

**Supporting Information:**

**Simulating Transient X-ray Photoelectron  
Spectra of Fe(CO)<sub>5</sub> and Its Photodissociation  
Products With Multireference Algebraic  
Diagrammatic Construction Theory**

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# 1 Optimized geometries of iron carbonyl complexes

Geometries of each iron carbonyl compound were optimized at the NEVPT2 level of theory with the CAS(10e, 10o) active space and def2-QZVPP basis set. These geometries are provided below in Cartesian coordinates, with distances given in Å. The  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  geometries including free CO were obtained through constrained optimization with the Fe–C bond distances fixed at 10.0 Å.

## 1.1 Ground-state $\text{Fe}(\text{CO})_5$

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | 0.0000033513  | 0.0000000000  | 0.0000000000  |
| C  | 0.0000120362  | 0.0000000000  | 1.7875478540  |
| C  | 0.0000120362  | 0.0000000000  | -1.7875478540 |
| C  | -0.8972187835 | -1.5540061679 | 0.0000000000  |
| C  | -0.8972187835 | 1.5540061679  | 0.0000000000  |
| C  | 1.7944036865  | 0.0000000000  | 0.0000000000  |
| O  | 0.0000196369  | 0.0000000000  | 2.9326301797  |
| O  | 0.0000196369  | 0.0000000000  | -2.9326301797 |
| O  | -1.4707073864 | -2.5472855808 | 0.0000000000  |
| O  | -1.4707073864 | 2.5472855808  | 0.0000000000  |
| O  | 2.9413819559  | 0.0000000000  | 0.0000000000  |

## 1.2 Singlet $\text{Fe}(\text{CO})_4$ ( $\text{C}_{2v}$ )

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | 0.0000000000  | 0.0000000000  | 0.5530178757  |
| C  | 0.0000000000  | 1.6808886300  | -0.0195822486 |
| C  | 1.7691291575  | 0.0000000000  | 0.2598542786  |
| C  | 0.0000000000  | -1.6808886300 | -0.0195822486 |
| C  | -1.7691291575 | 0.0000000000  | 0.2598542786  |
| O  | 0.0000000000  | 2.7271273761  | -0.5003264155 |
| O  | 2.8823189435  | 0.0000000000  | -0.0164545523 |
| O  | 0.0000000000  | -2.7271273761 | -0.5003264155 |
| O  | -2.8823189435 | 0.0000000000  | -0.0164545523 |

## 1.3 Singlet $\text{Fe}(\text{CO})_4$ ( $\text{C}_{2v}$ ) with free CO

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | 0.0000000000  | 0.0000000000  | 1.4694460727  |
| C  | 0.0000000000  | 0.0000000000  | -8.5305539272 |
| C  | -1.7728173159 | 0.0000000000  | 1.7454913077  |
| C  | 1.7728173159  | 0.0000000000  | 1.7454913077  |
| C  | 0.0000000000  | -1.6740281604 | 2.0585336468  |
| C  | 0.0000000000  | 1.6740281604  | 2.0585336468  |
| O  | 0.0000000000  | 0.0000000000  | -9.6651870246 |
| O  | -2.8886736731 | 0.0000000000  | 2.0093509889  |
| O  | 2.8886736731  | 0.0000000000  | 2.0093509889  |

|   |              |               |              |
|---|--------------|---------------|--------------|
| 0 | 0.0000000000 | -2.7156438926 | 2.5497714961 |
| 0 | 0.0000000000 | 2.7156438926  | 2.5497714961 |

#### 1.4 Singlet Fe(CO)<sub>4</sub> (C<sub>3v</sub>)

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | -0.0000001687 | 0.0000000000  | 0.5392800561  |
| C  | 0.0000055461  | 0.0000000000  | -1.1834348850 |
| C  | -1.8177144403 | 0.0000000000  | 0.5351886888  |
| C  | 0.9088716663  | -1.5742170596 | 0.5352449051  |
| C  | 0.9088716663  | 1.5742170596  | 0.5352449051  |
| O  | 0.0000131775  | 0.0000000000  | -2.3346463850 |
| O  | -2.9616974697 | 0.0000000000  | 0.4576620321  |
| O  | 1.4808250113  | 2.5649212180  | 0.4577303415  |
| O  | 1.4808250113  | -2.5649212180 | 0.4577303415  |

#### 1.5 Singlet Fe(CO)<sub>4</sub> (C<sub>3v</sub>) with free CO

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | 1.4947620721  | -0.1537388067 | 0.0000000000  |
| C  | -8.4466741381 | 0.9269304677  | 0.0000000000  |
| C  | 3.0466203952  | -0.3535444615 | 0.0000000000  |
| C  | 1.6023010142  | 0.6752882032  | -1.4488215109 |
| C  | 1.6023010142  | 0.6752882032  | 1.4488215109  |
| C  | 1.2828347424  | -1.8127043194 | 0.0000000000  |
| O  | -9.5653931119 | 1.0473720623  | 0.0000000000  |
| O  | 4.2056152559  | -0.5027094849 | 0.0000000000  |
| O  | 1.7727359349  | 1.2364510554  | -2.4532971170 |
| O  | 1.7727359349  | 1.2364510554  | 2.4532971170  |
| O  | 1.2321608861  | -2.9750839747 | 0.0000000000  |

