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# Computing L- and M-edge spectra using the DFT/CIS method with spin-orbit coupling†

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Modeling L-edge spectra at X-ray wavelengths requires consideration of spin-orbit splitting of the 2p orbitals. We introduce a low-cost tool to compute core-level spectra that combines a spin-orbit mean-field description of the Breit–Pauli Hamiltonian with nonrelativistic excited states computed using the semi-empirical density-functional theory configuration-interaction singles (DFT/CIS) method, within the state-interaction approach. Our version of DFT/CIS was introduced recently for K-edge spectra and includes a semi-empirical correction to the core orbital energies, significantly reducing *ad hoc* shifts that are typically required when time-dependent (TD-)DFT is applied to core-level excitations. In combination with the core/valence separation approximation and spin-orbit couplings, the DFT/CIS method affords semiquantitative L-edge spectra at CIS cost. Spin-orbit coupling has a qualitative effect on the spectra, as demonstrated for a variety of 3d transition metal systems and main-group compounds. The use of different active orbital spaces helps to facilitate spectral assignments. We find that spin-orbit splitting has a negligible effect on M-edge spectra for 3d transition metal species.

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## 1 Introduction

Near-edge X-ray absorption spectroscopy (XAS) is a powerful technique for investigating the electronic structure of molecules and materials, exhibiting atomic and even oxidation-state specificity. K-edge XAS corresponds to excitations originating from elemental 1s orbitals, the localized nature of which means that XAS serves as a reporter on the valence virtual orbitals.<sup>1–4</sup> This can be used to probe oxidation states<sup>5</sup> and orbital covalency<sup>6–8</sup> in transition-metal bonding. L- and M-edge spectra originate with transitions from 2p and 3p orbitals, respectively, that maintain elemental oxidation-state specificity.<sup>8–17</sup> This is especially useful for analyzing the electronic structure of transition metal compounds.<sup>6,18,19</sup> Probing the valence virtual orbitals enables determination of the local symmetry around a transition metal center,<sup>20–23</sup> and can serve as an indicator for strong correlation effects in the 3d orbitals.<sup>24</sup>

In moving beyond the standard technique of multiplet ligand-field theory,<sup>10,25–27</sup> the biggest obstacle to atomistic *ab initio* simulation of core-level spectra is the high cost of benchmark-quality quantum chemistry methods.<sup>3,28–32</sup> Time-dependent density functional theory (TD-DFT) can be applied to much larger systems,<sup>33–37</sup> and for X-ray spectroscopy it often

affords accurate results for peak splittings.<sup>38</sup> However, substantial absolute shifts are typically required in order to match experiment (*e.g.*, ~20 eV for the L-edge of 3d transition metals),<sup>39</sup> even if these shifts amount to only a few percent of the core-to-valence excitation energies. These shifts are primarily artifacts of differential self-interaction error (SIE) between compact core and delocalized valence orbitals,<sup>40–42</sup> as evidenced by improved results as the fraction of exact exchange is increased.<sup>39,43–45</sup> SIE artifacts are also present in the “real-time” approach to TD-DFT,<sup>35</sup> which is also subject to contamination by continuum states.<sup>35,37,46–48</sup>

To circumvent the need for large empirical shifts, specialized functionals have been developed for core-level spectroscopy,<sup>43,49–52</sup> and modified forms of linear response theory have also been suggested.<sup>53,54</sup> Alternatively, we have reported a new implementation<sup>55</sup> of the so-called DFT/CIS method.<sup>56</sup> This approach uses the formalism of configuration interaction with single substitutions (CIS) but incorporates molecular orbitals (MOs) and one-electron energy levels from Kohn–Sham DFT. A few empirical parameters are used to avoid double-counting of electron correlation effects.<sup>55,56</sup> Our implementation extends the original DFT/CIS method to core-level spectroscopy using the core/valence separation (CVS) approximation.<sup>30,35</sup> An empirical shift of the 1s orbital energies, based on atomic calculations with scalar relativistic corrections, is used to reduce differential SIE effects, with a concomitant reduction in the magnitude of the empirical shifts that are required to reproduce experimental spectra.<sup>55</sup>

In comparison to K-edge XAS, L-edge spectroscopy has several desirable characteristics including greater intensity

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because the most interesting transitions are dipole-allowed (e.g.,  $2p \rightarrow 3d$ ),<sup>57</sup> whereas  $1s \rightarrow 3d$  transitions that also probe metal–ligand covalency appear as relatively weak pre-edge features<sup>58–60</sup> that may be better probed by K-shell fluorescence spectroscopy.<sup>58</sup> L-edge linewidths are reduced due to longer core-hole lifetimes, as compared to K-edge transitions,<sup>10</sup> making L-edge XAS a formidable experimental tool. M-edge spectroscopy at extreme ultraviolet (XUV) wavelengths shares the same selection rules and is now accessible *via* tabletop instruments<sup>61–63</sup> with ultrafast time resolution,<sup>13–16,61–68</sup> providing a sensitive probe of transition metal spin and oxidation states.<sup>69</sup>

Theoretical simulation of L- and M-edge spectra is challenging due to spin–orbit coupling (SOC) that splits the  $2p$  and  $3p$  orbitals into states with  $J = 1/2$  or  $J = 3/2$ .<sup>39,70</sup> The present work extends our new DFT/CIS method to include SOC effects, without further parameterization. Results are presented for a variety of  $3d$  transition metal systems and some main-group compounds, indicating favorable agreement with experiment using only modest empirical shifts.

## 2 Theory

### 2.1 DFT/CIS method

The DFT/CIS formalism is similar to that of the CIS method,<sup>37,71</sup> with a few modifications necessitated by the use of Kohn–Sham orbitals. We use  $\psi_i, \psi_j, \dots$  to denote occupied MOs and  $\psi_a, \psi_b, \dots$  for virtual MOs, with indices  $r, s, \dots$  referring to arbitrary (occupied or virtual) MOs. We take these to be eigenfunctions of the Fock operator,

$$\hat{F}\psi_r = \varepsilon_r \psi_r, \quad (1)$$

with orbital energy levels  $\varepsilon_r$ .

Let  $|\Psi_0\rangle$  denote the reference determinant that solves the ground-state self-consistent field (SCF) problem, with ground-state energy  $E_0$ . Let  $|\Psi_i^a\rangle$  indicate a singly substituted Slater determinant with respect to that reference state. Using a closed-shell formalism for simplicity, diagonal matrix elements of the Hamiltonian in the singly substituted basis are<sup>71</sup>

$$\langle \Psi_i^a | \hat{H} | \Psi_i^a \rangle = E_0 + \varepsilon_a - \varepsilon_i + 2(\psi_i \psi_a | \psi_i \psi_a) - (\psi_i \psi_i | \psi_a \psi_a). \quad (2)$$

The off-diagonal elements are

$$\langle \Psi_i^a | \hat{H} | \Psi_j^b \rangle = 2(\psi_i \psi_a | \psi_j \psi_b) - (\psi_i \psi_j | \psi_a \psi_b). \quad (3)$$

Two-electron integrals in these equations are expressed using Mulliken notation.<sup>71</sup> In the CIS method, Brillouin's theorem ensures that

$$\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = 0. \quad (4)$$

Grimme introduced the first version of DFT/CIS,<sup>56</sup> based on MOs obtained using the B3LYP functional. For that reason, we refer to Grimme's original method as "B3LYP/CIS". In attempting to adapt it for core-level spectroscopy, we found that the parameterization was not appropriate for elements beyond the second row of the periodic table (*i.e.*, beyond Ne).

As such, we introduced a new parameterization based on the CAM-B3LYP functional,<sup>72</sup> a range-separated hybrid that is better suited to TD-DFT applications because it mitigates severe underestimation of Rydberg and other charge-transfer transitions.<sup>72–76</sup> We refer to this new parameterization as "CAM-B3LYP/CIS".<sup>55</sup> It was originally parameterized for use with the def2-TZVPD basis set,<sup>77</sup> although the results are not strongly sensitive to that choice and smaller basis sets can be used.<sup>55</sup>

For CAM-B3LYP/CIS we leave eqn (3) and (4) unchanged, following Grimme's prescription,<sup>56</sup> even though Brillouin's theorem is not generally satisfied by Kohn–Sham MOs. However, we modify the diagonal matrix elements in eqn (2) to obtain

$$\langle \Psi_i^a | \hat{H} | \Psi_i^a \rangle = E_0 + \varepsilon_a - \varepsilon_i + 2c_2 J_{ia} - c_1 K_{ia} - \Delta\varepsilon_i \quad (5)$$

where  $c_1$ ,  $c_2$ , and  $\Delta\varepsilon_i$  are empirical parameters (see below) and

$$J_{ia} = (\psi_i \psi_a | \psi_i \psi_a) \quad (6a)$$

$$K_{ia} = (\psi_i \psi_i | \psi_a \psi_a). \quad (6b)$$

These expressions are intended to be used with Kohn–Sham orbitals  $\{\psi_r\}$  and energy levels  $\{\varepsilon_r\}$ . Unlike the analogous TD-DFT linear-response equations,<sup>37</sup> there is no exchange–correlation kernel in the matrix elements defined in eqn (5). Recent work has shown that the effect of this kernel is negligible in core-level TD-DFT calculations.<sup>78</sup> Even for valence excitations, the parameterization of DFT/CIS means that it works well without this kernel.<sup>55,56</sup>

Parameters  $c_1 = 0.525$  and  $c_2 = 0.850$  in eqn (5) were determined<sup>55</sup> using a subset of QuestDB, a benchmark data set of excitation energies for small and medium-size molecules.<sup>79</sup> The correction  $\Delta\varepsilon_i$  in eqn (5) is an overall shift, which is different for the first two rows of the periodic table than it is for heavier atoms. Specifically,<sup>55</sup>

$$\Delta\varepsilon_i = \begin{cases} 0.0250\varepsilon_i & \text{if } |\varepsilon_i| \leq 102E_h \\ 0.0083\varepsilon_i - 1.4209E_h & \text{if } |\varepsilon_i| > 102E_h \end{cases}. \quad (7)$$

(Note that  $\varepsilon_i < 0$ .) This was determined in order to shift CAM-B3LYP  $1s$  orbital energies  $\{\varepsilon_i\}$  into agreement with those obtained using the short-range corrected (SRC) functional known as SRC1.<sup>43</sup> That functional was specifically parameterized to obtain K-edge spectra with experimental accuracy and uses a large fraction of exact exchange on a very short length scale ( $< 1 \text{ \AA}$ ), in order to reduce SIE for the core states. The correction  $\Delta\varepsilon_i$  reduces the inherent errors in core-level eigenvalues obtained from CAM-B3LYP and represents an alternative to shifting spectra to match experiment, as would be required in a XAS calculation using TD-CAM-B3LYP. Absent the  $\Delta\varepsilon_i$  correction,  $1s$  energy levels from CAM-B3LYP are less strongly bound as compared to the corresponding SRC1 values and this discrepancy is adjusted *via* eqn (7).

