Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ESI of

Rapid dissociation of H_2O_2 on the water surface (ice and water droplet)

Amit Kumar and Pradeep Kumar*

Department of Chemistry, Malaviya National Institute of Technology Jaipur, Jaipur, 302017, India

E-mail: pradeep.chy@mnit.ac.in

Sl. No. **Contents**

1 Computational details of modeling of water droplet and ice surface

To model the water droplet, we have consider a water cluster of 191 water molecules based on the previous studies,[1–4] which suggests that this size of water cluster is reasonable to include the surface effect on the reaction. To obtain the initial configuration of water droplets for BOMD simulation, the water cluster was first optimized with MD simulation using the AMBER force field followed by the full optimization at DFT functional. Further, we have relaxed the ozone molecules on the water droplets prior to the BOMD simulation. To model the ice surface, we have consider the water cluster of 270 water molecules having hexagonal structure.[5–7] Further, we have also optimized this ice surface using the AMBER force field method with MD simulation followed by full relaxation at DFT functional. Afterward, we have fully relaxed the ozone molecule on the ice surface using DFT functional, prior the BOMD simulation.

Table S1: Comparison of H_2O_2-H_2O stabilization energy (kcal mol^{-1}) and dissociation energy (kcal mol^{-1}) of H_2O_2 obtained at different DFT functional with the experimental value.

Method	Stabilization energy	Dissociation energy
CCSDT/aug-cc-pVTZ//M062X/aug-cc-pVTZ	-7.54	45.46
LC-ωHPBE/cc-pVTZ	-8.20	47.97
ωB97XD/cc-pVTZ	-8.69	47.83
LC-BLYP/cc-pVTZ	-11.55	53.35
Experimental	-	48.79

Table S2: Intrinsic bond strength index (IBSI) values for O-O bond of H_2O_2, IBSI values for the hydrogen bonding atoms between H_2O and H_2O_2, obtained using MultiWfn code in the presence of different number of water molecules (n) estimated at LC-ωHPBE/cc-pVTZ level of theory.

Bond	IBSI						
	n=0	n=1	n=2	n=3	W2(a) (n=40)	W2'(a) (n=40)	Ice (n=40)
O-O	0.4410	0.4520	0.4376	0.4464	0.3449	0.2156	0.3201
O(H_2O)-H(H_2O_2)	-	0.0294	-	-	0.0187	0.0365	0.0126
H(H_2O)-O(H_2O_2)	-	-	-	-	0.0057	-	0.0186

Table S3: Comparison of geometrical parameters obtained at different level of theory with the result obtained at CCSD(T)/aug-cc-pVQZ level of theory.

Geometrical parameters	ωB97XD/cc-pVTZ	LC-ωHPBE/cc-pVTZ	LC-BLYP/cc-pVTZ	CCSD(T)/aug-cc-pVQZ
O-H (Å)	0.96	0.96	0.96	0.96
O-O (Å)	1.42	1.41	1.40	1.45
H-O-O (deg.)	101.1	101.4	101.9	100.0

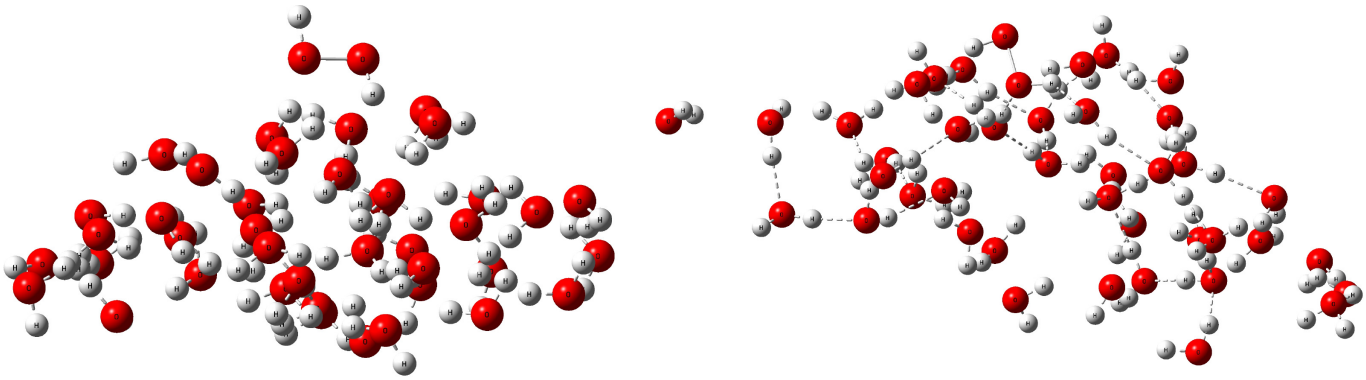

Figure S1: Initial (W2(a)) and critical geometry (W2'(a)) of W2(a) orientation obtained during the simulation at LC-ωHPBE/GTH-PTVZ level of theory.

