

Electronic Supporting Information

## In search of metal hydrides: An X-ray absorption and emission study of [NiFe] hydrogenase model complexes

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1. Optimized geometry of **1**
2. Optimized geometry of **2**
3. Hydrogen-optimized geometry of **1\***
4. Hydrogen-optimized geometry of **2\***

### 1. Optimized geometry of **1**

Ni	7.402228000	10.451270000	5.371538000
Fe	5.353534000	11.742933000	4.974958000
P	7.812795000	11.011900000	7.385181000
S	7.288053000	12.046016000	3.757883000
O	3.409040000	11.025969000	7.052446000
C	9.124254000	9.845832000	8.047810000
H	9.641808000	10.299281000	8.904852000
H	8.611821000	8.939041000	8.398394000
P	9.047966000	9.117772000	5.400398000
S	5.537192000	9.492378000	4.597007000
C	10.076390000	9.530631000	6.893352000
H	10.802505000	8.738617000	7.126905000
H	10.647025000	10.426879000	6.603821000
O	5.795225000	14.327475000	6.291433000
O	3.485907000	12.517771000	2.861870000
C	7.109265000	11.248819000	2.106424000
H	6.259061000	11.732270000	1.603006000
H	8.024520000	11.531343000	1.564681000
C	6.960930000	9.733988000	2.112209000
H	7.839297000	9.297360000	2.613091000
H	6.977683000	9.378587000	1.066227000
C	5.687872000	9.221087000	2.773219000
H	5.607011000	8.130207000	2.648669000
H	4.794398000	9.668519000	2.313974000
C	4.194974000	11.297697000	6.248315000
C	5.648952000	13.310414000	5.754442000
C	4.210210000	12.222324000	3.719031000
C	8.623034000	12.631342000	7.718045000
C	8.964920000	13.446742000	6.632966000
H	8.692291000	13.128599000	5.624773000
C	9.642161000	14.651747000	6.837923000
H	9.894948000	15.281604000	5.983907000
C	9.985366000	15.049844000	8.131245000
H	10.510244000	15.992469000	8.293607000
C	9.651434000	14.239188000	9.221998000
H	9.916562000	14.547360000	10.234647000
C	8.977018000	13.035309000	9.017428000
H	8.710670000	12.412852000	9.874103000
C	6.474779000	10.888218000	8.628700000
C	5.880925000	12.013341000	9.220402000
H	6.263294000	13.010863000	9.002502000
C	4.784848000	11.863807000	10.073165000
H	4.326093000	12.747532000	10.518870000

C	4.269994000	10.594541000	10.344395000
H	3.409702000	10.481209000	11.005521000
C	4.844447000	9.471116000	9.742045000
H	4.431146000	8.478677000	9.927195000
C	5.930988000	9.617032000	8.881148000
H	6.336976000	8.740611000	8.370534000
C	10.270314000	9.134689000	4.030405000
C	10.962769000	7.990695000	3.605987000
H	10.768891000	7.028217000	4.081774000
C	11.891657000	8.080057000	2.565878000
H	12.421066000	7.185015000	2.235428000
C	12.141832000	9.309469000	1.950096000
H	12.865222000	9.375281000	1.135640000
C	11.456207000	10.453354000	2.372647000
H	11.644213000	11.414358000	1.891391000
C	10.518830000	10.365207000	3.401656000
H	9.948880000	11.243114000	3.716504000
C	8.630197000	7.338887000	5.590209000
C	9.009422000	6.564958000	6.696909000
H	9.630348000	6.989743000	7.486308000
C	8.597100000	5.233040000	6.808656000
H	8.894459000	4.648324000	7.680805000
C	7.812248000	4.653778000	5.810550000
H	7.488841000	3.615987000	5.899733000
C	7.440038000	5.413782000	4.695942000
H	6.827257000	4.969913000	3.909571000
C	7.838748000	6.744181000	4.592807000
H	7.531386000	7.336955000	3.731156000

## 2. Optimized structure of **2**

Ni	9.094019000	11.316427000	15.107097000
Fe	8.223386000	11.917921000	12.746345000
H	8.797913000	12.679378000	14.056964000
S	9.972506000	10.439677000	13.266874000
S	7.063242000	10.727531000	14.417644000
P	11.059882000	11.885431000	15.784209000
P	8.309394000	12.178904000	16.915054000
O	6.148950000	13.980418000	12.693377000
O	7.213213000	10.345579000	10.467992000
O	10.110315000	13.589624000	11.257169000
C	11.881075000	12.968224000	14.578159000
C	11.509206000	14.321006000	14.493474000
H	10.779692000	14.739566000	15.188770000
C	12.067579000	15.141558000	13.515663000
H	11.779680000	16.191819000	13.460016000
C	12.987754000	14.615845000	12.603159000
H	13.418399000	15.257006000	11.833610000
C	13.348951000	13.268821000	12.672969000
H	14.063907000	12.856021000	11.960263000
C	12.798470000	12.442646000	13.654636000
H	13.086919000	11.393081000	13.708811000
C	12.235122000	10.550763000	16.158565000
C	13.544291000	10.857376000	16.567495000
H	13.878647000	11.895461000	16.612177000
C	14.426604000	9.829509000	16.900581000
H	15.442538000	10.070006000	17.214972000
C	14.010934000	8.495585000	16.828095000
H	14.704742000	7.695297000	17.087654000
C	12.710411000	8.188023000	16.420792000
H	12.386690000	7.148114000	16.360734000
C	11.824220000	9.213731000	16.086401000
H	10.808441000	8.988188000	15.759435000
C	8.191883000	11.010814000	18.304592000
C	8.524707000	9.665395000	18.097094000
H	8.813132000	9.342234000	17.095092000

