1 Single-crystal orientations

Table 1: Orientation of the single crystals with respect to the laboratory frame. The directional cosines of the crystal axes a, b, c are given with respect to the laboratory frame X, Y, Z for a crystal rotation denoted with 0° in the spectra. The magnetic field B_0 is parallel to the X-axis, and the rotation of the single crystal corresponds to a rotation of the B_0-vector around the Z-axis. The subscripts W and Q indicate the single crystal used in W- and Q-band, respectively.

	a_W	b_W	c_W	a_Q	b_Q	c_Q
X	0.4397	−0.1802	0.8799	−0.1294	0.0089	−0.9916
Y	−0.8944	−0.1769	0.4107	0.9780	0.1664	−0.1261
Z	0.0816	−0.9676	−0.2389	0.1639	−0.9860	−0.0302

2 High-field EPR and ENDOR on $Y_D^\bullet$

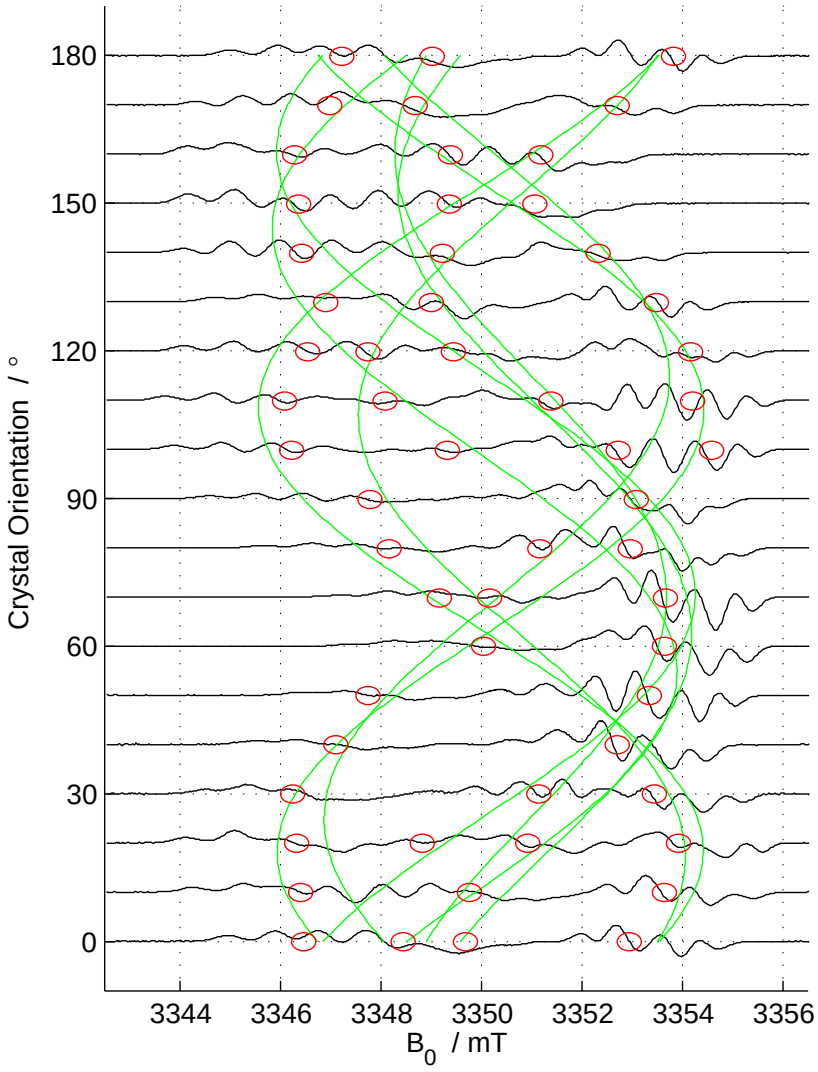

Figure 1: Pseudo-modulated FSE single crystal spectra of the $Y_D^\bullet$ measured at W-band. The effective g-values for the eight crystal sites are shown in green. The red circles denote the field positions at which ^{1}H-ENDOR spectra were taken. The field positions chosen follow the effective g-value orientation dependency. For some crystal orientations (e.g. 0°) four field positions were chosen to cover all crystal sites. At other crystal orientations (e.g. 40°) only two field positions are needed. All spectra were measured at $T = 40$ K with a π-pulse length of 128 ns, the shot repetition time was 2000 μs.

