Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Geometric and electronic structure analysis of calcium water complexes with one and two solvation shells

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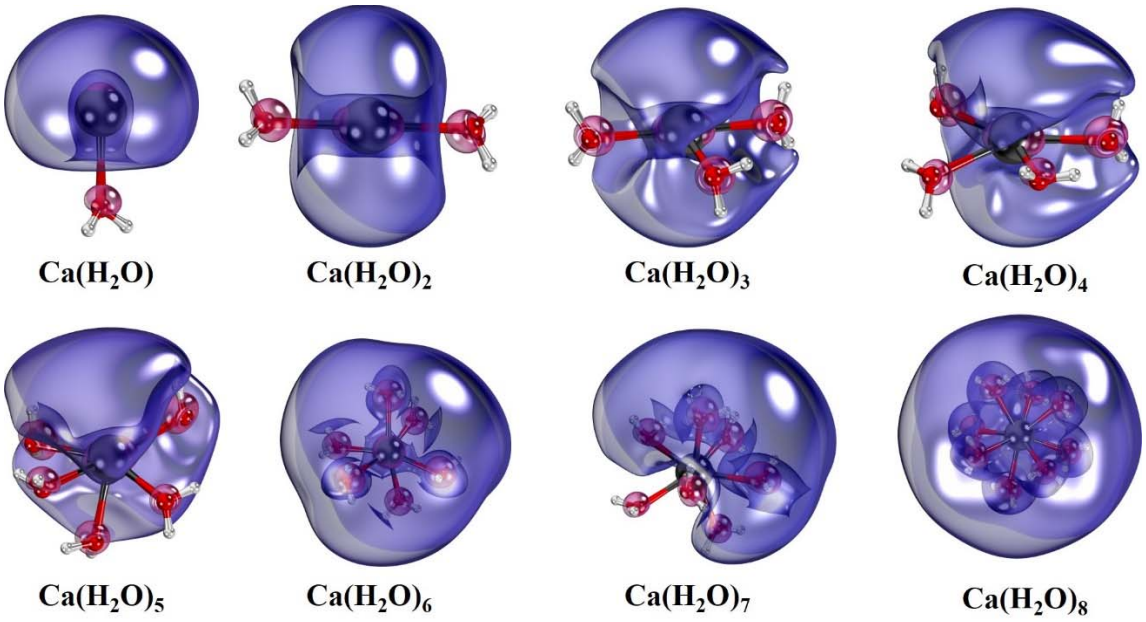

Figure S1. Contours of the highest (doubly) occupied molecular orbital of $Ca(H_2O)_{n=1-8}$.

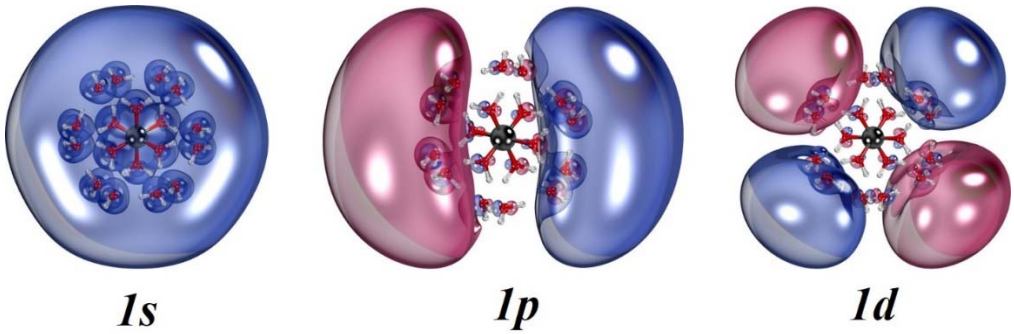

Figure S2. Selected 1s, 1p, and 1d orbitals of the $Ca(H_2O)_6^+$@$12H_2O$.

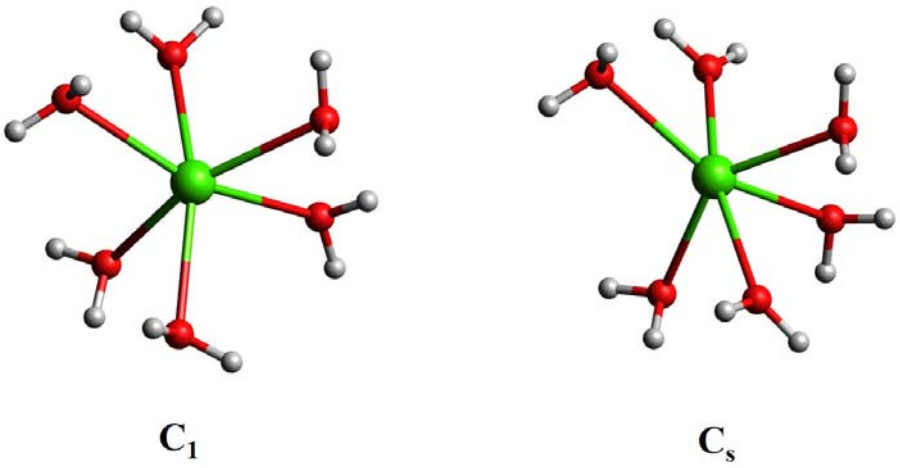

Figure S3. Optimized $Ca(H_2O)_6$ structure under C_1 and C_s point groups.

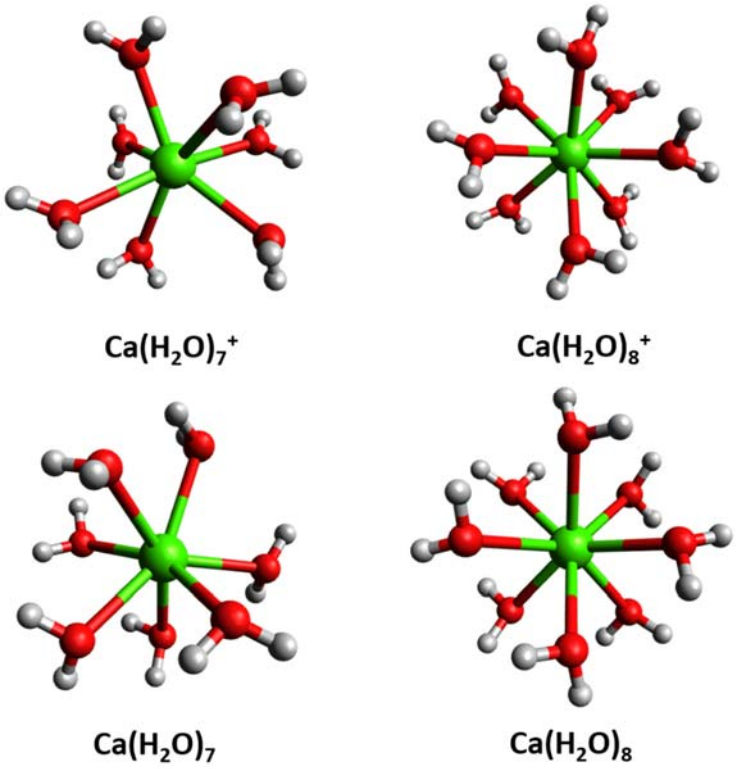

Figure S4. Optimized $Ca(H_2O)_{7,8}^{0,+}$ structures.

Table S1. MP2 and C-MP2 optimal geometries (coordinates in Å) and total energies (a.u.) of H_2O and $Ca(H_2O)_{n=1-8}^{+}$. The cc-pVTZ(Ca,O) aug-cc-pVTZ(H) basis sets are used for MP2 and cc-pCVTZ(Ca) cc-pVTZ(O) and aug-cc-pVTZ(H) for C-MP2.

		MP2				C-MP2		
H_2O		**-76.3256020000**				**-76.3256020000**		
	O	-0.000000	0.000000	0.118137	O	0.000000	-0.000000	0.118137
	H	-0.000000	0.757376	-0.472549	H	-0.000000	0.757376	-0.472549
	H	0.000000	-0.757376	-0.472549	H	-0.000000	-0.757376	-0.472549
$Ca(H_2O)_1^{+}$		**-752.9284159831**				**-753.2761699291**		
	Ca	-0.000004	-0.856123	0.000000	Ca	0.000101	-0.820320	0.000000
	O	-0.000004	1.595483	-0.000000	O	0.000101	1.523276	-0.000000
	H	0.000053	2.179295	0.746004	H	-0.001409	2.110094	0.768458
	H	0.000053	2.179295	-0.746004	H	-0.001409	2.110094	-0.768458
$Ca(H_2O)_2^{+}$		**-829.2871086699**				**-829.6399840928**		
	Ca	-0.000000	0.000031	-0.001390	Ca	-0.000001	0.000340	-0.001201
	O	2.448183	-0.000001	0.001285	O	2.347656	-0.000276	0.001086
	H	3.032091	0.757377	0.006189	H	2.933411	0.768420	0.006230
	H	3.031587	-0.757778	-0.002604	H	2.932420	-0.769738	-0.002927
	O	-2.448183	-0.000082	0.001291	O	-2.347655	-0.000369	0.001089
	H	-3.031456	0.757797	-0.002600	H	-2.932650	0.768918	-0.002924
	H	-3.032221	-0.757358	0.006201	H	-2.933178	-0.769240	0.006243
$Ca(H_2O)_3^{+}$		**-905.6389758247**				**-905.9957770612**		
	Ca	0.001165	-0.000605	-0.000045	Ca	0.001081	-0.000581	-0.000046
	O	-1.551567	-1.905862	0.000117	O	-1.493990	-1.819116	0.000144
	H	-1.918836	-2.356606	-0.762856	H	-1.863120	-2.268300	-0.772528
	H	-1.918912	-2.357079	0.762768	H	-1.863200	-2.268877	0.772438
	O	-0.878814	2.294360	-0.000040	O	-0.832243	2.201265	0.000009
	H	-1.086916	2.837874	0.762499	H	-1.037838	2.745813	0.772171
	H	-1.087163	2.837021	-0.763126	H	-1.038164	2.744801	-0.772788
	O	2.428290	-0.387347	0.000016	O	2.324260	-0.381082	-0.000060
	H	3.002102	-0.478968	0.763254	H	2.897613	-0.474950	0.772929
	H	3.003149	-0.479340	-0.762379	H	2.898870	-0.475408	-0.772046
$Ca(H_2O)_4^{+}$		**-981.9922301566**				**-982.3509749147**		
	Ca	0.135040	-0.000027	0.000001	Ca	0.118134	-0.000180	0.000091
	O	-0.285884	-2.451093	0.000207	O	-0.260128	-2.361505	0.000042
	H	-0.222528	-3.030638	0.765275	H	-0.164120	-2.936420	0.771631
	H	-0.222305	-3.030630	-0.764849	H	-0.162997	-2.936595	-0.771276
	O	-2.329725	0.003193	-0.000009	O	-2.254412	0.007574	0.000218
	H	-2.909349	-0.760758	-0.000075	H	-2.836199	-0.761432	-0.000304
	H	-2.907606	0.768463	0.000027	H	-2.831596	0.780040	0.000087
	O	2.597788	-0.004213	-0.000123	O	2.481886	-0.009172	-0.000249
	H	3.178326	-0.005060	0.766097	H	3.062315	-0.011333	0.773523
	H	3.178310	-0.005176	-0.766354	H	3.062147	-0.011281	-0.774145
	O	-0.278305	2.452251	-0.000073	O	-0.243182	2.363680	-0.000142
	H	-0.213207	3.031606	0.764990	H	-0.142895	2.938025	0.771325
	H	-0.213435	3.031628	-0.765139	H	-0.142646	2.937987	-0.771605
$Ca(H_2O)_5^{+}$		**-1058.3454625261**				**-1058.7046349732**		
	Ca	-0.004984	-0.002186	-0.750550	Ca	-0.004539	-0.004525	-0.566849
	O	-2.436460	0.047351	-0.059160	O	-2.356794	0.047981	0.029191

