Supporting information for

Application of the energetic span model to the electrochemical catalysis of proton reduction by a diiron azadithiolate complex

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Note about the calculation of transition free energies of electron transfer steps

In CV simulation studies of diiron hydrogenase models,[1–3] it is usually assumed that the electron transfers are fast compared to the proton transfers and the formation and release of H_2. To test the validity of this assumption, it is necessary to calculate the activation energy of an electron transfer, which depends on the driving force ΔG_{ET} and on the reorganization energy λ_{ET} as described by the Marcus' theory (eq. 1).[4,5] More sophisticated refinements of Marcus' theory, which take for instance into account the probability of occupancy of the Fermi levels of the electrode, have been developed but most of the parameters are not practically accessible.[6]

$$\Delta G^{\ddagger}_{ET} = \frac{\lambda_{ET}}{4}\left(1 + \frac{\Delta G_{ET}}{\lambda_{ET}}\right)^2 \qquad (1)$$

The reorganization energy of the electron transfer λ_{ET} corresponds to the total variation in energy due to both the change of geometry of the compound (λ_i) and to the response of the solvent (λ_s), within the solvation sphere of the substrate, consequently to the electron transfer. The inner-sphere reorganization energy (λ_i) can be accurately computed considering a thermodynamic cycle (eq. 2) which takes into account the energy of the oxidized, and reduced, substrate (E^{ox} and E^{red} respectively) for the geometry of the oxidized, and reduced, state of the substrate in the gas phase (R^{ox} and R^{red} respectively). [7,8]

$$\lambda_i = 0.5\ [E^{ox}(R^{red}) - E^{ox}(R^{ox}) + E^{red}(R^{ox}) - E^{red}(R^{red})\ ] \qquad (2)$$

The calculation of the outer-sphere reorganization energy is less straightforward, but a rough estimate can be obtained by considering the substrate as a sphere and the electrode as an infinite plane.[9] Using this procedure, we calculated a total reorganization energy value $\lambda_{ET} \sim 0.8$ eV for both **2** $\rightarrow$ **3** and **5** $\rightarrow$ **6**. This value corresponds to a heterogeneous rate constant of electron transfer at the electrode $k_s > 1$ cm s^{-1},[10] indicating that the electron transfers are fast and therefore not kinetically limiting.

Table S1. Comparison between experimental and calculated geometrical parameters for **1**. Experimental data from ref 16.

	experimental (Å or °) [11]	DFT (Å or °)	absolute error
Fe-Fe	2,515	2,533	0,018
Fe1-S1	2,258	2,3	0,042
Fe1-S2	2,258	2,3	0,042
Fe2-S1	2,258	2,309	0,051
Fe2-S2	2,258	2,309	0,051
Fe1-Coap	1,795	1,79	0,005
Fe2-Coap	1,795	1,789	0,006
S1-CH	1,855	1,874	0,019
S2-CH	1,861	1,874	0,013
C-N	1,401	1,426	0,025
	1,419	1,426	0,007
Fe-S-Fe	67,67	66,7	0,97
	67,7	66,7	1
S-Fe-S	85,08	84,9	0,18
HC-N-CH	117,82	117,1	0,72

	mean abs error	median abs error
distances	0,025363636	0,019

angles	0,7175	0,845

Cartesian coordinates for TS1

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Coordinates from ORCA-job adtHTS

C	4.16945247605324	9.01722174940759	2.47270498262390
C	5.59820113803191	10.94546851715979	1.87710820008900
C	5.34786191163822	9.98991918441226	4.58182732875753
C	7.67637785722816	6.85671175105073	5.62570327217660
C	8.42969680880012	9.36978226950908	5.82944171903318
C	9.93724655105410	7.61147137916490	4.24140283274304
C	6.86187622015669	6.95392978577455	1.33695190634244
H	7.52411163396210	6.11997768338700	1.08653692333323
H	5.90598059090271	6.84562445216877	0.81442111518198
C	8.62752318021701	8.83929872493175	1.40349367731617
H	9.08091885927404	9.47865666498857	0.65996441643597
H	6.62141782370161	8.92461505098769	0.99711157659710
Fe	8.13067262433917	8.20536917940678	4.45672096687603
Fe	5.81333110105709	9.52619582241933	2.90798457066223
N	7.42186015229574	8.22666338163538	0.75848623856267
O	3.09131040844154	8.69164322948740	2.23611599591801
O	5.43475998845622	11.90586912793717	1.26416570064080
O	4.92965818003056	10.46533407614791	5.53961236206190
O	7.40427526862964	5.98699326852636	6.32002121289112
O	8.66713017526846	10.08751541608802	6.69296752101633
O	11.07533490415856	7.48597991328789	4.28205281182625
S	8.22509434052013	9.85283756868032	2.87165849393034
S	6.43845368422896	7.17338981083443	3.07049694197204
H	9.29877873951540	8.03811585825061	1.66600699497511
H	7.58698538203862	8.13950613435610	-0.24100776196294

Cartesian coordinates for TS2

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Coordinates from ORCA-job adtHydNH_TS_MeCN

C	5.26608047508864	11.01018086016596	2.09000927373149
C	6.26120368815226	9.92440943405423	4.39245490381421
C	4.02891516095967	8.94192533122855	3.12068306337431
C	7.74938202648247	8.32179367974841	5.94621492357147
C	8.93450145114124	10.33868172371844	4.74483393602467
C	9.54532408733567	7.78891394276203	3.98647270085865
C	7.19139838009823	6.48616264732391	1.95442317910819
H	8.17714882987588	6.09033960903494	2.20560396726155
H	6.53867282220093	5.66598321514371	1.66616721995516
C	8.35038740732640	8.40614715670747	0.89121248820130
H	8.47316731061848	8.84410710415420	-0.09645661439046
H	6.14237264314682	8.17238183549821	0.95165889087684
Fe	8.05717313514452	8.85771034395585	4.26968472243978
Fe	5.68287247367289	9.37027914190314	2.63327235299778
N	7.26691311996740	7.42112207112018	0.82796784912024
O	5.02460351849654	12.07426749806011	1.75340289353616
O	5.81745645900505	10.55839028213899	5.29405993991514
O	2.97032513986741	8.64933639165898	3.43080959542544
O	7.52254274327966	7.99697082178325	7.01551453947480
O	9.48847016564872	11.30008232784275	5.01049749412107
O	10.49371486126147	7.15899687797058	3.94543359444513
S	7.96602075966261	9.77947680018937	2.05240990450557
S	6.45926110798728	7.25483095096651	3.45788203490491
H	9.28890104305372	7.93851837774941	1.19482242358932
H	5.35189470808827	8.73635325207642	1.11461676259504
H	7.27857648243766	6.92199832304436	-0.05774203945784

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