Theoretical study of the spin competition in small-sized Al clusters

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SUPPORTING INFORMATION

AL RESULTS

TABLE I. Total electronic energy for the Al atom (in a.u.) in the doublet (D) spin state at different levels of theory[a].

	PBE	PW91	TPSS	revTPSS
SDecp	-0.9411	-0.9437	-0.9502	-0.9499
D95	-0.2097	-0.3271	-0.3625	-0.2642
DGDZVP	-0.1906	-0.3087	-0.3397	-0.2396
DGTZVP	-0.2156	-0.3337	-0.3654	-0.2645
TZVP	-0.2245	-0.3416	-0.3777	-0.2789
Def2TZVPP	-0.2276	-0.3452	-0.3798	-0.2806
aug-cc-pVDZ	-0.2233	-0.3402	-0.3767	-0.2782
aug-cc-pVTZ	-0.2296	-0.3467	-0.3828	-0.2841
aug-cc-pVQZ	-0.2333	-0.3507	-0.3858	-0.2870
CBS[b]	-0.2373	-0.3551	-0.3890	-0.2898

[a] In order to simplify the numeric values is required to add -242 a.u. except por the SDecp computation where is required to add -1 a.u.
[b] The CBS extrapolation is computed for the aug-cc-pVxZ basis set (x=D,T,Q).

AL_2 RESULTS

TABLE II. Al_2 total electronic energy (in a.u.) for the $^1\Sigma_g^-$ and $^3\Sigma_g^-$, $^3\Pi_u$ spin states at different levels of theory[a].

		PBE			PW91	
	$^1\Sigma_g^-$	$^3\Sigma_g^-$	$^3\Pi_u$	$^1\Sigma_g^-$	$^3\Sigma_g^-$	$^3\Pi_u$
SDecp	-0.8976	-0.9352	-0.9375		-0.9404	-0.9429
D95	-0.4483	-0.4723	-0.4743	-0.6836	-0.7075	-0.7095
DGDZVP	-0.4140	-0.4400	-0.4391	-0.6505	-0.6763	-0.6756
DGTZVP	-0.4643	-0.4906	-0.4894	-0.7009	-0.7269	-0.7259
TZVP	-0.4829	-0.5090	-0.5080	-0.7175	-0.7433	-0.7425
Def2TZVPP	-0.4902	-0.5170	-0.5154	-0.7257	-0.7522	-0.7509
aug-cc-pVDZ	-0.4675	-0.5065	-0.5057	-0.7007	-0.7405	-0.7400
aug-cc-pVTZ	-0.4939	-0.5206	-0.5194	-0.7286	-0.7550	-0.7540
aug-cc-pVQZ	-0.4869	-0.5277	-0.5263	-0.7361	-0.7627	-0.7616
CBS	-0.4739	-0.5350	-0.5336	-0.7420	-0.7708	-0.7696
		TPSS			revTPSS	
	$^1\Sigma_g^-$	$^3\Sigma_g^-$	$^3\Pi_u$	$^1\Sigma_g^-$	$^3\Sigma_g^-$	$^3\Pi_u$
SDecp	-0.9238	-0.9371	-0.9423	-0.9188	-0.9315	-0.9373
D95	-0.7499	-0.7724	-0.7755	-0.5524	-0.5740	-0.5769
DGDZVP	-0.7088	-0.7343	-0.7341	-0.5147	-0.5329	-0.5325
DGTZVP	-0.7602	-0.7860	-0.7855	-0.5581	-0.5831	-0.5824
TZVP	-0.7175	-0.8105	-0.8104	-0.5868	-0.6115	-0.6112
Def2TZVPP	-0.7906	-0.8169	-0.8161	-0.5916	-0.6171	-0.6161
aug-cc-pVDZ	-0.7826	-0.8090	-0.8090	-0.5851	-0.6106	-0.6105
aug-cc-pVTZ	-0.7962	-0.8225	-0.8220	-0.5984	-0.6238	-0.6232
aug-cc-pVQZ	-0.8019	-0.8284	-0.8278	-0.6035	-0.6291	-0.6283
CBS	-0.8074	-0.8344	-0.8335	-0.6083	-0.6343	-0.6333

[a] In order to simplify the numeric values is required to add -484 a.u. except por the SDecp computation where is required to add -3 a.u.

TABLE III. Al_2 total energy (in a.u.) for the singlet $^1\Sigma_g^-$ and triplet $^3\Sigma_g^-$, $^3\Pi_u$ spin states obtained with aug-cc-pVxZ (x=D,T,Q.) basis sets and the complete basis set extrapolation (CBS) using perturbative MP4 and CCSD(T) methods[a], and energy difference $\Delta = {}^3\Pi_u - {}^3\Sigma_g^-$ (in eV/atom).

