SUPPORTING INFORMATION

Analysis of the EPR spectra of transferrin: the importance of a zero-field-splitting distribution and 4th-order terms

Mykhailo Azarkh,[a] Peter Gast,[b] Anne B. Mason,[c] Edgar J. J. Groenen,[b] and Guinevere Mathies*[a]

[a] Department of Chemistry, University of Konstanz, 78464 Konstanz, Germany.

[b] Department of Physics, Huygens-Kamerlingh Onnes Laboratory, Leiden University, PO Box 9504, 2300 RA Leiden, The Netherlands.

[c] Department of Biochemistry, University of Vermont College of Medicine, Burlington, VT 05405, United States.

*To whom correspondence should be addressed. E-mail: guinevere.mathies@uni-konstanz.de.

Table S1 Expression in S_+, S_-, and S_z of the extended Stevens operators $\boldsymbol{O}_k^q(\boldsymbol{S})$ with $k = 4$.

$\boldsymbol{q}$	$\boldsymbol{O_4^q}$
$\mathbf{0}$	$35S_z^4 - (30s - 25)S_z^2 + (3s^2 - 6s)\mathbb{I}$
$\pm\mathbf{1}$	$c_\pm[7S_z^3 - (3s + 1)S_z, S_+ \pm S_-]_+$
$\pm\mathbf{2}$	$c_\pm[7S_z^2 - (s + 5)\mathbb{I}, S_+^2 \pm S_-^2]_+$
$\pm\mathbf{3}$	$c_\pm[S_z, S_+^3 \pm S_-^3]_+$
$\pm\mathbf{4}$	$c_\pm(S_+^4 \pm S_-^4)$

$[A, B]_+ = (AB + BA)/2$, $s = S(S + 1)$, $c_+ = 1/2$, and $c_- = 1/2i$.

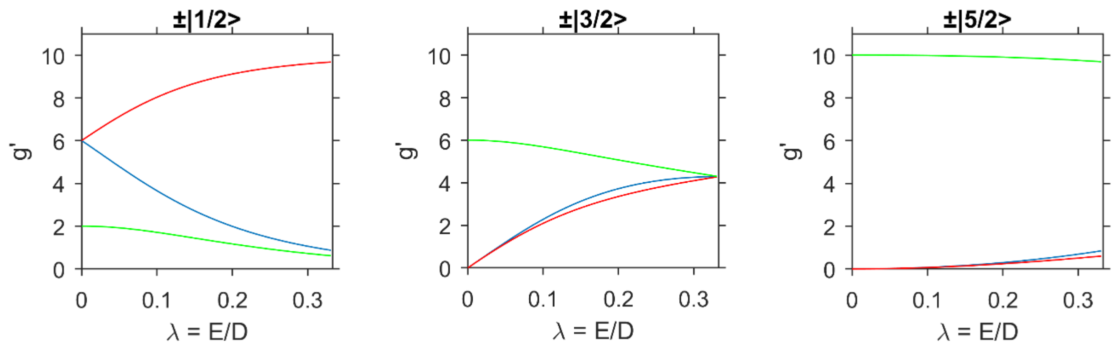

Fig. S1 Rhombograms for $S = 5/2$ showing the dependence of the effective g'–value on the rhombicity, E/D, for the three Kramers doublets. Blue: $g_x{}'$, red: $g_y{}'$, green: $g_z{}'$.

