Supporting Information
for

^{1}H-ENDOR Evidence for a Hydrogen Bonding Interaction That Modulates the Reactivity of a Nonheme Fe^{IV}=O Unit

Muralidharan Shanmugam,[H] Genqiang Xue,[I] Lawrence Que Jr.,[I]* Brian M. Hoffman[H]*

[H]*Chemistry Department, Northwestern University, Evanston, Illinois, 60208-3113,* [I]*Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, Minnesota-55455*

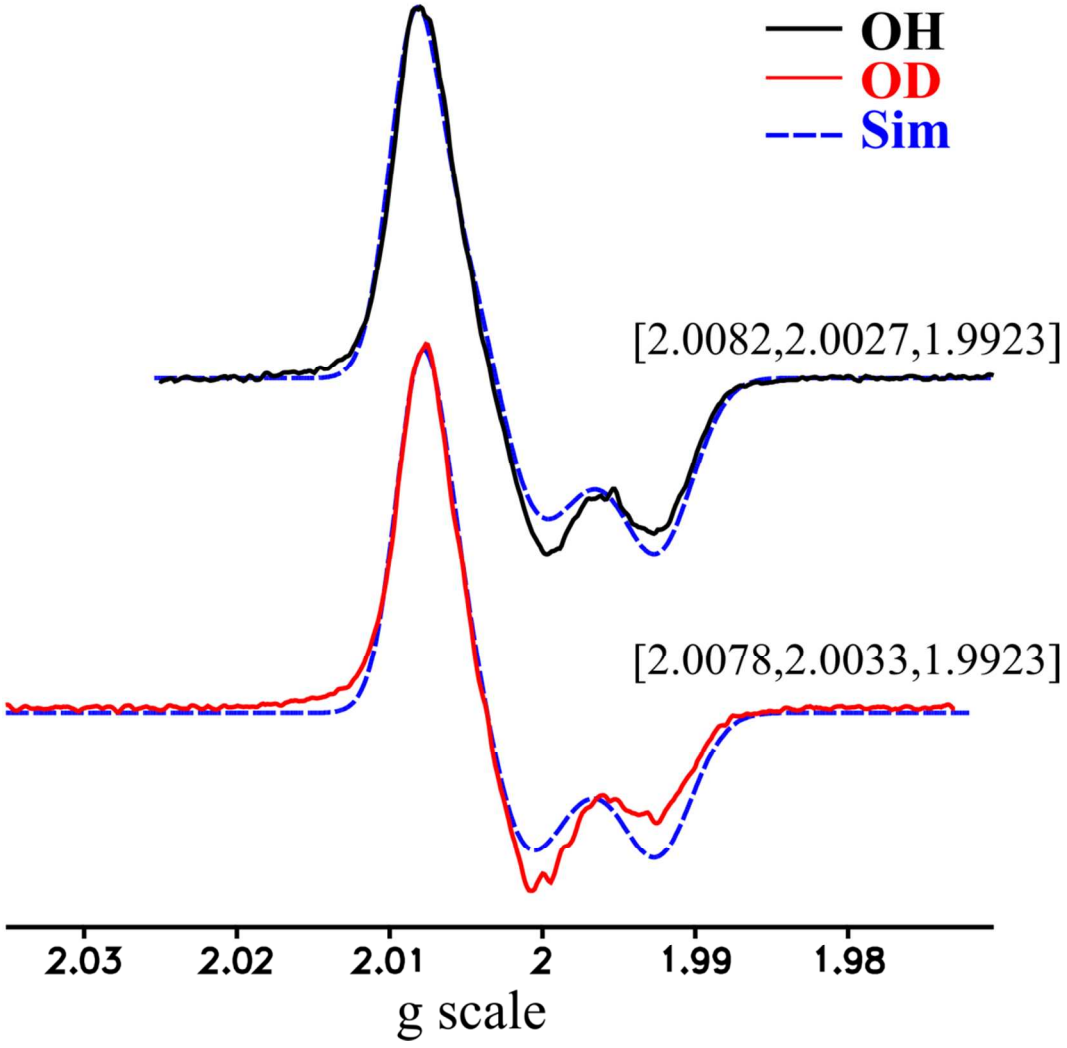

Fig S1: Solid lines: Echo-detected 35 GHz EPR spectra of **1** in OH/OD. Derivative spectra generated by numerical derivatives of absorption-display spectra. **Dashed lines:** Simulations performed using WIN-EPR program; g-values for the fits are listed. *Conditions:* Two-pulse echo, π-pulse = 80 ns, τ = 600 ns, repetition time = 50 ms, 34.698 GHz (OH), 34.75 GHZ (OD), T = 2 K.

