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Line lists for $X^3\Sigma^-$ and $a^1\Delta$ vibration-rotation bands of SO



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Peter F. Bernath^{a,b}, Ryan M. Johnson^{b,*}, Jacques Liévin^c

^a Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529, USA

^b Department of Physics, Old Dominion University, Norfolk, Virginia 23529, USA

^c Université Libre de Bruxelles, Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing, CP 160/09, Av. F. D. Roosevelt 50, Bruxelles, Belgium

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ABSTRACT

SO is found in several astronomical sources such as the atmospheres of Io and Venus. To complete our work on SO line lists, we used our previous fits for v = 0 to v = 6 for the $X^3 \Sigma^-$ state and v = 0-5 for the $a^1 \Delta$ state [JQSRT 272, 107772 (2021)] for line positions, and high-level ab initio calculations of electric dipole moments for line strengths for the vibration-rotation bands. LeRoy's RKR program was used to produce pointwise potential energy curves. *N*- and v-dependent dipole matrix elements were produced with LeRoy's LEVEL program and the final line lists were made with Western's PGOPHER program. All possible vibrational bands were calculated, and the line strengths included the Herman-Wallis effect caused by vibration-rotation interaction.

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1. Introduction

Sulfur monoxide (SO) is a free radical found in several astronomical sources including the Orion nebula [1]. More locally, SO has been detected by the ultraviolet $B^3 \Sigma^- X^3 \Sigma^-$ transition on Venus [2] as well as on Io [3], one of Jupiter's moons. Microwave [4,5] spectroscopy has detected SO on both Io and Venus and the forbidden $a^1 \Delta - X^3 \Sigma^-$ transition [6] has been used to characterize atmospheric SO on Io. However, SO has not been detected yet in astronomical sources using vibration-rotation spectra, but observations may be possible in the future using our new line lists.

The SO radical is isovalent with O_2 , with an $X^3 \Sigma^-$ ground state and a low-lying metastable $a^1 \Delta$ excited state. Unlike O_2 , there is no inversion symmetry; the SO ground state has a substantial dipole moment of 1.55 D [7] and dipole-allowed vibrational bands. The $X^3 \Sigma^-$ and $a^1 \Delta$ states have electron spin and orbital angular momentum, respectively, and the Herman-Wallis effect [8] was also taken into account for the vibration-rotation line intensities.

SO has been extensively studied by millimeter wave, microwave, infrared, and far infrared spectroscopy. In this paper, we relied mainly on the $X^3 \Sigma^-$ ground state rotational constants determined by Martin-Drummel et al. [9], the diode laser vibration-rotation measurements made by Kanamori et al. [10,11], and the Fourier transform infrared spectra of Burkholder et al. [12]. A more extensive discussion of SO spectroscopy can be found in our previous paper [13]. It should be noted that only the principal isotopo-

* Corresponding author. E-mail address: rjohn032@odu.edu (R.M. Johnson). logue ³²S¹⁶O was used for this paper. The stable isotopes of sulfur are ³²S, ³³S, ³⁴S, and ³⁶S and are found in terrestrial sources with abundances of 95%, 0.77%, 4.2%, and 0.017%, respectively [14].

2. Methods

2.1. Ab initio calculations

Large scale ab initio calculations have been carried out with the MOLPRO program package [15,16,17] in order to provide the electric dipole moment curves for the $X^3\Sigma^-$ and $a^1\Delta$ states. These calculations were performed with the internally contracted multireference configuration interaction (ic-MRCI) method [18], using molecular orbitals (MOs) optimized by state-specific complete active space self-consistent field (CASSCF) calculations [19,20] based on an active space including the 14 MOs correlating to the core and valence atomic orbitals. All electrons are thus correlated at the ic-MRCI level of calculation, and the Davidson correction for unlinked excitations [21] adapted to a relaxed reference [22] is taken into account in all energy calculations (ic-MRCI+Q). The scalar relativistic contributions were calculated by means of the exact 2component (X2C) relativistic Hamiltonian [23] using the aug-ccpCV6Z-X2C basis set (ACV6Z-X2C for short) [24,25], specifically contracted for X2C calculations [16]. This basis set is also optimized for describing the core and core-valence electron correlation and is augmented by diffuse functions, improving the convergence of electric properties like the dipole moment.

