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

**Short title: Abiotic Formation of HOOOH in Ice Analogs**

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**Abstract**

The formation and characterization of hydrogen trioxide (HOOOH) has fascinated scientists for more than a century, due to its role as a prototype model for oxygen-chain bonding and as a key transient in antibody-catalyzed oxidation reactions relevant to the origin of life. However, the abiotic formation pathways to HOOOH have remained elusive. Here we demonstrate in laboratory simulation experiments that HOOOHeffectively forms in water–molecular oxygen (H2O–O2) ice analogs at temperatures as low as 5 K under exposure to proxies of Galactic Cosmic Rays. Exploiting synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS), HOOOHalong with hydrogen peroxide (HOOH) and the hydroperoxyl (HOO) radical were identified during the temperature-programmed desorption (TPD) of the irradiated ices. This abiotic synthesis expands the oxidant inventory on interstellar grains, icy moons, and Kuiper Belt Objects (KBOs), offering a plausible source of essential oxidizers for prebiotic chemistry in space.

**Teaser**

Hydrogen trioxide and other oxidizers were synthesized abiotically in H2O–O2 ice analogs under extraterrestrial-like conditions.

**Introduction**

Hydrogen trioxide (HOOOH) — the simplest polyoxide — has long been regarded as a key intermediate in atmospheric (*1, 2*), biological (*3, 4*), and environmental processes (*1, 5*) since its initial proposal by Berthelot in 1880 (*6*). Extensive investigation of its preparation, reactivity, structural characterization, and quantum chemical properties began only in the 1960s (*7*). Czapski and Bielski first claimed the production of HOOOHin the pulse radiolysis of acidified air-saturated aqueous solutions (*8*), following by the ultraviolet (UV) absorption spectroscopy of HOOOHin the pulse radiolysis of air-saturated perchloric acid solution (*9, 10*). Giguère *et al* (*11, 12*) identified the fundamental skeletal vibrations of HOOOHvia infrared (IR) and Raman spectra exploiting electrically discharged mixtures of water (H2O), hydrogen peroxide (HOOH), and oxygen (O2) at cryogenic temperatures. Plesničar *et al* (*13-16*) prepared HOOOHat low temperatures in organic solvents via ozonation of 1,2-diphenylhydrazines, or through decomposition of hydrotrioxides (ROOOH) with R being an organic group.

Enlightened by the microscopic reversibility that HOOOHcan be reductively generated from ozone (O3) decomposition catalyzed by water (*17*), Wentworth *et al* (*3, 18*) suggested that antibodies adopt water as an electron source to catalyze its addition to singlet molecular oxygen (1O2) yielding HOOOHas a reactive intermediate. Engdahl and Nelander characterized the fundamental vibrations of HOOOHin argon matrices identifying its antisymmetric O–O stretch at 776 cm−1 as an ideal marker distinct from strong water absorption (*19*). Xu and Goddard *et al* (*1, 20*) theoretically delineated plausible mechanisms to HOOOHin a water-catalyzed reaction of water with 1O2 or via decomposition of [(HO2)(HO3)] hydrogen-bonded complexes. Suma *et al* (*21*) reported the first pure rotational spectra and precise geometrical structure of *trans*-HOOOH. High-level *ab initio* studies including the benchmark CCSD(T)-F12 calculations by Hollman and Schaefer confirmed a zigzag skew-chain helical-type structure of *trans*-HOOOHwith C2 symmetry (*22*).

Despite the astrochemical and astrobiological importance of HOOOH in the interstellar medium and in the Solar System, its formation mechanism under extraterrestrial-like conditions has remained poorly understood. Water ice — a potential precursor to HOOOH— is found ubiquitously in cold molecular clouds (*23, 24*) and throughout the Solar System including Kuiper Belt Objects (*25, 26*), comets (*27, 28*), and icy moons like Europa, Ganymede, and Callisto (*29, 30*). Molecular oxygen — a critical molecular building block of HOOOH— has been detected in molecular clouds, *e*.*g*., Orion (*31*) and *ρ* Oph A (*32*) as well as in the condensed phase on the Galilean and Saturnian moons (*33, 34*). Notably, molecular oxygen also exhibits remarkably high abundances in the coma of comet 67P/Churyumov–Gerasimenko (*35*).