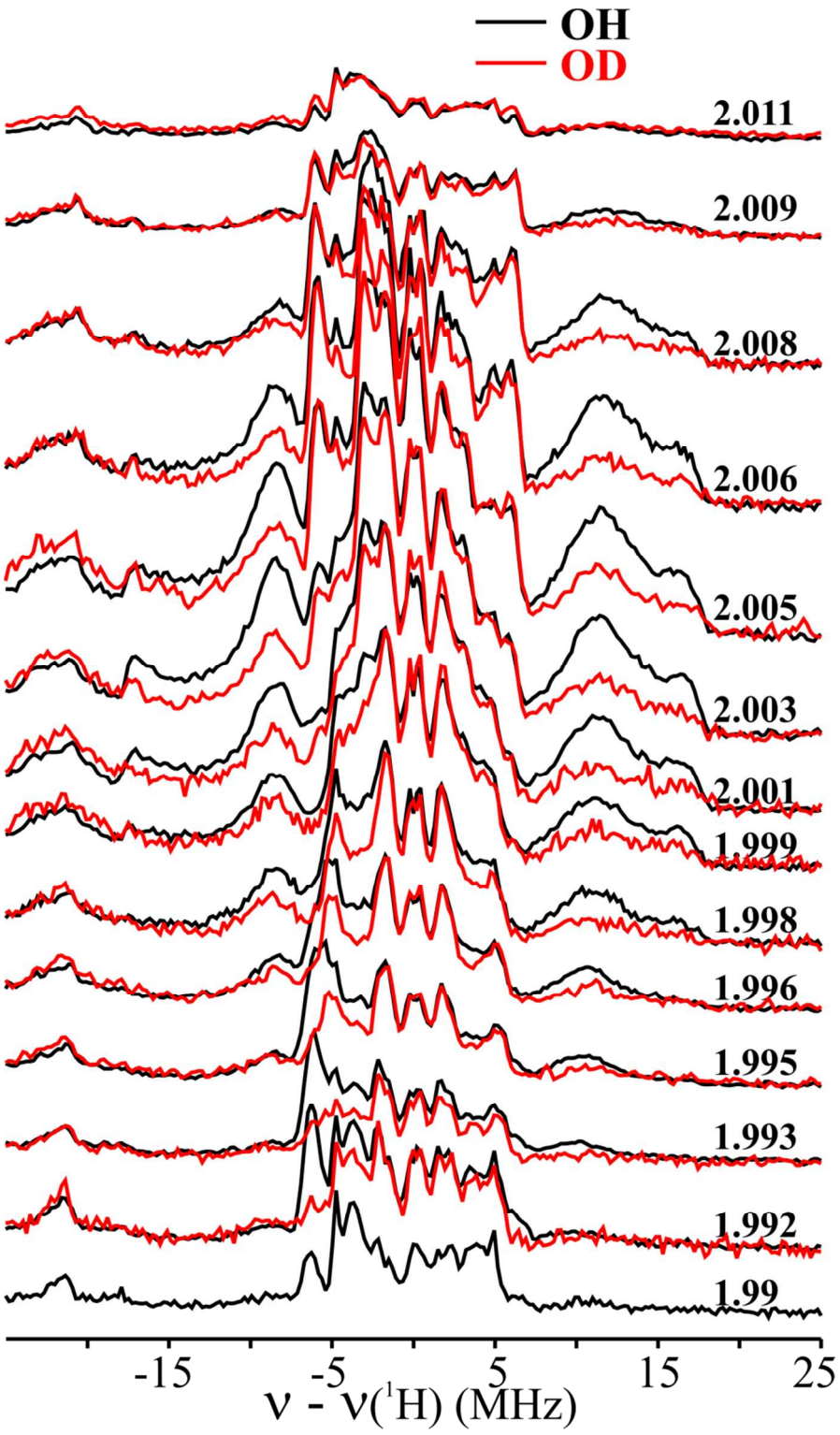

Fig S2: Experimental 2-D field-frequency plot of Davies ^{1}H-ENDOR spectra of **1** in OH (black) and OD (red). All spectra have been centered at ^{1}H nuclear Larmor frequency. *Conditions:* π pulse length = 120 ns, τ = 600 ns, repetition time = 40 ms, 34.698 GHz (OH), 34.75 GHz (OD), T = 2 K.

