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Supporting information for article:

Improved charge-transfer multiplet method to simulate *M*- and *L*-edge X-ray absorption spectra of metal-centered excited states

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Fe2_10Dq0d5_noSO.rac

```

Y
  % vertical 1 1
  butler 03
  to 0h
  to D4h
  to C4h
  endchain
  actor 0+ HAMILTONIAN ground PRINTEIG
  OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ > 0+ > 0+ 1.0
  OPER SHELL2
  BRANCH 4+ > 0 0+ > 0+ > 0+ 1.643
  BRANCH 4+ > 0 2+ > 0+ > 0+ 0.000
  BRANCH 2+ > 0 2+ > 0+ > 0+ 0.000
  actor 0+ HAMILTONIAN excite PRINTEIG
  OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ > 0+ > 0+ 1.0
  OPER SHELL2
  BRANCH 4+ > 0 0+ > 0+ > 0+ 1.643
  BRANCH 4+ > 0 2+ > 0+ > 0+ 0.000
  BRANCH 2+ > 0 2+ > 0+ > 0+ 0.000
  actor 1- left transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > 1- > 1- 1.000
  actor -1- right transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > 1- > -1- 1.000
  actor 0- parallel transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > ^0- > 0- 1.000
RUN

```

To turn on the additional outputs required for multiplet state assignment, the files should be modified to the following, where changes have been highlighted in yellow:

Fe2_10Dq0d5_noSO.rcg

```

  10  1  0  14  2  4  1  1 SHELL03000000 SPIN03000000
INTER8
  0 80998080 8065.47800 0000000
  1 2 1 12 1 10 00 6 00000000 0 8065.4790 .00 1
P 6 D 6
P 5 D 7
Fe2+ 3P06 3D06 4 0.0000 10.9661 6.8151 0.0002
0.0000HR99999999
Fe2+ 3P05 3D07 8 0.0000 11.0691 6.8821 0.0002
0.0002HR99999999
  7.6983 9.5694 5.7834
Fe2+ 3P06 3D06 Fe2+ 3P05 3D07 1.24596( 3P//R1// 3D)-0.992HR
-90 -96
-99999999.
-1

```

```
Fe2_10Dq0d5_noSO.rac
```

```
Y
  % vertical 1 1
  butler 03
  to 0h
  to D4h
  to C4h
  endchain
  actor 0+ HAMILTONIAN ground PRINTEIG 2
  OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ > 0+ > 0+ 1.0
  OPER SHELL2
  BRANCH 4+ > 0 0+ > 0+ > 0+ 1.643
  BRANCH 4+ > 0 2+ > 0+ > 0+ 0.000
  BRANCH 2+ > 0 2+ > 0+ > 0+ 0.000
  actor 0+ HAMILTONIAN excite PRINTEIG 2
  OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ > 0+ > 0+ 1.0
  OPER SHELL2
  BRANCH 4+ > 0 0+ > 0+ > 0+ 1.643
  BRANCH 4+ > 0 2+ > 0+ > 0+ 0.000
  BRANCH 2+ > 0 2+ > 0+ > 0+ 0.000
  actor 1- left transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > 1- > 1- 1.000
  actor -1- right transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > 1- > -1- 1.000
  actor 0- parallel transi PRINTTRANS
  oper MULTIPOLE
  branch 1- > 0 1- > ^0- > 0- 1.000
RUN
```

Running the input files using the following commands will generate the output files

Fe2_10Dq0d5_noSO.org and Fe2_10Dq0d5_noSO.ora necessary for assignment.

```
rcg2.bat Fe2_10Dq0d5_noSO
rac2.bat Fe2_10Dq0d5_noSO
```

Input files for point groups not supported by CTM4XAS GUI (e.g. D_{5d}) have to be constructed by hand according to the documented structure of the input files.

S1.3. Assignment of multiplet theory eigenstates

Continuing with the example of an octahedral Fe^{II} system, to perform multiplet state assignment on the special output files Fe2_10Dq0d5_noSO.org and Fe2_10Dq0d5_noSO.ora, one creates a Python script that begins with the following lines.

```
import coupl_coef2
import parse_complete2
groups=["03","0h","D4h","C4h"]
coupl_coef2.read_racah_outputs(groups)
```

These lines gathers the necessary data to support calculations in the $O_3 \supset O_h \supset D_{4h} \supset C_{4h}$ chain of groups used in the output files.

One then uses the function `parse_complete2.parse_complete` to read in the information contained in the output files.

parse_complete2.parse_complete(filename_prefix,j_basis,ex_j_basis,parity,groups)	
Parameter	Meaning
filename_prefix	Prefix of the filenames of the output files to be assigned. (i.e. "Fe2_10Dq0d5_noSO" for Fe2_10Dq0d5_noSO.org and Fe2_10Dq0d5_noSO.ora)
j_basis, ex_j_basis	A Python dict containing free-ion Russel-Saunders terms of the ground and the core-hole configurations, respectively, indexed by total angular momentum J. If not supplied, the program will automatically read the .org to extract these.
parity	A string being either "+" or "-" specifying the parity of the eigenstates that need to be read in from the output files. If not supplied, both parities will be read.
groups	A list of strings containing the names of the groups in the current group chain i.e. ["O3","Oh","D4h","C4h"] for the present example.
Return value	Meaning
basis_c4h, ex_basis_c4h	A Python dict containing all basis functions in the ground and the core-hole configurations, respectively, indexed by irreducible representation in the lowest point group ("C4h" in the present example).
irrep_eig	A Python dict containing lists of eigenvalues grouped by irreducible representation in the lowest point group.
irrep_matrix	A Python dict containing CTM theory eigenvectors in spin-orbit coupled basis indexed by irreducible representation in the lowest point group.