For elements H through Ne, corresponding to  $|\varepsilon_i| \leq 102E_h$ , the shift introduced in eqn (7) has essentially the same numerical value as the shift used by Grimme in B3LYP/CIS,<sup>56</sup> despite a rather different parameterization and functional form.<sup>55</sup>



This agreement reflects that fact that core-level eigenvalues from both B3LYP and CAM-B3LYP underestimate excitation energies for XAS by approximately the same amount. However, the CAM-B3LYP/CIS parameterization works for third-row elements ( $|\varepsilon_i| > 102E_h$ ), whereas Grimme's parameterization does not.

Our choice for the modifications in eqn (5) is motivated by the observation that the majority of the correction in B3LYP/CIS comes from the  $c_1$  parameter. Grimme introduced an alternative form for the shift in  $\langle \Psi_i^a | \hat{H} | \Psi_i^a \rangle$  that involves Coulomb integrals and is more difficult to evaluate.<sup>55</sup> This correction was intended to better describe Rydberg and charge-transfer states where the exchange integral  $K_{ia}$  is smaller than it is for localized valence excitations. However, the use of a range-separated hybrid functional means that CAM-B3LYP/CIS is inherently better equipped to deal with those types of transitions. Thus, we simplify the form of the empirical shift ( $\Delta\varepsilon_i$ ) by modernizing the DFT functional.

## 2.2 Spin-orbit coupling

Relativistic effects are present in all core-level spectra but in the context of electronic structure calculations they can be split into two categories: scalar and spin-orbit.<sup>80</sup> The latter do not play a significant role in K-edge spectroscopy because the 1s orbitals are energetically isolated. So long as peak splittings

become sufficiently large. However, variational treatment of SOC adds significantly to the complexity of the formalism and increases the computational cost by perhaps an order of magnitude, relative to a nonrelativistic calculation.<sup>87</sup> Perturbative treatment of SOC is more affordable and is sufficiently accurate for the first few rows of the periodic table.<sup>88</sup> This approach, which is the one adopted here, involves construction of the Breit–Pauli Hamiltonian using nonrelativistic (spin-orbit-free) wave functions as basis states.

**2.2.1 Breit–Pauli Hamiltonian.** We incorporate SOC as off-diagonal coupling matrix elements between eigenstates of the nonrelativistic (Coulomb electronic) Hamiltonian, in what has been called the “state-interaction” approach.<sup>89</sup> In the present work, the nonrelativistic basis states are obtained from DFT/CIS calculations that include a large number of singlet and triplet core-excited states. We denote the DFT/CIS or TD-DFT state energies as  $E(S_n)$  for the singlet state  $S_n$  and  $E(T_n^{(M)})$  for the triplet state  $T_n$ , with multiplet components ( $M \in \{-1, 0, +1\}$ ) that are degenerate in the DFT/CIS calculations:

$$E(T_n^{(-1)}) = E(T_n^{(0)}) = E(T_n^{(+1)}). \quad (8)$$

Within the state-interaction picture, the Breit–Pauli Hamiltonian incorporates SOC between the aforementioned spin-orbit-free basis states, and can be written in matrix form as

$$\mathbf{H}_{\text{BP}} = \begin{pmatrix} E(S_0) & 0 & \cdots & V(S_0, T_n^{(-1)}) & V(S_0, T_n^{(0)}) & V(S_0, T_n^{(+1)}) \\ 0 & E(S_1) & \cdots & V(S_1, T_n^{(-1)}) & V(S_1, T_n^{(0)}) & V(S_1, T_n^{(+1)}) \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ V(T_n^{(-1)}, S_0) & V(T_n^{(-1)}, S_1) & \cdots & E(T_n^{(-1)}) & 0 & 0 \\ V(T_n^{(0)}, S_0) & V(T_n^{(0)}, S_1) & \cdots & 0 & E(T_n^{(0)}) & 0 \\ V(T_n^{(+1)}, S_0) & V(T_n^{(+1)}, S_1) & \cdots & 0 & 0 & E(T_n^{(+1)}) \end{pmatrix}. \quad (9)$$

and other spectral features are accurate, K-edge spectra can simply be shifted to account for relativistic effects, using scalar relativistic corrections for the isolated atoms that can be computed, once and for all, across the periodic table.<sup>81–83</sup>

This is not the case for L-edge spectra, however, where SOC splits the triply degenerate 2p orbitals into one  $2p_{1/2}$  orbital and two  $2p_{3/2}$  orbitals. SOC leads to mixing of spin-orbit-free states with different multiplicities, resulting in two peaks at the L-edge: the  $L_2$  peak (originating from the  $2p_{1/2}$  orbital) and the  $L_3$  peak (from the  $2p_{3/2}$  orbitals). An analogous splitting of the 3p orbitals is observable in M-edge spectroscopy.

SOC effects can be incorporated using either variational or perturbative methods.<sup>80</sup> Variational treatments include the zeroth-order regular approximation (ZORA),<sup>84</sup> the Douglass–Kroll–Hess (DKH) method,<sup>85</sup> and the exact two-component (X2C) approach.<sup>86</sup> These methods incorporate spin-orbit operators into the wave function optimization, which is the formally more rigorous approach and is necessary when SOC effects

In principle, one might add scalar relativistic corrections to the diagonal matrix elements in  $\mathbf{H}_{\text{BP}}$ . For the  $L_{2,3}$ -edges of silicon and sulfur, such corrections are smaller than 0.05 eV.<sup>81</sup> For 3d transition metals considered here, these corrections range from 0.6–2.1 eV,<sup>81</sup> which is small compared to shifts that are applied to match experiment.

Off-diagonal matrix elements  $V(T_n^{(M)}, S_m)$ , containing the SOC interaction between spin-orbit-free states  $T_n^{(M)}$  and  $S_m$ , are evaluated here using the spin-orbit mean-field (SOMF) approximation.<sup>90,91</sup> These couplings are matrix elements of the Breit–Pauli spin-orbit operator,<sup>32,90–95</sup>

$$\hat{H}_{\text{SO}} = \frac{\alpha}{2} \sum_k^{\text{elec}} \left[ \hat{\mathbf{h}}_k^{\text{SSO}} \cdot \hat{\mathbf{s}}_k - \sum_{l \neq k}^{\text{elec}} \hat{\mathbf{h}}_{k,l}^{\text{SSO}} \cdot (\hat{\mathbf{s}}_k + 2\hat{\mathbf{s}}_l) \right]. \quad (10)$$

Here,  $\alpha$  is the fine-structure constant and  $\hat{\mathbf{s}}_k$  is the spin angular momentum for electron  $k$ . The one-electron operator  $\hat{\mathbf{h}}_k^{\text{SSO}}$  in



eqn (10) is the “spin-same-orbit” coupling, given by

$$\hat{\mathbf{h}}_k^{\text{SSO}} = \sum_K^{\text{nucl}} \frac{Z_K(\mathbf{r}_k - \mathbf{R}_K) \times \mathbf{p}_k}{\|\mathbf{r}_k - \mathbf{R}_K\|^3} \quad (11)$$

where  $\mathbf{r}_k$  and  $\mathbf{R}_K$  are the coordinates of electron  $k$  and nucleus  $K$ , respectively, with the latter having atomic number  $Z_K$ . One may recognize  $(\mathbf{r}_k - \mathbf{R}_K) \times \mathbf{p}_k$  in eqn (11) as the orbital angular momentum about nucleus  $K$ . The two-electron operator  $\hat{\mathbf{h}}_{k,l}^{\text{SOO}}$  in eqn (10) represents “spin-other-orbit” coupling,

$$\hat{\mathbf{h}}_{k,l}^{\text{SOO}} = \frac{(\mathbf{r}_k - \mathbf{r}_l) \times \mathbf{p}_l}{\|\mathbf{r}_k - \mathbf{r}_l\|^3}. \quad (12)$$

This form invokes the SOMF approximation,<sup>32,90–95</sup> which simplifies calculation of the coupling matrix elements insofar as explicit two-electron integrals are not required. Within this approximation, matrix elements of  $\hat{H}_{\text{SO}}$  can be evaluated using only one-electron integrals and transition density matrices.<sup>95</sup>

The formalism introduced above can be used with either DFT/CIS or TD-DFT.<sup>95</sup> Matrix elements  $\langle \Psi(S, M_S) | \hat{H}_{\text{SO}} | \Psi'(S', M'_S) \rangle$  in the basis of nonrelativistic states afford the off-diagonal terms in the matrix  $\mathbf{H}_{\text{BP}}$ . In the present work, these states are either singlets ( $S = 0 = M_S$ ) or triplets ( $S = 1$  and  $M_S \in \{-1, 0, +1\}$ ). Diagonalization of  $\mathbf{H}_{\text{BP}}$  in eqn (9) affords the coupled target states.

