Electronic Supplementary Information

Capture of SO_3 Isomers in the Oxidation of Sulfur Monoxide with Molecular Oxygen

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Experimental details

Sample preparation. Ethylene episulfoxide were prepared according to the published protocols[1]. The purity was checked by using ^{1}H and ^{13}C NMR spectroscopy (Bruker Avance III HD 400 spectrometer). Ar (≥ 99.999%, Messer), N_2 (≥ 99.999%, Messer), Ne (≥ 99.999%, Messer), and O_2 (≥ 99.999%, Messer) gases were used without further purification. For the labeling experiments, $^{18}O_2$ (97 atom %, Aldrich) was used.

Matrix-isolation IR spectroscopy. Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70V) in a reflectance mode by using a transfer optic. A KBr beam splitter and liquid-nitrogen cooled broadband MCT detector were used in the mid-IR region (4000–400 cm^{-1}). Typically, 200 scans at a resolution of 0.5 cm^{-1} were co-added for each spectrum. Gaseous ethylene episulfoxide was mixed by passing a flow of Ar, N_2, or Ne gas through a U-trap containing ca. 20 mg of ethylene episulfoxide at –27 °C. Then the mixture (estimated ratio of 1:1000) was passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), which can be heated over a length of ca. 25 mm by a tantalum wire (o.d. 0.4 mm, resistance 0.4 Ω), deposited (2 mmol h^{-1}) in a high vacuum (~10^{-6} pa) onto the Rh-plated Cu block matrix support (2.8 K for Ne or 15.0 K for Ar and N_2) using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled and monitored using a LakeShore 335 digital cryogenic temperature controller a Silicon Diode (DT-670). The voltage and current used in the pyrolysis experiments are 5.0 V and 3.45 A, respectively. Photolysis experiments were performed using an Nd^{3+}: YAG laser (266 nm, MPL-F-266, 10 mW), LED light (830 nm, FU830AD100-BXS22130, 100mW), and UV flashlight (365 nm, Boyu T648, 20 W).

Matrix-isolation UV/Vis spectroscopy.

The cryostat used was an APD Cryogenics HC-2 closed-cycle refrigerator system with CsI windows for IR and BaF_2 windows for UV/Vis measurements. IR spectra were recorded with a Bruker IFS 55 FT-IR spectrometer (spectral range of 4000–350 cm^{-1} with a resolution of 0.7 cm^{-1}, 50 scans per measurement), UV/Vis spectra with a Jasco V670 spectrometer (spectral range of 190–850 nm with a scanning speed of 1 nm s^{-1}). For the combination of high-vacuum flash pyrolysis with matrix isolation, a small, home-built, water-cooled oven directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax heating wire. The temperature was controlled through a Ni/CrNi thermocouple. A gas mixture of ethylene episulfoxide and Ar (1:1000) was prepared in a 2 L storage bulb and evaporated at room temperature into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, all pyrolysis products were condensed (typically 30 to 60 mbar in one hour) on the surface of the 12.0 K matrix window. For irradiation, LED light (850 nm), UV light (365 nm), and low-pressure mercury lamp (254 nm) were used.

Computational details

Molecular structures and IR frequencies of stationary points were computed using UB3LYP/6-311+G(3df),[2] UCCSD(T)/cc-pVTZ[3] and UCCSD(T)-F12/VTZ-F12.[4] Local minima were confirmed by vibrational frequency analysis. The time-dependent TD-B3LYP method was performed for the prediction of vertical excitations.[5] These computations were performed using the Gaussian 09 software package.[6] The CCSD(T) and CCSD(T)-F12 computations were performed using the CFOUR[7] and MOLPRO[8] packages, respectively.

