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Spectroscopic Characterization of HSO_2^{\bullet} and $HOSO^{\bullet}$ Intermediates Involved in SO_2 Geoengineering

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both radicals are crucial to understanding the chemical impact of SO₂ chemistry in the stratosphere. On the basis of the efficient generation of HOSO[•] by flash pyrolysis of gaseous sulfinic acid, CHF₂S(O)OH, a strong absorption is observed at 270 nm along with a shoulder up to 350 nm for HOSO[•] isolated in low-temperature noble gas matrixes (Ar and Ne). These mainly arise from the excitations from the ground state (X^2A) to the C²A/D²A and A²A/B²A states, respectively. Upon a 266 nm laser irradiation, the broad absorption band in the range 320–500 nm for HSO₂[•] appears, and it corresponds to the combination of three excitations from the X^2A state to the first (A²A), second (B²A), and



third (C^2A) excited states. Assignment of the UV-vis spectra is consistent with the photochemistry of HOSO[•] and HSO₂[•] as observed by matrix-isolation IR spectroscopy and also by the agreement with high-level *ab initio* calculations.

INTRODUCTION

The impacts of climate change are now being recognized as widespread and severe-and in many cases irreversible-as brought on by prolonged emissions of CO2 and other longlived greenhouse gases.¹⁻⁴ Limiting further warming to less than 2 °C above preindustrial levels requires dramatic decreases in the emissions of all greenhouse gases. An important step forward is to rapidly decrease greenhouse gas emission. While this action seems plausible, progress has been slow. As such, growing and urgent concerns have arisen that, until emissions of such long-lived greenhouse gases are driven to net zero and emissions of short-lived greenhouse are stabilized, risks from a changing climate will increase in the future. Crutzen⁵ and Wigley⁶ both suggest that geoengineering solutions should be considered as a possible mitigating strategy to counteract the consequences of the increasing emissions of greenhouse gases into the atmosphere. The concept of geoengineering to cool the planet is not a new idea,^{7,8} but since the proposal as a strategy to reduce the impact of climate change, there have been increasing studies in the literature.^{9,10} The central idea is to add a layer of aerosol particles to the upper atmosphere in order to reduce climate change caused by greenhouse gases. The layer of aerosol particles would reflect sunlight, thereby decreasing the amount of solar radiation reaching the Earth.

The inspiration for how to create a layer of aerosol particles to reflect sunlight comes from emulating volcanic eruptions.^{11,12} Volcanic eruptions inject massive amounts of sulfur dioxide (SO_2) gas into the atmosphere. The SO_2 is oxidized in the atmosphere to sulfuric acid, which has a low enough vapor pressure to form aerosol particles. The aerosol particles can then scatter some of the incoming sunlight back to space, thus cooling the surface¹³ and hence reducing the effects of climate change. Thus, implementing a solar geoengineering strategy with SO₂ involves spraying SO₂ into the stratosphere, thereby mimicking SO₂ gas from volcanoes to generate a layer of sulfate aerosol particles that can increase the reflection of incoming radiation from the sun and potentially reduce global temperatures.^{14–16} A recent Intergovernmental Panel on Climate Change (IPCC)^{17,18} and National Academies report¹⁹ suggest that geoengineering, by injecting SO₂ into the atmosphere, might become necessary.

However, such an action would come with risks, namely introducing an array of unknown or negative consequences.

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The Journal of Physical Chemistry A

One such unknown is the chemical implications on the sulfur cycle, demanding urgent studies to estimate the viability of this possible action against climate change. Moreover, the SO_2 geoengineering approach could also introduce other potential new risks related to critical atmospheric processes, e.g., loss of stratospheric ozone. In order to assess the chemical impact of SO_2 geoengineering, the impact of SO_2 chemistry in the stratosphere must be understood. The assumed underlying chemistry for which this geoengineering proposal is based, injection of SO_2 into the stratosphere to induce the subsequent formation of H_2SO_4 , is the traditional acid rain scheme (R1–R3) shown below:

$$SO_2 + {}^{\bullet}OH \rightarrow HOSO_2^{\bullet}$$
 (R1)

$$HOSO_2^{\bullet} + O_2 \to HO_2^{\bullet} + SO_3 \tag{R2}$$

$$SO_3 + nH_2O \rightarrow H_2SO_4 + (n-1)H_2O$$
 (R3)

To date many modeling studies of SO₂ geoengineering have not considered the chemistry of SO₂ after injection into the stratosphere, although it has shown that upon excitation of stratospheric SO₂ at 240–330 nm, followed by populating its lowest excited triplet state via intersystem crossing (R4),^{24,25} the excited ³SO₂ species can react with water in the gas phase (R5) yielding HOSO[•], as shown below:

$$SO_2 + hv(240 - 330 \text{ nm}) \rightarrow {}^3SO_2$$
 (R4)

$${}^{3}\text{SO}_{2} + \text{H}_{2}\text{O} \rightarrow {}^{\bullet}\text{OH} + \text{HOSO}^{\bullet}$$
 (R5)