This convergence has been tested at the equilibrium geometry of both states by extrapolating the dipole moment to the complete basis set limit (CBS), using a standard 2-point n^{-3} extrapolation





Fig. 1. Ab initio dipole moment curve for the X ${}^{3}\Sigma^{-}$ state of SO, calculated in this work and by Borin et al. [31] at the ic-MRCI+Q/ACV6Z-X2C/ED+Q and ic-MRCI/cc-pVQZ/EV levels of theory, respectively.

[26], with n=5 and 6, n being the cardinal number of the ACVnZ-X2C basis set series. In these tests, the dipole moment was evaluated as the expectation value (EV) of the dipole moment operator and as the energy derivative (ED) with respect to an external, weak and uniform electric field, for zero field strength [27]. The derivative has been calculated numerically by the two-point central difference formula with a field strength fixed to 3×10^{-4} a.u.. The derivative formalism, being based on the energy and not on the wave function, also permits the inclusion of the Davidson correction for unlinked clusters into the dipole moment calculations (ED+Q).

The ACV6Z-X2C results are found to be close to the CBS ones. the latter being smaller by less than 0.01 D. The tests also show that the ED+O values are larger than the EV ones by 0.18 and 0.22 D for the $X^3\Sigma^-$ and $a^1\Delta$ states, respectively. These significant differences indicate that the wave function still does not satisfy the Hellmann-Feynman theorem. As energies converge faster than wave functions, the ED formalism is expected to provide dipole moment values closer to the experimental ones (see [27-29] and references therein). We have thus adopted the ED+Q approach for calculating the dipole moment curves. They are shown in Fig. 1 and 2. We report here the projection of the dipole moment on the internuclear z-axis pointing arbitrarily from S to O. The $S^{(+)}O^{(-)}$ polarity explains the negative sign of the dipole moments. The calculations have been carried out at 57 points corresponding to internuclear distances (R) ranging from 1.1 to 2 Å, by steps of 0.025 Å, and from 2 to 3 Å, by steps of 0.05 Å. The curves were then interpolated using B-splines to create a set of 1592 points for each dipole moment curve. Both the calculated and interpolated data points are provided as supplementary material.

The value of the dipole moments for v=0, computed from our ACV6Z-X2C/ED+Q curves (see Tables 1 and 2, and discussion in the text) are 1.591 D and 1.444 D, for the $X^3\Sigma^-$ and $a^1\Delta$ states, respectively. They can be compared to the corresponding experimental

Fig. 2. Ab initio dipole moment curve for the a $^1\Delta$ state of SO, calculated in this work, by Borin et al. [31] and by Xing et al. [30] at the ic-MRCI+Q/ACV6Z-X2C/ED+Q, ic-MRCI/cc-pVQZ/EV and ic-MRCI/aug-cc-pV6Z/EV levels of theory, respectively.

values of Powell and Lide [7] of 1.55 \pm 0.02 D for the $X^3\Sigma^-$ state, and of Saito [30] of 1.336 \pm 0.045 D, for the $a^1\Delta$ state. Our calculated values overestimate these experimental findings by 2 and 7%, respectively.

Our dipole moment curves are compared in Figs. 1 and 2 to those previously calculated by Borin and Ornellas [31] at the ic-MRCI/cc-pVQZ/EV level of theory and by Xing et al. [32] at the ic-MRCI/aug-cc-pV6Z/EV level. These curves surprisingly agree with ours within a few percent, despite the many approximations impacting the dipole moment value they both use: EV formalism, frozen-core and non-relativistic approximations, averaging of the CASSCF optimization over many excited states, neglect of the Q correction in the dipole calculation, and in addition for Borin's calculations, use of a non-augmented lower zeta basis set. Some of these approximations tend to increase the dipole moment value while others to decrease it. One may thus explain the observed agreement by fortuitous compensations between them. Note however that their relative effect changes with the nature of the electronic structure, i.e. from one electronic state to another, but also as a function of internuclear distance. This directly impacts the shape of the calculated dipole functions. It can be seen from the figures that their slope at short and long distances changes from one calculation to another, which may influence the accuracy of high vibrational band intensities. Let us note the presence of unexpected deformations in Borin's curves.