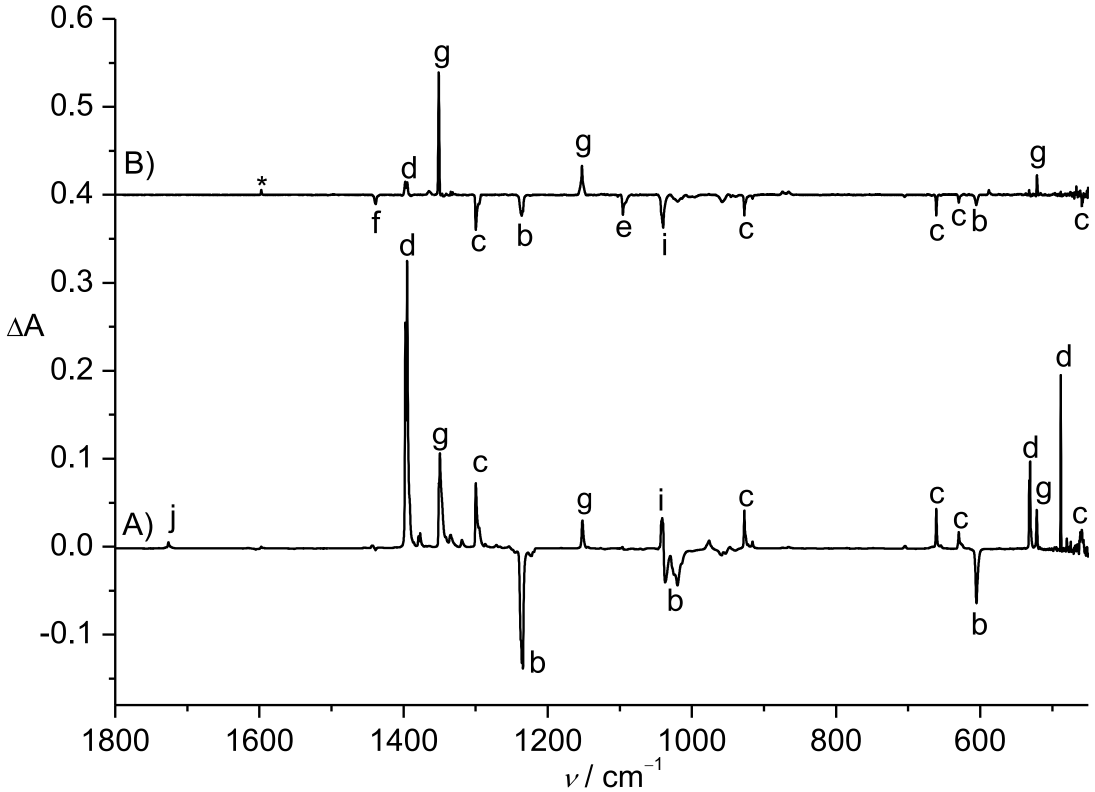

Figure S1. A) IR difference spectrum showing the change of the FVP (1000 K) products of a mixture of **e**/O_2/N_2 (1:50:1000) upon 830 nm LED irradiation (20 min) at 15.0 K. B) IR difference spectrum showing the change of the matrix upon 266 nm laser irradiation (10 min). IR bands of *cis*-OSOO (**b**), dioxathiirane (**c**), SO_3 (**d**), CH_2CH_2 (**f**), SO_2 (**g**), O_3 (**i**), $CH_3C(O)H$ (**j**), and H_2O (*) are labeled.

