

**ENDOR characterization of  $(\text{N}_2)\text{Fe}^{\text{II}}(\mu\text{-H})_2\text{Fe}^{\text{I}}(\text{N}_2)^{\cdot-}$ : a spectroscopic model for  $\text{N}_2$  binding by the di- $\mu$ -hydrido nitrogenase Janus intermediate**

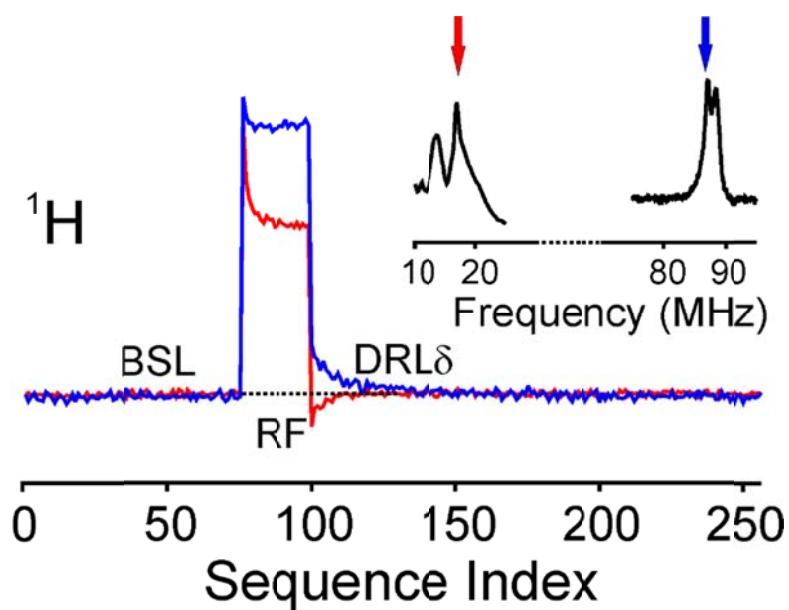
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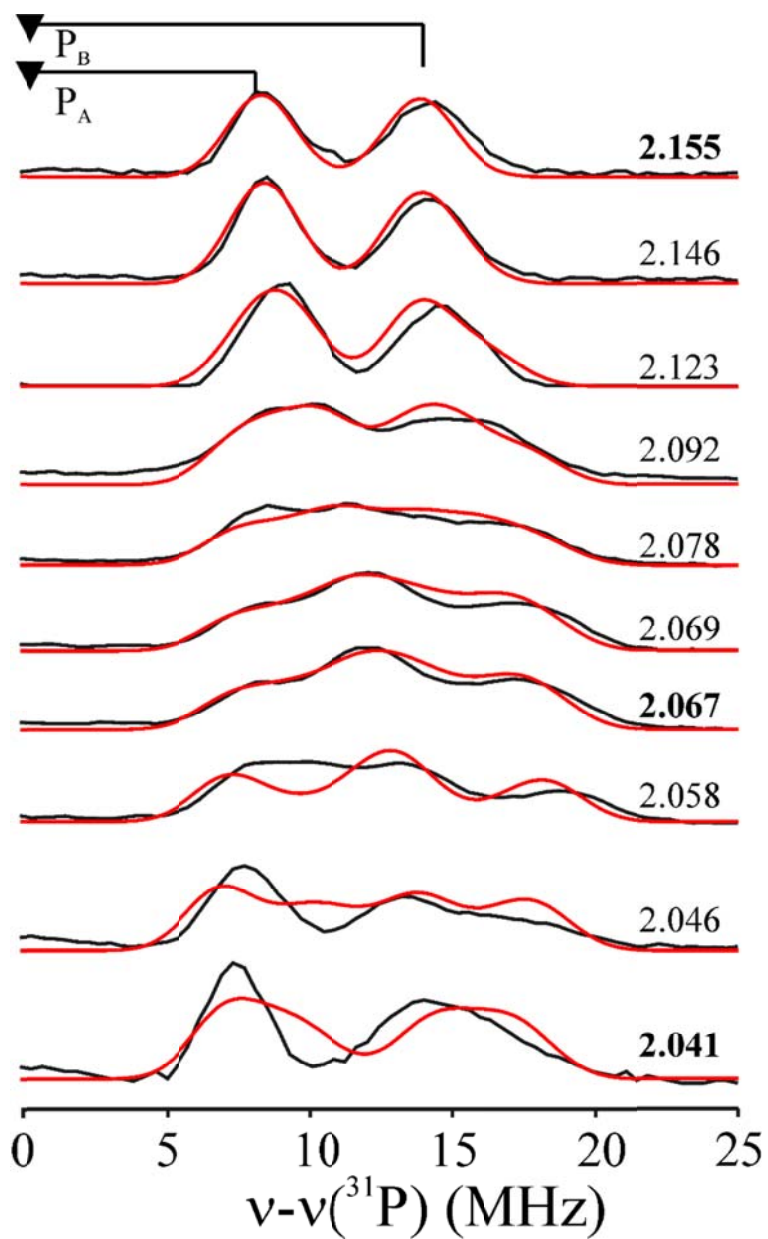
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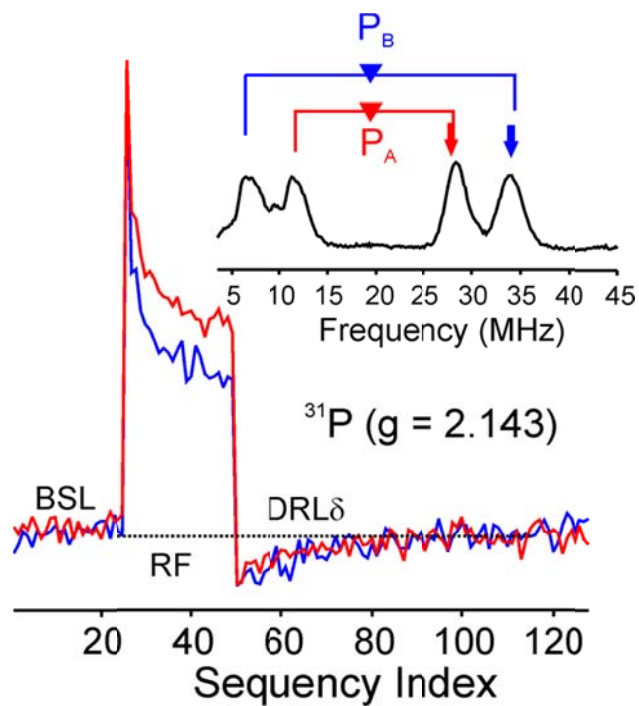
**SUPPORTING INFORMATION**