2.1.1. Line list calculations

We produced line positions and intensities up to J=75 with PGOPHER [33] for v=0-6 for $X^3 \Sigma^-$ and v=0-5 for $a^1 \Delta$. We included all of the possible vibration-rotation bands in the $X^3 \Sigma^-$ and $a^1 \Delta$ states. The line positions were calculated using the spectroscopic constants from our previous paper on line lists for the $b^1 \Sigma^+ - X^3 \Sigma^-$ and $a^1 \Delta - X^3 \Sigma^-$ electronic transitions [13]. The values of the final

Table 1

Dipole and	transition	dipole	moments	for	the	vibrational	levels	of	the	SO	X3	Σ^{-}	state in	n D.
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v'-v"	0	1	2	3	4	5	6
0	-1.591	-0.07090	0.01480	-0.002515	0.0003611	-2.426E-05	-7.185E-06
1	-0.07090	-1.592	-0.09726	0.02502	-0.004932	0.0008160	-7.199E-05
2	0.01480	-0.09726	-1.593	-0.1586	0.03457	-0.007644	0.001423
3	-0.002515	0.02502	-0.1586	-1.594	-0.1299	0.04361	-0.01060
4	0.0003611	-0.004932	0.03457	-0.1299	-1.595	-0.1407	0.05223
5	-2.426E-05	0.0008160	-0.007644	0.04361	-0.1407	-1.595	-0.1496
6	-7.185E-06	-7.199E-05	0.001423	-0.01060	0.05223	-0.1496	-1.596

Table 2

Dipole and transition dipole moments for the vibrational levels of the SO $a^1\Delta$ state in D.

v'-v"	0	1	2	3	4	5
0	-1.444	-0.06359	0.01331	-0.002527	0.0004743	-7.970E-05
1	-0.06359	-1.446	-0.08765	0.02256	-0.004947	0.001047
2	0.01331	-0.08765	-1.448	-0.1046	0.03121	-0.007650
3	-0.002527	0.02256	-0.1046	-1.449	-0.1176	0.03944
4	0.0004743	-0.004947	0.03121	-0.1176	-1.451	-0.1279
5	-7.970E-05	0.001047	-0.007650	0.03944	-0.1279	-1.452



Fig 3. Fortrat diagram of the $a^1 \Delta$ 1-0 band.

fitted constants as well as an exhaustive list of experimental data used in the fit can be found in our previous paper [13].

To calculate the line strengths, we used Rydberg-Klein-Rees (RKR) potentials [32] from the SO equilibrium constants [13]. The RKR potentials and dipole moment points were input to LeRoy's LEVEL program [35] to obtain the dipole moment vibrational matrix elements $\langle v', N' | \mu | v'', N'' \rangle$ for the X³ Σ^- and a¹ Δ states. LEVEL assumes singlet states so the rotational dependence of the vibrational wavefunctions (from the centrifugal potential [36]) depends on *N*. This *N*-dependence of the vibrational wavefunction interaction that leads to the Herman-Wallis effect. The matrix elements are used as input to PGOPHER to calculate line strengths; however, PGOPHER needs *J*-dependent matrix elements, not the *N*-dependent results from LEVEL for the X³ Σ^- state.

Brooke et al. [37] derived a formula for the conversion of Hund's case (b) *N*-dependent vibrational matrix elements to Hund's case (a) *J*-dependent matrix elements for the vibration-rotation bands of NH $X^3 \Sigma^-$. The formula was coded in Python by J.