		TZVP	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	CBS
MP4	$^1\Sigma_g^-$	-0.8555	-0.8729	-0.8973	-0.9033	-0.9077
	$^3\Sigma_g^-$	-0.8779	-0.8853	-0.9093	-0.9154	-0.9200
	$^3\Pi_u$	-0.8794	-0.8877	-0.9111	-0.9167	-0.9207
	Δ	-0.020	-0.068	-0.048	-0.035	-0.020
CCSD(T)	$^1\Sigma_g^-$	-0.8603	-0.8782	-0.9025	-0.9086	-0.9132
	$^3\Sigma_g^-$	-0.8797	-0.8874	-0.9115	-0.9178	-0.9227
	$^3\Pi_u$	-0.8821	-0.8903	-0.9137	-0.9196	-0.9240
	Δ	-0.032	-0.081	-0.061	-0.048	-0.037

[a] In order to simplify the numeric values is required to add -483 a.u.

TABLE IV. Al_2 difference in the total electronic energy between the $^3\Pi_u$ and the $^3\Sigma_g^-$ electronic states ($^3\Pi_u - {}^3\Sigma_g^-$ in eV/atom) at differents levels of theory. A positive value indicates that the $^3\Sigma_g^-$ state is the more stable structure.

	PBE	PW91	TPSS	revTPSS
SDecp	-0.031	-0.034	-0.071	-0.079
D95	-0.027	-0.027	-0.042	-0.039
DGDZVP	0.012	0.010	0.003	0.005
DGTZVP	0.016	0.014	0.007	0.010
TZVP	0.014	0.011	0.002	0.005
Def2TZVPP	0.022	0.018	0.011	0.014
aug-cc-pVDZ	0.011	0.007	0.000	0.001
aug-cc-pVTZ	0.016	0.014	0.007	0.008
aug-cc-pVQZ	0.019	0.015	0.008	0.011
CBS[a]	0.019	0.016	0.012	0.014

[a] The CBS extrapolation is computed for the aug-cc-pVxZ basis set (x=D,T,Q).

TABLE V. Al_2 bond length BL (in Å) and vibrational frequency ν (in cm^{-1}) at different levels of theory. [a]

		PBE		PW91		TPSS		revTPSS	
		BL	ν	BL	ν	BL	ν	BL	ν
$^3\Sigma_g^-$	SDD	2.57	312.6	2.57	310.9	2.59	294.5	2.61	282.4
	D95	2.57	298.3	2.57	298.5	2.57	295.9	2.57	295.0
	DGDZVP	2.50	338.9	2.50	337.5	2.48	347.0	2.48	346.8
	DGTZVP	2.49	340.1	2.49	338.8	2.48	347.5	2.48	347.7
	TZVP	2.50	342.8	2.49	341.3	2.49	349.8	2.49	349.0
	Def2TZVPP	2.49	344.0	2.49	342.9	2.48	349.9	2.48	349.6
	AUG-cc-pVDZ	2.51	340.4	2.50	338.7	2.50	346.2	2.50	345.4
	AUG-cc-pVTZ	2.49	343.0	2.49	341.9	2.48	348.9	2.49	348.2
	AUG-cc-pVQZ	2.49	342.1	2.49	341.1	2.48	349.0	2.48	348.5
$^3\Pi_u$	SDD	2.86	239.4	2.86	239.3	2.90	218.8	2.92	210.3
	D95	2.88	218.4	2.88	218.9	2.87	221.9	2.87	221.5
	DGDZVP	2.77	255.6	2.77	255.6	2.75	262.6	2.75	263.5
	DGTZVP	2.77	254.1	2.77	254.4	2.75	259.8	2.75	260.9
	TZVP	2.76	258.5	2.76	258.9	2.75	262.5	2.75	262.9
	Def2TZVPP	2.76	260.3	2.75	260.8	2.74	265.3	2.74	265.8
	AUG-cc-pVDZ	2.77	258.4	2.77	258.5	2.75	262.9	2.75	263.4
	AUG-cc-pVTZ	2.76	259.4	2.75	259.8	2.74	263.9	2.74	264.8
	AUG-cc-pVQZ	2.76	258.7	2.75	259.0	2.74	264.2	2.74	264.9

[a] Experimental data[1]: $^3\Sigma_g^-$ d=2.4665 ± 0.0024 Å and ν= 350.01 cm^{-1}, $^3\Pi_u$ d=2.7011 ± 0.0015 Å, ν=285.8 cm^{-1}

TABLE VI. Al_2 bond length BL (in Å) and vibrational frequency ν (in cm^{-1}) at MP4 and CCSD(T) levels of theory [a]

