

Table S1:

Unimolecular rate constants k (with fit errors) obtained from BIRD experiments as a function of absolute temperature T of the ICR cell.

T / K	314	324	334	342	352	355	364	374	383
k / s^{-1}	$8\text{E-}5$ $\pm 3\text{E-}6$	$1.9\text{E-}4$ $\pm 1\text{E-}5$	$7\text{E-}4$ $\pm 1\text{E-}5$	0.00239 ± 0.00012	0.00486 ± 0.00022	0.00704 ± 0.00029	0.01752 ± 0.0006	0.04422 ± 0.00243	0.05896 ± 0.0015

Table S2:

Total electronic energies (in Hartree) of the molecular anionic and neutral species.

	Anion/def-SV(P)	Anion/def-TZVP	Neutral/def2-TZVP
H ₂ O			-76.46721302625
Cage	-3309.629080704	-3313.145761060	-3313.033749343
Cage+H ₂ O	-3386.007629622	-3389.636638405	-3389.522147609
Cage+H ₂ O /(TS)	-3385.968823883	-3389.594994260	-3389.479033191

Table S3:

Cartesian coordinates (in atomic units) of the optimized ground state geometry of anionic H₂O@1a at the BP86-D/def2-SV(P) level of theory.

\$coord

4.58324554177047	5.48845679707893	-3.79928907607691	o
5.24755016078246	4.36269361097260	-5.19177814130856	h
-0.05976259194195	-0.13309650312687	3.98103025207063	o
-4.55358973070487	5.53145736438583	-3.77226227846953	o
-5.24000761111173	4.41503559483848	-5.15594184843133	h
-3.96394213820930	-2.50128514313084	-3.69097069432631	o
-0.07587821706564	-6.46455642349475	-3.33238992307906	o
3.87308373079178	-2.52060953134786	-3.73213614588605	o
-0.01631676171987	-1.12723711530095	-9.74172458666731	o
4.54490234620849	1.73791594525187	-7.29992092359907	n
-4.54271806411421	1.76705555423620	-7.29120213004746	n
2.98674822273915	3.86814944621324	-2.34303334072109	c
-2.96515097191064	3.89290397702755	-2.32315512786866	c
-4.58051695492426	-2.34128559032845	-1.46366734900939	c
-0.06039043168916	-6.28051319668091	-1.04272294137939	c
4.52037307851176	-2.39002674092976	-1.50352109360507	c
-0.00306878104605	0.13585777111696	-7.82114871583244	c
2.27272806234706	1.28813003458276	-6.46242720060157	c
1.31152969992838	2.42727436010303	-4.14562768397193	c
-1.31155818218565	2.43631839185168	-4.13204177297148	c
-2.28049317063636	1.30562289538153	-6.44983338833253	c
-1.36726429784469	-1.23980380394836	10.07141397837775	c
-2.70206033099873	-3.22661341154386	8.89446547016978	c
1.39420057628217	-1.25576209274309	10.05332454948126	c
4.41005759971130	1.85361475421495	8.24493091453609	c
-4.35266988396777	1.90757677450340	8.27305558787067	c
0.03930080477356	2.93550662886783	9.57002884790804	c
-4.31826671260081	4.05530597550015	6.57601107933049	c
-2.17849142664261	5.64915327929188	6.44876205180680	c
4.84163016567212	-4.40654411777791	5.16485601818454	c
-4.90786372488933	-2.65397576023024	7.35130619159283	c
-5.69160583555716	-0.13819250048633	7.02671691154407	c

