## Supplementary information for

## Mechanism for the formation of OH radicals in condensed-phase water under ultraviolet irradiation

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Fig. S1. The crystal structures with different proton arrangements in the orthorhombic supercell of ice-lh, including the proton-ordered structures of  $Cmc2_1$  and  $Pna2_1$  symmetries and the proton-disordered ice-lh. The lattice constants used in this paper are the ice-lh experimental values at 240K.<sup>1</sup>



Fig. S2. (a) Band structure of the perfect  $Pna2_1$  ice crystal calculated by DFT-LDA. (b) and (c) are charge density distributions of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) at  $\Gamma$  point in the perfect  $Pna2_1$  ice respectively. The isosurface is represented in green.



Fig. \$3. Exaited distribution soft to a stranding to the profession of the vacancy. The shaded denotes the water molecules behind.



displayed in green. The shaded denotes the Water molecules behind. Fig. S4. DFT-LDA band structures of the ion defect (a), vacancy defect (b), Bjerrum defects (c) and the (0001) basal plane (d) in the  $Pna2_1$  ice crystal. The valence band maximum is set to zero in each panel.



Fig. S8. Exciton distributions of the first excited state at 7.62 eV in the *Pna*2<sub>1</sub> ice crystal with Bjerrum defects. The electron (hole) is represented in blue (kelly).



Fig. S9. Charge density distributions of the band r (see Figure S3(d)) (a) and LUMO (b) at  $\Gamma$  point for the (0001) basal plane in the  $Pna2_1$  ice crystal.



Fig. S10. Exciton distributions of the lowest excited state at 7.78 eV for the (0001) basal plane in the *Pna*2<sub>1</sub> ice crystal. The electron (hole) is represented in blue (kelly).



Fig. S11. Charge density distributions of HOMO-1 (a), HOMO (b) and LUMO (c) at  $\Gamma$  point in the *Pna*2<sub>1</sub> ice crystal with ion defect. The isosurface is represented in green. The shaded denotes the water molecules behind.



Fig. S12. Theoretical optical absorption spectra of the perfect ice, the ice with defects and the (0001) basal plane from BSE for the  $Cmc2_1$  crystal (a) and the disordered crystal (b), together with the experimental optical absorption spectra of ice-Ih.



Fig. S13. Exciton distributions of the first state at 7.81 eV in the perfect Pna21 ice. The electron (hole) is represented in blue (kelly).



Fig. S14. (a) Energy surface for the total energy in the lowest excited state, which is the sum of  $E_{ground}$  and  $\Omega$ , along the proton transfer coordinates in the  $Cmc2_1$  ice crystal. Here,  $E_{ground}$  and  $\Omega$  are the ground-state total energy calculated by DFT and the excitation energy of the lowest excited state calculated by BSE for each configuration, respectively. (b) shows the variation of  $\Omega$  along the same proton transfer coordinates as (a).  $d_1$  and  $d_2$  denote the displacements of protons  $p_1$  and  $p_2$  in Fig. 5. In (c), the energy curve labelled by black squares is for the total energy in the lowest excited state when only the proton  $p_1$  transfers in the  $Cmc2_1$  ice; this curve corresponds to the profile of the energy surface in (a) with  $d_2=0$ . In (c), the energy curve labelled by red circles is for the total energy in the lowest excited state when  $O_1$  and  $O_2$ ; in this process the bond length and bond orientation of  $O_1$ - $p_3$  are fixed at their original data. (d) is the the energy curve for the total energy in the lowest excited state when the water molecule  $p_1$ - $O_1$ - $p_3$  moves rigidly towards  $O_2$ . In (a), (c) and (d), the energy at the maximum displacement [0.75 Å for (a) and (c), 0.15 Å for (d)] is set to zero.



Fig. S15. Variation of  $\Omega$  when one proton ( $p_1$  in Figure 5) transfers in the disordered ice.  $d_1$  denotes the displacement of proton  $p_1$  in Fig. 5. The meaning of  $\Omega$  is the same as that in Fig. S14.



Fig. S16. (a) Theoretical optical absorption spectrum of the  $Pna2_1$  ice with ion defects from BSE employing a supercell containing 32 water molecules. (b) and (c) Exciton distributions of the peak *i* which originates from the ion defect. The isosurface of electron (hole) is represented in blue (kelly). The shaded denotes the water molecules behind.

This work	Previous work					
S <sub>1</sub>						
	GW+BSE <sup>a</sup>	$\Delta SCF^{b}$	EOM-CCSD <sup>c</sup>	TDDFT <sup>c</sup>	CASSCF <sup>d</sup>	Exp <sup>e,f</sup> .
7.41	7.24	7.24	7.53	6.86	7.58	7.4
VIE						
12.57	GW			OVGF <sup>h</sup>		12.6
	11.94 <sup>a</sup> , 11.90 <sup>g</sup>			12.24		

TABLE S1. The lowest vertical ionization energy (VIE) and the first optical absorption peak ( $S_1$ ) of the water monomer (in eV) from our GW+BSE work, previous work using various theoretical methods and experiment.  $\Delta$ SCF: occupation-constrained DFT; EOM-CCSD: Equations-of-motion coupled cluster with singles and doubles; TDDFT: time-dependent density functional theory; CASSCF: complete active space self-consistent field; OVGF: outer-valence Green's function. The latter are labled by a, b, c, d, e, f, g and h for Ref.2, 3, 4, 5, 6, 7, 8 and 9, respectively.

<sup>a</sup> Ref. 2; <sup>b</sup> Ref. 3; <sup>c</sup> Ref. 4; <sup>d</sup> Ref. 5; <sup>e</sup> Ref. 6; <sup>f</sup> Ref. 7; <sup>g</sup> Ref. 8; <sup>h</sup> Ref. 9.

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- (1) Rick, S. W. J. Chem. Phys., 2005, 122, 094504.
- (2) P. H. Hahn, W. G. Schmidt and F. Bechstedt, Phys. Rev. B, 2005, 72, 245425.
- (3) A. Hermann, W. G. Schmidt and P. Schwerdtfeger, Phys. Rev. Lett., 2008, 100, 207403.
- (4) D. M. Chipman, J. Chem. Phys., 2005, 122, 044111.
- (5) B. D. Bursulaya, J. Jeon, D. A. Zichi and H. J. Kim, J. Chem. Phys., 1998, 108, 3286-3295.
- (6) M. Banna, B. McQuaide, R. Malutzki and V. Schmidt, J. Chem. Phys., 1986, 84, 4739-4744.
- (7) W. F. Chan, G. Cooper and C. E. Brion, *Chem. Phys.*, 1993, 178, 387-400.
- (8) Y. Shigeta, A. Ferreira, V. Zakrzewski and J. Ortiz, Int. J. Quantum Chem., 2001, 85, 411-420.
- (9) C. H. Hu and D. P. Chong, J. Chin. Chem. Soc. (Taipei), 2000, 47, 141-147.