Supplementary information

for

Confinement of hydrogen and hydroxyl radicals in water cages: a density functional theory study

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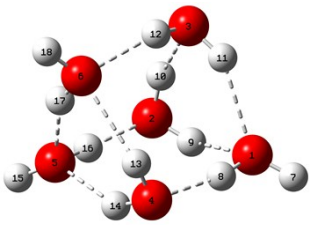
different angles θ.

Fig. S4 Energies for the approach of H· (top) or OH· (bottom) toward water, calculated at the CCSD(T)/6-311++G and UB97D-D3/6-311++G** levels of theory, $\Delta E = E_r - E_{r(\max)}$.**

Fig. S5 Energy decomposition analyses for H· attack at water, at different angles θ, using LMOEDA.

Fig. S6 Energy decomposition analyses for OH· attack at water, at different angles θ, using LMOEDA.

Table S1 Bondlength (Å) for the optimized water cluster W6 and the corresponding root-mean-square errors (RMSEs) by MP2 standard.



	1-7	1-8	2-9	2-10	3-11	3-12				RMSE
MP2	0.961	0.982	0.969	0.977	0.968	0.969				
B97-D3	0.964	0.991	0.975	0.985	0.974	0.976				
	0.003	0.009	0.006	0.008	0.006	0.007				
B3LYP-D3	0.962	0.987	0.972	0.982	0.971	0.973				
	0.001	0.005	0.003	0.005	0.003	0.004				
BLYP-D3	0.971	1.001	0.983	0.996	0.982	0.984				
	0.01	0.019	0.014	0.019	0.014	0.015				
PBE-D3	0.970	1.005	0.983	1.000	0.982	0.985				
	0.009	0.023	0.014	0.023	0.014	0.016				
	4-13	4-14	5-15	5-16	6-17	6-18				
MP2	0.967	0.970	0.961	0.995	0.977	0.961				
B97-D3	0.972	0.976	0.964	1.000	0.985	0.964				
	0.005	0.006	0.003	0.005	0.008	0.003				0.006
B3LYP-D3	0.970	0.973	0.962	1.003	0.981	0.962				
	0.003	0.003	0.001	0.008	0.004	0.001				0.003
BLYP-D3	0.981	0.985	0.971	1.020	0.994	0.971				
	0.014	0.015	0.01	0.025	0.017	0.01				0.015
PBE-D3	0.981	0.986	0.970	1.029	0.997	0.970				
	0.014	0.016	0.009	0.034	0.02	0.009				0.017
	1-9	1-11	2-16	3-10	4-8	5-14	5-17	6-12	6-13	
MP2	2.087	2.085	1.666	1.894	1.765	2.008	1.834	1.985	2.150	
B97-D3	2.075	2.078	1.656	1.903	1.775	2.022	1.830	1.987	2.151	
	-0.012	-0.007	-0.01	0.009	0.01	0.014	-0.004	0.002	0.001	0.008
B3LYP-D3	2.052	2.044	1.647	1.878	1.752	1.987	1.822	1.949	2.115	
	-0.035	-0.041	-0.019	-0.016	-0.013	-0.021	-0.012	-0.036	-0.035	0.025
BLYP-D3	2.048	2.037	1.633	1.868	1.745	1.986	1.821	1.949	2.106	
	-0.039	-0.048	-0.033	-0.026	-0.02	-0.022	-0.013	-0.036	-0.044	0.031
PBE-D3	2.020	2.009	1.574	1.804	1.695	1.943	1.770	1.913	2.078	
	-0.067	-0.076	-0.092	-0.09	-0.07	-0.065	-0.064	-0.072	-0.072	0.074

Table S2 Binding energies (BE, kcal/mol) for the water hexamer computed with different DFT-D3 functionals.

	MP2	B97D-D3	B3LYP-D3	BLYP-D3	PBE-D3
BE	45.3[a]	50.31	55.21	54.65	58.15

[a] MP2 complete basis set limit for 2/3*MP2/aDZ//MP2/6-31G*+1/3*MP2/aDZ//MP2/6-31G*[CP], ref R. M. Shields, B. Temelso, K. A. Archer, T. E. Morrell and G. C. Shields, *J. Phys. Chem. A*, 2010, **114**, 11725-11737.

Table S3 The coordination (in au) of water cage s1 optimized at the B97D-D3/def-TZVP level.