#### 1.6 Singlet Fe(CO)<sub>3</sub> (C<sub>s</sub>)

|    |               |               |               |
|----|---------------|---------------|---------------|
| Fe | -0.5904855200 | -0.7244440929 | 0.0000000000  |
| C  | -0.6631480917 | -0.0670633817 | 1.6494285842  |
| C  | 1.0614508288  | -0.2402051151 | 0.0000000000  |
| C  | -0.6631480917 | -0.0670633817 | -1.6494285842 |
| O  | -0.6549985938 | 0.5018880493  | -2.6511560793 |
| O  | -0.6549985938 | 0.5018880493  | 2.6511560793  |
| O  | 2.1653280623  | 0.0949998729  | 0.0000000000  |

#### 1.7 Singlet Fe(CO)<sub>3</sub> (C<sub>s</sub>) with free CO

|    |               |              |               |
|----|---------------|--------------|---------------|
| Fe | -0.3571414626 | 2.0686326990 | 0.0000000000  |
| C  | -1.7473441723 | 3.0836956592 | 0.0000000000  |
| C  | -0.0648317147 | 2.6622387084 | 1.6492275179  |
| C  | -0.0648317147 | 2.6622387084 | -1.6492275179 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| O | -2.6719221693 | 3.7738615177  | 0.0000000000  |
| O | 0.1214443097  | 3.1999566199  | 2.6508987869  |
| O | 0.1214443097  | 3.1999566199  | -2.6508987869 |
| C | 8.0648914205  | -3.3229683098 | 0.0000000000  |
| O | 9.0384809830  | -3.9059179796 | 0.0000000000  |
| C | -5.8235330937 | -6.3050499851 | 0.0000000000  |
| O | -6.6166566956 | -7.1166442581 | 0.0000000000  |

### 1.8 Singlet Fe(CO)<sub>3</sub> (D<sub>3h</sub>)

|    |               |               |              |
|----|---------------|---------------|--------------|
| Fe | 0.0000000000  | 0.0000000000  | 0.0000000000 |
| C  | -0.9279536992 | -1.6072629541 | 0.0000000000 |
| C  | 1.8559073984  | 0.0000000000  | 0.0000000000 |
| C  | -0.9279536992 | 1.6072629541  | 0.0000000000 |
| O  | -1.5012064313 | 2.6001658117  | 0.0000000000 |
| O  | -1.5012064313 | -2.6001658117 | 0.0000000000 |
| O  | 3.0024128627  | 0.0000000000  | 0.0000000000 |

### 1.9 Singlet Fe(CO)<sub>3</sub> (D<sub>3h</sub>) with free CO

|    |               |               |                |
|----|---------------|---------------|----------------|
| Fe | 0.0000000000  | 0.0000000000  | 0.0000000000   |
| C  | 0.0000000000  | 0.0000000000  | 10.0000000000  |
| C  | 1.8558987902  | 0.0000000000  | 0.0000000000   |
| C  | -0.9279493951 | 1.6072554992  | 0.0000000000   |
| C  | -0.9279493951 | -1.6072554992 | 0.0000000000   |
| O  | 0.0000000000  | 0.0000000000  | 11.1347191284  |
| O  | 3.0024280400  | 0.0000000000  | 0.0000000000   |
| O  | -1.5012140200 | 2.6001789556  | 0.0000000000   |
| O  | -1.5012140200 | -2.6001789556 | 0.0000000000   |
| C  | 0.0000000000  | 0.0000000000  | -10.0000000000 |
| O  | 0.0000000000  | 0.0000000000  | -11.1347191284 |

## 2 Selection of active spaces

Restricted Kohn–Sham B3LYP molecular orbitals were used as the guess for selecting the active space in the CASSCF calculations.

### 2.1 Ground-state Fe(CO)<sub>5</sub>

Listed orbitals included for CAS(10e, 13o)

Removed for CAS(10e, 10o)

Additionally removed for CAS(8e, 9o)

Additionally removed for CAS(8e, 8o)

```
MO #38 energy= -0.473240659748219 occ= 2
MO #45 energy= -0.317568684977186 occ= 2
MO #46 energy= -0.31756708404827 occ= 2
MO #47 energy= -0.260078469807197 occ= 2
MO #48 energy= -0.260075970393764 occ= 2
MO #49 energy= -0.051385737795196 occ= 0
MO #50 energy= -0.0513845263246786 occ= 0
MO #51 energy= -0.0431035847904987 occ= 0
MO #52 energy= -0.0431027407623284 occ= 0
MO #53 energy= -0.0371819956140942 occ= 0
MO #55 energy= -0.0269324570548654 occ= 0
MO #56 energy= -0.0213702122085298 occ= 0
MO #57 energy= -0.021368084226683 occ= 0
```

