Correlation between anisotropy, slow relaxation, and spectroscopic behaviour: the Ln(trensal) family

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Acknowledgments
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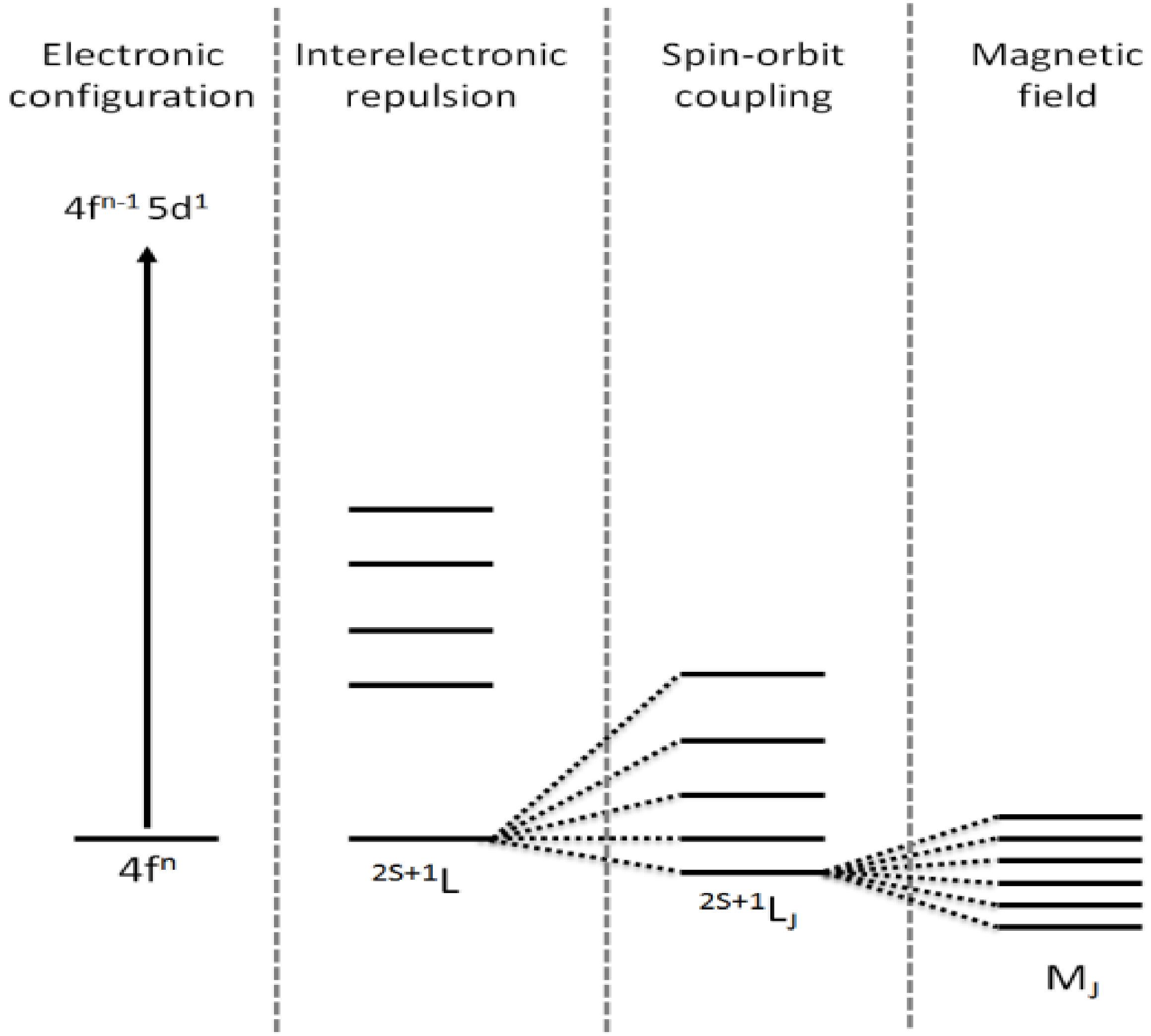
Outline

- Introduction
- Luminescence and electronic structure
- EPR and static magnetic behaviour
- Analysis of dynamic behaviour
- Correlation to the anisotropy