	H	-3.005943	-0.700895	-0.263082	H	-2.914734	-0.703003	-0.211735
	H	-2.974096	0.818096	-0.265750	H	-2.877857	0.824445	-0.213571
	O	-0.044478	-2.474200	-0.482947	O	-0.042474	-2.383988	-0.543820
	H	-0.057771	-3.022037	-1.274092	H	-0.053254	-2.775113	-1.429996
	H	-0.053782	-3.083274	0.259742	H	-0.055488	-3.121089	0.079486
	O	0.048007	2.469959	-0.484169	O	0.046423	2.375540	-0.545421
	H	0.055170	3.017760	-1.275422	H	0.050404	2.766451	-1.431741
	H	0.061236	3.079081	0.258432	H	0.060289	3.112840	0.077642
	O	0.006071	-0.000425	1.765344	O	0.006451	-0.001531	1.840504
	H	-0.758287	0.014712	2.346302	H	-0.761632	0.013443	2.422167
	H	0.777829	-0.014058	2.336493	H	0.783174	-0.015834	2.410628
	H	2.995967	0.706790	-0.286767	H	2.899663	0.716611	-0.233178
	H	2.971337	-0.812413	-0.284624	H	2.879460	-0.811251	-0.233565
	O	2.431577	-0.043570	-0.076547	O	2.352301	-0.040282	0.013462
$Ca(H_2O)_6^+$		**-1134.6883791036**				**-1135.0554150636**		
	Ca	0.000000	0.000000	0.000000	Ca	0.000000	0.000000	0.000000
	O	0.000000	-0.000000	2.442035	O	0.000000	-0.000000	2.366874
	O	0.000000	2.442035	-0.000000	O	0.000000	2.366874	-0.000000
	O	-0.000000	-2.442035	0.000000	O	-0.000000	-2.366874	0.000000
	O	0.000000	-0.000000	-2.442035	O	0.000000	-0.000000	-2.366874
	O	-2.442035	0.000000	-0.000000	O	-2.366874	0.000000	-0.000000
	O	2.442035	-0.000000	0.000000	O	2.366874	-0.000000	0.000000
	H	3.022936	-0.767814	0.000000	H	2.948767	-0.773754	0.000000
	H	3.022936	0.767814	-0.000000	H	2.948767	0.773754	-0.000000
	H	-0.000000	-3.022936	-0.767814	H	-0.000000	-2.948767	-0.773754
	H	-0.000000	-3.022936	0.767814	H	-0.000000	-2.948767	0.773754
	H	-0.767814	0.000000	3.022936	H	-0.773754	0.000000	2.948767
	H	0.767814	-0.000000	3.022936	H	0.773754	-0.000000	2.948767
	H	-3.022936	0.767814	0.000000	H	-2.948767	0.773754	-0.000000
	H	-3.022936	-0.767814	-0.000000	H	-2.948767	-0.773754	-0.000000
	H	0.000000	3.022936	0.767814	H	0.000000	2.948767	0.773754
	H	0.000000	3.022936	-0.767814	H	0.000000	2.948767	-0.773754
	H	-0.767814	0.000000	-3.022936	H	-0.773754	0.000000	-2.948767
	H	0.767814	-0.000000	-3.022936	H	0.773754	-0.000000	-2.948767
$Ca(H_2O)_7^+$		**-1211.0412210000**				**-1211.4115750000**		
	Ca	-0.020860	0.010663	-0.086474	Ca	0.087227	0.086650	0.065769
	o	1.607465	0.784251	1.641362	O	2.212511	1.099036	0.601026
	h	1.660968	1.460745	2.318201	H	2.542752	1.937104	0.938912
	h	2.382018	0.226071	1.748458	H	2.987869	0.562364	0.402462
	o	-0.556246	2.418486	0.277190	O	-0.100474	2.203906	-1.035660
	h	-1.388857	2.576785	-0.180331	H	-1.030281	2.297559	-1.283954
	h	-0.093050	3.256769	0.291219	H	0.388200	2.891937	-1.496964
	o	-2.321213	0.752659	-0.967940	O	-2.238384	0.667217	-0.435215
	h	-2.211023	0.589219	-1.920871	H	-2.580677	-0.081160	-0.981871
	h	-3.194474	0.404516	-0.756501	H	-2.943189	0.834747	0.207814
	o	1.774493	0.579807	-1.811486	O	-0.077974	-0.980139	-2.101793
	h	2.253623	1.393658	-2.000702	H	-0.114408	-0.573262	-2.981217
	h	1.286481	0.375860	-2.628230	H	-0.919413	-1.505345	-2.039650
	o	-1.177559	-2.203015	-0.614786	O	-1.125140	-1.851321	0.893705
	h	-1.397288	-2.040654	-1.548503	H	-1.831635	-1.994297	0.213672
	h	-0.809318	-3.092279	-0.616167	H	-0.795857	-2.744374	1.075021

	o	2.075179	-1.452496	0.045835	O	1.886653	-1.547628	-0.281488
	h	2.524386	-1.203461	-0.772525	H	1.601556	-1.896061	-1.140535
	h	2.238506	-2.392142	0.158126	H	2.294865	-2.286002	0.183206
	o	-1.326958	-0.831724	1.839506	O	-0.532639	0.429331	2.343834
	h	-1.910885	-1.561087	1.614300	H	-1.091890	-0.321281	2.585685
	h	-1.525167	-0.591009	2.745542	H	-0.448866	0.981860	3.126767
$Ca(H_2O)_8^+$		**-1287.3851542117**				**-1287.7548454495**		
	Ca	0.000000	0.000000	0.000842	Ca	0.000000	0.000000	0.000042
	O	1.459101	1.460522	-1.439957	O	0.000000	2.003757	-1.405415
	H	1.833672	2.331077	-1.266311	H	-0.303526	2.905049	-1.233338
	H	2.063898	1.030384	-2.055573	H	0.758711	2.083164	-2.000496
	O	0.000000	2.065665	1.439107	O	-1.415811	1.418135	1.405269
	H	-0.353690	2.945396	1.267908	H	-2.267905	1.840907	1.234186
	H	0.730174	2.189745	2.056562	H	-0.935080	2.010208	2.000607
	O	-1.460522	1.459101	-1.439957	O	-2.003757	0.000000	-1.405415
	H	-2.331077	1.833672	-1.266311	H	-2.905049	-0.303526	-1.233338
	H	-1.030384	2.063898	-2.055573	H	-2.083164	0.758711	-2.000496
	O	-2.065665	0.000000	1.439107	O	-1.418135	-1.415811	1.405269
	H	-2.945396	-0.353690	1.267908	H	-1.840907	-2.267905	1.234186
	H	-2.189745	0.730174	2.056562	H	-2.010208	-0.935080	2.000607
	O	-1.459101	-1.460522	-1.439957	O	-0.000000	-2.003757	-1.405415
	H	-2.063898	-1.030384	-2.055573	H	-0.758711	-2.083164	-2.000496
	H	-1.833672	-2.331077	-1.266311	H	0.303526	-2.905049	-1.233338
	O	-0.000000	-2.065665	1.439107	O	1.415811	-1.418135	1.405269
	H	-0.730174	-2.189745	2.056562	H	0.935080	-2.010208	2.000607
	H	0.353690	-2.945396	1.267908	H	2.267905	-1.840907	1.234186
	O	1.460522	-1.459101	-1.439957	O	2.003757	-0.000000	-1.405415
	H	1.030384	-2.063898	-2.055573	H	2.083164	-0.758711	-2.000496
	H	2.331077	-1.833672	-1.266311	H	2.905049	0.303526	-1.233338
	O	2.065665	-0.000000	1.439107	O	1.418135	1.415811	1.405269
	H	2.189745	-0.730174	2.056562	H	2.010208	0.935080	2.000607
	H	2.945396	0.353690	1.267908	H	1.840907	2.267905	1.234186

Table S2. MP2/aug-cc-pVTZ Optimized geometries (Cartesian coordinates in Å) and energies (a.u.) for different isomers of $Ca(H_2O)_{n=5-7}^{+}$.

$Ca(H_2O)_5^+$ **-1058.3631641744**	**$Ca(H_2O)_4@H_2O^+$** **-1058.3611351118**
Ca -0.0014900000 0.0019050000 -0.6331650000	Ca 0.0000000000 0.0000000000 0.7313920000
O 0.0005040000 2.4297410000 0.0492200000	O 0.0000000000 0.0000000000 -3.4738760000
H -0.7589480000 2.9839510000 -0.1581910000	H 0.7711200000 0.0000000000 -4.0530090000
H 0.7610960000 2.9817020000 -0.1600310000	H -0.7711200000 0.0000000000 -4.0530090000
O -2.4678610000 -0.0054010000 -0.3641330000	O 0.0000000000 1.8809490000 2.1623160000
H -3.0168750000 -0.0055240000 -1.1553820000	H 0.7796070000 2.2339160000 2.6142250000
H -3.0772160000 -0.0051630000 0.3791190000	H -0.7796070000 2.2339160000 2.6142250000
O 2.4652880000 -0.0018890000 -0.3655100000	O 0.0000000000 -1.8809490000 2.1623160000
H 3.0140820000 -0.0011940000 -1.1569150000	H 0.7796070000 -2.2339160000 2.6142250000
H 3.0748280000 -0.0005390000 0.3776010000	H -0.7796070000 -2.2339160000 2.6142250000
O 0.0004020000 -0.0001270000 1.8752800000	O 0.0000000000 -1.4877370000 -1.0980790000
H 0.0003800000 0.7666500000 2.4541620000	H 0.0000000000 -2.4498590000 -1.0796150000
H 0.0014550000 -0.7699830000 2.4500820000	H 0.0000000000 -1.1998440000 -2.0281370000
H 0.7657250000 -2.9766830000 -0.1600150000	H 0.0000000000 2.4498590000 -1.0796150000
H -0.7543940000 -2.9814180000 -0.1586400000	H 0.0000000000 1.1998440000 -2.0281370000
O 0.0041270000 -2.4260630000 0.0490820000	O 0.0000000000 1.4877370000 -1.0980790000
$Ca(H_2O)_6^+$ **-1134.7100703858**	**$Ca(H_2O)_5@H_2O^+$** **-1134.7161602512**
Ca 0.0000000000 0.0000000000 0.0000000000	Ca 0.5214080000 -0.0193620000 -0.2729490000
O 0.0000000000 0.0000000000 2.4403770000	O -1.2728560000 -1.5560630000 -0.1492590000
O 0.0000000000 2.4403770000 0.0000000000	O 2.0774250000 -1.7920720000 -0.5610060000
O 0.0000000000 -2.4403770000 0.0000000000	O -1.3072740000 1.4025640000 0.1993720000
O 0.0000000000 0.0000000000 -2.4403770000	O 1.4846270000 2.1007930000 -0.7811460000
O -2.4403770000 0.0000000000 0.0000000000	O 1.7359650000 0.0303090000 1.7963250000
O 2.4403770000 0.0000000000 0.0000000000	O -3.6702570000 -0.1124040000 0.1174410000
H 3.0218320000 -0.7681720000 0.0000000000	H -4.2408470000 -0.2202710000 0.8871920000
H 3.0218320000 0.7681720000 0.0000000000	H -4.2583510000 -0.0361350000 -0.6432300000
H 0.0000000000 -3.0218320000 -0.7681720000	H -1.2683270000 2.3429460000 -0.0059780000
H 0.0000000000 -3.0218320000 0.7681720000	H -2.2397950000 1.1260490000 0.2049100000
H -0.7681720000 0.0000000000 3.0218320000	H -2.1997070000 -1.2647350000 -0.0785720000
H 0.7681720000 0.0000000000 3.0218320000	H -1.2700250000 -2.4391080000 -0.5340930000
H -3.0218320000 0.7681720000 0.0000000000	H 2.5909800000 -0.4178310000 1.8322500000
H -3.0218320000 -0.7681720000 0.0000000000	H 1.5858180000 0.4246040000 2.6627820000
H 0.0000000000 3.0218320000 0.7681720000	H 2.2435060000 -2.7000210000 -0.2704630000
H 0.0000000000 3.0218320000 -0.7681720000	H 2.3820820000 -1.7230450000 -1.4847240000
H -0.7681720000 0.0000000000 -3.0218320000	H 2.1795700000 2.6185040000 -0.3519150000
H 0.7681720000 0.0000000000 -3.0218320000	H 1.6858850000 2.0912740000 -1.7329910000
$Ca(H_2O)_4@2H_2O^+$ **-1134.7154682042**	**$Ca(H_2O)_7^+$** **-1211.065943104**
Ca 0.0960070000 -0.9291190000 0.1880330000	Ca -0.0214200000 0.0136490000 -0.0769420000
O 2.3428950000 -0.2754400000 -0.0920250000	O 1.6028250000 0.8326360000 1.6232800000
O 0.3398580000 -3.2363120000 -0.1478550000	H 1.6458830000 1.5277280000 2.2826330000
O -0.1459310000 1.4011260000 -0.0350620000	H 2.3887640000 0.2922330000 1.7428320000
O -2.2369990000 -0.7521770000 -0.0932060000	O -0.5624450000 2.4195960000 0.2531870000
O -2.9208380000 1.9682790000 -0.0301280000	H -1.4020210000 2.5706950000 -0.1955110000
O 2.4523510000 2.5277310000 -0.0308220000	H -0.1009830000 3.2596710000 0.2498680000

