Rovibrational bound states of SO₂ isotopologues. II: Total angular momentum $J=11$ –20

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Abstract

In a two-part series, the rovibrational bound states of SO₂ are investigated in comprehensive detail, for all four stable sulfur isotopes ^{32–34,36}S. All low-lying rovibrational energy levels—both permutation-symmetry-allowed and not allowed—are computed, for all values of total angular momentum in the range $J=0$ –20. The calculations have been carried out using the *ScalIT* suite of parallel codes. The present study (Paper II) examines the $J=11$ –20 rovibrational levels, providing symmetry and rovibrational labels for every computed state, relying on a new *lambda-doublet splitting* technique to make completely unambiguous assignments. Isotope shifts are analyzed, as is the validity of “*J*-shifting” as a predictor of rotational fine structure. Among other ramifications, this work will facilitate understanding of mass-independent fractionation of sulfur isotopes (S-MIF) observed in the Archean rock record—particularly as this may have arisen from self shielding. S-MIF, in turn is highly relevant in the broader context of understanding the “oxygen revolution.”

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1. Introduction

Isotope effects have long been used as a standard research tool in many areas of science, including chemical and biological applications, geochemistry, electrochemistry, radiation chemistry, transport processes, and many more [1, 2, 3]. Within chemistry, isotopic analysis is closely linked to molecular structures, vis-à-vis vibrational and rotational spectroscopy. Almost always in this context, one encounters “mass-dependent” isotopic fractionation (MDF): heavier masses lead to monotonically smaller zero-point energies (ZPEs), vibrational frequencies, and rotational constants—and correspondingly larger partition functions. The impact on reaction equilibrium and rate constants is well understood, with these quantities also adhering to a straightforward monotonic MDF pattern.

The sulfur dioxide (SO₂) molecule—even when highly rovibrationally excited, as is the case considered here—is no exception. Nevertheless, highly accurate and comprehensive calculations of the rovibrational states of SO₂ are regarded as key for resolving one of the most important examples of mass-independent fractionation (MIF) of current interest [4]. To wit, in the year 2000, a startling and unexpected discovery was

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made with regard to sulfur MIF (S-MIF) in the rock record: namely, S-MIF is significant in Archean eon rocks older than 2.4 billion years [5, 6, 7, 8, 9, 10, 11, 12, 13], but almost completely absent in younger rocks. This finding is particularly propitious, given that it corresponds perfectly with the “oxygen revolution”—a seminal moment in the history of the Earth, giving rise to higher life forms as well as a host of other important geological and climatological changes. As such, the oxygen revolution or “great oxygenation event” is a subject of great interest to many scientific disciplines and funding agencies, including NASA’s Astrobiology program.

The occurrence of MIF in nature is so rare it is often called “anomalous.” There are very few known natural sources of MIF, which offers hope that the S-MIF observed in the Archean rock record (specifically, in Archean sulfide and sulfate samples) may ultimately admit an unambiguous mechanistic explanation. One primary motivation for pursuing this is the promise of new insights—both qualitative and quantitative—into the composition of the paleoatmosphere as a function of time [5]. In any event, Farquhar *et al.* have proposed that S-MIF might have originated from SO_2 photolysis in the atmosphere, at a variety of wavelengths [6]. This has come to be regarded, in broad brush-stroke terms, as the most likely explanation—although precise mechanistic details, necessary for the S-MIF signal to serve as a true proxy for conditions in the paleoatmosphere, are still lacking. Indeed, the passage of time seems only to have raised more possibilities. Thus for example, whereas for some time a predissociation mechanism involving the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ singlet transition in the 190–220 nm UV range was considered the most likely source of S-MIF, recent work by Whitehill *et al.* [8] suggests an alternative mechanism in the 250–350 nm range, involving intersystem crossing with the triplet states.

A completely unambiguous explanation of the origin of S-MIF in SO_2 photodissociation will no doubt require a detailed and accurate understanding of the ground and excited electronic state potential energy surfaces (PESs), together with non-adiabatic and spin-orbit couplings as well as transition dipole moments. These are being actively pursued, in ongoing efforts conducted in collaboration with expert colleagues. Meanwhile, however, we can still make very substantial progress on the S-MIF problem using existing ground state PESs. In the present two-part study (the first part [14] will be referred to as “Paper I”) we focus on the SO_2 rovibrational states, as these likely play a critical role in the origin of S-MIF despite their own highly MDF character. This is because S-MIF might be substantially influenced by the individual (and isotope-dependent) placement of rovibronic levels, and the resultant effect on the fine structure of the absorption spectra.

One such proposed S-MIF avenue is the “self-shielding hypothesis” [4, 9, 10, 15]: as radiation from the sun passes through the Earth’s atmosphere, $^{32}\text{SO}_2$ —by far the most abundant isotopologue—absorbs almost all of the UV photons at the frequencies needed for its own photodissociation. As a consequence, the other SO_2 isotopologues are preferentially photodissociated near the Earth’s surface. Assessing the viability of the self-shielding hypothesis depends on a detailed elucidation of the SO_2 rovibrational and rovibronic levels, at a level of precision that completely and unambiguously resolves all rotational splittings and isotope shifts. Although there are many other S-MIF and non-S-MIF-related contexts in which accurate modeling of the high-resolution rovibrational spectrum of SO_2 turns out to be important (e.g. atmospheric and astrophysical applications; see Paper I for a more detailed description), in this paper we focus primarily on self shielding. In particular, *with the results obtained here, we can already start providing unambiguous answers to questions posed in previous self-shielding studies*—thus directly addressing the assumptions made therein.

The prerequisite and most immediate objective, however, is to compute, assign, report, and analyze the rovibrational levels of SO_2 . We therefore continue, in this paper, our comprehensive analysis of the bound rovibrational states of SO_2 begun in Paper I, for all four sulfur-varying isotopologues (i.e. for ^{32}S , ^{33}S , ^{34}S , and ^{36}S). Whereas Paper I considered all J values ranging from 0–10, here we consider the $11 \leq J \leq 20$ case, again addressing every J value in this range explicitly. We use spectroscopically accurate quantum dynamics, i.e. no approximations are employed beyond Born-Oppenheimer. In particular, all rotation-vibration or “Coriolis” coupling is treated exactly. This is numerically much more difficult here than in Paper I, given the larger J values. Nevertheless, the expanded J range is necessary in order to adequately address the question of SO_2 self shielding (Sec. 2) [9, 10, 13, 14].

A discussion and identification of the major spectral patterns and trends is also provided here, especially

as these may relate to self shielding. In addition to understanding isotope shifts, the role of J and K splitting in the rotational fine structure is also examined—as is that of a new kind of *lambda-doublet splitting*. The latter feature has rarely (if ever!) been considered in the previous literature, because it only manifests in an exact Coriolis treatment for which Coriolis coupling is nevertheless relatively small (usually in that context, approximations are used). Lambda-doublet splitting nevertheless plays a vitally important role here, both with regard to analyzing self shielding, as well as the more fundamental goal of providing completely unambiguous state labels. Indeed, the latter task would be impossible in the $11 \leq J \leq 20$ range *without* relying on lambda-doublet splitting—yet this extremely useful technique has, to our knowledge, not been considered prior to Paper I. In any event, here, it enables us to adopt a “zero-tolerance policy,” wherein all potential ambiguity in our state labels is completely eliminated. That some labeling ambiguity still remains in the current literature, despite the highly regular nature of SO_2 , has recently been made clear—e.g., in a discussion [16] of incorrectly assigned states from the HITRAN database [17, 18]. There may yet be others; in any event, an independent check such as that provided here is certainly worthwhile.

SO_2 has a great many rovibrational states—even when considering just those that might be relevant for S-MIF. We therefore need to be able to compute many rovibrational energy levels accurately and efficiently. To this end, we continue to use the *ScalIT* suite of parallel codes as our work horse, as described in Paper I [14]. *ScalIT* employs a combination of the following techniques: (i) phase-space optimized discrete variable representation (PSO DVR) [19, 20, 21]; (ii) preconditioned inexact spectral transform (PIST) [22, 23, 24, 25]; (iii) optimal separable basis (OSB) [26, 27, 28]. *ScalIT* also offers massive parallelization—a necessity, given the sheer number of states to be computed, in addition to the numerical difficulty. A more detailed description of these methods is beyond the scope of this paper but is discussed in Paper I [14] and the above citations.

The remainder of this paper is organized as follows. In Sec. 2, the previous literature regarding SO_2 self shielding is summarized, by way of motivating some of the specific details of this study—e.g., the range of energies and J values considered. In Sec. 3, a basic theoretical framework is presented, along with computational details of the rovibrational calculations performed. In Sec. 4, the bound rovibrational energy levels for all SO_2 isotopologues are presented, and trends with respect to isotope shifts, vibrational excitation, J , K , and lambda-doublet splitting, are discussed. A final summary is provided in Sec. 5.

2. Motivation and Background

High resolution experimental absorption spectra for the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ singlet electronic transition of $^{32}\text{SO}_2$ have been obtained at 213 K in the relevant UV range by Freeman *et al.* [9, 10, 15, 29]. The spectrum exhibits very narrow ($\sim 0.1 \text{ cm}^{-1}$), clearly-resolved rovibronic features, reflecting long-lived resonances (100 ps or more) consistent with a predissociation mechanism. This aspect is critically important for self shielding, because it suggests that different isotopologues may well absorb photons of different frequencies. Since isotope shifts are on the order of tens of cm^{-1} (see below), self shielding would certainly not be viable if the spectrum were broader and rovibronic features were not resolved—as is the case, e.g., for H_2S , which is not considered a likely source of S-MIF, in part for this reason.

The strongest bands in the $^{32}\text{SO}_2$ absorption spectrum correspond to the $(1, \nu'_2, 2) \leftarrow (0, 0, 0)$ progression, as is also confirmed in a theoretical simulation conducted by Ran *et al.* [15]. The vibronic band origins computed in the Ran *et al.* study agree very well with experiment, typically to within a few cm^{-1} . Moreover, the latter authors also computed isotope shifts for the $^{33}\text{SO}_2$, $^{34}\text{SO}_2$, and $^{36}\text{SO}_2$ isotopologues. This represents an important contribution, as high-resolution experimental data for the rare isotopologues is not available (although lower-resolution, isotope-resolved spectra have since been published [30]). On the other hand, the computed fine structure does not agree even qualitatively with experiment, as the latter exhibits quite well resolved rovibronic features, whereas the Ran *et al.* simulation considered only pure vibration states (i.e. no rotation).