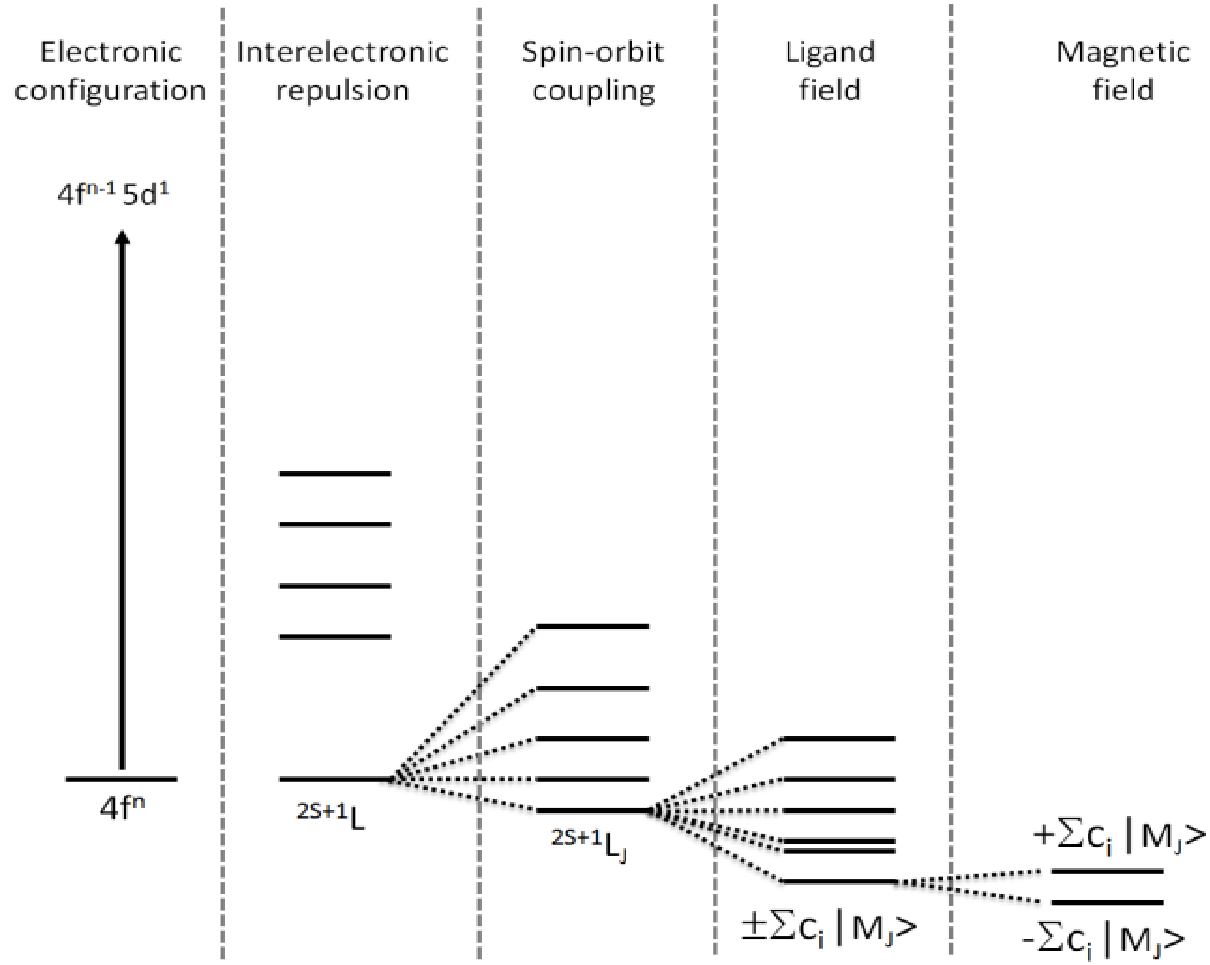
Free ion electronic structure



$$\Delta E = \mu_B g_J m_J H$$

$$g_J = \frac{3}{2} + \frac{L(L+1) - S(S+1)}{2J(J+1)}$$

Effect of the ligands



EPR provides information on wavefunction composition and anisotropy type

$$\Delta E = (1/2) g_{eff} \mu_B B$$

$$g_{//}^{eff} = 2 g_J \langle \Psi_+ | \hat{J}_z | \Psi_+ \rangle$$

$$g_{\perp}^{eff} = g_J \langle \Psi_+ | \hat{J}_+ | \Psi_- \rangle$$

Parametrization of ligand field: Stevens' formalism

$$\hat{\mathbf{H}}_{\mathbf{LF}}^{Stev} = \sum_{k=2,4,6} \rho^k \sum_{q=-k}^{k} A_k^q \left\langle r^k \right\rangle \hat{\mathbf{O}}_{\mathbf{k}}^{\mathbf{q}}$$

$A_k^q \left\langle r^k \right\rangle$ is a parameter, ρ^k is a number (tabulated)

$\hat{\mathbf{O}}_{\mathbf{k}}^{\mathbf{q}}$ are operator equivalents of the crystal field potential

which can be expanded in terms of J_+, J_-, J_z polynomials

- **Most used in magnetic and EPR studies**
- **It becomes too involved for treatment of excited multiplets**

Parametrization of Ligand field: Wybourne's formalism

$$\hat{\mathbf{H}}_{\mathbf{LF}}^{Wyb} = \sum_{k=0}^{\infty}\left[B_0^0 C_0^0(i) + \sum_{q=1}^{k} B_q^k \left(C_{-q}^k(i) + (-1)^q C_q^k(i) \right) + iB'^k_q \left(C_{-q}^k(i) - (-1)^q C_q^k(i) \right) \right]$$

B_q^k are parameters

$C_q^k(i)$ are related to spherical harmonics by: $C_q^k(i) = \sqrt{\frac{2k+1}{4\pi}} Y_q^k(i)$

The resulting matrix elements are:

$$\left\langle l^n \tau SLJM_J \right| \sum_i C_q^k(i) \left| l^n{}'\tau'S'L'J'M_J{}' \right\rangle = (-1)^{S+L'+2J-M_J+k+1}\, 7\left[(2J+1)(2J'+1)\right]^{1/2} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \times$$
$$\begin{pmatrix} J & k & J' \\ -M_J & q & M_J{}' \end{pmatrix} \begin{Bmatrix} J & J' & k \\ L & L & S \end{Bmatrix} \left\langle l^n \tau SL \| U^k \| l^n{}'\tau'SL' \right\rangle$$

- Allow direct comparison with luminescence data in literature
- Easy inclusion of excited multiplets
- Not much used in molecular magnetism (but see CONDON program)

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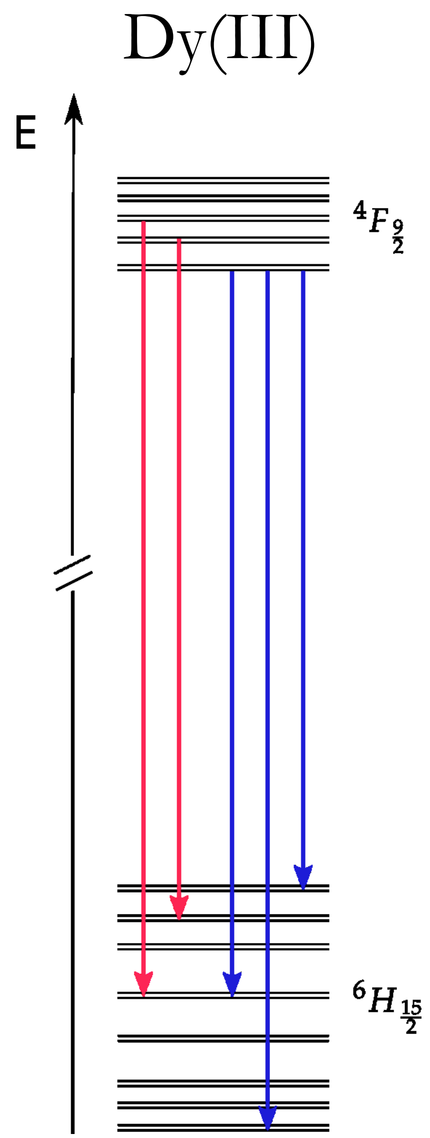
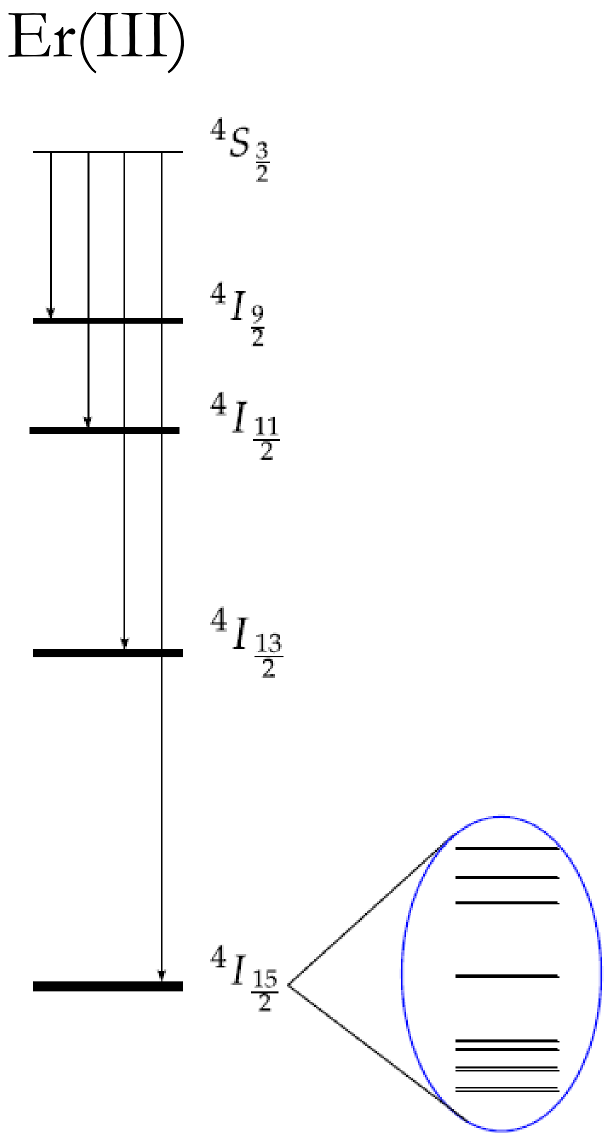
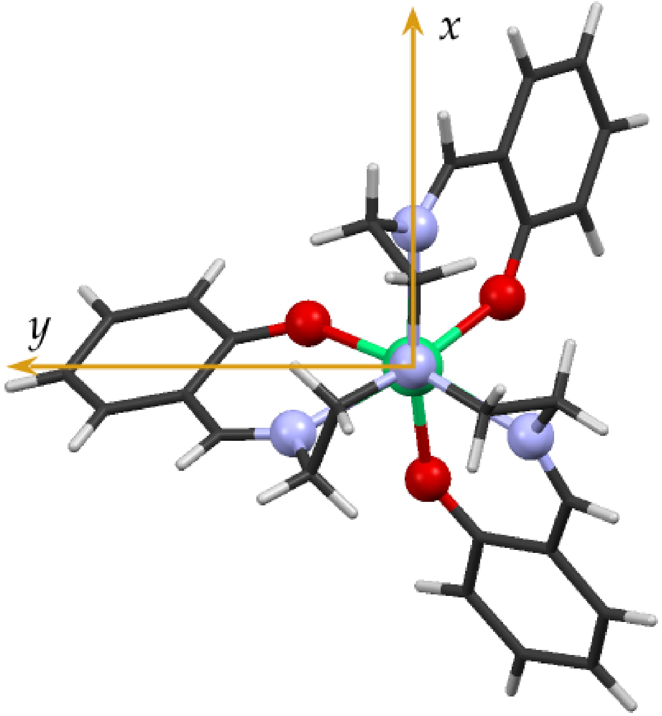
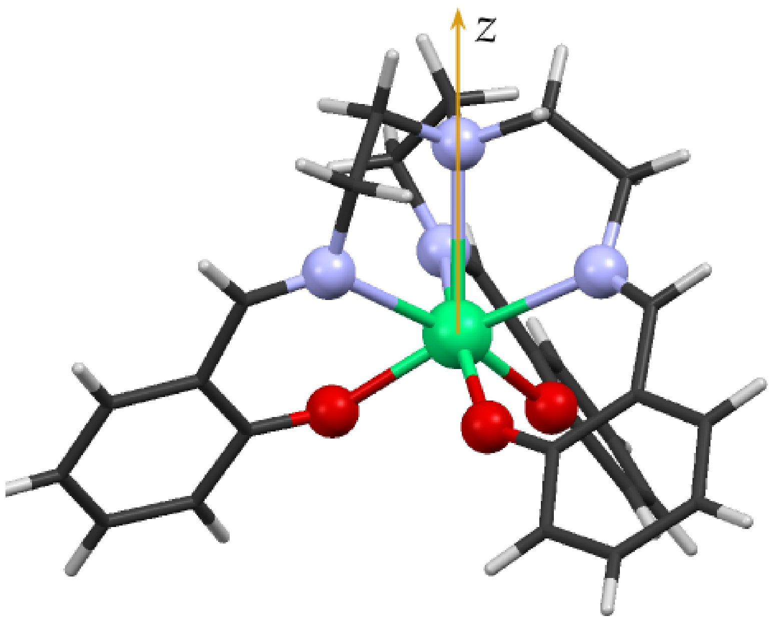
The importance of luminescence spectroscopy