### 2.2 Singlet Fe(CO)<sub>4</sub> (C<sub>2v</sub>)

Listed orbitals included for CAS(10e, 13o)

Removed for CAS(10e, 10o)

Additionally removed for CAS(8e, 9o)

Additionally removed for CAS(8e, 8o)

```
MO #34 energy= -0.455248169061573 occ= 2
MO #38 energy= -0.30181401438336 occ= 2
MO #39 energy= -0.266445760521372 occ= 2
MO #40 energy= -0.246895054159617 occ= 2
MO #41 energy= -0.241103457376167 occ= 2
MO #42 energy= -0.121430619156503 occ= 0
MO #43 energy= -0.0426490457319132 occ= 0
MO #44 energy= -0.0415692224873694 occ= 0
MO #45 energy= -0.0367555479003166 occ= 0
MO #46 energy= -0.0217548133102525 occ= 0
MO #47 energy= -0.0053484169621015 occ= 0
MO #48 energy= -0.00202638190503459 occ= 0
MO #49 energy= 0.00102125620255649 occ= 0
```

## 2.3 Singlet Fe(CO)<sub>4</sub> (C<sub>3v</sub>)

Orbitals for CAS(10e, 13o)

```
MO #35 energy= -0.451830428785213 occ= 2
MO #38 energy= -0.306086302299252 occ= 2
MO #39 energy= -0.306083957296835 occ= 2
MO #40 energy= -0.247332439006426 occ= 2
MO #41 energy= -0.24732935885856 occ= 2
MO #42 energy= -0.146422332948368 occ= 0
MO #43 energy= -0.0417729656109744 occ= 0
MO #44 energy= -0.0417710700105333 occ= 0
MO #46 energy= -0.0169668840138931 occ= 0
MO #47 energy= -0.0169644159569191 occ= 0
MO #48 energy= -0.00510389869495578 occ= 0
MO #49 energy= 0.00187230564446153 occ= 0
MO #50 energy= 0.00187590414947945 occ= 0
```

## 2.4 Singlet Fe(CO)<sub>3</sub> (C<sub>s</sub>)

Listed orbitals included for CAS(10e, 13o)

Removed for CAS(10e, 10o)

Additionally removed for CAS(8e, 9o)

Additionally removed for CAS(8e, 8o)

```
MO #29 energy= -0.434340864224717 occ= 2
MO #31 energy= -0.28921251252865 occ= 2
MO #32 energy= -0.261221927670599 occ= 2
MO #33 energy= -0.231210058346076 occ= 2
MO #34 energy= -0.229475121963493 occ= 2
MO #35 energy= -0.121926550643769 occ= 0
MO #36 energy= -0.0997992985424646 occ= 0
MO #37 energy= -0.0311013209948906 occ= 0
MO #38 energy= -0.00837210029613733 occ= 0
MO #39 energy= 0.00391172234960734 occ= 0
MO #40 energy= 0.0171881603020779 occ= 0
MO #41 energy= 0.0223078171054447 occ= 0
MO #42 energy= 0.0288797608426257 occ= 0
```

## 2.5 Singlet Fe(CO)<sub>3</sub> (D<sub>3h</sub>)

Orbitals for CAS(8e, 12o)

```
MO #31 energy= -0.289488351686681 occ= 2
MO #32 energy= -0.289480805509797 occ= 2
MO #33 energy= -0.229284224984664 occ= 2
```

MO #34 energy= -0.229270115012075 occ= 2  
MO #35 energy= -0.1500166065309 occ= 0  
MO #36 energy= -0.109580305834795 occ= 0  
MO #37 energy= -0.0232009559470306 occ= 0  
MO #38 energy= -0.0206476704611151 occ= 0  
MO #39 energy= -0.020644627280275 occ= 0  
MO #40 energy= -0.0112900652103888 occ= 0  
MO #41 energy= -0.0112794596722699 occ= 0  
MO #42 energy= 0.0248105347785993 occ= 0



### 3 Total CASSCF and NEVPT2 energies for optimized geometries

Table S1: NEVPT2 and CASSCF energies (in  $E_h$ ) computed at the optimized geometries using the CAS(10e, 13o) active space and unc-def2-TZVPP basis. The NEVPT2 energies were computed using  $10^{-5}$  and  $10^{-10}$  truncation parameters for the semi-internal and doubly external excitations, respectively.