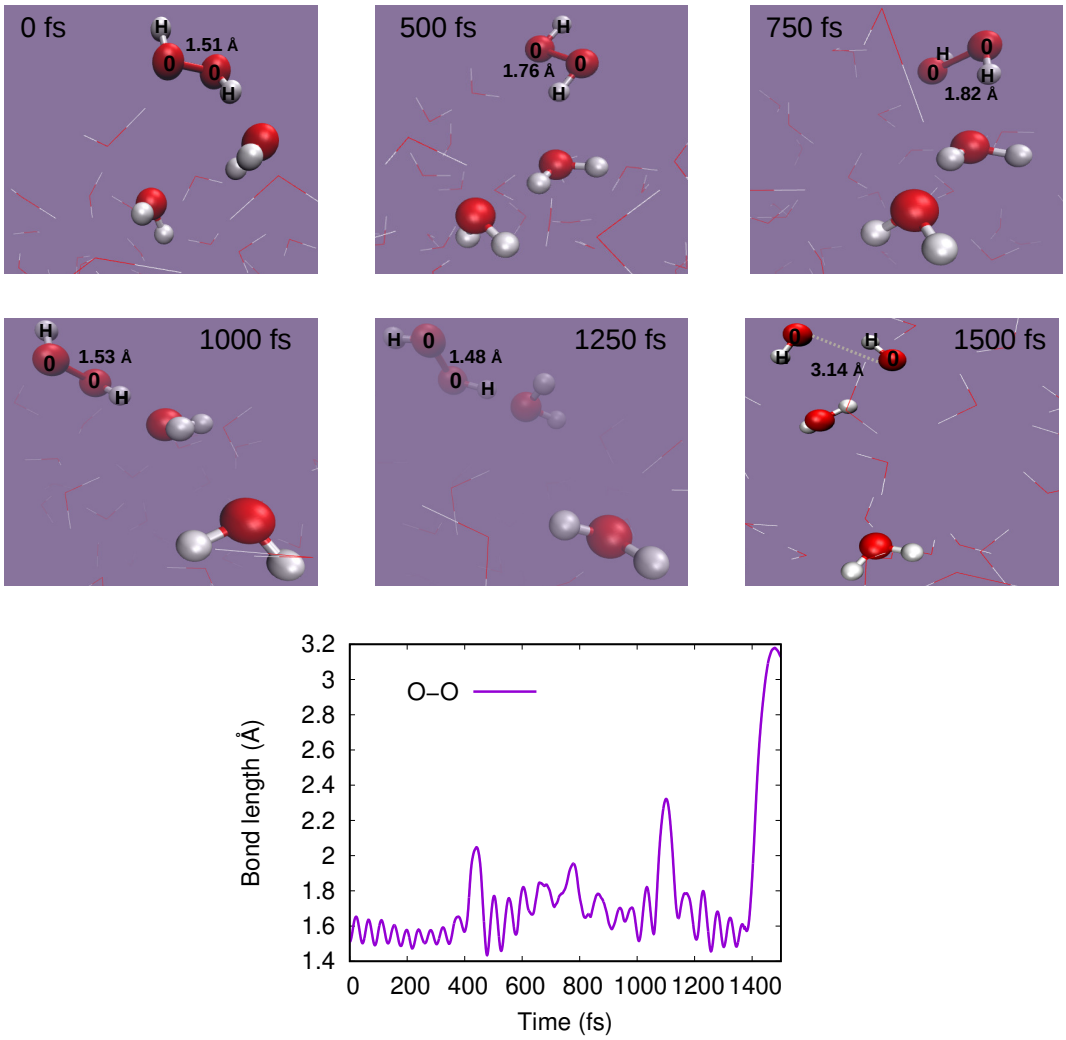

Figure S2: Top panel: Snapshot at different time interval for dissociation of H_2O_2 on water droplet at 300 K for W2(b) orientation. Lower panel: Time evolution of the O-O bond for dissociation of H_2O_2 on water droplet at 300 K for W2(b) orientation.

