

† Electronic Supplementary Information (ESI) for: Dissociative electron attachment and electronic excitation in Fe(CO)₅

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Contents

| | |
|---|-----------|
| S1 Geometry of Fe(CO)₅ | s2 |
| S2 Excited states | s2 |
| S2.1 Spin and dipole allowed transitions | s2 |
| S2.2 Spin allowed, dipole forbidden transitions | s4 |
| S2.3 Singlet-triplet transitions | s6 |

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S1 Geometry of Fe(CO)₅

Cartesian coordinates of Fe(CO)₅, D_{3h} point group, optimized at BP86/QZ4P level of theory (see section Experimental Methods, Electronically excited states of Fe(CO)₅, in the main text):

| | | | |
|------|-----------|-----------|-----------|
| 1.Fe | 0.000000 | 0.000000 | 0.000000 |
| 2.C | 0.903371 | 1.564685 | 0.000000 |
| 3.C | 0.903371 | -1.564685 | 0.000000 |
| 4.C | -1.806743 | 0.000000 | 0.000000 |
| 5.C | 0.000000 | 0.000000 | 1.807515 |
| 6.C | 0.000000 | 0.000000 | -1.807515 |
| 7.O | 1.479928 | 2.563310 | 0.000000 |
| 8.O | 1.479928 | -2.563310 | 0.000000 |
| 9.O | -2.959856 | 0.000000 | 0.000000 |
| 10.O | 0.000000 | 0.000000 | 2.957760 |
| 11.O | 0.000000 | 0.000000 | -2.957760 |

S2 Excited states

Tables S1, S2, S3, S4 list the calculated excited states, their energies and oscillator strengths. The excitation energies were calculated at the BP86/QZ4P level of theory (see Figure 10 in the main text). Ground electronic state of Fe(CO)₅ is $^1A'_1$, with electronic configuration: $\dots(1e'')^4(7e')^4(7a_2'')^2(8e')^4(13a_1')^2(1a_2')^2(2e'')^4(9e')^4(8a_2'')^2(3e'')^4(10e')^4(4e'')^0(14a_1')^0(11e')^0(9a_2'')^0(2a_2')^0(12e')^0(5e'')^0(15a_1')^0(10a_2'')^0(13e')^0(16a_1')^0(17a_1')^0(14e')^0(6e'')^0(11a_2'')^0(18a_1')^0\dots$ Description of electronic states by TD-DFT is given by linear combination of single excitations, as given in Tables S1, S2, S3, S4.

Dipole allowed transitions are to the excited $^1A''_2$ and $^1E'$ states, Tables S1 and S2, respectively. Spin allowed, dipole forbidden transitions are given in Table S3, while singlet-triplet transitions are collected in Table S4.

S2.1 Spin and dipole allowed transitions

Table S1 TDDFT (BP86/QZ4P) $^1A''_2$ transitions, the corresponding oscillator strengths (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of Fe(CO)₅

| E (eV) | f | Assignment | % |
|--------|-------------|---------------|-------|
| 4.1103 | 0.22461E-01 | 10e' → 4e'' | 95.68 |
| 5.3675 | 0.30392E-03 | 10e' → 5e'' | 83.39 |
| | | 3e'' → 11e' | 16.54 |
| 6.0659 | 0.12560E-02 | 3e'' → 12e' | 98.75 |
| 6.5274 | 0.36667 | 3e'' → 11e' | 67.20 |
| | | 10e' → 5e'' | 13.51 |
| 8.3599 | 0.30408E-02 | 3e'' → 13e' | 99.39 |
| 8.5621 | 0.10066 | 8a2'' → 14a1' | 61.93 |
| | | 9e' → 4e'' | 27.83 |
| 8.9261 | 0.10169 | 9e' → 4e'' | 53.40 |
| | | 2e'' → 11e' | 16.16 |
| | | 8a2'' → 14a1' | 12.46 |
| 9.1243 | 0.11369E-01 | 10e' → 6e'' | 95.69 |
| 9.2266 | 0.75825E-05 | 8e' → 4e'' | 97.66 |
| 9.3553 | 0.68589E-01 | 2e'' → 11e' | 59.33 |
| | | 7e' → 4e'' | 10.45 |
| 9.6609 | 0.25707E-03 | 13a1' → 9a2'' | 47.08 |
| | | 7a2'' → 14a1' | 36.48 |
| 9.7603 | 0.54551E-03 | 2e'' → 12e' | 85.49 |

