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

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S1  Newton-X UV-VIS Spectrum Simulation

S1.1 SO₂ Benchmark comparison

In this work the method from Farahani *et al.* is applied but with some small changes.\cite{1} The changes are: (1) The basis set used in this work is aug-cc-pV(T+d)Z while in the previous work it was a combination of aug-cc-pV(D+d)Z+3 and aug-cc-pV(T+d)Z+3 basis sets. The “+3” denotes a very diffuse set of basis functions placed on the central atom of each molecule and are normally useful for calculating Rydberg transitions. However, in this work we focus on the valence transitions and they are therefore not necessary. Additionally, the mix of the two basis sets means that most of the calculations were carried out with the smaller basis set (aug-cc-pV(D+d)Z+3), while a few of the calculations used the larger basis set (aug-cc-pV(T+d)Z+3) and were used to shift the overall spectrum. This was done to lower the computational cost for simulating the H₂SO₄ spectrum because it was found that only using the larger basis set was prohibitively time-consuming. In this work no molecules are larger than 4 atoms and thus it was feasible to use the aug-cc-pV(T+d)Z basis set exclusively. (2) In the previous work the initial calculations of ground-state geometries and vibrational frequencies were done with the CFOUR program, while in this work Molpro version 2012.1 was used.\cite{2,3} To illustrate that these changes to the method resulted in no significant change to the actual results, the SO₂ spectrum has been re-calculated here with the listed changes and compared to the SO₂ spectrum from previous work and the literature, see Figure S1. The nuclear ensemble for the calculated spectra reported in this work is 2000 geometries, consistent with the recommended ensemble size from Farahani *et al.* 2019.\cite{1} Note that neither spin-forbidden transitions nor vibrational progressions are calculated using this method, as can be seen from the calculated spectra.
Figure S1: Comparison of calculated SO$_2$ UV-VIS spectrum between this work and previous calculations and compared with an experimental spectrum.$^{[1,4]}$
S1.2 Supplementary OSSO UV-VIS Calculated Spectra Figure

As a supplement to Figure 2 in the main article we provide here the cis-OSSO and trans-OSSO calculated spectra on a linear y-scale. These are compared to the profiles from Frandsen et al.\textsuperscript{[5]}

Figure S2: Calculated cis- and trans-OSSO electronic spectra with a linear y-axis. The y-axis is identical between the two figures to showcase the relative intensities between the two OSSO isomers.
S2 Relative OSSO isomer population

The reported relative population of 76% cis-OSSO and 24% trans-OSSO at 64 km altitude in the main article was calculated by making the following assumptions: (1) The $^3\text{SO}^3\text{SO}$ association reaction forms equal amounts of cis- and trans-OSSO. (2) Any photon absorption by either of the two OSSO isomers results in the dissociation of said isomer to form $^3\text{SO}^3\text{SO}$, which is another way of saying that we assume the quantum yield is $\Phi = 1$ for photolytic cleavage of the S-S bond. These assumptions are the same as was used in Frandsen et al. 2016.[5] The population of trans-OSSO is thus

$$\% \text{ trans-OSSO} = \frac{(J_{\text{trans-OSSO}})^{-1}}{(J_{\text{trans-OSSO}})^{-1} + (J_{\text{cis-OSSO}})^{-1}} \times 100\%.$$ (S1)

with the population of cis-OSSO just being 100% minus the % population of trans-OSSO. The altitude dependent $J$ values, which are needed to calculate the OSSO population, are shown in Figure S3.

![Figure S3: The calculated $J$ values for cis-OSSO (blue) and trans-OSSO (red) in Venus’ middle atmosphere. These are calculated based on the UV-VIS spectra calculated in this work.](image)
S3  The Local Mode Model

The Local Mode (LM) Hamiltonian can be obtained by transforming the vibrational Hamiltonian in Cartesian coordinates, \{x\}, to internal curvilinear coordinates, \{q\}.\[^6,7^\] The resulting Hamiltonian takes the following form;

\[
\hat{H} = \frac{1}{2} \sum_{i,j} \hat{p}_i G_{i,j} \hat{p}_j + V(\{q\}) + V',
\]

(S2)

where \(\hat{p}_k = -i\hbar \frac{\partial}{\partial q_k}\), \(q_k\) is the \(k\)th internal displacement coordinate, \(V(\{q\})\) is the potential energy surface (PES), \(V'\) is the LM 'pseudopotential’, and \(G_{i,j}\) is the \(i,j\)’th element in the Wilson \(G\)-matrix.\[^8\] The LM pseudopotential is excluded in this work, as previous papers have shown this term to be negligible. The \(G\)-matrix elements are defined as

\[
G_{i,j} = \sum_\beta \frac{1}{m_\alpha} \frac{\partial q_i}{\partial x_\alpha} \frac{\partial q_j}{\partial x_\alpha},
\]

(S3)

where \(\beta\) expresses a summation over the Cartesian coordinates of each atom. To calculate potential energy and dipole moment single points, each LM coordinate is varied in steps of 0.05 Å or 5° around the equilibrium geometry. The dipole moments at each geometry is calculated with a finite field approach, with a field strength of \(\pm 0.0001\) atomic units. Each dipole moment single point is subsequently transformed to the Eckart frame.\[^9-11^\] We only include pairwise potential energy coupling between modes (two-mode coupling), and all 1D and 2D displacements ranges are given in Table S1.

