Supporting Information

Multifrequency EPR Studies of Manganese Catalases Provide a Complete Description of Proteinaceous Nitrogen Coordination

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Contents

Table S1. Effective Isotropic HFI for ^{14}N Atoms Coupled to Exchange Coupled Metal Clusters

Species	Coordination Geometry[a]	A_{iso} (MHz)	Ref.
Dinuclear Non-Heme Fe(II)Fe(III) Clusters			
methane monooxygenase hydroxylase	eq. to O_h Fe(III)	13.6	1
	eq. to O_h Fe(II)	5.0	2
	eq. to O_h Fe(III)	17.5	3
	eq. to O_h Fe(II)	5.2	
uteroferrin		12.6	4
semimethemerythrin	eq. to O_h Fe(III)	9.3	5
	eq. to O_h Fe(III)	≈15	
	ax. to O_h Fe(II)	5.1	
	eq. to O_h Fe(II)	6.7	
ribonucleotide reductase R2		7.31	6
		3.16	
Δ^9-desaturase		9.1	6
		3.34	
MiaE		6.4	7
		4.1	
Oxidized Rieske-type [2Fe2S] Clusters			
sulredoxin		4.6	8
		5.4	
oxygenase-associated ferredoxin		4.4	8
		5.4	
MitoNEET		6.25	9

a. Simple description of the geometry of the metal-ligand interaction. For example, "eq. to O_h Fe(III)" refers to a ^{14}N atom bound in the equatorial plane to a pseudo-octahedral Fe(III) ion.

Table S2. Measured HFI Parameters of ^{55}Mn Atoms in Exchange-Coupled Systems.

	Mn(III)			Mn(IV)				
Species	A_{iso}	$A_{\perp}$	$A_{\parallel}$	A_{iso}	$A_{\perp}$	$A_{\parallel}$	Meth.	Ref.
Ion in anatase	–247*2 = 494			–215				
LP MnCat	431	473	347	260	251	278	*a*	10
LP MnCat + N_3^-	417	457	337	257	249	273	*a*	10
LP MnCat + CN^-	414	457	327	249	242	263	*a*	10
TT MnCat	382	423	300	237	228	255	*b*	11
TT MnCat	387	424	312	235	228	250	*e*	12
TT MnCat	388	426	312	235	228	250	*a*	13
$bipy_2Mn(III)O_2Mn(IV)bipy_2$	440	480	360	218	212	231	*c*	14
TACN	393	444	297	213	208	223	*d*	15