O	-0.44874210	-0.07562020	4.98986470
H	-0.94735660	0.53435850	4.40326270
H	0.44201050	-0.17732890	4.59431910
O	-1.86301590	1.75016630	3.35884950
H	-2.74571240	1.41655080	2.99446380
H	-2.08332980	2.54002020	3.86917510
O	-1.49945710	-2.41413860	5.59592100
H	-1.12749940	-1.51071460	5.34137980
H	-1.57723300	-2.39550270	6.55833490
O	-4.17393530	0.99184600	2.36247740
H	-4.52376040	0.09970320	2.56986480
H	-4.19844410	1.08048550	1.38242090
O	-5.35810850	-1.51479450	3.01958660
H	-4.76463450	-2.13015420	3.60416820
H	-6.10748690	-1.28644470	3.58515170
O	-3.99748390	-3.09170640	4.49200290
H	-3.12413050	-2.81249930	4.84496610
H	-3.85798330	-3.98630920	4.07882090
O	2.09800320	-0.54491510	3.81754580
H	2.25480320	-1.52783200	3.71835170
H	2.88372920	-0.18368540	4.24672660
O	-0.19021860	2.25772720	1.16183340
H	-0.71615280	2.01424460	0.35029770
H	-0.78890760	2.11931060	1.93127420
O	1.91862930	0.52114480	1.23442600
H	1.92884530	0.12903250	2.13536260
H	1.15614960	1.15582500	1.22296450
O	-4.10559890	1.23854160	-0.42648030
H	-3.13930600	1.37029740	-0.68922550
H	-4.57622110	1.98727160	-0.81443390
O	-1.57054020	1.61890940	-1.07787750
H	-1.16232620	0.82635070	-1.53916260
H	-1.51432100	2.39115930	-1.71388050
O	-5.92914280	-2.78131340	0.72613460
H	-5.74567620	-2.30988540	1.59231180
H	-6.88202030	-2.72023610	0.58414560
O	-4.80458470	-1.29356930	-1.54740210
H	-4.60598990	-0.39871650	-1.20094610
H	-5.12747440	-1.79062030	-0.77461020
O	-3.62483920	-5.48169730	3.24908320
H	-3.89419600	-5.41883010	2.31469440
H	-2.68216100	-5.76321330	3.22487520

O	-4.62242710	-5.16611440	0.50111550
H	-5.13555840	-4.31839080	0.56479480
H	-5.27507950	-5.86073120	0.34826340
O	0.39141510	-4.33960840	4.72710660
H	-0.08690490	-5.00288330	4.17578740
H	-0.28859060	-3.70575940	5.04413470
O	-0.91069790	-6.16136090	3.07607980
H	-0.61029780	-5.97029170	2.11594560
H	-0.68892660	-7.08640760	3.24037820
O	2.33788120	-3.18331130	3.44263360
H	1.57920450	-3.64708500	3.94058160
H	3.14164810	-3.66303580	3.67865690
O	1.80425450	-3.82352650	0.62628370
H	1.72368570	-3.00960210	0.07821360
H	2.00400290	-3.51712420	1.52974250
O	1.63779050	-1.37839120	-0.79063380
H	1.73159130	-0.70746770	-0.07358630
H	2.46296520	-1.27642090	-1.34045020
O	-0.48825010	-0.50657720	-2.30264820
H	-1.16909590	-1.23493020	-2.38845400
H	0.26379390	-0.87657970	-1.76843330
O	-2.41036030	-2.37484100	-2.50392070
H	-3.28201550	-2.00148600	-2.23120450
H	-2.29657810	-3.17139480	-1.95430470
O	-2.32967700	-4.93593950	-1.07704030
H	-3.16667680	-5.04660830	-0.56973440
H	-2.39395940	-5.53960790	-1.82827020
O	-0.14744090	-5.68763810	0.64994350
H	0.57654100	-5.00366770	0.59294780
H	-0.85302980	-5.38644130	0.04529880
O	5.67580910	3.25623260	-2.81452760
H	5.18576330	3.00296080	-3.62085280
H	5.69024630	2.44897300	-2.25597350
O	2.20292170	4.30512250	-5.27777430
H	2.20268440	4.94557980	-4.53546170
H	1.31616380	3.87453130	-5.26051590
O	4.48619030	5.31662340	-1.47879650
H	4.95521040	4.59127530	-1.97315360
H	3.75767430	5.60468960	-2.06252460
O	4.18852060	2.60448050	-5.22046300
H	3.41509000	3.26279230	-5.23697930
H	4.73126540	2.82537070	-5.98781310
O	4.36333490	1.81576740	1.05070180
H	4.15757690	2.77588390	1.03388470