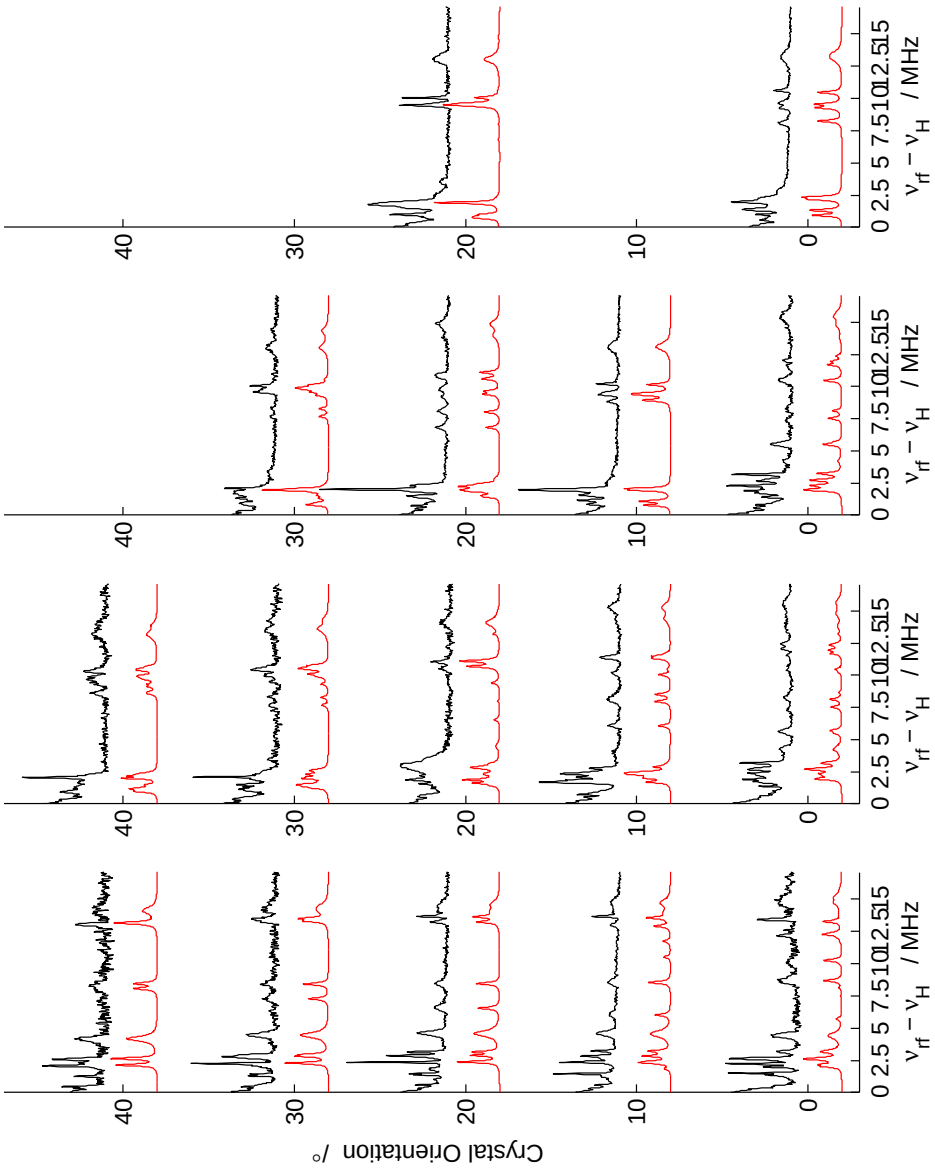

Figure 2: ^{1}H-ENDOR single-crystal spectra of the $Y_D^\bullet$ for the crystal orientations 0°–40°. Experimental spectra are shown in black, simulations in red. The four columns correspond to the field positions at which ENDOR-spectra were taken. The field positions are marked as red circles in Figure 1 and the spectra correspond to the field positions marked from left to right. Depending on