Ln(trensal) family



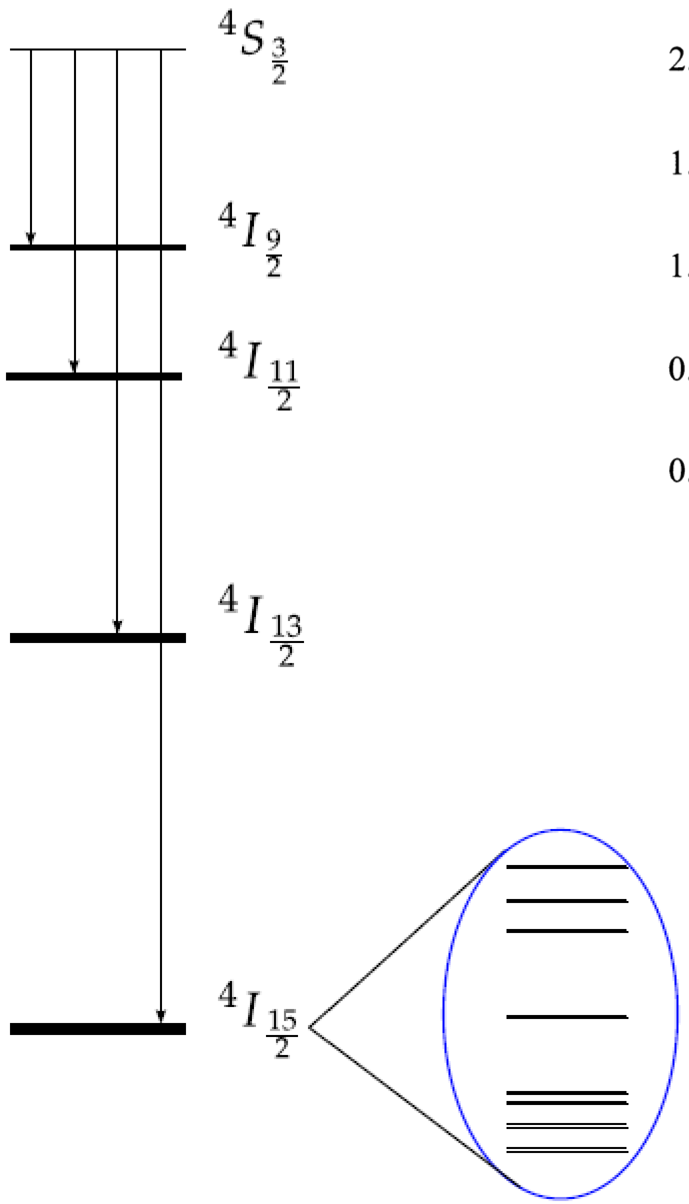


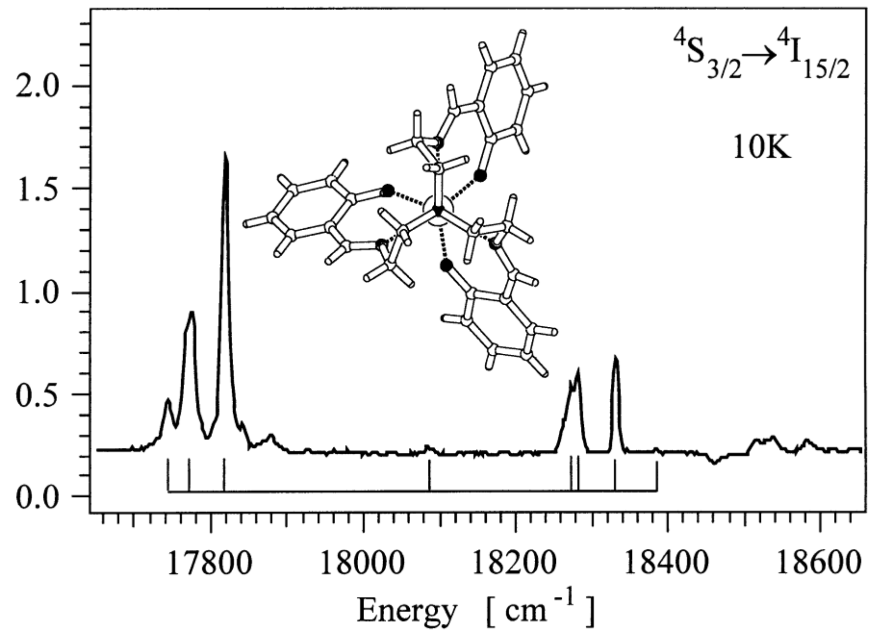
Space group: P-3c1

Ln(III) ions on a C_3 axis

B. M. Flanagan, P. V. Bernhardt, E. R. Krausz, S. R. Lüthi, M. J. Riley, *Inorg. Chem. 2002,* ***41, 5024-5033***

Luminescence spectra





- Single crystal data with polarized light
- Low temperature (no hot bands)
- Luminescence to ground multiplet levels observed for Er