The co-existence of H2O and O2 in interstellar and Solar System ices suggests that HOOOH could form via non-equilibrium processes such as through the interaction of H2O–O2 ices with ionizing radiation like Galactic Cosmic Rays (GCRs) or electrons trapped in the magnetospheres of the giant planets. However, experimental studies on irradiated H2O–O2 ices are limited. Under conditions simulating the icy Galilean moons, Cooper, Moore, and Hudson detected HOOH in proton irradiated H2O and H2O–O2 ices (*36*) along with the hydroperoxyl (HOO) and hydrotrioxyl (HOOO) radicals (*37, 38*). Zheng *et al* (*39*) conducted electron irradiation studies of H218O–O2ices and tentatively assigned the formation of HOOOHvia a single HOO bending mode at 1350 cm-1. However, the symmetric/anti-symmetric HOO bending modes of HOOOHat 1347 and 1359cm-1 overlap strongly with water absorption bands thus complicating unambiguous identification (*19*). Consequently, conclusive evidence for the formation and identification of HOOOHin simulated extraterrestrial environments still remains elusive.

In this study, we present persuasive evidence on the formation and identification of HOOOH,alongsideHOO, HOOH, and O3 in low-temperature H2O–O2 ice analogs exposed to proxies of GCRs. By exploiting the temperature-programmed desorption (TPD) technique, we investigate the sublimating products formed in the irradiated ices via the synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS) (*40-42*).We achieve unambiguous identification of HOOOH plus other key oxidants through photoionization efficiency (PIE) curve fitting, in conjunction with high-level quantum chemical calculations, quadrupole mass spectrometry, and isotopic labeling experiments. Our results demonstrate that HOOOH can form effectively on icy interstellar grains and surfaces of Galilean and Saturnian moons as well as comet 67P/Churyumov–Gerasimenko. These findings expand the molecular inventory of oxidants in space and enhance our understanding of their roles as key chemical sources to oxidize complex organics or even fuel extraterrestrial life in the outer Solar System. Our work may also motivate astronomical searches for HOOOH in star-forming regions and on the icy moons of Jupiter and Saturn, where HOOH has already been identified.

**Results**

**Computations**

The SVUV-PI-ReTOF-MS method represents a unique technique to identify sublimating species in the TPD phase based on the mass-to-charge ratio (*m*/*z*) of the ions and the adiabatic ionization energies (IEs) of the neutrals (*40, 41*). Since experimental ionization energies (IEs) of H2O3 isomers are unknown, we theoretically determined their adiabatic IEs at a level of sufficient accuracy (0.01 – 0.08 eV) (*43*). Our computations revealed two structural isomers, with geometries calculated at the CCSD(T)/aug-cc-pVTZ level of theory, and adiabatic IEs as well as relative energies computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory (Fig. 1, tables S1, S2 & S3). Two conformers of HOOOH were located: *trans*-HOOOH (*C*2 symmetry) and *cis*-HOOOH (*CS* symmetry); these conformers differ only by 9 kJ mol-1 and are interconvertible via a low *cis*-*trans* isomerization barrier of only 22 kJ mol–1 (*5, 44, 45*). The hyperconjugative interaction between the lone pair of electrons at the oxygen atoms and the σ\* orbital of the adjacent O–H bond optimizes the dihedral angle, thus achieving maximum stability and electron delocalization. Specifically, the dihedral angle for *trans*-HOOOH is 81.3°, whereas the corresponding angle for HOOH is 112° (*5*). This hyperconjugation effect also shortens the O–O bond length in *trans*-HOOOHto 143.5 pm, in contrast to the typical O–O bond length of 145.6 pm in HOOH. We also identified the water–oxygen molecular complex (O(H2O)O) isomer that is less stable by 485 kJ mol–1 compared to *trans*-HOOOH. This *C*2*v* symmetric isomer holds a central oxygen atom with a sp3 hybridization resulting in one unpaired electron on each of the terminal oxygen atoms. The adiabatic IEs of the aforementioned isomers were computed respectively to be 11.00 – 11.07 eV (*trans*-HOOOH), 10.90 – 10.97 eV (*cis*-HOOOH), and 11.09 – 11.16 eV (O(H2O)O) (*5, 45*).

