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CO_2 incorporation in hydroxide and hydroperoxide containing water clusters—unifying mechanism for hydrolysis and protolysis

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Supporting Information

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Experimental Analysis

The reactions of the clusters $OH^-(H_2O)_n$ and $HO_2^-(H_2O)_n$ with CO_2 was studied at the centre-of-mass (COM) collision energies given in Table S1 for values of n = 2–12.

Table S1. Overview of cluster sizes and centre-of-mass collision energies for which the reactions with CO_2 was studied experimentally.

Cluster	Number of water molecules, n	E_{COM} (eV)
$OH^-(H_2O)_n$	2–12	0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0
$HO_2^-(H_2O)_n$	2–12	0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0

The main reaction channel of the clusters with CO_2 can be expressed as:

$$OH^-(H_2O)_n + CO_2 \rightarrow HCO_3^-(H_2O)_{n-x} + xH_2O \quad \text{(S1)}$$

$$HO_2^-(H_2O)_n + CO_2 \rightarrow HCO_4^-(H_2O)_{n-x} + xH_2O. \quad \text{(S2)}$$

In addition to Eq. S1 and Eq. S2, some additional reaction pathways need to be considered. For the cluster $HO_2^-(H_2O)_n$ loss of hydrogen peroxide might occur upon incorporation of CO_2:

$$HO_2^-(H_2O)_n + CO_2 \rightarrow HCO_3^-(H_2O)_{n-x-1} + xH_2O + H_2O_2. \quad \text{(S3)}$$

Cluster–gas collisions that do not result in a reaction can occur, especially for larger clusters. Depending upon the energy associated with the collision, water molecules—or possibly hydrogen peroxide—might be lost from the cluster in excess to the losses occurring naturally from the clusters' meta-stable decay, *i.e.* collision induced dissociation (CID):

$$OH^-(H_2O)_n + CO_2 \rightarrow OH^-(H_2O)_{n-x} + CO_2 + xH_2O \quad \text{(S4)}$$

$$HO_2^-(H_2O)_n + CO_2 \rightarrow HO_2^-(H_2O)_{n-x} + CO_2 + xH_2O \quad \text{(S5)}$$

$$HO_2^-(H_2O)_n + CO_2 \rightarrow HO^-(H_2O)_{n-x-1} + CO_2 + xH_2O + H_2O_2. \quad \text{(S6)}$$

All of these reaction paths can be detected using the current experimental setup, with the exception of collisions of too low energy to induce fragmentation, *i.e.* Eq. S4–S5 with x = 0.

In order to compare results from different measurements, the peak intensities in the mass spectra were normalized to the reactant ion intensity in each measurement, the latter estimated as the sum of all product peaks, evaporation peaks, and the parent ion peak. The intensities in the background measurements were subtracted from the corresponding peaks in the measurements where CO_2 was present. This removes intensity originating from the clusters' meta-stable decay and possible restgas collisions from the fragmentation peaks, leaving only the intensity originating from the CID of the clusters. The combined (relative) intensity of all CID peaks in a spectrum is designated as the fraction of CID, ϕ_{CID}.

The fraction of reaction, ϕ_R, for a measurement corresponds to the sum of all normalized product peaks, *i.e.*, when CO_2 has been taken up by the reactant cluster. For almost all clusters, the majority of the product intensity was found in the peaks corresponding to adding CO_2 and losing 2–3H_2O (Eq. S1–S2). Loss of H_2O_2 from $HO_2^-(H_2O)_n$ clusters (Eq. S3) was a mostly insignificant reaction channel, being generally two orders of magnitude smaller than the primary one (Eq. S2).

The fraction of reactant clusters colliding with CO_2 can be estimated as

$$\phi_C = \phi_R + \phi_{CID}. \qquad \text{(S7)}$$

Due to the aforementioned inability of the current experimental setup to detect collisions that do not result in changes to the reactant cluster, Eq. S7 will most likely underestimate the degree of collisions occurring to some degree.

Experimentally, we can estimate a reaction rate coefficient as follows. The number of reactant clusters that react with the collision gas can be expressed using a Lambert–Beer law analogy:

$$-\ln(1-\phi_r) = \sigma_r L c, \qquad \text{(S8)}$$

where L is the length of the ion flight path, c is the concentration of the collision gas, and σ_r is the reaction cross section. Physically, the right hand side represents the volume of space covered by the ion's flight, and the number of gas molecules encountered and reacted with in

that volume. With the ion velocity v_i it is possible to calculate the volume covered and gas molecules encountered by the ion per unit time, *i.e.* the rate coefficient. The exact flight path of the ion is unknown due to the motion imposed on it by the hexapole ion guide in the collision cell, and so is also the actual ion velocity v_i along that path. However, the ratio L/v_i equals the residence time in collision cell, t, and can be calculated using the translational ion energy (E_{LAB}) and collision cell length. Hence:

$$-\ln(1-\phi_r) = k_r c t \qquad \text{(S9)}$$

where k_r is the reaction rate coefficient. It should be noted that the reaction rate coefficient as presented in Eq. S9 is not a true rate coefficient. The equation represents a nominal rate coefficient corresponding to a mono-energetic ion beam traversing a volume of stationary gas molecules, and can be considered a microcanonical rate coefficient. Several factors are neglected here: the ion beam might not be entirely mono-energetic, although this is likely of minor importance; the thermal motion of the collision gas will lead to a Doppler broadening of the collision energies; and in addition, the cross section might be dependent upon the relative ion–gas velocity, which in turn is dependent upon both the gas temperature and the axial motion of the ion imposed by the hexapole ion guide. While a more rigorous approach is possible,[1] it is unnecessary for the current purposes, especially considering the uncertainties in the CO_2 pressure with the current experimental setup.

Variations in CO_2 pressure with time is easily detected from the reference measurements. For the reasons stated immediately above, we consider estimating a quantitative rate coefficient meaningless. Instead, we calculate a relative reaction rate coefficient as

$$k_{rr} = -\ln(1-\phi_r)/(tR) \qquad \text{(S10)}$$

where R is a normalizing function calculated by a fit to the value of $-\ln(1-\phi_r)/t$ for our reference measurements as a function of time-of-day. In essence, this compensates for variations in CO_2 pressure and expresses the rate coefficients relative to the reaction rate coefficient for $OH^-(H_2O)_3 + CO_2$ at a nominal collision energy of 0.5 eV in the COM frame.

The fraction of reaction ϕ_r can be expressed to a good approximation as $\phi_r = \varphi_r + \varphi_r^2 + \varphi_r^3 \ldots$ where φ_r is the relative amount of single collision reactions; and φ_r^2 is approximately the relative amount of double collision reactions, etc. If φ_r is sufficiently small, the terms following it can be neglected. In the present experiments, the CO_2 pressure is high enough that double collisions is not entirely neglectable, and should be accounted for. However, the mass spectra reveal that incorporation of two CO_2 molecules into the clusters is not occurring, meaning that the reaction product of the first collision with CO_2 will not react further. Instead, a second collision will only result in additional water molecules being knocked out of the cluster.

Branching ratio model

A very simple model was used to estimate branching ratios for the products of Reaction (S1) from thermodynamic data. The basic assumption is that the clusters—being an evaporative ensemble—are metastable on the relevant experimental time-scale.[2] When entering the instrument, the evaporative ensemble will quickly cool down by successive evaporation of H_2O molecules; however, each evaporation removes enough energy from the clusters to result in an order of magnitude decrease in the evaporation rate.[3] Consequently, clusters traversing the collision cell without evaporating can be said to be stable on the time-scale corresponding to the flight time (or strictly speaking, from the cluster creation to detection). The first assumption is therefore that clusters will almost instantaneously reach a point where their internal energy is not enough to result in evaporation of H_2O during the flight time.