H	3.48501530	1.36762130	1.10158800
O	2.23580830	6.13637770	-3.10582560
H	1.43624950	6.06045260	-2.51693450
H	2.28662080	7.06316310	-3.37048060
O	-0.24812220	2.98847120	-5.09958800
H	-0.01557060	2.00690330	-4.94407620
H	-0.81333600	2.99720750	-5.88229830
O	5.58619600	0.97791890	-1.12966000
H	5.13442640	1.30540110	-0.28614010
H	6.44337050	0.63477580	-0.84808760
O	3.65865670	4.55710640	0.87292500
H	3.98609280	4.85413640	-0.04482530
H	4.10505280	5.13475990	1.50461520
O	-1.50434720	3.75233370	-2.69848730
H	-1.10121380	3.54078350	-3.57014210
H	-0.95447530	4.46772560	-2.31746230
O	0.09893850	5.79080450	-1.46974890
H	0.41335500	5.38907740	-0.58003980
H	-0.44770310	6.54916440	-1.22827030
O	3.86750770	-0.97809260	-2.29573040
H	4.48677110	-0.33307110	-1.89312660
H	3.64852880	-0.61046530	-3.17386450
O	3.17900410	0.09265970	-4.88731530
H	3.58956050	0.98131200	-5.05463530
H	3.47619100	-0.48190430	-5.60361980
O	0.35551630	0.49180530	-4.72662060
H	1.31315210	0.29737700	-4.78271150
H	0.04375460	0.08986460	-3.87603370
O	0.86788320	4.79418450	0.78883380
H	1.84505060	4.70319080	0.87355700
H	0.49022720	3.89867820	0.96418860

Table S4 The coordination (in au) of water cage s2 optimized at the B97D-D3/def-TZVP level.

O	3.42007810	-3.27751610	1.91410200
H	3.97454460	-2.65484430	2.50411560
H	3.29412520	-4.07958070	2.43589510
O	3.69177290	1.45767260	-3.45660670
H	2.81497140	1.27792200	-3.01966470
H	3.49434490	1.66598120	-4.37805730
O	1.15714720	2.41602830	0.20957700
H	2.01837890	2.87589650	0.33558740
H	1.10892910	1.70949310	0.93860270
O	7.33894220	-2.53808380	-0.09280530
H	6.42938860	-3.03097680	-0.19254730
H	8.01167960	-3.21606480	-0.23467210
O	5.22426260	3.18065640	-1.88758540
H	4.69466350	2.60809000	-2.48816840
H	4.64556930	3.35977570	-1.12090070
O	1.32273780	1.01228840	-2.21053110
H	1.25041610	1.50411580	-1.35710200
H	0.55176320	1.29777620	-2.75457090
O	7.53366810	-0.68819110	-2.28987870
H	7.53330090	0.20530800	-1.89756350
H	7.47372110	-1.30168220	-1.52988760
O	3.61884800	3.77243100	0.46236960
H	4.17659930	3.44674680	1.22910260
H	3.61601360	4.73476790	0.53851130
O	1.12217730	0.56549350	2.06350700
H	1.10390500	-0.34611820	1.67845840
H	0.38437530	0.60225090	2.74671120
O	5.13198350	-3.79127030	-0.32267770
H	4.51929170	-3.64789050	0.42730940
H	4.61072820	-3.55553210	-1.15103050
O	5.17667950	-1.08108880	-3.77242270
H	6.04742610	-0.97109040	-3.32359150
H	4.71521170	-0.23927640	-3.61296850
O	7.48633150	1.99864850	-1.14203280
H	6.63964120	2.44752400	-1.44640110
H	8.20907500	2.52293100	-1.50853260
O	7.34819290	-1.07408400	2.13488500
H	7.38775480	-1.64319460	1.30823760
H	8.09626260	-1.34712850	2.68056380
O	3.52112930	0.68402260	3.60419760
H	2.67333980	0.65252270	3.10945190
H	4.02689510	1.41447860	3.20123980
O	5.11863510	2.81908740	2.45637180

