

## Supplementary Information

### Hydroxyl radicals in ice: insights into local structure and dynamics

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#### Details of the metadynamics simulations

The metadynamics simulation was started from a small  $32 \cdot \text{H}_2\text{O-latt-OH}^*$  system, taken from an equilibrated Car-Parrinello MD simulation trajectory at 190 K. The chosen set of collective variables was  $CN_{O^*-O}$ , representing the coordination number of the oxygen atoms around the radical oxygen ( $O^*$ ) identified within a radius of 3 Å, and the  $CN_{O^*-H}$ , representing the coordination number of the hydrogen atoms around the radical oxygen ( $O^*$ ) identified within a radius of 2 Å. After extensive testing the only two collective variables were found to be successful in achieving a reasonable description of the process under study within metadynamics. The CN value was calculated as the sum of rational functions, as follows:

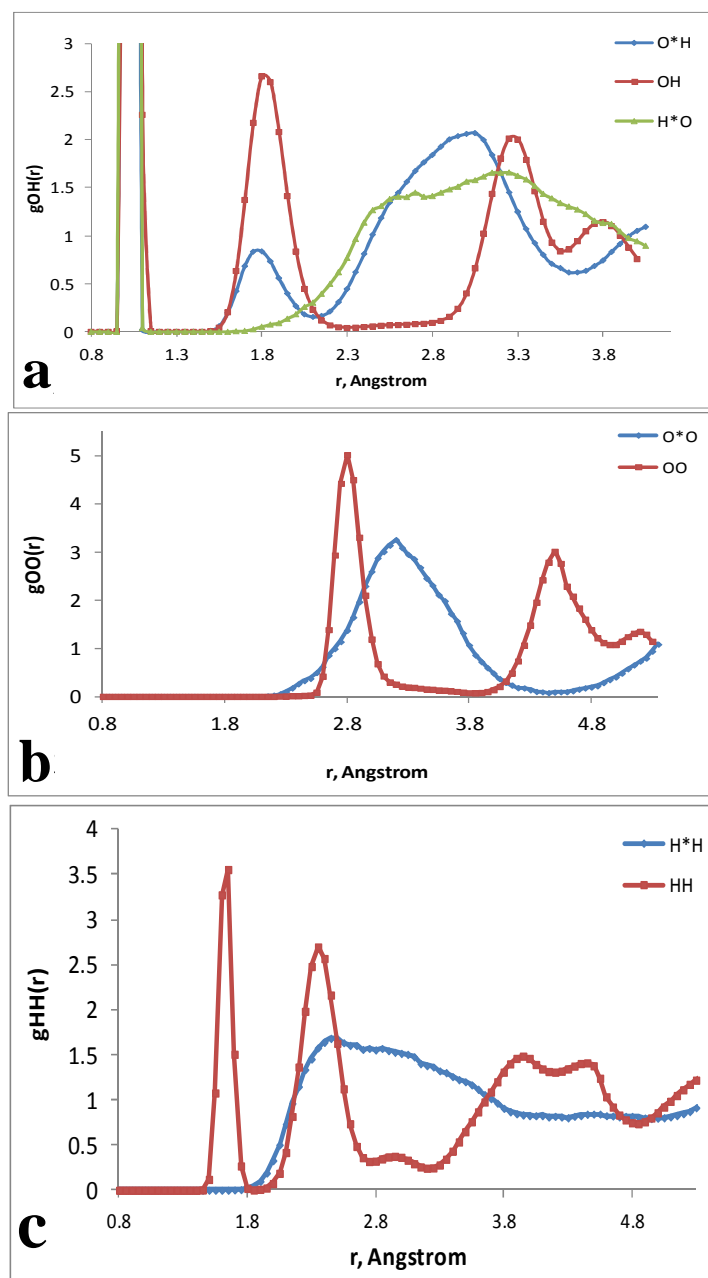
$$CN_i = \sum_{j \neq i}^{all\ Hs} \frac{1 - \left(\frac{d_{ij}}{d^o}\right)^p}{1 - \left(\frac{d_{ij}}{d^o}\right)^{p+q}} \quad (1)$$

where  $j$  runs over all hydrogen atoms,  $p$  and  $q$  were used as 6 and 12, respectively, and  $d^o$  was utilized as 1.2 Å for  $CN_{O^*-H}$  and 1.7 Å for  $CN_{H^*H}$ . Both collective variables were constrained to be between 0.7 and 1.5 for  $CN_{O^*-H}$  and 0 and 1 for  $CN_{H^*H}$ .