| Complex                                      | CASSCF     | NEVPT2     |
|--|------------|------------|
| Fe(CO) <sub>5</sub>                          | -1835.7345 | -1839.1437 |
| Fe(CO) <sub>4</sub> (C <sub>2v</sub> ) + CO  | -1835.6913 | -1839.0718 |
| Fe(CO) <sub>4</sub> (C <sub>3v</sub> ) + CO  | -1835.7056 | -1839.0522 |
| Fe(CO) <sub>3</sub> (C <sub>s</sub> ) + 2CO  | -1835.6649 | -1838.9987 |
| Fe(CO) <sub>3</sub> (D <sub>3h</sub> ) + 2CO | -1835.6372 | -1838.9556 |

## 4 MR-ADC(2)-X ionization energies and spectroscopic factors

Table S2: Ionization energies (in eV) and spectroscopic factors calculated using MR-ADC(2)-X for the Fe 3p edge of  $\text{Fe}(\text{CO})_n$  ( $n = 3, 4, 5$ ). Calculations used the unc-def2-TZVPP basis set and CAS(10e, 13o) active space. Results shown incorporate spin-orbit coupling corrections from Table S7. For  $\text{Fe}(\text{CO})_3$  ( $D_{3h}$ ), the CAS(8e, 12o) active space was used.

| Complex                               | Ionization energy | Spectroscopic intensity |
|---------------------------------------|-------------------|-------------------------|
| $\text{Fe}(\text{CO})_5$              | 62.24             | 1.298                   |
|                                       | 62.45             | 1.298                   |
|                                       | 64.25             | 1.322                   |
| $\text{Fe}(\text{CO})_4$ ( $C_{2v}$ ) | 61.48             | 1.264                   |
|                                       | 62.20             | 1.265                   |
|                                       | 63.57             | 1.263                   |
| $\text{Fe}(\text{CO})_4$ ( $C_{3v}$ ) | 62.03             | 1.288                   |
|                                       | 62.21             | 1.288                   |
|                                       | 64.37             | 1.310                   |
| $\text{Fe}(\text{CO})_3$ ( $C_s$ )    | 61.40             | 1.277                   |
|                                       | 61.97             | 1.271                   |
|                                       | 63.67             | 1.258                   |
| $\text{Fe}(\text{CO})_3$ ( $D_{3h}$ ) | 60.97             | 1.176                   |
|                                       | 61.11             | 1.171                   |
|                                       | 63.55             | 1.154                   |

Table S3: Ionization energies (in eV) and spectroscopic factors calculated using MR-ADC(2)-X for the CO  $3\sigma$  edge of  $\text{Fe}(\text{CO})_n$  ( $n = 3, 4, 5$ ). Calculations used the unc-def2-TZVPP basis set and CAS(10e, 13o) active space. For  $\text{Fe}(\text{CO})_3$  ( $D_{3h}$ ), the CAS(8e, 12o) active space was used.

| Complex                               | Ionization energy | Spectroscopic intensity |
|---------------------------------------|-------------------|-------------------------|
| $\text{Fe}(\text{CO})_5$              | 36.38             | 1.457                   |
|                                       | 36.38             | 1.457                   |
|                                       | 36.39             | 1.456                   |
|                                       | 36.89             | 1.472                   |
|                                       | 36.89             | 1.471                   |
| $\text{Fe}(\text{CO})_4$ ( $C_{2v}$ ) | 36.08             | 1.509                   |
|                                       | 36.08             | 1.509                   |
|                                       | 36.63             | 1.486                   |
|                                       | 36.64             | 1.486                   |
| $\text{Fe}(\text{CO})_4$ ( $C_{3v}$ ) | 36.30             | 1.551                   |
|                                       | 36.38             | 1.444                   |
|                                       | 36.38             | 1.444                   |
|                                       | 36.40             | 1.452                   |
| $\text{Fe}(\text{CO})_3$ ( $C_s$ )    | 35.97             | 1.545                   |
|                                       | 35.99             | 1.514                   |
|                                       | 36.04             | 1.558                   |
| $\text{Fe}(\text{CO})_3$ ( $D_{3h}$ ) | 35.96             | 1.394                   |
|                                       | 36.01             | 1.396                   |
|                                       | 36.01             | 1.396                   |
| CO                                    | 38.79             | 1.803                   |

## 5 X-ray photoelectron spectra at the CO $3\sigma$ edge

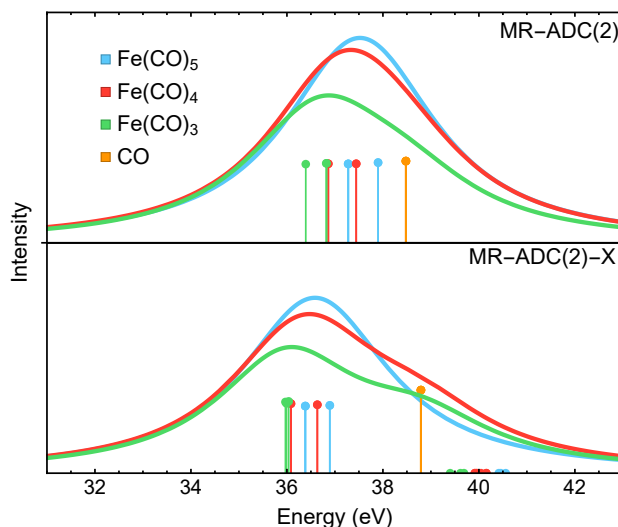


Figure S1: CO  $3\sigma^{-1}$  X-ray photoelectron spectra of  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_4$ , and  $\text{Fe}(\text{CO})_3$  simulated using MR-ADC(2) and MR-ADC(2)-X. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities. Calculations employed the CAS(10e, 13o) active space and uncontracted def2-TZVPP basis set.