a. *X*-band CW EPR

b. *X*-, *Q*-, and *W*-band CW and pulse EPR

c. *X*-band EPR and ENDOR

d. *X*- and *Q*-band CW EPR and ENDOR

e. *S*-, *X*-, and *P*-band CW EPR

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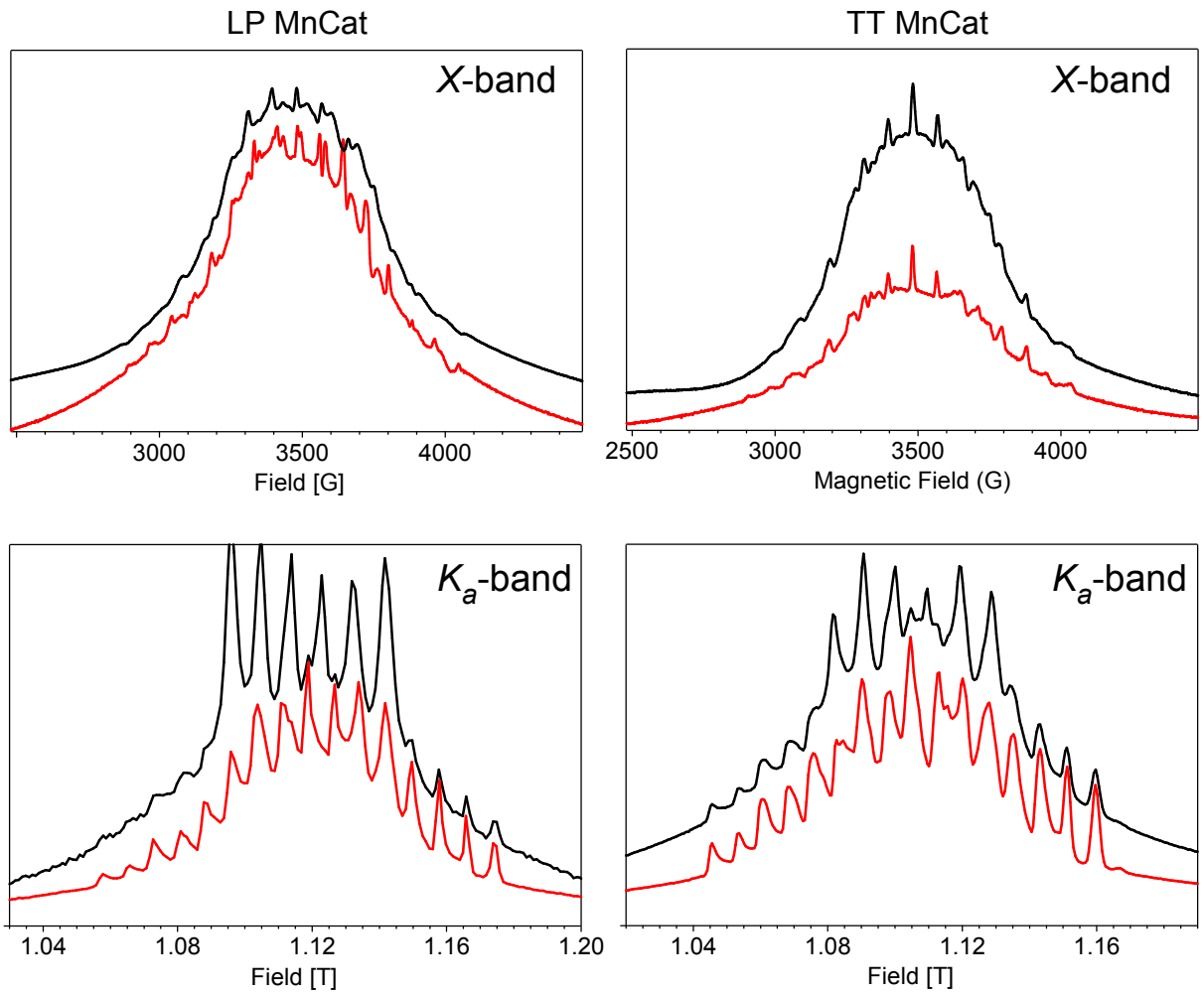

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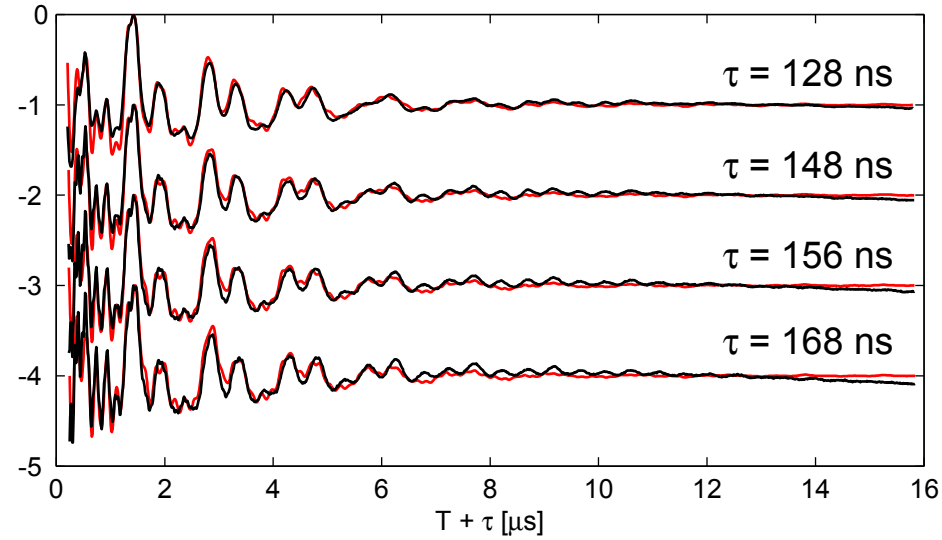

