Science Advances
AAAS

Supplementary Materials for

Formation of hydrogen trioxide (HOOOH) in extraterrestrial ice analogs and its role as an oxidizer in prebiotic chemistry

Xilin Bai *et al.*

Corresponding author: Tao Yang, tyang@lps.ecnu.edu.cn; Ralf I. Kaiser, ralfk@hawaii.edu; Rui Sun, ruisun@hawaii.edu; André K. Eckhardt, andre.eckhardt@ruhr-uni-bochum.de

Sci. Adv. **11**, eadw5720 (2025)
DOI: 10.1126/sciadv.adw5720

This PDF file includes:

Supplementary Methods

1. Ice thickness determination

The refractive index values $n_{H2O} = 1.27$ for solid water and $n_{O2} = 1.25$ for solid oxygen were utilized in Equation S1 to determine the thickness (d) of the ice using the interference pattern of a laser (λ = 632.8 nm) at an angle of incidence $\theta = 4°$:

$$d = \frac{m\lambda}{2\sqrt{n_{mix}^2 - sin^2\theta}} \qquad \text{(S1)}$$

Here, the interference pattern fringes (m) were determined using plots such as fig. S7, illustrating the interference pattern during ice deposition. Having observed 3 interference fringes, the thickness of H_2O and O_2 ice mixture was calculated to be 755 ± 50 nm.

2. Calibration Experiments

Calibration experiments aim to determine the ratio of water (H_2O) to molecular oxygen (O_2) in mixed ices. Initially, we employed laser interferometry to accurately measure the thicknesses of pure H_2O and O_2 ices deposited on a silver substrate respectively. The measured thicknesses were 250 ± 20 nm for H_2O ice and 254 ± 20 nm for O_2 ice. Subsequently, these ice samples were subjected to TPD, heated at a constant rate of 1 K min^{-1}. During the heating process, we monitored the sublimating species using electron-impact quadrupole mass spectrometer (EI-QMS), which detected both parent and fragment ions. The spectrometer was operated with an electron current of 2 mA, electron energy of 70 eV, and the Secondary Electron Multiplier (SEM) voltage of 1500 V. The ions observed corresponded to water (m/z = 18, H_2O^+; m/z = 17, OH^+; m/z = 16, O^+) and oxygen (m/z = 32, O_2^+; m/z = 16, O^+). Since the integrated ion counts are proportional to the number of molecules present in the sample, we were able to accurately establish the molecular ratio of H_2O to O_2 for a uniform layer thickness. Subsequent blank experiments were conducted to confirm the ratio of water to oxygen in the mixed ice. A dual-channel gas injection system was employed for these experiments, introducing water and molecular oxygen onto the silver substrate at pressures of (1 ± 0.1) × 10^{-8} Torr and (2 ± 0.2) × 10^{-8} Torr, respectively. The deposited thickness of the mixed ice was 755 ± 50 nm. The TPD signals of H_2O (H_2O^+ and OH^+) and O_2 (O_2^+ and O^+) were measured using QMS and compared with those obtained from pure H_2O and O_2 ice. From this comparison, we determined that the ratio of water to molecular oxygen in the mixed ice is 6.5 ± 1.0:1.

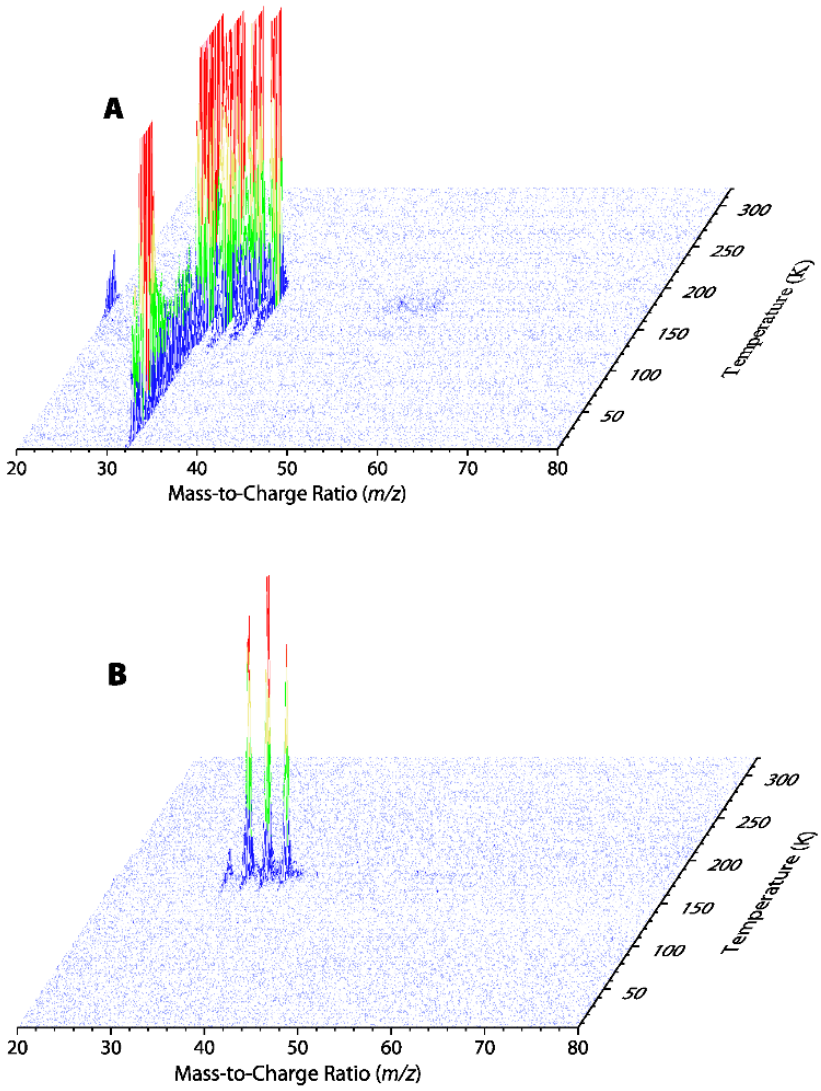


Fig. S1. Synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS). Data were recorded during the temperature-programmed desorption (TPD) phase of irradiated $H_2{}^{18}O$–O_2 ice at photon energies (PEs) of (**A**) 12.20, and (**B**) 11.40 eV, respectively. The irradiated ices were prepared under the exposure of 5 keV electrons of 1000 nA for 60 minutes.