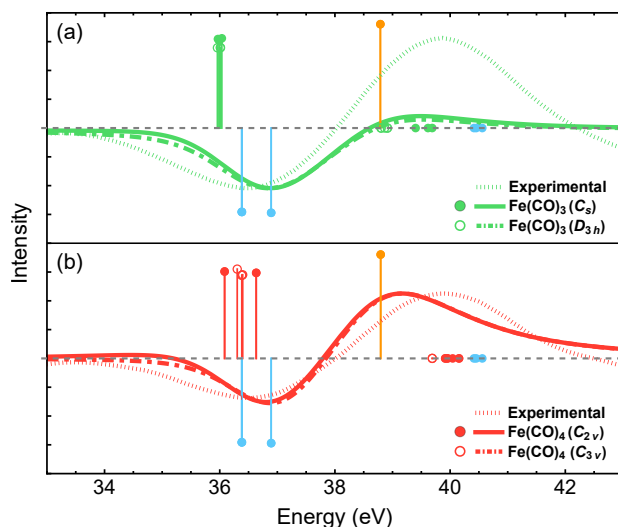


Figure S2: CO  $3\sigma^{-1}$  X-ray photoelectron difference spectra of different geometries of a)  $\text{Fe}(\text{CO})_3$  and b)  $\text{Fe}(\text{CO})_4$  relative to  $\text{Fe}(\text{CO})_5$  simulated using MR-ADC(2)-X. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities. Calculations employed the CAS(10e, 13o) active space and uncontracted def2-TZVPP basis set.

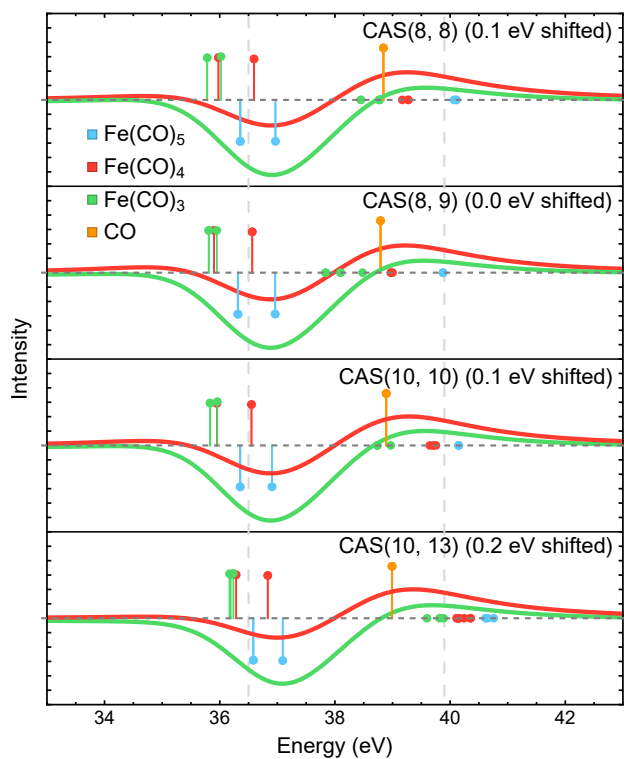


Figure S3: CO  $3\sigma^{-1}$  X-ray photoelectron difference spectra of  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  relative to  $\text{Fe}(\text{CO})_5$  simulated with MR-ADC(2)-X for different active space selections. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities. Calculations employed an uncontracted def2-TZVPP basis set.