To summarize, the isotope shifts for the relevant vibronic band origins are on the order of tens of cm^{-1} . Self shielding relies on there being fine structure spectral features that do *not* overlap, upon isotopic substitution. This question cannot be adequately addressed via the experimental study of Freeman *et al.* alone (because only one isotopologue was considered) nor in the theoretical study of Ran *et al.* alone (because

no rotational states were considered). Nevertheless by combining these two studies—specifically, by red-shifting the experimental spectrum using the isotope shifts computed in [15]—then at least a preliminary assessment of self shielding can be made. This is the approach that was adopted by Lyons [9, 10, 13], who concluded that self shielding may indeed constitute a plausible S-MIF source. However, he also lists several reasons why a definitive conclusion still remains out of reach. The list appears below (together with our own additions):

1. Less prominent vibronic progressions not included.
2. Anharmonicity/isotope-shift-nonlinearity mostly ignored.
3. Experimental data (213 K) reduces significance of hot bands.
4. Rotational fine structure of various isotopologues not considered.
5. Insufficient accuracy in the PESs and transition dipole surfaces.

Although clarified by the present calculations and those of Paper I, 1. and 2. will be primarily discussed elsewhere.

Regarding 3., it is clear that many rovibrational states of SO_2 are accessible at atmospherically relevant temperatures around ~ 300 K. However, only the (0, 0, 0) state was considered in [15], and even the 213 K experimental data also underestimates the role of hot bands. To ensure that the full range of atmospherically relevant states are considered, in the present study we compute rovibrational states excited up to ~ 2000 cm^{-1} . Also, an analysis of the experimental 213 K spectrum [29] reveals that transitions beyond $J \approx 12$ do not contribute appreciably to the absorption spectrum. The $J \leq 20$ calculations performed here should therefore suffice for realistic paleoatmospheric conditions.

Regarding 4., Lyons and others [4, 9, 10, 31] have advocated strongly for the need for accurate SO_2 rovibrational state calculations across the four sulfur-varying isotopologues, *thus motivating the present study*. Although rotational fine structure is evident in the experimental $^{32}\text{SO}_2$ absorption spectrum, in the absence of accurate theoretical calculations, it is difficult to disentangle individual rotational lines from other spectral features. A J -shifting approach might be employed (Sec. 3.2), wherein rotation and vibration are presumed to be perfectly decoupled, and the rotational energy contribution corresponds to a rigid (usually symmetric) rotor. This would represent an improvement over the Lyons strategy, in that the rotational fine structure would indeed exhibit isotope dependence beyond a simple vibronic band shift. However, the only completely reliable approach is to compute the rovibrational states exactly, as is done in this paper. One can then use the exact results to assess the validity of J -shifting, as is also considered here.

One prerequisite for computing accurate rovibrational energy levels is, of course, the availability of an accurate ground state PES. In this work we use the full variational Kauppi and Halonen (FVKH) PES [32], as this empirically fit PES yields very good agreement with the experimental data, to within a few cm^{-1} [14, 17, 18, 33, 34, 35, 36, 37, 38, 39]. A recent empirically fit PES due to D. W. Schwenke and coworkers [16] has achieved excellent, subwavenumber experimental agreement. Unfortunately, according to one of the authors of this “Ames1” PES, we cannot employ it ourselves, owing to the fact that the semiempirical refinement that they used was hard-wired to the Ames VTET rovibrational program, and will therefore lead to much less experimentally accurate results when used in conjunction with a more accurate rovibrational code such as *ScalIT* [40]. Moreover, there may still be misassigned experimental energy levels, as discussed. In any event, a much more comprehensive description of the FVKH PES, and a comparison with other available ground electronic state $\tilde{X}^1A_1$ ($1^1A'$) PESs, is given in Paper I [14]. Here, we simply point out that *the accuracy of the FVKH PES is sufficient to describe the vibronic spectrum and isotope shifts quantitatively well enough that an assessment of long-standing unresolved questions about self shielding can now be made*. This already represents a great advance beyond the present state of the art.

All of the above deficiencies except for 5., then, are remedied here (and in Paper I). This work will therefore greatly improve the current understanding of SO_2 self shielding. Moreover, 5. will be addressed in future publications, as the requisite PESs and coupling/transition surfaces, accurate to 1 cm^{-1} , are currently under development. In this endeavour, our strategy is similar to that employed by D. W. Schwenke and coworkers [16, 41] to achieve the excellent agreement described above. Namely, we will introduce minimal semiempirical corrections into an already very high-level *ab initio* PES—using *ScalIT*, and drawing from a broad range of *rovibrational* experimental spectral lines.

3. Theory and computational details

3.1. Exact rovibrational problem

The detailed theory for computing rovibrational energy levels and wavefunctions of triatomic molecules can be found in Paper I and elsewhere [42]. We repeat only a few of the essentials here. In Jacobi coordinates, the full dimensional Hamiltonian ($\hbar=1$) for a triatomic AB₂ molecule (such as SO₂) in the body-fixed reference frame can be expressed as

$$\hat{H} = -\frac{1}{2m_r} \frac{\partial^2}{\partial r^2} - \frac{1}{2M_R} \frac{\partial^2}{\partial R^2} + \frac{1}{2m_r r^2} \vec{J}^2 + \frac{1}{2M_R R^2} (\vec{J} - \vec{j})^2 + V(r, R, \theta), \quad (1)$$

where r represents the O–O separation, R the separation between the S atom and the O₂ center of mass, and m_r and M_R are the corresponding reduced masses. Likewise, $\vec{j}$, and $(\vec{J} - \vec{j})$ are the corresponding angular momenta, with $\vec{J}$ the total angular momentum. Since the latter quantity is conserved, both J and M (associated with the space-fixed Z component) are good quantum numbers, as is the total parity, $p = \pm 1$.

As in Paper I [14], PSO DVRs [19, 20, 21] are used as the basis functions for the radial coordinates (labeled v_1 and v_2 respectively), and parity-adapted associated Legendre functions are used as basis functions for θ [see, e.g., Eq. (4) in Paper I]. The latter are labeled (j, K) , where K is associated with the body-fixed z component of $\vec{J}$. Note that K is not a good quantum number, although only adjacent K values are coupled together, via Coriolis coupling.

In this representation, the Hamiltonian matrix takes the form

$$\begin{aligned} H^{JMp} &= H^{JMK} \left(\frac{1 + p\delta_{K0}}{1 + \delta_{K0}} \right) \delta_{K,K'} \\ &- \left[\frac{\lambda_{JK}^+ \lambda_{jK}^+}{2M_R R_{v_2}^2} \sqrt{1 + p\delta_{K0}} \delta_{K+1,K'} + \frac{\lambda_{JK}^- \lambda_{jK}^-}{2M_R R_{v_2}^2} \sqrt{1 + p\delta_{K1}} \delta_{K-1,K'} \right] \delta_{v_1,v_1'} \delta_{v_2,v_2'} \delta_{j,j'}, \end{aligned} \quad (2)$$

where

$$\lambda_{JK}^\pm = \sqrt{J(J+1) - K(K \pm 1)}, \quad (3)$$

$$\lambda_{jK}^\pm = \sqrt{j(j+1) - K(K \pm 1)}, \quad (4)$$

and the second line of Eq. (2) represents the Coriolis coupling. (Consult Paper I for further details).

3.2. J -shifting

If K is a “nearly” good quantum number, then the Coriolis coupling in Eq. (2) is small, and might be ignored. One then obtains an approximate separation between rotation and vibration, albeit one for which the H^{JMK} Hamiltonian blocks still depend on the value of K . The resultant approximate rovibrational eigenstate wavefunctions then become a product of vibration-like functions and symmetric rigid rotor functions. This is known as the “centrifugal sudden” (CS) approximation [42]. In contrast, J -shifting (JS) represents a more severe approximation, in which the rovibrational energies are presumed to be a sum of pure vibration plus pure rotation contributions. The former are taken to be the eigenvalues of the pure vibration Hamiltonian H^{000} , whereas the latter are presumed to adhere to a standard rigid rotor form.

JS methods often presume a symmetric rigid rotor, even if the molecular geometry corresponds to an asymmetric top, in terms of the moments of inertia. Thus,

$$E_{vJK}^{J\text{-shift}} = E_v + E_{JK}^{\text{rot}}, \quad \text{where} \quad (5)$$

$$E_{JK}^{\text{rot}} = (A - B)K^2 + BJ(J + 1), \quad (6)$$

$E_{vJK}^{J\text{-shift}}$ is the JS approximate rovibrational energy, E_v is the vibrational energy, and E_{JK}^{rot} is the rotational energy. The latter depends on the two rotational constants, A and B , and on the rotational state labels, (J, K) . For a highly prolate symmetric rotor such as SO₂, $A \gg B$ [43, 44, 45, 46, 47, 48].

The practice of using symmetric rotor energies even for asymmetric tops can be justified based on the form of the above CS H^{JMK} blocks, as examined in depth in a recent paper [49]. In that article, the focus was on predicting accurate JS rotational constants *a priori*, i.e. without knowledge of the true rovibrational energies. In this paper, in order to cast JS in the most favorable possible light, we fit symmetric rotor constants A and B to the exact rovibrational energy levels of Eq. (2). This procedure requires unambiguous K label assignments—which is in fact possible for SO_2 , owing to its highly prolate nature, and the fact that the Jacobi body-fixed z axis aligns very closely with the smallest moment of inertia (i.e., Coriolis coupling is relatively small). In this manner, we assess whether JS is sufficiently accurate to address the question of SO_2 self shielding.

