

## Electronic Supplementary Information

### Entangled Iodine and Hydrogen Peroxide Formation in Ice

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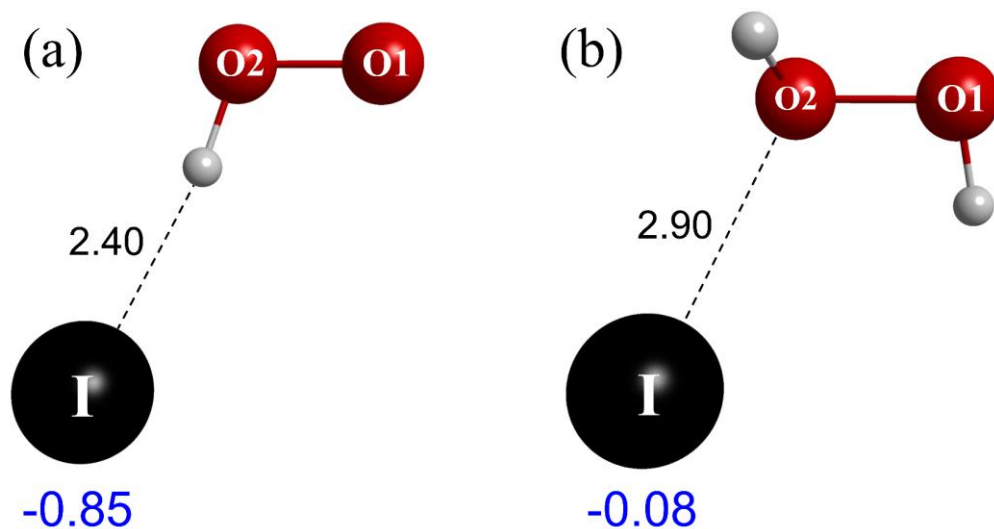
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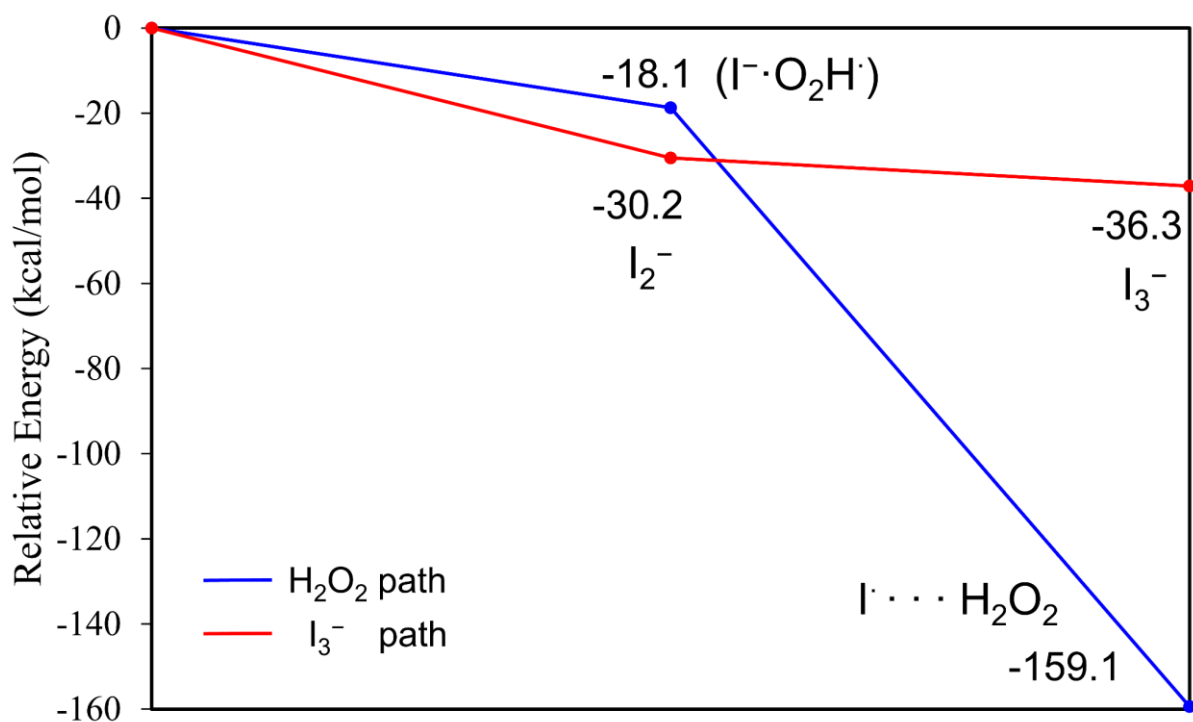
Figures SI 1 and 2

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**Fig. SI 1** The optimized structures of (a)  $\text{IO}_2\text{H}^-$  and (b)  $\text{IO}_2\text{H}_2$  complexes calculated using B3LYP/MIXED-level theory. The bond lengths (black) are in Å, while the Mulliken atomic charges (blue) are in atomic units. The binding energy between  $\text{I}^-$  and  $\text{O}_2\text{H}$  radical is  $-18.7$  kcal/mol, while the binding energy between  $\text{I}^-$  and  $\text{H}_2\text{O}_2$  is  $-3.5$  kcal/mol. Weak charge transfer is indicated in (a), while complete transfer occurs in (b). The MIXED basis set was composed of the Stevens-Krauss (SBKJC) VDZ effective core potential basis set for I and the standard cc-pVTZ basis set for O and H.