		MP4		CCSD(T)	
		BL	ν	BL	ν
$^3\Sigma_g^-$	TZVP	2.487	355.0	2.493	348.6
	aug-cc-pVDZ	2.524	343.0	2.538	330.5
	aug-cc-pVTZ	2.485	357.3	2.497	345.1
	aug-cc-pVQZ	2.473	361.7	2.485	348.2
$^3\Pi_u$	TZVP	2.711	292.8	2.714	289.8
	aug-cc-pVDZ	2.763	274.7	2.767	271.8
	aug-cc-pVTZ	2.725	284.4	2.728	282.1
	aug-cc-pVQZ	2.714	286.6	2.717	284.2

[a] Experimental data[1]: $^3\Sigma_g^-$ d=2.4665 ± 0.0024 Å and ν= 350.01 cm^{-1}, $^3\Pi_u$ d=2.7011 ± 0.0015 Å, ν=285.8 cm^{-1}

AL_3 RESULTS

TABLE VII. Al_3 total electronic energy (in a.u.) for the doublet $^2A_1'$ spin state in D_{3h} symmetry at different levels of theory[a].

	PBE	PW91	TPSS	revTPSS
SDecp	-0.9520	-0.9597	-0.9495	-0.9403
D95	-0.7529	-1.1059	-1.2031	-0.9069
DGDZVP	-0.7177	-1.0721	-1.1606	-0.8604
DGTZVP	-0.7939	-1.1484	-1.2379	-0.9356
TZVP	-0.8225	-1.1741	-1.2755	-0.9787
Def2TZVPP	-0.8351	-1.1882	-1.2856	-0.9876
aug-cc-pVDZ	-0.8168	-1.1678	-1.2713	-0.9755
aug-cc-pVTZ	-0.8401	-1.1919	-1.2935	-0.9971
aug-cc-pVQZ	-0.8505	-1.2032	-1.3022	-1.0049
CBS	-0.8608	-1.2147	-1.3105	-1.0121

[a] In order to simplify the numeric values is required to add -726 a.u. except por the SDecp computation where is required to add -5 a.u.

TABLE VIII. Al_3 difference in the total electronic energy between the doublet $^2A_1'$ (D) and the quadruplet $^4A_2$ (Q) spin states (D−Q in eV/atom) at different levels of theory. A negative value indicates that the doublet spin state is the more stable structure.

	PBE	PW91	TPSS	revTPSS
SDecp	-0.012	-0.011	0.021	0.028
D95	-0.001	-0.001	0.001	-0.008
DGDZVP	-0.066	-0.065	-0.065	-0.072
DGTZVP	-0.069	-0.069	-0.065	-0.073
TZVP	-0.073	-0.073	-0.070	-0.076
Def2TZVPP	-0.072	-0.072	-0.067	-0.073
aug-cc-pVDZ	-0.054	-0.054	-0.050	-0.057
aug-cc-pVTZ	-0.067	-0.067	-0.062	-0.067
aug-cc-pVQZ	-0.068	-0.069	-0.063	-0.069
CBS[a]	-0.068	-0.069	-0.064	-0.070

[a] The CBS extrapolation is computed for the aug-cc-pVxZ basis set (x=D,T,Q).

TABLE IX. Al_3 bond length (BL in Å), frequencies (ν in cm^{-1}) and vibrational symmetries for the doublet spin state at D_{3h} symmetry for different functional and basis sets.[a]

	PBE			PW91		
	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'
SDecp	2.6109	202.3425	322.1159	2.6112	201.8167	320.2566
D95	2.6117	196.7139	292.4224	2.6093	196.2349	292.6797
DGDZVP	2.5300	235.2321	359.8775	2.5295	234.2888	358.2569
DGTZVP	2.5242	237.3618	360.3572	2.5229	236.7903	359.2189
TZVP	2.5243	239.4787	363.4228	2.5230	238.7745	361.9902
Def2TZVPP	2.5195	242.1622	362.3698	2.5177	241.5804	361.2367
aug-cc-pVDZ	2.5436	234.1704	353.9313	2.5428	233.3984	352.2805
aug-cc-pVTZ	2.5248	240.8338	360.6088	2.5231	240.3785	359.5554
aug-cc-pVQZ	2.5200	241.0874	360.2354	2.5177	240.7388	359.3859
	TPSS			revTPSS		
	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'
SDecp	2.6271	187.9201	309.2057	2.6376	183.2245	303.7382
D95	2.6096	190.9166	290.8647	2.6072	191.2918	292.3834
DGDZVP	2.5155	236.295	368.8238	2.5140	237.6421	369.8634
DGTZVP	2.5126	237.4138	367.7554	2.5112	238.1355	368.5182
TZVP	2.5157	238.6849	369.1275	2.5140	239.175	369.7850
Def2TZVPP	2.5110	242.2057	368.1033	2.5091	242.3719	368.8246
aug-cc-pVDZ	2.5354	232.9805	358.9799	2.5332	234.3683	360.5695
aug-cc-pVTZ	2.5174	240.5467	365.3656	2.5162	240.3634	365.5279
aug-cc-pVQZ	2.5107	241.9420	366.7693	2.5099	241.7301	366.8882

