# Supporting Information

## Modeling the magnetic properties of lanthanide complexes: relation of the REC parameters with Pauling electronegativity and coordination number

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### Theoretical background: The Radial Effective Charge (REC) model

The calculations start with the crystallographic atomic coordinates of the first coordination sphere. These are introduced as an input for the portable *fortran77* software code SIMPRE.[1] This code parameterizes the electric field effect produced by the surrounding ligands, acting over the central ion, by using the following Crystal Field Hamiltonian expressed in terms of the Extended Stevens Operators (ESOs) [2]:

$$\hat{H}_{cf}(J) = \sum_{k=2,4,6}\sum_{q=-k}^{k} B_k^q O_k^q = \sum_{k=2,4,6}\sum_{q=-k}^{k} a_k(1-\sigma_k)A_k^q \left\langle r^k \right\rangle O_k^q \quad (1)$$

where $k$ is the order (also called rank or degree) and $q$ is the operator range, that varies between $k$ and $-k$, of the Stevens operator equivalents $O_k^q$ as defined by Ryabov in terms of the angular momentum operators $J_{\pm}$ and $J_z$,[3] where the components $O_k^q(c)$ and $O_k^q(s)$ correspond to the ESOs with q ≥ 0 and q < 0 respectively.[3] Note that all the Stevens CF parameters $B_k^q$ are real, whereas the matrix elements of $O_k^q$ (q < 0) are imaginary. $a_k$ are the $\alpha$, $\beta$ and $\gamma$ Stevens coefficients[4] for $k$ = 2, 4, 6, respectively, which are tabulated and depend on the number of $f$ electrons. $\sigma_k$ are the Sternheimer shielding parameters[5] of the 4*f* electronic shell, and $\langle r^k \rangle$ are the expectation values of the radius.[6]

In SIMPRE, the $A_k^q$ CF parameters are determined by the following relations:

$$A_k^0 = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{k0}(\theta_i,\varphi_i) p_{kq} \quad (2a)$$

$$A_k^q = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{kq}^c(\theta_i,\varphi_i) p_{kq} \quad (q>0) \quad (2b)$$

$$A_k^q = \frac{4\pi}{2k+1}\sum_{i=1}^{N}\frac{Z_i e^2}{R_i^{k+1}} Z_{k|q|}^s(\theta_i,\varphi_i) p_{k|q|} \quad (q<0) \quad (2c)$$

where $R_i$, $\theta_i$ and $\varphi_i$ are the effective polar coordinates of the point charges, and $Z_i$ is the effective point charge, associated to the $i$-th donor atom with the lanthanoid at the origin, $N$ is the number of ligands; $e$ is the electron charge, $p_{kq}$ are the prefactors of the spherical harmonics and $Z_{kq}$ are the tesseral harmonics expressed in terms of the polar coordinates for the i-th donor atom.

In the REC model[7] the ligand is modeled through an effective point charge situated between the lanthanoid and the coordinated atom at a distance $R_i$ from the magnetic centre, which is smaller than the real metal-ligand distance ($r_i$). To account for the effect of covalent electron sharing, a radial displacement vector ($\mathbf{D_r}$) is defined, in which the polar coordinate $r$ of each coordinated atom is varied, $R_i = r_i - D_r$. At the same time, the charge value ($Z_i$) is scanned in order to achieve the minimum deviation between calculated and experimental data, whereas $\theta_i$ and $\varphi_i$ remain constant.

In this communication, we have fitted the ground multiplet energy level scheme and, in a second step, the crystal field parameters of the 18 complexes grouped in four families. This has allowed us to obtain a particular solution of $D_r$ an $Z_i$ for each case. Finally, we have performed a collective fit for

each family, using the spectroscopic experimental data in order to model each kind of ligand.

