SUPPLEMENTARY MATERIAL ACCOMPANIING THE MANUSCRIPT ENTITLED

"Size, Adsorption Site and Spin Effects in the Reaction of Al Clusters with Water: Al_{17} and Al_{28} as Examples" by S. Álvarez-Barcia and J.R. Flores*, Departamento de Química Física, Facultad de Química, Universidade de Vigo, E-36310-Vigo (Pontevedra), Spain

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SM_T1: Absolutes energies (in a.u.), ZPE energies (scaled by 0.93) in a.u. and energy differences (in kcal/mol) relative to $Al_{17}(^2B_{2u})$ + *n* H_2O, with *n*=1-2. We have employed G03[1] and G09[2] computer programs.

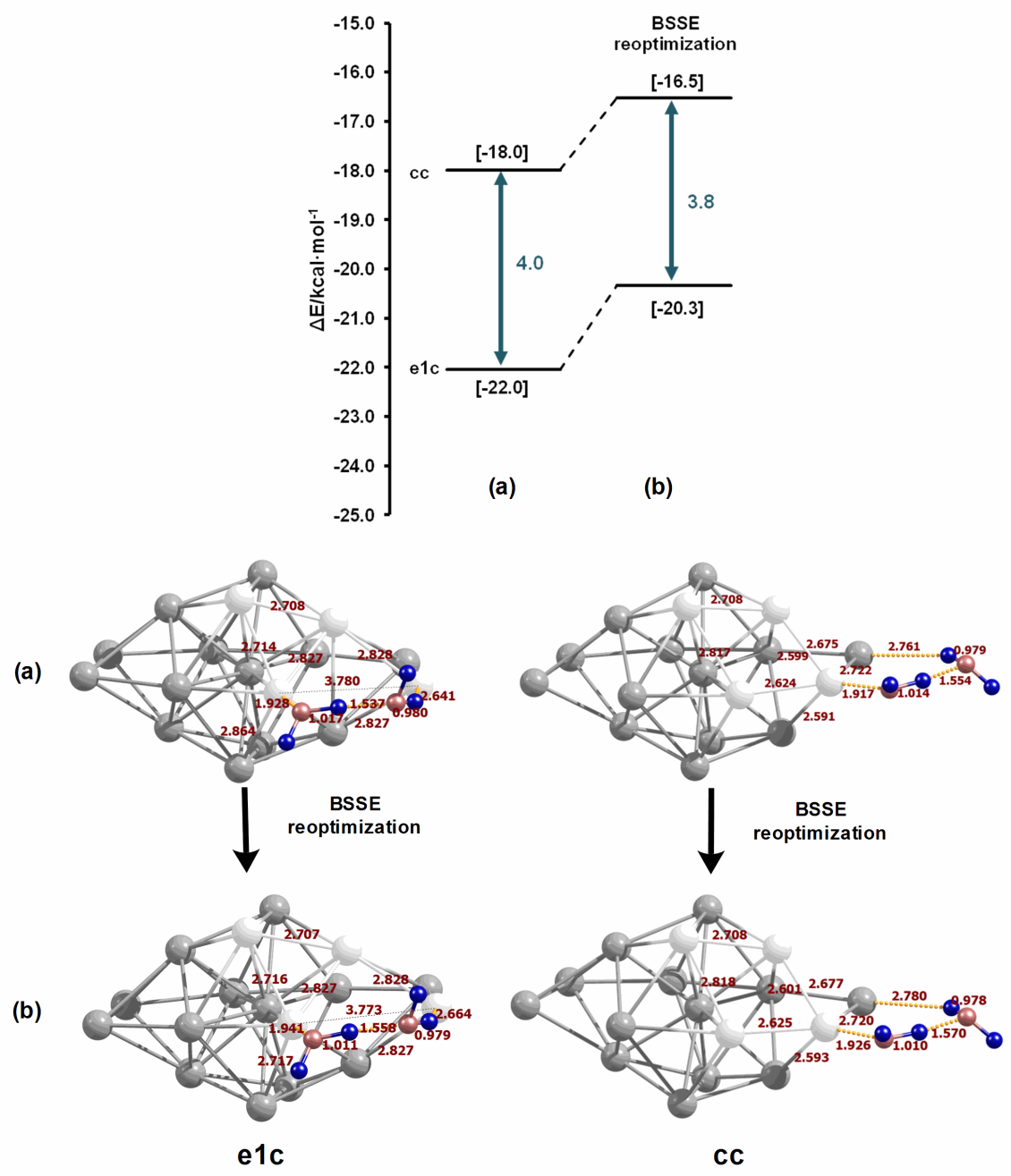
	E_{CEP} [(a)]	E_{6311} [(b)]	ZPE_{CEP} [(c)]	E_0^{6311}	ΔE_{CEP}	ΔE_{6311}	ΔZPE_{CEP}	ΔE^0_{6311} [(d)]
Al_{17}+H_2O	**-50.985969**	**-4197.894393**	**0.041061**	**-4197.853331**	**0.0**	**0.0**	**0.0**	**0.0**
M1_p	-51.000221	-4197.905795	0.043717	-4197.862077	-8.9	-7.2	1.7	-5.5
M1_c	-51.000236	-4197.905950	0.044162	-4197.861788	-9.0	-7.3	1.9	-5.3
M1_e1	-51.009322	-4197.914218	0.044608	-4197.869610	-14.7	-12.4	2.2	-10.2
M1_e2	-51.002860	-4197.908181	0.043656	-4197.864525	-10.6	-8.7	1.6	-7.0
Al_{17}+2·H_2O	**-68.100355**	**-4274.308545**	**0.061685**	**-4274.246860**	**0.0**	**0.0**	**0.0**	**0.0**
M1_pc	-68.140220	-4274.342839	0.068421	-4274.274418	-25.0	-21.5	4.2	-17.3
M1_pe1	-68.127998	-4274.330849	0.068008	-4274.262841	-17.3	-14.0	4.0	-10.0
M1_pe2	-68.136866	-4274.339719	0.067802	-4274.271917	-22.9	-19.6	3.8	-15.7
M1_cc	-68.144642	-4274.347044	0.068673	-4274.278371	-27.8	-24.2	4.4	-19.8
M1_ce1	-68.144360	-4274.347038	0.068907	-4274.278131	-27.6	-24.2	4.5	-19.6
M1_ce2	-68.136760	-4274.338970	0.068795	-4274.270175	-22.8	-19.1	4.5	-14.6
M1_e1c	-68.151390	-4274.353506	0.068807	-4274.284699	-32.0	-28.2	4.5	-23.7
M1_e1e2	-68.146981	-4274.349432	0.068598	-4274.280835	-24.6	-25.7	4.3	-21.3
M1_e2e1	-68.142870	-4274.345472	0.068240	-4274.277232	-26.7	-23.2	4.1	-19.1
M1_e2e2	-68.141933	-4274.344374	0.068260	-4274.276114	-26.1	-22.5	4.1	-18.4
TS_pc	-68.115279	-4274.315946	0.062503	-4274.253443	-9.4	-4.6	0.5	-4.1
TS_pe1	-68.110848	-4274.311402	0.062425	-4274.248976	-6.6	-1.8	0.5	-1.3
TS_pe2	-68.104448	-4274.304600	0.061821	-4274.242779	-2.6	2.5	0.1	2.6
TS_cc	-68.134936	-4274.335501	0.063638	-4274.271863	-21.7	-16.9	1.2	-15.7
TS_ce1	-68.131621	-4274.332584	0.063040	-4274.269544	-19.6	-15.1	0.9	-14.2
TS_ce2	-68.105839	-4274.306256	0.062357	-4274.243899	-3.4	1.4	0.4	1.9
TS_e1c	-68.139380	-4274.339654	0.063055	-4274.276599	-24.5	-19.5	0.9	-18.7
TS_e1e2	-68.115864	-4274.315760	0.062124	-4274.253636	-9.7	-4.5	0.3	-4.3
TS_e2e1	-68.108605	-4274.309063	0.061413	-4274.247650	-5.2	-0.3	-0.2	-0.5
TS_e2e2	-68.108819	-4274.308686	0.061363	-4274.247323	-5.3	-0.1	-0.2	-0.3
M2_cc	-68.191698	-4274.392681	0.062658	-4274.330024	-57.3	-52.8	0.6	-52.2
M2_ce1	-68.185458	-4274.386361	0.062700	-4274.323661	-53.4	-48.8	0.6	-48.2
M2_e1c	-68.222893	-4274.422551	0.065137	-4274.357414	-76.9	-71.5	2.2	-69.4