A preliminary unbiased run at 190 K was used to choose the Gaussian widths,  $\delta s$ , as half of the fluctuation of the collective variable with the smallest variation. The scaling factors were defined

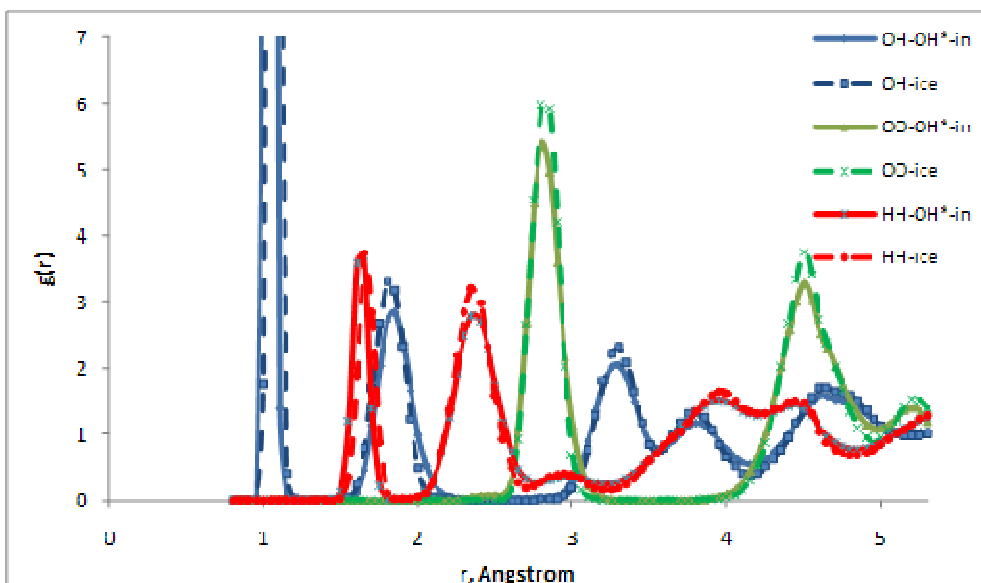
accordingly. In our case  $\delta s$  was utilized as 0.015. An initial simulation was performed with a value of the Gaussian height equal to 4 times the thermal energy. After verifying that the OH\* jumped to an adjacent cage, further metadynamics simulations were carried out, where the Gaussian heights were determined by the underlying potential energy surface with an imposed upper bound of 0.0005 kcal/mol. Biasing potentials were added with a minimum separation of 100 MD steps. The fictitious masses and force constants for both MTD variables were set to 0.1 a.u. and 10 a.m.u, respectively.

**Radial distribution functions,  $g(r)$  for 140 ps of a  $32\cdot\text{H}_2\text{O}$ -int- $\text{OH}^*$  system**



**Figure S1** Radial distribution functions obtained with the HCTH/120 for total simulation times of 140 ps of  $32\cdot\text{H}_2\text{O}$ - $\text{OH}^*$  (ice) systems, with interstitial  $\text{OH}^*$ , at a temperature of 190 K. (a) oxygen-hydrogen RDFs in which  $\text{O}^*\text{H}$  is represented by a blue solid line,  $\text{OH}$  by a red solid line, and  $\text{H}^*\text{O}$  by a green solid line; (b) oxygen-oxygen RDFs in which  $\text{O}^*\text{O}$  is represented by a blue solid line and  $\text{OO}$  by a red solid line; (c) hydrogen-hydrogen RDFs in which  $\text{H}^*\text{H}$  is represented by a blue solid line and  $\text{HH}$  by a red solid line.

