

SUPPORTING INFORMATION

The Hydration Structure of the Ti(III) Cation as Revealed by Pulse EPR and DFT Studies. New Insights into a Textbook Case

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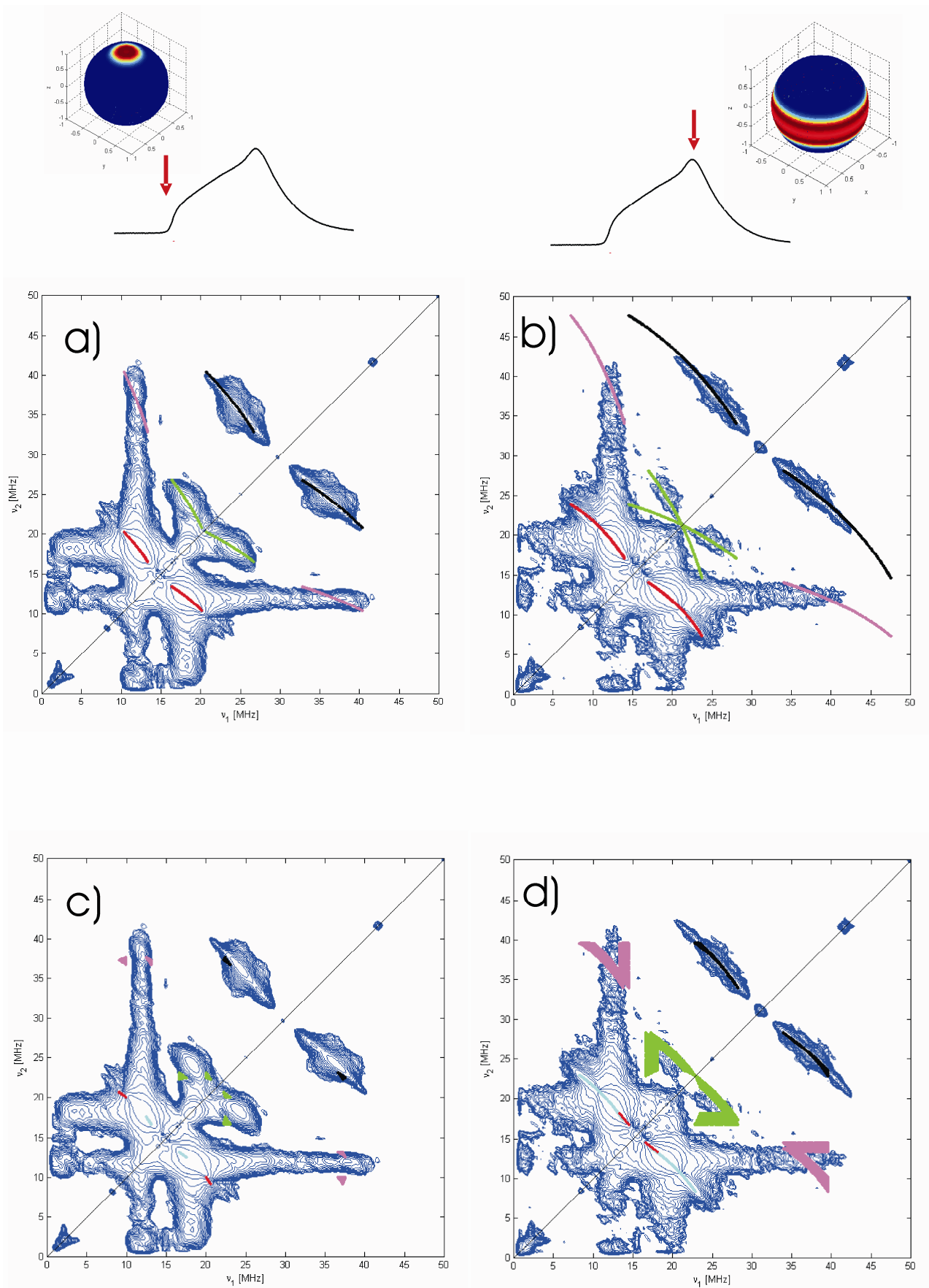