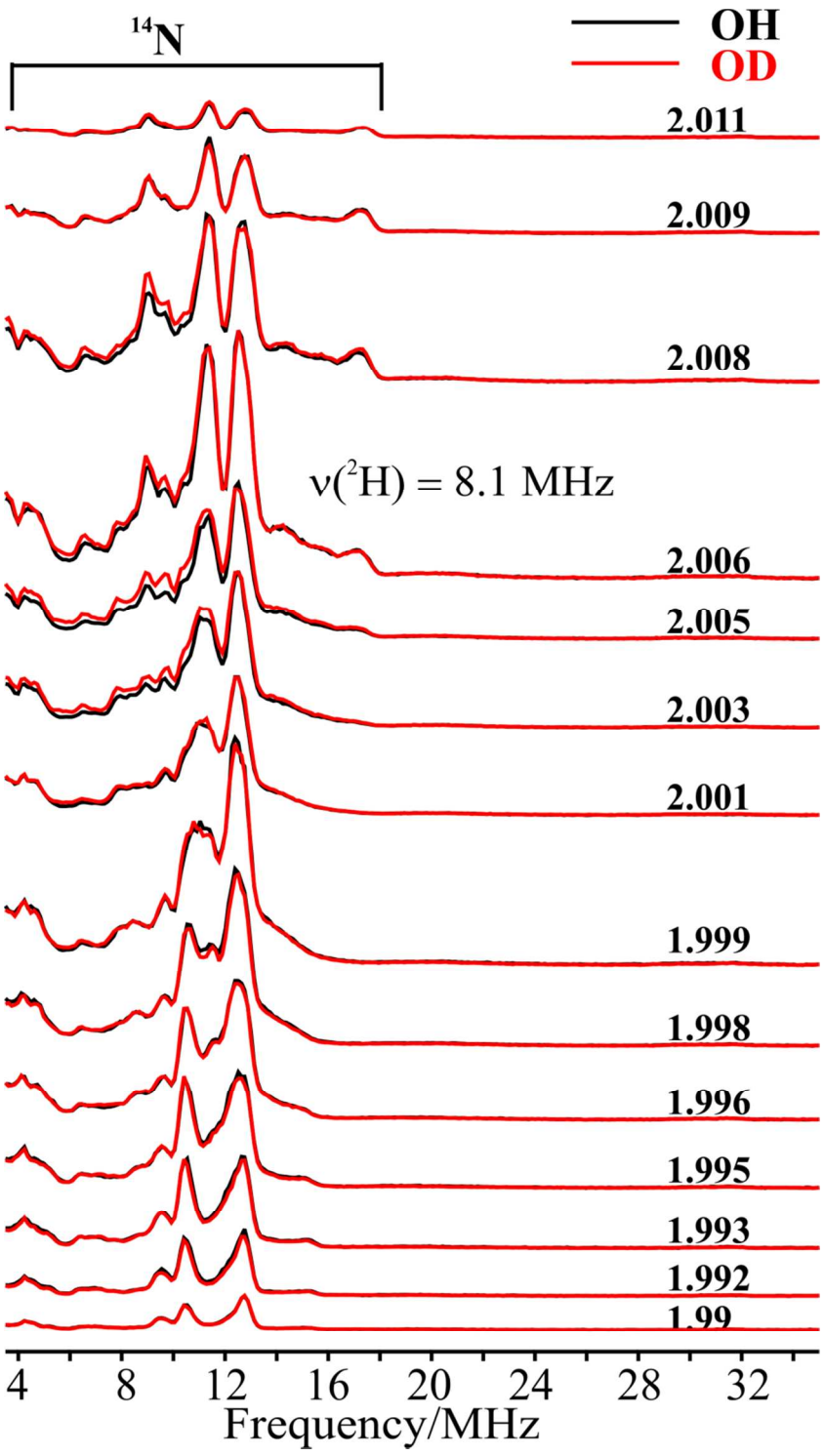

Fig S3: Experimental 2-D field-frequency plot of Davies ^{14}N-ENDOR spectra of **1** in OH (black) and OD (red). *Conditions:* π pulse length = 120 ns, τ = 600 ns, repetition time = 40 ms, 34.713 GHz (OH), 34.722 GHz (OD), T = 2 K.