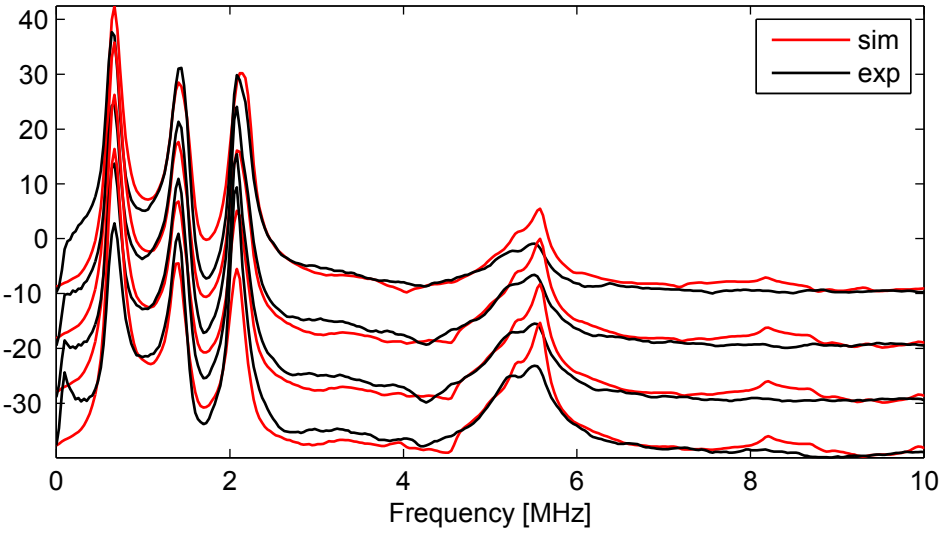

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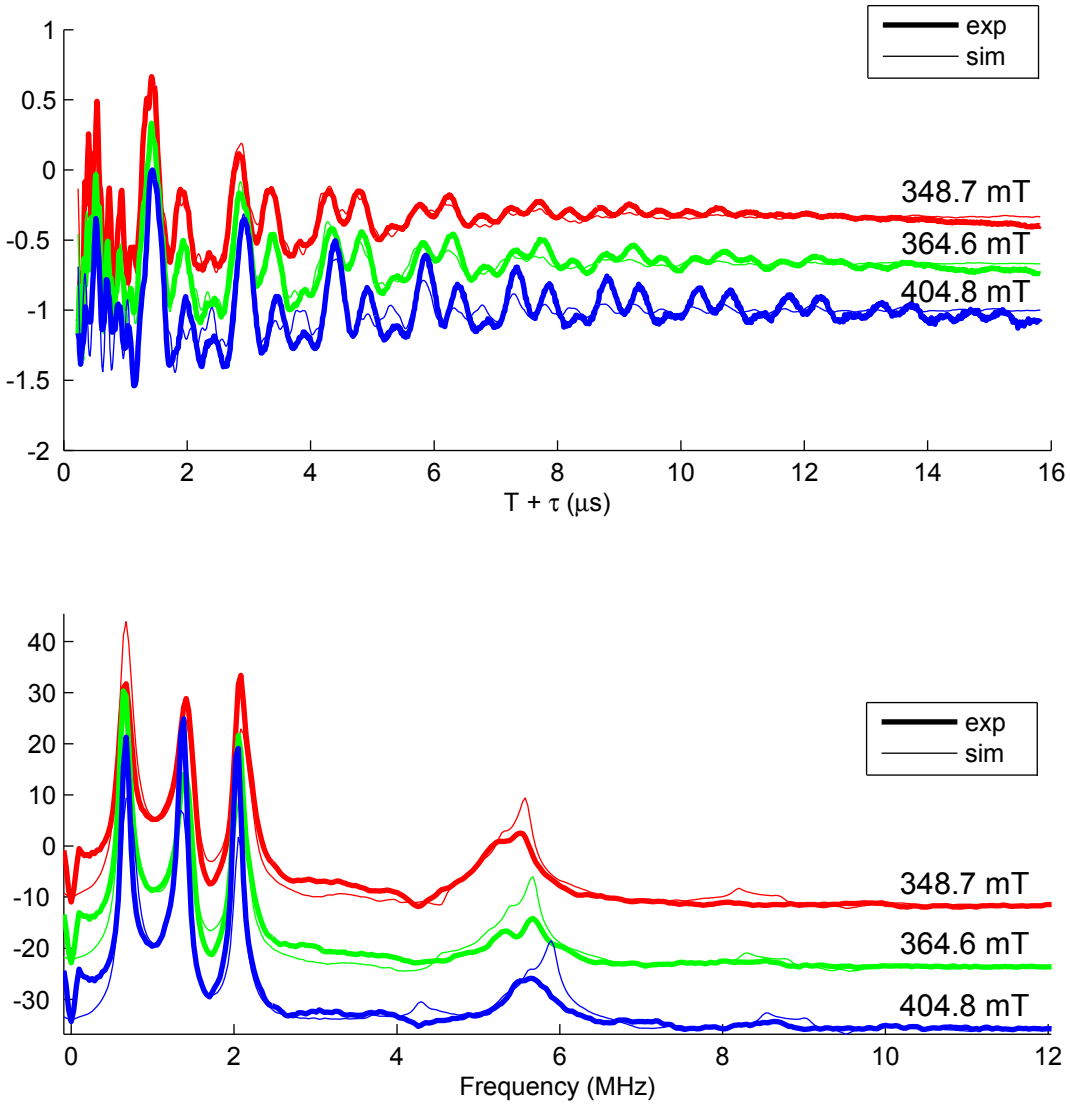