Table S1: Displacement ranges (min/max) used in the LM calculations.

<table>
<thead>
<tr>
<th>Mode</th>
<th>1D</th>
<th>2D</th>
<th>Step-size</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-stretch</td>
<td>-0.4/0.7 Å</td>
<td>-0.25/0.25 Å</td>
<td>0.05 Å</td>
</tr>
<tr>
<td>SO1-stretch</td>
<td>-0.4/0.7 Å</td>
<td>-0.25/0.25 Å</td>
<td>0.05 Å</td>
</tr>
<tr>
<td>SO2-stretch</td>
<td>-0.4/0.7 Å</td>
<td>-0.25/0.25 Å</td>
<td>0.05 Å</td>
</tr>
<tr>
<td>SSO1-bend</td>
<td>-50/50°</td>
<td>-25/25°</td>
<td>5°</td>
</tr>
<tr>
<td>SSO2-bend</td>
<td>-50/50°</td>
<td>-25/25°</td>
<td>5°</td>
</tr>
<tr>
<td>OSSO</td>
<td>-90/90°</td>
<td>-40/40°</td>
<td>5°</td>
</tr>
<tr>
<td>N_points</td>
<td>148</td>
<td>2145</td>
<td>-</td>
</tr>
</tbody>
</table>
The 1D LM eigenfunctions and eigenvalues are obtained with the method described by Meyer, for 1D PESs represented with a spline fit that is interpolated over 720 grid points. Cross terms in the PES and dipole moment function (DMF) are represented by polynomial expansions in the displacements coordinates, truncated at sixth-order \( f(q_1, q_2) = \sum_{n,m=0}^{6} F_{n,m} q_1^n q_2^m / (n+m)! \). The PES and DMF coefficients are found by solving a linear least squares problem with a Householder QR factorization, followed by a backward substitution.\(^{[12]}\) We subtract the 1D (decoupled) contributions from the 2D surfaces, and fit the remainder of the 2D surfaces.\(^{[11]}\) Solutions of the full-dimensional LM Schrödinger equation are obtained by diagonalizing the corresponding Hamiltonian in a product basis of the 1D eigenfunctions (see Section S3.1). To calculate transition intensities, transition dipole moment matrix elements needs to be obtained. The orthogonality of the 1D wavefunctions ensures that all PES and DMF matrix elements can be factorized into a product of integrals over the 1D LM wavefunctions. The 1D integrals are computed with trapezoidal integration, over the same 720 grid points used to represent the 1D LM wavefunctions. As opposed to cross terms in the DMF, the 1D DMFs are not represented by a polynomial expansion. Instead, the 1D DMFs are represented with a spline fit, and dipole moment matrix elements are calculated with trapezoidal integration, again, over the same 720 grid points used to represent the 1D LM wavefunctions.

**S3.1 The Local Mode Kinetic Energy Operator**

To obtain the kinetic energy numerically, first, the kinetic energy is written as

\[
\hat{T}_q = \sum_i \sum_j \frac{\partial}{\partial q_i} \sum_{\beta} \frac{3N}{m_{\beta}} \frac{\partial q_i}{\partial x_{\beta}} \frac{\partial q_j}{\partial x_{\beta}} = \sum_i \sum_j \frac{\partial}{\partial q_i} G_{ij}(\vec{R}) \frac{\partial}{\partial q_j} + \sum_i \sum_j G_{ij}(\vec{R}) \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j},
\]

(S4)

where \( \vec{R} \) represents the geometry of the molecule. The \( G \)-matrix elements are now expanded in the internal coordinates,

\[
G_{ij}(\vec{R}) = G_{ij}(\vec{R}_e) + \sum_k \frac{\partial G_{ij}(\vec{R})}{\partial q_k} \bigg|_{\vec{R}_e} q_k + \sum_{kl} \frac{\partial^2 G_{ij}(\vec{R})}{\partial q_k \partial q_l} \bigg|_{\vec{R}_e} q_k q_l + \ldots,
\]

(S5)
where $\bar{R}_e$ is the equilibrium geometry, corresponding to $q_i = 0$ for all $i$. This equation may also be written as a mode expansion.

$$G_{ij}(\bar{R}) = G_{ij}(\bar{R}_e) + \sum_k \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n + \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n \partial q_l^m} \bigg|_{\bar{R}_e} q_k^n q_l^m + \ldots$$ (S6)