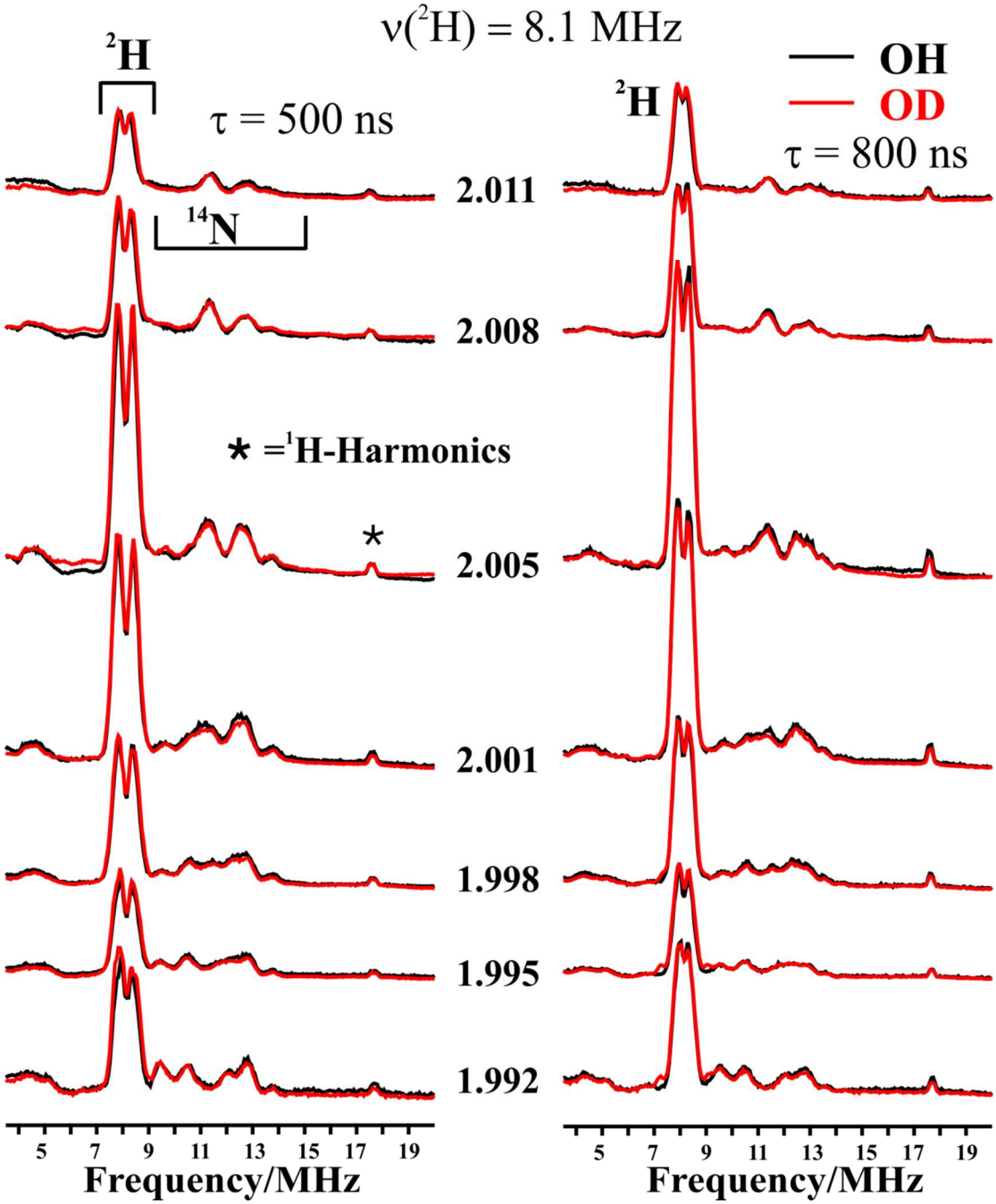

Fig S4: Experimental 2-D field-frequency plot of Mims ^{2}H and ^{14}N-ENDOR spectra of **1** in OH (black) and OD (red). The ^{2}H-doublet centered at ν_D arises from the deuterated methylene arms of **L** (**Scheme 1**). *Conditions: π/2* pulse length = 50 ns, repetition time = 40 ms, 34.713 GHz (OH), 34.722 GHz (OD), T = 2 K.

