Line lists for the $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions of SOPeter F. Bernath^{a,b,*}, Ryan Johnson^b, Jacques Liévin^c^a Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States^b Department of Physics, Old Dominion University, Norfolk, Virginia 23529, United States^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 many astronomical sources such as the atmospheres of Io and Venus. In order to create more complete line lists, we fit spectroscopic data on SO from the literature using PGOPHER. The fits covered $v = 0$ to $v = 6$ for the $X^3\Sigma^-$ state, $v = 0-5$ for the $a^1\Delta$ state and $v = 0-2$ for $b^1\Sigma^+$ state. LeRoy's RKR program was used to produce pointwise potential energy curves. High level *ab initio* calculations, including spin-orbit coupling, were carried out to obtain the electric transition dipole moment functions for the nominally forbidden $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions. The RKR potentials and transition dipole moment points were input into LeRoy's LEVEL program to calculate the transition dipole matrix elements for all possible b-X and a-X bands. For the $b^1\Sigma^+-X^3\Sigma^-$ transition, the electric and magnetic transition dipole matrix elements were scaled using the experimental values obtained by Setzer et al. [J Mol Spectrosc 1999;198:163–174] for the 0–0 band. The transition dipole moment matrix elements were used in PGOPHER to produce our line lists for all possible bands of the $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions.

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1. Introduction

The SO free radical has been detected in many astronomical sources. Pure rotational transitions of SO have been observed in the Orion nebula [1] and in oxygen-rich circumstellar envelopes [2] by radio astronomers. In our Solar System, SO has been detected in the atmosphere of Venus by the $B^3\Sigma^--X^3\Sigma^-$ ultraviolet transition [3] and by millimeter wave astronomy [4]. Microwave transitions [5], the $B^3\Sigma^--X^3\Sigma^-$ ultraviolet transition [6] and the near infrared emission of the forbidden $a^1\Delta-X^3\Sigma^-$ transition near 1.7 μm assigned by Bernath [7] have all been used to measure SO on Io, a moon of Jupiter.

The SO molecule is isovalent with O_2 with an $X^3\Sigma^-$ ground state and low-lying metastable $a^1\Delta$ and $b^1\Sigma^+$ states. The strong $B^3\Sigma^--X^3\Sigma^-$ UV transition [8] is analogous to the Schumann-Runge system of O_2 . The forbidden $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions have been measured in the near infrared region at 955 nm and 1.7 μm , respectively [9,10]. For symmetric O_2 these two electronic transitions are mainly magnetic dipole in character, but they are primarily electric dipole for SO due to the absence of inversion symmetry [11]. The $b^1\Sigma^+$, $a^1\Delta$ and $X^3\Sigma^-$ states in SO are not pure Hund's case (a) states because of spin-orbit coupling and this contamination makes the transitions weakly allowed [11].

In addition to electronic spectroscopy, SO has been studied numerous times by microwave, millimeter wave, far infrared and infrared spectroscopy. Many pure rotational transitions have been measured for the $X^3\Sigma^-$ ground state, e.g., by Martin-Drumel et al. [12] and references therein, and in the metastable $a^1\Delta$ state and $b^1\Sigma^+$ states, e.g., [13,14]. Diode laser [15,16] and Fourier transform [17] vibration-rotation spectra are also available. The electronic structure of SO has also been investigated by means of *ab initio* calculations, e.g., [17–21].

In order to simulate the $a^1\Delta-X^3\Sigma^-$ transition and to search for the $b^1\Sigma^+-X^3\Sigma^-$ transition on Io, reliable line lists are needed. A preliminary $a^1\Delta-X^3\Sigma^-$ line list has been published [22] for the 0–0 and 1–1 bands, but the line strengths are not accurate. We now report on the b-X and a-X transitions with improved line positions based on high precision data from microwave, infrared and near infrared measurements, and with line strengths based on state-of-the-art *ab initio* calculations.

2. Method

2.1. Spectroscopic constants

Line positions associated with the $b^1\Sigma^+$, $a^1\Delta$ and $X^3\Sigma^-$ states were obtained from the literature and fitted to obtain a set of spectroscopic constants for the $v = 0-2$ $b^1\Sigma^+$, $v = 0-5$ $a^1\Delta$ and $v = 0-6$ $X^3\Sigma^-$ energy levels. Western's PGOPHER [23] program was used for the analysis with the standard N^2 Hamiltonian [24].