(a) E_{CEP}: Energies at BHHLYP/CEP-31G*// BHHLYP/CEP-31G* level.
(b) E_{6311}: Energies at BHHLYP/6-311++G**// BHHLYP/CEP-31G* level.
(c) ZPE energies have been computed at the BHHLYP/CEP-31G* level and scaled by a factor of 0.93.
(d) $\Delta E^0_{6311} = \Delta E_{6311} + \Delta ZPE_{CEP}$.

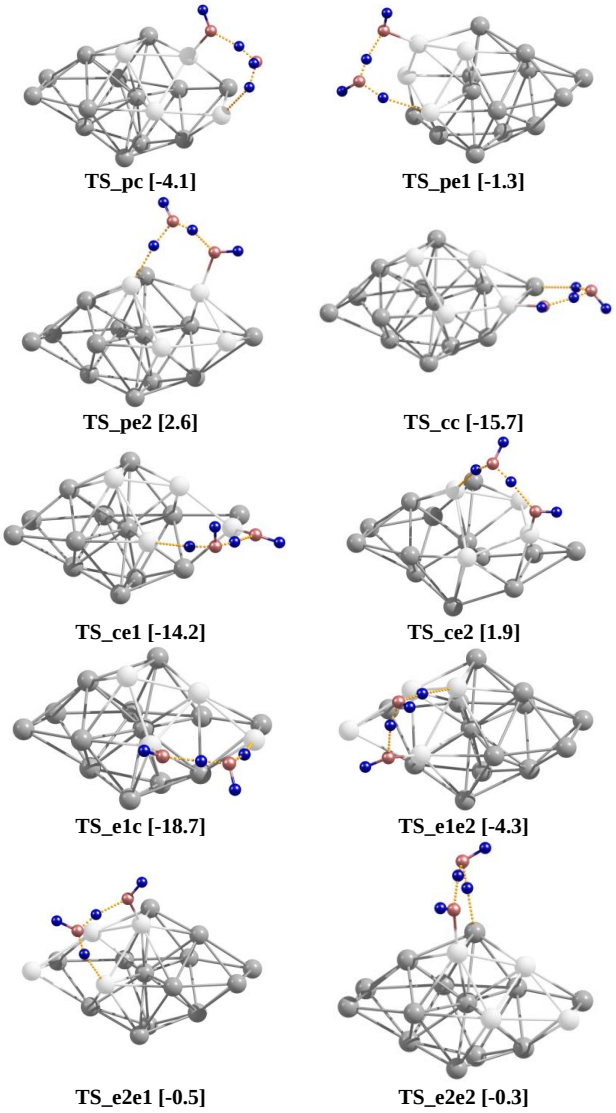
[1]Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[2]Gaussian 09, Revision B.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

