Electronic Supplementary Information

Reaction Mechanism between Small-Sized Ce Clusters and Water Molecules: An Ab Initio Investigation on Ce_n+H_2O

Table S1 The energies, compositions and occupancies of the high-energy molecular orbitals of the reaction products.

Isomers	Spin	Bond	Composition	Occupancy	Energy (a.u.)
CeO	α	Ce(LP)	$100\%(6s^{0.91}6p^{0.04}4d^{0.05})$	0.99	-0.13721
			$100\%(4f^{0.99})$	1.00	-0.20270
		Ce-O	$13\%Ce(5d^{0.77}4f^{0.23})+87\%O(2p^{1.0})$	1.00	-0.30391
			$13\%Ce(5d^{0.77}4f^{0.23})+87\%O(2p^{1.0})$	1.00	-0.30391
			$22\%Ce(5d^{0.60}4f^{0.30})+78\%O(2s^{0.13}2p^{0.87})$	1.00	-0.49433
	β	Ce-O	$11\%Ce(5d^{0.76}4f^{0.23})+89\%O(2p^{1.0})$	1.00	-0.30463
			$11\%Ce(5d^{0.76}4f^{0.23})+89\%O(2s^{0.04}2p^{0.96})$	1.00	-0.30463
			$21\%Ce(5d^{0.68}4f^{0.24})+79\%O(2s^{0.11}2p^{0.89})$	1.00	-0.48379
HCeOH	α	Ce(LP)	$100\%Ce(6s^{0.69}5d^{0.25})$	1.00	-0.13838
			100%Ce(4f)	1.00	-0.23434
		Ce-H	$24\%Ce(6s^{0.19}5d^{0.66}4f^{0.12})+76\%H(1s^{1.0})$	1.00	-0.26017
	β	Ce-H	$23\%Ce(6s^{0.33}5d^{0.57}4f^{0.07})+77\%H(1s^{1.0})$	1.00	-0.25932
H_2Ce_2O	α	Ce1(LP)	$100\%Ce1(6s^{0.69}5d^{0.21})$	1.00	-0.11910
		Ce1(LP)	100%Ce1(4f)	1.00	-0.21410
		Ce2(LP)	100%Ce2(4f)	1.00	-0.21995
		CeH	$18\%Ce(6s^{0.20}5d^{0.66}4f^{0.10})+82\%H(1s^{1.0})$	0.86	-0.23772
		CeH	$18\%Ce(6s^{0.20}5d^{0.66}4f^{0.10})+82\%H(1s^{1.0})$	0.86	-0.23772
	β	Ce2(LP)	100%Ce2(4f)	0.95	-0.11222
		CeH	$16\%Ce(6s^{0.09}5d^{0.75}4f^{0.08})+84\%H(1s^{1.0})$	0.86	-0.23138
		CeH	$16\%Ce(6s^{0.09}5d^{0.75}4f^{0.08})+84\%H(1s^{1.0})$	0.86	-0.23138

HCe_2OH	α	Ce1-Ce2	50%Ce1+50%Ce2($5d^{0.74}4f^{018}$)	1.00	-0.12588
		Ce1-Ce2	50%Ce1+50%Ce2($6s^{0.61}5d^{0.34}$)	1.00	-0.15049
		Ce2(LP^2)	100%Ce2(4f)	1.00	-0.18618
		Ce1(LP^1)	100%Ce1(4f)	1.00	-0.18620
		Ce-H	17%Ce($6s^{0.19}5d^{0.69}$)+83%H($1s^{1.0}$)	0.86	-0.22557
	β	Ce1-Ce2	50%Ce1+50%Ce2($6s^{0.28}5d^{0.66}$)	1.00	-0.11623
		Ce1-Ce2	50%Ce1+50%Ce2($6s^{0.41}5d^{0.52}$)	1.00	-0.15388
		Ce-H	16%Ce($6s^{0.16}5d^{0.71}$)+84%H($1s^{1.0}$)	0.87	-0.22809
H_2Ce_3O	α	Ce1-Ce3	43%Ce1($6s^{0.11}5d^{0.78}$)+57%Ce3($5d^{0.95}$)	0.73	-0.06841
		Ce2-Ce3	56%Ce2($6s^{0.55}5d^{0.40}$)+44%Ce3($6s^{0.32}5d^{0.62}$)	0.95	-0.13261
		Ce1-Ce3	55%Ce1($6s^{0.47}5d^{0.46}$)+45%Ce3($6s^{0.31}5d^{0.63}$)	0.96	-0.13822
		Ce1(LP)	100%Ce1(4f)	1.00	-0.17970
		Ce3(LP)	100%Ce3(4f)	1.00	-0.18680
	β	Ce2-Ce3	53%Ce2($6s^{0.46}5d^{0.48}$)+47%Ce3($6s^{0.24}5d^{0.73}$)	0.70	-0.05556
		Ce2-Ce3	33%Ce2($6s^{0.13}5d^{0.75}$)+67%Ce3($6s^{0.40}5d^{0.54}$)	0.76	-0.08027
		Ce2(LP)	100%Ce2(4f)	0.99	-0.17959
INT3	α	Ce2-Ce3	50%Ce2($6s^{0.23}5d^{0.70}$)+50%Ce3($5d^{0.85}$)	0.70	-0.08213
		Ce2-Ce3	43%Ce2($6s^{0.25}5d^{0.64}$)+54%Ce3($6s^{0.28}5d^{0.66}$)	0.76	-0.09457
		Ce1-Ce3	49%Ce1($6s^{0.54}5d^{0.39}$)+51%Ce3($6s^{49}5d^{0.48}$)	0.95	-0.16865
		Ce3(LP)	100%Ce3(4f)	0.99	-0.17951
		Ce1(LP)	100%Ce1(4f)	0.99	-0.19112
		Ce2(LP)	100%Ce2(4f)	1.00	-0.19693
	β	Ce2(LP)	100%Ce1($5d^{0.87}$)	0.35	-0.00253
		Ce1-Ce3	51%Ce1($5d^{0.93}$)+49%Ce3($5d^{0.92}$)	0.91	-0.10738
		Ce2-Ce3	63%Ce2($6s^{0.49}5d^{0.44}$)+37%Ce3($6s^{0.24}5d^{0.70}$)	0.96	-0.15069
		Ce1-Ce3	69%Ce1($6s^{0.89}$)+31%Ce3($6s^{0.60}5d^{0.35}$)	0.97	-0.18440