B. M. Flanagan, P. V. Bernhardt, E. R. Krausz, S. R. Lüthi, M. J. Riley, *Inorg. Chem. 2002*, ***41*, *5024-5033***

Luminescence spectra

Table 1. Experimental Energy Levels and Transition Line Strengths for Er(trensal)

		energy (cm^{-1})		obsd intens (10^{-42} esu^2 cm^2)				energy (cm^{-1})		obsd intens (10^{-42} esu^2 cm^2)	
multiplet	irrep[a]	obsd	calc	S_σ [D^2]	S_π [D^2]	multiplet	irrep[a]	obsd	calc	S_σ [D^2]	S_π [D^2]
$^4I_{15/2}$	$\Gamma_{4,5}$	0	0	0.005[b]		$^4F_{9/2}$	Γ_6	15 302	15 307	15.8	1.4
	$\Gamma_{4,5}$	54	54	0.235			$\Gamma_{4,5}$	15 328	15 317	16.4	4.2
	Γ_6	102	102	0.176			$\Gamma_{4,5}$	15 382	15 395	63.0	6.8
	$\Gamma_{4,5}$	110	110	0.202			Γ_6	15 538	15 552	100.2	7.2
	Γ_6	299	299	0.033			$\Gamma_{4,5}$	15 562	15 569	14.5	21.1
	$\Gamma_{4,5}$	568	567	1.000		$^4S_{3/2}$	$\Gamma_{4,5}$	18 395	18 420	1.3	3.8
	Γ_6	610	612	0.753			Γ_6	18 469	18 484	92.0	5.9
	$\Gamma_{4,5}$	642	641	0.229		$^2H_{11/2}$	$\Gamma_{4,5}$	19 157	19 186	34.3	12.1
$^4I_{13/2}$	$\Gamma_{4,5}$	6594	6590	21.9	14.9		Γ_6	19 165	19 194	87.0	7.2
	Γ_6	6611.5	6613	10.4	1.8		$\Gamma_{4,5}$	19 193	19 200	83.6	29.9
	$\Gamma_{4,5}$	6620.5	6630	34.1	31.4		$\Gamma_{4,5}$	19 371	19 359	143.5	32.7
	$\Gamma_{4,5}$	6690	6706	32.8	11.5		Γ_6	19 379	19 386	121.0	8.3
	$\Gamma_{4,5}$	6909	6937	19.0	0.0		$\Gamma_{4,5}$	19 412	19 404	56.2	20.1
	Γ_6	6928	6949	132.7	10.6	$^4F_{7/2}$	$\Gamma_{4,5}$	20 530	20 516	4.6	20.1
	$\Gamma_{4,5}$	6939	6967	12.2	0.0		$\Gamma_{4,5}$	20 613	20 615	2.5	25.3
$^4I_{11/2}$	$\Gamma_{4,5}$	10 290.5	10 270	17.2	2.1		Γ_6	20 679	20 665	6.5	1.9
	Γ_6	10 300.5	10 279	1.1	0.0		$\Gamma_{4,5}$	20 738	20 741	1.7	4.9
	$\Gamma_{4,5}$	10 315.5	10 302	2.5	0.0	$^4F_{5/2}$	$\Gamma_{4,5}$	22 244	22 234	3.7	13.6
	$\Gamma_{4,5}$	10 444	10 449	0.0	14.6		Γ_6	22 261	22 240	4.2	2.5
	Γ_6	10 448.5	10 459	27.5	14.8		$\Gamma_{4,5}$	22 353	22 326	1.6	11.9
	$\Gamma_{4,5}$	10 509.5	10 466	0.0	0.0	$^4F_{3/2}$	$\Gamma_{4,5}$	22 607	22 604	0.8	7.2
$^4I_{9/2}$	$\Gamma_{4,5}$	12 321	12 283	4.8	1.7		Γ_6	22 734	22 736	3.1	1.6
	Γ_6	12 532	12 531	1.5	0.0	$^2H_{9/2}$	$\Gamma_{4,5}$	24 434	24 424	16.5	2.2
	$\Gamma_{4,5}$		12 589	7.2	0.10		Γ_6	24 619	24 645	10.0	1.2
	Γ_6	12 768	12 728	21.5	2.4		$\Gamma_{4,5}$	24 628	24 672	5.0	3.9
	$\Gamma_{4,5}$	12 806	12 774	11.3	2.0		$\Gamma_{4,5}$	24 798	24 782	2.7	2.8
							Γ_6	24 841	24 836	11.7	2.9

About 50 observed transitions!

B. M. Flanagan, P. V. Bernhardt, E. R. Krausz, S. R. Lüthi, M. J. Riley, *Inorg. Chem. 2002*, ***41, 5024-5033***

Ln(trensal) family

Best fit LF parameters of luminescence data

	Dy	Er
B_0^2	-671(39)	-720
B_0^4	-186(77)	-44(106)
B_3^4	-2153(34)	-2121(83)
B_0^6	1241(57)	988(36)
B_3^6	439(41)	53(49)
B'^6_3	-284(83)	92(53)
B_6^6	660(49)	545(34)
B'^6_6	145(137)	311(36)

Ground multiplets splittings

Dy	Er
0	0
50	54
98	102
172	109
414	321
577	568
645	619
787	651

$$\hat{H}_{lf} = B_0^2\mathbf{C_0^2} + B_0^4\mathbf{C_0^4} + B_3^4\left(\mathbf{C_{-3}^4} - \mathbf{C_3^4}\right) + B_0^6\mathbf{C_0^6}$$

$$+ B_3^6\left(\mathbf{C_{-3}^6} - \mathbf{C_3^6}\right) + iB'^6_3\left(\mathbf{C_{-3}^6} + \mathbf{C_3^6}\right) + B_6^6\left(\mathbf{C_{-6}^6} + \mathbf{C_6^6}\right) + iB'^6_6\left(\mathbf{C_{-6}^6} - \mathbf{C_6^6}\right)$$