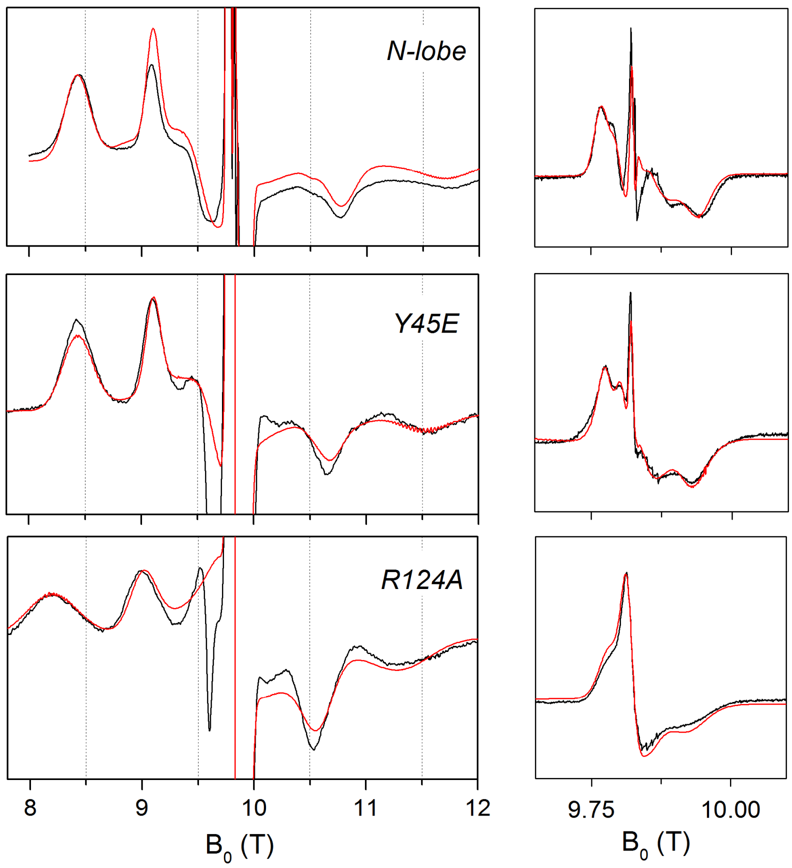

Fig. S2 J-band (275.7 GHz) CW EPR spectra of human serum transferrin. Black: experiment, red: simulation. Left: full-width spectra, right: the g_e–region.

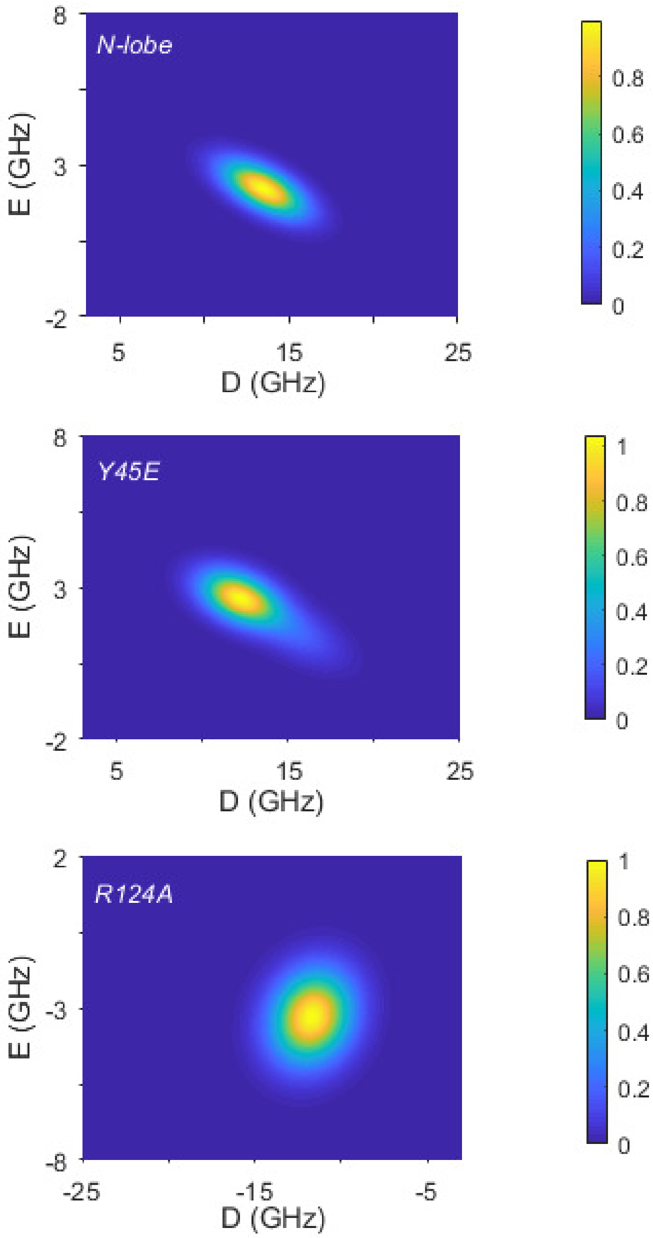

Fig. S3 D,E-space contour plots of the distribution of the ZFS parameters extracted from the J-band spectra in Figure S2.