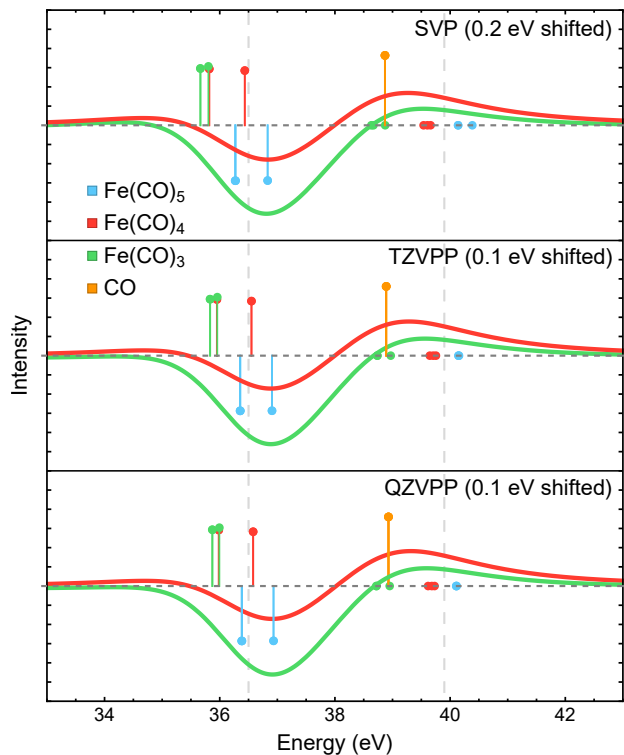


Figure S4: CO  $3\sigma^{-1}$  X-ray photoelectron difference spectra of  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  relative to  $\text{Fe}(\text{CO})_5$  simulated with MR-ADC(2)-X for different basis sets. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities. Calculations employed the CAS(10e, 13o) active space.

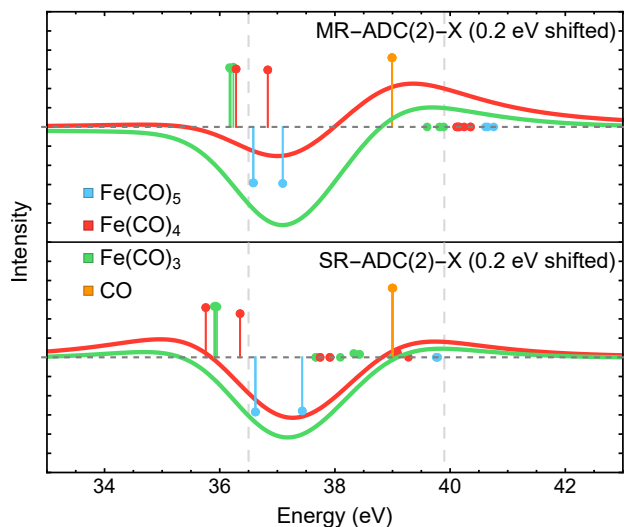


Figure S5: CO  $3\sigma^{-1}$  X-ray photoelectron difference spectra of  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  relative to  $\text{Fe}(\text{CO})_5$  simulated with MR-ADC(2)-X and SR-ADC(2)-X with an uncontracted def2-TZVPP basis set. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities. MR-ADC(2)-X calculations employed the CAS(10e, 13o) active space.

## 6 Spin-orbit coupling corrections for the Fe 3p edge

Table S4: Fe 3p ionization energies (in eV) of Fe(CO)<sub>5</sub> (D<sub>3h</sub> symmetry) computed using IP-MR-ADC(1) and unc-def2-TZVPP basis set with and without spin-orbit coupling effects. Scalar relativistic effects were incorporated for both calculations using the sf-X2C1e Hamiltonian. See Section 7 of the ESI for more details.

| Electronic state | Ionization energy without SOC | Ionization energy with SOC | $\Delta_{\text{SOC}}$ |
|------------------|-------------------------------|----------------------------|-----------------------|
| 3p <sub>1</sub>  | 75.82                         | 75.34                      | -0.48                 |
| 3p <sub>2</sub>  | 75.82                         | 75.55                      | -0.27                 |
| 3p <sub>3</sub>  | 76.16                         | 76.89                      | 0.73                  |

Table S5: Fe 3p ionization energies (in eV) of Fe(CO)<sub>4</sub> (C<sub>2v</sub> symmetry) computed using IP-MR-ADC(1) and unc-def2-TZVPP basis set with and without spin-orbit coupling effects. Scalar relativistic effects were incorporated for both calculations using the sf-X2C1e Hamiltonian. See Section 7 of the ESI for more details.

| Electronic state | Ionization energy without SOC | Ionization energy with SOC | $\Delta_{\text{SOC}}$ |
|------------------|-------------------------------|----------------------------|-----------------------|
| 3p <sub>1</sub>  | 74.87                         | 74.54                      | -0.33                 |
| 3p <sub>2</sub>  | 75.42                         | 74.98                      | -0.44                 |
| 3p <sub>3</sub>  | 75.50                         | 76.24                      | 0.74                  |

Table S6: Fe 3p ionization energies (in eV) of Fe(CO)<sub>4</sub> (C<sub>3v</sub> symmetry) computed using IP-MR-ADC(1) and unc-def2-TZVPP basis set with and without spin-orbit coupling effects. Scalar relativistic effects were incorporated for both calculations using the sf-X2C1e Hamiltonian. See Section 7 of the ESI for more details.