the effective g-values of different crystal sites two up to four field positions were chosen for taking ENDOR spectra. All spectra were measured at $T = 40$ K, the π-pulse had a length of 128 ns, the RF-pulse a length of 16 μs, the shot repetition time was 8000 μs.

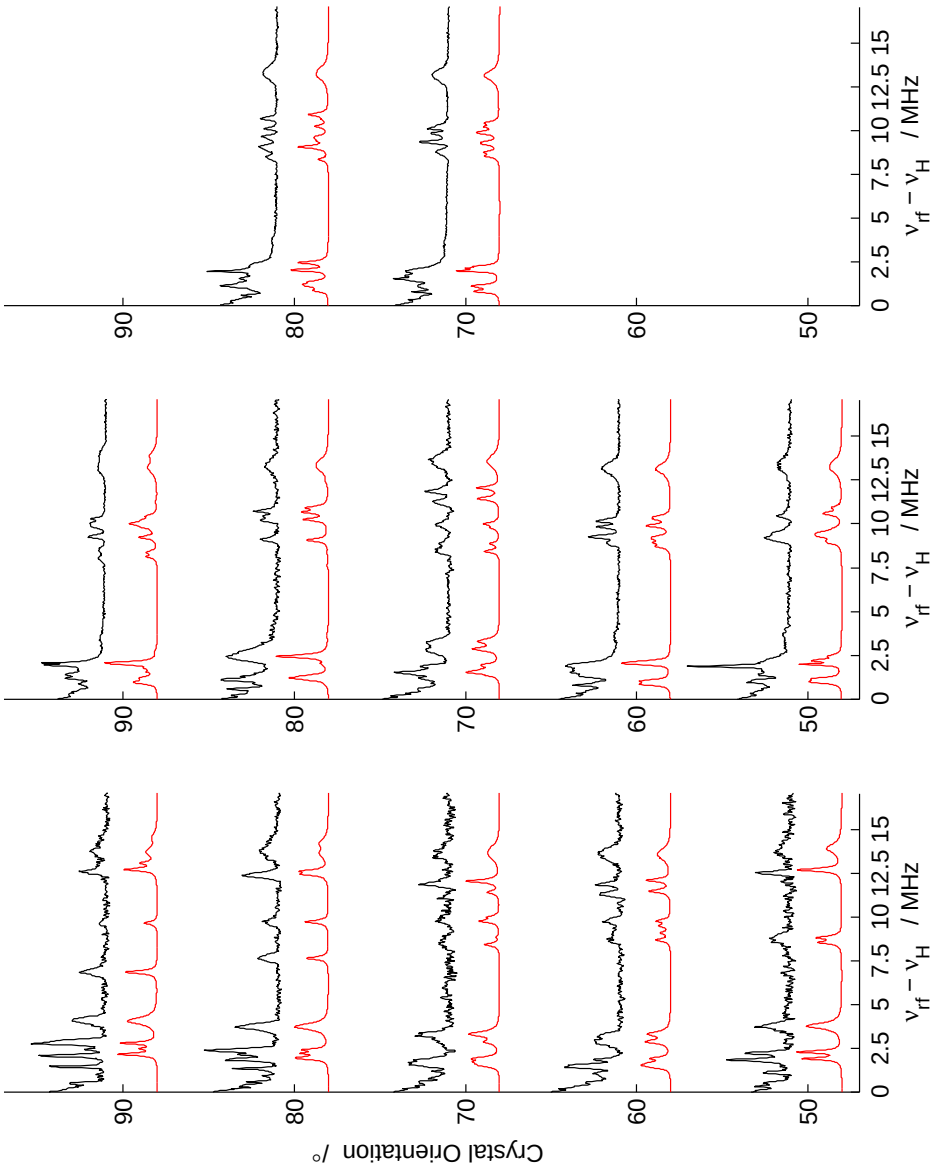

Figure 3: ^{1}H-ENDOR single-crystal spectra of the $Y_D^\bullet$ for the crystal orientations 50°–90°. For details see Figure 2