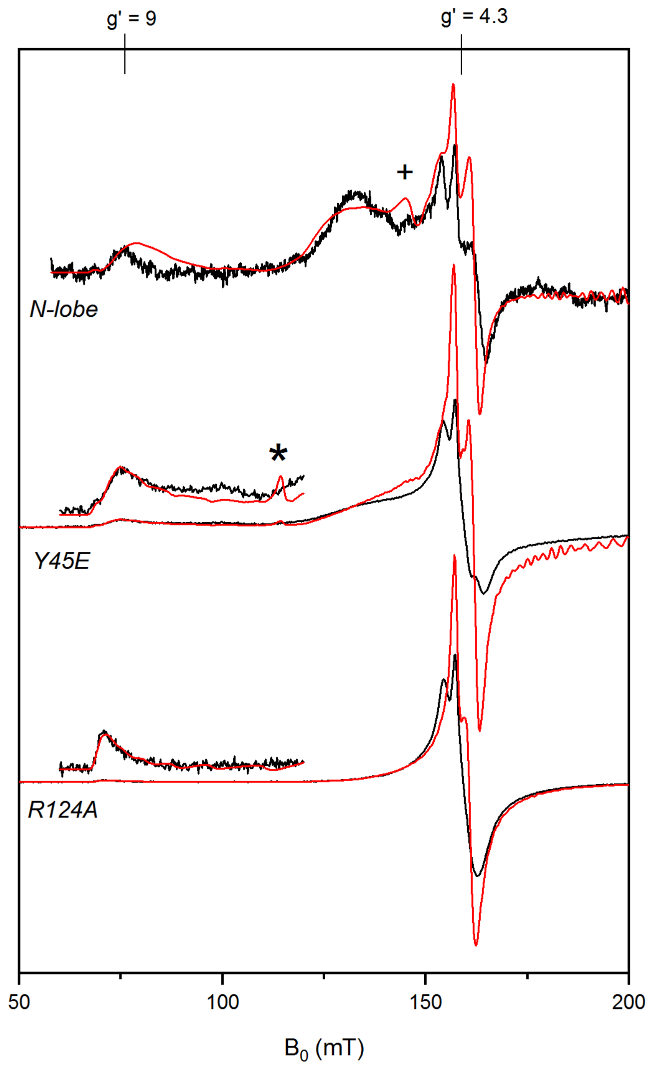

Fig. S4 X-band CW EPR spectra of human serum transferrin. Black: experiment, red: simulations with the ZFS distributions extracted from J band, see Table 1 in the main manuscript. The microwave frequency was 9.496 GHz.