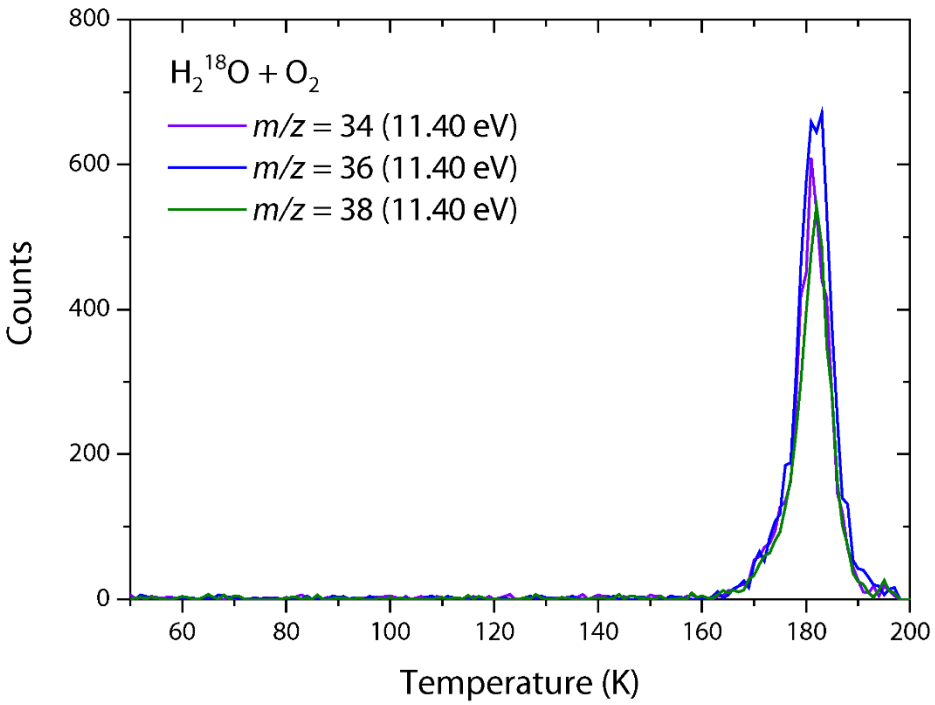


Fig. S2. TPD profiles obtained from the irradiated $H_2{}^{18}O$–O_2 ice mixtures. TPD profiles were obtained at *m/z* = 34, 36, and 38 at the photon energy of 11.40 eV. The irradiated ice was prepared under the exposure of 5 keV electrons of 1000 nA for 60 minutes.

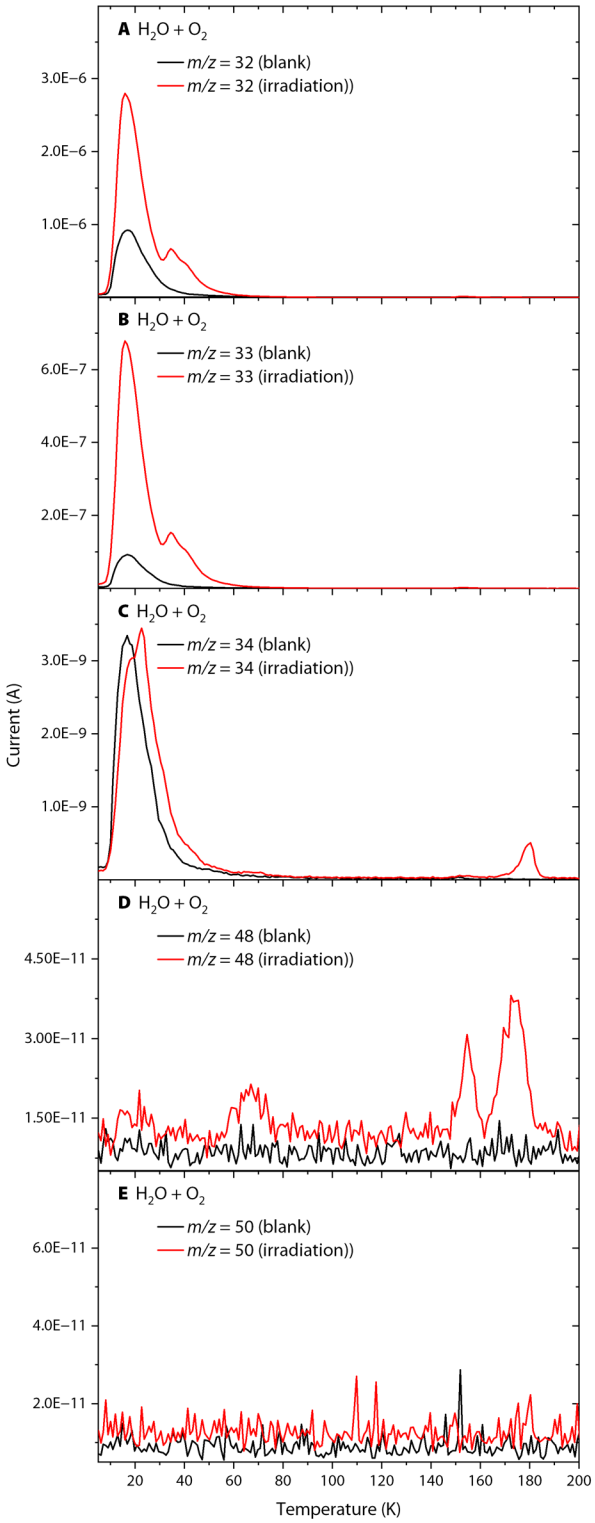


Fig. S3. Ion currents at distinct *m*/*z* obtained via EI-QMS in the TPD phase of irradiated and non-irradiated H_2O–O_2 ice mixtures. TPD profiles were collected at (**A**) *m*/*z* = 32, (**B**) *m*/*z* = 33, (**C**) *m*/*z* = 34, (**D**) *m*/*z* = 48, and (**E**) *m*/*z* = 50, respectively. The irradiated ice was prepared under the exposure of 5 keV electrons of 1000 nA for 60 minutes.

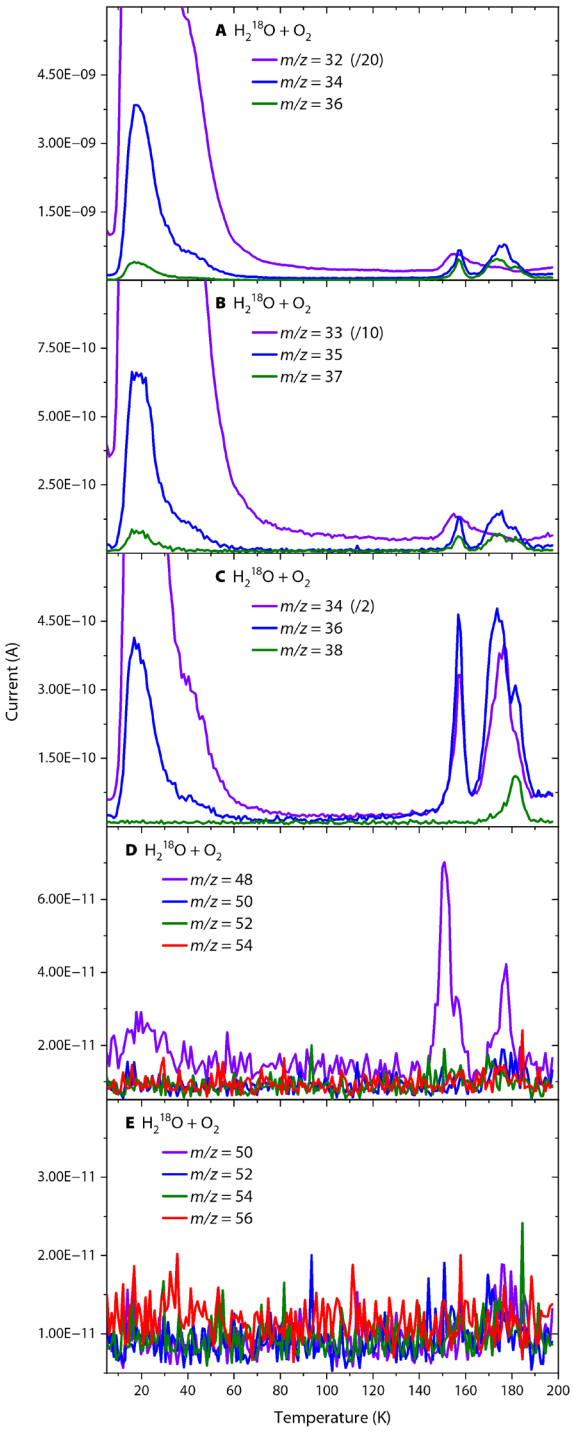


Fig. S4. Ion currents at distinct *m*/*z* obtained via EI-QMS in the TPD phase of irradiated $H_2{}^{18}O$–O_2 ice mixtures. For better comparison, TPD profiles are classified into (**A**) *m*/*z* = 32, 34, and 36; (**B**) *m*/*z* = 33, 35, and 37; (**C**) *m*/*z* = 34, 36, and 38; (**D**) *m*/*z* = 48, 50, 52, and 54; and (**E**) *m*/*z* = 50, 52, 54, and 56. Ion signals at *m*/*z* of 32, 33, and 34 are scaled down by factors of 20, 10, and 2, respectively. The irradiated ice was prepared under the exposure of 5 keV electrons of 1000 nA for 60 minutes.

