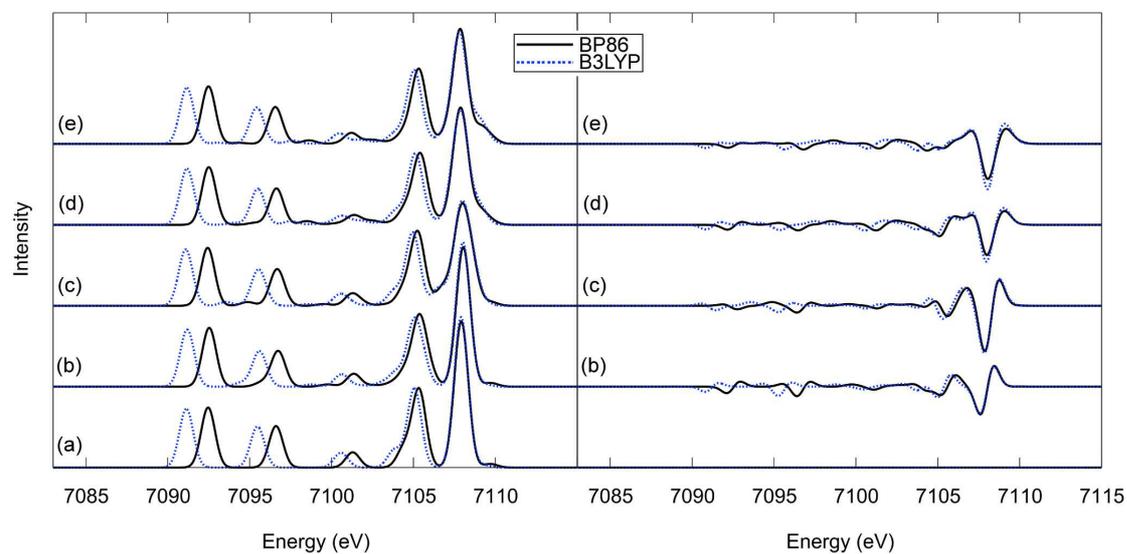
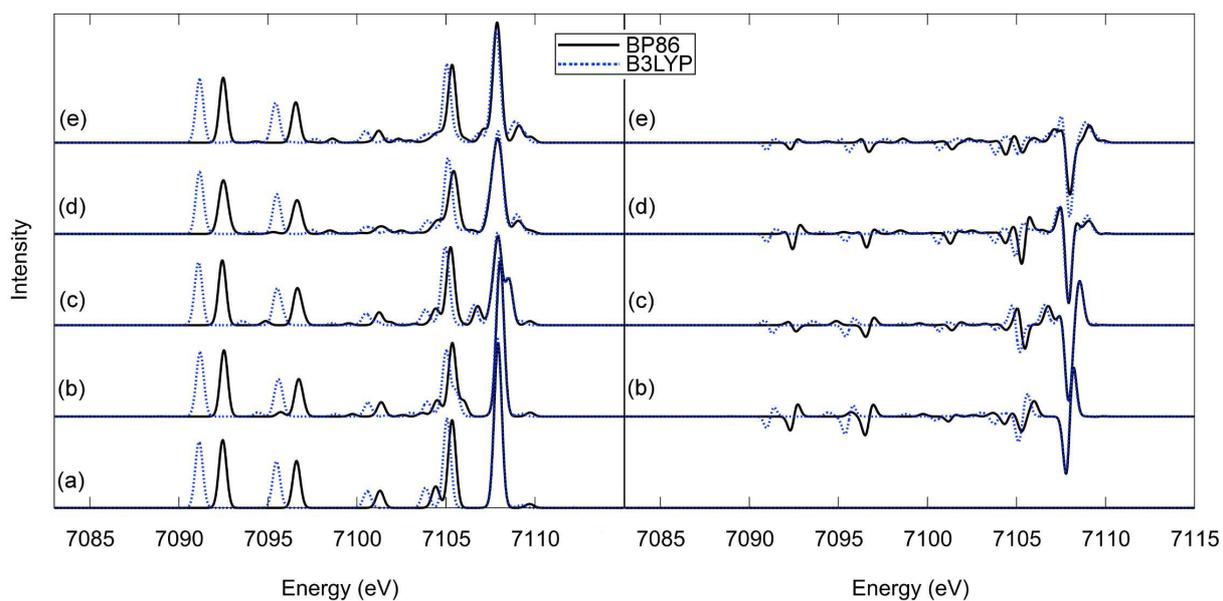


Figure 9: Calculated V2C-XES spectra plotted using Gaussians with a **FWHM of 0.5 eV** (left) and corresponding calculated difference spectra compared to ferrocene (a) (right).