Table S1 TDDFT (BP86/QZ4P) ${}^1A_2'$ transitions of Fe(CO)₅

| E (eV) | f | Assignment | % |
|--------|-------------|-------------|-------|
| 9.7860 | 0.53044E-03 | 7e' → 4e'' | 60.14 |
| | | 1e'' → 11e' | 14.01 |
| | | 9e' → 5e'' | 12.60 |
| 10.076 | 0.74607E-03 | 3e'' → 14e' | 99.23 |

Table S2 TDDFT (BP86/QZ4P) ${}^1E'$ transitions, the corresponding oscillator strengths (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of Fe(CO)₅

| E (eV) | f | Assignment | % |
|--------|-------------|---------------|-------|
| 4.1410 | 0.14305E-04 | 10e' → 11e' | 98.74 |
| 4.2445 | 0.18436E-03 | 10e' → 14a1' | 93.38 |
| 4.5853 | 0.19820E-02 | 10e' → 2a2' | 66.25 |
| | | 10e' → 12e' | 32.38 |
| 5.2567 | 0.55409E-01 | 10e' → 12e' | 45.08 |
| | | 3e'' → 9a2'' | 32.44 |
| | | 10e' → 2a2' | 15.71 |
| 5.6504 | 0.12531E-02 | 3e'' → 4e'' | 77.32 |
| | | 3e'' → 9a2'' | 18.67 |
| 6.0948 | 0.47277E-01 | 10e' → 15a1' | 49.65 |
| | | 3e'' → 9a2'' | 21.23 |
| 6.2033 | 0.13858 | 10e' → 15a1' | 49.33 |
| | | 3e'' → 9a2'' | 17.83 |
| | | 3e'' → 5e'' | 13.74 |
| 6.9906 | 0.16826 | 3e'' → 5e'' | 67.03 |
| | | 10e' → 13e' | 10.77 |
| 7.0221 | 0.39796E-01 | 10e' → 13e' | 89.03 |
| 7.6597 | 0.50695E-02 | 10e' → 16a1' | 99.78 |
| 8.1833 | 0.14764E-02 | 3e'' → 10a2'' | 98.55 |
| 8.2574 | 0.18657E-01 | 10e' → 17a1' | 95.88 |
| 8.3509 | 0.42221E-01 | 8a2'' → 4e'' | 85.97 |
| 8.7396 | 0.10690E-01 | 10e' → 14e' | 94.74 |
| 8.8102 | 0.17301E-01 | 9e' → 14a1' | 52.17 |
| | | 9e' → 11e' | 40.52 |
| | | 2e'' → 4e'' | 41.82 |
| 8.9812 | 0.30071E-01 | 9e' → 11e' | 28.42 |
| | | 9e' → 14a1' | 15.95 |
| | | 2e'' → 4e'' | 46.98 |
| 9.0993 | 0.43509E-01 | 9e' → 11e' | 20.70 |
| | | 1a2' → 11e' | 76.76 |
| 9.1620 | 0.13355E-04 | 9e' → 2a2' | 21.62 |
| | | 9e' → 2a2' | 48.58 |
| 9.2187 | 0.22392E-02 | 8e' → 14a1' | 20.81 |
| | | 1a2' → 11e' | 16.92 |
| | | 8e' → 14a1' | 63.26 |
| 9.3043 | 0.95784E-03 | 9e' → 2a2' | 12.87 |
| | | 8e' → 11e' | 89.77 |
| 9.3959 | 0.16112E-03 | 8e' → 11e' | 89.77 |
| 9.4282 | 0.12323E-02 | 2e'' → 9a2'' | 59.52 |
| | | 13a1' → 11e' | 12.93 |
| 9.5047 | 0.33184E-02 | 9e' → 12e' | 55.03 |

Table S2 TDDFT (BP86/QZ4P) ${}^1E'$ transitions of $\text{Fe}(\text{CO})_5$; f should be multiplied by two due to the degeneracy

