Supporting Information for

**The photochemistry of Fe2(S2C3H6)(CO)6(µ-CO) and its oxidized form, two simple [FeFe]-hydrogenase CO-inhibited models. A DFT and TDDFT investigation.**

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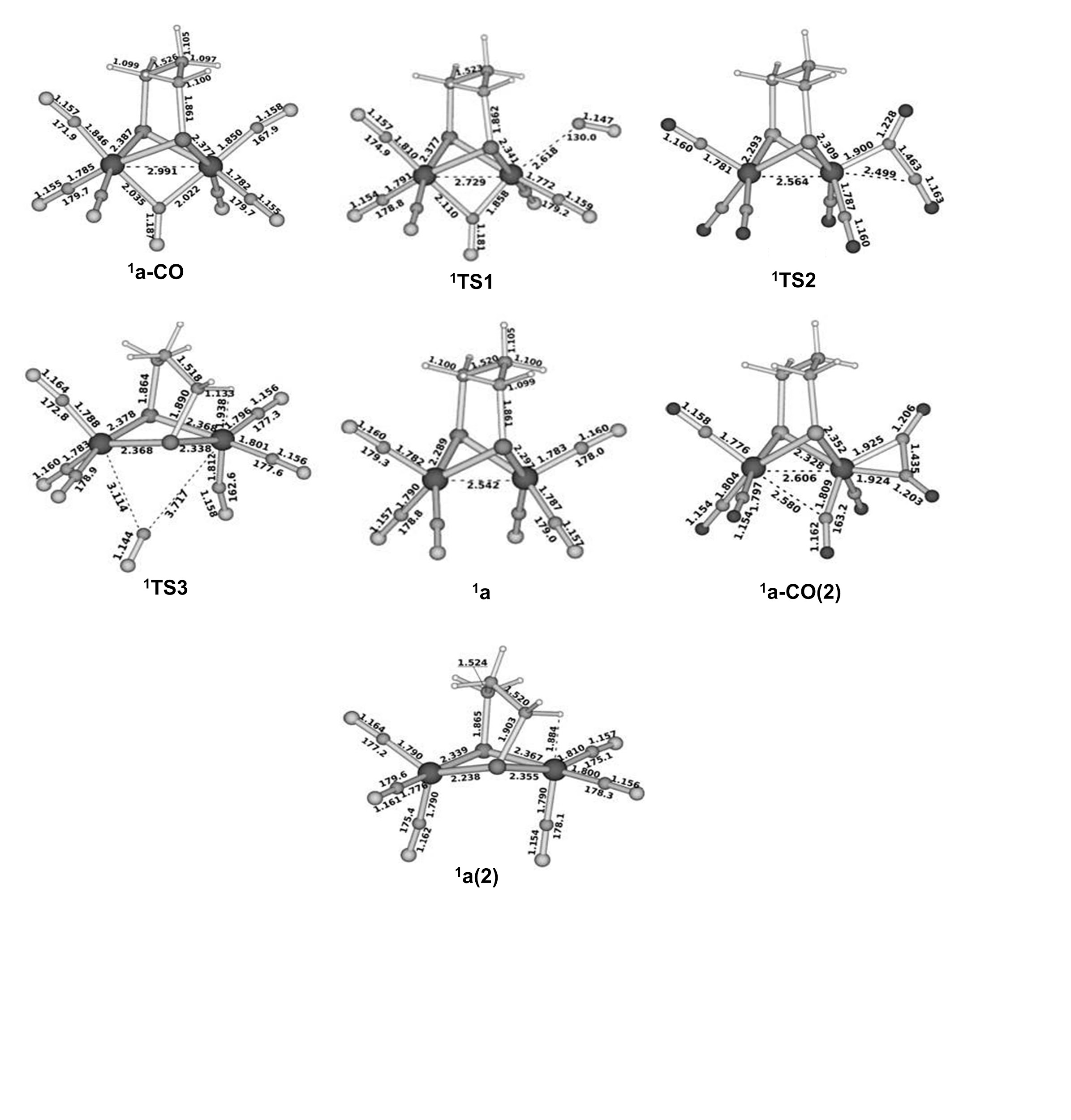
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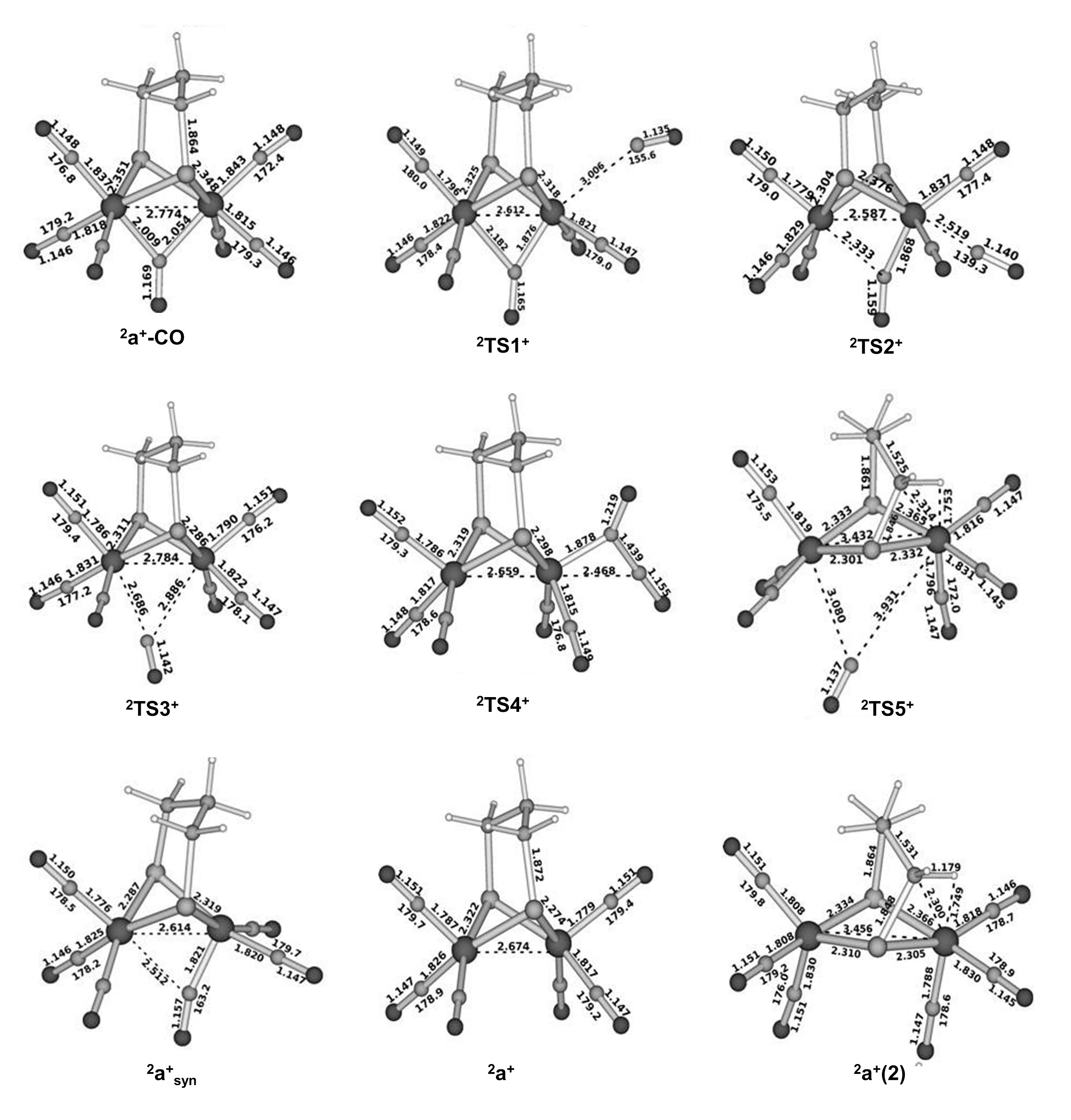
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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | **−2** | **−1** | **SOMO** | **LUMO** | **+1** | **+2** | **+3** | **+4** | **+5** | **+6** | **+7** | **+8** | **+9** | **+10** | **+11** |  |
| **α** |  | **101** | **102** | **103** | **104** | **105** | **106** | **107** | **108** | **109** | **110** | **111** | **112** | **113** | **114** | **115** |  |