In the fitting procedures concerning energy levels, we define the relative error *E* as:

$$E = \frac{1}{n}\sum_{i=1}^{n}\frac{\left[\Delta_{theo,i} - \Delta_{\exp,i}\right]^2}{\left[\Delta_{\exp,i}\right]^2} \quad (3)$$

where $\Delta_{exp}$ and $\Delta_{theo}$ are experimental and theoretical energy level values, respectively, and *n* is the number of points. In the case of the CFPs fit, the error is defined as follows:

$$E = \sum_{k=-q}^{k}\frac{\left[B_{kq,theo} - B_{kq,phen}\right]^2}{\left[B_{kq,phen}\right]^2} \quad (4)$$

where $B_{kq,phen}$ and $B_{kq,theo}$ are phenomenological (fitted from all the available spectroscopic information using the full hamiltonian) and the theoretical CFPs in Wybourne notation as calculated by the REC model, respectively. From the relations[8] between the ESOs and Wybourne operators, the Stevens CFPs and the Wybourne CFPs are obtained via the following conversion relations:

$$\lambda_{k0}A_k^0\left\langle r^k\right\rangle = B_{k0}\,,\ \lambda_{kq}A_k^q\left\langle r^k\right\rangle = \mathrm{Re}\,B_{kq}\ \text{for q <0},\ \lambda_{k|q|}A_k^q\left\langle r^k\right\rangle = \mathrm{Im}\,B_{k|q|}\ \text{for q <0.}$$

The conversion factors $\lambda_{kq}$ between the Stevens CFPs and the Wybourne CFPs can be found in table A2 of Ref. 8.

**Results: Systematic study of the four lanthanide families coordinated by halides**

**Table SI1:** Systematic $D_r$ and $Z_i$ calculation from fitting of the experimental ground multiplet energy levels and the reported CFPs for the 18 complexes studied in this work; the collective solution for each family using spectroscopic experimental data is also included.

| | $Ln^{3+}$ | **Energy levels individual fit** | | **CFPs individual fit** | |
|---|---|---|---|---|---|
| | | $D_r$ | $Z_i$ | $D_r$ | $Z_i$ |
| $Cs_2NaYF_6:Ln^{3+}$ (**F6**) | $Ho^{3+}$ | 0.68 | 0.46 | 0.51 | 0.66 |
| | $Er^{3+}$ | 0.46 | 1.00 | 0.62 | 0.60 |
| | $Tm^{3+}$ | 0.52 | 0.99 | 0.60 | 0.64 |
| | **Collective** | **0.51** | **0.85** | - | - |
| $LiYF_4:Ln^{3+}$ (**F8**) | $Tb^{3+}$ | 0.68 | 0.22 | 0.90 | 0.25 |
| | $Dy^{3+}$ | 0.87 | 0.14 | 0.95 | 0.15 |
| | $Ho^{3+}$ | 0.86 | 0.20 | 0.81 | 0.22 |
| | $Er^{3+}$ | 0.83 | 0.19 | 0.88 | 0.21 |
| | $Tm^{3+}$ | 0.81 | 0.20 | 0.83 | 0.21 |
| | **Collective** | **0.84** | **0.17** | **-** | **-** |
| $Cs_2NaYCl_6:Ln^{3+}$ (**Cl6**) | $Tb^{3+}$ | 0.45 | 0.99 | 0.74 | 0.57 |
| | $Dy^{3+}$ | 0.73 | 0.53 | 0.68 | 0.57 |
| | $Ho^{3+}$ | 0.98 | 0.23 | 0.92 | 0.38 |
| | $Er^{3+}$ | 0.85 | 0.39 | 0.96 | 0.33 |
| | $Tm^{3+}$ | 1.49 | 0.04 | 0.95 | 0.35 |
| | **Collective** | **0.86** | **0.36** | **-** | **-** |
| $LaCl_3:Ln^{3+}$ (**Cl9**) | $Tb^{3+}$ | 1.16 | 0.14 | 1.32 | 0.10 |
| | $Dy^{3+}$ | 1.23 | 0.13 | 1.27 | 0.13 |
| | $Ho^{3+}$ | 1.20 | 0.18 | 1.26 | 0.15 |
| | $Er^{3+}$ | 1.30 | 0.12 | 1.26 | 0.14 |
| | $Tm^{3+}$ | 1.29 | 0.15 | 1.26 | 0.15 |
| | **Collective** | **1.25** | **0.14** | **-** | **-** |

