**Supplementary information for:**

# Quantum Mechanics/Molecular Mechanics Study of Resting-State Vanadium Nitrogenase: Molecular and Electronic Structure of the Iron−Vanadium Cofactor

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## Contents



## Computational Details

**Force field parameters.** The CHARMM36 protein force field[1] was used in all MM and QM/MM calculations. As no forcefield parameters are available for FeVco, atomic charges were derived from Hirshfeld population analysis using the $[VFe_7S_8C(CO_3)]^{2-}$ charge configuration and crystal structure geometry for FeVco with relaxed protons (both extended carboxylate arms of FeVco were protonated, making the model 61 QM atoms in total) from a calculation performed with ORCA version 3.0.3 with TPSSh and Ahlrichs def2 triple-ζ basis set on V, Fe and S but def2 double-ζ basis set on other atoms and the protein matrix approximated with COSMO[2] (ε = 4). Same parameters were used for the P-cluster as in a previous study by us.[3] Lennard-Jones parameters were only added to inorganic sulfides (CHARMM atomtype SM used) and not to metals[4]. Forcefield parameters for homocitrate were adapted from those already available for citrate.[5] Water was modelled as TIP3P.[6]

**MM model preparation.**

Protonation state of titrable residues were decided via visual inspection of hydrogen bonds. The residues glutamine, asparagine and histidine were checked whether they were correctly orientated as in crystal structures it is generally not possible to distinguish between carbon and nitrogen. No arginine and lysine residues were deprotonated, and no glutamate was protonated. The aspartate residues α-$9^{Asp}$, β-$30^{Asp}$ and β-$73^{Asp}$ were protonated. As for histidine protonation state in the protein, the following were protonated on the ε nitrogen: α-$18^{His}$, α-$70^{His}$, α-$81^{His}$, α-$91^{His}$, α-$106^{His}$, α-$120^{His}$, α-$180^{His}$, α-$181^{His}$, α-$234^{His}$, α-$248^{His}$, α-$342^{His}$, α-$416^{His}$, α-$423^{His}$, α-$426^{His}$, α-$453^{His}$, β-$51^{His}$, β-$67^{His}$, β-$158^{His}$, β-$234^{His}$, β-$321^{His}$, β-$379^{His}$, β-$409^{His}$, β-$461^{His}$ and γ-$111^{His}$. The following histidine residues were protonated on the δ nitrogen: α-$364^{His}$, α-$448^{His}$, β-$80^{His}$, β-$177^{His}$, β-$334^{His}$, β-$386^{His}$, β-$80^{His}$, γ-$5^{His}$ and γ-$110^{His}$. Only β-$150^{His}$ is found to be doubly. Cysteine residues ligated to metals were modeled as deprotonated

cysteinate residues: α-49$^{Cys}$, α-138$^{Cys}$, α-75$^{Cys}$, α-257$^{Cys}$, β-31$^{His}$, β-56$^{Cys}$ and β-115$^{His}$. The following residues had their functional group flipped: α-120$^{His}$, α-249$^{Gln}$, α-426$^{His}$, β-243$^{His}$, β-260$^{Asn}$, β-267$^{Gln}$, β-361$^{Gln}$, γ-3$^{Gln}$ and γ-46$^{Gln}$

The total charge of the system after protonation by GROMACS is -62 and 62 sodium ions were generated in the solute (by randomly replacing water molecules) to neutralize the charge. The size of the periodic box is 174.97 * 174.97 * 174.97 Å with all angles set at 90°. The total volume of the system after solvation is 5356.17 nm$^3$ and has a density of 1006.33 g/l. The final MM model size is 531 080 atoms.

**MD simulations**

All hydrogen atoms, water molecules and sodium ions of the system were then relaxed (all other atoms were kept constrained) using the steepest descent algorithm. The MM model was simulated within the canonical ensemble, with the same constraints, using the velocity-Verlet algorithm[7,8] and coupled to a 4-chain Nosé-Hoover thermostat[9–12] . The system was heated up from 50 K to 300 K in 500 ps and maintained at 300 K for a total of 5 ns. At 1100 ps a snapshot was extracted.

**QM/MM preparation and calculations.**

A spherical cut-out cluster model was generated from a snapshot from the MD trajectory after 1100 ps (Figure 2 in article). All residues, as labelled in the 5N6Y X-ray structure,[13] from chain A (residues numbered 2 to 474), chain B (residues numbered 12 to 475), chain C (residues numbered from 2 to 113) and chain E (residues numbered 12 to 475) and water molecules within 42 Å of the carbide of FeVco are included. 35 sodium ions are included as well to keep the system charge neutral. In total, we are including all residues from $\alpha\beta_2\gamma$ subunits. The QM/MM model contains 32 562 atoms. An active region of 1038 atoms was used in all QM/MM optimizations except in separate calculations concerning the protonation state of FeVco. As the carboxylate arm of homocitrate reaches the boundary of the defined active region, the active region size was increased to include all residues within 13 Å of the central carbide (as compared to 10 Å for previous calculations) to accommodate for the area around the carboxylate group. All protonated models utilize this active region size. Three different QM regions were used: 57, 83 and 181 atoms, shown in Figure S2-S4.

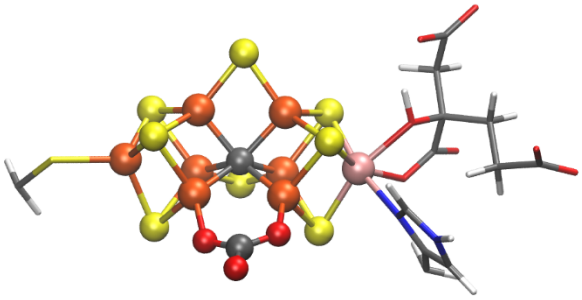

*Figure S 1: 57 QM atom region, [$VFe_7S_8CXO_3$], homocitrate, Cys$^{257}$ and His$^{423}$.*

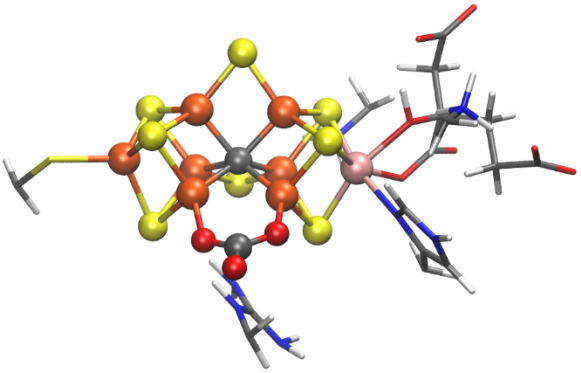

*Figure S 2: 83 QM atom region, [$VFe_7S_8CXO_3$], homocitrate, Cys$^{257}$, His$^{423}$, Arg$^{339}$, Lys$^{83}$ and Lys$^{361}$.*

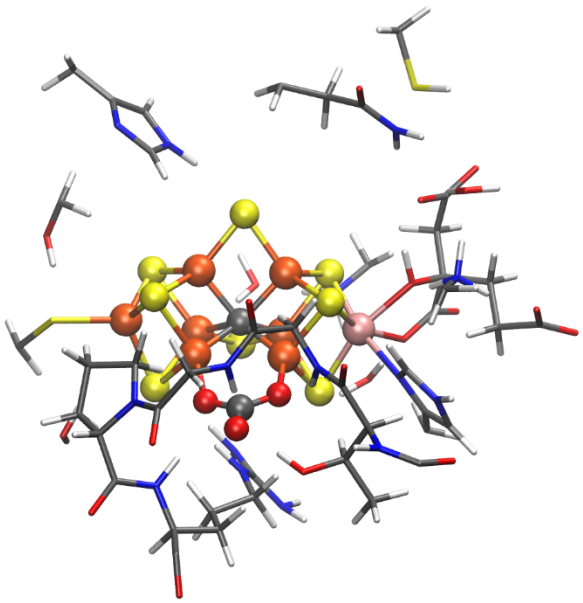

*Figure S 3: 181 QM atom region, [$VFe_7S_8CXO_3$], homocitrate, $Cys^{257}$, $His^{423}$, $Arg^{339*}$, $Lys^{83}$, $Lys^{361}$, $Ser^{260}$, $His^{180}$, $Gln^{176}$, $Cys^{52}$, Thr335, $Gly^{336}$, $Gly^{337}$ and $Pro^{338}$ (* the QM size of $Arg^{339}$ has been increased to include also the whole sidechain and the peptide backbone). Few water molecules have been included as well.*

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## Single Point Broken Symmetry Solution Comparison

We calculated 35 BS solutions for multiple combinations of ligand ($CO_3$, $NO_3$), redox state and spin state using the X-ray structure. Relative energies of the BS solutions are shown in Figures S5-S18 and Table S1 for each model. Energies are always relative the most stable BS7-235 solution for each model.

Figure S19 shows a BS-state comparison of different density functionals for the [**V**-$CO_3$]$^{2-}$ model and Figure S20 compares QM/MM vs. CPCM results.

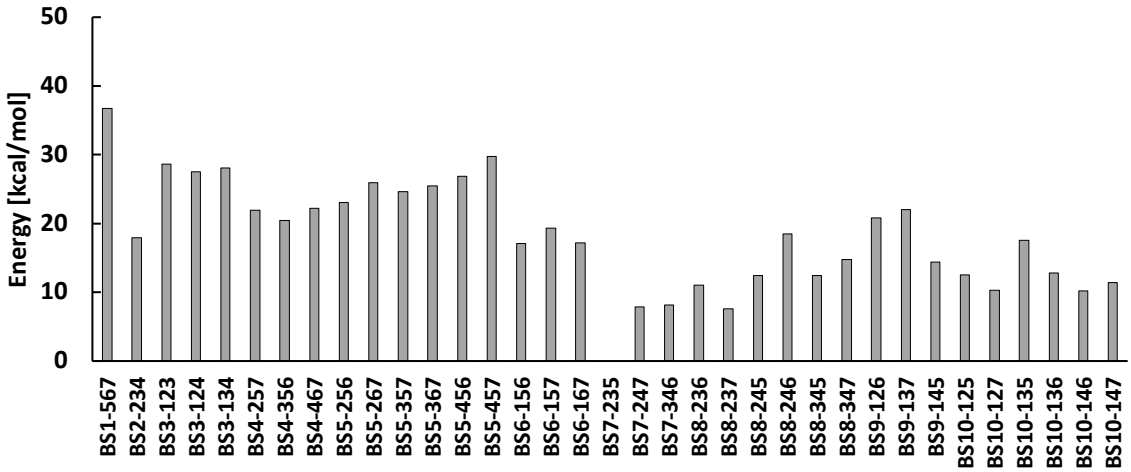



*Figure S 4: The relative energies of the 35 BS solutions for [**V**-$CO_3$]$^{2-}$ and $M_S$ = $^3/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S$ = $^3/_2$ BS7-235 solution.*

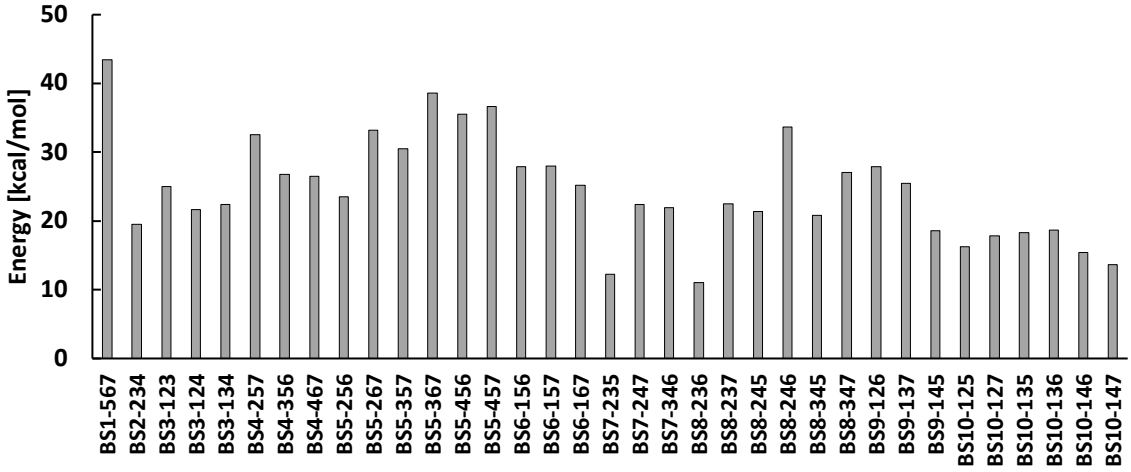



*Figure S 5: The relative energies of the 35 BS solutions for [**V**-$CO_3$]$^{2-}$ and $M_S$ = $^1/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S$ = $^3/_2$ BS7-235 solution.*

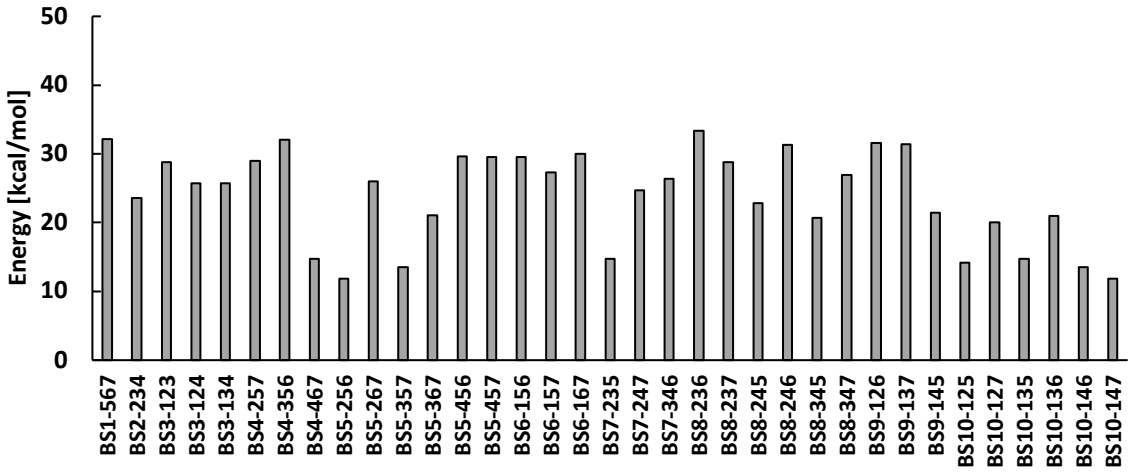



*Figure S 6: The relative energies of the 35 BS solutions for [**V**-$CO_3$]$^-$ and $M_S$ = 0. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S$ = 1 BS7-235 solution.*

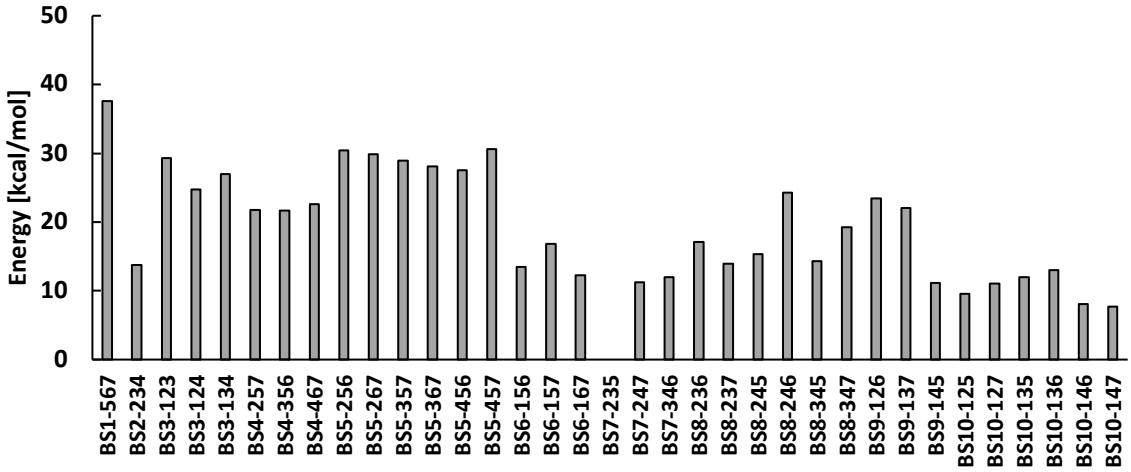



*Figure S 7: The relative energies of the 35 BS solutions for [**V**-$CO_3$]$^-$ and $M_S$ = 1. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S$ = 1 BS7-235 solution.*

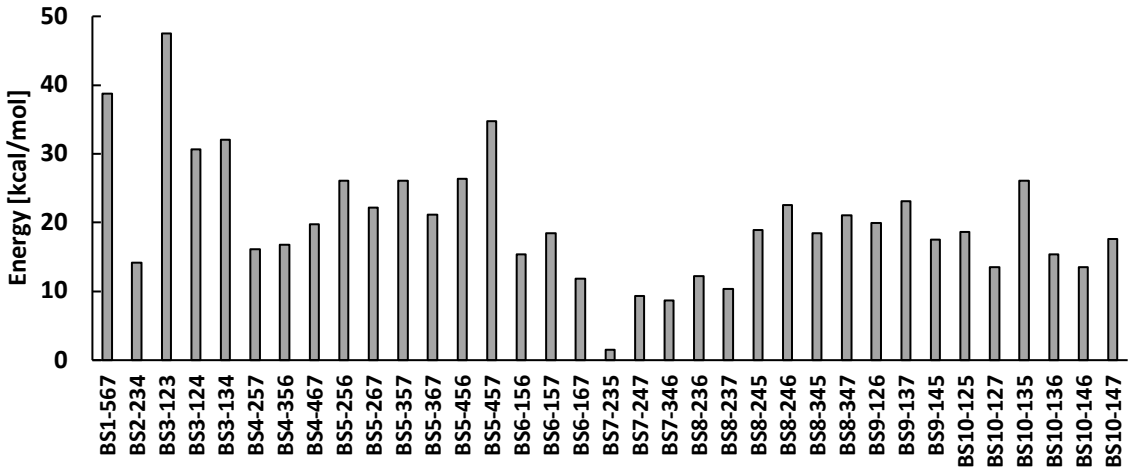



*Figure S 8: The relative energies of the 35 BS solutions for $[V\text{-}CO_3]^0$ and $M_S = 2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = 1$ BS7-235 solution.*

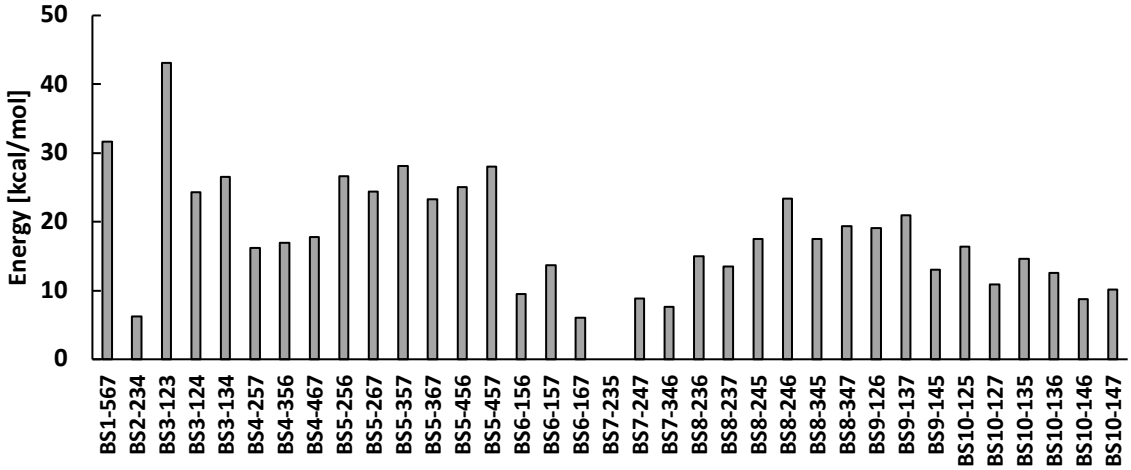



*Figure S 9: The relative energies of the 35 BS solutions for $[V\text{-}CO_3]^0$ and $M_S = {}^3/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = {}^3/_2$ BS7-235 solution.*

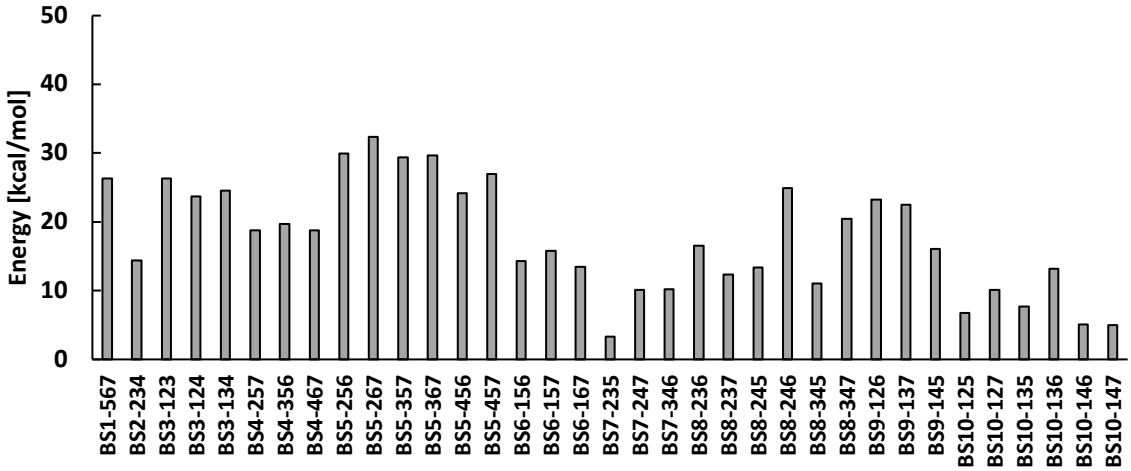



*Figure S 10: The relative energies of the 35 BS solutions for $[V\text{-}CO_3]^0$ and $M_S = {}^1/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = {}^3/_2$ BS7-235 solution.*

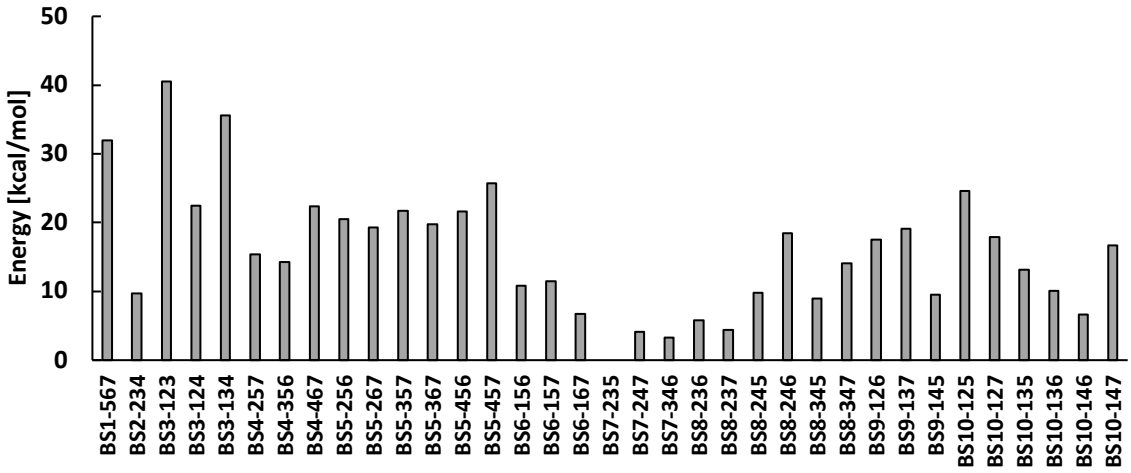



*Figure S 11: The relative energies of the 35 BS solutions for [**V**-$NO_3$]$^-$ and $M_S = {}^3/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = {}^3/_2$ BS7-235 solution.*

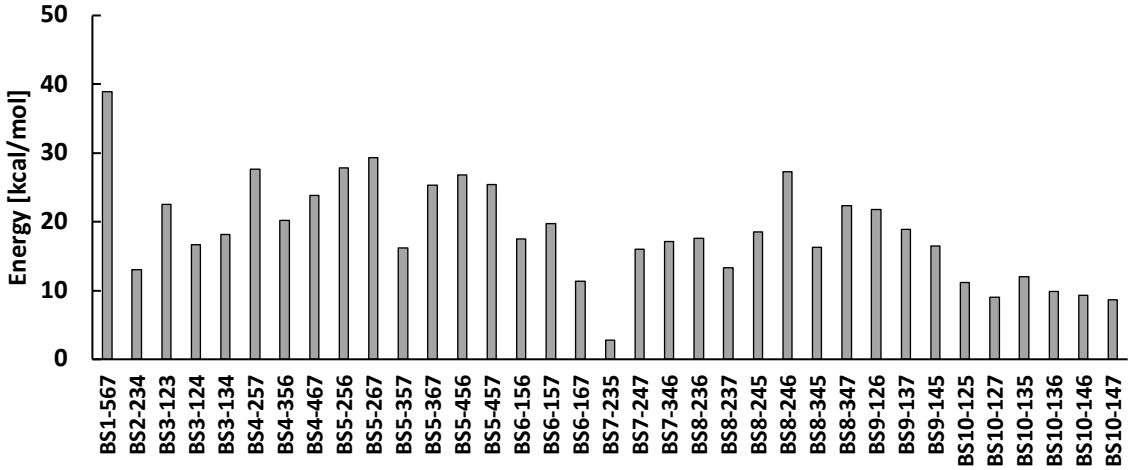



*Figure S 12: Figure S 13: The relative energies of the 35 BS solutions for [**V**-$NO_3$]$^-$ and $M_S = {}^1/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = {}^3/_2$ BS7-235 solution.*

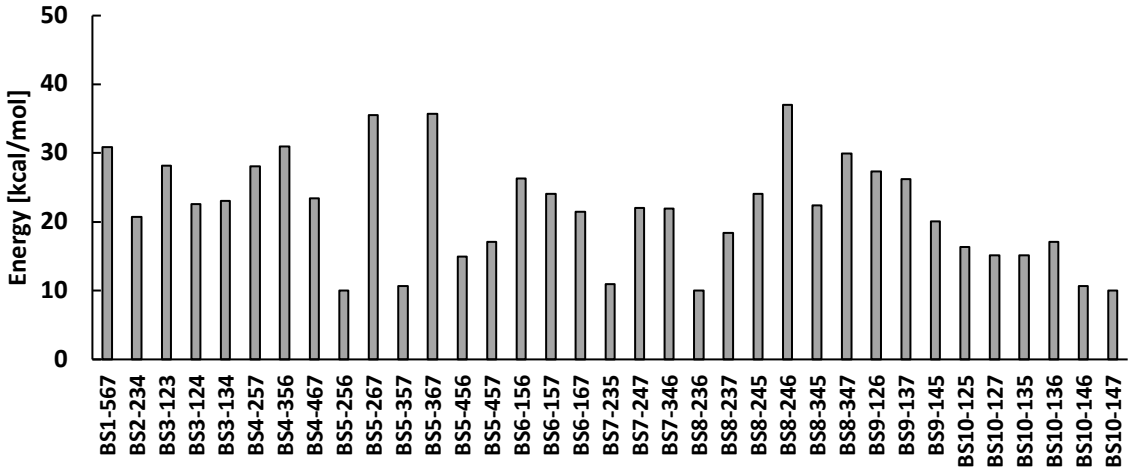



*Figure S 14: The relative energies of the 35 BS solutions for [**V**-$NO_3$]$^0$ and $M_S = 0$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = 1$ BS7-235 solution.*

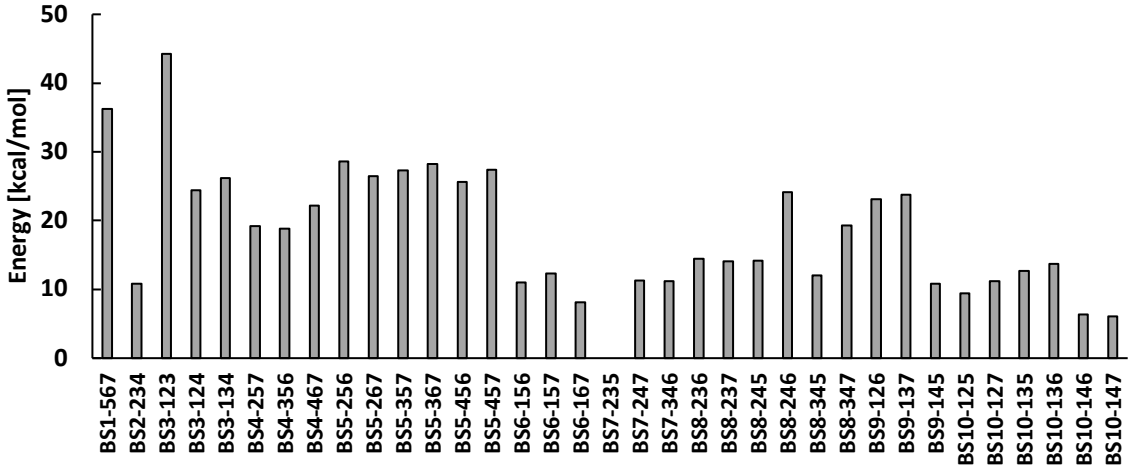



*Figure S 15: The relative energies of the 35 BS solutions for $[V\text{-}NO_3]^0$ and $M_S = 1$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = 1$ BS7-235 solution.*

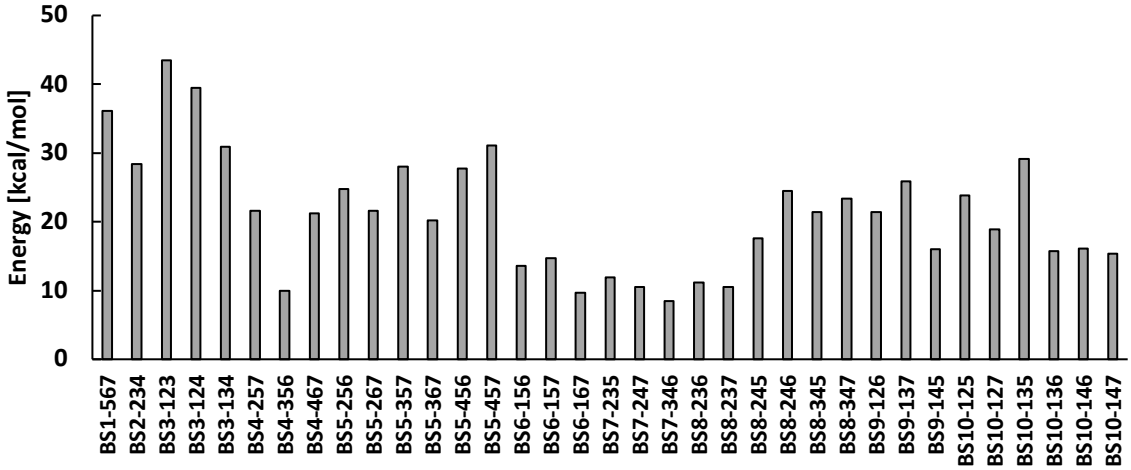



*Figure S 16: The relative energies of the 35 BS solutions for $[V\text{-}NO_3]^0$ and $M_S = 1$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = 1$ BS7-235 solution.*

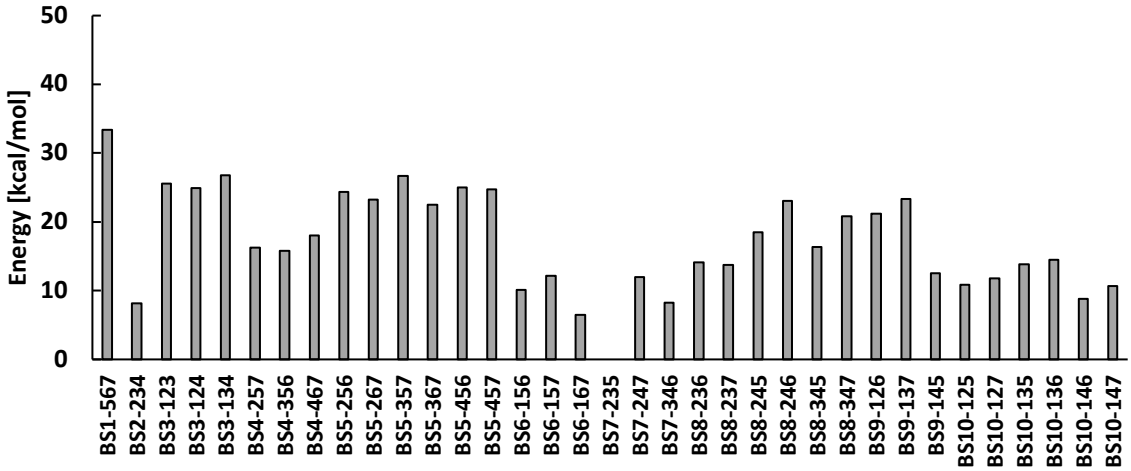



*Figure S 17: The relative energies of the 35 BS solutions for $[V\text{-}NO_3]^+$ and $M_S = {}^3/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S = {}^3/_2$ BS7-235 solution.*

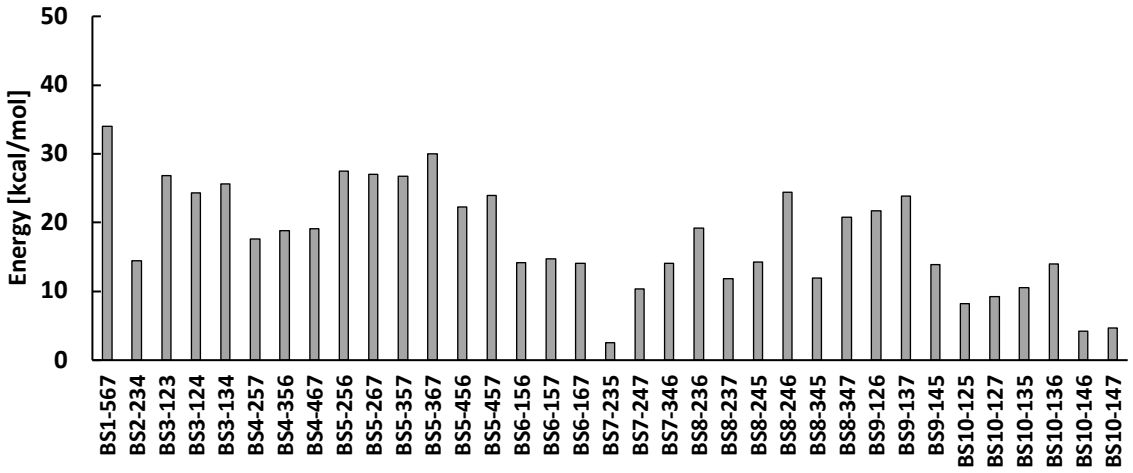



*Figure S 18: The relative energies of the 35 BS solutions for [**V**-$NO_3$]$^+$and $M_S$ = $^1/_2$. Functional: TPSSh. QM-region size: 57 atoms. Energies are relative to the $M_S$ = $^3/_2$ BS7-235 solution.*