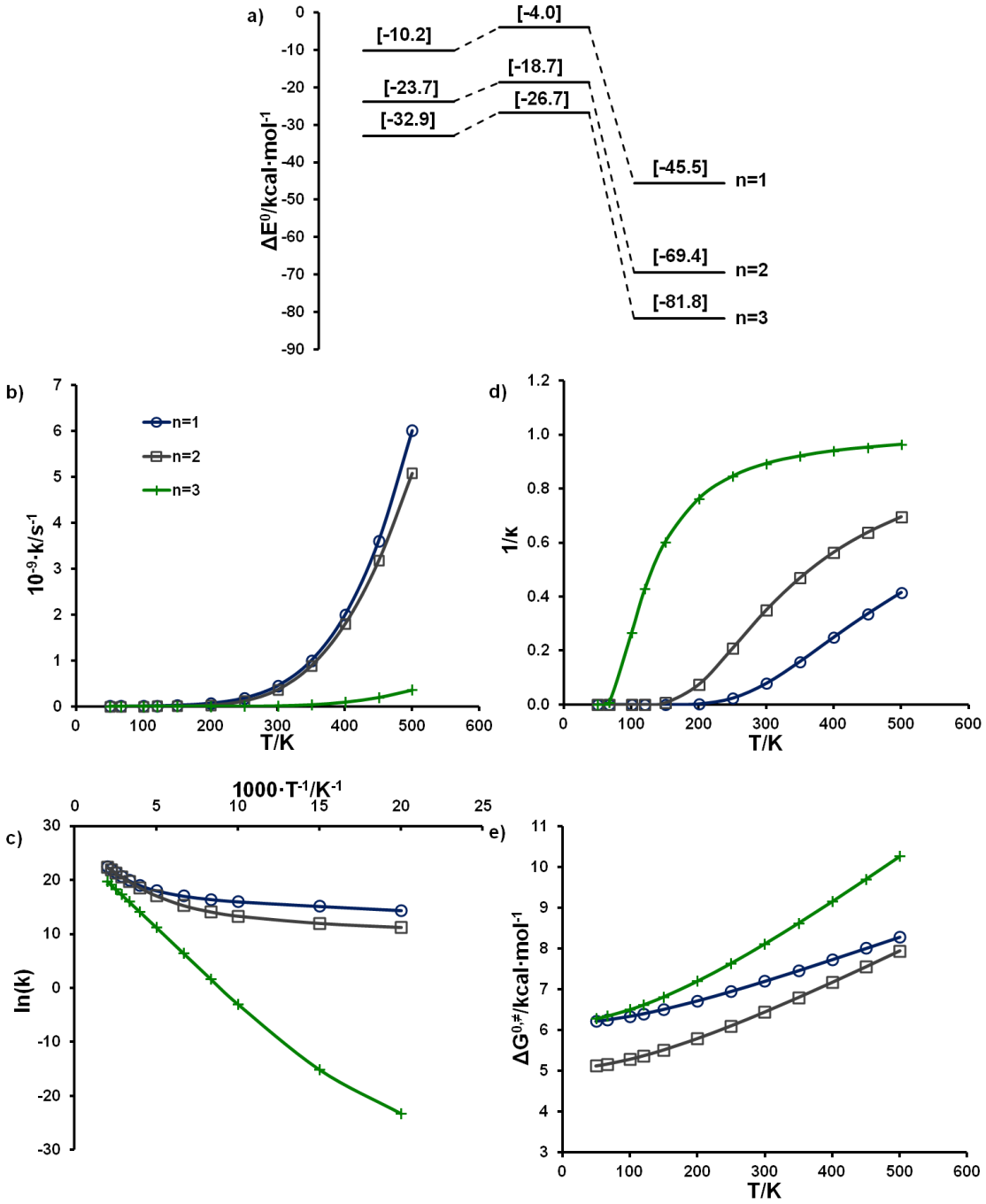
SM_F1: Effect of the BSSE (basis set superposition error) on the electronic energies through the geometry optimization for the $Al_{17}{\cdot}(H_2O)_2$ system. In (a), relatives energies in kcal/mol (for adducts e1c and cc) with respect to $Al_{17}(^2B_{2u})$ + $(H_2O)_2$ have been computed without taking into account BSSE. We have employed the BHHLYP/6-311++G**//BHHLYP/CEP-31G* level. In (b), relative energies have been obtained taking into account BSSE in the geometry optimization and energy (same level). The most representative geometrical parameters are displayed in both cases.



SM_F2: Schematic representation of the most relevant transition states of the $Al_{17}\cdot(H_2O)_2$ system (obtained by the BHHLYP/CEP-31G* method). The relative energies, with respect to Al_{17} + 2 H_2O computed at the BHHLYP/6-311++G**//BHHLYP/CEP-31G*+ZPE level (the ZPE is scaled by 0.93) are given in brackets.



SM_F3: a) Energy profile for the initial step of the reaction of the $Al_{17}\cdot(H_2O)_{n=1-3}$ (e1c) systems. Relative energies (ΔE^0, in kcal/mol) (including ZPE scaled by a factor of 0.93) in brackets have been computed with respect to $Al_{17}(^2B_{2u})$ + $2\cdot H_2O$. b) Representations of *k(T)* (s^{-1}) in the interval *T*=50 K to 500 K for the $Al_{17}\cdot(H_2O)_{n=1-3}$ (e1c) systems. c) Same for *Ln*(*k(T)*). c) *1/κ(T)* values. e) $\Delta G^{o,\ddagger}(T)$ values (kcal/mol).



SM_T2: Equilibrium constants ($K_p(T)$) and Gibbs energies ($\Delta G^0(T)$ in kcal/mol) for the H_2O elimination processes from the $Al_{17}\cdot(H_2O)_2$ aggregate in the gas phase. We have considered the equilibrium between M1_e1c and M1_e1, i.e. between the lowest-lying minima for each hydration.