C	8.492829000	8.761063000	19.160172000
H	8.756397000	7.715920000	18.994102000
C	8.124976000	9.198267000	20.434719000
H	8.099427000	8.493839000	21.266960000
C	7.786878000	10.539597000	20.647397000
H	7.495032000	10.878952000	21.641711000
C	7.819882000	11.446525000	19.588702000
H	7.541057000	12.487898000	19.759076000
C	6.715403000	13.030081000	16.769506000
C	6.649221000	14.189402000	15.978137000
H	7.545851000	14.576378000	15.490124000
C	5.429269000	14.834121000	15.782093000
H	5.384670000	15.731294000	15.164874000
C	4.265814000	14.318924000	16.360646000
H	3.311185000	14.821404000	16.202460000
C	4.323388000	13.154802000	17.131234000
H	3.414595000	12.746008000	17.573577000
C	5.542278000	12.505627000	17.334209000
H	5.580019000	11.592078000	17.928000000
C	9.385594000	8.714997000	13.004535000
H	9.027543000	8.651580000	11.966346000
H	10.301296000	8.112058000	13.083820000
C	8.333368000	8.214945000	13.983266000
H	8.145865000	7.147885000	13.774239000
H	8.728314000	8.279181000	15.010561000
C	7.007511000	8.958991000	13.912520000
H	6.281432000	8.509560000	14.604470000
H	6.579597000	8.919744000	12.899937000
C	6.959934000	13.162810000	12.726327000
C	7.606179000	10.957188000	11.362668000
C	9.369310000	12.930128000	11.841590000
C	10.922653000	12.855114000	17.372409000
H	11.104845000	12.127642000	18.176401000
H	11.713766000	13.616424000	17.415639000
C	9.521504000	13.454012000	17.496680000
H	9.394039000	14.334869000	16.853257000
H	9.286285000	13.754327000	18.527094000

### 3. Hydrogen-optimized geometry of 1\*

Ni	9.094019000	11.316427000	15.107097000
Fe	8.223386000	11.917921000	12.746345000
S	9.972506000	10.439677000	13.266874000
S	7.063242000	10.727531000	14.417644000
P	11.059882000	11.885431000	15.784209000
P	8.309394000	12.178904000	16.915054000
O	6.148950000	13.980418000	12.693377000
O	7.213213000	10.345579000	10.467992000
O	10.110315000	13.589624000	11.257169000
C	11.881075000	12.968224000	14.578159000
C	11.509206000	14.321006000	14.493474000
H	10.779692000	14.739566000	15.188770000
C	12.067579000	15.141558000	13.515663000
H	11.779680000	16.191819000	13.460016000
C	12.987754000	14.615845000	12.603159000
H	13.418399000	15.257006000	11.833610000
C	13.348951000	13.268821000	12.672969000
H	14.063907000	12.856021000	11.960263000
C	12.798470000	12.442646000	13.654636000
H	13.086919000	11.393081000	13.708811000
C	12.235122000	10.550763000	16.158565000
C	13.544291000	10.857376000	16.567495000
H	13.878647000	11.895461000	16.612177000
C	14.426604000	9.829509000	16.900581000
H	15.442538000	10.070006000	17.214972000
C	14.010934000	8.495585000	16.828095000