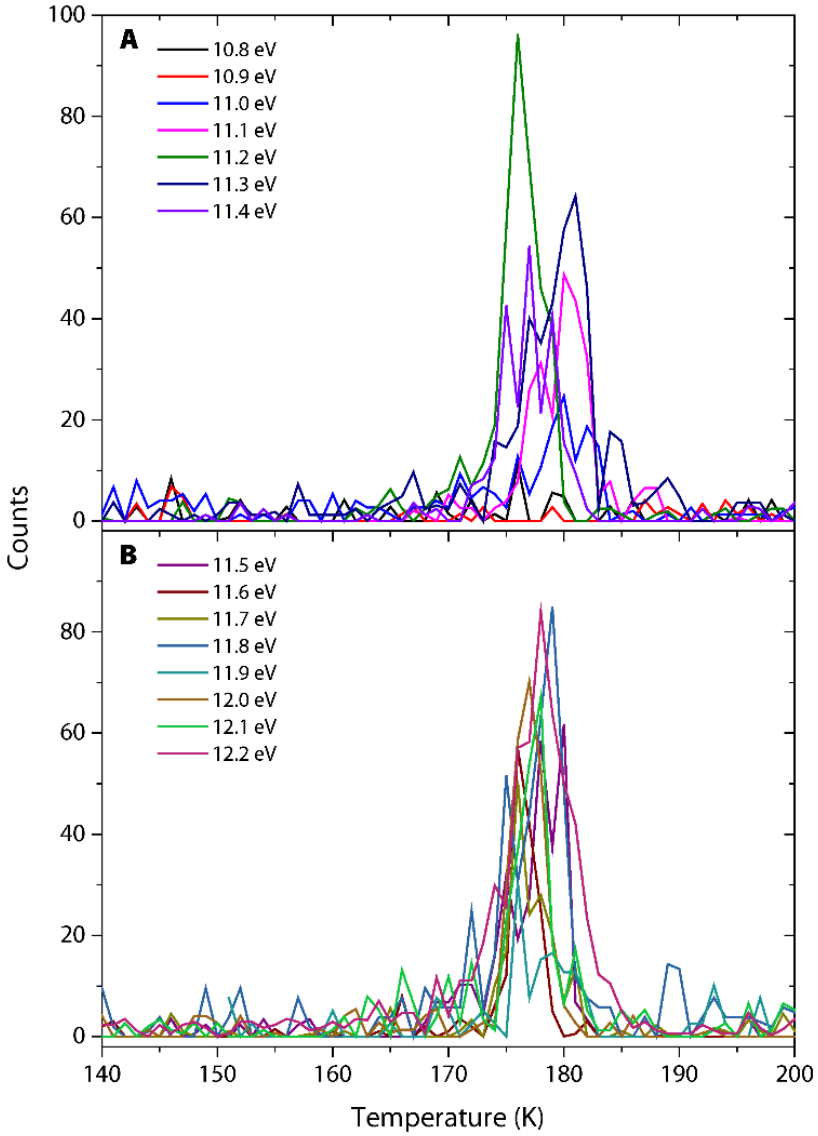


Fig. S5. TPD profiles obtained at *m/z* = 50 from the irradiated H_2O–O_2 ice mixtures under a range of photon energies. These TPD profiles have been normalized to photon fluxes at respective photon energy.

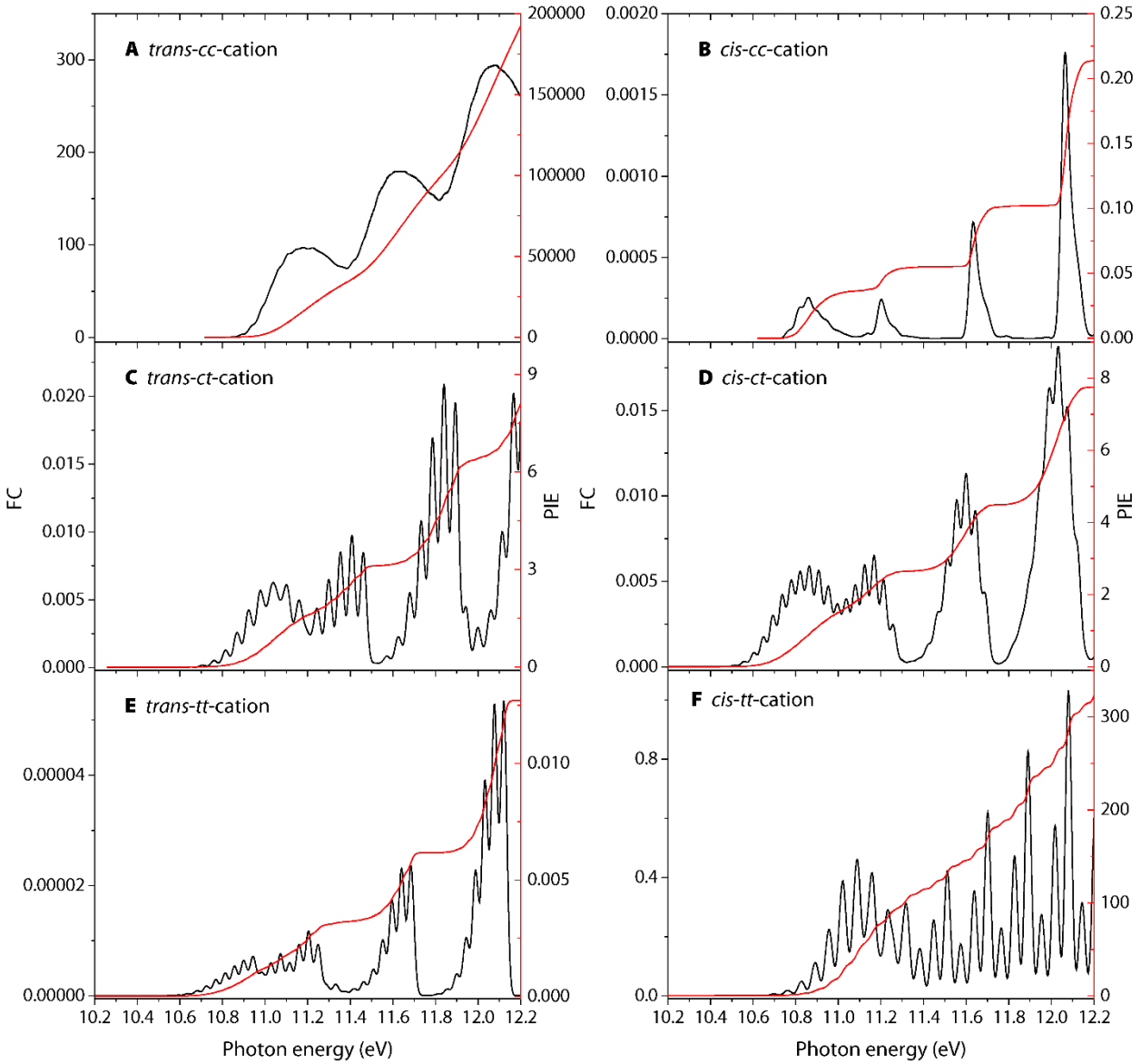


Fig. S6. Franck-Condon factors (FCFs) and photoionization efficiency (PIE) curves relevant to the HOOOH neutrals and cations. FCFs and PIE curves were calculated for the *trans*-/*cis*-HOOOH ionization producing (**A**/**B**) *cis*-*cis*-, (**C**/**D**) *cis*-*trans*-, and (**E**/**F**) *trans*-*trans*-HOOOH radical cation, respectively. The FCFs are in the unit of $dm^3/(mol \cdot cm)$.