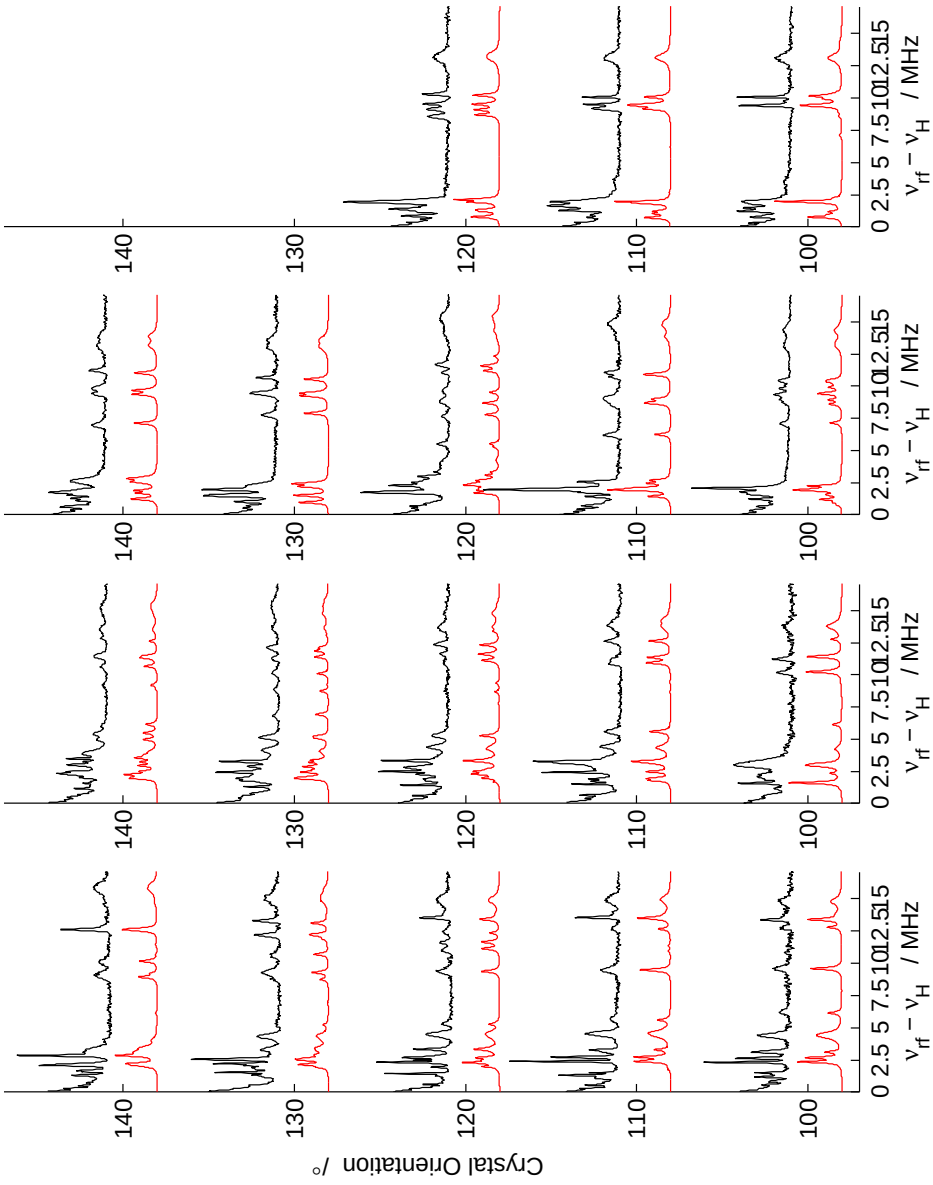

Figure 4: ^{1}H-ENDOR single-crystal spectra of the $Y_D^\bullet$ for the crystal orientations 100°–140°. For details see Figure 2