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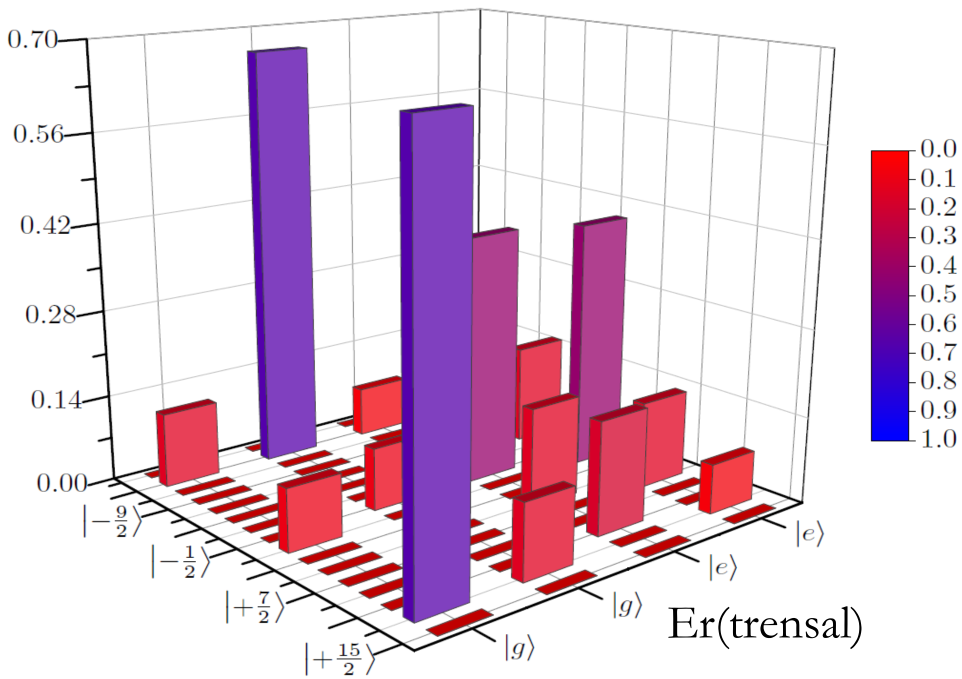
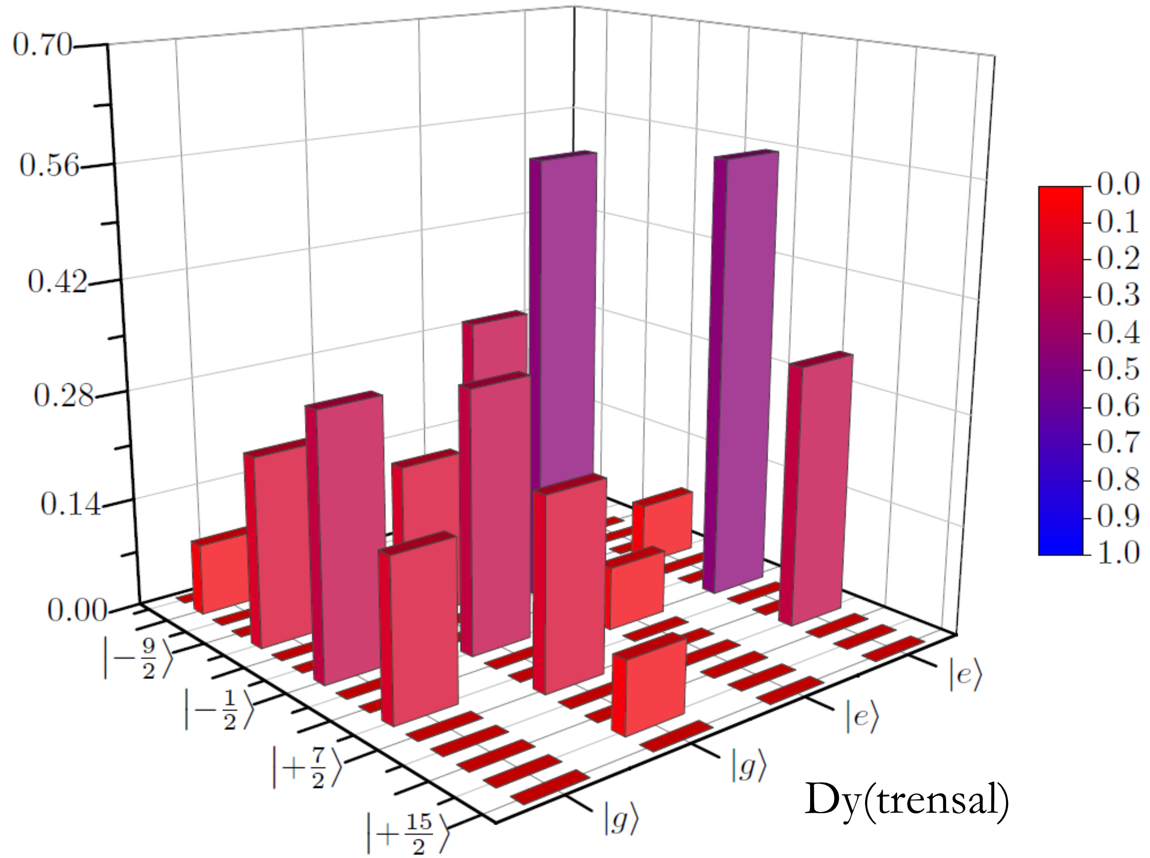
Er(trensal) wavefunction composition



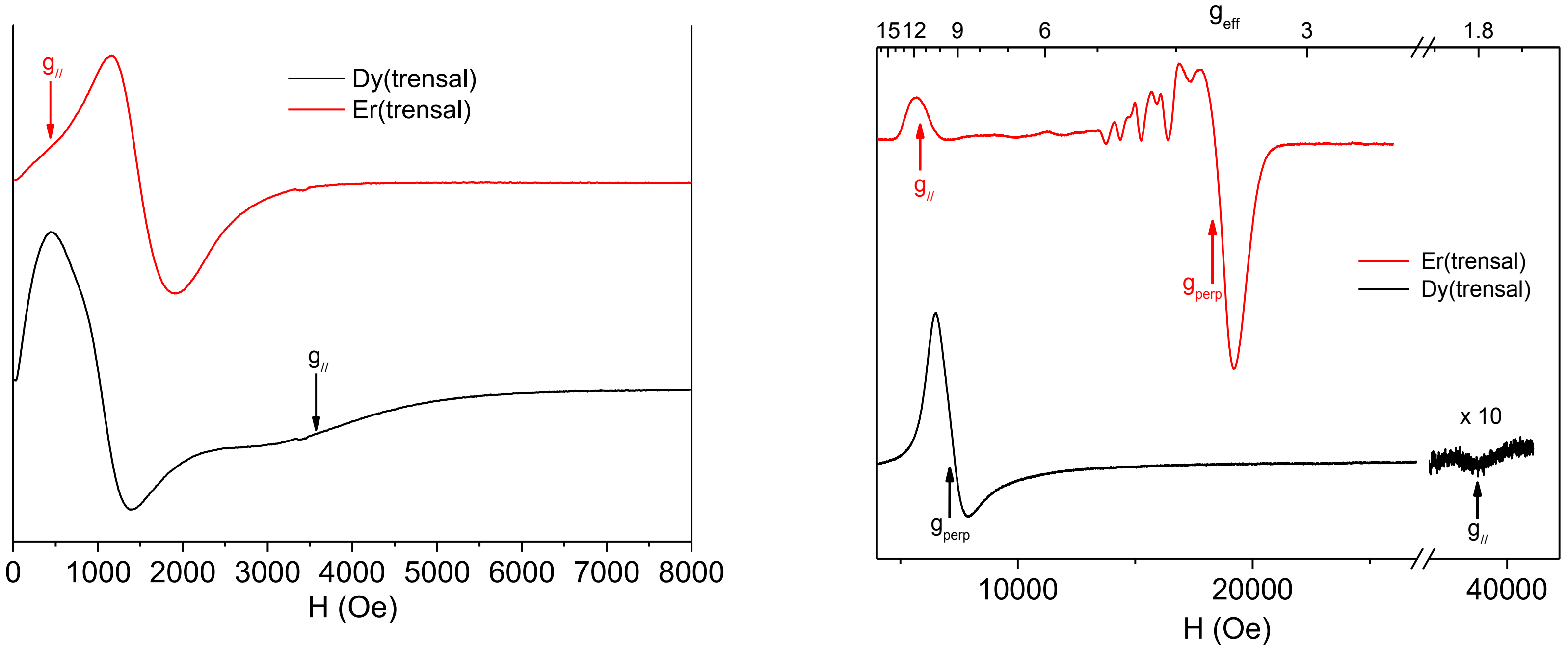
- |13/2> component is dominant for the ground state
- Small m_J components are dominant for the excited state