3.3. Lambda-doublet splitting

A very closely related issue is that of *lambda-doublet splitting*, introduced in Paper I. Note that for both the CS [Eq. (2)] and JS [Eq. (6)] approximations, there is a degenerate doublet associated with $\pm K$, for $|K| > 0$. In the true rovibrational energy levels, this degeneracy is lifted slightly by parity—much like the lambda-doublet splitting that occurs in diatomic molecular spectroscopy. From Eq. (2), it is clear that the Hamiltonian matrix representations for the two $p = \pm 1$ parities differ only by the presence of the H^{JM0} block, and its Coriolis coupling to the adjacent H^{JM1} block. If K is an approximately good quantum number—i.e., good enough to label the rovibrational states, as is the case here—then for any given exact rovibrational state, most of the wavefunction probability will be associated with a single K value, $K = \bar{K}$. Although all K blocks contribute, one can expect something like an exponential decay in wavefunction probability with respect to $|K - \bar{K}|$.

What are the ramifications for lambda-doublet splitting? Since the opposite-parity Hamiltonians differ only near $K = 0$, then the opposite-parity $\bar{K}$ states should be nearly identical for sufficiently large $\bar{K}$. Moreover, the magnitude of the lambda-doublet splitting should decrease exponentially or so with $\bar{K}$. Finally, since the magnitude of the Coriolis coupling between H^{JM0} and H^{JM1} is proportional to $\sqrt{J(J+1)}$, one expects a corresponding J dependence for the magnitude of the lambda-doublet splitting. These trends have already been clearly observed in Paper I, and continue to be seen here as well.

For purposes of this paper, lambda-doublet splitting plays two very important but different roles. First, it is an inherently Coriolis-coupling-based phenomenon, meaning that *no* CS or JS-based approximation will ever be able to simulate it. Thus, if the magnitude of the lambda-doublet splitting ever exceeds, say, a few cm^{-1} , then *these approximations will not be viable for purposes of evaluating self shielding*. Second, because of the highly prolate nature of SO_2 , $(A - B) \gg B$, leading to overlap in the rovibrational bands for sufficiently large $\bar{K}$. One can already start to see this in Paper I for the higher $J \approx 10$ calculations considered there. However, for the $11 \leq J \leq 20$ case considered here, the band overlap is much more pronounced. Thus, in order to unambiguously distinguish the high- $\bar{K}$ states of one vibrational band from the low- $\bar{K}$ states of the next excited band, *a lambda-doublet splitting analysis proves extremely useful—and indeed, even indispensable*.

3.4. Computational details

The SO_2 rovibrational bound state energy level calculations were performed using **ScalIT**—a suite of quantum dynamics codes designed for massively parallel computing architectures. **ScalIT** is particularly well suited for rovibrational bound state calculations, but it can also be used to compute resonance states and scattering quantities. It offers a number of predefined high-level modules for triatomic and tetraatomic calculations, though it is designed for more general use. A discussion of how the **ScalIT** codes are used to compute triatomic AB_2 rovibrational bound states is provided in Paper I.

For this work, SO_2 rovibrational energy levels were computed for every J value in the range $J=11$ –20, and for all four sulfur-varying isotopologues. Both permutation-symmetry-allowed (physical) and not allowed (unphysical) states were computed. The energy levels were converged to 10^{-5} cm^{-1} or better. In all cases, Coriolis coupling was treated exactly. The relevant coordinate ranges used to generate the PSO DVR basis sets, the one-dimensional basis sizes, and associated convergence parameters, are all given in Table 1. These are identical to those used in Paper I, although separate convergence tests were conducted

for the $J=11$ – 20 calculations performed here. Also, the total basis sizes are much larger than in Paper I (up to $\sim 3.3 \times 10^6$), owing to the larger J values and K ranges. The computed zero-point energies for all four isotopologues ($^{32}\text{SO}_2$, $^{33}\text{SO}_2$, $^{34}\text{SO}_2$, and $^{36}\text{SO}_2$) are also listed in Table 1. Since the system and FVKH PES are the same as in Paper I [14], the effective radial potentials, $V_r(r)$ and $V_R(R)$, are also the same as were used in Paper I (the interested reader is referred to Sec. 3.3 and Fig. 1 of Paper I).

The *ScalIT* calculations were run on three separate computing clusters. Most of the calculations were performed on Hrothgar, a 640 node (7680 cores) cluster, administered by the Texas Tech University (TTU) High Performance Computing Center. Each Hrothgar node contains two Westmere 2.8 GHz 6-core processors with 24 GB host memory. The Robinson cluster, administered by the TTU Department of Chemistry, was also used. Robinson has 96 compute nodes, each with 48 GB of memory and two 6-core 2.67 GHz Xeon X5650 processors. Lonestar, administered by the Texas Advanced Computation Center, has a similar architecture to Robinson (12 cores per node and low-latency, high-bandwidth Infiniband connectivity). Most calculations were done across 60 or 120 cores.

4. Results and discussion

4.1. Rovibrational states: $J=11$ – 20

As discussed, for this paper we computed the low-lying bound rovibrational energy levels of SO_2 for all total angular momentum values in the range $J=11$ – 20 . The $J=0$ – 10 energy levels were calculated in Paper I [14], but will also be considered here, e.g. in the determination of the rotational constants, A and B , and the assessment of JS. No previous calculations exist for comparison.

Unambiguous rotational and vibrational state assignments have been made for each computed state, and cross-checked against the permutation-inversion (PI) irrep labels to ensure accuracy. In this regard, the unphysical states are found to be extremely helpful, as is a lambda-doublet analysis based on inversion parity. Although K is not strictly a good quantum number, for every computed rovibrational level it is “good enough” for purposes of unambiguous labeling. Whereas in Sec. 3.3 we introduced $\bar{K}$ as the appropriate state label (in order to distinguish it from the rotational basis function or H^{JMK} Hamiltonian block label K), going forward we simply use ‘ K ’ as the state label, for simplicity. The distinction between the state label ‘ K ’ and the basis function ‘ K ’ should be clear from context.

The PI symmetry group for SO_2 has four irreps, labelled A^+ , A^- , B^+ , and B^- , where $A(B)$ denotes symmetric(anti-symmetric) permutation symmetry, and $+(-)$ denotes even(odd) inversion parity (system parity [42]). The physically allowed states are the A^+ and A^- states. For each J and parity value, the 30 lowest-lying rovibrational energy levels were obtained, from a single PIST window calculation. All rovibrational energies are reported in cm^{-1} , relative to the vibrational ground energy of $^{36}\text{SO}_2$, i.e. 1501.200334 cm^{-1} . Each calculation typically required around $L=139$ Lanczos iterations and $Q=11$ QMR iterations per Lanczos iteration to converge 30 states (see Paper I for an explanation of these parameters).

The full set of computed energy levels (about 4800 in all, not including the $J \leq 10$ states), presented in cm^{-1} to six digits past the decimal, can be found in the Supplementary Material, or obtained directly from the authors, on request. In this paper, only selected results are presented and discussed. In Tables 2–7, we list permutation-symmetry-allowed rovibrational energies, for both even and odd parity. The lowest-lying 30 energy levels are presented, for each irrep and isotopologue combination, for selected J values in the $11 \leq J \leq 20$ range (note that $n_i = v_i$).

Whereas the experimental accuracy of the FVKH PES [32] in relation to the low-lying vibrational states is well-documented, we note that a similar comparison with respect to the *rovibrational* states has never previously been made. Our first task, therefore, is to compare the rovibrational energy levels as computed here vs. those of previous experimental studies [16, 17, 18]. In Figure 1, the root mean square errors (σ_{rms}) between theory and experiment are presented in graphical form, for all of the $^{32}\text{SO}_2$ (0,0,0) rovibrational levels across the entire $J=1$ – 20 range considered here and in Paper I. Whereas the errors increase with J —from 0.0016 cm^{-1} for $J = 1$ to 0.285 cm^{-1} for $J = 20$ —they are still nevertheless very small throughout the relevant J range. The rovibrational errors are, in fact, less than the typical errors for the low-lying vibrational states, thus strongly justifying the use of the FVKH PES in the present rovibrational context.

A rovibrational energy level diagram for all $J=11$ – 15 is presented in Fig. 2 in the form of a line plot. Red solid lines indicate physically allowed states (A^+ and A^-) whereas blue dashed lines indicate unphysical states (B^+ and B^-). Rovibrational energy levels are presented relative to the $^{36}\text{SO}_2$ (0,0,0) vibrational ground state. The levels of lighter isotopologues always lie higher than the corresponding levels of heavier isotopologues, as expected based on MDF arguments. In fact, all of the energy levels exhibit a very clear MDF trend (Sec. 4.4) [14]. From Fig. 2, it is clear that there is no overlap in the lowest three vibrational bands, across the whole $J=11$ – 15 range. However, the rotational level spacing for the largest- K states does become quite large, i.e. on the order of 100 cm^{-1} . This is nearly comparable to the vibrational level spacing in the highest part of the spectrum that we have considered. On the other hand, the isotope shifts for these levels are comparatively quite small. In any case, it is clear that all vibrational bands above the lowest three exhibit significant overlap.

In the $J=16$ – 20 range, vibrational band overlap becomes significantly more pronounced—now encompassing even the lowest three bands, even though these are quite well separated energetically. This is clearly visible in Fig. 3, a line plot following the same conventions as in Fig. 2, but for $J=16$ – 20 . Assigning individual rovibrational lines to their appropriate vibrational bands—i.e., assigning (ν, K) labels—therefore becomes much more challenging than in the $J \leq 10$ calculation of Paper I. Nevertheless, we were able to unambiguously assign every level, using essentially a combination of lambda-doublet splitting and $(A - B)$ rotational constant fitting. Neither of these techniques on its own would have been able to avoid all labeling ambiguity, but the combination never fails (at least for this application).

The procedure works as follows. First, the $K = 0$ states are easily identified as those without a lambda-doublet partner. These are then used to define vibrational-state-dependent (VSD) B constants in Eq. (6). Next, a suitable VSD $(A - B)$ value is obtained by fitting the rovibrational states that lie between a given $K = 0$ state and the next $K = 0$ state, as all of these must be $K > 0$ states that belong to the vibrational band ν of interest. Finally, both VSD rotational constants A and B are used in Eq. (6) to extrapolate the (ν, K) states up to $K = J$ and into the overlapping region with the next vibrational band. We provide a few plots for $J = 15$ $^{36}\text{SO}_2$ in the Supplementary Material.