Addition of energy to the clusters will lead to evaporation of H_2O—with characteristic times shorter than the flight time—until the clusters have cooled down enough to again be metastable within the experimental time-frame. The second assumption of the model is thus: that energy in excess of the original internal energy of the clusters will lead to loss of H_2O if the excess is larger than the dissociation energy, and that the characteristic times of these evaporations are so short compared to the cluster flight time so that we do not have to explicitly consider actual reaction rates.

The energy available for evaporation of H_2O from the products of Reactions (S1) was calculated as the reaction enthalpy (from our QCC, Table 2) plus the reduced collision energy. Note that the reactant internal energy was used as a zero level for each cluster per the above

argument. The collision energy was corrected for Doppler broadening due to the thermal motions of the gas molecules,[1, 4] which leads to a distribution of energies for the reaction intermediates. This distribution was then integrated, with the integration limits consisting of the dissociation energies of H_2O from the product cluster (Table 2). This results in an estimate of the branching ratios for loss of 0, 1, 2,… H_2O in Reactions (S1).

Abundance spectra

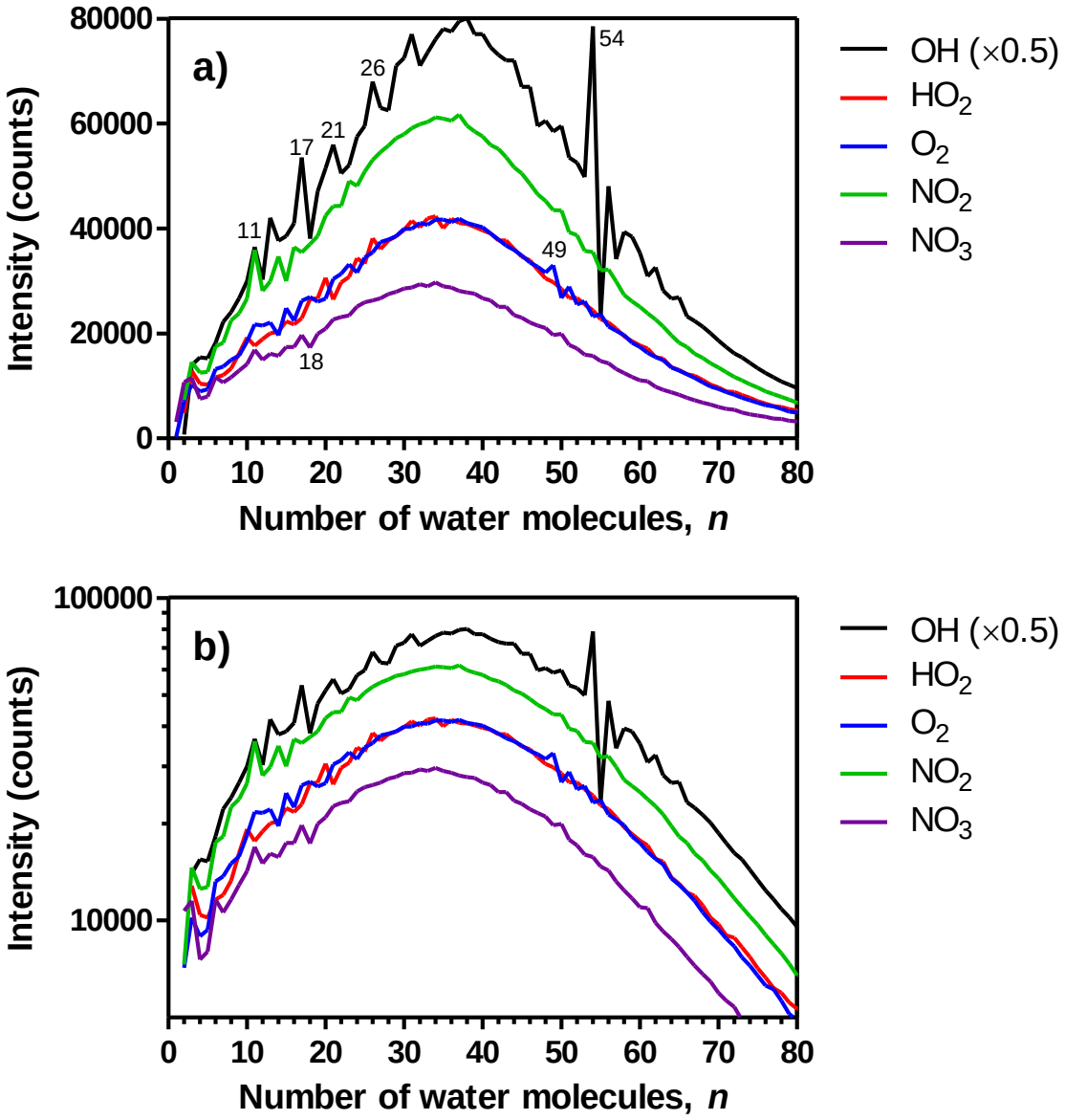

Figure S1. Abundance spectrum of various anionic water clusters $X^-(H_2O)_n$, with X = OH, HO_2, O_2, NO_2 and NO_3 as per the legend. The curve for $OH^-(H_2O)_m$ has been scaled by a factor 0.5. Panel a: linear scale; Panel b: logarithmic scale.

An abundance spectrum, *i.e.*, the distribution of various cluster sizes as produced by the electrospray ion source and detected by the instrument when no size selection is applied in the quadrupole, was collected during the experiments. Figure S1 shows the cluster intensities as a function of size for $X^-(H_2O)_n$, with X = OH, HO_2, O_2, NO_2, NO_3 and $n \leq 80$.

The abundance spectrum of $OH^-(H_2O)_n$ shows the expected magic numbers (in particular n = 11, 17 and 54) and is in perfect agreement with previously published spectra collected using the same instrument.[5] For the other cluster types shown in Fig. S1, no clear magic numbers can be detected, and certainly nothing comparable to $OH^-(H_2O)_{54}$. However, some "minor magic numbers" can be seen that exhibits the characteristic trait of increased intensity followed by a peak with decreased intensity as the next largest neighbour: $HO_2^-(H_2O)_{3,\ 10,\ 20}$, $O_2^-(H_2O)_{15,\ 49}$, $NO_2^-(H_2O)_{3,\ 11,\ 14}$, and $NO_3^-(H_2O)_{3,\ 6,\ 11,\ 17}$.

Evaporation

The evaporation of water molecules from clusters flying through the empty collision cell can be useful for identifying and confirming magic numbers occurring in the cluster population.[6] In addition, it can give valuable clues to other thermodynamic properties of clusters. Figure S2 shows the estimated rate coefficient for loss of H_2O in the background measurements for different cluster sizes and translational energies.