Figure S1. Simulation of the correlation ridges at the two field positions indicated on the ESE spectra above, expected for a three-spin system $S = 1/2$, $I_a = 1/2$ and $I_b = 1/2$ assuming different parameters: a) and b) ${}^1A_{\parallel} = {}^2A_{\parallel} = 15.5$ MHz ${}^1A_{\perp} = {}^2A_{\perp} = 3.5$ MHz and ${}^1\beta = {}^2\beta = 60^\circ$; c) and d) ${}^1A_{\parallel} = 11.4$ MHz ${}^2A_{\parallel} = 15.5$ MHz ${}^1A_{\perp} = 1.5$ MHz, ${}^2A_{\perp} = 3.5$ MHz, ${}^1\beta = 0$, ${}^2\beta = 90^\circ$

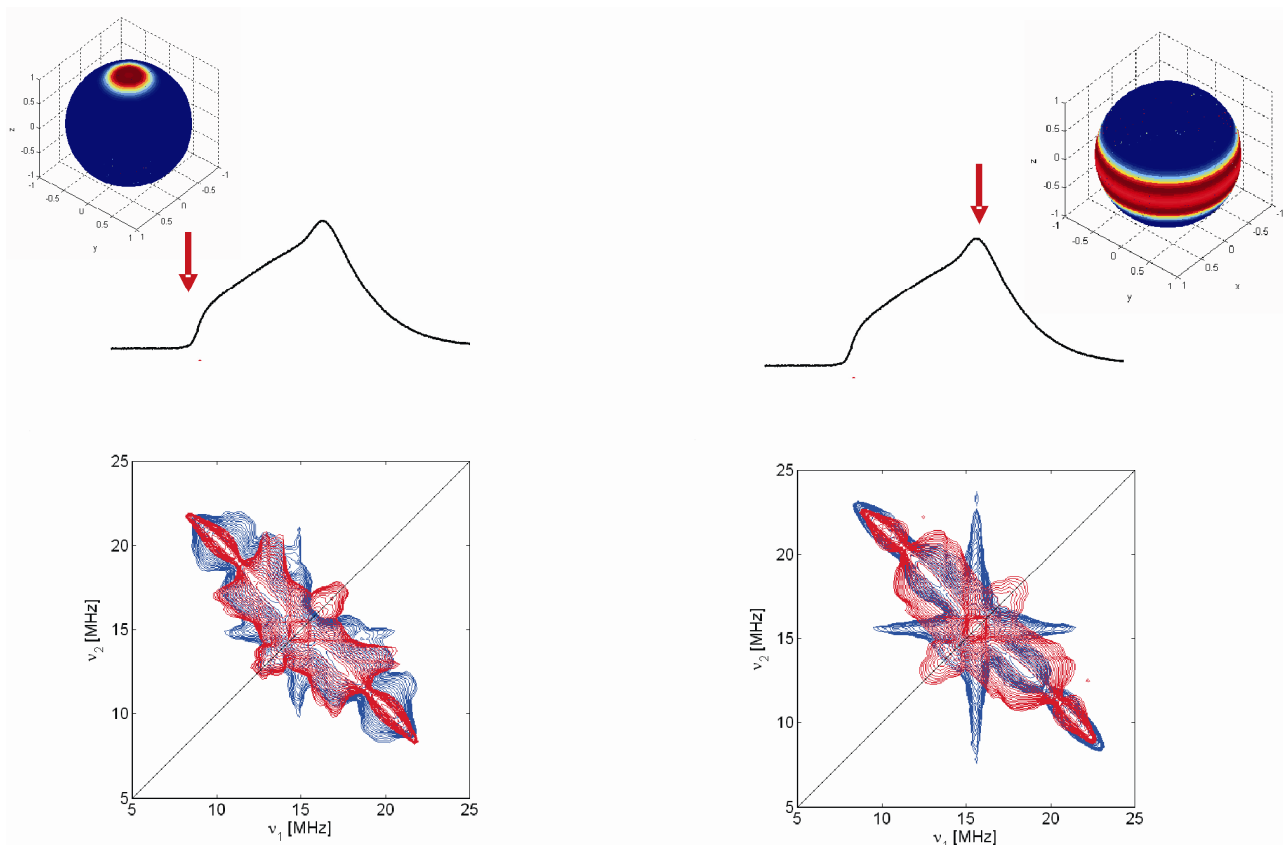


Figure S2 ^1H HYSCORE spectra of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ taken at the two field positions indicated on the ESE spectra above. Blue experimental, red simulation using the parameters listed in Table 1.