3 Assignment of Calculated XAS and XES spectra

Figure 10: Calculated pre-edge HERFD-XANES (top) and V2C-XES (bottom) spectra for ferrocene (left) and **acetylferrocene** (right). The calculated spectra are shown for both BP86 (black solid line) and for B3LYP (blue dashed line). For the BP86 calculation, the individual transitions are included as red sticks. Alongside the calculated spectra, the corresponding MO diagrams, as obtained from a DFT calculation with the BP86 exchange–correlation functional, are shown.

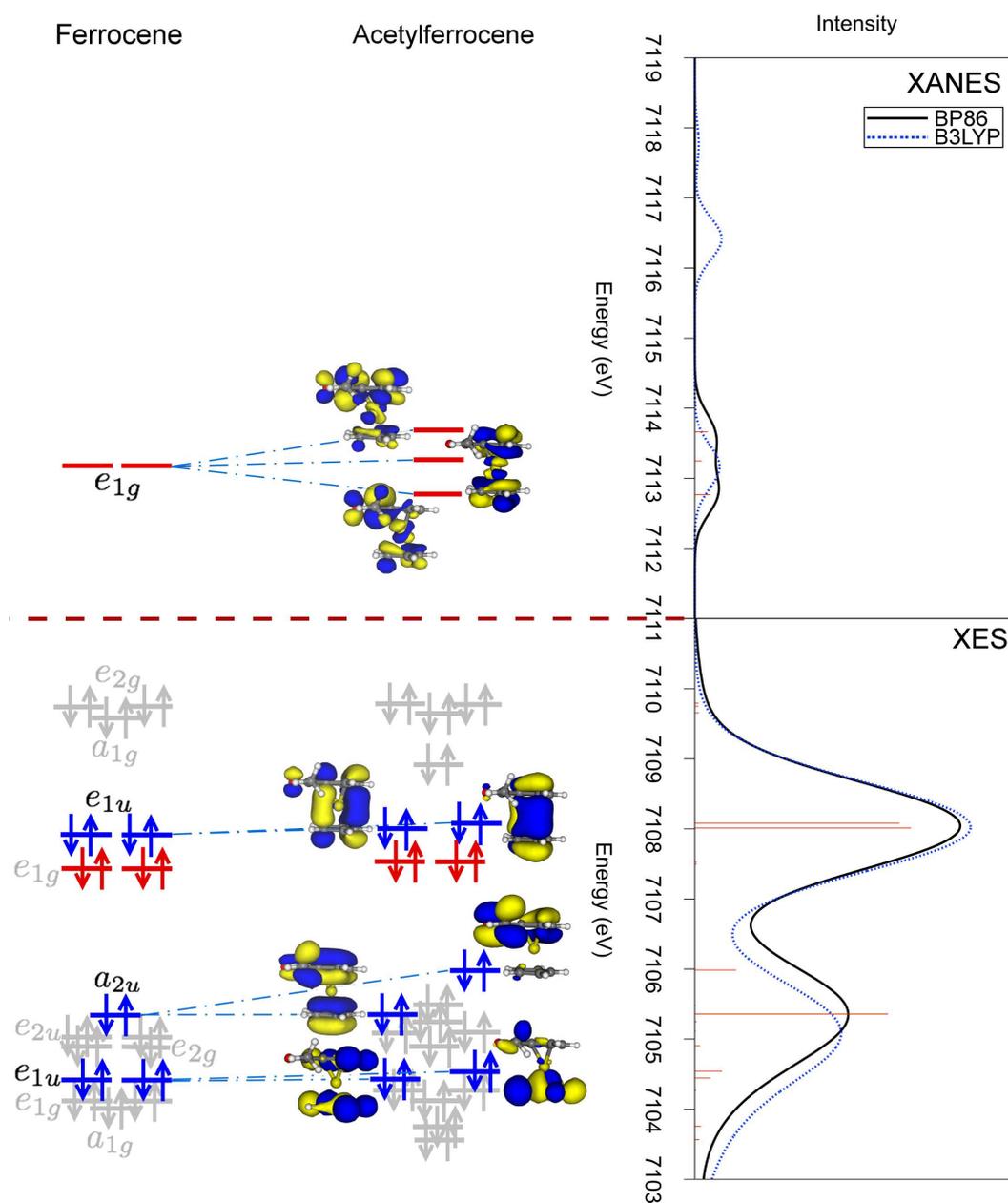


Figure 11: Calculated pre-edge HERFD-XANES (top) and V2C-XES (bottom) spectra for ferrocene (left) and **diisopropylferrocene** (right). The calculated spectra are shown for both BP86 (black solid line) and for B3LYP (blue dashed line). For the BP86 calculation, the individual transitions are included as red sticks. Alongside the calculated spectra, the corresponding MO diagrams, as obtained from a DFT calculation with the BP86 exchange–correlation functional, are shown.