The four objects returned by `parse_complete2.parse_complete` can be interpreted by the following functions:

- `coupl_coef.decompose_triads` transforms the eigenvectors into the decoupled basis, and organizes them into more structured representations. The analysis carried out in this function is valid regardless of the strength of spin-orbit coupling. This function forms the basis of all other interpretation functions

decompose_triads(basis_c4h, irrep_eig, irrep_matrix, groups, point_group, triads, threshold)	
Parameter	Meaning
basis_c4h	A Python dict containing all basis functions indexed by irreducible representation in the lowest point group.

irrep_eig	A Python dict containing lists of eigenvalues grouped by irreducible representation in the lowest point group.
irrep_matrix	A Python dict containing CTM theory eigenvectors in spin-orbit coupled basis indexed by irreducible representation in the lowest point group.
groups	A list of strings containing the names of the groups in the current group chain.
triads	A list of strings containing the names of the irreducible representations of the eigenvectors for which the basis transform should be carried out, defaulting to all irreducible representations if not specified.
threshold	A floating point number giving the minimum absolute value of a coefficient required for a basis function to be considered to contribution to an eigenvector, defaulting to zero if not specified.
Return value	Meaning
results	A list containing a list of transformed eigenvectors in internal representation for each irreducible representation requested through the triads parameter.

- `coupl_coef.analyze_per_triad` analyzes the composition of eigenfunctions in terms of irreducible representations of a given point group. The analysis carried out in this function is valid regardless of the strength of spin-orbit coupling. In fact, this function is particularly useful for uncovering the mixing of pure-spin terms by spin-orbit coupling.

<code>analyze_per_triad(basis_c4h, irrep_eig, irrep_matrix, groups, point_group, triads)</code>	
Parameter	Meaning
basis_c4h	Same as in <code>coupl_coef.decompose_triads</code> .
irrep_eig	
irrep_matrix	
groups	
point_group	A string giving the name of the point group for which the analysis should be carried out, defaulting to the lowest group in the chain if not specified.
triads	Same as in <code>coupl_coef.decompose_triads</code> .

Return value	Meaning
purity_lists	A list containing a summary list for each irreducible representation requested in triads. Each summary list contain a list of tuples (term, purity) for each eigenfunction under the irreducible representation where term is a pure-spin Russell-Saunders term symbol and purity the corresponding purity within the eigenfunction. A textual representation of purity_lists is also printed to the console as the function runs. All purities are specified as a floating point number between zero and one (inclusive).

- `coupl_coef.perform_assignment` collects eigenfunctions with identical eigenvalues into eigenstates and assigns a pure-spin Russell-Saunders term symbol to each eigenstate. The analysis carried out in this function is only meaningful with spin-orbit coupling set to zero.

perform_assignment(basis_c4h, irrep_eig, irrep_matrix, groups, point_group)	
Parameter	Meaning
basis_c4h	Same as in <code>coupl_coef.decompose_triads</code> .
irrep_eig	
irrep_matrix	
groups	
point_group	Same as in <code>coupl_coef.analyze_per_triad</code>
triads	Same as in <code>coupl_coef.decompose_triads</code> .
Return value	Meaning
gr	A list of eigenstates in internal representation. This table is also printed to the console as the function runs.

- `coupl_coef2.simulation_candidates` selects eigenfunctions as candidates for simulation based on their energies and their purities in user-specified pure-spin terms.

simulation_candidates(basis_c4h, irrep_eig, irrep_matrix, groups, targets, point_group, triads, purity_threshold, max_candidates, energy_cutoff)	
Parameter	Meaning
basis_c4h	Same as in <code>coupl_coef.decompose_triads</code> .
irrep_eig	
irrep_matrix	
groups	

targets	A list of tuples (S, L) each specifying a pure-spin term symbol to search for where S is a string giving the spin quantum number in Butler notation and L is a string giving the orbital irreducible representation.
point_group	Same as in <code>coupl_coef.analyze_per_triad</code>
triads	Same as in <code>coupl_coef.decompose_triads</code> .
purity_threshold	A floating point number giving the minimum purity required for an eigenfunction to be proposed as a candidate for a pure-spin term, defaulting to 0.05 if not specified.
max_candidates	An integer giving the maximum number of candidates to suggest for each target term, defaulting to five if not specified.
energy_cutoff	A floating point number giving the maximum energy above the least energetic candidate for which additional candidates should be suggested, defaulting to 1.0 eV if not specified.
Return value	Meaning
(N/A)	A list of candidates and their corresponding energies and purities are printed to the console as the function runs. The candidates functions are printed in a form compatible with the <code>state_spec</code> parameter of the simulation function <code>params_to_plot</code> (Section 2). All purities are specified as a floating point number between zero and one (inclusive).