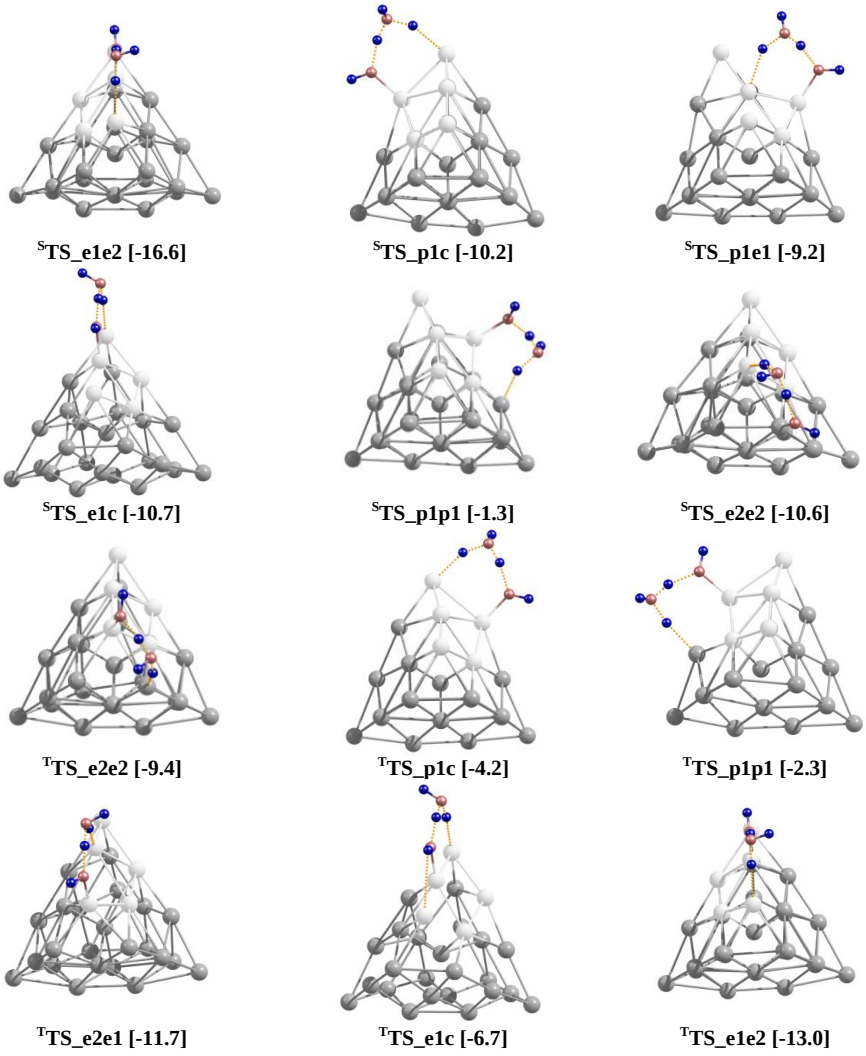
M1_e1c ↔ M1_e1 + H_2O		
T	$\Delta G^0(T)$	$K_p(T)$
50.0	12.6	1.11E-55
66.7	12.2	1.07E-40
100	11.4	1.01E-25
120	11.0	1.01E-20
150	10.3	1.01E-15
200	9.2	9.58E-11
250	8.1	8.82E-08
300	7.0	7.94E-06
350	6.0	1.89E-04
400	5.0	1.96E-03
450	4.0	1.17E-02
500	3.0	4.76E-02

SM_T3: Absolutes energies (in a.u.), ZPE energies (scaled by 0.93) in u.a. and energy differences (in kcal/mol) relative to $Al_{28}(^1A_1)$ + $n\cdot H_2O$ for the singlet state and $Al_{28}(^3A_2')$ + $n\cdot H_2O$ for the triplet state, with n=1-2.