The HOSO[•] radical is an important intermediate in the Earth's atmosphere since it is involved in the atmospheric oxidation of SO₂^{24,25} and CS₂.²⁶ Its molecular structure in the gas phase²⁷ and photochemistry in the condensed phase within solid noble gas (Ar, Kr, and Xe) matrixes have been studied by Fourier transform infrared spectroscopy (FTIR),^{28,29} and only the cis conformer of HOSO[•] has been identified, whereas the trans conformer was theoretically predicted to be a transition state. In matrix-isolation studies, the photodissociation threshold of HOSO[•] to H[•] and SO₂ is found to be 400 nm. Shorter wavelength irradiation at 266 nm causes additional isomerization to HSO_2^{\bullet} with concomitant O-S bond cleavage by yielding a highly unstable H-bonded complex between *OH and SO in the matrix cages. On the other hand, the photoexcitation of matrix-isolated HSO2 at wavelengths below 580 nm promotes isomerization to HOSO*, and the latter is more stable by about 20 kcal mol^{-1.27} However, no electronic spectroscopic data for HOSO[•] and HSO₂[•] currently exist that can be utilized to aid in understanding the photomechanism and role of these intermediates in the Earth's atmosphere and in SO₂ geoengineering schemes.

In this work, multireference configuration interaction (MRCI) methods are used to map the excited state potential energy surface of the lowest-lying electronic state of HSO_2^{\bullet} along the stretching coordinates to identify where the ultraviolet–visible (UV–vis) absorption bands are for HSO_2^{\bullet} with respect to $HOSO^{\bullet}$. Although recent computational studies of the photochemistry have theoretically characterized the absorption characteristics of $HOSO^{\bullet}$ in the UV–vis region, ³⁰ no experimental UV–vis spectrum has been reported. Moreover, there are no theoretical or experimental studies of the UV–vis spectra of HSO_2^{\bullet} . Herein, the first experimental UV–vis spectra of HSO_2^{\bullet} and $HOSO^{\bullet}$ are reported.

EXPERIMENTAL SECTION

Sample Preparation. Difluoromethylsulfinic acid (CHF₂S(O)OH) was prepared by reacting dry hydrogen chloride (HCl) with sodium difluoromethylsulfinate (CHF₂S-(O)ONa) according to the published protocol.²⁹ Ar (\geq 99.999%, Messer) and Ne (\geq 99.999%, Messer) gases were used without purification.

Matrix-Isolation Spectroscopy. Matrix IR spectra were recorded on an FTIR spectrometer (Bruker 70 V) in reflectance mode by using a transfer optic. A KBr beam splitter and liquid nitrogen cooled MCT detector were used in the mid-IR region $(5000-400 \text{ cm}^{-1})$. Typically, 200 scans at a resolution of 0.5 cm⁻¹ were coadded for each spectrum. Matrix UV-vis spectra were recorded on a UV-vis spectrometer (Lambda 850+, 800-190 nm) in transmission mode, and a scanning speed of 2 nm s⁻¹ at resolution of 1 nm was used. For the preparation of the matrix, the gaseous sample was mixed by passing a flow of argon or neon gas through a cold U-trap (ca. -10 °C) containing liquid sulfinic acid (ca. 0.2 g). The premix (acid/noble gas \approx 1:1500 estimated) was then directed 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) and immediately deposited (2 mmol h^{-1}) at a high vacuum (~10⁻⁶ Pa) onto a gold-plated copper block matrix support (10 K for Ar matrix, 3 K for Ne matrix) for IR spectroscopy and onto a CaF₂ window (10 K) for UV-vis spectroscopy using closed-cycle helium cryostats (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the high-vacuum chambers (10^{-5} Pa) . Temperatures at the second stage of the cold heads were controlled and monitored by using East Changing TC 290 (IR spectroscopy) and LakeShore 335 (UV-vis spectroscopy) digital cryogenic temperature controllers and silicon diodes (DT-670). The voltage and current used in the flash pyrolysis experiments are 5.8 V and 4 A, respectively. Photolysis experiments were performed with a Nd3+:YAG laser (266 nm, MPL-F-266, 10 mW) and visible-light emitting diodes (LED, 100 mW).