The evaporation rate coefficients shown in Fig. S2 were estimated as $k_{evap} = -\ln(1-\phi_{evap})/t$, where t is the flight time of the ions through the collision cell and ϕ_{evap} is the detected evaporation (*i.e.* loss of H_2O) in the background measurements. The rate coefficient can clearly be seen to increase with the translation energy, which indicate that a substantial part of it originate from collisions with restgas molecules. The loss of water molecules is generally higher for the $HO_2^-(H_2O)_n$ clusters compared to the $OH^-(H_2O)_n$ clusters, indicating that the former cluster type have a slightly lower dissociation energy (the evaporation is barrier-less). The difference is smaller for n = 2, and 8–10. Another interesting feature is the divergence of the two curves occurring at n = 11. This coincides with a similar but mirrored trend observable in the abundance spectra, *i.e.*, a slight magic number occurring for $OH^-(H_2O)_{11}$ and a slight anti–magic number occurring for $HO_2^-(H_2O)_{11}$. This is more clearly illustrated in Fig. S3: a direct comparison of the two plots. It can be shown that magic numbers in a decaying population of clusters arise as a direct consequence of variations in the evaporation rate with cluster size.[6]

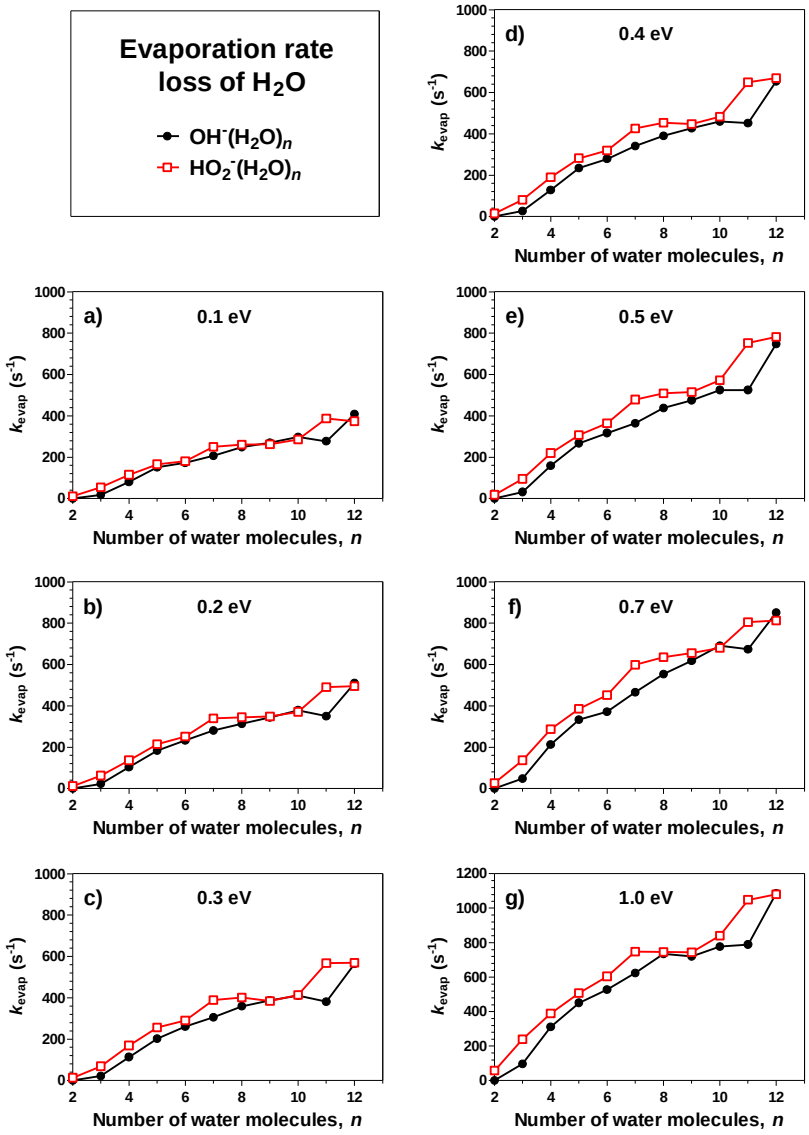

Figure S2. Estimated evaporation rate of $OH^-(H_2O)_n$ and $HO_2^-(H_2O)_n$ clusters when traversing the empty collision cell. The energies given correspond to the nominal reduced-frame collision energy the cluster would experience in a collision with CO_2.

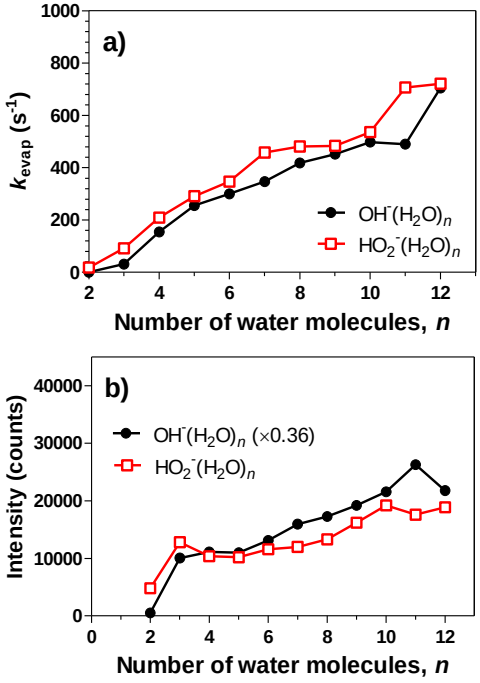

Figure S3. Comparison between the estimated evaporation rate coefficient (Panel a), and the corresponding abundance spectra (Panel b) for $OH^-(H_2O)_n$ and $HO_2^-(H_2O)_n$ clusters. Panel a is identical to Fig. S2e, and Panel b contains the same data as Fig. S1a.

Water loss during reaction and collision

A comparison of the average water loss from $OH^-(H_2O)_n$ and $HO_2^-(H_2O)_n$ clusters when they react or collide with CO_2 is shown in Fig. S4. The clusters show for the most part equal amounts of H_2O detachment after reactions and collisions. For n = 3–4, and to a lesser extent n = 5, the $HO_2^-(H_2O)_n$ clusters exhibit higher average water loss post collision. This indicates that for these particular cluster sizes, the balance between reaction and dehydration enthalpies differs for the two cluster types.

Of particular interest here is to note that the curves for loss of water after reaction show an initially higher amount of H_2O loss for E_{COM} = 0.1 eV, which then decreases for E_{COM} = 0.2–0.3 eV, before it starts to increase again. This behaviour is characteristic of a time dependent evaporation process occurring in addition to a collision/reaction induced one. The reactant clusters will have an internal energy low enough that they are meta-stable with regards to the experimental time-frame. After adding CO_2, clusters will quickly cool down by evaporation of water molecules. However, for many clusters, the last evaporation post reaction will still

leave them with some excess energy which will reduce their characteristic lifetime compared to the experimental time-frame, and result in additional H_2O loss of given enough time. Experimentally, this will be detected as a metastable decay superimposed on the reaction induced H_2O loss. The immediate reaction-induced evaporation increases with E_{COM}, while the metastable decay have a dependence on the nominal collision energy as $1-\exp(A\times E_{COM}^{-1/2})$, approximately proportional to $E_{COM}^{-1/2}$ (with A being some constant or function); the combined result being the characteristic curve shape observed for E_{COM} = 0.1–0.4 eV in Fig. S4.

The effect of the additional meta-stable decay is clear when comparing the experimentally determined average water loss to the modelled one, as is done in Fig. 6. The meta-stable effect is not included in the model, which therefore underestimates the detected average water loss for low E_{COM}. However, for medium to high E_{COM}, the effect can be disregarded; that is, the assumption of the model that the clusters after the reaction induced evaporation will have a lifetime longer than the experimental time frame, holds.

Figure S4 include error bars representing one standard deviation due to count statistics. The greater uncertainty of the larger reacting clusters is a consequence of their low reaction cross section leading to poor count statistics.