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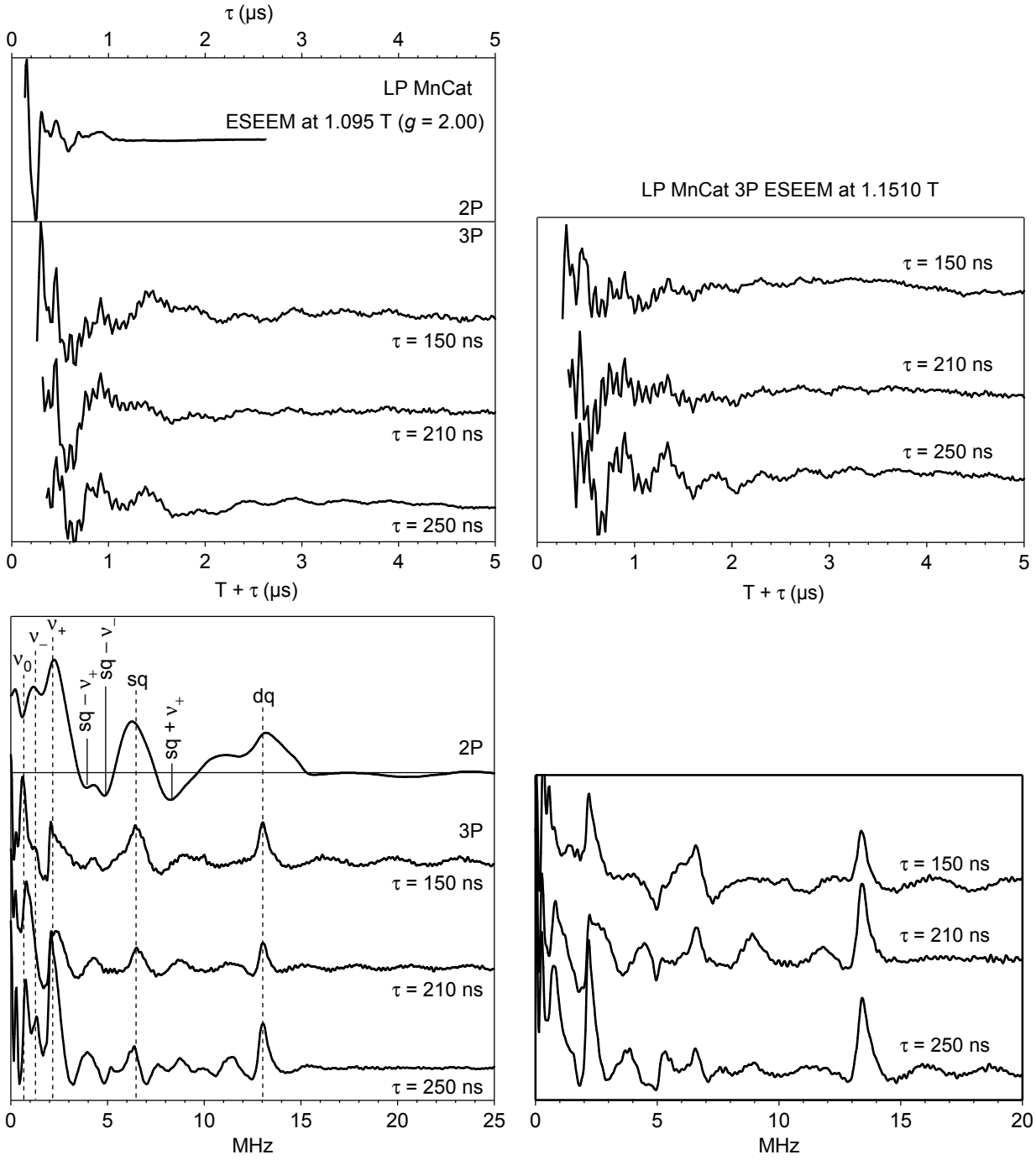