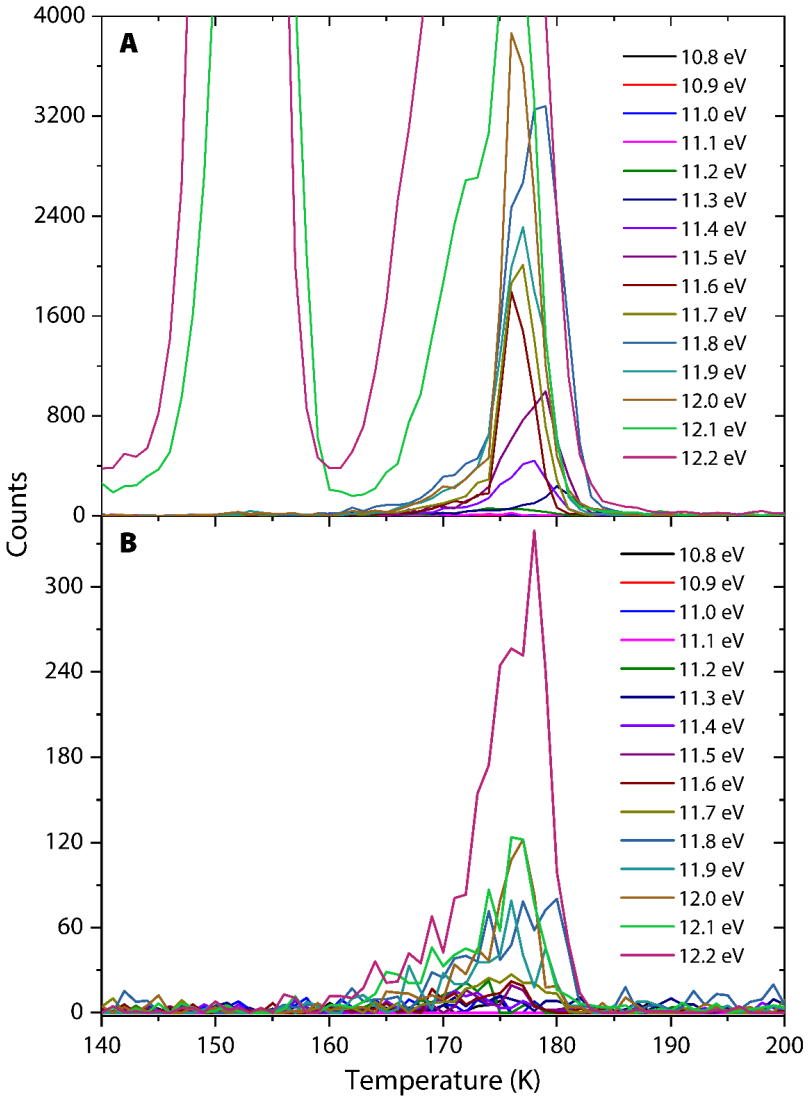


Fig. S7. TPD profiles obtained from the irradiated H_2O–O_2 ice mixtures under a range of photon energies. TPD profiles at *m/z* = 32 (**A**) and 18 (**B**) have been normalized to photon fluxes at respective photon energy. Note that TPD profiles at *m/z* = 32 exhibit strong signals at photon energies larger than 12.0 eV, since O_2 itself depicts ionization threshold of 12.071 ± 0.001 eV and its contribution has been corrected for the PIE curve of O_2^+ from the dissociative channel of H_2O plus O_2^+.

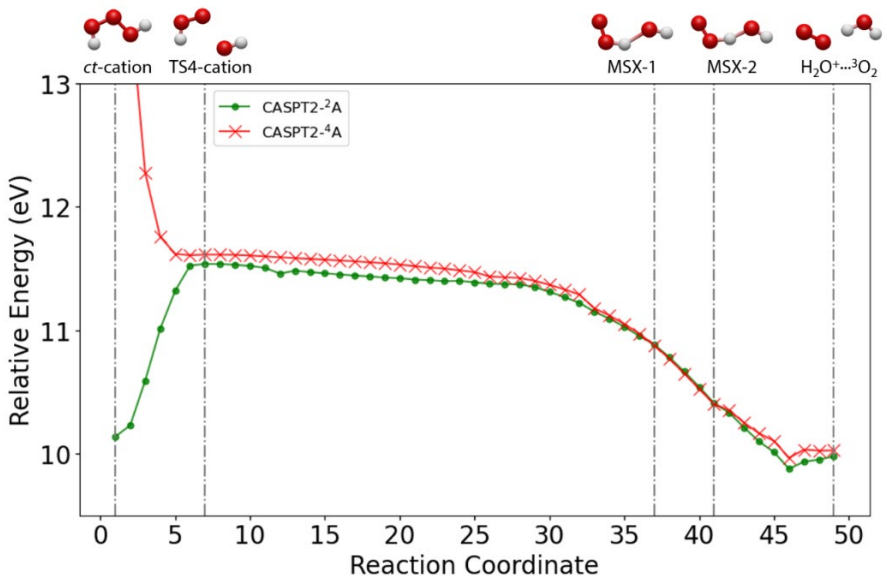


Fig. S8. Potential energy scan for the reaction path from *cis-trans*-HOOOH cation (*ct*-cation) to $H_2O^+\cdots{}^3O_2$ complex. The scan was completed using CASPT2(13,11)/def2-TZVP//B3LYP/aug-cc-pVTZ + ZPVE. Energies in eV are shown relative to *trans*-HOOOH. Only the lowest doublet (^{2}A) and lowest quartet (^{4}A) states are shown; the second doublet state is omitted in the figure for clarity. Structures at key stationary points and minimum-energy crossing points (MSX-1 and MSX-2) along the reaction coordinate are indicated.