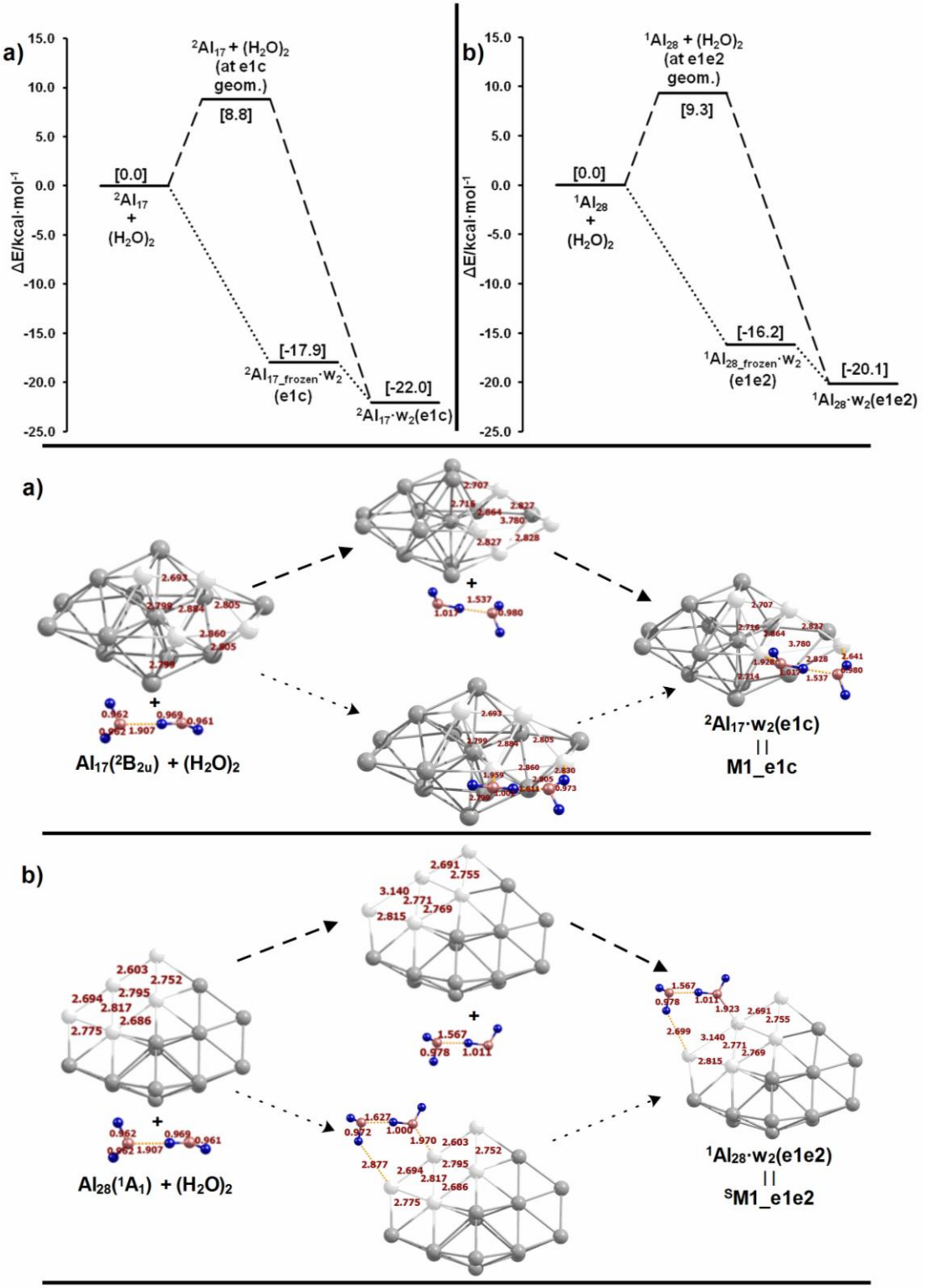
	E_{CEP} [a]	E_{6311} [b]	ZPE_{CEP} [c]	E_0^{6311}	ΔE_{CEP}	ΔE_{6311}	ΔZPE_{CEP}	ΔE^0_{6311} [d]
$^1Al_{28}+H_2O$	-73.006207	-6864.837881	0.055503	-6864.782378	**0.0**	**0.0**	**0.0**	**0.0**
^{S}M1_c	-73.020959	-6864.850278	0.058128	-6864.792150	-9.3	-7.8	1.6	-6.1
^{S}M1_p1	-73.026467	-6864.855963	0.058430	-6864.797533	-12.7	-11.3	1.8	-9.5
^{S}M1_e1	-73.028330	-6864.857217	0.058487	-6864.798730	-13.9	-12.1	1.9	-10.3
^{S}M1_p2	-73.021651	-6864.851014	0.058677	-6864.792336	-9.7	-8.2	2.0	-6.2
^{S}M1_e2	-73.024405	-6864.853823	0.058571	-6864.795251	-11.4	-10.0	1.9	-8.1
$^3Al_{28}+H_2O$	-73.005572	-6864.836062	0.055090	-6864.780971	0.0	0.0	0.0	0.0
^{T}M1_c	-73.014859	-6864.843436	0.057819	-6864.785617	-5.8	-4.6	1.7	-2.9
^{T}M1_p1	-73.024134	-6864.852479	0.058331	-6864.794148	-11.6	-10.3	2.0	-8.3
^{T}M1_e1	-73.022421	-6864.850306	0.057979	-6864.792327	-10.6	-8.9	1.8	-7.1
^{T}M1_p2	-73.019570	-6864.847752	0.058295	-6864.789457	-8.8	-7.3	2.0	-5.3
^{T}M1_e2	-73.023354	-6864.851463	0.058366	-6864.793097	-11.2	-9.7	2.1	-7.6
$^1Al_{28}+2\cdot H_2O$	-90.120593	-6941.252033	0.076127	-6941.175906	0.0	0.0	0.0	0.0
^{S}M1_e1e2	-90.167965	-6941.293935	0.083054	-6941.210881	-29.7	-26.3	4.3	-21.9
^{S}M1_p1c	-90.166884	-6941.293519	0.082963	-6941.210555	-29.0	-26.0	4.3	-21.7
^{S}M1_p1e1	-90.166627	-6941.293672	0.083210	-6941.210463	-28.9	-26.1	4.4	-21.7
^{S}M1_e1c	-90.166875	-6941.293113	0.082886	-6941.210227	-29.0	-25.8	4.2	-21.5
^{S}M1_p1p1	-90.165233	-6941.291920	0.082922	-6941.208999	-28.0	-25.0	4.3	-20.8
^{S}M1_p1p2	-90.165395	-6941.292001	0.082921	-6941.209081	-28.1	-25.1	4.3	-20.8
^{S}M1_e2e2	-90.166160	-6941.292244	0.083352	-6941.208891	-28.6	-25.2	4.5	-20.7
^{S}M1_e2e1	-90.163902	-6941.290389	0.082910	-6941.207478	-27.2	-24.1	4.3	-19.8
^{S}TS_e1e2	-90.155813	-6941.279882	0.077503	-6941.202379	-22.1	-17.5	0.9	-16.6
^{S}TS_p1c	-90.145023	-6941.269351	0.077146	-6941.192205	-15.3	-10.9	0.6	-10.2
^{S}TS_p1e1	-90.141899	-6941.267304	0.076670	-6941.190634	-13.4	-9.6	0.3	-9.2
^{S}TS_e1c	-90.146153	-6941.270203	0.077212	-6941.192990	-16.0	-11.4	0.7	-10.7
^{S}TS_p1p1	-90.129857	-6941.254287	0.076284	-6941.178002	-5.8	-1.4	0.1	-1.3
^{S}TS_e2e2	-90.146234	-6941.270131	0.077359	-6941.192771	-16.1	-11.4	0.8	-10.6
^{S}TS_e2e1	-90.149716	-6941.273614	0.077170	-6941.196444	-18.3	-13.5	0.7	-12.9
^{S}M2_e1e2	-90.216760	-6941.339138	0.078892	-6941.260246	-60.3	-54.7	1.7	-52.9
^{S}M2_e2e1	-90.215429	-6941.337562	0.079243	-6941.258318	-59.5	-53.7	2.0	-51.7
$^3Al_{28}+2\cdot H_2O$	-90.119958	-6941.250214	0.075714	-6941.174500	0.0	0.0	0.0	0.0
^{T}M1_e2e2	-90.164327	-6941.289377	0.082967	-6941.206410	-27.8	-24.6	4.6	-20.0
^{T}M1_p1c	-90.163444	-6941.288976	0.082767	-6941.206209	-27.3	-24.3	4.4	-19.9
^{T}M1_p1p1	-90.162625	-6941.288105	0.082708	-6941.205398	-26.8	-23.8	4.4	-19.4
^{T}M1_e2e1	-90.162610	-6941.287997	0.082680	-6941.205317	-26.8	-23.7	4.4	-19.3
^{T}M1_e1c	-90.160889	-6941.286121	0.082649	-6941.203472	-25.7	-22.5	4.4	-18.2
^{T}M1_e1e2	-90.160929	-6941.285912	0.082719	-6941.203193	-25.7	-22.4	4.4	-18.0
^{T}TS_e2e2	-90.143795	-6941.266492	0.076985	-6941.189507	-15.0	-10.2	0.8	-9.4
^{T}TS_p1c	-90.134089	-6941.257561	0.076437	-6941.181124	-8.9	-4.6	0.5	-4.2
^{T}TS_p1p1	-90.131559	-6941.254357	0.076222	-6941.178135	-7.3	-2.6	0.3	-2.3
^{T}TS_e2e1	-90.146672	-6941.270218	0.077012	-6941.193206	-16.8	-12.6	0.8	-11.7
^{T}TS_e1c	-90.139088	-6941.262025	0.076909	-6941.185116	-12.0	-7.4	0.7	-6.7
^{T}TS_e1e2	-90.149195	-6941.272163	0.077014	-6941.195148	-18.3	-13.8	0.8	-13.0
^{T}M2_e2e2	-90.210575	-6941.331934	0.078183	-6941.253750	-56.9	-51.3	1.5	-49.7
^{T}M2_e1e2	-90.213547	-6941.334830	0.078667	-6941.256163	-58.7	-53.1	1.9	-51.2
^{T}M2_e2e1	-90.210667	-6941.331926	0.078763	-6941.253164	-56.9	-51.3	1.9	-49.4