Returning to the example of `Fe2_10Dq0d5_noSO.org` and `Fe2_10Dq0d5_noSO.ora`, with spin-orbit coupling set to zero, `perform_assignment` can be invoked to carry out an assignment of octahedral terms.

```
coupl_coef2.perform_assignment(basis_c4h,irrep_eig,irrep_matrix,groups,"0h")
```

The full Python script for carrying out an assignment on `Fe2_10Dq0d5_noSO.org` and

`Fe2_10Dq0d5_noSO.ora` is reproduced below.

```
import coupl_coef2
import parse_complete2
groups=["03","0h","D4h","C4h"]
coupl_coef2.read_racah_outputs(groups)
filename_base='Fe2_10Dq0d5_noSO'
basis_c4h,ex_basis_c4h,irrep_eig,irrep_matrix=parse_complete2.parse_comple~
~te(filename_base,parity='+',groups=groups)
coupl_coef2.perform_assignment(basis_c4h,irrep_eig,irrep_matrix,groups,"0h")
```

When executed by Python, the script should produce output resembling the following.


```

03 Oh
Found 3jm response(s)
Oh D4h
Found 3jm response(s)
D4h C4h
Found 3jm response(s)
Processing triad 0+
Processing triad 1+
Processing triad -1+
Processing triad 2+
.....
^1+ 2+ -3.58684
^1+ 2+ -3.586838
2+ 2+ -3.08689
2+ 2+ -3.086889
2+ 2+ -3.086888
1+ 1+ -1.682914
1+ 1+ -1.68291
.....

```

The highlighted line indicates that the ground state has spin quantum number 2 and has orbital irreducible representation of 1A_1 which is T_{2g} in Butler notation. In other words, with spin-orbit coupling set to zero the ground state is $^5T_{2g}$.

Consider now the same Fe^{II} system with spin-orbit set to Hartree-Fock values. This system can be modelled in CTM4XAS using the following .rcg input file (named Fe2_10Dq0d5_hasSO.rcg). The .rac input is unchanged from before, but will be renamed Fe2_10Dq0d5_hasSO.rac to distinguish it from the previous example.

```

Fe2_10Dq0d5_hasSO.rcg
  10  1  0  14  2  4  1  1 SHELL03000000 SPIN03000000
INTER8
  0 80998080 8065.47800 0000000
  1 2 1 12 1 10 00 6 00000000 0 8065.4790 .00 1
P 6 D 6
P 5 D 7
Fe2+ 3P06 3D06 4 0.0000 10.9661 6.8151 0.0522
0.0000HR99999999
Fe2+ 3P05 3D07 8 0.0000 11.0691 6.8821 0.0002
0.0002HR99999999
  7.6983 9.5694 5.7834
Fe2+ 3P06 3D06 Fe2+ 3P05 3D07 1.24596( 3P//R1// 3D)-0.992HR
-90 -96
-99999999.
-1

```

The output files generated by running Fe2_10Dq0d5_hasSO.rcg and Fe2_10Dq0d5_hasSO.rac through the relevant helper scripts can also be parsed and analyzed by the assignment program albeit with a different set of functions. For example, the Python script below invokes the analyze_per_triad function to analyze the composition of the eigenfunctions of $1+$ (T_{1g}) symmetry in terms of pure-spin O_h Russell-Saunders terms.

```

import coupl_coef2
import parse_complete2
groups=["03","0h","D4h","C4h"]
coupl_coef2.read_racah_outputs(groups)
filename_base='Fe2_10Dq0d5_noSO'
basis_c4h,ex_basis_c4h,irrep_eig,irrep_matrix=parse_complete2.parse_comple~
~te(filename_base,parity='+',groups=groups)
coupl_coef2.analyze_per_triad(basis_c4h,irrep_eig,irrep_matrix,groups,"0h",("1+",))

```

When executed by Python, the script should produce output resembling the following.

```

03 0h
Found 3jm response(s)
0h D4h
Found 3jm response(s)
D4h C4h
Found 3jm response(s)
Processing triad 1+
-3.630365 + ('1+', 0)
('2+', '^1+') 0.997
('2+', '2+') 0.002
('1+', '^0+') 0.001
('1+', '^1+') 0.000
-3.605155 + ('1+', 1)
('2+', '^1+') 0.994
('2+', '2+') 0.005
('1+', '^1+') 0.001
('1+', '1+') 0.000
-3.568758 + ('1+', 2)
('2+', '^1+') 0.991
('2+', '2+') 0.007
('1+', '1+') 0.001
('1+', '2+') 0.000
.....

```

The highlighted lines indicate that the eigenfunction with eigenvalue -3.6304 eV is 99.7% of ${}^5T_{2g}$ character.

The CTM4XAS input files and Python analysis scripts used in producing the current article has been attached as examples. The files are organized into folders:

Folder	Content
Fe2_0h_simulation_candidates	Files for selecting excited state eigenfunctions for simulation in Case study 2
Ferrocenium_Tanabe-Sugano	Files for following the changes in the energies of ferrocenium excited states as a function of Nephelauxetic parameter (Figure 6 of main text)
Ferrocenium_simulation_candidates	Files for selecting excited state eigenfunctions for simulation in Case study 1

S1.4. Assignment of ferrocenium excited states with different 3d nephelauxetic scalings.**Table S1** Assignment of excited states of ferrocenium cation with 100% Slater-Condon scaling.

Energy	Γ^J , order within Γ^{J**}	Purity	Assignment
-6.22*	$\frac{1}{2}, 1$	99.5%	${}^6A_{1g}$
-6.22	$\frac{3}{2}, 1$	99.1%	
-6.24	$\frac{5}{2}, 1$	51.8%	
-5.37*	$\frac{1}{2}, 2$	99.4%	${}^4E_{1g}$
-5.34	$\frac{1}{2}, 3$	99.3%	
-5.39	$\frac{3}{2}, 3$	98.8%	
-5.41	$\frac{5}{2}, 3$	97.6%	
-5.14*	$\frac{1}{2}, 4$	100%	${}^4E_{2g}$
-5.12	$\frac{3}{2}, 4$	99.8%	
-5.08	$\frac{3}{2}, 5$	99.5%	
-5.10	$\frac{5}{2}, 4$	99.7%	
-4.81*	$\frac{1}{2}, 5$	98.7%	${}^2A_{1g}$
-6.10*	$\frac{3}{2}, 2$	98.9%	${}^2E_{2g}$
-6.22	$\frac{5}{2}, 2$	52.9%	

* Chosen as representative for simulation.