**Mass Spectrometry**

In the TPD phase of irradiated H2O–O2 ices, ion signals were observed at *m/z* of 32, 33, 34 and 50 at photon energies of 12.20 eV (Fig. 2, Figs. 3A-B). Since the products only contain hydrogen and oxygen atoms, we can link them to the molecular formulae of O2 (32 amu), HO2 (33 amu), H2O2 (34 amu) and H2O3 (50 amu), respectively. The blank experiment, which was conducted without exposing the ices to ionizing radiation, reveals only signal at *m/z* of 32 (O2+), *i*.*e*. the ionized molecular oxygen reactant, suggesting that HO2, H2O2, and H2O3 are the result of the radiation exposure of the H2O–O2 ices.

Isotopic labeling experiments involving the H218O–O2 ices provided additional evidence on the formation of isotopically substituted products (Figs. 3C-D, figs. S1 & S2). For clarity, we distinguish the oxygen atoms in the reactants and products as 16O and 18O, respectively. Here, TPD profiles at *m/z* of 50, 52, 54, and 56 in the H218O–16O2 ice at the photon energy of 12.20 eV can be respectively assigned to ion signals of H216O3, H218O16O2, H218O216O, and H218O3, which yield a branching ratio of 1 : 1.25 : 1.03 : 1.13 after the integration of each TPD profile at distinct *m/z*. Similarly, TPD profiles at *m/z* of 33, 35, and 37 at a photon energy of 11.40 eV correspond to ions of H16O2, H16O18O, and H18O2 whose branching ratio is 1 : 0.74 : 1.07, while those at *m/z* of 34, 36, and 38 at the photon energy of 11.40 eV correspond to ions of H216O2, H216O18O, and H218O2 whose branching ratio is 1 : 1.24 : 0.90.

We also analyzed the subliming molecules via an electron-impact quadrupole mass spectrometer (EI-QMS) operating with 70 eV electrons. Here, ion signals were detected at *m*/*z* of 34 and 48 in the H216O–16O2 ices, indicating the formation of H216O2 and 16O3 (fig. S3). We cannot assign ion signals at *m*/*z* of 33 to H16O2+ due to strong mass interference of 16O2+. The absence of signals at *m*/*z* of 50 (H216O3+) can be attributed to low ion counts and limited sensitivity of EI-QMS. In the irradiated H218O–16O2 ices, we may assign ion signals at *m*/*z* of 34, 36, and 38 as H216O2+/16O18O+, H216O18O+/18O2+, and H218O2+, respectively (fig. S4). Ion signals at *m*/*z* of 33, 35, and 37 can originate from either mass interference or fragmentation of neighboring ions. It should be noted that we detected ions at *m*/*z* of 48, implying preferential formation of 16O3 over other O3 isotopologues (*39*). Similarly, we did not observe any H2O3 isotopologues via EI-QMS in the irradiated H218O–16O2 ices.

**Photoionization Efficiency (PIE) Curves**

The PIE curves report the intensity of ion counts versus the photon energy at a distinct *m*/*z*. For the irradiated H2O–O2 ices, the experimental PIE curves of photoionized products at *m*/*z* of 33 (HO2+), 34 (H2O2+) and 50 (H2O3+) were collected by scanning the photon energies from 10.80 to 12.20 eV in an interval of 0.10 eV (HO2+ and H2O3+) and from 10.40 to 11.60 eV in an interval of 0.05 eV (H2O2+) respectively, in the temperature range of 175 K and 184 K (Fig. 4A-C, fig. S5). These PIE curves at *m*/*z* of 33, 34, and 50 display the onsets of ion counts at 11.35 ± 0.05 eV, 10.60 ± 0.03 eV and 10.95 ± 0.05 eV, respectively.