(a) E_{CEP}: Energies at BHHLYP/CEP-31G*// BHHLYP/CEP-31G* level.
(b) E_{6311}: Energies at BHHLYP/6-311++G**// BHHLYP/CEP-31G* level.
(c) ZPE energies have been computed at the BHHLYP/CEP-31G* level and scaled by a factor of 0.93.
(d) $\Delta E^0_{6311} = \Delta E_{6311} + \Delta ZPE_{CEP}$.

SM_F4: Schematic representation of the transition states of the $Al_{28}\cdot(H_2O)_2$ system (obtained by the BHHLYP/CEP-31G* method) and relative energies computed at the BHHLYP/6-311++G**//BHHLYP/CEP-31G*+ZPE level with respect to $Al_{28}(^1A_1)$ + 2 H_2O for the singlets and to $Al_{28}(^3A_2')$ + 2 H_2O for the triplets.



SM_F5: Energy variation due to the geometric change in the dimer and the Al-cluster ($^2Al_{17}$ and $^1Al_{28}$) when the $Al_m{\cdot}(H_2O)_2$ adduct is formed. It is shown the relative energies (ΔE in kcal/mol) with respect to a) $Al_{17}(^2B_{2u})$ + $(H_2O)_2$ and b) $Al_{28}(^1A_1)$ + $(H_2O)_2$; calculated at the BHHLYP/6-311++G**//BHHLYP/CEP-31G* level. In path (···), we have performed a partial optimization by keeping the Al-cluster geometry frozen. In path (– – –), we have calculated the energy of the fragments (independently) at the adduct's geometry. a) For $^2Al_{17}{\cdot}(H_2O)_2$ (M1_e1c). b) For $^1Al_{28}{\cdot}(H_2O)_2$ (^{S}M1_e1e2).



SM_T4: Comparison of PBE and BHHLYP functionals with respect to the geometry optimization. Energies are computed at the BHHLYP/6-311++G**//PBE/CEP-31G* and BHHLYP/6-311++G**//BHHLYP/CEP-31G* levels for the most important paths in the singlet (^{S}e1e2, ^{S}e2e1) and the triplet (^{T}e2e2, ^{T}e1e2 and ^{T}e2e1) states. See a complete description in the footnote of the table.

	BHHLYP/6-311++G//PBE/CEP-31G***					
	$E^{(a)}$	**ZPE1[(b)]**	**$E^{0(d)}$**	**$\Delta E^{0(e)}$**	**$\Delta\Delta E^{0(f)}$**	
Al_{28} ($^{1}A_1$) + $2H_2O$	-6941.243908	0.073343	-6941.170566	0.0		
^{S}M1_e1e2	-6941.282726	0.078824	-6941.203902	-20.9	0.0	
^{S}TS_e1e2	-6941.269743	0.073485	-6941.196258	-16.1	4.8	
^{S}M2_e1e2	-6941.326604	0.074652	-6941.251952	-51.1	-30.2	
	BHHLYP/6-311++G//BHHLYP/CEP-31G***					
	$E^{(a)}$	**ZPE2[(c)]**	**$E^{0\,(d)}$**	**$\Delta E^{0\,(e)}$**	**$\Delta\Delta E^{0\,(f)}$**	**$\Delta\Delta\Delta E^{0(g)}$**
Al_{28} ($^{1}A_1$) + $2H_2O$	-6941.252033	0.076127	-6941.175906	0.0		
^{S}M1_e1e2	-6941.293935	0.083054	-6941.210881	-21.9	0.0	
^{S}TS_e1e2	-6941.279882	0.077503	-6941.202379	-16.6	5.3	0.5
^{S}M2_e1e2	-6941.339138	0.078892	-6941.260246	-52.9	-31.0	-0.8
	BHHLYP/6-311++G//PBE/CEP-31G***					
	$E^{(a)}$	**ZPE1[(b)]**	**$E^{0(d)}$**	**$\Delta E^{0\,(e)}$**	**$\Delta\Delta E^{0(f)}$**	
Al_{28} ($^{1}A_1$) + $2H_2O$	-6941.243908	0.073343	-6941.170566	0.0		
^{S}M1_e2e1	-6941.276152	0.078707	-6941.197445	-16.9	0.0	
^{S}TS_e2e1	-6941.260944	0.073153	-6941.187792	-10.8	*6.1*	
^{S}M2_e2e1	-6941.319570	0.074865	-6941.244705	-46.5	-29.7	
	BHHLYP/6-311++G//BHHLYP/CEP-31G***					
	$E^{(a)}$	**ZPE2[(c)]**	**$E^{0\,(d)}$**	**$\Delta E^{0\,(e)}$**	**$\Delta\Delta E^{0\,(f)}$**	**$\Delta\Delta\Delta E^{0(g)}$**
Al_{28} ($^{1}A_1$) + $2H_2O$	-6941.252033	0.076127	-6941.175906	0.0		
^{S}M1_e2e1	-6941.290389	0.082910	-6941.207478	-19.8	0.0	
^{S}TS_e2e1	-6941.273614	0.077170	-6941.196444	-12.9	*6.9*	0.9
^{S}M2_e2e1	-6941.337562	0.079243	-6941.258318	-51.7	-31.9	-2.2
	BHHLYP/6-311++G//PBE/CEP-31G***					
	$E^{(a)}$	**ZPE1[(b)]**	**$E^{0(d)}$**	**$\Delta E^{0(e)}$**	**$\Delta\Delta E^{0(f)}$**	
Al_{28} ($^{3}A_2'$) + $2H_2O$	-6941.242512	0.073209	-6941.169304	0.0		
^{T}M1_e2e2	-6941.275661	0.078853	-6941.196808	-17.3	0.0	
^{T}TS_e2e2	-6941.253367	0.072771	-6941.180596	-7.1	*10.2*	
^{T}M2_e2e2	-6941.318683	0.073381	-6941.245302	-47.7	-30.4	
	BHHLYP/6-311++G//BHHLYP/CEP-31G***					
	$E^{(a)}$	**ZPE2[(c)]**	**$E^{0\,(d)}$**	**$\Delta E^{0\,(e)}$**	**$\Delta\Delta E^{0\,(f)}$**	**$\Delta\Delta\Delta E^{0(g)}$**
Al_{28} ($^{3}A_2'$) + $2H_2O$	-6941.250214	0.075714	-6941.174500	0.0		
^{T}M1_e2e2	-6941.289396	0.082947	-6941.206449	-20.0	0.0	
^{T}TS_e2e2	-6941.266492	0.076985	-6941.189507	-9.4	*10.6*	0.5
^{T}M2_e2e2	-6941.331934	0.078183	-6941.253750	-49.7	-29.7	0.7
	BHHLYP/6-311++G//PBE/CEP-31G***					
	$E^{(a)}$	**ZPE1[(b)]**	**$E^{0(d)}$**	**$\Delta E^{0(e)}$**	**$\Delta\Delta E^{0(f)}$**	
Al_{28} ($^{3}A_2'$) + $2H_2O$	-6941.242512	0.073209	-6941.169304	0.0		
^{T}M1_e1e2	-6941.273322	0.078246	-6941.195076	-16.2	0.0	
^{T}TS_e1e2	-6941.261202	0.073069	-6941.188133	-11.8	*4.4*	
^{T}M2_e1e2	-6941.322547	0.074591	-6941.247956	-49.4	-33.2	