Excited States Calculations. The lowest excited states of HSO_2^{\bullet} were calculated by using complete active space selfconsistent field $(CASSCF)^{31,32}$ followed by internally contracted multireference configuration interaction including the Davidson correction $(MRCI+Q)^{.33-35}$ In these calculations the atoms were described by aug-cc-pV(T+d)Z and the active space constructed by 19 electrons in 13 orbitals. The calculations were made with MOLPRO (ver. 2019.1) software.³⁶

Simulated Electronic Absorption Spectrum. To simulate the electronic absorption spectrum, the ground state geometry was optimized, and normal-mode analysis was performed at the MRCI+Q level of theory with the aug-ccpV(T+d)Z basis set. Following this, a set of initial geometries was obtained by using a Wigner distribution based on the ground state harmonic frequencies calculated at the MRCI+Q/ aug-c-pV(T+d)Z level of theory. At each Wigner geometry, vertical excitation energies and transition dipole moments were calculated. In these calculations, the CASSCF reference wave function was state-averaged over the lowest seven doublet states. To calculate the photoabsorption cross section, 200 Wigner geometries were generated and calculated at the MRCI +Q/aug-cc-pV(T+d)Z level in the C_1 symmetry group. The Wigner distribution was produced using NewtonX, while the ab initio calculations and absorption spectrum simulation were Table 1. Vertical Excitation Energies (nm), Oscillator Strengths (f), and Dominant Electron Configurations of the Low-Lying Electronic States of HSO₂^{•*a*}

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state	dominant electron configuration	EOM-CCSD ^b	MRCI+Q ^c	f
х	$0.95(Core)(12a^2)(13a^2)(14a^2)(15a^2)(16a^2)(17a^1)$	_	_	_
А	$0.91(\text{Core})(12a^2)(13a^2)(14a^2)(15a^2)(16a^1)(17a^2)$	384	369	0.0077
В	$0.92(\text{Core})(12a^2)(13a^2)(14a^1)(15a^2)(16a^2)(17a^2)$	344	329	0.0313
С	$0.94(Core)(12a^2)(13a^2)(14a^2)(15a^1)(16a^2)(17a^2)$	332	329	0.0034
D	$0.70(\text{Core})(12a^2)(13a^2)(14a^2)(15a^2)(16a^2)(17a^0)(18a^1) + 0.55(\text{Core})(12a)(13a^2)(14a^2)(15a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)($	218	207	0.0325
Е	$0.90(\text{Core})(12a^2)(13a^1)(14a^2)(15a^2)(16a^2)(17a^2)$	199	181	0.0106
F	$0.55(Core)(12a^2)(13a^2)(14a^2)(15a^2)(16a^2)(17a^0)(18a^1) + 0.70(Core)(12a)(13a^2)(14a^2)(15a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)(17a^2)(16a^2)(17a^2)$	179	176	0.0110

^a"Core" is the lowest 11 doubly occupied molecular orbitals. Numbers outside parentheses represent the weight of the configuration. ^bAt the 6-311++G^{**} basis set. ^cAt the aug-cc-pV(T+d)Z basis set.



Figure 1. (a) Potential energy surface of HSO_2^{\bullet} along the $H-SO_2^{\bullet}$ bond calculated at the MRCI+Q/aug-cc-pV(Q+d)Z level. (b) Potential energy surface of HSO_2^{\bullet} along the $HS(O)-O^{\bullet}$ bond calculated at the MRCI+Q/aug-cc-pV(Q+d)Z level.

performed using MOLPRO and the SArCASM package, respectively.³⁷

RESULTS AND DISCUSSION

Table 1 lists the CASSCF/aug-cc-pV(T+d)Z dominant electron configurations and the vertical excitation energies of HSO₂[•] calculated at the MRCI+Q and EOM-CCSD levels of theory. Figure 1 represents the one-dimensional potential energy surface of HSO2 • calculated as a function of the S-O distance (Figure 1a) and the H-S distance (Figure 1b). In these calculations, the remaining coordinates are kept fixed at their equilibrium values. In Figure 1a, the ground state correlates with the first dissociation limit $HSO^{\bullet}(X^2A'')$ + $O(^{3}P)$. The A, B, and C excited states present deep potential wells, and their minima are located below the HSO $^{\bullet}(X^2A'')$ + $O(^{3}P)$ dissociation limit, which makes them stable relative to this limit. The D state has an irregular shape, resulting from avoided crossing with other states not present in Figure 1. The D state arises from a promotion of two electrons from the 17a singly occupied molecular orbital (SOMO) to the 18a lowest unoccupied molecular orbital (LUMO) and from contributions from the 12a-17a MOs. The production of HSO[•] and O after UV-vis absorption is not plausible, and if it happens, it will be at a very low rate. Indeed, the production of HSO[•] and O must satisfy two criteria: (i) the population of the upper vibrational level of the B and C states and (ii) important spinorbit coupling at the crossing point with the repulsive quartet state. In Figure 1b, the ground state correlates to the first

dissociation limit of $H^{\bullet} + SO_2$ with low dissociation energy compared to $HSO^{\bullet} + O$. The bond dissociation energy is predicted to be 0.733 eV at the CCSD(T)/aug-cc-pV(Q+d)Z level. The population of the upper vibrational level of the ground state may produce H^{\bullet} and SO_2 in their ground electronic states. This is probably feasible at relatively high temperature or through IR excitation.