** Irreducible representations Γ^J are given in Butler notation. (Butler, 1981) The entries for $\Gamma^J = -\frac{5}{2}$ have been omitted, because those are identical to entries for $\Gamma^J = \frac{5}{2}$ of the corresponding terms.

Table S2 Assignment of excited states of ferrocenium cation with 71% Slater-Condon scaling.

Energy	Γ^J , order within Γ^{J**}	Purity	Assignment
-4.41*	$\frac{1}{2}, 5$	97.5%	
-4.41	$\frac{3}{2}, 5$	97.2%	${}^6A_{1g}$
-4.40	$\frac{5}{2}, 2$	96.3%	
-4.78*	$\frac{1}{2}, 2$	97.9%	
-4.73	$\frac{1}{2}, 3$	98.8%	
-4.82	$\frac{3}{2}, 2$	97.2%	${}^4E_{1g}$
-4.86	$\frac{5}{2}, 2$	96.2%	
-4.66*	$\frac{1}{2}, 4$	99.9%	
-4.65	$\frac{3}{2}, 3$	99.7%	
-4.60	$\frac{3}{2}, 4$	99.8%	${}^4E_{2g}$
-4.63	$\frac{5}{2}, 3$	99.6%	
-5.39*	$\frac{1}{2}, 1$	99.1%	${}^2A_{1g}$
-6.11	$\frac{3}{2}, 1$	99.6%	
-6.23*	$\frac{5}{2}, 1$	99.5%	${}^2E_{2g}$

* Chosen as representative for simulation.

** Irreducible representations Γ^J are given in Butler notation. (Butler, 1981) The entries for $\Gamma^J = -\frac{5}{2}$ have been omitted, because those are identical to entries for $\Gamma^J = \frac{5}{2}$ of the corresponding terms.

Table S3 Assignment of excited states of ferrocenium cation with 56.5% Slater-Condon scaling.

Energy	Γ^J , order within Γ^{J**}	Purity	Assignment
-3.51	$\frac{1}{2}, 7$	95.9%	
-3.58*	$\frac{3}{2}, 7$	99.7%	${}^6A_{1g}$
-3.49	$\frac{5}{2}, 5$	88.3%	
-4.49	$\frac{1}{2}, 2$	99.5%	
-4.44	$\frac{1}{2}, 3$	99.7%	
-4.53	$\frac{3}{2}, 2$	99.3%	${}^4E_{1g}$
-4.58*	$\frac{5}{2}, 2$	99.1%	
-4.44*	$\frac{1}{2}, 4$	99.9%	
-4.42	$\frac{3}{2}, 3$	99.5%	
-4.38	$\frac{3}{2}, 4$	99.8%	${}^4E_{2g}$
-4.40	$\frac{5}{2}, 3$	99.4%	
-5.71*	$\frac{1}{2}, 1$	99.7%	${}^2A_{1g}$
-6.12	$\frac{3}{2}, 1$	99.7%	
-6.24*	$\frac{5}{2}, 1$	99.7%	${}^2E_{2g}$

* Chosen as representative for simulation.

** Irreducible representations Γ^J are given in Butler notation. (Butler, 1981) The entries for $\Gamma^J = -\frac{5}{2}$ have been omitted, because those are identical to entries for $\Gamma^J = \frac{5}{2}$ of the corresponding terms.

Table S4 Assignment of excited states of ferrocenium cation with 42% Slater-Condon scaling.

Energy	Γ^J , order within Γ^{J**}	Purity	Assignment
-2.61*	$\frac{1}{2}$, 12	99.4%	
-2.61	$\frac{3}{2}$, 11	99.4%	${}^6A_{1g}$
-2.61	$\frac{5}{2}$, 7	99.4%	
-4.23	$\frac{1}{2}$, 2	99.6%	
-4.17	$\frac{1}{2}$, 4	99.8%	
-4.28	$\frac{3}{2}$, 2	99.5%	${}^4E_{1g}$
-4.33*	$\frac{5}{2}$, 2	99.5%	
-4.22*	$\frac{1}{2}$, 3	99.9%	
-4.21	$\frac{3}{2}$, 3	99.1%	
-4.16	$\frac{3}{2}$, 4	99.8%	${}^4E_{2g}$
-4.19	$\frac{5}{2}$, 3	99.0%	
-6.06*	$\frac{1}{2}$, 1	99.8%	${}^2A_{1g}$
-6.15	$\frac{3}{2}$, 1	99.8%	
-6.27*	$\frac{5}{2}$, 1	99.8%	${}^2E_{2g}$

* Chosen as representative for simulation.

** Irreducible representations Γ^J are given in Butler notation. (Butler, 1981) The entries for $\Gamma^J = -\frac{5}{2}$ have been omitted, because those are identical to entries for $\Gamma^J = \frac{5}{2}$ of the corresponding terms.

S2. Instructions for performing excited state simulations

S2.1. Software dependencies

The following software are necessary for performing excited state CTM simulations on a Windows 7 computer.