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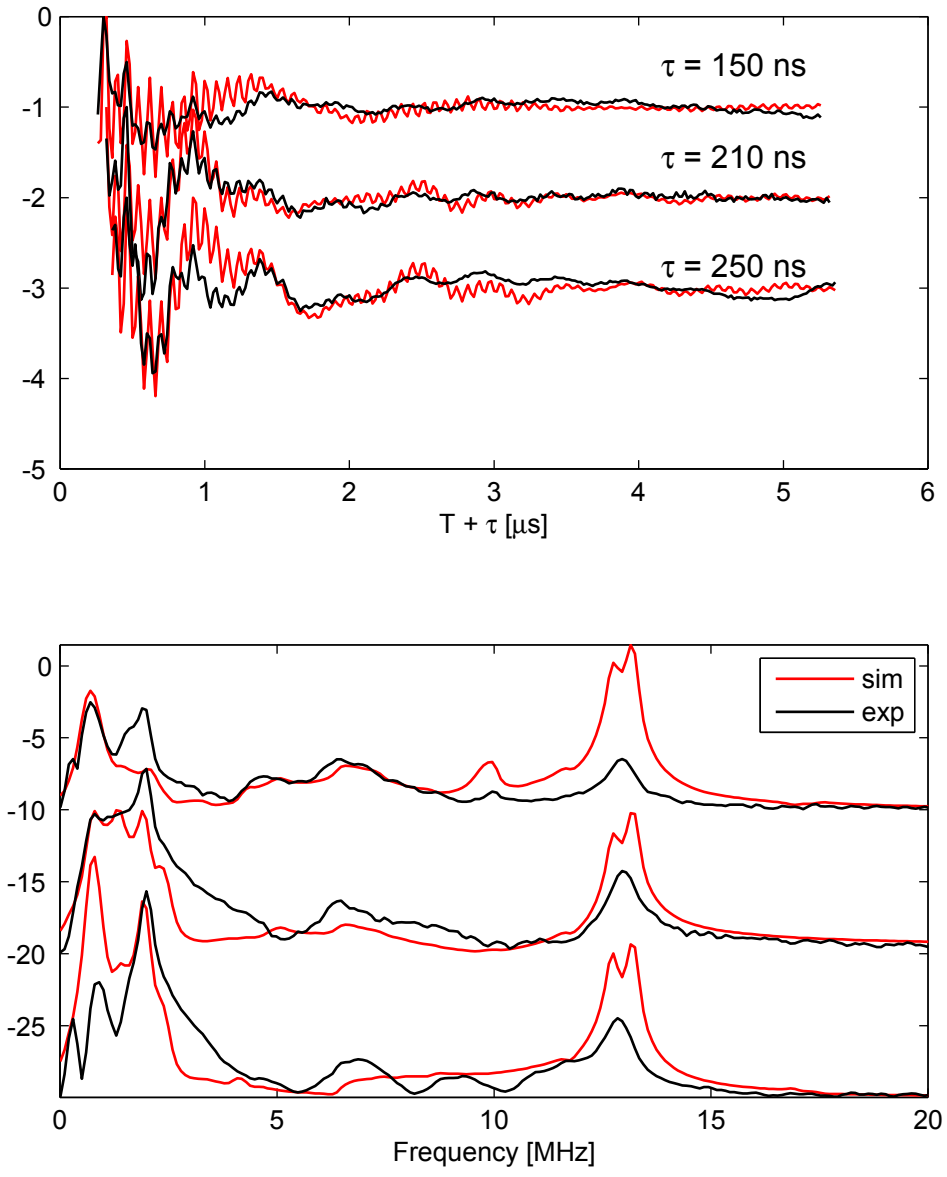

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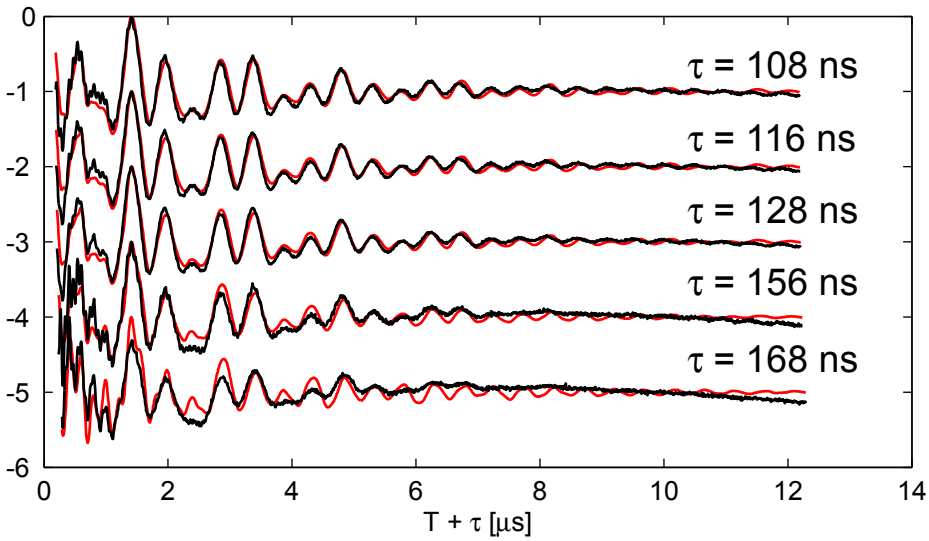