H 2.8129300000 3.0203820000 -0.7770310000 H 2.7855130000 2.9614350000 0.7633740000 H -0.9932350000 1.8734750000 -0.0393600000 H 0.5864200000 2.0372990000 -0.0395440000 H 2.6064130000 0.6626630000 -0.0780480000 H 3.1254100000 -0.8087070000 0.0838400000 H -3.3756390000 2.3771020000 -0.7754900000 H -3.3357850000 2.3228420000 0.7648250000 H 0.4037000000 -3.8417230000 -0.8992030000 H 0.3945610000 -3.7645790000 0.6661380000 H -2.6879730000 0.1116230000 -0.0794890000 H -2.8931360000 -1.4350950000 0.0821190000	O -2.3296280000 0.7247870000 -0.9415510000 H -2.2329120000 0.5542010000 -1.8959030000 H -3.2013490000 0.3799540000 -0.7161890000 O 1.7190580000 0.5455350000 -1.8575300000 H 2.1915600000 1.3556560000 -2.0795200000 H 1.2135320000 0.3189480000 -2.6589710000 O -1.1511550000 -2.2040280000 -0.6066540000 H -1.3812760000 -2.0487310000 -1.5401390000 H -0.7731140000 -3.0897770000 -0.6071260000 O 2.0834490000 -1.4229710000 0.0565320000 H 2.5206600000 -1.1984560000 -0.7759490000 H 2.2652380000 -2.3546880000 0.2048260000 O -1.2826900000 -0.8517040000 1.8617610000 H -1.8708000000 -1.5812640000 1.6453070000 H -1.4700990000 -0.6099600000 2.7704830000
$Ca(H_2O)_6@H_2O^+$ **-1211.0693002121**	**$Ca(H_2O)_5@2H_2O^+$** **-1211.0680333089**
Ca 0.4637300000 -0.0230700000 0.0504950000 O -1.1168730000 -1.2356530000 -1.2831030000 O 2.2357380000 0.6307630000 -1.4124450000 O -1.1694830000 -0.3341110000 1.7371530000 O -0.9530690000 1.8880780000 -0.5039760000 O 2.1147420000 1.0062260000 1.4062670000 O -3.1594490000 0.1945680000 -0.0268470000 H -4.1184770000 0.2764040000 -0.0564060000 H -2.7760110000 1.0416970000 -0.3149900000 H -1.2392640000 -0.7329210000 2.6084690000 H -2.0732100000 -0.1906540000 1.3906220000 H -2.0280640000 -0.9843370000 -1.0399400000 H -1.0521790000 -1.1298930000 -2.2420540000 H 2.7892220000 1.4047500000 0.8385260000 H 2.2320570000 1.3615230000 2.2933150000 H 2.8781380000 0.1241580000 -1.9323610000 H 1.8125770000 1.2645910000 -2.0375230000 H -0.8509400000 2.7586670000 -0.0798830000 H -0.6859960000 2.0290560000 -1.4516690000 O 1.2036790000 -2.2842350000 0.1794210000 H 1.9765490000 -2.7657620000 0.4910800000 H 0.6187150000 -2.9209610000 -0.2488330000	Ca 0.6071720000 0.4514460000 -0.2463820000 O -3.5633720000 0.5632810000 -0.3681100000 H -3.9511330000 0.4817950000 -1.2476850000 H -4.2997430000 0.7037270000 0.2383320000 O 1.6431680000 -1.6454620000 0.0561960000 H 2.5378140000 -1.8062320000 -0.2621180000 H 1.1726600000 -2.4948260000 0.1120790000 O 2.8479640000 0.9377810000 -0.9039550000 H 2.7521660000 1.1582840000 -1.8497320000 H 3.5315890000 1.5231500000 -0.5498140000 O -0.3172750000 -3.6424530000 0.2478550000 H -0.3925480000 -4.1872170000 1.0395090000 H -0.4729430000 -4.2324220000 -0.4985170000 O -1.1664220000 2.0978050000 -0.2819890000 H -1.0356480000 2.6469020000 -1.0705670000 H -2.0822780000 1.7655960000 -0.3244490000 O -1.2434610000 -0.9489460000 0.1693150000 H -1.2030840000 -1.9169030000 0.2101360000 H -2.1616000000 -0.6666300000 0.0262290000 O 0.7964420000 1.8258840000 1.6996050000 H 0.1306610000 2.5263240000 1.6815760000 H 1.3543000000 1.9664110000 2.4713350000

Table S3. MP2 and C-MP2 optimized geometries (Cartesian coordinates in Å) and total energies (a.u.) of $Ca(H_2O)_{n=1-8}$. The cc-pVTZ(Ca,O) aug-cc-pVTZ(H) basis sets are used for MP2 and cc-pCVTZ(Ca) cc-pVTZ(O) and aug-cc-pVTZ(H) for C-MP2.

		MP2				C-MP2		
$Ca(H_2O)$		**-753.1125291362**				**-753.4634537218**		
	Ca	-0.014774	-0.890637	-0.000000	Ca	-0.022072	-0.842263	0.000000
	O	-0.014774	1.673874	0.000000	O	-0.022072	1.588514	-0.000000
	H	0.206830	2.210873	0.767388	H	0.309012	2.068576	0.773191
	H	0.206830	2.210873	-0.767388	H	0.309012	2.068576	-0.773191
$Ca(H_2O)_2$		**-829.4492880312**				**-829.8042716811**		
	Ca	-0.000002	-0.000298	0.000089	Ca	0.000002	-0.000082	0.000422
	O	2.504950	0.000293	0.079789	O	2.386877	0.000095	-0.093341
	H	2.972166	-0.767057	-0.269215	H	2.805841	0.773678	0.315877
	H	2.971840	0.767690	-0.269552	H	2.805828	-0.773624	0.315637
	O	-2.504972	0.000293	-0.080013	O	-2.386960	0.000094	0.092580
	H	-2.972057	-0.767043	0.269217	H	-2.805519	0.773680	-0.317046
	H	-2.971732	0.767675	0.269555	H	-2.805529	-0.773611	-0.316816
$Ca(H_2O)_3$		**-905.7890045243**				**-906.1463760867**		
	Ca	0.199290	-0.453814	0.003896	Ca	-0.335820	-0.060163	-0.024638
	O	-0.717014	1.948808	0.066839	O	1.698374	-1.365349	-0.066759
	H	-1.586815	1.984480	0.478339	H	2.414299	-0.742014	0.131930
	H	-0.878794	2.298221	-0.818476	H	1.893149	-2.175861	0.418272
	O	-2.273328	-0.839910	0.004342	O	1.675996	1.382494	0.023709
	H	-2.555740	-1.166525	-0.862127	H	1.558326	1.964460	-0.748986
	H	-2.500072	-1.553056	0.615884	H	1.477433	1.954552	0.787616
	O	2.647900	-0.071688	0.003526	O	-2.701712	-0.094459	0.011111
	H	3.119084	-0.308199	-0.805316	H	-3.027453	0.500316	-0.687954
	H	3.156082	-0.476313	0.716127	H	-2.980628	0.320324	0.847395
$Ca(H_2O)_4$		**-982.1310609207**				**-982.4910060113**		
	Ca	-0.000009	0.387035	0.000844	Ca	-0.013889	0.211660	-0.086320
	O	-1.589303	-1.568742	-0.179195	O	-1.612537	-1.599948	0.213165
	H	-1.566666	-2.229443	-0.876436	H	-2.455845	-1.136113	0.084615
	H	-2.463736	-1.163811	-0.226089	H	-1.628755	-1.880932	1.140658
	O	1.589436	-1.568381	0.178871	O	1.710081	-1.447254	-0.292895
	H	1.568464	-2.229708	0.875579	H	1.784230	-2.392547	-0.123267
	H	2.463835	-1.163206	0.224605	H	2.540855	-1.039801	-0.007364
	O	-2.452648	1.090295	0.156428	O	-2.229216	1.181584	-0.158168
	H	-2.562339	1.759613	-0.536642	H	-2.184596	1.837799	-0.879995
	H	-2.540456	1.588501	0.983314	H	-2.194831	1.717667	0.661148
	O	2.452498	1.090438	-0.157464	O	2.161314	1.241489	0.253782
	H	2.564253	1.760294	0.534707	H	1.986540	1.677625	1.111694
	H	2.536949	1.588174	-0.985035	H	2.193048	1.976132	-0.388168
$Ca(H_2O)_5$		**-1058.4728279921**				**-1058.8374449500**		
	Ca	-0.200924	-0.426689	-0.043002	Ca	0.131323	0.078049	-0.206500
	O	1.747002	0.660207	1.307693	O	2.100105	1.443041	-0.029868
	H	2.395896	-0.045077	1.163484	H	1.992624	1.786321	0.884709
	H	1.683729	0.755477	2.263904	H	1.969268	2.225372	-0.602796
	O	0.848967	1.623024	-1.168725	O	-0.776373	-1.818887	1.009080
	H	1.635541	1.846942	-0.654454	H	-0.775633	-1.570518	1.948273