[a] Experimental frequencies: stretching a_1' 357 ± 10 cm^{-1}, bending mode e' 240 ± 10 cm^{-1},[2]

TABLE X. Al_3 total energy (in a.u.) for the doublet $^2A_1'$ spin state obtained with aug-cc-pVxZ (x=D,T,Q.) basis sets and the complete basis set extrapolation (CBS) using perturbative CCSD(T) and MP4 methods[a].

	CCSD(T)	MP4
TZVP	-0.8770	-0.8757
aug-cc-pVDZ	-0.8825	-0.8827
aug-cc-pVTZ	-0.9274	-0.9263
aug-cc-pVQZ	-0.9392	-0.9382
CBS	-0.9483	-0.9477

[a] In order to simplify the numeric values is required to add -725 a.u.

TABLE XI. Al_3 bond length (BL in Å), frequencies (ν in cm^{-1}) and vibrational symmetries for the doublet spin state in D_{3h} symmetry at CCSD(T) and MP4 theory level and different basis sets.[a]

	CCSD(T)			MP4		
	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'	$BL_{1,2,3}$	ν_1 e′	ν_2 a_1'
TZVP	2.5396	240.2741	366.4829	2.6037	182.0016	335.6776
aug-cc-pVDZ	2.5165	257.4809	393.2657	2.6721	240.4952	326.8684
aug-cc-pVTZ	2.5493	232.1042	353.8035	2.6408	195.4111	313.5326
aug-cc-pVQZ	2.5315	238.0173	359.8348	2.6205	191.0311	303.2244

[a] Experimental frequencies: stretching a_1' 357 ± 10 cm^{-1}, bending mode e' 240 ± 10 cm^{-1},[2]

TABLE XII. Al_3^+ vertical ionization energy (in eV) from the neutral doublet spin ground state at D_{3h} symmetry to the $^1A_2''$ and to the $^3A_1'$ states, at different levels of theory. The experimental value has been reported to be 6.46 ± 0.04 eV[3].

	PBE		PW91		TPSS		revTPSS	
	$^1A_1'$	$^3A_2''$	$^1A_1'$	$^3A_2''$	$^1A_1'$	$^3A_2''$	$^1A_1'$	$^3A_2''$
SDecp	7.57	6.53	7.59	6.56	6.81	6.44	6.77	6.41
D95	6.89	6.65	6.91	6.68	6.91	6.71	6.92	6.75
DGDZVP	6.78	6.58	6.82	6.62	6.82	6.63	6.83	6.66
DGTZVP	6.78	6.58	6.82	6.62	6.81	6.63	6.83	6.66
TZVP	6.81	6.60	6.84	6.62	6.82	6.62	6.83	6.65
Def2TZVPP	6.77	6.55	6.81	6.58	6.79	6.57	6.80	6.60
aug-cc-pVDZ	6.78	6.52	6.81	6.55	6.79	6.54	6.80	6.57
aug-cc-pVTZ	6.77	6.54	6.81	6.57	6.78	6.56	6.79	6.58
aug-cc-pVQZ	6.76	6.54	6.80	6.57	6.79	6.57	6.80	6.59

AL_4 RESULTS

TABLE XIII. Al_4 total electronic energy (in a.u.) for the singlet (S) and the triplet (T) spin states at different levels of theory[a].

	PBE		PW91		TPSS		revTPSS	
	S	T	S	T	S	T	S	T
SDecp	-0.9644	-0.9742	-0.9747	-0.9848	-0.9582	-0.9700	-0.9450	-0.9565
D95	-1.0359	-1.0466	-1.5067	-1.5174	-1.6356	-1.6413	-1.2403	-1.2462
DGDZVP	-0.9827	-0.9909	-1.4551	-1.4633	-1.5728	-1.5597	-1.1726	-1.1594
DGTZVP	-1.0841	-1.0923	-1.5566	-1.5648	-1.6757	-1.6622	-1.2726	-1.2591
TZVP	-1.1220	-1.1303	-1.5907	-1.5990	-1.7253	-1.7335	-1.3298	-1.3379
Def2TZVPP	-1.1385	-1.1475	-1.6090	-1.6181	-1.7387	-1.7476	-1.3416	-1.3504
aug-cc-pVDZ	-1.1147	-1.1238	-1.5826	-1.5917	-1.7206	-1.7294	-1.3262	-1.3121
aug-cc-pVTZ	-1.1454	-1.1546	-1.6143	-1.6234	-1.7493	-1.7585	-1.3542	-1.3633
aug-cc-pVQZ	-1.1587	-1.1679	-1.6288	-1.6381	-1.7606	-1.7697	-1.3643	-1.3733
CBS	-1.1718	-1.1811	-1.6436	-1.6528	-1.7714	-1.7803	-1.3737	-1.3791

[a] In order to simplify the numeric values is required to add -968 a.u. except por the SDecp computation where is required to add -7 a.u.