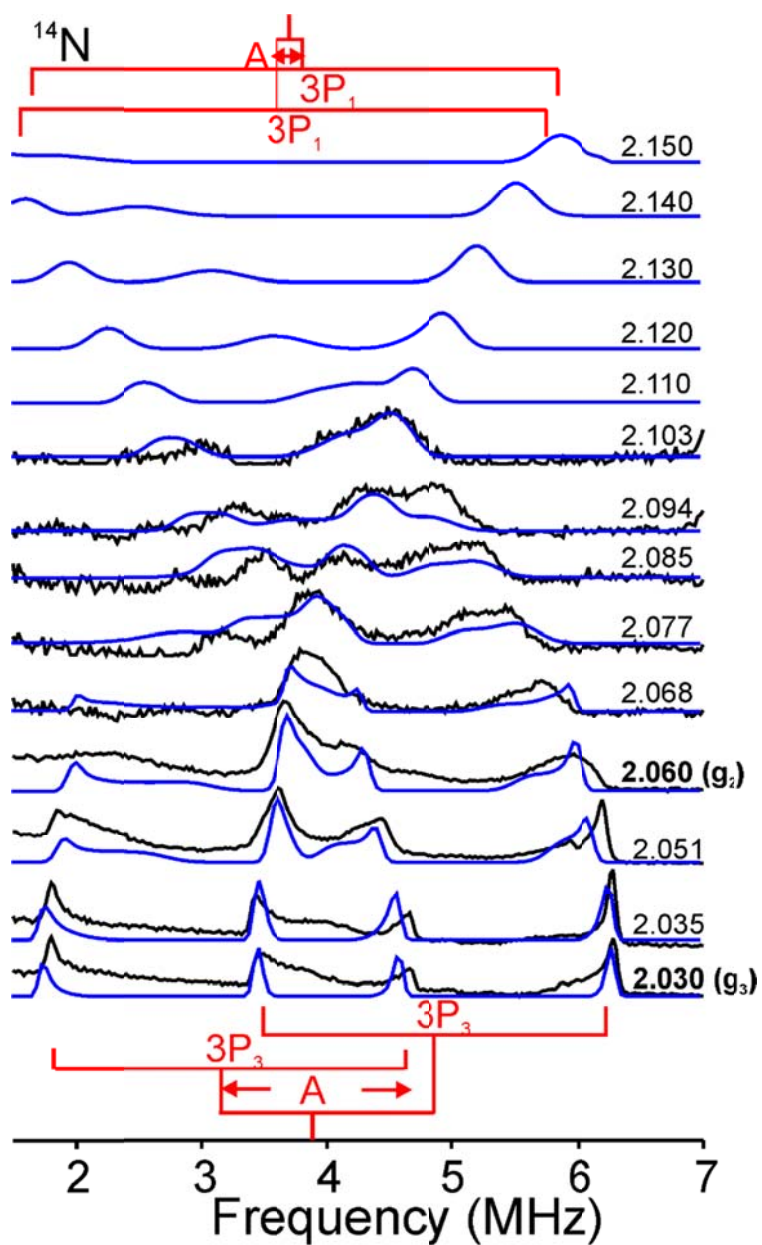
**Figure S1.** PESTRE measurement of  $^1\text{H}$  ENDOR response at  $g_3$  of  $4\text{-(N}_2)_2$ . PESTRE Conditions: microwave frequency, 34.739 GHz;  $\pi = 80$  ns,  $\tau = 600$  ns; repetition time, 50 ms;  $t_{\text{RF}} = 35$   $\mu\text{s}$ ; RF frequency, 17.1 MHz (red,  $\nu_-$ ) and 87.1 MHz (blue,  $\nu_+$ ).  $^1\text{H}$  ENDOR condition:  $\pi = 80$  ns;  $\tau = 600$  ns, repetition time, 50 ms;  $t_{\text{RF}} = 15$   $\mu\text{s}$ ; temperature 2K.