*Table S 1: Relative QM/MM energies (kcal/mol) of all BS solutions for all FeVco models using the crystal structure geometry. The * indicates the high-spin energy relative to the preferred BS solution. ($M_S$ = 34/2 for [V-$CO_3$]$^{2-}$ and [V-$NO_3$]$^-$, $M_S$ = 35/2 for [V-$CO_3$]$^-$ and [V-$NO_3$]$^0$, and $M_S$ = 36/2 for [V-$CO_3$]$^0$ and [V-$NO_3$]$^+$).*

| | Carbonate | | | | | | | Nitrate | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | [**V**-$CO_3$]$^{2-}$ $M_S = {}^3/_2$ | [**V**-$CO_3$]$^{2-}$ $M_S = {}^1/_2$ | [**V**-$CO_3$]$^-$ $M_S = 0$ | [**V**-$CO_3$]$^-$ $M_S = 1$ | [**V**-$CO_3$]$^-$ $M_S = 2$ | [**V**-$CO_3$] $M_S = {}^3/_2$ | [**V**-$CO_3$] $M_S = {}^1/_2$ | [**V**-$NO_3$]$^-$ $M_S = {}^3/_2$ | [**V**-$NO_3$]$^-$ $M_S = {}^1/_2$ | [**V**-$NO_3$] $M_S = 0$ | [**V**-$NO_3$] $M_S = 1$ | [**V**-$NO_3$] $M_S = 2$ | [**V**-$NO_3$]$^+$ $M_S = {}^3/_2$ | [**V**-$NO_3$]$^+$ $M_S = {}^1/_2$ |
| BS1-567 | 36.77 | 43.47 | 32.16 | 37.57 | 38.74 | 31.68 | 26.30 | 31.94 | 38.92 | 30.83 | 36.20 | 36.10 | 33.37 | 34.00 |
| BS2-234 | 17.90 | 19.47 | 23.62 | 13.75 | 14.15 | 6.19 | 14.36 | 9.71 | 13.06 | 20.69 | 10.86 | 28.37 | 8.20 | 14.47 |
| BS3-123 | 28.68 | 24.98 | 28.77 | 29.26 | 47.47 | 43.10 | 26.35 | 40.52 | 22.56 | 28.22 | 44.29 | 43.47 | 25.60 | 26.82 |
| BS3-124 | 27.49 | 21.62 | 25.70 | 24.69 | 30.64 | 24.29 | 23.67 | 22.48 | 16.63 | 22.62 | 24.42 | 39.49 | 24.92 | 24.31 |
| BS3-134 | 28.12 | 22.37 | 25.76 | 26.94 | 32.06 | 26.52 | 24.57 | 35.55 | 18.14 | 23.02 | 26.21 | 30.95 | 26.75 | 25.60 |
| BS4-257 | 21.91 | 32.56 | 28.98 | 21.72 | 16.18 | 16.20 | 18.75 | 15.41 | 27.64 | 28.10 | 19.21 | 21.60 | 16.30 | 17.66 |
| BS4-356 | 20.40 | 26.75 | 32.01 | 21.69 | 16.74 | 16.90 | 19.70 | 14.23 | 20.18 | 30.94 | 18.85 | 9.99 | 15.79 | 18.81 |
| BS4-467 | 22.18 | 26.52 | 14.75 | 22.64 | 19.81 | 17.78 | 18.74 | 22.34 | 23.82 | 23.42 | 22.22 | 21.23 | 18.05 | 19.10 |
| BS5-256 | 23.01 | 23.54 | 11.83 | 30.43 | 26.10 | 26.62 | 29.95 | 20.51 | 27.87 | 9.99 | 28.57 | 24.73 | 24.33 | 27.50 |
| BS5-267 | 25.94 | 33.23 | 26.04 | 29.89 | 22.17 | 24.43 | 32.35 | 19.31 | 29.36 | 35.53 | 26.44 | 21.55 | 23.28 | 27.06 |
| BS5-357 | 24.60 | 30.45 | 13.49 | 28.97 | 26.13 | 28.08 | 29.34 | 21.72 | 16.21 | 10.68 | 27.32 | 28.06 | 26.69 | 26.78 |
| BS5-367 | 25.47 | 38.61 | 21.09 | 28.12 | 21.15 | 23.29 | 29.63 | 19.76 | 25.28 | 35.69 | 28.24 | 20.17 | 22.51 | 30.03 |
| BS5-456 | 26.86 | 35.49 | 29.62 | 27.57 | 26.33 | 25.05 | 24.16 | 21.64 | 26.78 | 14.99 | 25.66 | 27.72 | 24.98 | 22.30 |
| BS5-457 | 29.78 | 36.61 | 29.51 | 30.65 | 34.77 | 27.98 | 26.93 | 25.68 | 25.44 | 17.14 | 27.42 | 31.07 | 24.78 | 23.98 |
| BS6-156 | 17.12 | 27.90 | 29.55 | 13.49 | 15.38 | 9.47 | 14.32 | 10.81 | 17.54 | 26.35 | 11.04 | 13.63 | 10.11 | 14.15 |
| BS6-157 | 19.30 | 27.99 | 27.32 | 16.87 | 18.42 | 13.70 | 15.80 | 11.50 | 19.76 | 24.03 | 12.30 | 14.74 | 12.19 | 14.75 |
| BS6-167 | 17.16 | 25.21 | 30.00 | 12.27 | 11.83 | 6.09 | 13.45 | 6.72 | 11.34 | 21.43 | 8.10 | 9.67 | 6.50 | 14.06 |
| BS7-235 | 0.00 | 12.29 | 14.75 | 0.00 | 1.51 | 0.00 | 3.27 | 0.00 | 2.76 | 10.90 | 0.00 | 11.95 | 0.00 | 2.51 |
| BS7-247 | 7.83 | 22.41 | 24.67 | 11.20 | 9.37 | 8.84 | 10.09 | 4.09 | 15.97 | 22.03 | 11.27 | 10.49 | 11.94 | 10.38 |
| BS7-346 | 8.18 | 21.98 | 26.40 | 11.99 | 8.67 | 7.63 | 10.16 | 3.30 | 17.13 | 21.90 | 11.24 | 8.42 | 8.25 | 14.13 |
| BS8-236 | 11.08 | 11.08 | 33.39 | 17.10 | 12.24 | 15.02 | 16.51 | 5.77 | 17.63 | 9.99 | 14.46 | 11.16 | 14.11 | 19.19 |
| BS8-237 | 7.58 | 22.47 | 28.79 | 13.95 | 10.32 | 13.52 | 12.31 | 4.41 | 13.27 | 18.42 | 14.05 | 10.55 | 13.74 | 11.86 |
| BS8-245 | 12.42 | 21.39 | 22.79 | 15.33 | 18.92 | 17.51 | 13.38 | 9.77 | 18.52 | 24.07 | 14.13 | 17.62 | 18.51 | 14.24 |
| BS8-246 | 18.52 | 33.68 | 31.33 | 24.29 | 22.59 | 23.40 | 24.90 | 18.46 | 27.25 | 37.00 | 24.13 | 24.46 | 23.02 | 24.44 |
| BS8-345 | 12.48 | 20.86 | 20.74 | 14.27 | 18.47 | 17.46 | 11.01 | 8.92 | 16.29 | 22.41 | 12.08 | 21.44 | 16.39 | 11.97 |
| BS8-347 | 14.77 | 27.08 | 26.96 | 19.29 | 21.03 | 19.32 | 20.40 | 14.09 | 22.33 | 29.98 | 19.29 | 23.33 | 20.80 | 20.75 |
| BS9-126 | 20.77 | 27.93 | 31.55 | 23.41 | 19.91 | 19.12 | 23.24 | 17.50 | 21.80 | 27.36 | 23.09 | 21.41 | 21.16 | 21.74 |
| BS9-137 | 22.00 | 25.48 | 31.42 | 22.06 | 23.16 | 20.98 | 22.52 | 19.09 | 18.92 | 26.23 | 23.72 | 25.84 | 23.34 | 23.91 |
| BS9-145 | 14.40 | 18.56 | 21.41 | 11.16 | 17.53 | 13.04 | 16.05 | 9.52 | 16.51 | 20.06 | 10.85 | 16.04 | 12.50 | 13.88 |
| BS10-125 | 12.56 | 16.21 | 14.20 | 9.60 | 18.64 | 16.38 | 6.74 | 24.61 | 11.18 | 16.38 | 9.45 | 23.81 | 10.86 | 8.24 |
| BS10-127 | 10.28 | 17.80 | 20.04 | 11.06 | 13.56 | 10.84 | 10.12 | 17.93 | 9.02 | 15.16 | 11.17 | 18.93 | 11.77 | 9.22 |
| BS10-135 | 17.56 | 18.32 | 14.71 | 12.02 | 26.06 | 14.63 | 7.66 | 13.20 | 12.02 | 15.10 | 12.69 | 29.17 | 13.85 | 10.53 |
| BS10-136 | 12.79 | 18.64 | 20.94 | 12.98 | 15.42 | 12.59 | 13.22 | 10.09 | 9.85 | 17.14 | 13.67 | 15.69 | 14.51 | 13.98 |
| BS10-146 | 10.18 | 15.44 | 13.49 | 8.12 | 13.53 | 8.75 | 5.06 | 6.64 | 9.32 | 10.68 | 6.38 | 16.10 | 8.84 | 4.22 |
| BS10-147 | 11.38 | 13.64 | 11.83 | 7.73 | 17.65 | 10.18 | 4.95 | 16.70 | 8.68 | 9.99 | 6.10 | 15.39 | 10.63 | 4.70 |
| Hi-Spin* | 132.53 | | | 149.53 | | 160.57 | | 128.07 | | | 147.79 | | 162.17 | |

*Table S 2: Relative QM/MM energies (kcal/mol) of different spin-flip procedures for $[V\text{-}CO_3]^{2-}$, where the spin of V is either flipped after the BS solution is converged or the spin of V is flipped along with the spins of the irons from the high spin solution.. All energies are relative to the BS7-235 solution of the 'normal flip spin' column (which is the same as BS7-235 in the first column, $[V\text{-}CO_3]^{2-}$ and $M_S = 3/2$ in Table S1).*

| | Normal flip spin[a] | V-flip from low spin[b] | V-flip from high spin[c] | Difference between 'V-flip from low spin' and 'normal flip spin' | Difference between 'V-flip from high spin' and 'normal flip spin' |
|---|---|---|---|---|---|
| BS1-567 | 36.77 | 36.77 | 36.77 | 0.00 | 0.00 |
| BS2-234 | 17.90 | 17.85 | 16.48 | -0.05 | -1.41 |
| BS3-123 | 28.68 | 28.68 | 28.68 | 0.00 | 0.00 |
| BS3-124 | 27.49 | 27.48 | 29.05 | 0.00 | 1.57 |
| BS3-134 | 28.12 | 28.12 | 28.12 | 0.00 | 0.00 |
| BS4-257 | 21.91 | 21.91 | 21.91 | 0.00 | 0.00 |
| BS4-356 | 20.40 | 20.40 | 20.40 | 0.00 | 0.00 |
| BS4-467 | 22.18 | 22.18 | 22.18 | 0.00 | 0.00 |
| BS5-256 | 23.01 | 23.01 | 23.01 | 0.00 | 0.00 |
| BS5-267 | 25.94 | 25.94 | 25.94 | 0.00 | 0.00 |
| BS5-357 | 24.60 | 24.60 | 24.60 | 0.00 | 0.00 |
| BS5-367 | 25.47 | 25.47 | 25.47 | 0.00 | 0.00 |
| BS5-456 | 26.86 | 26.86 | 26.86 | 0.00 | 0.00 |
| BS5-457 | 29.78 | 29.78 | 29.71 | 0.00 | -0.07 |
| BS6-156 | 17.12 | 17.12 | 17.12 | 0.00 | 0.00 |
| BS6-157 | 19.30 | 19.30 | 19.30 | 0.00 | 0.00 |
| BS6-167 | 17.16 | 17.16 | 17.16 | 0.00 | 0.00 |
| BS7-235 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| BS7-247 | 7.83 | 7.83 | 7.83 | 0.00 | 0.00 |
| BS7-346 | 8.18 | 8.18 | 8.18 | 0.00 | 0.00 |
| BS8-236 | 11.08 | 11.08 | 11.08 | 0.00 | 0.00 |
| BS8-237 | 7.58 | 7.58 | 7.58 | 0.00 | 0.00 |
| BS8-245 | 12.42 | 12.42 | 12.42 | 0.00 | 0.00 |
| BS8-246 | 18.52 | 18.52 | 18.52 | 0.00 | 0.00 |
| BS8-345 | 12.48 | 12.48 | 12.48 | 0.00 | 0.00 |
| BS8-347 | 14.77 | 14.77 | 14.77 | 0.00 | 0.00 |
| BS9-126 | 20.77 | 20.77 | 20.77 | 0.00 | 0.00 |
| BS9-137 | 22.00 | 22.00 | 22.00 | 0.00 | 0.00 |
| BS9-145 | 14.40 | 14.40 | 14.40 | 0.00 | 0.00 |
| BS10-125 | 12.56 | 12.56 | 12.56 | 0.00 | 0.00 |
| BS10-127 | 10.28 | 10.28 | 10.28 | 0.00 | 0.00 |
| BS10-135 | 17.56 | 17.56 | 17.56 | 0.00 | 0.00 |
| BS10-136 | 12.79 | 12.79 | 12.79 | 0.00 | 0.00 |
| BS10-146 | 10.18 | 10.18 | 10.18 | 0.00 | 0.00 |
| BS10-147 | 11.38 | 11.38 | 11.38 | 0.00 | 0.00 |

a) Normal flip spin is the same BS solution as acquired with no specific flipping of vanadium

b) V-flip from low spin means that a fully converged BS solution is used as a "high spin" solution and then vanadium is flipped

c) V-flip from high spin means that first a high spin solution is converged and then in the BS step, the vanadium is included in the flip spin procedure.

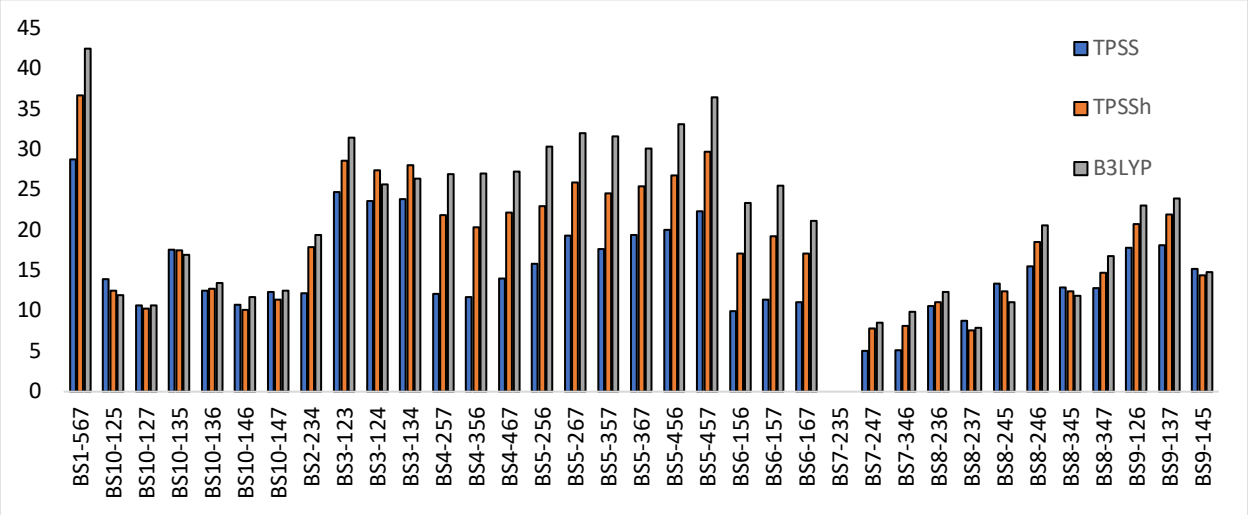



*Figure S 19: Relative QM/MM energies of the 35 BS solutions for the $[V\text{-}CO_3]^{2-}$ model using the X-ray structure with different functionals.*

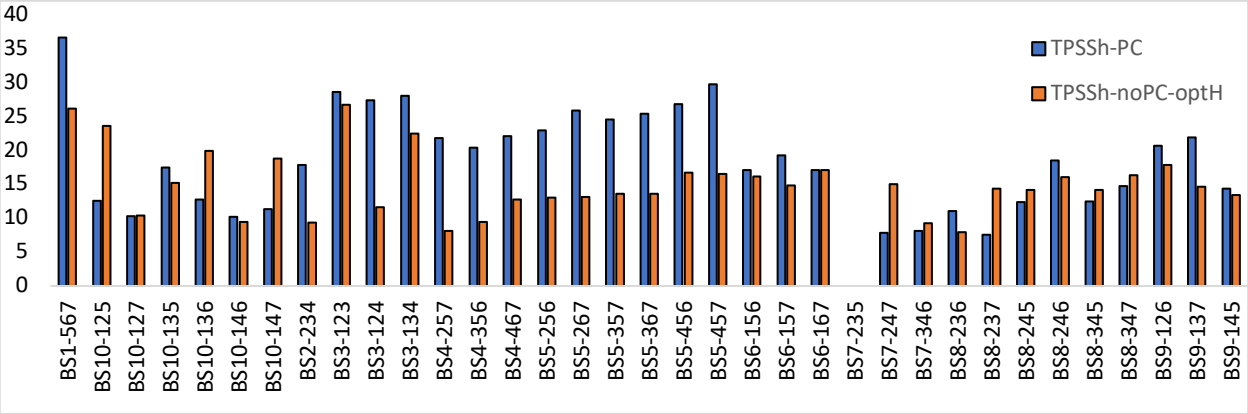



*Figure S 20: Comparison of CPCM-DFT energies and QM/MM energies of the 35 BS solutions for the $[V\text{-}CO_3]^{2-}$ model using the X-ray structure. Functional: TPSSh. Homocitrate was calculated as triply protonated.*

# Mulliken spin populations of the 181 QM-atom QM/MM optimized structures

*Table S 3: Mulliken spin population of the QM/MM optimized models. C* is carbide and X is either nitrogen or carbon of the $XO_3$ ligand.*

| Model | [**V**-$CO_3$]$^n$ | | | | | | | | | | [**V**-$NO_3$]$^n$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Charge | 2- | 1- | 1- | 1- | 0 | 2- | 1- | 1- | 1- | 0 | 1- | 0 | 0 | 0 | 1+ | 1- | 0 | 0 | 0 | 1+ |
| Spin | $^3/_2$ | 2 | 1 | 0 | $^3/_2$ | $^3/_2$ | 2 | 1 | 0 | $^3/_2$ | $^3/_2$ | 2 | 1 | 0 | $^3/_2$ | $^3/_2$ | 2 | 1 | 0 | $^3/_2$ |
| QM size | 181 | 181 | 181 | 181 | 181 | 57 | 57 | 57 | 57 | 57 | 181 | 181 | 181 | 181 | 181 | 57 | 57 | 57 | 57 | 57 |
| V | -1.62 | 1.00 | -1.58 | -1.59 | -1.52 | -1.65 | 1.02 | -1.61 | -1.61 | -0.65 | -1.69 | -1.66 | -1.67 | -1.62 | -1.56 | -1.73 | 0.85 | -1.69 | -1.65 | -0.84 |
| Fe1 | 3.45 | 3.47 | 3.46 | 3.37 | 3.46 | 3.48 | 3.49 | 3.49 | 2.33 | 3.49 | 3.47 | 3.48 | 3.48 | 3.39 | 3.48 | 3.50 | 3.50 | 3.50 | 3.43 | 3.49 |
| Fe2 | -3.29 | -3.43 | -3.44 | -3.43 | -3.42 | -3.29 | -3.44 | -3.45 | -3.49 | -3.45 | -3.26 | -3.17 | -3.42 | -3.43 | -3.40 | -3.27 | -3.41 | -3.42 | -3.43 | -3.43 |
| Fe3 | -3.27 | -3.44 | -3.45 | -3.45 | -3.42 | -3.29 | -3.48 | -3.48 | -3.47 | -3.46 | -3.25 | -3.17 | -3.43 | -3.44 | -3.39 | -3.27 | -3.45 | -3.45 | -3.47 | -3.42 |
| Fe4 | 3.39 | 3.40 | 3.40 | 2.27 | 3.43 | 3.43 | 3.43 | 3.42 | 3.26 | 3.42 | 3.24 | 3.29 | 3.28 | 2.15 | 3.32 | 3.26 | 3.28 | 3.28 | 2.15 | 3.29 |
| Fe5 | -3.19 | -3.34 | -3.23 | -3.27 | -3.18 | -3.22 | -3.37 | -3.25 | -3.27 | -3.30 | -3.04 | -3.00 | -3.09 | -3.11 | -3.06 | -3.06 | -3.19 | -3.10 | -3.13 | -3.14 |
| Fe6 | 3.29 | 3.29 | 3.15 | 3.06 | 3.39 | 3.28 | 3.30 | 3.18 | 3.19 | 3.19 | 3.27 | 3.44 | 3.13 | 3.05 | 3.36 | 3.27 | 3.28 | 3.15 | 3.06 | 3.17 |
| Fe7 | 3.21 | 2.84 | 3.07 | 2.97 | 3.31 | 3.23 | 2.88 | 3.10 | 3.11 | 3.18 | 3.20 | 3.37 | 3.06 | 2.97 | 3.30 | 3.22 | 2.89 | 3.07 | 2.97 | 3.16 |
| S1A | 0.20 | 0.15 | 0.15 | -0.04 | 0.12 | 0.18 | 0.13 | 0.13 | -0.09 | 0.11 | 0.20 | 0.20 | 0.16 | -0.04 | 0.14 | 0.18 | 0.14 | 0.15 | -0.04 | 0.13 |
| S2A | -0.02 | -0.12 | -0.13 | -0.14 | -0.15 | -0.02 | -0.12 | -0.13 | -0.32 | -0.15 | -0.01 | -0.05 | -0.11 | -0.13 | -0.14 | -0.01 | -0.10 | -0.11 | -0.13 | -0.12 |
| S4A | 0.17 | 0.13 | 0.13 | -0.06 | 0.11 | 0.16 | 0.12 | 0.12 | -0.03 | 0.10 | 0.18 | 0.18 | 0.15 | -0.05 | 0.13 | 0.18 | 0.15 | 0.14 | -0.07 | 0.13 |
| S1B | 0.08 | 0.01 | 0.09 | 0.09 | 0.14 | 0.09 | 0.01 | 0.10 | 0.10 | 0.03 | 0.07 | 0.11 | 0.08 | 0.08 | 0.11 | 0.08 | 0.00 | 0.08 | 0.08 | 0.03 |
| S3B | 0.27 | 0.20 | 0.28 | 0.23 | 0.36 | 0.27 | 0.20 | 0.28 | 0.28 | 0.28 | 0.29 | 0.37 | 0.28 | 0.24 | 0.36 | 0.29 | 0.22 | 0.29 | 0.23 | 0.31 |
| S4B | 0.10 | -0.06 | 0.11 | 0.10 | 0.14 | 0.11 | -0.06 | 0.12 | 0.12 | 0.06 | 0.09 | 0.11 | 0.09 | 0.08 | 0.11 | 0.09 | -0.06 | 0.09 | 0.09 | 0.06 |
| S2B | 0.01 | -0.07 | -0.07 | -0.06 | 0.02 | 0.02 | -0.07 | -0.07 | -0.08 | -0.03 | 0.01 | 0.11 | -0.07 | -0.07 | 0.01 | 0.00 | -0.08 | -0.08 | -0.07 | -0.04 |
| S5A | 0.00 | -0.15 | -0.10 | -0.08 | -0.02 | 0.02 | -0.15 | -0.09 | -0.08 | -0.02 | 0.00 | 0.08 | -0.10 | -0.09 | -0.02 | 0.01 | -0.14 | -0.09 | -0.08 | -0.03 |
| C* | 0.06 | -0.07 | -0.04 | -0.13 | 0.02 | 0.06 | -0.07 | -0.03 | -0.03 | -0.05 | 0.06 | 0.13 | -0.03 | -0.13 | 0.03 | 0.07 | -0.06 | -0.02 | -0.13 | -0.04 |
| X | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | 0.01 | 0.00 | -0.02 | 0.00 |
| O3 | 0.03 | 0.04 | 0.04 | 0.02 | 0.05 | 0.04 | 0.05 | 0.05 | 0.04 | 0.05 | -0.01 | -0.01 | -0.01 | 0.01 | 0.00 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 |
| O1 | -0.01 | -0.02 | -0.02 | -0.02 | -0.03 | -0.02 | -0.04 | -0.03 | -0.03 | -0.05 | 0.02 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 |
| O2 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 |

# Mulliken spin populations of all 35 BS solutions for different FeVco models: Single-point QM/MM calculations using X-ray structure

*Table S 4: Mulliken spin populations of the [**V**-$CO_3$]$^{2-}$ model, $M_S = 3/2$. Functional: TPSSh*

| No. | *1* | *2* | *3* | *3* | *3* | *4* | *4* | *4* | *5* | *5* | *5* | *5* | *5* | *5* | *6* | *6* | *6* | *7* | *7* | *7* | *8* | *8* | *8* | *8* | *8* | *8* | *9* | *9* | *9* | *10* | *10* | *10* | *10* | *10* | *10* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | *567* | *234* | *123* | *124* | *134* | *257* | *356* | *467* | *256* | *267* | *357* | *367* | *456* | *457* | *156* | *157* | *167* | *235* | *247* | *346* | *236* | *237* | *245* | *246* | *345* | *347* | *126* | *137* | *145* | *125* | *127* | *135* | *136* | *146* | *147* |
| V | 2.12 | -2.12 | -2.18 | -2.07 | -2.04 | 0.48 | 1.11 | 1.61 | 0.90 | 1.35 | 0.57 | 1.38 | 0.99 | 0.60 | 0.88 | 0.57 | 1.43 | -1.60 | -1.13 | -0.71 | -0.66 | -1.03 | -1.45 | -0.57 | -1.42 | -0.86 | -0.52 | -0.77 | -1.48 | -1.50 | -1.01 | -1.45 | -0.61 | -0.60 | -0.92 |
| Fe1 | 0.81 | 3.46 | -2.34 | -3.38 | -3.37 | 3.31 | 3.32 | 2.15 | 3.28 | 3.20 | 3.31 | 3.29 | 3.15 | 3.23 | -3.45 | -3.45 | -3.48 | 3.44 | 3.37 | 3.34 | 3.40 | 3.41 | 3.36 | 3.34 | 3.34 | 3.32 | -3.32 | -3.33 | -3.39 | -3.32 | -3.32 | -3.35 | -3.35 | -3.41 | -3.40 |
| Fe2 | 3.27 | -3.04 | -3.27 | -3.01 | 3.41 | -3.36 | 2.21 | 3.22 | -3.34 | -3.36 | 2.46 | 2.38 | 3.31 | 2.42 | 3.12 | 3.04 | 3.09 | -3.22 | -3.25 | 3.32 | -3.28 | -3.35 | -3.31 | -3.24 | 3.36 | 3.31 | -3.30 | 3.27 | 3.34 | -3.28 | -3.29 | 3.37 | 3.29 | 3.30 | 3.37 |
| Fe3 | 3.30 | -3.11 | -3.29 | 3.42 | -3.13 | 3.08 | -3.35 | 3.22 | 2.42 | 2.55 | -3.33 | -3.37 | 2.54 | 3.34 | 3.13 | 3.21 | 3.13 | -3.23 | 3.34 | -3.30 | -3.37 | -3.32 | 3.37 | 3.29 | -3.33 | -3.28 | 3.32 | -3.28 | 3.37 | 3.39 | 3.32 | -3.30 | -3.30 | 3.37 | 3.32 |
| Fe4 | 3.32 | -3.23 | 3.41 | -3.28 | -3.23 | 3.13 | 3.29 | -3.44 | 3.38 | 3.26 | 3.38 | 3.28 | -3.43 | -3.41 | 3.20 | 3.21 | 3.20 | 3.43 | -3.36 | -3.35 | 3.39 | 3.41 | -3.38 | -3.47 | -3.35 | -3.44 | 3.42 | 3.45 | -3.32 | 3.44 | 3.45 | 3.47 | 3.47 | -3.34 | -3.34 |
| Fe5 | -3.27 | 3.46 | 3.51 | 3.54 | 3.56 | -3.44 | -3.31 | 3.15 | -3.39 | 3.17 | -3.38 | 3.17 | -3.36 | -3.32 | -3.33 | -3.29 | 3.18 | -3.18 | 3.27 | 3.26 | 3.29 | 3.33 | -3.18 | 3.34 | -3.18 | 3.36 | 3.33 | 3.37 | -3.06 | -3.06 | 3.42 | -3.02 | 3.39 | 3.36 | 3.38 |
| Fe6 | -3.20 | 3.14 | 3.23 | 3.37 | 3.30 | 3.11 | -3.22 | -3.17 | -3.19 | -3.23 | 3.09 | -3.28 | -3.26 | 3.11 | -3.19 | 3.17 | -3.26 | 3.17 | 3.17 | -3.18 | -3.21 | 3.24 | 3.26 | -3.19 | 3.21 | 3.16 | -3.15 | 3.18 | 3.26 | 3.24 | 3.22 | 3.31 | -3.12 | -3.15 | 3.30 |
| Fe7 | -3.28 | 3.24 | 3.28 | 3.36 | 3.45 | -3.28 | 3.12 | -3.23 | 3.06 | -3.33 | -3.21 | -3.28 | 3.07 | -3.27 | 3.13 | -3.21 | -3.31 | 3.22 | -3.14 | 3.20 | 3.24 | -3.15 | 3.26 | 3.16 | 3.30 | -3.14 | 3.22 | -3.10 | 3.33 | 3.33 | -3.09 | 3.28 | 3.22 | 3.29 | -3.11 |
| S1A | 0.31 | 0.00 | -0.04 | -0.41 | -0.03 | -0.01 | 0.26 | -0.05 | 0.10 | 0.04 | 0.28 | 0.24 | 0.09 | 0.05 | 0.02 | 0.01 | 0.00 | 0.18 | -0.13 | 0.15 | 0.14 | 0.12 | -0.16 | -0.17 | 0.15 | 0.10 | -0.11 | 0.19 | -0.10 | -0.09 | -0.11 | 0.17 | 0.17 | -0.12 | -0.14 |
| S2A | 0.27 | 0.02 | -0.27 | -0.05 | -0.08 | 0.05 | -0.01 | 0.20 | 0.07 | 0.07 | 0.08 | 0.05 | 0.26 | 0.28 | -0.02 | -0.01 | 0.00 | -0.06 | 0.17 | 0.13 | -0.11 | -0.11 | 0.14 | 0.15 | 0.12 | 0.13 | -0.11 | -0.12 | 0.13 | -0.11 | -0.11 | -0.15 | -0.14 | 0.11 | 0.11 |
| S4A | 0.27 | -0.03 | -0.03 | -0.03 | -0.38 | 0.36 | 0.03 | -0.01 | 0.25 | 0.22 | 0.08 | 0.05 | 0.05 | 0.11 | 0.04 | 0.05 | 0.03 | 0.15 | 0.15 | -0.14 | 0.09 | 0.13 | 0.14 | 0.09 | -0.15 | -0.16 | 0.17 | -0.10 | -0.09 | 0.17 | 0.17 | -0.10 | -0.12 | -0.11 | -0.10 |
| S1B | -0.25 | 0.29 | 0.31 | 0.30 | 0.30 | -0.01 | -0.24 | -0.08 | -0.25 | -0.08 | -0.02 | -0.09 | -0.26 | 0.00 | -0.25 | 0.01 | -0.08 | 0.08 | 0.23 | -0.01 | -0.01 | 0.26 | 0.09 | 0.01 | 0.07 | 0.24 | 0.00 | 0.25 | 0.11 | 0.10 | 0.26 | 0.10 | 0.01 | 0.01 | 0.25 |
| S3B | -0.32 | 0.25 | 0.27 | 0.31 | 0.32 | 0.00 | -0.05 | -0.27 | -0.04 | -0.29 | 0.01 | -0.29 | -0.07 | -0.01 | -0.04 | 0.01 | -0.31 | 0.26 | 0.04 | -0.02 | 0.00 | 0.06 | 0.29 | -0.03 | 0.28 | 0.03 | 0.01 | 0.07 | 0.30 | 0.30 | 0.06 | 0.30 | 0.01 | 0.00 | 0.07 |
| S4B | -0.29 | 0.30 | 0.33 | 0.32 | 0.33 | -0.26 | -0.02 | -0.10 | -0.03 | -0.10 | -0.24 | -0.09 | -0.02 | -0.25 | 0.00 | -0.24 | -0.10 | 0.10 | 0.01 | 0.23 | 0.24 | 0.01 | 0.08 | 0.23 | 0.10 | 0.02 | 0.24 | 0.01 | 0.12 | 0.11 | 0.03 | 0.12 | 0.25 | 0.25 | 0.02 |
| S2B | -0.03 | 0.06 | 0.03 | 0.24 | 0.50 | 0.04 | -0.19 | -0.06 | -0.46 | -0.47 | 0.21 | -0.21 | -0.07 | 0.23 | -0.09 | 0.40 | -0.12 | 0.03 | 0.03 | -0.05 | -0.45 | 0.01 | 0.03 | -0.45 | 0.46 | 0.44 | -0.45 | 0.42 | 0.46 | 0.03 | 0.03 | 0.49 | -0.02 | -0.04 | 0.48 |
| S5A | 0.01 | 0.02 | -0.02 | 0.46 | 0.17 | -0.15 | -0.07 | -0.01 | 0.14 | -0.19 | -0.41 | -0.44 | 0.15 | -0.01 | 0.36 | -0.04 | -0.08 | -0.01 | 0.03 | -0.03 | -0.04 | -0.38 | 0.42 | 0.38 | 0.00 | -0.38 | 0.39 | -0.38 | 0.43 | 0.44 | 0.03 | -0.02 | -0.04 | 0.41 | 0.03 |
| C* | -0.03 | 0.03 | -0.09 | 0.00 | 0.01 | -0.14 | -0.03 | -0.08 | -0.03 | -0.03 | -0.03 | -0.03 | -0.12 | -0.11 | -0.24 | -0.22 | -0.21 | 0.03 | -0.01 | -0.03 | 0.03 | 0.04 | -0.03 | -0.04 | -0.03 | -0.02 | -0.13 | -0.11 | -0.13 | -0.09 | -0.06 | -0.09 | -0.09 | -0.16 | -0.14 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.03 | -0.04 | 0.06 | -0.02 | -0.01 | 0.02 | 0.03 | -0.05 | 0.03 | 0.04 | 0.04 | 0.05 | -0.06 | -0.06 | 0.03 | 0.03 | 0.05 | 0.04 | -0.04 | -0.04 | 0.06 | 0.05 | -0.06 | -0.06 | -0.06 | -0.05 | 0.06 | 0.07 | -0.05 | 0.05 | 0.06 | 0.05 | 0.07 | -0.04 | -0.04 |
| O1 | -0.03 | 0.04 | 0.06 | 0.05 | 0.05 | -0.05 | -0.03 | 0.02 | -0.04 | 0.04 | -0.04 | 0.04 | -0.05 | -0.05 | -0.04 | -0.04 | 0.04 | -0.02 | 0.03 | 0.03 | 0.05 | 0.05 | -0.04 | 0.03 | -0.04 | 0.03 | 0.04 | 0.04 | -0.03 | -0.02 | 0.04 | -0.02 | 0.05 | 0.03 | 0.03 |
| O2 | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | -0.03 | -0.02 | 0.00 | -0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | -0.02 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | 0.02 | 0.00 | 0.03 | 0.00 | 0.00 |