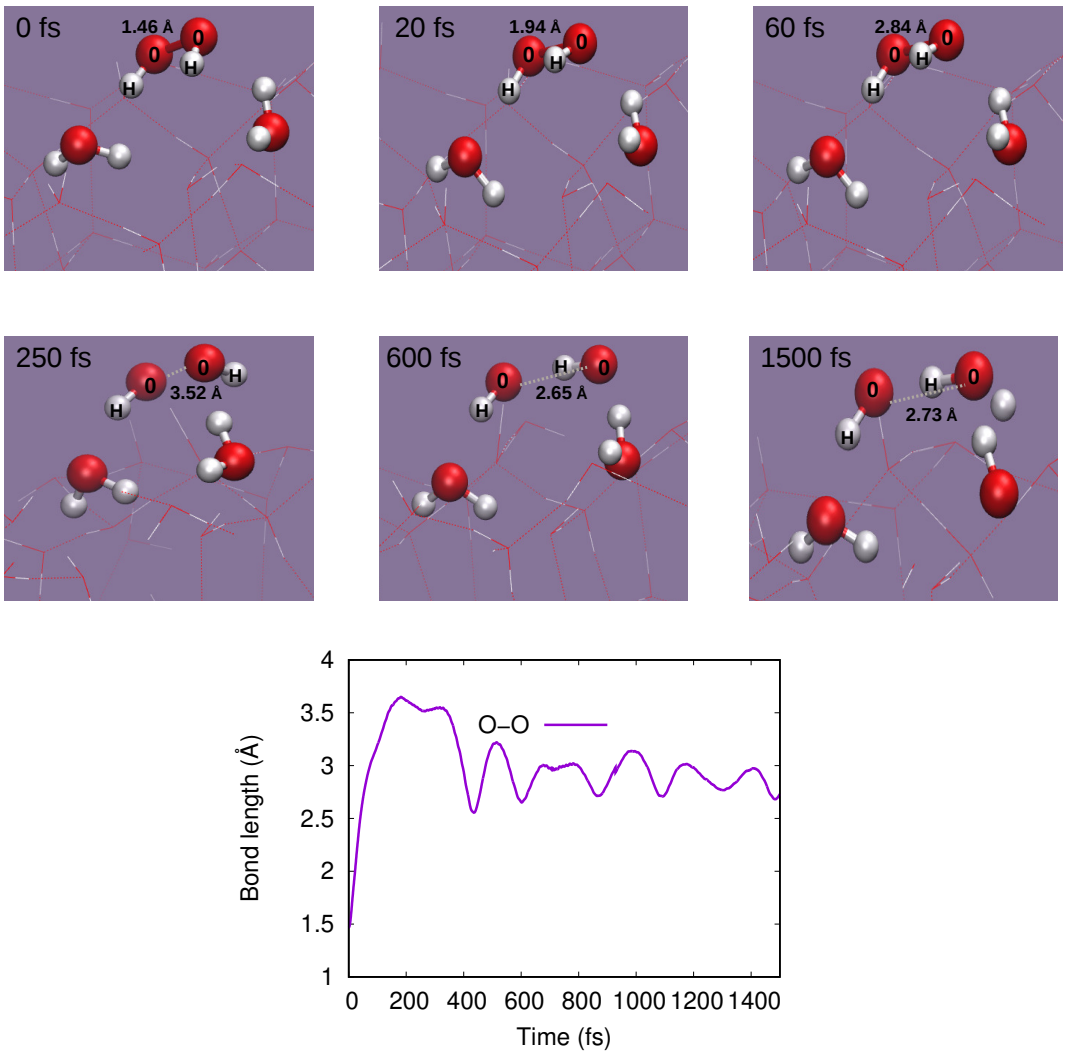

Figure S3: Top panel: Snapshot at different time interval for dissociation of H_2O_2 on water droplet at 190 K for I1(b) orientation. Lower panel: Time evolution of the O-O bond for dissociation of H_2O_2 on water droplet at 190 K for I1(b) orientation.