**Fig. SI 2** Relative changes in energy along the  $I\cdot \rightarrow I_2^- \rightarrow I_3^-$  (red) and  $O_2H\cdot \rightarrow IO_2H^- \rightarrow I\cdot \dots H_2O_2$  (blue) pathways calculated using B3LYP/MIXED-level theory. The corresponding reaction enthalpies are presented in Table SI 1d–g. The MIXED basis set was composed of the Stevens-Krauss (SBKJC) VDZ effective core potential basis set for I and the standard cc-pVTZ basis set for O and H.

**Table SI 1.** The enthalpies of various elementary reactions calculated using B3LYP/MIXED-level theory, including zero-point energies. **a**, Formation of  $\Gamma \cdot \text{O}_2$  complexes in the singlet and triplet states. **b**, Formation of  $\text{IO}_2\text{H}$  complexes in the singlet and triplet states through protonation by hydronium at low pH. **c**, Formation of  $\text{IO}_2\text{H}$  complexes in the singlet and triplet states at neutral pH in water. **d**, Formation of  $\text{I}_2^-$  in the doublet state. **e**, Formation of  $\text{I}_3^-$  in the singlet state. **f**, Formation of  $\text{IO}_2\text{H}^-$  in the doublet state. **g**, Formation of  $\text{IO}_2\text{H}_2$  in the doublet state at low pH with hydronium ion. **h**, Dissociation of  $\text{IO}_2\text{H}_2$  to  $\Gamma$  and  $\text{H}_2\text{O}_2$ . The MIXED basis set was composed of the Stevens-Krauss (SBKJJC) VDZ effective core potential basis set for I and the standard cc-pVTZ basis set for O and H.

Elementary reactions	Singlet	Triplet
(a) $\Gamma^- + \text{O}_2 \rightarrow \Gamma \cdot \text{O}_2$	-5.1* (0.3 <sup>a</sup> )	0.2* (-0.3 <sup>a</sup> )
(b) $\Gamma \cdot \text{O}_2 + \text{H}_3\text{O}^+ \rightarrow \text{IO}_2\text{H} + \text{H}_2\text{O}$	-170.7	-127.7
(c) $\Gamma \cdot \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{IO}_2\text{H} + \text{OH}^-$	74.8	117.8
(d) $\text{I} \cdot + \Gamma^- \rightarrow \text{I}_2^-$	-30.2 <sup>b</sup>	
(e) $\text{I}_2^- + \text{I}_2^- \rightarrow \text{I}_3^- + \Gamma^-$	-6.1 <sup>b</sup>	
(f) $\Gamma^- + \text{O}_2\text{H} \cdot \rightarrow \text{IO}_2\text{H}^-$	-18.1 <sup>b</sup>	
(g) $\text{IO}_2\text{H}^- + \text{H}_3\text{O}^+ \rightarrow \text{IO}_2\text{H}_2 + \text{H}_2\text{O}$	-141.0 <sup>b</sup>	
(h) $\text{IO}_2\text{H}_2 \rightarrow \text{I} \cdot + \text{H}_2\text{O}_2$	2.8 <sup>b</sup>	

\*The  $\Gamma \cdot \text{O}_2$  structures were obtained using CASSCF(12,7)/MIXED-level theory. <sup>a</sup>Values were obtained with MCQDPT2(12,7)/MIXED, not including zero-point energy. <sup>b</sup>The spin states of  $\text{I} \cdot$ ,  $\Gamma^-$ ,  $\text{I}_2^-$ ,  $\text{I}_3^-$ ,  $\text{O}_2\text{H} \cdot$ ,  $\Gamma \cdot \text{O}_2\text{H} \cdot$ ,  $\text{IO}_2\text{H}_2$  and  $\text{H}_2\text{O}_2$  are doublet, singlet, doublet, singlet, doublet, doublet, doublet and singlet, respectively.