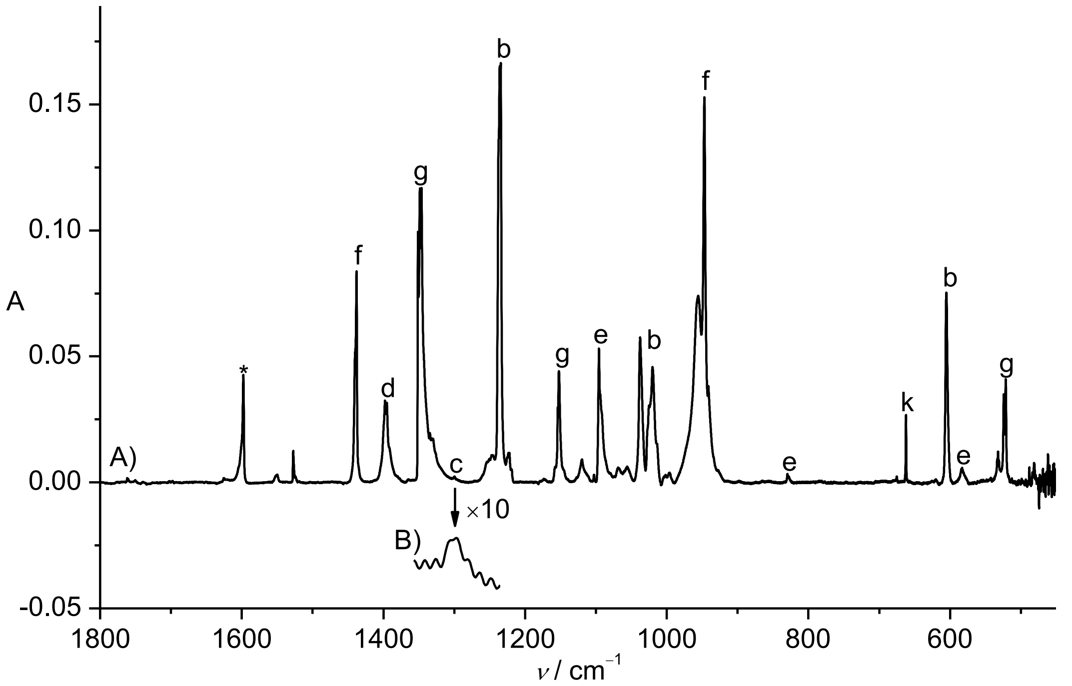

Figure S2. A) IR spectrum of matrix isolated HVFP (1000 K) products of a mixture of e/O_2/N_2 (1:50:1000) at 15.0 K. B) Part of spectrum A expanded 10 times. IR bands of *cis*-OSOO (**b**), dioxathiirane (**c**), SO_3 (**d**), CH_2CH_2 (**f**), SO_2 (**g**), O_3 (**i**), CO_2 (**k**), and H_2O (*) are labeled.

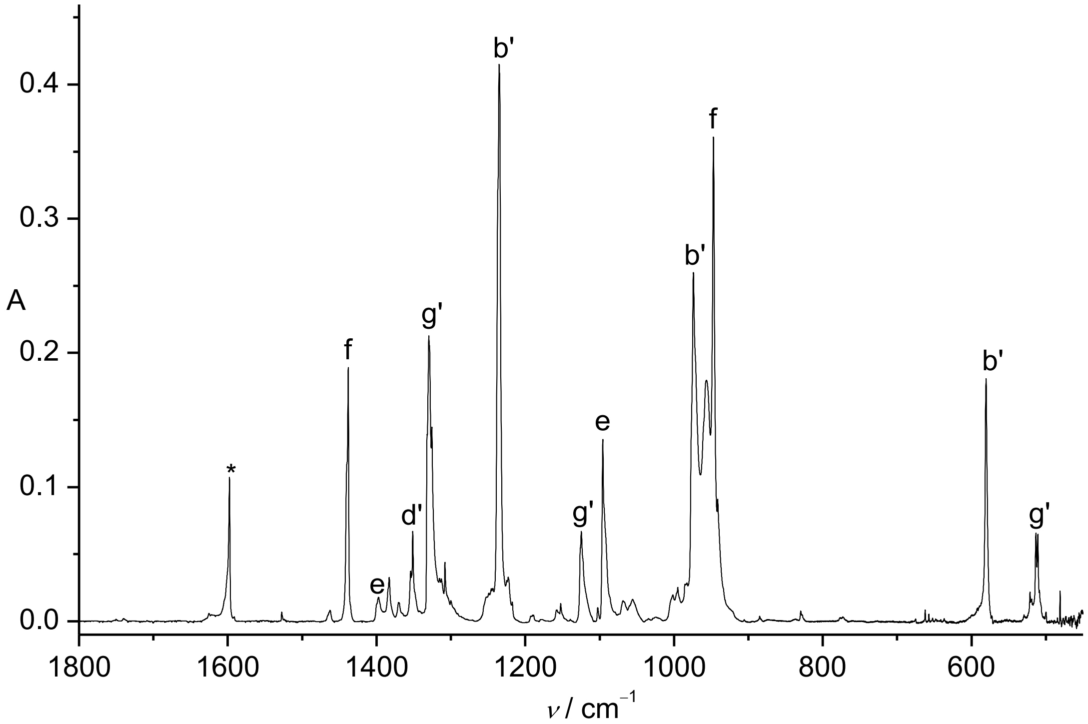

Figure S3. A) IR spectrum of matrix isolated HVFP (1000 K) products of a mixture of **e**/$^{18}O_2/N_2$ (1:50:1000) at 15.0 K. IR bands of *cis*-$OS^{18}O^{18}O$ (**b'**), doubly ^{18}O labeled SO_3 (**d'**), CH_2CH_2 (**f**), $OS^{18}O$ (**g'**), and H_2O (*) are labeled.

