magnetochemistry

Supplementary Information

Reciprocating thermal behavior in multichannel relaxation of cobalt(II) based single ion magnets

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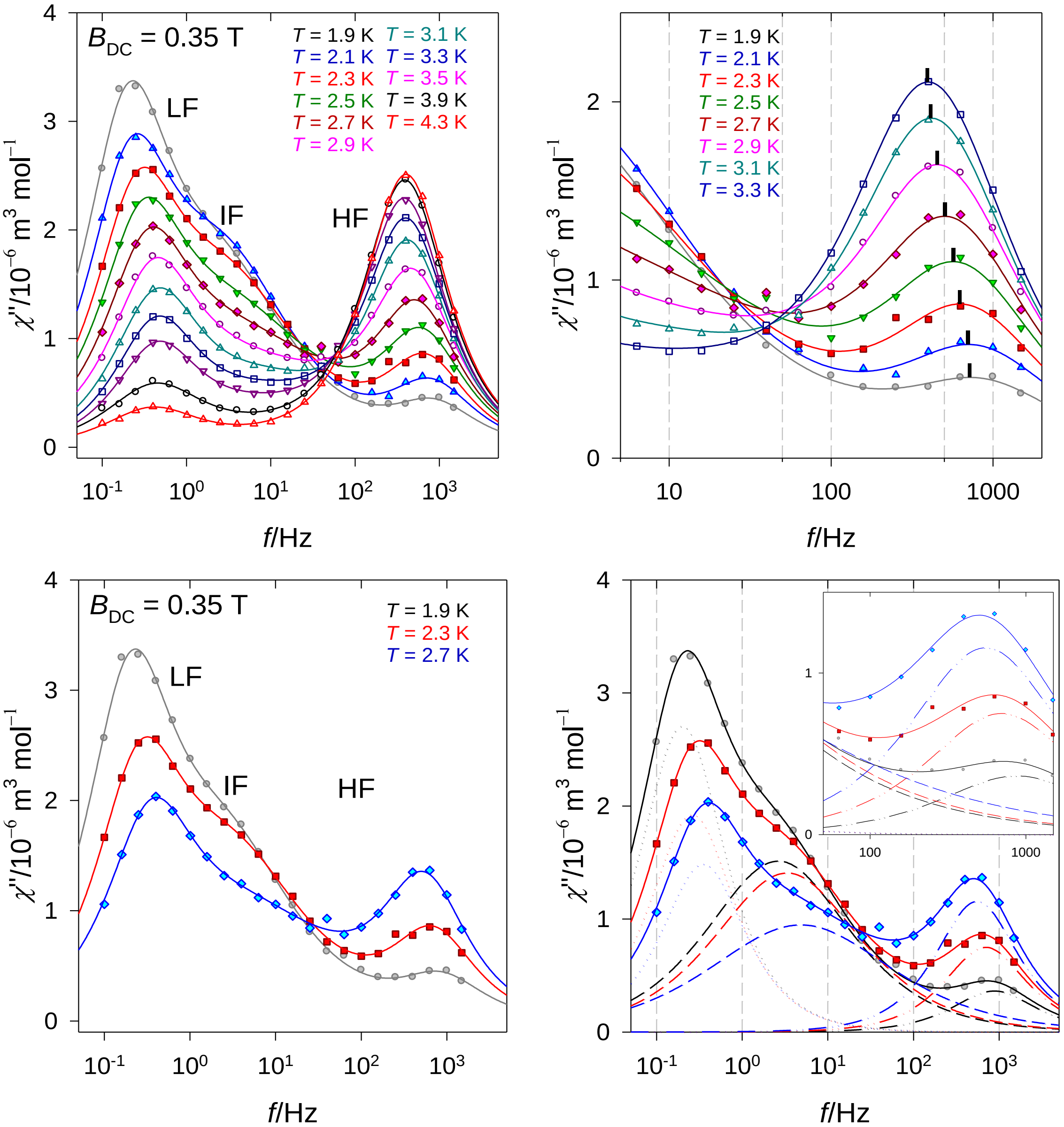

Figure S1. Deconvolution curves for the three-set Debye model for **1**. Solid line – convolution of three primitive curves (dotted, dashed, dot-dot-dashed).

This figure demonstrates that the maximum of the dot-dot-dashed curves (that determines the HF relaxation time) matches the maximum of the convoluted curve so that the reciprocating thermal behavior is not a numerical artifact and refers to the HF relaxation mode.

Table S1. Stability test of the data fitting with incomplete and/or reduced data points for [Co(*biq*)Cl_2], **12**. Data taken at B_{DC} = 0.2 T and T = 2.7 K.