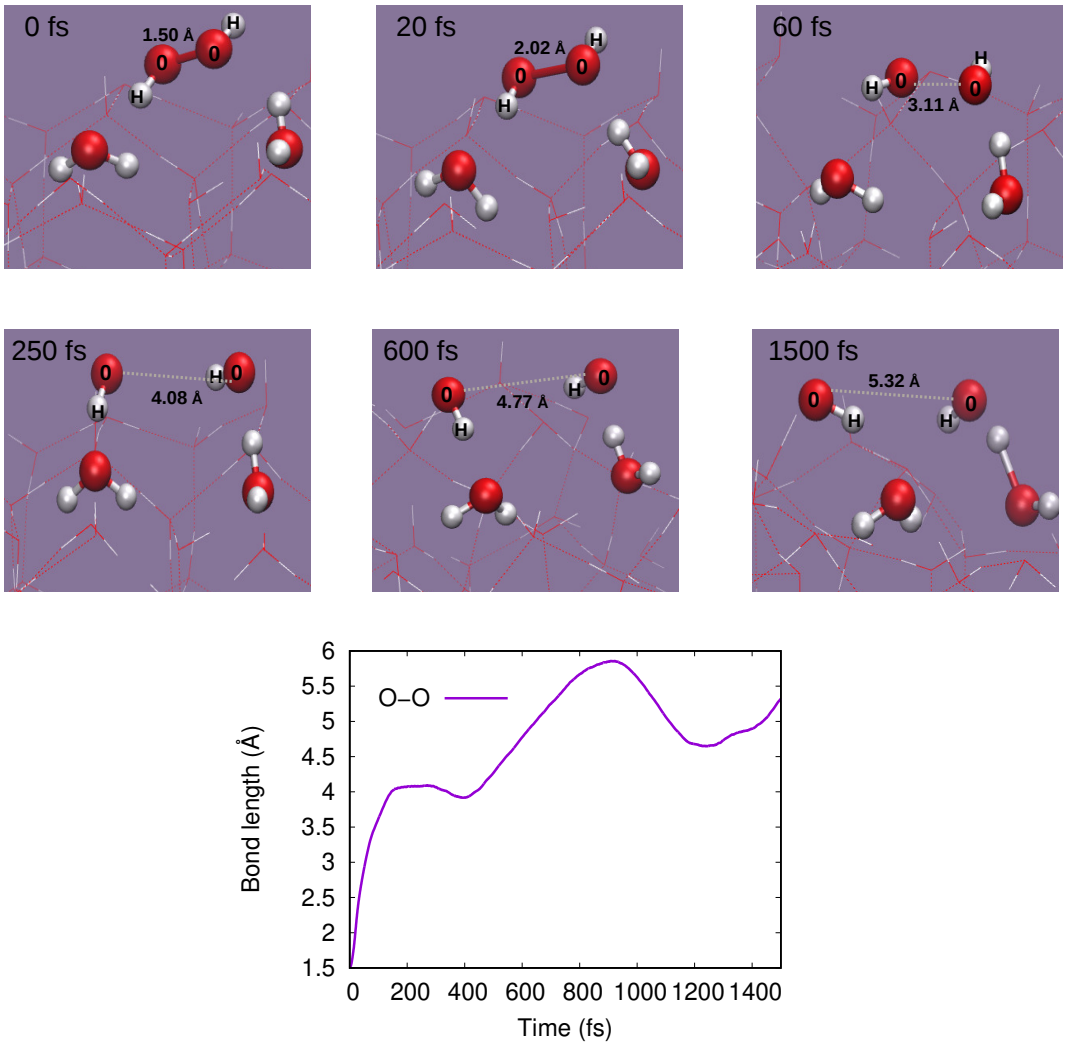

Figure S4: Top panel: Snapshot at different time interval for dissociation of H_2O_2 on water droplet at 190 K for I2(b) orientation. Lower panel: Time evolution of the O-O bond for dissociation of H_2O_2 on water droplet at 190 K for I2(b) orientation.

References

(1) Kumar, M.; Zhong, J.; Zeng, X. C.; Francisco, J. S. *J. Am. Chem. Soc.* **2018**, *140*, 4913–4921.

(2) Zhong, J.; Li, H.; Kumar, M.; Liu, J.; Liu, L.; Zhang, X.; Zeng, X. C.; Francisco, J. S. *Angew. Chem.* **2019**, *131*, 8439–8443.

(3) Kumar, M.; Francisco, J. S. *Chem. Sci.* **2019**, *10*, 743–751.

(4) Mallick, S.; Kumar, P. *J. Phys. Chem. B* **2020**, *124*, 2465–2472.

(5) Kumar, A.; Kumar, P. *J. Phys. Chem. A* **2022**, *126*, 1504–1510.

(6) Ignatov, S. K.; Gadzhiev, O. B.; Razuvaev, A. G.; Masunov, A. E.; Schrems, O. *J. Phys. Chem. C* **2014**, *118*, 7398–7413.

(7) Ignatov, S. K.; Gadzhiev, O. B.; Kulikov, M. Y.; Petrov, A. I.; Razuvaev, A. G.; Gand, M.; Feigin, A. M.; Schrems, O. *J. Phys. Chem. C* **2011**, *115*, 9081–9089.