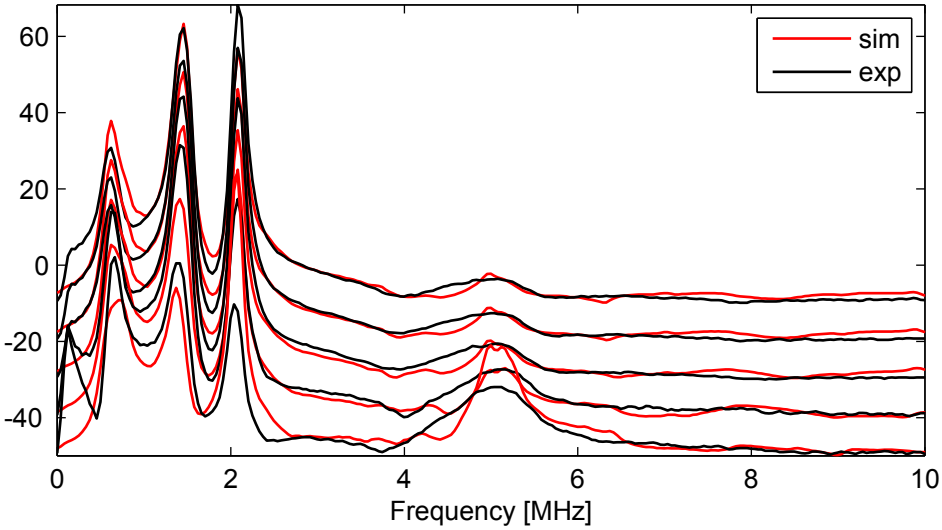

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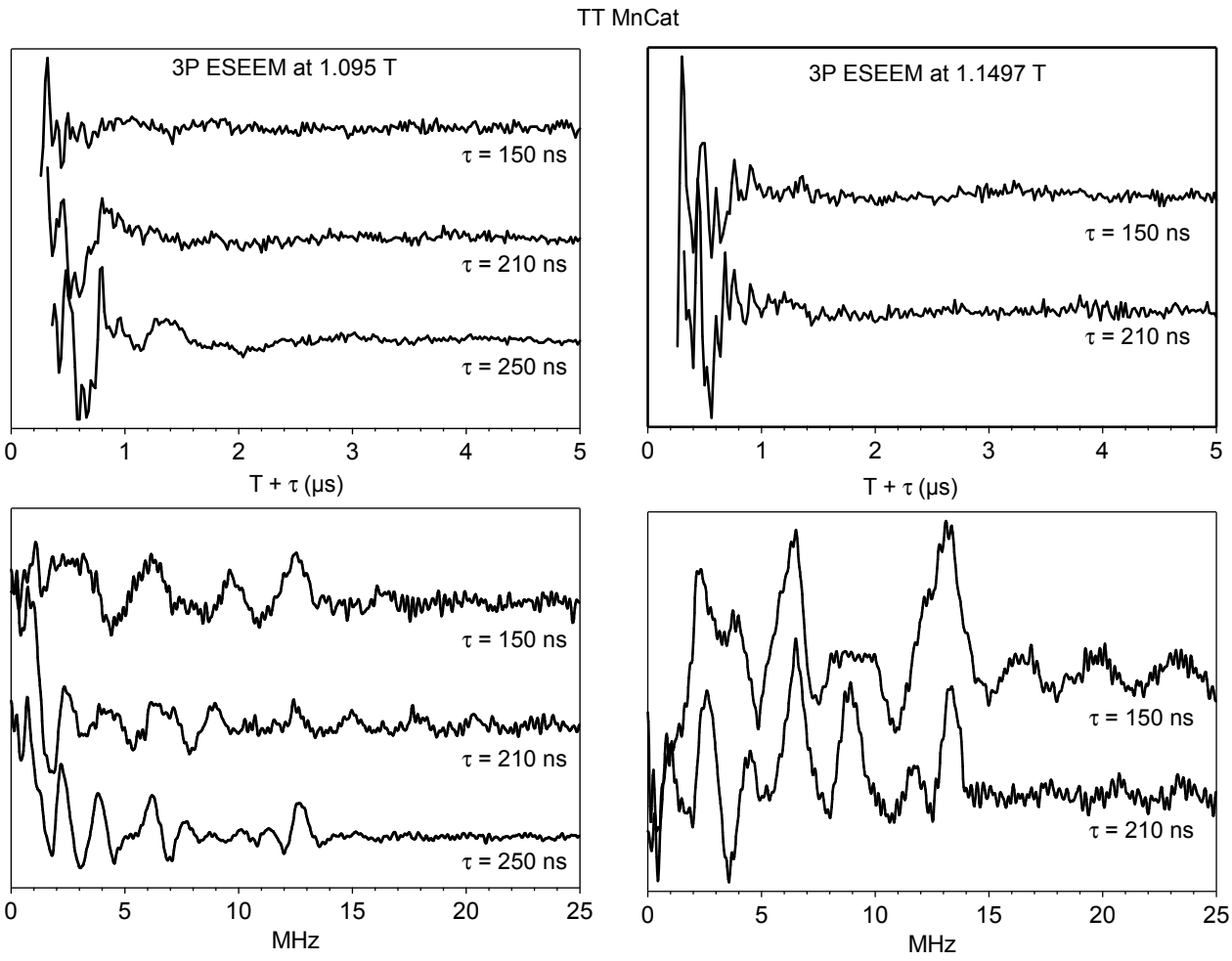