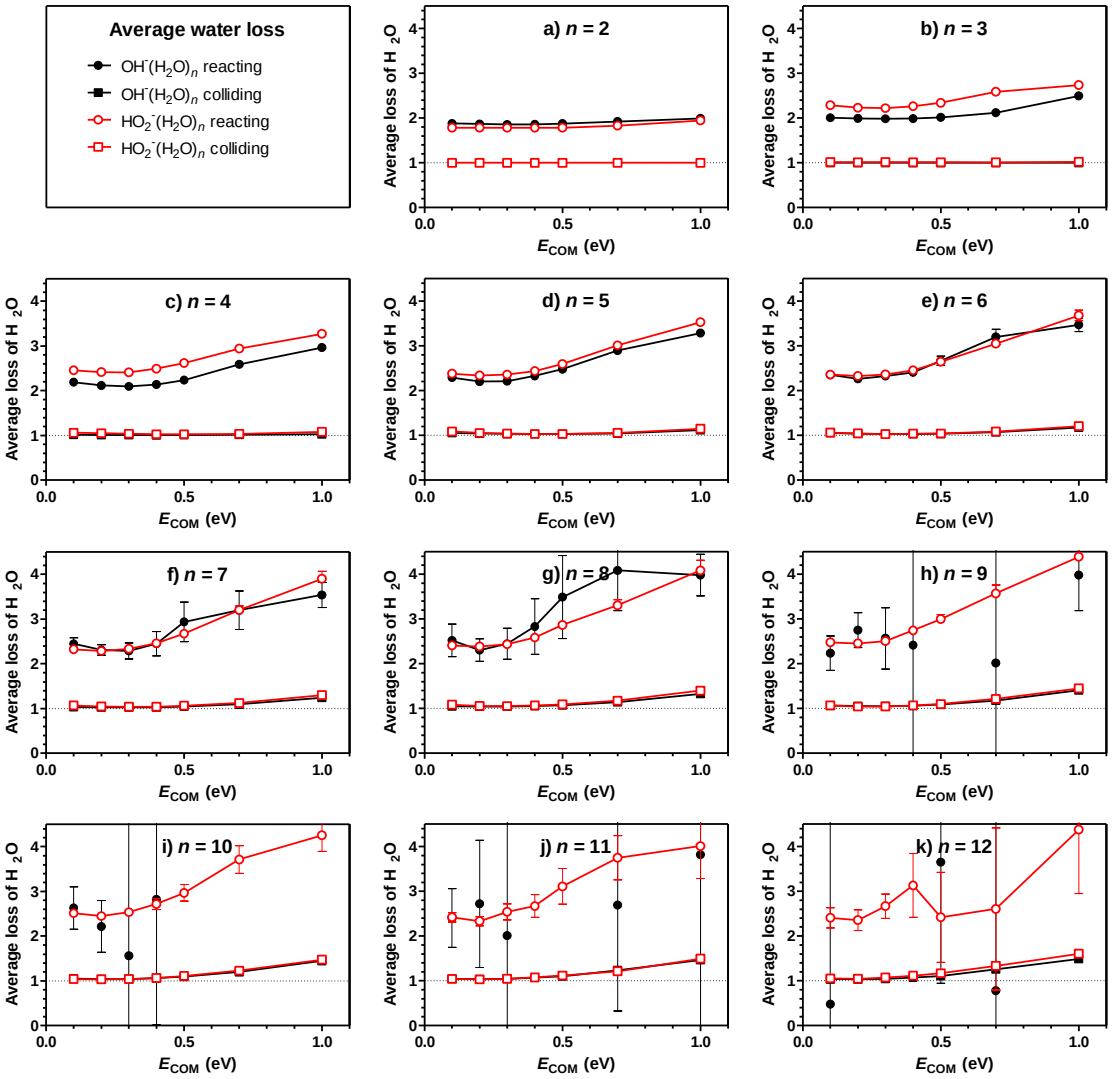

Figure S4. Comparison of the average number of water molecules lost when $OH^-(H_2O)_n$ and $HO_2^-(H_2O)_n$ clusters react with or collide with CO_2. Data given as a function of nominal centre-of-mass collision energy for different cluster sizes *n*. The error bars represent one standard deviation due to count statistics.

Quantum Chemical Calculations

Energy levels

The potential energies (ZPVE included) of all structures in the potential energy diagram Fig. 4 is given below. The structures are numbered 2–15 as per Fig. S5; the energies are given in Table S2.

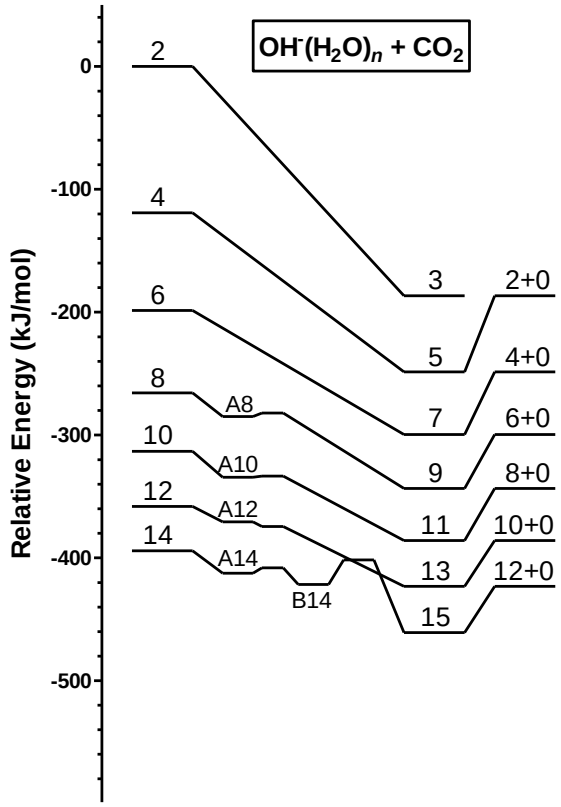

Figure S5. Designation of structures in the potential energy diagram.

Table S2. Energies, in Hartrees (ZPVE included), of the structures in the potential energy diagram, and estimated thermal energies (kJ/mol).

Structure No.	Description	E + ZPVE	Thermal energy (298 K)
0	H_2O	−76,440653	
2	OH^-	−75,820796	
4	$OH^-(H_2O)$	−152,306853	6.2
6	$OH^-(H_2O)_2$	−228,777759	11.1
8	$OH^-(H_2O)_3$	−305,243968	16.5
10	$OH^-(H_2O)_4$	−381,702768	26.0
12	$OH^-(H_2O)_5$	−458,160503	32.5
14	$OH^-(H_2O)_6$	−534,614886	42.6
1	CO_2	−188,638984	
3	$HOCO_2^-$	−264,530851	
5	$HOCO2^-(H_2O)$	−340,995154	
7	$HOCO2^-(H_2O)_2$	−417,455198	
9	$HOCO2^-(H_2O)_3$	−493,912604	
11	$HOCO2^-(H_2O)_4$	−570,369427	
13	$HOCO2^-(H_2O)_5$	−646,824221	
15	$HOCO2^-(H_2O)_6$	−723,279241	
17	$HOCO2^-(H_2O)$	−340,995154	
18	$HOCO_2^-(H_2O)_2$	−417,455198	
A8	$(OH^-)(CO_2)(H_2O)_3$	−493,890253	
A10	$(OH^-)(CO_2)(H_2O)_4$	−570,349726	
A12	$(OH^-)(CO_2)(H_2O)_5$	−646,804244	
A14	$(OH^-)(CO_2)(H_2O)_6$	−723,260816	
B14	$(OH^-)(CO_2)(H_2O)_6$	−723,264306	
16	H_2O_2	−151,582125	
17	HO_2^-	−150,986807	
18	$HOOCO_2^-$	−339,699364	
19	$(H_2O_2)(H_2O)5(OH^-)$	−609,776139	
A19	$(H_2O_2)(H_2O)_5(OH^-)(CO_2)$	−798,420177	
20		−798,435616	
TS(A8 → 9)		−493,889213	
TS(A10 → 11)		−570,349365	
TS(A12 → 13)		−646,805673	
TS(B14 → 15)		−723,256701	
TS(A14 → B14)		−723,259200	
TS(A19 → 20)		−798,415613	