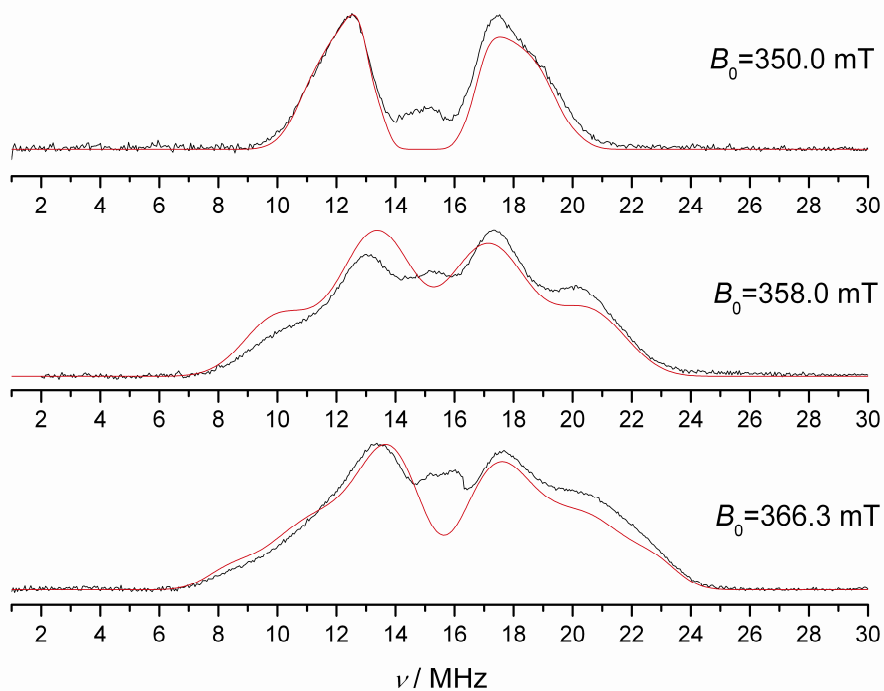


Figure S3 Experimental (black) and simulated (red) ^1H Davies-ENDOR spectra of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ taken at different field positions indicated beside each spectrum. Spectra were measured at 10 K. Length of the three m.w. pulses, $t_{\pi}^{(1)} = 80$ ns, $t_{\pi/2}^{(2)} = 16$ ns $t_{\pi}^{(3)} = 32$ ns; length of the r. f. pulse $t_{\text{rf}} = 12$ μs . The rf and mw data were optimized to obtain good ^1H ENDOR spectra, conditions which are unfavorable for the ^{17}O contributions. The parameters used in the simulations are the same adopted for the simulation of the ^1H HYSCORE spectra and listed in Table 1.

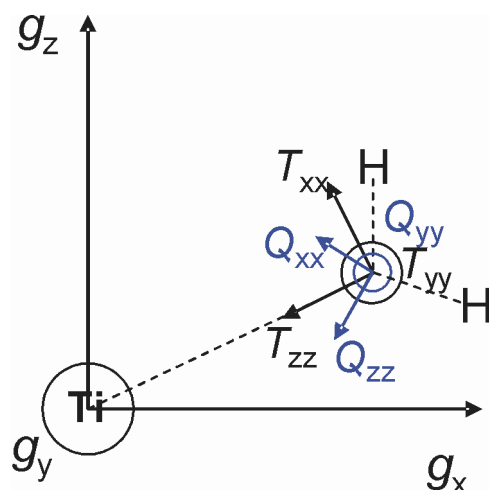


Figure S4 Schematic illustration of the ^{17}O hyperfine and quadrupole tensors orientations obtained from the DFT computations for the D_{3d} symmetry case and adopted in the simulations of the ^{17}O HYSCORE spectra reported in Figure 4. The corresponding Euler angles (α β γ) are $(0+n60, 64, 0)$ and $(0+n60, 31, 0)$ for the hyperfine and quadrupole tensors respectively, where n ranges from 1 to 6 and accounts for the orientations of the six oxygens in the xy plane of the complex.