| E (eV) | f | Assignment | % |
|--------|-------------|--------------------------|-------|
| 9.6211 | 0.60699E-05 | $13a1' \rightarrow 11e'$ | 16.64 |
| | | $7a2'' \rightarrow 4e''$ | 51.49 |
| | | $8a2'' \rightarrow 5e''$ | 40.12 |
| 9.6866 | 0.48115E-01 | $7e' \rightarrow 14a1'$ | 55.91 |
| 9.7055 | 0.29019E-02 | $8e' \rightarrow 2a2'$ | 47.33 |
| 9.8111 | 0.26884E-01 | $1a2' \rightarrow 12e'$ | 27.55 |
| | | $7e' \rightarrow 14a1'$ | 13.12 |
| | | $1e'' \rightarrow 4e''$ | 32.29 |
| | | $7e' \rightarrow 11e'$ | 18.16 |
| 9.8827 | 0.84912E-02 | $7a2'' \rightarrow 4e''$ | 10.40 |
| | | $10e' \rightarrow 18a1'$ | 61.68 |
| | | $8e' \rightarrow 12e'$ | 14.93 |
| 9.9054 | 0.24826E-01 | $1a2' \rightarrow 12e'$ | 11.13 |
| | | $10e' \rightarrow 18a1'$ | 30.32 |
| | | $13a1' \rightarrow 12e'$ | 13.97 |
| | | $1a2' \rightarrow 12e'$ | 10.41 |
| 9.9526 | 0.40831E-01 | $1e'' \rightarrow 4e''$ | 17.78 |
| | | $8e' \rightarrow 12e'$ | 11.56 |
| | | $8a2'' \rightarrow 5e''$ | 27.72 |
| | | $7e' \rightarrow 14a1'$ | 17.71 |
| 10.028 | 0.44501E-01 | $8e' \rightarrow 12e'$ | 24.66 |
| 10.069 | 0.95595E-02 | $7e' \rightarrow 2a2'$ | 19.66 |
| | | $7e' \rightarrow 11e'$ | 54.13 |
| 10.123 | 0.35522E-01 | $1e'' \rightarrow 4e''$ | 30.68 |
| | | $7e' \rightarrow 2a2'$ | 51.08 |
| | | $13a1' \rightarrow 12e'$ | 11.00 |
| | | $1e'' \rightarrow 9a2''$ | 10.62 |

S2.2 Spin allowed, dipole forbidden transitions

Table S3 TDDFT (BP86/QZ4P) spin allowed dipole forbidden, their symmetry label, the corresponding oscillator strengths (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of $\text{Fe}(\text{CO})_5$

| E (eV) | f | Symmetry | Assignment | % |
|---------|------------|----------|--------------------------|-------|
| 3.97882 | 0.000 | $A1''$ | $10e' \rightarrow 4e''$ | 99.86 |
| 4.09309 | 0.1546E-34 | $A2'$ | $10e' \rightarrow 11e'$ | 99.79 |
| 4.13733 | 0.000 | E'' | $10e' \rightarrow 4e''$ | 97.38 |
| 4.31740 | 0.000 | E'' | $10e' \rightarrow 9a2''$ | 99.74 |
| 4.52799 | 0.9080E-34 | $A1'$ | $10e' \rightarrow 11e'$ | 92.14 |
| 4.76975 | 0.2796E-32 | $A2'$ | $10e' \rightarrow 12e'$ | 99.58 |
| 5.24317 | 0.7592E-33 | $A2'$ | $3e'' \rightarrow 4e''$ | 99.98 |
| 5.37378 | 0.000 | $A1''$ | $10e' \rightarrow 5e''$ | 98.45 |
| 5.37440 | 0.000 | E'' | $10e' \rightarrow 5e''$ | 89.68 |
| 5.42123 | 0.000 | $A1''$ | $3e'' \rightarrow 11e'$ | 98.47 |
| 5.42185 | 0.000 | E'' | $3e'' \rightarrow 14a1'$ | 77.67 |
| | | | $3e'' \rightarrow 11e'$ | 14.17 |
| 5.43420 | 0.2321E-32 | $A1'$ | $10e' \rightarrow 12e'$ | 66.27 |
| | | | $3e'' \rightarrow 4e''$ | 30.04 |
| 5.52647 | 0.000 | E'' | $3e'' \rightarrow 11e'$ | 75.83 |