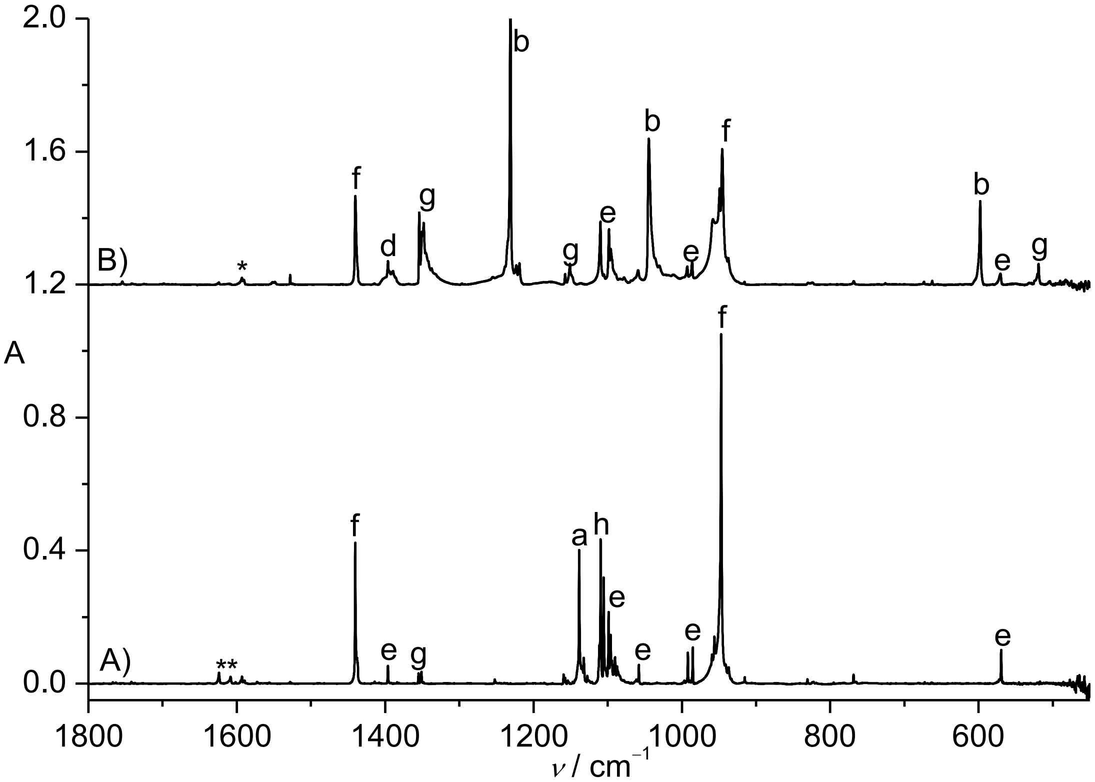

Figure S4. A) IR spectrum of matrix isolated HVFP (1000 K) products of ethylene episulfoxide (**e**) in Ar (1:1000) at 15.0 K. B) IR spectrum of matrix isolated HVFP (1000 K) products of a mixture of **e**/O_2/Ar (1:50:1000) at 15.0 K. IR bands of SO (**a**), *cis*-OSOO (**b**), SO_3 (**d**), CH_2CH_2 (**f**), SO_2 (**g**), and H_2O (*) are labeled.