	H	1.145365	1.531281	-2.080685	H	-1.708981	-1.940698	0.772205
	O	-2.625529	-1.176171	0.014693	O	-2.134658	-0.362067	-1.082120
	H	-2.676759	-1.860705	0.698486	H	-2.259668	-0.270320	-2.036976
	H	-2.756478	-1.664653	-0.811976	H	-2.554903	0.426916	-0.695604
	O	-1.704452	1.534365	0.369988	O	2.004980	-1.416759	-0.345661
	H	-1.574062	2.282457	-0.219117	H	2.046530	-2.133086	0.301306
	H	-2.619997	1.259072	0.258320	H	2.783117	-0.863249	-0.181241
	H	2.197845	-1.707407	-1.287115	H	-1.144296	2.580784	0.314730
	H	1.888978	-2.458072	0.009453	H	-1.111870	1.724878	1.609974
	O	2.071315	-1.567116	-0.333683	O	-1.426886	1.713750	0.675495
$Ca(H_2O)_6$		**-1134.8144741157**				**-1135.1843537168**		
	Ca	-0.000371	0.003107	0.189369	Ca	-0.000436	0.000119	-0.179455
	O	0.577008	-2.319369	1.013833	O	1.637287	-1.133549	1.186127
	O	-0.976609	-1.757160	-1.254987	O	0.521168	-2.090897	-1.206471
	O	1.730960	1.653772	1.016727	O	0.163448	1.986760	1.183476
	O	-1.038207	1.736358	-1.243882	O	-2.070919	0.594196	-1.208598
	O	2.011287	0.030587	-1.255376	O	1.552390	1.493662	-1.207502
	O	-2.303469	0.651373	1.014618	O	-1.802383	-0.850628	1.184703
	H	-2.108500	0.969874	1.913752	H	-1.615021	-0.422562	2.054875
	H	-2.903976	-0.094970	1.166071	H	-1.779598	-1.807162	1.389714
	H	1.390780	2.547696	1.177052	H	-0.676148	2.446327	1.386876
	H	1.912571	1.317984	1.912351	H	0.438903	1.610971	2.054367
	H	0.197464	-2.311563	1.910372	H	1.172791	-1.184715	2.056270
	H	1.522315	-2.468003	1.171640	H	2.454089	-0.635103	1.390824
	H	2.468624	-0.693697	-1.689978	H	2.440087	1.328495	-1.550538
	H	2.685324	0.532068	-0.779479	H	1.651395	2.169892	-0.515234
	H	-0.872530	-2.590286	-0.778030	H	1.056704	-2.513546	-0.512993
	H	-1.834823	-1.796551	-1.684657	H	-0.064007	-2.778184	-1.550210
	H	-1.813100	2.057872	-0.765798	H	-2.705591	0.342227	-0.515746
	H	-0.644498	2.502954	-1.668145	H	-2.372814	1.444624	-1.552967
$Ca(H_2O)_7$		**-1211.1609160325**				**-1211.5335376682**		
	Ca	-0.039220	0.068204	-0.062464	Ca	-0.076075	0.038568	-0.067308
	O	-2.206444	0.774350	-1.050541	O	-2.313090	0.274191	-0.983175
	H	-2.443685	1.703886	-1.118684	H	-2.680492	1.165634	-1.023464
	H	-2.920568	0.348888	-0.561783	H	-2.887269	-0.226027	-0.386253
	O	0.035495	2.568344	-0.018521	O	-0.490136	2.442822	0.012625
	H	0.981571	2.773229	-0.031552	H	0.421680	2.765764	-0.090398
	H	-0.299227	3.026567	0.763220	H	-0.782498	2.810328	0.861542
	O	2.332029	0.895384	-0.192456	O	2.016806	1.253367	-0.379222
	H	2.742124	0.772771	0.683878	H	2.510441	1.131625	0.462853
	H	2.953152	0.471533	-0.802341	H	2.635756	0.949897	-1.065027
	O	0.056170	0.048544	2.426876	O	0.312612	0.171478	2.308965
	H	0.179267	0.885191	2.904489	H	0.336575	1.038438	2.764398
	H	0.809001	-0.502397	2.718301	H	1.213226	-0.210965	2.467873
	O	1.267434	-2.075873	0.074276	O	1.546119	-1.785767	0.039774
	H	2.072332	-1.943731	0.612004	H	2.314963	-1.455696	0.566705
	H	0.831304	-2.833140	0.500352	H	1.272171	-2.596183	0.515751
	O	-1.932353	-1.325306	0.858270	O	-1.571760	-1.536126	1.071637
	H	-1.757487	-1.257310	1.811062	H	-1.264530	-1.337140	1.976641
	H	-1.969995	-2.277276	0.688086	H	-1.427622	-2.492221	0.971057
	O	0.334832	-0.864174	-2.310668	O	0.387818	-0.782435	-2.275750

	H	0.790394	-1.706111	-2.179955	H	0.977328	-1.528795	-2.079172
	H	-0.281085	-0.996327	-3.035687	H	-0.225181	-1.086269	-2.955169
$Ca(H_2O)_8$		**-1287.5043779205**				**-1287.8764081051**		
	Ca	-0.000025	0.000008	-0.000047	Ca	0.000002	-0.000021	-0.000059
	O	-1.674545	1.175511	-1.473729	O	-0.454241	-1.940790	-1.433073
	H	-2.513856	1.525966	-1.145199	H	-0.522129	-2.846904	-1.091716
	H	-1.254230	1.909218	-1.944815	H	-1.295912	-1.765161	-1.886146
	O	-2.015206	-0.352777	1.473791	O	1.051277	-1.694011	1.432351
	H	-2.856584	-0.698384	1.145409	H	1.644055	-2.382669	1.090967
	H	-2.236661	0.463217	1.944989	H	0.331968	-2.165054	1.885398
	O	-1.175425	-1.674442	-1.473871	O	1.941118	-0.453891	-1.432755
	H	-1.525832	-2.513780	-1.145350	H	2.847167	-0.521673	-1.091192
	H	-1.909147	-1.254183	-1.944983	H	1.765745	-1.295539	-1.885975
	O	0.352750	-2.015259	1.473697	O	1.693694	1.051006	1.432889
	H	0.698342	-2.856609	1.145221	H	2.382407	1.643835	1.091694
	H	-0.463265	-2.236759	1.944842	H	2.164673	0.331584	1.885829
	O	1.674524	-1.175290	-1.473894	O	0.454177	1.941355	-1.432324
	H	1.254211	-1.908977	-1.945018	H	1.295870	1.765927	-1.885443
	H	2.513802	-1.525792	-1.145318	H	0.522093	2.847303	-1.090517
	O	2.015197	0.352630	1.473823	O	-1.051324	1.693421	1.433015
	H	2.236553	-0.463462	1.944902	H	-0.331894	2.164152	1.886204
	H	2.856610	0.698118	1.145402	H	-1.643925	2.382339	1.091844
	O	1.175378	1.674579	-1.473772	O	-1.941071	0.454465	-1.432677
	H	1.909001	1.254194	-1.944928	H	-1.765458	1.296267	-1.885518
	H	1.525985	2.513803	-1.145176	H	-2.847111	0.522338	-1.091117
	O	-0.352638	2.015091	1.473980	O	-1.693698	-1.051554	1.432553
	H	0.463457	2.236393	1.945074	H	-2.164485	-0.332204	1.885804
	H	-0.698160	2.856537	1.145689	H	-2.382568	-1.644120	1.091232

Table S4. MP2/aug-cc-pVTZ Optimized geometries (Cartesian coordinates in Å) and energies (a.u.) for different isomers of $Ca(H_2O)_{n=5-7}$.

$Ca(H_2O)$ **-753.116458635**	**$Ca(H_2O)_2$** **-829.45724273102**
Ca 0.8856570000 -0.0000260000 0.0036820000 H -2.1979530000 0.7684090000 0.1751360000 H -2.2010550000 -0.7664210000 0.1756900000 O -1.6642670000 -0.0001840000 -0.0530580000	Ca 0.0000000000 0.0000380000 -0.0227060000 O 2.4955730000 -0.0001760000 -0.0542680000 H 2.9377470000 -0.7662140000 0.3305460000 H 2.9340160000 0.7680030000 0.3306630000 H -2.9374250000 0.7662810000 0.3305690000 H -2.9342170000 -0.7679340000 0.3307850000 O -2.4955880000 0.0000640000 -0.0542870000
$Ca(H_2O)@H_2O$ **-829.45839483075**	**$Ca(H_2O)_3$** **-905.8003411313**
Ca 1.6464860000 -0.2902080000 0.0021310000 O -2.7447260000 -0.4531700000 -0.0436240000 H -2.5201200000 -1.2342540000 -0.5621290000 H -3.0192530000 -0.8018080000 0.8111960000 H -1.3090060000 0.6629380000 0.0094520000 H -0.5796500000 1.9922360000 -0.2785070000 O -0.4429860000 1.1013010000 0.0407940000	Ca 0.0031210000 -0.8111140000 -0.0268530000 O 2.4196480000 -0.0114350000 0.0434860000 H 2.9130800000 -0.2729400000 -0.7462970000 H 2.8880910000 -0.4377190000 0.7745630000 O -0.0080400000 1.6925030000 -0.0803540000 H 0.7575520000 2.1929680000 0.2157240000 H -0.7858380000 2.1771810000 0.2103970000 H -2.8813990000 -0.4465990000 0.7763880000 H -2.9096080000 -0.2870820000 -0.7449950000 O -2.4171440000 -0.0190100000 0.0432790000
$Ca(H_2O)_2@H_2O$ **-905.80212192541**	**$Ca(H_2O)@2H_2O$** **-905.79787050138**
Ca 1.6946890000 -0.0447470000 -0.0664320000 O -0.2901680000 -1.5614110000 0.0837920000 H -0.3349490000 -2.4465830000 0.4380850000 H -1.2045610000 -1.2342410000 0.0396490000 H -0.1315570000 2.3145250000 -0.5506210000 H -0.2601860000 2.0872330000 0.9556900000 O -0.4079470000 1.6498910000 0.1011440000 O -2.6292400000 -0.1389850000 -0.0242790000 H -3.2392140000 -0.0978460000 -0.7664290000 H -2.1044770000 0.6758850000 -0.0730030000	Ca -2.0341440000 -0.0028990000 0.0022980000 O 1.8161590000 -2.4760100000 0.0063880000 H 1.5764590000 -3.0143990000 -0.7548790000 H 1.5511430000 -3.0028250000 0.7674070000 O 0.4312160000 0.0001980000 -0.0186980000 H 1.0022360000 -0.7719870000 -0.0117810000 H 0.9997470000 0.7741790000 -0.0112880000 H 1.5702400000 3.0173550000 -0.7568300000 H 1.5388200000 3.0097400000 0.7653620000 O 1.8081540000 2.4815510000 0.0068160000
$Ca(H_2O)_4$ **-982.1459897904**	**$Ca(H_2O)_3@H_2O$** **-982.14579176664**
Ca 0.0000860000 -0.3888760000 -0.0010960000 O 2.4433130000 -1.0902200000 -0.1566310000 H 2.5319100000 -1.5894680000 -0.9835260000 H 2.5585910000 -1.7585150000 0.5373280000 O 1.5707900000 1.5697330000 0.1813260000 H 2.4523730000 1.1797190000 0.2310190000 H 1.5337690000 2.2269920000 0.8820620000 O -2.4426700000 -1.0910570000 0.1581300000 H -2.5591310000 -1.7589090000 -0.5360670000 H -2.5285080000 -1.5910940000 0.9848690000 H -2.4528580000 1.1785870000 -0.2276190000 H -1.5368520000 2.2253650000 -0.8830350000 O -1.5715590000 1.5696480000 -0.1807140000	Ca -0.8777300000 0.8061310000 0.0489620000 O -2.8897880000 -0.7178410000 -0.0586230000 H -3.5400330000 -0.4108140000 -0.7029950000 H -3.3798910000 -0.7860050000 0.7707600000 O 0.1641080000 -1.4494080000 0.0426840000 H -0.2191070000 -2.2364520000 -0.3399360000 H 1.1298660000 -1.5490760000 -0.0034250000 H 1.6618420000 2.1551540000 0.6750860000 H 1.6406180000 2.0561230000 -0.8556230000 O 1.6077620000 1.5089420000 -0.0509550000 O 2.8723930000 -1.0844150000 -0.0740650000 H 3.4992590000 -1.2838810000 0.6274820000 H 2.7262520000 -0.1258920000 -0.0229170000