| **μCO** |  | 3 | 9 | 10 | 8 | 6 | 8 | 5 | 15 | 5 | 6 | 7 | 4 | 2 | 10 | 10 |  |
| **2Fe** |  | 23 | 32 | 36 | 22 | 22 | 24 | 18 | 19 | 18 | 15 | 17 | 17 | 16 | 16 | 17 |  |
| **2S** |  | 25 | 15 | 13 | 21 | 24 | 17 | 8 | 9 | 6 | 5 | 6 | 5 | 5 | 4 | 5 |  |
| **2CO** | **cis** | 10 | 6 | 17 | 8 | 5 | 20 | 23 | 6 | 21 | 21 | 19 | 9 | 9 | 25 | 24 |  |
|  | **/2** | 5 | 3 | 9 | 4 | 2 | 10 | 11 | 3 | 11 | 11 | 10 | 5 | 4 | 12 | 12 |  |
| **4CO** | **trans** | 25 | 24 | 14 | 30 | 31 | 20 | 33 | 40 | 40 | 44 | 43 | 59 | 55 | 34 | 28 |  |
|  | **/4** | 6 | 6 | 3 | 7 | 8 | 5 | 8 | 10 | 10 | 11 | 11 | 15 | 14 | 8 | 7 |  |
| **pdt** |  | 15.2 | 14.9 | 9.7 | 12 | 12 | 11 | 14 | 11 | 10 | 9 | 8 | 6 | 13 | 12 | 17 |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | **−1** | **SOMO** | **LUMO** | **+1** | **+2** | **+3** | **+4** | **+5** | **+6** | **+7** | **+8** | **+9** | **+10** | **+11** | **+12** |