**Table SI 2.** The singlet and triplet excitation energies of the  $\Gamma \cdot \text{O}_2$  complex calculated using MCQDPT2(12,7)/MIXED-level theory. The optimized structures of the  $\Gamma \cdot \text{O}_2$  complex were obtained using CASSCF(12,7)/MIXED-level theory. Experimentally observed absorption from 280 to 330 nm did not correspond well to the theoretical excitation energies of the  $\Gamma \cdot \text{O}_2$  complex. The MIXED basis set was composed of the Stevens-Krauss (SBKJC) VDZ effective core potential basis set for I and the standard cc-pVTZ basis set for O and H. The values are shown in nm.

	Singlet		Triplet
S <sub>1</sub>	309,960	T <sub>1</sub>	517
S <sub>2</sub>	1675	T <sub>2</sub>	510
S <sub>3</sub>	932	T <sub>3</sub>	173
S <sub>4</sub>	843	T <sub>4</sub>	172
S <sub>5</sub>	226	T <sub>5</sub>	169

**Table SI 3.** Values in the TD-DFT/B3LYP column correspond to the excitation energies of IO<sub>2</sub>H in the singlet and triplet states. Values were calculated using TDDFT/B3LYP/MIXED at the optimized geometries. The oscillator strengths are shown in parentheses. Values in the MCQDPT2 column were obtained using the MCQDPT2(20,12)/MIXED-level theory for singlets and the MCQDPT2(12,7)/MIXED-level theory for triplets. The IO<sub>2</sub>H singlet geometry was obtained with CASSCF(20,12)/MIXED, and the IO<sub>2</sub>H triplet geometry was obtained with CASSCF(12,7)/MIXED. Experimentally observed absorption from 280 to 330 nm corresponded well to the singlet S<sub>3</sub> and S<sub>4</sub> states according to the TDDFT and MCQDPT2 theories. The MIXED basis set was composed of the Stevens-Krauss (SBKJC) VDZ effective core potential basis set for I and the standard cc-pVTZ basis set for O and H. The values are shown in nm.

	TD-DFT/B3LYP	MCQDPT2	Expt.
Singlet			
S <sub>1</sub>	502 (0.001)	544	
S <sub>2</sub>	387 (0.002)	437	
S <sub>3</sub>	291 (0.005)	328	280 ~ 330
S <sub>4</sub>	260 (0.221)	308	280 ~ 330
S <sub>5</sub>	194 (0.004)	278	
Triplet			
T <sub>1</sub>	1016 (0.000)	41328	
T <sub>2</sub>	1008 (0.000)	1252	
T <sub>3</sub>	892 (0.000)	574	
T <sub>4</sub>	832 (0.002)	546	
T <sub>5</sub>	742 (0.000)	541	

$T_6$	639 (0.000)	238
$T_7$	633 (0.003)	220
$T_8$	215 (0.000)	219
$T_9$	195 (0.837)	135

**Table SI 4.** Correlations between iodine concentration [I] (Fig. 4a) in an ice core from the east coast of Greenland (71° 30' N, 26° 72' W)<sup>1</sup> and hydrogen peroxide concentrations in ice cores from central Greenland, [H<sub>2</sub>O<sub>2</sub>]<sub>A</sub> (72° 34' N, 37° 38' W), and south Greenland, [H<sub>2</sub>O<sub>2</sub>]<sub>B</sub> (65° 11' N, 43° 49' W)<sup>2</sup> from 1773 to 1986 (Fig. 4b). Correlations between H<sub>2</sub>O<sub>2</sub> concentrations and ozone [O<sub>3</sub>] (Fig. 4c) over the North Atlantic (20° N–70° N, 75° W–0°)<sup>1</sup> and their significance are shown below. [I], [H<sub>2</sub>O<sub>2</sub>]<sub>A</sub> and [H<sub>2</sub>O<sub>2</sub>]<sub>B</sub> reflect data from 1950 to 1986.  $\rho$  is the Pearson's correlation coefficient, while significance is denoted by 'Sig.'

	[I]-[H <sub>2</sub> O <sub>2</sub> ] <sub>A</sub>	[I]-[H <sub>2</sub> O <sub>2</sub> ] <sub>B</sub>	[H <sub>2</sub> O <sub>2</sub> ] <sub>A</sub> -[H <sub>2</sub> O <sub>2</sub> ] <sub>B</sub>
1773-1986			
$\rho$	0.164	0.218	0.371
Sig.	0.028	0.003	0.000
	[O <sub>3</sub> ]-[I]	[O <sub>3</sub> ]-[H <sub>2</sub> O <sub>2</sub> ] <sub>A</sub>	[O <sub>3</sub> ] <sub>A</sub> -[H <sub>2</sub> O <sub>2</sub> ] <sub>B</sub>
1950-1986			
$\rho$	0.420	0.406	0.519
Sig.	0.011	0.014	0.001



## Supplementary References

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2. A. Sigg and A. Neftel, *Nature*, 1991, **351**, 557–559.