Cartesian coordinates of structures

0 (water)

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.116780
2	1	0	0.000000	0.762889	-0.467119
3	1	0	0.000000	-0.762889	-0.467119

1 (carbon dioxide)

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.160310
3	8	0	0.000000	0.000000	-1.160310

2 (hydroxide)

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.107161
2	1	0	0.000000	0.000000	-0.857286

3 (bicarbonate)

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.173853	0.000000
2	8	0	1.224451	0.425323	0.000000
3	8	0	-1.000619	0.895347	0.000000
4	8	0	-0.296674	-1.246396	0.000000
5	1	0	0.582735	-1.637311	0.000000

4 ((OH-)(H2O))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.234078	0.093151	-0.064364
2	1	0	-1.531407	-0.595877	0.536170
3	8	0	1.228296	-0.096047	-0.055960
4	1	0	0.096245	-0.024430	-0.074960
5	1	0	1.481420	0.643474	0.501381

5 ((HOCO2-)(H2O))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.527078	-0.046364	0.000084
2	1	0	1.913092	0.708273	-0.000007
3	1	0	1.853920	-0.750175	-0.000351
4	6	0	-0.619218	0.045868	-0.000019
5	8	0	-2.042757	0.071453	0.000060
6	1	0	-2.275412	-0.862882	0.000084
7	8	0	-0.124777	-1.107645	-0.000039
8	8	0	-0.081580	1.161253	-0.000057

6 ((OH-)(H2O)2)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000033	1.513202	-0.008893
2	8	0	2.428386	-0.295593	-0.094641
3	1	0	1.454791	0.055198	-0.096974
4	1	0	2.519510	-0.659347	0.788435
5	8	0	-2.428998	-0.293863	0.094274
6	1	0	-2.513686	-0.674835	-0.782159
7	1	0	-1.455383	0.057075	0.096864
8	8	0	-0.000047	0.553044	0.000708

7 ((HOCO2-)(H2O)2)

Center	Atomic	Atomic	Coordinates (Angstroms)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.838800	-1.182103	0.001840
2	1	0	1.857265	-1.098078	0.000134
3	1	0	3.104273	-0.258651	0.001761
4	8	0	-2.821928	-1.137684	0.000048
5	1	0	-1.942521	-1.539745	-0.001740
6	1	0	-2.550406	-0.200085	0.001760
7	6	0	-0.124331	0.586958	-0.000455
8	8	0	1.028358	1.413053	-0.001999
9	1	0	0.667003	2.305517	0.000228
10	8	0	-1.211619	1.199297	0.002777
11	8	0	0.117685	-0.633901	-0.002592

8 ((OH-)(H2O)3)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	1.608265
2	8	0	0.057954	2.488742	-0.214872
3	1	0	0.892573	2.487995	-0.688535
4	1	0	0.000000	1.542128	0.143744
5	8	0	-2.184290	-1.194182	-0.214872
6	1	0	-1.335522	-0.771064	0.143744
7	1	0	-2.600954	-0.471007	-0.688535
8	8	0	2.126337	-1.294560	-0.214872
9	1	0	1.708381	-2.016988	-0.688535
10	1	0	1.335522	-0.771064	0.143744
11	8	0	0.000000	0.000000	0.647879

A8 ((OH-)(H2O)3(CO2))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.419052	0.227093	1.457715
2	8	0	-3.038175	-2.124044	0.229201
3	1	0	-3.837167	-1.746333	-0.145010
4	1	0	-2.451183	-1.315216	0.371512
5	8	0	0.660334	-0.197080	-0.725531
6	1	0	-0.214804	-0.055118	-0.203490

7	1	0	0.547980	-1.062161	-1.125985
8	8	0	-3.084031	2.045798	-0.368692
9	1	0	-2.517763	2.487976	-1.004768
10	1	0	-2.507891	1.287761	-0.026524
11	8	0	-1.579806	0.066756	0.524673
12	6	0	3.070137	0.077960	0.138390
13	8	0	3.459873	-0.819831	-0.491431
14	8	0	2.829188	0.991931	0.812557

TS(A8->9)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.238941	-0.346335	1.531527
2	8	0	-3.539799	-1.708994	-0.182825
3	1	0	-4.129288	-1.046145	-0.548489
4	1	0	-2.755675	-1.175378	0.127028
5	8	0	0.487599	0.341331	-0.648606
6	1	0	-0.498392	0.047457	-0.005040
7	1	0	0.387758	-0.065566	-1.512885
8	8	0	-1.284175	2.612014	-0.161898
9	1	0	-0.484306	2.192899	-0.519515
10	1	0	-1.674399	1.836203	0.278843
11	8	0	-1.517017	-0.136437	0.637039
12	6	0	2.493751	-0.429309	0.119736
13	8	0	2.928529	-0.811581	-0.898775
14	8	0	2.353706	-0.154743	1.246329

9 ((HOCO2-)(H2O)3)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.806238	1.099209	1.321595
2	1	0	-2.227020	1.181519	0.454652
3	1	0	-0.862340	1.076687	1.063792
4	8	0	-1.572115	-1.724858	0.231200
5	1	0	-0.591295	-1.648397	0.177902
6	1	0	-1.805392	-1.012489	0.843928
7	8	0	-1.706013	0.539056	-1.621345
8	1	0	-1.810173	-0.355262	-1.252609

9	1	0	-0.829945	0.789306	-1.276014
10	6	0	1.443154	-0.045989	0.025968
11	8	0	2.813406	0.243809	-0.034330
12	1	0	2.843950	1.204484	-0.096866
13	8	0	0.690218	0.968387	-0.016036
14	8	0	1.158652	-1.245592	0.110093

10 ((OH-)(H2O)3)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.001547	-0.002780	1.938903
2	8	0	-1.920349	-1.464930	-0.247782
3	1	0	-2.302690	-0.734210	-0.742559
4	1	0	-1.228242	-1.000930	0.296563
5	8	0	1.477962	-1.901959	-0.251154
6	1	0	1.001057	-1.219132	0.294880
7	1	0	0.756804	-2.291068	-0.754355
8	8	0	1.915235	1.465967	-0.246511
9	1	0	1.224939	0.999604	0.297980
10	1	0	2.300295	0.736362	-0.740849
11	8	0	-1.472498	1.904254	-0.250572
12	1	0	-0.747316	2.289923	-0.750725
13	1	0	-1.001176	1.217856	0.295386
14	8	0	-0.000616	-0.002785	0.979117