$Ca(H_2O)_5$ **-1058.4911179421**	**$Ca(H_2O)_4@H_2O$** **-1058.4885700036**
Ca 0.1973740000 0.4047070000 -0.0319180000	Ca 0.0000000000 0.0000000000 1.0246870000
O -2.0502220000 1.5708630000 -0.3582670000	O 0.0000000000 0.0000000000 -3.4607920000
H -2.1539660000 1.7107030000 -1.3152530000	H 0.7651650000 0.0000000000 -4.0471350000
H -1.8659990000 2.4615070000 -0.0133970000	H -0.7651650000 0.0000000000 -4.0471350000
O -0.8533400000 -1.6313340000 -1.1556700000	O 0.0000000000 2.4488860000 1.6949330000
H -1.1319740000 -1.5370650000 -2.0736070000	H 0.7630630000 2.5414920000 2.2866010000
H -1.6507000000 -1.8573890000 -0.6584500000	H -0.7630630000 2.5414920000 2.2866010000
O 2.6011750000 1.1960180000 0.0136240000	O 0.0000000000 -2.4488860000 1.6949330000
H 2.7185260000 1.6810700000 -0.8180670000	H 0.7630630000 -2.5414920000 2.2866010000
H 2.6421370000 1.8876520000 0.6919340000	H -0.7630630000 -2.5414920000 2.2866010000
O -1.7600740000 -0.6432420000 1.3118770000	O 0.0000000000 -1.4661520000 -0.9673670000
H -2.4063850000 0.0620590000 1.1527520000	H 0.0000000000 -2.4174460000 -0.8372820000
H -1.6996060000 -0.7182050000 2.2705600000	H 0.0000000000 -1.2838800000 -1.9130150000
H 2.6423670000 -1.2363820000 0.2495570000	H 0.0000000000 2.4174460000 -0.8372820000
H 1.6172160000 -2.2869040000 -0.2159110000	H 0.0000000000 1.2838800000 -1.9130150000
O 1.7300740000 -1.5249550000 0.3594650000	O 0.0000000000 1.4661520000 -0.9673670000
$Ca(H_2O)_3@2H_2O$ **-1058.4886476611**	
Ca 0.0000440000 -1.2167340000 -0.3952640000	
O -2.4005230000 -1.0032370000 0.2805870000	
O -0.0000260000 0.7152510000 1.2648400000	
O 2.4005900000 -1.0031260000 0.2806720000	
O 2.2243050000 1.7103990000 -0.3376310000	
O -2.2244270000 1.7103280000 -0.3375450000	
H -2.7688120000 2.4774820000 -0.5554380000	
H -1.6549280000 1.5689640000 -1.1195400000	
H 0.7591100000 1.2795900000 1.0749190000	
H -0.7591910000 1.2795600000 1.0749450000	
H -2.6912580000 -0.0983730000 0.0813010000	
H -3.0477520000 -1.5789200000 -0.1322700000	
H 2.7686200000 2.4775850000 -0.5555930000	
H 1.6548340000 1.5689080000 -1.1196290000	
H 2.6912660000 -0.0982490000 0.0813560000	
H 3.0478720000 -1.5787780000 -0.1321460000	
$Ca(H_2O)_6$ **-1134.8363108788**	**$Ca(H_2O)_5@H_2O$** **-1134.836852258**
Ca -0.0001620000 -0.0032500000 -0.1813960000	Ca 0.3139760000 -0.7352370000 -0.2012870000
O 0.4898100000 2.3278230000 -1.0202300000	O -1.6872850000 -0.0201480000 1.1689100000
O -1.0373560000 1.7178410000 1.2589950000	O -1.5210490000 -2.4248080000 -0.4885440000
O 1.7827130000 -1.5807240000 -1.0247530000	O 0.6835770000 1.7969130000 0.2830270000
O -0.9746270000 -1.7699790000 1.2466960000	O 2.3438600000 0.1225400000 -1.4441680000
O 2.0074650000 0.0397530000 1.2599190000	O 1.6321670000 -0.1980360000 1.8850420000
O -2.2674930000 -0.7302220000 -1.0224830000	O -1.9397460000 2.1758530000 -0.6503950000
H -2.0545640000 -1.0678560000 -1.9113590000	H -2.5545180000 2.8484880000 -0.9717470000
H -2.8759860000 0.0042520000 -1.2028780000	H -1.7862090000 1.5829750000 -1.4145710000
H 1.4572050000 -2.4751550000 -1.2151950000	H 1.3635460000 2.0359990000 -0.3581310000
H 1.9717290000 -1.2186480000 -1.9094050000	H -0.1163560000 2.2637230000 -0.0082650000
H 0.0854900000 2.3138550000 -1.9066720000	H -2.0752790000 0.7642640000 0.7546430000
H 1.4285910000 2.4904130000 -1.2060890000	H -2.3472240000 -0.7107750000 1.0513240000

H 2.4343910000 0.7834710000 1.6938610000	H 1.6331920000 -0.6178800000 2.7475470000
H 2.7037870000 -0.4346840000 0.7872390000	H 1.4313320000 0.7348910000 2.0314160000
H -0.9672750000 2.5572280000 0.7856780000	H -1.8398420000 -2.1283520000 -1.3608810000
H -1.8979930000 1.7208100000 1.6868580000	H -1.1753770000 -3.3121280000 -0.6585680000
H -1.7380530000 -2.1238440000 0.7718920000	H 3.1011190000 -0.4784310000 -1.4678640000
H -0.5481750000 -2.5207710000 1.6688340000	H 1.9939100000 0.1034610000 -2.3501510000

Table S5. Constrained C_s optimal geometry (Cartesian coordinates in Å) and the total energy (a.u.) of $Ca(H_2O)_6$.

	MP2		
	-1134.8127138677		
Ca	-0.294072	-0.008243	0.000000
O	-2.291487	-1.565968	0.000000
O	0.354034	-2.375528	0.000000
O	-0.182632	2.461910	-0.000000
O	0.354034	0.537226	2.360687
O	2.189620	0.209249	-0.000000
O	0.354034	0.537226	-2.360687
H	-0.389193	-2.987896	0.000000
H	-1.034157	2.922698	-0.000000
H	1.161756	-2.891572	0.000000
H	0.501373	3.147548	-0.000000
H	2.567705	0.647731	0.769575
H	2.567705	0.647731	-0.769575
H	-2.841320	-1.317859	0.761779
H	-2.841320	-1.317859	-0.761779
H	-0.021292	0.012047	3.078510
H	-0.021292	0.012047	-3.078510
H	0.005333	1.428666	2.511499
H	0.005333	1.428666	-2.511499

Table S6. Harmonic vibrational frequencies (cm^{-1}) at the DFT/B3LYP/cc-pVTZ(Ca,O) and aug-cc-pVTZ(H) level for the $Ca(H_2O)_{n=1-8}^{+}$.

$Ca(H_2O)^+$	$Ca(H_2O)_2^+$	$Ca(H_2O)_3^+$	$Ca(H_2O)_4^+$	$Ca(H_2O)_5^+$	$Ca(H_2O)_6^+$	$Ca(H_2O)_7^+$	$Ca(H_2O)_8^{+\,a}$
322.7	37.5	32.5	23.5	19.3	41.8	20.0	38.5 *i*
356.2	45.4	32.9	57.0	24.4	41.8	30.3	37.9 *i*
435.5	74.5	64.6	68.9	33.8	41.8	47.8	40.4
1645.7	265.4	145.3	69.1	44.8	52.8	55.5	41.2
3712.5	326.7	148.6	70.0	53.4	52.8	62.4	55.4
3793.3	328.7	149.1	70.2	56.8	52.8	64.7	68.7
	338.2	255.1	121.2	61.2	68.0	85.3	69.0
	394.1	291.9	151.6	99.0	68.0	101.6	80.1
	401.8	306.6	225.5	132.7	68.0	103.4	88.9
	1638.0	306.7	231.8	176.3	149.8	115.9	92.5
	1641.1	313.1	241.3	182.5	149.8	122.3	94.2
	3719.5	313.1	245.6	231.6	182.5	154.8	109.1
	3720.9	328.1	260.9	238.7	182.5	165.8	109.2
	3803.8	362.4	289.6	244.0	182.5	172.5	168.9
	3805.2	362.6	292.1	244.2	201.4	184.2	169.5
		1617.3	296.6	255.2	201.4	187.7	176.7
		1617.4	302.7	264.3	201.4	194.7	176.8
		1624.6	314.8	268.4	232.2	199.0	181.1
		3687.4	340.3	279.6	232.2	209.9	190.5
		3687.5	351.3	281.0	239.1	216.8	190.9
		3693.5	395.5	300.4	239.1	224.1	196.0
		3781.2	1610.3	305.0	239.1	228.8	198.5
		3781.2	1612.1	342.1	243.4	249.6	223.5
		3783.0	1618.4	346.8	260.0	252.9	230.8
			1631.8	381.5	301.9	264.6	231.1
			3675.2	391.8	301.9	271.1	239.2
			3679.2	399.2	301.9	283.3	251.6
			3687.5	1591.8	369.4	297.6	256.7
			3742.0	1593.8	369.4	302.0	256.8
			3774.9	1614.6	369.4	309.2	271.5
			3775.6	1620.1	381.2	352.8	272.2
			3776.9	1620.7	381.2	367.7	298.4
			3836.7	3604.9	381.2	380.1	299.3
				3611.0	1600.2	386.9	300.5
				3657.8	1600.2	389.3	300.8
				3665.4	1602.5	397.9	356.2
				3676.6	1602.5	398.7	365.1
				3703.0	1602.5	401.3	365.2
				3708.0	1604.8	407.1	373.6
				3760.9	3603.6	1580.3	390.4
				3761.9	3603.6	1596.2	391.3
				3763.3	3614.0	1599.1	391.7
					3614.0	1599.8	400.6

3614.0	1601.1	400.9
3671.3	1605.3	418.6
3713.2	1607.1	1591.7
3713.2	3545.3	1591.9
3713.2	3592.7	1592.8
3717.3	3597.1	1592.8
3717.3	3628.1	1593.9
3717.3	3629.1	1594.0
	3671.7	1594.2
	3691.7	1595.3
	3703.4	3650.1
	3708.2	3654.3
	3715.1	3654.4
	3724.6	3658.4
	3780.4	3658.4
	3813.1	3664.6
	3818.3	3665.1
		3698.4
		3758.6
		3759.7
		3760.2
		3761.3
		3761.4
		3762.4
		3762.6
		3763.3

[a] The two imaginary frequencies correspond to small rotations of water molecules. We were not able to eliminate them.