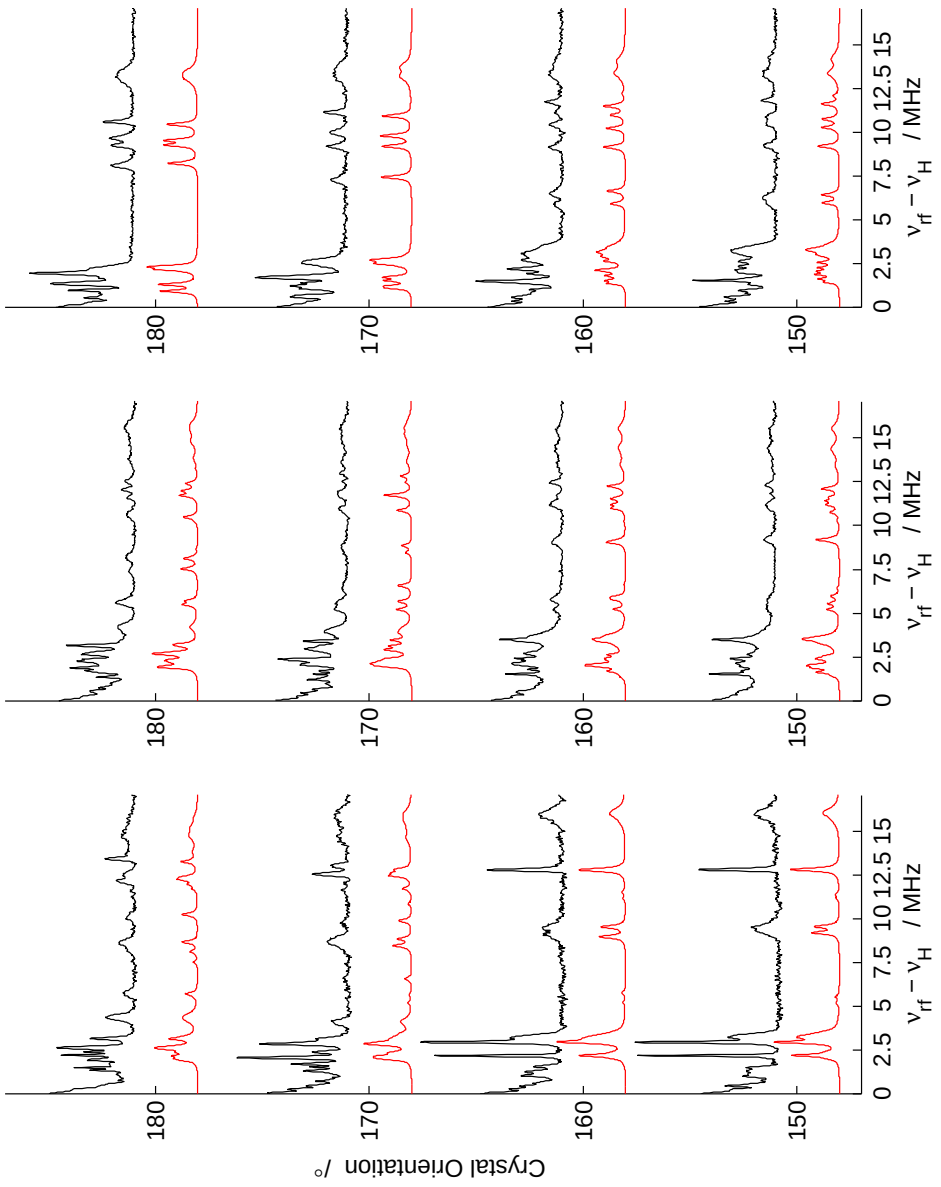

Figure 5: ^{1}H-ENDOR single-crystal spectra of the $Y_D^\bullet$ for the crystal orientations 150°–180°. For details see Figure 2