**2.2.2 Oscillator strengths.** To compute spectra we need oscillator strengths for the coupled states. We start from the transition dipole moments in the nonrelativistic basis, which have the form

$$\mu_{S, M_S; S', M'_S}^\alpha = \langle \Psi(S, M_S) | \hat{\mu}_\alpha | \Psi'(S', M'_S) \rangle \quad (13)$$

where  $\alpha \in \{x, y, z\}$  and  $\hat{\mu}_\alpha = e\hat{\alpha}$  is the  $\alpha$  component of the dipole moment operator. Suppressing the spin quantum numbers ( $S, M_S$ ) for brevity, the states  $|\Psi\rangle$  and  $|\Psi'\rangle$  in eqn (13) range over the SCF ground state  $|\Psi_0\rangle$  and all of the DFT/CIS or TD-DFT excited states. Each of the excited states is a CIS-style linear combination of singly substituted Slater determinants,

$$|\Psi\rangle = \sum_{ia} x_{ia} |\Psi_i^a\rangle. \quad (14)$$

This is reminiscent of the Tamm–Dancoff approximation (TDA) in TD-DFT,<sup>37,96</sup> which is implicit in the DFT/CIS approach. The requisite matrix elements in eqn (13) are evaluated using the Slater–Condon rules, in what has been called a “pseudo-wave function” approach to computing transition dipole moments between TD-DFT excited states.<sup>97–100</sup> This treatment is consistent with how the Breit–Pauli Hamiltonian has long been used in TD-DFT calculations.<sup>101–103</sup> Formally speaking, state-to-state transition dipoles require quadratic rather than linear response theory,<sup>100,104</sup> but the pseudo-wave function method is consistent with invocation of the TDA.

The nonrelativistic transition dipole moments in eqn (13) vanish if  $S \neq S'$ , and they are identical for all values of  $M_S$  within a given spin multiplet. However, we retain the indices  $M_S$  and  $M'_S$  in eqn (13) to clarify that the dimension of the matrix  $\mu^\alpha$  matches the dimension of  $\mathbf{H}_{\text{BP}}$ . The former can then

be transformed into the coupled SOMF basis, using the matrix  $\mathbf{U}_{\text{BP}}$  that diagonalizes  $\mathbf{H}_{\text{BP}}$ :

$$\tilde{\mu}^\alpha = \mathbf{U}_{\text{BP}}^\dagger \mu^\alpha \mathbf{U}_{\text{BP}}. \quad (15)$$

The matrix  $\tilde{\mu}^\alpha$  contains the  $\alpha$  components of the transition dipole moments between SOC states, including the ground state. The oscillator strength for  $|0\rangle \rightarrow |n\rangle$  excitation, from the ground state to coupled state  $|n\rangle$ , is given by<sup>37</sup>

$$f_{0 \rightarrow n} = \frac{2m_e(E_n - E_0)}{3e^2\hbar^2} \sum_{\alpha \in \{x, y, z\}} \left( \tilde{\mu}_{0,n}^\alpha \right)^2. \quad (16)$$

## 3 Computational details

### 3.1 Implementation

The DFT/CIS method has been implemented in the Q-Chem program,<sup>105</sup> and is available starting from v. 6.2.<sup>55</sup> SOC matrix elements have been implemented in Q-Chem by Krylov and co-workers,<sup>32,92–95</sup> see ref. 95 for the TD-DFT implementation.

Core-level spectra without SOC are computed using either DFT/CIS or TD-DFT within the CVS approximation.<sup>35</sup> Subsequently, in a post-processing step, these spin-orbit-free states are transformed to the coupled basis by diagonalizing  $\mathbf{H}_{\text{BP}}$  in eqn (9). For this, we have written a Python code called pySETSOC.<sup>106</sup> This program extracts SOC terms from the Q-Chem output, along with state-to-state transition dipole moments that are computed within the pseudo-wave function approach. It then constructs and diagonalizes  $\mathbf{H}_{\text{BP}}$  and computes oscillator strengths for the coupled states. The pySETSOC program can be applied to Q-Chem outputs from TD-DFT or DFT/CIS, using the pseudo-wave function approximation to evaluate the requisite state-to-state transition dipole matrix elements as discussed in Section 2.2.2. The pySETSOC program will also read the output from restricted active-space (RAS)-CI methods,<sup>94,107</sup> although that functionality is not used here.

Finally, spectra are plotted using either Lorentzian or Gaussian broadening. The former is probably more appropriate for core-level spectra that are subject to lifetime broadening arising from the core hole. In many cases, we use a Lorentzian function with a full width at half-maximum (FWHM) of 0.3 eV. Although chosen empirically, this is roughly consistent with 2p core-hole states having natural line widths of  $\sim 0.1$  eV.<sup>108,109</sup>

### 3.2 Core/valence separation

The CVS approximation extends standard excited-state methods to core-level states by eliminating the amplitudes  $x_{ia}$  [eqn (14)] associated with all but a small number of occupied MOs,  $\psi_i$ .<sup>33–35</sup> This dramatically reduces computational cost by eliminating valence excited states, so that core-to-valence excitations appear as the lowest energy states in the spectrum. Furthermore, the CVS approximation decouples these states from the continuum, which is otherwise problematic (e.g., in real-time approaches).<sup>35,37</sup> Finally, the CVS approximation enables separation of K-, L-, and M-edge spectra in cases where different elemental edges might overlap with one another.





In such situations, peak assignments can be made by comparing DFT/CIS or TD-DFT spectra using different active-space approximations.

All calculations reported here invoke the CVS approximation, which affords negligible errors for K- and L-edge spectra.<sup>32,110</sup> For the L-edge spectra presented here, the occupied orbital active space consists of the 2p orbitals for the element in question along with the entire virtual space. In molecules containing more than one atom with the same atomic number, we include all of the 2p orbitals for that element. M-edge spectra are computed using the analogous procedure with 3p orbitals in the active space. For most calculations, we use 200 singlet and 200 triplet (nonrelativistic) basis states to construct  $\mathbf{H}_{\text{BP}}$ .

Conventional TD-DFT calculations reported here also use the CVS approximation as well as the TDA. This is consistent with the CIS-style matrix elements used in DFT/CIS, and with the CIS-style pseudo-wave function method that is used to compute oscillator strengths. Previous work suggests that the TDA has a negligible effect on core-level spectra.<sup>35,111</sup>

### 3.3 Functionals and basis sets

DFT/CIS calculations were performed using CAM-B3LYP,<sup>72</sup> for which the method was parameterized in previous work.<sup>55</sup> The B3LYP-based parameterization introduced by Grimme is not used here, because CAM-B3LYP/CIS is more suitable for computing core-level spectra.

As a point of comparison, conventional TD-DFT calculations are reported using the functionals B3LYP, CAM-B3LYP,<sup>72</sup> and SRC1-r2.<sup>33,43</sup> The latter is specifically parameterized for K-edge spectra of third-row elements, using a large fraction of exact exchange (87%) on a very short length scale ( $\lesssim 1$  Å). Although TD-SRC1 is quite accurate for K-edge spectra,<sup>33,35,43,52</sup> it has not yet been tested for L-edge spectra.

CAM-B3LYP/CIS parameters were developed based on calculations using def2-TZVPD.<sup>77</sup> That basis set should be sufficient to converge TD-DFT excitation energies,<sup>37,112–116</sup> but in fact CAM-B3LYP/CIS provides satisfactory results in smaller basis sets also.<sup>55</sup> Except where specified otherwise, the def2-TZVPD basis set is used for all calculations.

## 4 Results and discussion

### 4.1 Functional and basis-set effects

The effect of exact exchange on K-edge TD-DFT calculations is well documented,<sup>39,43–45</sup> with larger fractions generally affording more accurate results in the sense that smaller absolute shifts are required. This is primarily due to larger SIE associated with the compact 1s orbital, as compared to the relatively delocalized valence virtual orbitals. Core-to-valence excitations can also be considered to manifest a certain type of charge transfer, whose excitation energy is dramatically underestimated by functionals that lack correct asymptotic behavior.<sup>37,117–119</sup> Although the latter problem is ameliorated as the fraction of exact exchange is increased, this must be balanced against a semilocal correlation functional that is not designed for fully

nonlocal Hartree–Fock exchange. Accuracy may be significantly degraded when the fraction of exact exchange rises above 50%.<sup>120</sup> Besley and co-workers solved this problem by introducing SRC functionals with unusually large fractions of exact exchange ( $>50\%$ ) on very short length scales.<sup>43</sup> The range-separation scheme and the fractions of exact exchange that are used in these SRC functionals were determined in order to match experimental K-edge excitation energies and these functionals have not previously been examined for L-edge spectra.

