# SUPPLEMENTARY INFORMATION

## **BEHAVIOR OF HYDROXYL RADICALS IN AQUEOUS ENVIRONMENTS**

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# 1. The triplet O(aq)

The evolution of the electronic spin density during the disproportionation reaction 2 OH\* (aq)  $\rightarrow$  O(aq) + H<sub>2</sub>O in the triplet state can be observed in the Video1\_O(aq)\_production (only the molecules involved in the reaction are shown). Details on the generation of the videos are presented in the Methods section. A full analysis of the reaction mechanism (including local structure, electronic localization functions, and HOMO) will be provided in a forthcoming article. The evolution of the electronic spin density of the reaction product, O(aq), during 5 ps after the reaction is shown in Video2\_triplet\_O. The existence of an O-H<sub>2</sub>O complex has been documented in the gas phase. However, as can be observed in this video, the dynamic behavior

of the isosurfaces does not show any strong coupling with the hydration within 2.5 Å of O(aq). O(aq) seems to be a weakly hydrated species. This is in agreement with the  $g_{OO}$  and  $g_{OH}$  radial distribution functions for this simulation presented in Fig. S1; within a 2.5 Å cutoff O(aq) does not exhibit a peak as would be expected if there was a persistent interaction with any water molecule. The O-H<sub>2</sub>O complex described in the gas phase simulations is not evident in solution.



**Figure S1:** Radial distribution functions, g(r), after the formation of the triplet O(aq) from a OH\* pair in the triplet state, averaged over 5 ps for a  $63 \cdot H_2O-O^*$  system at a temperature of 310 K. (a) oxygen-hydrogen RDFs in which O<sub>1</sub>\*H (O<sub>1</sub> represents O(aq)) is represented by a blue solid line, O<sub>2</sub>\*H (O<sub>2</sub> being the oxygen atom of the second OH\* after being converted into a water molecule) is represented by a green solid line, and OH is represented by a red solid lines (b) oxygen-oxygen RDFs in which O<sub>1</sub>\*O is represented by a blue solid line, O<sub>2</sub>\*O is represented by a green solid line.

## 2. The OH\*-dimer

The evolution of the spin density isosurfaces of the OH\* dimer (hemibonded interaction) can be observed in Video\_3\_OH\*-dimer (0.9 ps of Car-Parrinello molecular dynamics simulations) in which positive and negative spin density values are represented as yellow and green isosurfaces, respectively. The spin density is delocalized among the four atoms, showing a persistent complex with a very short O\*-O\* distance of about 2.11 Å (see Fig. S2). The variation in the O\*-O\* distance appears to be oscillatory in nature and resembles bond stretching vibrations for heavy atoms experiencing a relatively weak interaction. Fig. S3 shows the RAMT plot corresponding to this simulation (RAMT-4). Consistent with the information provided in Fig. S2, the O\*-O\* separation remains around 2.0 Å during the simulation.



**Figure S2:** Evolution of O\*-O\* (blue solid line),  $O_1^*-H_2^*$  (red solid line) and  $O_2^*-H_1^*$  (green solid line) separations of the OH\*-dimer (hemibonded) during 0.9 ps of Car-Parrinello molecular dynamics simulations of a  $62 \cdot H_2O$ -2OH\* at 310 K. The colors of the lines shown in the inset correspond to the same line colors in the graphs.

#### 3. RAMT-plots for different Car-Parrinello MD simulations

The RAMT plots in Fig. S3 are trajectory traces plotted in a semicircular projection of spherical polar coordinates (r,  $\theta$ ,  $\varphi$ ). We place an oxygen atom at the origin and align the H-O bond with zenith direction. OH\* has a C<sub>∞</sub> symmetry axis that coincides with the H-O bond, so OH\* cannot distinguish different  $\varphi$ -values in terms of its own structure. Therefore, only the terms of (r,  $\theta$ ) are significant. A plot in this space reveals the atomic trajectories of the atoms in the system from the perspective of the centrally placed OH\*. Given that the RAMT plot for a OH\* is only semicircular, two of these RAMT plots be placed back to back such that they appear to have the same layout as polar coordinates or a radar view.