Hodges and used for the OH⁺ [38] and NH A³ Π - X³ Σ ⁻ [39] transitions. We include this program as supplementary data. The table output from our Python program was included in PGOPHER as the line strengths utilizing the custom transition moment function. The line strength tables for the X³ Σ ⁻ and a¹ Δ states as well as the line lists are provided as supplementary data.

3. Results and discussion

The selection rules for electric dipole transitions require $\Delta J=0$, ± 1 and $+\leftrightarrow$ - for total parity [36]. For a¹ Δ vibration-rotation transitions, there are nominally 6 branches ${}^{r}R_{e/f}$, ${}^{q}Q_{e/f}$, and ${}^{p}P_{e/f}$ in each band. All of the lines are doubled by lambda doubling, labeled by e or f in the lower state, which is very small and unresolved. The lines are labeled in PGOPHER using the notation: ${}^{\Delta N}\Delta J_{e''|f''}(J'')$ in which p, q and r refer to $\Delta N=-1$, 0, 1, respectively; P, Q, and R refer to $\Delta J=-1$, 0, and 1, respectively. For the singlet a¹ Δ state N=J. The Fortrat diagram and simulated spectrum for SO at 300 K are dis-



Fig 4. Absorbance spectrum of the $a^1 \Delta$ 1-0 band of SO at 300 K.



Fig 5. Fortrat diagram of the $X^3 \Sigma^-$ 1-0 band

played as Figs. 3 and 4. Notice the relatively weak Q branch which deceases rapidly in relative intensity as *J* increases.

For the $X^3 \Sigma^-$ state, each rotational level (*N*) is split into 3 *J* levels due to electron spin with J=N+1, J=N and J=N-1, labeled conventionally as F_i , i=1, 2 and 3, respectively. The transitions are labeled in PGOPHER as ${}^{\Delta N}\Delta J_{Fi'Fi''}(J'')$. Primes and double primes refer to the upper and lower states, respectively. There are 6 main branches: ${}^{P}P_1$, ${}^{P}P_2$, ${}^{P}P_3$, ${}^{r}R_1$, ${}^{r}R_2$ and ${}^{r}R_3$ with $\Delta F_i=0$ plus a number of weaker satellite branches that change F_i . The Fortrat diagram and a simulated spectrum for the 1-0 band are presented in Figs. 5 and 6. The lines are tripled due to electron spin and the weak satellite lines mostly track the main branches.

In Tables 1 and 2 we report the rotationless dipole and transition dipole moments for the vibrations of the $X^3\Sigma^-$ and $a^1\Delta$ states. Additionally, we replaced the dipole moment function with the one from Borin and Ornellas [31] to produce dipole and transition dipole moment values. The 1-0 band transition dipole moments from this calculation were 0.0678 D for the $X^3 \Sigma^-$ state and 0.0682 D for the $a^1 \Delta$ state. Compared with our dipole moment values in Tables 1 and 2, the values calculated using the Borin and Ornellas data agree with experiment slightly less than our own for the $X^3 \Sigma^-$ state and is closer to experiment for the $a^1 \Delta$ state than our value; all of the values calculated agree within 10% of the experimental values. For our 1-0 transition dipole moments, we calculated values of 0.07968 D and 0.06359 D for the $X^3 \Sigma^-$ state and the $a^1 \Delta$ state, respectively, for our data, in reasonable agreement with Borin and Ornellas. Intensities in our spectra for the $X^3 \Sigma^$ state agree roughly to Fig. 1 in Burkholder et al. [12].

The Einstein A_{1-0} value for the $X^3\Sigma^-$ 1-0 band is calculated to be 2.93 s⁻¹ from equation 5.141 from Bernath's book [36],



Fig 6. Absorbance spectrum of the $X^3 \Sigma^-$ 1-0 band of SO at 300 K.