Truncation of this expansion yields;

$$G_{ij}(\bar{R}) \approx G_{ij}(\bar{R}_e) + \sum_k \sum_{n} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n + \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n \partial q_l^m} \bigg|_{\bar{R}_e} q_k^n q_l^m,$$ (S7)

and is inserted in Equation S4, for which we get $\hat{T}_q = \hat{T}_{q1} + \hat{T}_{q2} + \hat{T}_{q3}$, where each of the terms are;

$$\hat{T}_{q1} = 0 + \sum_i \sum_j G_{ij}(\bar{R}_e) \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j}$$ (S8)

$$\hat{T}_{q2} = \sum_i \sum_j \left[ \frac{\partial}{\partial q_i} \sum_k \sum_{n} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n \right] \frac{\partial}{\partial q_j} + \sum_i \sum_j \sum_k \sum_{n} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j}$$ (S9)

$$\hat{T}_{q3} = \sum_i \sum_j \left[ \frac{\partial}{\partial q_i} \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n \partial q_l^m} \bigg|_{\bar{R}_e} q_k^n q_l^m \right] \frac{\partial}{\partial q_j} + \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n \partial q_l^m} \bigg|_{\bar{R}_e} q_k^n q_l^m \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j}$$ (S10)

Here, a square bracket denotes that a derivative should only be taken inside. Now $T_{q2A}$ is written as;

$$\hat{T}_{q2A} = \sum_i \sum_j \left[ \frac{\partial}{\partial q_i} \sum_k \sum_{n} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n \right] \frac{\partial}{\partial q_j} = \sum_i \sum_j \sum_k \sum_{n} \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} q_k^n \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j},$$ (S12)
where the term \( \frac{\partial q_i}{\partial q_i} \) is zero if \( k \neq i \) and \( nq_i^{n-1} \) if \( k = i \), and we used that \( \frac{n}{n!} = \frac{1}{(n-1)!} \), to further simplify the expression

\[
\hat{T}_{qa} = \sum_i \sum_j \sum_n \frac{1}{(n-1)!} \frac{\partial^n G_{ij}(\vec{R})}{\partial q^n_i} \left|_{\vec{R}_c} \right. q_i^{n-1} \frac{\partial}{\partial q_j}.
\]

Similarly, \( \hat{T}_{qa} \) is written as:

\[
\hat{T}_{qa} = \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. \frac{\partial q^n_i}{\partial q_j} q^m_l \frac{\partial}{\partial q_j} + \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. \frac{\partial q^m_l}{\partial q_j} q^n_i \frac{\partial}{\partial q_j}.
\]

Again, the term \( \frac{\partial q_i}{\partial q_i} \) (and \( \frac{\partial q_i^n}{\partial q_i} \)) is zero if \( k \neq i \) and \( nq_i^{n-1} \) if \( k = i \).

\[
\hat{T}_{qa} = \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. q_i^{n-1} q^m_l \frac{\partial}{\partial q_j} + \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. q^m_i q^n_l \frac{\partial}{\partial q_j}.
\]

In the last term, interchanging \( n \) and \( m \) and letting \( k \to l \) (\( n \) and \( m \) runs over the same range and \( k \) and \( l \) are dummy indices) gives:

\[
\hat{T}_{qa} = \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{2}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. q_i^{n-1} q^m_l \frac{\partial}{\partial q_j} + \sum_i \sum_j \sum_k \sum_{l \neq k} \sum_{n,m} \frac{1}{n!m!} \frac{2}{n!m!} \frac{\partial^{n+m} G_{ij}(\vec{R})}{\partial q^n_i \partial q^m_l} \left|_{\vec{R}_c} \right. q^m_i q^n_l \frac{\partial}{\partial q_j}.
\]
All terms in $\hat{T}_q$ are now collected,

\[
\hat{T}_q = \sum_i \sum_j \left[ \frac{G_{ij}(\bar{R}_e)}{\partial q_i} + \sum_n \frac{1}{n(n-1)!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_i^n} q_i^{n-1} + \sum_k \frac{1}{n!} \frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} q_k^{n-1} \right] \frac{\partial^{n+1} G_{ij}(\bar{R}_e)}{\partial q_i^{n+1} \partial q_j} + \sum_{l \neq i} \sum_{n,m} \frac{2}{(n-1)!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_i^n \partial q_l^m} q_i^{n-1} q_l^{m-1} + \sum_{l \neq i} \sum_{n,m} \frac{1}{n!m!} \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n q_l^m} q_k^{n-1} q_l^{m-1} \right] \frac{\partial^{m+1} G_{ij}(\bar{R}_e)}{\partial q_i^m \partial q_j}.
\]