2.69755016410660	-3.25492674011904	8.86987992810637	c
-1.43124599252369	-6.73554812443677	3.23566365431144	c
-1.36260032315715	-5.30866258068477	7.72016687717649	c
2.64836098998209	-6.03697738622353	5.42456848843263	c
2.20175168598405	-6.09286558989846	0.72559963934406	c
-1.32982062700397	6.57836043459468	4.01633958935219	c
-4.89052160648110	-4.35353740829309	5.20501344496531	c
-6.44025703151042	0.74046035461179	4.53413065542332	c
-5.55147055665976	-3.48201971689238	2.78667836776763	c
1.31950804932638	-5.32084078531328	7.69937586710141	c
6.26084669554109	-0.92871838910613	2.39749069308156	c
4.89912995789083	-2.70974391910040	7.31344330026978	c
-5.59065043436086	3.31502197269356	4.25766108957412	c
2.25922653456750	1.32345996315900	9.75052346698854	c
-4.33456915966500	-4.37850838975924	0.52357470390017	c
0.04597845171968	5.04512129419537	7.94574839475572	c
1.41647229356013	6.56179116289079	4.00678475758632	c
-2.19690751000952	1.34741252640881	9.76373425264929	c
2.27256235498875	5.62315118264376	6.43547611092099	c
-2.60310011662759	5.89099934861071	1.78013341898389	c
5.49781486168507	-3.54108693865281	2.74232177455762	c
1.33603730766718	-6.74361770130977	3.21714786440272	c
-4.70281774058629	4.12737274494175	1.89390094808952	c
-6.26675760327432	-0.85929622823945	2.43799419234932	c
-2.31205461056941	-6.07281678934582	0.74962512520336	c
-2.71447517645607	-6.00160382272078	5.44512874501354	c
4.25362168869222	-4.41305223127259	0.47507823329607	c
1.32925775564105	5.43584031404547	-0.55693691900050	c
4.75327433499347	4.07837959603831	1.86337602576845	c
-4.62721885093022	2.49153933619270	-0.31130310523036	c
-1.28288237429172	5.44663367507991	-0.54620732993093	c
5.71978810369243	-0.20194124107291	6.99301939865644	c
4.64542949226736	2.44342640347939	-0.34229557623017	c
4.39203842550450	4.00752528405395	6.54704363876291	c
6.46171772077300	0.66808383235042	4.49409252751738	c
5.41476802719077	-0.07252903876123	-0.07513645997701	c
5.64732590727416	3.25664893501104	4.22459739316192	c
-5.42518148037243	-0.01166647422037	-0.03189987267738	c
2.66884040898329	5.86346644365684	1.76343743219592	c
5.71176768149836	0.52323329993079	-9.31988759622326	c
5.55247005835514	-2.12616654826851	-9.72188787574503	c
4.41455717378887	-3.27991673046725	-8.42338342217012	h
6.90712354335351	-3.24539541126567	-11.69944296415226	c
6.77651060673223	-5.30587928150030	-11.98030121705504	h
8.41650741084676	-1.77459922097454	-13.32206805109374	c
9.46437770807236	-2.67278646089494	-14.88261994724992	h
8.60090658822320	0.84726776122398	-12.91902981947381	c
9.79337393179899	2.01604138748092	-14.16615410234146	h
7.29655378111078	1.98315395912297	-10.91623556404125	c
7.45455266454141	4.02962474239255	-10.56508490943173	h
-5.70777790953822	0.56502353859948	-9.32287823627765	c
-5.58202669061699	-2.08697069008777	-9.71161900281260	c
-4.46703566943729	-3.25110335634697	-8.40243707018490	h
-6.93741125612554	-3.19479072363175	-11.69554945298720	c
-6.83334434383275	-5.25774839400880	-11.96835034839022	h
-8.41064970754220	-1.70809568325698	-13.33608397103644	c
-9.45824913783627	-2.59698591656297	-14.90208917060236	h
-8.55942231693303	0.91800337155871	-12.94624006201721	c
-9.72342242686210	2.09878044790667	-14.20867175183299	h
-7.25682553156280	2.04274083982871	-10.93594298829194	c
-7.38888673893760	4.09233048500363	-10.59281347983435	h
0.26475468452285	1.60149521014769	3.40800148141751	h
1.05655787636918	-1.17936380114473	2.93044140415074	h

\$end

Table S4:

Cartesian coordinates (in atomic units) of the optimized ground state geometry of anionic **1a** at the BP86-D/def2-SV(P) level of theory.