TABLE XIV. Al_4 difference in the total electronic energy between the singlet (S) and the triplet (T) spin states (T−S in eV/atom) at different levels of theory. A negative value indicates that the triplet spin state is the more stable structure.

	PBE	PW91	TPSS	revTPSS
SDecp	-0.067	-0.068	-0.080	-0.078
D95	-0.073	-0.073	-0.039	-0.040
DGDZVP	-0.056	-0.056	0.090	0.090
DGTZVP	-0.056	-0.055	0.092	0.092
TZVP	-0.057	-0.057	-0.056	-0.055
Def2TZVPP	-0.061	-0.061	-0.061	-0.060
aug-cc-pVDZ	-0.062	-0.062	-0.060	0.096
aug-cc-pVTZ	-0.063	-0.062	-0.062	-0.062
aug-cc-pVQZ	-0.063	-0.063	-0.062	-0.061
CBS	-0.063	-0.063	-0.061	-0.037

TABLE XV. Al_4 BL and angle (θ) at different levels of theory.

	PBE		PW91		TPSS		revTPSS	
	BL	θ	BL	θ	BL	θ	BL	θ
SDecp	2.723	81.093	2.724	81.499	2.723	78.864	2.728	78.318
D95	2.755	83.321	2.754	83.730	2.666	71.561	2.663	71.376
DGDZVP	2.572	68.227	2.572	68.419	2.6165	63.9555	2.6165	63.9555
DGTZVP	2.568	68.127	2.567	68.215	2.619	63.8675	2.619	63.8675
TZVP	2.567	67.898	2.566	68.140	2.559	67.606	2.556	67.531
Def2TZVPP	2.563	68.178	2.561	68.334	2.554	67.805	2.552	67.733
aug-cc-pVDZ	2.582	68.487	2.581	68.632	2.573	68.114	2.6504	64.4807
aug-cc-pVTZ	2.567	68.164	2.566	68.333	2.559	67.891	2.559	67.832
aug-cc-pVQZ	2.564	68.267	2.562	68.421	2.554	67.845	2.553	67.772

AL_6 RESULTS

TABLE XVI. Al_6 total electronic energy (in a.u.) for the singlet (S) and the triplet (T) spin states at different levels of theory[a].

	PBE		PW91		TPSS		revTPSS	
	S	T	S	T	S	T	S	T
SDecp	-0.0329	-0.0357	-0.0473	-0.0505	-0.0202	-0.0230	-0.0022	-0.0043
D95	-0.6457	-0.6481	-1.3507	-1.3535	-1.5437	-1.5456	-0.9550	-0.9544
DGDZVP	-0.5787	-0.5772	-1.2859	-1.2841	-1.4641	-1.4629	-0.8671	-0.8658
DGTZVP	-0.7310	-0.7296	-1.4384	-1.4366	-1.6186	-1.6176	-1.0173	-1.0160
TZVP	-0.7880	-0.7864	-1.4898	-1.4880	-1.6931	-1.6920	-1.1029	-1.1016
Def2TZVPP	-0.8170	-0.8172	-1.5213	-1.5211	-1.7174	-1.7179	-1.1248	-1.1250
aug-cc-pVDZ	-0.7794	-0.7788	-1.4796	-1.4786	-1.6885	-1.6882	-1.1000	-1.0994
aug-cc-pVTZ	-0.8267	-0.8269	-1.5285	-1.5283	-1.7328	-1.7333	-1.1433	-1.1435
aug-cc-pVQZ	-0.8463	-0.8465	-1.5500	-1.5499	-1.7491	-1.7496	-1.1578	-1.1580
CBS[b]	-0.8653	-0.8655	-1.5715	-1.5713	-1.7642	-1.7647	-1.1998	-1.2017

[a] In order to simplify the numeric values is required to add -1453 a.u. except for the SDecp computation where is required to add -12 a.u.
[b] The CBS extrapolation is computed for the aug-cc-pVxZ basis set (x=D,T,Q).

TABLE XVII. Al_6 difference in the total electronic energy between the singlet (S) and the triplet (T) spin states (S−T in eV/atom) at different levels of theory. A positive value indicates that the triplet spin state is the more stable structure.