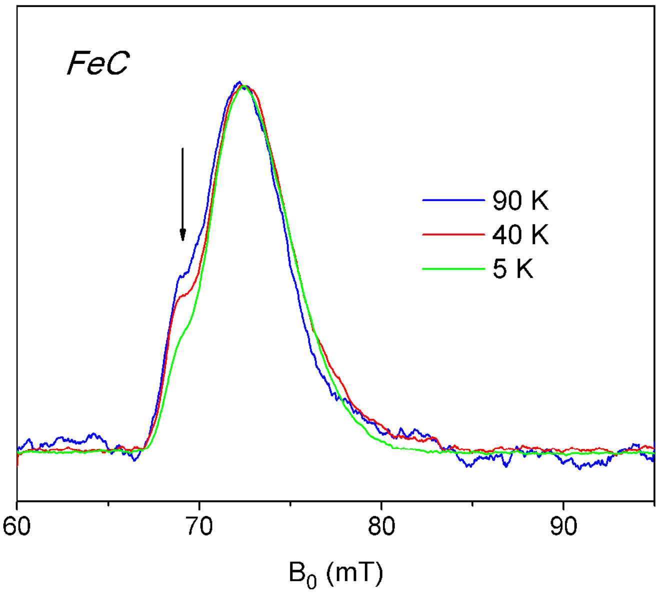

Fig. S5 g' = 9 region of the X-band (9.495 GHz) CW EPR spectra of monoferric human serum transferrin FeC at three temperatures. The spectra are normalized on the main peak (at 72 mT). The amplitude of the shoulder (at 69 mT) relative to the main peak decreases as the temperature is lowered.

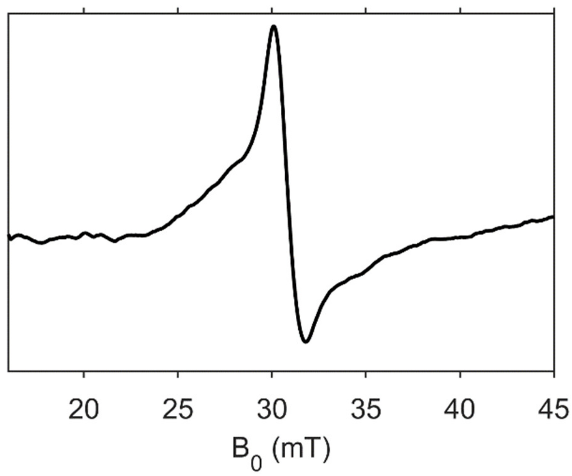

Fig. S6 L-band (1.8404 GHz) CW EPR spectrum of human serum transferrin isolated N-lobe. Courtesy of Aaron Kittell and Bill Antholine at the Medical College of Wisconsin. The spectrum was recorded at a temperature of 110 K with a modulation amplitude of 0.55 mT and a microwave power of 0.3 mW.