| **β** |  |  | 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 |
| **μCO** |  |  | 7 | 9 | 10 | 8 | 4 | 7 | 6 | 14 | 6 | 5 | 7 | 4 | 2 | 8 | 6 |
| **2Fe** |  |  | 31 | 34 | 36 | 22 | 26 | 22 | 18 | 19 | 19 | 16 | 17 | 17 | 16 | 15 | 5 |
| **2S** |  |  | 15 | 14 | 13 | 19 | 18 | 17 | 8 | 9 | 7 | 5 | 6 | 5 | 5 | 5 | 11 |
| **2CO** | **cis** |  | 5 | 6 | 17 | 9 | 5 | 25 | 21 | 6 | 17 | 23 | 21 | 9 | 9 | 29 | 7 |
|  | **/2** |  | 3 | 3 | 9 | 5 | 2 | 12 | 11 | 3 | 8 | 11 | 10 | 4 | 5 | 14 | 4 |
| **4CO** | **trans** |  | 28 | 24 | 14 | 29 | 36 | 19 | 34 | 40 | 42 | 45 | 41 | 57 | 55 | 32 | 58 |
|  | **/4** |  | 7 | 6 | 4 | 7 | 9 | 5 | 9 | 10 | 10 | 11 | 10 | 14 | 14 | 8 | 14 |
| **pdt** |  |  | 14 | 14 | 10 | 3 | 11 | 11 | 13 | 11 | 11 | 7 | 8 | 8 | 13 | 11 | 14 |