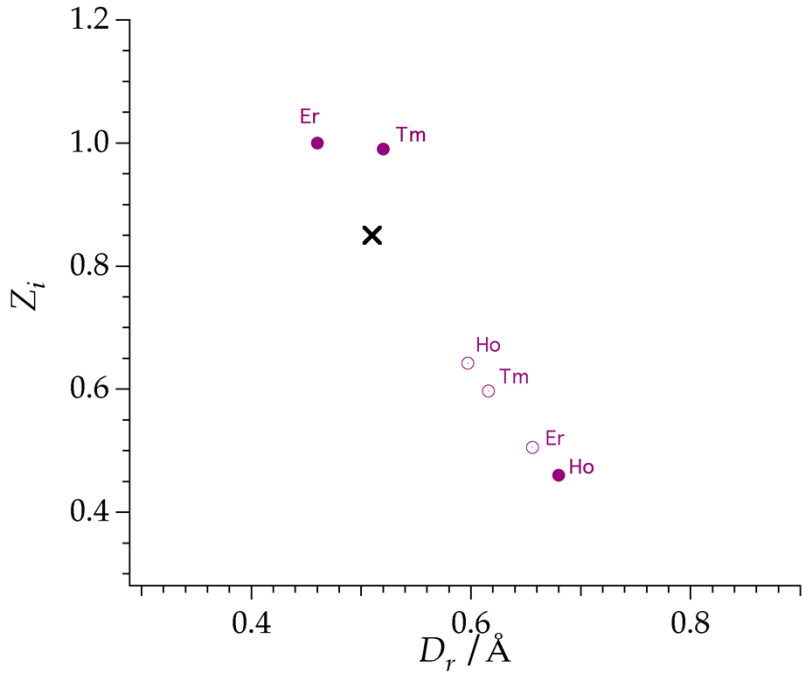


**Figure SI1**: Dispersion of the $D_r$ and *Zi* values obtained by fitting: 1) the experimental energy levels (purple circles) and, 2) the phenomenological CFPs (purple open circles) of the family $Cs_2NaYF_6:Ln^{3+}$. The black cross represents the collective fit of energy levels solution for this family.

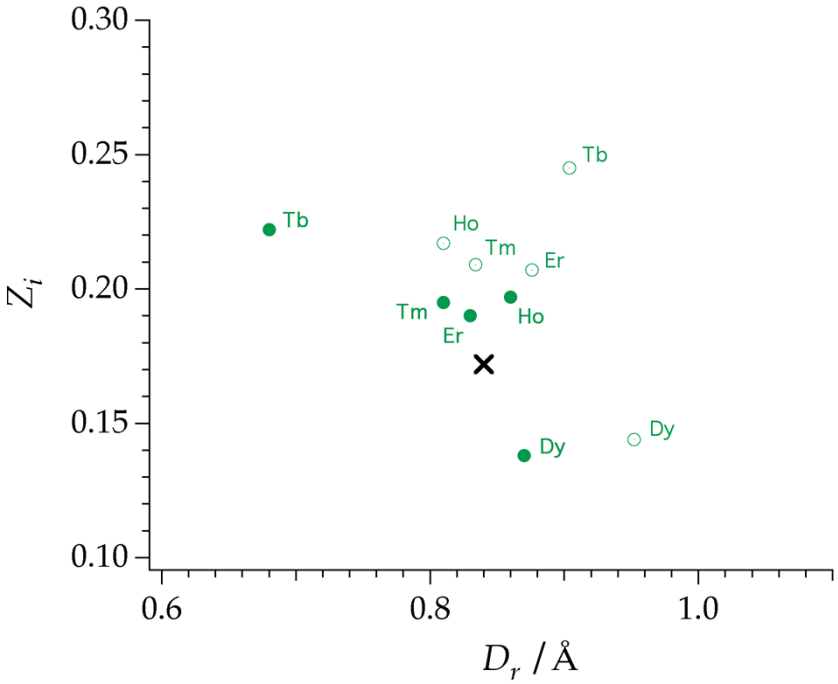


**Figure SI2**: Dispersion of the $D_r$ and *Zi* values obtained by fitting: 1) the experimental energy levels (green circles) and, 2) the phenomenological CFPs (green open circles) of the family $LiYF_4:Ln^{3+}$. The black cross represents the collective fit of energy levels solution for this family.