Dy(trensal) wavefunction composition



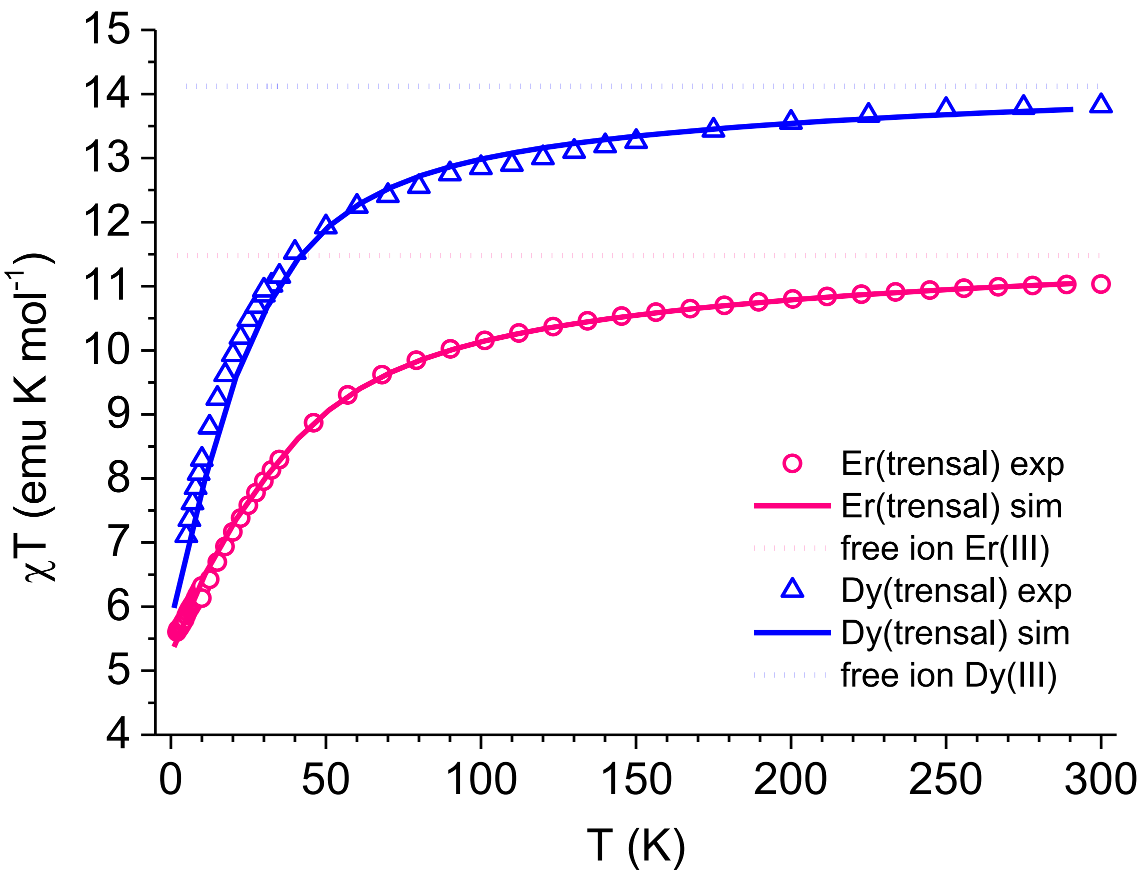
- small m_J components are dominant in the ground state
- Large |+3/2> and |-9/2> components in the first exc. state

EPR spectroscopy



	Dy(trensal)		Er(trensal)	
	exp	calc	exp	calc
$g_{//}$	1.8 ± 0.1	2.6	11.8 ± 0.4	13
$g_{\perp}$	9.4 ± 0.5	9.6	3.6 ± 0.1	1.2

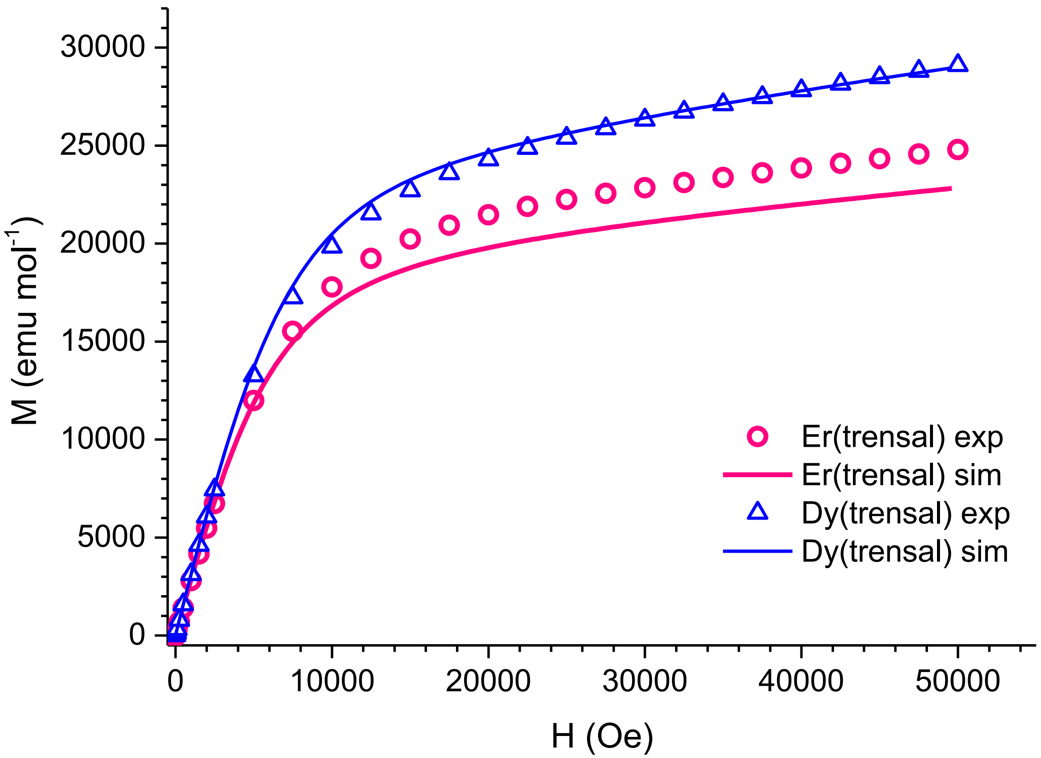
DC magnetic data/2



•No free parameters.
•Good reproduction of magnetic data

BUT…

DC magnetic data/1

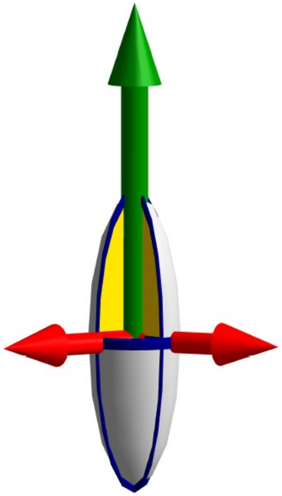


…some discrepancy for the high-field magnetization

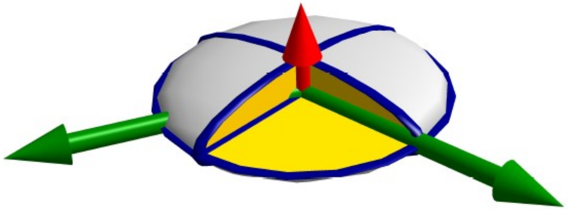
	Dy(trensal)		Er(trensal)	
	exp	calc	exp	calc
$g_{//}$	1.8 ± 0.1	2.6	11.8 ± 0.4	13
$g_{\perp}$	9.4 ± 0.5	9.6	3.6 ± 0.1	1.2