	PBE	PW91	TPSS	revTPSS
SDecp	0.012	0.015	0.013	0.010
D95	0.011	0.013	0.008	-0.003
DGDZVP	-0.007	-0.008	-0.005	-0.006
DGTZVP	-0.007	-0.008	-0.005	-0.006
TZVP	-0.007	-0.009	-0.005	-0.006
Def2TZVPP	0.001	-0.001	0.002	0.001
aug-cc-pVDZ	-0.003	-0.005	-0.001	-0.003
aug-cc-pVTZ	0.001	-0.001	0.002	0.001
aug-cc-pVQZ	0.001	-0.001	0.002	0.001

TABLE XVIII. Al_6 average nearest-neighbor $\langle d \rangle$ (in Å) and dispersion σ (in Å) at different levels of theory.

	PBE		PW91		TPSS		revTPSS	
	$\langle d \rangle$	σ	$\langle d \rangle$	σ	$\langle d \rangle$	σ	$\langle d \rangle$	σ
SDecp	3.02	0.51	3.03	0.51	3.03	0.51	3.04	0.51
D95	3.06	0.51	3.06	0.51	3.06	0.51	3.10	0.57
DGDZVP	2.77	0.20	2.78	0.20	2.76	0.20	2.75	0.19
DGTZVP	2.77	0.20	2.77	0.20	2.76	0.20	2.76	0.20
TZVP	2.76	0.20	2.76	0.20	2.75	0.19	2.75	0.19
Def2TZVPP	2.73	0.10	2.76	0.20	2.72	0.10	2.72	0.10
aug-cc-pVDZ	2.79	0.20	2.80	0.21	2.78	0.20	2.78	0.20
aug-cc-pVTZ	2.74	0.10	2.77	0.20	2.76	0.20	2.73	0.10
aug-cc-pVQZ	2.73	0.10	2.77	0.20	2.75	0.19	2.72	0.10

AL_8 RESULTS

TABLE XIX. Al_8 total electronic energy (in a.u.) for the singlet (S) and the triplet (T) spin states at different levels of theory[a].

	PBE		PW91		TPSS		revTPSS	
	S	T	S	T	S	T	S	T
SDecp	-0.1138	-0.1030	-0.1330	-0.1216	-0.0950	-0.0860	-0.0717	-0.0631
D95	-0.2706	-0.2598	-1.2100	-1.1989	-1.4713	-1.4606	-0.6855	-0.6748
DGDZVP	-0.1754	-0.1658	-1.1177	-1.1071	-1.3502	-1.3535	-0.5558	-0.5595
DGTZVP	-0.3789	-0.3695	-1.3216	-1.3134	-1.5565	-1.5601	-0.7562	-0.7601
TZVP	-0.4462	-0.4453	-1.3903	-1.3796	-1.6547	-1.6585	-0.8695	-0.8734
Def2TZVPP	-0.4911	-0.4842	-1.4297	-1.4212	-1.6861	-1.6904	-0.8976	-0.9021
aug-cc-pVDZ	-0.4398	-0.4299	-1.3730	-1.3621	-1.6556	-1.6481	-0.8637	-0.8651
aug-cc-pVTZ	-0.5043	-0.4972	-1.4396	-1.4302	-1.7063	-1.7098	-0.9217	-0.9253
aug-cc-pVQZ	-0.5298	-0.5219	-1.4678	-1.4588	-1.7279	-1.7320	-0.9410	-0.9452
CBS[b]	-0.5543	-0.5448	-1.4957	-1.4868	-1.7491	-1.7525	-0.9581	-0.9628

[a] In order to simplify the numeric values is required to add -1938 a.u. except for the SDecp computation where is required to add -16 a.u.
[b] The CBS extrapolation is computed for the aug-cc-pVXZ basis set (x=D,T,Q).

TABLE XX. Al_8 difference in the total electronic energy between the singlet (S) and the triplet (T) spin states (S−T in eV/atom) at different levels of theory. A positive value indicates that the triplet spin state is the more stable structure.

	PBE	PW91	TPSS	revTPSS
SDecp	-0.037	-0.039	-0.031	-0.029
D95	-0.037	-0.038	-0.036	-0.037
DGDZVP	-0.033	-0.036	0.011	0.013
DGTZVP	-0.032	-0.028	0.012	0.013
TZVP	-0.003	-0.036	0.013	0.013
Def2TZVPP	-0.024	-0.029	0.015	0.015
aug-cc-pVDZ	-0.034	-0.037	-0.026	0.005
aug-cc-pVTZ	-0.024	-0.032	0.012	0.012
aug-cc-pVQZ	-0.027	-0.031	0.014	0.014

TABLE XXI. Al_8 average nearest-neighbor $\langle d \rangle$ (in Å) and dispersion σ (in Å) at different levels of theory.