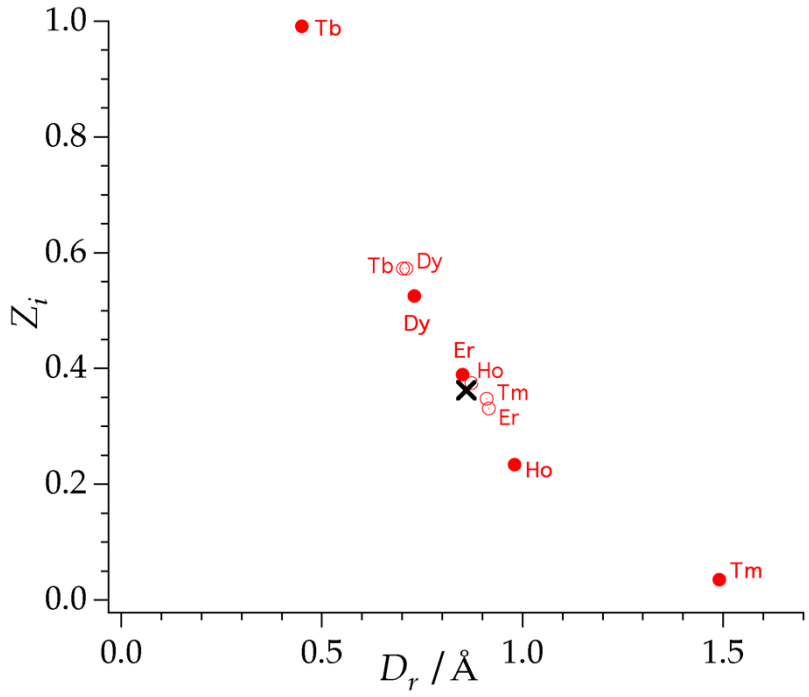


**Figure SI3**: Dispersion of the $D_r$ and *Zi* values obtained by fitting: 1) the experimental energy levels (red circles) and, 2) the phenomenological CFPs (red open circles) of the family $Cs_2NaYCl_6:Ln^{3+}$. The black cross represents the collective fit of energy levels solution for this family.

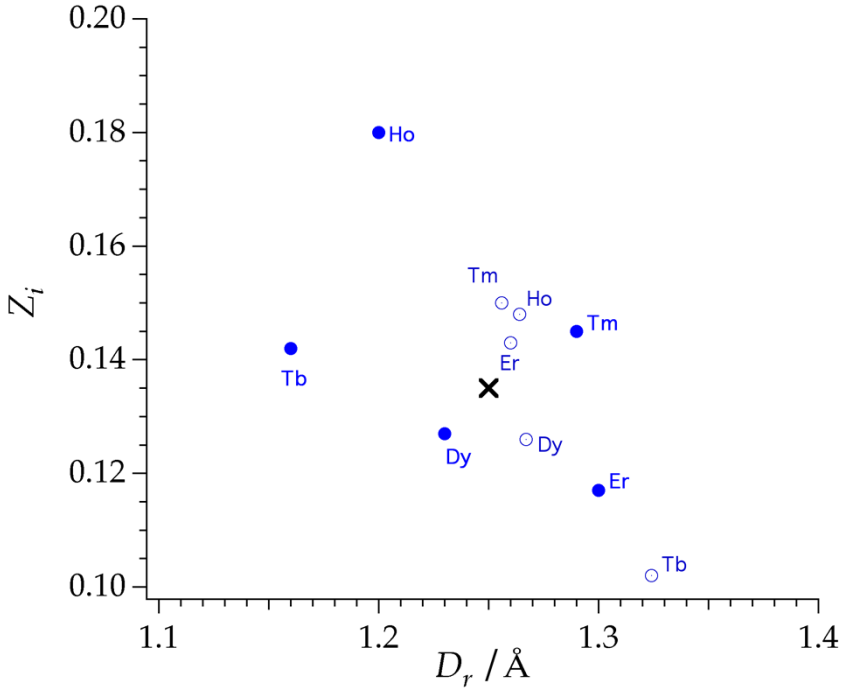


**Figure SI4**: Dispersion of the $D_r$ and *Zi* values obtained by fitting: 1) the experimental energy levels (blue circles) and, 2) the phenomenological CFPs (blue open circles) of the family $LaCl_3:Ln^{3+}$. The black cross represents the collective fit of energy levels solution for this family.