Fig. 1 presents conventional TD-DFT results for the Ti  $L_{2,3}$ -edge spectrum of  $\text{TiCl}_4$  using several different functionals, in comparison to CAM-B3LYP/CIS calculations and to experiment.<sup>121</sup> All calculations include SOC so that distinct  $L_2$  and  $L_3$  edges are apparent, separated by  $\sim 12$  eV. Conventional TD-B3LYP and TD-CAM-B3LYP calculations underestimate the  $2p \rightarrow$  valence excitation energies by  $\sim 15$  eV, while CAM-B3LYP/CIS and TD-SRC1-r2 underestimate them by only 5.0 eV (TD-SRC1-r2) or 6.8 eV (CAM-B3LYP/CIS). The fact that all four methods underestimate the excitation energies with respect to experiment suggests that differential SIE remains significant even for the 2p orbitals. Note that the core orbital correction  $\Delta\epsilon_i$  that is used in CAM-B3LYP/CIS was parameterized using 1s orbital energies yet continues to work reasonably well for excitations from the 2p orbitals, as we observed previously.<sup>55</sup>

Notably, relative intensities of  $L_2$  versus  $L_3$  are different between theory and experiment. The same artifact has been noted previously in real-time TD-DFT calculations of the same spectrum.<sup>122</sup> Correct intensities are obtained using the ZORA

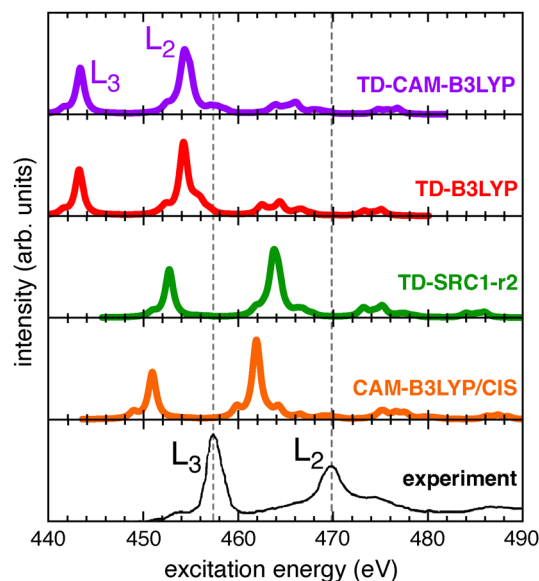
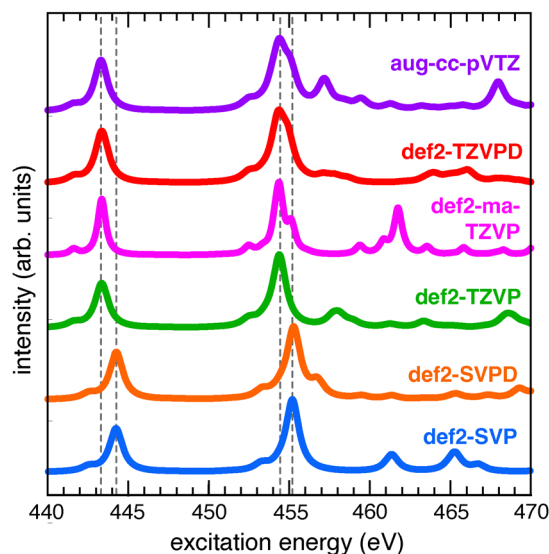


Fig. 1 Direct relation between the accuracy of TD-DFT calculations and the fraction of exact exchange, for Ti  $L_{2,3}$ -edge spectra of  $\text{TiCl}_4$ . Shown are four different TD-DFT approaches along with CAM-B3LYP/CIS, in comparison to an experimental spectrum from ref. 121. All calculations used the def2-TZVPD basis set and include 200 singlet and 200 triplet basis states. Individual transitions were broadened using a Lorentzian function with FWHM = 0.3 eV.





**Fig. 2** Basis set effects on the Ti  $L_{2,3}$ -edge spectrum of  $\text{TiCl}_4$ , computed at the CAM-B3LYP/CIS + SOC level as described in Fig. 1. Spectra are normalized separately so that the main feature (around 455 eV) has the same intensity in each case. Vertical dashed lines are guides to the eye, aligned with the most intense  $L_2$  and  $L_3$  features at the top and at the bottom.

method in conjunction with relativistic basis sets,<sup>123,124</sup> pointing to a limitation of the present approach.

Fig. 2 documents basis-set effects on this  $\text{TiCl}_4$  spectrum. The position of both the  $L_2$  and  $L_3$  peaks is unchanged amongst the def2-TZVP, def2-TZVPD and aug-cc-pVTZ basis sets. A shoulder on the higher-energy side of the  $L_2$  peak becomes progressively more pronounced as one goes from def2-SVPD to def2-TZVPD to aug-cc-pVTZ, but is absent when diffuse functions are omitted. The minimally augmented def2-ma-TZVP basis set,<sup>125</sup> which removes higher angular momentum diffuse functions from def2-TZVPD, exaggerates the peak splitting near 455 eV and predicts inconsistent intensities at higher energies, as compared to other basis sets. This suggests a role for the diffuse d functions that are present in def2-TZVPD and aug-cc-pVTZ, at least when it comes to lineshapes.

Peak excitation energies are a different matter. Using double- $\zeta$  rather than triple- $\zeta$  basis sets introduces a shift of about 1 eV in both the  $L_2$  and  $L_3$  features but the  $L_{2,3}$  splitting is essentially identically in all of the basis sets tested, as documented in Table 1. In our view, 1 eV shifts in the absolute

excitation energies are of no consequence at X-ray wavelengths, where the empirical shifts required to match experiment are 5–7 eV at a minimum. Thus, smaller basis seem to suffice for excitation energies, even while converged lineshapes require diffuse functions.

## 4.2 Benchmarking $L_{2,3}$ energies

Fig. 3 shows experimental  $X(2p) \rightarrow$  valence excitation spectra for  $\text{TiCl}_4$ ,<sup>121</sup>  $\text{SiCl}_4$ ,<sup>126</sup> and  $\text{CrO}_2\text{Cl}_2$ ,<sup>127</sup> at the  $L_{2,3}$ -edge of the central atom ( $X = \text{Ti}, \text{Si},$  or  $\text{Cr}$ ), along with CAM-B3LYP/CIS + SOC calculations. Splitting of the  $L_{2,3}$  features is rather dramatic for  $\text{TiCl}_4$  (Fig. 3a), highlighting the fact that a spin-orbit-free spectrum contains only one bright feature and is qualitatively incorrect. Additional features in the  $L_{2,3}$  spectrum correspond to splitting of the 3d orbitals into  $t_2$  and  $e$  sets. Even with SOC, however, intensities of the  $L_2$  and  $L_3$  peaks are inverted relative to experiment, as noted in Section 4.1.

Spectra of  $\text{SiCl}_4$  at the Si  $L_{2,3}$ -edge are more complicated (Fig. 3b). One explanation is that the Si(2p) orbitals are less localized as compared to Ti(2p) orbitals, and thus undergo more mixing with the ligand orbitals. Splitting of the Si( $2p_{3/2}$ ) and Si( $2p_{1/2}$ ) features is very small,<sup>126</sup> hence the difference between SOC and nonrelativistic spectra is not as striking in this case as it was for  $\text{TiCl}_4$ . For  $\text{CrO}_2\text{Cl}_2$  (Fig. 3c), inclusion of SOC is once again necessary to obtain a spectrum that is even qualitatively correct. The  $L_2$  and  $L_3$  edges are well separated, as they were in  $\text{TiCl}_4$ , and the low symmetry  $C_{2v}$  environment leads to distinctive peak shapes.

Overall, the Breit–Pauli formalism, combined with the SOMF approximation, works rather well for reproducing the L-edge spectra of these third-row elements. Spectral features contain important information about the nature of the valence virtual orbitals that can be connected to features in the experimental spectra by means of the DFT/CIS + SOC calculations.

Table 2 compares the accuracy of CAM-B3LYP/CIS and conventional TD-DFT, with SOC included in either case and compared to experimental transition energies.<sup>121,126–131</sup> CIS + SOC results are also tabulated, in order to set a baseline. These L-edge results follow the same trend as the K-edge values that we reported previously.<sup>55</sup> Specifically, both the TD-B3LYP and TD-CAM-B3LYP methods underestimate the excitation energies in all cases. This indicates that range separation alone is insufficient to correct the excitation energies, as the errors originate in 2p eigenvalues that are insufficiently bound. The TD-SRC1-r2 method performs better, despite being parameterized for main-group K-edge spectra, because the large fraction of exact exchange at ultrashort range mitigates the eigenvalue problem to some extent. Finally, CAM-B3LYP/CIS + SOC exhibits a mean absolute error (MAE) that is very similar to TD-SRC1-r2 + SOC. This is expected since the  $\Delta\epsilon_i$  correction in the former was based on SRC1-r2 orbital energies.

Mean errors in Table 2 provide an additional indication as to the source of the errors. The CIS method, for example, is SIE-free but lacks complete orbital relaxation and as a result the errors are strictly positive, with a mean error of 10.6 eV. On the other hand, the TD-B3LYP and TD-CAM-B3LYP errors are

**Table 1** Basis set effects for CAM-B3LYP/CIS + SOC calculations at the Ti  $L_{2,3}$ -edge of  $\text{TiCl}_4$

| Basis        | Exc. energy (eV) |       | Splitting (eV) |
|--------------|------------------|-------|----------------|
|              | $L_3$            | $L_2$ |                |
| def2-SVP     | 444.2            | 455.2 | 11.0           |
| def2-SVPD    | 444.2            | 455.3 | 11.0           |
| def2-TZVP    | 443.4            | 454.4 | 11.0           |
| def2-ma-TZVP | 443.4            | 454.4 | 11.0           |
| def2-TZVPD   | 443.4            | 454.4 | 11.0           |
| aug-cc-pVTZ  | 443.3            | 454.4 | 11.1           |