A10 ((OH-)(H2O)4(CO2))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.238373	-0.958337	1.501249
2	8	0	-0.542944	2.821399	-0.577643
3	1	0	-0.021667	2.001922	-0.625980
4	1	0	-1.366199	2.521558	-0.154206
5	8	0	-2.892075	1.479722	0.562792
6	1	0	-2.349165	0.620176	0.626605
7	1	0	-3.453658	1.346832	-0.204213
8	8	0	-2.732732	-2.744529	-0.526059
9	1	0	-2.215052	-1.991457	-0.104340
10	1	0	-3.647958	-2.512410	-0.356310

11	8	0	0.649331	0.126393	-0.599319
12	1	0	0.549003	-0.219555	-1.489359
13	1	0	-0.175476	-0.229566	-0.088428
14	8	0	-1.458617	-0.700281	0.602832
15	6	0	3.126748	-0.375304	0.223825
16	8	0	3.503904	-0.517663	-0.867123
17	8	0	2.867892	-0.255959	1.348524

TS(A10->11)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.259737	0.856445	1.527394
2	8	0	-0.250480	-2.638289	-0.763830
3	1	0	-0.346754	-1.647556	-0.781371
4	1	0	-0.554866	-2.883701	0.113201
5	8	0	2.495668	-1.988652	0.471483
6	1	0	2.236355	-1.045982	0.588440
7	1	0	1.760037	-2.350241	-0.041510
8	8	0	3.258339	2.420568	-0.355005
9	1	0	2.574925	1.795839	0.019776
10	1	0	3.982160	1.837027	-0.592799
11	8	0	-0.475166	0.050752	-0.648766
12	1	0	-0.374892	0.490766	-1.496327
13	1	0	0.446688	0.349401	-0.036474
14	8	0	1.517311	0.628707	0.631174
15	6	0	-2.826997	0.661097	0.254610
16	8	0	-3.145159	1.222545	-0.713398
17	8	0	-2.653188	0.133296	1.274843

11 ((HOCO2-)(H2O)4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.387402	1.635360	-1.286379
2	1	0	0.446539	1.504019	-1.057480
3	1	0	1.779378	1.677663	-0.399688
4	8	0	1.448514	-1.245708	-1.601925
5	1	0	1.578400	-0.280757	-1.640921
6	1	0	0.545259	-1.323074	-1.246698

7	8	0	1.474216	-1.564728	1.301158
8	1	0	0.525762	-1.517760	1.077833
9	1	0	1.863178	-1.571358	0.411222
10	8	0	1.328573	1.309284	1.630118
11	1	0	1.524176	0.354990	1.664002
12	1	0	0.437127	1.327821	1.239924
13	6	0	-1.595599	-0.069789	-0.016129
14	8	0	-2.990496	-0.114313	0.012293
15	1	0	-3.255616	0.811789	0.027883
16	8	0	-1.098978	1.087403	-0.013246
17	8	0	-1.033058	-1.177874	-0.039431

12 ((OH-)(H2O)5)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.501389	-0.910566	-2.172523
2	8	0	-1.422869	1.159901	1.286791
3	1	0	-0.674346	1.573949	0.815909
4	1	0	-1.905454	0.713246	0.568117
5	8	0	0.758657	1.948070	-0.439700
6	1	0	1.576127	1.696530	0.007475
7	1	0	0.545236	1.106272	-0.928989
8	8	0	2.650527	-0.410154	0.183132
9	1	0	2.237491	-0.784537	0.970624
10	1	0	1.915247	-0.496160	-0.473191
11	8	0	-0.023089	-1.506169	1.310657
12	1	0	0.115793	-1.376789	0.347805
13	1	0	-0.458363	-0.676783	1.566739
14	8	0	-2.299344	-0.518115	-0.932581
15	1	0	-2.400684	-1.308290	-0.394551
16	1	0	-1.314305	-0.521867	-1.158935
17	8	0	0.318852	-0.550408	-1.301859

A12 ((OH-)(H2O)5(CO2))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.314736	-2.241736	-1.298520
2	8	0	-0.875017	0.979826	1.621351

3	1	0	-1.280757	0.089693	1.692932
4	1	0	-0.127310	0.833617	1.006871
5	8	0	-1.979544	-1.618272	1.369783
6	1	0	-2.847509	-1.444553	0.988682
7	1	0	-1.406828	-1.680275	0.541635
8	8	0	-3.226846	-0.515590	-1.381960
9	1	0	-3.175792	0.352567	-0.957368
10	1	0	-2.306989	-0.869221	-1.330185
11	8	0	-2.697848	2.196449	-0.047290
12	1	0	-2.156510	2.470125	-0.791536
13	1	0	-2.054516	1.802977	0.592612
14	8	0	1.036925	0.321370	-0.396098
15	1	0	0.962404	0.944344	-1.122715
16	1	0	0.365649	-0.467161	-0.641890
17	8	0	-0.657143	-1.444368	-0.890230
18	6	0	3.660926	0.041522	-0.044642
19	8	0	3.569221	-0.914608	0.605446
20	8	0	3.877419	0.990254	-0.682586

TS(A12->13)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.092161	2.164428	-1.417632
2	8	0	0.768894	-0.982697	1.560398
3	1	0	1.188869	-0.111078	1.680578
4	1	0	0.044976	-0.800967	0.906808
5	8	0	1.999797	1.653506	1.319351
6	1	0	2.788635	1.370777	0.836428
7	1	0	1.357527	1.751273	0.576193
8	8	0	3.201374	0.480387	-1.215935
9	1	0	3.090523	-0.425982	-0.885754
10	1	0	2.287833	0.820800	-1.304594
11	8	0	2.589759	-2.193817	-0.062874
12	1	0	2.045573	-2.584266	-0.750792
13	1	0	1.936331	-1.800479	0.573414
14	8	0	-1.023520	-0.325080	-0.404034
15	1	0	-0.984053	-0.986097	-1.099469
16	1	0	-0.264067	0.588347	-0.737043
17	8	0	0.537553	1.438232	-0.977774
18	6	0	-3.481622	-0.032388	-0.015439
19	8	0	-3.377540	0.934386	0.620881

20	8	0	-3.783139	-0.978971	-0.625701

13 ((HOCO2-)(H2O)5)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.370393	0.666873	1.647310
2	1	0	2.053353	-0.000361	2.261888
3	1	0	2.230391	0.264199	0.755971
4	8	0	0.025457	2.335896	1.034828
5	1	0	0.817560	1.868816	1.349255
6	1	0	-0.606489	1.629223	0.826163
7	8	0	4.687102	-0.971811	-0.418459
8	1	0	3.766792	-0.910625	-0.728991
9	1	0	4.684535	-0.418719	0.368112
10	8	0	-4.432954	0.589399	-0.188365
11	1	0	-3.457971	0.584828	-0.236940
12	1	0	-4.613316	-0.294251	0.143270
13	8	0	0.257701	1.640038	-1.798390
14	1	0	-0.473404	1.067780	-1.499429
15	1	0	0.362475	2.220315	-1.027137
16	8	0	1.901419	-0.440201	-0.817749
17	1	0	1.512921	0.304792	-1.318447
18	1	0	1.111328	-0.977173	-0.555291
19	6	0	-1.381882	-1.065859	0.081870
20	8	0	-2.504354	-1.769434	0.521211
21	1	0	-2.182245	-2.662235	0.686860
22	8	0	-0.319613	-1.719102	0.035038
23	8	0	-1.599483	0.133164	-0.204986

14 ((OH-)(H2O)6)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.001328	-1.095529	2.021567
2	8	0	0.002517	2.140807	-1.183856
3	1	0	-0.758441	2.010616	-0.587509
4	1	0	0.762530	2.008961	-0.586622
5	8	0	-0.000101	-0.721632	-1.716399
6	1	0	0.000969	0.250140	-1.792504