Table S3 TDDFT (BP86/QZ4P) spin allowed dipole forbidden transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|------------|----------|---------------|-------|
| | | | 3e'' → 14a1' | 15.87 |
| 5.69542 | 0.000 | E'' | 3e'' → 2a2' | 99.71 |
| 6.08401 | 0.000 | A1'' | 3e'' → 12e' | 99.70 |
| 6.36004 | 0.000 | E'' | 3e'' → 12e' | 92.82 |
| 6.66475 | 0.9962E-33 | A2' | 3e'' → 5e'' | 99.97 |
| 6.85310 | 0.000 | E'' | 10e' → 10a2'' | 99.91 |
| 6.95526 | 0.1722E-34 | A1' | 10e' → 13e' | 87.12 |
| 7.03373 | 0.1868E-34 | A2' | 10e' → 13e' | 99.91 |
| 7.13085 | 0.2123E-33 | A1' | 3e'' → 5e'' | 74.30 |
| 7.45306 | 0.000 | E'' | 3e'' → 15a1' | 99.93 |
| 7.63541 | 0.7835E-33 | A1' | 13a1' → 14a1' | 18.42 |
| | | | 3e'' → 4e'' | 33.15 |
| | | | 10e' → 12e' | 11.07 |
| | | | 3e'' → 5e'' | 10.61 |
| 8.35928 | 0.000 | A1'' | 3e'' → 13e' | 99.98 |
| 8.36098 | 0.000 | E'' | 3e'' → 13e' | 99.47 |
| 8.56178 | 0.000 | E'' | 8a2'' → 11e' | 94.24 |
| 8.62347 | 0.000 | A1'' | 8a2'' → 2a2' | 92.79 |
| 8.65780 | 0.000 | A1'' | 9e' → 4e'' | 93.25 |
| 8.70583 | 0.1571E-35 | A1' | 10e' → 14e' | 85.98 |
| 8.74494 | 0.000 | E'' | 9e' → 4e'' | 94.42 |
| 8.75117 | 0.7824E-34 | A2' | 10e' → 14e' | 99.57 |
| 8.78016 | 0.1269E-35 | A1' | 8a2'' → 9a2'' | 66.08 |
| | | | 10e' → 14e' | 12.60 |
| | | | 2e'' → 4e'' | 11.90 |
| 8.81353 | 0.3702E-33 | A2' | 9e' → 11e' | 99.70 |
| 8.94885 | 0.000 | E'' | 8a2'' → 12e' | 92.67 |
| 8.97453 | 0.1356E-32 | A2' | 2e'' → 4e'' | 99.97 |
| 8.98506 | 0.000 | E'' | 3e'' → 16a1' | 98.36 |
| 9.00755 | 0.000 | E'' | 2e'' → 14a1' | 79.33 |
| | | | 9e' → 9a2'' | 15.14 |
| 9.01863 | 0.2102E-37 | A1' | 9e' → 11e' | 51.41 |
| | | | 2e'' → 4e'' | 39.06 |
| 9.02306 | 0.000 | E'' | 1a2' → 4e'' | 88.22 |
| 9.03057 | 0.3692E-35 | A2' | 1a2' → 14a1' | 98.46 |
| 9.10851 | 0.000 | E'' | 9e' → 9a2'' | 36.43 |
| | | | 10e' → 6e'' | 48.01 |
| 9.14287 | 0.000 | A1'' | 2e'' → 11e' | 99.64 |
| 9.14701 | 0.000 | E'' | 9e' → 9a2'' | 27.76 |
| | | | 10e' → 6e'' | 50.64 |
| 9.15846 | 0.000 | A1'' | 10e' → 6e'' | 99.26 |
| 9.19953 | 0.000 | E'' | 2e'' → 11e' | 95.49 |
| 9.24456 | 0.000 | A1'' | 8e' → 4e'' | 87.74 |
| | | | 1a2' → 9a2'' | 11.23 |
| 9.26854 | 0.000 | E'' | 8e' → 4e'' | 65.07 |
| | | | 10e' → 11a2'' | 26.58 |
| 9.27450 | 0.000 | E'' | 10e' → 11a2'' | 71.96 |
| | | | 8e' → 4e'' | 21.59 |
| 9.32098 | 0.000 | E'' | 13a1' → 4e'' | 87.49 |