Table S7. Harmonic vibrational frequencies (cm^{-1}) at the DFT/B3LYP (Ca, O: cc-pVTZ and H/aug-cc-pVTZ level for the $Ca(H_2O)_{n=1-8}$.

$Ca(H_2O)$	$Ca(H_2O)_2$	$Ca(H_2O)_3$	$Ca(H_2O)_4$	$Ca(H_2O)_5$	$Ca(H_2O)_6$	$Ca(H_2O)_7$	$Ca(H_2O)_8$
180.1	41.6	28.2	26.5	21.5	31.2	26.8	42.8
261.4	46.1	37.9	35.1	30.1	31.9	30.0	44.6
314.3	62.1	47.0	42.5	38.2	39.5	54.4	61.2
1572.1	214.7	57.7	56.7	48.7	44.2	64.7	74.5
3592.6	243.2	108.8	59.7	54.6	49.0	69.4	74.5
3695.8	245.7	118.9	97.7	59.6	51.0	75.7	92.5
	310.7	230.9	112.8	64.4	55.6	84.3	100.9
	331.4	245.0	133.0	65.4	66.5	98.8	102.9
	336.1	256.5	179.3	79.3	69.0	104.9	102.9
	1564.7	270.3	223.6	113.3	75.6	106.4	115.6
	1565.1	293.5	229.9	116.0	100.4	120.0	115.6
	3579.5	307.7	250.0	128.4	100.9	125.8	122.8
	3580.1	323.5	279.5	142.4	169.3	147.1	124.7
	3673.4	336.0	288.7	166.1	170.3	157.8	171.8
	3676.7	360.8	300.0	168.1	189.2	182.2	174.0
		1551.4	308.8	242.1	225.6	193.9	180.2
		1553.4	318.2	263.3	225.9	204.6	181.2
		1560.7	335.0	266.9	244.4	210.9	194.5
		3533.8	353.8	286.3	245.6	215.3	194.5
		3542.4	399.3	306.2	251.7	234.4	195.3
		3571.8	404.0	316.3	267.2	248.8	195.3
		3622.2	1534.2	321.0	275.6	273.2	213.8
		3630.2	1542.9	348.8	288.3	279.6	214.8
		3661.7	1558.8	358.3	288.6	281.5	214.8
			1586.3	363.8	301.5	296.2	239.9
			3483.4	390.6	312.3	304.2	251.4
			3502.8	428.4	312.6	313.1	262.8
			3551.8	1541.1	405.4	337.3	270.1
			3568.8	1541.2	405.9	346.9	270.1
			3581.6	1548.4	411.6	349.9	311.1
			3639.5	1551.5	412.4	367.8	312.4
			3646.1	1561.0	420.2	372.6	312.4
			3748.2	3451.2	421.0	424.4	312.7
				3452.5	1551.3	437.8	343.0
				3473.1	1551.4	441.6	345.0
				3487.9	1557.0	443.4	345.0
				3519.2	1575.2	444.7	393.9
				3528.3	1575.4	452.1	423.8
				3546.2	1576.5	461.9	423.8
				3551.6	3461.1	1546.5	431.7
				3569.5	3461.2	1552.4	433.3
				3573.8	3494.9	1565.6	434.5
					3540.6	1570.5	444.8

3540.8	1576.0	444.8
3546.2	1578.8	456.9
3580.5	1585.6	1562.2
3580.6	3427.0	1562.2
3608.8	3443.3	1562.8
3685.0	3477.0	1562.9
3685.2	3519.4	1563.1
3687.7	3531.1	1563.7
	3542.9	1567.1
	3585.7	1567.1
	3611.6	3568.1
	3619.7	3571.6
	3638.1	3571.6
	3658.1	3585.8
	3660.8	3585.8
	3748.0	3587.6
		3587.7
		3618.0
		3661.6
		3664.9
		3670.6
		3670.6
		3672.5
		3672.5
		3673.0
		3673.1

Table S8. Electron attachment energies (eV) and pole strengths (in parentheses) of $Ca(H_2O)_6^{2+}$ from diagonal electron propagator methods calculated at the geometry of $Ca(H_2O)_6^{+}$ using the cc-pVTZ(Ca) cc-pVTZ(O) d-aug-cc-pVTZ(H) basis sets. 1s, 2s, 2p, 3s, 3p orbitals of Ca and 1s of O were frozen.

State (T_h)	Config.	KT	D2	P3	P3+
1^2A_g	$1s^1$	-5.528	-6.114 (0.983)	-6.122 (0.980)	-6.122 (0.980)
1^2T_u	$1p^1$	-4.767	-5.185 (0.987)	-5.195 (0.984)	-5.195 (0.984)
		-4.767	-5.185 (0.987)	-5.195 (0.984)	-5.195 (0.984)
		-4.767	-5.185 (0.987)	-5.195 (0.984)	-5.195 (0.984)
1^2E_g	$1d^1$	-4.040	-4.418 (0.988)	-4.429 (0.986)	-4.428 (0.986)
		-4.040	-4.418 (0.988)	-4.429 (0.986)	-4.428 (0.986)
1^2T_g		-3.826	-4.043 (0.992)	-4.053 (0.990)	-4.053 (0.991)
		-3.826	-4.043 (0.992)	-4.053 (0.990)	-4.053 (0.991)
		-3.826	-4.043 (0.992)	-4.053 (0.990)	-4.053 (0.991)
2^2A_g	$2s^1$	-3.199	-3.431 (0.993)	-3.431 (0.992)	-3.431 (0.992)
3^2T_u	$1f^1$	-3.105	-3.326 (0.993)	-3.335 (0.991)	-3.334 (0.991)
		-3.105	-3.326 (0.993)	-3.335 (0.991)	-3.334 (0.991)
		-3.105	-3.326 (0.993)	-3.335 (0.991)	-3.334 (0.991)
1^2A_u		-2.841	-3.042 (0.994)	-3.059 (0.992)	-3.058 (0.992)
4^2T_u		-2.691	-2.866 (0.994)	-2.878 (0.993)	-2.877 (0.993)
		-2.691	-2.866 (0.994)	-2.878 (0.993)	-2.877 (0.993)
		-2.691	-2.866 (0.994)	-2.878 (0.993)	-2.877 (0.993)
2^2T_u	$2p^1$	-2.832	-3.012 (0.994)	-3.016 (0.993)	-3.016 (0.993)
		-2.832	-3.012 (0.994)	-3.016 (0.993)	-3.016 (0.993)
		-2.832	-3.012 (0.994)	-3.016 (0.993)	-3.016 (0.993)
2^2E_g	$2d^1$	-2.420	-2.596 (0.995)	-2.598 (0.994)	-2.598 (0.994)
		-2.420	-2.596 (0.995)	-2.598 (0.994)	-2.598 (0.994)
2^2T_g		-2.359	-2.531 (0.994)	-2.531 (0.993)	-2.531 (0.993)
		-2.359	-2.531 (0.994)	-2.531 (0.993)	-2.531 (0.993)
		-2.359	-2.531 (0.994)	-2.531 (0.993)	-2.531 (0.993)
3^2T_g	$1g^1$	-2.000	-2.413 (0.987)	-2.416 (0.985)	-2.415 (0.985)
		-2.000	-2.413 (0.987)	-2.416 (0.985)	-2.415 (0.985)
		-2.000	-2.413 (0.987)	-2.416 (0.985)	-2.415 (0.985)

Accuracy of the methods increases in the order of KT < D2 < P3 < P3+ (Dolgounitcheva, O.; Díaz-Tinoco, M.; Zakrzewski, V. G.; Richard, R. M.; Marom, N.; Sherill, C. D.; Ortiz J. V. *J. Chem. Theory Comput.* **2016**, *12*, 627-637)

KT: Koopmans's theorem
D2: Diagonal second-order approximation
P3: Partial third-order quasiparticle method
P3+: Renormalized partial third-order quasiparticle method

Table S9. Excitation energies (eV) of $Ca(H_2O)_6^+$ inferred from electron attachment energies in Table S8.

State (T_h)	Config.	KT	D2	P3	P3+
1^2A_g	$1s^1$	0.000	0.000	0.000	0.000
1^2T_u	$1p^1$	0.761	0.929	0.927	0.927
		0.761	0.929	0.927	0.927
		0.761	0.929	0.927	0.927
1^2E_g	$1d^1$	1.488	1.696	1.694	1.694
		1.488	1.696	1.694	1.694
1^2T_g		1.702	2.071	2.069	2.069
		1.702	2.071	2.069	2.069
		1.702	2.071	2.069	2.069
2^2A_g	$2s^1$	2.329	2.683	2.691	2.691
3^2T_u	$1f^1$	2.423	2.788	2.788	2.788
		2.423	2.788	2.788	2.788
		2.423	2.788	2.788	2.788
1^2A_u		2.687	3.072	3.064	3.064
4^2T_u		2.837	3.248	3.245	3.245
		2.837	3.248	3.245	3.245
		2.837	3.248	3.245	3.245
2^2T_u	$2p^1$	2.696	3.102	3.106	3.106
		2.696	3.102	3.106	3.106
		2.696	3.102	3.106	3.106
2^2E_g	$2d^1$	3.108	3.518	3.524	3.524
		3.108	3.518	3.524	3.524
2^2T_g		3.169	3.583	3.591	3.591
		3.169	3.583	3.591	3.591
		3.169	3.583	3.591	3.591
3^2T_g	$1g^1$	3.528	3.701	3.707	3.707
		3.528	3.701	3.707	3.707
		3.528	3.701	3.707	3.707

Table S10. Electron attachment energies (eV) and pole strengths (in parentheses) of $Ca(H_2O)_6^{2+}$ from diagonal electron propagator methods[a] calculated at the geometry of $Ca(H_2O)_6^{+}$ using the cc-pCVTZ(Ca) cc-pVTZ(O) d-aug-cc-pVTZ(H) basis sets. Only the 1s orbitals of Ca and O were frozen.

State (T_h)	Config.	KT	D2	P3	P3+
1^2A_g	$1s^1$	-5.528	-6.159 (0.982)	-6.158 (0.979)	-6.158 (0.979)
1^2T_u	$1p^1$	-4.767	-5.205 (0.986)	-5.212 (0.984)	-5.211 (0.984)
		-4.767	-5.205 (0.986)	-5.212 (0.984)	-5.211 (0.984)
		-4.767	-5.205 (0.986)	-5.212 (0.984)	-5.211 (0.984)
1^2E_g	$1d^1$	-4.040	-4.435 (0.988)	-4.445 (0.985)	-4.444 (0.986)
		-4.040	-4.435 (0.988)	-4.445 (0.985)	-4.444 (0.986)
1^2T_g		-3.826	-4.055 (0.992)	-4.062 (0.990)	-4.062 (0.990)
		-3.826	-4.055 (0.992)	-4.062 (0.990)	-4.062 (0.990)
		-3.826	-4.055 (0.992)	-4.062 (0.990)	-4.062 (0.990)
2^2A_g	$2s^1$	-3.199	-3.461 (0.992)	-3.455 (0.991)	-3.455 (0.991)
3^2T_u	$1f^1$	-3.105	-3.334 (0.992)	-3.342 (0.991)	-3.341 (0.991)
		-3.105	-3.334 (0.992)	-3.342 (0.991)	-3.341 (0.991)
		-3.105	-3.334 (0.992)	-3.342 (0.991)	-3.341 (0.991)
1^2A_u		-2.841	-3.054 (0.994)	-3.069 (0.992)	-3.068 (0.992)
4^2T_u		-2.691	-2.873 (0.994)	-2.885 (0.993)	-2.884 (0.993)
		-2.691	-2.873 (0.994)	-2.885 (0.993)	-2.884 (0.993)
		-2.691	-2.873 (0.994)	-2.885 (0.993)	-2.884 (0.993)
2^2T_u	$2p^1$	-2.832	-3.025 (0.994)	-3.026 (0.993)	-3.026 (0.993)
		-2.832	-3.025 (0.994)	-3.026 (0.993)	-3.026 (0.993)
		-2.832	-3.025 (0.994)	-3.026 (0.993)	-3.026 (0.993)
2^2E_g	$2d^1$	-2.420	-2.607 (0.994)	-2.609 (0.993)	-2.608 (0.993)
		-2.420	-2.607 (0.994)	-2.609 (0.993)	-2.608 (0.993)
2^2T_g		-2.359	-2.564 (0.993)	-2.559 (0.992)	-2.560 (0.992)
		-2.359	-2.564 (0.993)	-2.559 (0.992)	-2.560 (0.992)
		-2.359	-2.564 (0.993)	-2.559 (0.992)	-2.560 (0.992)
3^2T_g	$1g^1$	-2.000	-2.536 (0.984)	-2.524 (0.982)	-2.525 (0.982)
		-2.000	-2.536 (0.984)	-2.524 (0.982)	-2.525(0.982)
		-2.000	-2.536 (0.984)	-2.524 (0.982)	-2.525 (0.982)

Table S11. Excitation energies (eV) of $Ca(H_2O)_6^+$ inferred from electron attachment energies in Table S10.

State (T_h)	Config.	KT	D2	P3	P3+
1^2A_g	$1s^1$	0.000	0.000	0.000	0.000
1^2T_u	$1p^1$	0.761	0.954	0.946	0.947
		0.761	0.954	0.946	0.947
		0.761	0.954	0.946	0.947
1^2E_g	$1d^1$	1.488	1.724	1.713	1.714
		1.488	1.724	1.713	1.714
1^2T_g		1.702	2.104	2.096	2.096
		1.702	2.104	2.096	2.096
		1.702	2.104	2.096	2.096
2^2A_g	$2s^1$	2.329	2.698	2.703	2.703
3^2T_u	$1f^1$	2.423	2.825	2.816	2.817
		2.423	2.825	2.816	2.817
		2.423	2.825	2.816	2.817
1^2A_u		2.687	3.105	3.089	3.090
4^2T_u		2.837	3.286	3.273	3.274
		2.837	3.286	3.273	3.274
		2.837	3.286	3.273	3.274
2^2T_u	$2p^1$	2.696	3.134	3.132	3.132
		2.696	3.134	3.132	3.132
		2.696	3.134	3.132	3.132
2^2E_g	$2d^1$	3.108	3.552	3.549	3.550
		3.108	3.552	3.549	3.550
2^2T_g		3.169	3.595	3.599	3.598
		3.169	3.595	3.599	3.598
		3.169	3.595	3.599	3.598
3^2T_g	$1g^1$	3.528	3.623	3.634	3.633
		3.528	3.623	3.634	3.633
		3.528	3.623	3.634	3.633

Table S12. Electron attachment energies (eV) and pole strengths (in parentheses) of $Ca(H_2O)_8^{2+}$ from diagonal electron propagator methods calculated at the geometry of $Ca(H_2O)_8^{+}$ using the cc-pVTZ(Ca) cc-pVTZ(O) d-aug-cc-pVTZ(H) basis sets. 1s, 2s, 2p, 3s, 3p orbitals of Ca and 1s of O were frozen.

State (C_4)	Config.	KT	D2	P3	P3+
^2A	$1s^1$	-5.171	-5.766 (0.982)	-5.772 (0.979)	-5.772 (0.980)
^2E	$1p^1$	-4.615	-5.053 (0.986)	-5.062 (0.983)	-5.062 (0.983)
		-4.615	-5.053 (0.986)	-5.062 (0.983)	-5.062 (0.983)
^2A		-4.343	-4.752 (0.987)	-4.760 (0.984)	-4.759 (0.984)
^2E	$1d^1$	-3.888	-4.197 (0.989)	-4.208 (0.987)	-4.207 (0.987)
		-3.888	-4.197 (0.989)	-4.208 (0.987)	-4.207 (0.987)
^2E		-3.739	-4.063 (0.989)	-4.073 (0.987)	-4.073 (0.987)
		-3.739	-4.063 (0.989)	-4.073 (0.987)	-4.073 (0.987)
^2A		-3.592	-3.807 (0.992)	-3.817 (0.991)	-3.816 (0.991)
^2A	$2s^1$	-2.985	-3.219 (0.993)	-3.218 (0.992)	-3.218 (0.992)
^2E	$1f^1$	-3.074	-3.296 (0.993)	-3.308 (0.991)	-3.307 (0.991)
		-3.074	-3.296 (0.993)	-3.308 (0.991)	-3.307 (0.991)
^2E		-2.972	-3.190 (0.993)	-3.201 (0.991)	-3.200 (0.991)
		-2.972	-3.190 (0.993)	-3.201 (0.991)	-3.200 (0.991)
^2E		-2.865	-3.040 (0.994)	-3.050 (0.992)	-3.049 (0.993)
		-2.865	-3.040 (0.994)	-3.050 (0.992)	-3.049 (0.993)
^2A		-2.834	-3.012 (0.994)	-3.022 (0.993)	-3.022 (0.993)
^2E	$2p^1$	-2.696	-2.882 (0.994)	-2.884 (0.993)	-2.884 (0.993)
		-2.696	-2.882 (0.994)	-2.884 (0.993)	-2.884 (0.993)
^2A		-2.595	-2.789 (0.994)	-2.790 (0.993)	-2.790 (0.993)

Table S13. Excitation energies (eV) of $Ca(H_2O)_8^+$ inferred from electron attachment energies in Table S12.

State (C_4)	Config.	KT	D2	P3	P3+
^2A	$1s^1$	0.000	0.000	0.000	0.000
^2E	$1p^1$	0.556	0.713	0.710	0.710
		0.556	0.713	0.710	0.710
^2A		0.828	1.014	1.012	1.013
^2E	$1d^1$	1.283	1.569	1.564	1.565
		1.283	1.569	1.564	1.565
^2E		1.432	1.703	1.699	1.699
		1.432	1.703	1.699	1.699
^2A		1.579	1.959	1.955	1.956
^2A	$2s^1$	2.186	2.547	2.554	2.554
^2E	$1f^1$	2.097	2.470	2.464	2.465
		2.097	2.470	2.464	2.465
^2E		2.199	2.576	2.571	2.572
		2.199	2.576	2.571	2.572
^2E		2.306	2.726	2.722	2.723
		2.306	2.726	2.722	2.723
^2A		2.337	2.754	2.750	2.750
^2E	$2p^1$	2.475	2.884	2.888	2.888
		2.475	2.884	2.888	2.888
^2A		2.576	2.977	2.982	2.982

Table S14. Electron attachment energies (eV) and pole strengths (in parentheses) of $Ca(H_2O)_8^{2+}$ from diagonal electron propagator methods calculated at the geometry of $Ca(H_2O)_8^{+}$ using the cc-pCVTZ(Ca) cc-pVTZ(O) d-aug-cc-pVTZ(H) basis sets. Only the 1s orbitals of Ca and O were frozen.

State (C_4)	Config.	KT	D2	P3	P3+
^2A	$1s^1$	-5.171	-5.792 (0.982)	-5.792 (0.979)	-5.792 (0.979)
^2E	$1p^1$	-4.615	-5.066 (0.985)	-5.073 (0.983)	-5.072 (0.983)
		-4.615	-5.066 (0.985)	-5.073 (0.983)	-5.072 (0.983)
^2A		-4.343	-4.765 (0.986)	-4.77 (0.984)	-4.77 (0.984)
^2E	$1d^1$	-3.888	-4.206 (0.989)	-4.215 (0.987)	-4.215 (0.987)
		-3.888	-4.206 (0.989)	-4.215 (0.987)	-4.215 (0.987)
^2E		-3.739	-4.073 (0.989)	-4.082 (0.987)	-4.081 (0.987)
		-3.739	-4.073 (0.989)	-4.082 (0.987)	-4.081 (0.987)
^2A		-3.592	-3.815 (0.992)	-3.823 (0.991)	-3.822 (0.991)
^2A	$2s^1$	-2.985	-3.234 (0.993)	-3.229 (0.992)	-3.230 (0.992)
^2E	$1f^1$	-3.074	-3.304 (0.992)	-3.315 (0.991)	-3.314 (0.991)
		-3.074	-3.304 (0.992)	-3.315 (0.991)	-3.314 (0.991)
^2E		-2.972	-3.199 (0.993)	-3.209 (0.991)	-3.208 (0.991)
		-2.972	-3.199 (0.993)	-3.209 (0.991)	-3.208 (0.991)
^2E		-2.865	-3.045 (0.994)	-3.054 (0.992)	-3.054 (0.992)
		-2.865	-3.045 (0.994)	-3.054 (0.992)	-3.054 (0.992)
^2A		-2.834	-3.018 (0.994)	-3.028 (0.993)	-3.027 (0.993)
^2E	$2p^1$	-2.696	-2.889 (0.994)	-2.889 (0.993)	-2.889 (0.993)
		-2.696	-2.889 (0.994)	-2.889 (0.993)	-2.889 (0.993)
^2A		-2.595	-2.798 (0.994)	-2.796 (0.993)	-2.796 (0.993)

Table S15. Excitation energies (eV) of $Ca(H_2O)_8^+$ inferred from electron attachment energies in Table S14.

State (C_4)	Config.	KT	D2	P3	P3+
^2A	$1s^1$	0.000	0.000	0.000	0.000
^2E	$1p^1$	0.556	0.726	0.719	0.720
		0.556	0.726	0.719	0.720
^2A		0.828	1.027	1.022	1.022
^2E	$1d^1$	1.283	1.586	1.577	1.577
		1.283	1.586	1.577	1.577
^2E		1.432	1.719	1.710	1.711
		1.432	1.719	1.710	1.711
^2A		1.579	1.977	1.969	1.970
^2A	$2s^1$	2.186	2.558	2.563	2.562
^2E	$1f^1$	2.097	2.488	2.477	2.478
		2.097	2.488	2.477	2.478
^2E		2.199	2.593	2.583	2.584
		2.199	2.593	2.583	2.584
^2E		2.306	2.747	2.738	2.738
		2.306	2.747	2.738	2.738
^2A		2.337	2.774	2.764	2.765
^2E	$2p^1$	2.475	2.903	2.903	2.903
		2.475	2.903	2.903	2.903
^2A		2.576	2.994	2.996	2.996

Table S16. Electron attachment energies (eV) and pole strengths (in parentheses) of $[Ca(H_2O)_6@12H_2O]^{2+}$ from diagonal electron propagator methods calculated at the geometry of $[Ca(H_2O)_6@12H_2O]^{+}$ using the cc-pVDZ(Ca) cc-pVDZ(O) d-aug-cc-pVDZ(H) basis sets. 1s, 2s, 2p, 3s, 3p orbitals of Ca and 1s of O were frozen.

