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Supplemental Material for:

Assessment of TD-DFT and LF-DFT for study of $d-d$ transitions in first row transition metal hexaaqua complexes

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S1. TD-DFT AND LF-DFT RESULTS ON PW91 OPTIMIZED GEOMETRIES

TABLE S1. TD-DFT excitation energies (in cm^{-1}) of $[V(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[1]
^3T_g $(t_g^2e_g^0)$	0	0	0	0	0	0	0	0	0	0	0
	2,700	2,958	2,422	2,885	6,330	2,012	2,515	2,218	12,314	3,491	1,940[2]
^1T_g $(t_g^2e_g^0)$	6,626	7,222	9,740	6,956	13,613	8,992	6,480	6,915	25,587	9,320	9,860
	11,299	12,683	15,399	12,341	18,716	14,874	11,440	12,597	26,557	14,901	12,200
^3T_g $(t_g^1e_g^1)$	18,228	19,366	18,145	19,200	23,205	16,914	18,125	17,679	12,314	18,928	17,200
	22,418	23,170	24,580	22,859	30493	23,736	22,475	22,435	40,201	24,470	19,600
^3T_g $(t_g^1e_g^1)$	25,737	24,937	23,009	24,762	29,721	24,206	25,858	25,317	28,623	24,296	25,200
	27,305	26,354	28,417	26,646	35,123	28,511	27,522	27,169	44,865	28,429	27,900
MAE ($^3\Gamma \rightarrow ^3\Gamma$)	1,147	1,713	1,823	1,579	6,606	1,220	1,082	888	11,250	1,916	
MAE ($^3\Gamma \rightarrow ^1\Gamma$)	2,067	1,560	1,659	1,522	5,134	1,771	2,070	1,671	15,042	1,620	
MAE	1,410	1,669	1,776	1,563	6,185	1,377	1,364	1,112	12,333	1,831	

TABLE S2. LF-DFT excitation energies (in cm^{-1}) of $[V(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[1]
	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^2e_g^0)$	863	917	848	907	805	852	845	908	1,940[2]
	981	1,113	1,094	1,107	960	949	975	1,077	
	9,499	9,648	10,512	9,550	10,705	9,487	10,000	10,401	9,860
^1T_g $(t_g^2e_g^0)$	10,324	10,630	11,496	10,526	11,527	10,304	10,828	11,339	12,200
	10,784	11,046	11,870	10,938	11,942	10,742	11,266	11,777	
	15,081	15,343	14,902	15,299	14,936	15,317	15,234	14,494	17,200
^3T_g $(t_g^1e_g^1)$	15,912	16,321	15,863	16,272	15,748	16,109	16,058	15,434	19,600
	17,499	17,715	17,348	17,672	17,435	17,815	17,704	16,819	
	24,120	23,940	22,989	23,873	23,269	24,207	23,830	22,957	25,200
^3T_g $(t_g^1e_g^1)$	26,371	25,971	24,989	25,897	25,518	26,582	26,105	25,002	27,900
	27,573	27,291	26,283	27,210	26,689	27,755	27,295	26,289	
MAE ($^3\Gamma \rightarrow ^3\Gamma$)	1,366	1,341	1,902	1,390	1,762	1,207	1,410	2,092	
MAE ($^3\Gamma \rightarrow ^1\Gamma$)	1,003	787	584	889	655	1,025	646	591	
MAE	1,262	1,183	1,526	1,246	1,445	1,155	1,191	1,663	

TABLE S3. TD-DFT excitation energies (in cm^{-1}) of $[V(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[3]
^4A_g $(t_g^3e_g^0)$	0	0	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^2e_g^1)$	16,604	17,560	15,938	17,279	23,427	14,754	16,476	15,836	24,586	16,892	12,400
^4T_g $(t_g^2e_g^1)$	20,880	20,124	18,599	18,297	26,146	1,9537	20,917	20,534	27,222	19,522	18,500
^4T_g $(t_g^1e_g^2)$	-	-	-	-	-	-	-	-	-	-	28,000
MAE	3,292	3,392	1,818	2,541	9,336	1,695	3,246	2,735	10,454	2,757	

TABLE S4. LF-DFT excitation energies (in cm^{-1}) of $[V(H_2O)_6]^{2+}$with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[3]
^4A_g $(t_g^3e_g^0)$	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^2e_g^1)$	13,086	12,460	11,761	12,530	12,621	15,732	13,224	11,706	12,400
^4T_g $(t_g^2e_g^1)$	19,093	18,354	17,298	18,226	18,428	21,716	19,180	17,352	18,500
^4T_g $(t_g^1e_g^2)$	29,696	28,525	26,886	28,358	28,659	34,316	29,855	26,967	28,000
MAE	992	244	985	254	317	4288	1,120	958	