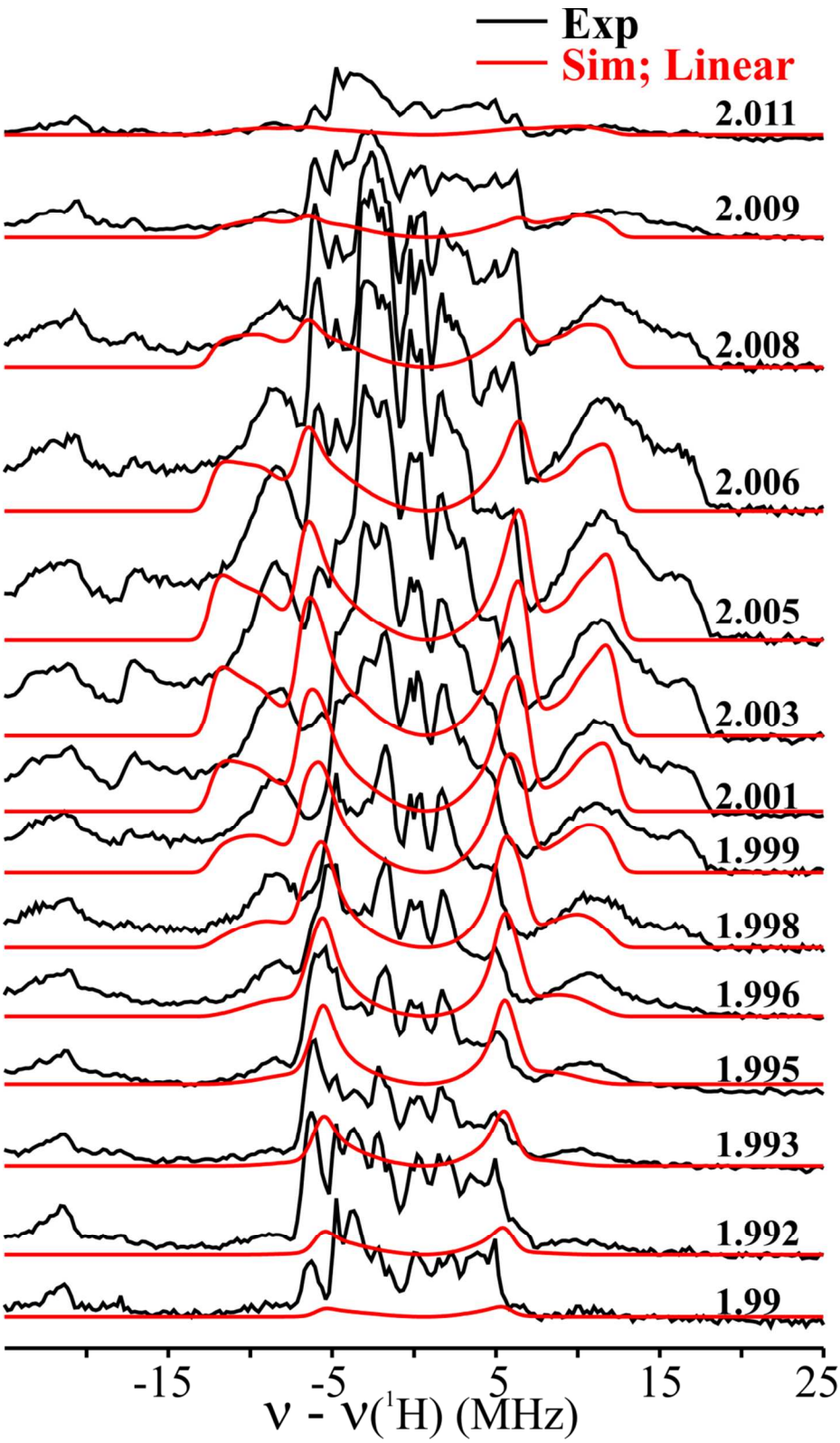

Fig S5: Comparisons of experimental 2-D ^{1}H-ENDOR pattern of **1**(OH) with simulation performed by assuming a liner Fe(III)-μ(O)-Fe(IV) geometry. The metrical and Spin-Hamiltonian parameters used to do the simulation are given in table **S1**.