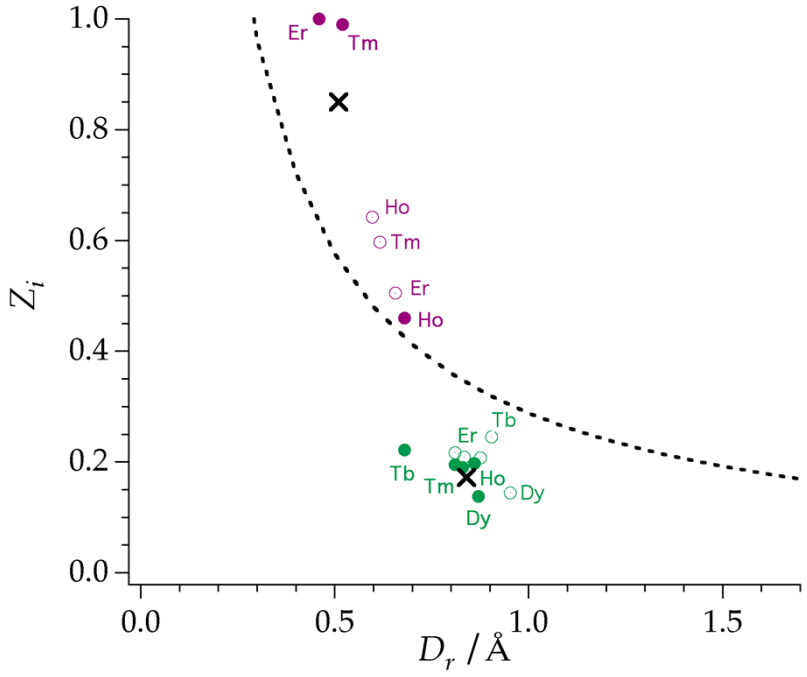


**Figure SI5**: Radial displacement ($D_r$) and effective charge ($Z_i$) values obtained fitting the ground multiplet energy levels (circles) and crystal field parameters (open circles); $Cs_2NaYCl_6$:$Ln^{3+}$ (purple) and $LiYF_4$ $^{3+}$ (green). Collective fit (black cross). Function $Z_i = f_F/D_r$ ; where $f_F$ = 0.2882.

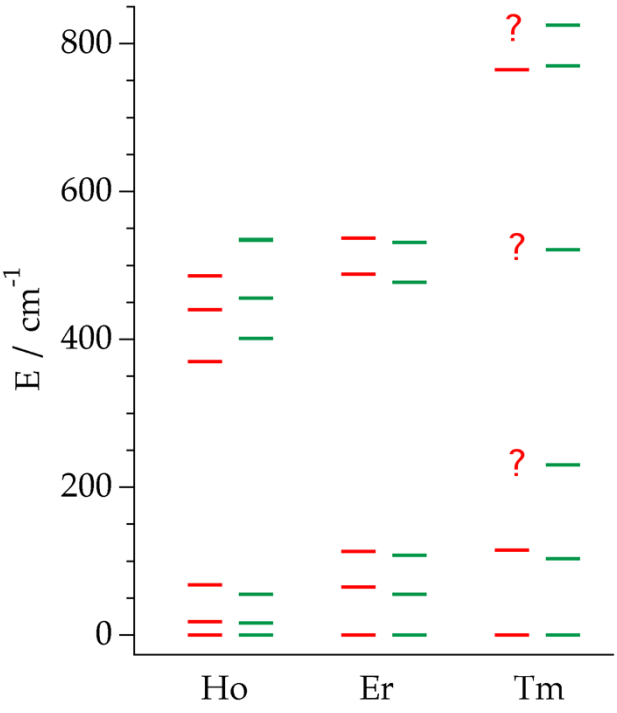


**Figure SI6**: Experimental ground multiplet energy levels (red) and calculated ones using the collective fitting value for $D_r$ and $Z_i$ (green) in $Cs_2NaYF_6$:$Ln^{3+}$; non-determined levels are marked with the question mark.