	PBE		PW91		TPSS		revTPSS	
	$\langle d \rangle$	σ	$\langle d \rangle$	σ	$\langle d \rangle$	σ	$\langle d \rangle$	σ
SDecp	3.00	0.49	3.01	0.48	3.01	0.49	3.01	0.50
D95	2.92	0.35	2.92	0.35	2.84	0.25	2.91	0.35
DGDZVP	2.90	0.55	2.90	0.55	2.69	0.09	2.69	0.09
DGTZVP	2.90	0.55	2.90	0.55	2.69	0.09	2.69	0.09
TZVP	2.78	0.25	2.89	0.54	2.69	0.08	2.68	0.08
Def2TZVPP	2.69	0.16	2.89	0.54	2.81	0.39	2.68	0.08
aug-cc-pVDZ	2.92	0.55	2.92	0.55	2.90	0.55	2.71	0.09
aug-cc-pVTZ	2.90	0.55	2.90	0.55	2.69	0.08	2.69	0.08
aug-cc-pVQZ	2.89	0.54	2.89	0.54	2.69	0.08	2.68	0.08

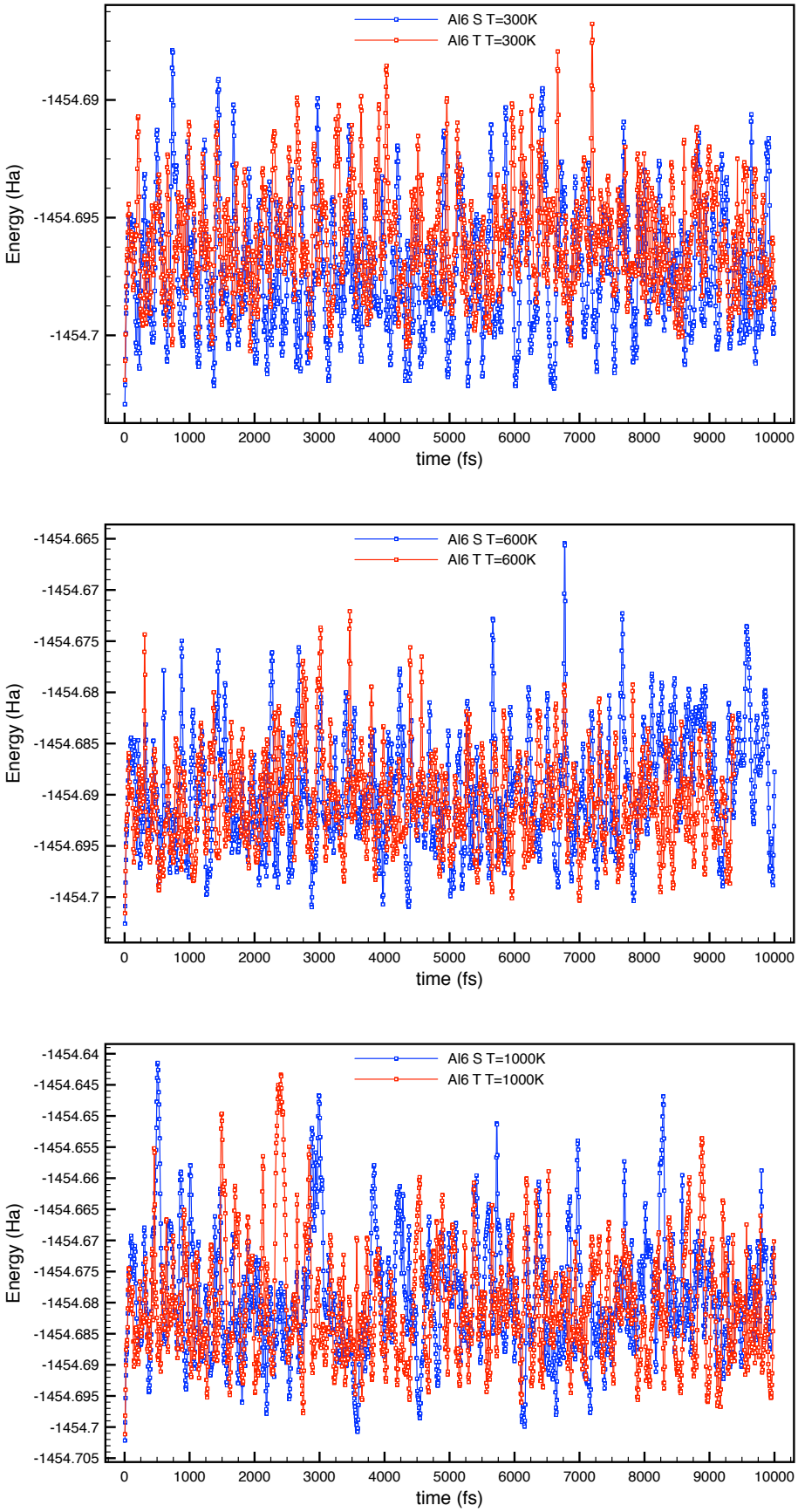

FIG. 1. Al_6 Born-Oppenheimer molecular dynamics trajectories computed at TPSS/aug-cc-DVZP level theory at T=300, 600 and 1000K.