The largest quadrupole and hyperfine (a_{iso} is positive) are perpendicular to the water plane (y direction). The smallest hyperfine is directed along the Ti-O bond making an angle of 64° with the g_z direction. The largest negative quadrupole is in the zx plane making an angle of 31° with the g_z direction. The largest H hyperfines (T_{zz} not shown in the scheme) lay in the zx plane making an angle of 45° and 72° with the z direction

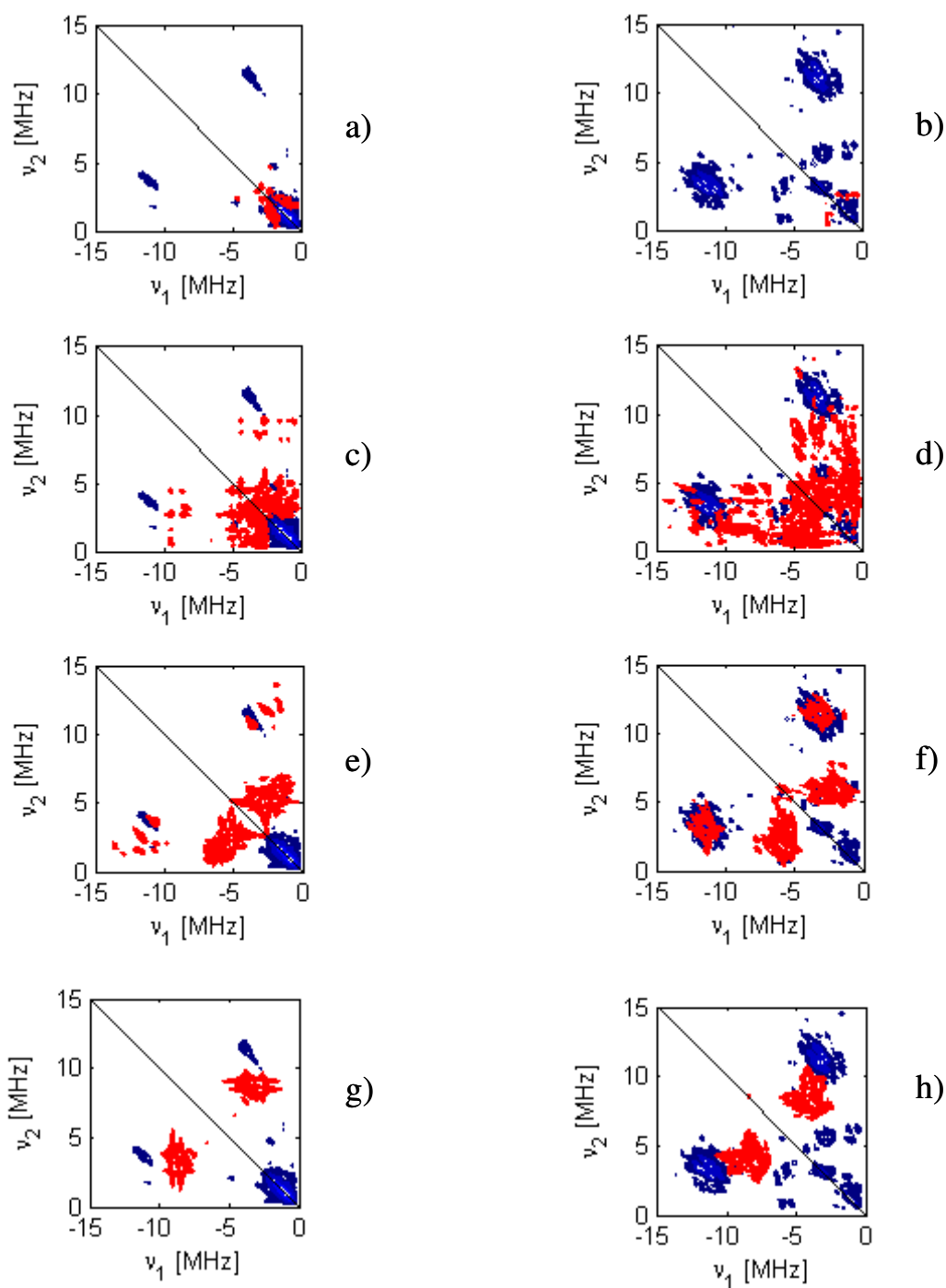


Figure S5 Effect of increasing a_{iso} on the ^{17}O HYSORE spectrum taken at $B_0 = 352.0$ mT (position 2 in Figure 1a) and $B_0 = 366.0$ mT (position 3 in Figure 1a) respectively. (a) and (b) $|a_{\text{iso}}| = 0$ MHz; (c) and (d) $|a_{\text{iso}}| = 4$ MHz; (e) and (f) $|a_{\text{iso}}| = 8$ MHz; (g) and (h) $|a_{\text{iso}}| = 12$ MHz. For all spectra $T = 1$ MHz, $e2qQ/h = 4$ MHz, $\eta = 0.75$.