- CTM4XAS ver 5.5 with the attached helper batch scripts
- Python (2.7.11+) with numpy (1.10+), scipy (0.13.2+), matplotlib (1.3.1+)
- Modified bander program (source code attached) with helper batch script
- Python scripts `gen_input_raw.py`, `FitAndPlotFuns_KZ.py` and `plot_lifetime.py`

The helper batch scripts should be added to the PATH variable so that the scripts are accessible from the command line.

S2.2. Excited state simulation

To perform an excited state CTM simulation, one creates a Python script that imports `gen_input_raw.py` as a library module. Spectrum computation and plotting is carried out by invoking the function `gen_input_raw.params_to_plot` with the desired parameters.

Parameter name	Meaning
ion	A string identifying the ion, defaulting to the empty string "" if not specified.
dnum	An integer giving the number of 3d-electrons, defaulting to zero if not specified.
nuc_charge	An integer giving the nuclear charge in units of elementary charges, defaulting to zero if not specified.
Ek	A floating point number giving the kinetic energy of the Auger electron in Rydbergs, defaulting to zero if not specified.
group	A string identifying the point group of the system. Currently only supports "Oh" for octahedral, "D4h" for D _{4h} and "D5d" for D _{5d} .
If_params	Interpretation of this parameter varies depending on the parameter group. If group is "Oh", If_params should be a floating point number giving the octahedral field strength 10Dq. If group is "D4h", If_params should be a tuple of three floating point numbers giving the tetragonal parameters 10Dq, Dσ and Dτ in order. If group is "D5d", If_params should be a tuple of two floating point numbers giving the five-fold parameters Δ ₁ and Δ ₂ in order. (Gray <i>et al.</i> , 1971)

fdd_scaling, fpd_scaling, gpd_scaling, zeta3d_scaling, zeta3p_scaling	Floating point numbers giving the factors by which the Coulombic, exchange and spin-orbit coupling radial integrals, respectively, should be rescaled from Hartree-Fock values beyond a default 80% rescale. For example, fdd_scaling=0.6 will cause the Hartree-Fock F_{dd}^2 and F_{dd}^4 to be multiplied by $0.6 \times 0.8 = 0.48$ before being used.
state_spec	A tuple (a,b) specifying the state for which plotting is to be done. a is string containing the irreducible representation of the state in Butler notation and b an integer specifying the index of the desired state in that irreducible representation with states indexed in ascending order by energy beginning with 0 for the lowest energy state. If state_spec is not specified, the global ground state will be plotted. If only a is specified, the ground state within irreducible representation a will be plotted.
energy_min, energy_max	Floating point numbers giving the minimum and the maximum of the energy window in which the spectrum is to be simulated.
dG	Floating point number giving the σ for Gaussian broadening.
q	Floating point number giving the Fano asymmetry parameter.
shift	Floating point number giving the horizontal shift to be applied to the simulated spectrum, defaulting to zero if not specified.
gamma_floor	Floating point number giving the enforced minimum Lorentzian linewidths of simulated peaks, defaulting to zero if not specified.
plot_only	Boolean value specifying whether eigenfunctions and transition matrix elements should be computed (false) before generating the simulated spectra.
xy_filename	String giving the file name for storing the raw simulated spectrum.

A number of optional parameters can be supplied to request additional outputs.

Parameter name	Meaning
sticks_filename	A string giving the file name for storing a list of stick transitions.
intensity_threshold	A floating point number giving the minimum intensity for which a stick transition should be included in a sticks_filename output.
linewidths_filename	A string giving the file name for storing a list of computed Auger-limited linewidths.
framed_filename	A string giving the file name for storing the simulation with intensity rescaled to between zero and one.
const_widths_filename	A string giving the file name for storing a simulated spectrum with a constant Lorentzian linewidth.
const_widths	A floating point number giving the constant linewidth to be used in a const_widths_filename output.

zero_bounded_filename	A string giving the file name for storing the simulation vertically shifted such that the minimum intensity becomes zero.
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Python scripts for producing the simulated spectra used in the present article have been attached as examples. They are organized into folders:

Folder	Content
Ferrocene_M_simulation	Script for simulating the ground state M _{2,3} -edge absorption spectrum of neutral ferrocene.
Ferrocenium_M_simulations	Sub-folders each contain a script for simulating the ground and excited state M _{2,3} -edge absorption spectra of ferrocenium cation with a specific set of parameters.
Fe2_L_simulations	Sub-folders each contain a script for simulating the ground and excited state L _{2,3} -edge absorption spectra of Fe ^{II} cation with a different 10Dq.

S2.3. Parameters for CTM theory simulations in the main text

Table S5 Parameters for simulating the M_{2,3}-edge spectra of ferrocene and ferrocenium.

Species	Number of 3d-electrons	Scaling of Slater-Condon parameters		Scaling of spin-orbit coupling	Δ_1 (eV) *	Δ_2 (eV) *
		3d-3d	3p-3d			
Ferrocene	6	0.41	0.625	1.0	-0.8804	2.728
Ferrocenium	5	0.855	0.625	1.0	-0.8804	2.728
* (Gray <i>et al.</i> , 1971)						

Table S6 Parameters for simulating the L_{2,3}-edge spectra of Fe^{II} polypyridyl complexes.

Species	Number of 3d-electrons	Scaling of Slater-Condon parameters		Scaling of spin-orbit coupling	10 Dq (eV)
		3d-3d	2p-3d		
Fe ^{II}	6	1.0	1.0	1.0	Variable, see main text.

S3. Dependence of simulated difference spectrum of 6A_1 state on the choice of spin-orbit component.