TABLE S5. TD-DFT excitation energies (in cm^{-1}) of $[Cr(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[3]
^4A_g $(t_g^3e_g^0)$	0	0	0	0	0	0	0	0	0	0	0
^2E_g $(t_g^3e_g^0)$	15,885	16,291	19,866	15,966	24,392	20,667	16,177	17,607	32,538	19,407	15,000
^4T_g $(t_g^2e_g^1)$	21,233	21,492	19,472	21,391	26,483	19,342	21,321	25,971	20,527	20,833	17,400
^4T_g $(t_g^2e_g^1)$	25,379	23,594	21,474	23,504	28,537	23,915	25,712	25,133	27,719	22,883	24,700
^4T_g $(t_g^1e_g^2)$											37,800
MAE ($^4\Gamma \rightarrow ^4\Gamma$)	2,256	2,599	2,649	2,593	6,460	1,365	2,466	4,502	3,073	2,625	
MAE ($^4\Gamma \rightarrow ^2\Gamma$)	885	1,291	4,866	966	9,392	5,667	1,177	2,607	17,538	4,407	
MAE	1,799	2,163	3,388	2,051	7,437	2,798	2,037	3,870	7,895	3,219	

TABLE S6. LF-DFT excitation energies (in cm^{-1}) of $[Cr(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[3]
^4A_g $(t_g^3e_g^0)$	0	0	0	0	0	0	0	0	0
^2E_g $(t_g^3e_g^0)$	12,682	12,905	14,336	12,786	14,745	12,756	13,640	14,140	15,000
^4T_g $(t_g^2e_g^1)$	16,806	17,154	16,743	17,119	16,636	16,938	16,888	16,240	17,400
^4T_g $(t_g^2e_g^1)$	24,197	24,140	23,266	24,095	23,594	24,332	24,096	23,036	24,700
^4T_g $(t_g^1e_g^2)$	37,716	37,866	36,664	37,793	36,918	37,945	37,639	36,043	37,800
MAE ($^4\Gamma \rightarrow ^4\Gamma$)	394	291	1,075	298	917	325	425	1,527	
MAE ($^4\Gamma \rightarrow ^2\Gamma$)	2,318	2,095	664	2,214	255	2,244	1,360	860	
MAE	612	546	513	578	407	805	659	1,360	

TABLE S7. TD-DFT excitation energies (in cm^{-1}) of $[Cr(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[4]
^5E_g $(t_g^3e_g^1)$	0	0	0	0	0	0	0	0	0	0	0
	7,823	7,905	7,147	7,968	12,230	7,095	7,717	7,559	13,921	8,291	8,000
^5T_g $(t_g^2e_g^2)$	14,751	15,345	14,227	15,154	21,044	13,646	14,629	14,347	20,600	15,172	14,550
	16,471	17,465	16,185	17,285	23,169	14,884	16,274	16,064	22,499	17,245	18,050
	17,114	18,061	16,369	17,892	23,433	15,347	16,999	16,142	22,561	17,637	
MAE	724	654	1,063	620	5,723	1,297	745	1,001	5,810	787	

TABLE S8. LF-DFT excitation energies (in cm^{-1}) of $[Cr(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[4]
^5E_g $(t_g^3e_g^1)$	0	0	0	0	0	0	0	0	0
	7,231	7,170	6,697	7,092	6,910	7,332	7,177	6,886	8,000
^5T_g $(t_g^2e_g^2)$	12,890	13,130	12,463	13,056	12,495	13,105	12,906	12,337	14,550
	13,171	13,163	12,562	13,075	12,659	13,422	13,153	12,489	18,050
	14,864	15,185	14,373	15,083	14,229	15,037	14,801	14,423	
MAE	1,824	1,699	2,339	1,786	2,295	1,656	1,864	2,293	

TABLE S9. TD-DFT excitation energies (in cm^{-1}) of $[Mn(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[5]
^5E_g $(t_g^3e_g^1)$	0	0	0	0	0	0	0	0	0	0	0
	7,227	6,568	5,796	6,501	9,595	6,732	7,380	7,113	10,085	6,839	9,800
^5T_g $(t_g^2e_g^2)$	18,110	15,539	11,853	15,547	16,090	17,044	18,653	18,061	12,887	11,911	20,000
	19,882	16,639	14,451	16,604	18,782	18,181	20,746	19,667	16,563	14,690	21,100
	20,109	18,629	15,855	18,608	20,212	18,758	20,992	20,150	17,632	16,183	
MAE	1,522	3,204	5,365	3,238	1,219	2,599	942	1,591	3,009	3,446	