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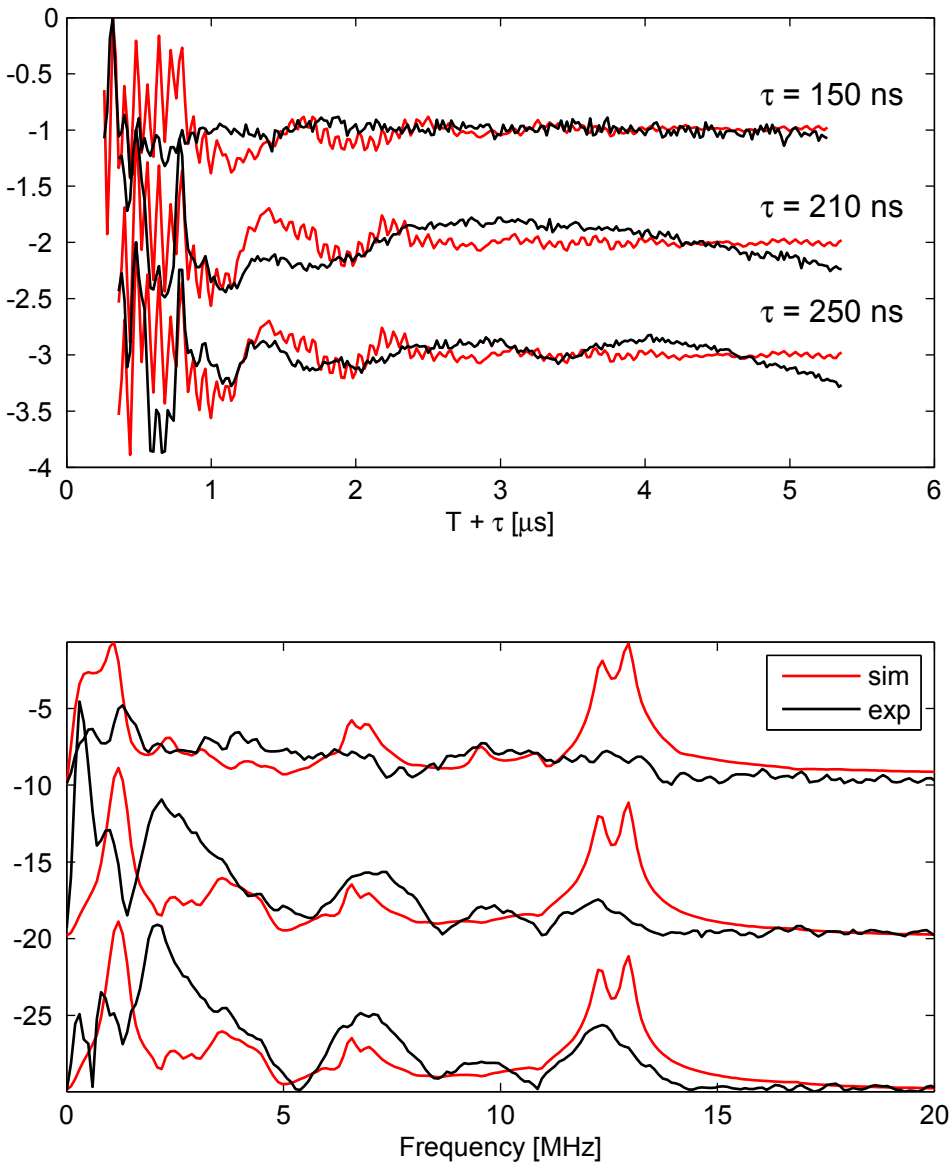