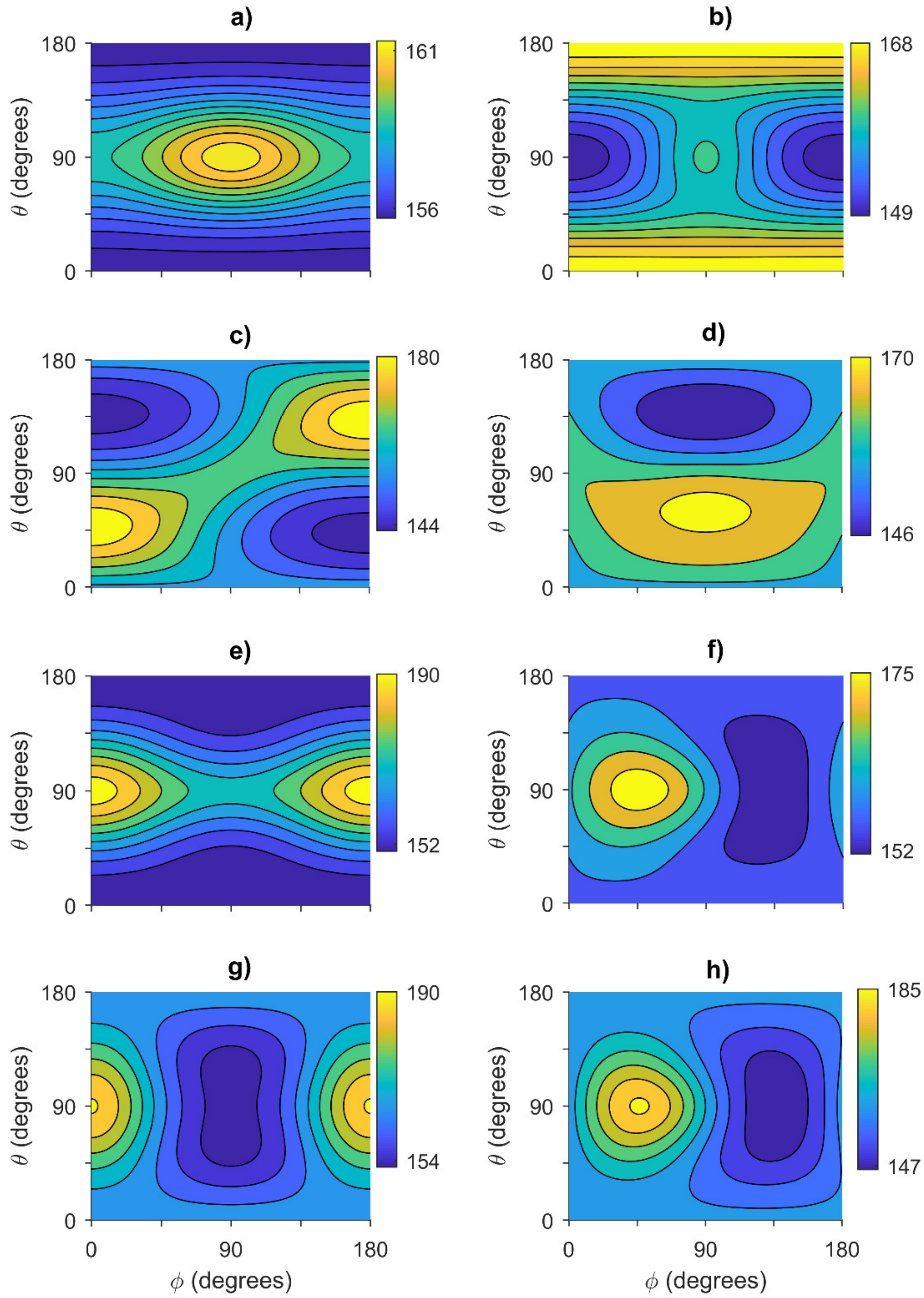

Fig. S7 Maps showing dependence of the resonance field position of the $|\pm 3/2\rangle$ intra-doublet transition on the relative orientation of the magnetic field vector. ϕ is the azimuth and θ is the polar angle. (a) D = 30 GHz, λ = 0.32, and all 4th-order terms are zero. For the other maps, D = 9.38 GHz (FeC), λ = 0.32, and all 4th-order terms are zero, except for B_4^0 = 10 MHz (b), B_4^1 = 70 MHz (c), B_4^{-1} = 70 MHz (d), B_4^2 = 70 MHz (e), B_4^{-2} = 70 MHz (f), B_4^4 = 70 MHz (g), and B_4^{-4} = 70 MHz (h).

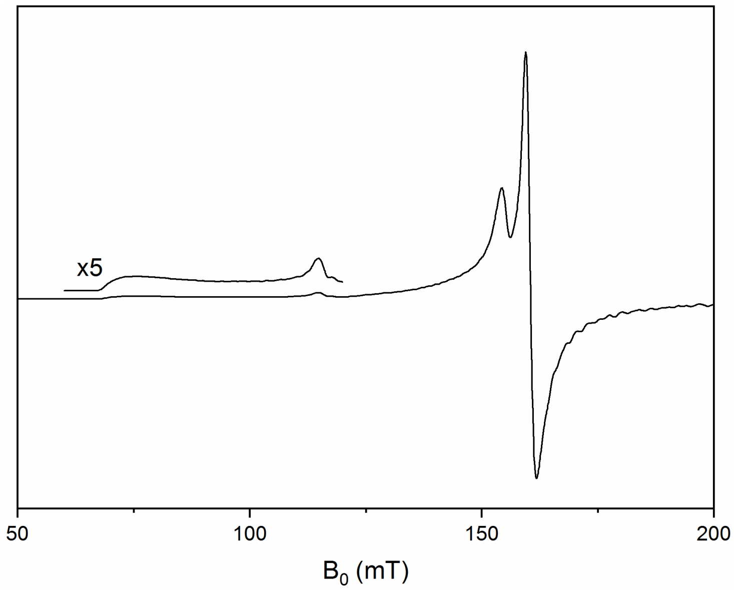

Fig. S8 Simulated X-band spectrum of E83A based on the ZFS distribution extracted from J band (Table 1). The spectra in the library were calculated with B_4^{-3} = 70 MHz.