Points/missing	$R(\chi')$/%	$R(\chi'')$/%	χ_S	χ_{LF}	α_{LF}	$\tau_{LF}/10^{-3}$ s	χ_{HF}	α_{HF}	$\tau_{HF}/10^{-3}$ s	x_{HF}
22/0	**0.32**	**1.6**	**1.44(3)**	**2.84(10)**	**.31(3)**	**33.0(33)**	**8.44(2)**	**.14(1)**	**0.64(1)**	**.80**
21/1	**0.35**	**1.4**	**1.49(3)**	**2.93(10)**	**.31(3)**	**32.9(34)**	**8.43(1)**	**.13(1)**	**0.65(1)**	**.79**
20/2	**0.34**	**1.3**	**1.49(5)**	**2.93(12)**	**.31(3)**	**31.9(34)**	**8.43(1)**	**.13(1)**	**0.65(1)**	**.79**
19/3	**0.33**	**1.4**	**1.49(7)**	**2.93(16)**	**.31(3)**	**31.9(38)**	**8.42(2)**	**.13(1)**	**0.65(1)**	**.79**
18/4	0.24	1.4	1.47(11)	2.93(19)	.31(2)	31.3(35)	8.44(2)	.12(2)	0.64(2)	.79
17/5	0.24	1.1	1.47(21)	2.93(31)	.31(2)	31.3(38)	8.44(1)	.12(2)	0.64(3)	.79
16/6	0.22	1.2	1.47(47)	2.93(58)	.31(3)	31.3(46)	8.44(1)	.11(4)	0.64(8)	.79
15/7	0.21	1.2	1.47(117)	2.93(135)	.31(3)	31.3(62)	8.44(1)	.11(8)	0.64(20)	.79
14/8	0.22	1.5	*1.47(339)*	*2.93(370)*	.31(4)	31.3(96)	8.44(2)	*.11(17)*	*0.64(59)*	.79
13/9	0.27	1.6	*1.47(1261)*	*2.93(1332)*	.31(5)	*31.3(183)*	8.43(2)	*.12(50)*	*0.63(219)*	.79

Note: 2.93(31) means 2.93 ± 0.31, 2.93(135) means 2.93 ± 1.35, .31(3) means 0.31 ± 0.03.
Data in blue (bold) refer to the dataset above the maximum of the out-of-phase susceptibility.
Data in red (*Italic*) means that the standard deviation in parenthesis is higher than the value of the fitted parameter, i.e. such a fit is out of acceptance (irrespective that the value is the same as for the full data set).

This test demonstrates that the data fitting using the (two-set) Debye model is stable even in the case when the maximum of the peak is not supported by measured values. However, monitoring of the standard deviations is crucial. The parameters of the interest, i.e. the relaxation times (and eventually the mole fraction of the relaxing species) are well stable and thus reliable.

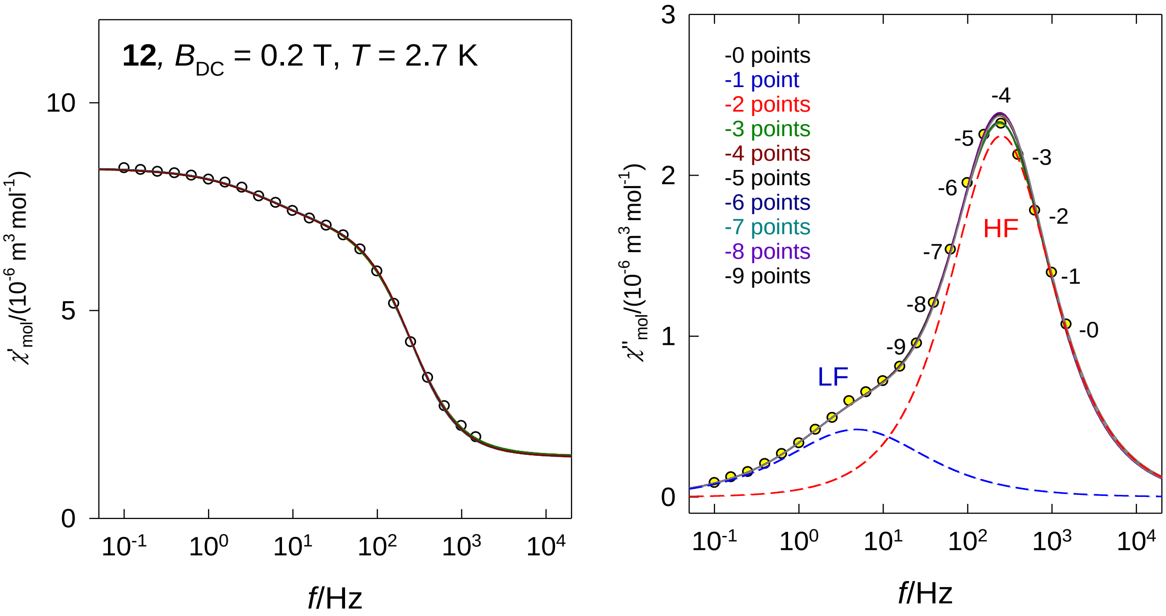

Figure S2. Test of the stability of the fitted relaxation time when 1 to 9 data points from the HF range are gradually omitted. Solid lines for individual fits are overlapped. Dashed lines: primitive low-frequency (LF) and high-frequency (HF) com-ponents. Experimental data points from [38] for [Co(*biq*)Cl_2], **12**.