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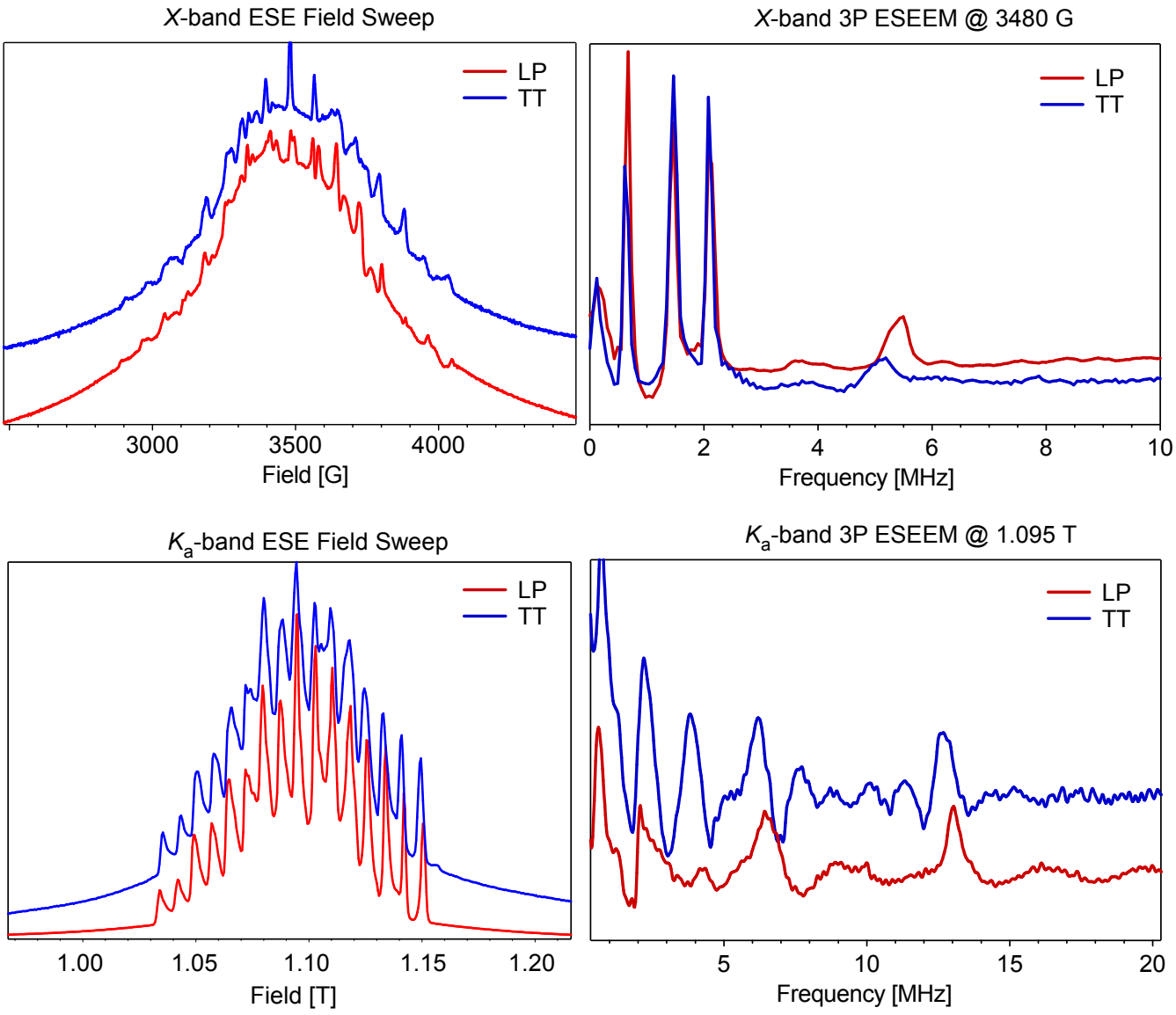

Stich et al. Supplemental Figure S9.