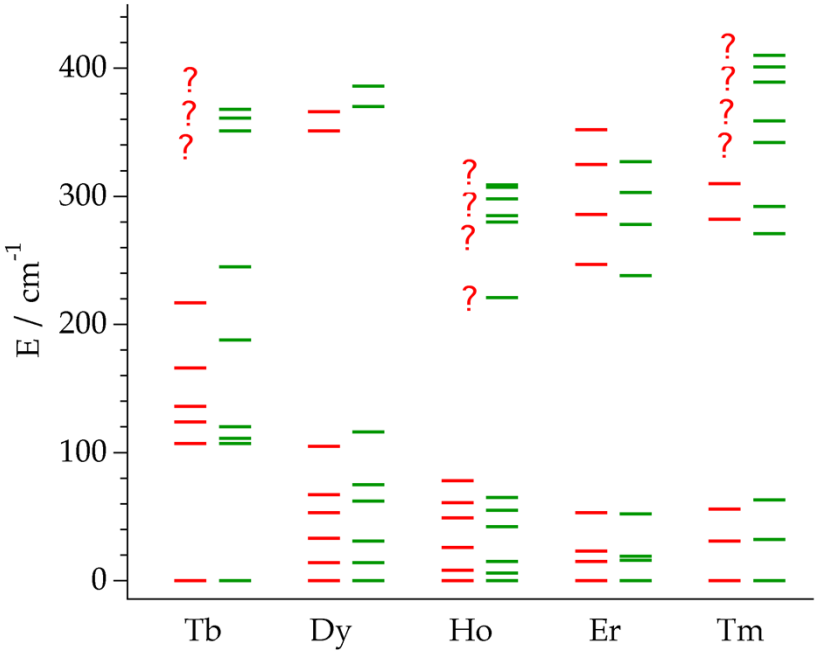


**Figure SI7**: Experimental ground multiplet energy levels (red) and calculated ones using the collective fitting value for $D_r$ and $Z_i$ (green) in $LiYF_4:Ln^{3+}$; non-determined levels are marked with the question mark.

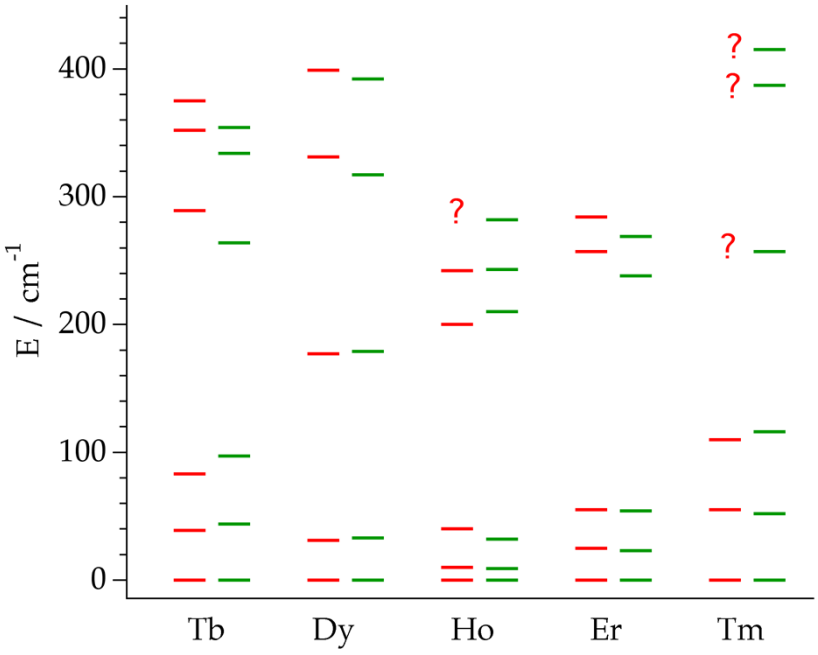


**Figure SI8**: Experimental ground multiplet energy levels (red) and calculated ones using the collective fitting value for $D_r$ and $Z_i$ (green) in $Cs_2NaYCl_6:Ln^{3+}$; non-determined levels are marked with the question mark.