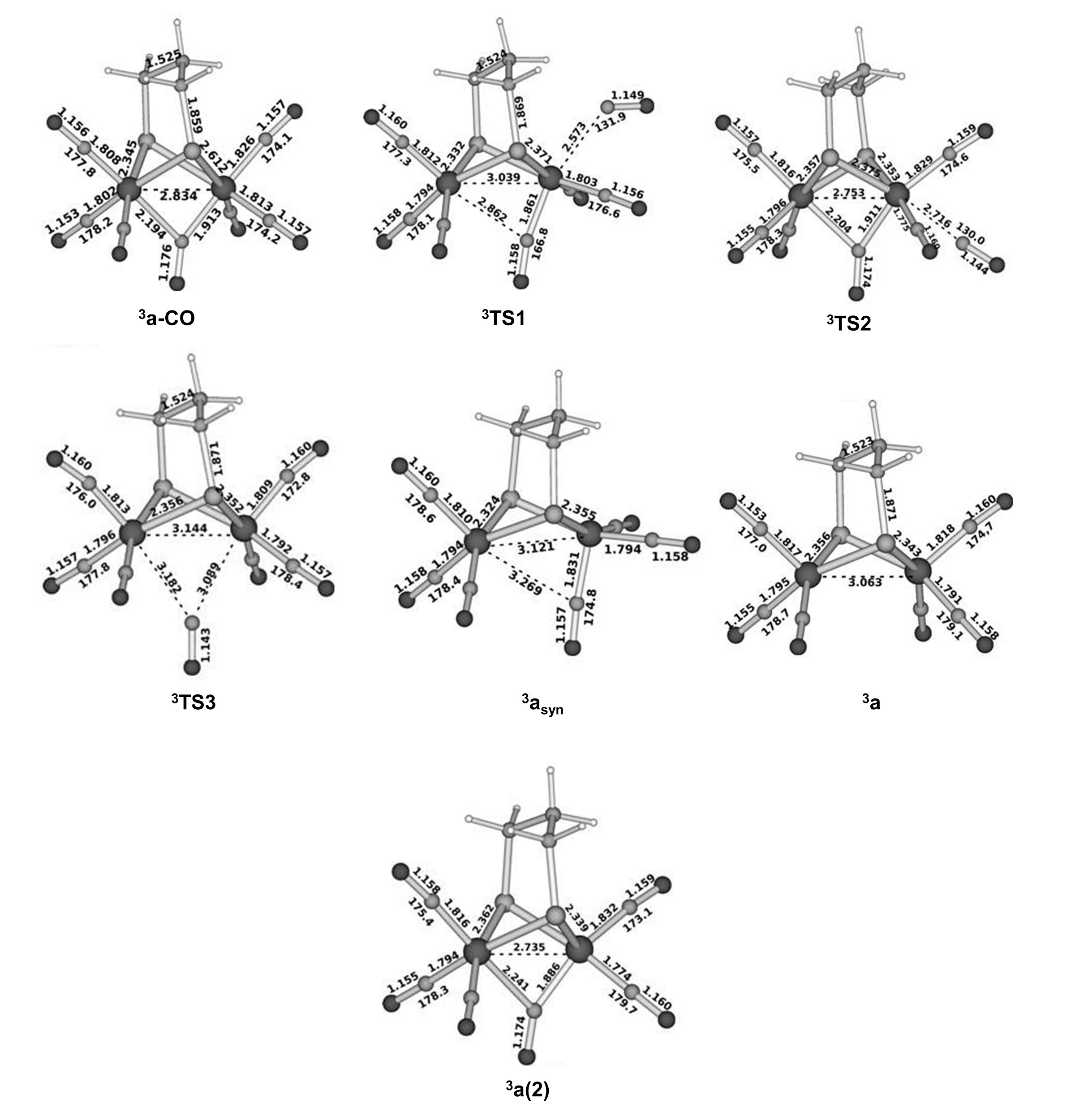
**Table S1.** Mulliken population analysis (in percentage) of **2a+-CO** FMOs.