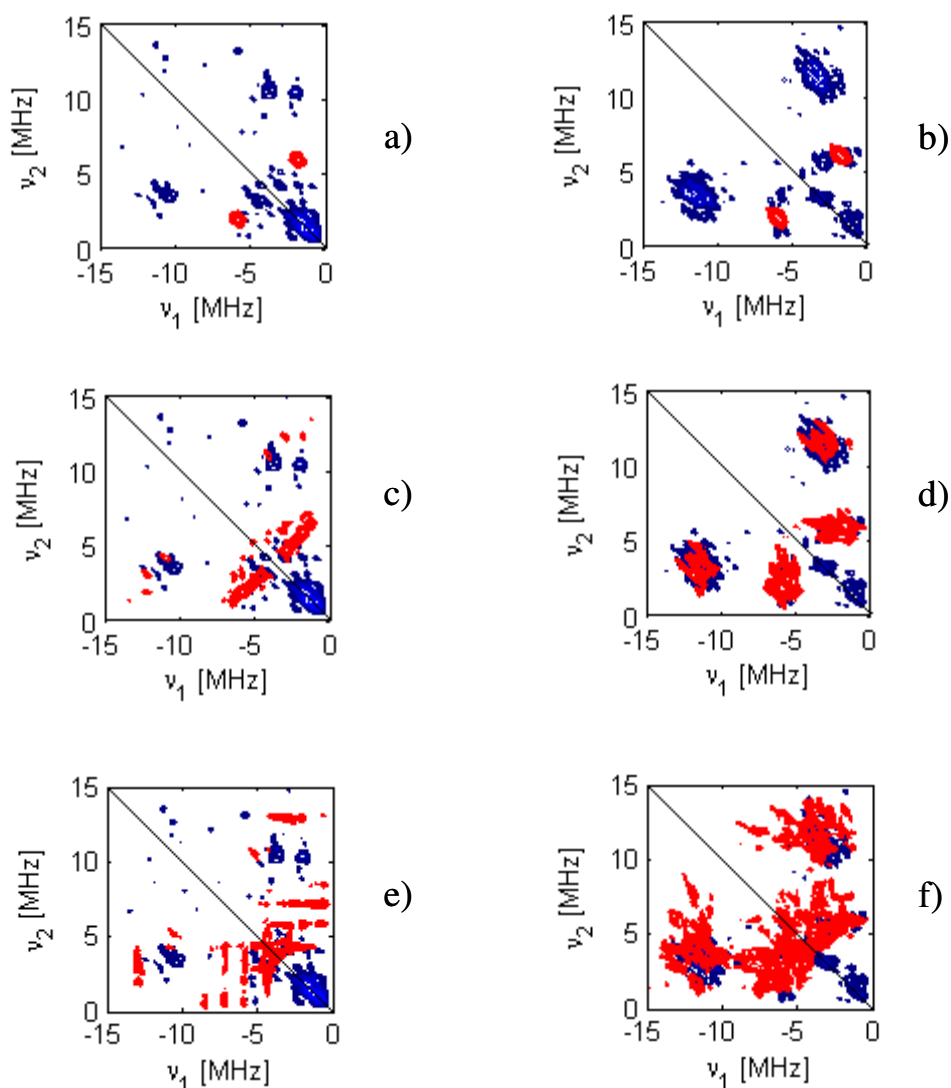


Figure S6 Effect of increasing quadrupole coupling on the ^{17}O HSCORE spectrum taken at $B_0 = 352.0$ mT (position 2 in Figure 1a) and $B_0 = 366.0$ mT (position 3 in Figure 1a) respectively. (a) and (b) $e2qQ/h = 0$; (c) and (d) $e2qQ/h = 4$ MHz; (e) and (f) $e2qQ/h = 9$ MHz. For all spectra $a_{\text{iso}} = 7.84$ MHz and $T = 0.84$ MHz.