H	5.97000000	2.36142650	2.11631700
H	5.39558310	3.37429200	3.19595690
O	4.83607100	-1.69432600	3.40397900
H	5.69778280	-1.46953760	2.99914080
H	4.36711410	-0.82713260	3.53654160
O	3.74750250	-3.09449650	-2.48659110
H	4.24458110	-2.41787950	-3.00941730
H	2.89179390	-2.67503440	-2.26606200
O	1.27729860	-1.79590870	-1.66851060
H	1.30422680	-0.84166250	-1.89336700
H	0.50499860	-2.16841600	-2.18626670
O	1.15076850	-2.00313690	0.99354360
H	1.17950240	-1.96302570	-0.00966720
H	1.98869510	-2.44422100	1.28191090
O	7.27552800	1.68065230	1.60927700
H	7.42165480	1.79447080	0.64086550
H	7.31797290	0.71257800	1.78068080
O	-5.50630360	3.97685030	0.63716250
H	-4.63231130	4.01455000	1.06475550
H	-5.31477860	3.84705990	-0.31063250
O	-7.03281980	1.77382250	1.59411340
H	-6.52940490	1.45116200	2.37956430
H	-6.56352740	2.58734410	1.30652540
O	-2.87458750	4.35510640	1.92313050
H	-2.10445160	4.25794380	1.30606400
H	-2.90792720	5.29032160	2.16057650
O	-5.49732290	0.91379610	3.75115190
H	-5.21508960	-0.02045690	3.73836040
H	-4.67009310	1.42752370	3.81950960
O	-3.04005180	2.43136960	3.92778670
H	-2.93489240	2.86873490	4.78224250
H	-2.97758890	3.14146790	3.24830190
O	-0.82083470	4.16273940	0.10752980
H	-0.35442490	4.99272920	-0.05639950
H	-0.09016150	3.46510860	0.19506620
O	-0.76701730	0.63101540	3.92364490
H	-1.13132660	-0.26954030	4.11574460
H	-1.54615080	1.20825960	3.82455760
O	-7.21356730	0.07344370	-0.40722730
H	-7.15209570	0.70069740	0.38453630
H	-6.75116380	0.51138540	-1.14371660
O	-6.83008150	-2.44116390	-0.26441660
H	-6.94862160	-1.41334020	-0.26917640
H	-7.72355680	-2.78875990	-0.38425640

O	-5.46896910	-3.48940860	1.80136880
H	-5.99321690	-3.06764890	1.05937580
H	-5.92786410	-4.31325500	2.00953540
O	-4.71812090	-1.86552290	3.91976250
H	-5.02603340	-2.43665080	3.17605610
H	-5.16529010	-2.19575170	4.70933700
O	-1.83275140	-1.88859470	4.26442690
H	-2.80115150	-1.88787740	4.14196570
H	-1.48259370	-2.44827640	3.54190490
O	-4.93227000	3.59532340	-2.19160450
H	-5.37930460	2.75791610	-2.47960520
H	-5.34353560	4.30183970	-2.70556410
O	-6.22155250	1.29316470	-2.88725740
H	-5.74845840	0.56125360	-3.38197310
H	-7.10028530	1.35795980	-3.28245210
O	-2.12425470	3.73830250	-2.41348260
H	-1.76209200	3.84002410	-1.51005830
H	-3.09665720	3.64779050	-2.32003220
O	-4.96156460	-0.73874730	-4.08156060
H	-5.10305310	-1.57585480	-3.51449470
H	-5.20186260	-0.99473160	-4.98158980
O	-2.06739680	-0.60559580	-4.46414520
H	-3.01823150	-0.57033240	-4.25117560
H	-1.69901010	0.25372610	-4.18090150
O	-0.81151050	1.88825890	-3.77824990
H	-1.34206380	2.57872650	-3.27595570
H	-0.56434150	2.30649920	-4.61256730
O	-2.97597650	-4.41296290	0.66734130
H	-3.76773770	-4.03046420	1.09256650
H	-2.19685610	-4.03556630	1.13658910
O	-0.78535740	-3.45695590	2.09945660
H	-0.29918040	-4.21947880	2.43866790
H	-0.09336890	-2.89325830	1.63234070
O	-5.34761620	-2.87823200	-2.66547250
H	-5.84126600	-2.76137330	-1.82581940
H	-4.52326830	-3.37126380	-2.43519160
O	-3.01116560	-4.18899650	-1.96585730
H	-2.89332050	-5.08370600	-2.30947660
H	-2.96690360	-4.27426280	-0.96391010
O	-0.79977020	-2.70101900	-3.10142960
H	-1.22834200	-1.99315830	-3.63574100
H	-1.53225720	-3.16794650	-2.65655630

Table S5 The bondlength (Å) for optimized water cages s1 and s2.

