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Thermal Spin Crossover in Fe(II) and Fe(III). Accurate Spin State Energetics at the Solid State

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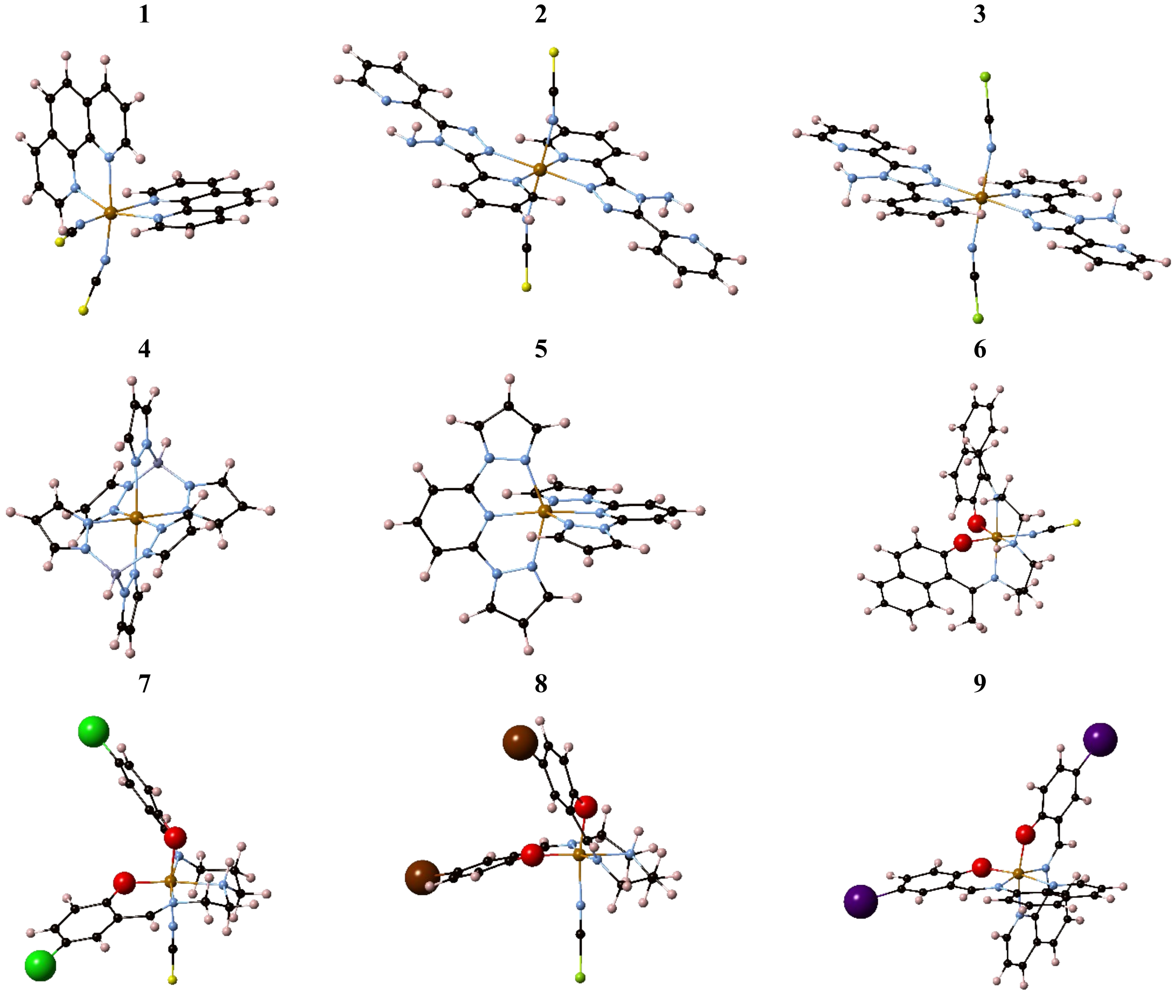
S1. List of Compounds


1 **2** **3**

4 **5** **6**

7 **8** **9**

Figure S1. HS-minima of Fe^{II} Compounds (**1-5**) and Fe^{III} Compounds (**6-9**). Color code for atoms: Iron=Brown, Hydrogen=Pink, Carbon=**Black**, Oxygen=Red, Nitrogen=Blue, Sulfur=Yellow, Selenium=Green, Clorine=Green, Bromine=Brown, Iodine=Violet.