The reported IE of 11.352 ± 0.007 eV for the hydroperoxyl radical HOO (*46*) matches well with the experimental onset of ion counts for *m/z* of 33 at 11.35 ± 0.05 eV, whereas the IE of hydrogen peroxide (HOOH) of 10.631 ± 0.007 eV (*46*) correlates nicely with the onset of ion counts for *m/z* of 34 at 10.60 ± 0.03 eV. We emphasize that the appearance energy of HO2+ fragment from HOOH was determined to be 15.112 ± 0.035 eV (*46*), which cannot contribute to our experimental PIE curve recorded at *m/z* of 33. Also, PIE curves collected in the present experiments at *m/z* of 33 and 34 agree exceptionally well with known literature PIE curves of hydroperoxyl (*46*) and hydrogen peroxide (*47*), respectively.

The onset of ion counts for *m/z* of 50 (H2O3+) at 10.95 ± 0.05 eV are in line with the calculated IEs of *trans*-HOOOH (11.00 – 11.07 eV) and *cis*-HOOOH(10.90 – 10.97 eV), indicating the formation of *trans*-/*cis*-HOOOH, but not O(H2O)O (11.09 – 11.16 eV). Nevertheless, no reference PIE curve of any H2O3 isomer is available. Our computations in Franck-Condon factors (FCFs) from *trans*-/*cis*-HOOOH to the resulting cations including *trans*-*trans*-HOOOH+, *cis*-*trans*-HOOOH+ and *cis*-*cis*-HOOOH+ (fig. S6) revealed that, FCFs for the ionization from *trans*-HOOOHto *cis*-*cis*-HOOOH+ are at least two orders of magnitude higher than the others. The computations correlate with the rapidly increasing PIE profile at *m/z* of 50, which indicates an efficient adiabatic ionization at 10.95 ± 0.05 eV (Fig. 4C). Such a PIE curve then drops sharply in intensity beyond 11.25 ± 0.05 eV suggesting an efficient dissociative ionization.

**Discussion**

We further conducted an extensive computational search of entrance and exit channels leading to HOOOH on the global potential energy surface (PES) involving HOOOH neutrals and cations, for elucidating of the confirmative detection of HOOOH (Fig. 5). The computations predict that *cis*-*cis*-HOOOH+ isomerizes promptly to the *cis*-*trans*-HOOOH+, which undergoes unimolecular decomposition via a barrier of 1.09 eV to H2O plus O2+ at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ + ZPVE level of theory. To account for potential multireference characters of this transition state, the dissociation barrier was further explored at the CASPT2(15,13)/def2tzvp//B3LYP/aug-cc-pVTZ + ZPVE level of theory. At this level, the barrier turns out to be 11.30 eV and matches well the experimental PIE drop at 11.25 ± 0.05 eV for *m/z* of 50. In addition, this barrier also coincides with the appearance energy of 11.25 ± 0.05 eV in the dissociative channel of H2O plus O2+ as indicated in the experimental PIE curve of O2+ (Fig. 4D, fig. S7). Notice that the ionization threshold of O2 itself was measured to be 12.071 ± 0.001 eV (*48*).

We also carried out the comprehensive analysis of potential intersystem crossings (ISCs) in the reaction pathway involving the dissociative channel H2O+ plus 3O2 (fig. S8). Starting from *cis*-*trans*-HOOOH+, the CASPT2 energy scans showed that the energy on the doublet manifold increases while the quartet state energy decreases as the HOO–OH bond stretches, resulting in the identification of the transition state (TS4) at 11.54 eV. We located two minimum-energy crossing points MSX-1 and MSX-2 connecting to this transition state between the doublet and quartet surfaces, either of which can lead to the H2O+···3O2 complex that dissociates barrierlessly to H2O+ plus 3O2. This dissociative pathway could be responsible for the ionization onset of 11.55 ± 0.05 eV in the experimental PIE curve of H2O+ (Fig. 4D, fig. S7); this value is lower than the ionization threshold of H2O located at 12.619 ± 0.006 eV (*49*). Alternative dissociative pathways of HOOOH+ leading to H2O+ plus 1O2, HO2+ plus OH, HO3+ plus H, and HO2 plus OH+ are located 12.32 eV, 12.98 eV, 14.44 eV and 16.87 eV higher than *trans*-HOOOH, respectively, and hence are closed energetically in our photoionization studies (tables S1-S4). Overall, the agreement on the PIE curves and the ionization onsets of HOOOH along with the dissociative channels of H2O plus O2+ and H2O+ plus 3O2 between experiments and computations strongly support the formation and detection of HOOOH molecules in our irradiated H2O–O2 ices.