		O-H[a]	O-H[b]	HB[c]	O-H	O-H	HB
			B97-D3			B3LYP-D3	
s1	Max	0.966	1.035	1.971	0.964	1.026	1.935
	Min	0.965	0.974	1.560	0.963	0.971	1.521
s2	Max	0.966	1.039	1.987	0.964	1.029	1.953
	Min	0.965	0.973	1.509	0.963	0.970	1.516
			BLYP-D3			PBE-D3	
s1	Max	0.974	1.050	1.935	0.972	1.082	1.889
	Min	0.973	0.981	1.495	0.971	0.982	1.401
s2	Max	0.974	1.055	1.958	0.972	1.093	1.908
	Min	0.973	0.981	1.485	0.971	0.981	1.395
			B3LYP/6-31G(*d*)[56]				
5^{12}	Max	0.970	1.040	1.871			
	Min	0.969	0.980	1.505			

[a] without hydrogen bonding linked. [b] H atom linked to other O atom by hydrogen bonding. [c] HB represents hydrogen bonding.

Table S6 Zero point vibrational energy (ZPE) (Ha) and <S2> values for the molecular species investigated in this work.

	ZPE				S^2			
	UB97D-D3	UB3LYP-D3	UBLYP-D3	UPBE-D3	UB97D-D3	UB3LYP-D3	UBLYP-D3	UPBE-D3
				H·				
s1-L	0.9811	1.0000	0.9640	0.9672	0.7520	0.7501	0.7505	0.7502
s1-S	0.9821	0.9998	0.9635	0.9673	0.7508	0.7504	0.7509	0.7502
s2-L	1.0799	1.0993	1.0594	1.0624	0.7520	0.7502	0.7506	0.7502
s2-S	1.0799	1.0988	1.0589	1.0622	0.7500	0.7506	0.7509	0.7502
				OH·				
s1-L	0.9920	1.0095	0.9731	0.9774	0.7547	0.7526	0.7526	0.7524
s1-S	0.9934	1.0111	0.9746	0.9783	0.7547	0.7530	0.7526	0.7523
s2-L	1.0899	1.1093	1.0692	1.0720	0.7549	0.7536	0.7527	0.7526
s2-S	1.0888	1.1100	1.0699	1.0731	0.7545	0.7525	0.7525	0.7525
s1	0.9791	0.9992	0.9627	0.9663				
s2	1.0762	1.0983	1.0580	1.0618				
H					0.7500	0.7500	0.7500	0.7500
OH	0.0082	0.0084	0.0080	0.0082	0.7537	0.7521	0.7518	0.7517
				THF existence				
				H·				
s1-S	1.0992				0.7519			
s2-S	1.1951				0.7520			
				OH·				
s1-S	1.1122				0.7550			
s2-S	1.2064				0.7547			
s1[a]	1.0980							
s2[a]	1.1952							
THF	0.1142							

[a] THF occupies the larger cage of s1 or s2 structure.

Table S7 Stabilization energies (SE, kcal/mol), net charges, spin densities and electronic configurations for the s1 and s2 structures, which occupied with H· or OH·, calculated at the UB97D/def-TZVP level.

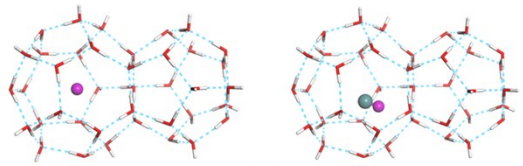
	SE_a	SE_b	Net charge	Spin density	configuration			
				H·				
					1s			
s1-L	-237.0	2.5	0	0.998	1.00			
s1-S	-233.7	5.9	-0.011	0.974	1.01			
s2-L	-247.7	3.4	0	1.000	1.00			
s2-S	-246.9	4.4	-0.011	0.976	1.01			
				OH·				
					H		O	
					1*s*	2*s*	2*p*	3*p*
s1-L	-237.4	0.4	-0.108	0.865	0.59	1.89	4.61	0.01
s1-S	-242.1	-1.5	-0.400	0.984	0.57	1.88	4.56	0.01
s2-L	-249.4	0.4	-0.118	0.859	0.59	1.89	4.63	
s2-S	-251.6	-0.5	-0.161	0.812	0.58	1.88	4.68	
s1	-241.5							
s2	-253.0							

Table S8 The control file for natural bond orbital (NBO) analyses with Turbomole suite.