S2. Linear Response *U*

In the linear response (LR) approach[1] to obtain U, the response function that is calculated is:

$$\chi = \frac{\partial n}{\partial \alpha}$$

In order to obtain U, the inverse of the self-consistent function χ is subtracted from the inverse of the bare non-interacting function χ_0 such as:

$$U = {\chi_0}^{-1} - \chi^{-1}$$

For the LS and HS states of **1**, we obtained χ_0 and χ from linear repressions of the relationship between the occupations n obtained within a range of potential shifts α:

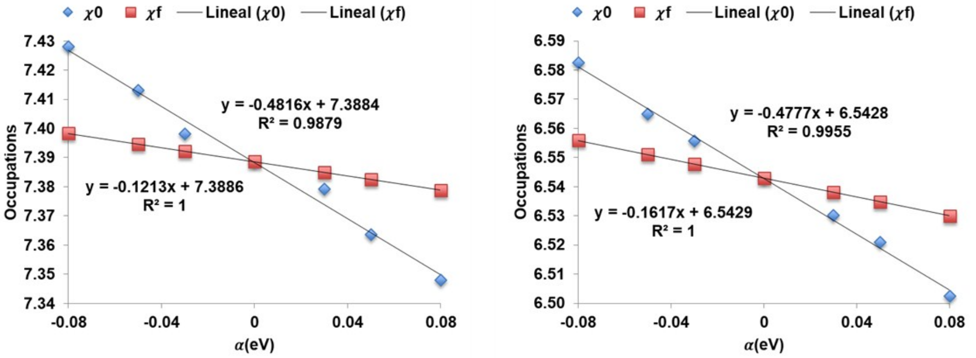


Figure S2. Occupation of the Fe 3d orbitals (n) with respect to the potential shift α applied for the LS (left) and HS (right) state of **1**.

The resulting U obtained with the LR approach are 6.17 and 4.09 eV for the LS and HS state of **1**, respectively. With these U values, the resulting ΔH_{elec} of **1** at the D3-BJ minima is −175.0 kJ/mol, very far from the reference value of 15.0 kJ/mol.

S3. Evolution of ΔH_{elec} vs. *U*

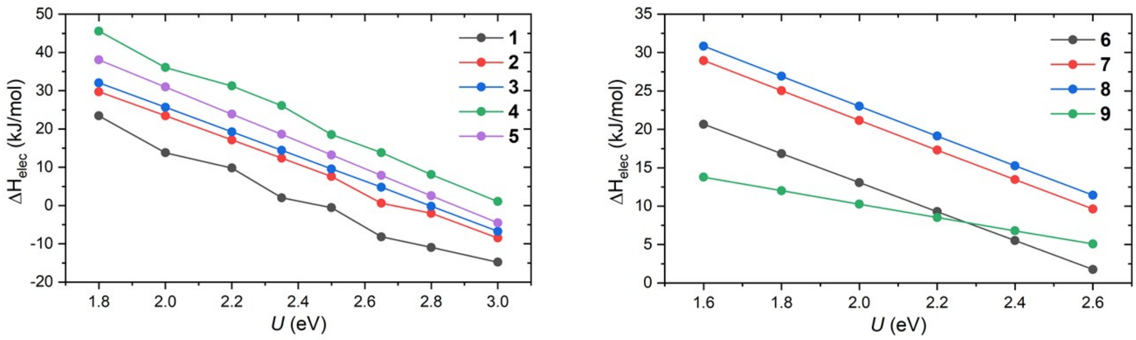


Figure S3. Evolution of ΔH_{elec} with U for (left) Fe^{II} and (right) Fe^{III} compounds.

S4. Unit cell volumes

Table S1. Volumes (in Angstrom^3) of the HS and LS computed and experimentally reported unit cells, together with the expansion along SCO, computed as $(V_{HS}-V_{LS})/V_{LS}$.