Of course, there may be accidental near-degeneracies that prevent the above procedure from being 100% reliable. In the present calculation, this happens, for instance, for the $\nu = (0, 2, 0), K = 11$ and $\nu = (1, 0, 0), K = 7$ states. In such cases, the regular, exponential decay of the lambda-doublet splitting with respect to K —which, in any event, itself allows for nearly unambiguous K labeling—is used as an independent check.

Finally, all symmetry properties based on the PI irrep labels—applied to both the physically allowed and unphysical states—are also fully exploited to aid in proper state labeling. For each ν and J value, there are a total of $(2J + 1)$ associated rovibrational levels, (ν, K) . For even (odd) J values, $(J + 1)$ of these are associated with the even(odd) parity irreps, and the other J levels with the odd(even) parity irreps. Since K is in fact a parity-adapted quantum number, the first category corresponds to K values in the range $0 \leq K \leq J$, and the second to $1 \leq K \leq J$. We can further subdivide the K values based on permutation symmetry. More specifically, for those states for which $(J + \nu_3)$ is even(odd), the even(odd) K values are associated with the A irreps, whereas the odd(even) K values are associated with the B irreps. All of this further facilitates unambiguous state labeling, particular at the larger energy and J values.

4.2. Lambda-doublet splitting

We have predicted that the magnitude of lambda-doublet splitting should decrease exponentially with K , and increase monotonically with J . These trends are clearly evident in Tables 2–7, in which each horizontally adjacent pair of energy levels is a lambda-doublet pair. For clarity, we also present the lambda-doublet splittings explicitly in Table 8, for all of the $^{32}\text{SO}_2$ $J = 20$ rovibrational states (including unphysical) corresponding to $\nu = (0, 0, 0)$.

For any given ν , the lambda-doublet splitting is reduced by something like a factor of 3 from one K value to the next, with the $K = 1$ splitting being the largest by far. Interestingly, for fixed J , the magnitude of the $K = 1$ lambda-doublet splitting is remarkably consistent across ν . For $J = 11$ for example (Table 2), the $^{32}\text{SO}_2$ $\nu = (0, 0, 0)$ $K = 1$ splitting is 3.29 cm^{-1} , whereas the $\nu = (1, 0, 0)$ $K = 1$ splitting is 3.28 cm^{-1} .

Of course, this property is partly what enables lambda-doublet splitting to be such a precise state labeling tool.

From Table 8, it appears that the decrease in lambda-doublet splitting with K is at least as fast as exponential, possibly Gaussian. Thus, whereas lambda-doublet splittings alone may suffice to label K nearly unambiguously up to about $K \approx 8$ or so, for larger K values, the splittings are smaller than the numerical precision, and can no longer be relied upon. For this reason, we anticipate that for J values much larger than $J = 20$, assignment difficulties may indeed be encountered.

The fact that the lambda-doublet splitting magnitude reaches as high as $\sim 10 \text{ cm}^{-1}$ over the relevant energy and J range implies that *no CS or JS scheme can serve as a fully reliable method for assessing SO₂ self shielding*. As discussed in Sec. 3.3, no such approximation can resolve lambda-doublet splittings at all, whereas $\sim 10 \text{ cm}^{-1}$ discrepancies are simply too large to adequately accommodate self shielding.

4.3. Rotational constants and J -shifting

The best that can be hoped for is to be able to accurately fit a rigid rotor form to the *doublet-averaged* energy levels. Note that $K = 0$ should not be included in this fit, and must be treated separately. The reason is that in the large J limit, the lower of the two $K = 1$ doublet energies approaches the corresponding $K = 0$ singlet—as is evident, e.g., in Table 8. By combining such a strategy with the use of state-dependent rotational constants—together with other, more sophisticated ideas [49]—it may well become possible to predict every rovibrational level to subwavenumber precision. This approach will be considered in future papers.

Here, we content ourselves with the more straightforward JS approach, wherein a single pair of (A , B) rotational constants is computed, to be applied across a range of J and K values. However, we do this in the most favorable manner possible, i.e. via a least squares fit to exact rovibrational level data. Specifically, we have performed a least squares fit to the functional form of Eqs. (5) and (6), for all of the $^{32}\text{SO}_2$ $v = (0, 0, 0)$ rovibrational energy levels across the full range $0 \leq J \leq 20$, as computed here and in Paper I. All K values and PI irreps are considered, including physically allowed as well as unphysical levels.

The resultant $^{32}\text{SO}_2$ $v = (0, 0, 0)$ rotational constants are $A = 2.00924 \text{ cm}^{-1}$ and $B = 0.320999 \text{ cm}^{-1}$, which agree quite well with the corresponding experimental values [50, 51, 52] (Table 9). The RMS error for the resultant JS energy level predictions is 1.25 cm^{-1} . This is not bad; the SO_2 molecule really is quite rigid-rotor-like, as a consequence of the relatively heavy masses. However, the maximum error for the $v = (0, 0, 0)$ band is 7.6 cm^{-1} . Moreover, when the above rotational constants are applied to other v bands for which they were not explicitly fit, the errors are larger still.

Perhaps the most damning feature of the above JS fit, however, is that the *largest* errors correspond to the spectroscopically *most important* states, i.e. those with the lowest K values. A more careful study reveals that the largest errors are associated with the largest J and smallest K values—again, due to the increasingly pronounced role of lambda-doublet splitting in this regime, and the special role of $K = 0$. This lends further support to the conclusion from Sec. 4.2, i.e. that even the best possible JS fit described above is insufficiently accurate for purposes of conducting a reliable analysis of self shielding.

The rotational constant A is about six times larger than B , reflecting the highly prolate nature of the SO_2 top. This has important ramifications for the rovibrational level structure, and possibly also for the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ vibronic fine structure. Namely, it does not require a great many K excitations—around $K \approx 10$ or so—for a given vibrational band to reach the threshold energy for the next vibrational band. In contrast, for “perpendicular” rotational excitations (i.e. $K = 0$), this is not achieved until $J \approx 50$, which is likely well outside the spectroscopically relevant J range. These trends, which can be observed clearly in Fig. 4, may have important ramifications for self shielding, as will be explored in future work.

Because the $K = 0$ states are not expected to adhere closely to the same pattern as the other rotational states (for reasons previously discussed), we have also performed a fit of all of the $v = (0, 0, 0)$ $K = 0$ levels to the form $E_{(000),J0}^{J\text{-shift}} = E_{(000)} + BJ(J+1)$. The results, presented in Table 10, exhibit surprisingly small RMS errors. However, the $K = 0$ $^{32}\text{SO}_2$ B value is substantially smaller than that obtained by fitting across all $v = (0, 0, 0)$ rovibrational states—once again highlighting the need to separate out the $K = 0$ states from the others.

4.4. Isotope shifts

Although knowledge of the overall isotope shifts for vibrational (or vibronic) band origins is necessary, real progress towards resolving the self-shielding issue requires a detailed understanding of the effect of isotopic substitution on the spectroscopic fine structure. The effect on individual rovibrational lines can be seen in Fig. 4, but is best summarized in an analysis of rotational constants. In Table 10, we present isotope shifts for the $\nu = (0, 0, 0)$ $K = 0$ rotational constants B . The B values decrease monotonically with increasing S atom mass, adhering to an MDF pattern as expected. However, the isotope shifts are clearly seen to be very small, e.g. $(^{32}B - ^{36}B) = 0.0023 \text{ cm}^{-1}$.

With regard to fitting rotational constants across rovibrational levels that vary with respect to both J and K , as was done in Sec. 4.3, we have computed separate VSD A and B constants for all $(0, \nu_2, 0)$ vibrational states up to $\nu_2 = 2$, by fitting the exact rovibrational level data to Eqs. (5) and (6). Here though, only rovibrational level data up to $J = 15$ is incorporated, in order to be consistent across all ν_2 values considered. The results, for all four SO_2 isotopologues, are presented in Table 9. From the table, similar trends for B isotope shifts are observed as in Table 10, although the table also indicates that isotope shifts for A are substantially larger. A more detailed analysis will be presented in future publications.

Isotope shifts for individual (ν, K) rovibrational frequencies, relative to $^{32}\text{SO}_2$, are presented in increasing energetic order, in Fig. 5 (for $J=11-15$) and Fig. 6 (for $J=16-20$). By “rovibrational frequency” is meant rovibrational energy levels relative to the $\nu = (0, 0, 0)$, $K = 0$ state for a given J . In these figures, the sign has been reversed, to make all shifts positive. Also, only the irrep that includes both permutation-symmetry-allowed and $K = 0$ (even total parity) states is considered—i.e., A^+ for even J , and A^- for odd J .

Continuing the trends first observed in Paper I (Figs. 5 and 7), clear and regular MDF behavior is observed in the frequency isotope shifts for every single rovibrational state considered. Moreover, the shift magnitudes are on the whole comparable to the $J = 0-10$ case, and thus largely independent of J . There is a general increase in the isotope shifts with respect to both vibrational and rotational excitation, although the form of this increase is quite different in each case. In Paper I, the increase was seen to be less than linear with respect to vibrational excitation, but more than linear with respect to rotational (K) excitation. These same trends are evident in Figs. 5 and 6, except that now it is also evident that the K progression appears quadratic. These findings are consistent with a linear isotope shift in the rotational constants themselves.

5. Summary and conclusions

UV photon absorption in the 190–220 nm range, associated with the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ singlet transition in atmospheric SO_2 , is regarded as an important potential source of S-MIF. In particular, the self-shielding hypothesis proposes that the Archean paleoatmosphere may have been “optically thick” with regard to those UV photons required to (pre)dissociate $^{32}\text{SO}_2$, but not optically thick for the rare isotopologues. The self-shielding hypothesis is plausible because the experimental SO_2 absorption spectrum exhibits a rich fine structure, and because the isotope shifts in the vibronic band origins are on the order of tens of cm^{-1} . Conversely, however, an unambiguous assessment of the self-shielding hypothesis requires a comprehensive understanding of the rovibronic spectral features, across all four sulfur-varying SO_2 isotopologues.

Prior to this work (and Paper I), such an understanding was largely lacking. On the one hand, it is well-known that the main features in the experimental absorption spectrum (Sec. 2) [29], are due to the $(1, \nu'_2, 2) \leftarrow (0, 0, 0)$ progression—as confirmed, e.g. in a spectral simulation by Ran *et al.* [15], which also provides accurate isotope shifts for the vibronic band origins. On the other hand, the Ran *et al.* study does not capture any fine structure at all (apart from that due to weaker progressions), and high-resolution experimental spectra are only available for $^{32}\text{SO}_2$ but not for the rare isotopologues.

In reality, between successive $(1, \nu'_2, 2) \leftarrow (0, 0, 0)$ band origins, spaced roughly 350 cm^{-1} apart, the fine structure is determined by many competing factors. J and K splittings, lambda-doublet splittings, less prominent band progressions, and hot bands, all play a significant role in determining the fine structure features. Disentangling each of these competing factors—and assessing the separate impact of isotopic substitution on each—is no small challenge. This work makes a very substantial contribution towards that

goal—even though only the ground $\tilde{X}^1A_1$ electronic state is considered, and even though the FVKH PES is only accurate to a few cm^{-1} . In particular, all rotational splittings, lambda-doublet splittings, and isotope shifts are shown to be resolvable.

To this end, in this paper and in Paper I, we report bound rovibrational energy levels of SO_2 for all four isotopes, ^{32}S , ^{33}S , ^{34}S , and ^{36}S , for all total angular momentum values in the range $J=0\text{--}20$, across a spectroscopically relevant energy range. All energy levels are reported relative to the ground vibrational level of $^{36}\text{SO}_2$. All four PI irreps are considered, including the two B irreps corresponding to unphysical states. Results were obtained using the *ScalIT* suite of parallel codes, treating Coriolis coupling exactly. To our best knowledge, these are the first computational rovibrational levels reported for SO_2 using an exact quantum method and high degree of basis convergence accuracy (10^{-5} cm^{-1} or better), although vibrational levels for $^{32}\text{SO}_2$ have been previously reported [16, 32, 33, 37, 38, 39].

Both the physically allowed and unphysical rovibrational states are computed, in order to assist with spectroscopic labeling. A careful consideration of lambda-doublet splitting—i.e., the lifting of the usual double degeneracy associated with the $|K| > 0$ states, similar to the lambda-doublet splitting observed in diatomic electronic spectroscopy, or the Renner-Teller effect in polyatomic vibronic spectroscopy—is also vitally important in this regard. Unambiguous state labels are needed, not only for disentangling the various trends described above, but also for establishing spectroscopic selection rules. In particular, though K is not a good quantum number per se, it may be sufficiently good that $\Delta K \neq 0$ spectroscopic transitions are not significant—as has indeed been previously observed in the experimental rovibrational spectrum [51]. This feature could also have an impact on self shielding.

The energy and J ranges considered here—encompassing some $\sim 10,000$ rovibrational states with completely unambiguous assignments—almost certainly span all rovibrational states that might reasonably contribute to hot bands in the absorption spectrum. Throughout this range, the magnitude of the isotope shifts is on the order of tens of cm^{-1} —i.e., certainly larger than the errors in the FVKH PES itself. The J variation of the isotope shifts is very small—as is that of the rotational levels themselves. However, the K and ν variations of the isotope shifts are comparable in magnitude, but with different trends (Paper I and Sec. 4.4). Understanding these trends, together with the others discussed in this paper (e.g. for lambda-doublet splitting) may prove beneficial for understanding S-MIF, whether due to self shielding or some other cause.

With regard to the role of self shielding in S-MIF, a final determination will have to wait for a comprehensive analysis of the absorption fine structure. This in turn will require more accurate $\tilde{X}^1A_1$ and $\tilde{C}^1B_2$ PESs, together with a transition dipole surface, all of which are currently under development. Nevertheless, even the ground state FVKH PES rovibrational state calculation performed here already suffices to clarify several very important issues pertaining to self shielding. First, the *fine structure is not simply “translatable” from one isotope to the next*, nor across a bend progression. Second, *neither the JS nor the CS approximations* (of rotation-vibration separability) *is sufficiently accurate to address self shielding*. Coriolis coupling *must* be accounted for, particularly when it manifests as lambda-doublet splitting, which perturbs the spectroscopically most important low- K rovibrational states by as much as 10 cm^{-1} . Third, *isotope shifts associated with rotational excitations are at least as large as for pure vibrational excitations at the same energy*.

In addition to clarifying the points above, it is anticipated that the results obtained here may be directly relevant for identifying individual fine structure features in the experimental absorption spectrum. Other researchers, moreover, may find our comprehensive data, as provided in the Supplementary Material, to be a useful tool for evaluating their own JS schemes, or for testing various aspects of self-shielding/S-MIF.

In addition to PES development, calculation of the $\tilde{C}^1B_2$ rovibronic levels, and simulation of the corresponding absorption spectra, future work will also involve the calculation of a great many more rovibrational levels—well beyond the energy range, and also the J range, considered here. The reason is that the long-lived nature of the $\tilde{C}^1B_2$ predissociation states allows for spontaneous emission back to the $\tilde{X}^1A_1$ state [15]. Energetically speaking, then, almost any rovibrationally excited state might be accessible—although these may be greatly restricted by a consideration of other factors such as Franck-Condon overlaps. In any event, since the emission process may also lead to S-MIF, a greatly expanded set of rovibrational states may have to be considered—perhaps $\sim 100,000$ in all.

Even using *ScalIT* and massively parallel computers, we have no intention of computing all of these

states explicitly. Instead, we will compute only selected rovibrational states, which will then be fit via a modified version of JS that exploits two improvements over the basic scheme considered here. First, we will use both VSD and “RSD” (rotational state dependent) rotational constants. Such a strategy was considered in Ref. [49] for a much floppier system, and found to be remarkably effective. However, based on point 5. above, we know that even this approach alone will not suffice. We will therefore fit rotational constants to lambda-doublet-averaged rovibrational level values with $K > 0$, and model separately the $K = 0$ levels and the lambda-doublet splitting itself. This combined strategy should allow us to predict any desired rovibrational level to wavenumber accuracy.

Finally, oxygen cofractionation—i.e., isotope effects arising from the *oxygen*-varying SO₂ isotopologues—may also contribute to S-MIF, or can at least provide clues as to its origin, be it self shielding or some other mechanism [9, 53]. Accordingly, oxygen cofractionation effects will also be explored in future work.

Conflict of interest

There is no conflict of interest.

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Table 1. Parameters used for the calculation of PSO DVR basis and rovibrational bound states of SO₂ isotopologues; computed zero point energies (ZPEs). Note that “(a.u.)” stands for “atomic units,” and “(u)” stands for “(atomic mass units)” [formerly denoted “(amu)”].

Coordinate range (a.u.)	Basis size	Atomic Mass (u)	ZPE (cm ⁻¹)
$3.5 \leq r \leq 6.1$ $0.25 \leq R \leq 2.25$ $0 \leq \theta \leq \pi$	$N_r=40$ $N_R=40$ $j_{\max}=200$	¹⁶ O=15.99491462 ³² S=31.97207100 ³³ S=32.97145876 ³⁴ S=33.96786690 ³⁶ S=35.96708076	³² SO ₂ =1528.826716 ³³ SO ₂ =1521.357196 ³⁴ SO ₂ =1514.300335 ³⁶ SO ₂ = 1501.200334

Table 2. Lowest-lying rovibrational energies (cm⁻¹) of SO₂ for $J=11$, relative to the vibrational ground state of ³⁶SO₂, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	³⁶ SO ₂ (A ⁺)	³⁶ SO ₂ (A ⁻)	³⁴ SO ₂ (A ⁺)	³⁴ SO ₂ (A ⁻)	³³ SO ₂ (A ⁺)	³³ SO ₂ (A ⁻)	³² SO ₂ (A ⁺)	³² SO ₂ (A ⁻)
1	0,0,0	1	45.0277	41.5818	58.2393	54.8660	65.3549	62.0199	72.8863	69.5914
2	0,0,0	3	56.4806	56.4201	70.1177	70.0647	77.4656	77.4161	85.2453	85.1993
3	0,0,0	5	81.9051	81.9051	96.3917	96.3917	104.2011	104.2011	112.4723	112.4723
4	0,0,0	7	120.1154	120.1154	135.8587	135.8587	144.3514	144.3514	153.3510	153.3510
5	0,0,0	9	170.9453	170.9453	188.3551	188.3551	197.7541	197.7541	207.7195	207.7195
6	0,0,0	11	234.2731	234.2731	253.7537	253.7537	264.2786	264.2786	275.4439	275.4439
7	0,1,0	1	554.8132	551.3313	572.0609	568.6515	581.3096	577.9385	591.0681	587.7371
8	0,1,0	3	566.5679	566.5085	584.2511	584.1990	593.7373	593.6887	603.7497	603.7045
9	0,1,0	5	592.6348	592.6348	611.1858	611.1858	621.1435	621.1435	631.6580	631.6580
10	0,0,0	7	631.7990	631.7990	651.6341	651.6341	662.2899	662.2899	673.5483	673.5483
11	0,1,0	9	683.8855	683.8855	705.4227	705.4227	717.0039	717.0039	729.2484	729.2484
12	0,1,0	11	748.7604	748.7604	772.4114	772.4114	785.1417	785.1417	798.6105	798.6105
13	0,2,0	1	1064.1116	1060.5935	1085.3767	1081.9310	1096.7486	1093.3413	1108.7242	1105.3570
14	0,2,0	3	1076.1789	1076.1207	1097.8896	1097.8385	1109.5046	1109.4569	1121.7398	1121.6955
15	0,2,0	5	1102.9096	1102.9096	1125.5072	1125.5072	1137.6040	1137.6040	1150.3523	1150.3523
16	0,2,0	7	1143.0589	1143.0589	1166.9688	1166.9688	1179.7790	1179.7790	1193.2874	1193.2874
17	0,2,0	9	1196.4420	1196.4420	1222.0907	1222.0907	1235.8461	1235.8461	1250.3615	1250.3615
18	0,2,0	11	1262.9114	1262.9114	1290.7181	1290.7181	1305.6464	1305.6464	1321.4113	1321.4113
19	1,0,0	1	1182.8650	1179.4305	1202.4901	1199.1282	1213.0969	1209.7733	1224.3516	1221.0681
20	1,0,0	3	1194.3191	1194.2592	1214.3744	1214.3219	1225.2162	1225.1673	1236.7221	1236.6767
21	1,0,0	5	1219.7409	1219.7409	1240.6547	1240.6547	1251.9632	1251.9632	1263.9663	1263.9663
22	1,0,0	7	1257.9451	1257.9451	1280.1292	1280.1292	1292.1288	1292.1288	1304.8687	1304.8687
23	1,0,0	9	1308.7654	1308.7654	1332.6339	1332.6339	1345.5499	1345.5499	1359.2669	1359.2669
24	1,0,0	11	1372.0791	1372.0791	1398.0403	1398.0403	1412.0948	1412.0948	1427.0253	1427.0253
25	0,0,1	0		1370.3783		1398.8951		1414.2546		1430.5124
26	0,0,1	2	1377.4145	1378.2669	1406.0918	1406.8883	1421.5401	1422.3080	1437.8937	1438.6325
27	0,0,1	4	1396.5803	1396.5821	1425.8600	1425.8614	1441.6364	1441.6377	1458.3402	1458.3414
28	0,0,1	6	1428.0760	1428.0760	1458.3865	1458.3865	1474.7233	1474.7233	1492.0242	1492.0242
29	0,0,1	8	1472.1073	1472.1073	1503.8526	1503.8526	1520.9696	1520.9696	1539.1017	1539.1017
30	0,0,1	10	1528.5581	1528.5581	1562.1381	1562.1381	1580.2524	1580.2524	1599.4472	1599.4472

Table 3. Lowest-lying rovibrational energies (cm^{-1}) of SO_2 for $J=12$, relative to the vibrational ground state of $^{36}\text{SO}_2$, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	$^{36}\text{SO}_2 (\text{A}^+)$	$^{36}\text{SO}_2 (\text{A}^-)$	$^{34}\text{SO}_2 (\text{A}^+)$	$^{34}\text{SO}_2 (\text{A}^-)$	$^{33}\text{SO}_2 (\text{A}^+)$	$^{33}\text{SO}_2 (\text{A}^-)$	$^{32}\text{SO}_2 (\text{A}^+)$	$^{32}\text{SO}_2 (\text{A}^-)$
1	0,0,0	0	48.4110		61.6763		68.8186		76.3768	
2	0,0,0	2	56.8958	55.7537	70.2406	69.1710	77.4302	76.3977	85.0418	84.0472
3	0,0,0	4	75.2247	75.2213	89.2494	89.2466	96.8074	96.8049	104.8107	104.8084
4	0,0,0	6	107.0657	107.0657	122.1424	122.1424	130.2724	130.2724	138.8853	138.8853
5	0,0,0	8	151.5977	151.5977	168.1370	168.1370	177.0624	177.0624	186.5230	186.5230
6	0,0,0	10	208.6936	208.6936	227.1027	227.1027	237.0449	237.0449	247.5889	247.5889
7	0,0,0	12	278.2212	278.2212	298.9008	298.9008	310.0774	310.0774	321.9369	321.9369
8	0,1,0	0	558.1335		575.4337		584.7084		594.4929	
9	0,1,0	2	566.7770	565.6367	584.1622	583.0939	593.4871	592.4557	603.3282	602.3344
10	0,1,0	4	585.5887	585.5854	603.6676	603.6648	613.3684	613.3660	623.6091	623.6069
11	0,1,0	6	618.2286	618.2286	637.3826	637.3826	647.6678	647.6678	658.5312	658.5312
12	0,1,0	8	663.8673	663.8673	684.5155	684.5155	695.6131	695.6131	707.3422	707.3422
13	0,1,0	10	722.3669	722.3669	744.9243	744.9243	757.0598	757.0598	769.8948	769.8948
14	0,1,0	12	793.5817	793.5817	818.4559	818.4559	831.8509	831.8509	846.0277	846.0277
15	0,2,0	0	1067.3679		1088.6840		1100.0813		1112.0822	
16	0,2,0	2	1076.1749	1075.0367	1097.5817	1096.5151	1109.0323	1108.0024	1121.0929	1120.1004
17	0,2,0	4	1095.4858	1095.4826	1117.6007	1117.5981	1129.4350	1129.4326	1141.9035	1141.9013
18	0,2,0	6	1128.9511	1128.9511	1152.1650	1152.1649	1164.5965	1164.5965	1177.7013	1177.7013
19	0,2,0	8	1175.7324	1175.7324	1200.4729	1200.4729	1213.7344	1213.7344	1227.7235	1227.7235
20	0,2,0	10	1235.6795	1235.6795	1262.3698	1262.3698	1276.6911	1276.6911	1290.3554	1290.3554
21	0,2,0	12	1308.6320	1308.6320	1337.6869	1337.6869	1353.2932	1353.2932	1369.7802	1369.7802
22	1,0,0	0	1186.2262		1205.9038		1216.5367		1227.8174	
23	1,0,0	2	1194.6978	1193.5625	1214.4572	1213.3944	1225.1387	1224.1130	1236.4742	1235.4864
24	1,0,0	4	1213.0289	1213.0256	1233.4750	1233.4722	1244.5288	1244.5263	1256.2604	1256.2581
25	1,0,0	6	1244.8653	1244.8653	1266.3748	1266.3748	1278.0072	1278.0072	1291.8092	1291.8092
26	1,0,0	8	1289.3895	1289.3895	1312.3774	1312.3774	1324.8141	1324.8141	1338.0198	1338.0198
27	1,0,0	10	1346.4736	1346.4736	1371.3512	1371.3512	1384.8159	1384.8159	1399.1177	1399.1177
28	1,0,0	12	1415.9842	1415.9842	1443.1563	1443.1563	1457.8691	1457.8691	1473.5012	1473.5012
29	0,0,1	1	1378.0679	1382.1057	1406.6595	1410.6154	1422.0597	1425.9721	1438.3610	1442.2278
30	0,0,1	3	1393.1874	1393.2891	1422.1180	1422.2074	1437.7044	1437.7878	1454.2054	1454.2829

Table 4. Lowest-lying rovibrational energies (cm^{-1}) of SO_2 for $J=13$, relative to the vibrational ground state of $^{36}\text{SO}_2$, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	$^{36}\text{SO}_2 (\text{A}^+)$	$^{36}\text{SO}_2 (\text{A}^-)$	$^{34}\text{SO}_2 (\text{A}^+)$	$^{34}\text{SO}_2 (\text{A}^-)$	$^{33}\text{SO}_2 (\text{A}^+)$	$^{33}\text{SO}_2 (\text{A}^-)$	$^{32}\text{SO}_2 (\text{A}^+)$	$^{32}\text{SO}_2 (\text{A}^-)$
1	0,0,0	1	61.3114	56.6355	74.5595	69.9748	81.6935	77.1575	89.2438	84.7588
2	0,0,0	3	72.5286	72.3710	86.1806	86.0421	93.5367	93.4075	101.3253	101.2051
3	0,0,0	5	97.8330	97.8329	112.3462	112.3461	120.1696	120.1695	128.4554	128.4554
4	0,0,0	7	136.0294	136.0294	151.8008	151.8008	160.3084	160.3084	169.3233	169.3233
5	0,0,0	9	186.8577	186.8577	204.2964	204.2964	213.7106	213.7106	223.6918	223.6918
6	0,0,0	11	250.1887	250.1887	269.6988	269.6988	280.2393	280.2393	291.4207	291.4207
7	0,0,0	13	325.8795	325.8795	347.8578	347.8578	359.7401	359.7401	372.3514	372.3514
8	0,1,0	1	571.0945	566.3677	588.3788	583.7434	597.6460	593.0592	607.4234	602.8878
9	0,1,0	3	582.6034	582.4488	600.3022	600.1662	609.7970	609.6700	619.8186	619.7004
10	0,1,0	5	608.5517	608.5516	627.1298	627.1297	637.1017	637.1016	647.6310	647.6309
11	0,1,0	7	647.7022	647.7022	667.5659	667.5659	678.2367	678.2367	689.5108	689.5108
12	0,1,0	9	699.7874	699.7874	721.3539	721.3539	732.9506	732.9506	745.2111	745.2111
13	0,1,0	11	764.6658	764.6658	788.3467	788.3467	801.0928	801.0928	814.5780	814.5780
14	0,1,0	13	842.1800	842.1800	868.3787	868.3787	882.4932	882.4932	897.4364	897.4364
15	0,2,0	1	1080.3909	1075.6128	1101.6925	1097.0059	1113.0831	1108.4453	1125.0776	1120.4911
16	0,2,0	3	1092.2021	1092.0505	1113.9290	1113.7954	1125.5529	1125.4282	1137.7978	1137.6816
17	0,2,0	5	1118.8157	1118.8155	1141.4407	1141.4406	1153.5520	1153.5519	1166.3154	1166.3153
18	0,2,0	7	1158.9516	1158.9516	1182.8905	1182.8905	1195.7159	1195.7159	1209.2403	1209.2403
19	0,2,0	9	1212.3336	1212.3336	1238.0121	1238.0121	1251.7831	1251.7831	1266.3148	1266.3148
20	0,2,0	11	1278.8068	1278.8068	1306.6439	1306.6439	1321.5882	1321.5882	1337.3698	1337.3698
21	0,2,0	13	1358.1976	1358.1976	1388.6033	1388.6033	1404.9433	1404.9433	1422.2118	1422.2118
22	1,0,0	1	1199.0790	1194.4182	1218.7391	1214.1695	1229.3637	1224.8427	1240.6363	1236.1664
23	1,0,0	3	1210.2965	1210.1405	1230.3653	1230.2283	1241.2146	1241.0867	1252.7285	1252.6097
24	1,0,0	5	1235.5990	1235.5989	1256.5380	1256.5379	1267.8598	1267.8597	1279.8767	1279.8766
25	1,0,0	7	1273.7893	1273.7893	1296.0001	1296.0001	1308.0137	1308.0137	1320.7682	1320.7682
26	1,0,0	9	1324.6077	1324.6077	1348.5037	1348.5037	1361.4342	1361.4342	1375.1661	1375.1661
27	1,0,0	11	1387.9244	1387.9244	1413.9137	1413.9137	1427.9829	1427.9829	1442.9287	1442.9287
28	0,0,1	0		1385.5500		1414.1314		1429.5246		1445.8174
29	0,0,1	2	1393.1076	1394.6111	1421.8240	1423.2367	1437.2925	1438.6585	1453.6669	1454.9850
30	0,0,1	4	1412.4726	1412.4792	1441.7770	1441.7824	1457.5664	1457.5714	1474.2837	1474.2882