Table S3 TDDFT (BP86/QZ4P) spin allowed dipole forbidden transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|----------|------------|----------|---------------|-------|
| 9.38548 | 0.3322E-37 | A1' | 8e' → 11e' | 94.85 |
| 9.39458 | 0.1073E-33 | A2' | 8e' → 11e' | 88.31 |
| | | | 9e' → 12e' | 11.50 |
| 9.40585 | 0.000 | A1'' | 1a2' → 9a2'' | 84.53 |
| 9.44782 | 0.000 | E'' | 2e'' → 2a2' | 86.06 |
| 9.47821 | 0.1555E-34 | A1' | 9e' → 12e' | 36.14 |
| | | | 2e'' → 4e'' | 21.66 |
| 9.52448 | 0.1497E-33 | A2' | 13a1' → 2a2' | 32.04 |
| | | | 9e' → 12e' | 59.46 |
| 9.54249 | 0.9112E-37 | A1' | 1a2' → 2a2' | 55.35 |
| | | | 9e' → 12e' | 16.03 |
| 9.62617 | 0.000 | E'' | 8e' → 9a2'' | 76.46 |
| 9.65950 | 0.000 | A1'' | 7e' → 4e'' | 99.37 |
| 9.68546 | 0.000 | E'' | 3e'' → 17a1' | 90.12 |
| 9.72193 | 0.4563E-36 | A1' | 13a1' → 14a1' | 29.81 |
| | | | 1a2' → 2a2' | 12.09 |
| | | | 1e'' → 4e'' | 12.45 |
| | | | 7e' → 11e' | 11.38 |
| 9.73461 | 0.000 | E'' | 7e' → 4e'' | 78.66 |
| 9.80336 | 0.000 | E'' | 2e'' → 12e' | 84.01 |
| 9.81139 | 0.000 | A1'' | 2e'' → 12e' | 89.52 |
| 9.82638 | 0.1086E-33 | A2' | 7e' → 11e' | 99.77 |
| 9.85113 | 0.2226E-34 | A2' | 1e'' → 4e'' | 99.53 |
| 9.86674 | 0.000 | E'' | 7a2'' → 11e' | 58.58 |
| | | | 1e'' → 14a1' | 39.63 |
| 9.87010 | 0.3470E-36 | A1' | 1e'' → 4e'' | 48.23 |
| | | | 7a2'' → 9a2'' | 13.33 |
| | | | 7e' → 11e' | 10.56 |
| 9.91135 | 0.1455E-35 | A2' | 13a1' → 2a2' | 62.14 |
| | | | 9e' → 12e' | 23.67 |
| 9.97269 | 0.000 | E'' | 1e'' → 14a1' | 39.42 |
| | | | 7e' → 9a2'' | 32.05 |
| | | | 7a2'' → 11e' | 21.62 |
| 10.10506 | 0.6112E-36 | A1' | 7a2'' → 9a2'' | 65.89 |
| | | | 2e'' → 5e'' | 12.94 |
| | | | 8e' → 12e' | 10.93 |
| 10.27079 | 0.3501E-35 | A1' | 10e' → 15e' | 42.12 |
| | | | 7e' → 12e' | 12.83 |
| 10.35836 | 0.1181E-38 | A1' | 2e'' → 5e'' | 39.45 |
| | | | 10e' → 15e' | 25.76 |
| | | | 8e' → 12e' | 14.38 |
| 10.39938 | 0.9964E-38 | A1' | 7e' → 12e' | 72.64 |
| | | | 10e' → 15e' | 16.74 |

S2.3 Singlet-triplet transitions

Table S4 TDDFT (BP86/QZ4P) singlet-triplet transitions, their symmetry label, the corresponding oscillator strengths (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|-------|----------|---------------|-------|
| 3.67716 | 0.000 | E' | 10e' → 14a1' | 99.65 |
| 3.72867 | 0.000 | A1' | 10e' → 11e' | 55.00 |
| | | | 10e' → 12e' | 30.92 |
| | | | 3e'' → 4e'' | 13.35 |
| 3.74874 | 0.000 | A2'' | 10e' → 4e'' | 99.26 |
| 3.76176 | 0.000 | E'' | 10e' → 4e'' | 99.33 |
| 3.77672 | 0.000 | A1'' | 10e' → 4e'' | 99.43 |
| 3.98357 | 0.000 | E' | 10e' → 11e' | 93.87 |
| 4.07214 | 0.000 | A2' | 10e' → 11e' | 99.79 |
| 4.13400 | 0.000 | A1' | 10e' → 12e' | 50.13 |
| | | | 10e' → 11e' | 43.33 |
| 4.16576 | 0.000 | E' | 10e' → 2a2' | 85.08 |
| | | | 10e' → 12e' | 10.56 |
| 4.17921 | 0.000 | E'' | 10e' → 9a2'' | 99.74 |
| 4.43947 | 0.000 | E' | 10e' → 12e' | 85.19 |
| | | | 10e' → 2a2' | 12.72 |
| 4.60474 | 0.000 | A2' | 10e' → 12e' | 99.68 |
| 4.69541 | 0.000 | A1' | 3e'' → 4e'' | 79.85 |
| | | | 10e' → 12e' | 18.42 |
| 4.92178 | 0.000 | E' | 3e'' → 4e'' | 99.37 |
| 4.95119 | 0.000 | E'' | 3e'' → 14a1' | 99.64 |
| 5.18203 | 0.000 | A2'' | 3e'' → 11e' | 59.59 |
| | | | 10e' → 5e'' | 39.59 |
| 5.24168 | 0.000 | A2' | 3e'' → 4e'' | 100.0 |
| 5.25542 | 0.000 | E'' | 10e' → 5e'' | 68.40 |
| | | | 3e'' → 11e' | 31.09 |
| 5.29160 | 0.000 | A1'' | 10e' → 5e'' | 99.58 |
| 5.33972 | 0.000 | A2'' | 10e' → 5e'' | 60.28 |
| | | | 3e'' → 11e' | 39.53 |
| 5.34391 | 0.000 | E'' | 3e'' → 11e' | 68.10 |
| | | | 10e' → 5e'' | 31.18 |
| 5.38661 | 0.000 | A1'' | 3e'' → 11e' | 98.79 |
| 5.51096 | 0.000 | E' | 3e'' → 9a2'' | 99.42 |
| 5.65626 | 0.000 | E'' | 3e'' → 2a2' | 99.35 |
| 5.87695 | 0.000 | A1'' | 3e'' → 12e' | 98.52 |
| 5.88006 | 0.000 | E'' | 3e'' → 12e' | 98.80 |
| 5.88854 | 0.000 | A2'' | 3e'' → 12e' | 99.41 |
| 6.10064 | 0.000 | E' | 10e' → 15a1' | 99.96 |
| 6.53885 | 0.000 | A1' | 3e'' → 5e'' | 99.47 |
| 6.60214 | 0.000 | E' | 3e'' → 5e'' | 99.73 |
| 6.65961 | 0.000 | A2' | 3e'' → 5e'' | 99.99 |
| 6.85316 | 0.000 | E'' | 10e' → 10a2'' | 99.98 |
| 7.01127 | 0.000 | A1' | 10e' → 13e' | 99.88 |
| 7.01616 | 0.000 | E' | 10e' → 13e' | 99.93 |
| 7.02197 | 0.000 | A2' | 10e' → 13e' | 99.99 |
| 7.43546 | 0.000 | E'' | 3e'' → 15a1' | 99.94 |