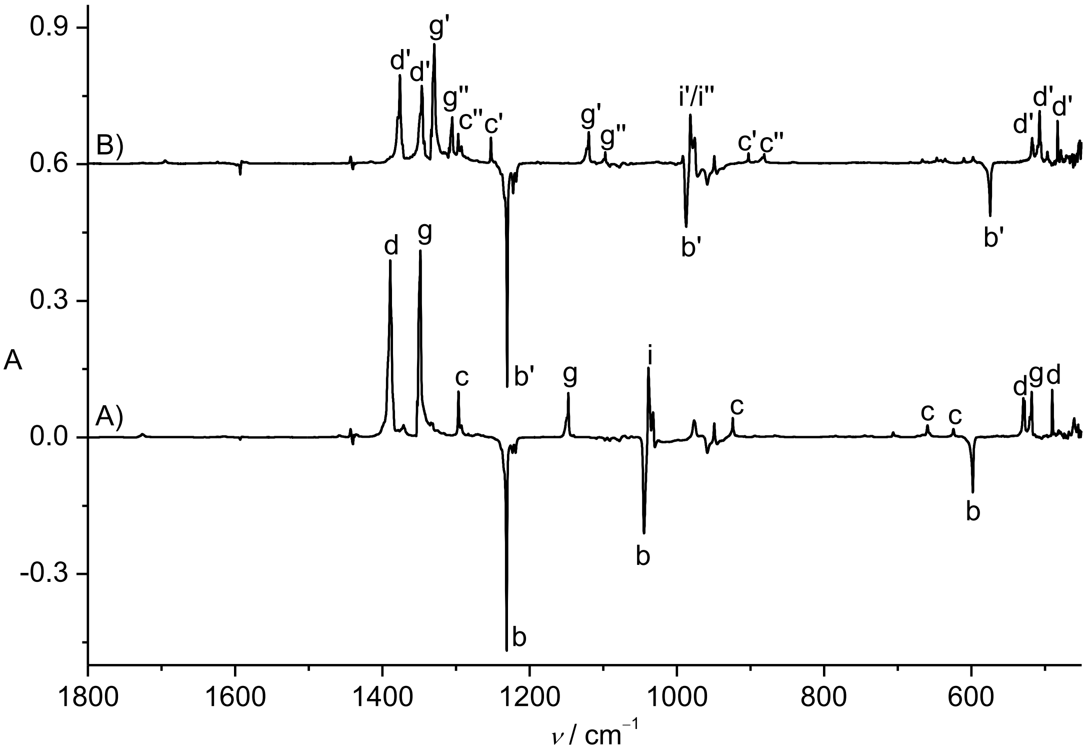

Figure S5. A) IR difference spectrum showing the change of the Ar-matrix isolated HVFP (1000 K) products of a mixture of **e**/O_2/Ar (1:50:1000) upon 830 nm LED irradiation (20 min). IR difference spectrum showing the change of the Ar-matrix isolated HVFP (1000 K) products of a mixture of **e**/$^{18}O_2$/Ar (1:50:1000) upon 830 nm LED irradiation (20 min). IR bands of *cis*-OSOO (**b**), *cis*-$OS^{18}O^{18}O$ (**b'**), cyclic OS(=O)O (**c**), cyclic $OS(=^{18}O)^{18}O$ (**c'**), cyclic $^{18}OS(=O)^{18}O$ (**c''**), SO_3 (**d**), $OS(^{18}O)_2$ (**d**),CH_2CH_2 (**f**), SO_2 (**g**), $OS^{18}O$ (**g'**), $S^{18}O_2$ (**g''**), O_3 (**i**), $OO^{18}O$ (**i'**), $O^{18}O^{18}O$ (**i''**), are labeled.