Table 5. Lowest-lying rovibrational energies (cm^{-1}) of SO_2 for $J=15$, relative to the vibrational ground state of $^{36}\text{SO}_2$, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	$^{36}\text{SO}_2 (\text{A}^+)$	$^{36}\text{SO}_2 (\text{A}^-)$	$^{34}\text{SO}_2 (\text{A}^+)$	$^{34}\text{SO}_2 (\text{A}^-)$	$^{33}\text{SO}_2 (\text{A}^+)$	$^{33}\text{SO}_2 (\text{A}^-)$	$^{32}\text{SO}_2 (\text{A}^+)$	$^{32}\text{SO}_2 (\text{A}^-)$
1	0,0,0	1	80.0699	74.0498	93.3712	87.4551	100.5322	94.6723	108.1098	102.3093
2	0,0,0	3	91.2284	90.8768	104.8902	104.5798	112.2520	111.9617	120.0470	119.7765
3	0,0,0	5	116.3226	116.3221	130.8655	130.8651	138.7046	138.7042	147.0068	147.0064
4	0,0,0	7	154.4955	154.4955	170.2989	170.2989	178.8234	178.8234	187.8560	187.8560
5	0,0,0	9	205.3189	205.3189	222.7909	222.7909	232.2226	232.2226	242.2220	242.2220
6	0,0,0	11	268.6523	268.6523	288.1964	288.1964	298.7548	298.7548	309.9548	309.9548
7	0,0,0	13	344.3494	344.3494	366.3623	366.3623	378.2629	378.2629	390.8931	390.8931
8	0,0,0	15	432.2455	432.2455	457.1156	457.1156	470.5692	470.5692	484.8541	484.8541
9	0,1,0	1	589.8513	583.7617	607.1888	601.2038	616.4829	610.5543	626.2877	620.4187
10	0,1,0	3	601.2881	600.9426	618.9974	618.6922	628.4984	628.2129	638.5269	638.2607
11	0,1,0	5	627.0285	627.0279	645.6368	645.6363	655.6247	655.6243	666.1706	666.1703
12	0,1,0	7	666.1558	666.1558	686.0520	686.0520	696.7401	696.7401	708.0320	708.0320
13	0,1,0	9	718.2365	718.2365	739.8367	739.8367	751.4512	751.4512	763.7302	763.7302
14	0,1,0	11	783.1177	783.1177	806.8331	806.8331	819.5973	819.5973	833.1014	833.1014
15	0,1,0	13	860.6384	860.6384	886.8723	886.8723	901.0053	901.0053	915.9678	915.9678
16	0,1,0	15	950.6178	950.6178	979.7640	979.7640	995.4797	995.4797	1012.1281	1012.1281
17	0,2,0	1	1099.1463	1092.9867	1120.5010	1114.4466	1131.9185	1125.9207	1143.9404	1138.0026
18	0,2,0	3	1110.8717	1110.5325	1132.6099	1132.3100	1144.2405	1143.9598	1156.4927	1156.2309
19	0,2,0	5	1137.2797	1137.2792	1159.9355	1159.9351	1172.0630	1172.0627	1184.8434	1184.8431
20	0,2,0	7	1177.3928	1177.3928	1201.3648	1201.3648	1214.2077	1214.2077	1227.7502	1227.7502
21	0,2,0	9	1230.7707	1230.7707	1256.4834	1256.4834	1270.2725	1270.2725	1284.8230	1284.8230
22	0,2,0	11	1297.2470	1297.2470	1325.1191	1325.1191	1340.0818	1340.0818	1355.8826	1355.8826
23	0,2,0	13	1376.6448	1376.6448	1407.0862	1407.0862	1423.4450	1423.4450	1440.7331	1440.7331
24	1,0,0	1	1217.7576	1211.7561	1237.4693	1231.5718	1248.1199	1242.2786	1259.4189	1253.6370
25	1,0,0	3	1228.9138	1228.5655	1248.9906	1248.6835	1259.8448	1259.5576	1271.3642	1271.0968
26	1,0,0	5	1254.0076	1254.0071	1274.9747	1274.9742	1286.3112	1286.3108	1298.3435	1298.3432
27	1,0,0	7	1292.1743	1292.1743	1314.4155	1314.4155	1326.4451	1326.4451	1339.2163	1339.2163
28	1,0,0	9	1342.9877	1342.9877	1366.9153	1366.9153	1379.8623	1379.8623	1393.6115	1393.6115
29	1,0,0	11	1406.3064	1406.3064	1432.3280	1431.6781	1446.4142	1446.4142	1461.3777	1461.3777
30	0,0,1	0		1403.0210		1432.3280		1447.1110		1463.4449

Table 6. Lowest-lying rovibrational energies (cm^{-1}) of SO_2 for $J=17$, relative to the vibrational ground state of $^{36}\text{SO}_2$, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	$^{36}\text{SO}_2 (\text{A}^+)$	$^{36}\text{SO}_2 (\text{A}^-)$	$^{34}\text{SO}_2 (\text{A}^+)$	$^{34}\text{SO}_2 (\text{A}^-)$	$^{33}\text{SO}_2 (\text{A}^+)$	$^{33}\text{SO}_2 (\text{A}^-)$	$^{32}\text{SO}_2 (\text{A}^+)$	$^{32}\text{SO}_2 (\text{A}^-)$
1	0,0,0	1	101.2407	93.8139	114.6158	107.2963	121.8143	114.5537	129.4298	122.2324
2	0,0,0	3	112.6217	111.9281	126.2857	125.6697	133.6495	133.0716	141.4471	140.9070
3	0,0,0	5	137.3802	137.3783	151.9553	151.9537	159.8114	159.8100	168.1315	168.1303
4	0,0,0	7	175.5161	175.5161	191.3554	191.3554	199.8987	199.8987	208.9509	208.9509
5	0,0,0	9	226.3304	226.3304	243.8397	243.8397	253.2911	253.2911	263.3109	263.3109
6	0,0,0	11	289.6646	289.6646	309.2471	309.2471	319.8256	319.8256	331.0467	331.0467
7	0,0,0	13	365.3677	365.3677	387.4198	387.4198	399.3410	399.3410	411.9927	411.9927
8	0,0,0	15	453.2733	453.2733	478.1833	478.1833	491.6579	491.6579	505.9647	505.9647
9	0,0,0	17	553.1969	553.1969	581.3435	581.3435	596.5773	596.5773	612.7580	612.7580
10	0,1,0	1	611.0211	603.5025	628.4322	621.0219	637.7637	630.4129	647.6064	640.3193
11	0,1,0	3	622.6636	621.9810	640.3760	639.7695	649.8795	649.3103	659.9111	659.3790
12	0,1,0	5	648.0713	648.0694	666.7124	666.7109	676.7177	676.7164	687.2819	687.2808
13	0,1,0	7	687.1622	687.1622	707.0948	707.0948	717.8020	717.8020	729.1140	729.1140
14	0,1,0	9	739.2341	739.2341	760.8723	760.8723	772.5067	772.5067	784.8065	784.8065
15	0,1,0	11	804.1165	804.1165	827.8709	827.8709	840.6556	840.6556	854.1811	854.1811
16	0,1,0	13	881.6438	881.6438	907.9174	907.9174	922.0714	922.0714	937.0557	937.0557
17	0,1,0	15	971.6330	971.6330	1000.8198	1000.8198	1016.5569	1016.5569	1033.2275	1033.2275
18	0,1,0	17	1073.8819	1073.8819	1106.3651	1106.3651	1123.8934	1123.8934	1142.4718	1142.4718
19	0,2,0	1	1120.3154	1112.7044	1141.7436	1134.2420	1153.1985	1145.7568	1165.2583	1157.8808
20	0,2,0	3	1132.2294	1131.5579	1153.9717	1153.3748	1165.6052	1165.0450	1177.8611	1177.3371
21	0,2,0	5	1158.3080	1158.3062	1180.9972	1180.9958	1193.1425	1193.1412	1205.9414	1205.9403
22	0,2,0	7	1198.3852	1198.3852	1222.3941	1222.3941	1235.2565	1235.2565	1248.8193	1248.8193
23	0,2,0	9	1251.7546	1251.7546	1277.5059	1277.5059	1291.3152	1291.3152	1305.8869	1305.8869
24	0,2,0	11	1318.2326	1318.2326	1346.1443	1346.1443	1361.1278	1361.1278	1376.9503	1376.9503
25	0,2,0	13	1397.6374	1397.6374	1428.1191	1428.1191	1444.4993	1444.4993	1461.8095	1461.8095
26	1,0,0	1	1238.8387	1231.4336	1258.6223	1251.3244	1269.3093	1262.0704	1280.6451	1273.4694
27	1,0,0	3	1250.2124	1249.5251	1270.2895	1269.6798	1281.1446	1280.5729	1292.6656	1292.1315
28	1,0,0	5	1274.9729	1274.9710	1295.9702	1295.9687	1307.3228	1307.3215	1319.3719	1319.3707
29	1,0,0	7	1313.1027	1313.1027	1335.3778	1335.3778	1347.4253	1347.4253	1360.2150	1360.2150
30	1,0,0	9	1363.9067	1363.9067	1387.8698	1387.8698	1400.8354	1400.8354	1414.6040	1414.6040