Unlike Figure 1a, along the H–SO₂ stretching coordinate the lowest excited states are unstable relative to the first dissociation limit H[•] + SO₂. Inspection of the vertical excitation energies show that the B and D states absorb strongly compared to the A and C states. In near-UV–vis, the B state may be populated after the absorption around 344 nm and the molecule may fluoresce. The D \leftarrow X transition is predicted to be 218 nm with an oscillator strength of 0.0325 at the EOM-CCSD level. The D state is crossed by a repulsive quartet state, and the production of hydrogen atom and excited SO₂ may occur via spin–orbit coupling at that crossing.

The simulated UV absorption spectrum of HSO_2^{\bullet} from the *ab initio* excited state potential energy surface, shown in Figure 2, consists of two broad bands at 260–450 and 160–250 nm. The analysis of the computed bands reveals that the major absorption around 340 nm arises from the combination of three excitations from the ground state (X²A) to the first (A²A), second (B²A), and third (C²A) doublet excited states, with almost equal contributions from the B²A and C²A states. Meanwhile, the peak in the 160–250 nm range consists of two overlapping absorption features. The first, ranging from 200 to 250 nm is attributed to the D²A $\leftarrow X^2A$ excitation, while the

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Figure 2. Simulated UV–vis absorption spectrum and absolute cross sections (σ/cm^2) of HSO₂[•] and contributions to the spectrum of the stratospherically relevant doublet excited states.

second at 160–200 nm contains two almost identical shapes corresponding to the E²A $\leftarrow X^2$ A and F²A $\leftarrow X^2$ A excitations. The two broad bands in the spectrum have a maximum calculated absorption cross section of ~3.25 × 10⁻¹⁸ cm² molecule⁻¹, approximately half the strength of the isomeric species HOSO[•] (~5.5 × 10⁻¹⁸ cm² molecule⁻¹)³⁸ and an order of magnitude greater than that of SO₂ (~10⁻¹⁹ cm² molecule⁻¹) at 248 nm.³⁹

Experimentally, HSO_2^{\bullet} can be generated in solid noble gas matrixes (Ne and Ar) through photoinduced (266 nm) isomerization of HOSO^{\bullet} , and the latter is produced in the gas phase by high-vacuum flash pyrolysis (HVFP) of the molecular precursor $\text{CHF}_2\text{S}(\text{O})\text{OH}$ at ca. 700 °C (Figure 3A).²⁹ The efficient conversion of HOSO^{\bullet} to HSO_2^{\bullet} (Figure 3B) via either straightforward intramolecular 1,2-H shift or dissociation-recombination ($\text{HOSO}^{\bullet} \rightarrow \text{H}^{\bullet} + \text{SO}_2 \rightarrow$ HSO_2^{\bullet})⁴⁰ in the matrix cages enables identification of several very weak IR absorptions (Table 2) that were not observed in the previous matrix-isolation IR spectroscopic study.²⁸ There-

Table 2. Calculated and Observed IR Frequencies ((cm^{-1})) of
HOSO [•] and HSO ₂ [•]		

	HOSO•			HSO₂ [●]	
${\nu_{ m calcd}}^a$ CcCR	$ u_{\rm obsd}^{\ b}$ Ne matrix	mode ^c	$ \frac{\nu_{\mathrm{calcd}}^{a}}{\mathrm{CcCR}} $	$\nu_{ m obsd}^{\ \ b}$ Ne matrix	mode ^c
2331.6	2329.6	$2\nu_2$			
2195.0	2220.1	$\nu_2 + \nu_3$			
2044.3	2084.2	$2\nu_3$	2583.5	2562.0	$2\nu_2$
1952.8	1945.6	$\nu_2+\nu_4$	2367.1	2347.5	$\nu_2 + \nu_3$
1550.7	1535.5	$2\nu_4$	2161.4	2152.4	$2\nu_3$
1171.8	1166.5	$\nu_4 + \nu_5$	2091.7	2076.1	$\nu_2 + \nu_5$
790.2	781.2	$2\nu_5$	1760.5	1741.3	$\nu_2 + \nu_6$
3567.3	3566.6	ν_1	2167.9	2125.0	$ u_1 $
1172.2	1173.8	ν_2	1298.3	1288.1	ν_2
1034.1	1051.2	$ u_3 $	1084.8	1075.0	ν_3
781.0	772.4	$ u_4$	957.5	952.4	$ u_4$
395.6	390.6 ^d	ν_5	799.4	794.3	ν_5
31.0	n.o.	ν_6	466.7	464.6	ν_6

^{*a*}CcCR calculated anharmonic frequencies. ^{*b*}Observed band positions in Ne matrix at 3 K. ^{*c*}Tentative assignment of the vibrational modes. ^{*d*}Derived from its overtone.

in, both radicals are generated through the photoinduced reactions of SO₂ with hydrogen atoms in solid Ar, Kr, and Xe matrixes. As an example of this sensitivity, the band at 1051.2 cm⁻¹ for the S–O–H bending mode (ν_3 , calcd 1034.1 cm⁻¹), its overtone at 2084.2 cm⁻¹ ($2\nu_3$, calcd 2044.3 cm⁻¹), and combination bands at 2220.1 cm⁻¹ ($\nu_2 + \nu_3$, calcd 2195.0 cm⁻¹) are observable, and the assignment is supported by the agreement with the recent CcCR ("C" represents CBS energy, "cC represents core correlation, and "R" represents relativistic inclusions) computed anharmonic IR frequencies.⁴¹ For HSO₂[•], two overtone modes at 2562.0 ($2\nu_2$, calcd 2583.5 cm⁻¹) and 2152.4 cm⁻¹ ($2\nu_3$, calcd 2161.4 cm⁻¹) along with three combination bands at 2347.5 ($\nu_2 + \nu_3$, calcd 2367.1 cm⁻¹), 2076.1 ($\nu_2 + \nu_5$, calcd 2091.7 cm⁻¹), and 1741.3 cm⁻¹ ($\nu_2 + \nu_6$, calcd 1760.5 cm⁻¹) can also be identified. The



Figure 3. (A) IR spectrum of HVFP products of $CHF_2S(O)OH$ in Ne matrix at 3 K. (B) IR difference spectrum reflecting the change of the Ne matrix upon irradiation with a 266 nm laser (50 min). (C) UV–vis spectra of $CHF_2S(O)OH$ and its HVFP products in Ar (10 K) and Ne matrixes (3 K). (D) Enlarged UV–vis spectra in the range 230–600 nm.

The Journal of Physical Chemistry A

frequencies observed in the Ne matrix for the IR fundamentals of HSO_2^{\bullet} are also in good agreement with the very recent CcCR computations (Table 2).⁴²

Recently, the UV-vis spectrum of HOSO[•] in the gas phase has been computationally explored^{30,43} with the highly accurate multireference methods MRCI+Q and MS-CASPT2, and three absorptions above 200 nm have been predicted. The strongest absorption is located around 250 nm with an oscillator strength (f) of 0.0184 corresponding to the combination of two excitations from the ground state (X^2A) to the third (C^2A) and fourth (D^2A) excited states. In the UVvis spectrum of the Ne matrix isolated HVFP products of $CHF_2S(O)OH$ (Figure 3C), an intense absorption at 270 nm (λ_{max}) occurs, and it differs from the main absorption of the acid precursor at 215 nm. This band is assigned to HOSO[•] and is close to the calculated transition around 250 nm. However, the remaining decomposition product (${}^{\bullet}CHF_{2}$) of the acid displays negligible absorption features above 250 nm. Furthermore, the strong band exhibits a shoulder in the range 300-350 nm, and it also belongs to HOSO[•] by comparison with the predicted weaker transitions at 324 (f =0.0035) and 315 nm (f = 0.0009).⁴² In the Ar matrix, the strongest absorption of HOSO[•] shifts to 250 nm due to overlap with the band of an unknown photostable species in the range 250-300 nm which also exhibits vibrational spacings.

In line with the photoinduced isomerization of $HOSO^{\bullet} \rightarrow$ HSO_2^{\bullet} in the IR spectrum (Figure 3B), the intensities for the bands in the range 240-320 nm for HOSO[•] in both Ar and Ne matrixes decrease dramatically upon 266 nm laser irradiation (Figure 3C). In sharp contrast, a very broad and weak band in the range 320-500 nm appears (Figure 3D) and is in good agreement with the calculated vertical transitions in the range 250–500 nm for HSO_2^{\bullet} at the MRCI+Q/aug-ccpV(T+d)Z level of theory (Figure 2). The assignment of this band to HSO₂[•] is consistent with the photochemistry that this radical can be destroyed under further visible-light irradiation (420 or 530 nm) through fragmentation (HSO₂ \rightarrow H[•] + SO₂) and concomitant reformation of HOSO[•]. Formation of SO₂ among the photolysis products of HOSO[•] is clearly evidenced by the occurrence of the absorption at 280 nm^{44,45} after the irradiation. The absorption of HSO2 • in the range 320-500 nm is notable in that it resembles $CH_3SO_2^{\bullet}$, for which a broad absorption in the range 250-450 nm has been identified in Ar matrix studies.4

According to the MRCI+Q calculations (Figure 2), HSO_2^{\bullet} has another strong absorption at about 220 nm. However, its identification is blurred by the overlap with the absorptions of the accompanying species including $CHF_2S(O)OH$, $HOSO^{\bullet}$, SO_2 , and ${}^{\bullet}CHF_2$ in the same matrix. The electronic absorption for HSO_2^{\bullet} in the range 320–500 nm is reproducible in Ar matrix analysis (Figure 3D).

CONCLUSIONS

In summary, a joint theoretical and experimental characterization is reported for the electronic properties of two sulfurcontaining radicals, HSO_2^{\bullet} and $HOSO^{\bullet}$, which are considered as key intermediates in SO_2 geoengineering. In line with the MRCI+Q/aug-cc-pV(T+d)Z calculated vertical transitions above 300 nm for HSO_2^{\bullet} , a very broad absorption band in the range 320–500 nm has been observed in both solid Ar and Ne matrixes for the first time, which reasonably accounts for the previously reported photochemistry of HSO_2^{\bullet} in solid pubs.acs.org/JPCA

noble gas (Ar, Kr, and Xe) matrixes.^{28,29} Additionally, the stronger absorptions for HOSO[•] in the range 250-350 nm have been identified, coinciding with the photodissociation of HOSO[•] to [•]OH and SO under ultraviolet light irradiation conditions in the stratosphere as disclosed by multiconfigurational quantum chemistry.³⁰ Therefore, the electronic spectra of HSO_2^{\bullet} and $HOSO^{\bullet}$ computed with high-level multireference and multiconfiguration quantum chemical methods are experimentally validated. The efficient photoinduced interconversion between HOSO[•] and $HSO_2^{•}$ in the matrix also allows for the identification of several weak IR absorptions for the combination and overtone modes of the fundamental vibrations. The new experimental UV-vis and IR spectra and photochemistry are complementary to the intensively explored²⁴⁻³⁰ properties of HOSO $^{\bullet}$ and HSO₂ $^{\bullet}$, which are expected to aid modeling and laboratory studies on the complex SO₂ chemistry in the Earth's atmosphere and even also in the interstellar medium (ISM).^{47,48}

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Abatzoglou, J. T.; Williams, A. P. Impact of Anthropogenic Climate Change on Wildfire across Western US Forests. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 11770–11775.

(2) Diffenbaugh, N. S.; Burke, M. Global Warming Has Increased Global Economic Inequality. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 9808–9813.

(3) Duffy, P. B.; Field, C. B.; Diffenbaugh, N. S.; Doney, S. C.; Dutton, Z.; Goodman, S.; Heinzerling, L.; Hsiang, S.; Lobell, D. B.; Mickley, L. J.; Myers, S.; Natali, S. M.; Parmesan, C.; Tierney, S.; Williams, A. P. Strengthened Scientific Support for the Endangerment Finding for Atmospheric Greenhouse Gases. *Science* **2019**, *363*, No. eaat5982.

(4) Irvine, P.; Emanuel, K.; He, J.; Horowitz, L. W.; Vecchi, G.; Keith, D. Halving Warming with Idealized Solar Geoengineering Moderates Key Climate Hazards. *Nat. Clim. Change* **2019**, *9*, 295–299.

(5) Crutzen, P. J. Albedo Enhancement by Stratospheric Sulfur Injections: A Contribution to Resolve a Policy Dilemma? *Clim. Change* **2006**, *77*, 211.

(6) Wigley, T. M. L. A Combined Mitigation/Geoengineering Approach to Climate Stabilization. *Science* **2006**, *314*, 452–454.

(7) Budyko, M. I. Climate and Life; Academic: New York, 1974.

(8) Dickinson, R. E. Climate Engineering A Review of Aerosol Approaches to Changing the Global Energy Balance. *Clim. Change* **1996**, 33, 279–290.

(9) Aubry, T. J.; Staunton-Sykes, J.; Marshall, L. R.; Haywood, J.; Abraham, N. L.; Schmidt, A. Climate Change Modulates the Stratospheric Volcanic Sulfate Aerosol Lifecycle and Radiative Forcing from Tropical Eruptions. *Nat. Commun.* **2021**, *12*, 4708.

(10) Tilmes, S.; Müller, R.; Salawitch, R. The Sensitivity of Polar Ozone Depletion to Proposed Geoengineering Schemes. *Science* **2008**, 320, 1201–1204.

(11) Dutton, E. G.; Christy, J. R. Solar Radiative Forcing at Selected Locations and Evidence for Global Lower Tropospheric Cooling following the Eruptions of El Chichón and Pinatubo. *Geophys. Res. Lett.* **1992**, *19*, 2313–2316.

(12) Robock, A.; MacMartin, D. G.; Duren, R.; Christensen, M. W. Studying Geoengineering with Natural and Anthropogenic Analogs. *Clim. Change* **2013**, *121*, 445–458.

(13) Robock, A. Volcanic Eruptions and Climate. *Rev. Geophys.* 2000, 38, 191–219.

(14) Kravitz, B.; MacMartin, D. G.; Robock, A.; Rasch, P. J.; Ricke, K. L.; Cole, J. N. S.; Curry, C. L.; Irvine, P. J.; Ji, D.; Keith, D. W.; Kristjánsson, J. E.; Moore, J. C.; Muri, H.; Singh, B.; Tilmes, S.; Watanabe, S.; Yang, S.; Yoon, J.-H. A Multi-model Assessment of Regional Climate Disparities Caused by Solar Geoengineering. *Environ. Res. Lett.* **2014**, *9*, 074013.

(15) Weisenstein, D. K.; Keith, D. W.; Dykema, J. A. Solar Geoengineering using Solid Aerosol in the Stratosphere. *Atmos. Chem. Phys.* **2015**, *15*, 11835–11859.

(16) Keith, D. W.; MacMartin, D. G. A Temporary, Moderate and Responsive Scenario for Solar Geoengineering. *Nat. Clim. Change* **2015**, *5*, 201–206.

(17) Masson-Delmotte, V.; Zhai, P.; Pörtner, H.-O.; Roberts, D.; Skea, J.; Shukla, P. R.; Pirani, A.; Moufouma-Okia, W.; Péan, C.; Pidcock, R.; Connors, S.; Matthews, J. B. R.; Chen, Y.; Zhou, X.; Gomis, M. I.; Lonnoy, E.; Maycock, T.; Tignor, M.; Waterfield, T. Global Warming of 1.5 °C, An IPCC Special Report on the Impacts of Global Warming of 1.5 °C above Pre-industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty; World Meteorological Organization: Geneva, Switzerland, 2018.

(18) Masson-Delmotte, V.; Zhai, P.; Pirani, A.; Connors, S. L.; Péan, C.; Berger, S.; Caud, N.; Chen, Y.; Goldfarb, L.; Gomis, M. I.; Huang, M.; Leitzell, K.; Lonnoy, E.; Matthews, J. B. R.; Maycock, T. K.; Waterfield, T.; Yelekçi, O.; Yu, R.; Zhou, B. Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth

Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge, U.K., 2021.

(19) Reflecting Sunlight: Recommendations for Solar Geoengineering Research and Research Governance; National Academies of Sciences, Engineering, and Medicine; The National Academies Press: Washington, DC, 2021.

(20) Shepherd, J. G. Geoengineering the Climate: An Overview and Update. *Philos. Trans. R. Soc., A* 2012, 370, 4166-4175.

(21) Pierce, J. R.; Weisenstein, D. K.; Heckendorn, P.; Peter, T.; Keith, D. W. Efficient Formation of Stratospheric Aerosol for Climate Engineering by Emission of Condensible Vapor from Aircraft. *Geophys. Res. Lett.* **2010**, *37*, L18805.

(22) Crutzen, P. J. The Possible Importance of COS for the Sulfate Layer of the Stratosphere. *Geophys. Res. Lett.* **1976**, *3*, 73–76.

(23) Tuck, A. F.; Donaldson, D. J.; Hitchman, M. H.; Richard, E. C.; Tervahattu, H.; Vaida, V.; Wilson, J. C. On Geoengineering with Sulphate Aerosols in the Tropical upper Troposphere and lower Stratosphere. *Clim. Change* **2008**, *90*, 315–331.

(24) Kroll, J. A.; Frandsen, B. N.; Kjaergaard, H. G.; Vaida, V. Atmospheric Hydroxyl Radical Source: Reaction of Triplet SO_2 and Water. J. Phys. Chem. A **2018**, 122, 4465–4469.

(25) Anglada, J. M.; Martins-Costa, M. T. C.; Francisco, J. S.; Ruiz-López, M. F. Triplet State Promoted Reaction of SO_2 with H_2O by Competition between Proton Coupled Electron Transfer (pcet) and Hydrogen Atom Transfer (hat) Processes. *Phys. Chem. Chem. Phys.* **2019**, *21*, 9779–9784.

(26) McKee, M. L.; Wine, P. H. Ab Initio Study of the Atmospheric Oxidation of CS₂. J. Am. Chem. Soc. **2001**, 123, 2344–2353.

(27) McCarthy, M. C.; Lattanzi, V.; Martinez, O., Jr.; Gauss, J.; Thorwirth, S. Spectroscopic Detection and Structure of Hydroxidooxidosulfur (HOSO) Radical, An Important Intermediate in the Chemistry of Sulfur-Bearing Compounds. J. Phys. Chem. Lett. **2013**, 4, 4074–4079.

(28) Isoniemi, E.; Khriachtchev, L.; Lundell, J.; Räsänen, M. HSO₂ Isomers in Rare-gas Solids. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1549– 1554.

(29) Chen, C.; Lu, B.; Zhao, X.; Qian, W.; Liu, J.; Trabelsi, T.; Francisco, J. S.; Qin, J.; Li, J.; Wang, L. N.; Zeng, X. Q. Capture of the Sulfur Monoxide-Hydroxyl Radical Complex. *J. Am. Chem. Soc.* **2020**, *142*, 2175–2179.

(30) Carmona-García, J.; Francés-Monerris, A.; Cuevas, C. A.; Trabelsi, T.; Saiz-Lopez, A.; Francisco, J. S.; Roca-Sanjuán, D. Photochemistry and Non-adiabatic Photodynamics of the HOSO Radical. J. Am. Chem. Soc. **2021**, *143*, 10836–10841.

(31) Knowles, P. J.; Werner, H.-J. An Efficient Second-order MC SCF Method for Long Configuration Expansions. *Chem. Phys. Lett.* **1985**, *115*, 259–267.

(32) Werner, H.-J.; Knowles, P. J. A Second Order Multiconfiguration SCF Procedure with Optimum Convergence. *J. Chem. Phys.* **1985**, *82*, 5053–5063.

(33) Werner, H.-J.; Knowles, P. J. An Efficient Internally Contracted Multiconfiguration-reference Configuration Interaction Method. *J. Chem. Phys.* **1988**, *89*, 5803–5814.

(34) Werner, H.-J.; Knowles, P. J. An Efficient Method for the Evaluation of Coupling Coefficients in Configuration Interaction Calculations. *Chem. Phys. Lett.* **1988**, *145*, 514–522.

(35) Szalay, P. G.; Bartlett, R. J. Multi-reference Averaged Quadratic Coupled-cluster Method: A Size-extensive Modification of Multi-reference CI. *Chem. Phys. Lett.* **1993**, *214*, 481–488.

(36) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Shamasundar, K. R.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselman, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; O'Neill, D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R. M.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni,

The Journal of Physical Chemistry A

R.; Thorsteinsson, T.; Wang, M.; Welborn, M. MOLPRO, A Package of Ab Initio Programs, ver. 2019.1. http://www.molpro.net.

(37) Karsili, T. N. V.; Thodika, M.; Nguyen, L.; Matsika, S. The Origin of Fluorescence in DNA Thio-analogues. *Chem. Phys.* **2018**, *515*, 434–440.

(38) Esposito, V. J.; Trabelsi, T.; Rohacs, N.; Francisco, J. S. Spectroscopic Characterization of the First and Second Excited States of the HOSO Radical. *J. Phys. Chem. A* **2021**, *125*, 6254–6262.

(39) Blackie, D.; Blackwell-Whitehead, R.; Stark, G.; Pickering, J. C.; Smith, P. L.; Rufus, J.; Thorne, A. P. High-resolution Photoabsorption Cross-section Measurements of SO₂ at 198 K from 213 to 325 nm. *J. Geophys. Res.: Planets* **2011**, *116*, E03006.

(40) Qin, J.; Li, J. An Accurate Full-dimensional Potential Energy Surface for the Reaction OH + SO \rightarrow H + SO₂. *Phys. Chem. Chem. Phys.* **2021**, 23, 487–497.

(41) Fortenberry, R. C.; Francisco, J. S.; Lee, T. J. Quantum Chemical Rovibrational Analysis of the HOSO Radical. *J. Phys. Chem.* A **2017**, *121*, 8108–8114.

(42) Fortenberry, R. C.; Francisco, J. S. Anharmonic Fundamental Vibrational Frequencies and Spectroscopic Constants of the Potential HSO₂ Radical Astromolecule. *J. Chem. Phys.* **2021**, *155*, 114301.

(43) Trabelsi, T.; Anglada, J. M.; Ruiz-López, M. F.; Francisco, J. S. Photochemistry of HOSO Radical in the Gas Phase. *J. Chem. Phys.* **2019**, *151*, 111103.

(44) Danielache, S. O.; Eskebjerg, C.; Johnson, M. S.; Ueno, Y.; Yoshida, N. High-precision Spectroscopy of ³²S, ³³S, and ³⁴S Sulfur Dioxide: Ultraviolet Absorption Cross Sections and Isotope Effects. *J. Geophys. Res.* **2008**, *113*, D17314.

(45) Whitehill, A. R.; Xie, C.; Hu, X.; Xie, D.; Guo, H.; Ono, S. Vibronic Origin of Sulfur Mass-independent Isotope Effect in Photoexcitation of SO_2 and the Implications to the Early Earth's Atmosphere. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 17697–17702.

(46) Reisenauer, H. P.; Schreiner, P. R.; Romanski, J.; Mloston, G. Gas-phase Generation and Matrix Isolation of the Methylsulfonyl Radical CH₃SO₂• from Allylmethylsulfone. *J. Phys. Chem. A* **2015**, *119*, 2211–2216.

(47) Góbi, S.; Csonka, I. P.; Bazsó, G.; Tarczay, G. Successive Hydrogenation of SO and SO₂ in Solid *para*-H₂: Formation of Elusive Small Oxoacids of Sulfur. *ACS Earth Space Chem.* **2021**, *5*, 1180–1195.

(48) Hobbs, R.; Rimmer, P. B.; Shorttle, O.; Madhusudhan, N. Sulfur chemistry in the atmospheres of warm and hot Jupiters. *Mon. Not. R. Astron. Soc.* **2021**, *506*, 3186–3204.