Table S2. Stability test of the data fitting with incomplete and/or reduced data points for [$C_{28}H_{26}Co_{0.52}N_4O_{13}Zn_{1.48}$], **2a**. Data taken at B_{DC} = 0.4 T and T = 2.1 K.

Points/missing	$R(\chi')$/%	$R(\chi'')$/%	χ_{HF} /10^{-6} SI	α_{HF}	τ_{HF} /10^{-3} s
22/0	1.5	2.9	0.55(1)	.15(1)	18.1(2)
17/5	1.3	2.0	0.55(1)	.15(1)	18.1(2)
12/10	0.86	1.6	0.55(1)	.15(1)	18.1(2)
10/12	0.78	2.6	0.55(1)	.17(1)	18.0(2)
9/13	0.53	5.8	0.55(1)	.20(1)	16.1(5)
8/14	0.54	3.4	0.55(1)	.20(1)	16.2(5)
7/15	0.51	1.5	0.55(1)	.20(1)	16.8(6)
6/16	0.19	6.0	0.56(2)	.26(2)	15.0(11)

This test demonstrates that the data fitting using the (two-set) Debye model is stable even in the case when the maximum of the peak is not supported by measured values.

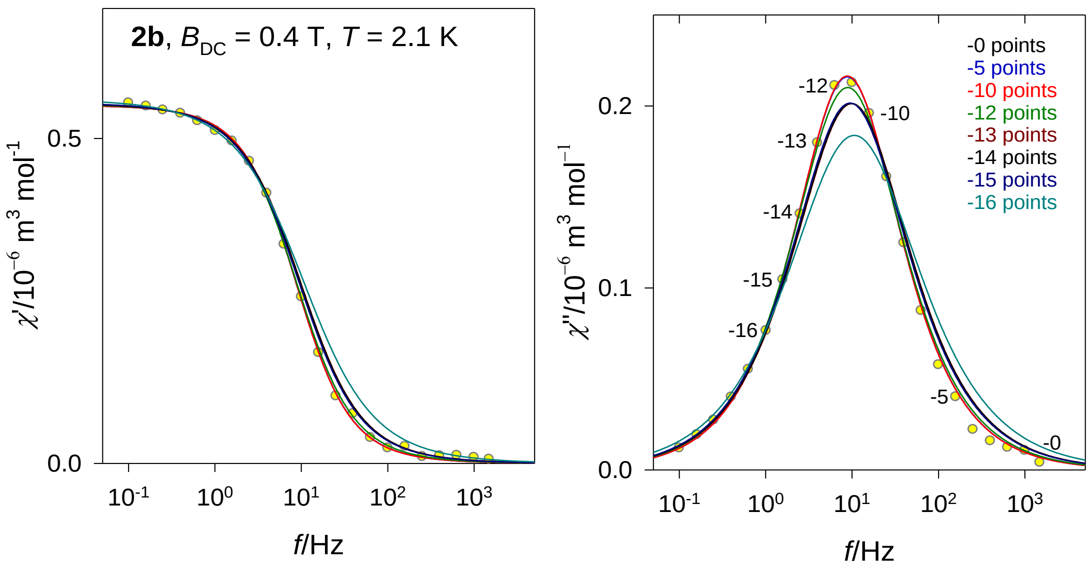

Figure S3. Test of the stability of the fitted relaxation time when data points from the HF range are gradually omitted. Experimental data for a doped sample $C_{28}H_{26}Co_{0.52}N_4O_{13}Zn_{1.48}$ (**2b**). From: Boča, R.; Rajnák, C.; Moncoľ, J.; Titiš, J.; Valigura, D. Breaking the Magic Border of One Second for Slow Magnetic Relaxation of Cobalt-Based Single Ion Magnets. *Inorg. Chem.* **2018**, *57*, 14314-14321. [https://doi.org/10.1021/acs.inorgchem.8b02287].

Table S3. Fitted relaxation time for **5** at B_{DC} = 0.6 T with three Debye components.

T/K	$R(\chi')$/%	$R(\chi'')$/%	τ_{LF} 10^{-3} s	τ_{IF} /10^{-3} s	τ_{HF} /10^{-6} s	x_{HF}
1.9	0.69	1.4	632(19)	92.0(483)	**51.2(14)**	0.28
2.1	0.92	1.7	523(33)	75.0(920)	**57.1(16)**	0.33
2.3	1.3	2.1	467(42)	49.8(857)	**61.4(22)**	0.39
2.5	0.51	2.4	445(22)	48.4(378)	**65.9(10)**	0.47
2.7	0.47	2.3	355(20)	15.0(33)	**68.5(8)**	0.55
2.9	0.61	1.9	343(38)	14.7(207)	**68.6(10)**	0.60
3.1	0.26	2.4	357(16)	13.0(35)	68.6(5)	0.68
3.3	0.56	2.2	337(19)	10.1(41)	66.9(8)	0.75
3.7	0.48	2.8	363(21)		60.7(6)	0.83
4.1	0.31	1.9	415(22)		52.2(4)	0.89
4.5	0.28	2.2	494(43)		43.0(3)	0.92

Bold data demonstrate the RTB effect.