*Table S 5 Mulliken spin populations of the [**V**-$CO_3$]$^{2-}$ model, $M_S = 1/2$. Functional: TPSSh*

| No. | *1* | *2* | *3* | *3* | *3* | *4* | *4* | *4* | *5* | *5* | *5* | *5* | *5* | *5* | *6* | *6* | *6* | *7* | *7* | *7* | *8* | *8* | *8* | *8* | *8* | *8* | *9* | *9* | *9* | *10* | *10* | *10* | *10* | *10* | *10* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | *567* | *234* | *123* | *124* | *134* | *257* | *356* | *467* | *256* | *267* | *357* | *367* | *456* | *457* | *156* | *157* | *167* | *235* | *247* | *346* | *236* | *237* | *245* | *246* | *345* | *347* | *126* | *137* | *145* | *125* | *127* | *135* | *136* | *146* | *147* |
| V | 2.09 | -2.15 | -2.12 | -2.12 | -2.12 | 0.33 | 1.09 | 1.60 | 1.06 | 1.50 | 0.58 | 1.42 | 0.86 | 0.54 | 0.88 | 0.60 | 1.66 | -1.55 | -1.09 | -0.75 | -0.66 | -1.34 | -1.41 | -0.53 | -1.37 | -0.89 | -0.70 | -0.99 | -1.55 | -1.49 | -1.14 | -1.48 | -0.76 | -0.67 | -1.04 |
| Fe1 | 0.78 | 3.46 | -3.42 | -3.48 | -3.42 | 2.27 | 3.42 | 0.05 | 3.43 | 3.40 | 3.41 | 1.72 | 2.37 | 2.41 | -3.49 | -3.49 | -3.47 | 3.34 | 2.82 | 1.84 | 3.40 | 3.40 | 3.33 | 3.32 | 3.30 | 3.29 | -3.36 | -3.37 | -3.41 | -3.33 | -3.38 | -3.34 | -3.38 | -3.41 | -3.40 |
| Fe2 | 3.02 | -3.19 | 3.28 | -3.34 | 3.28 | -3.38 | -0.61 | 3.20 | -2.24 | -3.33 | 0.12 | 2.32 | 2.99 | 2.50 | 2.77 | 2.41 | 2.91 | -3.39 | -3.41 | 3.27 | -3.28 | -3.35 | -3.31 | -3.34 | 2.91 | 2.74 | -3.32 | 2.82 | 3.06 | -3.35 | -3.32 | 2.88 | 2.94 | 3.07 | 2.87 |
| Fe3 | 3.04 | -3.32 | -3.32 | 3.33 | -3.32 | 3.08 | -3.22 | 3.25 | -2.91 | -0.29 | -3.32 | -3.36 | 2.52 | 3.01 | 2.57 | 2.95 | 3.01 | -3.46 | 3.20 | -3.31 | -3.37 | -3.35 | 2.95 | 3.22 | -3.34 | -3.31 | 2.89 | -3.35 | 3.17 | 3.12 | 3.11 | -3.36 | -3.36 | 2.85 | 3.14 |
| Fe4 | 3.19 | -3.35 | -3.33 | -3.36 | -3.33 | 3.24 | 3.34 | -3.43 | 3.48 | 3.32 | 3.40 | 3.30 | -3.42 | -3.40 | 3.07 | 3.08 | 2.89 | 3.01 | -3.57 | -3.37 | 3.39 | 3.34 | -3.42 | -3.49 | -3.37 | -3.45 | 3.15 | 3.14 | -3.40 | 3.31 | 3.02 | 3.34 | 2.95 | -3.41 | -3.39 |
| Fe5 | -3.49 | 3.18 | 3.39 | 3.34 | 3.39 | -3.44 | -3.29 | 3.16 | -3.14 | 3.18 | -3.38 | 3.16 | -3.40 | -3.36 | -3.36 | -3.32 | 2.18 | -3.23 | 3.22 | 3.27 | 3.29 | 2.00 | -3.23 | 3.25 | -3.23 | 3.17 | 3.25 | 3.33 | -3.15 | -3.16 | 3.17 | -3.17 | 3.23 | 3.20 | 3.24 |
| Fe6 | -3.34 | 2.91 | 3.08 | 3.15 | 3.08 | 2.69 | -3.16 | -3.18 | -2.56 | -3.17 | 3.14 | -3.26 | -3.28 | 2.90 | -3.21 | 2.76 | -3.31 | 3.05 | 3.13 | -3.18 | -3.21 | 3.15 | 2.98 | -3.27 | 2.67 | 2.67 | -3.17 | 2.99 | 3.01 | 2.98 | 3.05 | 2.99 | -3.14 | -3.21 | 2.98 |
| Fe7 | -3.41 | 2.97 | 3.15 | 3.28 | 3.15 | -3.34 | 3.18 | -3.22 | 3.17 | -3.32 | -3.25 | -3.28 | 2.90 | -3.30 | 2.74 | -3.23 | -3.36 | 3.06 | -3.18 | 3.20 | 3.24 | -3.14 | 2.74 | 1.81 | 3.09 | -3.15 | 2.97 | -3.11 | 3.13 | 2.89 | -3.13 | 3.12 | 3.16 | 3.06 | -3.19 |
| S1A | 0.26 | -0.05 | -0.05 | -0.53 | -0.05 | 0.03 | 0.33 | -0.06 | 0.24 | 0.11 | 0.30 | -0.03 | 0.06 | 0.01 | -0.04 | -0.01 | -0.01 | 0.01 | -0.39 | 0.00 | 0.14 | 0.11 | -0.17 | -0.17 | 0.05 | 0.03 | -0.23 | 0.06 | -0.20 | -0.12 | -0.23 | 0.09 | 0.03 | -0.14 | -0.21 |
| S2A | 0.19 | -0.03 | -0.14 | -0.16 | -0.14 | 0.03 | 0.05 | 0.19 | 0.08 | 0.07 | 0.05 | -0.09 | 0.04 | 0.03 | -0.04 | -0.03 | -0.04 | -0.20 | 0.06 | 0.03 | -0.11 | -0.13 | 0.06 | 0.13 | 0.05 | 0.04 | -0.20 | -0.22 | 0.06 | -0.21 | -0.13 | -0.23 | -0.16 | 0.02 | 0.03 |
| S4A | 0.26 | -0.03 | -0.45 | -0.04 | -0.45 | 0.21 | 0.08 | 0.01 | 0.18 | 0.26 | 0.10 | 0.00 | 0.01 | 0.09 | 0.02 | 0.00 | 0.02 | -0.01 | -0.01 | -0.27 | 0.09 | 0.13 | 0.07 | 0.07 | -0.16 | -0.16 | 0.06 | -0.21 | -0.16 | 0.11 | 0.04 | -0.12 | -0.22 | -0.20 | -0.11 |
| S1B | -0.31 | 0.23 | 0.28 | 0.25 | 0.28 | -0.09 | -0.22 | -0.08 | -0.15 | -0.07 | -0.04 | -0.09 | -0.25 | -0.02 | -0.23 | -0.03 | -0.20 | 0.07 | 0.22 | -0.01 | -0.01 | 0.10 | 0.07 | -0.01 | 0.05 | 0.16 | 0.00 | 0.23 | 0.05 | 0.08 | 0.19 | 0.04 | 0.00 | 0.00 | 0.20 |
| S3B | -0.33 | 0.24 | 0.28 | 0.31 | 0.28 | -0.09 | -0.02 | -0.27 | 0.00 | -0.28 | 0.01 | -0.29 | -0.09 | -0.04 | -0.08 | -0.03 | -0.33 | 0.23 | 0.04 | -0.01 | 0.00 | 0.08 | 0.17 | -0.01 | 0.18 | 0.02 | -0.05 | 0.02 | 0.25 | 0.21 | 0.05 | 0.24 | 0.01 | -0.06 | -0.01 |
| S4B | -0.33 | 0.27 | 0.27 | 0.30 | 0.27 | -0.26 | -0.02 | -0.10 | -0.01 | -0.10 | -0.23 | -0.09 | -0.03 | -0.24 | -0.04 | -0.22 | -0.20 | 0.08 | 0.01 | 0.24 | 0.24 | 0.03 | 0.07 | 0.14 | 0.09 | 0.01 | 0.22 | 0.02 | 0.08 | 0.06 | 0.02 | 0.10 | 0.21 | 0.20 | 0.02 |
| S2B | -0.18 | -0.06 | 0.41 | 0.00 | 0.41 | -0.07 | -0.29 | -0.04 | -0.22 | -0.46 | 0.26 | -0.18 | -0.13 | 0.23 | -0.14 | 0.23 | -0.13 | -0.02 | -0.01 | -0.02 | -0.45 | 0.00 | -0.02 | -0.48 | 0.22 | 0.20 | -0.45 | 0.35 | 0.37 | 0.00 | 0.01 | 0.36 | -0.10 | -0.08 | 0.35 |
| S5A | -0.14 | -0.13 | -0.01 | 0.41 | -0.01 | -0.07 | -0.01 | 0.01 | 0.03 | -0.21 | -0.42 | -0.42 | 0.18 | -0.07 | 0.18 | -0.08 | -0.09 | -0.09 | -0.07 | -0.02 | -0.04 | -0.36 | 0.19 | 0.28 | -0.05 | -0.40 | 0.29 | -0.38 | 0.36 | 0.32 | -0.03 | -0.04 | -0.04 | 0.30 | 0.00 |
| C* | -0.25 | -0.18 | -0.18 | -0.18 | -0.18 | -0.13 | 0.17 | -0.06 | 0.37 | 0.13 | 0.08 | -0.01 | -0.19 | -0.16 | -0.37 | -0.35 | -0.34 | -0.08 | -0.07 | 0.01 | 0.03 | 0.02 | -0.15 | -0.05 | -0.15 | -0.11 | -0.30 | -0.30 | -0.38 | -0.30 | -0.25 | -0.29 | -0.28 | -0.34 | -0.32 |
| C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.02 | 0.02 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.02 | -0.05 | -0.03 | -0.03 | -0.03 | 0.03 | 0.03 | -0.04 | 0.04 | 0.05 | 0.04 | 0.05 | -0.06 | -0.06 | 0.03 | 0.03 | 0.03 | 0.02 | -0.06 | -0.04 | 0.06 | 0.05 | -0.07 | -0.06 | -0.06 | -0.05 | 0.04 | 0.04 | -0.05 | 0.05 | 0.04 | 0.05 | 0.03 | -0.04 | -0.04 |
| O1 | -0.04 | 0.02 | 0.04 | 0.03 | 0.04 | -0.04 | -0.03 | 0.02 | -0.02 | 0.04 | -0.03 | 0.04 | -0.05 | -0.05 | -0.04 | -0.04 | 0.01 | -0.03 | 0.02 | 0.03 | 0.05 | 0.03 | -0.04 | 0.03 | -0.04 | 0.02 | 0.04 | 0.05 | -0.03 | -0.02 | 0.04 | -0.02 | 0.04 | 0.03 | 0.03 |
| O2 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | -0.03 | -0.02 | -0.01 | -0.01 | 0.01 | 0.00 | -0.01 | 0.00 | 0.02 | 0.01 | -0.02 | 0.00 | -0.02 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | 0.02 | 0.00 | 0.02 | 0.00 | 0.00 |

*Table S 6: Mulliken spin populations of the [**V**-$CO_3$]$^-$ model, $M_S$ = 0. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.97 | -2.04 | -2.06 | -1.97 | -2.01 | 0.35 | 0.83 | 1.60 | 1.01 | 1.64 | 0.54 | 1.57 | 1.13 | 0.58 | 0.68 | 0.35 | 1.68 | -1.60 | -1.24 | -0.70 | -0.33 | -1.25 | -1.67 | -0.40 | -1.64 | -0.76 | -0.55 | -1.02 | -1.55 | -1.55 | -1.15 | -1.53 | -0.72 | -0.54 | -1.01 |
| Fe1 | -1.41 | 3.48 | -3.59 | -3.54 | -3.55 | 0.33 | 0.35 | -2.64 | 3.45 | -2.68 | 3.45 | 3.43 | 3.28 | 3.32 | -3.50 | -3.50 | -3.49 | 2.64 | 2.61 | 2.41 | 3.41 | 2.35 | 3.29 | 3.45 | 3.25 | 3.48 | -3.61 | -3.34 | -3.43 | -3.35 | -3.43 | -3.37 | -3.43 | -3.45 | -3.45 |
| Fe2 | 3.26 | -3.19 | -3.42 | -3.40 | 3.17 | -3.41 | 3.14 | 3.41 | -2.40 | -2.74 | -3.01 | -1.73 | 3.29 | -1.06 | 2.84 | 1.91 | 2.48 | -3.41 | -3.40 | 2.80 | -3.38 | -3.43 | -3.36 | -3.14 | 2.93 | -0.31 | -3.45 | 1.45 | 3.15 | -3.33 | -3.34 | 2.99 | 2.89 | 3.01 | 2.40 |
| Fe3 | 3.29 | -3.28 | -3.45 | 3.16 | -3.43 | 3.20 | -3.45 | 3.46 | -3.09 | 3.44 | -2.49 | -3.27 | -1.00 | 3.33 | 1.98 | 3.02 | 2.76 | -3.46 | 2.70 | -3.44 | -3.41 | -3.44 | 2.96 | -0.25 | -3.40 | -3.20 | 2.78 | -3.32 | 1.97 | 3.11 | 2.89 | -3.36 | -3.39 | 2.49 | 3.09 |
| Fe4 | 3.31 | -3.35 | 3.37 | -3.44 | -3.40 | 3.29 | 3.27 | -3.12 | 3.45 | 3.48 | 3.46 | 3.40 | -3.43 | -3.38 | 3.14 | 3.13 | 2.97 | 3.12 | -3.59 | -3.57 | 3.28 | 3.16 | -3.53 | -3.41 | -3.49 | -3.38 | 2.96 | 3.32 | -3.41 | 3.27 | 2.81 | 3.30 | 2.75 | -3.46 | -3.45 |
| Fe5 | -3.48 | 3.32 | 3.41 | 3.31 | 3.38 | -3.45 | -3.46 | 3.25 | -3.20 | 3.27 | -3.13 | 3.24 | -3.39 | -3.33 | -3.50 | -3.48 | 2.10 | -3.25 | 3.22 | 3.24 | 1.31 | 3.30 | -3.33 | 3.32 | -3.32 | 3.38 | 3.29 | 3.37 | -3.25 | -3.25 | 3.13 | -3.24 | 3.10 | 3.13 | 3.20 |
| Fe6 | -3.31 | 3.12 | 3.08 | 3.05 | 2.87 | 3.16 | -3.30 | -3.11 | -2.87 | -3.10 | 3.25 | -3.15 | -3.24 | 3.19 | -3.29 | 2.74 | -3.39 | 3.11 | 3.12 | -3.21 | -3.32 | 3.00 | 2.88 | -3.22 | 2.42 | 3.13 | -3.20 | 3.10 | 3.13 | 2.90 | 2.96 | 2.38 | -3.22 | -3.25 | 2.87 |
| Fe7 | -3.38 | 1.22 | 3.17 | 3.06 | 3.14 | -3.33 | 3.12 | -3.12 | 3.20 | -3.18 | -2.88 | -3.22 | 3.10 | -3.25 | 2.73 | -3.32 | -3.44 | 3.12 | -3.14 | 3.11 | 2.85 | -3.16 | 2.46 | 3.14 | 2.99 | -3.16 | 3.01 | -3.20 | 3.19 | 2.36 | -3.18 | 3.05 | 2.99 | 2.88 | -3.20 |
| S1A | 0.32 | -0.08 | -0.19 | -0.56 | -0.10 | -0.08 | 0.26 | 0.14 | 0.21 | 0.11 | 0.15 | 0.19 | 0.08 | 0.04 | 0.01 | 0.02 | 0.00 | -0.14 | -0.39 | -0.13 | 0.07 | -0.13 | -0.19 | -0.08 | 0.03 | 0.06 | -0.35 | 0.00 | -0.15 | -0.13 | -0.28 | 0.10 | -0.02 | -0.15 | -0.21 |
| S2A | 0.36 | -0.03 | -0.56 | -0.16 | -0.18 | -0.04 | -0.06 | 0.35 | 0.03 | 0.06 | 0.04 | 0.01 | 0.19 | 0.20 | -0.01 | 0.00 | -0.01 | -0.35 | -0.05 | -0.07 | -0.16 | -0.33 | 0.05 | 0.13 | 0.03 | 0.15 | -0.30 | -0.21 | -0.01 | -0.16 | -0.14 | -0.19 | -0.16 | -0.04 | -0.03 |
| S4A | 0.29 | -0.06 | -0.20 | -0.08 | -0.50 | 0.30 | -0.07 | 0.11 | 0.11 | 0.31 | 0.19 | 0.12 | 0.04 | 0.12 | 0.05 | 0.04 | 0.05 | -0.11 | -0.06 | -0.36 | 0.06 | -0.10 | 0.04 | 0.05 | -0.18 | -0.09 | -0.05 | -0.15 | -0.16 | 0.10 | -0.02 | -0.12 | -0.26 | -0.19 | -0.11 |
| S1B | -0.33 | 0.31 | 0.31 | 0.26 | 0.29 | 0.01 | -0.29 | -0.10 | -0.19 | -0.09 | 0.01 | -0.09 | -0.27 | 0.00 | -0.27 | -0.04 | -0.23 | 0.10 | 0.24 | -0.01 | -0.03 | 0.25 | 0.11 | -0.01 | 0.08 | 0.25 | -0.02 | 0.27 | 0.08 | 0.10 | 0.19 | 0.06 | -0.03 | -0.01 | 0.19 |
| S3B | -0.34 | 0.19 | 0.25 | 0.29 | 0.26 | 0.01 | -0.04 | -0.25 | -0.02 | -0.27 | 0.05 | -0.29 | -0.08 | -0.01 | -0.08 | -0.03 | -0.36 | 0.25 | 0.07 | -0.02 | -0.04 | 0.09 | 0.15 | -0.03 | 0.16 | 0.04 | -0.06 | 0.05 | 0.28 | 0.13 | 0.05 | 0.14 | -0.01 | -0.05 | 0.02 |
| S4B | -0.35 | 0.18 | 0.34 | 0.31 | 0.30 | -0.27 | -0.02 | -0.10 | -0.02 | -0.13 | -0.16 | -0.09 | -0.04 | -0.24 | -0.05 | -0.25 | -0.25 | 0.10 | 0.03 | 0.23 | 0.05 | 0.04 | 0.09 | 0.23 | 0.12 | 0.01 | 0.23 | 0.02 | 0.11 | 0.09 | -0.01 | 0.12 | 0.18 | 0.16 | 0.02 |
| S2B | -0.12 | 0.04 | -0.06 | -0.08 | 0.33 | 0.02 | -0.13 | 0.05 | -0.24 | -0.27 | 0.08 | -0.29 | -0.04 | 0.30 | -0.19 | 0.19 | -0.15 | -0.05 | -0.06 | -0.10 | -0.51 | -0.10 | -0.04 | -0.44 | 0.17 | 0.32 | -0.52 | 0.24 | 0.43 | 0.02 | 0.02 | 0.25 | -0.10 | -0.08 | 0.24 |
| S5A | -0.05 | -0.18 | -0.12 | 0.28 | -0.10 | -0.07 | -0.07 | 0.12 | -0.01 | 0.08 | -0.17 | -0.42 | 0.27 | 0.02 | 0.16 | -0.12 | -0.10 | -0.12 | -0.05 | -0.15 | -0.15 | -0.42 | 0.15 | 0.27 | -0.09 | -0.37 | 0.30 | -0.38 | 0.24 | 0.23 | -0.03 | -0.03 | -0.06 | 0.17 | 0.01 |
| C* | -0.13 | 0.03 | -0.23 | -0.25 | -0.24 | -0.08 | -0.09 | 0.07 | 0.37 | 0.06 | 0.39 | 0.27 | 0.11 | 0.16 | -0.35 | -0.37 | -0.39 | -0.07 | -0.06 | -0.09 | -0.03 | -0.05 | -0.14 | 0.13 | -0.13 | 0.15 | -0.31 | -0.17 | -0.29 | -0.36 | -0.38 | -0.35 | -0.40 | -0.39 | -0.37 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.03 | -0.05 | 0.08 | -0.05 | -0.05 | 0.04 | 0.03 | -0.03 | 0.05 | 0.08 | 0.05 | 0.06 | -0.07 | -0.08 | 0.03 | 0.03 | 0.04 | 0.03 | -0.07 | -0.07 | 0.05 | 0.05 | -0.09 | -0.06 | -0.08 | -0.05 | 0.04 | 0.06 | -0.06 | 0.05 | 0.02 | 0.05 | 0.02 | -0.05 | -0.05 |
| O1 | -0.05 | 0.04 | 0.06 | 0.04 | 0.04 | -0.05 | -0.05 | 0.03 | -0.03 | 0.05 | -0.03 | 0.04 | -0.05 | -0.06 | -0.06 | -0.05 | 0.01 | -0.03 | 0.03 | 0.03 | 0.02 | 0.05 | -0.05 | 0.04 | -0.04 | 0.05 | 0.05 | 0.06 | -0.04 | -0.03 | 0.05 | -0.03 | 0.05 | 0.03 | 0.03 |
| O2 | -0.01 | 0.00 | 0.03 | 0.00 | 0.00 | -0.01 | -0.01 | 0.00 | 0.00 | 0.03 | 0.00 | 0.03 | -0.03 | -0.03 | -0.01 | -0.01 | 0.01 | 0.00 | -0.01 | -0.01 | 0.02 | 0.02 | -0.03 | 0.00 | -0.03 | 0.00 | 0.03 | 0.03 | -0.03 | 0.00 | 0.02 | 0.00 | 0.02 | 0.00 | 0.00 |

*Table S 7 Mulliken spin populations of the [**V**-$CO_3$]$^-$ model, $M_S$ = 1. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.97 | -2.02 | -2.02 | -1.93 | -1.90 | 0.36 | 0.85 | 1.59 | 0.94 | 1.45 | 0.55 | 1.50 | 1.09 | 0.59 | 0.85 | 0.45 | 1.42 | -1.60 | -1.10 | -0.60 | -0.55 | -0.92 | -1.47 | -0.40 | -1.44 | -0.74 | -0.31 | -0.75 | -1.52 | -1.49 | -1.13 | -1.46 | -0.68 | -0.57 | -0.97 |
| Fe1 | 0.96 | 3.47 | -3.43 | -3.52 | -3.53 | 2.42 | 2.52 | 2.08 | 2.46 | 2.37 | 3.38 | 2.56 | 2.43 | 2.41 | -3.50 | -3.50 | -3.49 | 3.44 | 3.33 | 3.27 | 3.42 | 3.43 | 3.37 | 3.32 | 3.34 | 3.29 | -3.35 | -3.36 | -3.43 | -3.35 | -3.40 | -3.37 | -3.39 | -3.44 | -3.43 |
| Fe2 | 3.25 | -3.21 | -3.35 | -3.34 | 3.37 | -3.37 | 3.03 | 3.16 | -3.30 | -3.36 | 0.90 | 2.79 | 3.19 | 2.64 | 2.91 | 2.90 | 2.87 | -3.38 | -3.37 | 3.29 | -3.35 | -3.37 | -3.28 | -3.22 | 3.13 | 2.98 | -3.29 | 3.09 | 3.23 | -3.28 | -3.28 | 3.23 | 3.14 | 3.13 | 3.20 |
| Fe3 | 3.27 | -3.31 | -3.31 | 3.38 | -3.39 | 3.10 | -3.40 | 2.82 | 2.60 | 2.87 | -3.26 | -3.38 | 2.68 | 3.24 | 2.99 | 3.09 | 3.03 | -3.44 | 3.31 | -3.41 | -3.45 | -3.33 | 3.17 | 2.99 | -3.32 | -3.26 | 3.17 | -3.31 | 3.32 | 3.29 | 3.23 | -3.31 | -3.32 | 3.22 | 3.21 |
| Fe4 | 3.25 | -3.36 | 3.46 | -3.36 | -3.31 | 3.26 | 3.21 | -3.46 | 3.34 | 3.17 | 3.46 | 3.06 | -3.41 | -3.37 | 3.21 | 3.21 | 3.02 | 3.43 | -3.56 | -3.53 | 3.30 | 3.26 | -3.38 | -3.47 | -3.35 | -3.44 | 3.42 | 3.43 | -3.37 | 3.43 | 3.40 | 3.44 | 3.39 | -3.39 | -3.37 |
| Fe5 | -3.48 | 3.22 | 3.48 | 3.55 | 3.56 | -3.45 | -3.47 | 3.16 | -3.40 | 3.16 | -3.36 | 3.17 | -3.39 | -3.35 | -3.41 | -3.36 | 3.07 | -3.23 | 3.17 | 3.22 | 3.18 | 3.15 | -3.22 | 3.26 | -3.20 | 3.31 | 3.24 | 3.32 | -3.17 | -3.18 | 3.32 | -3.16 | 3.29 | 3.31 | 3.30 |
| Fe6 | -3.31 | 3.15 | 3.33 | 3.33 | 3.26 | 3.16 | -3.30 | -3.23 | -3.17 | -3.27 | 3.18 | -3.33 | -3.27 | 3.15 | -3.20 | 2.99 | -3.28 | 3.11 | 3.10 | -3.22 | -3.26 | 2.90 | 3.13 | -3.22 | 2.91 | 2.87 | -3.22 | 2.97 | 3.15 | 3.05 | 3.04 | 3.14 | -3.19 | -3.22 | 3.13 |
| Fe7 | -3.38 | 3.25 | 3.39 | 3.32 | 3.40 | -3.33 | 3.11 | -3.31 | 3.05 | -3.37 | -3.16 | -3.30 | 3.07 | -3.29 | 2.95 | -3.24 | -3.34 | 3.10 | -3.18 | 3.08 | 2.94 | -3.18 | 2.92 | 2.83 | 3.20 | -3.17 | 2.87 | -3.17 | 3.24 | 3.14 | -3.14 | 3.14 | 3.12 | 3.16 | -3.17 |
| S1A | 0.30 | -0.09 | -0.10 | -0.52 | -0.05 | 0.03 | 0.17 | -0.03 | 0.10 | 0.02 | 0.19 | 0.05 | 0.08 | 0.03 | 0.01 | 0.04 | 0.02 | 0.14 | -0.24 | 0.05 | 0.08 | 0.07 | -0.17 | -0.17 | 0.07 | 0.05 | -0.12 | 0.16 | -0.16 | -0.08 | -0.12 | 0.15 | 0.12 | -0.15 | -0.14 |
| S2A | 0.27 | -0.07 | -0.50 | -0.15 | -0.17 | 0.02 | -0.02 | 0.02 | -0.04 | 0.02 | 0.05 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | -0.01 | -0.17 | 0.14 | 0.09 | -0.16 | -0.14 | 0.10 | 0.06 | 0.10 | 0.04 | -0.16 | -0.18 | 0.11 | -0.13 | -0.12 | -0.15 | -0.15 | 0.08 | 0.09 |
| S4A | 0.27 | -0.05 | -0.06 | -0.04 | -0.47 | 0.22 | 0.00 | -0.03 | 0.03 | 0.08 | 0.13 | 0.03 | 0.02 | 0.09 | 0.06 | 0.04 | 0.06 | 0.10 | 0.08 | -0.22 | 0.06 | 0.06 | 0.09 | 0.06 | -0.17 | -0.16 | 0.15 | -0.10 | -0.11 | 0.15 | 0.12 | -0.09 | -0.11 | -0.12 | -0.10 |
| S1B | -0.33 | 0.25 | 0.33 | 0.33 | 0.31 | 0.00 | -0.29 | -0.10 | -0.27 | -0.11 | 0.00 | -0.12 | -0.29 | 0.00 | -0.27 | -0.01 | -0.11 | 0.10 | 0.23 | -0.02 | -0.03 | 0.18 | 0.10 | 0.00 | 0.10 | 0.19 | -0.02 | 0.22 | 0.09 | 0.09 | 0.22 | 0.09 | 0.02 | 0.02 | 0.23 |
| S3B | -0.34 | 0.33 | 0.34 | 0.32 | 0.32 | 0.01 | -0.05 | -0.31 | -0.05 | -0.32 | 0.05 | -0.33 | -0.08 | 0.00 | -0.07 | 0.00 | -0.33 | 0.26 | 0.05 | -0.03 | -0.02 | 0.06 | 0.21 | -0.04 | 0.22 | 0.03 | -0.07 | 0.01 | 0.28 | 0.25 | 0.06 | 0.26 | 0.00 | -0.03 | 0.04 |
| S4B | -0.35 | 0.30 | 0.35 | 0.34 | 0.35 | -0.27 | -0.02 | -0.12 | -0.03 | -0.13 | -0.24 | -0.11 | -0.03 | -0.27 | -0.03 | -0.25 | -0.12 | 0.11 | 0.01 | 0.22 | 0.19 | 0.00 | 0.11 | 0.16 | 0.12 | 0.02 | 0.18 | 0.00 | 0.11 | 0.11 | 0.05 | 0.10 | 0.21 | 0.21 | 0.03 |
| S2B | -0.11 | -0.01 | 0.08 | 0.10 | 0.50 | 0.03 | -0.17 | -0.06 | -0.47 | -0.51 | 0.17 | -0.18 | -0.06 | 0.28 | -0.12 | 0.34 | -0.17 | -0.05 | -0.08 | -0.04 | -0.49 | -0.08 | 0.03 | -0.46 | 0.27 | 0.24 | -0.48 | 0.38 | 0.43 | 0.03 | 0.01 | 0.41 | -0.08 | -0.06 | 0.40 |
| S5A | -0.06 | -0.08 | 0.07 | 0.47 | 0.02 | -0.09 | -0.07 | -0.08 | 0.17 | -0.14 | -0.39 | -0.48 | 0.18 | 0.01 | 0.28 | -0.06 | -0.12 | -0.12 | 0.04 | -0.15 | -0.18 | -0.42 | 0.23 | 0.14 | -0.02 | -0.40 | 0.32 | -0.41 | 0.41 | 0.37 | 0.01 | -0.02 | -0.05 | 0.36 | 0.02 |
| C* | -0.12 | -0.08 | -0.06 | -0.11 | -0.11 | -0.09 | -0.10 | -0.06 | 0.03 | -0.05 | 0.12 | -0.07 | -0.08 | -0.05 | -0.35 | -0.34 | -0.36 | -0.06 | -0.11 | -0.13 | -0.06 | -0.06 | -0.05 | -0.03 | -0.06 | -0.05 | -0.25 | -0.26 | -0.28 | -0.24 | -0.21 | -0.25 | -0.26 | -0.31 | -0.28 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.03 | -0.05 | 0.08 | -0.03 | -0.03 | 0.03 | 0.02 | -0.06 | 0.04 | 0.04 | 0.05 | 0.04 | -0.07 | -0.07 | 0.04 | 0.04 | 0.05 | 0.05 | -0.08 | -0.08 | 0.06 | 0.06 | -0.08 | -0.07 | -0.07 | -0.06 | 0.08 | 0.08 | -0.06 | 0.07 | 0.08 | 0.07 | 0.08 | -0.05 | -0.05 |
| O1 | -0.05 | 0.03 | 0.07 | 0.06 | 0.06 | -0.05 | -0.05 | 0.03 | -0.04 | 0.04 | -0.04 | 0.04 | -0.06 | -0.06 | -0.05 | -0.05 | 0.04 | -0.03 | 0.02 | 0.03 | 0.05 | 0.04 | -0.05 | 0.03 | -0.04 | 0.04 | 0.04 | 0.05 | -0.04 | -0.03 | 0.05 | -0.03 | 0.05 | 0.04 | 0.04 |
| O2 | -0.01 | 0.00 | 0.04 | 0.01 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | -0.03 | -0.03 | -0.01 | -0.01 | 0.02 | 0.00 | -0.01 | -0.01 | 0.02 | 0.02 | -0.03 | 0.00 | -0.03 | 0.00 | 0.03 | 0.03 | -0.03 | 0.00 | 0.03 | 0.00 | 0.03 | 0.00 | 0.00 |