Table S4 TDDFT (BP86/QZ4P) singlet-triplet transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|-------|----------|---------------|-------|
| 7.65156 | 0.000 | E' | 10e' → 16a1' | 99.88 |
| 7.93391 | 0.000 | E' | 8a2'' → 4e'' | 83.29 |
| 7.97096 | 0.000 | A2'' | 8a2'' → 14a1' | 82.14 |
| 8.01477 | 0.000 | A1' | 8a2'' → 9a2'' | 52.31 |
| 8.07725 | 0.000 | E'' | 8a2'' → 11e' | 97.05 |
| 8.17355 | 0.000 | E' | 3e'' → 10a2'' | 99.18 |
| 8.19416 | 0.000 | A1' | 9e' → 11e' | 38.28 |
| | | | 2e'' → 4e'' | 28.81 |
| | | | 7e' → 11e' | 16.58 |
| 8.26261 | 0.000 | A2'' | 9e' → 4e'' | 51.93 |
| | | | 8a2'' → 14a1' | 14.82 |
| | | | 2e'' → 11e' | 14.58 |
| 8.34414 | 0.000 | A2'' | 3e'' → 13e' | 98.13 |
| 8.34827 | 0.000 | E' | 10e' → 17a1' | 85.85 |
| 8.35030 | 0.000 | E'' | 3e'' → 13e' | 99.64 |
| 8.35684 | 0.000 | A1'' | 3e'' → 13e' | 99.90 |
| 8.35809 | 0.000 | E' | 9e' → 14a1' | 17.41 |
| | | | 10e' → 17a1' | 13.57 |
| | | | 2e'' → 9a2'' | 11.51 |
| | | | 8a2'' → 4e'' | 10.82 |
| | | | 2e'' → 4e'' | 10.18 |
| 8.48589 | 0.000 | E'' | 9e' → 4e'' | 88.06 |
| 8.50451 | 0.000 | A1'' | 8a2'' → 2a2' | 86.97 |
| 8.56342 | 0.000 | E' | 9e' → 14a1' | 62.35 |
| | | | 2e'' → 4e'' | 11.56 |
| | | | 9e' → 11e' | 11.48 |
| 8.56649 | 0.000 | A1' | 8a2'' → 9a2'' | 37.83 |
| | | | 1a2' → 2a2' | 15.99 |
| | | | 2e'' → 4e'' | 14.29 |
| 8.62190 | 0.000 | A1'' | 9e' → 4e'' | 94.42 |
| 8.63726 | 0.000 | E' | 9e' → 11e' | 71.40 |
| | | | 9e' → 14a1' | 14.31 |
| 8.65179 | 0.000 | A2'' | 9e' → 4e'' | 37.81 |
| | | | 2e'' → 11e' | 32.26 |
| | | | 7e' → 4e'' | 10.50 |
| 8.69675 | 0.000 | A1' | 10e' → 14e' | 89.50 |
| 8.71535 | 0.000 | E' | 10e' → 14e' | 96.12 |
| 8.74389 | 0.000 | A2' | 10e' → 14e' | 98.06 |
| 8.74711 | 0.000 | E'' | 9e' → 9a2'' | 41.07 |
| | | | 8a2'' → 12e' | 18.55 |
| | | | 1a2' → 4e'' | 15.84 |
| 8.78994 | 0.000 | A1' | 13a1' → 14a1' | 85.35 |
| 8.80157 | 0.000 | A2' | 9e' → 11e' | 98.58 |
| 8.81108 | 0.000 | E'' | 9e' → 9a2'' | 28.87 |
| | | | 8a2'' → 12e' | 25.88 |
| | | | 1a2' → 4e'' | 12.38 |
| 8.83194 | 0.000 | E' | 9e' → 2a2' | 72.12 |
| 8.89685 | 0.000 | A1' | 1a2' → 2a2' | 36.38 |
| | | | 2e'' → 4e'' | 28.29 |