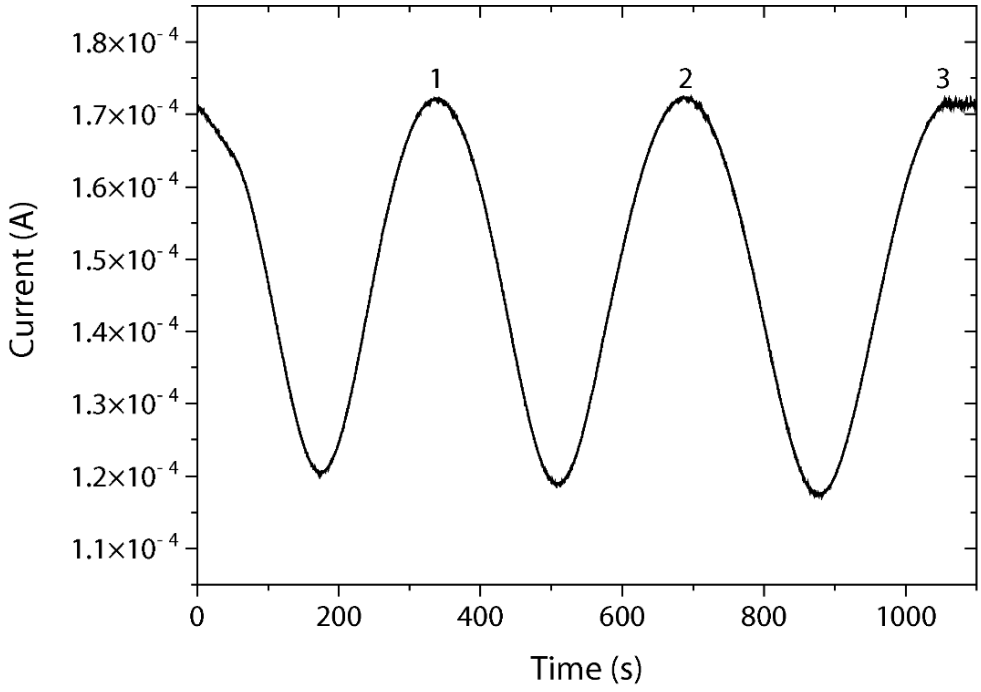


Fig. S9. Interference pattern observed during depositing the H_2O–O_2 ice mixture. The pattern was obtained by a 632.8 nm laser at an incidence angle of 4°. Integer numbers of fringes are indicated above signal maxima. At the end of the deposition process, three fringes had accumulated.

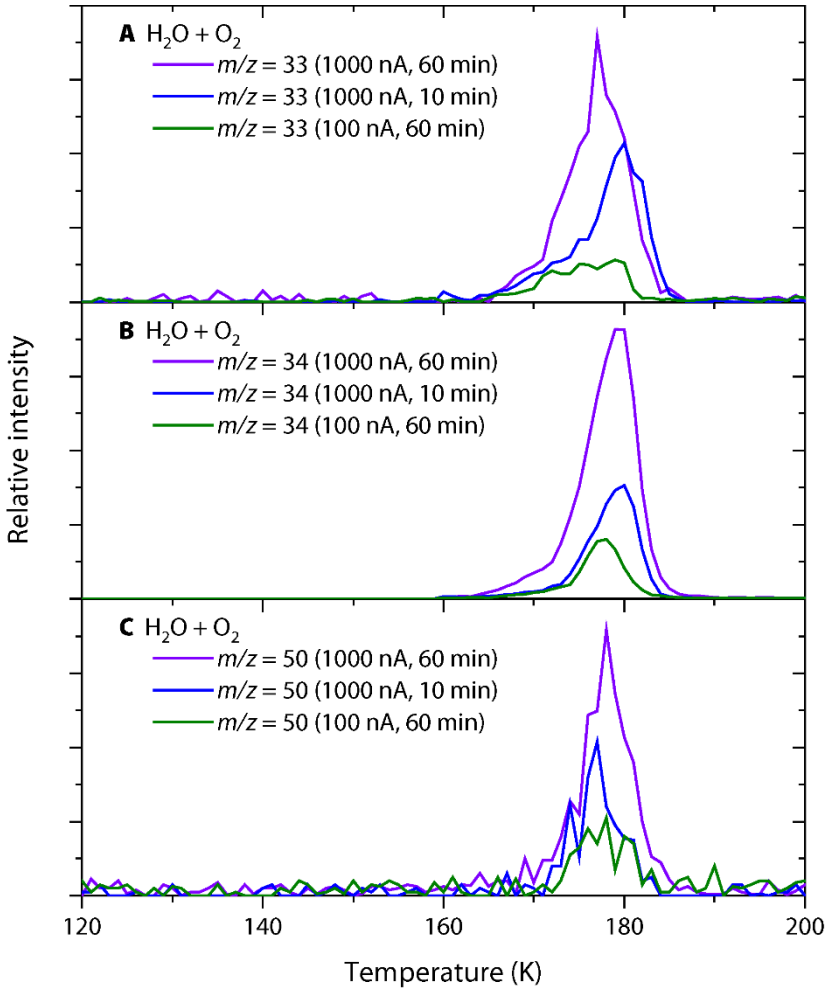


Fig. S10. TPD profiles obtained from the irradiated H_2O–O_2 ice mixtures under different doses. TPD profiles obtained at *m/z* of (**A**) 33, (**B**) 34, and (**C**) 50 at three different doses (1000 nA, 60 minutes; 1000 nA, 10 minutes; 100 nA, 60 minutes) for H_2O–O_2 ice mixtures (6.5 ± 1.0:1), respectively.

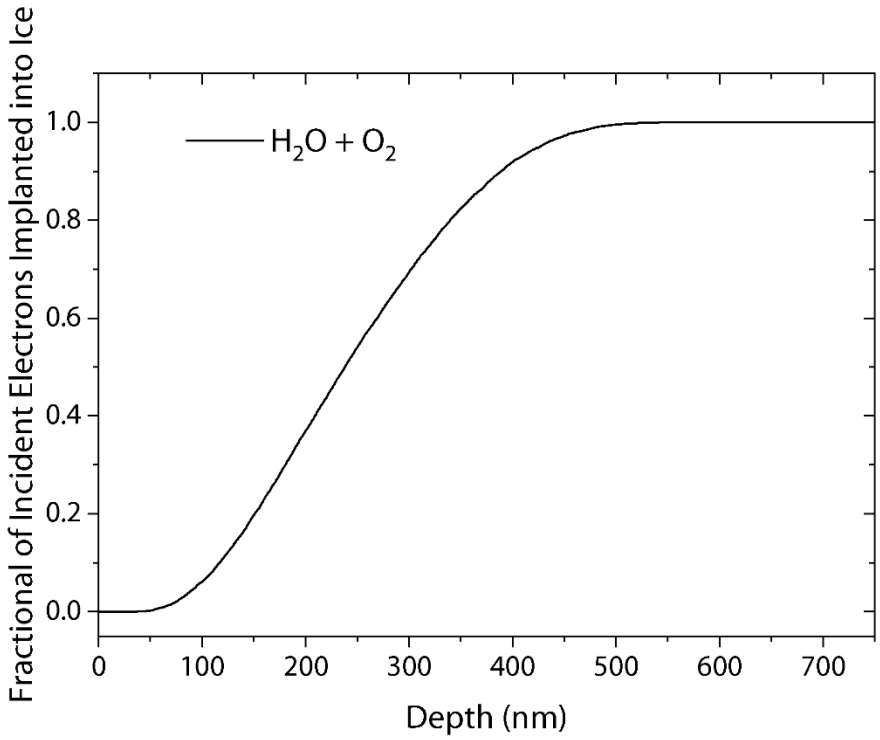


Fig. S11. CASINO simulation of the electron penetration. The maximum penetration depth of 5 keV electrons in the H_2O–O_2 ice is less than 600 nm.

Table S1. Relative energies and error analysis of H_2O_3 isomers. Relative energies and error analysis of adiabatic ionization energies (AIEs) of H_2O_3 isomers are computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory including the zero-point vibrational energy corrections. The IE ranges are calculated based on the computed AIE error limits of 0.01 – 0.08 eV and the electrical filed effect of −0.02 eV.