* Corresponding author.

E-mail address: pbernath@odu.edu (P.F. Bernath).

Table 1

$X^3\Sigma^-$ vibrational energy levels, one standard deviation in the last 2 digits is in parentheses.

v	Energy (cm^{-1})
0	0
1	1138.00953(28)
2	2263.31610(39)
3	3375.98685(43)
4	4476.08656(51)
5	5563.67728(58)
6	6638.81795(63)

Table 2

Rotational constants for $X^3\Sigma^-$ $v = 6$, one standard deviation in the last digits is in parentheses.

Constant	Value (cm^{-1})
B	0.683737834(77)
λ	5.4799854(161)
γ	-5.85081(203)e-3
D	1.135193(167)e-6
λ_D	1.148(11)e-5
γ_D	-1.550(450)e-8

For $v = 0-5$ of the $X^3\Sigma^-$ state, the rotational constants were taken from Table 9 of Martin-Drumel et al. [12] for ^{32}SO and held fixed. The vibrational energy levels were obtained fitting the diode laser measurements of Kanamori et al. [15] for the 1-0 to 6-5 vibration-rotation bands. The microwave and millimeter wave data for $v = 6$ [13,25-27] were added to the fit. The vibrational band origins for the X state and spectroscopic constants for $v = 6$ are provided in Tables 1 and 2, respectively. In Table 2, the customary symbols for the rotational constant B , the electron spin-spin constant λ , the (electron) spin-rotation constant γ as well as their centrifugal distortion constants (D , λ_D , γ_D) are used. The corresponding operators and their matrix elements can be conveniently printed using PGOPHER.

For $v = 0-5$ of the $a^1\Delta$ state, the 1-0 to 5-4 vibration-rotation bands of Kanamori et al. [16] were fitted along with pure rotational transitions [13,14,27-31]. In order to determine the $a^1\Delta-X^3\Sigma^-$ 0-0 band origin and connect all the $a^1\Delta$ vibrational levels to the ground state, 5 low- J transitions ($^9R_{13}(1-4)$ and $^1R_{12}(3)$ 0-0 $a^1\Delta-X^3\Sigma^-$) from Setzer et al. [10] were included in the fit. Note that $v = 0-6$ $X^3\Sigma^-$ and $v = 0-5$ $a^1\Delta$ were fitted simultaneously. The $a^1\Delta$ spectroscopic constants are reported in Table 3.

For $v = 0-2$ of the $b^1\Sigma^+$ state, no infrared vibration-rotation bands are available so the 0-0, 1-1 and 2-2 $b^1\Sigma^+-X^3\Sigma^-$ bands [10] were fitted separately with the $X^3\Sigma^-$ constants held fixed to the values obtained in the $X^3\Sigma^-$ and $a^1\Delta$ state fits (Table 1) described above. The pure rotational transitions [13,14,22,32,33] were also fitted separately (Table 4) and the $v = 0-2$ $b^1\Sigma^+$ rotational constants were held fixed in the $b^1\Sigma^+-X^3\Sigma^-$ fits. Only the energy origins were determined (also Table 4) in the 0-0, 1-1 and 2-2 $b^1\Sigma^+-X^3\Sigma^-$ fits; the errors for the rotational constants reported in Table 4 are from the separate fits of the pure rotational lines.

2.2. Ab initio calculations

Large scale *ab initio* spin-orbit calculations aiming to provide the electric transition dipole moment (TDM) curves for the $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions were performed using the MOLPRO program package [34,35] running on the Hydra and Vega clusters of the ULB/VUB computer center. The state interacting method [36] was used, in which the $\hat{H}_{SO} = \hat{H}_{el} + \hat{H}_{BP}$ Hamiltonian is diagonalized in a zeroth order basis set formed by the eigenfunctions of the electronic Hamiltonian $\hat{H}_{el}$. $\hat{H}_{BP}$ is the full Breit-Pauli spin-orbit

Hamiltonian. The requirements to be met for ensuring the accuracy of the TDM of spin forbidden transitions are the following: i) calculation of highly correlated solutions of the electronic Hamiltonian $\hat{H}_{el}$; ii) use of an extended polarized correlation consistent basis set augmented by diffuse functions, and optimized for the description of core-valence correlation and scalar relativistic corrections; and iii) inclusion in the spin-orbit calculations of a set of (Λ , S) zeroth order states covering the entire network of excited electronic states contributing to the spin-orbit transition properties at all internuclear distances.