To proceed, the following notation is introduced:

\[
\frac{\partial^n G_{ij}(\bar{R}_e)}{\partial q_k^n} \bigg|_{\bar{R}_e} = k G_{ij} \quad \& \quad \frac{\partial^{n+m} G_{ij}(\bar{R}_e)}{\partial q_k^n q_l^m} \bigg|_{\bar{R}_e} = \frac{nm}{kl} G_{ij} \quad \& \quad G_{ij}(\bar{R}_e) = G_{ij},
\]

which results in the following expression for $\hat{T}_q$

\[
\hat{T}_q = \sum_i \sum_j \left[ G_{ij} \frac{\partial^2}{\partial q_i^2} + \sum_n \frac{n! G_{ij}}{(n-1)!} q_i^{n-1} \frac{\partial}{\partial q_i} + \sum_k \frac{n! G_{ij}}{n!} q_k^{n-1} \frac{\partial}{\partial q_i} \right] + \sum_{l \neq i} \sum_{n,m} \frac{2 \cdot \frac{n!}{(n-1)!m!} G_{ij}}{m!} q_i^{n-1} q_l^{m-1} + \sum_{l \neq i} \sum_{n,m} \frac{m \cdot \frac{n!}{n!} G_{ij}}{m!} q_k^{n-1} q_l^{m-1} + \sum_{l \neq i} \sum_{n,m} \frac{1 \cdot \frac{n!}{(n-1)!m!} G_{ij}}{m!} q_k^{n-1} q_l^{m-1} \frac{\partial^{n+1} G_{ij}(\bar{R}_e)}{\partial q_i^{n+1} \partial q_j}.
\]

We now expand this expression and use the following notation: $\frac{\partial}{\partial q_i} = \partial q_i$ and $\frac{\partial^2}{\partial q_i^2} = \partial^2 q_i$.

\[
\hat{T}_q = \sum_i \left[ G_{ii} \frac{\partial^2}{\partial q_i^2} + \sum_n \frac{n! G_{ii}}{(n-1)!} q_i^{n-1} \frac{\partial}{\partial q_i} + \sum_n \frac{n! G_{ii}}{n!} q_i^{n-1} \frac{\partial}{\partial q_i} \right] + \sum_{j \neq i} \sum_n \frac{n! G_{ij}}{n!} q_j^{n-1} \frac{\partial}{\partial q_i} + \sum_{l \neq i} \sum_{n,m} \frac{2 \cdot \frac{n!}{(n-1)!m!} G_{ij}}{m!} q_i^{n-1} q_l^{m-1} + \sum_{l \neq i} \sum_{n,m} \frac{m \cdot \frac{n!}{n!} G_{ij}}{m!} q_k^{n-1} q_l^{m-1} + \sum_{l \neq i} \sum_{n,m} \frac{1 \cdot \frac{n!}{(n-1)!m!} G_{ij}}{m!} q_k^{n-1} q_l^{m-1} \frac{\partial^{n+1} G_{ij}(\bar{R}_e)}{\partial q_i^{n+1} \partial q_j}.
\]
where the fourth-mode term, \( q_k q_l \partial_{q_i} \partial_{q_j} \), has been excluded. In practice, we calculate the \( G \)-matrix elements, and its derivative with respect to the internal coordinates from

\[
G(q_i, q_j) = \sum_\alpha^N \frac{1}{m_\alpha} \partial_{q_i} \partial_{q_j} = \sum_\beta^N \sum_\phi^N \left[ \left( J^{-1}\right)_i^j \right]_{\phi \beta} \left[ M^{-1}\right]_{\phi \beta} \left[ J^{-1}\right]_{\beta j},
\]

with \( J \) being the Jacobian of the coordinate transformation \( \left( J^{-1}\right)_\phi^i = \frac{\partial q_i}{\partial x_\phi} \) and \( M \) is the mass matrix \( \left( M_{\phi \beta} = m_\phi \delta_{\phi \beta} \right) \). First, we calculate elements of the Jacobian with finite differences with \( \delta q = 0.001 \, \text{Å} \) for stretching displacements and \( \delta q = 0.001^\circ \) for angular displacements. The internal curvilinear coordinates are defined from a molecular \( Z \)-matrix. The molecular \( Z \)-matrix only includes the \( 3N - 6 \) (vibrational) degrees of freedom, and the Jacobian is therefore augmented with rotation and translation. The small displacements along the rotational coordinates are calculated from a rotation matrix expressed from three quaternions, each describing the rotation around the \( x-, y- \) and \( z \)-axis of the space-fixed Cartesian coordinate system defined from the \( Z \)-matrix of the equilibrium geometry. The inverse \( G \)-matrix is calculated from the Jacobian, i.e. \( G^{-1} = JMJ^T \), and the \( G \)-matrix is obtained by inverting \( G^{-1} \). With this approach, \( G \)-matrix elements are calculated with approximately 10 digits accuracy compared with analytical \( G \)-matrix elements.\(^{[13,14]}\)

The \( G \)-matrix is calculated at each displacement used for the PES, and the derivatives are also obtained by solving a linear-least squares problem with a Householder QR-factorization, followed by a backward substitution.

