Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Non-uniform Sampling in EPR – optimizing data acquisition for HYSCORE spectroscopy

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Supporting Information

Content

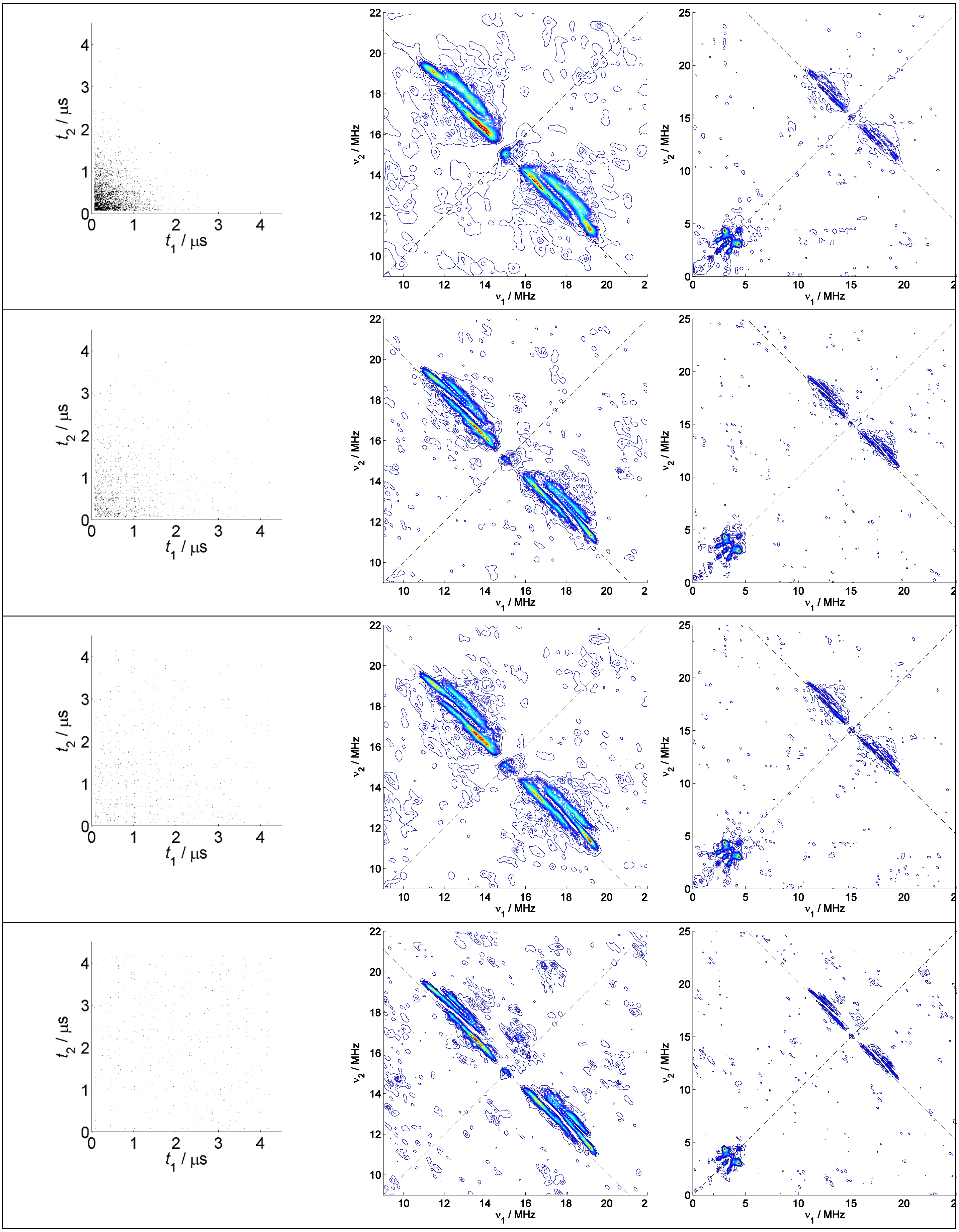

Figure S1: X-band (9.7822 GHz) HYSCORE data from the paramagnetic $[2Fe\text{-}2S]^+$ cluster. (Left) NUS scheme using 5% of the linearly sampled time domain data (350 × 350), and with the decay rate (eq. 3) decreasing down the column. (Middle / Right) the corresponding absolute value MaxEnt spectrum showing only the ^1H region (Middle) and the entire (+,+) quadrant (Right). The cross-peaks around 4 MHz are due to ^{14}N.