\$coord

5.50130151361710	-3.71683528290047	4.58224163066741	o
4.37613557058398	-5.11548399405094	5.23882824600975	h
5.50130151361710	-3.71683528290047	-4.58224163066741	o
4.37613557058398	-5.11548399405094	-5.23882824600975	h
-2.55442560558141	-3.65623924892853	-4.00466946415212	o
-6.44717950832392	-3.29265093607828	0.00000000000000	o
-2.55442560558141	-3.65623924892853	4.00466946415212	o
-1.02441379333668	-9.77400695352639	0.00000000000000	o
1.75057979055574	-7.21666323174098	4.54739196885165	n
1.75057979055574	-7.21666323174098	-4.54739196885165	n
3.87952890444760	-2.27196280415985	2.97550702876263	c
3.87952890444760	-2.27196280415985	-2.97550702876263	c
-2.39382297281404	-1.41726986582709	-4.54820604475669	c
-6.32589015306931	-0.99087182865265	0.00000000000000	c
-2.39382297281404	-1.41726986582709	4.54820604475669	c
0.17496217073970	-7.79653681232508	0.00000000000000	c
1.30154778863615	-6.41652272908119	2.26192998689606	c
2.45145117381769	-4.08672873202571	1.30365743337020	c
2.45145117381769	-4.08672873202571	-1.30365743337020	c
1.30154778863615	-6.41652272908119	-2.26192998689606	c
-1.25524485007251	10.14698534795726	-1.36660917080144	c
-3.24862213076003	8.96284804272206	-2.70729765107165	c
-1.25524485007251	10.14698534795726	1.36660917080144	c
1.87877326476017	8.31975446927404	4.35568826711097	c
1.87877326476017	8.31975446927404	-4.35568826711097	c
2.96260875552874	9.65215719512490	0.00000000000000	c
4.04875376862622	6.62859729974221	-4.34547994328335	c
5.64099942604955	6.50187045945678	-2.21330013423164	c
-4.39103599305485	5.25717235456889	4.85450773345253	c
-2.69379013306965	7.41004251893718	-4.89589923791751	c
-0.17144219606543	7.08919873005780	-5.71916952674989	c
-3.24862213076003	8.96284804272206	2.70729765107165	c
-6.75934506958662	3.30147338357581	-1.37529511289586	c
-5.30941836068593	7.77124531988902	-1.33054375369058	c
-6.05195959866647	5.49759684978402	2.68551818800714	c
-6.11326899607593	0.79058132694067	2.23829238914064	c
6.59037036764933	4.06601837647975	-1.37065506292242	c
-4.39103599305485	5.25717235456889	-4.85450773345253	c
0.69913516323139	4.59515590102400	-6.43227459081448	c
-3.51935367904906	2.83315371004134	-5.50068528040184	c
-5.30941836068593	7.77124531988902	1.33054375369058	c
-0.90319788581377	2.48318443779745	6.25908288368518	c
-2.69379013306965	7.41004251893718	4.89589923791751	c
3.28429384659858	4.30958733684253	-5.60717261301323	c
1.35083879034483	9.81940904596544	2.21621787528487	c
-4.42986055968803	0.56996273559954	-4.28250153873430	c
5.09092785494744	8.02629199200207	0.00000000000000	c
6.59037036764933	4.06601837647975	1.37065506292242	c
1.35083879034483	9.81940904596544	-2.21621787528487	c
5.64099942604955	6.50187045945678	2.21330013423164	c
5.87651117547268	1.83915412237467	-2.63217403279386	c
-3.51935367904906	2.83315371004134	5.50068528040184	c
-6.75934506958662	3.30147338357581	1.37529511289586	c
4.10515437677801	1.94511090577237	-4.72383838263099	c
-0.90319788581377	2.48318443779745	-6.25908288368518	c
-6.11326899607593	0.79058132694067	-2.23829238914064	c
-6.05195959866647	5.49759684978402	-2.68551818800714	c
-4.42986055968803	0.56996273559954	4.28250153873430	c