**S4 Vibrational transitions of Trigonal-S\(_2\)O\(_2\) and C\(_1\)-S\(_2\)O\(_2\)**

The full set of fundamental vibrational transitions calculated in this work of cis-OSSO, trans-OSSO, Trigonal-S\(_2\)O\(_2\) and C\(_1\)-S\(_2\)O\(_2\) are listed in this section. These have been calculated using VPT2 at the CCSD(T)/AV(T+d)Z level of theory in CFOUR.\(^{[2]}\) In addition we used a full-dimensional (6-D) local mode model to calculate the vibrational frequencies and intensities of the two OSSO isomers, see section S3 for details. In the local mode model we also used the
CCSD(T)/AV(T+d)Z level of theory and ran those calculations in Molpro.[3] The cis-OSSO transition frequencies and intensities can be found in Table S2 where they are compared to those calculated by Martin Drumel et al. 2015 and the anharmonic coupled-cluster results in Wu et al. 2018.[15,16] The results for trans-OSSO are listed in Table S3 and compared to the anharmonic coupled-cluster results from Wu et al. 2018.[16] The transition frequencies and intensities of Trigonal-S\(_2\)O\(_2\) are listed in Table S4. The calculated transitions in C\(_1\)-S\(_2\)O\(_2\) are given in Table S5 where they are compared to the Wu et al. 2018 calculated transitions and those assigned in their matrix-isolation spectroscopy experiments.[16]

Table S2: The calculated vibrational transition frequencies and intensities for cis-OSSO. Vibrational frequencies are in cm\(^{-1}\) and calculated intensities in parenthesis are in km/mol.

<table>
<thead>
<tr>
<th></th>
<th>VPT2(^a)</th>
<th>6-D LM(^b)</th>
<th>Martin-Drumel et al.(^c)</th>
<th>Wu et al.(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_1)</td>
<td>1160 (51)</td>
<td>1154 (53)</td>
<td>1171 (47)</td>
<td>1173 (125)</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>1107 (168)</td>
<td>1102.7 (160)</td>
<td>1120 (165)</td>
<td>1122 (738)</td>
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<tr>
<td>(\nu_3)</td>
<td>477 (0.1)</td>
<td>464 (0.2)</td>
<td>478 (0.3)</td>
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<tr>
<td>(\nu_4)</td>
<td>464 (15)</td>
<td>462 (15)</td>
<td>470 (17)</td>
<td>471 (40)</td>
</tr>
<tr>
<td>(\nu_5)</td>
<td>270 (0)</td>
<td>268 (0)</td>
<td>274 (0)</td>
<td>275 (0)</td>
</tr>
<tr>
<td>(\nu_6)</td>
<td>131 (4)</td>
<td>131 (4)</td>
<td>131 (5)</td>
<td>136 (8)</td>
</tr>
<tr>
<td>(2\nu_1)</td>
<td>2313 (0.2)*</td>
<td>2305 (0.8)</td>
<td>—</td>
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</tr>
<tr>
<td>(\nu_1 + \nu_2)</td>
<td>2252 (0.2)*</td>
<td>2246 (4.0)</td>
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</tr>
<tr>
<td>(2\nu_2)</td>
<td>2208 (0.6)</td>
<td>2204 (0.7)</td>
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</tbody>
</table>

\(^{a}\)VPT2 using CCSD(T)/AV(T+d)Z level of theory. \(^{b}\)See section S3 for details on the local mode model. The \textit{ab initio} method employed for this was CCSD(T)/AV(T+d)Z. \(^{c}\)VPT2 using CCSD(T)/cc-pV(Q+d)Z with frozen-core approximation.\(^{15}\) \(^{d}\)CCSD(T)-F12b/VTZ-F12 calculated with anharmonicity.\(^{16}\) \(^*\)In 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 S3: The calculated vibrational transition frequencies and intensities for \textit{trans}-OSSO. Vibrational frequencies are in \text{cm}^{-1} and calculated intensities in parenthesis are in \text{km/mol}.