3 Q-band EPR and ENDOR on the S_2 MLS

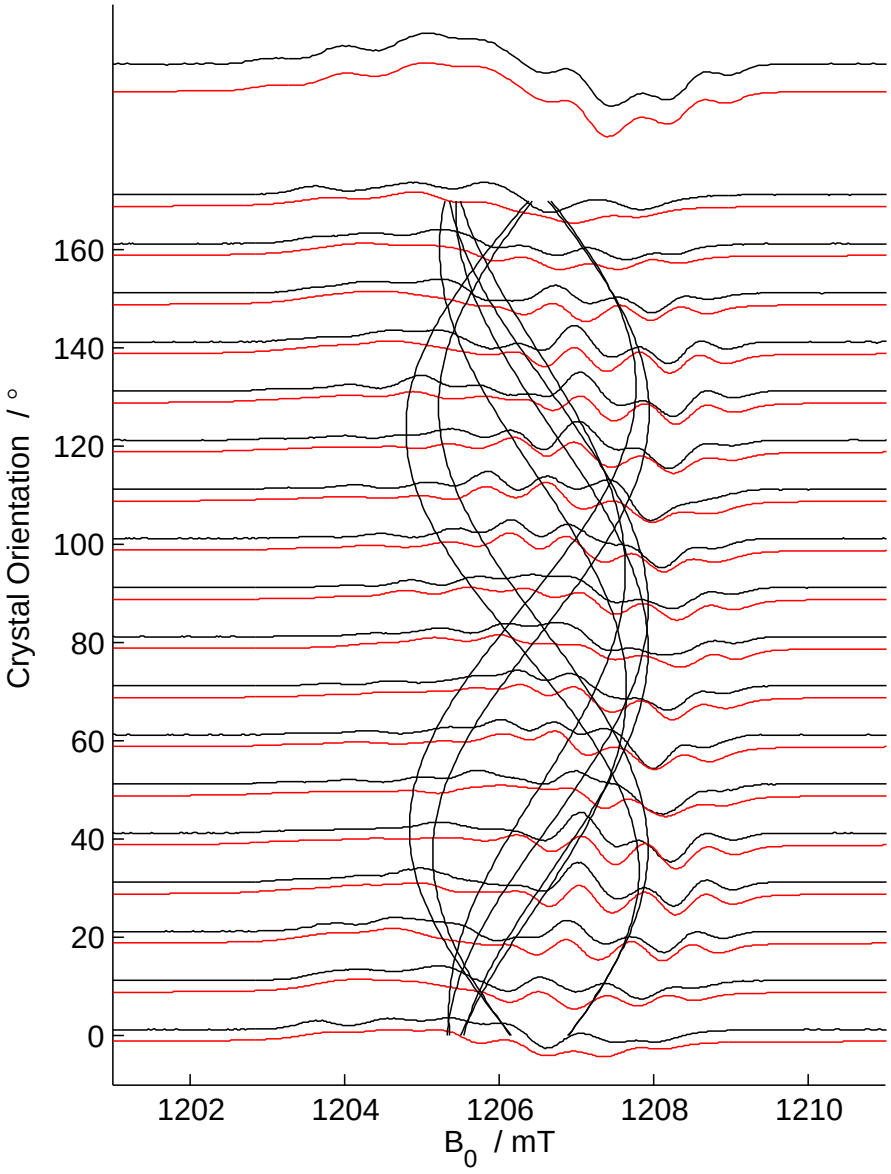

Figure 6: Pseudo-modulated FSE single-crystal spectra of the $Y_D^\bullet$ measured at Q-band are shown in black, simulations in red. The orientation dependence of the effective g-values for $Y_D^\bullet$ at the eight crystal sites is shown in black. All spectra were measured at $T = 5$ K with a π-pulse length of 40 ns and a shot repetition time of 140 ms.