| Electronic state | Ionization energy without SOC | Ionization energy with SOC | $\Delta_{\text{SOC}}$ |
|------------------|-------------------------------|----------------------------|-----------------------|
| 3p <sub>1</sub>  | 75.42                         | 74.94                      | -0.48                 |
| 3p <sub>2</sub>  | 75.42                         | 75.12                      | -0.30                 |
| 3p <sub>3</sub>  | 75.70                         | 76.46                      | 0.76                  |

Table S7: Fe 3p ionization energies (in eV) of  $\text{Fe}(\text{CO})_3$  ( $C_s$  symmetry) computed using IP-MR-ADC(1) and unc-def2-TZVPP basis set with and without spin-orbit coupling effects. Scalar relativistic effects were incorporated for both calculations using the sf-X2C1e Hamiltonian. See Section 7 of the ESI for more details.

| Electronic state | Ionization energy without SOC | Ionization energy with SOC | $\Delta_{\text{SOC}}$ |
|------------------|-------------------------------|----------------------------|-----------------------|
| 3p <sub>1</sub>  | 74.39                         | 74.07                      | -0.32                 |
| 3p <sub>2</sub>  | 74.93                         | 74.52                      | -0.41                 |
| 3p <sub>3</sub>  | 75.05                         | 75.77                      | 0.72                  |

Table S8: Fe 3p ionization energies (in eV) of  $\text{Fe}(\text{CO})_3$  ( $D_{3h}$  symmetry) computed using IP-MR-ADC(1) and unc-def2-TZVPP basis set with and without spin-orbit coupling effects. Scalar relativistic effects were incorporated for both calculations using the sf-X2C1e Hamiltonian. See Section 7 of the ESI for more details.

| Electronic state | Ionization energy without SOC | Ionization energy with SOC | $\Delta_{\text{SOC}}$ |
|------------------|-------------------------------|----------------------------|-----------------------|
| 3p <sub>1</sub>  | 74.34                         | 73.87                      | -0.47                 |
| 3p <sub>2</sub>  | 74.36                         | 74.01                      | -0.35                 |
| 3p <sub>3</sub>  | 74.56                         | 75.36                      | 0.80                  |

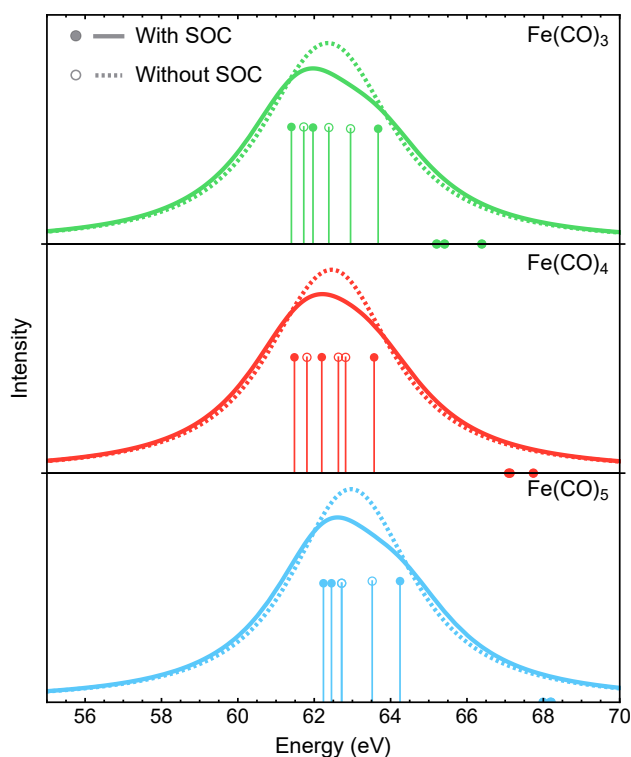


Figure S6: Fe 3p X-ray photoelectron spectra of  $\text{Fe}(\text{CO})_3$ ,  $\text{Fe}(\text{CO})_4$ , and  $\text{Fe}(\text{CO})_5$  simulated using MR-ADC(2)-X with and without spin-orbit coupling (SOC) effects. Vertical lines represent the computed core ionization energies and the corresponding photoelectron intensities.



## 7 Implementation of spin–orbit coupling effects

### 7.1 Form of the spin–orbit coupling Hamiltonian

The implementation of spin–orbit coupling (SOC) effects in IP-MR-ADC(1) utilized the Breit–Pauli (BP) SOC Hamiltonian. In addition, spin–orbit mean-field (SOMF) approximation was invoked, resulting in a Hamiltonian that we term BP-SOMF.