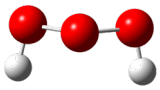
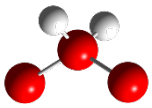
Structure	Isomer	ΔE (kcal/mol)	Computed IE (eV)	IE range after error analysis (eV)	Corrected IE with electric field effect (eV)
	*trans*-HOOOH	0.0	11.01	11.02 – 11.09	11.00 – 11.07
	*cis*-HOOOH	2.2	10.91	10.92 – 10.99	10.90 – 10.97
	$O(H_2O)O$	116.0	11.10	11.11 – 11.18	11.09 – 11.16

Table S2. Geometries, energies, and frequencies of H_2O_3 isomers. Computed Cartesian coordinates (Å), electronic energies (hartree), vibrational frequencies (cm^{-1}) at the CCSD(T)/aug-cc-pVTZ level of theory (Fig. 1).

trans-HOOOH

O	–0.008745847	1.152627068	–0.241409666
O	0.008745847	–1.152627068	–0.241409666
O	0.000000000	0.000000000	0.612995193
H	0.931798423	1.222762542	–0.467706492
H	–0.931798423	–1.222762542	–0.467706492

Frequency
360.11
416.06
521.16
797.51
896.10
1382.84
1391.98
3726.95
3730.16

cis-HOOOH

O	0.074180549	–0.257468623	1.154801458
O	0.074180549	–0.257468623	–1.154801458
O	0.073738020	0.594896597	0.000000000
H	–0.873727676	–0.315682717	1.350970930
H	–0.873727676	–0.315682717	–1.350970930

Frequency
271.64
436.69
504.36
797.77
896.76
1364.64
1398.71
3722.58
3725.84

$O(H_2O)O$

O	1.335475604	–0.310038942	0.000145972
O	0.000298810	0.381995169	0.000009105
O	–1.334911543	–0.309974127	–0.000167464
H	0.000216630	0.925868222	0.812921845
H	0.000407499	0.925914800	–0.812872458

Frequency
309.92
655.98
675.66
690.07
908.58
979.38
1558.93
3597.14
3690.30

Table S3. Geometries, energies, frequencies, and infrared intensities relevant to HOOOH neutrals, cations, and dissociation channels. Computed Cartesian coordinates (Å), electronic energies (hartree), vibrational frequencies (cm^{-1}), infrared intensities (km mol^{-1}), zero-point vibrational energies (kcal mol^{-1}), and extrapolated CCSD(T)/CBS, CASSCF/def2-TZVP and CASPT2/def2-TZVP energies (hartree) at the B3LYP/aug-cc-pVTZ level of theory involved in the potential energy surface of *trans*-/*cis*-HOOOH neutrals and cations.

trans-HOOOH

O	0.000000	1.153889	–0.241757
O	–0.000000	–0.000000	0.598547
H	0.940851	1.245513	–0.460135
O	–0.000000	–1.153889	–0.241757
H	–0.940851	–1.245513	–0.460135

E = –226.7924131
E[CCSD(T)/CBS] = –226.5228221
E[CASSCF(16,13)] = –225.8376467
E[CASPT2(16,13)] = –226.3671208
E[CASPT2(14,11)] = –226.3665029
ZPVE = 18.9473 kcal mol^{-1}

Frequency	Intensity
373.6184	122.3541
425.0267	93.5789
526.6237	24.8962
799.8598	92.8979
940.8801	2.8719
1384.4163	30.5073
1392.5038	45.6469
3703.2575	65.6485
3707.6675	3.1218

cis-HOOOH

O	0.259652	–0.068755	–1.155403
O	–0.573597	0.028892	0.000000
H	0.430833	0.861915	–1.368881
O	0.259652	–0.068755	1.155403
H	0.430833	0.861915	1.368881

E = –226.7886986
E[CCSD(T)/CBS] = –226.5190315
ZPVE = 18.8144 kcal mol^{-1}

Frequency	Intensity
288.5912	43.6655
446.3997	105.2649
513.1470	6.1986
801.9920	109.8807
941.0334	0.6920
1367.3283	48.4211
1399.3240	30.2627
3700.2964	27.1542

3702.7400	19.8012		
$O(H_2O)O$			
O	–1.340721	–0.305854	–0.000653
O	0.001167	0.378309	–0.000034
O	1.339851	–0.307258	0.000739
H	0.000329	0.920609	–0.814461
H	–0.001142	0.920852	0.814231
E = –226.6100566			
E[CCSD(T)/CBS] = –226.3368655			
ZPVE = 18.3240 kcal mol^{-1}			
Frequency	Intensity		
312.1305	21.0081		
523.0318	2.9464		
677.6033	8.3757		
691.2704	2.6411		
883.6063	0.0035		
980.0557	104.2825		
1540.5321	92.9894		
3562.7697	136.8218		
3646.8619	339.6294		
$O(H_2O)O$ radical cation			
O	–1.294664	–0.316178	–0.000762
O	0.000699	0.367098	–0.000019
O	1.293540	–0.317118	0.000831
H	0.000513	0.936293	–0.837435
H	–0.000604	0.936564	0.837207
E = –226.2100876			
E[CCSD(T)/CBS] = –225.9263411			
ZPVE = 16.6955 kcal mol^{-1}			
Frequency	Intensity		
381.4139	22.2467		
393.8592	705.2367		
408.2749	7.4560		
717.2247	0.0120		
896.5254	0.0016		
1029.2970	152.7616		
1467.0424	158.4060		
3184.4169	341.1396		
3200.6170	512.1769		

cis-cis-HOOOH radical cation

O	–1.149106	0.150975	0.046269
O	–0.000040	–0.555748	0.000104
H	–1.015166	1.016154	–0.417790
O	1.149087	0.150962	–0.046501
H	1.015693	1.015513	0.418863

E = –226.3927823
E[CCSD(T)/CBS] = –226.1171142
E[CASSCF(15,13)] = –225.4774152
E[CASPT2(15,13)] = –225.9736805
ZPVE = 18.2014 kcal mol^{-1}

Frequency	Intensity
74.7500	173.7585
372.3526	57.1596
582.6921	2.5207
939.2840	156.6072
1000.6514	5.4017
1338.5291	157.0482
1488.5455	31.4926
3454.6521	192.1943
3480.6210	240.4468

cis-trans-HOOOH radical cation

O	1.127043	0.189300	–0.000000
O	0.010965	–0.528848	0.000000
H	0.875242	1.151041	–0.000000
O	–1.077857	0.289341	–0.000000
H	–1.829878	–0.354210	0.000000

E = –226.4106956
E[CCSD(T)/CBS] = –226.1353020
E[CASSCF(15,13)] = –225.4978661
E[CASPT2(15,13)] = –225.9930498
ZPVE = 18.8837 kcal mol^{-1}

Frequency	Intensity
361.1758	315.8211
433.3952	0.0004
542.3986	20.8944
968.9926	87.6555
1042.3496	87.3539
1416.1519	72.1615
1515.8318	94.1990
3426.5770	299.2641
3502.4421	365.6578

trans-trans-HOOOH radical cation

O	–1.070829	0.000000	–0.281811
O	–0.000000	0.000000	0.531481
H	–1.821621	0.000000	0.363427

O	1.070829	–0.000000	–0.281811
H	1.821621	–0.000000	0.363427

E = –226.4149654
E[CCSD(T)/CBS] = –226.1391932
E[CASSCF(15,13)] = –225.5022175
E[CASPT2(15,13)] = –225.9975454
ZPVE = 19.2100 kcal mol^{-1}