The inclusion of spin-orbit coupling introduces the quantum number $\Omega = |\Lambda + \Sigma|$ (Σ is the projection of S on the internuclear axis), which is used to label the spin-orbit components of a (Λ , S) term. The Ω value appears as a right subscript on the term symbol: $b^1\Sigma^+_{0+}$, $a^1\Delta_2$ and $X^3\Sigma^-_1$, $X^3\Sigma^-_{0+}$ for the lowest energy states of SO. It is convenient, particularly for forbidden transitions that are allowed by spin-orbit mixing, to use just the Ω value in the corresponding Hund's case (c) state notation: $b0^+$, $a2$ and $X1$, $X0^+$. The selection rule for Ω is $\Delta\Omega = 0, \pm 1$; 0^+-0^+ and 0^+-1 transitions are called parallel and perpendicular, respectively, because of the direction of the transition dipole moment relative to the internuclear axis.

The internally contracted configuration interaction method (ic-MRCI) [37] has been adopted to answer i). These calculations were performed with an active correlation space including all core and valence molecular orbitals, except for the sulfur 1s-like molecular orbital, which lies too deep to interact appreciably with the valence shell. The aug-cc-pCVQZ-DK basis set [38-40] obeying to all criteria of ii) has been used. The second order Douglas-Kroll scalar relativistic correction has been taken into account in all calculations [41,42]. Finally, systematic test calculations, performed at a few relevant internuclear distances, were used to select the following 24 (Λ , S) electronic states satisfying iii), and thus included in the zeroth-order basis set (the number of states of each species is given in parentheses): $^1\Sigma^+(5)$, $^1\Sigma^-(2)$, $^1\Pi(3)$, $^1\Delta(3)$, $^3\Sigma^+(3)$, $^3\Sigma^-(3)$, $^3\Pi(3)$ and $^3\Delta(2)$. This selection is illustrated for the most important terms in Fig. 1 for the three transitions studied in this work. It highlights the network of electric dipole coupling terms contributing to the intensity of these transitions. Each line connects a pair of (Λ , S) states A and B, positioned at their relative ic-MRCI energies at the equilibrium geometry of the ground state; the x-axis is arbitrary. These lines indicate the matrix element $\langle A | \mu | B \rangle$ of the dipole moment operator μ , weighted by the product of coefficients of A and B in the corresponding spin-orbit eigenvectors, that contributes to the TDM value. These graphs interestingly show the dipolar coupling terms between pairs of zeroth order states, which are carrying the intensity of the different transitions. Let us draw attention to the horizontal lines appearing in the case of the $b0^+-X0^+$ transition, revealing the contribution of $\langle A | \mu | A \rangle$ expectation values in the corresponding TDM. This information was already discussed by Klotz et al. [11].

All ic-MRCI calculations have been performed using the symmetry of the C_{2v} abelian subgroup of $C_{\infty v}$, which means that the electronic calculations were carried out in the C_{2v} projected basis set of the following 35 states: $^1A_1(8)$, $^1B_1(3)$, $^1B_2(3)$, $^1A_2(5)$, $^3A_1(5)$, $^3B_1(3)$, $^3B_2(3)$ and $^3A_2(5)$. Let us note that the spatial degeneracy of $\Lambda \neq 0$ states is ensured by the state-averaged complete active space self-consistent field (SA-CASSCF) calculation [43] preceding the ic-MRCI runs. Combining the ic-MRCI electronic wavefunctions with spin functions, also adapted to C_{2v} symmetry, leads to the final basis set of 67 zeroth order spin-orbit functions, in which the $\hat{H}_{SO}$ matrix is diagonalized. The non-diagonal elements are calculated at the ic-MRCI level, using the effective Hamiltonian approach implemented in MOLPRO [34,35], while the diagonal elements include the Davidson correction for unlinked clusters adapted to a relaxed reference [44,45], which has been added to the ic-MRCI

Table 3Spectroscopic constants (in cm⁻¹) for the a¹Δ state, one standard deviation in the last digits is in parentheses.

Const.	v = 0	v = 1	v = 2	v = 3	v = 4	v = 5
T _{v=0}	5862.86874(40)	6964.28715(46)	8052.07391(53)	9126.26615(58)	10,186.89430(63)	11,233.98377(67)
B _v	0.710347530(27)	0.704302311(30)	0.698260115(28)	0.692219409(26)	0.686178903(26)	0.680136861(28)
D _v	1.168519(56)e-6	1.170995(44)e-6	1.173874(41)e-6	1.176777(36)e-6	1.180019(36)e-6	1.183271(37)e-6
H _v	-6.87(34)e-13	-6.5e-13 ^a	-6.5e-13 ^a	-6.5e-13 ^a	-6.5e-13 ^a	-6.5e-13 ^a

^a Fixed.**Table 4**Spectroscopic constants (in cm⁻¹) for the b¹Σ⁺ state, one standard deviation in the last digits is in parentheses.

Const.	v = 0	v = 1	v = 2
T _{v=0}	10,472.753681(52)	11,527.011444(28)	12,566.84664(16)
B _v	0.699465229(13)	0.693088427(24)	0.686706305(28)
D _v	1.217056(42)e-6	1.221617(32)e-6	1.226393(36)e-6
H _v	-6.29(38)e-13	-6.29e-13 ^a	-6.29e-13 ^a

^a Fixed.

energy value to improve the relative energies between the zeroth order states.

The analysis of the 67 spin-orbit eigenvectors of $\hat{H}_{SO}$ led to the characterization of 43 states corresponding to the following Ω values: 0⁺(11), 0⁻(8), 1(14), 2(8) and 3(2), among which the 6 eigenfunctions describing the X0⁺, X1, a2 and b0⁺ states are identified, noting that two degenerate complex eigenvectors arise from the two-fold degeneracy of the $\Omega \neq 0$ spin-orbit states.

The transition matrix elements of the Cartesian components (μ_x , μ_y , μ_z) of the electric dipole moment operator are calculated by Molpro. In order to match the spectroscopic analysis, unitary transformations were applied to the spin-orbit functions to transform them from C_{2v} to C_{∞v} symmetry, and the dipole moment operator has been put in spherical tensor form ($(\mu_x \pm i\mu_y)/\sqrt{2}$, μ_z). The resulting TDMs, which have been used to model the line intensities (see next section), are:

$$\mu_0 = \langle {}^1\Sigma_0^+ | \mu_z | {}^3\Sigma_0^- \rangle \quad (1)$$

$$\mu_1 = \langle {}^1\Sigma_0^+ | 1/\sqrt{2}(\mu_x - i\mu_y) | {}^3\Sigma_{+1}^- \rangle = -\langle {}^1\Sigma_0^+ | 1/\sqrt{2}(\mu_x + i\mu_y) | {}^3\Sigma_{-1}^- \rangle \quad (2)$$

$$\mu_2 = \langle {}^1\Delta_2 | 1/\sqrt{2}(\mu_x + i\mu_y) | {}^3\Sigma_{+1}^- \rangle = -\langle {}^1\Delta_{-2} | 1/\sqrt{2}(\mu_x - i\mu_y) | {}^3\Sigma_{-1}^- \rangle, \quad (3)$$

where the right subscript of the state labels corresponds to the signed $\Lambda + \Sigma$ value. Eq. (1) for μ_0 is for the b0⁺-X0⁺ transition, Eq. (2) for μ_1 is for the b0⁺-X1 transition and Eq. (3) for μ_3 is for the a2-X1 transition. The two matrix elements reported in Eqs. (2) and (3) are related by a σ_{xz} symmetry operation, explaining the sign change, as detailed by Watson for ¹Σ⁺-³Σ transitions [46].

The transition dipole moment calculations have been carried out at 24 points corresponding to internuclear distances, R , ranging from 1.05 to 1.9 Å, by steps of 0.05 Å, and from 1.9 to 2.5 Å, by steps of 0.1 Å. The μ_0 , μ_1 and μ_2 curves were then interpolated using B-splines to create a set of 1592 points for each transition function. These curves are shown in Fig. 2, and both the calculated and interpolated data points are provided as supplementary material.

All calculated values of μ_0 , μ_1 and μ_2 are real, as expected. The TDM of each transition is determined within a phase factor, which depends on the phase of the eigensolutions arising from the successive matrix diagonalizations of the computational procedure.