*Table S 8: Mulliken spin populations of the [**V**-$CO_3$]$^-$ model, $M_S$ = 2. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 2.01 | -1.98 | 0.55 | -1.93 | -1.90 | 0.38 | 0.89 | 1.61 | 1.05 | 1.53 | 0.56 | 1.55 | 1.08 | 2.21 | 0.81 | 0.42 | 1.54 | -1.59 | -0.77 | -0.32 | -0.34 | -0.71 | -1.52 | -0.28 | -1.40 | -0.62 | -0.22 | -0.52 | -1.52 | -1.55 | -0.89 | 1.23 | -0.33 | -0.23 | 1.76 |
| Fe1 | 1.19 | 3.47 | -3.37 | -3.32 | -2.58 | 3.52 | 3.51 | 2.37 | 3.46 | 3.39 | 3.47 | 3.42 | 3.40 | 2.39 | -3.44 | -3.46 | -3.49 | 3.46 | 3.39 | 3.36 | 3.47 | 3.47 | 3.60 | 3.38 | 3.36 | 3.37 | -3.28 | -3.31 | -3.40 | -3.23 | -3.29 | -3.37 | -3.37 | -3.44 | -3.43 |
| Fe2 | 3.35 | -3.03 | -3.30 | -2.27 | 3.39 | -3.35 | 3.19 | 3.33 | -3.31 | -3.36 | 2.83 | 2.81 | 3.39 | 2.89 | 3.28 | 3.30 | 3.24 | -3.16 | -3.20 | 3.32 | -3.26 | -3.26 | -3.26 | -3.21 | 3.38 | 3.37 | -3.24 | 3.36 | 3.49 | -3.23 | -3.21 | 3.22 | 3.37 | 3.42 | 3.21 |
| Fe3 | 3.41 | -3.08 | -3.38 | 3.40 | -3.12 | 3.27 | -3.39 | 3.35 | 2.82 | 2.80 | -3.29 | -3.37 | 2.80 | 3.27 | 3.29 | 3.38 | 3.29 | -3.18 | 3.35 | -3.26 | -3.29 | -3.30 | 3.46 | 3.39 | -3.20 | -3.22 | 3.38 | -3.24 | 3.50 | 3.42 | 3.41 | -3.31 | -3.25 | 3.41 | 3.25 |
| Fe4 | 3.49 | -3.23 | 3.49 | -3.33 | -3.26 | 3.32 | 3.33 | -3.45 | 3.38 | 3.33 | 3.43 | 3.34 | -3.40 | -3.37 | 3.41 | 3.42 | 3.44 | 3.45 | -3.33 | -3.33 | 3.44 | 3.45 | -3.32 | -3.41 | -3.31 | -3.38 | 3.51 | 3.55 | -3.29 | 3.57 | 3.48 | 3.44 | 3.50 | -3.32 | -3.38 |
| Fe5 | -3.24 | 3.49 | 3.40 | 3.57 | 3.56 | -3.45 | -3.47 | 3.21 | -3.40 | 3.22 | -3.40 | 3.21 | -3.38 | -3.33 | -3.26 | -3.26 | 3.23 | -3.14 | 3.45 | 3.44 | 3.41 | 3.44 | -3.20 | 3.42 | -3.12 | 3.45 | 3.44 | 3.46 | -3.05 | -3.03 | 3.53 | -3.32 | 3.52 | 3.51 | 3.03 |
| Fe6 | -3.19 | 3.33 | 3.37 | 3.40 | 3.26 | 3.18 | -3.27 | -3.13 | -3.18 | -3.24 | 3.14 | -3.25 | -3.24 | 3.31 | -3.18 | 3.25 | -3.27 | 3.35 | 3.30 | -3.16 | -3.22 | 3.32 | 3.31 | -3.19 | 3.34 | 3.26 | -3.15 | 3.32 | 3.42 | 3.39 | 3.34 | 3.22 | -3.09 | -3.12 | 3.18 |
| Fe7 | -3.27 | 3.41 | 3.19 | 3.36 | 3.44 | -3.30 | 3.13 | -3.14 | 3.09 | -3.28 | -3.20 | -3.29 | 3.08 | -3.30 | 3.22 | -3.18 | -3.29 | 3.39 | -3.13 | 3.32 | 3.32 | -3.17 | 3.29 | 3.29 | 3.42 | -3.13 | 3.32 | -3.10 | 3.44 | 3.44 | -3.05 | 2.98 | 3.38 | 3.39 | -3.28 |
| S1A | 0.35 | -0.04 | -0.04 | -0.25 | -0.05 | 0.04 | 0.49 | 0.00 | 0.12 | 0.07 | 0.32 | 0.32 | 0.15 | 0.03 | 0.08 | 0.10 | 0.08 | 0.17 | -0.14 | 0.14 | 0.17 | 0.13 | -0.05 | -0.16 | 0.16 | 0.12 | -0.04 | 0.23 | -0.06 | -0.04 | -0.05 | 0.15 | 0.20 | -0.09 | -0.14 |
| S2A | 0.25 | 0.00 | -0.51 | -0.03 | -0.05 | 0.12 | 0.08 | 0.25 | 0.15 | 0.12 | 0.17 | 0.13 | 0.29 | 0.08 | 0.05 | 0.07 | 0.02 | -0.08 | 0.16 | 0.12 | -0.10 | -0.11 | 0.23 | 0.20 | 0.13 | 0.19 | -0.07 | -0.08 | 0.20 | -0.06 | -0.06 | -0.15 | -0.11 | 0.15 | 0.10 |
| S4A | 0.34 | -0.06 | -0.05 | -0.06 | -0.21 | 0.46 | 0.02 | 0.01 | 0.28 | 0.28 | 0.10 | 0.04 | 0.09 | 0.08 | 0.07 | 0.08 | 0.10 | 0.14 | 0.14 | -0.15 | 0.09 | 0.14 | 0.23 | 0.11 | -0.15 | -0.14 | 0.21 | -0.05 | -0.05 | 0.21 | 0.20 | -0.09 | -0.09 | -0.10 | -0.09 |
| S1B | -0.26 | 0.32 | 0.26 | 0.34 | 0.31 | 0.01 | -0.29 | -0.10 | -0.27 | -0.09 | 0.00 | -0.12 | -0.29 | -0.03 | -0.26 | 0.02 | -0.10 | 0.12 | 0.29 | -0.01 | 0.00 | 0.28 | 0.11 | 0.00 | 0.12 | 0.26 | 0.00 | 0.27 | 0.15 | 0.14 | 0.30 | 0.04 | 0.02 | 0.01 | 0.12 |
| S3B | -0.34 | 0.35 | 0.27 | 0.33 | 0.33 | 0.02 | -0.04 | -0.27 | -0.04 | -0.30 | 0.04 | -0.31 | -0.08 | -0.01 | -0.04 | 0.02 | -0.33 | 0.34 | 0.04 | -0.01 | 0.00 | 0.06 | 0.32 | -0.01 | 0.33 | 0.06 | 0.01 | 0.07 | 0.35 | 0.34 | 0.08 | 0.18 | 0.02 | 0.00 | 0.01 |
| S4B | -0.30 | 0.34 | 0.17 | 0.33 | 0.35 | -0.27 | -0.03 | -0.10 | -0.04 | -0.13 | -0.26 | -0.11 | -0.03 | -0.34 | 0.01 | -0.25 | -0.12 | 0.14 | 0.01 | 0.27 | 0.26 | 0.02 | 0.11 | 0.25 | 0.13 | 0.01 | 0.25 | 0.01 | 0.15 | 0.14 | 0.04 | -0.05 | 0.27 | 0.26 | -0.14 |
| S2B | 0.04 | 0.14 | 0.11 | 0.23 | 0.48 | 0.03 | -0.15 | 0.01 | -0.48 | -0.50 | 0.27 | -0.19 | 0.01 | 0.32 | -0.02 | 0.45 | -0.06 | 0.14 | 0.12 | -0.09 | -0.47 | 0.11 | 0.02 | -0.47 | 0.52 | 0.49 | -0.44 | 0.48 | 0.53 | 0.13 | 0.13 | 0.40 | 0.00 | -0.02 | 0.40 |
| S5A | 0.10 | 0.10 | -0.02 | 0.47 | 0.09 | -0.08 | -0.07 | 0.07 | 0.18 | -0.14 | -0.42 | -0.46 | 0.16 | 0.00 | 0.41 | 0.06 | 0.02 | 0.09 | -0.01 | 0.06 | 0.03 | -0.40 | 0.50 | 0.42 | 0.12 | -0.39 | 0.44 | -0.37 | 0.49 | 0.50 | 0.08 | -0.08 | 0.06 | 0.47 | -0.02 |
| C* | 0.08 | 0.14 | -0.09 | -0.13 | -0.10 | -0.10 | -0.11 | 0.01 | 0.00 | -0.01 | 0.02 | -0.04 | -0.07 | -0.04 | -0.18 | -0.16 | -0.15 | 0.10 | 0.06 | 0.06 | 0.07 | 0.09 | -0.02 | 0.04 | 0.06 | 0.03 | -0.10 | -0.08 | -0.05 | -0.03 | -0.04 | -0.28 | -0.05 | -0.10 | -0.30 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.05 | -0.04 | 0.08 | -0.03 | -0.02 | 0.03 | 0.03 | -0.07 | 0.05 | 0.06 | 0.05 | 0.06 | -0.07 | -0.07 | 0.06 | 0.05 | 0.08 | 0.05 | -0.04 | -0.05 | 0.06 | 0.06 | -0.07 | -0.05 | -0.07 | -0.04 | 0.09 | 0.10 | -0.06 | 0.08 | 0.08 | 0.07 | 0.09 | -0.04 | -0.05 |
| O1 | -0.03 | 0.05 | 0.06 | 0.06 | 0.06 | -0.05 | -0.05 | 0.03 | -0.04 | 0.05 | -0.05 | 0.05 | -0.06 | -0.06 | -0.03 | -0.03 | 0.04 | -0.03 | 0.05 | 0.05 | 0.06 | 0.06 | -0.04 | 0.05 | -0.04 | 0.05 | 0.06 | 0.06 | -0.04 | -0.03 | 0.07 | -0.04 | 0.07 | 0.05 | 0.02 |
| O2 | 0.00 | 0.01 | 0.03 | 0.01 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.03 | 0.00 | 0.03 | -0.03 | -0.03 | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | 0.01 | 0.03 | 0.03 | -0.03 | 0.00 | -0.03 | 0.01 | 0.03 | 0.03 | -0.03 | 0.00 | 0.03 | 0.00 | 0.03 | 0.01 | 0.00 |

*Table S 9: Mulliken spin populations of the [**V**-$CO_3$]$^0$ model, $M_S$ = $^3/_2$. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.85 | -1.84 | 0.73 | -1.81 | -1.79 | 0.22 | 0.82 | 1.55 | 1.82 | 1.54 | 1.79 | 1.54 | 0.49 | 0.03 | 0.66 | 0.28 | 1.42 | -1.53 | -0.63 | -0.13 | -0.05 | -0.34 | -1.42 | -0.26 | -1.35 | -0.65 | -0.06 | -0.44 | -1.48 | -0.05 | -0.76 | -1.46 | -0.29 | -0.13 | -0.51 |
| Fe1 | 1.67 | 3.46 | -3.60 | -2.82 | -2.74 | 3.28 | 3.46 | 2.50 | 2.37 | 2.70 | 2.74 | 2.84 | 3.30 | 3.32 | -3.47 | -3.49 | -3.47 | 3.43 | 3.31 | 3.22 | 3.46 | 3.42 | 3.32 | 3.59 | 3.30 | 3.59 | -3.57 | -3.30 | -3.42 | -3.37 | -3.54 | -2.80 | -3.47 | -3.45 | -3.44 |
| Fe2 | 3.27 | -3.24 | -3.36 | -3.15 | 3.23 | -3.32 | 3.23 | 3.26 | -3.32 | -3.34 | 2.48 | 2.84 | 3.29 | 2.71 | 3.10 | 3.11 | 3.05 | -3.36 | -3.35 | 3.29 | -3.41 | -3.22 | -2.96 | -3.15 | 3.01 | 3.27 | -3.34 | 3.16 | 3.38 | -3.25 | -3.28 | 3.23 | 3.19 | 3.25 | 3.17 |
| Fe3 | 3.35 | -3.31 | -3.47 | 3.26 | -3.22 | 2.68 | -3.37 | 3.29 | 2.72 | 2.89 | -3.33 | -3.37 | 2.78 | 3.35 | 3.13 | 3.30 | 3.22 | -3.42 | 3.31 | -3.39 | -3.44 | -3.25 | 3.07 | 3.33 | -3.12 | -3.19 | 3.30 | -3.21 | 3.44 | 3.25 | 3.32 | -3.17 | -3.28 | 3.18 | 3.35 |
| Fe4 | 3.44 | -3.35 | 3.48 | -3.28 | -3.34 | 3.45 | 2.64 | -3.48 | 3.39 | 3.28 | 3.31 | 3.24 | -3.46 | -3.46 | 3.40 | 3.41 | 3.28 | 3.44 | -3.56 | -3.52 | 3.35 | 3.15 | -3.19 | -3.47 | -3.20 | -3.45 | 3.51 | 3.49 | -3.32 | 3.43 | 3.45 | 3.43 | 3.43 | -3.34 | -3.32 |
| Fe5 | -3.49 | 3.46 | 3.37 | 3.53 | 3.53 | -3.44 | -3.49 | 3.18 | -3.42 | 3.22 | -3.46 | 3.21 | -3.43 | -3.39 | -3.32 | -3.33 | 3.13 | -3.19 | 3.40 | 3.41 | 3.35 | 3.25 | -3.17 | 3.23 | -3.14 | 3.24 | 3.43 | 3.39 | -3.14 | -3.33 | 3.53 | -3.16 | 3.48 | 3.47 | 3.46 |
| Fe6 | -3.31 | 3.29 | 3.29 | 3.23 | 3.10 | 3.21 | -3.29 | -3.31 | -3.16 | -3.21 | 3.19 | -3.22 | -3.26 | 3.21 | -3.17 | 3.04 | -3.27 | 3.32 | 3.26 | -3.20 | -3.31 | 3.09 | 3.23 | -3.24 | 3.10 | 2.71 | -3.18 | 3.16 | 3.33 | 3.06 | 3.30 | 3.14 | -3.15 | -3.18 | 3.24 |
| Fe7 | -3.36 | 3.35 | 3.17 | 3.17 | 3.32 | -3.30 | 3.11 | -3.34 | 3.23 | -3.23 | -3.20 | -3.26 | 3.15 | -3.26 | 3.07 | -3.19 | -3.31 | 3.34 | -3.18 | 3.27 | 3.19 | -3.21 | 3.04 | 2.55 | 3.31 | -3.19 | 3.29 | -3.17 | 3.35 | 3.18 | -3.11 | 3.14 | 3.31 | 3.30 | -3.17 |
| S1A | 0.33 | -0.12 | -0.15 | -0.19 | -0.07 | 0.07 | 0.21 | 0.00 | 0.08 | 0.05 | 0.00 | 0.09 | 0.11 | 0.00 | 0.08 | 0.13 | 0.10 | 0.11 | -0.24 | 0.03 | 0.09 | 0.01 | -0.10 | -0.09 | 0.05 | 0.19 | -0.16 | 0.18 | -0.10 | -0.08 | -0.15 | 0.12 | 0.13 | -0.11 | -0.12 |
| S2A | 0.18 | -0.11 | -0.56 | -0.09 | -0.06 | 0.01 | 0.09 | 0.19 | -0.06 | 0.02 | -0.05 | 0.04 | 0.25 | 0.25 | 0.08 | 0.07 | 0.01 | -0.19 | 0.11 | 0.06 | -0.19 | -0.13 | 0.07 | 0.19 | 0.07 | 0.16 | -0.16 | -0.14 | 0.17 | -0.13 | -0.14 | 0.00 | -0.14 | 0.10 | 0.12 |
| S4A | 0.31 | -0.09 | -0.16 | -0.01 | -0.21 | 0.26 | 0.00 | 0.01 | 0.03 | 0.08 | 0.06 | 0.03 | 0.04 | 0.13 | 0.09 | 0.08 | 0.13 | 0.07 | 0.05 | -0.23 | 0.04 | 0.01 | 0.06 | 0.18 | -0.12 | -0.10 | 0.15 | -0.06 | -0.07 | 0.15 | 0.13 | -0.02 | -0.11 | -0.09 | -0.06 |
| S1B | -0.34 | 0.34 | 0.25 | 0.33 | 0.32 | 0.02 | -0.30 | -0.13 | -0.30 | -0.12 | -0.07 | -0.14 | -0.27 | 0.05 | -0.26 | 0.01 | -0.13 | 0.13 | 0.27 | -0.03 | -0.06 | 0.20 | 0.12 | 0.00 | 0.13 | 0.15 | -0.03 | 0.23 | 0.12 | 0.00 | 0.29 | 0.11 | 0.00 | 0.00 | 0.25 |
| S3B | -0.36 | 0.35 | 0.25 | 0.31 | 0.30 | 0.03 | -0.06 | -0.34 | -0.07 | -0.30 | -0.02 | -0.31 | -0.05 | 0.02 | -0.06 | 0.01 | -0.34 | 0.34 | 0.04 | -0.03 | -0.03 | 0.04 | 0.25 | -0.07 | 0.27 | 0.03 | -0.03 | 0.00 | 0.32 | 0.19 | 0.06 | 0.26 | 0.00 | -0.02 | 0.03 |
| S4B | -0.36 | 0.36 | 0.17 | 0.34 | 0.33 | -0.26 | -0.03 | -0.14 | -0.06 | -0.15 | -0.32 | -0.13 | 0.01 | -0.23 | 0.00 | -0.24 | -0.14 | 0.15 | -0.01 | 0.25 | 0.23 | -0.04 | 0.13 | 0.11 | 0.13 | 0.01 | 0.24 | -0.03 | 0.13 | 0.01 | 0.03 | 0.12 | 0.25 | 0.23 | 0.01 |
| S2B | -0.05 | 0.06 | 0.03 | 0.09 | 0.38 | 0.00 | -0.08 | -0.10 | -0.49 | -0.50 | 0.27 | -0.14 | -0.07 | 0.29 | -0.03 | 0.36 | -0.11 | 0.05 | 0.01 | -0.08 | -0.53 | 0.03 | 0.11 | -0.46 | 0.29 | 0.35 | -0.52 | 0.38 | 0.46 | 0.11 | 0.07 | 0.42 | -0.07 | -0.06 | 0.43 |
| S5A | 0.02 | -0.02 | -0.10 | 0.34 | 0.04 | -0.11 | -0.10 | -0.04 | 0.25 | -0.10 | -0.45 | -0.48 | 0.19 | 0.01 | 0.31 | 0.06 | -0.02 | -0.03 | -0.01 | -0.07 | -0.12 | -0.42 | 0.24 | 0.25 | 0.08 | -0.40 | 0.42 | -0.37 | 0.45 | 0.39 | 0.04 | -0.05 | 0.03 | 0.38 | 0.04 |
| C* | -0.02 | 0.02 | -0.18 | -0.23 | -0.21 | 0.00 | -0.05 | -0.05 | 0.03 | 0.01 | 0.03 | -0.01 | -0.06 | -0.05 | -0.30 | -0.27 | -0.33 | 0.01 | -0.04 | -0.04 | -0.03 | -0.01 | 0.05 | -0.03 | 0.03 | -0.06 | -0.16 | -0.27 | -0.23 | -0.31 | -0.13 | -0.26 | -0.20 | -0.25 | -0.25 |
| C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| O3 | 0.05 | -0.06 | 0.10 | -0.03 | -0.03 | 0.06 | 0.00 | -0.08 | 0.06 | 0.07 | 0.04 | 0.06 | -0.10 | -0.10 | 0.07 | 0.06 | 0.07 | 0.05 | -0.09 | -0.08 | 0.07 | 0.06 | -0.07 | -0.08 | -0.07 | -0.08 | 0.11 | 0.11 | -0.07 | 0.08 | 0.10 | 0.08 | 0.10 | -0.04 | -0.04 |
| O1 | -0.06 | 0.05 | 0.06 | 0.07 | 0.07 | -0.06 | -0.06 | 0.04 | -0.06 | 0.05 | -0.06 | 0.05 | -0.07 | -0.07 | -0.03 | -0.05 | 0.06 | -0.04 | 0.05 | 0.05 | 0.06 | 0.05 | -0.05 | 0.03 | -0.05 | 0.03 | 0.07 | 0.07 | -0.05 | -0.06 | 0.08 | -0.03 | 0.08 | 0.07 | 0.07 |
| O2 | 0.00 | 0.00 | 0.04 | 0.01 | 0.01 | 0.00 | -0.02 | 0.00 | 0.00 | 0.03 | -0.01 | 0.03 | -0.04 | -0.04 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.03 | 0.02 | -0.03 | -0.01 | -0.03 | -0.01 | 0.04 | 0.04 | -0.03 | 0.00 | 0.04 | 0.00 | 0.04 | 0.01 | 0.01 |

*Table S 10: Mulliken spin populations of the [**V**-$CO_3$]$^0$ model, $M_S = {}^1/_2$. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.84 | -1.89 | -1.87 | -1.82 | -1.79 | 0.26 | 0.83 | 1.56 | 0.59 | 1.38 | 0.19 | 1.43 | 0.61 | 0.06 | 0.68 | 0.30 | 1.41 | -1.60 | -1.81 | -1.78 | -1.81 | -1.86 | -1.70 | -0.21 | -1.65 | -0.69 | -0.10 | -0.69 | -1.49 | -1.55 | -1.78 | -1.53 | -0.73 | -0.30 | -0.86 |
| Fe1 | -1.31 | 3.44 | -3.63 | -3.55 | -3.55 | 1.56 | 2.27 | 1.73 | 2.47 | 2.61 | 2.69 | 2.69 | 2.07 | 2.12 | -3.50 | -3.50 | -3.48 | 3.38 | 3.33 | 3.26 | 3.43 | 3.42 | 3.25 | 2.88 | 3.21 | 3.02 | -3.59 | -3.58 | -3.45 | -3.38 | -3.58 | -3.36 | -3.55 | -3.46 | -3.46 |
| Fe2 | 3.37 | -3.38 | -3.38 | -3.38 | 3.18 | -3.34 | 2.67 | 3.06 | -3.42 | -3.41 | 2.48 | 2.99 | 3.12 | 2.75 | 2.41 | 2.58 | 1.72 | -3.38 | -3.37 | 3.25 | -3.33 | -3.38 | -3.37 | -3.22 | 3.07 | 2.96 | -3.45 | 3.08 | 3.16 | -3.29 | -3.39 | 3.07 | 3.12 | 3.10 | 3.00 |
| Fe3 | 3.44 | -3.46 | -3.45 | 3.17 | -3.46 | 3.12 | -3.39 | 3.03 | 2.62 | 3.07 | -3.45 | -3.47 | 2.79 | 3.18 | 2.96 | 3.02 | 3.18 | -3.43 | 3.25 | -3.41 | -3.44 | -3.37 | 3.08 | 2.91 | -3.41 | -3.34 | 3.20 | -3.47 | 3.33 | 3.18 | 3.25 | -3.31 | -3.44 | 3.11 | 3.16 |
| Fe4 | 3.51 | -3.51 | 3.43 | -3.40 | -3.39 | 3.32 | 3.22 | -3.53 | 3.31 | 2.24 | 3.28 | 2.30 | -3.42 | -3.43 | 3.25 | 3.22 | 3.12 | 3.29 | -3.58 | -3.54 | 3.21 | 3.18 | -3.52 | -3.47 | -3.48 | -3.46 | 3.35 | 3.39 | -3.42 | 3.28 | 3.43 | 3.32 | 3.26 | -3.42 | -3.41 |
| Fe5 | -3.48 | 3.44 | 3.44 | 3.52 | 3.52 | -3.44 | -3.47 | 3.12 | -3.49 | 3.16 | -3.45 | 3.15 | -3.45 | -3.39 | -3.48 | -3.48 | 3.11 | -3.28 | 3.24 | 3.32 | 3.22 | 3.20 | -3.30 | 3.17 | -3.28 | 3.14 | 3.20 | 3.31 | -3.20 | -3.24 | 3.45 | -3.23 | 3.27 | 3.13 | 3.19 |
| Fe6 | -3.31 | 2.97 | 3.29 | 3.24 | 3.06 | 3.17 | -3.33 | -3.36 | -3.32 | -3.38 | 3.11 | -3.37 | -3.29 | 3.19 | -3.26 | 2.90 | -3.28 | 2.93 | 3.11 | -3.29 | -3.31 | 3.03 | 3.09 | -3.28 | 2.93 | 2.82 | -3.24 | 2.92 | 2.85 | 2.98 | 3.18 | 2.96 | -3.19 | -3.25 | 2.92 |
| Fe7 | -3.36 | 3.00 | 3.34 | 3.10 | 3.33 | -3.33 | 3.10 | -3.40 | 3.05 | -3.40 | -3.33 | -3.45 | 3.13 | -3.29 | 2.94 | -3.29 | -3.38 | 2.98 | -3.36 | 3.16 | 3.06 | -3.32 | 2.96 | 2.66 | 3.14 | -3.28 | 2.75 | -3.18 | 3.09 | 3.00 | -3.27 | 3.09 | 3.06 | 2.82 | -3.19 |
| S1A | 0.39 | -0.14 | -0.19 | -0.54 | -0.08 | 0.02 | -0.02 | -0.04 | 0.06 | -0.03 | 0.01 | 0.00 | 0.03 | -0.01 | 0.00 | 0.05 | -0.09 | 0.04 | -0.24 | 0.04 | 0.02 | 0.03 | -0.21 | -0.13 | 0.01 | 0.03 | -0.23 | 0.07 | -0.16 | -0.12 | -0.21 | 0.10 | 0.06 | -0.13 | -0.12 |
| S2A | 0.39 | -0.12 | -0.55 | -0.15 | -0.16 | -0.08 | -0.11 | -0.05 | -0.09 | 0.02 | -0.09 | 0.00 | -0.04 | -0.04 | -0.05 | 0.01 | -0.05 | -0.22 | 0.12 | 0.07 | -0.19 | -0.17 | 0.05 | -0.04 | 0.05 | -0.02 | -0.23 | -0.27 | 0.09 | -0.12 | -0.18 | -0.13 | -0.21 | 0.03 | 0.02 |
| S4A | 0.39 | -0.15 | -0.19 | -0.04 | -0.50 | 0.12 | 0.00 | -0.03 | 0.02 | -0.01 | 0.04 | -0.02 | 0.00 | 0.04 | 0.10 | 0.07 | 0.08 | 0.00 | 0.06 | -0.23 | 0.03 | 0.01 | 0.03 | 0.03 | -0.21 | -0.17 | 0.08 | -0.19 | -0.10 | 0.10 | 0.11 | -0.10 | -0.18 | -0.09 | -0.09 |
| S1B | -0.34 | 0.32 | 0.34 | 0.33 | 0.31 | 0.02 | -0.30 | -0.14 | -0.29 | -0.13 | 0.02 | -0.14 | -0.29 | 0.04 | -0.28 | 0.00 | -0.12 | 0.12 | 0.27 | 0.04 | 0.04 | 0.23 | 0.14 | -0.02 | 0.12 | 0.15 | -0.05 | 0.20 | 0.12 | 0.12 | 0.31 | 0.12 | 0.00 | -0.01 | 0.16 |
| S3B | -0.36 | 0.23 | 0.34 | 0.30 | 0.30 | 0.02 | -0.06 | -0.36 | -0.07 | -0.34 | 0.01 | -0.36 | -0.06 | 0.02 | -0.06 | 0.00 | -0.34 | 0.13 | 0.02 | 0.00 | 0.03 | 0.07 | 0.23 | -0.08 | 0.23 | 0.00 | -0.09 | 0.01 | 0.13 | 0.19 | 0.05 | 0.19 | 0.00 | -0.04 | 0.05 |
| S4B | -0.36 | 0.35 | 0.36 | 0.34 | 0.34 | -0.27 | -0.02 | -0.15 | 0.00 | -0.14 | -0.26 | -0.15 | 0.00 | -0.24 | -0.03 | -0.26 | -0.15 | 0.13 | 0.01 | 0.29 | 0.26 | 0.03 | 0.13 | 0.11 | 0.14 | 0.00 | 0.13 | -0.01 | 0.14 | 0.13 | 0.05 | 0.13 | 0.19 | 0.11 | 0.01 |
| S2B | -0.04 | -0.12 | 0.04 | 0.04 | 0.34 | -0.05 | -0.16 | -0.10 | -0.53 | -0.54 | 0.21 | -0.14 | -0.09 | 0.31 | -0.17 | 0.25 | -0.16 | -0.09 | -0.03 | -0.20 | -0.52 | -0.02 | -0.03 | -0.49 | 0.24 | 0.23 | -0.56 | 0.38 | 0.29 | 0.04 | -0.05 | 0.30 | -0.04 | -0.06 | 0.29 |
| S5A | 0.06 | -0.20 | -0.05 | 0.27 | -0.03 | -0.02 | -0.15 | -0.05 | 0.18 | -0.08 | -0.49 | -0.52 | 0.23 | -0.02 | 0.26 | -0.09 | -0.05 | -0.16 | -0.16 | -0.10 | -0.12 | -0.48 | 0.20 | 0.12 | -0.10 | -0.44 | 0.31 | -0.51 | 0.40 | 0.30 | -0.07 | -0.01 | -0.16 | 0.21 | 0.03 |
| C* | -0.03 | -0.14 | -0.16 | -0.19 | -0.20 | -0.04 | -0.03 | -0.13 | -0.03 | -0.03 | -0.03 | -0.07 | -0.07 | -0.05 | -0.36 | -0.42 | -0.28 | -0.15 | -0.10 | -0.10 | -0.05 | -0.06 | -0.09 | -0.03 | -0.08 | -0.06 | -0.27 | -0.29 | -0.33 | -0.37 | -0.16 | -0.37 | -0.32 | -0.40 | -0.39 |
| C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | -0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| O3 | 0.06 | -0.08 | 0.10 | -0.05 | -0.04 | 0.05 | 0.02 | -0.08 | 0.03 | 0.00 | 0.03 | 0.02 | -0.08 | -0.09 | 0.05 | 0.05 | 0.07 | 0.06 | -0.09 | -0.09 | 0.06 | 0.05 | -0.11 | -0.08 | -0.11 | -0.09 | 0.09 | 0.10 | -0.08 | 0.04 | 0.09 | 0.05 | 0.08 | -0.06 | -0.06 |
| O1 | -0.05 | 0.04 | 0.07 | 0.07 | 0.07 | -0.06 | -0.06 | 0.03 | -0.06 | 0.04 | -0.06 | 0.05 | -0.07 | -0.07 | -0.07 | -0.06 | 0.05 | -0.05 | 0.04 | 0.05 | 0.06 | 0.05 | -0.06 | 0.02 | -0.06 | 0.02 | 0.04 | 0.05 | -0.05 | -0.05 | 0.07 | -0.04 | 0.06 | 0.02 | 0.03 |
| O2 | 0.00 | 0.00 | 0.04 | 0.01 | 0.01 | -0.01 | -0.01 | 0.00 | -0.01 | 0.01 | -0.01 | 0.02 | -0.04 | -0.04 | -0.01 | -0.01 | 0.03 | 0.00 | -0.01 | -0.01 | 0.02 | 0.02 | -0.04 | -0.01 | -0.04 | -0.01 | 0.04 | 0.04 | -0.03 | -0.01 | 0.04 | -0.01 | 0.03 | -0.01 | -0.01 |