	DFT+D2 (ref. [2])			DFT+D3 (this work)			DFT+D3-BJ (this work)		
	HS	LS	Expansion	HS	LS	Expansion	HS	LS	Expansion
1	14957.6	14435.4	+3.6%	15620.7	15111.7	+3.4%	15413.7	14929.0	+3.2%
2	9047.2	8713.4	+3.8%	9629.4	9369.6	+2.8%	9453.3	9151.9	+3.3%
3	9242.2	8862.0	+4.3%	9839.1	9531.1	+3.2%	9721.3	9423.7	+3.2%
4	14066.3	13406.4	+4.9%	15201.5	14363.7	+5.8%	15174.4	14513.5	+4.6%
5	17440.2	16935.1	+3.0%	18278.3	17931.0	+1.9%	18259.5	17986.4	+1.5%
6	-	-	-	18182.1	17489.0	+4.0%	17949.3	17418.2	+3.0%
7	-	-	-	14769.3	14308.4	+3.2%	14613.7	14159.0	+3.2%
8	-	-	-	15405.4	14809.3	+4.0%	15142.3	14625.8	+3.5%
9	-	-	-	11803.1	11576.6	+2.0%	11709.6	11484.3	+2.0%

	Crystal (.cif files)		
	HS	LS	Temp (HS/LS)
1	15779.2	14975.2	RT/130
2	9687.8	-	295/-
3	9870.2	-	295/-
4	14718.1	14561.6	298/180
5	17789.9	17394.5	30/30
6	-	17391.8	-/100
7	-	13905.6	-/100
8	-	14621.0	-/193
9	11600.6	11461.4	293/163

S5. Tables

Table S2. Energy contribution to ΔH_{elec} arising from dispersion interactions as described by the dispersion correction schemes (in kJ/mol) at the solid-state minima computed with PBE+*U*+D3. Inter- and intra-molecular (for SCO) contributions are given. All energy contributions are given *per* molecule.

	D2			***D3***			***D3-BJ***		
	Total	***Inter***	***Intra***	***Total***	***Inter***	***Intra***	***Total***	***Inter***	***Intra***
1	11.8	0.4	11.4	−1.1	−4.4	3.3	0.1	−4.5	4.6
2	12.2	5.6	6.6	−0.3	−0.6	0.3	1.7	2.2	−0.5
3	15.5	6.7	8.8	3.8	2.0	1.8	4.4	3.5	0.9
4	23.8	−0.5	24.3	11.8	3.6	8.3	13.8	2.4	11.4
5	9.8	−3.9	13.7	0.5	−7.7	8.2	0.9	−7.6	8.5
6	19.7	11.2	8.5	7.5	5.4	2.1	7.3	5.2	2.1
7	12.2	4.7	7.5	2.3	0.8	1.6	1.5	0.2	1.3
8	16.9	9.0	7.9	5.7	3.9	1.8	4.9	3.3	1.5
9	13.5	13.2	0.3	1.9	8.0	−6.1	0.4	6.1	−5.7

Table S3. ΔH_{elec}^{iso} values (in kJ/mol) obtained with various DFT functionals complemented with the D3 and D3-BJ dispersion correction schemes. The reference is the ΔH_{elec}^{iso} value obtained with PBE+*U* using the benchmarked U (different for each compound, see Table 2) at isolated molecules of **1-9** excised from the PBE+*U*+D3 and PBE+*U*+D3-BJ solid-state minima.

		D3 Dispersion Correction						
	ΔH_{elec}^{iso}	***OLYP***	***OPBE***	***TPSSh***	***B3LYP***	***B3LYP****	***M06L***	***SCAN***
1	9.4	2.8	22.1	35.9	−24.1	0.5	−14.6	46.1
2	16.6	14.1	26.6	41.8	−12.8	14.9	11.7	61.1
3	21.3	17.7	31.5	47.4	−8.0	19.3	11.1	67.6
4	35.5	50.3	67.6	69.7	11.7	31.7	41.3	98.5
5	20.6	40.1	58.6	55.4	−4.7	24.0	14.5	76.2
6	2.3	−2.3	6.4	46.4	−4.5	17.7	−35.4	29.6
7	5.2	8.4	18.5	55.6	4.9	26.5	−28.5	39.0
8	6.1	10.7	21.4	58.3	7.7	28.6	−25.9	42.1
9	10.9	13.5	23.9	54.8	6.1	31.2	−21.5	42.9
		D3-BJ Dispersion Correction						
	ΔH_{elec}^{iso}	***OLYP***	***OPBE***	***TPSSh***	***B3LYP***	***B3LYP****	***M06L***	***SCAN***
1	9.0	2.5	21.5	33.8	−24.8	0.8	−7.0	40.6
2	15.4	15.8	30.9	45.2	−11.0	15.9	19.6	63.7
3	17.8	17.2	32.1	47.0	−8.8	19.0	22.6	67.1
4	35.0	57.9	76.8	72.1	14.2	38.1	63.6	98.8
5	20.6	43.3	64.0	55.7	−4.5	25.0	28.0	76.5
6	1.8	−4.9	5.2	46.1	−6.0	16.2	−26.4	29.5
7	5.1	5.4	16.6	54.8	2.7	24.0	−20.3	39.9
8	6.9	7.7	19.4	57.4	5.3	26.3	−17.3	42.6
9	11.6	8.0	18.4	52.2	1.8	27.2	−15.6	42.4