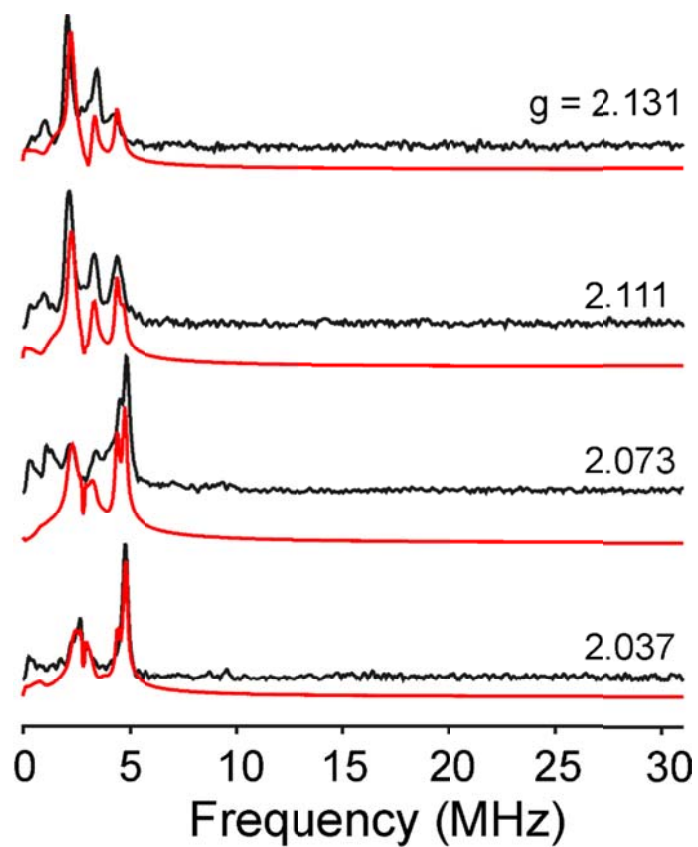
**Figure S2.** 2D pattern of stochastic  $^{31}\text{P}$  ENDOR (Black) and the simulation sum of  $P_A$  and  $P_B$  (Red) of  $4\text{-(N}_2\text{)}_2$ . The simulation parameters for  $P_A$  are  $A = + [16.5, 25, 13]$ ,  $(\alpha, \beta, \gamma) = (30, 10, 0)$ , for  $P_B$  are  $A = + [27, 38, 26]$ ,  $(\alpha, \beta, \gamma) = (45, 20, 0)$ .



**Figure S3.** PESTRE measurement of  $^{31}\text{P}$  ENDOR response at  $g = 2.143$  of  $4\text{-(N}_2)_2$ . PESTRE Conditions: microwave frequency, 34.858 GHz;  $\pi = 80$  ns,  $\tau = 400$  ns; repetition time, 50 ms;  $t_{\text{RF}} = 35$   $\mu\text{s}$ ; RF frequency, 28.5 MHz (red,  $\nu_+$  of  $P_A$ ) and 34.0 MHz (blue,  $\nu_+$  of  $P_{B,C}$ ).  $^1\text{H}$  ENDOR condition:  $\pi = 80$  ns;  $\tau = 600$  ns; repetition time, 50 ms;  $t_{\text{RF}} = 15$   $\mu\text{s}$ ; temperature, 2K.



**Figure S4.** Full 2D  $^{14}\text{N}$  ENDOR pattern simulation (blue) superimposed with the partial 2D pattern of the experimental data of  $4-(\text{N}_2)_2$ . The experimental condition is described in the legend of the main text Figure 8.



**Figure S5.** FT spectra of X-band three-pulse ESEEM (black), and simulation (red) of 4-(N<sub>2</sub>)<sub>2</sub>. Simulation parameters: <sup>14</sup>N, A = [0.7, 1.3, 1.85] MHz, e<sup>2</sup>Qq/h = 3.7 MHz, η = 0.03. Experimental conditions: mw frequency = 9.771 GHz, T<sub>0</sub> = 48 ns, ΔT = 24 ns, τ = 136 ns.