

Supp. Info

Unraveling the magnetoelectric effect using electric field-controlled magnetic anisotropy: a theoretical study

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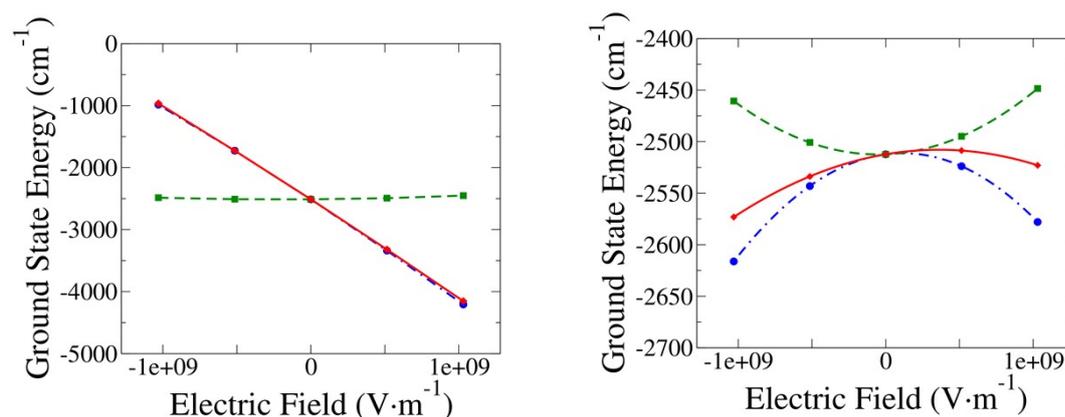


Figure S1. Energies in cm⁻¹ (shifted by 58.35795.10⁷ cm⁻¹) of the ground state obtained for the cases (a) in blue and dot-dashed line, (b) in green an dashed line and (c) in red and plain line as functions of the field applied in the Z (left) and Y (right) directions.

In complement to the perturbative evaluation of the contributions to D and in order to better treat the contribution of the first excited state which is relatively close in energy, we also calculate the variational contribution $C(D)_{VAR}$ by diagonalizing the 2×2 SOC matrices in the basis of $T_{\pm 1}^0$ and $T_{\pm 1}^1$ given in equation 2 of the article:

$$C(D)_{VAR} = \frac{\Delta E - \sqrt{\Delta E^2 + 4|SOC|^2}}{2}$$

where $|SOC|^2$ is the square of the off-diagonal element of H^{SOC} between ground and excited components.

In case(a) for $F//Z$, the energy variation of the states is so small that it is more reasonable to invoke the increase of the SOC (Table S1). Examining the wave functions of both the ground and first excited states for $-F$ and $+F$, one may rationalize this SOC increase. Indeed, the product of the coefficients of the determinants coupled through SOC increase due to both a slight increase from 96.68% to 96.71% of the weights of the determinant $|d_{xz}\bar{d}_{xz}d_{yz}\bar{d}_{yz}d_{xy}\bar{d}_{xy}d_{x^2-y^2}d_{z^2}|$ in the ground state and a very slight increase of the spin-orbit constant ζ from 659.33 cm^{-1} to 659.46 cm^{-1} .

Table S1. F parallel to Z Contributions to the axial parameter D (in cm^{-1}) of the most contributing excited states and their variations $\Delta C(D)$ between the $-F$ and $+F$ in the Z direction either provided by ORCA or calculated variationally. $\Delta|\text{SOC}|^2$ is the variation of the square of the module of the SOC between the ground and the first excited triplet states while $\Delta(\Delta E)$ is the variation between the $-F$ and $+F$ of their energy difference (in cm^{-1}) obtained at the NEVPT2 level.

Excited state	C(D) for -F	C(D) for +F	$\Delta C(D)$ ORCA	$\Delta C(D)$ VAR.	$\Delta C(D)$ PERT..	$\Delta \text{SOC} ^2$	$\Delta(\Delta E)$	
(a)	T ₁	-179.18	-180.06	-0.88	-0.82	-0.96	1722.78	-1.60
	T ₂	23.84	23.72	-0.12				
	T ₃	19.61	19.68	0.07				
	S ₃	20.48	20.57	0.09				
(b)	T ₁	-180.95	-178.25	2.70	2.70	3.42	-209.90	36.2
	T ₂	23.82	23.72	-0.10				
	T ₃	19.71	19.58	-0.13				
	S ₃	20.55	20.51	-0.04				
(c)	T ₁	-180.49	-178.66	1.83	1.90	2.47	1509.15	34.7
	T ₂	23.88	23.66	-0.22				
	T ₃	19.67	19.61	-0.06				
	S ₃	20.51	20.56	0.05				

Table S2: F perpendicular to Z applied along Y . Contributions to the axial parameter D (in cm^{-1}) of the most contributing excited states and their variations $\Delta C(D)$ between the $-F$ and $+F$ either provided by ORCA or calculated perturbatively and variationally (see text). $\Delta|\text{SOC}|^2$ is the variation of the square of the module of the SOC between the ground and the first excited triplet state while $\Delta(\Delta E)$ is the variation between the two extreme values of the field of the

energy difference (in cm^{-1}) obtained at the NEVPT2 level between ground and the first excited state.

Excited state		C(D) for -F	C(D) for +F	$\Delta C(D)$ ORCA	$\Delta C(D)$ VAR.	$\Delta C(D)$ PERT.	$\Delta \text{SOC} ^2$	$\Delta(\Delta E)$
(a)	T ₁	-179.99	-178.26	1.73	1.74	2.21	36.05	24.40
	T ₂	23.66	24.05	0.39				
	T ₃	19.60	19.61	0.01				
	S ₃	20.53	20.50	-0.03				
(b)	T ₁	-174.84	-183.67	-8.83	-8.76	-11.10	-162.22	-122.40
	T ₂	23.91	23.82	-0.09				
	T ₃	19.56	19.65	0.09				
	S ₃	20.44	20.60	0.16				
(c)	T ₁	-175.65	-182.76	-7.11	-7.02	-8.91	-124.89	-98.20
	T ₂	23.71	24.02	0.31				
	T ₃	19.56	19.65	0.09				
	S ₃	20.45	20.59	0.14				

Table S3: Weights $w(d_{xz})$ and $w(d_{yz})$ of the determinants having a single occupation in the d_{xz} and d_{yz} orbitals, their differences $\Delta w(X-Y)$ and their variations $\Delta(\Delta w(Y-X))$ between the $-F$ and $+F$ values of the field applied along Z and Y.

		F//Z			F//Y		
		-F	+F	$\Delta(\Delta w(Y-X))$	-F	+F	$\Delta(\Delta w(X-Y))$
case (a)	$w(d_{xz})$	96.200	96.742	-0.528	96.603	96.738	-0.174
	$w(d_{yz})$	97.210	97.224		97.191	97.152	
	$\Delta w(Y-X)$	1.010	0.482		0.588	0.414	
case (b)	$w(d_{xz})$	96.543	96.494	-0.088	96.661	96.695	+0.002
	$w(d_{yz})$	97.282	97.145		97.159	97.195	
	$\Delta w(X-Y)$	0.739	0.651		0.498	0.500	
case (c)	$w(d_{xz})$	96.271	96.762		96.597	96.762	

	$w(d_{yz})$	97.282	97.152		97.175	97.170	
	$\Delta w(X-Y)$	1.011	0.390	-0.621	0.578	0.408	-0.170