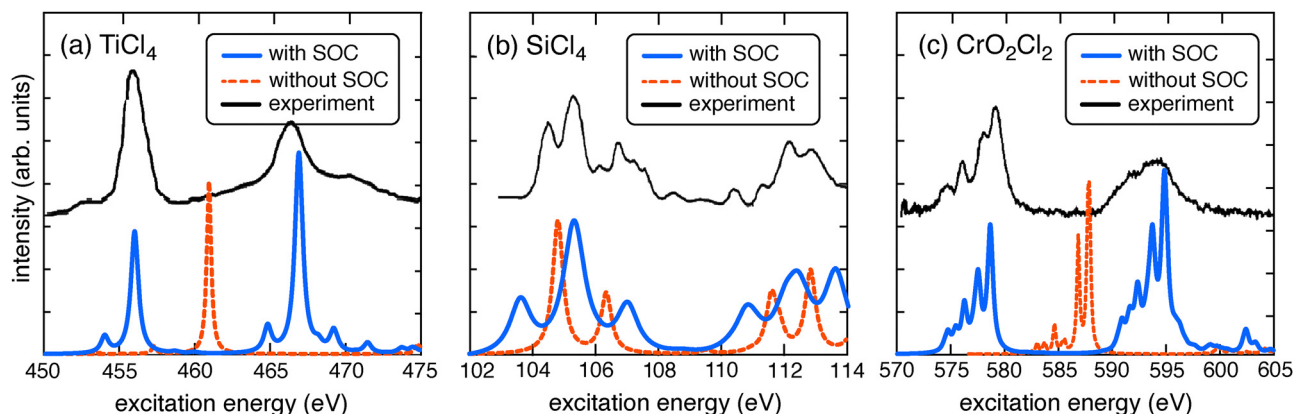


Fig. 3 Experimental  $L_{2,3}$ -edge spectra for (a) Ti in  $\text{TiCl}_4$ ,<sup>121</sup> (b) Si in  $\text{SiCl}_4$ ,<sup>126</sup> and (c) Cr in  $\text{CrO}_2\text{Cl}_2$ ,<sup>127</sup> in comparison to CAM-B3LYP/CIS + SOC calculations. The latter employ the def2-TZVPD basis set with 200 singlet and 200 triplet excited states. Calculated transition energies were broadened using a Lorentzian function (FWHM = 0.3 eV) and shifted by (a) 5.0 eV, (b) 3.2 eV, and (c) 4.8 eV.

Table 2 Simulated  $L_{2,3}$  excitation energies in comparison to experimental values<sup>a</sup>

| Molecule                  | Edge <sup>b</sup> | Expt. (eV)         | Errors in computed values (eV) |                      |         |           |       |
|---------------------------|-------------------|--------------------|--------------------------------|----------------------|---------|-----------|-------|
|                           |                   |                    | CIS                            |                      | TD-DFT  |           |       |
|                           |                   |                    | Standard <sup>c</sup>          | DFT/CIS <sup>d</sup> | SRC1-r2 | CAM-B3LYP | B3LYP |
| $\text{SiCl}_4$           | $L_3$             | 104.3 <sup>e</sup> | 6.8                            | -3.2                 | -3.9    | -5.3      | -5.6  |
|                           | $L_2$             | 104.9 <sup>e</sup> | 6.5                            | -2.6                 | -3.3    | -4.6      | -5.0  |
| $\text{H}_2\text{S}$      | $L_3$             | 164.9 <sup>f</sup> | 7.9                            | -3.4                 | -1.7    | -4.4      | -5.0  |
|                           | $L_2$             | 166.5 <sup>f</sup> | 8.7                            | -2.6                 | 0.6     | -2.2      | -3.0  |
| Ar                        | $L_3$             | 244.5 <sup>g</sup> | 12.0                           | -0.7                 | -1.4    | -6.7      | -6.7  |
|                           | $L_2$             | 246.4 <sup>g</sup> | 14.2                           | 0.5                  | 1.0     | -4.4      | -4.5  |
| $\text{TiCl}_4$           | $L_3$             | 457.7 <sup>h</sup> | 6.7                            | -6.8                 | -5.0    | -14.3     | -14.5 |
|                           | $L_2$             | 462.8 <sup>h</sup> | 13.0                           | -0.9                 | 0.9     | -8.5      | -8.6  |
| $\text{VO}_4^{3-}$        | $L_3$             | 518.2 <sup>i</sup> | 6.8                            | -7.9                 | -5.4    | -16.0     | -15.9 |
|                           | $L_2$             | 525.1 <sup>i</sup> | 13.8                           | -1.5                 | 1.1     | -9.6      | -9.2  |
| $\text{CrO}_2\text{Cl}_2$ | $L_3$             | 577.2 <sup>j</sup> | 11.8                           | -3.4                 | -2.0    | -13.9     | -14.0 |
|                           | $L_2$             | 585.9 <sup>j</sup> | 19.7                           | 4.0                  | 5.6     | -6.6      | -6.5  |
| $\text{MnO}_4^-$          | $L_3$             | 645.6 <sup>i</sup> | 9.5                            | -6.9                 | -5.3    | -18.8     | -18.8 |
|                           | $L_2$             | 656.0 <sup>i</sup> | 18.6                           | 2.0                  | 3.9     | -9.6      | -9.7  |
| $\text{Fe}(\text{Cp})_2$  | $L_3$             | 709.1 <sup>k</sup> | 1.5                            | -10.4                | -7.9    | -22.6     | -22.3 |
|                           | $L_2$             | 722.2 <sup>k</sup> | 11.8                           | -0.3                 | 2.2     | -12.5     | -12.2 |
| Mean error                |                   |                    | 10.6                           | -2.8                 | -1.3    | -10.0     | -10.1 |
| MAE <sup>l</sup>          |                   |                    | 10.6                           | 3.6                  | 3.2     | 10.0      | 10.1  |

<sup>a</sup> All calculations use def2-TZVPD. <sup>b</sup>  $L_2$  or  $L_3$  for the central atom. <sup>c</sup> Conventional CIS. <sup>d</sup> CAM-B3LYP/CIS. <sup>e</sup> Ref. 126. <sup>f</sup> Ref. 129. <sup>g</sup> Ref. 128. <sup>h</sup> Ref. 121. <sup>i</sup> Ref. 131. <sup>j</sup> Ref. 127. <sup>k</sup> Ref. 130. <sup>l</sup> Mean absolute error.

strictly negative, indicating that SIE dominates over orbital relaxation error. The TD-SRC1-r2 approach, which balances these errors (by virtue of its parameterization using experimental data),<sup>54</sup> exhibits errors of either sign. The same is true of CAM-B3LYP/CIS.

Table 3 lists the  $L_{2,3}$  splitting [ $\Delta E(L_2) - \Delta E(L_3)$ ] from Table 2, along with the error in this splitting as computed using each of the methods examined here. In many cases, the errors are of the same order of magnitude as the experimental splitting itself. Errors are also roughly independent of the theoretical method used, averaging about 5 eV but increasing in magnitude as the splitting itself increases. This means that TD-SRC1-r2 is no more accurate than other TD-DFT methods that weren't parameterized to remove the need for absolute shifts, and furthermore the accuracy of CIS is quite similar.

(This is not altogether unexpected, as it speaks to the rather small electron correlation effects on the SOC values, consistent with the accuracy of the SOMF approximation.<sup>90,132,133</sup>) While the origin of the discrepancies in  $L_{2,3}$  splittings with respect to experiment are unclear, it seems that they have more to do with the treatment of SOC than with the description of electron correlation.

### 4.3 CVS as a diagnostic tool

The CVS approximation is needed to extend CIS-type methods to core-level excitations, because it removes valence excitations that appear at lower transition energies so that core-to-valence transitions can be obtained using reasonable subspace sizes in the iterative eigensolver.<sup>35</sup> By performing several calculations with different active occupied orbitals, the CVS approximation



Table 3 Errors in  $L_{2,3}$  splittings in comparison to experimental values<sup>a</sup>

| Molecule                         | Expt. <sup>b</sup> (eV) | Error (eV) |                      |         |           |       |
|----------------------------------|-------------------------|------------|----------------------|---------|-----------|-------|
|                                  |                         | CIS        | DFT/CIS <sup>c</sup> | TD-DFT  |           |       |
|                                  |                         |            |                      | SRC1-r2 | CAM-B3LYP | B3LYP |
| SiCl <sub>4</sub>                | 0.6                     | 0.3        | 0.6                  | 0.6     | 0.7       | 0.6   |
| H <sub>2</sub> S                 | 1.6                     | 0.8        | 0.8                  | 2.3     | 2.2       | 2.0   |
| Ar                               | 1.9                     | 2.2        | 1.2                  | 2.4     | 2.3       | 2.2   |
| TiCl <sub>4</sub>                | 5.1                     | 6.3        | 5.9                  | 5.9     | 5.8       | 5.9   |
| VO <sub>4</sub> <sup>3−</sup>    | 6.9                     | 7.0        | 6.5                  | 6.5     | 6.4       | 6.8   |
| CrO <sub>2</sub> Cl <sub>2</sub> | 8.7                     | 7.9        | 7.4                  | 7.6     | 7.3       | 7.5   |
| MnO <sub>4</sub> <sup>−</sup>    | 10.4                    | 9.1        | 8.9                  | 9.2     | 9.2       | 9.1   |
| Fe(Cp) <sub>2</sub>              | 13.1                    | 10.3       | 10.1                 | 10.1    | 10.1      | 10.1  |
| Mean                             |                         | 5.5        | 5.2                  | 5.6     | 5.5       | 5.5   |

<sup>a</sup> All calculations use def2-TZVPD. <sup>b</sup>  $L_{2,3}$  splitting for the central atom, equal to the difference between experimental  $L_2$  and  $L_3$  values from Table 2. <sup>c</sup> CAM-B3LYP/CIS.

also facilitates separation of the K-, L-, and M-edges of different elements. This is a useful feature because overlapping edges can otherwise make it difficult to assign peaks. The vanadate ion (VO<sub>4</sub><sup>3−</sup>) affords an example, insofar as the O(1s) K-edge and the V(2p) L-edge are quite close in energy as shown in Fig. 4.