Frequency	Intensity
354.4690	0.0000
506.7892	294.2430
573.4165	14.8414
977.8242	227.4017
1044.9394	10.0086
1448.4972	72.8097
1528.9680	52.4247
3487.7073	752.3037
3514.9954	94.7564

H_2O

H	–0.763511	0.000000	–0.515934
O	0.000000	0.000000	0.068997
H	0.763511	–0.000000	–0.515934

E = –76.4661983
E[CCSD(T)/CBS] = –76.3763063
E[CASSCF(6,5)] = –76.1111560
E[CASPT2(6,5)] = –76.3108262
ZPVE = 13.3290 kcal mol^{-1}

Frequency	Intensity
1627.2978	75.7766
3796.9001	4.6432
3899.5522	63.0484

O_2 radical cation

O	–1.045720	0.087249	0.041993
O	–0.103479	–0.492070	0.004260

E = –149.9235830
E[CCSD(T)/CBS] = –149.7572818
E[CASSCF(10,8)] = –149.4113825
E[CASPT2(10,8)] = –149.6769369
ZPVE = 2.9233 kcal mol^{-1}

Frequency	Intensity
2044.8960	0.0000

TS_*ct*-cation-*cc*-radical cation (TS1)

O	–1.165672	0.129720	0.001770
O	–0.007506	–0.546398	0.062224
H	–1.006344	1.015214	–0.417859
O	1.125208	0.185377	–0.106416
H	1.054762	0.993718	0.461216

E = –226.3927632
E[CCSD(T)/CBS] = –226.1172416
E[CASSCF(15,13)] = –225.4795434
E[CASPT2(15,13)] = –225.9732504
ZPVE = 18.0740 kcal mol^{-1}
ν_i = 129.9 cm^{-1}

Frequency	Intensity
–129.8831	147.4393
390.8945	77.2137
580.6442	9.6375
921.2253	122.2430
1012.2588	27.4823
1340.7279	156.8149
1477.5844	33.0776
3440.3631	208.4464
3479.2641	232.8951

TS_H_2O + O_2^+_*ct*- radical cation (TS3)

O	0.931113	0.201202	0.186009
O	0.078946	–0.713737	–0.109090
H	–0.101695	0.962103	0.020267
O	–1.069186	0.209047	–0.362819
H	–1.792101	–0.044415	0.266639

E = –226.3626776
E[CCSD(T)/CBS] = –226.0908310
E[CASSCF(15,13)] = –225.4590409
E[CASPT2(15,13)] = –225.9505305
ZPVE = 15.9953 kcal mol^{-1}
ν_i = 1876.5 cm^{-1}

Frequency	Intensity
–1876.5132	303.7688
543.2498	112.7760
731.0976	44.9985
839.9479	0.1457
1127.4487	122.7638
1173.8318	16.9347
1309.4350	77.3721
1982.3776	214.3045
3481.4982	317.0087

TS_*tt*-cation-*ct*- radical cation (TS2)

O	0.000474	1.118688	–0.244792
O	–0.040030	–0.012172	0.519323
H	0.960008	1.337239	–0.344084
O	0.089347	–1.079017	–0.279883
H	–0.049998	–1.845252	0.341321

E = –226.4002273
E[CCSD(T)/CBS] = –226.1251301

E[CASSCF(15,13)] = –225.4880068
E[CASPT2(15,13)] = –225.9818884
ZPVE = 18.2584 kcal mol^{-1}
ν_i = 591.4 cm^{-1}

Frequency	Intensity
–591.4202	120.4252
554.4230	53.0279
578.8359	127.9768
857.1542	132.0856
1050.4874	4.2592
1375.7674	76.3410
1440.9465	94.7525
3420.9913	503.5621
3493.3629	195.6495

cis-HOOH

O	0.259652	–0.068755	–1.155403
O	–0.573597	0.028892	0.000000
H	0.430833	0.861915	–1.368881
O	0.259652	–0.068755	1.155403
H	0.430833	0.861915	1.368881

E = –226.7886986
E[CCSD(T)/CBS] = –226.5190315
ZPVE = 18.8144 kcal mol^{-1}

Frequency	Intensity
288.5912	43.6655
446.3997	105.2649
513.1470	6.1986
801.9920	109.8807
941.0334	0.6920
1367.3283	48.4211
1399.3240	30.2627
3700.2964	27.1542
3702.7400	19.8012

trans-HOOH

O	0.000000	1.153889	–0.241757
O	–0.000000	–0.000000	0.598547
H	0.940851	1.245513	–0.460135
O	–0.000000	–1.153889	–0.241757
H	–0.940851	–1.245513	–0.460135

E = –226.7924131
E[CCSD(T)/CBS] = –226.5228221
ZPVE = 18.9473 kcal mol^{-1}

Frequency	Intensity
373.6184	122.3541
425.0267	93.5789
526.6237	24.8962

799.8598	92.8979	
940.8801	2.8719	
1384.4163	30.5073	
1392.5038	45.6469	
3703.2575	65.6485	
3707.6675	3.1218	
H_2O-radical cation		
H	–0.013819	–0.008688	–0.037522
O	–0.316336	–0.198892	0.902998
H	0.330155	0.207581	1.558105
E = –76.0003009		
E[CCSD(T)/CBS] = –75.9100052		
E[CASSCF(5,5)] = –75.7076898		
E[CASPT2(5,5)] = –75.8597374		
ZPVE = 11.6129 kcal mol^{-1}		
Frequency	Intensity	
1441.8605	168.7340	
3318.0294	114.5744	
3363.4480	455.4290	
O_2 singlet		
O	–1.087625	0.113013	0.043671
O	–0.061574	–0.517834	0.002582
E = –150.3233607		
E[CCSD(T)/CBS] = –150.1541580		
E[CASSCF(10,8)] = –149.7549079		
E[CASPT2(10,8)] = –150.0645875		
ZPVE = 2.3078 kcal mol^{-1}		
O_2 triplet		
O	–1.087784	0.113111	0.043677
O	–0.061415	–0.517932	0.002576
E = –150.3846123		
E[CCSD(T)/CBS] = –150.2009742		
E[CASSCF(10,8)] = –149.7856677		
E[CASPT2(10,8)] = –150.1192771		
ZPVE = 2.3241 kcal mol^{-1}		
$H_2O^+\cdots{}^3O_2$ complex		
O	0.459265	0.000647	–0.605536
O	–0.331960	–0.000574	–1.516121
H	0.079550	–0.000064	0.879878
O	–0.173348	0.000536	1.910311
H	0.651313	–0.009617	2.474899
E = –226.30895300		
E[CASPT2(13,11)-^{2}A] = –225.99286574		
E[CASPT2(13,11)-^{4}A] = –225.99181247		
ZPVE = 14.9173 kcal mol^{-1}		
Frequency	Intensity	

128.97	1.06
312.55	146.76
519.14	82.09
587.39	130.45
1463.31	102.78
1599.72	33.17
2407.44	2077.65
3416.28	270.59
10.28	0.00

TS4-cation doublet

O	–0.368743	0.000001	–1.251602
O	0.611373	–0.000000	–0.451270
H	–1.231590	–0.000007	–0.749860
O	–0.202359	0.000000	1.611264
H	0.592352	–0.000002	2.203996