TABLE S10. LF-DFT excitation energies (in cm^{-1}) of $[Mn(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[5]
^5E_g $(t_g^3e_g^1)$	0	0	0	0	0	0	0	0	0
	6,486	6,449	6,300	6,433	6,400	6,543	6,488	6,285	9,800
^5T_g $(t_g^2e_g^2)$	16,833	16,935	16,513	16,908	16,711	16,949	16,902	16,147	20,000
	16,913	17,075	16,734	17,051	16,723	17,061	16,965	16,219	21,100
	18,841	19,092	18,607	19,056	18,573	18,937	18,853	18,206	
MAE	2,900	2,784	3,123	2,810	3,070	2,805	2,875	3,408	

TABLE S11. TD-DFT excitation energies (in cm^{-1}) of $[Mn(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[6]
^6A_g $(t_g^3e_g^2)$	0	0	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^1)$	18,897	20,059	26,875	19,710	32,050	27,067	18,910	21,610	42,584	27,744	18,870
^4T_g $(t_g^4e_g^1)$	19,892	20,183	26,985	19,833	32,171	28,309	19,973	22,869	42,694	27,851	23,120
^4A_g +^{4} E_g $(t_g^3e_g^2)$	23,832	24,705	30,799	24,376	36,291	31,379	24,032	26,388	24,425	36,404	24,960
	23,878	25,226	31,516	24,874	37,037	31,459	24,059	26,493	24,432	32,326	25,270
^4T_g $(t_g^3e_g^2)$	24,373	25,825	32,463	25,438	37,996	32,735	24,449	27,366	47,869	32,701	27,980
^4E_g $(t_g^3e_g^2)$	23,878	25,833	32,491	25,448	38,015	33,147	25,351	28,001	46,909	32,798	29,750
MAE	2,542	1,749	5,196	1,991	10,601	5,691	2,213	1,334	1,3618	6,645	

TABLE S12. LF-DFT excitation energies (in cm^{-1}) of $[Mn(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[6]
^6A_g $(t_g^3e_g^2)$	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^1)$	15,458	16,044	20,031	15,838	20,668	15,536	17,744	19,151	18,870
^4T_g $(t_g^4e_g^1)$	19,650	20,186	23,564	19,988	24,102	19,688	2,1611	22,889	23,120
^4A_g +^{4} E_g $(t_g^3e_g^2)$	21,829	22,749	25,742	22,542	25,913	21,847	23,672	25,012	24,960 25,270
^4T_g $(t_g^3e_g^2)$	25,745	26,323	29,239	26,116	29,754	25,744	27,522	28,750	27,980
^4E_g $(t_g^3e_g^2)$	27,753	28,390	31,070	28,181	31,486	27,736	29,423	30,635	29,750
MAE	2,880	2,228	962	2,434	1,418	2,857	973	454	

TABLE S13. TD-DFT excitation energies (in cm^{-1}) of $[Fe(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[7]
^6A_g $(t_g^3e_g^2)$	0	0	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^1)$	13,137	11,695	16,310	11,453	22,272	19,417	13,709	15,289	24,127	18,138	12,600
^4T_g $(t_g^4e_g^1)$	14,401	11,830	16,452	11,587	22,396	20,963	15,056	16,857	24,351	18,282	18,500
^4A_g +^{4} E_g $(t_g^3e_g^2)$	22,223 26,591	17,470 19,382	19,399 20,585	17,288 19,230	23,678 24,598	28,063 31,577	23,695 29,110	24,927 29,722	24,473 24,720	20,246 21,343	24,300
MAE	1,581	4,483	3,355	4,700	4,576	4,121	2,218	2,452	5,891	3,087	

TABLE S14. LF-DFT excitation energies (in cm^{-1}) of $[Fe(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[7]
^6A_g $(t_g^3e_g^2)$	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^1)$	10,001	11,040	14,047	10,885	13,688	9,906	11,600	14,178	12,600
^4T_g $(t_g^4e_g^1)$	15,244	15,968	18,475	15,823	18,388	15,163	16,623	18,765	18,500
^4A_g +^{4} E_g $(t_g^3e_g^2)$	20,650	21,313	23,472	21,169	23,563	20,672	21,998	23,395	24,300
MAE	3,168	2,359	766	2,507	645	3,219	1,726	916	

TABLE S15. TD-DFT excitation energies (in cm^{-1}) of $[Fe(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[8]
^5T_g $(t_g^4e_g^2)$	0	0	0	0	0	0	0	0	0	0	0
^5E_g $(t_g^3e_g^3)$	10,628	12,104	11,878	11,916	17,165	10,986	10,523	10,928	23,035	12,642	8,300
	14,394	16,956	15,847	16,689	24,117	21,947	14,204	14,394	25,116	17,357	10,400
MAE	3,161	5,180	4,512	4,952	11,291	7,116	3,013	3,311	14,725	5,649	