<table>
<thead>
<tr>
<th></th>
<th>VPT2$^a$</th>
<th>6-D LM$^b$</th>
<th>Wu \textit{et al.}$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>1135 (0)</td>
<td>1124.5 (0)</td>
<td>1148 (0)</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1103 (289)</td>
<td>1097.2 (264)</td>
<td>1122 (1552)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>556 (0)</td>
<td>544 (0)</td>
<td>561 (0)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>336 (0)</td>
<td>330 (0)</td>
<td>339 (0)</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>183 (11)</td>
<td>180 (11)</td>
<td>186 (20)</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>176 (19)</td>
<td>172 (19)</td>
<td>180 (55)</td>
</tr>
<tr>
<td>$2\nu_1$</td>
<td>2263 (0)*</td>
<td>2244 (0)</td>
<td>—</td>
</tr>
<tr>
<td>$\nu_1 + \nu_2$</td>
<td>2223 (0.3)*</td>
<td>2208 (6.8)</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$VPT2 using CCSD(T)/AV(T+d)Z level of theory. $^b$See section S3 for details on the local mode model. The \textit{ab initio} method employed for this was CCSD(T)/AV(T+d)Z. $^c$CCSD(T)-F12b/VTZ-F12 calculated with anharmonicity.$^{[16]}$

*In 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 S4: The calculated vibrational transition frequencies and intensities for Trigonal-S$_2$O$_2$. Vibrational frequencies are in \text{cm}^{-1} and calculated intensities in parenthesis are in \text{km/mol}.

<table>
<thead>
<tr>
<th></th>
<th>VPT2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>1360 (125)</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1169 (186)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>675 (63)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>468 (21)</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>408 (9)</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>346 (2)</td>
</tr>
</tbody>
</table>

$^a$VPT2 using CCSD(T)/AV(T+d)Z level of theory.
Table S5: The calculated vibrational transition frequencies and intensities for C\textsubscript{1}-S\textsubscript{2}O\textsubscript{2} Vibrational frequencies are in cm\textsuperscript{-1} and calculated intensities in parenthesis are in km/mol.

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Matrix-isolation IR spectroscopy.\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VPT2\textsuperscript{a}</td>
<td>Wu \textit{et al.} 2018\textsuperscript{b}</td>
</tr>
<tr>
<td>(\nu_1)</td>
<td>1255 (180)</td>
<td>1266 (339)</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>796 (40)</td>
<td>803 (58)</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>557 (26)</td>
<td>559 (29)</td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>456 (29)</td>
<td>459 (55)</td>
</tr>
<tr>
<td>(\nu_5)</td>
<td>411 (12)</td>
<td>417 (20)</td>
</tr>
<tr>
<td>(\nu_6)</td>
<td>271 (0.4)</td>
<td>272 (0.8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experiments by Wu \textit{et al.} with the intensities normalized relative to the most intense transition.\textsuperscript{[16]} \textsuperscript{b}VPT2 (this work) using CCSD(T)/AV(T+d)Z level of theory. \textsuperscript{c}CCSD(T)-F12b/VTZ-F12 calculated with anharmonicity.\textsuperscript{[16]}

S5 Supplementary Matrix-isolation FTIR Spectra

Here we show an expanded view of the matrix-isolation FTIR spectra (1100 cm\textsuperscript{-1} to 1170 cm\textsuperscript{-1}) which includes the \(\nu_1\) SO\textsubscript{2} region, see Figures S4 and S5. We made sure to record spectra of mixtures of SO\textsubscript{2} and argon without microwave discharging to confirm that all signals assigned to SO\textsubscript{2} here were present in the undischarged spectra, and that none of the signals belonging to \(3\)\textsuperscript{SO}, S\textsubscript{2}O or OSSO were present in the undischarged spectra. The assignment of signals belonging to cis- and trans-OSSO are discussed in the main text. The assignment of the (stable) \(3\)\textsuperscript{SO} signal is in agreement with Salama \textit{et al.}\textsuperscript{[17]} and Wu \textit{et al.},\textsuperscript{[16]} while the metastable \(3\)\textsuperscript{SO} site signal appers to be novel to the best of our knowledge.\textsuperscript{[18,19]} The assignment of the four signals attributed to the \(\nu_1\) transition in the SO\textsubscript{2} monomer is based on the literature.\textsuperscript{[20]} We note that the broad features in the region around 1150 cm\textsuperscript{-1} can be attributed to SO\textsubscript{2} clustering, which Ito \textit{et al.}\textsuperscript{[20]} discuss in detail. Assignment of the \(\nu_1\) \(^{34}\)SO\textsubscript{2} signal was based on the work by Nxumalo \textit{et al.}\textsuperscript{[21]} and the two signals belonging to S\textsubscript{2}O are assigned based on the work by Lo \textit{et al.}\textsuperscript{[22]} and Hopkins \textit{et al.}\textsuperscript{[23]}
Figure S4: Matrix-isolation FTIR spectrum of SO$_2$:Ar at a 1:500 ratio. The spectra are offset for clarity. Sample was deposited at a rate of 0.9 mmol/h while subjected to a microwave discharge power set to 50 W. The temperature was set to T=12 K both during deposition and the recording of spectra. See text for details on assignments.
Figure S5: Matrix-isolation FTIR spectrum of SO$_2$:Ar at a 1:2000 ratio. The spectra are offset for clarity. Sample was deposited at a rate of 1.1 mmol/h while subjected to a microwave discharge power set to 60 W. The temperature was set to $T=6$ K both during deposition and the recording of spectra. See text for details on assignments.
S6 $^3$SO + $^3$SO rate constant