5.43960845905294	-0.49272918203024	1.30307612711058	c
4.10515437677801	1.94511090577237	4.72383838263099	c
2.46403034164258	-0.26158685748023	-4.62638453628420	c
5.43960845905294	-0.49272918203024	-1.30307612711058	c
-0.17144219606543	7.08919873005780	5.71916952674989	c
2.46403034164258	-0.26158685748023	4.62638453628420	c
4.04875376862622	6.62859729974221	4.34547994328335	c
0.69913516323139	4.59515590102400	6.43227459081448	c
-0.04424389454042	0.02924132522452	5.40291724414173	c
3.28429384659858	4.30958733684253	5.60717261301323	c
-0.04424389454042	0.02924132522452	-5.40291724414173	c
5.87651117547268	1.83915412237467	2.63217403279386	c
0.54490837857373	-9.23116078242330	5.73401907503087	c
-2.09338099187716	-9.68272691959407	5.53264197083649	c
-3.24845127341747	-8.43339111248753	4.34314567821877	h
-3.20450335749032	-11.64942779836725	6.90974697385509	c
-5.25669654612491	-11.97022203573971	6.74558151361770	h
-1.73521822608523	-13.21268303759368	8.48168093545952	c
-2.62678766599796	-14.76582391424691	9.54622591622089	h
0.87554370710275	-12.76074697254183	8.70690990880948	c
2.04205646585243	-13.96146827955930	9.94817237643358	h
2.00113206002208	-10.76665076749140	7.38071995396759	c
4.03783818911964	-10.37568172558879	7.56916475993809	h
0.54490837857373	-9.23116078242330	-5.73401907503087	c
-2.09338099187716	-9.68272691959407	-5.53264197083649	c
-3.24845127341747	-8.43339111248753	-4.34314567821877	h
-3.20450335749032	-11.64942779836725	-6.90974697385509	c
-5.25669654612491	-11.97022203573971	-6.74558151361770	h
-1.73521822608523	-13.21268303759368	-8.48168093545952	c
-2.62678766599796	-14.76582391424691	-9.54622591622089	h
0.87554370710275	-12.76074697254183	-8.70690990880948	c
2.04205646585243	-13.96146827955930	-9.94817237643358	h
2.00113206002208	-10.76665076749140	-7.38071995396759	c
4.03783818911964	-10.37568172558879	-7.56916475993809	h
\$end			

Table S5:

Cartesian coordinates (in atomic units) of the transition state geometry of anionic H₂O@**1a** at the BP86-D/def2-SV(P) level of theory.

\$coord			
-7.62177324356175	1.64068769278209	-10.88576839849473	c
-5.81940141494260	0.34713330856031	-9.37714467274349	c
-5.37398318417363	-2.25828708872019	-9.84816476234998	c
-6.65686564639679	-3.48963657748706	-11.80549854765058	c
-8.38188064632346	-2.17325633196005	-13.34444236639201	c
-8.85488810056474	0.40023862450822	-12.87156038406286	c
-4.72605554586913	1.65232169530963	-7.37772765433049	n
-2.37631168127395	1.46939305908714	-6.63448603437513	c
-0.03640930139033	0.54585262097751	-8.03011546444505	c
2.18073830204037	1.60332111994934	-6.47953286839260	c
1.11986930922134	2.64681650249353	-4.16446865255616	c
-1.50792778609365	2.58431374963912	-4.28344388332049	c
-3.29009471155018	3.69120601293908	-2.36460982098738	c
-1.73218790385046	5.30529861051750	-0.54022034203097	c
0.87729580666319	5.46459072434215	-0.48141061456580	c
2.69830015590323	4.03239353664222	-2.22072458711835	c
2.11782024957973	6.01471651681544	1.85945425512707	c
4.32722937363913	4.40463559703424	2.03829330883073	c
4.45732122663815	2.73210782305092	-0.15227148631545	c
-3.13401408993346	5.63378678882811	1.75495469600656	c