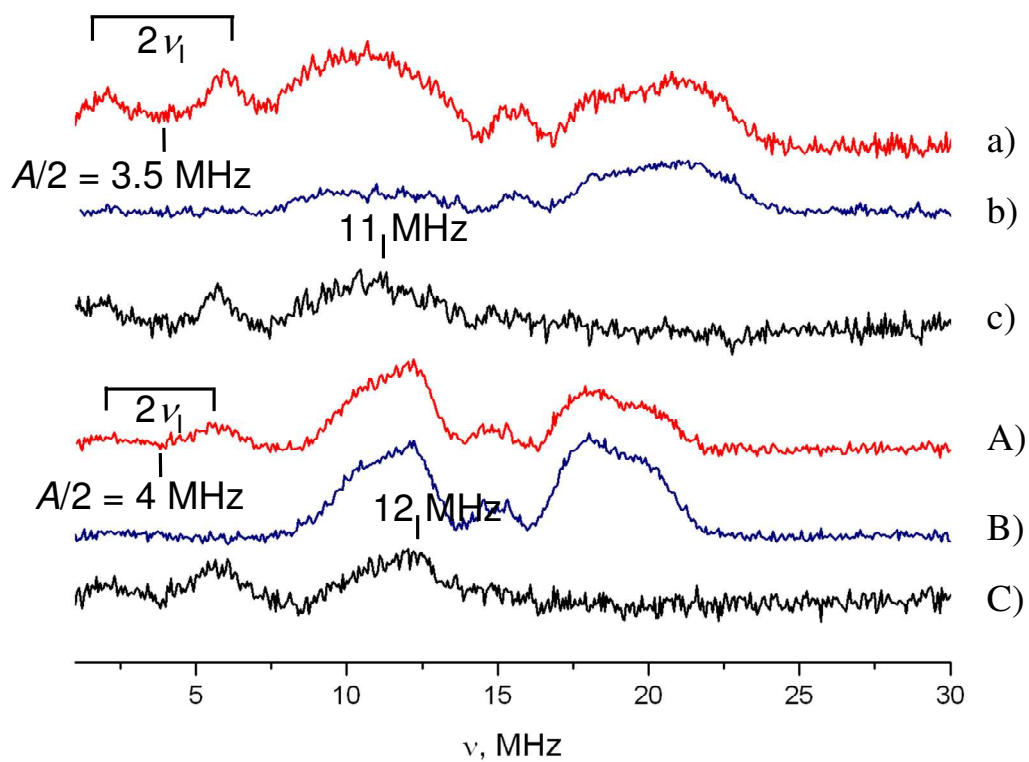


Figure S7 ^{17}O Davies ENDOR spectra taken at (a,b,c) $B_0 = 366.0$ mT and (A;B;C) $B_0 = 352.0$ mT. $t_{\text{rf}} = 12 \mu\text{s}$, $t_{\pi/2} = 16$ ns, $t_{\pi} = 32$ ns. Red spectra ^{17}O , blue spectra ^{16}O , black trace is the difference between red and blue.