For the $^3$SO self-reaction

$$^3\text{SO} + ^3\text{SO} \rightarrow \text{OSSO} \quad (S22)$$

the potential energy surface (PES) was sampled using VRC-TST with unrestricted M06-L/jun-cc-pv(D+d)z to get $\mu$VTST rate constants. The number of points per step was set to 500 in the Monte-Carlo sampling procedure and the potential energy surface was sampled between in distances of 3.0 Å and 7.0 Å with a step size of 0.2 Å between the center of mass of the two SO units. The reported Monte-Carlo sampling error is less than 1%. The resulting rate constant calculated at different temperatures can be seen in Table S6. Note that these numbers assume that all $^3$SO + $^3$SO collisions result in an overall spin singlet state, which is not true. According to spin statistics 1 in 9 times the overall spin will be a singlet, while for 3 in 9 it will be a triplet and finally 5 in 9 will result in a quintet.$^{[24]}$ Thus to account for this the rate constant has to be multiplied by a factor of 1/9 to account for this. Alternatively, if the spin triplet PES is assumed to contribute to OSSO formation at the same rate as the singlet, the rate constant has to be multiplied by a factor of $(1/9 + 3/9) = 4/9$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{\mu\text{VTST}}$ (molecule$^{-1}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$4.00 \times 10^{-11}$</td>
</tr>
<tr>
<td>250</td>
<td>$3.89 \times 10^{-11}$</td>
</tr>
<tr>
<td>300</td>
<td>$3.83 \times 10^{-11}$</td>
</tr>
<tr>
<td>350</td>
<td>$3.80 \times 10^{-11}$</td>
</tr>
<tr>
<td>400</td>
<td>$3.79 \times 10^{-11}$</td>
</tr>
<tr>
<td>500</td>
<td>$3.77 \times 10^{-11}$</td>
</tr>
<tr>
<td>600</td>
<td>$3.65 \times 10^{-11}$</td>
</tr>
<tr>
<td>700</td>
<td>$3.54 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Summarily, the $k_\infty$ rate constant, where spin statistics has been accounted for at T=245 K is thus $k_\infty^{\text{Singlet}} = 4.3 \times 10^{-12}$ molecule$^{-1}$ cm$^3$ s$^{-1}$ or $k_\infty^{\text{Singlet+triplet}} = 1.7 \times 10^{-11}$ molecule$^{-1}$ cm$^3$ s$^{-1}$. 
S7  \(^3\)SO formation from SO\(_2\) photochemistry

To calculate the photo-excitation rate of SO\(_2\) we use the equation

\[
J = \int_{\lambda_1}^{\lambda_2} F(\lambda) \times \sigma(\lambda) \times \Phi(\lambda) d\lambda. \tag{S23}
\]

Where \(F(\lambda)\) is the actinic flux, \(\sigma(\lambda)\) the absorption cross-section of the molecule and \(\Phi(\lambda)\) is the quantum yield. The actinic flux for the Venusian middle atmosphere is from Zhang et al. 2012.\(^{25}\) Note that the original data corresponds to a 45\(^\circ\) latitude. The absorption cross section for SO\(_2\) is taken from Manatt & Lane 1993 and accessed via the MPI-Mainz UV/VIS Spectral Atlas.\(^{4,26}\) The quantum yield is set to \(\Phi = 1\) for each photon absorption process within the indicated wavelength range and zero otherwise in accordance with Hu et al. 2012.\(^{27}\)

\[
\text{SO}_2 + h\nu(<220 \text{ nm}) \rightarrow \text{SO} + \text{O}. \tag{S24}
\]

\[
\text{SO}_2 + h\nu(220 - 340 \text{ nm}) \rightarrow ^1\text{SO}_2 \left(^1\text{B}_2/ ^1\text{A}_2\right). \tag{S25}
\]

\[
\text{SO}_2 + h\nu(340 - 400 \text{ nm}) \rightarrow ^3\text{SO}_2 \left(^3\text{B}_1\right) \tag{S26}
\]

The resulting altitude dependent \(J\) value for each process is given in Figure S6.
Figure S6: Altitude dependent $J$ values for SO$_2$: Direct dissociation (blue), excitation to the singlet state (red) and excitation to the triplet (yellow).