Table S4 TDDFT (BP86/QZ4P) singlet-triplet transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|-------|----------|---------------|-------|
| | | | 9e' → 11e' | 17.08 |
| | | | 8e' → 12e' | 10.20 |
| 8.94145 | 0.000 | E' | 2e'' → 4e'' | 46.39 |
| | | | 8e' → 2a2' | 17.90 |
| 8.94911 | 0.000 | E'' | 8a2'' → 12e' | 40.51 |
| | | | 1a2' → 4e'' | 30.06 |
| | | | 2e'' → 11e' | 16.01 |
| 8.94950 | 0.000 | E'' | 2e'' → 14a1' | 86.10 |
| 8.95070 | 0.000 | A2' | 1a2' → 14a1' | 87.55 |
| 8.97401 | 0.000 | E'' | 2e'' → 11e' | 53.71 |
| | | | 1a2' → 4e'' | 19.67 |
| 8.97425 | 0.000 | A2' | 2e'' → 4e'' | 99.86 |
| 8.97772 | 0.000 | E'' | 3e'' → 16a1' | 94.04 |
| 8.99430 | 0.000 | A1'' | 8e' → 4e'' | 50.09 |
| | | | 1a2' → 9a2'' | 28.10 |
| 9.08442 | 0.000 | E' | 2e'' → 9a2'' | 35.05 |
| | | | 8e' → 2a2' | 11.01 |
| 9.11158 | 0.000 | E'' | 13a1' → 4e'' | 87.50 |
| 9.11553 | 0.000 | A2'' | 10e' → 6e'' | 99.54 |
| 9.13439 | 0.000 | E'' | 10e' → 6e'' | 88.26 |
| 9.13489 | 0.000 | A1' | 7e' → 11e' | 35.70 |
| | | | 1e'' → 4e'' | 19.95 |
| | | | 9e' → 11e' | 18.41 |
| 9.13818 | 0.000 | E'' | 8e' → 4e'' | 56.66 |
| | | | 1a2' → 4e'' | 14.60 |
| 9.14258 | 0.000 | E' | 1a2' → 11e' | 64.48 |
| | | | 8e' → 14a1' | 26.75 |
| 9.14279 | 0.000 | A1'' | 2e'' → 11e' | 96.13 |
| 9.14668 | 0.000 | A2' | 9e' → 12e' | 65.78 |
| | | | 13a1' → 2a2' | 12.38 |
| | | | 1a2' → 14a1' | 11.57 |
| 9.15778 | 0.000 | A1'' | 10e' → 6e'' | 94.61 |
| 9.18554 | 0.000 | E' | 8e' → 14a1' | 64.38 |
| | | | 1a2' → 11e' | 28.61 |
| 9.19469 | 0.000 | A2'' | 8e' → 4e'' | 94.12 |
| 9.24596 | 0.000 | E' | 13a1' → 11e' | 68.58 |
| | | | 8a2'' → 5e'' | 10.18 |
| 9.26948 | 0.000 | A1'' | 1a2' → 9a2'' | 58.78 |
| | | | 8e' → 4e'' | 39.10 |
| 9.27251 | 0.000 | E'' | 10e' → 11a2'' | 95.78 |
| 9.30057 | 0.000 | E'' | 2e'' → 2a2' | 47.48 |
| | | | 8e' → 9a2'' | 14.00 |
| | | | 8e' → 4e'' | 25.71 |
| 9.31790 | 0.000 | A1' | 9e' → 12e' | 76.99 |
| 9.33294 | 0.000 | A2'' | 13a1' → 9a2'' | 19.17 |
| | | | 2e'' → 11e' | 36.79 |
| | | | 7e' → 4e'' | 26.53 |
| 9.33312 | 0.000 | E' | 9e' → 12e' | 62.77 |
| 9.37018 | 0.000 | A2' | 8e' → 11e' | 89.33 |

