

Supplementary Materials for

**Formation of Hydrogen Trioxide (HOOOH) in Extraterrestrial Ice Analogs and its Role as an Oxidizer in Prebiotic Chemistry**

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**This PDF file includes:**

Supplementary Methods

Figs. S1 to S11

Tables S1 to S5

**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 *θ* = 4°:

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 H2O and O2 ice mixture was calculated to be 755 ± 50 nm.

2. Calibration Experiments

Calibration experiments aim to determine the ratio of water (H2O) to molecular oxygen (O2) in mixed ices. Initially, we employed laser interferometry to accurately measure the thicknesses of pure H2O and O2 ices deposited on a silver substrate respectively. The measured thicknesses were 250 ± 20 nm for H2O ice and 254 ± 20 nm for O2 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, H2O⁺; *m/z* = 17, OH⁺; *m/z* = 16, O⁺) and oxygen (*m/z* = 32, O2⁺; *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 H2O to O2 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 H2O (H2O⁺ and OH⁺) and O2 (O2⁺ and O⁺) were measured using QMS and compared with those obtained from pure H2O and O2 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 H218O–O2 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 H218O–O2 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 H2O–O2 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 H218O–O2 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.



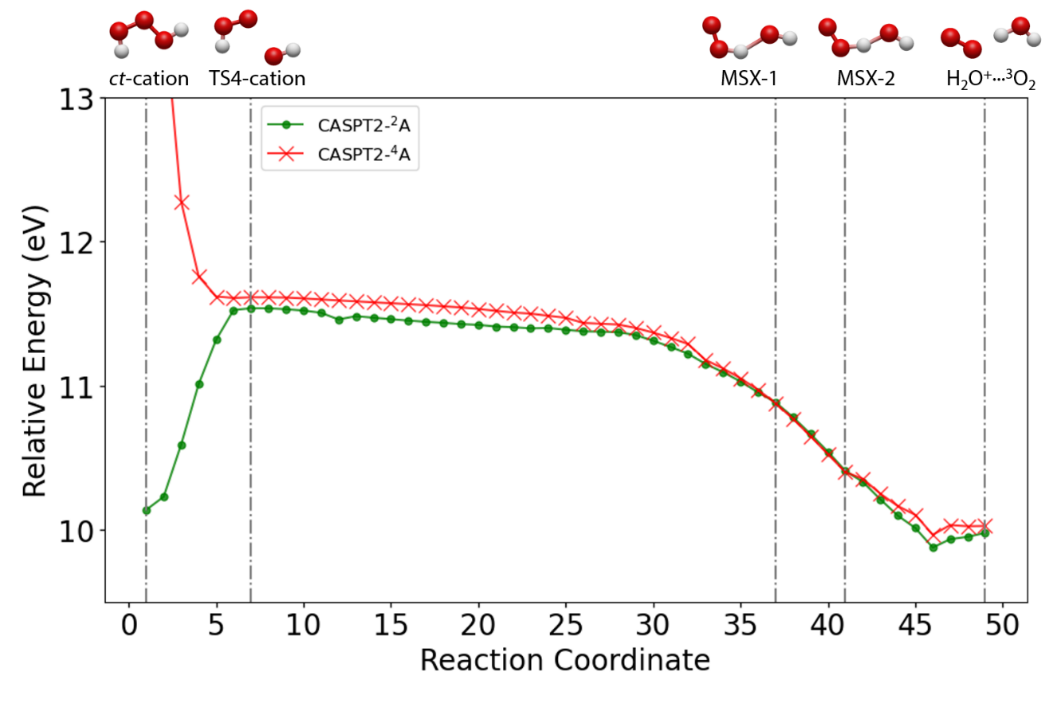
**Fig. S5. TPD profiles obtained at *m/z* = 50 from the irradiated H2O–O2 ice mixtures under a range of photon energies.** These TPD profiles have been normalized to photon fluxes at respective photon energy.



**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 dm3/(mol·cm).



**Fig. S7. TPD profiles obtained from the irradiated H2O–O2 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 O2 itself depicts ionization threshold of 12.071 ± 0.001 eV and its contribution has been corrected for the PIE curve of O2+ from the dissociative channel of H2O plus O2+.



**Fig. S8. Potential energy scan for the reaction path from *cis*-*trans*-HOOOH cation (*ct*-cation) to H2O+···3O2 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 (2A) and lowest quartet (4A) 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 H2O–O2 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 H2O–O2 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 H2O–O2 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 H2O–O2 ice is less than 600 nm.

**Table S1.** **Relative energies and error analysis of H2O3 isomers.** Relative energies and error analysis of adiabatic ionization energies (AIEs) of H2O3 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 | *Δ*E (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(H2O)O | 116.0 | 11.10 | 11.11 – 11.18 | 11.09 – 11.16 |

**Table S2.** **Geometries, energies, and frequencies of H2O3 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(H2O)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(H2O)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(H2O)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 |
| H2O  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 |
| O2 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  νi = 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\_H2O + O2+\_*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  νi = 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  νi = 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 |
| H2O-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 |
| O2 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 |
| O2 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 |
| H2O+···3O2 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)-2A] = –225.99286574  E[CASPT2(13,11)-4A] = –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)-2A] = –225.93808671  E[CASPT2(13,11)-4A] = –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)-2A] = –225.95843659  E[CASPT2(13,11)-4A] = –225.95871710  ZPVE = 13.8796 kcal mol–1  νi = 264.92 cm–1  νi = 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)-2A] = –225.97490142  E[CASPT2(13,11)-4A] = –225.97571073  ZPVE = 13.2206 kcal mol–1  νi = 110.59 cm–1  νi = 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 H2O3+ 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 H2O3+ isomers.

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| --- |
| H2O2  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 |
| H2O2 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.

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|  |  |
| 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*bsa | 3.33 ± 0.3 keV |
| Fraction of backscattered electrons, *f*bsa | 0.36 ± 0.04 |
| Average kinetic energy of transmitted electrons, *E*transa, | 0.0 keV |
| Fraction of transmitted electrons, *f*transa | 0 |
| Average density of the ice mixture, *ρ* | 1.26 g cm–3 |
| Irradiated area, *A* | 1.0 ± 0.2 cm2 |
| Total number of electrons | 8.6 ± 0.9 × 1017 |
| Dose per molecule, *D* | water: 99.2 eV  oxygen: 176.4 eV |

a Values from CASINO simulations.