TABLE S16. LF-DFT excitation energies (in cm^{-1}) of $[Fe(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[8]
^5T_g $(t_g^4e_g^2)$	0	0	0	0	0	0	0	0	0
^5E_g $(t_g^3e_g^3)$	7,656	8,392	8,050	8,400	7,226	7,531	7,501	7,915	8,300
	9,642	10,403	9,939	10,394	9,099	9,523	9,455	9,826	10,400
MAE	701	47	355	53	1187	823	872	479	

TABLE S17. TD-DFT excitation energies (in cm^{-1}) of $[Co(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[1]
^1A_g $(t_g^6e_g^0)$	0	0	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^5e_g^1)$	8,915	8,826	7,106	8,789	14,940	5,984	7,858	7,233	15,248	8,612	8,000
^3T_g $(t_g^5e_g^1)$	10,610	9,059	7,333	9,018	15,241	8,109	12,214	9,342	15,581	8,851	12,500
^1T_g $(t_g^5e_g^1)$	14,486	13,055	11,415	13,019	18,850	11,816	14,781	13,051	18,704	12,814	16,600
^1T_g $(t_g^5e_g^1)$	20,239	15,384	13,764	15,351	20,723	18,447	21,188	19,697	20,180	14,990	24,900
MAE ($^1\Gamma \rightarrow ^3\Gamma$)	1,402	2,133	3,030	2,135	4,840	3,203	214	1,962	5,164	2,130	
MAE ($^1\Gamma \rightarrow ^1\Gamma$)	3,387	6,530	8,160	6,565	3,213	5,618	2,765	4,376	3,412	6,848	
MAE	2,395	4,332	5,595	4,350	4,027	4,411	1,489	3,169	4,288	4,489	

TABLE S18. LF-DFT excitation energies (in cm^{-1}) of $[Co(H_2O)_6]^{3+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[1]
^1A_g $(t_g^6e_g^0)$	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^5e_g^1)$	7,706	6,253	4,783	6,312	6,281	7,999	7,212	4,617	8,000
^3T_g $(t_g^5e_g^1)$	12,076	10,311	8,532	10,375	10,369	12,410	11,488	8,454	12,500
^1T_g $(t_g^5e_g^1)$	13,109	12,018	11,403	12,031	12,747	13,374	13,080	11,147	16,600
^1T_g $(t_g^5e_g^1)$	21,757	20,068	18,918	20,088	20,934	22,112	21,589	18,774	24,900
MAE ($^1\Gamma \rightarrow ^1\Gamma$)	3,317	3,863	5,589	4,690	3,909	3,007	3,415	5,789	
MAE ($^1\Gamma \rightarrow ^3\Gamma$)	359	1,968	3,592	1,906	1,925	45	900	3,714	
MAE	1,838	2,915	4,304	3,298	2,917	1,526	2,158	4,752	

TABLE S19. TD-DFT excitation energies (in cm^{-1}) of $[Co(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[3]
^4T_g $(t_g^5e_g^2)$	0	0	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^3)$	10,219	12,776	11,966	12,608	19,449	9,595	10,048	9,997	19,634	14,066	8,100
	11,231	13,473	12,689	13,317	19,811	10,604	11,075	11,048	20,434	14,665	
$^2E_g(t_g^6e_g^1)$	7,070	6,683	10,404	6,471	17,325	12,560	7,243	9,349	15,567	12,762	11,300
	11,482	11,337	15,082	11,186	22,588	16,414	11,789	13,156	20,014	17,571	
^4A_g $(t_g^3e_g^4)$	-	-	-	-	-	-	-	-	-	-	16,000
^4T_g $(t_g^4e_g^3)$	19144	20,255	18,770	20,020	29,610	18,661	19,025	19,358	25,364	21,893	19,400
	20133	20,785	19,260	20,554	30,036	19,547	20,055	20,336	26,067	22,282	2,1550
MAE ($^4\Gamma \rightarrow ^4\Gamma$)	1,433	2,215	2,382	2,159	10,075	1,580	1,444	1,226	7,471	3,163	
MAE ($^4\Gamma \rightarrow ^2\Gamma$)	2,024	2,290	1,443	2,471	8,656	3,187	1,784	47	6,490	3,866	
MAE	1,580	2,234	2,148	2,237	9,721	1,982	1,529	931	7,226	3,339	