Figure S1 shows that the spectra of difference spin-orbit split components of 6A_1 states are not significantly different.

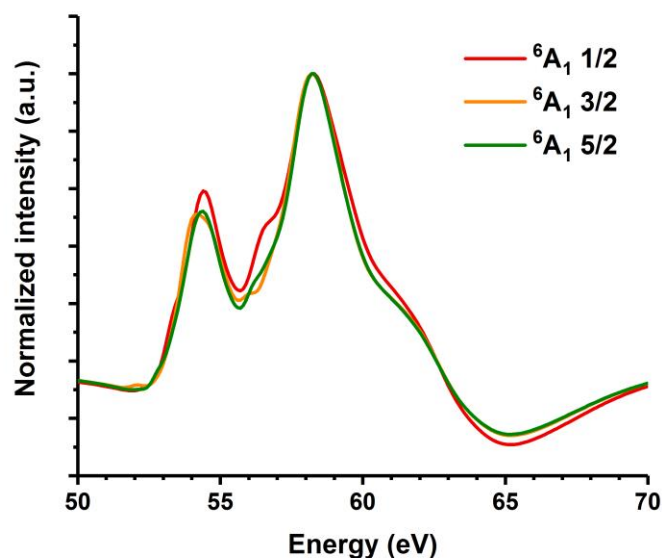


Figure S1 Simulated difference spectra of the spin-orbit split components of 6A_1 : $\frac{1}{2}$, $\frac{3}{2}$ and $\frac{5}{2}$.

S4. Dependence of simulated difference spectrum of 6A_1 state on the magnitude of horizontal shift applied to the computed ferrocenium spectrum.

A simulated difference spectrum of ferrocenium contains two horizontal shift parameters. One for computed spectrum of ground state ferrocene and another for that of ferrocenium. As detailed in the main text, the horizontal shift for the spectrum of ground state ferrocene is fixed at 3.7 eV. The shift for the spectrum of ferrocenium is adjusted for better agreement between experiment and theory.

Figure S2 shows that within a reasonable range, increasing the shift applied to the computed ferrocenium spectrum leads to an overall shift to higher energies of both peaks in the computed difference spectrum and a broadening of the peak at 58-59 eV.

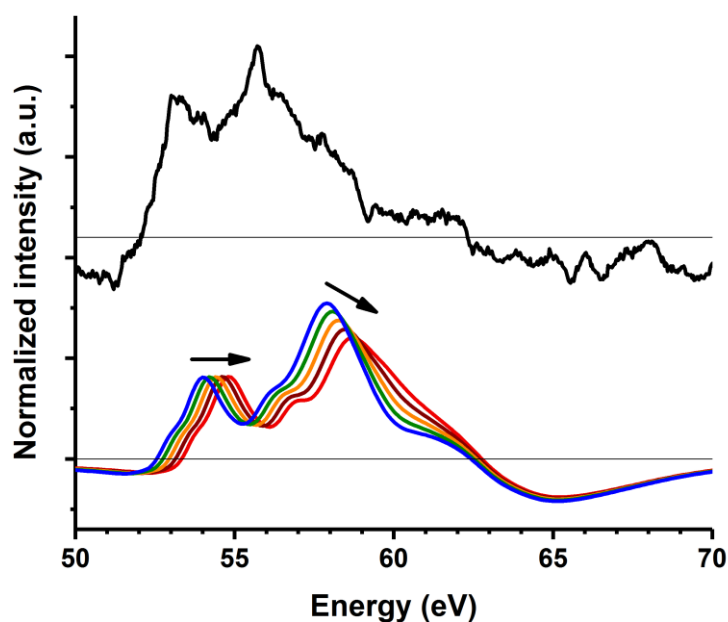


Figure S2 Simulated difference spectra of the 6A_1 state with the computed spectrum of ferrocenium shifted by 2.0, 1.8, 1.6, 1.4 and 1.2 eV, respectively. The arrows indicate the direction of increasing magnitude of the shift applied.

S5. Dependence of simulated difference spectrum of 6A_1 state on the magnitude of p-d interaction parameters.

Unless otherwise stated, the simulated $M_{2,3}$ -edge spectra in this work were all computed with 3p-3d Slater-Condon parameters scaled to 62.5% of free-ion values following literature precedents (Berlazzo *et al.*, 2006; Vura-Weis *et al.*, 2013; Zhang *et al.*, 2016; Ryland *et al.*, 2018).

The interpeak spacing in the simulated difference spectrum decreases as 3p-3d Slater-Condon parameters are down scaled from free-ion values (Figure S3).

