Supporting Information

L-Tryptophan Radical Cation Electron Spin Resonance Studies: Connecting Solution-derived Hyperfine Coupling Constants with Protein Spectral Interpretations

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Table 4. Values of dihedral angles (θ_1 and θ_1 - 120°) and ρ_C^{π} B" (mT) calculated from reported β-methylene hydrogen HFCs (a_β^H (1) and a_β^H (2) in mT) for L-tyrosine radicals in proteins.

Protein- L-Tyrosine free radical	a_β^H (1)	a_β^H (2)	Θ 1	Θ 1-120	ρ_C^{π} B"	Reference
Bovine liver catalase	0.61	0.41	56.6	-63.4	2.02	[1]
Bovine liver catalase	0.47	0.62	62.1	-57.9	2.17	[2]
C. reinhardtii PSII	0.20	1.07	72.7	-47.3	2.32	[3]
C. synechocystis TD PSII	0.75	0.28	52.0	-68.0	1.99	[4]
E. coli RNR	2.01	0.08	19.2	-100.8	2.26	[5]
E. coli RNR WT R2 W191G	1.03	0.23	48.2	-71.8	2.32	[6]
Horse metMb	1.67	1.42	-25.8	-145.8	2.07	[7]
M. tuberculosis KatG	0.19	0.93	47.5	-72.48	2.06	[8]
Mouse RNR	1.95	0.49	0.0	-120.0	1.96	[9]
Mouse RNR WT R2 Y177	2.06	0.59	-2.2	-122.2	2.07	[10]
P. denitrificans CCO	1.59	1.37	-26.1	-146.1	1.98	[11]
P. laminosum PSII	0.29	0.93	69.3	-50.7	2.31	[4]
Ram seminal vesicle PGHS	1.82	0.02	24.5	-95.5	2.20	[12,13]
Ram seminal vesicle PGHS	2.12	0.13	16.6	-103.4	2.32	[14]
Ram seminal vesicle PGHS	1.07	0.14	44.8	-75.2	2.14	[14]
Spinach PSII	1.01	0.19	47.1	-72.9	2.19	[1]
Spinach PSII	1.01	0.20	47.4	-72.6	2.21	[15]
Spinach PSII	0.23	1.03	71.7	-48.3	2.31	[3,16]
Synechocystis 6803 PSII	1.11	0.13	43.9	-76.1	2.15	[16]
Synechocystis PSII	0.79	0.25	50.8	-69.2	1.98	[9]
Synechocystis PSII	0.83	0.30	51.6	-68.4	2.17	[6]
E. coli RNR[a]	2.01	0.01	26.0	-94.0	2.49	[9]
E. coli RNR[a]	2.06	0.02	24.9	-95.1	2.51	[10]
M. tuberculosis KatG[b]	0.60	0.60	60.0	60.0	2.40	[8]
Ram seminal vesicle PGHS[a]	1.90	0.01	26.3	-93.7	2.36	[13]
Bovine SOD[b]	1.17	0.22	47.1	-72.9	2.54	[17]
S. oligorrhiza PSII[b]	0.80	0.18	48.3	-71.7	1.82	[18]

[a] Irregular ρ_C^{π} B" values due to a coupling that is less than the ESR linewidth and could be adjusted to give an appropriate ρ_C^{π} B" value (< 2.35 mT)

[b] Irregular ρ_C^{π} B" values for unknown reasons

Abbreviations: PSII, photosystem II; RNR, ribonucleotide reductase; metMB, metmyoglobin; KatG, catalase-peroxidase; CCO, cytochrome c oxidase; PGHS, prostaglandin H synthase; SOD, superoxide dismutase

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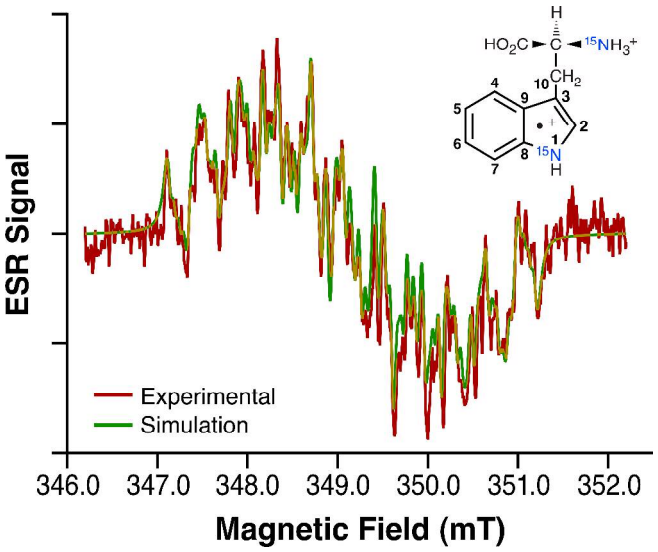

Fig. 6 L-[$^{15}N_2$]tryptophan radical cation ESR spectrum.
ESR fast-flow spectrum of L- [$^{15}N_2$]tryptophan radical cation produced in a system of $^{15}N_2$ L-tryptophan, Ce^{4+}, and H_2SO_4 having concentrations of 0.5 mM, 0.25 mM, and 0.225 M, respectively. Equal volumes of aqueous solutions of indole ^{15}N L-tryptophan/ H_2SO_4 and Ce^{4+}/ H_2SO_4 were mixed milliseconds before entering the ESR flat cell at a total flow rate of 40 mL/min. ESR spectra were recorded at 20 mW microwave power, 0.05 mT field modulation, 6.0 mT field sweep width, 163 ms time constant, 81 ms conversion time and 123 scans of 1024 data points (*Red*). Also shown is the L-[$^{15}N_2$]tryptophan radical cation simulation spectrum produced using coupling constants given in Table 1 (*Green*).

