Lanthanide-induced relaxation anisotropy

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SUPPLEMENTARY INFORMATION

S1. Connection between ZFS and Zeeman limits

To illustrate the connection between the relaxation rates in the ZFS limit and their Zeeman limit counterparts in Equations (1), some less realistic assumptions will now be made. These are not necessary for the application of Equations (31), but help illustrate the relationship between the two limits. We need to assume high temperature, in which case

$$\rho_{pq}^{\text{eq}} = \frac{\delta_{pq}}{2J+1}$$

* MERGEFORMAT (S1)

and extreme narrowing on the electron

$$\tau_{\text{R},pq} = \tau_{\text{E}}, \qquad \left(\omega + \omega_{pq}\right)^2 \tau_{\text{E}}^2 = 1 \qquad \forall p,q$$

* MERGEFORMAT (S2)

where τ_{E} is the electron relaxation time that is assumed to be the same for all populations and coherences. With this in place, Equation (37) simplifies into

$$G_{nk}(\omega) = \text{Tr}\left[\hat{\rho}^{\text{eq}}\hat{\mu}_n\hat{\mu}_k\right]\tau_{\text{E}} = \frac{\tau_{\text{E}}}{2J+1}\text{Tr}\left[\hat{\mu}_n\hat{\mu}_k\right] = \frac{g_J^2\mu_{\text{B}}^2\tau_{\text{E}}}{2J+1}\text{Tr}\left[\hat{J}_n\hat{J}_k\right]$$

* MERGEFORMAT (S3)

The Cartesian components of the total electron momentum operator are orthogonal

$$\text{Tr}\left[\hat{J}_n\hat{J}_k\right] = \delta_{nk}\sum_{m=-J}^{J}m^2 = \frac{\delta_{nk}}{3}J(J+1)(2J+1)$$

* MERGEFORMAT (S4)

and Equation * MERGEFORMAT (S3) therefore further simplifies into

$$G_{nk}(\omega) = g_J^2 \mu_B^2 \frac{J(J+1)}{3} \delta_{nk} \tau_E \qquad \text{* MERGEFORMAT (S5)}$$

After placing this into Equation (31):

$$R_1^{dip} = \frac{2}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_N^2 g_J^2 \mu_B^2}{r^6} \frac{J(J+1)\tau_E}{3} \text{Tr}\left[\left(3\hat{r}\cdot\hat{r}^T - \mathbf{1}\right)^2\right] \qquad \text{* MERGEFORMAT (S6)}$$

and noting that the trace is the same for any unit vector $\hat{r}$

$$\text{Tr}\left[\left(3\hat{r}\cdot\hat{r}^T - \mathbf{1}\right)^2\right] = 6 \qquad \text{* MERGEFORMAT (S7)}$$

we obtain exactly the same expression as the extreme narrowing limit of Equation (1):

$$R_1^{dip} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_N^2 \mu_{eff}^2 \tau_E}{r^6} \qquad \text{* MERGEFORMAT (S8)}$$

where $\mu_{eff}^2 = \mu_B^2 g_J^2 J(J+1)$. The same happens with the transverse relaxation rate.

That these expressions should be equal between the ZFS and the Zeeman limit is to be expected – when electron relaxation is much faster than coherent interactions, the dynamics are dominated by the stochastic noise, and the difference between the two limits disappears.

S2. Spherical coordinate form of Equations 18 and 19

It is useful to express the invariants of the Curie contribution to the chemical shielding tensor in spherical coordinates centred on the lanthanide, and to expose the anisotropy of the magnetic susceptibility tensor of the lanthanide ion explicitly. The second rank invariant in Equations (17) becomes:

$$\Delta_{\mathbf{D}\cdot\chi}^2 = \chi_{iso}^2 \frac{9}{16\pi^2 r^6} + \chi_{iso}\delta_{PCS}\frac{9}{4\pi r^3} + \chi_{ax}^2 f_1(r,\theta) + \chi_{rh}^2 f_2(r,\theta,\varphi) + \chi_{ax}\chi_{rh}f_3(r,\theta,\varphi) \text{ * MERGEFORMAT }$$

where $\delta_{PCS} = \text{Tr}(\mathbf{D}\cdot\chi)/3$ is the pseudocontact shift and $\{\theta,\varphi\}$ are spherical coordinates of the nucleus relative to the eigenframe of the magnetic susceptibility tensor. The three eigenvalues of χ, expressed *via* its isotropic part, axiality, and rhombicity, are

$$\left[\chi_{iso} - \frac{\chi_{ax}}{3} + \chi_{rh}; \quad \chi_{iso} - \frac{\chi_{ax}}{3} - \chi_{rh}; \quad \chi_{iso} + \frac{2\chi_{ax}}{3}\right] \qquad \text{* MERGEFORMAT (S10)}$$

The second term in Equation * MERGEFORMAT (S9) indicates that the relaxation rate would appear to be correlated with the sign of the pseudocontact shift – the experimental confirmation may be seen in Figure 4 of the main text. The first rank term in Equations (17):

$$\Lambda_{\mathbf{D}\cdot\chi}^2 = \chi_{ax}^2 \frac{9\sin^2 2\theta}{64\pi^2 r^6} + \chi_{rh}^2 \frac{9\sin^2\theta\left(3+\cos 2\theta - 2\cos 4\phi\sin^2\theta\right)}{64\pi^2 r^6} - \chi_{ax}\chi_{rh}\frac{9\cos 2\phi\sin^2 2\theta}{32\pi^2 r^6} \text{ * MERGEFORMA}$$

is only non-zero when the magnetic susceptibility tensor is anisotropic.