TABLE S20. LF-DFT excitation energies (in cm^{-1}) of $[Co(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[3]
^4T_g $(t_g^5e_g^2)$	0	0	0	0	0	0	0	0	0
^4T_g $(t_g^4e_g^3)$	7,156	7,821	7,501	7,807	6,776	7,017	6,989	7,318	8,100
	7,365	8,255	7,915	8,245	6,902	7,169	7,143	7,734	
	8,574	9,413	9,084	9,398	8,155	8,417	8,382	8,855	
^2E_g $(t_g^6e_g^1)$	5,514	5,363	7,646	5,253	8,483	5,674	6,873	7,678	11,300
	7,447	7,372	9,603	7,258	10,326	7,603	8,760	9,628	
^4A_g $(t_g^3e_g^4)$	16,292	17,829	17,133	17,801	15,445	15,980	15,914	16,740	1,6000
^4T_g $(t_g^4e_g^3)$	16,292	19,159	18,129	19,147	17,855	18,739	18,500	18,611	19,400
	18,941	20,493	19,485	20,478	19,227	20,119	19,864	19,997	21,550
	20,306	21,484	20,429	21,464	19,892	20,837	20,570	20,915	
MAE ($^4\Gamma \rightarrow ^4\Gamma$)	930	679	728	671	974	332	470	400	
MAE ($^4\Gamma \rightarrow ^2\Gamma$)	4,819	4,932	2,675	5,044	1,895	4,661	3,483	2,647	
MAE	1,708	1,530	1,118	1,545	1,158	1,198	1,072	850	

TABLE S21. TD-DFT excitation energies (in cm^{-1}) of $[Ni(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	M06L	OPBE0	CAMB3LYP	PBE0	SAOP	SSBD	Exp.[9]
^3A_g $(t_g^6e_g^2)$	0	0	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^5e_g^3)$	14,463	16,211	14,420	16,064	25,038	12,870	14,423	13,987	18,562	16,963	8,500
^3T_g $(t_g^5e_g^3)$	20,481	19,625	17,946	19,480	28,656	19,592	20,543	20,607	21,468	20,485	13,500
^1E_g $(t_g^6e_g^2)$	14,766	14,105	15,005	13,845	24,920	17,333	15,494	16,263	15,223	18,128	15,400
^1T_g $(t_g^5e_g^3)$	20,186	20,301	20,795	20,076	31,783	23,644	20,304	20,138	21,063	23,401	22,000
^3T_g $(t_g^4e_g^4)$	-	-	-	-	-	-	-	-	-	-	25,300
MAE ($^3\Gamma \rightarrow ^3\Gamma$)	6,472	6,918	5,183	6,772	15,847	5,231	6,483	6,297	9,015	7,724	
MAE ($^3\Gamma \rightarrow ^1\Gamma$)	1,224	1,497	800	1,739	9,651	1,788	895	1,362	557	2,064	
MAE	3,848	4,207	2,991	4,256	12,749	3,510	3,689	3,830	4,786	4,894	

TABLE S22. LF-DFT excitation energies (in cm^{-1}) of $[Ni(H_2O)_6]^{2+}$ with different XC functionals and comparison with available experimental data; mean absolute error (MAE) is given in cm^{-1}; assignement (electronic state and its configuration) in formally T_h point group is indicated

Assignment	B3LYP	BP86	OPBE	PW91	OPBE0	CAMB3LYP	PBE0	SSBD	Exp.[9]
^3A_g $(t_g^6e_g^2)$	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^5e_g^3)$	9,362	9,594	9,268	9,586	9,157	9,276	9,272	9,056	8,500
^3T_g $(t_g^5e_g^3)$	15,340	15,610	15,013	15,598	14,930	15,210	15,172	14,827	13,500
^1E_g $(t_g^6e_g^2)$	12,231	12,480	13,262	12,412	13,321	12,215	12,758	13,471	15,400
^1T_g $(t_g^5e_g^3)$	21,209	21,715	22,201	21,638	22,126	21,107	21,657	22,160	22,000
^3T_g $(t_g^4e_g^4)$	26,131	26,145	24,915	26,131	25,127	25,956	25,752	25,202	25,300
MAE ($^3\Gamma \rightarrow ^3\Gamma$)	1,178	1,350	889	1,338	753	1,047	965	660	
MAE ($^3\Gamma \rightarrow ^1\Gamma$)	1,980	1,602	1,169	1,675	1,102	2,039	1,492	1,044	
MAE	1,499	1,451	1,001	1,473	893	1,444	1,176	814	

S2. ALL NON-EMPIRICALLY DETERMINED PARAMETERS OBTAINED BY THE LF-DFT PROCEDURE

A. Complexes with T_h symmetry

TABLE S23. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[V(H_2O)_6]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	839	2,437	17,119
	BP86	635	2,519	12,311
	CAMB3LYP	594	2,400	15,251
	OPBE	594	3,142	11,605
	OPBE0	616	3,040	12,432
	PBE0	629	2,590	13,048
	PW91	615	2,501	12,343
	SSB-D	617	2,904	11,563
PW91	B3LYP	635	2,258	13,086
	BP86	633	2,516	12,460
	CAMB3LYP	589	2,458	15,732
	OPBE	593	3,135	11,761
	OPBE0	615	3,035	12,621
	PBE0	624	2,600	13,224
	PW91	599	2,519	12,530
	SSB-D	613	2,905	11,706