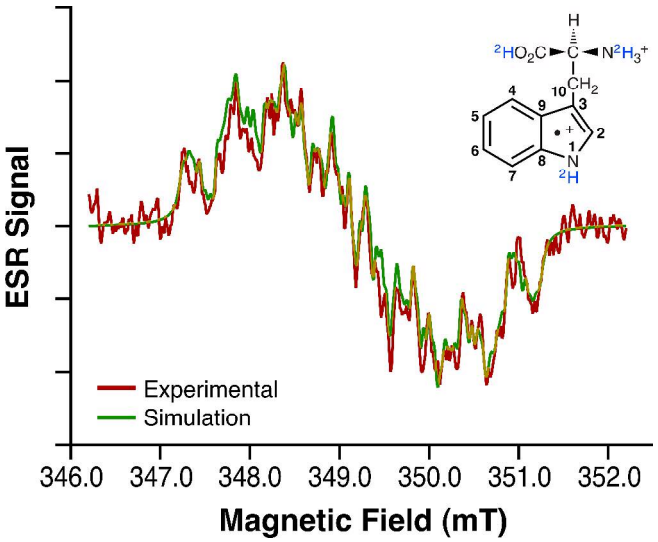

Fig. 7 L-Tryptophan radical cation in ^2H_2O ESR spectrum.
ESR fast-flow spectrum of L-tryptophan radical cation produced in a system of L-tryptophan, Ce^{4+}, and $^2H_2SO_4$ having concentrations of 0.5 mM, 0.25 mM, and 0.225 M, respectively, with ^2H_2O as solvent. Equal volumes of ^2H_2O solutions of L-tryptophan/ $^2H_2SO_4$ and Ce^{4+}/ $^2H_2SO_4$ were mixed milliseconds before entering the ESR flat cell at a total flow rate of 60 mL/min. ESR spectra were recorded at 10 mW microwave power, 0.08 mT field modulation, 6.0 mT field sweep width, 327 ms time constant, 163 ms conversion time, and 107 scans of 512 data points (*Red*). Also shown is the L- ^{2}H(N-1)-tryptophan radical cation simulation spectrum produced using coupling constants given in Table 1 (*Green*).

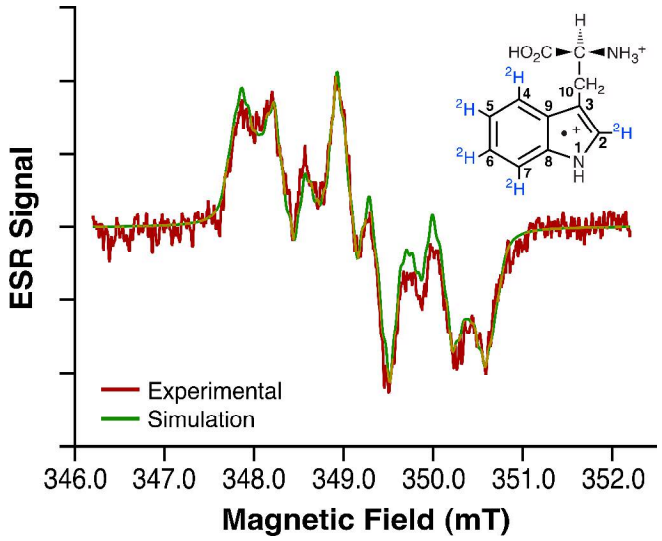

Fig. 8. L-[2,4,5,6,7-$^2H_5$]tryptophan radical cation ESR spectrum.
ESR fast-flow spectrum of L-[2,4,5,6,7-$^2H_5$]tryptophan radical cation produced in a system of L-[2,4,5,6,7-$^2H_5$]tryptophan, Ce^{4+}, and H_2SO_4 having concentrations of 0.5 mM, 0.25 mM, and 0.225 M, respectively. Equal volumes of aqueous solutions of $^2H_5$[2, 4, 5, 6, 7]-L-tryptophan/H_2SO_4 and Ce^{4+}/H_2SO_4 were mixed milliseconds before entering the ESR flat cell at a total flow rate of 40 mL/min. ESR spectra were recorded at 20 mW microwave power, 0.05 mT field modulation, 6.0 mT field sweep width, 163 ms time constant, 81 ms conversion time and 115 scans of 1024 data points (*Red*). Also shown is the L-[2,4,5,6,7-$^2H_5$]tryptophan radical cation simulation spectrum produced using coupling constants given in Table 1 (*Green).*