H	14.704742000	7.695297000	17.087654000
C	12.710411000	8.188023000	16.420792000
H	12.386690000	7.148114000	16.360734000
C	11.824220000	9.213731000	16.086401000
H	10.808441000	8.988188000	15.759435000
C	8.191883000	11.010814000	18.304592000
C	8.524707000	9.665395000	18.097094000
H	8.813132000	9.342234000	17.095092000
C	8.492829000	8.761063000	19.160172000
H	8.756397000	7.715920000	18.994102000
C	8.124976000	9.198267000	20.434719000
H	8.099427000	8.493839000	21.266960000
C	7.786878000	10.539597000	20.647397000
H	7.495032000	10.878952000	21.641711000
C	7.819882000	11.446525000	19.588702000
H	7.541057000	12.487898000	19.759076000
C	6.715403000	13.030081000	16.769506000
C	6.649221000	14.189402000	15.978137000
H	7.545851000	14.576378000	15.490124000
C	5.429269000	14.834121000	15.782093000
H	5.384670000	15.731294000	15.164874000
C	4.265814000	14.318924000	16.360646000
H	3.311185000	14.821404000	16.202460000
C	4.323388000	13.154802000	17.131234000
H	3.414595000	12.746008000	17.573577000
C	5.542278000	12.505627000	17.334209000
H	5.580019000	11.592078000	17.928000000
C	9.385594000	8.714997000	13.004535000
H	9.027543000	8.651580000	11.966346000
H	10.301296000	8.112058000	13.083820000
C	8.333368000	8.214945000	13.983266000
H	8.145865000	7.147885000	13.774239000
H	8.728314000	8.279181000	15.010561000
C	7.007511000	8.958991000	13.912520000
H	6.281432000	8.509560000	14.604470000
H	6.579597000	8.919744000	12.899937000
C	6.959934000	13.162810000	12.726327000
C	7.606179000	10.957188000	11.362668000
C	9.369310000	12.930128000	11.841590000
C	10.922653000	12.855114000	17.372409000
H	11.104845000	12.127642000	18.176401000
H	11.713766000	13.616424000	17.415639000
C	9.521504000	13.454012000	17.496680000
H	9.394039000	14.334869000	16.853257000
H	9.286285000	13.754327000	18.527094000

#### 4. Hydrogen-optimized geometry of 2\*

Ni	7.401498000	10.451412000	5.371428000
Fe	5.352835000	11.743028000	4.974532000
P	7.811799000	11.012131000	7.385101000
S	7.287506000	12.046090000	3.757692000
O	3.408086000	11.026121000	7.051801000
C	9.123190000	9.846110000	8.047946000
H	9.624637000	10.327059000	8.897953000
H	8.614089000	8.942830000	8.409905000
P	9.047252000	9.117940000	5.400554000
S	5.536575000	9.492460000	4.596698000
C	10.075479000	9.530875000	6.893622000
H	10.783835000	8.720720000	7.111059000
H	10.662097000	10.418253000	6.610358000
O	5.794319000	14.327631000	6.290957000
O	3.485467000	12.517751000	2.861173000
C	7.108941000	11.248822000	2.106243000
H	6.266731000	11.740682000	1.599537000
H	8.029480000	11.535135000	1.577230000

C	6.960628000	9.733989000	2.112072000
H	7.842798000	9.289534000	2.598289000
H	6.962989000	9.386669000	1.064983000
C	5.687493000	9.221096000	2.772940000
H	5.606723000	8.129863000	2.661820000
H	4.788875000	9.659759000	2.316725000
C	4.194119000	11.297827000	6.247759000
C	5.648130000	13.310546000	5.753989000
C	4.209665000	12.222350000	3.718439000
C	8.621971000	12.631599000	7.718001000
C	8.963984000	13.446960000	6.632932000
H	8.701689000	13.134608000	5.620490000
C	9.641181000	14.651983000	6.837926000
H	9.896765000	15.279948000	5.984032000
C	9.984214000	15.050139000	8.131276000
H	10.509600000	15.991826000	8.292707000
C	9.650154000	14.239523000	9.222020000
H	9.913975000	14.544251000	10.235020000
C	8.975783000	13.035625000	9.017413000
H	8.710079000	12.416214000	9.876244000
C	6.473625000	10.888481000	8.628453000
C	5.879679000	12.013619000	9.220033000
H	6.266630000	13.011759000	9.012502000
C	4.783494000	11.864104000	10.072662000
H	4.332213000	12.747330000	10.525360000
C	4.268624000	10.594842000	10.343878000
H	3.412462000	10.480847000	11.009323000
C	4.843171000	9.471400000	9.741648000
H	4.436090000	8.478326000	9.933250000
C	5.929821000	9.617297000	8.880884000
H	6.340754000	8.735355000	8.383614000
C	10.269776000	9.134818000	4.030717000
C	10.962302000	7.990817000	3.606435000
H	10.767278000	7.026372000	4.077098000
C	11.891322000	8.080150000	2.566441000
H	12.420112000	7.184404000	2.239672000
C	12.141557000	9.309540000	1.950640000
H	12.864644000	9.375887000	1.136784000
C	11.455861000	10.453432000	2.373056000
H	11.647141000	11.414506000	1.894362000
C	10.518354000	10.365314000	3.401948000
H	9.964585000	11.252120000	3.718195000
C	8.629485000	7.339056000	5.590385000
C	9.008580000	6.565179000	6.697166000
H	9.632369000	6.982211000	7.488394000
C	8.596264000	5.233259000	6.808915000
H	8.899395000	4.648876000	7.678334000
C	7.811548000	4.653944000	5.810732000
H	7.489900000	3.616063000	5.898552000
C	7.439469000	5.413896000	4.696045000
H	6.832316000	4.967894000	3.907197000
C	7.838173000	6.744297000	4.592906000
H	7.537948000	7.330080000	3.723549000
H	6.423012000	11.414494000	6.177720000