TABLE S24. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[Cr(H_2O)_6]^{3+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	765	2,389	16,730
	BP86	702	2,582	17,078
	CAMB3LYP	764	2,416	16,861
	OPBE	647	3,174	16,665
	OPBE0	705	3,187	16,559
	PBE0	736	2,758	16,812
	PW91	701	2,547	17,043
	SSB-D	690	3,022	16,167
PW91	B3LYP	766	2,388	16,806
	BP86	703	2,586	17,154
	CAMB3LYP	764	2,415	16,938
	OPBE	647	3,177	16,743
	OPBE0	707	3,186	16,636
	PBE0	738	2,757	16,888
	PW91	702	2,550	17,119
	SSB-D	691	3,026	16,240

TABLE S25. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[Mn(H_2O)_6]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	847	2,674	8,066
	BP86	806	2,939	8,671
	CAMB3LYP	842	2,687	8,019
	OPBE	762	3,627	8,176
	OPBE0	797	3,591	7,618
	PBE0	822	3,092	7,958
	PW91	806	2,898	8,637
	SSB-D	804	3,396	8,135
PW91	B3LYP	846	2,673	8,134
	BP86	806	2,938	8,744
	CAMB3LYP	841	2,687	8,087
	OPBE	761	3,626	8,247
	OPBE0	796	3,590	7,685
	PBE0	821	3,092	8,026
	PW91	806	2,897	8,710
	SSB-D	803	3,396	8,204

TABLE S26. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[Fe(H_2O)_6]^{3+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	822	2,488	12,389
	BP86	779	2,702	12,219
	CAMB3LYP	822	2,494	12,517
	OPBE	726	3,240	11,836
	OPBE0	768	3,184	12,237
	PBE0	801	2,803	12,428
	PW91	779	2,673	12,203
	SSB-D	765	3,148	11,515
PW91	B3LYP	822	2,486	12,454
	BP86	780	2,702	12,294
	CAMB3LYP	821	2,492	12,581
	OPBE	727	3,240	11,912
	OPBE0	766	3,180	12,300
	PBE0	799	2,801	12,492
	PW9	780	2,673	12,279
	SSB-D	766	3,148	11,588

TABLE S27. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[Co(H_2O)_6]^{3+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	839	2,437	17,119
	BP86	787	2,723	16,911
	CAMB3LYP	859	2,299	17,434
	OPBE	733	3,213	16,594
	OPBE0	842	2,695	17,139
	PBE0	894	2,262	17,245
	PW91	787	2,697	16,902
	SSB-D	771	3,151	16,112
PW91	B3LYP	771	2,383	14,432
	BP86	733	2,578	13,440
	CAMB3LYP	774	2,370	14,697
	OPBE	687	3,029	13,074
	OPBE0	729	2,939	14,398
	PBE0	757	2,625	14,551
	PW91	733	2,555	13,440
	SSB-D	716	2,964	12,753

TABLE S28. All non-empirically determined parameters (Racah's parameters B and C, and ligand field splitting Δ) obtained by the LF-DFT procedure (in cm^{-1}) for $[Ni(H_2O)_6]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ
BP86	B3LYP	892	2,785	9,316
	BP86	865	3,001	9,529
	CAMB3LYP	889	2,791	9,233
	OPBE	808	3,596	9,201
	OPBE0	839	3,520	9,114
	PBE0	874	3,116	9,229
	PW91	865	2,967	9,521
	SSB-D	857	3,532	8,992
PW91	B3LYP	892	2,784	9,362
	BP86	865	3,000	9,594
	CAMB3LYP	889	2,789	9,276
	OPBE	808	3,596	9,268
	OPBE0	839	3,520	9,157
	PBE0	874	3,114	9,272
	PW91	865	2,966	9,586
	SSB-D	857	3,533	9,056