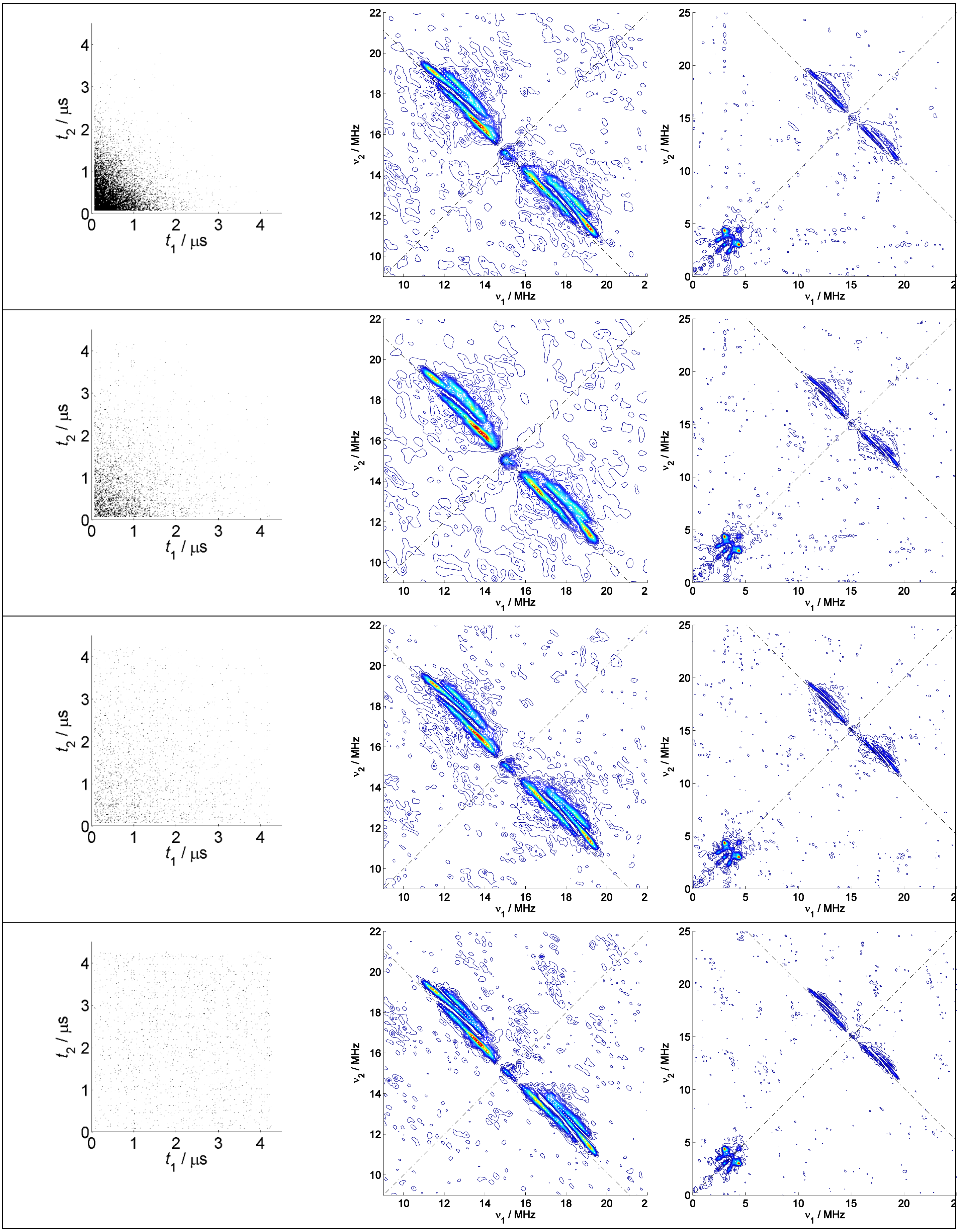

Figure S2: X-band (9.7822 GHz) HYSCORE data from the paramagnetic [2Fe-2S]$^+$ cluster. (Left) NUS scheme using 10% of the linearly sampled time domain data (350 × 350), and with the decay rate (eq. 3) decreasing down the column. (Middle / Right) the corresponding absolute value MaxEnt spectrum showing only the ^1H region (Middle) and the entire (+,+) quadrant (Right). The cross-peaks around 4 MHz are due to ^{14}N.