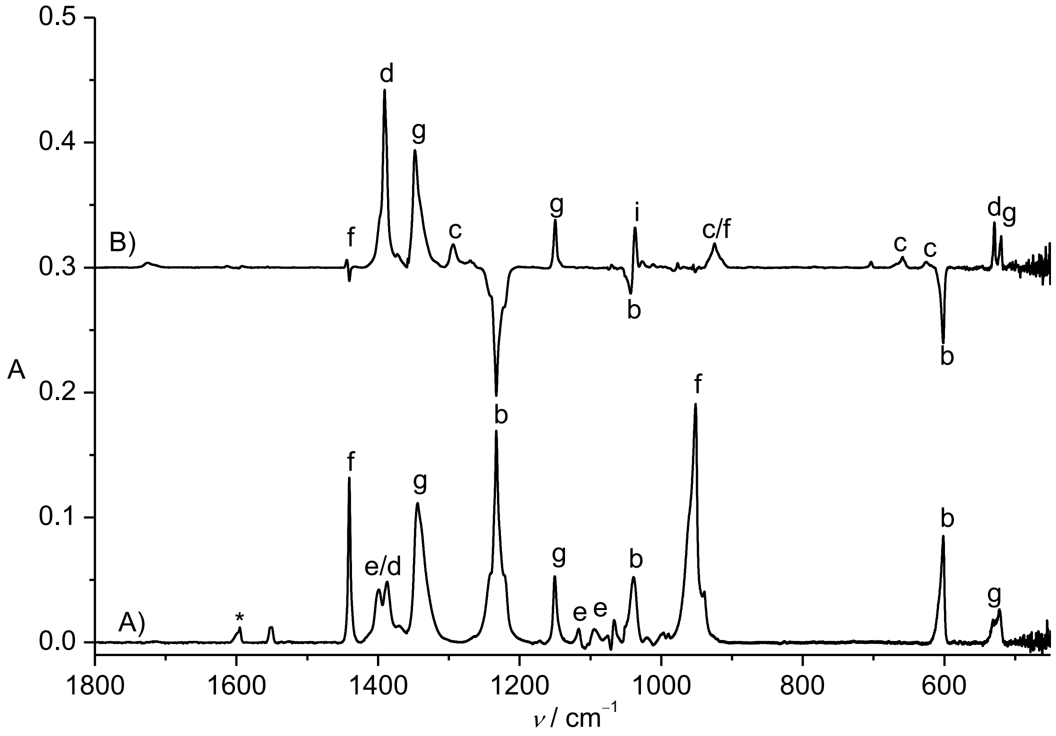

Figure S6. A) IR spectrum of matrix isolated HVFP (1000 K) products of a mixture of **e**/O_2/Ne (1:50:1000) at 2.8 K. B) IR difference spectrum showing the change of the matrix upon 830 nm LED irradiation (20 min). IR bands of *cis*-OSOO (**b**), SO_3 (**d**), CH_2CH_2 (**f**), SO_2 (**g**), O_3 (**i**), and H_2O (*) are labeled.

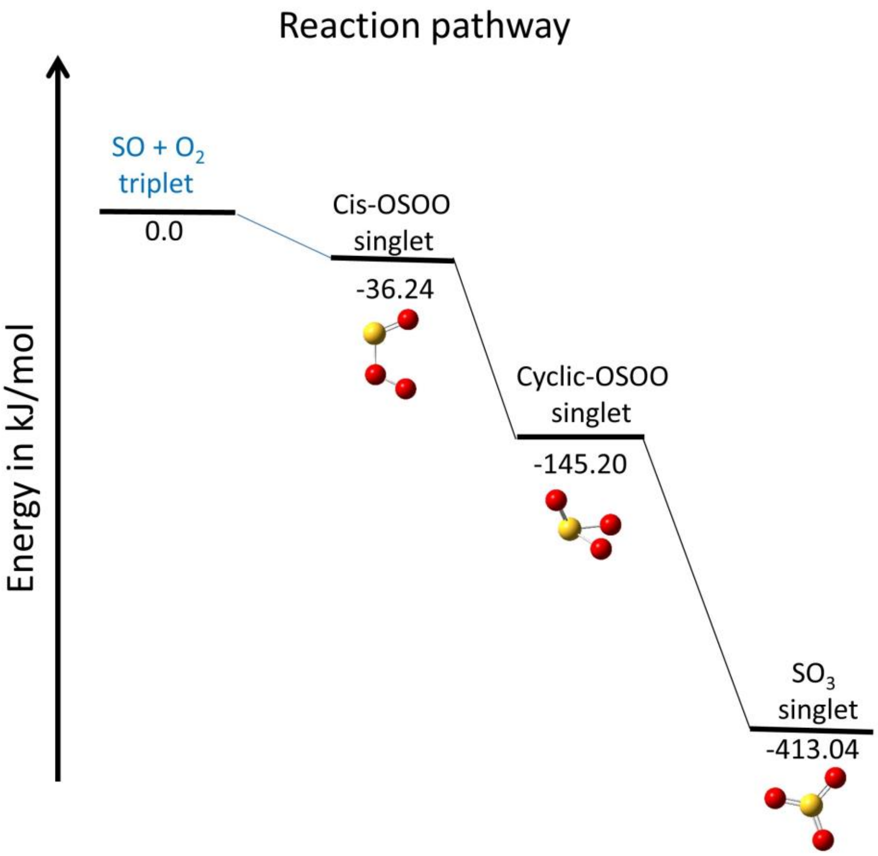

Figure S7. Calculated relative energies for the SO_3 isomers at the CCSD(T)-F12/VTZ-F12 level.