7	1	0	-0.001546	-0.846761	-0.750270
8	8	0	-1.881107	1.284833	0.842344
9	1	0	-2.537859	0.686191	0.465734
10	1	0	-1.166122	0.646523	1.099356
11	8	0	-2.422661	-1.600203	-0.010563
12	1	0	-2.099715	-1.520423	-0.916211
13	1	0	-1.611309	-1.399722	0.509326
14	8	0	2.419840	-1.603024	-0.010937
15	1	0	1.608728	-1.402008	0.509092
16	1	0	2.096736	-1.522457	-0.916477
17	8	0	1.882522	1.281952	0.844025
18	1	0	2.538729	0.682701	0.467432
19	1	0	1.166463	0.644416	1.100108
20	8	0	-0.000740	-0.675564	1.157509

A14 ((OH-)(H2O)5(CO2))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.286177	-0.061171	-1.238078
2	8	0	1.009505	-0.145701	-0.057135
3	1	0	0.581773	-0.954383	-0.402253
4	1	0	0.613701	0.560636	-0.598614
5	8	0	-1.426604	0.517251	1.617273
6	1	0	-0.516907	0.306393	1.353451
7	1	0	-1.931441	0.335460	0.790270
8	8	0	-0.625859	-2.214609	-1.192039
9	1	0	-0.968233	-2.733292	-0.453025
10	1	0	-1.323062	-1.513141	-1.271865
11	8	0	-2.740651	-2.290865	1.007373
12	1	0	-2.361456	-1.801261	1.745917
13	1	0	-2.766552	-1.598863	0.304992
14	8	0	-1.315597	3.348506	0.764506
15	1	0	-1.108770	3.027600	-0.125310
16	1	0	-1.396497	2.518298	1.262953
17	8	0	-0.744503	1.591106	-1.561221
18	1	0	-0.640823	1.576228	-2.514763
19	1	0	-1.458786	0.889326	-1.340622
20	8	0	-2.424598	-0.240179	-0.854889
21	6	0	3.723126	-0.229295	0.209684
22	8	0	3.868710	0.802433	-0.302774
23	8	0	3.677657	-1.264950	0.732511

TS(A14->B14)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.226171	0.489495	-1.782209
2	8	0	-0.844886	0.271770	-0.042462
3	1	0	-0.435306	1.129439	-0.284223
4	1	0	-0.394643	-0.367951	-0.632893
5	8	0	0.911248	-0.647788	1.994398
6	1	0	0.233132	-0.292189	1.381870
7	1	0	1.594331	-0.986887	1.405548
8	8	0	0.718337	2.502523	-0.838893
9	1	0	1.133356	2.749048	-0.001509
10	1	0	1.372995	1.831846	-1.176648
11	8	0	2.756720	1.706157	1.262398
12	1	0	2.197546	1.128325	1.798251
13	1	0	2.784455	1.245742	0.388785
14	8	0	1.084519	-3.488853	0.400617
15	1	0	1.050503	-2.831894	-0.324336
16	1	0	0.693116	-3.023920	1.147048
17	8	0	0.906196	-1.392314	-1.466437
18	1	0	0.717611	-1.542249	-2.394826
19	1	0	1.641121	-0.588444	-1.411534
20	8	0	2.452978	0.509372	-1.215299
21	6	0	-3.587056	0.244553	0.049933
22	8	0	-3.658760	-0.720459	-0.591993
23	8	0	-3.612859	1.208632	0.696057

B14 ((H2O) (OH-)(H2O)4(CO2))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.419507	-0.186393	-1.922952
2	8	0	0.843328	-0.423809	-0.101514
3	1	0	0.377015	-1.275071	-0.151772
4	1	0	0.316967	0.179266	-0.702465
5	8	0	-0.578518	0.832156	2.059573
6	1	0	0.013671	0.367424	1.435677
7	1	0	-0.807441	1.648557	1.576547

8	8	0	-1.099885	-2.668711	-0.262500
9	1	0	-1.553746	-2.333754	0.532461
10	1	0	-1.577662	-2.193745	-0.960280
11	8	0	-2.700094	-0.977230	1.438633
12	1	0	-2.041421	-0.331747	1.765289
13	1	0	-2.864104	-0.698503	0.520823
14	8	0	-0.961426	3.063830	0.251745
15	1	0	-0.908638	2.382695	-0.498334
16	1	0	-0.078102	3.437623	0.295375
17	8	0	-0.769375	1.163541	-1.522176
18	1	0	-0.472632	1.392964	-2.405103
19	1	0	-1.914850	0.196461	-1.531581
20	8	0	-2.660235	-0.523640	-1.444424
21	6	0	3.519177	-0.289546	-0.060374
22	8	0	3.519874	0.812091	-0.428178
23	8	0	3.633255	-1.384291	0.309912

TS(B14->15)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.271519	1.821947	-0.960012
2	8	0	0.767143	-0.636911	-0.095117
3	1	0	0.403334	-1.526874	-0.185621
4	1	0	0.154638	0.162983	-0.872923
5	8	0	-0.385336	0.528742	2.096517
6	1	0	0.095585	0.014638	1.402787
7	1	0	-0.227361	1.440358	1.809972
8	8	0	-1.589312	-2.772038	-0.251155
9	1	0	-2.015032	-2.097299	0.322138
10	1	0	-1.758900	-2.452774	-1.141116
11	8	0	-2.791185	-0.654708	1.178750
12	1	0	-2.026805	-0.201400	1.591331
13	1	0	-2.990440	-0.116756	0.391872
14	8	0	0.701882	2.757711	0.370436
15	1	0	0.264079	2.263147	-0.354219
16	1	0	1.544688	2.295300	0.453759
17	8	0	-0.398778	0.971537	-1.487993
18	1	0	-0.008262	0.991033	-2.364162
19	1	0	-2.074899	0.938922	-1.388928
20	8	0	-3.059081	0.927469	-1.236803
21	6	0	2.822497	-0.579899	-0.146694

22	8	0	3.000835	0.579267	-0.010651
23	8	0	3.125822	-1.707798	-0.292071

15 ((HOCO2-)(H2O)6)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.894899	-0.873393	1.751646
2	1	0	1.198695	-1.169375	1.137284
3	1	0	2.683490	-0.777167	1.190274
4	8	0	0.548163	1.652325	1.750725
5	1	0	1.105701	0.859129	1.871082
6	1	0	-0.275469	1.286365	1.391998
7	8	0	3.985651	-0.362023	-0.218654
8	1	0	3.245780	-0.312997	-0.874444
9	1	0	4.233166	0.552865	-0.063460
10	8	0	-4.336081	0.803416	0.006292
11	1	0	-3.359456	0.776491	0.011304
12	1	0	-4.558909	-0.130058	-0.037704
13	8	0	0.484680	2.180949	-1.080949
14	1	0	-0.328161	1.656178	-0.978568
15	1	0	0.776030	2.240811	-0.153692
16	8	0	1.790971	-0.215297	-1.835262
17	1	0	1.449194	0.693170	-1.712711
18	1	0	1.138875	-0.748077	-1.339177
19	6	0	-1.270207	-0.876228	-0.107478
20	8	0	-2.392507	-1.699741	-0.121859
21	1	0	-2.039378	-2.593365	-0.194630
22	8	0	-0.165837	-1.464965	-0.187053
23	8	0	-1.515978	0.344154	-0.015221