Table S4 TDDFT (BP86/QZ4P) singlet-triplet transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|-------|----------|---------------|-------|
| | | | 9e' → 12e' | 10.14 |
| 9.37154 | 0.000 | E' | 8e' → 11e' | 87.12 |
| 9.38292 | 0.000 | A1' | 8e' → 11e' | 89.32 |
| | | | 9e' → 12e' | 10.35 |
| 9.42491 | 0.000 | A2'' | 13a1' → 9a2'' | 64.78 |
| 9.43319 | 0.000 | E' | 8a2'' → 5e'' | 25.95 |
| | | | 2e'' → 9a2'' | 17.40 |
| | | | 13a1' → 11e' | 15.79 |
| | | | 7a2'' → 4e'' | 12.22 |
| 9.46698 | 0.000 | E'' | 8e' → 9a2'' | 31.63 |
| | | | 2e'' → 2a2' | 22.62 |
| | | | 7e' → 4e'' | 29.91 |
| 9.47270 | 0.000 | E' | 7e' → 11e' | 44.12 |
| | | | 8a2'' → 5e'' | 19.00 |
| | | | 1e'' → 4e'' | 16.88 |
| 9.49702 | 0.000 | E'' | 8e' → 9a2'' | 33.86 |
| | | | 7e' → 4e'' | 39.32 |
| 9.54262 | 0.000 | A2'' | 7a2'' → 14a1' | 85.75 |
| 9.56330 | 0.000 | E' | 7a2'' → 4e'' | 51.46 |
| | | | 7e' → 14a1' | 32.48 |
| 9.57784 | 0.000 | A2' | 13a1' → 2a2' | 83.85 |
| | | | 9e' → 12e' | 14.88 |
| 9.59796 | 0.000 | A1' | 7a2'' → 9a2'' | 38.04 |
| | | | 1a2' → 2a2' | 13.03 |
| | | | 7e' → 11e' | 17.74 |
| 9.60363 | 0.000 | E' | 7e' → 14a1' | 56.39 |
| | | | 8a2'' → 5e'' | 22.93 |
| | | | 7a2'' → 4e'' | 19.28 |
| 9.63833 | 0.000 | A1'' | 2e'' → 12e' | 51.57 |
| | | | 7e' → 4e'' | 36.35 |
| 9.65075 | 0.000 | E'' | 7a2'' → 11e' | 71.84 |
| | | | 1e'' → 14a1' | 10.91 |
| 9.66293 | 0.000 | A1'' | 7e' → 4e'' | 63.35 |
| | | | 2e'' → 12e' | 32.59 |
| 9.69348 | 0.000 | E'' | 3e'' → 17a1' | 99.54 |
| 9.70348 | 0.000 | E'' | 2e'' → 12e' | 79.78 |
| | | | 7a2'' → 11e' | 12.26 |
| 9.70843 | 0.000 | E' | 1a2' → 12e' | 56.72 |
| | | | 8e' → 2a2' | 39.12 |
| 9.72155 | 0.000 | A2'' | 2e'' → 12e' | 92.34 |
| 9.76476 | 0.000 | A1' | 8e' → 12e' | 67.52 |
| | | | 1a2' → 2a2' | 18.07 |
| 9.78156 | 0.000 | E'' | 1e'' → 14a1' | 81.93 |
| | | | 7a2'' → 11e' | 11.66 |
| 9.80169 | 0.000 | E' | 1e'' → 4e'' | 56.65 |
| | | | 7e' → 11e' | 24.94 |
| 9.82366 | 0.000 | A2' | 7e' → 11e' | 99.83 |
| 9.84326 | 0.000 | E' | 13a1' → 12e' | 46.08 |
| | | | 8e' → 12e' | 26.35 |

Table S4 TDDFT (BP86/QZ4P) singlet-triplet transitions of Fe(CO)₅

| E (eV) | f | Symmetry | Assignment | % |
|---------|-------|----------|---------------|-------|
| 9.84939 | 0.000 | A1' | 7a2'' → 9a2'' | 31.21 |
| | | | 1e'' → 4e'' | 50.21 |
| | | | 7e' → 11e' | 16.88 |
| 9.85111 | 0.000 | A2' | 1e'' → 4e'' | 100.0 |
| 9.88891 | 0.000 | E' | 10e' → 18a1' | 95.89 |