 $A = 3.136 \times 10^{-7} \nu^3 S$, with the frequency ν in cm⁻¹ and the band strength *S* in debye². The vibrational lifetime $\tau = 1/A_{1-0}$ is therefore 0.341 s. To check this value, we summed the three Einstein $A_{2-J''}$ values arising from J'=2f and also found an *A* value of 2.93 s⁻¹. Similarly, for the a¹ Δ 1-0 band, a value of $A_{1-0} = 1.69 \text{ s}^{-1}$ and a vibrational lifetime of $\tau = 0.590 \text{ s}$ was obtained. A similar check using J'=3f yields the same results.

The size of the Herman-Wallis effect was assessed by using a single band strength for each vibration-rotation band from LEVEL and ignoring the *N*-dependence. These values for the $X^3\Sigma^-$ and $a^1\Delta$ states are provided as Tables 1 and 2. After input into PGO-PHER, the Einstein A values for the corresponding lines with and without the Herman-Wallis effect were compared. For the $X^3\Sigma^$ state, the three main ^pP branches all increased in Einstein A values while the rR branches saw a significant decrease, particularly for large J values. For example, the ${}^{r}R_{1}(10)$ line of the 1-0 band changed from an Einstein A of 1.15 s⁻¹ to 1.11 s⁻¹, a 3% decrease, while the ${}^{r}R_{1}(73)$ line was altered from 1.39 s⁻¹ to 0.954 s⁻¹, a 31% decrease. In the P branches, the ${}^{p}P_{1}(10)$ value rose 2% from 1.18 s⁻¹ to 1.21 s⁻¹ while ${}^{p}P_{1}(71)$ was raised 9% from 0.821 s⁻¹ to 0.898 s⁻¹. In the satellite branches, we saw a very small increase of around 0.4% in the Einstein A for the ${}^{p}Q_{12}$, ${}^{p}Q_{23}$, ${}^{r}Q_{32}$, and ${}^{r}Q_{21}$ branches. Similarly, in the 1-0 band of the $a^1 \Delta$ state, the ${}^p\mathrm{P}_{e/f}$ branch saw a noticeable increase while the ${}^{\mathrm{r}}\mathrm{R}_{\mathrm{e/f}}$ branch mostly decreased. The ${}^{p}P_{e/f}(8)$ line increased from 0.821 s⁻¹ to 0.841 s⁻¹ and the ${}^{p}P_{e/f}(71)$ line rose from 0.586 s⁻¹ to 0.649 s⁻¹, a boost of 2% and 11%, respectively. The opposite occurred in the ${}^{\rm r}R_{e/f}$ branch, as ${}^{\rm r}R_{e/f}$ (8) decreased 3% from 0.789 s $^{-1}$ to 0.769 s $^{-1}$ and ${}^{\rm r}R_{e/f}$ (71) fell 31% from 1.01 s⁻¹ to 0.697 s⁻¹. The ^qQ_{e/f} branch was mostly unchanged or saw a very small shift in A value. We provided the .pgo file as a supplementary material for those who would like to visually explore any transitions. Note this file requires use of the PGOPHER program [33].

4. Conclusion

We have calculated vibration-rotation line lists for v=0-6 for the $X^3\Sigma^-$ and v=0-5 $a^1\Delta$ states from fitting spectroscopic data from the literature to obtain line positions, and *ab initio* dipole moment calculations for line intensities. The 1-0 bands of the $X^3\Sigma^$ state and the metastable $a^1\Delta$ state may be observable with the Mid-Infrared Instrument (MIRI) on the James Webb Space Telescope that was launched in December 2021. The line lists include quantum numbers, line positions and lower state energies in cm⁻¹, and Einstein $A_{J^-J^*}$ values. If necessary, these Einstein A values can be converted to other units such as oscillator strengths or HITRAN units using formulas found in Bernath's book [34,38,40]. Partition functions for SO as needed for astronomical retrievals are available, for example, from Barklem and Collet [41].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Peter F. Bernath: Writing – original draft, Supervision, Conceptualization. **Ryan M. Johnson:** Writing – review & editing, Formal analysis, Visualization. **Jacques Liévin:** Writing – review & editing, Formal analysis, Visualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2022.108317.

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