BHHLYP/6-311++G//BHHLYP/CEP-31G***

	$E^{(a)}$	$ZPE2^{(c)}$	$E^{0(d)}$	$\Delta E^{0(e)}$	$\Delta\Delta E^{0(f)}$	$\Delta\Delta\Delta E^{0(g)}$
Al_{28} ($^3A_2$') + $2H_2O$	-6941.250214	0.075714	-6941.174500	0.0		
^{T}M1_e1e2	-6941.285912	0.082719	-6941.203193	-18.0	0.0	
^{T}TS_e1e2	-6941.272163	0.077014	-6941.195148	-13.0	*5.0*	0.7
^{T}M2_e1e2	-6941.339138	0.078667	-6941.260471	-53.9	-35.9	-2.8

BHHLYP/6-311++G//PBE/CEP-31G***

	$E^{(a)}$	$ZPE1^{(b)}$	$E^{0\,(d)}$	$\Delta E^{0(e)}$	$\Delta\Delta E^{0(f)}$
Al_{28} ($^3A_2$') + $2H_2O$	-6941.242512	0.073209	-6941.169304	0.0	
^{T}M1_e2e1	-6941.273782	0.078686	-6941.195096	-16.2	0.0
^{T}TS_e2e1	-6941.256707	0.072949	-6941.183758	-9.1	*7.1*
^{T}M2_e2e1	-6941.317046	0.074798	-6941.242248	-45.8	-29.6

BHHLYP/6-311++G//BHHLYP/CEP-31G***

	$E^{(a)}$	$ZPE2^{(c)}$	$E^{0(d)}$	$\Delta E^{0(e)}$	$\Delta\Delta E^{0(f)}$	$\Delta\Delta\Delta E^{0(g)}$
Al_{28} ($^3A_2$') + $2H_2O$	-6941.250214	0.075714	-6941.174500	0.0		
^{T}M1_e2e1	-6941.287997	0.082680	-6941.205317	-19.3	0.0	
^{T}TS_e2e1	-6941.270218	0.077012	-6941.193206	-11.7	*7.6*	0.5
^{T}M2_e2e1	-6941.337562	0.079243	-6941.258318	-52.6	-33.3	-3.7

(a) E: Energy calculated at BHHLYP/6-311++G**//PBE/CEP-31G* (first case) or BHHLYP /6-311++G**//BHHLYP/CEP-31G* (second case) level (in a.u.).

(b) ZPE1: ZPE calculated at PBE/CEP-31G* and scaled by a factor of 0.93 (in a.u.).

(c) ZPE2: ZPE calculated at BHHLYP/CEP-31G* and scaled by a factor of 0.93 (in a.u.).