*Table S 11: Mulliken spin population of the [**V**-$NO_3$]$^-$, $M_S = {}^3/_2$. Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 2.00 | -2.02 | 0.56 | -1.98 | 0.44 | 0.51 | 1.00 | 1.65 | 0.75 | 1.47 | 0.40 | 1.41 | 1.02 | 0.56 | 0.85 | 0.49 | 1.49 | -1.67 | -0.89 | -0.44 | -0.48 | -1.01 | -1.45 | -0.39 | -1.54 | -0.68 | -0.23 | -0.63 | -1.40 | 1.16 | 1.73 | -1.55 | -0.37 | -0.38 | 1.88 |
| Fe1 | 1.03 | 3.47 | -3.39 | -3.34 | -3.48 | 3.22 | 3.34 | 2.10 | 3.29 | 3.27 | 3.32 | 3.35 | 2.40 | 2.49 | -3.47 | -3.47 | -3.49 | 3.47 | 3.36 | 3.33 | 3.46 | 3.42 | 3.35 | 3.33 | 3.32 | 3.32 | -3.32 | -3.33 | -3.41 | -3.34 | -3.38 | -3.34 | -3.35 | -3.44 | -3.42 |
| Fe2 | 3.26 | -3.11 | -3.32 | -2.41 | 3.28 | -3.34 | 2.40 | 3.18 | -3.35 | -3.36 | 2.51 | 2.77 | 3.22 | 2.97 | 3.20 | 3.07 | 3.22 | -3.18 | -3.29 | 3.30 | -3.25 | -3.28 | -3.33 | -3.21 | 3.30 | 3.29 | -3.23 | 3.36 | 3.21 | -3.32 | -3.24 | 3.28 | 3.36 | 3.31 | 2.91 |
| Fe3 | 3.33 | -3.20 | -3.39 | 3.36 | -3.35 | 2.53 | -3.37 | 3.04 | 2.53 | 2.74 | -3.33 | -3.38 | 3.01 | 3.22 | 3.20 | 3.29 | 3.27 | -3.21 | 3.33 | -3.35 | -3.36 | -3.25 | 3.31 | 3.26 | -3.40 | -3.32 | 3.36 | -3.25 | 3.35 | 3.21 | 3.30 | -3.30 | -3.29 | 3.37 | 3.13 |
| Fe4 | 3.13 | -3.06 | 3.34 | -3.12 | -3.17 | 3.09 | 3.01 | -3.28 | 3.18 | 3.18 | 3.17 | 3.19 | -3.26 | -3.24 | 3.07 | 3.07 | 3.19 | 3.24 | -3.21 | -3.21 | 3.28 | 3.27 | -3.23 | -3.33 | -3.25 | -3.29 | 3.38 | 3.37 | -3.20 | 3.23 | 3.21 | 3.37 | 3.39 | -3.14 | -3.24 |
| Fe5 | -3.13 | 3.16 | 3.15 | 3.24 | 3.03 | -3.10 | -3.15 | 3.05 | -3.21 | 3.05 | -3.18 | 3.05 | -3.24 | -3.21 | -3.14 | -3.10 | 3.09 | -3.03 | 3.07 | 3.02 | 3.19 | 3.20 | -3.05 | 3.11 | -3.04 | 3.16 | 3.22 | 3.32 | -2.98 | -3.16 | 2.69 | -2.79 | 3.31 | 3.19 | 2.65 |
| Fe6 | -3.23 | 3.22 | 3.32 | 3.30 | 3.22 | 3.19 | -3.25 | -3.16 | -3.22 | -3.21 | 3.11 | -3.23 | -3.30 | 3.14 | -3.21 | 3.19 | -3.27 | 3.15 | 3.22 | -3.20 | -3.22 | 3.29 | 3.17 | -3.19 | 3.15 | 3.21 | -3.15 | 3.30 | 3.12 | 3.04 | 3.04 | 3.21 | -3.12 | -3.17 | 3.23 |
| Fe7 | -3.33 | 3.36 | 3.20 | 3.34 | 3.18 | -3.28 | 3.14 | -3.24 | 3.06 | -3.29 | -3.23 | -3.30 | 3.06 | -3.32 | 3.12 | -3.23 | -3.31 | 3.21 | -3.17 | 3.25 | 3.32 | -3.09 | 3.11 | 3.20 | 3.24 | -3.15 | 3.32 | -3.10 | 3.29 | 2.81 | -3.31 | 3.23 | 3.34 | 3.32 | -3.34 |
| S1A | 0.25 | -0.01 | -0.05 | -0.23 | -0.04 | 0.04 | 0.19 | -0.03 | 0.08 | 0.05 | 0.18 | 0.28 | 0.08 | 0.03 | 0.02 | 0.00 | 0.03 | 0.17 | -0.12 | 0.13 | 0.16 | 0.13 | -0.17 | -0.14 | 0.14 | 0.09 | -0.06 | 0.20 | -0.13 | -0.13 | -0.18 | 0.13 | 0.17 | -0.09 | -0.18 |
| S2A | 0.26 | -0.01 | -0.49 | -0.07 | -0.15 | 0.04 | 0.01 | 0.08 | 0.07 | 0.09 | 0.08 | 0.12 | 0.10 | 0.11 | 0.01 | 0.02 | 0.02 | -0.03 | 0.16 | 0.11 | -0.10 | -0.08 | 0.09 | 0.14 | 0.10 | 0.13 | -0.09 | -0.08 | 0.11 | -0.15 | -0.11 | -0.15 | -0.12 | 0.12 | 0.05 |
| S4A | 0.26 | -0.04 | -0.04 | -0.07 | -0.43 | 0.21 | 0.02 | -0.07 | 0.24 | 0.26 | 0.08 | 0.05 | 0.00 | 0.08 | 0.04 | 0.06 | 0.06 | 0.16 | 0.14 | -0.14 | 0.10 | 0.13 | 0.13 | 0.07 | -0.16 | -0.16 | 0.19 | -0.07 | -0.12 | 0.12 | 0.13 | -0.07 | -0.12 | -0.10 | -0.11 |
| S1B | -0.23 | 0.22 | 0.22 | 0.25 | 0.20 | 0.03 | -0.23 | -0.09 | -0.22 | -0.08 | 0.01 | -0.10 | -0.27 | 0.00 | -0.23 | 0.02 | -0.08 | 0.08 | 0.21 | -0.04 | -0.02 | 0.27 | 0.10 | -0.03 | 0.07 | 0.21 | -0.03 | 0.26 | 0.08 | 0.02 | 0.05 | 0.15 | 0.00 | -0.02 | 0.09 |
| S3B | -0.34 | 0.34 | 0.26 | 0.32 | 0.24 | 0.01 | -0.05 | -0.29 | -0.04 | -0.29 | 0.02 | -0.30 | -0.08 | 0.00 | -0.05 | 0.00 | -0.32 | 0.27 | 0.04 | -0.02 | -0.01 | 0.07 | 0.27 | -0.04 | 0.27 | 0.03 | 0.01 | 0.07 | 0.28 | 0.16 | 0.03 | 0.31 | 0.01 | -0.01 | -0.01 |
| S4B | -0.28 | 0.27 | 0.15 | 0.29 | 0.14 | -0.22 | 0.00 | -0.10 | -0.01 | -0.13 | -0.21 | -0.09 | -0.03 | -0.26 | 0.00 | -0.22 | -0.11 | 0.10 | -0.02 | 0.21 | 0.25 | 0.03 | 0.09 | 0.20 | 0.12 | -0.01 | 0.22 | 0.01 | 0.09 | -0.07 | -0.16 | 0.17 | 0.24 | 0.22 | -0.19 |
| S2B | -0.04 | 0.07 | 0.06 | 0.18 | 0.42 | 0.00 | -0.20 | -0.04 | -0.47 | -0.49 | 0.21 | -0.17 | -0.08 | 0.34 | -0.08 | 0.42 | -0.08 | 0.03 | 0.03 | -0.07 | -0.46 | 0.04 | -0.02 | -0.44 | 0.43 | 0.44 | -0.44 | 0.47 | 0.41 | 0.00 | -0.02 | 0.43 | 0.00 | -0.05 | 0.39 |
| S5A | 0.01 | 0.04 | -0.04 | 0.45 | -0.03 | -0.13 | -0.08 | -0.03 | 0.14 | -0.14 | -0.42 | -0.46 | 0.26 | -0.03 | 0.38 | 0.00 | -0.01 | -0.01 | 0.01 | -0.04 | -0.02 | -0.35 | 0.35 | 0.39 | -0.07 | -0.40 | 0.42 | -0.37 | 0.43 | 0.28 | -0.03 | -0.04 | 0.02 | 0.43 | -0.06 |
| C* | -0.02 | 0.02 | -0.09 | -0.21 | -0.21 | 0.00 | -0.01 | -0.06 | -0.01 | 0.02 | -0.02 | -0.04 | -0.13 | -0.10 | -0.26 | -0.24 | -0.17 | 0.03 | -0.01 | -0.03 | 0.08 | 0.11 | -0.13 | -0.03 | -0.09 | -0.04 | -0.10 | -0.10 | -0.24 | -0.36 | -0.22 | -0.21 | -0.04 | -0.18 | -0.35 |
| N | 0.07 | -0.02 | -0.17 | -0.09 | -0.05 | 0.03 | 0.04 | 0.19 | 0.03 | -0.19 | 0.07 | -0.23 | 0.18 | 0.18 | -0.10 | -0.06 | -0.19 | -0.03 | -0.06 | -0.01 | -0.13 | -0.11 | 0.13 | -0.07 | 0.14 | -0.03 | -0.21 | -0.21 | 0.21 | -0.17 | -0.20 | 0.20 | -0.18 | -0.10 | -0.10 |
| O3 | 0.02 | -0.04 | 0.01 | -0.01 | -0.01 | 0.02 | 0.00 | -0.02 | 0.00 | 0.02 | 0.00 | 0.02 | -0.02 | -0.03 | 0.02 | 0.02 | 0.06 | -0.01 | -0.03 | -0.03 | 0.00 | 0.00 | -0.01 | -0.02 | -0.04 | -0.03 | 0.00 | 0.04 | -0.02 | 0.03 | 0.02 | 0.06 | 0.02 | -0.02 | -0.03 |
| O1 | -0.01 | 0.02 | 0.03 | 0.01 | 0.01 | -0.01 | -0.01 | 0.04 | 0.00 | -0.02 | 0.01 | 0.00 | -0.02 | -0.01 | -0.02 | -0.02 | -0.03 | 0.01 | 0.01 | 0.02 | 0.01 | 0.02 | 0.00 | -0.01 | 0.02 | 0.01 | 0.03 | 0.01 | 0.01 | -0.05 | -0.01 | 0.00 | 0.02 | 0.00 | -0.01 |
| O2 | 0.03 | -0.01 | -0.08 | -0.05 | -0.03 | 0.01 | 0.02 | 0.09 | 0.02 | -0.08 | 0.04 | -0.10 | 0.08 | 0.07 | -0.06 | -0.04 | -0.09 | -0.01 | -0.03 | 0.00 | -0.05 | -0.03 | 0.05 | -0.03 | 0.06 | -0.01 | -0.10 | -0.10 | 0.09 | -0.09 | -0.09 | 0.09 | -0.08 | -0.05 | -0.05 |

*Table S 12: Mulliken spin population of the [**V**-NO$_3$]$^-$, $M_S$ = $^1/_2$ Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 2.00 | -2.04 | -2.03 | -1.99 | -1.95 | 0.32 | 1.00 | 1.65 | 0.80 | 1.46 | 0.57 | 1.44 | 1.14 | 0.67 | 0.76 | 0.37 | 1.23 | -1.62 | -1.28 | -0.49 | -0.64 | -1.21 | -1.63 | -0.60 | -1.57 | -0.84 | -0.45 | -0.84 | -1.63 | -1.51 | -1.27 | -1.44 | -0.78 | -0.47 | -0.90 |
| Fe1 | 0.95 | 3.45 | -3.41 | -3.51 | -3.51 | 2.26 | 3.46 | -0.61 | 3.42 | 2.28 | 3.47 | 3.41 | 3.28 | 3.35 | -3.50 | -3.49 | -3.49 | 3.40 | 3.30 | 1.82 | 3.43 | 3.43 | 3.31 | 3.33 | 3.24 | 3.26 | -3.39 | -3.37 | -3.47 | -3.34 | -3.41 | -3.38 | -3.41 | -3.44 | -3.43 |
| Fe2 | 3.07 | -3.23 | -3.34 | -3.36 | 3.31 | -3.36 | -0.46 | 3.21 | -3.26 | -3.34 | -3.10 | 0.99 | 3.29 | -0.84 | 2.90 | 2.51 | 2.88 | -3.40 | -3.37 | 3.25 | -3.28 | -3.33 | -3.34 | -3.28 | 2.88 | 2.85 | -3.29 | 3.03 | 2.97 | -3.33 | -3.29 | 3.13 | 3.10 | 3.07 | 2.87 |
| Fe3 | 3.12 | -3.35 | -3.35 | 3.34 | -3.38 | 3.13 | -3.25 | 3.19 | -0.13 | 2.89 | -2.64 | -3.36 | -0.81 | 3.33 | 2.92 | 3.10 | 3.00 | -3.47 | 3.31 | -3.34 | -3.35 | -3.32 | 3.00 | 3.05 | -3.41 | -3.31 | 3.11 | -3.32 | 3.13 | 3.22 | 3.23 | -3.35 | -3.34 | 2.99 | 3.12 |
| Fe4 | 3.17 | -3.27 | 3.32 | -3.20 | -3.14 | 3.01 | 3.07 | -3.16 | 3.20 | 3.08 | 3.40 | 3.13 | -3.28 | -3.22 | 2.95 | 2.91 | 2.90 | 3.13 | -3.50 | -3.21 | 3.27 | 3.26 | -3.32 | -3.42 | -3.28 | -3.35 | 3.27 | 3.20 | -3.27 | 3.25 | 3.25 | 3.13 | 3.16 | -3.27 | -3.19 |
| Fe5 | -3.38 | 3.15 | 3.26 | 3.21 | 3.21 | -3.40 | -3.13 | 3.08 | -3.21 | 2.89 | -2.90 | 3.07 | -3.27 | -3.25 | -3.34 | -3.14 | 2.91 | -3.17 | 2.90 | 3.06 | 1.66 | 2.08 | -3.17 | 3.05 | -3.13 | 3.12 | 3.10 | 3.23 | -3.08 | -3.03 | 3.16 | -3.05 | 3.20 | 3.09 | 3.12 |
| Fe6 | -3.36 | 3.03 | 3.30 | 3.22 | 3.16 | 3.10 | -3.22 | -3.17 | -3.25 | -3.28 | 3.24 | -3.29 | -3.27 | 3.15 | -3.21 | 2.78 | -3.26 | 3.09 | 3.06 | -3.20 | -3.21 | 3.20 | 2.95 | -3.22 | 2.53 | 2.88 | -3.20 | 3.01 | 2.98 | 2.99 | 3.06 | 3.08 | -3.16 | -3.25 | 3.11 |
| Fe7 | -3.42 | 3.05 | 3.36 | 3.28 | 3.24 | -3.33 | 3.19 | -3.22 | 3.12 | -3.39 | -2.38 | -3.29 | 3.09 | -3.29 | 2.92 | -3.26 | -3.33 | 3.09 | -3.15 | 3.26 | 3.26 | -3.16 | 2.53 | 2.68 | 3.10 | -3.18 | 2.99 | -3.15 | 3.07 | 3.01 | -3.13 | 3.14 | 3.15 | 3.13 | -3.21 |
| S1A | 0.26 | -0.06 | -0.09 | -0.48 | -0.05 | -0.03 | 0.28 | -0.01 | 0.12 | 0.00 | 0.17 | 0.14 | 0.16 | 0.10 | -0.02 | -0.02 | 0.01 | 0.07 | -0.23 | 0.00 | 0.16 | 0.11 | -0.17 | -0.17 | 0.05 | 0.02 | -0.17 | 0.10 | -0.21 | -0.13 | -0.18 | 0.09 | 0.07 | -0.14 | -0.18 |
| S2A | 0.17 | -0.06 | -0.48 | -0.17 | -0.17 | 0.03 | 0.05 | 0.12 | 0.09 | 0.02 | 0.01 | 0.07 | 0.19 | 0.21 | 0.00 | -0.01 | -0.01 | -0.19 | 0.13 | 0.01 | -0.12 | -0.12 | 0.04 | 0.09 | 0.03 | 0.04 | -0.17 | -0.19 | 0.04 | -0.15 | -0.13 | -0.15 | -0.14 | 0.04 | 0.04 |
| S4A | 0.26 | -0.06 | -0.05 | -0.05 | -0.45 | 0.23 | 0.07 | 0.03 | 0.25 | 0.11 | 0.22 | 0.07 | 0.03 | 0.13 | 0.02 | 0.01 | 0.04 | 0.04 | 0.06 | -0.27 | 0.09 | 0.14 | 0.05 | 0.05 | -0.16 | -0.16 | 0.10 | -0.14 | -0.16 | 0.12 | 0.12 | -0.17 | -0.17 | -0.18 | -0.11 |
| S1B | -0.31 | 0.24 | 0.29 | 0.24 | 0.25 | -0.02 | -0.21 | -0.09 | -0.22 | -0.14 | 0.02 | -0.11 | -0.25 | -0.01 | -0.26 | 0.00 | -0.09 | 0.08 | 0.21 | -0.04 | 0.00 | 0.12 | 0.09 | 0.01 | 0.05 | 0.17 | -0.02 | 0.23 | 0.07 | 0.08 | 0.20 | 0.07 | 0.02 | -0.03 | 0.19 |
| S3B | -0.34 | 0.25 | 0.33 | 0.32 | 0.30 | 0.00 | -0.03 | -0.28 | -0.04 | -0.32 | 0.07 | -0.31 | -0.09 | -0.02 | -0.06 | -0.03 | -0.32 | 0.25 | 0.07 | -0.02 | 0.02 | 0.10 | 0.16 | -0.04 | 0.18 | 0.04 | -0.05 | 0.02 | 0.25 | 0.23 | 0.07 | 0.25 | 0.00 | -0.05 | 0.01 |
| S4B | -0.34 | 0.27 | 0.31 | 0.28 | 0.27 | -0.26 | -0.01 | -0.10 | -0.02 | -0.16 | -0.06 | -0.09 | -0.02 | -0.25 | -0.02 | -0.20 | -0.12 | 0.09 | -0.01 | 0.22 | 0.14 | 0.03 | 0.09 | 0.11 | 0.12 | -0.01 | 0.19 | 0.01 | 0.07 | 0.08 | 0.04 | 0.10 | 0.22 | 0.18 | 0.00 |
| S2B | -0.18 | -0.05 | 0.05 | 0.01 | 0.45 | 0.01 | -0.20 | 0.00 | -0.47 | -0.50 | 0.04 | -0.23 | -0.06 | 0.30 | -0.13 | 0.24 | -0.15 | -0.03 | -0.09 | -0.03 | -0.45 | 0.03 | -0.03 | -0.47 | 0.18 | 0.22 | -0.48 | 0.37 | 0.36 | 0.02 | 0.01 | 0.40 | -0.08 | -0.09 | 0.36 |
| S5A | -0.11 | -0.14 | 0.01 | 0.43 | -0.03 | -0.09 | -0.01 | 0.04 | 0.18 | -0.13 | -0.14 | -0.45 | 0.26 | 0.00 | 0.26 | -0.04 | -0.12 | -0.10 | 0.05 | -0.03 | -0.02 | -0.38 | 0.17 | 0.14 | -0.08 | -0.41 | 0.31 | -0.40 | 0.35 | 0.34 | 0.01 | -0.01 | -0.04 | 0.33 | -0.02 |
| C* | -0.21 | -0.17 | -0.07 | -0.21 | -0.23 | -0.12 | 0.18 | -0.03 | 0.14 | -0.07 | 0.37 | 0.00 | 0.11 | 0.14 | -0.42 | -0.34 | -0.39 | -0.07 | -0.15 | 0.01 | 0.10 | 0.05 | -0.17 | -0.08 | -0.14 | -0.12 | -0.27 | -0.26 | -0.44 | -0.31 | -0.23 | -0.30 | -0.27 | -0.37 | -0.35 |
| N | -0.18 | -0.18 | -0.17 | -0.10 | -0.06 | -0.28 | 0.00 | 0.18 | 0.07 | -0.26 | 0.23 | -0.27 | 0.24 | 0.22 | -0.28 | -0.08 | -0.30 | -0.25 | -0.29 | -0.06 | -0.21 | -0.20 | 0.16 | -0.25 | 0.16 | -0.25 | -0.27 | -0.24 | 0.12 | -0.21 | -0.25 | -0.21 | -0.25 | -0.18 | -0.12 |
| O3 | 0.02 | -0.07 | 0.00 | -0.02 | -0.01 | 0.01 | 0.01 | -0.03 | 0.01 | 0.00 | 0.07 | 0.03 | -0.02 | -0.06 | 0.03 | 0.02 | 0.02 | 0.03 | -0.10 | -0.03 | -0.01 | -0.01 | -0.03 | -0.09 | -0.04 | -0.08 | 0.05 | 0.05 | 0.00 | 0.03 | 0.02 | 0.04 | 0.06 | -0.05 | -0.03 |
| O1 | -0.06 | 0.02 | 0.04 | 0.01 | 0.01 | -0.08 | -0.02 | 0.04 | 0.00 | 0.02 | -0.02 | -0.01 | -0.02 | 0.01 | -0.08 | -0.03 | 0.02 | -0.07 | 0.01 | 0.01 | 0.05 | 0.03 | 0.01 | 0.03 | 0.02 | 0.02 | 0.01 | 0.00 | 0.00 | -0.05 | 0.02 | -0.06 | -0.01 | 0.01 | 0.01 |
| O2 | -0.10 | -0.09 | -0.08 | -0.06 | -0.03 | -0.14 | 0.00 | 0.10 | 0.04 | -0.13 | 0.12 | -0.13 | 0.12 | 0.11 | -0.15 | -0.04 | -0.15 | -0.13 | -0.15 | -0.03 | -0.11 | -0.10 | 0.06 | -0.13 | 0.07 | -0.12 | -0.14 | -0.12 | 0.04 | -0.11 | -0.12 | -0.12 | -0.13 | -0.09 | -0.06 |

*Table S 13: Mulliken spin population of the [**V**-NO$_3$]$^0$, $M_S$ = 0, Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.97 | -2.04 | -2.06 | -1.97 | -2.01 | 0.35 | 0.83 | 1.60 | 1.01 | 1.64 | 0.54 | 1.57 | 1.13 | 0.58 | 0.68 | 0.35 | 1.68 | -1.60 | -1.24 | -0.70 | -0.33 | -1.25 | -1.67 | -0.40 | -1.64 | -0.76 | -0.55 | -1.02 | -1.55 | -1.55 | -1.15 | -1.53 | -0.72 | -0.54 | -1.01 |
| Fe1 | -1.41 | 3.48 | -3.59 | -3.54 | -3.55 | 0.33 | 0.35 | -2.64 | 3.45 | -2.68 | 3.45 | 3.43 | 3.28 | 3.32 | -3.50 | -3.50 | -3.49 | 2.64 | 2.61 | 2.41 | 3.41 | 2.35 | 3.29 | 3.45 | 3.25 | 3.48 | -3.61 | -3.34 | -3.43 | -3.35 | -3.43 | -3.37 | -3.43 | -3.45 | -3.45 |
| Fe2 | 3.26 | -3.19 | -3.42 | -3.40 | 3.17 | -3.41 | 3.14 | 3.41 | -2.40 | -2.74 | -3.01 | -1.73 | 3.29 | -1.06 | 2.84 | 1.91 | 2.48 | -3.41 | -3.40 | 2.80 | -3.38 | -3.43 | -3.36 | -3.14 | 2.93 | -0.31 | -3.45 | 1.45 | 3.15 | -3.33 | -3.34 | 2.99 | 2.89 | 3.01 | 2.40 |
| Fe3 | 3.29 | -3.28 | -3.45 | 3.16 | -3.43 | 3.20 | -3.45 | 3.46 | -3.09 | 3.44 | -2.49 | -3.27 | -1.00 | 3.33 | 1.98 | 3.02 | 2.76 | -3.46 | 2.70 | -3.44 | -3.41 | -3.44 | 2.96 | -0.25 | -3.40 | -3.20 | 2.78 | -3.32 | 1.97 | 3.11 | 2.89 | -3.36 | -3.39 | 2.49 | 3.09 |
| Fe4 | 3.31 | -3.35 | 3.37 | -3.44 | -3.40 | 3.29 | 3.27 | -3.12 | 3.45 | 3.48 | 3.46 | 3.40 | -3.43 | -3.38 | 3.14 | 3.13 | 2.97 | 3.12 | -3.59 | -3.57 | 3.28 | 3.16 | -3.53 | -3.41 | -3.49 | -3.38 | 2.96 | 3.32 | -3.41 | 3.27 | 2.81 | 3.30 | 2.75 | -3.46 | -3.45 |
| Fe5 | -3.48 | 3.32 | 3.41 | 3.31 | 3.38 | -3.45 | -3.46 | 3.25 | -3.20 | 3.27 | -3.13 | 3.24 | -3.39 | -3.33 | -3.50 | -3.48 | 2.10 | -3.25 | 3.22 | 3.24 | 1.31 | 3.30 | -3.33 | 3.32 | -3.32 | 3.38 | 3.29 | 3.37 | -3.25 | -3.25 | 3.13 | -3.24 | 3.10 | 3.13 | 3.20 |
| Fe6 | -3.31 | 3.12 | 3.08 | 3.05 | 2.87 | 3.16 | -3.30 | -3.11 | -2.87 | -3.10 | 3.25 | -3.15 | -3.24 | 3.19 | -3.29 | 2.74 | -3.39 | 3.11 | 3.12 | -3.21 | -3.32 | 3.00 | 2.88 | -3.22 | 2.42 | 3.13 | -3.20 | 3.10 | 3.13 | 2.90 | 2.96 | 2.38 | -3.22 | -3.25 | 2.87 |
| Fe7 | -3.38 | 1.22 | 3.17 | 3.06 | 3.14 | -3.33 | 3.12 | -3.12 | 3.20 | -3.18 | -2.88 | -3.22 | 3.10 | -3.25 | 2.73 | -3.32 | -3.44 | 3.12 | -3.14 | 3.11 | 2.85 | -3.16 | 2.46 | 3.14 | 2.99 | -3.16 | 3.01 | -3.20 | 3.19 | 2.36 | -3.18 | 3.05 | 2.99 | 2.88 | -3.20 |
| S1A | 0.32 | -0.08 | -0.19 | -0.56 | -0.10 | -0.08 | 0.26 | 0.14 | 0.21 | 0.11 | 0.15 | 0.19 | 0.08 | 0.04 | 0.01 | 0.02 | 0.00 | -0.14 | -0.39 | -0.13 | 0.07 | -0.13 | -0.19 | -0.08 | 0.03 | 0.06 | -0.35 | 0.00 | -0.15 | -0.13 | -0.28 | 0.10 | -0.02 | -0.15 | -0.21 |
| S2A | 0.36 | -0.03 | -0.56 | -0.16 | -0.18 | -0.04 | -0.06 | 0.35 | 0.03 | 0.06 | 0.04 | 0.01 | 0.19 | 0.20 | -0.01 | 0.00 | -0.01 | -0.35 | -0.05 | -0.07 | -0.16 | -0.33 | 0.05 | 0.13 | 0.03 | 0.15 | -0.30 | -0.21 | -0.01 | -0.16 | -0.14 | -0.19 | -0.16 | -0.04 | -0.03 |
| S4A | 0.29 | -0.06 | -0.20 | -0.08 | -0.50 | 0.30 | -0.07 | 0.11 | 0.11 | 0.31 | 0.19 | 0.12 | 0.04 | 0.12 | 0.05 | 0.04 | 0.05 | -0.11 | -0.06 | -0.36 | 0.06 | -0.10 | 0.04 | 0.05 | -0.18 | -0.09 | -0.05 | -0.15 | -0.16 | 0.10 | -0.02 | -0.12 | -0.26 | -0.19 | -0.11 |
| S1B | -0.33 | 0.31 | 0.31 | 0.26 | 0.29 | 0.01 | -0.29 | -0.10 | -0.19 | -0.09 | 0.01 | -0.09 | -0.27 | 0.00 | -0.27 | -0.04 | -0.23 | 0.10 | 0.24 | -0.01 | -0.03 | 0.25 | 0.11 | -0.01 | 0.08 | 0.25 | -0.02 | 0.27 | 0.08 | 0.10 | 0.19 | 0.06 | -0.03 | -0.01 | 0.19 |
| S3B | -0.34 | 0.19 | 0.25 | 0.29 | 0.26 | 0.01 | -0.04 | -0.25 | -0.02 | -0.27 | 0.05 | -0.29 | -0.08 | -0.01 | -0.08 | -0.03 | -0.36 | 0.25 | 0.07 | -0.02 | -0.04 | 0.09 | 0.15 | -0.03 | 0.16 | 0.04 | -0.06 | 0.05 | 0.28 | 0.13 | 0.05 | 0.14 | -0.01 | -0.05 | 0.02 |
| S4B | -0.35 | 0.18 | 0.34 | 0.31 | 0.30 | -0.27 | -0.02 | -0.10 | -0.02 | -0.13 | -0.16 | -0.09 | -0.04 | -0.24 | -0.05 | -0.25 | -0.25 | 0.10 | 0.03 | 0.23 | 0.05 | 0.04 | 0.09 | 0.23 | 0.12 | 0.01 | 0.23 | 0.02 | 0.11 | 0.09 | -0.01 | 0.12 | 0.18 | 0.16 | 0.02 |
| S2B | -0.12 | 0.04 | -0.06 | -0.08 | 0.33 | 0.02 | -0.13 | 0.05 | -0.24 | -0.27 | 0.08 | -0.29 | -0.04 | 0.30 | -0.19 | 0.19 | -0.15 | -0.05 | -0.06 | -0.10 | -0.51 | -0.10 | -0.04 | -0.44 | 0.17 | 0.32 | -0.52 | 0.24 | 0.43 | 0.02 | 0.02 | 0.25 | -0.10 | -0.08 | 0.24 |
| S5A | -0.05 | -0.18 | -0.12 | 0.28 | -0.10 | -0.07 | -0.07 | 0.12 | -0.01 | 0.08 | -0.17 | -0.42 | 0.27 | 0.02 | 0.16 | -0.12 | -0.10 | -0.12 | -0.05 | -0.15 | -0.15 | -0.42 | 0.15 | 0.27 | -0.09 | -0.37 | 0.30 | -0.38 | 0.24 | 0.23 | -0.03 | -0.03 | -0.06 | 0.17 | 0.01 |
| C* | -0.13 | 0.03 | -0.23 | -0.25 | -0.24 | -0.08 | -0.09 | 0.07 | 0.37 | 0.06 | 0.39 | 0.27 | 0.11 | 0.16 | -0.35 | -0.37 | -0.39 | -0.07 | -0.06 | -0.09 | -0.03 | -0.05 | -0.14 | 0.13 | -0.13 | 0.15 | -0.31 | -0.17 | -0.29 | -0.36 | -0.38 | -0.35 | -0.40 | -0.39 | -0.37 |
| N | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O3 | 0.03 | -0.05 | 0.08 | -0.05 | -0.05 | 0.04 | 0.03 | -0.03 | 0.05 | 0.08 | 0.05 | 0.06 | -0.07 | -0.08 | 0.03 | 0.03 | 0.04 | 0.03 | -0.07 | -0.07 | 0.05 | 0.05 | -0.09 | -0.06 | -0.08 | -0.05 | 0.04 | 0.06 | -0.06 | 0.05 | 0.02 | 0.05 | 0.02 | -0.05 | -0.05 |
| O1 | -0.05 | 0.04 | 0.06 | 0.04 | 0.04 | -0.05 | -0.05 | 0.03 | -0.03 | 0.05 | -0.03 | 0.04 | -0.05 | -0.06 | -0.06 | -0.05 | 0.01 | -0.03 | 0.03 | 0.03 | 0.02 | 0.05 | -0.05 | 0.04 | -0.04 | 0.05 | 0.05 | 0.06 | -0.04 | -0.03 | 0.05 | -0.03 | 0.05 | 0.03 | 0.03 |
| O2 | -0.01 | 0.00 | 0.03 | 0.00 | 0.00 | -0.01 | -0.01 | 0.00 | 0.00 | 0.03 | 0.00 | 0.03 | -0.03 | -0.03 | -0.01 | -0.01 | 0.01 | 0.00 | -0.01 | -0.01 | 0.02 | 0.02 | -0.03 | 0.00 | -0.03 | 0.00 | 0.03 | 0.03 | -0.03 | 0.00 | 0.02 | 0.00 | 0.02 | 0.00 | 0.00 |

*Table S 14: Mulliken spin population of the [**V**-NO$_3$]$^0$, $M_S$ = 1, Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.89 | -1.87 | 0.71 | -1.81 | -1.81 | 0.16 | 0.63 | 1.63 | 0.67 | 1.56 | 0.26 | 1.47 | 0.90 | 0.35 | 0.48 | 0.10 | 1.44 | -1.66 | -0.72 | -0.21 | -0.37 | -0.83 | -1.55 | -0.15 | -1.53 | -0.45 | 0.06 | -0.54 | -1.61 | -1.53 | -0.85 | -1.50 | -0.29 | -0.25 | -0.74 |
| Fe1 | 1.37 | 3.45 | -3.59 | -3.54 | -3.55 | 2.65 | 2.69 | 1.96 | 2.61 | 1.30 | 3.43 | 3.37 | 2.16 | 2.30 | -3.49 | -3.50 | -3.47 | 3.47 | 3.29 | 3.18 | 3.44 | 3.44 | 3.32 | 3.21 | 3.25 | 3.22 | -3.39 | -3.33 | -3.47 | -3.32 | -3.42 | -3.34 | -3.40 | -3.46 | -3.45 |
| Fe2 | 3.20 | -3.23 | -3.35 | -3.30 | 3.36 | -3.37 | 3.02 | 3.07 | -3.31 | -3.25 | 0.73 | 2.77 | 3.23 | 2.65 | 3.02 | 2.92 | 2.97 | -3.35 | -3.37 | 3.27 | -3.39 | -3.36 | -3.33 | -3.23 | 3.10 | 2.86 | -3.23 | 3.15 | 3.22 | -3.26 | -3.28 | 3.26 | 3.18 | 3.14 | 3.18 |
| Fe3 | 3.29 | -3.35 | -3.46 | 3.36 | -3.37 | 3.15 | -3.41 | 3.06 | 2.65 | 3.27 | -3.24 | -3.41 | 2.76 | 3.26 | 3.03 | 3.17 | 3.16 | -3.43 | 3.29 | -3.40 | -3.48 | -3.32 | 3.19 | 2.80 | -3.39 | -3.30 | 3.20 | -3.26 | 3.31 | 3.33 | 3.32 | -3.30 | -3.31 | 3.21 | 3.19 |
| Fe4 | 3.03 | -3.23 | 3.32 | -3.15 | -3.13 | 3.05 | 2.96 | -3.23 | 3.20 | 3.13 | 3.32 | 2.01 | -3.27 | -3.27 | 3.03 | 3.05 | 2.95 | 3.27 | -3.39 | -3.36 | 3.20 | 3.11 | -3.27 | -3.33 | -3.22 | -3.29 | 3.29 | 3.31 | -3.23 | 3.28 | 3.30 | 3.33 | 3.32 | -3.22 | -3.19 |
| Fe5 | -3.34 | 3.04 | 3.05 | 3.39 | 3.39 | -3.30 | -3.27 | 3.02 | -3.18 | 3.09 | -3.09 | 3.04 | -3.23 | -3.17 | -3.17 | -3.11 | 2.99 | -3.11 | 2.93 | 2.92 | 3.06 | 3.04 | -3.12 | 3.05 | -3.10 | 3.08 | 2.94 | 3.16 | -3.06 | -3.00 | 3.18 | -2.97 | 3.11 | 3.07 | 3.12 |
| Fe6 | -3.32 | 3.19 | 3.23 | 3.32 | 3.24 | 3.17 | -3.30 | -3.29 | -3.19 | -3.12 | 3.21 | -3.21 | -3.31 | 3.18 | -3.21 | 3.04 | -3.27 | 3.09 | 3.10 | -3.24 | -3.30 | 3.00 | 3.16 | -3.24 | 2.88 | 2.99 | -3.22 | 3.09 | 3.14 | 3.05 | 3.13 | 3.10 | -3.22 | -3.25 | 3.17 |
| Fe7 | -3.39 | 3.29 | 3.13 | 3.29 | 3.42 | -3.33 | 3.15 | -3.35 | 3.07 | -3.28 | -3.17 | -3.30 | 3.11 | -3.32 | 3.00 | -3.24 | -3.34 | 3.06 | -3.22 | 3.13 | 3.15 | -3.17 | 2.88 | 3.05 | 3.23 | -3.19 | 3.11 | -3.19 | 3.22 | 3.11 | -3.18 | 3.13 | 3.17 | 3.19 | -3.21 |
| S1A | 0.21 | -0.09 | -0.14 | -0.42 | -0.05 | 0.03 | 0.07 | -0.04 | 0.09 | 0.03 | 0.17 | 0.10 | 0.02 | 0.00 | 0.02 | 0.03 | 0.03 | 0.14 | -0.22 | 0.02 | 0.10 | 0.07 | -0.18 | -0.12 | 0.06 | 0.03 | -0.13 | 0.17 | -0.16 | -0.05 | -0.13 | 0.14 | 0.12 | -0.13 | -0.13 |
| S2A | 0.21 | -0.10 | -0.54 | -0.16 | -0.18 | 0.02 | -0.01 | 0.07 | -0.06 | 0.00 | 0.06 | 0.13 | -0.01 | -0.02 | 0.03 | 0.03 | 0.01 | -0.15 | 0.12 | 0.06 | -0.18 | -0.13 | 0.07 | 0.02 | 0.07 | 0.02 | -0.17 | -0.17 | 0.10 | -0.11 | -0.12 | -0.14 | -0.15 | 0.07 | 0.08 |
| S4A | 0.23 | -0.08 | -0.15 | -0.04 | -0.43 | 0.18 | 0.00 | -0.03 | 0.03 | 0.16 | 0.14 | 0.02 | -0.01 | 0.02 | 0.06 | 0.06 | 0.08 | 0.11 | 0.04 | -0.20 | 0.07 | 0.07 | 0.05 | 0.03 | -0.18 | -0.15 | 0.15 | -0.06 | -0.12 | 0.15 | 0.13 | -0.06 | -0.10 | -0.13 | -0.11 |
| S1B | -0.31 | 0.23 | 0.20 | 0.30 | 0.28 | 0.02 | -0.25 | -0.11 | -0.22 | -0.08 | 0.05 | -0.11 | -0.28 | 0.02 | -0.21 | 0.04 | -0.11 | 0.09 | 0.16 | -0.07 | -0.06 | 0.19 | 0.10 | -0.04 | 0.08 | 0.16 | -0.08 | 0.21 | 0.09 | 0.10 | 0.21 | 0.10 | -0.02 | -0.03 | 0.21 |
| S3B | -0.35 | 0.34 | 0.24 | 0.32 | 0.33 | 0.02 | -0.04 | -0.34 | -0.04 | -0.28 | 0.06 | -0.31 | -0.07 | 0.02 | -0.06 | 0.00 | -0.34 | 0.25 | 0.03 | -0.05 | -0.04 | 0.06 | 0.22 | -0.05 | 0.23 | 0.02 | -0.08 | 0.01 | 0.28 | 0.25 | 0.05 | 0.25 | -0.02 | -0.04 | 0.03 |
| S4B | -0.35 | 0.28 | 0.14 | 0.31 | 0.34 | -0.24 | 0.00 | -0.12 | 0.01 | -0.13 | -0.19 | -0.11 | -0.02 | -0.25 | 0.02 | -0.20 | -0.12 | 0.09 | -0.04 | 0.16 | 0.22 | 0.00 | 0.11 | 0.16 | 0.13 | -0.03 | 0.15 | -0.02 | 0.09 | 0.10 | 0.02 | 0.11 | 0.18 | 0.18 | 0.01 |
| S2B | -0.12 | -0.02 | -0.02 | 0.11 | 0.50 | 0.02 | -0.17 | -0.12 | -0.48 | -0.43 | 0.17 | -0.16 | -0.04 | 0.29 | -0.10 | 0.35 | -0.15 | -0.05 | -0.08 | -0.08 | -0.52 | -0.08 | 0.00 | -0.46 | 0.24 | 0.24 | -0.48 | 0.38 | 0.43 | 0.04 | 0.03 | 0.41 | -0.08 | -0.07 | 0.41 |
| S5A | -0.05 | -0.09 | -0.13 | 0.47 | 0.05 | -0.07 | -0.07 | -0.09 | 0.15 | 0.06 | -0.39 | -0.47 | 0.22 | 0.02 | 0.29 | -0.03 | -0.08 | -0.13 | 0.00 | -0.15 | -0.17 | -0.42 | 0.21 | 0.14 | -0.04 | -0.42 | 0.33 | -0.40 | 0.41 | 0.37 | 0.04 | -0.02 | -0.03 | 0.37 | 0.01 |
| C* | -0.11 | -0.07 | -0.20 | -0.17 | -0.16 | -0.09 | -0.08 | -0.07 | 0.03 | 0.07 | 0.14 | 0.03 | -0.10 | -0.08 | -0.35 | -0.34 | -0.34 | -0.04 | -0.13 | -0.12 | -0.03 | -0.01 | -0.11 | -0.03 | -0.10 | -0.05 | -0.21 | -0.23 | -0.35 | -0.26 | -0.16 | -0.29 | -0.22 | -0.33 | -0.32 |
| N | -0.01 | -0.04 | -0.09 | -0.04 | -0.01 | -0.05 | 0.02 | 0.04 | 0.01 | -0.07 | 0.04 | -0.04 | 0.02 | 0.02 | -0.03 | -0.04 | -0.07 | 0.02 | -0.02 | -0.02 | -0.03 | 0.00 | 0.00 | -0.01 | 0.03 | 0.02 | -0.01 | -0.05 | -0.01 | -0.02 | -0.04 | 0.00 | -0.01 | -0.03 | -0.02 |
| O3 | -0.01 | -0.03 | 0.01 | 0.02 | 0.01 | 0.00 | -0.01 | 0.00 | 0.00 | 0.04 | 0.00 | 0.03 | -0.01 | -0.02 | 0.01 | 0.02 | 0.05 | -0.01 | -0.03 | -0.03 | 0.01 | 0.01 | -0.02 | -0.01 | -0.04 | -0.02 | 0.01 | 0.01 | 0.00 | 0.01 | 0.03 | 0.01 | 0.02 | 0.00 | 0.00 |
| O1 | -0.01 | 0.01 | 0.03 | 0.00 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | -0.01 | 0.01 | -0.01 | -0.01 | 0.00 | -0.01 | -0.01 | -0.02 | 0.02 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | -0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 |
| O2 | -0.01 | -0.02 | -0.03 | -0.03 | -0.01 | -0.04 | 0.01 | 0.03 | 0.00 | -0.02 | 0.02 | -0.01 | -0.01 | -0.02 | -0.03 | -0.03 | -0.03 | 0.01 | -0.01 | -0.01 | 0.01 | 0.02 | -0.03 | 0.00 | 0.00 | 0.01 | 0.02 | 0.00 | -0.03 | -0.02 | 0.00 | -0.01 | 0.02 | -0.02 | -0.01 |