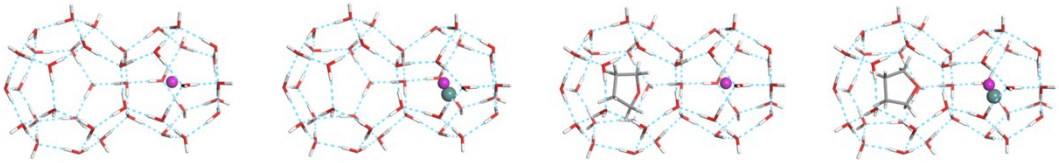
```
$title
$operating system unix
$symmetry c1
$coord    file=coord
$user-defined bonds    file=coord
$atoms
o    1-24,73,76,79,82,85,88,91,94,97,100,103,106,109,112,115                \
     basis =o def-TZVP                                                      \
     jbas  =o def-TZVP
h    25-72,74-75,77-78,80-81,83-84,86-87,89-90,92-93,95-96,98-99,101-102,104-105 \
     107-108,110-111,113-114,116-118                                        \
     basis =h def-TZVP                                                      \
     jbas  =h def-TZVP
$basis    file=basis
$rundimensions
     dim(fock,dens)=788058
     natoms=118
     nshell=667
     nbf(CAO)=1254
     nbf(AO)=1215
     dim(trafo[SAO<-->AO/CAO])=1332
     rhfshells=2
$uhfmo_alpha   file=alpha
$uhfmo_beta    file=beta
$uhf
$alpha shells
 a          1-196                                        ( 1 )
$beta shells
 a          1-195                                        ( 1 )
$scfiterlimit          30
$thize       0.10000000E-04
$thime          5
$scfdump
$scfintunit
 unit=30          size=0          file=twoint
$scfdiis
$drvopt
     cartesian  on
     basis      off
     global     off
     hessian    on
     dipole     on
     nuclear polarizability
```

```
$interconversion    off
    qconv=1.d-7
    maxiter=25
$optimize
    internal      off
    cartesian     on
    global        off
    basis         off      logarithm
$coordinateupdate
    dqmax=0.3
    interpolate   on
    statistics    5
$forceupdate
    ahlrichs numgeo=0    mingeo=3 maxgeo=4 modus=<g|dq> dynamic fail=0.3
    threig=0.005    reseig=0.005    thrbig=3.0    scale=1.00    damping=0.0
$forceinit on
    diag=default
$energy       file=energy
$grad       file=gradient
$forceapprox       file=forceapprox
$lock off
$dft
    functional b97-d
    gridsize      m3
$scfconv      6
$scfdamp      start=0.700    step=0.050    min=0.050
$scforbitalshift    closedshell=.05
$ricore           500
$rij
$jbas       file=auxbasis
$marij
$disp3
$pop nbo
$last step          define
$end
```

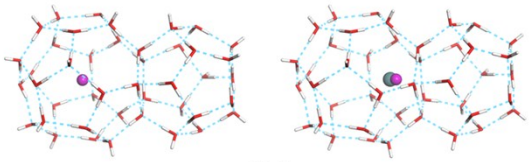
Fig. S1 Structures of the radical-included clathrate hydrates optimized at the UB97D-D3/def-TZVP level. O atoms are red, H atoms are lightgray, C atoms are dark grey, H· radicals and the H atoms in the OH· radical are purple, and O atoms in OH· are blue-green.



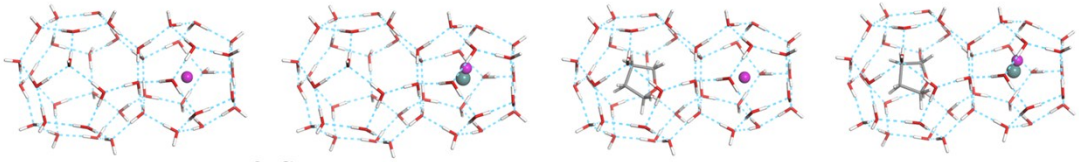
s1-L



s1-S



s2-L



s2-S

Fig. S2 Schematic diagram for the diffusion of H· and OH· between the water cages in s1 (left) and s2 (right).