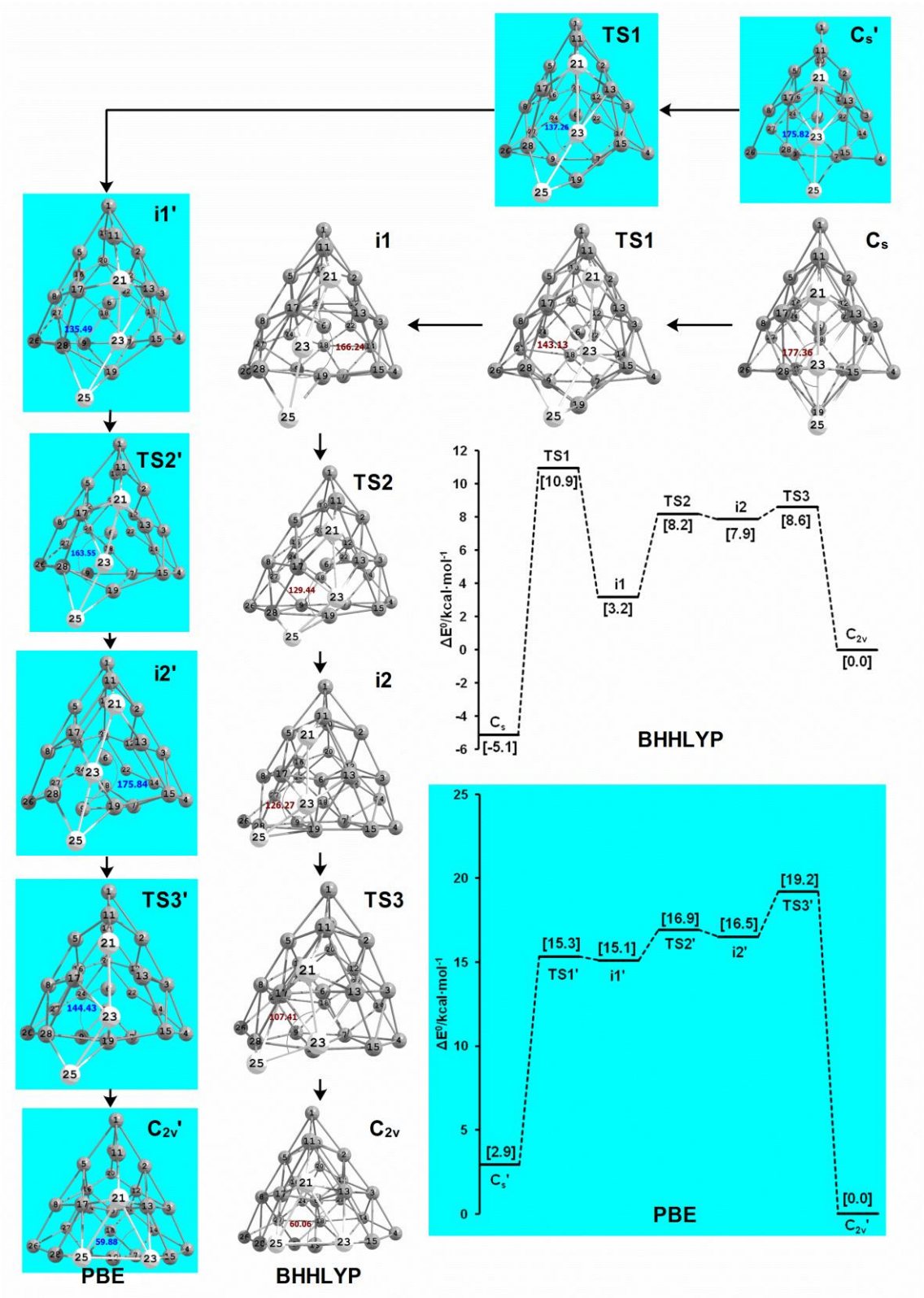
(d) E^0=E + ZPE1 or E^0=E + ZPE2 (in a.u.)

(e) ΔE^0: Relative energies (including ZPE) with respect to $Al_{28}(^1A_1)$ + 2 H_2O and $Al_{28}(^3A_2')$ + 2 H_2O for the singlet and triplet states, respectively (in kcal/mol).

(f) $\Delta\Delta E^0$: Relative energies (including ZPE) with respect to the corresponding minima M1 (in kcal/mol).

(g) $\Delta\Delta\Delta E^0$: Energy differences between the two levels; we have compared the energy barriers and the energies of reaction at 0K (in kcal/mol).

SM_F6: Energy profiles at the BHHLYP/6-311++G**//BHHLYP/CEP-31G*+ZPE (transparent background) and PBE/6-311++G**//PBE/CEP-31G*+ZPE (Fluorescent blue background) levels for the $Al_{28}(^1A')\leftrightarrow Al_{28}(^1A_1)$ conversion. Relative energies (ΔE^0 in kcal/mol) (including ZPE scaled by a factor of 0.93) with respect to $Al_{28}(^1A_1)$ have been presented.



SM_T5: Equilibrium constants ($K_p(T)$) and Gibbs energies ($\Delta G^0(T)$ in kcal/mol) for the H_2O elimination processes from the $Al_{28}\cdot(H_2O)_2$ complex in the gas phase (singlet and the triplet states). In the case of the singlet state, we have studied the equilibrium between ^{S}M1_e1e2 and ^{S}M1_e1, i.e. between the lowest-lying minima for each hydration. In the case of the triplet state we have considered two different equilibria: a) ^{T}M1_e2e2 (lowest-lying minimum) ↔ ^{T}M1_e1 + H_2O and b) ^{T}M1_p1c ↔ ^{T}M1_p1 (lowest-lying minimum) + H_2O.

	^{S}M1_e1e2 ↔ ^{S}M1_e1 + H_2O	
T	$\Delta G^0(T)$	$K_p(T)$
50.0	10.7	1.56E-47
66.7	10.3	1.56E-34
100	9.5	1.57E-21
120	9.0	3.50E-17
150	8.3	7.81E-13
200	7.1	1.69E-08
250	5.9	6.46E-06
300	4.8	3.26E-04
350	3.7	5.14E-03
400	2.6	3.93E-02
450	1.5	1.85E-01
500	0.5	6.23E-01

	a) ^{T}M1_e1e2 ↔ ^{T}M1_e1 + H_2O		**b) ^{T}M1_p1c ↔ ^{T}M1_p1 + H_2O**	
T	$\Delta G^0(T)$	$K_p(T)$	$\Delta G^0(T)$	$K_p(T)$
50.0	11.5	6.37E-51	11.3	2.56E-50
66.7	11.1	4.21E-37	11.0	9.74E-37
100	10.3	2.81E-23	10.3	3.62E-23
120	9.8	1.19E-18	9.8	1.24E-18
150	9.1	5.02E-14	9.2	4.23E-14
200	7.9	2.08E-09	8.1	1.38E-09
250	6.8	1.17E-06	7.1	6.68E-07
300	5.6	7.67E-05	6.0	3.92E-05
350	4.5	1.46E-03	5.1	6.85E-04
400	3.5	1.28E-02	4.1	5.64E-03
450	2.4	6.72E-02	3.2	2.81E-02
500	1.4	2.47E-01	2.3	9.87E-02

NOTE: In MRCI calculations we have employed the MOLPRO2010 program. MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf .