Spectroscopy of OSSO and Other Sulfur Compounds Thought to be Present in the Venus Atmosphere

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ABSTRACT: The spectroscopy of *cis*-OSSO and *trans*-OSSO is explored and put into the context of the Venusian atmosphere, along with other sulfur compounds potentially present there, namely, S₂O, C₁-S₂O₂, trigonal-S₂O₂, and S₃. UV-vis spectra were calculated using the nuclear ensemble approach. The calculated OSSO spectra are shown to match well with the 320–400 nm near-UV absorption previously measured on Venus, and we discuss the challenges of assigning OSSO as the Venusian near-UV absorber. The largest source of uncertainty is getting accurate concentrations of sulfur monoxide (³SO) in the upper cloud layer of Venus (60–70 km altitude) since the ³SO self-reaction is what causes *cis*- and *trans*-OSSO to form. Additionally, we employed the matrix-isolation technique to trap OSSO formed by microwave discharging a gas mixture of argon and SO₂ and then depositing the mixture onto a cold window (6–12 K). Anharmonic vibrational transition frequencies and intensities were calculated at the coupled cluster level to corroborate the matrix-isolation FTIR spectra. The computationally calculated UV-vis and experimentally recorded IR spectra presented in this work aid future attempts at detecting these sulfur compounds in the Venusian atmosphere.

■ INTRODUCTION

On Venus, SO₂ is the main UV absorber at wavelengths from 200 to 320 nm.^{1–3} However, at wavelengths longer than 320 nm, something other than SO₂ is absorbing, which has not yet been assigned with certainty.^{4–6} There have been several proposed candidates to match the absorption, including S₂O, sulfur allotropes (S₃ and S₄), SCl₂, croconic acid, FeCl₃ in aerosols, and even biomolecules formed by living organisms and recently *cis*-OSSO and *trans*-OSSO.^{6–14} The two OSSO isomers must exist on Venus to some degree because sulfur monoxide (³SO, ground state is a triplet) has been observed on Venus in several ways,^{15–19} and it has previously been found that ³SO self-reacts with no barrier to form either *cis*-OSSO or *trans*-OSSO.¹²

Additionally, the calculation of the vertical electronic transitions of the two OSSO isomers has unravelled where in the UV-vis spectrum they will absorb, though the actual spectral shape cannot be confidently obtained from a single excitation from the equilibrium geometries.¹² At the altitudes where the unknown UV absorber is mainly located (60–70 km altitude), the ³SO concentration is hard to determine.^{5,20,21} Recently, Marcq et al. have estimated that the ³SO concentration is 10% of the SO₂ concentration based on Hubble telescope measurements that constrain the ³SO concentration at 74–81 km altitudes.^{19,22} Earlier measure-

ments done by the International UV Explorer arrive at ³SO concentrations of 12–20 ppb below 70 km.^{15,16} However, there is expressed skepticism of these results based on photochemical modeling.²³ Consensus on whether or not OSSO can be assigned to the near-UV absorption on Venus has not been established yet, and although it remains a promising candidate it depends largely on the ³SO concentration at 60–70 km altitude.^{6,12,22–24}

The potential near-UV absorber needs to absorb in the right region and be present in sufficient concentration. Recently, Pérez-Hoyos et al.⁶ concluded that S₂O and the two OSSO isomers currently “provide the best agreement” with the near-UV absorption on Venus. Pérez-Hoyos et al.⁶ used simulated OSSO spectra based on calculated vertical electronic transition energies and oscillator strengths and spectra of the higher energy conformer of the cyc-S₂O (vide infra).^{12,25} This illustrates the need for high-quality absorption spectra of these sulfur oxides. Recently, we showed that for a series of sulfur compounds (SO₂, SO₃, H₂S, OCS, and CS₂), the nuclear

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ensemble approach, developed by Barbatti et al., can be used to calculate the full electronic spectra, including the bandwidths, in good agreement with experiments.^{26–31} Here we use this relatively new finding to calculate high-quality UV–vis spectra for *cis*- and *trans*-OSSO and compare them to the unknown near-UV absorber on Venus. Additionally, we calculate the UV–vis spectra of S₃ and two S₂O isomers, as these sulfur compounds have also been suggested as potentially matching the unknown Venus absorber.^{6,8,10} Finally, for completeness, we calculate the spectra of two other S₂O₂ isomers, C₁-S₂O₂ and trigonal-S₂O₂, for which no UV–vis spectral data are available in the literature. These isomers are predicted to be stable compounds and may be formed from the complex sulfur chemistry in the Venusian atmosphere, and knowing their UV–vis spectral profiles could be an important improvement for future photochemical modeling studies on Venus.^{12,23,32} Where possible, the calculated spectra are compared with experimental data available.^{25,33–38}

It is difficult to get a good estimate of the OSSO concentration with a high degree of confidence due to a lack of accurate estimates of the OSSO precursor concentration, ³SO, and the rate constant of OSSO formation, in the altitude range of the Venusian near-UV absorption (60–70 km altitude).^{5,39} Previously, the rate constant of OSSO formation was calculated in the high-pressure limit, based on collision theory with a collision diameter estimated from a potential energy surface scan.¹² Here, we improve the level of kinetics theory by using variable reaction coordinate transition state theory (VRC-TST) to calculate the high-pressure rate constant. The advantage of this method is that we avoid having to choose the reactive collisional diameter of the ³SO molecules based on a visual inspection of the potential energy surface. Instead, the rate constant is calculated with microcanonical variational transition state theory (μ VTST).^{40–42}

Experimental observation of spectral signatures belonging to *cis*- and *trans*-OSSO is important to aid in the potential assignment of the OSSO isomers and other compounds predicted to exist in the Venusian atmosphere. Spectral assignment of vibrational transitions belonging to OSSO and other relevant compounds gives a fingerprint to look for in the infrared spectra from the Venusian atmosphere. A matrix-isolation instrument was set up with an FTIR spectrometer in an attempt to detect IR signatures of the OSSO isomers. To produce OSSO, the system was set up so SO₂ could be subjected to a microwave discharge, which would break the bonds in SO₂ and form new sulfur oxides as products. Previously, discharge methods have been shown to produce ³SO, S₂O, and *cis*-OSSO.^{43–45}

Computational Details. Electronic absorption spectra calculated in this work follow a similar approach to that recently shown to accurately reproduce electronic absorption spectra of small sulfur-containing molecules.³¹ For the UV–vis spectral simulation, the molecules investigated, *cis*-OSSO, *trans*-OSSO, C₁-S₂O₂, trigonal-S₂O₂, S₃, S₂O, and cyc-S₂O, were first structurally optimized, and normal modes were calculated using CCSD(T) with the aug-cc-pV(T+d)Z basis set with the Molpro 2012 program.^{46,47} To calculate the UV–vis spectra, the Newton-X program was used, which employs the nuclear ensemble approximation.^{27,28} Newton-X was used to generate a nuclear ensemble using a Wigner distribution,⁴⁸ with the normal coordinates obtained from the CCSD(T)/aug-cc-pV(T+d)Z frequency calculations. The size of each nuclear ensemble is 2000 geometries, which was found

appropriate for the benchmark molecules investigated by Farahani et al. (SO₂, SO₃, H₂S, OCS, and CS₂), and further increasing the size has a diminishing return on improving spectral quality.³¹ As shorthand for describing the combination of ab initio methods employed for the geometry optimizations and electronic excitation calculations, we write CCSD(T)//EOM-CCSD/aug-cc-pV(T+d)Z, where CCSD(T) is the geometry optimization method and EOM-CCSD the electronic excitation calculation method, with both calculations using the aug-cc-pV(T+d)Z basis set. Vertical excitation energies and oscillator strengths for the first five excited states were calculated for each geometric structure in the ensemble using the EOM-CCSD/aug-cc-pV(T+d)Z method in Gaussian 09.⁴⁹ Each individual vertical excitation was convoluted using a $\delta = 0.1$ eV full width at half-maximum (fwhm) Gaussian function, as recommended.³¹ In the [Supporting Information](#) we compare the approach used here with the approach used in the previous work and find that the two approaches produce essentially equivalent data for the calculated SO₂ spectrum.³¹

To get accurate vibrational transition frequencies and intensities, vibrational second-order perturbation theory (VPT2) was used. VPT2 is implemented in the CFOUR program and includes anharmonicity in the calculation of transition frequencies and intensities.^{50–56} For the VPT2 calculations, the molecules, *cis*-OSSO, *trans*-OSSO, C₁-S₂O₂, and trigonal-S₂O₂, were geometry optimized in the CFOUR program before running the VPT2 calculations themselves. Both the geometry optimizations and VPT2 calculations were done at the CCSD(T)/aug-cc-pV(T+d)Z level of theory. For both OSSO isomers, we also performed full-dimensional (6-D) local mode (LM) calculations, including Eckart axis-embedding, with an in-house code (see the [Supporting Information](#) for a detailed description).^{57–59} The single points used for the LM calculations were computed with the Molpro 2012 program,⁴⁶ also at the CCSD(T)/aug-cc-pV(T+d)Z level of theory.

Variable reaction coordinate transition state theory (VRC-TST) was employed to calculate microcanonical variational transition state theory (μ VTST) rate constants for the ³SO + ³SO reaction to form *cis*-OSSO and *trans*-OSSO. It has been shown that using this method provides results in good agreement with experiments for association/dissociation reactions.^{40,41} The calculations of VRC-TST rate constants were carried out using the Polyrate17 program which was combined with Gaussrate version 17-B.^{42,60} The M06-L functional was used for this part with the jun-cc-pV(D+d)Z basis set in the Gaussian 09 program.⁴⁹ The “jun” basis set prefix was preferred over the “aug” basis set prefix, as it alleviated some convergence issues encountered for the larger (“aug”) basis set due to linear dependencies.⁶¹ The program procedure involves a Monte Carlo sampling of the potential energy surface, and to avoid discontinuities and/or convergence problems in the Gaussian 09 program, the calculations were unrestricted and the following keywords were used: guess = mix, scf = xqc, and geom = nocrowd.

■ EXPERIMENTAL SECTION

The matrix-isolation technique was employed to isolate molecules and probe them using infrared spectroscopy. Argon (Alphagaz $\geq 99.999\%$) was used as a host gas with SO₂ (Aldrich $\geq 99.98\%$) mixed in. We used a closed cycle cryostat from Advanced Research Systems (CS202-SI-DMX-1-2-SS) with a DE-202SI cryocooler that has pressurized helium

as its coolant. The matrix sample window was made of CsI, and the shrouds were made of KBr. A thermostat (CryoCon 32) was connected to the setup with a silicon diode (LakeShore Cryotronics) and was used to monitor and control the temperature of the matrix sample window. We used an Edwards turbomolecular vacuum pump (EXT 750X) to keep a high vacuum in the experiments, and a pressure gauge (Balzers Compact Full Range Gauge, PKR 250) was connected to monitor the pressure inside the matrix chamber. To generate new sulfur compounds from SO_2 , such as ^3SO and the OSSO isomers, a microwave discharge was used on the $\text{Ar} + \text{SO}_2$ mixture during deposition to generate a plasma. This technique has been used previously to generate novel compounds in matrix-isolation spectroscopy.^{62–68} In the experiments, an adjustable 0–200 W, 2450 MHz solid state microwave generator from Sairem (GMS200WSM) was used as a microwave source and was connected to an Evenson cavity (CAVITE EVENSON 01/01). This cavity was attached onto a quartz tube, which leads the gas mixture onto the cold sample window. The quartz tube had a 5.5 mm inner diameter, which narrows down to about half of that at the entry point to the matrix chamber. The generated plasma can cause the SO_2 molecules to dissociate inside the tube due to the vacuum-UV radiation, the high temperature, and/or collisions with charged argon species and free electrons. The products are immediately trapped on the cold window after traversing the quartz tube. A commercial FTIR spectrometer (Bruker VERTEX 70) was used to carry out the spectral measurements on the cryogenic matrix. The spectral resolution was set to 0.2 cm^{-1} , and each spectrum was recorded using 500 scans. We used an MCT detector, an MIR light source, and a KBr beamsplitter in these experiments. Background spectra were taken of the window after cooling it, before depositing any gases onto it. Temperatures for recording spectra were between 6 and 12 K, while the window would be annealed to temperatures between 20 and 30 K between spectrum recordings, which allowed the atoms and molecules in the matrix to move around so reactions could occur. To anneal the matrix, the attached thermostat was set to the desired temperature for 10 min before the matrix was cooled back down to the temperature used when recording the spectra. After annealing was done, the system was allowed at least 5 min to thermally stabilize before recording a spectrum.

RESULTS AND DISCUSSION

Photochemistry of SO_2 and ^3SO in a Venus Context.

The mechanism for the formation of ^3SO is naturally quite important, as it is the precursor for OSSO. Direct photolysis of SO_2 is considered to be the main source of ^3SO in the middle atmosphere of Venus.^{23,69–74} This direct photolysis happens with radiation at wavelengths shorter than 220 nm.^{75–77}

SO_2 dominates the UV spectrum of the Venusian atmosphere at wavelengths shorter than 320 nm, and the excited states of SO_2 are known to participate in a variety of reactions.^{73,78–86} Some of these reactions have been brought to attention previously in the literature and are said to be “worthwhile to consider” in a Venus context.^{87–90} Excitation by the first singlet band with a maximum near 280 nm is known to result in a significant portion of excited SO_2 molecules.

In this first excited state the molecule can self-react with ground state SO_2 .⁸⁰

From its excited singlet state, SO_2 can also cross into its lowest energy triplet state ($^3\text{B}_1$). Direct excitation to the triplet state is also possible with radiation at 340–400 nm wavelength, although the absorption cross section for this transition is orders of magnitude lower than for the first singlet band.⁹¹

The triplet state has a phosphorescence lifetime of ~ 0.9 ms and is proposed to be involved in several interesting atmospheric reactions.^{75,77,84–87,92–95} The $^3\text{SO}_2$ molecule is known to react with carbon monoxide (CO) and with ground state SO_2 .^{92,96,97}

Both CO and SO_2 are quite abundant in the Venusian atmosphere, and both of these reactions form ^3SO . Notably, SO_2 absorption at wavelengths shorter than 320 nm is most significant in the Venus UV spectrum at the altitudes where the unknown UV absorber is mainly present (60–70 km altitude).^{5,6,73} In an effort to uncover the impact that these processes actually have on Venus, the photolytic production of ^3SO through the reactions 2, 4, 6, and 7 was calculated and is shown in Figure 1. To calculate these production rates, the values of SO_2 concentration, CO concentration, atmospheric number density, and photon flux on Venus from Zhang et al. were used.⁷³ We calculated the ^3SO formation rate with steady-

Figure 1. Photolytic production of ^3SO on Venus from SO_2 through different channels, including direct photolytic cleavage of SO_2 at wavelengths shorter than 220 nm and indirect pathways through reactions of either photoexcited $^1\text{SO}_2$ or $^3\text{SO}_2$; see the text for details.

Figure 2. UV–vis spectrum of *cis*-OSSO (left) and *trans*-OSSO (right) with the single vertical excitation profile calculated at the CC3/aug-cc-pV(T+d)Z level based on a MRCI/cc-pV(T+d)Z optimized geometry by Frandsen et al.¹² (red) and the new calculated spectrum using the nuclear ensemble approach calculated at the CCSD(T)//EOM-CCSD/aug-cc-pV(T+d)Z level of theory (blue). See the [Supporting Information](#) for a linear y-axis version of this figure.

state approximations for both $^1\text{SO}_2$ and $^3\text{SO}_2$; see the [Supporting Information](#) for further details. The results in [Figure 1](#) show that the direct photolysis of SO_2 to form ^3SO dominates at almost all altitudes, compared to the indirect pathways through $^1\text{SO}_2$ and $^3\text{SO}_2$. This confirms that indirect pathways exceed the direct SO_2 photolysis only at the lower boundary of 58 km altitude. However, these results indicate that SO_2 could still do excited state chemistry, especially close to the lower boundary, and it should possibly be taken into account in future work on the Venus atmosphere.^{23,69–74} Identification of potentially important processes is needed to improve the Venus atmosphere models.^{98,99} Recently, it was suggested that excited state SO_2 can abstract hydrogen atoms from water and alkanes, and further studies have suggested that SO_2 can coat the interface of water-based aerosols, which potentially impacts its chemistry and photochemistry.^{85,86,100,101} It shows that there might be more to the photochemistry of SO_2 than what is currently accounted for. Given how rich the Venusian atmosphere is in aerosols, it is probable that SO_2 chemistry at the aerosol interface plays an important role.

The rate constant for OSSO formation from the ^3SO self-reaction was calculated in previous work using an experimental low-pressure rate constant from Herron and Huie and an estimated high-pressure (collision limit) rate constant.¹⁰² These were combined in a Troe scheme to calculate the rate constant over the Venusian middle atmosphere (58–112 km altitude).¹² In this work, the high-pressure rate constant is calculated using microcanonical variational transition state theory (μVTST). It is important to take spin statistics into account for the reaction, since it is two triplet state molecules reacting to form a single molecule. Only 1 in 9 random $^3\text{SO} + ^3\text{SO}$ collisions follow a singlet potential energy surface (PES) while 3 in 9 follow a triplet PES and finally 5 in 9 a quintet PES.¹⁰³ In the previous work, both the singlet and triplet PES were assumed to result in OSSO formation, and the estimated rate constant was $k_\infty = 1.4 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at $T = 245 \text{ K}$. The reasoning behind the triplet PES leading to OSSO formation is that a downhill product, a $^3\text{OSSO}$ isomer, was identified with a geometry that resembles the transition state between the *cis*- and *trans*-OSSO isomers, which was suggested

to convert to the singlet PES after its formation.¹² In this work, using the same assumption that both singlet and triplet PES result in OSSO, we calculate a $k_{\infty, \mu\text{VTST}} = 1.7 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at $T = 245 \text{ K}$. This different approach for calculating the rate constant is in very good agreement with the previous estimate, which helps validate the rate constant for OSSO formation. The μVTST rate constant was found to have a small negative temperature dependence, which is consistent with a barrierless reaction; see the [Supporting Information](#). Note that the ab initio calculations were only done on the singlet PES and were simply assumed to have the same end result following the triplet PES. This is a source of uncertainty in the high-pressure rate constant, and a lower estimate can be made by dividing the rate constant(s) above by a factor of 4, which assumes that the singlet PES pathway is the only one which forms OSSO; see the [Supporting Information](#) for details. Furthermore, the sampling procedure used to calculate the rate constant here does not distinguish between the two OSSO isomers, and thus the rate constant refers to the overall formation of OSSO. It can be safely assumed that the formation of OSSO via the singlet PES results in approximately equal amounts of *cis*- and *trans*-OSSO, based on the geometry of the *cis/trans* isomerization transition state identified in earlier work.¹² It is however unknown if the triplet PES will result in more of one OSSO isomer than the other.

UV–Vis Spectra for *cis*-OSSO and *trans*-OSSO.

Previously, the vertical electronic transition energy and oscillator strength were calculated at the CC3/aug-cc-pV(T+d)Z level of theory for the two lowest energy transitions of both OSSO isomers. However, the spectral shape of each transition was estimated using a simple Lorentzian function with a line width estimated from electronic transitions in other small sulfur species. These simulated spectra were sufficient to suggest OSSO as the unknown UV absorber.^{6,12} Here, we use the nuclear ensemble approach within the Newton-X program to directly calculate the spectral shape and width of the UV–vis spectra. The new calculated spectra of *cis*-OSSO and *trans*-OSSO using the nuclear ensemble approach are shown in [Figure 2](#). The simulated spectra reported by Frandsen et al. are also shown for comparison.¹² An interesting result is that for *cis*- and *trans*-

OSSO, the peak maxima, which are located at 339 and 381 nm, respectively, are both red-shifted compared to the CCSD calculation in earlier work.¹² Note that the difference between CC3 and CCSD vertical excitation energies was explored by Frandsen et al. and was found to be small, <0.04 eV, which corresponds to a few nanometer shift for the two OSSO isomers.¹² There are other more significant factors that cause this shift. First, the geometry of the OSSO isomers was optimized at the MRCI/cc-pV(T+d)Z level of theory in earlier work, while in this work the geometry was optimized at the CCSD(T)/aug-cc-pV(T+d)Z level. Second, as part of this work we have tried manually displacing the molecular geometry of *cis*- and *trans*-OSSO along each normal mode and found that most displacements away from the equilibrium geometry cause a red shift of the dominant electronic transition. Thus, when we use the nuclear ensemble approach, which generates molecular geometries randomly displaced along the normal coordinates, the peak will on average shift toward the red. The vertical excitation energy from the equilibrium geometry was calculated using the exact same ab initio method for calculating the electronic transitions as was employed in the nuclear ensemble approach in this work. We find that the second vertical transition for *cis*-OSSO is at 333 nm and for *trans*-OSSO at 374 nm, which means the sampling approach alone caused a red shift of 0.08 and 0.05 eV for the second electronic transition in *cis*- and *trans*-OSSO, respectively. The new calculated spectra have additional features that arise from including more electronic transitions in the calculations. The nuclear ensemble approach with the Gaussian line broadening for the individual transitions decays much faster and more realistically than the single broad Lorentzian that Frandsen et al. used.¹²

Recently, Wu et al. assigned *cis*- and *trans*-OSSO in a matrix-isolation experiment.¹⁰⁴ They assigned a transition at 517 nm to the first electronic transition in *trans*-OSSO in an N₂ matrix at 12 K. Additional features at 375 and 390 nm were assigned to the second electronic transition in *cis*- and *trans*-OSSO, respectively.¹⁰⁴ The peak maxima in our calculated spectra for the first electronic transitions in *cis*- and *trans*-OSSO are at 473 and 538 nm, respectively, and the second transitions are at 339 and 381 nm. Peak maxima placements appear to be somewhat in agreement with the Wu et al. assignments, with the biggest difference being between their assigned *cis*-OSSO peak maximum and our calculated electronic transition, 375 and 339 nm, respectively.¹⁰⁴ The 375 nm band that they assign to *cis*-OSSO is broad and potentially includes two overlapping bands, with the *cis*-OSSO signal belonging to the shorter wavelength part of the bands at ~360 nm. It can be seen in their spectra that the second *trans*-OSSO transition is around a factor of 3–4 times more intense than the first transition.¹⁰⁴ In this work, the corresponding calculated difference in intensity exceeds a factor of 1000, which is in disagreement with what Wu et al. assigned experimentally.¹⁰⁴ Additionally, they calculated a zero oscillator strength for the first vertical excitation in *trans*-OSSO with their TD-DFT calculations, which was also found in previous work using coupled-cluster calculations.¹² The calculated spectra here show the first band with a nonzero cross section as the sampling procedure generates nonequilibrium geometries that break the molecular symmetry. However, as expected based on the vertical excitation calculations, the cross section for the symmetry-forbidden first transition in *cis*- and *trans*-OSSO is still orders of magnitude lower than for the second transition. We

therefore suggest that the 517 nm band Wu et al.¹⁰⁴ observed is unlikely to be caused by *trans*-OSSO.

The calculated UV–vis cross sections of *cis*- and *trans*-OSSO can be used to calculate the photolysis rate constant, *J*, which is important in trying to assign the enigmatic UV absorber on Venus. To do so, we set the Venusian altitude to 64 km altitude and the latitude to 0° to be able to directly compare the values with the ones calculated in previous work.¹² We calculate *J* values of 0.20 s^{−1} for *cis*-OSSO and 0.62 s^{−1} for *trans*-OSSO, in agreement with the earlier values of 0.16 and 0.39 s^{−1}, respectively.¹² This photolysis rate calculation includes the bands corresponding to the first transition in *cis*- and *trans*-OSSO, and in the interest of uncovering their impact on the overall OSSO photolysis rate, we calculate how much they contribute to the *J* values at 64 km altitude. We find that these bands contribute less than 0.3% to the *J* value, which is negligible. Note that the calculated OSSO spectra cut off at around ~250 nm, which means contributions from shorter wavelength photons are missed in the calculation of the *J* values. This should mainly be a source of systematic error at high altitudes in the Venusian atmosphere (100–110 km), where most of the short-wavelength photon flux from the sun has not been filtered by the atmosphere.

The enigmatic Venusian UV absorber was investigated by both Haus et al. and Pérez-Hoyos et al. in an attempt to retrieve its UV spectrum.^{5,6} Their resulting spectral profile can be compared to our calculated OSSO spectra; see Figure 3. We

Figure 3. Retrieved spectral profile of the Venus near-UV absorber (top) and the calculated spectral profiles of the *cis*- and *trans*-OSSO isomers (bottom). The dashed lines for OSSO are the profiles from Frandsen et al.¹² while the solid lines are from this work. These are the same profiles as in Figure 2, but here they are all normalized and shown on a linear scale.

note that the two studies appear to have significant differences at wavelengths 300–330 and 420–500 nm, while they seem to be in relatively good agreement between 330 and 420 nm.^{5,6} Thus, while we show the whole 300–500 nm spectral range, we wish to draw focus on the spectral match between OSSO and the retrieved UV profiles of the unknown UV absorber in the 330–420 nm range. A direct comparison of mixed spectral

profiles of OSSO to the unknown UV absorber spectral profiles is made in Figure 4. The two mixed *cis*- and *trans*-OSSO

Figure 4. Retrieved spectral profiles of the unknown absorber on Venus compared to two different mixed *cis*- and *trans*-OSSO absorption profiles. The 76%/24% OSSO profile (black) is based on the photolysis lifetime of the two OSSO isomers at 64 km altitude. The 50%/50% OSSO profile (green) is based on the assumed isomer distribution upon formation from the ^3SO self-reaction.

profiles are based on our calculated spectra but with different population ratios. The population ratio in the black trace is calculated using the J values for *cis*- and *trans*-OSSO; see the Supporting Information for details. The green trace profile is a straight 50%/50% mix of the two OSSO isomers, which agrees with the observed population ratio in the matrix-isolation FTIR experiments discussed *vide infra*. The best spectral match between the unknown UV absorber profiles and our calculated OSSO spectra is clearly obtained with the 50%/50% mix of OSSO isomers. Based on the calculated J values for the two OSSO isomers, and assuming photochemical control of the two OSSO isomer lifetimes, a 74%/26% ratio should be found in the Venusian atmosphere. However, the real population distribution cannot easily be determined because it depends on much more than just the photolysis rate for each isomer, and several assumptions are made to arrive at the 74%/

26% mix. For one, the ^3SO self-reaction is assumed to form *cis*- and *trans*-OSSO in equal amounts, which at this point is not known. Furthermore, the quantum yield for photolytic cleavage of OSSO is assumed to be $\Phi = 1$ at all wavelengths. Alternative routes to OSSO formation should also be considered, as these might result in more of one OSSO isomer than the other, such as the formation of *trans*-OSSO from the $\text{C}_1\text{-S}_2\text{O}_2$ isomer; see Frandsen et al. for details.¹² We also assumed that destruction of the two OSSO isomers exclusively happens through photolytic cleavage based on their short photolysis lifetimes, but reactions could also be controlling the OSSO lifetimes if the quantum yield for OSSO photolysis is significantly lower than the assumed $\Phi = 1$. Additionally, at lower altitudes where temperatures and pressures are higher and the actinic flux is lower, the two OSSO isomers might participate in chemistry since their photolytic lifetimes will be longer there, while they will encounter more molecules with a higher thermal energy. It is therefore not possible to arrive at an accurate population ratio of *cis*- and *trans*-OSSO until the discussed assumptions have been either validated or corrected. In a recent modeling study, the total OSSO abundance has been predicted to be 2 orders of magnitude lower than that needed to explain the near-UV absorption. This lower OSSO concentration originates primarily from a lower ^3SO concentration on which the OSSO concentration is very dependent.²³

Matrix-Isolation FTIR Spectroscopy on OSSO. The matrix-isolation FTIR spectroscopy experiments carried out in this work gave rise to several peaks, which we assign to *cis*- and *trans*-OSSO based on full-dimensionality VPT2 and LM calculations; see Tables 1 and 2.^{45,104,105} We have also identified signals belonging to SO_2 , ^3SO , and S_2O , in agreement with the literature, which we discuss and show in the Supporting Information.^{25,104,106–109} We assign the ν_2 mode in *cis*-OSSO to the peak at 1111.4 cm^{-1} and in *trans*-OSSO to the peak at 1105.7 cm^{-1} ; see Figure 5. The 1105.7 cm^{-1} transition matches the one Wu et al. identified at 1105.5 cm^{-1} , which they also assigned to *trans*-OSSO.¹⁰⁴ A weaker band is also seen in our experiments at 1105.1 cm^{-1} , which is assigned to a site-splitting band from the main peak at 1105.7 cm^{-1} because these two appear with a constant intensity ratio. We note that Wu et al. did not assign two site split bands; this is likely due to the lower resolution (0.5 cm^{-1}) that they used compared with our resolution of 0.2 cm^{-1} .¹⁰⁴ The transition at 1111.4 cm^{-1} seen here is close to the transition that Wu et al.

Table 1. Calculated and Experimental SO-Stretching Vibrational Transition Frequencies (cm^{-1}) and Intensities (in Parentheses in km/mol) in *cis*-OSSO

	calculated ab initio				matrix IR spectroscopy ^a	
	VPT2 ^b	6-D LM ^c	Wu et al. ^d	Drumel et al. ^e	this work	Wu et al.
ν_2	1107 (168)	1103 (160)	1122 (738)	1120 (165)	1111.4	1112.5 (38) ^g
ν_1	1160 (51)	1154 (53)	1173 (125)	1171 (47)	$\sim 1159^f$	1159.3 (100) ^g
$2\nu_2$	2208 (0.6)	2204 (0.7)	—	—	—	—
$\nu_1 + \nu_2$	2252 (0.2) ^h	2246 (4.0)	—	—	—	—
$2\nu_1$	2313 (0.2) ^h	2305 (0.8)	—	—	—	—

^aThe matrix-isolation experiments with argon as host gas. ^bVPT2 using the CCSD(T)/AV(T+d)Z level of theory. ^cFull-dimensionality local mode model with the CCSD(T)/AV(T+d)Z level of theory; see the Supporting Information for details. ^dCCSD(T)-F12b/VTZ-F12 calculated with anharmonicity.¹⁰⁴ ^eVPT2 using CCSD(T)/cc-pV(Q+d)Z with frozen-core approximation.⁴⁵ ^fTentative assignment of a weak signal observed here; see the Supporting Information for details. ^gIntensities were set relative to the most intense transition observed. These relative intensities have likely been switched by accident in the Wu et al. paper.¹⁰⁴ ^hIn the VPT2 calculations, the states associated with the $2\nu_1$ and $\nu_1 + \nu_2$ transitions are deperturbed and should be interpreted with caution.

Table 2. Calculated and Experimental SO-Stretching Vibrational Transition Frequencies (cm^{-1}) and Intensities (in Parentheses in km/mol) in *trans*-OSSO

	calculated ab initio			matrix IR spectroscopy ^a	
	VPT2 ^b	6-D LM ^c	Wu et al. ^d	this work	Wu et al.
ν_2	1103 (289)	1097 (264)	1122 (1552)	1105.7, 1105.1 ^e	1105.5
ν_1	1135 (0)	1125 (0)	1148 (0)	—	—
$2\nu_2$	2199 (0)	2187 (0)	—	—	^f
$\nu_1 + \nu_2$	2223 (0.3) ^h	2208 (6.8)	—	—	2219.7 ^f
$2\nu_1$	2263 (0) ^h	2244 (0)	—	—	—

^aThe matrix-isolation experiments used argon as host gas. ^bVPT2 using the CCSD(T)/AV(T+d)Z level of theory. ^cFull-dimensionality local mode model with the CCSD(T)/AV(T+d)Z level of theory, see the Supporting Information for details. ^dCCSD(T)-F12b/VTZ-F12 calculated with anharmonicity. ^eSite split band. ^fWu et al. assign a weak signal observed at 2219.7 cm^{-1} to the first ν_2 overtone in *trans*-OSSO. We suggest a better agreement with the $\nu_1 + \nu_2$ combination band. ^hIn the VPT2 calculations, the states associated with the $2\nu_1$ and $\nu_1 + \nu_2$ transitions are deperturbed and should be interpreted with caution.

Figure 5. Matrix-isolation infrared spectroscopy of *cis*-OSSO and *trans*-OSSO formed after microwave discharge on SO_2 in argon. Stable and metastable sites of ^3SO are assigned too. The spectra are offset for clarity. Left spectra: SO_2 :Ar ratio of 1:500, deposited and spectra recorded at $T = 12 \text{ K}$. Deposition rate of 0.9 mmol/h . Microwave discharge power set to 50 W . Right spectra: SO_2 :Ar ratio of 1:2000, deposited and spectra recorded at $T = 6 \text{ K}$. Deposition rate of 1.1 mmol/h . Microwave discharge power set to 60 W .

observed at 1112.5 cm^{-1} and assigned to *cis*-OSSO, but the difference in the peak maximum is outside the spectral resolution in both our and their experiments.¹⁰⁴ In Figure 5, the spectra with a 1:500 SO_2 :Ar ratio (left spectra, $T = 12 \text{ K}$) show that the peaks assigned to *cis*-OSSO and *trans*-OSSO can be observed in the “after deposition” spectrum, while in the 1:2000 SO_2 :Ar ratio experiments (right spectra, $T = 6 \text{ K}$) OSSO is observed only after annealing the matrix. We attribute this to more bimolecular chemistry happening in the plasma during deposition when the concentration of SO_2 is higher, consistent with what has been observed in the literature.^{43,44} In the more dilute experiment, the OSSO signals grow in, which is attributed to bimolecular association of ^3SO happening in the matrix during annealing. An interesting observation is the

signal at 1134.5 cm^{-1} , which we assign to ^3SO in a metastable site, and to the best of our knowledge, this has not previously been reported; see Figure 5 (right spectra). It disappears after the first annealing to 20 K , which coincides with the formation of OSSO. Additionally, the intensity of the stable ^3SO site increases as the metastable signal disappears, although this could also be attributed to free sulfur and oxygen atoms combining during annealing. The likely reason why this transition has not been assigned previously is because it is so unstable that the temperature of the matrix needs to be around 6 K , which is lower than what previous studies used.^{104,107,110,111} For *cis*-OSSO an additional feature was assigned to the ν_1 mode by Wu et al. at 1159.3 cm^{-1} . We observe a very weak signal at that same wavenumber in the

1:2000 SO₂:Ar matrix-isolation experiment which grows in with annealing. We tentatively assign this to the ν_1 mode in *cis*-OSSO; see the [Supporting Information](#) for extended spectra that cover this region.¹⁰⁴ In the experiment by Wu et al., they find that the *cis*-OSSO ν_1 transition is three times more intense than the ν_2 transition; however, this is perhaps a typo in their table. We find a calculated ratio of about 1:3 in favor of the ν_2 transition from both the VPT2 and 6D LM calculations, which agrees with the work of Martin-Drumel et al.⁴⁵ and also agrees with the fact that the signal we see at ~ 1159 cm⁻¹ is significantly weaker than the ν_2 *cis*-OSSO signal at 1111.4 cm⁻¹.

Integration of the ν_2 peaks in both *cis*-OSSO and *trans*-OSSO in our experiments gave a 1:2 intensity ratio of *cis*:*trans*, which with our calculated intensity ratio (VPT2/LM) of 160/168 to 264/289 km/mol for the two ν_2 transitions in *cis*-OSSO and *trans*-OSSO, respectively, yields a 50%/50% population ratio of *cis*/*trans*-OSSO formation in the matrix experiments.

Wu et al. assign the first overtone of the ν_2 transition in *trans*-OSSO at 2219.7 cm⁻¹.¹⁰⁴ Based on our calculations, we find this peak in better agreement with the $\nu_1 + \nu_2$ combination band, see [Table 2](#), as the $2\nu_2$ transitions have zero intensity and the wavenumber match is better for the combination transition (a pure local mode and expected to carry the intensity in the overtone).

The possibility of the two S₂O₂ isomers, trigonal-S₂O₂ and C₁-S₂O₂, being formed in the matrix was also considered, but no spectral features belonging to these two isomers were identified in this work. However, both of these S₂O₂ isomers could be formed in an atmospheric setting like on Venus, which is discussed in the next section. As part of our efforts to try and find these in the experiments, we calculated the vibrational frequencies and intensities of both trigonal-S₂O₂ and C₁-S₂O₂ and have listed those results in the [Supporting Information](#) along with the full set of fundamental transition frequencies and intensities for *cis*- and *trans*-OSSO.

UV–Vis Spectra of Trigonal-S₂O₂, C₁-S₂O₂, S₂O, and S₃. The two other S₂O₂ isomers, C₁-S₂O₂ and trigonal-S₂O₂, are both relatively stable and could also be formed in the Venusian atmosphere. Previously, we limited our study of S₂O₂ formation on Venus to the ³SO self-reaction.¹² It is worth noting that other mechanisms of S₂O₂ formation exist, such as a sulfur atom reacting with SO₂

which has been studied in a combustion context where it leads to SO + SO formation.³² At the lower temperatures of the Venus atmosphere (58–112 km altitude), this reaction should terminate at the S₂O₂ intermediates. Free sulfur atoms are formed in the Venusian atmosphere through the UV photolysis of OCS.^{73,112} Therefore, we calculated the UV–vis spectra of trigonal-S₂O₂ and C₁-S₂O₂ using the nuclear ensemble approach; see [Figure 6](#). These can be useful when modeling S₂O₂ photochemistry and can aid in assigning spectral features in future experiments or observations. On a logarithmic scale, the wavelengths longer than 325 nm catch the eye, but it should be noted that these have low cross sections, less than 10⁻¹⁹ cm² molecule⁻¹, and are unlikely to be responsible for the atmospheric Venus absorption from 320 to 400 nm. It is mostly at wavelengths shorter than 300 nm where they absorb significantly, and in the case of Venus, such features are probably overshadowed by the much more abundant SO₂ molecule's absorption features.

Figure 6. Calculated UV–vis spectrum of C₁-S₂O₂ (blue) and trigonal-S₂O₂ (red). Calculated using the nuclear ensemble approach at the CCSD(T)//EOM-CCSD/aug-cc-pV(T+d)Z level of theory.

Pérez-Hoyos et al. concluded that OSSO was the overall best match for the enigmatic near-UV absorber on Venus, but it was actually “only” the second best spectral match.⁶ The best spectral match they reported was with a high-energy cyclic isomer of S₂O (cyc-S₂O).²⁵ The Gibbs energy difference calculated at the CCSD(T)/aug-cc-pV(T+d)Z level between the cyc-S₂O isomer and the normal S₂O isomer (SSO, similar geometry to SO₂) is 44 kcal/mol. The normal S₂O isomer was observed in our microwave discharge experiments (see the [Supporting Information](#)), while cyc-S₂O was not observed, which is in agreement with the work of Tiemann et al. and the calculated relative stability.⁴⁴ The cyc-S₂O isomer was observed by Lo et al. only after irradiating matrix-isolated S₂O in argon with a 308 nm laser.²⁵ The cyclic isomer is either not formed during the discharge experiments or is so short-lived that it isomerizes to normal S₂O before being isolated in the matrices. Our calculated S₂O and cyc-S₂O spectra are shown in [Figure 7](#) with comparisons to the literature included.^{25,113} Note that multiplying the SO₂ UV cross section by a factor of 30 in the 260–340 nm region to obtain the spectral profile of S₂O was recommended by Mills,¹¹³ based on earlier work by Jones,¹¹⁴ and is in surprisingly good agreement with our calculated spectrum. Based on the work of Cobos et al.,³⁷ there seems to be an overall good agreement in the literature with the normal S₂O isomer spectrum.^{33,37,113,114} In the cyc-S₂O spectrum the spectral feature at 530 nm, which at peak maximum has about half the cross section of the 344 nm peak, is something that should be clearly seen in the UV–vis spectrum of Venus if cyc-S₂O was actually the unknown UV absorber. It can therefore be discarded as a potential match to the unknown UV absorber. Another high-energy isomer of S₂O, the SOS isomer, has previously been studied computationally but was predicted to be extremely unstable and was therefore not included in this project.¹¹⁵

Spectral simulation of S₃ was also carried out in this work. The UV–vis spectral data on this molecule is limited, yet it was one of the early candidates suggested to match the unknown UV absorber on Venus along with S₄, and it is part of the Venusian atmospheric models.^{6,8,11,34–36,71–74,116} The calculated spectrum of S₃ ([Figure 8](#)) has a large absorption cross section in the region around 365 nm where the unknown near-

Figure 7. Calculated UV–vis spectra of S_2O (left) and $cyc-S_2O$ (right) with the nuclear ensemble approach at the CCSD(T)//EOM-CCSD/aug-cc-pV(T+d)Z level of theory. The “30 times SO_2 cross section” for the S_2O spectral profile is based on the recommendation by Mills.¹¹³ The $cyc-S_2O$ Ar matrix spectrum is obtained from Pérez-Hoyos et al. who cite Lo et al. for the data.^{6,25} Note that since no absolute intensity was obtained in the $cyc-S_2O$ experimental spectrum by Lo et al.²⁵ we have scaled it to match the maximum absorption of our calculated spectral profile. The y-axis is identical in both the left and the right spectrum.

Figure 8. Calculated S_3 UV–vis spectrum (blue) at the CCSD(T)//EOM-CCSD/aug-cc-pV(T+d)Z level with the nuclear ensemble approach and experimental spectrum from Billmers and Smith³⁶ (red) and Krasnopolsky (1987)³⁵ (yellow).

UV absorber on Venus mainly absorbs. However, as discussed earlier, a spectral match alone is not enough, but pure sulfur species or very low oxides might be interesting targets for future computational studies in a Venus context to aid modeling.^{6,8,73} The agreement between the experimental data sets from Krasnopolsky (1987)³⁵ and Billmers and Smith³⁶ is good; however, our simulated spectrum does not have an excellent agreement with the experiments. It should be noted that the temperature is quite high in the two experimental data sets while no temperature effect has been included in the calculated spectrum ($T = 0$ K); see the legend in Figure 8.^{35,36} The temperature effect on UV–vis spectra can be quite noteworthy, resulting in both a clear shift of band maxima and changes in intensity.¹¹⁷

CONCLUSION

In this work, the photochemistry of SO_2 , which results in the formation of 3SO and precedes OSSO formation, was

discussed in the context of the Venusian middle atmosphere. The chemistry of SO_2 's first excited singlet state and triplet state was explored, and it was shown that the production of 3SO via direct photodissociation of SO_2 at wavelengths <220 nm exceeds the 3SO production through the photochemistry of SO_2 initiated by photon absorption at wavelengths >220 nm at altitudes 60 km and up. This is despite the higher photon flux at longer wavelengths. We conclude that the excited state chemistry of SO_2 is worth considering in future modeling studies on the Venusian atmosphere. The rate constant for OSSO formation from the 3SO self-reaction was calculated using an improved level of kinetics theory compared to the previous work, and we found that it was in very good agreement with the rate constant calculated in the previous work.

The UV–vis spectra for the Venus relevant sulfur compounds, *cis*-OSSO, *trans*-OSSO, $C_1-S_2O_2$, trigonal- S_2O_2 , S_2O , $cyc-S_2O$, and S_3 , were calculated. These calculated spectra all have the potential to impact future Venusian atmospheric modeling as well as aid future experimental/observational studies in assigning these molecules. We have shown that a mix of *cis*- and *trans*-OSSO matches the enigmatic UV absorption on Venus quite well and thus OSSO remains a promising candidate to explain the unknown UV absorption on Venus, although further work is still needed. Vibrational transition frequencies and intensities were calculated for the S_2O_2 isomers, which assisted us in the assignment of *cis*-OSSO and *trans*-OSSO seen in the matrix-isolation FTIR spectroscopy experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.0c04388>.

Details on the UV–vis spectral calculations including validation of the method with SO_2 as the test molecule; a linear y-axis version of Figure 2; details on how the relative OSSO isomer populations were obtained; a

detailed description of the full-dimensionality local mode model used to calculate vibrational frequencies and intensities for the OSSO isomers; additional output from the calculations of vibrational transition frequencies and intensities; supplementary spectra from the matrix-isolation IR spectroscopy experiments; additional details on the rate constant for the $^3\text{SO} + ^3\text{SO}$ reaction to form OSSO; details on how the formation rate of ^3SO from the photochemistry of SO_2 was calculated (PDF)

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Notes

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