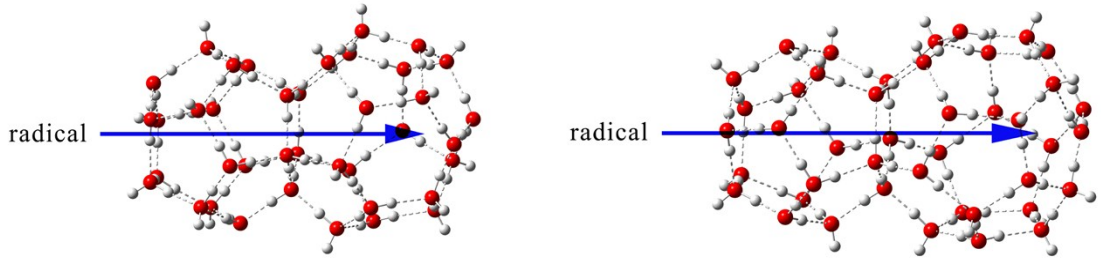


Fig. S3 Schematic diagram showing the interactions of H· and OH· with the water cage, at different angles θ.

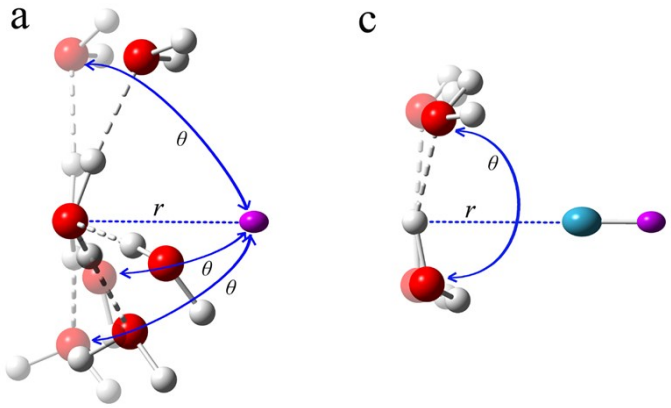


Fig. S4 Energies for the approach of H· (top) or OH· (bottom) toward water, calculated at the CCSD(T)/6-311++G** and UB97D-D3/6-311++G** levels of theory, $\Delta E = E_r - E_{r(\max)}$.