*Table S 15: Mulliken spin population of the [**V**-NO$_3$]$^0$, $M_S$ = 2, Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.87 | 0.53 | 0.70 | 1.01 | -1.80 | 1.77 | 2.32 | 1.65 | 0.81 | 1.55 | 1.83 | 1.59 | 1.90 | 2.02 | 0.69 | 1.98 | 1.51 | -0.08 | -0.54 | -0.13 | 0.02 | -0.38 | -1.44 | -0.05 | 0.13 | 1.24 | -0.04 | -0.27 | -1.64 | 1.78 | 1.90 | 2.05 | -0.21 | 0.77 | 1.84 |
| Fe1 | 1.57 | 3.45 | -2.67 | -3.54 | -2.70 | 2.66 | 3.77 | 2.33 | 3.47 | 3.41 | 3.31 | 3.41 | 2.46 | 2.28 | -3.43 | -3.48 | -3.46 | 3.47 | 3.36 | 3.32 | 3.48 | 3.49 | 3.37 | 3.39 | 3.32 | 3.34 | -3.15 | -3.18 | -3.45 | -3.32 | -3.39 | -3.36 | -3.30 | -3.46 | -3.45 |
| Fe2 | 3.30 | -3.19 | -3.19 | -3.30 | 3.36 | -3.33 | 3.80 | 3.29 | -3.32 | -3.34 | 2.52 | 2.86 | 3.27 | 2.94 | 3.26 | 3.00 | 3.32 | -3.37 | -3.22 | 3.29 | -3.14 | -3.18 | -3.31 | -3.14 | 3.26 | 3.25 | -3.11 | 3.34 | 3.45 | -3.25 | -3.24 | 3.16 | 3.40 | 3.31 | 3.20 |
| Fe3 | 3.39 | -3.34 | -3.31 | 3.37 | -3.07 | 3.18 | 3.73 | 3.32 | 2.87 | 2.84 | -3.35 | -3.35 | 3.09 | 3.29 | 3.29 | 3.26 | 3.40 | -3.43 | 3.33 | -3.32 | -3.20 | -3.24 | 3.40 | 3.35 | -3.40 | -3.30 | 3.40 | -3.10 | 3.49 | 3.30 | 3.33 | -3.31 | -3.23 | 3.39 | 3.21 |
| Fe4 | 3.33 | -3.23 | 3.29 | -3.19 | -3.06 | 3.06 | 3.80 | -3.26 | 3.22 | 3.18 | 3.19 | 3.20 | -3.27 | -3.26 | 3.32 | 3.07 | 3.17 | 3.30 | -3.19 | -3.19 | 3.29 | 3.29 | -3.24 | -3.28 | -3.25 | -3.32 | 3.32 | 3.39 | -3.14 | 3.23 | 3.28 | 3.21 | 3.41 | -3.15 | -3.22 |
| Fe5 | -3.10 | 2.87 | 3.01 | 3.11 | 3.38 | -3.21 | 3.79 | 3.08 | -3.20 | 3.11 | -3.29 | 3.10 | -3.23 | -3.16 | -2.98 | -3.14 | 3.14 | -3.00 | 3.23 | 3.27 | 3.13 | 3.21 | -2.99 | 3.16 | -3.18 | 3.02 | 3.23 | 3.25 | -2.88 | -3.10 | 2.81 | -3.08 | 3.35 | 3.19 | 2.85 |
| Fe6 | -3.20 | 3.28 | 3.16 | 3.37 | 3.24 | 3.24 | 3.61 | -3.09 | -3.20 | -3.20 | 3.13 | -3.22 | -3.31 | 3.26 | -3.17 | 3.19 | -3.23 | 3.17 | 3.30 | -3.15 | -3.21 | 3.28 | 3.36 | -3.22 | 3.09 | 2.92 | -3.14 | 3.28 | 3.39 | 3.14 | 3.18 | 2.76 | -3.09 | -3.14 | 3.27 |
| Fe7 | -3.30 | 3.18 | 3.12 | 3.27 | 3.45 | -3.27 | 3.69 | -3.10 | 3.11 | -3.25 | -3.25 | -3.23 | 3.22 | -3.34 | 3.22 | -3.26 | -3.24 | 3.18 | -3.15 | 3.32 | 3.29 | -3.18 | 3.39 | 3.26 | 3.25 | -3.23 | 3.32 | -3.09 | 3.44 | 2.64 | -3.27 | 3.08 | 3.37 | 3.30 | -3.27 |
| S1A | 0.30 | -0.08 | -0.02 | -0.45 | -0.05 | 0.02 | 0.64 | -0.03 | 0.11 | 0.07 | 0.17 | 0.27 | 0.07 | 0.00 | 0.08 | 0.03 | 0.05 | 0.13 | -0.12 | 0.11 | 0.16 | 0.13 | -0.17 | -0.12 | 0.11 | 0.08 | 0.00 | 0.20 | -0.07 | -0.08 | -0.12 | 0.10 | 0.20 | -0.09 | -0.13 |
| S2A | 0.18 | -0.09 | -0.16 | -0.14 | -0.03 | 0.03 | 0.61 | 0.21 | 0.16 | 0.13 | 0.08 | 0.14 | 0.12 | 0.09 | 0.07 | 0.04 | 0.11 | -0.17 | 0.15 | 0.10 | -0.08 | -0.08 | 0.14 | 0.21 | 0.11 | 0.14 | -0.04 | -0.04 | 0.19 | -0.12 | -0.09 | -0.15 | -0.07 | 0.14 | 0.09 |
| S4A | 0.30 | -0.08 | -0.01 | -0.04 | -0.14 | 0.19 | 0.54 | -0.02 | 0.27 | 0.28 | 0.07 | 0.05 | -0.03 | 0.02 | 0.09 | 0.07 | 0.10 | 0.10 | 0.12 | -0.15 | 0.10 | 0.14 | 0.13 | 0.09 | -0.17 | -0.17 | 0.19 | 0.00 | -0.06 | 0.13 | 0.14 | -0.13 | -0.02 | -0.11 | -0.11 |
| S1B | -0.24 | 0.20 | 0.18 | 0.19 | 0.27 | -0.04 | 0.36 | -0.09 | -0.24 | -0.08 | -0.07 | -0.12 | -0.30 | -0.04 | -0.22 | -0.05 | -0.09 | 0.06 | 0.24 | -0.02 | -0.06 | 0.23 | 0.12 | -0.04 | 0.01 | 0.01 | -0.03 | 0.22 | 0.17 | 0.01 | 0.09 | -0.04 | 0.01 | -0.04 | 0.12 |
| S3B | -0.34 | 0.30 | 0.23 | 0.24 | 0.33 | -0.02 | 0.38 | -0.27 | -0.03 | -0.30 | -0.04 | -0.31 | -0.10 | -0.03 | -0.04 | -0.05 | -0.32 | 0.24 | 0.04 | -0.02 | 0.00 | 0.05 | 0.35 | -0.02 | 0.17 | -0.01 | -0.01 | 0.05 | 0.37 | 0.11 | 0.02 | 0.11 | 0.01 | 0.00 | 0.01 |
| S4B | -0.29 | 0.13 | 0.14 | 0.10 | 0.34 | -0.29 | 0.34 | -0.09 | -0.01 | -0.11 | -0.29 | -0.09 | -0.06 | -0.32 | 0.02 | -0.30 | -0.11 | 0.08 | -0.01 | 0.24 | 0.20 | -0.02 | 0.13 | 0.19 | 0.00 | -0.11 | 0.22 | -0.03 | 0.16 | -0.13 | -0.17 | -0.02 | 0.25 | 0.09 | -0.15 |
| S2B | 0.04 | 0.00 | -0.01 | 0.09 | 0.49 | 0.11 | 0.65 | 0.01 | -0.49 | -0.48 | 0.25 | -0.17 | -0.12 | 0.34 | 0.00 | 0.39 | -0.02 | -0.03 | 0.12 | -0.11 | -0.44 | 0.10 | 0.09 | -0.47 | 0.40 | 0.33 | -0.38 | 0.46 | 0.52 | 0.05 | 0.05 | 0.33 | 0.05 | -0.10 | 0.42 |
| S5A | 0.09 | -0.14 | -0.08 | 0.44 | 0.11 | -0.05 | 0.62 | 0.07 | 0.18 | -0.13 | -0.46 | -0.45 | 0.36 | -0.01 | 0.42 | -0.05 | 0.08 | -0.08 | -0.03 | 0.03 | 0.03 | -0.38 | 0.48 | 0.43 | -0.02 | -0.43 | 0.44 | -0.31 | 0.51 | 0.25 | -0.02 | 0.02 | 0.05 | 0.42 | -0.03 |
| C* | 0.08 | -0.07 | -0.24 | -0.16 | -0.15 | -0.02 | 0.19 | 0.00 | 0.01 | 0.06 | -0.03 | 0.06 | -0.14 | -0.08 | -0.24 | -0.29 | -0.08 | -0.05 | 0.06 | 0.05 | 0.13 | 0.16 | -0.03 | 0.02 | -0.08 | -0.01 | -0.09 | -0.10 | -0.16 | -0.34 | -0.19 | -0.36 | -0.01 | -0.17 | -0.33 |
| N | 0.06 | -0.01 | -0.08 | -0.05 | 0.01 | -0.01 | 0.32 | 0.01 | 0.01 | 0.03 | 0.05 | 0.03 | 0.10 | 0.06 | -0.03 | -0.03 | -0.01 | 0.11 | 0.03 | 0.06 | -0.02 | 0.01 | -0.02 | -0.02 | 0.05 | 0.02 | 0.00 | 0.04 | -0.02 | -0.01 | -0.01 | -0.05 | 0.00 | -0.04 | 0.00 |
| O3 | 0.02 | -0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.11 | -0.01 | 0.00 | 0.00 | -0.01 | 0.00 | -0.03 | -0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.00 | -0.02 | 0.00 | 0.00 | -0.02 | -0.01 | -0.03 | -0.01 | 0.03 | 0.02 | -0.01 | 0.02 | 0.03 | 0.02 | 0.02 | 0.01 | 0.00 |
| O1 | 0.00 | 0.00 | 0.02 | -0.01 | 0.01 | -0.02 | 0.10 | -0.01 | 0.00 | 0.00 | 0.00 | 0.01 | -0.02 | -0.01 | 0.01 | -0.02 | -0.01 | -0.02 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | -0.01 | -0.02 | -0.01 | 0.01 | -0.01 | -0.02 |
| O2 | 0.04 | 0.00 | -0.03 | -0.03 | 0.00 | -0.01 | 0.17 | 0.01 | 0.01 | 0.04 | 0.03 | 0.04 | 0.04 | 0.01 | -0.03 | -0.03 | 0.02 | 0.07 | 0.02 | 0.04 | 0.01 | 0.03 | -0.04 | -0.01 | 0.00 | 0.01 | 0.02 | 0.04 | -0.03 | -0.01 | 0.01 | -0.03 | 0.03 | -0.03 | 0.00 |

*Table S 16: Mulliken spin population of the [**V**-NO$_3$]$^0$, $M_S$ = $^3/_2$, Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.75 | -1.74 | -1.81 | -1.69 | -1.69 | 0.04 | 0.57 | 1.58 | 1.76 | 1.58 | 1.73 | 1.57 | 0.34 | 1.78 | 0.16 | -0.17 | 1.39 | -1.58 | 0.40 | -0.02 | 0.31 | -0.08 | -0.18 | 0.88 | -0.40 | 0.81 | 0.15 | -0.20 | -1.56 | -1.55 | -0.72 | -1.50 | 0.16 | 0.92 | 1.34 |
| Fe1 | 1.92 | 3.42 | -2.83 | -2.87 | -2.90 | 3.34 | 3.42 | 2.25 | 2.60 | 2.83 | 2.77 | 2.90 | 3.11 | 1.91 | -3.44 | -3.46 | -3.44 | 3.46 | 2.92 | 2.97 | 3.44 | 3.40 | 3.17 | 2.85 | 3.17 | 3.11 | -3.52 | -3.11 | -3.46 | -2.88 | -3.52 | -2.87 | -3.51 | -3.47 | -3.47 |
| Fe2 | 3.23 | -3.23 | -3.21 | -3.12 | 3.21 | -3.32 | 2.64 | 3.23 | -3.34 | -3.34 | 2.59 | 2.82 | 3.21 | 3.01 | 3.11 | 3.16 | 3.10 | -3.33 | -3.22 | 3.25 | -3.17 | -3.17 | -3.34 | -3.24 | 3.01 | 2.87 | -3.29 | 3.19 | 3.38 | -3.18 | -3.28 | 3.28 | 3.31 | 3.16 | 3.11 |
| Fe3 | 3.32 | -3.33 | -3.30 | 3.24 | -3.21 | 2.79 | -3.36 | 3.27 | 2.75 | 2.90 | -3.32 | -3.34 | 2.82 | 3.28 | 3.16 | 3.36 | 3.29 | -3.40 | 3.27 | -3.30 | -3.28 | -3.19 | 2.92 | 3.09 | -3.32 | -3.30 | 3.32 | -3.04 | 3.43 | 3.34 | 3.38 | -3.22 | -3.32 | 3.19 | 3.22 |
| Fe4 | 3.30 | -3.22 | 3.31 | -3.14 | -3.17 | 3.29 | 3.24 | -3.25 | 3.23 | 3.17 | 3.19 | 3.13 | -3.28 | -3.27 | 3.29 | 3.26 | 3.03 | 3.32 | -3.21 | -3.21 | 3.18 | 3.10 | -3.26 | -3.34 | -3.17 | -3.32 | 3.39 | 3.31 | -3.21 | 3.30 | 3.37 | 3.34 | 3.43 | -3.23 | -3.24 |
| Fe5 | -3.34 | 3.29 | 3.34 | 3.38 | 3.39 | -3.29 | -3.29 | 3.11 | -3.28 | 3.15 | -3.30 | 3.12 | -3.23 | -3.24 | -3.02 | -3.03 | 3.06 | -3.11 | 3.07 | 3.27 | 2.97 | 3.03 | -3.20 | 3.09 | -3.17 | 3.09 | 3.29 | 3.09 | -3.05 | -3.04 | 3.37 | -3.00 | 3.23 | 3.13 | 3.04 |
| Fe6 | -3.29 | 3.28 | 3.27 | 3.24 | 3.09 | 3.20 | -3.28 | -3.27 | -3.20 | -3.16 | 3.19 | -3.15 | -3.24 | 3.26 | -3.15 | 3.11 | -3.21 | 3.28 | 3.13 | -3.17 | -3.25 | 3.10 | 3.20 | -3.27 | 3.01 | 3.03 | -3.15 | 3.07 | 3.31 | 3.06 | 3.30 | 3.10 | -3.19 | -3.25 | 2.99 |
| Fe7 | -3.35 | 3.35 | 3.34 | 3.16 | 3.31 | -3.29 | 3.16 | -3.29 | 3.23 | -3.19 | -3.22 | -3.19 | 3.16 | -3.36 | 3.13 | -3.18 | -3.26 | 3.30 | -3.28 | 3.29 | 3.08 | -3.20 | 3.17 | 3.16 | 3.23 | -3.24 | 3.27 | -3.19 | 3.33 | 3.09 | -3.08 | 3.12 | 3.26 | 3.17 | -3.27 |
| S1A | 0.29 | -0.12 | -0.03 | -0.14 | -0.06 | 0.08 | 0.22 | 0.00 | 0.09 | 0.07 | 0.00 | 0.08 | 0.14 | -0.01 | 0.08 | 0.12 | 0.09 | 0.12 | -0.10 | 0.04 | 0.06 | 0.04 | -0.15 | -0.13 | 0.03 | 0.01 | -0.11 | 0.15 | -0.12 | 0.00 | -0.11 | 0.12 | 0.15 | -0.12 | -0.13 |
| S2A | 0.13 | -0.14 | -0.15 | -0.09 | -0.06 | 0.01 | 0.03 | 0.16 | -0.07 | -0.01 | -0.07 | 0.01 | 0.15 | 0.00 | 0.09 | 0.12 | 0.09 | -0.18 | -0.01 | -0.03 | -0.14 | -0.13 | 0.02 | -0.01 | 0.05 | 0.03 | -0.14 | -0.10 | 0.16 | 0.03 | -0.12 | 0.02 | -0.14 | 0.08 | 0.09 |
| S4A | 0.28 | -0.12 | -0.01 | -0.03 | -0.17 | 0.26 | 0.06 | 0.00 | 0.04 | 0.09 | 0.06 | 0.04 | 0.04 | 0.02 | 0.12 | 0.10 | 0.12 | 0.09 | 0.05 | -0.16 | 0.05 | 0.02 | 0.03 | 0.02 | -0.17 | -0.16 | 0.17 | -0.01 | -0.08 | 0.17 | 0.15 | -0.02 | -0.11 | -0.11 | -0.10 |
| S1B | -0.31 | 0.31 | 0.33 | 0.30 | 0.29 | 0.03 | -0.24 | -0.11 | -0.29 | -0.10 | -0.06 | -0.12 | -0.24 | -0.05 | -0.17 | 0.08 | -0.11 | 0.12 | 0.12 | -0.04 | -0.11 | 0.15 | 0.03 | -0.09 | 0.00 | 0.07 | -0.04 | 0.17 | 0.11 | 0.11 | 0.27 | 0.10 | -0.04 | -0.06 | -0.02 |
| S3B | -0.35 | 0.36 | 0.33 | 0.30 | 0.29 | 0.04 | -0.04 | -0.34 | -0.06 | -0.28 | -0.02 | -0.29 | -0.05 | -0.05 | -0.05 | 0.00 | -0.32 | 0.33 | -0.01 | -0.04 | -0.03 | 0.03 | 0.21 | -0.03 | 0.20 | 0.00 | -0.04 | -0.03 | 0.32 | 0.24 | 0.07 | 0.25 | -0.04 | -0.05 | -0.04 |
| S4B | -0.35 | 0.34 | 0.36 | 0.32 | 0.32 | -0.23 | -0.01 | -0.11 | -0.05 | -0.12 | -0.31 | -0.10 | 0.03 | -0.34 | 0.07 | -0.17 | -0.11 | 0.12 | -0.10 | 0.22 | 0.11 | -0.08 | 0.01 | 0.08 | 0.04 | -0.09 | 0.21 | -0.06 | 0.11 | 0.11 | 0.04 | 0.11 | 0.20 | 0.05 | -0.13 |
| S2B | -0.05 | 0.04 | 0.08 | 0.09 | 0.39 | -0.01 | -0.18 | -0.07 | -0.51 | -0.49 | 0.27 | -0.11 | -0.06 | 0.44 | -0.02 | 0.40 | -0.07 | 0.04 | -0.01 | -0.04 | -0.48 | 0.02 | 0.03 | -0.51 | 0.28 | 0.30 | -0.50 | 0.39 | 0.47 | -0.03 | 0.05 | 0.43 | 0.00 | -0.14 | 0.32 |
| S5A | 0.03 | -0.04 | -0.01 | 0.35 | 0.05 | -0.10 | -0.11 | -0.01 | 0.25 | -0.09 | -0.47 | -0.47 | 0.22 | 0.00 | 0.34 | 0.08 | 0.03 | -0.04 | 0.00 | -0.10 | -0.09 | -0.40 | 0.25 | 0.34 | 0.00 | -0.45 | 0.41 | -0.31 | 0.46 | 0.40 | 0.12 | -0.09 | -0.03 | 0.35 | -0.05 |
| C* | -0.01 | 0.02 | -0.15 | -0.26 | -0.25 | -0.01 | -0.02 | -0.01 | 0.02 | 0.07 | 0.01 | 0.07 | -0.12 | -0.11 | -0.33 | -0.31 | -0.26 | 0.00 | 0.02 | 0.04 | 0.06 | 0.08 | -0.11 | 0.00 | -0.09 | -0.01 | -0.13 | -0.27 | -0.29 | -0.25 | -0.08 | -0.27 | -0.12 | -0.30 | -0.30 |
| N | 0.02 | 0.01 | 0.00 | -0.03 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.03 | 0.02 | 0.03 | -0.02 | 0.00 | -0.02 | -0.02 | 0.01 | 0.00 | 0.00 | 0.03 | 0.02 | 0.03 | -0.03 | 0.00 | -0.01 | 0.01 | 0.01 | 0.02 | -0.03 | -0.02 | 0.01 | -0.01 | 0.02 | -0.01 | 0.00 |
| O3 | -0.01 | -0.01 | 0.03 | 0.01 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | -0.02 | -0.03 | 0.02 | 0.01 | 0.02 | -0.01 | -0.01 | -0.01 | 0.01 | 0.01 | -0.01 | -0.01 | -0.02 | -0.02 | 0.03 | 0.01 | 0.00 | 0.01 | 0.03 | 0.01 | 0.02 | 0.01 | 0.01 |
| O1 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | -0.01 | -0.01 |
| O2 | 0.01 | 0.02 | 0.03 | -0.02 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.05 | 0.01 | 0.04 | -0.04 | -0.04 | -0.02 | -0.02 | 0.03 | 0.00 | 0.00 | 0.03 | 0.04 | 0.05 | -0.05 | 0.00 | -0.04 | 0.01 | 0.03 | 0.04 | -0.04 | -0.02 | 0.03 | -0.01 | 0.05 | -0.01 | 0.00 |

*Table S 17: Mulliken spin population of the [**V**-NO$_3$]$^0$, $M_S$ = $^1/_2$, Functional: TPSSh*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 1.75 | -1.76 | -1.80 | -1.72 | -1.70 | 0.05 | 0.58 | 1.58 | -0.86 | 1.38 | -0.87 | 1.44 | 0.34 | -0.12 | 0.27 | 0.04 | 0.17 | -1.62 | -1.71 | 0.01 | -0.26 | -1.83 | -1.69 | 0.00 | -1.68 | -0.32 | 0.16 | -0.28 | -1.56 | -1.56 | -1.71 | -1.58 | -0.19 | 0.01 | -0.53 |
| Fe1 | -0.08 | 3.42 | -3.63 | -3.59 | -3.60 | 1.78 | 2.24 | 1.78 | 2.62 | 1.50 | 3.33 | 2.79 | 1.97 | 2.02 | -3.48 | -3.48 | -3.46 | 3.41 | 3.24 | 2.91 | 3.20 | 3.28 | 3.14 | 2.86 | 3.12 | 2.96 | -3.58 | -3.56 | -3.46 | -3.53 | -3.56 | -3.32 | -3.55 | -3.49 | -3.49 |
| Fe2 | 3.22 | -3.34 | -3.36 | -3.35 | 3.16 | -3.34 | 2.93 | 2.99 | -3.34 | -3.34 | 1.33 | 3.02 | 3.05 | 2.77 | 2.50 | 2.70 | 2.93 | -3.36 | -3.36 | 3.18 | -3.39 | -3.33 | -3.37 | -3.22 | 2.99 | 2.87 | -3.43 | 3.16 | 3.10 | -3.38 | -3.39 | 3.13 | 3.16 | 3.12 | 2.98 |
| Fe3 | 3.29 | -3.44 | -3.45 | 3.16 | -3.43 | 3.15 | -3.38 | 2.99 | 2.70 | 3.16 | -3.33 | -3.45 | 2.81 | 3.08 | 3.04 | 3.14 | 3.11 | -3.42 | 3.23 | -3.39 | -3.46 | -3.30 | 2.87 | 2.89 | -3.40 | -3.32 | 3.26 | -3.45 | 3.26 | 3.36 | 3.33 | -3.28 | -3.47 | 3.08 | 3.16 |
| Fe4 | 3.26 | -3.38 | 3.34 | -3.22 | -3.20 | 3.19 | 3.09 | -3.36 | 3.25 | 3.09 | 3.31 | 2.17 | -3.29 | -3.29 | 3.12 | 3.07 | 3.02 | 3.22 | -3.37 | -3.27 | 3.16 | 3.10 | -3.29 | -3.35 | -3.29 | -3.33 | 3.14 | 3.32 | -3.26 | 3.24 | 3.31 | 3.21 | 3.16 | -3.30 | -3.29 |
| Fe5 | -3.32 | 2.98 | 3.37 | 3.40 | 3.41 | -3.28 | -3.29 | 3.02 | -3.14 | 3.05 | -3.10 | 3.03 | -3.23 | -3.16 | -3.24 | -3.30 | 3.13 | -3.15 | 3.09 | 2.78 | 3.03 | 3.18 | -3.24 | 2.98 | -3.22 | 2.95 | 2.98 | 3.07 | -3.10 | -3.06 | 3.36 | -3.11 | 3.10 | 2.88 | 2.98 |
| Fe6 | -3.31 | 3.09 | 3.32 | 3.26 | 3.06 | 3.17 | -3.32 | -3.32 | -3.09 | -3.27 | 3.24 | -3.33 | -3.28 | 3.21 | -3.23 | 2.90 | -3.25 | 2.91 | 3.14 | -3.24 | -3.32 | 3.22 | 3.15 | -3.27 | 2.90 | 2.86 | -3.23 | 2.99 | 3.02 | 3.01 | 3.25 | 2.93 | -3.22 | -3.26 | 3.00 |
| Fe7 | -3.37 | 3.24 | 3.37 | 3.12 | 3.33 | -3.32 | 3.12 | -3.39 | 3.17 | -3.39 | -3.15 | -3.40 | 3.17 | -3.28 | 3.01 | -3.28 | -3.34 | 2.95 | -3.33 | 2.78 | 3.06 | -3.30 | 2.95 | 2.78 | 3.14 | -3.27 | 3.06 | -3.21 | 3.18 | 3.09 | -3.26 | 3.08 | 3.16 | 2.94 | -3.23 |
| S1A | 0.24 | -0.17 | -0.15 | -0.46 | -0.07 | 0.03 | 0.02 | -0.06 | 0.08 | 0.00 | 0.07 | 0.01 | 0.03 | 0.00 | -0.02 | 0.03 | 0.06 | 0.07 | -0.21 | 0.03 | 0.01 | 0.02 | -0.15 | -0.12 | 0.00 | 0.01 | -0.25 | 0.10 | -0.14 | -0.14 | -0.19 | 0.10 | 0.07 | -0.13 | -0.13 |
| S2A | 0.15 | -0.13 | -0.55 | -0.16 | -0.17 | -0.10 | -0.15 | -0.07 | -0.09 | -0.02 | -0.02 | 0.00 | -0.08 | -0.10 | -0.05 | 0.04 | 0.03 | -0.22 | 0.09 | -0.06 | -0.23 | -0.19 | 0.04 | -0.08 | 0.04 | -0.06 | -0.21 | -0.26 | 0.00 | -0.18 | -0.16 | -0.11 | -0.22 | 0.01 | 0.00 |
| S4A | 0.21 | -0.18 | -0.14 | -0.05 | -0.45 | 0.12 | -0.01 | -0.05 | 0.04 | 0.14 | 0.11 | -0.01 | 0.00 | 0.02 | 0.09 | 0.08 | 0.11 | 0.04 | 0.01 | -0.18 | -0.02 | -0.01 | 0.03 | 0.01 | -0.18 | -0.16 | 0.08 | -0.15 | -0.10 | 0.11 | 0.13 | -0.04 | -0.18 | -0.11 | -0.10 |
| S1B | -0.31 | 0.21 | 0.34 | 0.31 | 0.29 | 0.04 | -0.25 | -0.13 | -0.07 | -0.11 | 0.09 | -0.13 | -0.24 | 0.07 | -0.20 | 0.03 | -0.03 | 0.10 | 0.24 | -0.08 | -0.07 | 0.28 | 0.11 | -0.05 | 0.09 | 0.11 | -0.09 | 0.16 | 0.11 | 0.11 | 0.31 | 0.11 | -0.04 | -0.06 | 0.14 |
| S3B | -0.36 | 0.35 | 0.35 | 0.30 | 0.29 | 0.03 | -0.04 | -0.36 | 0.00 | -0.33 | 0.06 | -0.36 | -0.05 | 0.02 | -0.05 | 0.00 | -0.26 | 0.12 | 0.03 | -0.08 | -0.06 | 0.07 | 0.24 | -0.09 | 0.22 | -0.02 | -0.09 | -0.02 | 0.20 | 0.23 | 0.06 | 0.17 | -0.01 | -0.06 | 0.03 |
| S4B | -0.35 | 0.27 | 0.36 | 0.32 | 0.33 | -0.24 | 0.00 | -0.14 | 0.08 | -0.13 | -0.07 | -0.13 | 0.03 | -0.21 | 0.02 | -0.22 | -0.04 | 0.11 | 0.01 | 0.06 | 0.17 | 0.04 | 0.09 | 0.08 | 0.12 | -0.05 | 0.13 | -0.06 | 0.11 | 0.11 | 0.05 | 0.12 | 0.17 | 0.08 | -0.03 |
| S2B | -0.03 | -0.13 | 0.04 | 0.06 | 0.34 | -0.06 | -0.12 | -0.11 | -0.47 | -0.52 | 0.10 | -0.11 | -0.07 | 0.33 | -0.19 | 0.22 | -0.21 | -0.10 | -0.05 | -0.03 | -0.54 | 0.02 | -0.04 | -0.50 | 0.21 | 0.22 | -0.56 | 0.39 | 0.24 | -0.09 | -0.02 | 0.28 | -0.05 | -0.06 | 0.29 |
| S5A | 0.05 | -0.19 | -0.06 | 0.28 | -0.01 | 0.01 | -0.18 | -0.04 | 0.21 | -0.04 | -0.44 | -0.53 | 0.25 | -0.02 | 0.30 | -0.07 | -0.17 | -0.18 | -0.17 | -0.24 | -0.29 | -0.48 | 0.17 | 0.10 | -0.09 | -0.47 | 0.32 | -0.53 | 0.36 | 0.39 | -0.05 | 0.01 | -0.17 | 0.20 | 0.03 |
| C* | -0.03 | -0.14 | -0.10 | -0.21 | -0.21 | -0.03 | -0.04 | -0.14 | 0.00 | 0.01 | 0.05 | 0.00 | -0.12 | -0.10 | -0.33 | -0.38 | -0.36 | -0.09 | -0.09 | -0.07 | -0.04 | 0.04 | -0.10 | -0.02 | -0.11 | -0.06 | -0.23 | -0.26 | -0.36 | -0.26 | -0.10 | -0.35 | -0.27 | -0.39 | -0.39 |
| N | -0.01 | -0.01 | 0.00 | -0.03 | 0.00 | -0.03 | -0.01 | 0.03 | 0.00 | 0.00 | 0.02 | 0.02 | -0.02 | -0.02 | -0.02 | -0.03 | -0.03 | 0.01 | 0.00 | 0.01 | 0.01 | 0.02 | -0.02 | 0.00 | -0.01 | 0.01 | 0.02 | 0.02 | -0.02 | -0.02 | 0.00 | -0.01 | 0.01 | -0.01 | 0.00 |
| O3 | 0.01 | -0.03 | 0.03 | 0.02 | 0.01 | 0.00 | -0.01 | -0.02 | 0.00 | 0.02 | -0.01 | 0.00 | -0.01 | -0.02 | 0.01 | 0.01 | 0.03 | -0.01 | -0.02 | -0.02 | 0.02 | 0.01 | -0.01 | -0.01 | -0.02 | -0.02 | 0.02 | 0.01 | -0.01 | 0.01 | 0.03 | 0.00 | 0.02 | 0.00 | 0.00 |
| O1 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | 0.00 | -0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.01 | 0.00 | -0.02 | 0.00 | 0.01 | -0.01 | -0.02 | 0.00 | -0.01 | -0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 | -0.02 | -0.01 |
| O2 | -0.02 | -0.01 | 0.03 | -0.02 | 0.00 | -0.03 | -0.01 | 0.02 | 0.00 | 0.03 | 0.01 | 0.04 | -0.04 | -0.04 | -0.02 | -0.03 | 0.00 | 0.00 | 0.00 | 0.01 | 0.04 | 0.04 | -0.05 | 0.00 | -0.03 | 0.01 | 0.04 | 0.04 | -0.04 | -0.02 | 0.02 | -0.01 | 0.04 | -0.01 | -0.01 |

*Table S 18: Mulliken spin populations of the [**V**-$CO_3$]$^{2-}$ model, $M_S = 3/2$. Functional: TPSSh. The spin of the vanadium ion is flipped from a low spin BS solution for each BS solution.*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 2.12 | -2.12 | -2.18 | -2.07 | -2.04 | 0.48 | 1.11 | 1.61 | 0.90 | 1.35 | 0.57 | 1.38 | 0.99 | 0.60 | 0.88 | 0.57 | 1.43 | -1.60 | -1.12 | -0.71 | -0.66 | -1.03 | -1.45 | -0.57 | -1.42 | -0.86 | -0.51 | -0.77 | -1.48 | -1.50 | -1.01 | -1.45 | -0.61 | -0.60 | -0.92 |
| Fe1 | 0.81 | 3.46 | -2.34 | -3.38 | -3.37 | 3.31 | 3.32 | 2.15 | 3.28 | 3.20 | 3.31 | 3.29 | 3.15 | 3.23 | -3.45 | -3.45 | -3.48 | 3.44 | 3.37 | 3.34 | 3.40 | 3.41 | 3.36 | 3.34 | 3.34 | 3.32 | -3.32 | -3.33 | -3.39 | -3.32 | -3.32 | -3.35 | -3.35 | -3.41 | -3.40 |
| Fe2 | 3.27 | -3.03 | -3.27 | -3.00 | 3.41 | -3.36 | 2.21 | 3.22 | -3.34 | -3.36 | 2.46 | 2.38 | 3.31 | 2.42 | 3.12 | 3.04 | 3.09 | -3.22 | -3.25 | 3.32 | -3.28 | -3.35 | -3.31 | -3.24 | 3.36 | 3.31 | -3.30 | 3.27 | 3.34 | -3.28 | -3.29 | 3.37 | 3.29 | 3.30 | 3.37 |
| Fe3 | 3.30 | -3.11 | -3.29 | 3.42 | -3.13 | 3.08 | -3.35 | 3.22 | 2.42 | 2.56 | -3.33 | -3.37 | 2.54 | 3.34 | 3.13 | 3.21 | 3.13 | -3.23 | 3.34 | -3.30 | -3.37 | -3.32 | 3.37 | 3.29 | -3.33 | -3.28 | 3.32 | -3.28 | 3.37 | 3.39 | 3.32 | -3.30 | -3.30 | 3.37 | 3.32 |
| Fe4 | 3.32 | -3.22 | 3.41 | -3.28 | -3.23 | 3.13 | 3.29 | -3.44 | 3.38 | 3.26 | 3.38 | 3.28 | -3.43 | -3.41 | 3.20 | 3.21 | 3.20 | 3.43 | -3.36 | -3.35 | 3.39 | 3.41 | -3.38 | -3.47 | -3.35 | -3.44 | 3.42 | 3.45 | -3.32 | 3.44 | 3.45 | 3.47 | 3.47 | -3.34 | -3.34 |
| Fe5 | -3.27 | 3.45 | 3.51 | 3.54 | 3.56 | -3.44 | -3.31 | 3.15 | -3.39 | 3.17 | -3.38 | 3.17 | -3.36 | -3.32 | -3.33 | -3.29 | 3.18 | -3.18 | 3.27 | 3.26 | 3.29 | 3.33 | -3.18 | 3.34 | -3.18 | 3.36 | 3.33 | 3.37 | -3.06 | -3.06 | 3.42 | -3.02 | 3.39 | 3.36 | 3.38 |
| Fe6 | -3.20 | 3.13 | 3.23 | 3.37 | 3.30 | 3.11 | -3.22 | -3.17 | -3.19 | -3.23 | 3.09 | -3.28 | -3.26 | 3.11 | -3.19 | 3.17 | -3.26 | 3.17 | 3.17 | -3.18 | -3.21 | 3.24 | 3.26 | -3.19 | 3.21 | 3.16 | -3.15 | 3.18 | 3.26 | 3.24 | 3.22 | 3.31 | -3.12 | -3.15 | 3.30 |
| Fe7 | -3.28 | 3.25 | 3.28 | 3.36 | 3.45 | -3.28 | 3.12 | -3.23 | 3.06 | -3.33 | -3.21 | -3.28 | 3.07 | -3.27 | 3.13 | -3.21 | -3.31 | 3.22 | -3.14 | 3.20 | 3.24 | -3.15 | 3.26 | 3.16 | 3.30 | -3.14 | 3.22 | -3.10 | 3.33 | 3.33 | -3.09 | 3.28 | 3.22 | 3.29 | -3.11 |
| S1 | 0.31 | 0.00 | -0.04 | -0.41 | -0.03 | -0.01 | 0.26 | -0.05 | 0.10 | 0.04 | 0.28 | 0.24 | 0.09 | 0.05 | 0.02 | 0.01 | 0.00 | 0.18 | -0.13 | 0.15 | 0.14 | 0.12 | -0.16 | -0.17 | 0.15 | 0.10 | -0.11 | 0.19 | -0.10 | -0.09 | -0.11 | 0.17 | 0.17 | -0.12 | -0.14 |
| S2 | 0.27 | 0.02 | -0.27 | -0.05 | -0.08 | 0.04 | -0.01 | 0.20 | 0.07 | 0.07 | 0.08 | 0.05 | 0.26 | 0.28 | -0.02 | -0.01 | 0.00 | -0.06 | 0.17 | 0.13 | -0.11 | -0.11 | 0.14 | 0.15 | 0.12 | 0.13 | -0.11 | -0.12 | 0.13 | -0.11 | -0.11 | -0.15 | -0.14 | 0.11 | 0.11 |
| S3 | 0.27 | -0.04 | -0.03 | -0.03 | -0.38 | 0.36 | 0.03 | -0.01 | 0.25 | 0.22 | 0.08 | 0.05 | 0.05 | 0.11 | 0.04 | 0.05 | 0.03 | 0.15 | 0.15 | -0.14 | 0.09 | 0.13 | 0.14 | 0.09 | -0.15 | -0.16 | 0.17 | -0.10 | -0.09 | 0.17 | 0.17 | -0.10 | -0.12 | -0.11 | -0.10 |
| S4 | -0.25 | 0.29 | 0.31 | 0.30 | 0.30 | -0.01 | -0.24 | -0.08 | -0.25 | -0.08 | -0.02 | -0.09 | -0.26 | 0.00 | -0.25 | 0.01 | -0.08 | 0.08 | 0.23 | -0.01 | -0.01 | 0.26 | 0.09 | 0.01 | 0.07 | 0.24 | 0.00 | 0.25 | 0.11 | 0.10 | 0.26 | 0.10 | 0.01 | 0.01 | 0.25 |
| S5 | -0.32 | 0.25 | 0.27 | 0.31 | 0.32 | 0.00 | -0.05 | -0.27 | -0.04 | -0.29 | 0.01 | -0.29 | -0.07 | -0.01 | -0.04 | 0.01 | -0.31 | 0.26 | 0.04 | -0.02 | 0.00 | 0.06 | 0.29 | -0.03 | 0.28 | 0.03 | 0.01 | 0.07 | 0.30 | 0.30 | 0.06 | 0.30 | 0.01 | 0.00 | 0.07 |
| S6 | -0.29 | 0.29 | 0.33 | 0.32 | 0.33 | -0.26 | -0.02 | -0.10 | -0.03 | -0.10 | -0.24 | -0.09 | -0.02 | -0.25 | 0.00 | -0.24 | -0.10 | 0.10 | 0.01 | 0.23 | 0.24 | 0.01 | 0.08 | 0.23 | 0.10 | 0.02 | 0.24 | 0.01 | 0.12 | 0.11 | 0.03 | 0.12 | 0.25 | 0.25 | 0.02 |
| S7 | -0.03 | 0.06 | 0.03 | 0.24 | 0.50 | 0.04 | -0.19 | -0.06 | -0.46 | -0.47 | 0.21 | -0.21 | -0.07 | 0.23 | -0.09 | 0.40 | -0.12 | 0.03 | 0.03 | -0.05 | -0.45 | 0.01 | 0.03 | -0.45 | 0.46 | 0.44 | -0.45 | 0.42 | 0.46 | 0.03 | 0.03 | 0.49 | -0.02 | -0.04 | 0.48 |
| S8 | 0.01 | 0.03 | -0.02 | 0.46 | 0.17 | -0.15 | -0.07 | -0.01 | 0.14 | -0.19 | -0.41 | -0.44 | 0.15 | -0.01 | 0.36 | -0.04 | -0.08 | -0.01 | 0.03 | -0.03 | -0.04 | -0.38 | 0.42 | 0.38 | 0.00 | -0.38 | 0.39 | -0.38 | 0.43 | 0.44 | 0.03 | -0.02 | -0.04 | 0.41 | 0.03 |
| C | -0.03 | 0.03 | -0.09 | 0.00 | 0.01 | -0.14 | -0.03 | -0.08 | -0.03 | -0.03 | -0.03 | -0.03 | -0.12 | -0.11 | -0.24 | -0.22 | -0.21 | 0.03 | -0.01 | -0.03 | 0.03 | 0.04 | -0.03 | -0.04 | -0.03 | -0.02 | -0.13 | -0.11 | -0.13 | -0.09 | -0.06 | -0.09 | -0.09 | -0.16 | -0.14 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O | 0.03 | -0.04 | 0.06 | -0.02 | -0.01 | 0.02 | 0.03 | -0.05 | 0.03 | 0.04 | 0.04 | 0.05 | -0.06 | -0.06 | 0.03 | 0.03 | 0.05 | 0.04 | -0.04 | -0.04 | 0.06 | 0.05 | -0.06 | -0.06 | -0.06 | -0.05 | 0.06 | 0.07 | -0.05 | 0.05 | 0.06 | 0.05 | 0.07 | -0.04 | -0.04 |
| O | -0.03 | 0.04 | 0.06 | 0.05 | 0.05 | -0.05 | -0.03 | 0.02 | -0.04 | 0.04 | -0.04 | 0.04 | -0.05 | -0.05 | -0.04 | -0.04 | 0.04 | -0.02 | 0.03 | 0.03 | 0.05 | 0.05 | -0.04 | 0.03 | -0.04 | 0.03 | 0.04 | 0.04 | -0.03 | -0.02 | 0.04 | -0.02 | 0.05 | 0.03 | 0.03 |
| O | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | -0.03 | -0.02 | 0.00 | -0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | -0.02 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | 0.02 | 0.00 | 0.03 | 0.00 | 0.00 |

*Table S 19: Mulliken spin populations of the [**V**-$CO_3$]$^{2-}$ model, $M_S = 3/2$. Functional: TPSSh. The spin of the vanadium is flipped along the irons from a high spin solution.*

| BS | 1 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flip | 567 | 234 | 123 | 124 | 134 | 257 | 356 | 467 | 256 | 267 | 357 | 367 | 456 | 457 | 156 | 157 | 167 | 235 | 247 | 346 | 236 | 237 | 245 | 246 | 345 | 347 | 126 | 137 | 145 | 125 | 127 | 135 | 136 | 146 | 147 |
| V | 2.12 | -2.13 | -2.18 | -2.13 | -2.04 | 0.48 | 1.11 | 1.61 | 0.90 | 1.35 | 0.57 | 1.38 | 0.99 | 0.61 | 0.88 | 0.57 | 1.43 | -1.60 | -1.12 | -0.71 | -0.66 | -1.03 | -1.45 | -0.57 | -1.42 | -0.86 | -0.52 | -0.77 | -1.48 | -1.50 | -1.01 | -1.45 | -0.61 | -0.60 | -0.92 |
| Fe1 | 0.81 | 3.46 | -2.34 | -2.54 | -3.37 | 3.31 | 3.32 | 2.15 | 3.28 | 3.20 | 3.31 | 3.29 | 3.15 | 2.34 | -3.45 | -3.45 | -3.48 | 3.44 | 3.37 | 3.34 | 3.40 | 3.41 | 3.36 | 3.34 | 3.34 | 3.32 | -3.32 | -3.33 | -3.39 | -3.32 | -3.32 | -3.35 | -3.35 | -3.41 | -3.40 |
| Fe2 | 3.27 | -3.03 | -3.27 | -3.16 | 3.41 | -3.36 | 2.21 | 3.22 | -3.34 | -3.36 | 2.46 | 2.38 | 3.31 | 3.21 | 3.12 | 3.04 | 3.09 | -3.22 | -3.25 | 3.32 | -3.28 | -3.35 | -3.31 | -3.24 | 3.36 | 3.31 | -3.30 | 3.27 | 3.34 | -3.28 | -3.29 | 3.37 | 3.29 | 3.30 | 3.37 |
| Fe3 | 3.30 | -3.10 | -3.29 | 3.35 | -3.13 | 3.08 | -3.35 | 3.22 | 2.42 | 2.56 | -3.33 | -3.37 | 2.54 | 3.33 | 3.13 | 3.21 | 3.13 | -3.23 | 3.34 | -3.30 | -3.37 | -3.32 | 3.37 | 3.29 | -3.33 | -3.28 | 3.32 | -3.28 | 3.37 | 3.39 | 3.32 | -3.30 | -3.30 | 3.37 | 3.32 |
| Fe4 | 3.32 | -3.21 | 3.41 | -3.31 | -3.23 | 3.13 | 3.29 | -3.44 | 3.38 | 3.26 | 3.38 | 3.28 | -3.43 | -3.37 | 3.20 | 3.21 | 3.20 | 3.43 | -3.36 | -3.35 | 3.39 | 3.41 | -3.38 | -3.47 | -3.35 | -3.44 | 3.42 | 3.45 | -3.32 | 3.44 | 3.45 | 3.47 | 3.47 | -3.34 | -3.34 |
| Fe5 | -3.27 | 3.28 | 3.51 | 3.35 | 3.56 | -3.44 | -3.31 | 3.15 | -3.39 | 3.17 | -3.38 | 3.17 | -3.36 | -3.31 | -3.33 | -3.29 | 3.18 | -3.18 | 3.27 | 3.26 | 3.29 | 3.33 | -3.18 | 3.34 | -3.18 | 3.36 | 3.33 | 3.37 | -3.06 | -3.06 | 3.42 | -3.02 | 3.39 | 3.36 | 3.38 |
| Fe6 | -3.20 | 3.20 | 3.23 | 3.26 | 3.30 | 3.11 | -3.22 | -3.17 | -3.19 | -3.23 | 3.09 | -3.28 | -3.26 | 3.18 | -3.19 | 3.17 | -3.26 | 3.17 | 3.17 | -3.18 | -3.21 | 3.24 | 3.26 | -3.19 | 3.21 | 3.16 | -3.15 | 3.18 | 3.26 | 3.24 | 3.22 | 3.31 | -3.12 | -3.15 | 3.30 |
| Fe7 | -3.28 | 3.30 | 3.28 | 3.33 | 3.45 | -3.28 | 3.12 | -3.23 | 3.06 | -3.33 | -3.21 | -3.28 | 3.07 | -3.28 | 3.13 | -3.21 | -3.31 | 3.22 | -3.14 | 3.20 | 3.24 | -3.15 | 3.26 | 3.16 | 3.30 | -3.14 | 3.22 | -3.10 | 3.33 | 3.33 | -3.09 | 3.28 | 3.22 | 3.29 | -3.11 |
| S1 | 0.31 | -0.01 | -0.04 | -0.22 | -0.03 | -0.01 | 0.26 | -0.05 | 0.10 | 0.04 | 0.28 | 0.24 | 0.09 | 0.03 | 0.02 | 0.01 | 0.00 | 0.18 | -0.13 | 0.15 | 0.14 | 0.12 | -0.16 | -0.17 | 0.15 | 0.10 | -0.11 | 0.19 | -0.10 | -0.09 | -0.11 | 0.17 | 0.17 | -0.12 | -0.14 |
| S2 | 0.27 | 0.03 | -0.27 | -0.03 | -0.08 | 0.05 | -0.01 | 0.20 | 0.07 | 0.07 | 0.08 | 0.05 | 0.26 | 0.24 | -0.02 | -0.01 | 0.00 | -0.06 | 0.17 | 0.13 | -0.11 | -0.11 | 0.14 | 0.15 | 0.12 | 0.13 | -0.11 | -0.12 | 0.13 | -0.11 | -0.11 | -0.15 | -0.14 | 0.11 | 0.11 |
| S3 | 0.27 | -0.03 | -0.03 | -0.04 | -0.38 | 0.36 | 0.03 | -0.01 | 0.25 | 0.22 | 0.08 | 0.05 | 0.05 | 0.06 | 0.04 | 0.05 | 0.03 | 0.15 | 0.15 | -0.14 | 0.09 | 0.13 | 0.14 | 0.09 | -0.15 | -0.16 | 0.17 | -0.10 | -0.09 | 0.17 | 0.17 | -0.10 | -0.12 | -0.11 | -0.10 |
| S4 | -0.25 | 0.24 | 0.31 | 0.26 | 0.30 | -0.01 | -0.24 | -0.08 | -0.25 | -0.08 | -0.02 | -0.09 | -0.26 | 0.00 | -0.25 | 0.01 | -0.08 | 0.08 | 0.23 | -0.01 | -0.01 | 0.26 | 0.09 | 0.01 | 0.07 | 0.24 | 0.00 | 0.25 | 0.11 | 0.10 | 0.26 | 0.10 | 0.01 | 0.01 | 0.25 |
| S5 | -0.32 | 0.32 | 0.27 | 0.32 | 0.32 | 0.00 | -0.05 | -0.27 | -0.04 | -0.29 | 0.01 | -0.29 | -0.07 | -0.01 | -0.04 | 0.01 | -0.31 | 0.26 | 0.04 | -0.02 | 0.00 | 0.06 | 0.29 | -0.03 | 0.28 | 0.03 | 0.01 | 0.07 | 0.30 | 0.30 | 0.06 | 0.30 | 0.01 | 0.00 | 0.07 |
| S6 | -0.29 | 0.27 | 0.33 | 0.30 | 0.33 | -0.26 | -0.02 | -0.10 | -0.03 | -0.10 | -0.24 | -0.09 | -0.02 | -0.25 | 0.00 | -0.24 | -0.10 | 0.10 | 0.01 | 0.23 | 0.24 | 0.01 | 0.08 | 0.23 | 0.10 | 0.02 | 0.24 | 0.01 | 0.12 | 0.11 | 0.03 | 0.12 | 0.25 | 0.25 | 0.02 |
| S7 | -0.03 | 0.07 | 0.03 | 0.02 | 0.50 | 0.04 | -0.19 | -0.06 | -0.46 | -0.47 | 0.21 | -0.21 | -0.07 | 0.41 | -0.09 | 0.40 | -0.12 | 0.03 | 0.03 | -0.05 | -0.45 | 0.01 | 0.03 | -0.45 | 0.46 | 0.44 | -0.45 | 0.42 | 0.46 | 0.03 | 0.03 | 0.49 | -0.02 | -0.04 | 0.48 |
| S8 | 0.01 | 0.05 | -0.02 | 0.44 | 0.17 | -0.15 | -0.07 | -0.01 | 0.14 | -0.19 | -0.41 | -0.44 | 0.15 | 0.01 | 0.36 | -0.04 | -0.08 | -0.01 | 0.03 | -0.03 | -0.04 | -0.38 | 0.42 | 0.38 | 0.00 | -0.38 | 0.39 | -0.38 | 0.43 | 0.44 | 0.03 | -0.02 | -0.04 | 0.41 | 0.03 |
| C | -0.03 | 0.04 | -0.09 | -0.17 | 0.01 | -0.14 | -0.03 | -0.08 | -0.03 | -0.03 | -0.03 | -0.03 | -0.12 | -0.09 | -0.24 | -0.22 | -0.21 | 0.03 | -0.01 | -0.03 | 0.03 | 0.04 | -0.03 | -0.04 | -0.03 | -0.02 | -0.13 | -0.11 | -0.13 | -0.09 | -0.06 | -0.09 | -0.09 | -0.16 | -0.14 |
| C | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | -0.01 | -0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | -0.01 | 0.00 | 0.01 | 0.01 | -0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| O | 0.03 | -0.03 | 0.06 | -0.03 | -0.01 | 0.02 | 0.03 | -0.05 | 0.03 | 0.04 | 0.04 | 0.05 | -0.06 | -0.06 | 0.03 | 0.03 | 0.05 | 0.04 | -0.04 | -0.04 | 0.06 | 0.05 | -0.06 | -0.06 | -0.06 | -0.05 | 0.06 | 0.07 | -0.05 | 0.05 | 0.06 | 0.05 | 0.07 | -0.04 | -0.04 |
| O | -0.03 | 0.03 | 0.06 | 0.03 | 0.05 | -0.05 | -0.03 | 0.02 | -0.04 | 0.04 | -0.04 | 0.04 | -0.05 | -0.05 | -0.04 | -0.04 | 0.04 | -0.02 | 0.03 | 0.03 | 0.05 | 0.05 | -0.04 | 0.03 | -0.04 | 0.03 | 0.04 | 0.04 | -0.03 | -0.02 | 0.04 | -0.02 | 0.05 | 0.03 | 0.03 |
| O | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | -0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | -0.03 | -0.02 | 0.00 | -0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | -0.02 | 0.00 | 0.02 | 0.02 | -0.02 | 0.00 | 0.02 | 0.00 | 0.03 | 0.00 | 0.00 |

## Mayer bond orders for FeMoco and FeVco

*Table S 20: Mayer bond order for metal-metal, metal-sulfide and carbide-metal interaction in QM/MM models of FeMoco and FeVco*

| Cofactor | FeVco | FeMoco | FeVco | FeVco | FeMoco |
|---|---|---|---|---|---|
| Model | X-ray[a] | X-ray[a] | QM/MM | QM/MM | QM/MM |
| QM size | 57 | 57 | 57 | 181 | 247 |
| M-Fe5 | 0.42 | 0.41 | 0.38 | 0.37 | 0.47 |
| M-Fe6 | 0.20 | 0.40 | 0.16 | 0.18 | 0.45 |
| M-Fe7 | 0.28 | 0.42 | 0.27 | 0.30 | 0.49 |
| Fe1-Fe2 | 0.19 | 0.20 | 0.20 | 0.21 | 0.20 |
| Fe1-Fe3 | 0.23 | 0.20 | 0.22 | 0.24 | 0.23 |
| Fe1-Fe4 | 0.44 | 0.38 | 0.42 | 0.43 | 0.41 |
| Fe2-Fe3 | 0.39 | 0.40 | 0.40 | 0.42 | 0.41 |
| Fe2-Fe4 | 0.26 | 0.24 | 0.23 | 0.23 | 0.24 |
| Fe3-Fe4 | 0.27 | 0.23 | 0.23 | 0.24 | 0.29 |
| Fe5-Fe6 | 0.26 | 0.28 | 0.24 | 0.24 | 0.28 |
| Fe5-Fe7 | 0.24 | 0.28 | 0.21 | 0.25 | 0.31 |
| Fe6-Fe7 | 0.40 | 0.45 | 0.40 | 0.42 | 0.47 |
| Fe2-Fe6 | 0.29 | 0.32 | 0.28 | 0.32 | 0.32 |
| Fe3-Fe7 | 0.29 | 0.33 | 0.28 | 0.32 | 0.34 |
| Fe4-Fe5 | 0.27 | 0.29 | 0.29 | 0.33 | 0.30 |
| C-Fe2 | 0.36 | 0.30 | 0.36 | 0.32 | 0.31 |
| C-Fe3 | 0.31 | 0.34 | 0.37 | 0.27 | 0.27 |
| C-Fe4 | 0.43 | 0.40 | 0.48 | 0.36 | 0.35 |
| C-Fe5 | 0.49 | 0.40 | 0.50 | 0.37 | 0.36 |
| C-Fe6 | 0.39 | 0.32 | 0.38 | 0.30 | 0.33 |
| C-Fe7 | 0.35 | 0.34 | 0.33 | 0.29 | 0.35 |
| S1A-Fe1 | 0.68 | 0.64 | 0.68 | 0.69 | 0.68 |
| S1A-Fe2 | 0.91 | 0.77 | 0.88 | 0.85 | 0.86 |
| S1A-Fe4 | 0.82 | 0.80 | 0.82 | 0.77 | 0.82 |
| S2A-Fe1 | 0.90 | 0.87 | 0.96 | 1.00 | 0.88 |
| S2A-Fe2 | 0.79 | 0.76 | 0.80 | 0.80 | 0.77 |
| S2A-Fe3 | 0.78 | 0.81 | 0.80 | 0.78 | 0.76 |
| S4A-Fe1 | 0.65 | 0.67 | 0.65 | 0.73 | 0.70 |
| S4A-Fe3 | 0.95 | 0.85 | 0.82 | 0.85 | 0.93 |
| S4A-Fe4 | 0.77 | 0.81 | 0.74 | 0.76 | 0.90 |
| S1B-V | 0.86 | 1.03 | 0.87 | 0.81 | 1.00 |
| S1B-Fe5 | 0.69 | 0.75 | 0.66 | 0.68 | 0.71 |
| S1B-Fe6 | 0.76 | 0.72 | 0.76 | 0.78 | 0.78 |
| S3B-Fe6 | 0.69 | 1.04 | 0.62 | 0.71 | 0.99 |
| S3B-Fe5 | 0.71 | 0.66 | 0.70 | 0.71 | 0.67 |
| S3B-Fe7 | 0.76 | 0.67 | 0.84 | 0.70 | 0.65 |
| S4B-V | 0.89 | 1.01 | 0.88 | 0.84 | 1.02 |
| S4B-Fe5 | 0.74 | 0.71 | 0.72 | 0.75 | 0.75 |
| S4B-Fe7 | 0.80 | 0.72 | 0.82 | 0.81 | 0.80 |
| S2B-Fe2 | 1.04 | 0.92 | 1.05 | 0.99 | 0.77 |
| S2B-Fe2 | 1.04 | 1.10 | 1.02 | 1.03 | 1.04 |
| S5A-Fe3 | 1.09 | 1.01 | 0.99 | 1.03 | 0.95 |
| S5A-Fe7 | 0.97 | 1.09 | 1.00 | 0.96 | 1.02 |
| S3A-Fe4 | N/A | 0.94 | N/A | N/A | 0.70 |
| S3A-Fe5 | N/A | 0.97 | N/A | N/A | 0.91 |
| Ave. non bridging Fe-S | 0.78 | 0.75 | 0.78 | 0.78 | 0.78 |
| Ave. bridging Fe-S | 1.03 | 1.01 | 1.01 | 1.00 | 0.90 |
| Average M-S | 0.81 | 1.03 | 0.79 | 0.79 | 1.00 |

[a] Single point QM/MM using crystal structure geometry with the protein matrix as pointcharges.

## Localized Orbital Analysis of FeVco

The electronic structure of FeVco in redox states $[V\text{-}CO_3]^{2-/1-/0}$ as interpreted via IAOIBO localized orbital analysis is shown in Figures S21-S23.

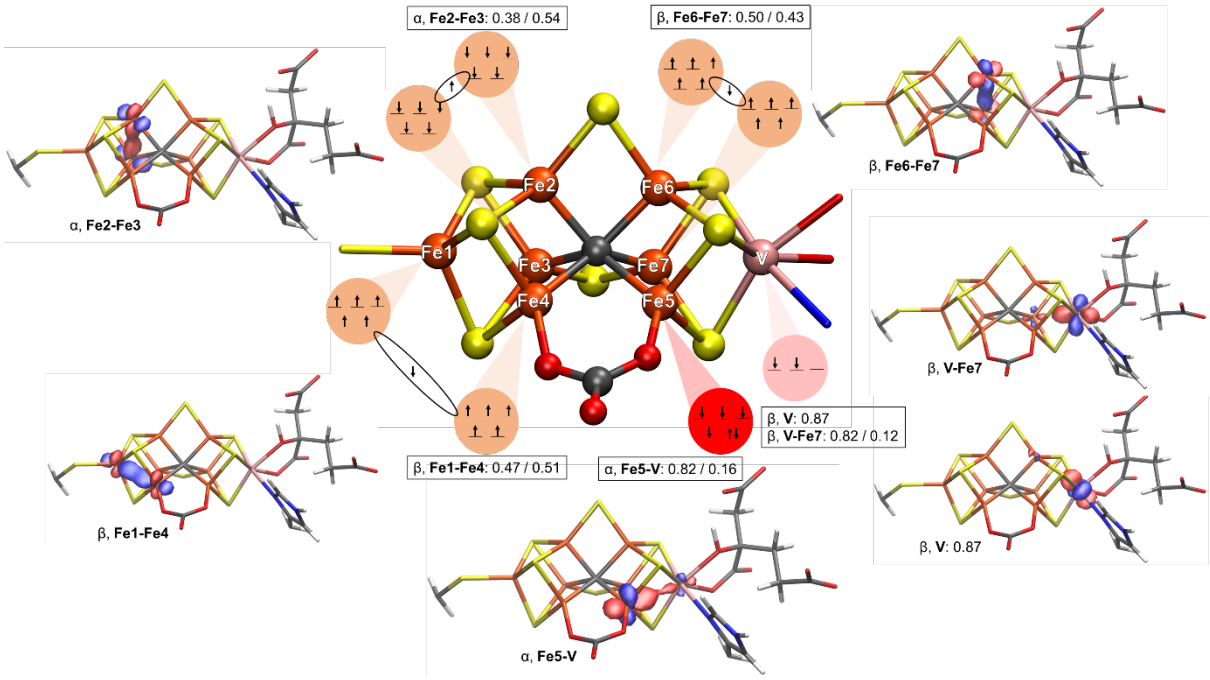



*Figure S 21: Electronic structure of $[V\text{-}CO_3]^{2-}$ with $M_S = {}^3/_2$ as interpreted by IAOIBOs. 181 QM atom QM/MM model. Iso value of 0.1 was used to generate the figures of the orbitals.*

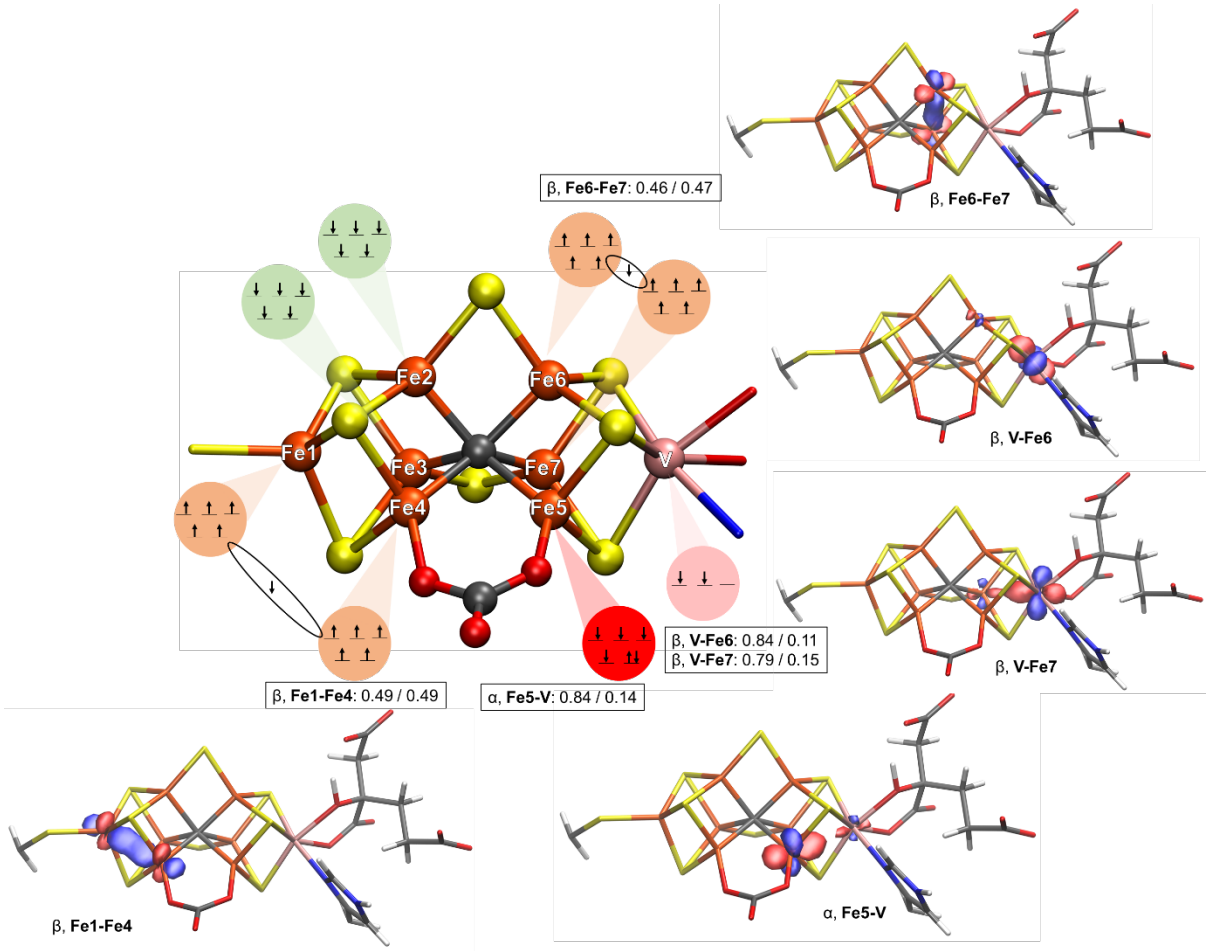



*Figure S 22: The electronic structure of $[V\text{-}CO_3]^{1-}$ $M_S$ = 1 BS7-235 model as interpreted by IAOIBOs. Shown are localized orbitals for the minority-spin electrons and the vanadium electrons and the atomic populations. Using 181 QM atom QM/MM model. Iso value of 0.1 was used to generate the figures of the orbitals.*

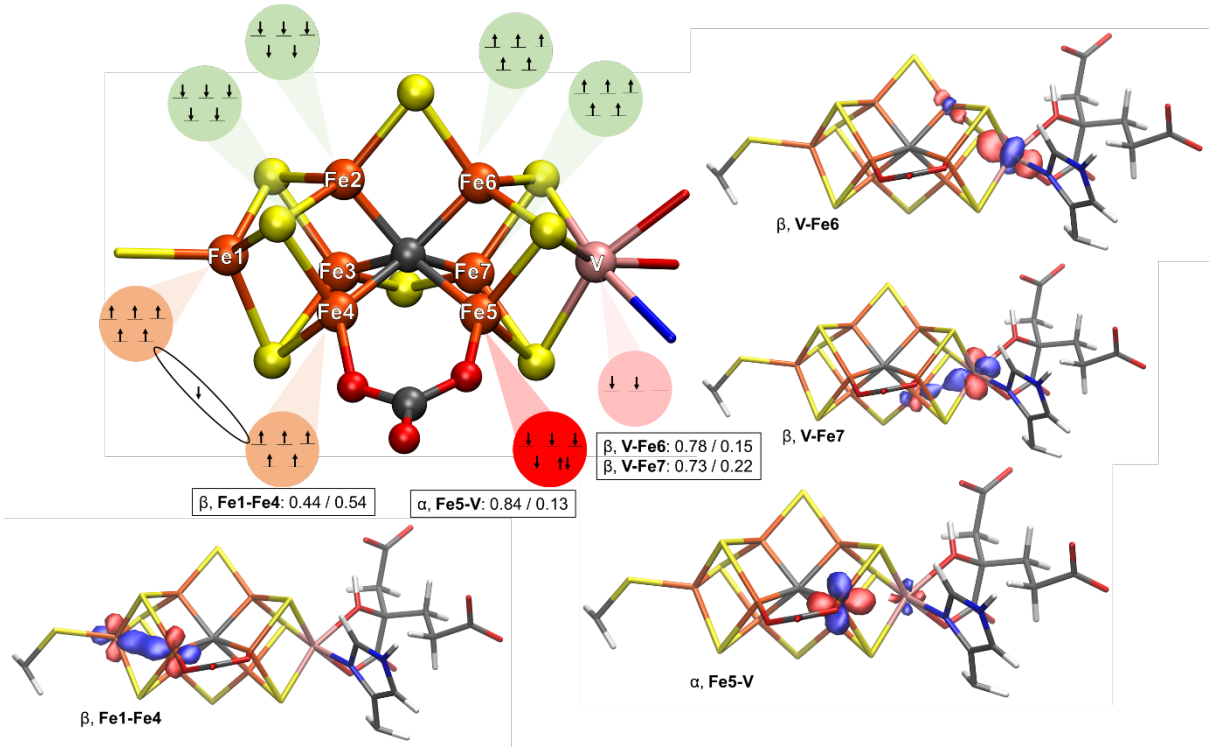



*Figure S 23: The electronic structure of $[V\text{-}CO_3]^0$ $M_S = {}^3/_2$ BS7-235 model as interpreted by IAOIBOs. Shown are localized orbitals for the minority-spin electrons and the vanadium electrons and the atomic populations. Using 181 QM atom QM/MM model. Iso value of 0.1 was used to generate the figures of the orbitals.*

## The BS7 solutions: FeMoco vs. FeVco

As discussed in the manuscript, for FeVco the BS7-235 solution is considerably lower in energy (by 6 kcal/mol) than the analogous BS7-247 and BS7-346 solutions. For FeMoco the 3 BS7 solutions are all within 1 kcal/mol for FeMoco (Benediktsson, B.; Bjornsson, R. QM/MM Study of the Nitrogenase MoFe Protein Resting State: Broken-Symmetry States, Protonation States, and QM Region Convergence in the FeMoco Active Site. *Inorg. Chem.* **2017**, *56* (21), 13417–13429)

To separate out the effects of carbonate vs. sulfide, V vs. Mo and the different Fe redox state, we carried out calculations where the carbonate of FeVco was substituted by a sulfide, V was substituted by Mo or with both substitutions. When the carbonate ligand in FeVco is exchanged for a sulfide, the difference between the BS7-235 and the other BS7 solutions drops by ~4 kcal/mol (Table S22) and the three BS7 solutions are much more similar in energy. A similar change in energy difference is, however, observed when the vanadium is substituted for molybdenum (and the negative charge is reduced by 1). Simultaneously substituting the vanadium for molybdenum and carbonate for sulfide in FeVco within the VFe protein matrix (essentially substituting FeVco for FeMoco), we see a further drop in the energy difference between the three BS7 solutions which is now less than 1 kcal/mol. Overall this suggests that the preference for BS7-235 in FeVco arises from both the carbonate ligand as well as the presence of V instead of Mo (and the reduced Fe environment).