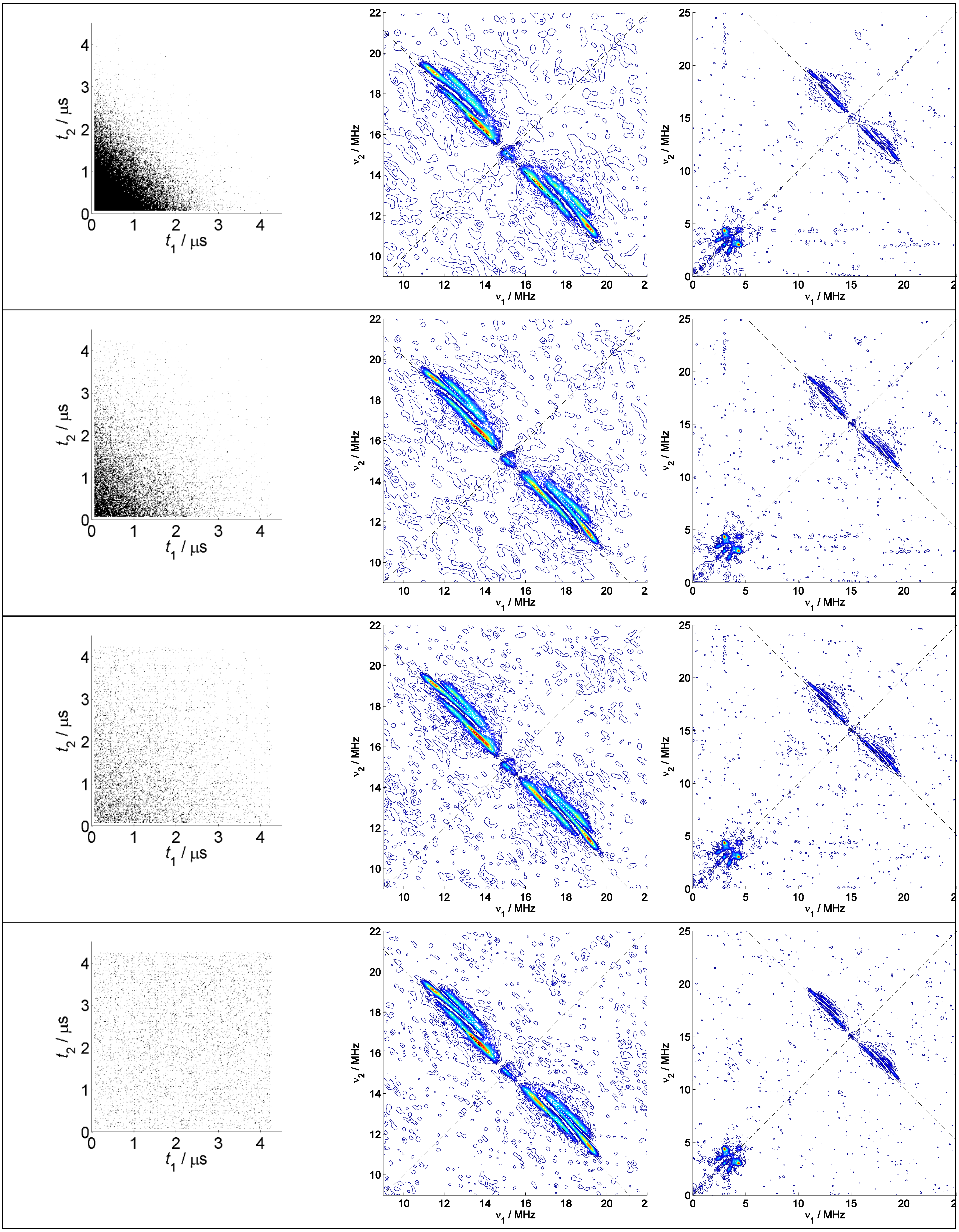

Figure S3: X-band HYSCORE data from the paramagnetic $[2Fe\text{-}2S]^+$ cluster. (Left) NUS scheme using 20% of the linearly sampled time domain data (350 × 350), and with the decay rate (eq. 3) decreasing down the column. (Middle / Right) the corresponding absolute value MaxEnt spectrum showing only the ^1H region (Middle) and the entire (+,+) quadrant (Right). The cross-peaks around 4 MHz are due to ^{14}N.