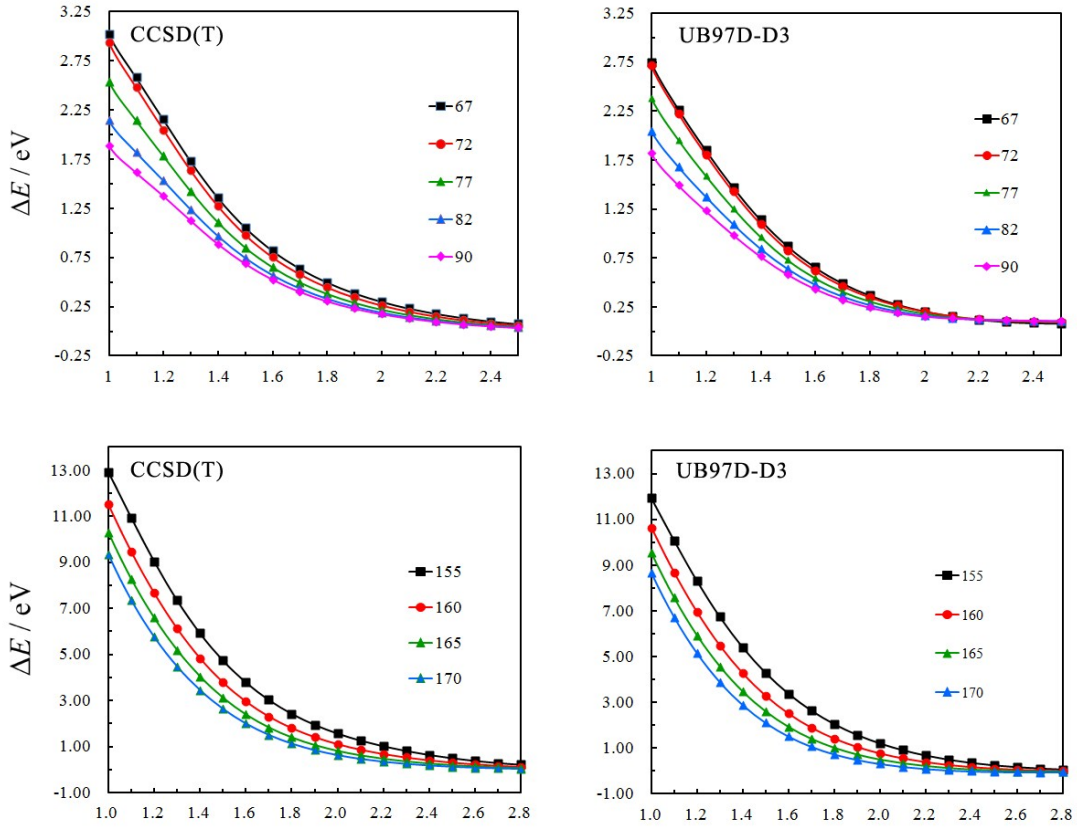


Fig. S5 Energy decomposition analyses for H· attack at water, at different angles θ, using LMOEDA.

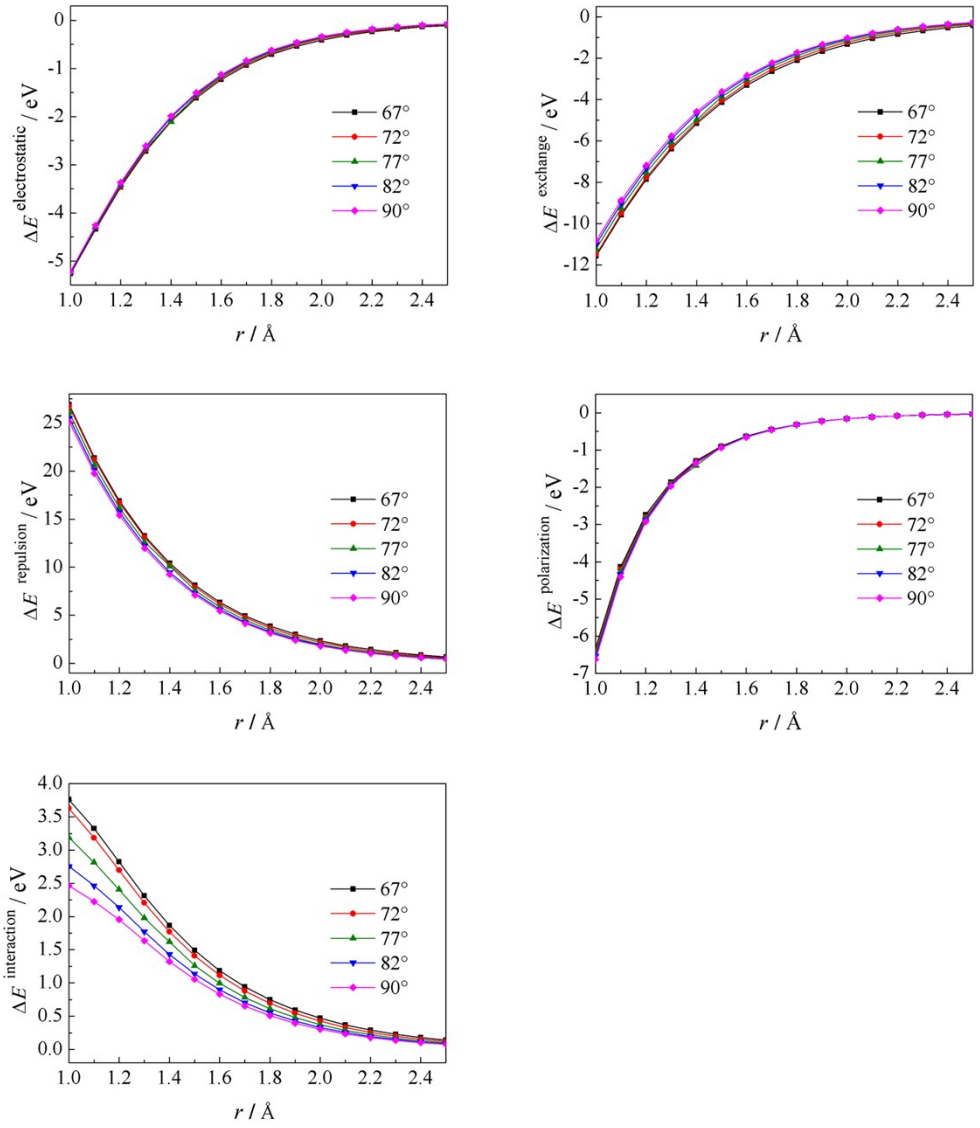


Fig. S6 Energy decomposition analyses for OH· attack at water, at different angles θ, using LMOEDA.