-5.08019388090899	3.69529831301691	1.82713193222012	c
-4.83570765377416	2.05825552271447	-0.37180873675549	c
-5.95942629497486	2.84341359905946	4.18779263679231	c
-4.79902611829208	3.71648862269218	6.51193311627310	c
-2.80636882202857	5.48468698591104	6.42196394402205	c
-1.97617561662441	6.45701085072564	3.99908471874726	c
-6.58783372433179	0.20484776958781	4.49355988966292	c
-5.82162552964337	-0.58159444588634	7.01405023176015	c
-4.68332259902357	1.58413971316146	8.23786334019675	c
-0.57536894483443	5.08804701804148	7.96943653487131	c
-0.42950737000603	2.98458996642467	9.58914698047147	c
-2.51036561930773	1.20926498018151	9.73144575663143	c
-1.50284189369350	-1.26968322128487	10.32523241609061	c
-2.60643725718030	-3.36064563546542	9.04507203472479	c
-4.80417501461410	-3.00496805207074	7.41085743572787	c
-1.04118436754396	-5.31269780322185	7.89739472702310	c
1.63031290198138	-5.09278627089100	7.97338076579201	c
2.78416867958367	-2.91299976953078	9.17397215625051	c
1.27123459082040	-1.02976558475444	10.31719635208098	c
1.91032139262541	1.60768173393645	9.92695790292923	c
-2.24933301321556	-6.12974083031251	5.58188162985258	c
-4.55811416502690	-4.69907355213835	5.26793755842193	c
4.05043988431245	2.32526201426057	8.47440864780952	c
5.58436699678244	0.37715019716095	7.31014771518270	c
4.97918587004670	-2.18628925335343	7.66511025989017	c
1.62719522017513	5.84681272577231	6.51250629092911	c
3.87542391789253	4.42831545061502	6.72025775439557	c
5.25067040123542	3.74383767845058	4.44125567230964	c
6.32354533410286	1.26944900881367	4.81314440500737	c
0.75938782761076	6.67153283183390	4.05354369142471	c
-5.24835686569376	-3.92346447195268	2.82365153081448	c
-6.23333037104097	-1.39365661789373	2.42652521670491	c
5.15580813155245	-3.90806617916270	5.54262135849770	c
3.09065811609306	-5.69360600988004	5.73079854531310	c
1.92076489638676	-6.49516630471881	3.48208332563697	c
2.85012656221060	-5.83445376645183	1.01286217936525	c
4.83678097161297	-4.08042745990783	0.83233527668545	c
5.85937580941816	-3.04139573082593	3.13024481811604	c
6.37685368690784	-0.36887774666328	2.74629067734736	c
-0.83608398908310	-6.70892113682441	3.39569863109821	c
0.64667810502193	-6.30905680169785	-0.82820880771577	c
-1.69836380712978	-6.16387389903529	0.87936486052000	c
-3.92349604568055	-4.72119376246355	0.56845431096900	c
-5.46291644187966	-0.50698326085655	-0.06605964044225	c
-4.50870132251972	-2.80239074097481	-1.45117345243946	c
5.31246246920024	-2.11610069006487	-1.21157880906270	c
5.58960680752217	0.35796837260317	0.21014014587622	c
4.24835057378641	5.78763180402567	-3.58852992429846	o
-5.06782093589439	5.23869595279878	-3.69202983004804	o
-4.01780039146147	-2.94968894139759	-3.74205460661296	o
0.75534762697494	-6.87563266809541	-3.05490682822313	o
5.35710024530770	-2.45800764117350	-3.50707946704120	o
0.07127851574578	-0.53681557046614	-10.06360248536987	o
4.53313394642184	1.94894367842294	-7.10273866885647	n
5.80521719859731	0.77507197277109	-9.08210501242766	c
5.58091873490307	-1.84252343665802	-9.61973901813111	c
7.03009402926767	-2.92628394579204	-11.54758722148975	c
8.70263487899997	-1.44223181834652	-12.98760074241880	c
8.95517908431536	1.14854764546827	-12.44671568638150	c
7.55759099334692	2.24154704874670	-10.48344048038611	c
0.56011727758486	-1.61953354225188	-2.04118591004959	o
5.09586154005461	4.71038612937519	-4.90273334648759	h
-5.65293691611466	4.13022470591324	-5.13175326378482	h
4.32470275480394	-3.01579706369891	-8.45565260213243	h
6.85039282047962	-4.96601925837615	-11.93033391423272	h
9.82838748131812	-2.31017517137669	-14.51034640502420	h
10.27733329328959	2.32360745791254	-13.54804085656493	h

```

7.76906311487653 4.26004101027923 -10.01822903066970 h
-4.07871552618427 -3.30382756096652 -8.60722275784072 h
-6.30346805736262 -5.51671698793623 -12.13384355472046 h
-9.37402135524625 -3.15702545233573 -14.88961949262527 h
-10.21838789590799 1.44694302696678 -14.04998502000710 h
-8.00338318928063 3.64740432958215 -10.48167676841150 h
1.8548888055560 -2.33423035344429 -3.17032408001566 h
-1.01427241320682 -1.97371683025098 -2.98589426821908 h
$end

```

Table S4:

Cartesian coordinates (in atomic units) of the optimized ground state geometry of H₂O at the BP86-D/def2-SV(P) level of theory.

```

$coord
0.000000000000000 -0.12833454782429 0.000000000000000 o
1.45651988189996 1.01852027563322 0.000000000000000 h
-1.45651988189991 1.01852027563320 0.000000000000000 h
$end

```