Is it possible to detectHOOOHin deep space? Notably, HOO and HOOH – two co-products of the interaction of ionizing radiation with H2O–O2 ices in the present experiments – have been detected toward the cloud complex *ρ* Oph A (*50, 51*). The *ρ* Oph A also represents one of two interstellar clouds in which gas phase O2 was detected with abundance ratios of HOO/O2 ≈ HOOH/O2 ≈ 0.6 × 10-3 (*32, 52*). Therefore, since both H2O and O2 are present toward *ρ* Oph A and the co-products HOO and HOOH have been also detected, HOOOH should be existing after formation and sublimation from icy grains. On the other side, the abundance ratios of HOOand HOOH versus O2 in the coma of comet 67P/Churyumov–Gerasimenko as determined by ROSINA-DFMS are very close to those interstellar ones (*53*). The *in situ* measurement revealed local abundances of O2 relative to H2O ranging from 1% to 10%, suggesting that O2 is chemically relevant to H2O ice by radiolysis rather than CO2 or CO ices (*35*). Therefore, astrophysical H2O–O2 ices under the exposure of GCRs can be regarded as chemical and energetic sources in producing oxidizing agents including HOOOH, HOOH, HOO, and O3 relevant to the extraterrestrial origin of life in deep space and in the outer Solar System. It is interesting to note that the rotational frequency of *trans*-HOOOH (20838.6 MHz) (*21*) is potentially linked to the unidentified line (20838.2 MHz) observed in the W51 region (*54*), a massive molecular complex containing clusters of H2O masers.

In conclusion, the present work provides compelling evidence on the identification of key oxidizing agents hydrogen trioxide (HOOOH), hydrogen peroxide (HOOH), hydroperoxyl (HOO), and ozone (O3) prepared in water–molecular oxygen (H2O–O2) ice analogs upon the exposure to ionizing radiation in form of proxies of Galactic Cosmic Rays. Although HOOOH has been studied extensively for more than one century, for the first time we demonstrate the formation and detection of HOOOHin interstellar and Solar System analog ices exploiting state-of-the-art synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS), in association with high-level quantum chemical calculations, quadrupole mass spectrometry, and isotopic labeling experiments. The laboratory experiments conducted under conditions simulating astrophysical ones, suggest that HOOOHcan be produced in ices rich in H2O and O2 under the influence of ionizing radiation. The studies further suggest that HOOOHshould be searched for and detectable in the gas phase after sublimation from the icy grains toward *ρ* Oph A. The detection of interstellar HOOOHcombined with updated astrochemical modellingwould provide fundamental constraints and new knowledge on the chemistry of oxygen-containing inorganic molecules in deep space. It would further provide a hitherto overlooked entry point to key oxidizers in prebiotic chemistry, eventually deciphering prebiotic redox cycles that could fuel microbial life on icy moons (*55*), or even oxygen-driven catalytic cycles such as the antibody catalysis in the oxidation of water (*56*).