Experimental and Measurement Time

1. X-band HYSCORE data from the paramagnetic [2Fe-2S]$^+$ cluster (S = ½) from palustrisredoxin-B (PuxB).

The X-band (9.7822 GHz) HYSCORE measurements were carried out on an X-/W-band Bruker Elexsys 680 spectrometer equipped with a 1 kW TWT amplifier and a helium gas-flow cryostat from Oxford Instruments Inc. The HYSCORE data set was recorded at 15°K and at B_0=353 mT, and employed the pulse sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau-echo$ with mw pulses of lengths $t_{\pi/2} = t_\pi = 16$ ns, a tau value $\tau = 116$ ns and starting times $t^o_1 = t^o_2 = 64$ ns with increments $\Delta t = 12$ ns (data matrix 350 × 350). The shot repetition time was 1.5 ms, and an eight-step phase cycle was used to remove unwanted echoes. The HYSCORE traces were processed with MATLAB R2013a (The MathWorks, Inc.). The time traces were baseline corrected with an exponential, apodized with a Gaussian window and zero filled. After a two-dimensional Fourier transformation absolute-value spectra were calculated.

Experimental Measurement Time

The total experimental time was measured; **134 minutes** for the 350 × 350 matrix. This comprises measurement and pulse programming time. The calculated measurement time is,

$$measurement = \left(\sum_{i=1}^{350}\sum_{j=1}^{350}(t_{1,i} + t_{1,j}) + shot\ repetition\ rate\right) \times shots/point \times no.\ phase\ cycles \times no.\ loops$$

$$= \left(\sum_{i=1}^{350}\sum_{j=1}^{350}(t_{1,i} + t_{1,j}) + 1.5 \times 10^{-3} seconds\right) \times 2 \times 8 \times 2$$

$$= 98.3\ \text{minutes.}$$

The difference between 134 minutes (total experimental time) and 98 minutes (calculated measurement time) is the pulse programming overhead.

2. Q-band HYSCORE data from the complex [Rh(trop2N)(bipy)]OTf$^-$, S = ½.

The Q-band (35.3 GHz) experiment was carried out on a home-built instrument (see reference S1) equipped with a 100 W TWT amplifier and a helium gas-flow cryostat from Oxford Instruments Inc. The HYSCORE data set was recorded at 25°K and at B_0=1210.2 mT, and employed the pulse sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau-echo$ with mw pulses of lengths $t_{\pi/2} = t_\pi = 16$ ns, a tau value $\tau = 96$ ns and starting times $t^o_1 = t^o_2 = 32$ ns with time increments $\Delta t = 8$ ns (data matrix 175 × 175). The shot repetition time was 1 ms and an eight-step phase cycle was used to remove unwanted echoes. The HYSCORE data were processed with MATLAB R2013a (The MathWorks, Inc.). The time traces were baseline corrected with a 2nd order polynomial, apodized with a Gaussian window and zero filled. After a two-dimensional Fourier transformation absolute-value spectra were calculated.

Experimental Measurement Time

The total experimental time was measured; **82 minutes** for the 175 × 175 matrix. This comprises of measurement and pulse programming time. The calculated measurement time is,

$$measurement = \left(\sum_{i=1}^{175}\sum_{j=1}^{175}(t_{1,i} + t_{1,j}) + shot\ repetition\ rate\right) \times shots/point \times no.\ phase\ cycles \times no.\ loops$$

$$= \left(\sum_{i=1}^{350}\sum_{j=1}^{350}(t_{1,i} + t_{1,j}) + 1 \times 10^{-3} seconds\right) \times 4 \times 8 \times 3$$

$$= 49.1\ \text{minutes.}$$

The difference between 82 minutes (total experimental time) and 49 minutes (calculate measurement time) is the pulse programming overhead.

References

S1 Gromov, I.; Shane, J.; Forrer, J.; Rakhmatoullin, R.; Rozentzwaig, Y.; Schweiger, A., *A Q-band pulse EPR/ENDOR spectrometer and the implementation of advanced one- and two-dimensional pulse EPR methodology*. JMR **2001**, 149 (2), 196-203.