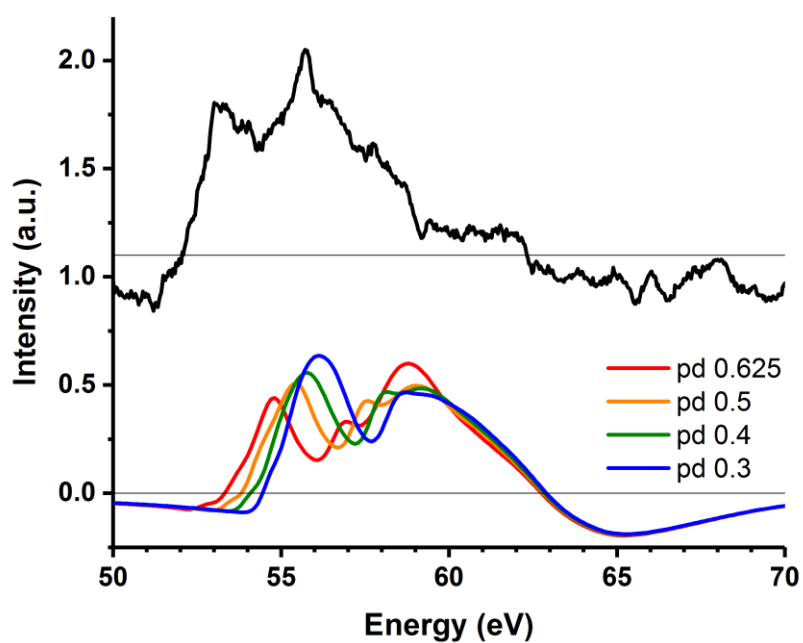


Figure S3 Top: Experimental difference spectrum of photogenerated ferrocenium (Chatterley *et al.*, 2016). Bottom: Simulated difference spectra of 6A_1 state of ferrocenium with F_{pd} and G_{pd} parameters scaled to 62.5%, 50%, 40% and 30% of free ion values.

S6. Dependence of simulated difference spectrum of 6A_1 state on the magnitude of d-d interaction parameters.

The shape of the difference features is not significantly sensitive to the magnitude of 3d-3d Slater-Condon parameters. An increase in 3d-3d Slater-Condon parameters is accompanied by a slight blueshift of difference features (Figure S4).

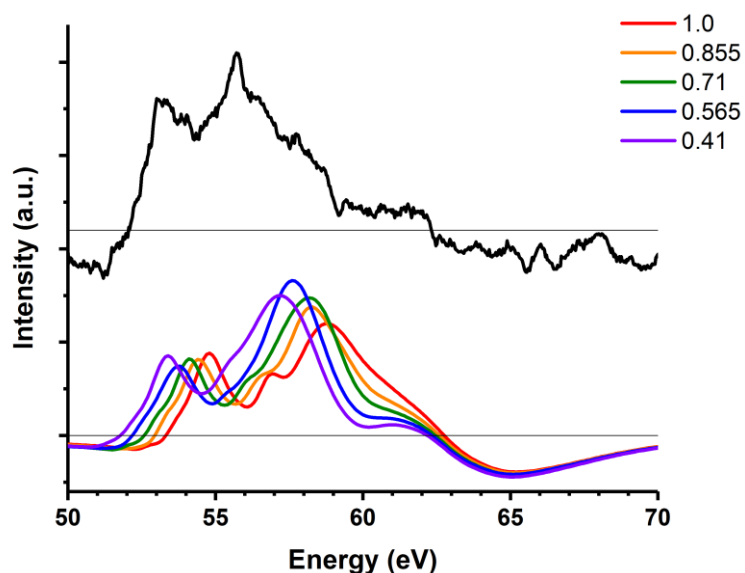


Figure S4 Top: Experimental difference spectrum of photogenerated ferrocenium (Chatterley *et al.*, 2016). Bottom: Simulated difference spectra of 6A_1 state of ferrocenium with F_{dd} parameter scaled to 100%, 85.5%, 71%, 56.5% and 42% of free ion values.

The observations of sections S3 and S6 suggest that downscaling both 3d-3d and 3p-3d Slater-Condon parameters can lead to a simulated difference spectrum in better agreement with experiment both in peak positions and in interpeak spacing (Figure S5).

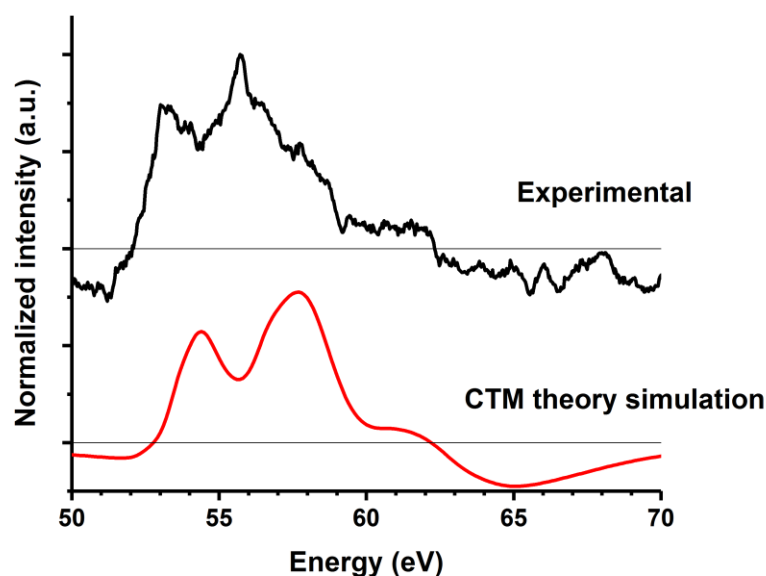


Figure S5 Top: Experimental difference spectrum of photogenerated ferrocenium (Chatterley *et al.*, 2016). Bottom: Simulated difference spectra of 6A_1 state of ferrocenium with F_{dd} parameter scaled to 42% of free ion values and F_{pd} and G_{pd} parameters scaled to 40% of free ion values.

S7. CTM theory simulation of $L_{2,3}$ -edge spectra of ferrocene and ferrocenium hexafluorophosphate.