For this small ion, it is possible to perform the calculations without invoking the CVS approximation by computing both valence and core excitations. Upon doing so, subtle dipole-forbidden pre-edge features appear whose origin might at first be unclear. For that matter, given the magnitude of the shifts that are needed to match experiment, it is not clear *a priori* which features in the “no CVS” spectrum in Fig. 4 even correspond to the oxygen K-edge. Using active-space approximations involving only the O(1s) or V(2p) orbitals, these features are readily assignable and it is clear that the oxygen K-edge appears at 529 eV. Moreover, the close resemblance of the V(2p) spectrum and the exact linear-response result (sans CVS approximation) suggests there is little mixing between O(1s) and V(2p) orbitals in the ground state of VO<sub>4</sub><sup>3−</sup>.

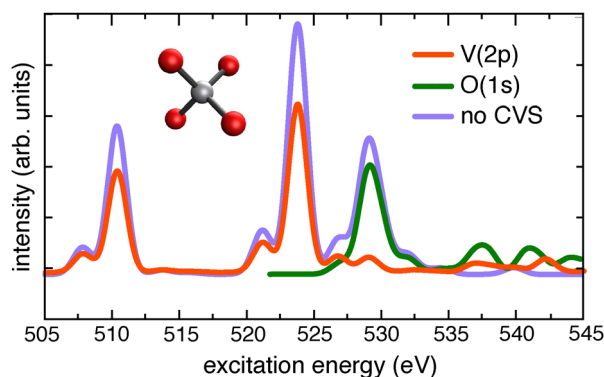


Fig. 4 XAS of VO<sub>4</sub><sup>3−</sup>, illustrating the important role of the CVS approximation in assigning spectral features. All calculations were performed at the CAM-B3LYP/CIS + SOC level using the def2-TZVPD basis set, including 100 singlet and 100 triplet states broadened with a Lorentzian function (FWHM = 0.3 eV). The calculations labeled V(2p) and O(1s) employ the indicated active occupied orbitals, whereas the “no CVS” calculation uses all MOs. For clarity, the three spectra are normalized separately.

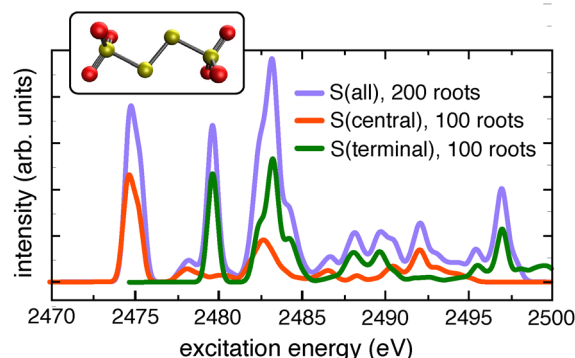


Fig. 5 XAS of (S<sub>4</sub>O<sub>6</sub>)<sup>2−</sup> at the sulfur K-edge, illustrating how calculations with different active spaces can be used to assign spectral features. Spectra were computed using CAM-B3LYP/CIS + SOC with the def2-TZVPD basis set and Lorentzian broadening (FWHM = 0.3 eV). CVS active spaces contain S(1s) orbitals on the atoms indicated in the legend.

The CVS approximation can also be a helpful tool when the same element appears more than once in a molecule, in different coordination environments. An example is the tetrathionate ion, (S<sub>4</sub>O<sub>6</sub>)<sup>2−</sup>, whose terminal sulfur atoms have formal charges of +5 whereas the two interior sulfur atoms have formal charges of zero. Simulated K-edge spectra for this species are shown in Fig. 5 using three different CVS active spaces, consisting of either the S(1s) orbitals on the terminal sulfur atoms, or those on the interior sulfur atoms, or both. The latter spectrum is the true K-edge result but the other two spectra aid in assigning features. These spectra clearly demonstrate how the interior S<sup>0</sup> atoms give rise to lower-energy XAS features as compared to the terminal S<sup>5+</sup> atoms, which is expected due to the stronger electron-hole interaction when the formal charge is larger.

Note that this decomposition is not exact, in the sense that the sum of the spectra with limited active spaces need not equal the spectrum that is obtained with the union of these active spaces, which is evident from the feature at 2475 eV in Fig. 5. These discrepancies arise due to coupling between S(1s) orbitals on different atoms, when such coupling is available within the active space. Despite their approximate nature, however, such decompositions can be useful diagnostic tools to understand the origins of various spectral features.

Fig. 6 shows the analogous decomposition of the L-edge spectrum of (S<sub>4</sub>O<sub>6</sub>)<sup>2−</sup>. Here, we use the S(2p) orbitals on either the terminal or the interior sulfur atoms (or both) as the CVS active space, and these calculations once again demonstrate how the lower-energy features originate in transitions localized on the interior S<sup>0</sup> atoms. The approximate nature of the decomposition is evident in some of the features above 165 eV in Fig. 6a. When a significantly larger number of nonrelativistic states is used, spectral features fill in at higher energies (Fig. 6b). The larger calculation is significantly more expensive because it requires computing 800 DFT/CIS singlet states, including state-to-state transition moments between them, then another 800 triplet states and SOC couplings between the singlet and triplet states. The total dimension of



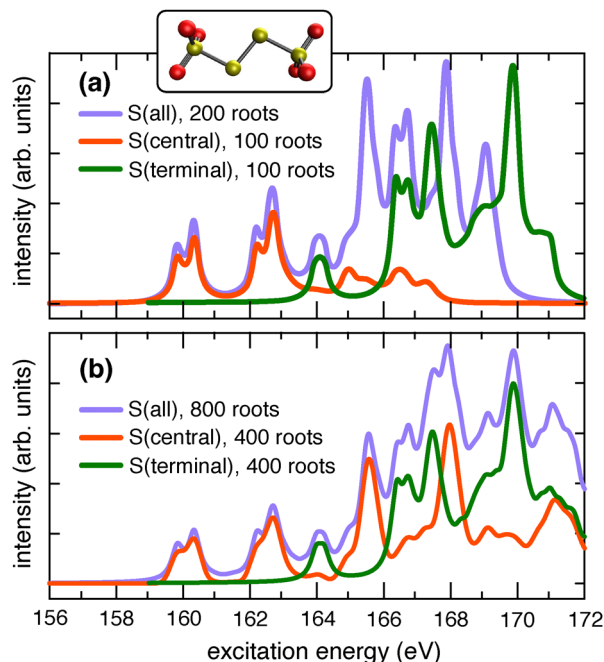


Fig. 6 XAS of  $(\text{S}_4\text{O}_6)^{2-}$  at the sulfur L-edge. All calculations were performed using CAM-B3LYP/CIS + SOC with def2-TZVPD, computing either (a) 200 or (b) 800 singlet and triplet excited states, which were then broadened using a Lorentzian function (FWHM = 0.2 eV). Spectra labeled S(terminal) and S(central) employ only the S(2p) orbitals on the indicated atoms, with a correspondingly smaller number of excited states, whereas S(all) uses all of the S(2p) orbitals.

$H_{\text{BP}}$  in eqn (9) is 3200 states. Nevertheless, such a calculation is feasible at the DFT/CIS level using the high-quality def2-TZVPD

basis set. At the same time, even an approximate decomposition using atom-specific active spaces can be a useful diagnostic and interpretative tool.

#### 4.4 Miscellaneous L-edge applications

We next consider a variety of applications of CAM-B3LYP/CIS + SOC to compute L-edge spectra of main-group compounds and transition metal complexes.

**4.4.1 L-edge spectra of  $\text{SF}_6$ .** XAS of  $\text{SF}_6$  at the S(2p) L-edge is considered in Fig. 7, juxtaposing the CAM-B3LYP/CIS spectrum with an experimental one.<sup>134</sup> Peaks labeled 1 and 2, in the region from 172–175 eV, are assigned as  $a_{1g}$  symmetry and correspond to excitation of S(2p<sub>3/2</sub>) and S(2p<sub>1/2</sub>) electrons into the lowest unoccupied MO (LUMO). As compared to those features, peaks 3 and 4 (representing transitions into  $t_{2g}$  orbitals) are much more intense, in both the computed and the experimental spectrum, although peak 3 has a doublet structure in the CAM-B3LYP/CIS calculation that is not evident in the experiment. Weaker doublet peaks 5 and 6, representing transitions into a second set of  $t_{2g}$  orbitals, are not observed experimentally although they have been observed in real-time TD-DFT calculations.<sup>46</sup> Finally, peaks 7 and 8 in the simulated spectrum correspond to transitions with  $e_g$  symmetry. These features are narrow and intense whereas the corresponding region of the experimental spectrum is broad and diffuse.

Some Rydberg states between 179–182 eV are highlighted in an inset to Fig. 7. These appear at slightly higher energies as compared to the Rydberg features identified in the experimental spectrum, from 177–180 eV and identified as  $a_{1g}$ ,  $e_g$  and  $t_{2g}$  transitions.<sup>134</sup> Only two peaks can be discerned in the highlighted region of the CAM-B3LYP/CIS spectrum. Ruud and