Fig. S3 shows RAMT plots for three different simulations of  $62 \cdot H_2O-2OH^*$  at 310 K, in RAMT-1, RAMT-2 and RAMT-3, respectively. The outcome of all these three simulations is the disproportionation reaction 2 OH\* (aq) $\rightarrow$  O(aq) + H<sub>2</sub>O in the triplet state. RAMT-4 in Fig. S3 shows a non-reactive system, in which an OH\*-dimer (hemibonded) forms instead of an O(aq) atom. Here, the two hydroxyl radicals appear to move relative to one another such that the oxygen atom of one hydroxyl radical forms a roughly 60° to 120° with the O-H bond of the other radical (O\*<sub>1</sub>O\*<sub>2</sub>H angle). This qualitative range is comparable to the range of 43° to 123° that Chipman<sup>21</sup> found to be the optimum range of angles between the oxygen of a water molecule and the O-H bond of a hydroxyl radical for hemibonding to occur. The hemibonding between water and a hydroxyl radical is described in the literature as a three electron two center interaction.<sup>21-23</sup> In the first three plots, sides A and B correspond to the RAMT plots for the OH\* that becomes the triplet oxygen and the OH\* that becomes the water molecule, respectively. In RAMT-4, each side corresponds to each OH\* forming the dimer. The two semicircular RAMT plots are divided by a white vertical line. The yellow, red, green and blue traces correspond to the projected trajectory traces of the OH\* hydrogen, the OH\* oxygen, the H<sub>2</sub>O oxygen atoms and the H<sub>2</sub>O hydrogen atoms, respectively, up to 10 fs after the transition state of the reaction with the exception of the RAMT plots in RAMT-4, which are drawn until the end of the simulation. A large dot is used to indicate the final position of each OH\* atom in the other radical's RAMT plot. The final positions of the OH\* atoms that define the frame of reference of a given RAMT plot are shown as semi-circles along the line. In this figure, X refers to any atom of the system, and the distance scale refers to the separation between X and the HO\* oxygen atom that defines the local frame of reference for a given RAMT plot. The distance scale is not constant from 0.0 Å to the outer edge of the RAMT plot. The distance scale has two linear regions, from 0.0 Å to 4.0 Å and from 4.0 Å Å to the outer edge of the RAMT plot, the maximum distance that any atom can be from the HO\* oxygen atom based on periodic boundary conditions. The simulation details have been provided in the Methods section.



**Figure S3:** Local frame representation (as a RAMT plot) of four different trajectories showing three reactive systems (RAMT-1, RAMT-2 and RAMT-3) in which the OH\* radical pair form O(aq) in the triplet state, and one non-reactive system (RAMT-4) in which an OH\*-dimer (hemibonded) forms.

#### 4. Hydrogen peroxide formed from a OH\* pair in water in the singlet state

The local structure and the isosurfaces from the electronic localization functions (ELF), highest occupied molecular orbital (HOMO) and HOMO-1, corresponding to different states during the formation of hydrogen peroxide in water from an OH\* pair, are presented in Fig. S4. In the local structure, the two H-bond acceptor water molecules for each OH\* are also shown to highlight the persistence of these interaction during the simulation. In the initial state, the OH\* are separated by a water molecule and one of the OH\* is hemibonded (O\*-Ow distance of 2.5 Å). The ELF isosurfaces for this state are typical for OH\* and water molecules, and the HOMO and HOMO-1 are localized on one of the OH\*. The radicals adopt a "side-by-side" arrangement after about 0.5 ps (see Fig. 1, Int1), reminiscent of the hemibonded interaction in the triplet state (with a O\*-O\* separation of 2.4 Å). A change in the electronic localization function is evident for both OH\* radicals, and the HOMO and HOMO-1 remain localized on the same OH\*. In a more advanced stage (Int2), at ~ 0.8 ps, the O\*-O\* separation decreases to 1.8 Å and the HOMO and HOMO-1 are delocalized on both OH\* oxygens. In the post-reaction state, the hydrogen peroxide molecule has formed and the ELF shows paired electrons between the two oxygen atoms.