**Figure S1**. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **1a-CO.** Distances are in Å and angles in degrees.



**Figure S2**. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **2a+-CO.** Distances are in Å and angles in degrees.



**Figure S3**. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **3a-CO.** Distances are in Å and angles in degrees.

**Coordinates (xyz) of selected structures.**

**1a-CO**

C -1.717554 2.422086 -1.318767

O -2.258892 2.972767 -2.177573

Fe -0.876923 1.567050 0.000000

C 0.525037 2.773916 0.000000

O 1.223355 3.697262 0.000000

S -0.066616 -0.024747 1.583104

C 1.748089 -0.326515 1.303189

C 2.362337 0.175711 0.000000

C 1.748089 -0.326515 -1.303189

S -0.066616 -0.024747 -1.583104

Fe -1.177487 -1.409792 0.000000

C 0.054120 -2.782241 0.000000

O 0.699058 -3.742964 0.000000

C -1.717554 2.422086 1.318767

O -2.258892 2.972767 2.177573

C -2.159886 -2.115816 -1.312110

O -2.801697 -2.572022 -2.156934

C -2.159886 -2.115816 1.312110

O -2.801697 -2.572022 2.156934

H 2.370691 1.273292 0.000000

H 3.423166 -0.133272 0.000000

H 1.882656 -1.412550 1.413572

H 2.247213 0.159414 2.153096

H 2.247213 0.159414 -2.153096

H 1.882656 -1.412550 -1.413572

C -2.390991 0.207030 0.000000

O -3.572006 0.328117 0.000000

**2a+-CO**

C -1.610432 2.341502 -1.337983

O -2.129982 2.915625 -2.182959

Fe -0.772017 1.446021 0.000000

C 0.593983 2.683711 0.000000

O 1.334511 3.560837 0.000000

S 0.108741 -0.045441 1.585224

C 1.927160 -0.337907 1.301645

C 2.540961 0.162292 0.000000

C 1.927160 -0.337907 -1.301645

S 0.108741 -0.045441 -1.585224

Fe -1.079630 -1.311271 0.000000

C 0.111490 -2.709170 0.000000

O 0.805930 -3.622910 0.000000

C -1.610432 2.341502 1.337983

O -2.129982 2.915625 2.182959

C -2.055327 -2.058731 -1.338843

O -2.659669 -2.540754 -2.184677

C -2.055327 -2.058731 1.338843

O -2.659669 -2.540754 2.184677

H 2.569046 1.259062 0.000000

H 3.597605 -0.157050 0.000000

H 2.069098 -1.419601 1.435840

H 2.402622 0.163282 2.155976

H 2.402622 0.163282 -2.155976

H 2.069098 -1.419601 -1.435840

C -2.404433 0.199358 0.000000

O -3.564251 0.343477 0.000000

**3a-CO**

C -1.819138 2.377071 -1.406053

O -2.350059 3.001413 -2.222482

Fe -1.050682 1.528317 0.000000

C 0.348105 2.702225 0.000000

O 1.153868 3.532314 0.000000

S 0.083807 -0.160096 1.638490

C 1.885229 -0.470393 1.299281

C 2.462784 0.082503 0.000000

C 1.885229 -0.470393 -1.299281

S 0.083807 -0.160096 -1.638490

Fe -1.145196 -1.301692 0.000000

C -0.030352 -2.723099 0.000000

O 0.640063 -3.664785 0.000000

C -1.819138 2.377071 1.406053

O -2.350059 3.001413 2.222482

C -2.158043 -1.954672 -1.340000

O -2.782761 -2.405282 -2.198490

C -2.158043 -1.954672 1.340000

O -2.782761 -2.405282 2.198490

H 2.388596 1.177941 0.000000

H 3.543546 -0.151268 0.000000

H 2.044333 -1.555982 1.375702

H 2.396795 -0.006907 2.154660

H 2.396795 -0.006907 -2.154660

H 2.044333 -1.555982 -1.375702

C -2.570472 0.365476 0.000000

O -3.743760 0.291323 0.000000

**2a+-CO 12A’’**

C -1.759593 2.271068 -1.462777

O -2.226010 2.890667 -2.307894

Fe -1.058888 1.382200 0.000000

C 0.302105 2.599369 0.000000

O 1.079330 3.443405 0.000000

S 0.147500 -0.230953 1.602579

C 1.971690 -0.424907 1.294534

C 2.542194 0.135673 0.000000

C 1.971690 -0.424907 -1.294534

S 0.147500 -0.230953 -1.602579

Fe -1.080210 -1.291201 0.000000

C -0.033416 -2.717957 0.000000

O 0.668204 -3.628910 0.000000

C -1.759593 2.271068 1.462777

O -2.226010 2.890667 2.307894

C -2.149508 -1.953955 -1.338878

O -2.789871 -2.403434 -2.175049

C -2.149508 -1.953955 1.338878

O -2.789871 -2.403434 2.175049

H 2.462856 1.230046 0.000000

H 3.623920 -0.085288 0.000000

H 2.177281 -1.499163 1.405582

H 2.424387 0.079234 2.159744

H 2.424387 0.079234 -2.159744

H 2.177281 -1.499163 -1.405582

C -2.673080 0.454876 0.000000

O -3.820828 0.296126 0.000000