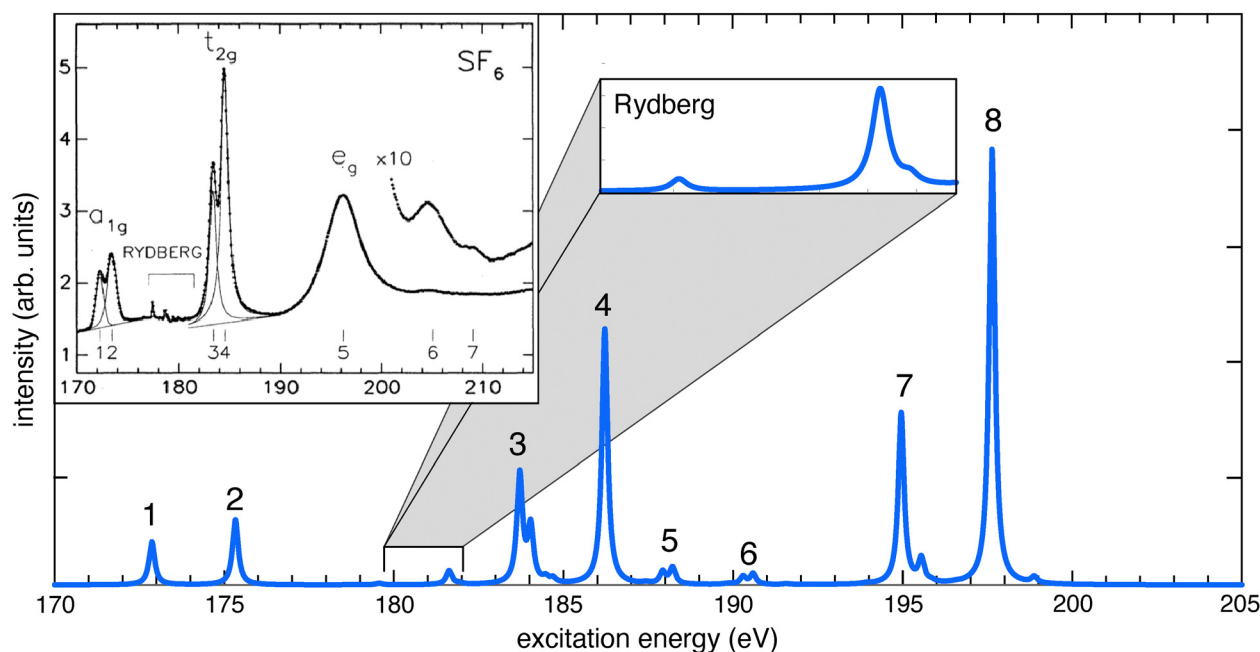


Fig. 7 L-edge XAS of  $\text{SF}_6$ . The CAM-B3LYP/CIS + SOC spectrum (in blue) was obtained using the def2-TZVPD basis set with 200 singlet and 200 triplet states. Individual transition energies were shifted by 5 eV and broadened with a Lorentzian function (FWHM = 0.3 eV). The experimental spectrum (inset) is reproduced from ref. 134; copyright 1993 American Physical Society.



co-workers have identified the same Rydberg features in real-time TD-DFT calculations,<sup>46</sup> which are found to be quite sensitive to basis-set effects. Since these features are not as important in the context of using L-edge spectroscopy to probe valence virtual orbitals, they are not discussed any further.

The DFT/CIS spectrum for SF<sub>6</sub> in Fig. 7 shows doublet peak structure in all features, with an average splitting of  $\approx 2.5$  eV as compared to experimental splittings of  $\approx 1.2$  eV. Nominally, the intensity ratio of the 2p<sub>3/2</sub> to 2p<sub>1/2</sub> features should be about 2 : 1 for each pair of peaks, corresponding to the 4 : 2 ratio of microstates. However, both experimental and ligand-field multiplet intensity ratios can deviate from this result in practice,<sup>124,135</sup> and in the present example this ratio is inverted. The calculated (CAM-B3LYP/CIS + SOC) intensity ratio is 1 : 1.5 for the a<sub>1g</sub> features (peaks 1 and 2 in Fig. 7), as compared to an experimental ratio of 1 : 1.6. For the t<sub>2g</sub> features (peaks 3 and 4), the calculations afford an intensity ratio of 1 : 2.24 as compared to an experimental ratio of 1 : 2.04. Previous work indicates that a significant exchange interaction between the core-excited electron and the valence electrons is responsible for this inversion in the 2p<sub>3/2</sub> : 2p<sub>1/2</sub> intensity ratio.<sup>134</sup>

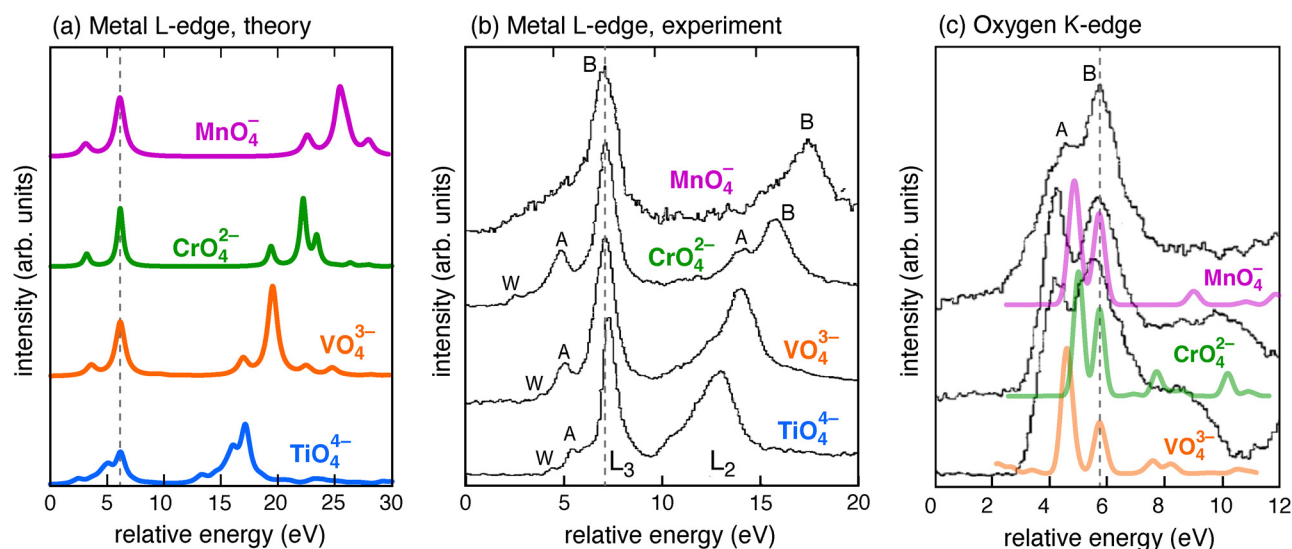
**4.4.2 3d<sup>0</sup> complexes.** Core-level spectra of tetrahedrally coordinated 3d<sup>0</sup> metal oxide anions MO<sub>4</sub><sup>n−</sup> (M = Ti, V, Cr, Mn) are examined in Fig. 8. The 2p → 3d transition is dipole-allowed and the peak splitting affords insight into the electronic structure of the metal 3d band and the effect of the ligand field. The d<sup>0</sup> nature of the ground state means that each ion has only one reasonable ground-state electron configuration, thus a single-reference method like DFT/CIS may be adequate.

Spectra at the metal L<sub>2,3</sub> edge are shown in Fig. 8a and b. The most apparent feature is the magnitude of the spin-orbit splitting between the L<sub>3</sub> and L<sub>2</sub> edges, which decreases in the

order MnO<sub>4</sub><sup>−</sup> > CrO<sub>4</sub><sup>2−</sup> > VO<sub>4</sub><sup>3−</sup> > TiO<sub>4</sub><sup>4−</sup> in both CAM-B3LYP/CIS + SOC simulations and experiment. The splitting between experimental features labeled A and B (Fig. 8b) decreases in the same order. A similar trend is observed at the oxygen K-edge; see Fig. 8c. The biggest discrepancy between theory and experiment is an inversion of peak intensities between the L<sub>2</sub> and L<sub>3</sub> edges, as observed in previous calculations.<sup>123,124</sup> This is similar to what we observed for TiCl<sub>4</sub> (Fig. 1), where it appears that a variational description of SOC is required in order to obtain the correct relative intensities, as discussed in Section 4.1.

SOC increases with atomic number [eqn (11)] and this is reflected in both theory and experiment. However, these MO<sub>4</sub><sup>n−</sup> spectra exhibit ligand-field splitting (into e and t<sub>2g</sub> orbitals) at both the L<sub>3</sub> and L<sub>2</sub> edges,<sup>131</sup> such that there are two sets of metal d orbitals available to a 3d<sup>0</sup> transition metal. Oxygen K-edge spectra of these MO<sub>4</sub><sup>n−</sup> complexes show a splitting in their most intense features that correlates well with the L<sub>2,3</sub> splitting,<sup>131</sup> indicating that the transition from O(1s) either the e or t<sub>2g</sub> orbitals is dipole-allowed. Brydson *et al.*<sup>131</sup> argue that there is considerable mixing between the O(2p) and M(3d) orbitals, along with some contribution from M(4p) and O(2s) orbitals, resulting in the nominal O(1s) → M(3d) transition becoming dipole-allowed. The increased splitting between the A and B features at the metal L<sub>3</sub> edge has been attributed to the increasing X–O bond lengths and decreasing formal charge on the metal ion.<sup>131</sup>

**4.4.3 Ligand effects at the Fe L-edge.** Sensitivity of transition metal 3d orbital energies to ligand substitution is especially pronounced for Fe(CO)<sub>5</sub> and Fe(Cp)<sub>2</sub> (ferrocene),<sup>130,136</sup> where “Cp” indicates the cyclopentadienyl anion, (C<sub>5</sub>H<sub>6</sub>)<sup>−</sup>. L<sub>2,3</sub>-edge spectra of Fe(CO)<sub>5</sub> exhibit a splitting in both the L<sub>3</sub> and L<sub>2</sub>



**Fig. 8** XAS of 3d<sup>0</sup> metal oxide ions, MO<sub>4</sub><sup>n−</sup>, including (a) spectra at the metal L-edge from CAM-B3LYP/CIS + SOC calculations, (b) the corresponding experimental L-edge spectra, and (c) oxygen K-edge spectra, overlaying theory (in translucent color) and experiment. Spectra are shifted to align the L<sub>3</sub>- or K-edge feature labeled “B”, as indicated by the dashed vertical lines. This places all spectra within the same energy window, consistent with the presentation in ref. 131. Simulated spectra were computed using def2-TZPVD including 200 singlet and 200 triplet basis states and broadened using a Lorentzian function (FWHM = 0.3 eV). Experimental spectra are reproduced from ref. 131.