Ground doublet anisotropy

g^2 tensor shape

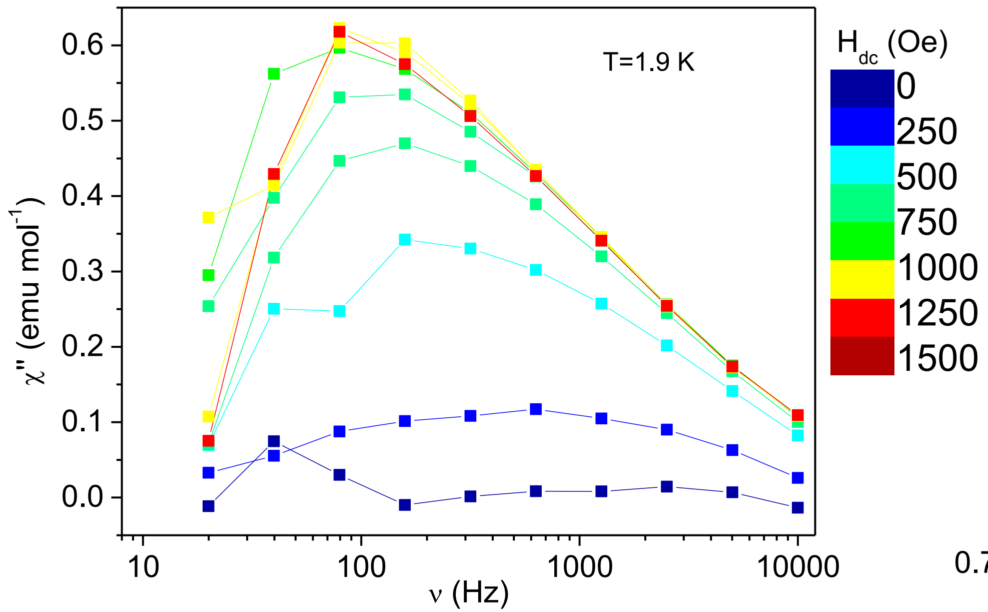


Er(trensal)
Easy axis



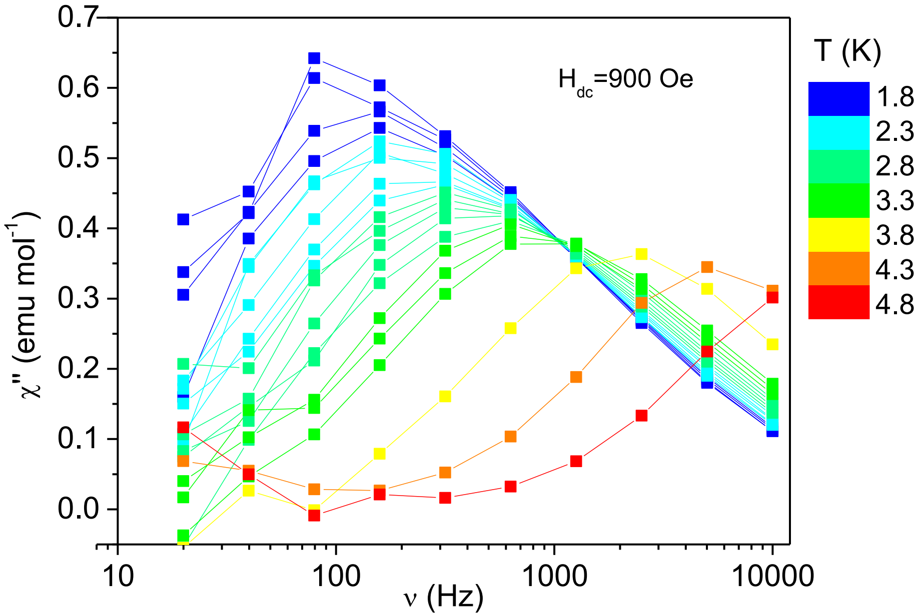
Dy(trensal)
Hard axis

Er(trensal) AC susceptibility



- Field induced slow relaxation
- Slowest at 900 Oe

- As expected for an easy axis rare-earth complex, frequency dependence of χ"(T) is observed at low T



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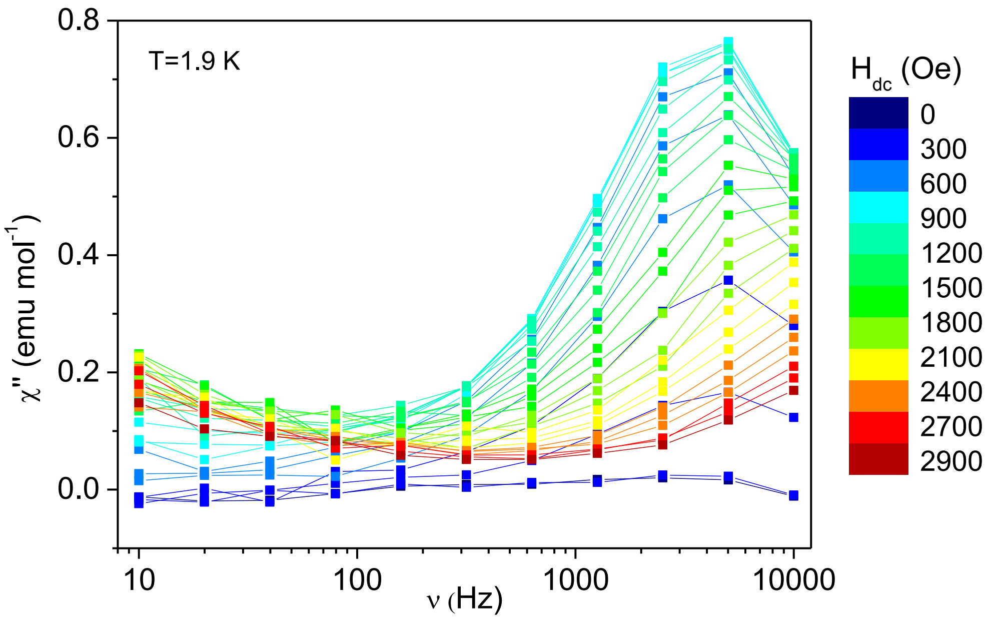
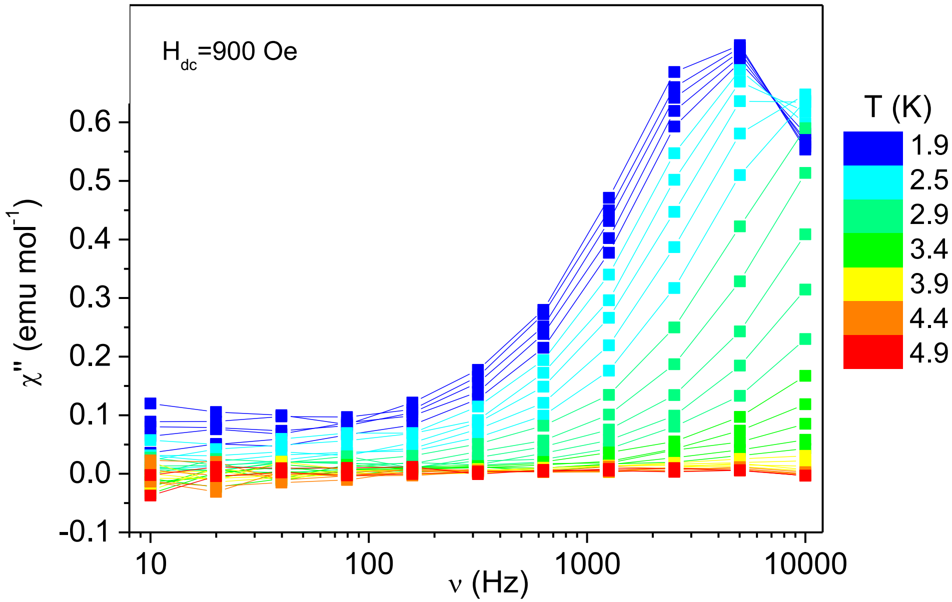
Dy(trensal) dynamic behaviour