Table S4. Error associated with ΔH_{elec}^{iso} values (in kJ/mol) obtained with various DFT functionals and the D3 dispersion correction scheme.

		OLYP	***OPBE***	***TPSSh***	***B3LYP***	***B3LYP****	***M06L***	***SCAN***
1		6.6	12.7	26.5	33.6	8.9	24.0	36.7
2		2.5	10.0	25.2	29.4	1.8	4.9	44.5
3		3.6	10.2	26.1	29.3	2.0	10.3	46.3
4		14.8	32.1	34.2	23.8	3.8	5.8	63.0
5		19.4	37.9	34.8	25.3	3.4	6.2	55.6
MAE-Fe^{II}		9.4	20.6	29.4	28.3	4.0	10.2	49.2
6		4.6	4.1	44.1	6.8	15.4	37.7	27.3
7		3.2	13.3	50.4	0.3	21.4	33.7	33.9
8		4.6	15.3	52.2	1.6	22.5	32.0	36.0
9		2.6	13.0	43.9	4.8	20.3	32.4	32.0
MAE-Fe^{III}		3.7	11.4	47.6	3.4	19.9	33.9	32.3
MAE-All		6.9	16.5	37.5	17.2	11.0	20.8	41.7

Table S5. Error associated with ΔH_{elec}^{iso} values (in kJ/mol) obtained with various DFT functionals and the D3-BJ dispersion correction scheme.

		OLYP	***OPBE***	***TPSSh***	***B3LYP***	***B3LYP****	***M06L***	***SCAN***
1		6.5	12.5	24.8	33.8	8.2	16.0	31.6
2		0.4	15.5	29.8	26.4	0.5	4.2	48.3
3		0.6	14.3	29.2	26.6	1.2	4.8	49.3
4		22.9	41.8	37.1	20.8	3.1	28.6	63.8
5		22.7	43.4	35.1	25.1	4.4	7.4	55.9
MAE-Fe^{II}		10.6	25.5	31.2	26.5	**3.5**	12.2	49.8
6		6.7	3.4	44.3	7.8	14.4	28.2	27.7
7		0.3	11.5	49.7	2.4	18.9	25.4	34.8
8		0.8	12.5	50.5	1.6	19.4	24.2	35.7
9		3.6	6.8	40.6	9.8	15.6	27.2	30.8
MAE-Fe^{III}		**2.9**	8.5	46.3	5.4	17.1	26.3	32.2
MAE-All		7.2	18.0	37.9	17.1	9.5	18.5	42.0

Table S6. Electronic enthalpy differences (in kJ/mol) obtained for **1**-**9** when using the average *U* values benchmarked for D3 and D3-BJ, for all compounds, ΔH_{elec}^{Uavg}. This value is compared to the reference electronic enthalpy, ΔH_{elec}^{ref}.

		D3		***D3-BJ***	
	ΔH_{elec}^{ref}	ΔH_{elec}^{Uavg}	***Error***	ΔH_{elec}^{Uavg}	***Error***
1	15.0	4.1	−11.0	3.6	11.4
2	13.2	14.3	1.1	11.9	1.3
3	14.5	16.4	1.9	15.8	1.3
4	21.4	28.4	6.9	29.1	7.6
5	19.1	20.7	1.6	19.2	0.1
MAE			**4.5**		**4.4**
6	10.3	4.8	5.5	6.5	3.7
7	11.7	12.7	1.0	13.3	1.7
8	11.9	14.5	2.6	15.1	3.3
9	10.9	12.9	2.0	11.4	0.6
MAE			**2.8**		**2.3**

References

1. M. Cococcioni and S. de Gironcoli, *Phys. Rev. B*, 2005, **71**, 035105.
2. S. Vela, M. Fumanal, J. Ribas-Arino and V. Robert, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16306-16314.