**Radial distribution functions,  $g(r)$ , and coordination numbers,  $n(r)$  of a pure ice for comparison with a  $31 \cdot \text{H}_2\text{O-latt-OH}^*$  system**



**Figure S2.** Radial distribution functions obtained with the HCTH/120 for total simulation times of 50 ps of 32 water molecules of pure hexagonal ice at a temperature of 190 K and a total simulation times of 50 ps of  $31 \cdot \text{H}_2\text{O-latt-OH}^*$  (ice) systems at a temperature of 190 K . Oxygen-hydrogen, Oxygen-oxygen and hydrogen-hydrogen RDFs are represented by blue, green and red lines, respectively (solid line for OH-RDFs for  $31 \cdot \text{H}_2\text{O-latt-OH}^*$  systems and dashed line for pure ice OH-RDFs).

**Table S1.** Coordination Numbers,  $n(r)$ , obtained with the HCTH/120 functional for total simulation times of 50 ps of 32 water molecules of hexagonal ice at a temperature of 190 K and a total simulation times of 50 ps of  $31 \cdot \text{H}_2\text{O-latt-OH}^*$  systems at a temperature of 190 K .

	<b>r</b>	<b>Ice-CPMD</b>	<b><math>31 \cdot \text{H}_2\text{O-latt-OH}^*</math></b>
<b>OH</b>	1.15	1.9	1.9
	2.05	3.9	3.8
	3.55	10.4	10.2
	4.15	16.4	16.1
	5.30	34.2	33.7
<b>OO</b>	3.10	3.9	3.9
	5.30	17.1	17.1
<b>HH</b>	1.80	0.9	0.9
	2.70	5.1	4.9
	3.20	5.9	5.9
	4.15	16.1	15.8
	4.80	26.0	25.6
	5.30	26.9	26.6

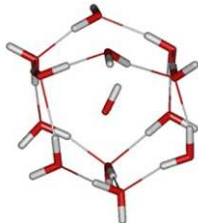
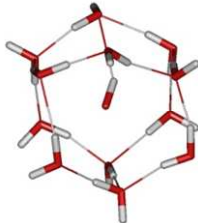
### *Ab initio* gas phase calculations

Although a full *ab initio* study will be published in a forthcoming paper, here we want to show further evidences of the reliability of the DFT functional we have selected for our Car-Parrinello simulations in an ice environment.

#### 1) Constrained ice cage cluster with an interstitial OH\*

The first model was created to compare the outcome of the HCTH DFT functional in the gas phase optimization of an interstitial OH\* located in a constrained ice model cage, with an *ab initio* method. The HCTH functional was utilized, as well a post-Hartree-Fock method, specifically using Møller-Plesset Perturbation Theory up to second order (MP2). All calculations were done in conjunction with Dunning's basis sets of triple and quadruple-zeta quality with diffuse functions on all atoms, denoted aug-cc-pVTZ, and aug-cc-pVQZ, respectively. As it can be observed in Table S1, both methods yielded very similar relative energies and both found the OH\* acting as a H-donor to one of the oxygen waters of the ice cage, as the global minimum.