**Materials and Methods**

**Experimental**. The surface scattering experiments were conducted at the Shanghai-Hawaii-Hefei Advanced Research Center (SHHARC), utilizing the vacuum ultraviolet (VUV) synchrotron radiation at the Combustion and Flame Beamline (BL03U) of the National Synchrotron Radiation Laboratory (NSRL) (*40, 41*). The surface machine consists of a hydrogen-free stainless steel ultra-high vacuum (UHV) chamber that can be pumped down to a few 10-11 Torr. The ice analogs were deposited onto a mirror-polished silver substrate (12.6 × 15.1 mm2) attached to oxygen-free high thermal conductivity (OFHC) copper coldfinger at 4.8 ± 0.1 K. High-purity water (H2O, Macklin, HPLC grade) and molecular oxygen (O2, Air Liquide, 99.999%) were introduced and condensed onto the silver substrate via two sets of leak valves and glass capillary arrays (10 mm array diameter) at pressures of (1 ± 0.1) × 10-8 Torr and (2 ± 0.2) × 10-8 Torr respectively, achieving an actual depositing ratio ([H2O]/[O2]) of 6.5 ± 1.0 : 1. This ratio was determined by an electron-impact quadrupole mass spectrometer (EI-QMS) (Pfeiffer, QMG 220 M2). Prior to experiments using H218O (Aladdin, 97.0 atom % 18O), tubings and chambers were purged with H218O vapor to allow any 16O/18O isotopic exchange to occur before the preparation of H218O–O2 ices. The thickness of deposited ices was measured via laser interferometry with a He-Ne 632.8 nm laser (Thorlabs, HNL008L), which was determined to be 755 ± 50 nm based on analyzing the interference patterns and the average of refractive index of two components in amorphous ices, 1.26 ± 0.02 (Supplementary Methods, fig. S9) (*57, 58*).

After deposition, the silver substrate was rotated and translated to the irradiation position, and subjected to isothermal irradiation with 5 keV electrons (SPECS GmbH, EQ 22/35 electron source) at an incident angle of 70° relative to the surface normal. Distinct experiments were carried out on blank (0 nA, 60 minutes) and irradiated (1000 nA, 60 minutes; 1000 nA, 10 minutes; 100 nA, 60 minutes) conditions (fig. S10). Using the CASINO 2.42 simulation software (*59*), the average penetration depth of the electrons (1000 nA current) was calculated to be 226 ± 23 nm (fig. S11), significantly less than the ice thickness ensuring no interaction between the electrons and the silver substrate. The highest irradiation doses were calculated to be 99.2 eV/H2O and 176.4 eV/O2, respectively (table S5).

After irradiation, the ice sample was repositioned for temperature-programmed desorption (TPD), annealing from 5 to 320 K at a rate of 1 K min-1 controlled and monitored by a programmable temperature controller (Lakeshore, Model 336) in an accuracy of ± 0.1 K. Simultaneously, sublimating molecules were mass-analyzed via synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS). Molecular ions at distinct mass-to-charge ratio (*m*/*z*) generated upon the selected photon energy were extracted by pulsed grid voltage (−150 V, 2.5 μs) and detected by a 40 mm dual-multichannel plate detector (Jordan TOF Products, C-726), whose signals were pre-amplified (AMETEK Inc., Ortec 9306), discriminated & amplified (Advanced Research Instruments Corp., F-100TD), and recorded by a multichannel scaler (FAST ComTec, P7889) with 3.2 ns accuracy. Typical ReTOF mass spectra were generated at an experimental repetition rate of 15 kHz and a data acquisition time of 60 seconds, in accordance with the TPD rate. In the TPD range between 175 K and 184 K, the SVUV photon energy was tuned from 10.80 to 12.20 eV in an interval of 0.10 eV or from 10.40 to 11.60 eV in an interval of 0.05 eV, in order to extract photoionization of efficiency (PIE) curves of targeted molecules, which report the intensities of ions at specific *m/z* as a function of photon energy. During the SVUV photon energy scan, the obtained TPD spectra were normalized with respect to the TPD spectrum at 12.20 eV or 11.60 eV and the corresponding photon flux. Subliming molecules were also detected during TPD via the EI-QMS in the residual gas analyzer mode.

**Computational**.All density functional theory computations were carried out with Gaussian 16, Revision C.01 (*60*). For geometry optimizations and frequency computations, the B3LYP functional (*61*) was employed utilizing the Dunning correlation consistent split valence basis set aug-cc‑pVTZ (*62*). Vibrational frequency calculations were used to characterize stationary points, and to obtain zero-point vibrational energy (ZPVE) corrections. Minima structures were characterized by zero imaginary frequencies, while transition states exactly showed one imaginary frequency. Based on the minima geometries, the corresponding frozen-core coupled cluster (*63*) CCSD(T)/aug-cc‑pVTZ, and CCSD(T)/aug-cc‑pVQZ single point energies were computed and extrapolated to complete basis set limit (*64*) CCSD(T)/CBS utilizing the built-in extrapolation routine in ORCA 5.0.4 (*65*). The adiabatic ionization energies were computed by taking the electronic CCSD(T)/CBS energies and the B3LYP/aug-cc-pVTZ ZPVE corrected energy difference between the neutral and ionic species that correspond to similar conformations.