Simulated $L_{2,3}$ -edge spectra of ferrocenium cation were computed using the same crystal field parameters as in the main text (Gray *et al.*, 1971) and nephelauxetic parameter being 0.86 or 0.42. Comparison with the experimental spectrum shows that a nephelauxetic parameter of 0.86 better reproduces the shape of the experimental absorption features (Figure S6) (Otero *et al.*, 2009). In particular, the simulation with nephelauxetic parameter being 0.86 reproduces the shoulder at 709 eV absent in the simulation with nephelauxetic parameter being 0.42.

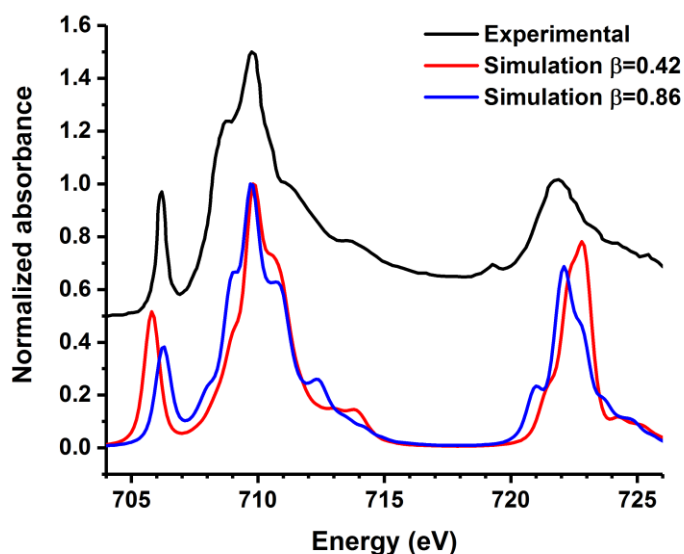


Figure S6 Top: experimental $L_{2,3}$ -edge absorption spectrum of ferrocenium hexafluorophosphate (Otero *et al.*, 2009). Bottom: Simulated $L_{2,3}$ -edge absorption spectra of ferrocenium cation with the nephelauxetic parameter being 0.42 (red) or 0.86 (blue).

The simulated $L_{2,3}$ -edge absorption spectrum of ferrocene computed using the same parameters underestimates the intensities of the peaks at 711.4 eV and 724 eV observed in the experimental spectrum (Figure S7) (Otero *et al.*, 2009). The peak at 711.4 eV has been given two assignments: a simultaneous 2p-3d and 3d-3d double excitation (Otero *et al.*, 2009) or to a 2p-Cp π^* transition (Godehusen *et al.*, 2017). The simulation of this feature using CTM theory is currently under investigation.

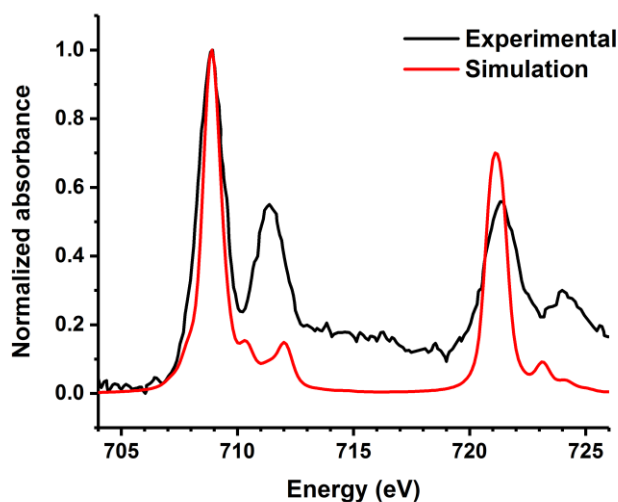


Figure S7 Black: experimental $L_{2,3}$ -edge absorption spectrum of ferrocene (Otero *et al.*, 2009). Bottom: Simulated $L_{2,3}$ -edge absorption spectra of ferrocene.

S8. References

- Berlazzo, R., Dallera, C., Borgatti, F., Vozzi, C., Sansone, G., Stagira, S., Nisoli, M., Ghiringhelli, G., Villorresi, P., Poletto, L., Pascolini, M., Nannarone, S., De Silvestri, S. & Braicovich, L. (2006). *Phys. Rev. B* **73**, 115101.
- Butler, P. H. (1981). *Point Group Symmetry Applications, Methods and Tables* Springer US.
- Chatterley, A. S., Lackner, F., Pemmaraju, C. D., Neumark, D. M., Leone, S. R. & Gessner, O. (2016). *J. Phys. Chem. A* **120**, 9509–9518.
- Godehusen, K., Richter, T., Zimmermann, P. & Wernet, P. (2017). *J. Phys. Chem. A* **121**, 66–72.
- Gray, H. B., Sohn, Y. S. & Hendrickson, N. (1971). *J. Am. Chem. Soc.* **93**, 3603–3612.
- Otero, E., Kosugi, N. & Urquhart, S. G. (2009). *J. Chem. Phys.* **131**, 114313.
- Ryland, E. S., Lin, M.-F., Verkamp, M. A., Zhang, K., Benke, K., Carlson, M. & Vura-Weis, J. (2018). *J. Am. Chem. Soc.* **140**, 4691–4696.
- Vura-Weis, J., Jiang, C.-M., Liu, C., Gao, H., Lucas, J. M., de Groot, F. M. F., Yang, P., Alivisatos, A. P. & Leone, S. R. (2013). *J. Phys. Chem. Lett.* **4**, 3667–3671.
- Zhang, K., Lin, M.-F., Ryland, E. S., Verkamp, M. A., Benke, K., de Groot, F. M. F., Girolami, G. S. & Vura-Weis, J. (2016). *J. Phys. Chem. Lett.* **7**, 3383–3387.