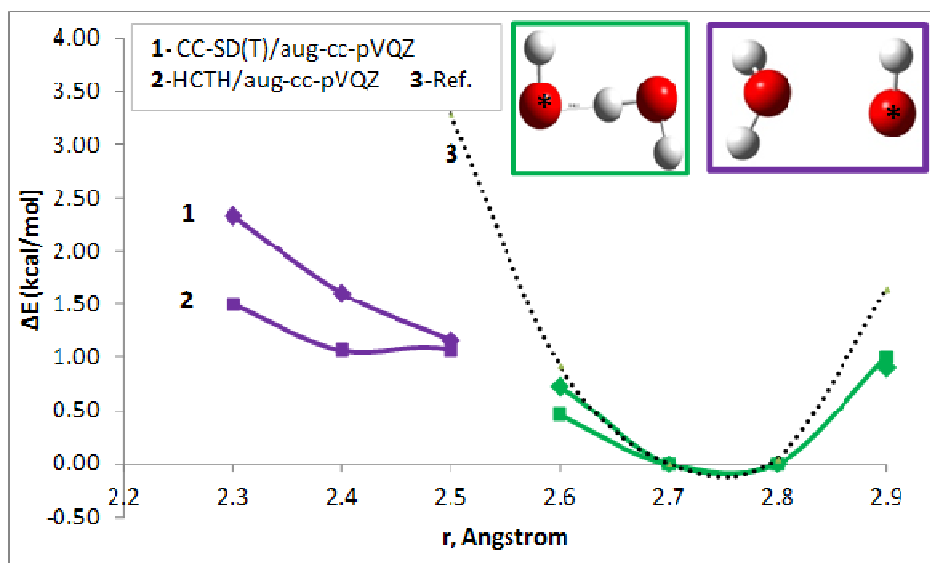
**Table S2.** Relative energies (kcal/mol) obtained from HCTH and MP2 methods, in combination with aug-cc-pVTZ, and aug-cc-pVQZ basis sets' for an (int-OH\*) in a constrained ice cage model. The structures of this gas phase cluster for the initial and converged final states are shown. In the initial state (taken from MD simulations) OH\* was in the center of the cage. After convergence OH\* is found in all cases to act as a H-bond donor to one of the oxygens in the ice cage.

Method	$\Delta E$ (kcal/mol)	Initial Structure	Optimized Structure
MP2/aug-cc-pVTZ	-2.98		
HCTH/ aug-cc-pVTZ	-2.95		
MP2/aug-cc-pVQZ	-2.99		
HCTH/ aug-cc-pVQZ	-2.97		

## 2) OH\*-H<sub>2</sub>O dimer

The OH\*-H<sub>2</sub>O dimer was studied in the gas phase with a full optimization of the system at every constrained O\*-O distance (Fig. S3). The HCTH DFT functional (curve 2) was utilized, as well as the highly correlated CC-SD(T) *ab initio* method (curve 1), both in combination with the aug-cc-pVQZ basis set. In the range 2.6-2.8 Å the distance O\*-H<sub>w</sub> (where H<sub>w</sub> is the water hydrogen H-bonded to the OH\*) was also constrained, to avoid the conversion to the 2 kcal/mol more stable configuration in which the radical donates a H-bond to the water molecule (results not shown). The two configurations explored by the system have been represented by the corresponding colored energy curves. The purple segment shows that at shorter O\*-O distances a shoulder in the potential energy surface is obtained for both methods, corresponding to a hemibonding arrangement. An additional structure has been optimized for the HF-H<sub>2</sub>O dimer at corresponding distances, for comparison with the behavior of the radical and the resulting energies have been represented with a dashed black curve and labeled “reference” (Ref). As can be observed, this system shows the expected repulsive behavior in the energy surface at short distances.

Although the HCTH functional slightly overestimates the stability of the hemibonded structure for this dimer, it can be seen that the coupled cluster method predicts the existence of the hemibond (purple segment) and that is only about 2 kcal/mol less stable than the appropriate H-bonding configuration (green segment) when the O\*-O distance is constrained. These results are consistent with very recent reports (see Refs. 27 and 28) suggesting that the hemibond can be an alternative structure in the chemistry of the OH\* when the formation of H-bonds is constrained, and not a DFT artefact.



**Figure S3.** Relative energy (kcal/mol) vs O\*-O distance (Angstrom) in the OH\*-H<sub>2</sub>O dimer in the gas phase. The HCTH DFT functional (curve 2) was utilized, as well as the highly correlated CC-SD(T) *ab initio* method (curve 1), both in combination with the aug-cc-pVQZ basis set. The O\*-O distance has been constrained at every point, allowing the system to explore different configurations at each particular distance. The different configurations explored by the system have been represented consistently with the colors used in the energy curve. The global minimum corresponds to the H-bond donation from the OH\* to the water molecule (not shown for clarity) which is around 2 kcal/mol more stable than the H-bond configuration (green segment).