The BP-SOMF Hamiltonian in second quantization takes the following form:

$$\hat{\mathcal{H}}^{SOMF} = \sum_{\xi} \sum_{pq} F_{pq}^{\xi} \hat{D}_{pq}^{\xi} \quad (1)$$

where  $\hat{D}_{pq}^{\xi}$  is the one-electron spin excitation operator

$$\begin{aligned} \hat{D}_{pq}^x &= \frac{1}{2}(a_{p\alpha}^{\dagger}a_{q\beta} + a_{p\beta}^{\dagger}a_{q\alpha}) , \\ \hat{D}_{pq}^y &= \frac{i}{2}(a_{p\beta}^{\dagger}a_{q\alpha} - a_{p\alpha}^{\dagger}a_{q\beta}) , \\ \hat{D}_{pq}^z &= \frac{1}{2}(a_{p\alpha}^{\dagger}a_{q\alpha} - a_{p\beta}^{\dagger}a_{q\beta}) , \end{aligned} \quad (2)$$

$F_{pq}^{\xi}$  is defined as

$$F_{pq}^{\xi} = h_{pq}^{\xi} + \sum_{rs} P_r^s \left( g_{rspq}^{\xi} - \frac{3}{2}g_{prsq}^{\xi} + \frac{3}{2}g_{qrsp}^{\xi} \right) , \quad (3)$$

and  $P_r^s = P_{r\alpha}^{s\alpha} + P_{r\beta}^{s\beta}$  is the spinless one-particle reduced density matrix of the state-specific CASSCF reference wavefunction. In Eq. (3),  $h_{pq}^{\xi}$  and  $g_{pqrs}^{\xi}$  are the one- and two-electron integrals calculated in the spatial molecular orbital basis ( $\phi_p$ )

$$\begin{aligned} h_{pq}^{\xi} &= \langle \phi_p(1) | \hat{h}_{\xi}(1) | \phi_q(1) \rangle , \\ g_{pqrs}^{\xi} &= \langle \phi_p(1)\phi_r(2) | \hat{g}_{\xi,soo}(1,2) | \phi_q(1)\phi_s(2) \rangle , \end{aligned} \quad (4)$$

with  $\hat{h}_{\xi}(i)$  being the one–electron spin–orbit operator and  $\hat{g}_{\xi,soo}(i,j)$  being the ‘spin–other orbit’ two-electron operator

$$\begin{aligned} \hat{h}_{\xi}(i) &= \frac{1}{2c^2} \sum_A \frac{Z_A [\mathbf{r}_{iA} \times \hat{\mathbf{p}}(i)]_{\xi}}{r_{iA}^3} , \\ \hat{g}_{\xi,soo}(i,j) &= -\frac{1}{2c^2} \frac{[\mathbf{r}_{ij} \times \hat{\mathbf{p}}(j)]_{\xi}}{r_{ij}^3} , \end{aligned} \quad (5)$$

where  $Z_A$  denotes the nuclear charge on nucleus  $A$ ,  $\mathbf{r}_{ij}$  and  $\mathbf{r}_{iA}$  are the relative coordinates of electron  $i$  with respect to electron  $j$  and nucleus  $A$ , respectively,  $\hat{\mathbf{p}}(i)$  is the momentum operator of electron  $i$ , and  $\xi = x, y, z$ .

## 7.2 Implementation of spin–orbit coupling effects in IP-MR-ADC(1)

Here, we outline modifications in the IP-MR-ADC(1) that incorporate the SOC effects. For details about the theory behind IP-MR-ADC(1) we refer to [*J. Chem. Theory Comput.* **15**, 5908–5924 (2019)] and [*J. Chem. Theory Comput.* **16**, 6343–6357 (2020)], here referred to as [1] and [2].

To incorporate spin–orbit coupling effects in IP-MR-ADC(1), we include  $\hat{\mathcal{H}}^{SOMF}$  (Eq. (1)) in the perturbation operator  $\hat{V}$  that is used to define the order series for the effective Hamiltonian matrix  $\mathbf{M}$  and effective transition moments matrix  $\mathbf{T}$ . At first order,  $\mathbf{M}$  contains the following effective Hamiltonian contributions

$$\tilde{H}^{(1)} = \hat{V} + [\hat{H}^{(0)}, \hat{T}^{(1)} - \hat{T}^{(1)\dagger}] \quad (6)$$

where  $\hat{T}^{(1)}$  and  $\hat{T}^{(1)\dagger}$  are the excitation and de-excitation operators, respectively.

In addition to augmenting  $\hat{V}$  with  $\hat{\mathcal{H}}^{SOMF}$ , consistent implementation of spin–orbit MR-ADC(1) also requires incorporating SOC in the calculations of amplitudes that define  $\hat{T}^{(1)}$  and  $\hat{T}^{(1)\dagger}$ . For this reason, we also include  $\hat{\mathcal{H}}^{SOMF}$  as part of the perturbation operator in Eq. 42 of Ref. [1]. The resulting amplitudes become complex-valued, making the effective Hamiltonian matrix  $\mathbf{M}$  complex-Hermitian. Diagonalizing the resulting  $\mathbf{M}$  matrix yields real-valued ionization energies that incorporate SOC effects to first order in perturbation theory. Due to the fact that the size of  $\mathbf{M}$  at the MR-ADC(1) is rather small, we did not invoke the CVS approximation in these calculations.