B. Complexes with D_{2h} symmetry

TABLE S29. All non-empirically determined parameters (Racah's parameters B and C, ligand field splitting Δ, and elements of the ligand field matrix, $< d_i|h_{\mathrm{LF}}|d_j >$; $< d_{xy}|h_{\mathrm{LF}}|d_{xy} >= 0$) obtained by the LF-DFT procedure (in cm^{-1}) for $[\mathrm{V(H_2O)_6}]^{3+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ	$< d_{yz}\|h_{\mathrm{LF}}\|d_{yz} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{z^2} >$	$< d_{xz}\|h_{\mathrm{LF}}\|d_{xz} >$	$< d_{x^2-y^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$
BP86	B3LYP	738	2,267	16,964	993	18,813	-37	15,752	132
	BP86	696	2,493	17,148	1033	18,888	-129	16,009	123
	CAMB3LYP	730	2,288	17,234	980	19,146	-14	15,966	135
	OPBE	654	3,077	16,693	955	18,393	-184	15,506	120
	OPBE0	682	3,068	16,802	920	18,623	-82	15,539	128
	PBE0	705	2,637	17,110	965	18,960	-53	15,868	130
	PW91	694	2,452	17,104	1,022	18,837	-134	15,963	122
	SSB-D	687	2,896	16,248	1,030	17,990	-98	15,128	125
PW91	B3LYP	737	2,266	17,058	1,002	18,929	-49	15,823	149
	BP86	696	2,493	17,243	1,041	19,002	-144	16,082	139
	CAMB3LYP	730	2,288	17,331	989	19,266	-27	16,037	152
	OPBE	654	3,076	16,790	962	18,508	-199	15,579	137
	OPBE0	682	3,066	16,898	928	18,741	-95	15,611	145
	PBE0	704	2,636	17,206	974	19,077	-66	15,940	147
	PW91	694	2,452	17,199	1,030	18,951	-148	16,035	139
	SSB-D	686	2,896	16,341	1,039	18,103	-111	15,198	142

TABLE S30. All non-empirically determined parameters (Racah's parameters B and C, ligand field splitting Δ, and elements of the ligand field matrix, $< d_i|h_{\mathrm{LF}}|d_j >$; $< d_{xy}|h_{\mathrm{LF}}|d_{xy} >= 0$) obtained by the LF-DFT procedure (in cm^{-1}) for $[\mathrm{Cr}(\mathrm{H_2O})_6]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ	$< d_{yz}\|h_{\mathrm{LF}}\|d_{yz} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{z^2} >$	$< d_{xz}\|h_{\mathrm{LF}}\|d_{xz} >$	$< d_{x^2-y^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$
BP86	B3LYP	768	2,455	9,896	1,726	13,010	1,993	9,261	-3,168
	BP86	728	2,758	10,107	2,063	13,325	2,070	9,645	-3,157
	CAMB3LYP	762	2,458	10,055	1,645	13,158	1,950	9,349	-3,208
	OPBE	680	3,432	9,657	1,949	12,641	1,824	9,190	-2,941
	OPBE0	713	3,361	9,547	1,601	12,459	1,750	8,870	-3,021
	PBE0	740	2,865	9,901	1,680	12,960	1,911	9,237	-3,142
	PW91	724	2,715	10,059	2,048	13,239	2,042	9,605	-3,125
	SSB-D	725	3,158	9,513	1,976	12,636	2,104	9,110	-3,034
PW91	B3LYP	767	2,453	10,026	1,693	13,063	1,975	9,434	-3,127
	BP86	728	2,756	10,241	2,022	13,382	2,054	9,818	-3,111
	CAMB3LYP	762	2,457	10,189	1,615	13,214	1,932	9,528	-3,169
	OPBE	680	3,428	9,784	1,910	12,692	1,811	9,358	-2,904
	OPBE0	713	3,358	9,673	1,570	12,508	1,735	9,040	-2,989
	PBE0	740	2,863	10,031	1,649	13,013	1,895	9,411	-3,104
	PW91	724	2,713	10,192	2,008	13,296	2,027	9,777	-3,079
	SSB-D	725	3,156	9,640	1,933	12,680	2,086	9,279	-2,994

TABLE S31. All non-empirically determined parameters (Racah's parameters B and C, ligand field splitting Δ, and elements of the ligand field matrix, $< d_i|h_{\mathrm{LF}}|d_j >$; $< d_{xy}|h_{\mathrm{LF}}|d_{xy} >= 0$) obtained by the LF-DFT procedure (in cm^{-1}) for $[\mathrm{Mn(H_2O)_6}]^{3+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ	$< d_{yz}\|h_{\mathrm{LF}}\|d_{yz} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{z^2} >$	$< d_{xz}\|h_{\mathrm{LF}}\|d_{xz} >$	$< d_{x^2-y^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$
BP86	B3LYP	798	2,486	14,196	1,933	17,211	1,996	13,800	-2,751
	BP86	760	2,658	14,380	2,160	17,425	2,001	14,109	-2,758
	CAMB3LYP	795	2,518	14,287	1,881	17,304	1,976	13,842	-2,769
	OPBE	702	3,237	14,038	2,095	16,971	1,856	13,739	-2,696
	OPBE0	734	3,268	14,045	1,853	16,961	1,849	13,596	-2,714
	PBE0	770	2,846	14,239	1,893	17,224	1,939	13,809	-2,751
	PW91	759	2,626	14,360	2,150	17,393	1,989	14,086	-2,752
	SSB-D	747	3,091	13,622	2,061	16,582	1,971	13,351	-2,688
PW91	B3LYP	798	2,487	14,286	1,928	17,288	2,008	13,907	-2,768
	BP86	759	2,659	14,476	2,157	17,511	2,017	14,223	-2,774
	CAMB3LYP	798	2,486	14,284	1,928	17,298	2,008	13,897	-2,762
	OPBE	701	3,237	14,135	2,094	17,059	1,873	13,855	-2,712
	OPBE0	734	3,268	14,136	1,849	17,040	1,861	13,706	-2,731
	PBE0	770	2,847	14,329	1,889	17,302	1,952	13,917	-2,767
	PW91	759	2,627	14,455	2,148	17,479	2,006	14,201	-2,767
	SSB-D	747	3,091	13,715	2,059	16,666	1,987	13,461	-2,703