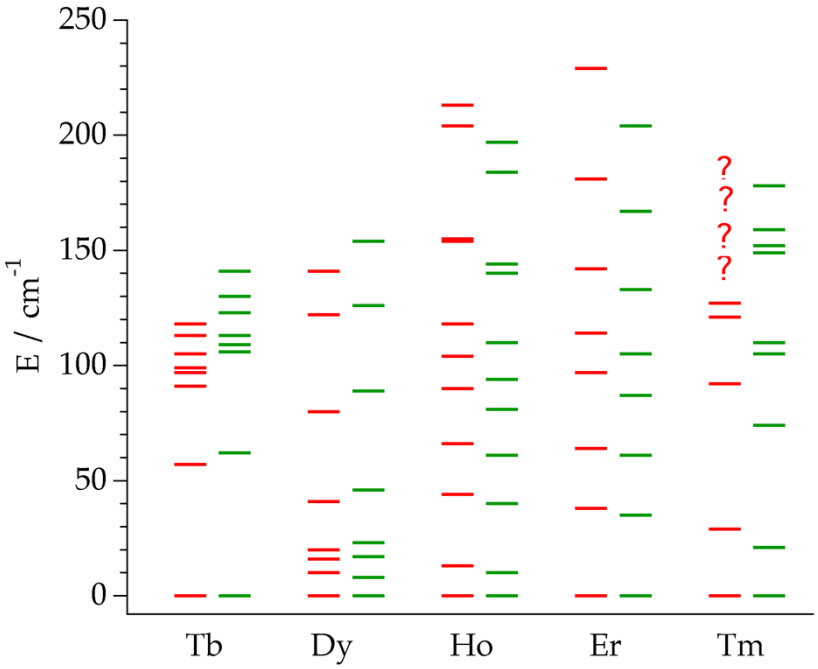


**Figure SI9**: Experimental ground multiplet energy levels (red) and calculated ones using the collective fitting value for $D_r$ and $Z_i$ (green) in $LaCl_3:Ln^{3+}$; non-determined levels are marked with the question mark.

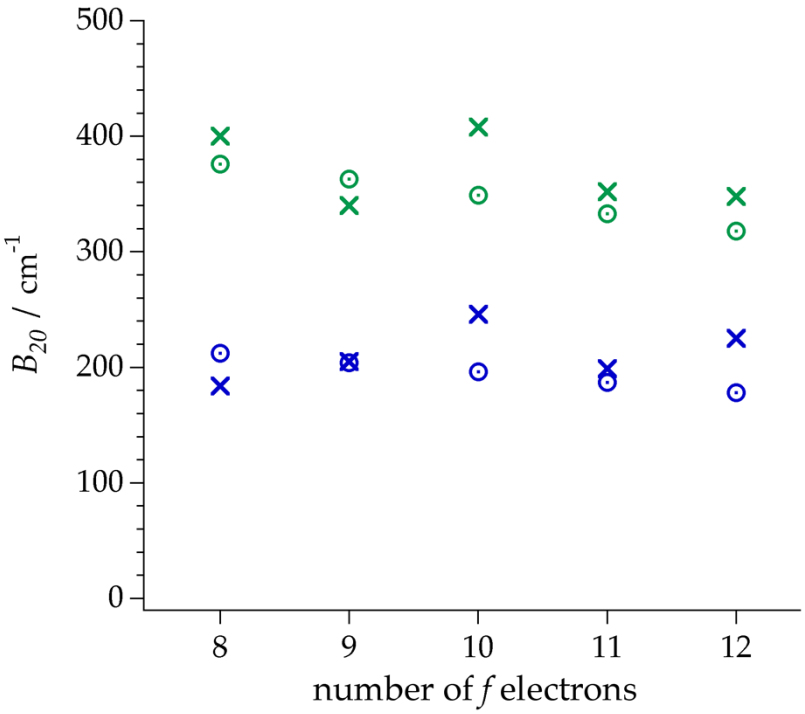


**Figure SI10**: Phenomenological (crosses) and calculated $B_{20}$ (open circles) in Wybourne notation, using the collective fitting value for $D_r$ and $Z_i$, in $LiYF_4$: $Ln^{3+}$ (green) and $LaCl_3:Ln^{3+}$ (blue).