Table S1. TD-DFT B3LYP/6-311+G(3df) calculated vertical excitation energy of SO_3 isomers..

species	energy (nm)	oscillator strength (*f*)
cis-OSOO	699	0.0001
	349	0.0962
	270	0.0016
	242	0.0014
	229	0.0246
	214	0.0002
	197	0.0732
	191	0.0018
	176	0.0391
dioxathiirane	290	0.0015
	246	0.0026
	232	0.0035
	203	0.0029
	198	0.0059
	176	0.0024
	172	0.0340
	164	0.0018

Table S2. Calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}, in parentheses.) of dioxathiirane at the CCSD(T)/cc-pVTZ level.

cyclic ^{16}OS(=^{16}O)^{16}O		cyclic ^{18}OS(=^{16}O)^{18}O		cyclic^{18}OS(=^{18}O)^{16}O	
harmonic	anharmonic	harmonic	anharmonic	harmonic	anharmonic
1308.5 (155)	1291.9 (138)	1261.4 (150)	1256.7 (128)	1308.0 (153)	1293.2 (126)
947.1 (46)	925.3 (38)	925.1 (45)	911.8 (38)	905.0 (49)	898.1 (43)
672.8 (44)	658.1 (40)	659.8 (41)	646.5 (18)	647.9 (39)	641.6 (38)
630.9 (19)	618.4 (18)	616.2 (19)	608.5 (18)	603.4 (18)	598.8 (18)
449.7 (17)	444.9 (17)	433.7 (16)	430.2 (15)	441.1 (16)	437.6 (16)
342.0 (5)	337.6 (5)	330.4 (5)	326.2 (5)	331.0 (5)	327.1 (15)

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Computed atomic coordinates (in Angstroms) and energies (in Hartrees).

cis-OSOO
B3LYP/6-311+G(3df)

S	0.68063000	-0.45832600	-0.00004700
O	1.19548500	0.88892600	0.00005000
O	-0.91031600	-0.53408900	0.00010200
O	-1.64642900	0.56181400	-0.00005900

Zero-point correction= 0.009468
Thermal correction to Energy= 0.013509
Thermal correction to Enthalpy= 0.014453
Thermal correction to Gibbs Free Energy= -0.017534
Sum of electronic and zero-point Energies= -623.794533
Sum of electronic and thermal Energies= -623.790493
Sum of electronic and thermal Enthalpies= -623.789549
Sum of electronic and thermal Free Energies= -623.821536

CCSD(T)/cc-pVTZ Energy=-622.939288153486

O	-2.11179494	1.76848503	0.00000000
S	-1.34925082	-0.88433064	0.00000000
O	1.78646287	-1.09401999	0.00000000
O	3.02233568	1.09321440	0.00000000

CCSD(T)-F12/VTZ-F12 ENERGY=-623.07600224

S	-0.0007047893	0.8345707707	0.0000000000
O	-0.9835286247	-0.4616812480	0.0000000000
O	-0.3993940401	-1.6520116250	0.0000000000
O	1.3836274539	0.4308461024	0.0000000000

dioxathiirane
B3LYP/6-311+G(3df)

O	-1.02061100	-0.75567800	-0.19502600
S	0.30545200	-0.00001600	0.42543100
O	1.42806300	-0.00067900	-0.46059900
O	-1.01835600	0.75639000	-0.19523700

Zero-point correction= 0.010013
Thermal correction to Energy= 0.013799
Thermal correction to Enthalpy= 0.014743
Thermal correction to Gibbs Free Energy= -0.016442
Sum of electronic and zero-point Energies= -623.826770
Sum of electronic and thermal Energies= -623.822984
Sum of electronic and thermal Enthalpies= -623.822040
Sum of electronic and thermal Free Energies= -623.853225

CCSD(T)/cc-pVTZ Energy= -622.973772480117

O	0.37559094	1.92442772	-1.45354951
S	-0.81310980	-0.56894223	0.00000000
O	0.37559095	1.92442772	1.45354951

O	0.87413494	-2.71160266	-0.00000000

CCSD(T)-F12/VTZ-F12 ENERGY=-623.11750236

S	-0.2906853711	0.0004637471	0.4206392981
O	1.0092427062	0.7674848899	-0.1955427453
O	1.0089639762	-0.7683876736	-0.1938434845
O	-1.4124003114	-0.0003099634	-0.4611810683