State (S_6)	Config.	KT	D2	P3	P3+
^2A_g	$1s^1$	-3.759	-4.191 (0.986)	-4.208 (0.983)	-4.207 (0.983)
^2E_u	$1p^1$	-3.517	-3.870 (0.988)	-3.888 (0.985)	-3.887 (0.985)
^2E_u		-3.517	-3.870 (0.988)	-3.888 (0.985)	-3.887 (0.985)
^2A_u		-3.300	-3.545 (0.991)	-3.562 (0.989)	-3.560 (0.989)
^2E_g	$1d^1$	-3.121	-3.388 (0.990)	-3.406 (0.988)	-3.405 (0.988)
^2E_g		-3.121	-3.388 (0.990)	-3.406 (0.988)	-3.405 (0.988)
^2E_g		-3.010	-3.230 (0.992)	-3.246 (0.990)	-3.245 (0.990)
^2E_g		-3.010	-3.230 (0.992)	-3.246 (0.990)	-3.245 (0.990)
^2A_g		-2.821	-2.970 (0.994)	-2.983 (0.993)	-2.982 (0.993)

Table S17. Excitation energies (eV) of $[Ca(H_2O)_6@12H_2O]^{+}$ inferred from electron attachment energies in Table S16.

State (S_6)	Config.	KT	D2	P3	P3+
^2A_g	$1s^1$	0.000	0.000	0.000	0.000
^2E_u	$1p^1$	0.242	0.321	0.320	0.320
^2E_u		0.242	0.321	0.320	0.320
^2A_u		0.459	0.646	0.646	0.647
^2E_g	$1d^1$	0.638	0.803	0.802	0.802
^2E_g		0.638	0.803	0.802	0.802
^2E_g		0.749	0.961	0.962	0.962
^2E_g		0.749	0.961	0.962	0.962
^2A_g		0.938	1.221	1.225	1.225

Table S18. Electron attachment energies (eV) and pole strengths (in parentheses) of $[Ca(H_2O)_6@12H_2O]^{2+}$ from D2: Diagonal second-order approximation calculated at the geometry of $[Ca(H_2O)_6@12H_2O]^{+}$ using the cc-pVTZ(Ca) cc-pVTZ(O) d-aug-cc-pVTZ(H) basis sets. 1s, 2s, 2p, 3s, 3p orbitals of Ca and 1s of O were frozen.

State (S_6)	Config.	D2
^2A_g	$1s^1$	-4.243 (0.985)
^2E_u	$1p^1$	-3.916 (0.987)
^2E_u		-3.916 (0.987)
^2A_u		-3.580 (0.990)
^2E_g	$1d^1$	-3.425 (0.990)
^2E_g		-3.425 (0.990)
^2E_g		-3.260 (0.991)
^2E_g		-3.260 (0.991)
^2A_g		-2.993 (0.994)

Table S19. Excitation energies (eV) of $[Ca(H_2O)_6@12H_2O]^{+}$ inferred from electron attachment energies in Table S18.

State (S_6)	Config.	D2
^2A_g	$1s^1$	0.000
^2E_u	$1p^1$	0.327
^2E_u		0.327
^2A_u		0.663
^2E_g	$1d^1$	0.818
^2E_g		0.818
^2E_g		0.983
^2E_g		0.983
^2A_g		1.250

Table S20. Cartesian coordinates (Å) of the CAM-B3LYP/aug-cc-pVTZ optimized $Ca(H_2O)_6@12H_2O^+$ structure.

Ca	0.000000	0.000000	0.000000
O	-1.159813	1.554471	1.315858
O	-1.926118	-0.227192	-1.315858
O	0.766305	1.781663	-1.315858
O	-0.766305	-1.781663	1.315858
O	1.926118	0.227192	1.315858
O	1.159813	-1.554471	-1.315858
H	-2.103878	1.493699	1.538009
H	-0.824473	2.441917	1.530488
H	-2.345521	-1.075163	-1.538009
H	-2.526998	0.506944	-1.530488
H	1.702526	1.934973	-1.530488
H	0.241642	2.568862	-1.538009
H	-1.702526	-1.934973	1.530488
H	-0.241642	-2.568862	1.538009
H	2.526998	-0.506944	1.530488
H	2.345521	1.075163	1.538009
H	2.103878	-1.493699	-1.538009
H	0.824473	-2.441917	-1.530488
O	-3.895558	0.991970	1.175411
O	0.219244	3.973081	1.270403
O	-2.806851	-2.877667	-1.175411
O	-3.331167	2.176411	-1.270403
O	3.550411	1.796670	-1.270403
O	-1.088708	3.869638	-1.175411
O	-3.550411	-1.796670	1.270403
O	1.088708	-3.869638	1.175411
O	3.331167	-2.176411	1.270403
O	2.806851	2.877667	1.175411
O	3.895558	-0.991970	-1.175411
O	-0.219244	-3.973081	-1.270403
H	-4.619779	1.382296	1.677713
H	-3.876854	1.443883	0.305010
H	0.196041	4.699351	1.903312
H	1.152246	3.671338	1.218573
H	-3.188866	-2.635513	-0.305010
H	-3.506993	-3.309698	-1.677713
H	-2.603349	2.833543	-1.218573
H	-3.971737	2.519452	-1.903312
H	3.755595	0.837795	-1.218573
H	4.167778	2.179899	-1.903312
H	-0.687988	4.079395	-0.305010
H	-1.112786	4.691994	-1.677713

H	-4.167778	-2.179899	1.903312
H	-3.755595	-0.837795	1.218573
H	1.112786	-4.691994	1.677713
H	0.687988	-4.079395	0.305010
H	3.971737	-2.519452	1.903312
H	2.603349	-2.833543	1.218573
H	3.506993	3.309698	1.677713
H	3.188866	2.635513	0.305010
H	3.876854	-1.443883	-0.305010
H	4.619779	-1.382296	-1.677713
H	-1.152246	-3.671338	-1.218573
H	-0.196041	-4.699351	-1.903312

Table S21. Electronic terms, electronic configurations (Config.), and vertical excitation energies (eV) at CASSCF and CASPT2 for several low-lying states of $Ca(H_2O)_6$.

State (C_s)	Config.	CASSCF	CASPT2
$1^1A'$	$1s^2$	0.00	0.00
$1^3A'$	$1s^1 1p^1$	0.44	0.60
$1^3A''$	$1s^1 1p^1$	0.43	0.64
$2^3A'$	$1s^1 1p^1$	0.69	0.92
$2^1A'$	$1s^1 1p^1/1s^1 1d^1$	0.92	1.14
$1^1A''$	$1s^1 1p^1/1s^1 1d^1$	1.05	1.27
$3^1A'$	$1s^1 1p^1/1s^1 1d^1$	1.04	1.33
$2^1A''$	$1s^1 1d^1/1p^2$	1.25	1.58
$4^1A'$	$1s^1 1d^1/1p^2$	1.28	1.58
$3^3A'$	$1s^1 1d^1$	1.48	1.64
$4^3A'$	$1s^1 1d^1$	1.41	1.68
$5^1A'$	$1s^1 1p^1/1p^2/1s^1 1d^1$	1.71	1.73
$5^3A'$	$1s^1 1d^1$	1.60	1.79
$2^3A''$	$1s^1 1d^1$	1.60	1.84
$3^3A''$	$1s^1 1d^1$	1.66	1.89
$3^1A''$	$1s^1 1p^1/1p^2/1s^1 1d^1$	1.76	1.91
$6^1A'$	$1p^2$	1.86	1.97
$4^3A''$	$1p^2$	1.71	1.98
$6^3A'$	$1p^2$	2.00	2.28
$5^3A''$	$1p^2$	1.97	2.29
$7^1A'$	$1s^1 1d^1/1p^2/1p^1 1d^1$	2.23	
$4^1A''$	$1s^1 1d^1/1p^2$	2.33	2.56
$7^3A'$	$1p^1 1d^1$	2.40	
$6^3A''$	$1p^1 1d^1$	2.41	
$8^1A'$	$1s^1 1d^1/1p^2/1p^1 1d^1$	2.42	
$5^1A''$	$1p^1 1d^1$	2.49	2.84
$7^3A''$	$1p^1 1d^1$	2.53	
$8^3A'$	$1p^1 1d^1$	2.57	
$9^1A'$	$1p^1 1d^1$	2.58	
$6^1A''$	$1p^1 1d^1$	2.60	2.96
$8^3A''$	$1p^1 1d^1$	2.61	
$9^3A'$	$1p^1 1d^1$	2.66	
$7^1A''$	$1p^1 1d^1/1s^1 1d^1$	2.88	
$9^3A''$	$1p^1 1d^1$	2.90	
$8^1A''$	$1p^1 1d^1$	3.28	
$9^1A''$	$1p^1 1d^1$	3.31	

Table S22. Electronic terms, electronic configurations (Config.), and vertical excitation energies (eV) at CASSCF and CASPT2 for several low-lying states of $Ca(H_2O)_8$.

State (S_8)	Config.	CASSCF	CASPT2
^1A	$1s^2$	0.00	0.00
$^3E_1$	$1s^1 1p^1$	0.23	0.33
^3B	$1s^1 1p^1$	0.56	0.69
$^1E_2$	$1s^1 1d^1/1p^2$	0.70	0.93
$^1E_1$	$1s^1 1p^1$	0.89	0.99
$^1E_3$	$1s^1 1d^1/1p^2$	0.93	1.16
^1B	$1s^1 1p^1$	0.97	1.09
^3A	$1p^2$	0.99	1.21
^1A	$1s^1 1d^1/1p^2$	1.09	1.32
$^3E_3$	$1p^2$	1.21	1.43
$^3E_2$	$1s^1 1d^1$	1.31	1.33
$^3E_1$ or $^3E_3$	$1p^1 1d^1$	1.40	1.59
$^3E_3$	$1s^1 1d^1$	1.50	
^3A	$1s^1 1d^1$	1.54	1.64
$^3E_2$	$1p^1 1d^1$	1.62	
^1A	$1s^2/1p^2/1d^2$	1.68	1.81
^1B	$1p^1 1d^1$	1.69	
$^1E_2$	$1p^1 1d^1$	1.70	
$^3E_1$	$1p^1 1d^1$	1.76	
$^1E_1$	$1p^1 1d^1$	1.78	2.08
^3B	$1p^1 1d^1$	1.81	
^1A	$1s^1 1d^1/1p^2/1d^2$	2.05	
$^1E_3$	$1s^1 1d^1/1p^1 1p^1$	2.05	
$^3E_1$ or $^3E_3$	$1p^1 1d^1$	2.07	
^3B	$1p^1 1d^1$	2.10	
$^1E_2$	$1s^1 1d^1/1p^1 1p^1/1d^1 1d^1$	2.20	
$^3E_1$	$1p^1 1d^1$	2.26	
$^3E_2$	$1p^1 1d^1$	2.29	
^3B	$1p^1 1d^1$	2.39	