

Magnetic anisotropy of single-ion magnet (PPh₄)₂[ReF₆] · 2H₂O

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In the present work we studied the magnetocrystalline anisotropy of two related single-molecule magnets [1] with a single rhenium ion in irregular tilted octahedra (PPh₄)₂[ReF₆]·2H₂O, (**1**), (PPh₄ stands for tetraphenylphosphonium, (C₆H₅)₄P), and [Zn(viz)₄(ReF₆)], (**2**), (viz = 1-vinylimidazole) [2].

All density functional theory (DFT) calculations were performed using the VASP code [3–6] with projector-augmented wave method (PAW) [7], employing Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange–correlation functional [8] and taking into account strong Coulomb correlations *via* rotationally invariant DFT + *U* approach after Dudarev et al. [9].

In order to estimate single-ion anisotropy (SIA) we performed total energy calculations with spin-orbit coupling (GGA + *U* + SOC) for different spin directions and mapped these results onto the model, where the SIA is described by the following Hamiltonian:

$$\hat{H}_{\text{SIA}} = D \cdot \hat{S}_z^2. \quad (1)$$

The obtained results have shown the easy-plane anisotropy for these 5*d*³ systems with large single-ion anisotropy parameters *D* equal to 11.7 K for (**1**) and 16.8 K for (**2**). Magnetic moments for both complexes are less than expected 3*μ_B*. It can be explained by the covalency effects and substantial spin-orbit coupling. Due to irregular tilted [ReF₆]²⁻ octahedra, there is a strong *t*_{2*g*} – *e_g* crystal-field splitting of the order of 3.5 eV. Since symmetry of the crystal-field is lower than cubic, *t*_{2*g*} levels get an additional splitting onto nearly degenerate *xz* and *yz* orbitals, that are lower in energy than *xy* orbital (see Fig. 1). The spin-orbit coupling mixes the ground state singlet Γ₂ with orbital triplet Γ₅, lying on 10*Dq* higher (*t*_{2*g*} – *e_g* crystal field splitting parameter in spectroscopy) [10]. This triplet is split by the non-cubic crystal-field onto a doublet, characterized by

fictitious orbital moment $\tilde{l}_z = \pm 1$ and having energy Δ₁, and a singlet with $\tilde{l}_z = 0$ and Δ₀.

In the second order of the perturbation theory one can take into account the mixing of these Γ₅ states with the ground state (Γ₂) due to the spin-orbit coupling. This admixture splits the ground state into two spin doublets and the value of this splitting is proportional to the spin-orbit coupling constant λ [10]:

$$2D = -\frac{8\lambda^2}{\Delta_0} + \frac{8\lambda^2}{\Delta_1}. \quad (2)$$

Using estimation of λ = 320 meV for Re⁴⁺ [11] and the crystal-field splittings shown in Fig. 1 for (PPh₄)₂[ReF₆]·2H₂O, one can see that such a consideration gives a reasonable estimation of *D* = 14.6 K. This agrees with the obtained single-ion anisotropy parameters *D* presented above.

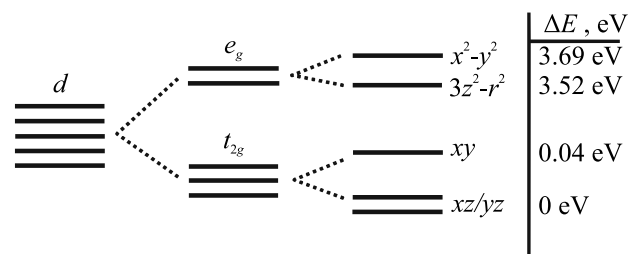


Fig. 1. Results of the Wannier function projection of the non-magnetic DFT Hamiltonian for (**1**). We used the local coordinate system where axes are directed as much as possible to the ligand to calculate on-site energies of different Re 5*d* orbitals

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