The analysis of intersystem crossings (ISC) between doublet and quartet states was carried out on a set of 49 smoothly transitioning structures along this pathway using Molpro (Version 2025.1) (*66, 67*). Calculations were performed using state-averaged complete active space self-consistent field (SA-CASSCF) (*68*) wavefunctions followed by complete active-space second-order perturbation theory (CASPT2) (*69-71*) with the def2-TZVP basis set (*72*). The active space consisted of nine 2p orbitals from oxygen atoms and two 1s orbitals from hydrogen atoms. Two lowest doublet states and one lowest quartet state were considered to avoid root-flipping issues associated with nearly degenerate doublet states. A level shift of 0.3 was applied during CASPT2 calculations to prevent intruder state problems as recommended by Roos and Andersson (*73*).

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**Supplementary Materials Table of Contents:**

Supplementary Methods

Figs. S1 to S11

Tables S1 to S5

**Fig. 1.** **CCSD(T)/aug-cc-pVTZ optimized geometries of H2O3 isomers.** Bond lengths and angles are in the units of picometers (pm) and degrees (°) respectively, while relative energies with respect to *trans*-HOOOH (ΔE) are given in the units of kJ mol-1. Corresponding adiabatic ionization energies are provided in electron volts (eV).

**Fig. 2.** **Synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS) at selected photon energies.** SVUV-PI-ReTOF-MS data recorded during the temperature-programmed desorption (TPD) phase of non-irradiated water–molecular oxygen (H2O–O2) ice at the photon energy (PE) of (**A**) 12.20 eV (blank experiment) and irradiated H2O–O2 ice at PEs of (**B**) 12.20 eV, (**C**) 11.40 eV, (**D**) 11.30 eV, (**E**) 11.00 eV, and (**F**) 10.90 eV, respectively.

**Fig.** **3.** **Temperature-programmed desorption (TPD) profiles**. TPD profiles for (**A**) *m/z* = 50 of non-irradiated H2O–O2 ice at the PE of 12.20 eV (blank experiment) and irradiated H2O–O2 ices at PEs of 12.20, 11.00, and 10.90 eV, and (**B**) *m/z* = 33 of non-irradiated H2O–O2 ice at the PE of 12.20 eV and irradiated H2O–O2 ices at PEs of 12.20, 11.40, and 11.30 eV, respectively. TPD profiles obtained at **(C)** *m/z* = 50, 52, 54, and 56 at the PE of 12.20 eV, and **(D)** *m/z* = 33, 35, and 37 at the PE of 11.40 eV of irradiated H218O–O2 ices.

**Fig. 4.** **Photoionization efficiency (PIE) curves.** PIE curves for the species linked to (**A**) *m/z* = 33, (**B**) *m/z* = 34, (**C**) *m/z* = 50, and (**D**) *m/z* = 18 and 32. The black, blue and green dots represent the experimental data, while the red lines indicate the calculated or reference PIE curves. The experimental PIE curve at *m*/*z* = 50 drops at 11.25 ± 0.05 eV, while the experimental PIE curves at *m*/*z* = 32 and 18 rise at 11.25 ± 0.05 eV and 11.55 ± 0.05 eV, respectively. The uncertainties in the fit are noted with dark-gray (1σ) and light-gray (2σ) shaded regions.

**Fig. 5.** **The potential energy surface of the HOOOH neutral, cations and dissociative channels.** The *tt*-/*ct*-/*cc*-cation stands for the radical cations *trans*-*trans*-/*cis*-*trans*-/*cis-cis*-HOOOH, respectively. The dashed arrow indicates the adiabatic ionization process from *trans*-HOOOH to *cc*-cation, while the dashed lines connecting two minimum-energy crossing points (MSX-1 and MSX-2) represent the pathways involving the intersystem crossing (ISC). Atoms are color coded in white (hydrogen) and red (oxygen).