*Table S 21 The electronic energy of the three BS7 spin isomers of FeVco, FeVco-triS[a], FeVco-Mo[b], FeVco-triS-Mo[c] and FeMoco[d], using a 57 QM atom QM/MM model for FeVco and 54 QM atom QM/MM model for FeMoco.*

| | FeVco | FeVco-triS[a] | FeVco-Mo[b] | FeVco-triS-Mo[c] | FeMoco[d] |
|---|---|---|---|---|---|
| BS7-235 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| BS7-247 | 6.0 | 2.0 | 2.3 | 0.3 | 1.1 |
| BS7-346 | 6.5 | 1.6 | 1.4 | 0.6 | 0.0 |

[a]FeVco-triS: A 54 QM atom QM/MM optimized model (of the VFe protein) where carbonate has been substituted for a sulfide. $[VFe_7S_9C]^{2-}$ and $M_S = {}^3/_2$

[b]FeVco-Mo: A 57 QM atom QM/MM optimized model (of the VFe protein) where vanadium has been substituted for a molybdenum. $[MoFe_7S_8C(CO_3)]^-$ and $M_S = {}^3/_2$

[c]FeVco-triS-Mo: A 54 QM atom QM/MM optimized model (of the VFe protein) where carbonate has been substituted for sulfide and vanadium has been substituted for molybdenum (essentially FeMoco within the VFe protein matrix). $[MoFe_7S_9C]^-$ and $M_S = {}^3/_2$

[d]FeMoco: A 54 QM atom QM/MM optimized model (of the MoFe protein) as previously described. $[MoFe_7S_9C]^-$ and $M_S = {}^3/_2$.

The energy difference between the BS7 solutions of FeVco is not very sensitive to the QM region size, however, the geometries of all BS7 solutions when optimized are systematically improved with respect to the 5NY6 X-ray structure (Table S20) as the QM region increases. The BS7-235 structure is still in best agreement with the 5N6Y X-ray structure.

*Table S 22: Root-Mean-Square Deviations (in Å) of different QM/MM Optimized Geometries with the Possible FeVco structure compared to the Experimentally Determined Crystal Structure). The RMSD is defined as the deviation of the $[VFe_7S_8C(XO_3)]$ part with respect to both cofactors in the crystal structure.*

| Model | RMSD [Å] | Relative energy difference [kcal/mol] | V-Fe1 distance [Å] (crystal 7.11 Å) |
|---|---|---|---|
| BS7-235-57QM | 0.080 | 0 | 7.11 |
| BS7-247-57QM | 0.101 | 6.00 | 7.15 |
| BS7-346-57QM | 0.096 | 6.53 | 7.10 |
| BS235-83QM | 0.083 | 0 | 7.09 |
| BS7-247-83QM | 0.098 | 5.58 | 7.10 |
| BS7-346-83QM | 0.091 | 5.52 | 7.12 |
| BS7-235-181QM | 0.076 | 0 | 7.05 |
| BS7-247-181QM | 0.088 | 5.27 | 7.11 |
| BS7-346-181QM | 0.089 | 6.13 | 7.09 |

*Table S 23: The effect of geometry optimization on the relative energy difference of BS7 class of broken symmetry solutions.*

| BS | Geometry type | QM region | Relative energy difference [kcal/mol] |
|---|---|---|---|
| BS7-235 | X-ray | 57 | 0 |
| BS7-247 | X-ray | 57 | 7.83 |
| BS7-346 | X-ray | 57 | 8.18 |
| BS7-235 | QM/MM opt | 57 | 0 |
| BS7-247 | QM/MM opt | 57 | 6.00 |
| BS7-346 | QM/MM opt | 57 | 6.53 |
| BS7-235 | QM/MM opt | 83 | 0 |
| BS7-247 | QM/MM opt | 83 | 5.58 |
| BS7-346 | QM/MM opt | 83 | 5.52 |
| BS7-235 | QM/MM opt | 181 | 0 |
| BS7-247 | QM/MM opt | 181 | 5.27 |
| BS7-346 | QM/MM opt | 181 | 6.13 |

## Protonation state of homocitrate

QM/MM calculations of FeVco ([**V**-$CO_3$]$^{2-}$ model) with and without the alcohol group of homocitrate protonated were carried out. A comparison of the computed structures with the X-ray crystal structure (PDB ID: 5N6Y) reveal that the alcohol group is most likely protonated. This is consistent with our previous finding for FeMoco in MoFe protein Benediktsson, B.; Bjornsson, R. QM/MM Study of the Nitrogenase MoFe Protein Resting State: Broken-Symmetry States, Protonation States, and QM Region Convergence in the FeMoco Active Site. *Inorg. Chem.* **2017**, *56* (21), 13417–13429). and another study (Cao, L.; Caldararu, O.; Ryde, U. Protonation States of Homocitrate and Nearby Residues in Nitrogenase Studied by Computational Methods and Quantum Refinement. *J. Phys. Chem. B* **2017**, *121* (35), 8242–8262.)

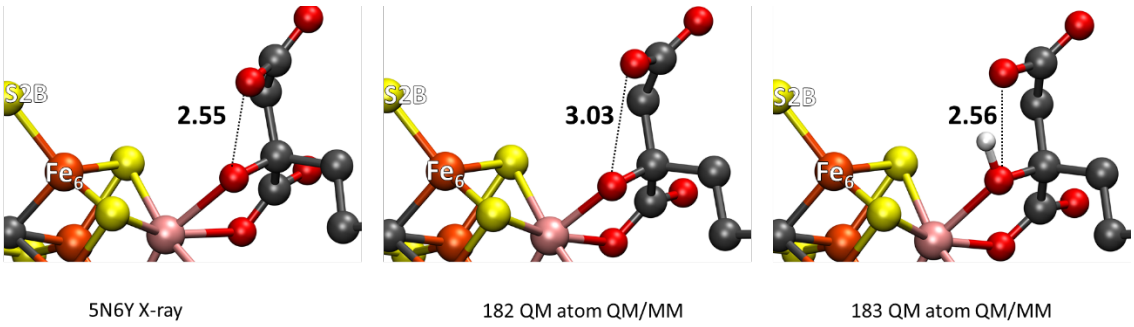



*Figure S 24: Protonation state of the alcohol group of homocitrate of FeVco. Left: Close-up of the alcohol group of homocitrate of FeVco in the 5N6Y X-ray structure with the O-O distance between the alcohol group and the shorter carboxylate arm indicated. Middle: Computed structure with no proton present. Right: Computed structure with alcohol proton present.*

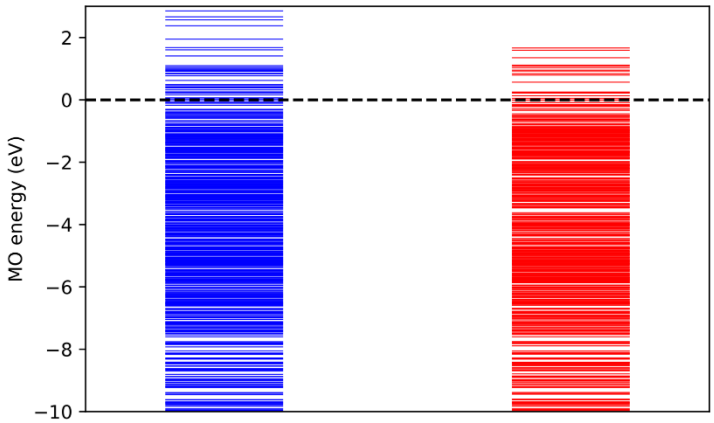
## Protonated FeVco

*Table S 24: Structural parameters comparing the average of the two FeVco cofactors of the X-ray structure to QM/MM calculated structures of protonated forms of the cofactors. HS2B: Sulfide S2B protonated, HS5A: Sulfide S5A protonated, 2XHCA: longer carboxylate arm of FeVco protonated. 58 QM atom QM/MM calculations.*

| | Crystal | HS2B | HS5A | 2XHCA |
|---|---|---|---|---|
| Fe1-Fe2 | 2.71 | 2.69 | 2.69 | 2.72 |
| Fe1-Fe3 | 2.66 | 2.64 | 2.61 | 2.65 |
| Fe1-Fe4 | 2.58 | 2.66 | 2.66 | 2.63 |
| V-Fe5 | 2.70 | 2.71 | 2.69 | 2.70 |
| V-Fe6 | 2.77 | 2.74 | 2.82 | 2.90 |
| V-Fe7 | 2.73 | 2.72 | 2.66 | 2.73 |
| Fe2-Fe3 | 2.63 | 2.56 | 2.59 | 2.60 |
| Fe2-Fe4 | 2.62 | 2.62 | 2.63 | 2.63 |
| Fe3-Fe4 | 2.63 | 2.67 | 2.64 | 2.67 |
| Fe5-Fe6 | 2.60 | 2.62 | 2.66 | 2.67 |
| Fe5-Fe7 | 2.63 | 2.65 | 2.63 | 2.66 |
| Fe6-Fe7 | 2.60 | 2.53 | 2.51 | 2.57 |
| V-Fe1 | 7.11 | 7.12 | 7.10 | 7.15 |
| C-Fe1 | 3.48 | 3.51 | 3.50 | 3.53 |
| C-V | 3.63 | 3.61 | 3.61 | 3.63 |
| Fe2-Fe6 | 2.61 | 2.67 | 2.61 | 2.62 |
| Fe3-Fe7 | 2.60 | 2.59 | 2.64 | 2.60 |
| Fe4-Fe5 | 2.76 | 2.72 | 2.72 | 2.72 |
| C-Fe2 | 1.95 | 2.01 | 2.01 | 2.03 |
| C-Fe3 | 2.04 | 2.02 | 2.01 | 2.04 |
| C-Fe4 | 2.02 | 2.00 | 1.99 | 2.00 |
| C-Fe5 | 2.05 | 2.01 | 2.00 | 1.99 |
| C-Fe6 | 1.98 | 2.02 | 2.02 | 2.02 |
| C-Fe7 | 2.01 | 2.01 | 2.02 | 2.02 |
| Fe4-OX | 1.97 | 1.91 | 1.91 | 1.93 |
| Fe5-Ocarb | 1.93 | 1.91 | 1.91 | 1.92 |
| Fe4-O-O-Fe5 | -11.30 | -2.57 | -2.89 | -5.06 |

| | | | | |
|---|---|---|---|---|
| V-Oalk | 2.20 | 2.12 | 2.11 | 2.16 |
| V-Ocarb | 2.35 | 2.05 | 2.06 | 2.08 |
| V-His | 2.35 | 2.20 | 2.21 | 2.22 |
| Fe1-Scys | 2.16 | 2.26 | 2.26 | 2.29 |
| Fe2-S2B | 2.21 | 2.35 | 2.19 | 2.21 |
| Fe6-S2B | 2.17 | 2.34 | 2.19 | 2.19 |
| Fe3-S5A | 2.23 | 2.20 | 2.34 | 2.22 |
| Fe7-S5A | 2.27 | 2.20 | 2.34 | 2.20 |

## Unbound electrons




**Alpha electrons:**
497α: 0.0064 eV
498α: 0.0662 eV
499α: 0.2503 eV
500α: 0.2547 eV
501α: 0.3847 eV
502α: 0.4911 eV
503α: 0.6242 eV
504α: 0.8518 eV
505α: 0.9152 eV
506α: 0.9676 eV
507α: 1.0450 eV
508α: 1.4082 eV
509α: 1.6039 eV
510α: 1.6793 eV

**Beta electrons:**
496β: 0.0497 eV
497β: 0.1307 eV
498β: 0.2392 eV
499β: 0.2514 eV
500β: 0.7961 eV
501β :0.8426 eV
502β: 0.9262 eV
503β 1.0820 eV
504β: 1.1137 eV
505β :1.3524 eV
506β: 1.5942 eV
507β 1.6636 eV

*Figure S 25: MO diagram showing the occupied valence orbitals in the 181 QM atom QM/MM model of [**V**-$CO_3$]$^{2-}$. Orbitals with positive energies correspond to unbound electrons and are listed to the right.*

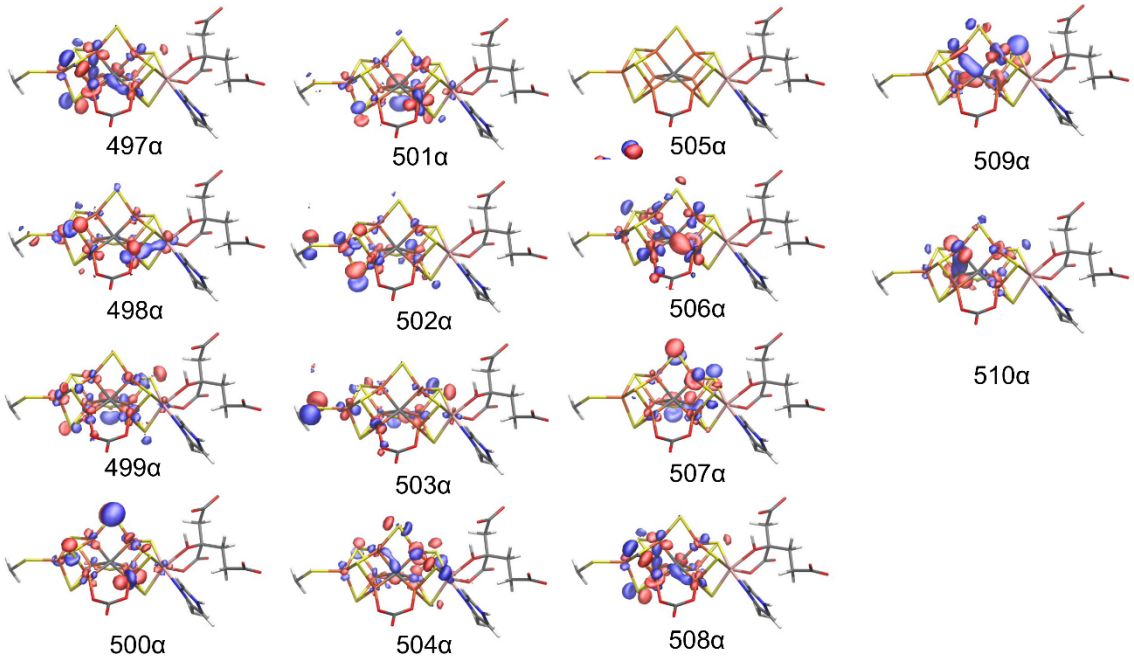



*Figure S 26: Molecular orbitals of α electrons that that have positive orbital energies in a 181 QM atom QM/MM model of the [**V**-$CO_3$]$^{2-}$ model. These high energy orbitals show mainly, but not only, sulfide and iron character*

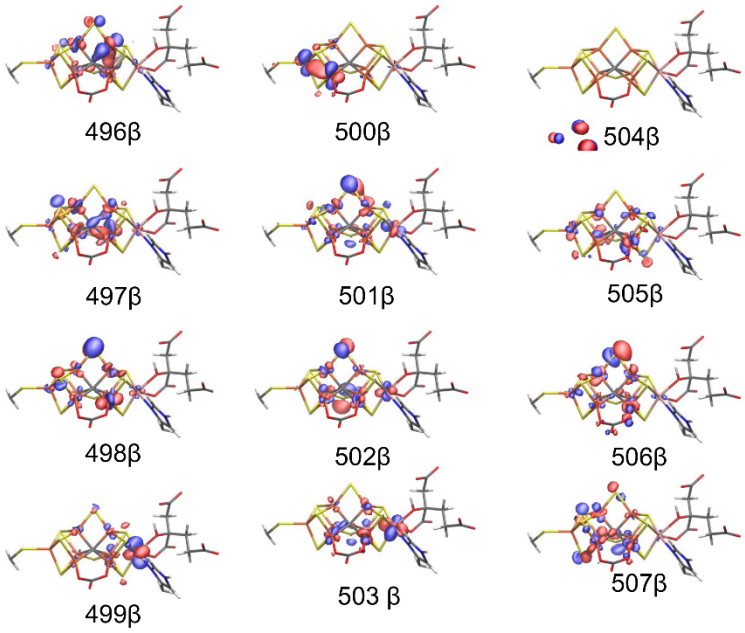



*Figure S 27: Molecular orbitals of β electrons that that have positive orbital energies in a 181 QM atom QM/MM model of the [**V**-$CO_3$]$^{2-}$ model. These high energy orbitals show mainly, but not only, sulfide and iron character*

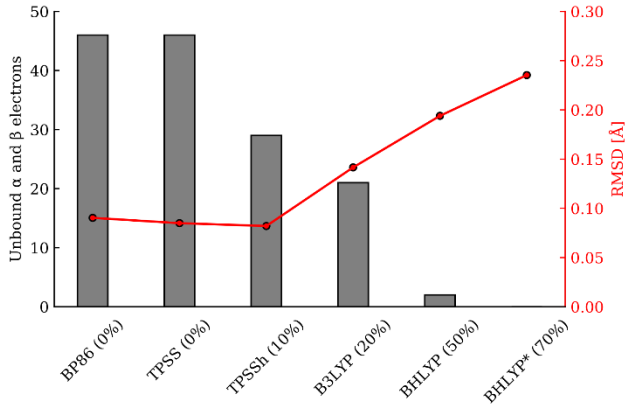



*Figure S 28: The dependence of unbound electrons in the [**V**-$CO_3$]$^{2-}$ resting state model on density functionals with different amount of HF exchange. Also shown (right y-axis) is the RMSD of the optimized cofactor with the respective functional. QM/MM model with a QM region size of 57 atoms. The RMSD is defined as the deviation of the [$VFe_7S_8C(XO_3)$] part with respect to both cofactors in the crystal structure.*

## Alternative QM/MM model of whole protein

The model is prepared similarly as the spherical QM/MM model. The difference between the two models is that instead of a spherical cut from the MD step, the whole protein is included as well as all water molecules within 3 Å of the protein matrix. This new QM/MM model 47 516 atoms in size.

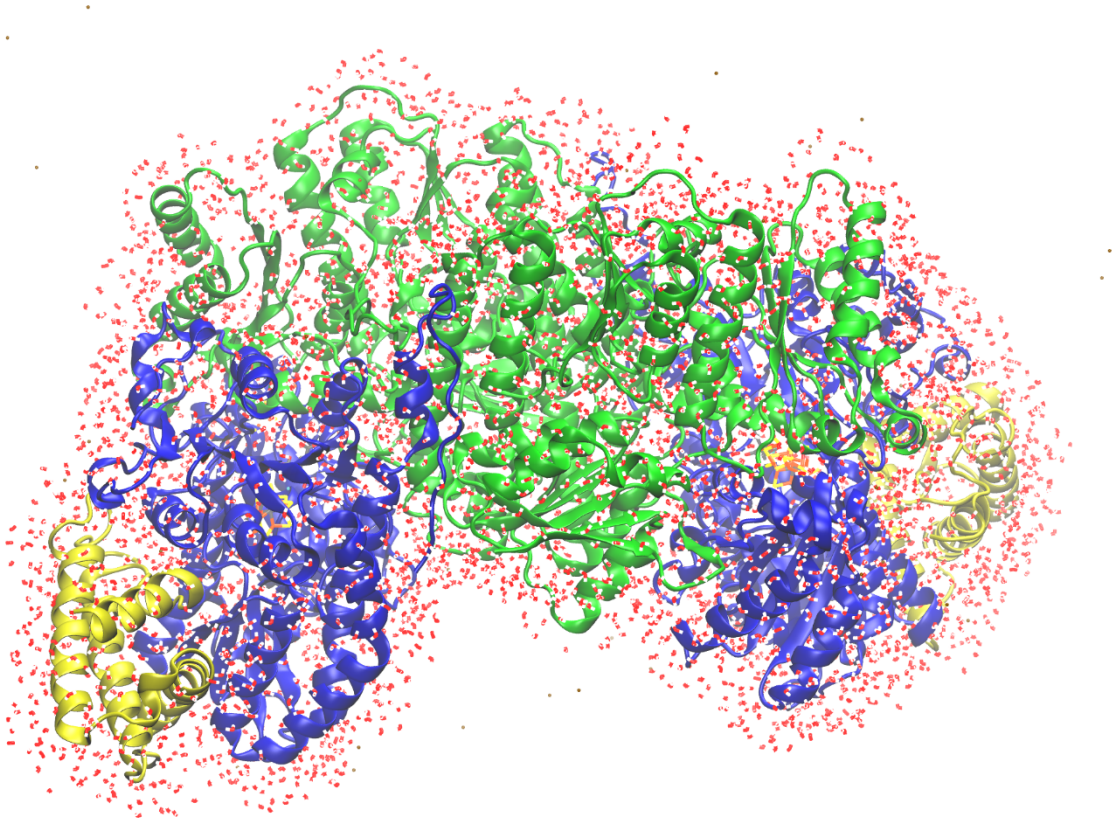


*Figure S 29: The new QM/MM model (47 516 atoms) includes the whole VFe protein as well as sodium ion counterions and 3 Å thick water layer at the edge of the VFe protein.*

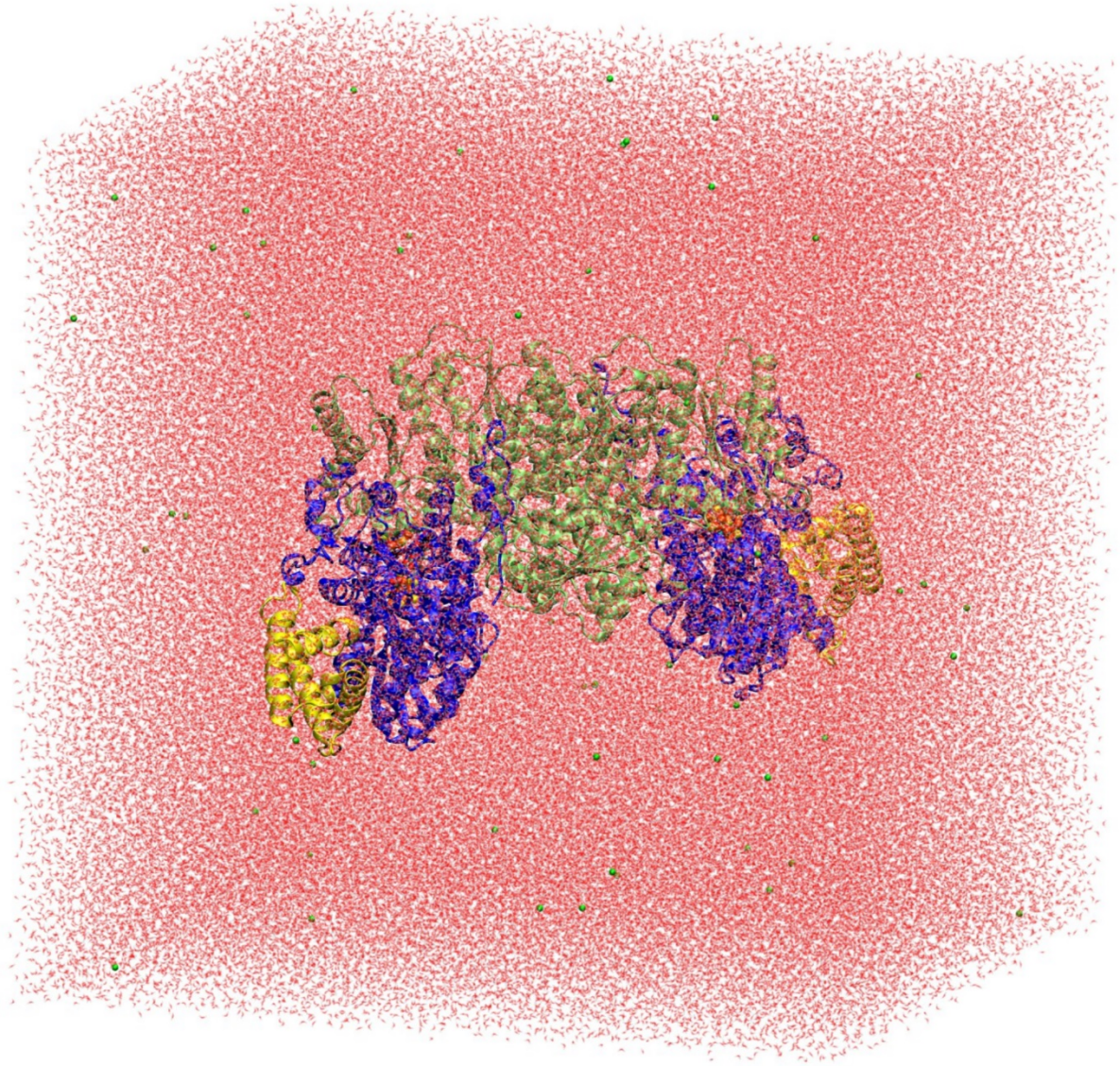


Figure S 30: *The 531 080 atom QM/MM model (full box from the MM setup).*

*Table S 25: Mulliken spin populations of the FeVco $[VFe_7S_8C(CO_3)]^{2-}$ model using 47 516 atom and 531 080 atom QM/MM model setups.*

| QM atoms | 57 | 57 | 181 | 181 |
|---|---|---|---|---|
| QM/MM Model size | 47 516 | 531 080 | 47 516 | 531 080 |
| V | -1.650 | -1.649 | -1.634 | -1.630 |
| Fe1 | 3.477 | 3.479 | 3.459 | 3.462 |
| Fe2 | -3.292 | -3.292 | -3.286 | -3.288 |
| Fe3 | -3.290 | -3.293 | -3.274 | -3.277 |
| Fe4 | 3.428 | 3.427 | 3.387 | 3.388 |
| Fe5 | -3.218 | -3.218 | -3.187 | -3.186 |
| Fe6 | 3.289 | 3.288 | 3.291 | 3.289 |
| Fe7 | 3.221 | 3.222 | 3.210 | 3.208 |
| S1A | 0.183 | 0.182 | 0.200 | 0.199 |
| S2A | -0.014 | -0.019 | -0.013 | -0.018 |
| S4A | 0.164 | 0.161 | 0.169 | 0.167 |
| S1B | 0.084 | 0.084 | 0.079 | 0.079 |
| S3B | 0.273 | 0.270 | 0.279 | 0.275 |
| S4B | 0.106 | 0.105 | 0.099 | 0.098 |
| S2B | 0.012 | 0.015 | 0.009 | 0.013 |
| S5A | 0.014 | 0.019 | -0.008 | -0.004 |
| C* | 0.059 | 0.061 | 0.055 | 0.057 |
| C | -0.001 | 0.000 | -0.005 | -0.005 |
| O3 | 0.041 | 0.043 | 0.026 | 0.027 |
| O1 | -0.020 | -0.022 | -0.008 | -0.009 |
| O2 | -0.001 | -0.001 | 0.000 | 0.000 |

*Table S 26: Comparison of metal-metal distances in different X-ray structures of MoFe: the deviation of metal-metal distances of each FeMoco unit in various X-ray structures to one FeMoco unit in the 1.0 Å resolution crystal structure (PDB ID: 3U7Q).*

| Resolution [Å] | 1.00 | 1.16 | 1.16 | 1.16 | 1.16 | 1.43 | 1.43 | QM/MM |
|---|---|---|---|---|---|---|---|---|
| PDB ID | 3U7Q | 1M1N[b] | 1M1N[b] | 1M1N[b] | 1M1N[b] | 4TKU[c] | 4TKU[c] | 367 QM atoms[d] |
| FeMoco unit number[a] | 2 | 1 | 2 | 3 | 4 | 1 | 2 | |
| Fe1-Fe2 | -0.012 | -0.004 | 0.008 | -0.012 | -0.001 | -0.006 | 0.001 | 0.021 |
| Fe1-Fe3 | 0.005 | -0.004 | 0.010 | -0.001 | -0.002 | -0.003 | -0.001 | 0.034 |
| Fe1-Fe4 | -0.007 | 0.004 | 0.002 | -0.006 | -0.005 | 0.004 | 0.007 | 0.013 |
| Mo-Fe6 | 0.007 | 0.002 | 0.004 | 0.011 | -0.001 | 0.017 | 0.015 | 0.025 |
| Mo-Fe7 | 0.005 | -0.005 | -0.002 | -0.007 | -0.006 | 0.014 | 0.005 | 0.055 |
| Mo-Fe5 | 0.003 | -0.003 | 0.001 | 0.014 | 0.001 | 0.010 | 0.004 | 0.022 |
| Fe2-Fe3 | 0.002 | -0.001 | 0.013 | -0.002 | 0.009 | 0.008 | 0.005 | 0.019 |
| Fe3-Fe4 | -0.002 | -0.003 | -0.002 | 0.000 | -0.009 | 0.005 | -0.002 | 0.028 |
| Fe2-Fe4 | 0.000 | 0.001 | 0.013 | -0.003 | 0.003 | 0.017 | 0.015 | 0.026 |
| Fe6-Fe7 | 0.003 | -0.004 | 0.015 | 0.017 | 0.007 | 0.013 | 0.001 | 0.040 |
| Fe5-Fe6 | 0.001 | -0.006 | 0.002 | 0.018 | 0.000 | 0.001 | -0.007 | -0.002 |
| Fe5-Fe7 | -0.002 | 0.004 | 0.006 | 0.011 | 0.008 | 0.004 | -0.008 | 0.010 |
| Fe2-Fe6 | -0.003 | -0.004 | -0.001 | 0.003 | 0.003 | -0.004 | -0.007 | -0.010 |
| Fe3-Fe7 | -0.001 | 0.026 | 0.028 | 0.031 | 0.032 | 0.035 | 0.032 | 0.003 |
| Fe4-Fe5 | -0.006 | -0.032 | -0.041 | -0.041 | -0.035 | -0.030 | -0.034 | -0.011 |
| Absolute average deviation | 0.004 | 0.007 | 0.010 | 0.012 | 0.008 | 0.011 | 0.010 | 0.021 |

[a] As the MoFe protein is a dimer, there are two units of FeMoco per protein.

[b] In the case of 1M1N, there are two units of the MoFe protein in the X-ray structure and therefore 4 units of FeMoco (Reference: Einsle, O. Nitrogenase MoFe-Protein at 1.16 A Resolution: A Central Ligand in the FeMo-Cofactor. *Science.* **2002**, *297* (5587), 1696–1700. https://doi.org/10.1126/science.1073877.)

[c] As the MoFe protein is a dimer, there are two units of FeMoco per protein (Reference: Spatzal, T.; Perez, K. A.; Einsle, O.; Howard, J. B.; Rees, D. C. Ligand Binding to the FeMo-Cofactor: Structures of Co-Bound and Reactivated Nitrogenase. *Science.* **2014**, *345* (6204), 1620–1623.)

[d] From a previous study by us (Reference: Benediktsson, B.; Bjornsson, R. QM/MM Study of the Nitrogenase MoFe Protein Resting State: Broken-Symmetry States, Protonation States, and QM Region Convergence in the FeMoco Active Site. *Inorg. Chem.* **2017**, *56* (21), 13417–13429)