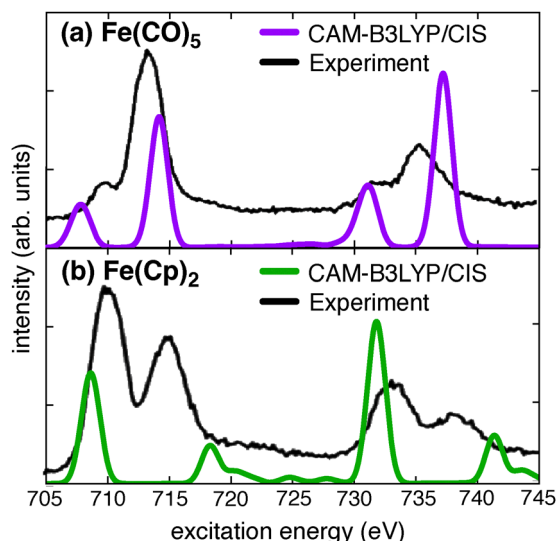


Fig. 9  $L_{2,3}$ -edge spectra of (a)  $\text{Fe}(\text{CO})_5$  and (b)  $\text{Fe}(\text{Cp})_2$ , comparing experiment (with an offset baseline) to CAM-B3LYP/CIS + SOC simulations. The calculations employ the def2-TZVPD basis set with 200 singlet and 200 triplet states, broadened using a Lorentzian function (FWHM = 0.7 eV). The computed spectra were shifted by (a) 8.0 eV and (b) 10.0 eV in order to align with experimental spectra that are reproduced from ref. 130.

bands, with one peak that is much stronger than the other. This is characteristic of the metal 2p spectra of all near-covalent complexes.<sup>137</sup> In Fig. 9a, we see that this feature is present in both the experimental spectra of  $\text{Fe}(\text{CO})_5$  and in CAM-B3LYP/CIS + SOC simulations.

The  $L_{2,3}$ -edge spectrum of ferrocene shows significant differences as compared to the iron pentacarbonyl complex, and these differences are reflected in the calculations. This highlights L-edge sensitivity to metal oxidation state and ligand identity. In  $\text{Fe}(\text{Cp})_2$ , the more intense first peak at 709 eV is a  $\text{Fe}(2p) \rightarrow e_{1g}$  transition, as determined in previous calculations.<sup>137</sup> The second peak has been attributed to a  $\text{Fe}(2p) \rightarrow e_{2u}$  transition where the  $3e_{2u}$  MO contains a significant contribution from  $\text{Fe}(3d)$  orbitals, giving it metal-to-ligand charge-transfer character.<sup>137</sup>

CAM-B3LYP/CIS + SOC calculations predict a larger  $L_{2,3}$  splitting for  $\text{Fe}(\text{Cp})_2$  as compared to what is observed experimentally. This might be due to the presence of large amounts of exact exchange in the CAM-B3LYP/CIS method, which is known to adversely affect the splitting between high- and low-spin configurations of 3d transition metals.<sup>138–141</sup> Specifically in the context of L-edge spectroscopy, Kasper *et al.*<sup>122</sup> observe larger d-orbital splittings when the half-and-half functional BH&H-LYP is used, as compared to B3LYP or PBE0. Indeed, ligand-field splittings often vary directly with the fraction of exact exchange,<sup>142</sup> and functionals with larger fractions (even 20%) tend to overestimate the d-orbital splitting.<sup>138</sup> Overall, the CAM-B3LYP/CIS + SOC approach replicates experimental features and ligand effects with reasonable accuracy, however. This is important for L-edge X-ray spectroscopy where changes in the coordination environment around a metal center are directly observable in experimental spectra.

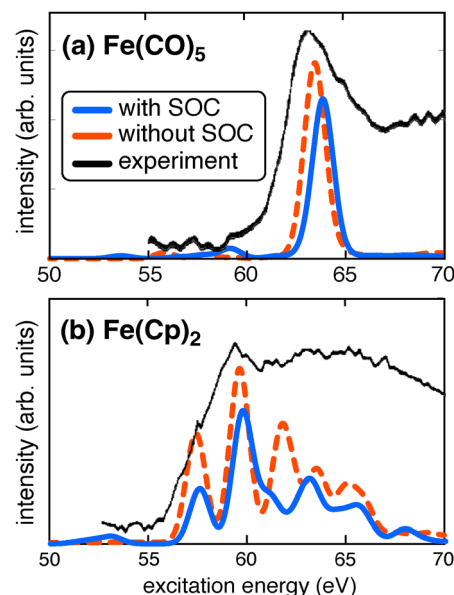


Fig. 10 XUV spectra of (a)  $\text{Fe}(\text{CO})_5$  and (b)  $\text{Fe}(\text{Cp})_2$  at the Fe M-edge, comparing CAM-B3LYP/CIS simulations to experimental spectra from ref. 130. Calculations employ the def2-TZVPD basis set with 200 singlet and 200 triplet states. Transition energies were broadened using a Lorentzian function (FWHM = 0.5 eV) but have not been shifted.

#### 4.5 M-edge spectra

Finally, we consider  $M_{2,3}$ -edge spectra of some 3d transition metal complexes. Fig. 10 presents M-edge spectra of the same two iron complexes whose L-edge spectra were discussed in Section 4.4.3, namely,  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}(\text{Cp})_2$ .<sup>130</sup> The M-edge spectrum of  $\text{TiO}_2$  is plotted in Fig. 11, from a thin film of the rutile polymorph,<sup>143,144</sup> and juxtaposed with a CAM-B3LYP/CIS spectrum of its fundamental octahedral unit,  $(\text{TiO}_6)^{8-}$ .

Unlike the L-edge spectra, no shifts are needed to match with experiment in any of these M-edge cases, demonstrating that errors due to SIE are reduced for orbitals with principal quantum number  $n = 3$  (M-edge), as compared to those with  $n = 2$  (L-edge). Furthermore, SOC effects are no longer

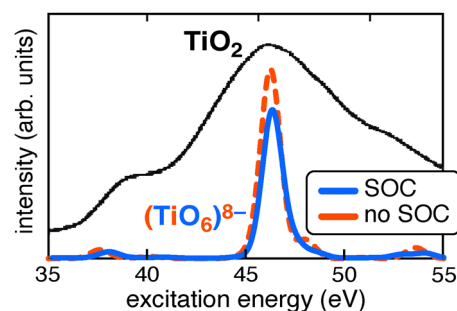


Fig. 11 XUV spectra at the Ti M-edge, for a rutile  $\text{TiO}_2$  film (experiment) and its fundamental octahedral unit  $(\text{TiO}_6)^{8-}$  (CAM-B3LYP/CIS calculation). The experimental spectrum is reproduced from ref. 144 but was originally recorded in ref. 143. Calculations use the def2-TZVPD basis set and include 200 singlet and 200 triplet states, with transition energies that are broadened using a Lorentzian function (FWHM = 0.5 eV) but not shifted.

significant and similar spectral features are obtained using nonrelativistic calculations. This is consistent with the larger electron–nucleus separation for the 3p orbitals and the  $r^{-3}$  distance dependence of SOC [eqn (11) and (12)]. With or without SOC, the CAM-B3LYP/CIS spectra resemble the experimental ones, including the abrupt M-edge in Fe(CO)<sub>5</sub>, the broad multiplet in Fe(Cp)<sub>2</sub>, and a low-energy shoulder in TiO<sub>2</sub>. The spin–orbit splitting is much reduced even as compared to the same Fe complexes at the L-edge (*cf.* Fig. 9).

## 5 Conclusions

This work extends a new CAM-B3LYP/CIS variant<sup>55</sup> of the DFT/CIS method<sup>56</sup> to core-level spectroscopy at elemental L- and M-edges. Specifically, a state-interaction treatment of SOC, using the Breit–Pauli Hamiltonian within a mean-field approximation for the matrix elements, is used to correct the non-relativistic (SOC-free) DFT/CIS states. The same approach works for TD-DFT calculations as well,<sup>95</sup> but CAM-B3LYP/CIS was parameterized in such a way that it significantly reduces the *ad hoc* shifts that are necessary to match experiment for core-to-valence excitation energies. Although these shifts were parameterized at elemental K-edges,<sup>55</sup> we find that the same parameterization also yields more accurate results for L- and M-edge spectra, as compared to TD-DFT with general-purpose functionals.

The cost of the DFT/CIS calculations is the same as that of CIS calculations and, when combined with the CVS approximation, is significantly cheaper than the real-time TD-DFT approach.<sup>35</sup> SOC corrections implemented in the Q-Chem program<sup>105</sup> can be added to nonrelativistic DFT/CIS and TD-DFT calculations *a posteriori*, using a Python package developed for this work.<sup>106</sup>

The CAM-B3LYP/CIS + SOC method accurately models L- and M-edge spectra, as assessed herein by comparison to experimental results. The CVS approximation, which reduces the active space to a small number of occupied orbitals appropriate for the elemental edge in question, significantly reduces the cost although a large number of excited states is required to converge spectral lineshapes. The CVS approximation is also vital for disentangling overlapping spectral features and making peak assignments. At present, the SOC corrections are implemented only for closed-shell species and we hope to introduce an open-shell variant in due course, enabling simulations of core-level spectra on a wider range of transition metal systems.

## Author contributions

Aniket Mandal: conceptualization (contributing); data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); software (lead); validation (lead); visualization (lead); writing – original draft (lead); writing – review and editing (equal). John M. Herbert: conceptualization (lead); formal analysis (contributing); funding acquisition (lead); methodology (contributing); project administration (lead); supervision

(lead); visualization (contributing); writing – review and editing (equal).

## Conflicts of interest

J. M. H. is part owner of Q-Chem Inc. and serves on its board of directors.

## Data availability

The data that support these findings are available from the corresponding author upon reasonable request.

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