E = –226.26178758

E[CASPT2(13,11)-^{2}A] = –225.93808671

E[CASPT2(13,11)-^{4}A] = –225.93480025

ZPVE = 16.1561 kcal mol^{-1}

Frequency	Intensity
157.99	18.80
293.47	1.07
319.60	48.09
533.68	90.25
604.45	190.76
1192.77	276.33
1334.45	24.91
3356.43	284.78
3508.50	314.05

MSX-1

O	–0.612366	0.000000	–0.767747
O	0.557801	–0.000000	–1.116094
H	–0.734826	0.000000	0.297158
O	0.106045	0.000001	1.697284
H	–0.082324	–0.000008	2.664127

E = –226.27798633

E[CASPT2(13,11)-^{2}A] = –225.95843659

E[CASPT2(13,11)-^{4}A] = –225.95871710

ZPVE = 13.8796 kcal mol^{-1}

ν_i = 264.92 cm^{-1}

ν_i = 103.02cm^{-1}

Frequency	Intensity
197.57	20.99
460.29	109.02
629.83	86.64
1129.90	277.33

1487.57	15.73
2222.58	1325.24
3581.18	260.81

MSX-2

O	–0.572256	0.000000	–0.643750
O	0.455710	–0.000000	–1.288988
H	–0.444591	0.000001	0.498241
O	0.166204	0.000001	1.738471
H	–0.343641	–0.000009	2.585424

E = –226.29310359

E[CASPT2(13,11)-^{2}A] = –225.97490142

E[CASPT2(13,11)-^{4}A] = –225.97571073

ZPVE = 13.2206 kcal mol^{-1}

ν_i = 110.59 cm^{-1}

ν_i = 81.83 cm^{-1}

Frequency	Intensity
221.17	88.10
584.33	51.87
777.16	102.73
1191.38	1918.35
1392.42	604.83
1540.82	4.58
3540.66	236.23

Table S4. Geometries, energies, frequencies, and infrared intensities relevant to other $H_2O_3^+$ dissociation channels. Computed Cartesian coordinates (Å), electronic energies (hartree), vibrational frequencies (cm^{-1}), infrared intensities (km mol^{-1}), zero-point vibrational energies (kcal mol^{-1}), and extrapolated CCSD(T)/CBS energies (hartree) optimized at the B3LYP/aug-cc-pVTZ level of theory involved in the potential energy surface of dissociation channels leading from $H_2O_3^+$ isomers.

H_2O_2			
O	0.183482	0.367201	0.089919
O	–1.109524	–0.238624	–0.169640
H	–1.437792	–0.355917	0.732039
H	0.045646	1.250240	–0.278546
E = –151.6179514			
E[CCSD(T)/CBS] = –151.4383770			
ZPVE = 16.5714 kcal mol^{-1}			
Frequency	Intensity		
374.1468	165.0681		
949.7231	0.6070		
1322.2452	98.6232		
1434.3059	0.5260		
3755.1477	56.1485		
3756.3143	13.1595		
H_2O_2 radical cation			
O	0.004100	0.507466	0.253195
O	–1.163245	0.004024	–0.066301
H	–1.371926	–0.630724	0.673099
H	0.212884	1.142136	–0.486220
E = –151.2308258			
E[CCSD(T)/CBS] = –151.0474889			
ZPVE = 16.9184 kcal mol^{-1}			
Frequency	Intensity		
860.8664	310.0047		
1238.6910	0.0000		
1312.4261	238.1287		
1587.9260	0.0000		
3406.9642	635.4744		
3427.7275	0.0158		
HO-OH-O radical cation			
O	–1.203540	–0.323917	0.055168
O	–0.131568	0.419983	–0.151571
O	1.163473	–0.195731	0.147773
H	1.435025	–0.503017	–0.748188
H	–0.162573	1.283986	0.350479
E = –226.3542148			
E[CCSD(T)/CBS] = –226.0787746			
ZPVE = 18.3167 kcal mol^{-1}			
Frequency	Intensity		
271.8942	132.9534		
453.5918	10.5378		
675.8456	142.7064		

758.6858	31.0461		
1005.5079	18.9249		
1293.0693	89.5200		
1443.1668	38.9399		
3348.7109	411.4060		
3562.2720	212.8380		
H			
H	0.000000	0.000000	0.000000
E = –0.5022597			
E[CCSD(T)/CBS] = –0.5000407			
ZPVE = 0.0000 kcal mol^{-1}			
O radical cation			
O	0.000000	0.000000	0.000000
E = –74.5743832			
E[CCSD(T)/CBS] = –74.5055873			
ZPVE = 0.0000 kcal mol^{-1}			
OH radical cation			
O	1.168983	–0.181370	0.172292
H	1.431851	–0.524068	–0.773771
E = –75.1714543			
E[CCSD(T)/CBS] = –75.1051198			
ZPVE = 4.3339 kcal mol^{-1}			
Frequency	Intensity		
3031.6403	295.4788		
OH			
O	1.177158	–0.192027	0.142871
H	1.423676	–0.513411	–0.744350
E = –75.7685987			
E[CCSD(T)/CBS] = –75.6757199			
ZPVE = 5.2796 kcal mol^{-1}			
Frequency	Intensity		
3693.0993	13.3270		
OOH radical cation			
O	0.635953	–0.010884	0.000000
O	–0.559218	–0.049405	–0.000000
H	–0.954611	0.895824	–0.000000
E = –150.5302271			
E[CCSD(T)/CBS] = –150.3623175			
ZPVE = 8.7218 kcal mol^{-1}			
Frequency	Intensity		
1470.9509	119.5864		
1578.3843	2.6472		
3051.6459	206.2686		
OOH			
O	0.691267	0.004988	0.000000
O	–0.635826	–0.049479	0.000000
H	–0.933317	0.880026	0.000000
E = –150.9733511			
E[CCSD(T)/CBS] = –150.7885358			
ZPVE = 8.8360 kcal mol^{-1}			

Frequency	Intensity		
1157.4963	26.6849		
1430.9084	39.9450		
3592.4290	25.0761		
OOOH radical cation			
O	–1.049151	0.116027	0.108041
O	–0.070709	–0.507687	–0.102697
O	1.158172	0.107280	0.061083
H	0.978095	1.045995	0.352484
E = –225.7422691			
E[CCSD(T)/CBS] = –225.4809171			
ZPVE = 12.0039 kcal mol^{-1}			
Frequency	Intensity		
590.9802	4.5603		
637.6397	129.6891		
871.7461	154.8450		
1369.6723	6.5908		
1544.9553	119.4623		
3381.8651	229.6473		
O			
O	0.000000	0.000000	0.000000
E = –75.0941778			
E[CCSD(T)/CBS] = –75.0048260			
ZPVE = 0.0000 kcal mol^{-1}			

Table S5. Data applied to calculate the average dose per molecule.

Initial Kinetic energy of the electrons	5 keV
Irradiation current (I)	1000 ± 50 nA
Irradiation time (t)	3600 s
Average penetration depth, l	226 ± 30 nm
Average kinetic energy of backscattered electrons, E_{bs}[a]	3.33 ± 0.3 keV
Fraction of backscattered electrons, f_{bs}[a]	0.36 ± 0.04
Average kinetic energy of transmitted electrons, E_{trans}[a],	0.0 keV
Fraction of transmitted electrons, f_{trans}[a]	0
Average density of the ice mixture, ρ	1.26 g cm^{-3}
Irradiated area, A	1.0 ± 0.2 cm^2
Total number of electrons	$8.6 \pm 0.9 \times 10^{17}$
Dose per molecule, D	water: 99.2 eV
	oxygen: 176.4 eV

[a] Values from CASINO simulations.