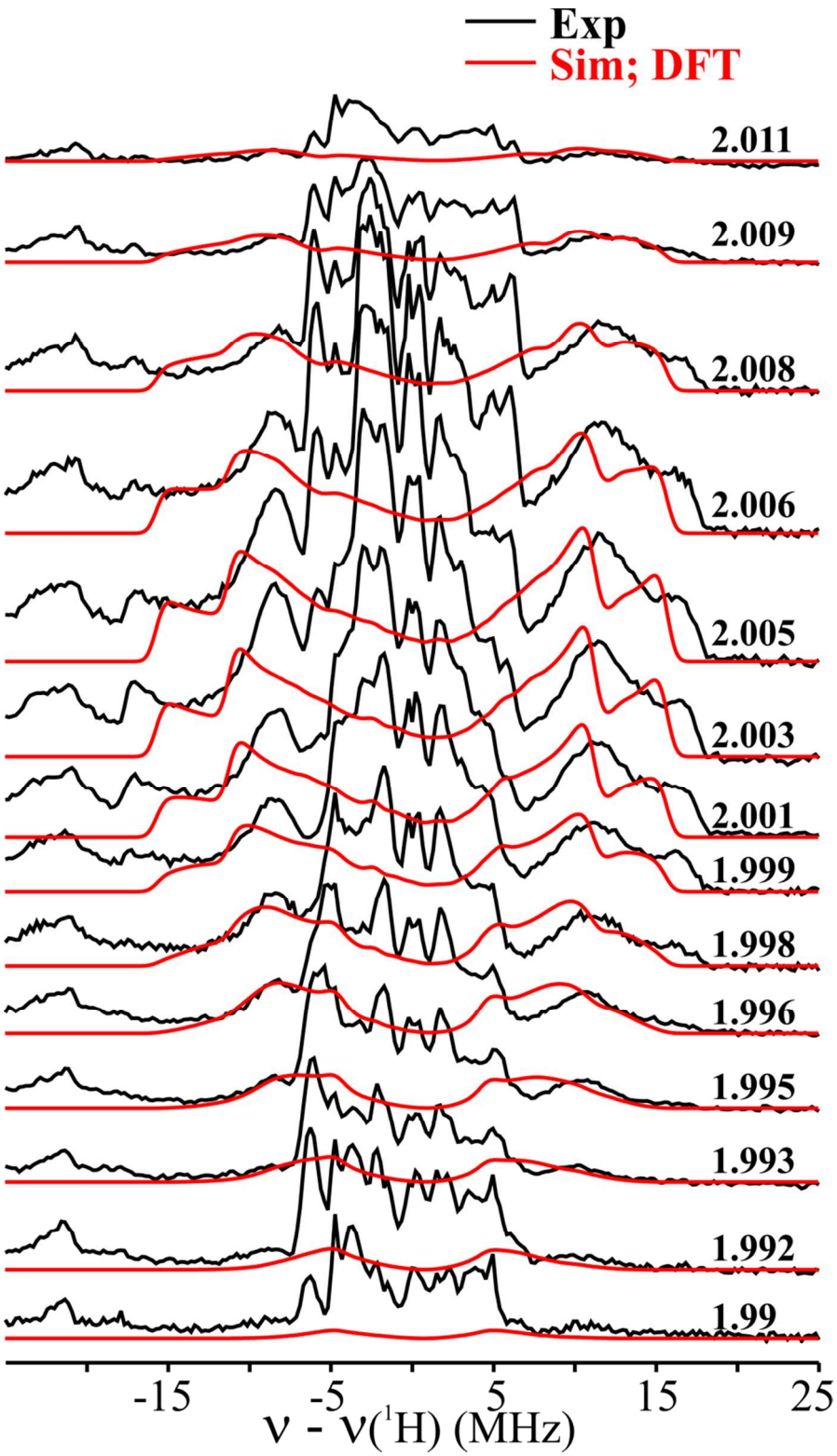

Fig S6: Comparisons of experimental 2-D ^{1}H-ENDOR pattern of **1**(OH) with simulation performed by assuming DFT optimized location of $^{1}H_{A}$, whose metrical and Spin-Hamiltonian parameters are given in table **S1**.