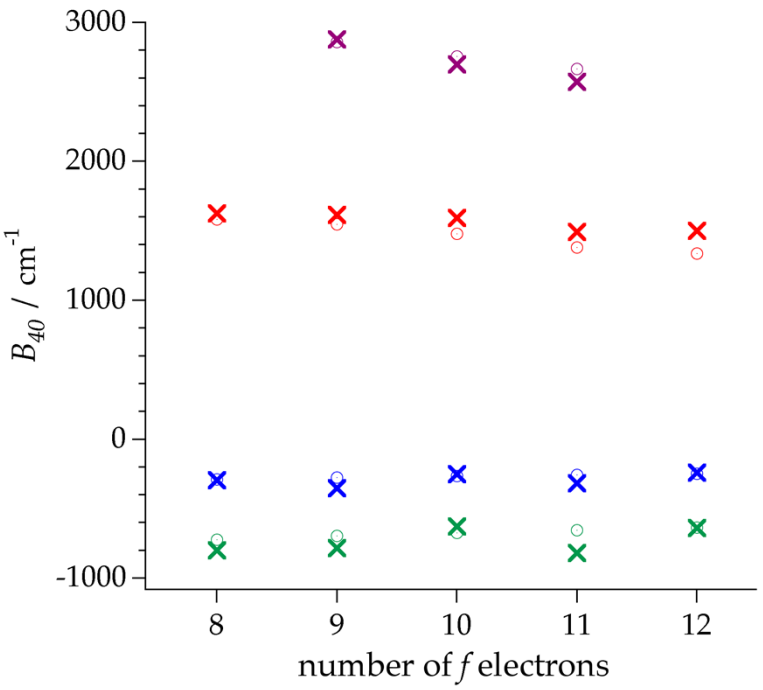


**Figure SI11**: Phenomenological (crosses) and calculated $B_{40}$ (open circles) in Wybourne notation, using the collective fitting value for $D_r$ and $Z_i$, in $Cs_2NaYF_6$:$Ln^{3+}$ (purple), $LiYF_4$:$Ln^{3+}$ (green), $Cs_2NaYCl_6$:$Ln^{3+}$ (red) and $LaCl_3$:$Ln^{3+}$ (blue).

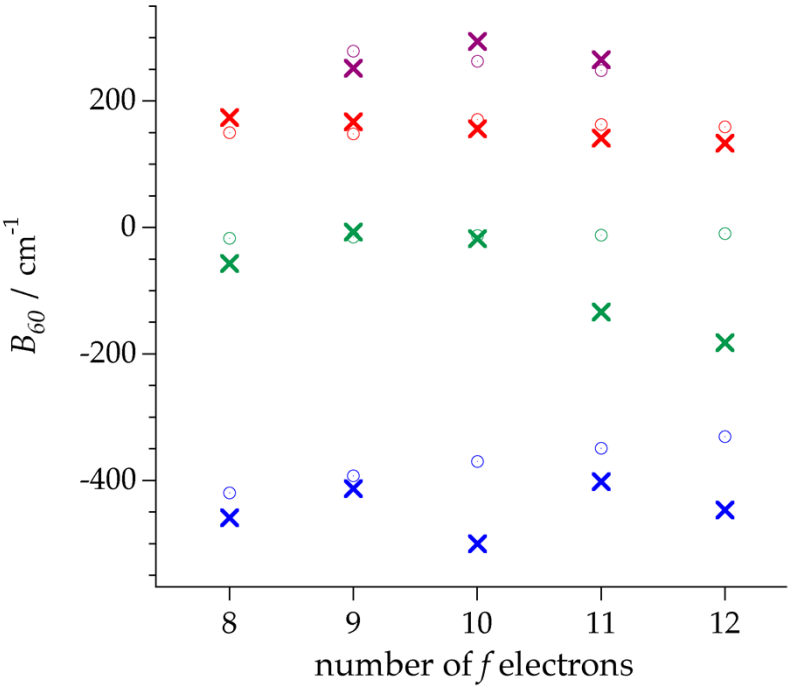


**Figure SI12**: Phenomenological (crosses) and calculated $B_{60}$ (open circles) in Wybourne notation, using the collective fitting value for $D_r$ and $Z_i$, in $Cs_2NaYF_6$:$Ln^{3+}$ (purple), $LiYF_4$:$Ln^{3+}$ (green), $Cs_2NaYCl_6$:$Ln^{3+}$ (red) and $LaCl_3$:$Ln^{3+}$ (blue).

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