Table 7. Lowest-lying rovibrational energies (cm^{-1}) of SO_2 for $J=20$, relative to the vibrational ground state of $^{36}\text{SO}_2$, for each isotopologue, with Even Permutation Symmetry and both Even and Odd Parity.

n	n_1, n_2, n_3	K	$^{36}\text{SO}_2 (\text{A}^+)$	$^{36}\text{SO}_2 (\text{A}^-)$	$^{34}\text{SO}_2 (\text{A}^+)$	$^{34}\text{SO}_2 (\text{A}^-)$	$^{33}\text{SO}_2 (\text{A}^+)$	$^{33}\text{SO}_2 (\text{A}^-)$	$^{32}\text{SO}_2 (\text{A}^+)$	$^{32}\text{SO}_2 (\text{A}^-)$
1	0,0,0	0	127.7974		141.4046		148.7265		156.4713	
2	0,0,0	2	143.7411	138.3204	157.1752	151.9841	164.4079	159.3383	172.0618	167.1190
3	0,0,0	4	159.7699	159.5910	173.8897	173.7403	181.4997	181.3640	189.5584	189.4357
4	0,0,0	6	191.2091	191.2087	206.4227	206.4225	214.6251	214.6249	223.3134	223.3132
5	0,0,0	8	235.6599	235.6599	252.3455	252.3455	261.3479	261.3479	270.8886	270.8886
6	0,0,0	10	292.7403	292.7403	311.3008	311.3008	321.3226	321.3226	331.9495	331.9495
7	0,0,0	12	362.2817	362.2817	383.1164	383.1164	394.3745	394.3745	406.3189	406.3189
8	0,0,0	14	444.1195	444.1195	467.6205	467.6205	480.3281	480.3281	493.8168	493.8168
9	0,0,0	16	538.0755	538.0755	564.6263	564.6263	578.9916	578.9916	594.2464	594.2464
10	0,0,0	18	643.9550	643.9550	671.0700	665.8551	680.4382	675.3451	690.3217	685.3558
11	0,0,0	20	761.5478	761.5478	795.3089	795.3089	813.5921	813.5921	833.0202	833.0202
12	0,1,0	0	637.4411		655.0855		664.5410		674.5135	
13	0,1,0	2	653.5957	648.1505	673.9294	673.9294	690.1552	690.1552	707.3918	707.3918
14	0,1,0	4	670.0702	669.8970	688.2476	688.1028	698.0022	697.8706	708.3000	708.1810
15	0,1,0	6	702.3141	702.3138	721.6074	721.6072	731.9663	731.9661	742.9065	742.9063
16	0,1,0	8	747.8733	747.8733	768.6700	768.6700	779.8460	779.8460	791.6566	791.6566
17	0,1,0	10	806.3590	806.3590	829.0701	829.0701	841.2865	841.2865	854.2058	854.2058
18	0,1,0	12	877.5893	877.5893	902.6209	902.6209	916.0987	916.0987	930.3618	930.3618
19	0,1,0	14	961.3840	961.3840	989.1345	989.1345	1004.0900	1004.0900	1019.9272	1019.9272
20	0,1,0	16	1057.5476	1057.5476	1088.4057	1088.4057	1105.0498	1105.0498	1122.6857	1122.6857
21	0,1,0	18	1165.8670	1165.8670	1200.2105	1200.2105	1214.0107	1213.8832	1226.5380	1226.4227
22	0,1,0	20	1286.1127	1286.1127	1317.7363	1317.5889	1328.8381	1328.7044	1340.6208	1340.5000
23	0,2,0	0	1146.5982		1168.2607		1179.8401		1192.0303	
24	0,2,0	2	1162.9674	1157.4986	1184.4629	1179.2255	1195.9567	1190.8415	1208.0599	1203.0722
25	0,2,0	4	1179.9043	1179.7369	1202.1210	1201.9808	1218.7482	1218.7482	1238.4008	1238.4008
26	0,2,0	6	1212.9794	1212.9791	1236.3349	1236.3347	1248.8413	1248.8411	1262.0243	1262.0241
27	0,2,0	8	1259.6828	1259.6828	1284.5742	1284.5742	1297.9152	1297.9152	1311.9872	1311.9872
28	1,0,0	0	1265.2672		1285.2795		1296.0880		1307.5512	
29	1,0,0	2	1281.1673	1275.7716	1301.0077	1295.8422	1311.7280	1306.6842	1323.1012	1318.1845
30	1,0,0	4	1297.2024	1297.0258	1324.3077	1324.3077	1344.9376	1344.9376	1366.8181	1366.8181

Table 8. Rovibrational energy levels for the ground $v = (0, 0, 0)$ vibrational state of $^{32}\text{SO}_2$, for $J=20$. All energies are in cm^{-1} and relative to the $^{32}\text{SO}_2$ ground vibrational state. Lambda-doublet splittings are represented explicitly in Columns IV and VII.

K	$J=20 (\text{A}^+)$	$J=20 (\text{A}^-)$	$\Delta_{\text{A}^+-\text{A}^-}$	$J=20 (\text{B}^+)$	$J=20 (\text{B}^-)$	$\Delta_{\text{B}^+-\text{B}^-}$
0	128.844875					
1				128.921329	138.263858	-9.34(+00)
2	144.435449	139.492607	4.94(+00)			
3				149.749842	151.017739	-1.27(+00)
4	161.931994	161.809354	1.23(-01)			
5				177.024960	177.030849	-5.89(-03)
6	195.686977	195.686805	1.73(-04)			
7				217.776755	217.776758	-3.39(-06)
8	243.262248	243.262248	7.72(-08)			
9				272.118348	272.118348	-3.02(-09)
10	304.323116	304.323116	-1.57(-08)			
11				339.855135	339.855135	1.00(-12)
12	378.692471	378.692471	2.65(-08)			
13				420.812241	420.812241	-7.96(-09)
14	466.190424	466.190424	-4.22(-09)			
15				514.801803	514.801803	-9.46(-09)
16	566.619978	566.619978	2.29(-08)			
17				621.617398	621.617398	-2.54(-08)
18	679.765426	679.765426	-4.41(-08)			
19				741.034411	741.034411	-3.43(-09)
20	805.393762	805.393762	-1.03(-08)			

Table 9. Rotational constants A and B for all four SO_2 isotopologues, in cm^{-1} , obtained by fitting $E_{vJK}^{J\text{-shift}} = E_v + (A - B)K^2 + BJ(J + 1)$ to all rovibrational levels in the range $J=0\text{--}15$, for three different vibrational states in the bend progression $v = (0, v_2, 0)$. For $^{32}\text{SO}_2$ $v = (0, 0, 0)$, two other sets of rotational constant values are also provided: theoretical, for all $J \leq 20$, from Sec. 4.3; experimental, from Refs. [50] and [51].

v_1, v_2, v_3	^{32}A	^{33}A	^{34}A	^{36}A	^{32}B	^{33}B	^{34}B	^{36}B
0,0,0 (expt.)	2.02735				0.31885 ¹			
0,0,0 (theory)	2.00924				0.320999			
0,0,0	2.01749	1.98705	1.95848	1.90592	0.32008	0.31971	0.319375	0.318683
0,1,0	2.05876	2.02655	1.99852	1.94486	0.32003	0.319652	0.319288	0.318599
0,2,0	2.10334	2.07194	2.0421	1.98718	0.319571	0.319106	0.31875	0.318066

Table 10. Rotational constant B for all four SO_2 isotopologues, in cm^{-1} , obtained by fitting $E_{(000)J0}^{J\text{-shift}} = E_{(000)} + BJ(J + 1)$ to all $v = (0, 0, 0)$ $K = 0$ rovibrational levels in the range $J=0\text{--}20$. RMS errors for the resultant $E^{J\text{-shift}}$ energy level predictions are also reported.

Isotopologue	B	$^{32}B - B$	RMS Error
$^{32}\text{SO}_2$	0.308792		0.42027
$^{33}\text{SO}_2$	0.308164	6.28(-04)	0.427755
$^{34}\text{SO}_2$	0.307556	1.24(-03)	0.435053
$^{36}\text{SO}_2$	0.306457	2.34(-03)	0.463403

Fig. 1. Root mean square errors (σ_{rms}) of present rovibrational energy levels relative to experimental HITRAN values [17, 18], as a function of J , for $^{32}\text{SO}_2$ $v=(0,0,0)$.

Fig. 2. Rovibrational energy level diagram for SO_2 isotopologues relative to the ground vibrational state of $^{36}\text{SO}_2$, for all PI irreps A^+ , A^- , B^+ , and B^- , for $J=11$ – 15 .

Fig. 3. Rovibrational energy level diagram for SO_2 isotopologues relative to the ground vibrational state of $^{36}\text{SO}_2$, for all PI irreps A^+ , A^- , B^+ , and B^- , for $J=16$ – 20 .

Fig. 4. Rovibrational energy level diagram for SO_2 isotopologues relative to the ground vibrational state of $^{36}SO_2$, for the A^+ irrep, for $J=0, 5, 10, 15$, and 20 .

Fig. 5. Isotope shifts for SO_2 rovibrational frequencies relative to the $^{32}\text{SO}_2$ isotopologue, for PI irreps A^+ and A^- , for $J=11-15$: $\Delta E_{^{32}\text{SO}_2 \rightarrow ^{36}\text{SO}_2}$ (red solid line with filled squares), $\Delta E_{^{32}\text{SO}_2 \rightarrow ^{34}\text{SO}_2}$ (blue dashed line with empty circles), $\Delta E_{^{32}\text{SO}_2 \rightarrow ^{33}\text{SO}_2}$ (cyan dot-dashed line with filled circles).

Fig. 6. Isotope shifts for SO_2 rovibrational frequencies relative to the $^{32}\text{SO}_2$ isotopologue, for PI irreps A^+ and A^- , for $J=16$ – 20 . Description of the plots is same as in Fig. 5.