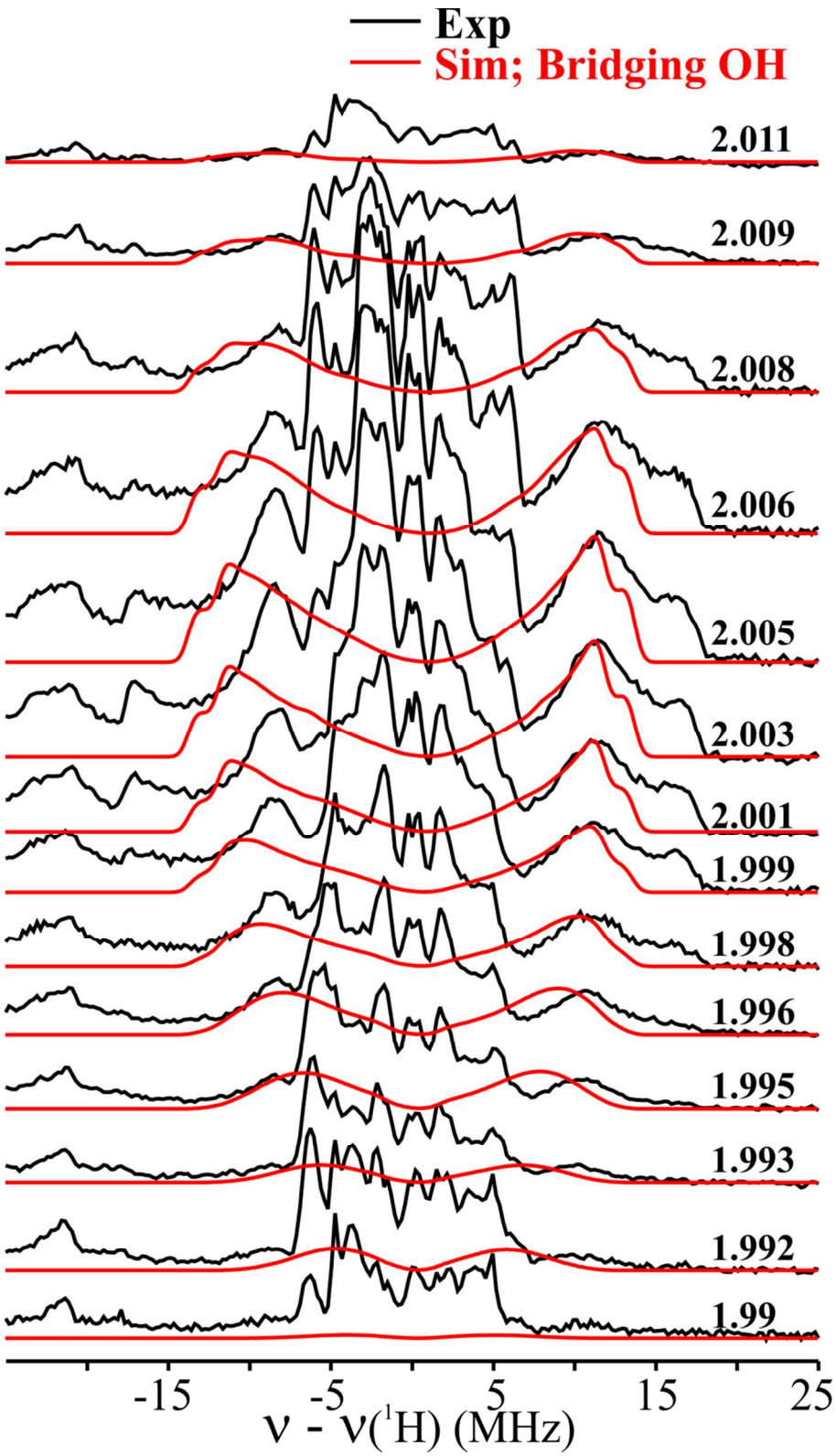

Fig S7: Comparisons of experimental 2-D ^{1}H-ENDOR pattern of **1**(OH) with simulation performed by assuming a bridging μ(OH) hydroxide, by adding to proton to a μ(O) bridge, whose metrical and Spin-Hamiltonian parameters are given in table **S1**.