TABLE S32. All non-empirically determined parameters (Racah's parameters B and C, ligand field splitting Δ, and elements of the ligand field matrix, $< d_i|h_{\mathrm{LF}}|d_j >$; $< d_{xy}|h_{\mathrm{LF}}|d_{xy} >= 0$) obtained by the LF-DFT procedure (in cm^{-1}) for $[\mathrm{Fe}(\mathrm{H_2O})_6]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ	$< d_{yz}\|h_{\mathrm{LF}}\|d_{yz} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{z^2} >$	$< d_{xz}\|h_{\mathrm{LF}}\|d_{xz} >$	$< d_{x^2-y^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$
BP86	B3LYP	877	2,819	8,178	-12	-8,377	468	-7,675	-787
	BP86	854	2,977	8,771	11	-8,974	489	-8,234	-814
	CAMB3LYP	873	2,835	8,076	-23	-8,292	433	-7,586	-789
	OPBE	785	3,732	8,468	100	-8,576	583	-7,905	-743
	OPBE0	822	3,725	7,739	7	-7,932	409	-7,270	-741
	PBE0	854	3,229	8,031	-9	-8,236	434	-7,544	-774
	PW91	843	2,980	8,809	45	-8,970	554	-8,248	-796
	SSB-D	835	3,543	8,333	59	-8,453	593	-7,778	-752
PW91	B3LYP	876	2,819	8,290	-18	-8,515	530	-7,723	-911
	BP86	840	3,033	8,973	69	-9,134	672	-8,319	-919
	CAMB3LYP	872	2,834	8,190	-31	-8,435	490	-7,639	-913
	OPBE	784	3,733	8,586	110	-8,708	667	-7,947	-865
	OPBE0	821	3,725	7,855	1	-8,074	462	-7,328	-859
	PBE0	853	3,228	8,146	-16	-8,377	491	-7,597	-896
	PW91	838	3,002	8,965	80	-9,114	687	-8,306	-912
	SSB-D	834	3,542	8,441	62	-8,578	676	-7,813	-876

TABLE S33. All non-empirically determined parameters (Racah's parameters B and C, ligand field splitting Δ, and elements of the ligand field matrix, $< d_i|h_{\mathrm{LF}}|d_j >$; $< d_{xy}|h_{\mathrm{LF}}|d_{xy} >= 0$) obtained by the LF-DFT procedure (in cm^{-1}) for $[\mathrm{Co(H_2O)_6}]^{2+}$ with different XC functionals on BP86 and PW91 geometries

Geometry	XC	B	C	Δ	$< d_{yz}\|h_{\mathrm{LF}}\|d_{yz} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{z^2} >$	$< d_{xz}\|h_{\mathrm{LF}}\|d_{xz} >$	$< d_{x^2-y^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$	$< d_{z^2}\|h_{\mathrm{LF}}\|d_{x^2-y^2} >$
BP86	B3LYP	896	2,865	8,463	565	-7,363	614	-8,777	-863
	BP86	863	3,063	9,185	811	-7,935	746	-9,396	-895
	CAMB3LYP	892	2,884	8,315	502	-7,252	570	-8,663	-863
	OPBE	813	3,712	8,817	773	-7,598	724	-9,039	-897
	OPBE0	846	3,709	8,038	457	-7,021	528	-8,397	-852
	PBE0	877	3,249	8,280	496	-7,233	556	-8,625	-855
	PW91	863	3,027	9,171	810	-7,927	744	-9,380	-894
	SSB-D	859	3,590	8,632	762	-7,411	760	-8,838	-897
PW91	B3LYP	895	2,867	8,560	549	-7,480	578	-8,889	-803
	BP86	862	3,065	9,293	781	-8,071	697	-9,529	-833
	CAMB3LYP	891	2,886	8,412	489	-7,367	537	-8,773	-804
	OPBE	812	3,714	8,925	744	-7,733	675	-9,170	-835
	OPBE0	845	3,711	8,133	444	-7,134	498	-8,504	-794
	PBE0	876	3,250	8,376	482	-7,347	524	-8,734	-796
	PW91	862	3,029	9,279	781	-8,062	695	-9,513	-832
	SSB-D	859	3,591	8,733	735	-7,541	711	-8,962	-838

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