Stage	(a) Local structure	(b) ELF	(c) HOMO	(d) HOMO-1
Initial	1.8 Å 1.8 Å 1.8 Å 1.8 Å 2.5 Å			
<b>Int1</b> (t~0.5 ps)	1.9 Å 2.0 Å 2.4 Å			° ● ● ● ● ● ● ● ●
Int2 (t~0.8 ps)	1.4 Å 1.8 Å			2000 - 1000 2000 - 1000 2000 - 1000
Post- reaction (t~ 1ps)	1.7 Å 1.3 Å		<b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b> <b>3</b>	

**Figure S4:** Molecular configurations and electronic features for different stages during the spontaneous formation of hydrogen peroxide from an OH\* pair. Dark blue and purple spheres represent the oxygen atoms of the initial radicals. Column (a) shows molecular configurations in which the black numbers are atomic distances, (b) presents the electron localization functions (ELF) as light green isosurfaces (0.85), and columns (c) and (d) shows the evolution of the HOMO and HOMO-1, respectively, where the blue isosurfaces have values of -0.03.

Figure S5 shows the  $g_{OO}$  and  $g_{OH}$  radial distribution functions averaged over the full simulation trajectory in which  $H_2O_2$  is formed. Examination of Fig. S5 reveals very similar solvation features for both hydrogen peroxide oxygen atoms. This is consistent with the coordination numbers provided in Fig. S6; hydrogen peroxide donates two hydrogen bonds and accepts a total of four hydrogen bonds (two from each oxygen atom).



**Figure S5:** Radial distribution functions, g(r), of a 62·H<sub>2</sub>O-2OH\* system in the singlet state, averaged over 10 ps during the formation of hydrogen peroxide from a OH\* pair, at a temperature of 310 K. (a) oxygen-oxygen RDFs in which O\*<sub>1</sub>O (O<sub>1</sub> represents the oxygen atom of one of the two OH\*) is represented by a blue solid line, O\*<sub>2</sub>O (O<sub>2</sub> being in the second OH\*) is represented by a red solid line, O<sub>1</sub>O<sub>2</sub> by a green solid line, and OO by a purple solid line; (b) oxygen-hydrogen RDFs in which O\*<sub>1</sub>H is represented by a blue solid line, O<sub>2</sub>\*H is represented by a red solid line, and H\*<sub>3</sub>O (H\*<sub>3</sub> being the hydrogen atom bonded to O\*<sub>1</sub>) and H\*<sub>4</sub>O (H\*<sub>4</sub> being the hydrogen atom bonded to O\*<sub>2</sub>), represented by purple and light blue solid lines, respectively, shows the RDFs for both OH\* hydrogens with respect to the oxygen atoms in the system.



**Figure S6:** Coordination Numbers, n(r), for the hydrogen peroxide. The numbers of hydrogen and oxygen atoms around the oxygen and hydrogen atoms of H<sub>2</sub>O<sub>2</sub> are provided (O\*H and O\*O, respectively) as well as the coordination of oxygen atoms around the radical hydrogen (H\*O). O\*<sub>1</sub> and O\*<sub>2</sub> are shown as blue and purple in the inset, respectively. H\*<sub>3</sub> and H\*<sub>4</sub> are bonded to O\*<sub>1</sub> and O\*<sub>2</sub>, respectively.

### 5. Contour plot from Metadynamics Simulations

Figure S7 is an alternative representation of the free energy landscape obtained for the formation of O(aq) utilizing metadynamics simulations (see Methods section). In Fig. S7  $\Delta$ G is represented as a function of the O\*H separation and the O\*H\*O\* angle (where H\* is the hydrogen atom that is going to be transferred). Fig. 4 provides a better description of the free energy separation of the minima, however details on the dependence upon the O\*H\*O\* angle are not easily extracted due to the use of a colour ramp to encode this angular information. These details are better described in the contour plot provided in Fig. S7. As evidenced in this figure the O\*H\*O\* angle changes from about 55° for the dimer (V) to about 110° for O(aq) + H<sub>2</sub>O (VII).



**Figure S7:** Alternative contour plot view of the free energy data, given in Fig. 4. These  $\Delta G$  values were obtained from metadynamics simulations (see details in the Methods section), utilizing the O\*H\* distance between the transferred hydrogen atom and the oxygen atom donating the hydrogen and the O\*H\*O\* angle as collective variables (see details in the Methods section).