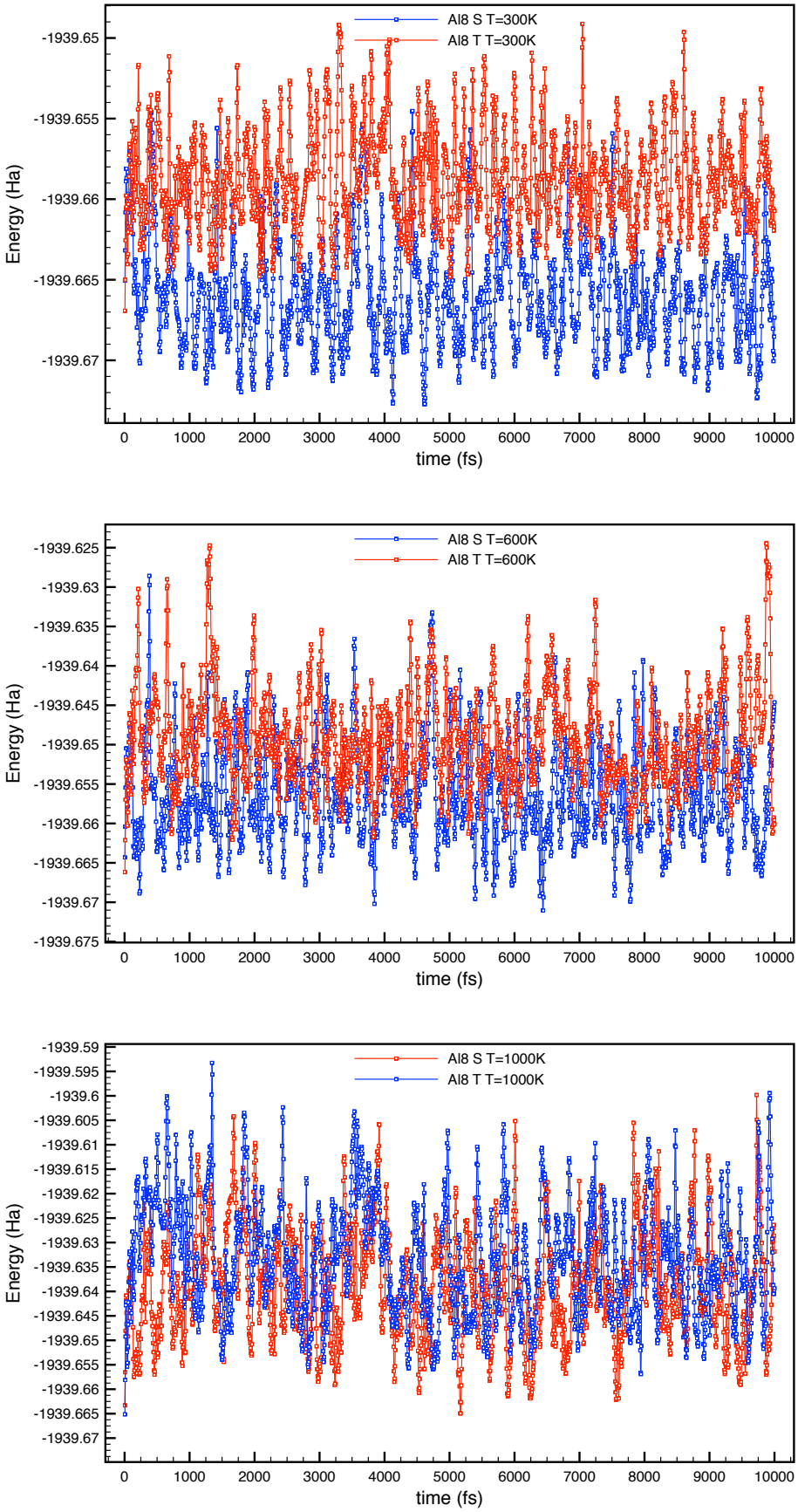

FIG. 2. Al_8 Born-Oppenheimer molecular dynamics trajectories computed at TPSS/aug-cc-DVZP level theory at T=300, 600 and 1000K.

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