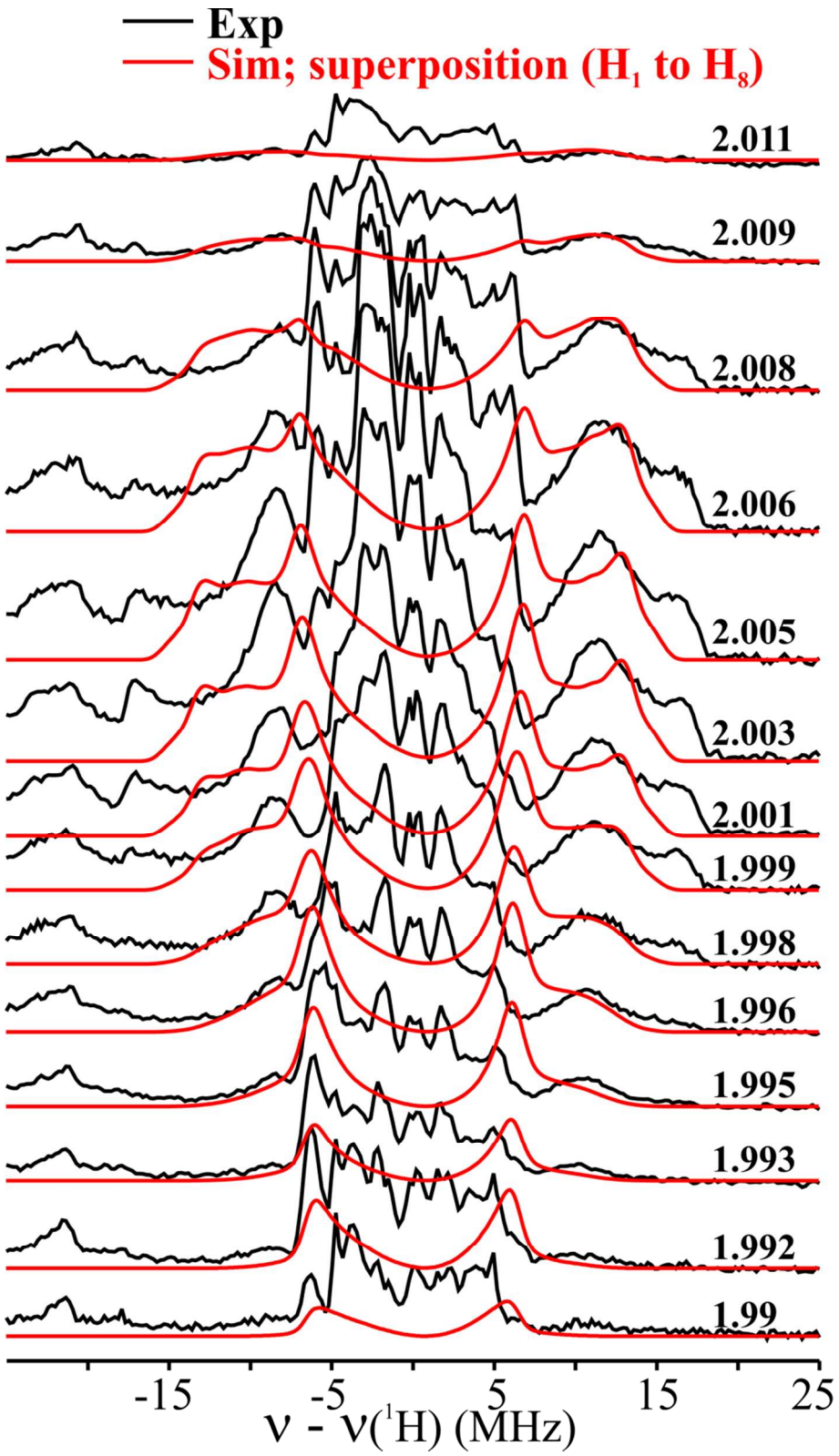

Fig S8: Comparisons of experimental 2-D ^{1}H-ENDOR pattern of **1**(OH) with simulation performed by assuming $^{1}H_A$ to be randomly rotated around the Fe(III)-O bond, with the superposition 2-D spectra obtained by summing the simulations, corresponding to multiple $^{1}H_A$ orientations whose metrical and dipolar tensors are given in table **S2**.

Table S1: Metrical and ^{1}H Spin-Hamiltonian Parameters used to simulate 2-D pattern for ^1H_A

^1H_A Hyperfine tensors						
Metrical Parameters	Experiment[a] $\mathbf{A_{exp}}$	$\mathbf{T_{exp}}$	**T:** Modified DFT[b]	**T:** Linear[c] geometry	**T:** DFT[d]	**T:** Bridging[e] OH
A_1/T_1 (MHz)	-25	-24.3	-24.3	-14.0	-22.4	-23.7
A_2/T_2 (MHz)	-12	-11.3	-11.3	-10.9	-9.0	-3.7
A_3/T_3 (MHz)	34.8	+35.6	+35.6	+24.9	+31.4	+27.4
a_{iso} (MHz)	-	0	0	0	0	0
$\lambda = (T_2\text{-}T_1)/T_3$	0.73	0.365	0.365	0.126	0.427	0.73
$d_{Fe\text{-}Fe}$ (Å)				3.7	3.341	3.341
r_1 (Å)			**2.198**	**2.387**	**2.387**	**2.52**
(β_1) (deg)			**53.8**	**80.6**	**56.6**	**44.4**
γ (deg)				78.4	53.8	43.1
r_2 (Å)				4.1	2.843	2.341
(β_2) (deg)				144.5	135.5	131.1

[a] Tensor used in simulations of experiment, **Figure 2**, using **g** = [2.008, 2.003, 1.992].

[b] Tensor calculated using Fe-Fe distance from DFT optimized geometry[1] with slightly repositioned ^1H_A exactly matches **T** derived from experiment.

[c] Tensor calculated using metrical parameters of DFT optimized[1] geometry of **1** as modified by linearizing the Fe-O-Fe fragment. Simulations with this tensor, **Figure S5** do not match.

[d] Tensor calculated using metrical parameters of DFT optimized[1] geometry of **1**; simulations with this tensor, **Figure S6** do not match.

[e] Tensor calculated using metrical parameters of DFT optimized[1] geometry of **1** as modified by adding a proton to a μ(O)-bridge. Simulations with this tensor, **Figure S7**, do not match.

Table S2: Metrical and ^{1}H Spin-Hamiltonian Parameters used to simulate the superposition 2-D ^{1}H-ENDOR pattern displayed in Figure **S8**.

	DFT Optimized geometry for **X**-Model							
Metrical Parameters	H_1 (DFT)	H_2 (+45°)	H_3 (-44°)	H_4 (+89°)	H_5 (-87°)	H_6 (+124°)	H_7 (-121°)	H_8 (+141°)
A_1/T_1 (MHz)	-22.4	-18.6	-20.5	-15.5	-16.6	-14.5	-14.9	-14.3
A_2/T_2 (MHz)	-9.0	-10.6	-9.8	-11.9	-11.4	-12.3	-12.2	-12.4
A_3/T_3 (MHz)	+31.4	+29.2	+30.3	+27.4	+28.0	+26.8	+27.1	+26.7
a_{iso} (MHz)	0	0	0	0	0	0	0	0
$\lambda = (T_2\text{-}T_1)/T_3$	0.427	0.274	0.353	0.131	0.186	0.082	0.10	0.071
$d_{Fe\text{-}Fe}$ (Å)	3.341							
r_1 (Å)	2.387							
(β_1) (deg)	**56.6**	**68.0**	**61.3**	**86.5**	**77.7**	**99.4**	**93.1**	**102.3**
γ (deg)	53.8	64.6	58.1	83.4	74.4	83.1	89.7	80.1
r_2 (Å)	2.843	3.3	3.0	4.0	3.7	4.4	4.2	4.5
(β_2) (deg)	135.5	137.9	136.3	143.3	140.5	147.7	145.5	148.8

References:

(1) De Hont, R. F.; Xue, G.; Hendrich, M. P.; Que, L.; Bominaar, E. L.; Munck, E. *Inorg. Chem.* **2010**, *49*, 8310-8322.