16 (HOOH)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.716788	0.114479	0.057278
2	1	0	-1.018461	-0.644586	-0.458182
3	8	0	0.716799	-0.114487	0.057264
4	1	0	1.018367	0.644645	-0.458154

17 (HOO-)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.055795	0.811896	0.000000
2	8	0	0.055795	-0.705056	0.000000
3	1	0	-0.892728	-0.854721	0.000000

18 (HOOCO2-)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.608826	0.078298	-0.000006
2	8	0	0.284184	1.286761	-0.000048
3	8	0	1.688821	-0.507136	0.000043
4	8	0	-0.500409	-0.843172	-0.000037
5	8	0	-1.760645	-0.096113	0.000002
6	1	0	-1.348567	0.807487	0.000359

19 ((OH-)(H2O2)(H2O)5)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.082959	-2.179089	0.123768
2	8	0	-0.577957	-1.621850	-1.129483
3	1	0	-0.552349	-1.626359	0.792612
4	1	0	0.131300	-0.932607	-1.375776
5	8	0	1.103961	0.275764	-1.700588
6	1	0	1.408700	0.278509	-2.609499
7	8	0	2.483479	-0.591142	0.413987
8	1	0	2.150325	-0.217283	-0.445401
9	1	0	1.889144	-1.347336	0.522167
10	8	0	0.900797	1.342336	1.791773
11	1	0	1.547936	0.705825	1.423058
12	1	0	0.559673	1.800146	1.002715
13	8	0	-0.194687	2.203372	-0.743942
14	1	0	-0.015390	3.030197	-1.195024
15	1	0	0.368831	1.464665	-1.227032

16	8	0	-2.478300	0.481229	-0.521037
17	1	0	-1.989353	-0.300769	-0.837744
18	1	0	-1.841048	1.206542	-0.653853
19	8	0	-1.306247	-0.437989	1.932178
20	1	0	-0.562328	0.194453	2.017342
21	1	0	-1.880126	-0.037026	1.253174

A19 ((OH-)(H2O2)(CO2)(H2O)5)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.523188	-0.387876	-1.477804
2	8	0	0.990692	0.116770	-0.193856
3	1	0	-0.200079	0.247624	-1.697219
4	1	0	0.451511	-0.432527	0.491977
5	8	0	-0.452283	-1.116232	1.530656
6	1	0	0.057352	-1.467296	2.263066
7	8	0	-1.436394	-2.509391	-0.526554
8	1	0	-1.104311	-2.161646	0.343152
9	1	0	-0.805719	-2.099334	-1.134996
10	8	0	-3.388063	-0.427949	-0.541862
11	1	0	-2.827891	-1.230149	-0.591450
12	1	0	-3.173964	-0.055666	0.331816
13	8	0	-2.223573	0.641982	1.889436
14	1	0	-2.601713	0.614555	2.770107
15	1	0	-1.491260	-0.099246	1.850391
16	8	0	-0.561774	2.496359	0.472823
17	1	0	0.120875	1.827164	0.286774
18	1	0	-1.168219	2.029013	1.076004
19	8	0	-1.625779	1.322508	-1.918248
20	1	0	-2.326394	0.750885	-1.540087
21	1	0	-1.390506	1.923671	-1.187389
22	6	0	3.683546	-0.041941	0.123626
23	8	0	3.910700	0.015765	-1.012771
24	8	0	3.558166	-0.101361	1.277692

TS(A19->20)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	0.524933	-1.260701	0.861840
2	8	0	0.993899	-0.215132	-0.046299
3	1	0	-0.117311	-1.749245	0.304456
4	1	0	0.405164	1.037045	0.351963
5	8	0	-0.057867	1.964984	0.579229
6	1	0	0.646814	2.612417	0.497150
7	8	0	-1.216964	0.179715	2.525951
8	1	0	-0.926684	1.037949	2.182399
9	1	0	-0.582873	-0.428557	2.088630
10	8	0	-3.267025	-0.322176	0.595920
11	1	0	-2.665224	-0.166534	1.351655
12	1	0	-3.043903	0.387866	-0.025572
13	8	0	-2.085864	1.758235	-1.168402
14	1	0	-2.471430	2.606783	-1.395296
15	1	0	-1.333584	1.949993	-0.548511
16	8	0	-0.408142	-0.411374	-2.425462
17	1	0	0.206061	-0.354742	-1.655029
18	1	0	-1.007879	0.334434	-2.286950
19	8	0	-1.611210	-2.331919	-0.699812
20	1	0	-2.277098	-1.766176	-0.266265
21	1	0	-1.313192	-1.801806	-1.463055
22	6	0	3.103332	0.035409	-0.037786
23	8	0	3.498300	-0.971499	0.411925
24	8	0	3.112583	1.120882	-0.498499

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20 ((HOOCO2-)(H2O)5)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.055453	-0.694769	1.838253
2	1	0	1.301215	-0.989271	1.300901
3	1	0	2.821528	-0.769831	1.242256
4	8	0	1.011157	1.944746	1.533181
5	1	0	1.484315	1.117377	1.748093
6	1	0	0.127132	1.631475	1.282593
7	8	0	4.095822	-0.709214	-0.223967
8	1	0	3.356316	-0.606044	-0.871668
9	1	0	4.516787	0.153363	-0.192024
10	8	0	-4.005194	1.718794	-0.020588
11	1	0	-3.061848	1.482373	0.039756
12	1	0	-4.432016	0.860849	-0.089074
13	8	0	0.969316	2.224437	-1.285251

14	1	0	0.052459	1.921477	-1.219649
15	1	0	1.219724	2.273630	-0.341150
16	8	0	1.889246	-0.393274	-1.808827
17	1	0	1.661662	0.557554	-1.750972
18	1	0	1.196002	-0.811369	-1.268918
19	6	0	-1.199560	-0.506666	0.036245
20	8	0	-2.444343	-1.131878	-0.041424
21	8	0	-0.195540	-1.258481	0.027615
22	8	0	-1.287654	0.730652	0.102292
23	8	0	-2.303929	-2.575201	-0.122445
24	1	0	-1.320600	-2.628089	-0.088334

Additional information

On the liquid phase equilibrium of CO_2

Combining the equilibriums of Eq. 2 and Eq. 3, respectively

$$\frac{[H_2CO_3]}{[CO_2]} = K_H \quad \text{(S11)}$$

$$\frac{[H_3O^+][HOCO_2^-]}{[H_2CO_3]} = K_A, \quad \text{(S12)}$$

with $[H_3O^+][OH^-] = K_W$ yields

$$\frac{[HOCO_2^-]}{[CO_2]} = \frac{K_A K_H}{K_W}[OH^-]. \quad \text{(S13)}$$

Note that the acid dissociation constant for H_2CO_3 is often given for

$$\frac{[H_3O^+][HOCO_2^-]}{[CO_2]+[H_2CO_3]} = K_A^*. \quad \text{(S14)}$$

However, it is easily shown that

$$K_A = K_A^* * (1 + \frac{1}{K_H}), \quad \text{(S15)}$$

which gives

$$\frac{[HCO_3^-]}{[CO_2]} = \frac{K_A^*(1+K_H)}{K_W}[OH^-]. \quad \text{(S16)}$$

Using values[7] for $K_H = 1.5\times10^{-3}$ and $K_A = 2.0\times10^{-4}$ M (pK_A = 3.70), the right hand side of Eq. S13 becomes 3.0×10^7 $[OH^-]$ at 298 K.

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