## Supplementary Material for:

## A new parameterization of the DFT/CIS method with applications to core-level spectroscopy

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Fig. S1: Fitting of CAM-B3LYP eigenvalue shift to SRC1-r2 eigenvalues for 3rd-row elements. A simple linear regression is used to obtain  $\Delta \varepsilon$  in Eq. (6). Values are in Hartree.



Fig. S2: Simulated XANES at the titanium K-edge, for the organotitanium complexes considered also in Fig. 6, using the same simulation parameters. As compared to CAM-B3LYP/CIS/def2-TZVPD, the TD-CAM-B3LYP/def2-TZVPD spectra require an additional shift of 76 eV to match experiment.



Fig. S3: Simulated XANES at the chlorine K-edge, for the organotitanium complexes considered also in Fig. 6, using the same simulation parameters. As compared to CAM-B3LYP/CIS/def2-TZVPD, the TD-CAM-B3LYP/def2-TZVPD spectra require an additional shift of 56 eV to match experiment.



Fig. S4: Simulated XES for  $CH_3Cl$  at the chlorine K-edge, using 200 states with a 1.0 eV Gaussian broadening. The CAM-B3LYP/CIS/def2-TZVPD spectrum is the same as in Fig. 7(b) and has been shifted to match experiment. The TD-CAM-B3LYP/def2-TZVPD spectrum requires a further shift of 45 eV.



Fig. S5: Simulated XES for  $H_2S$  at the sulfur K-edge, using 200 states with a 1.0 eV Gaussian broadening. The CAM-B3LYP/CIS/def2-TZVPD spectrum is the same as in Fig. 7(a) and has been shifted to match experiment. The TD-CAM-B3LYP/def2-TZVPD spectrum requires a further shift of 41 eV.