The set of reactions used to calculate $^3$SO production and their rate constants are given in Table S7. This reaction list is similar to those in earlier work by Krasnoposlky and Parshev concering excited state SO$_2$ chemistry.$^{[28,29]}$
Table S7: List of reaction processes involved in production of $^3\text{SO}$ from $\text{SO}_2$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{SO}_2 \rightarrow \text{SO}_2 + h\nu$</td>
<td>$a_k_1$</td>
<td>$2.2 \times 10^4 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^1\text{SO}_2 \rightarrow ^3\text{SO}_2$</td>
<td>$a_k_2$</td>
<td>$1.5 \times 10^3 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^1\text{SO}_2 + \text{M} \rightarrow \text{SO}_2 + \text{M}$</td>
<td>$b_k_3$</td>
<td>$1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^1\text{SO}_2 + \text{M} \rightarrow ^3\text{SO}_2 + \text{M}$</td>
<td>$b_k_4$</td>
<td>$1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^1\text{SO}_2 + \text{SO}_2 \rightarrow \text{SO} + \text{SO}_3$</td>
<td>$c_k_5$</td>
<td>$4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^3\text{SO}_2 \rightarrow \text{SO}_2 + h\nu$</td>
<td>$d_k_6$</td>
<td>$1.1 \times 10^3 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^3\text{SO}_2 + \text{M} \rightarrow \text{SO}_2$</td>
<td>$e_k_7$</td>
<td>$2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^3\text{SO}_2 + \text{SO}_2 \rightarrow ^3\text{SO} + \text{SO}_3$</td>
<td>$e_k_8$</td>
<td>$8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$^3\text{SO}_2 + \text{CO} \rightarrow ^3\text{SO} + \text{CO}_2$</td>
<td>$f_k_9$</td>
<td>$1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>

Overview of reactions can be found in Whitehill & Ono 2012 and Turco et al. 1982. Specific rate constant references: $^a$Rao et al. 1969, $^b$Calvert et al. 1978, $^c$Chung et al. 1975, $^d$Otsuka & Calvert 1971, $^e$Su et al. 1977, $^f$Jackson & Calvert 1971. The fluorescence lifetime actually depends on excitation wavelength and has both a short- and long-lived component, see the review by Heicklen et al. 1980 for a detailed discussion of this. Here, for simplicity, just one value is used just as both Whitehill & Ono 2012 and Turco et al. 1982 does.

The steady-state approximation is used both for the $^1\text{SO}_2$ and $^3\text{SO}_2$ excited states:

\[
\frac{d[^1\text{SO}_2]}{dt} = 0 = J_{\text{singlet}}[^\text{SO}_2] - k_1[^1\text{SO}_2] - k_2[^1\text{SO}_2] - k_3[^1\text{SO}_2][M] - k_4[^1\text{SO}_2][M] - k_5[^1\text{SO}_2][\text{SO}_2] \quad \rightarrow \\
[^1\text{SO}_2] = \frac{J_{\text{singlet}}[^\text{SO}_2]}{k_1 + k_2 + k_3[M] + k_4[M] + k_5[\text{SO}_2]} 
\]

\[
\frac{d[^3\text{SO}_2]}{dt} = 0 = J_{\text{triplet}}[^\text{SO}_2] + k_2[^1\text{SO}_2] + k_4[^1\text{SO}_2][M] - k_6[^3\text{SO}_2] - k_7[^3\text{SO}_2][M] - k_8[^3\text{SO}_2][\text{SO}_2] - k_9[^3\text{SO}_2][\text{CO}] \quad \rightarrow \\
[^3\text{SO}_2] = \frac{J_{\text{triplet}}[^\text{SO}_2] + k_2[^1\text{SO}_2] + k_4[^1\text{SO}_2][M]}{k_6 + k_7[M] + k_8[\text{SO}_2] + k_9[\text{CO}]} 
\]

S21
To proceed the number density of the Venusian atmosphere, M, and concentration of SO$_2$ and CO are all needed. These have all been obtained from digitizing the figures in Zhang et al. 2012.[25]

Note that the CO concentration from 58 to 80 km altitude remains virtually constant in their model at 45 ppm. It should also be mentioned that their model is set to a latitude of 70°. The photochemical production of $^3$SO from SO$_2$ contains a direct dissociation pathway, a singlet pathway and two triplet pathways

$$\frac{d[^3\text{SO}]}{dt} = J_{\text{dissoc}}[^1\text{SO}_2] + k_5[^1\text{SO}_2][\text{SO}_2] + k_8[^3\text{SO}_2][\text{SO}_2] + k_9[^3\text{SO}_2][\text{CO}].$$  \hspace{1cm} (S29)

We assume that all SO formed in a singlet state decays to its ground-state (triplet). This assumption is needed for equation S29 to be valid.
References


(31) Turco, R. P.; Whitten, R. C.; Toon, O. B. Stratospheric aerosols: Observation and theory. 


(37) Jackson, G. E.; Calvert, J. G. Triplet sulfur dioxide-carbon monoxide reaction excited with the SO$_2$(^1$A_1$) → SO$_2$(^3$B_1$) "forbidden" band. *Journal of the American Chemical Society* **1971**, *93*, 2593–2599.