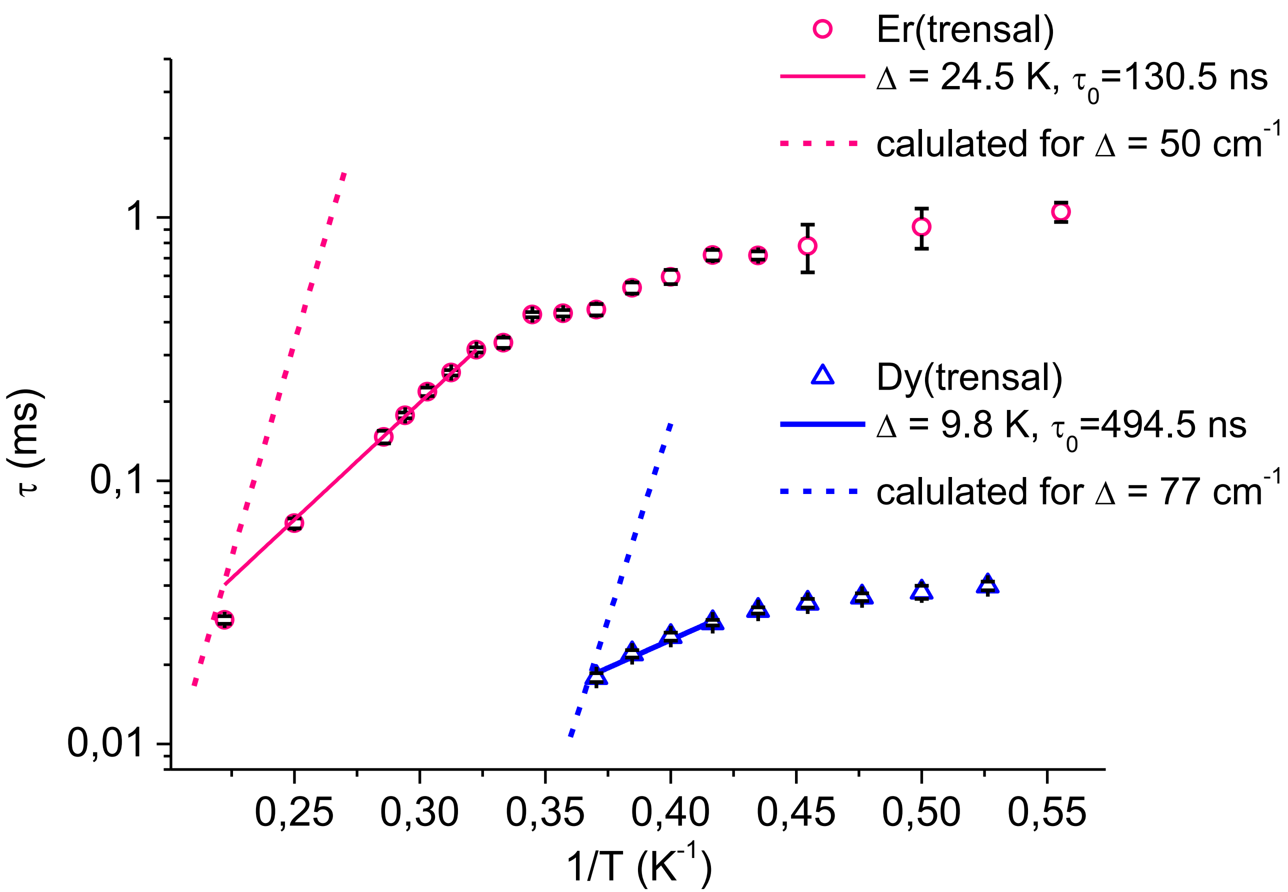


- Field induced slow relaxation
- Slowest at 900 Oe

Quite surprisingly, Dy(trensal) is also slowly relaxing



Temperature dependence of relaxation time



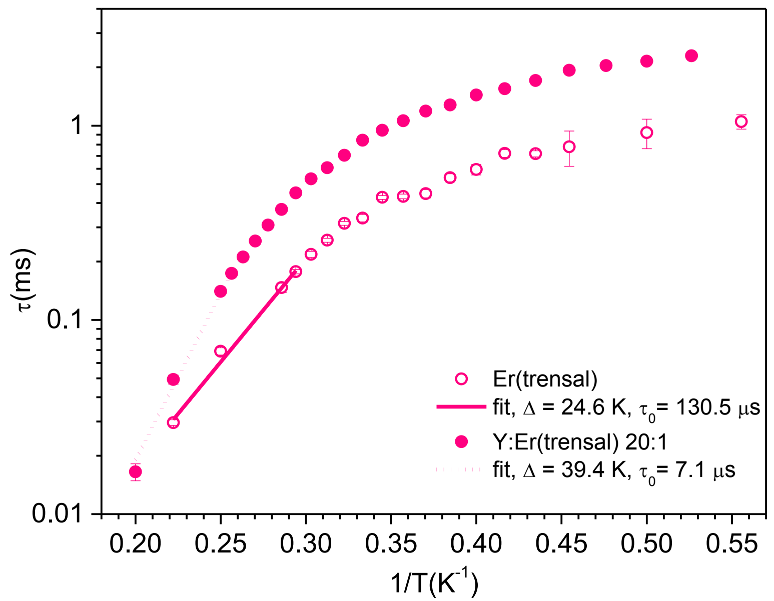
E(cm^{-1})

Dy	Er
0	0
50	54
98	102
172	109
414	321
577	568
645	619
787	651

- Both systems are far from linear (Arrhenius) behaviour
- The relaxation is not related to magnetic anisotropy barrier

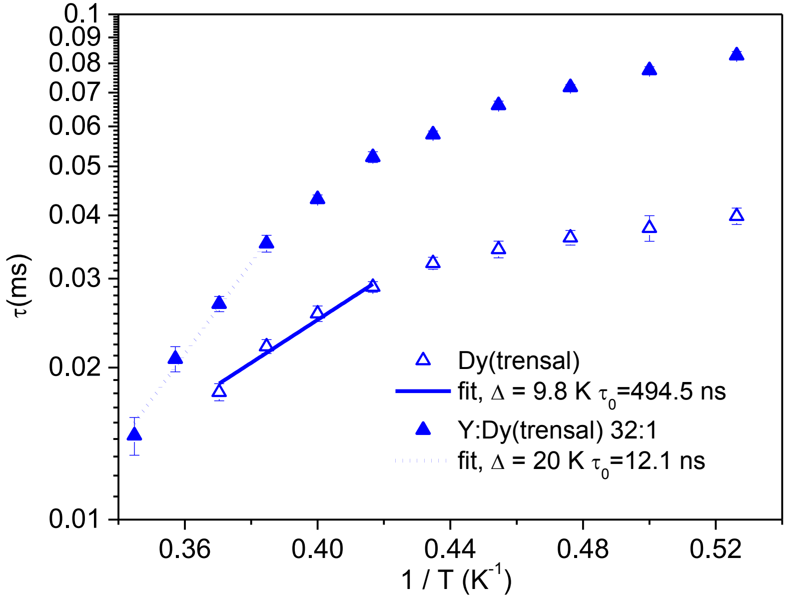
Does dilution affect this behaviour?

Y:Er(trensal) 20:1



System is still far from Arrhenius behaviour

Y:Dy(trensal) 32:1



Slow relaxation persist in diluted system

Concluding remarks

- EPR and DC data confirm the LF parametrization obtained by luminescence spectrscopy
- Dy(trensal) is hard-axis type, Er(trensal) is easy axis type
- Both derivatives show field induced slow relaxation of the magnetization in a static magnetic field
- The thermal activation barrier is not consistent with the energy differences obtained by luminescence data.
- This observation invalidates the general assumption that the slow dynamics of the magnetization is associated in these systems to the magnetic anisotropy
- Spectroscopic techniques are fundamental to understand the factors affecting the magnetization dynamics and relaxation mechanisms in these systems