The relative sign, however, between two transitions is unambiguously predicted because it results from the same matrix diagonalization based on a common set of optimized molecular orbitals. This allows us to predict that the sign of the μ_1/μ_0 ratio is negative within a range of R values covering the lowest vibrations of the system. This agrees with the observation made by Setzer et al. [11] for the 0-0 band. This ratio is of particular importance for the interpretation of the intensities in the b-X transition, as shown below. However, the ratio becomes positive at values of R smaller than 1.25 Å as can be seen in Fig. 2. This is explained by a competition between two major indirect couplings of opposite sign contributing to the value of μ_0 , namely the expectation values of the dipole moments of the X and b states (see Fig. 1). This competition affecting μ_0 and not μ_1 causes the sign inversion of μ_1/μ_0 . This inversion affects however internuclear distances which are too short to be explored by the vibrational wavepackets involved in the observed bands. The left turning points of the corresponding vibrational levels are indeed larger than 1.35 Å.

2.3. Line list calculation

Line positions up to $J = 75$ were generated with PGOPHER [23] using the spectroscopic constants of Tables 1–4 and the rotational constants of Martin-Drumel et al. [12] for X³Σ⁻ $v = 0-5$. The b¹Σ⁺, a¹Δ and X³Σ⁻ states all arise from the same electronic configuration so the vibrational and rotational constants are relatively similar. All possible bands were included in our line lists for the b-X and a-X transitions.

The band strengths were calculated using Le Roy's LEVEL program [47] with the new *ab initio* b-X and a-X transition dipole moment functions. Semi-classical RKR potentials [48] were first calculated using the $B_v = B_e - \alpha_e(v + 1/2) + \dots$ rotational parameters of Bogey et al. [13] for all 3 states. The $G_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots$ vibrational parameters for the X³Σ⁻ and a¹Δ states were from Kanamori et al. [15,16], while $\omega_e = 1068.680$ cm⁻¹ and $\omega_e x_e = 7.2113$ cm⁻¹ for the b¹Σ⁺ state are derived from an exact fit of the differences between the T_{v=0} values in Table 4 to the G_v expression.

Using the three RKR potential energy curves, we input the points into LEVEL [47] along with the pointwise interpolated b-X and a-X electric transition dipole moments. LEVEL produces calculated energy levels, Einstein A factors, Franck-Condon factors, and vibration-rotation transition dipole moment matrix elements. The R(0) matrix elements were used to obtain purely vibrational matrix elements because the rotational parts (Hönl-London factors) are 1 in this case.

For the magnetic transition dipole moment matrix elements of the b¹Σ⁺-X³Σ⁻ transition, we used the 0-0 band value of 0.16 μ_B (Bohr magnetons) obtained by Setzer et al. [10] scaled by the ratio of the square root of the Franck-Condon factors (i.e., $M_{v'v''} = M_e |\langle v' | v'' \rangle|$ for the magnetic dipole matrix elements). For the electric transition dipole matrix elements for b¹Σ⁺-X³Σ⁻ transition, values of $\mu_0 = 0.0107$ D and $\mu_1 = -0.0119$ D, respectively, were reported by Setzer et al. [10] for the 0-0 band compared to our *ab initio* values of $\mu_0 = 0.00135$ D and $\mu_1 = -0.001755$ D obtained from LEVEL, which evaluates

Fig. 1. Network of electric dipole coupling terms contributing to the intensity of the studied transitions. Each line connects two electronic states involved in a matrix element of the dipole moment operator contributing to the considered transition.

Fig. 2. *Ab initio* transition dipole moment functions for μ_0 ($b0^+-X0^+$), μ_1 ($b0^+-X1$) and μ_2 ($a2-X1$); see Eqs. (1), (2) and (3), respectively.

the $\langle v'=0 | \mu(R) | v''=0 \rangle$ integrals using the unscaled transition dipole moment functions and the vibrational wavefunctions. The vibrationally-averaged *ab initio* matrix elements provided by LEVEL were therefore scaled using the experimental values (i.e., the matrix elements were multiplied by a factor of 7.92 for the parallel moment μ_0 and 6.78 for the perpendicular moment μ_1). These scaled matrix elements are provided in Table 5. The scaling factors are surprisingly large, and the magnitude of the experimental values are based on the experimental b state lifetime of 6.8 ± 0.4 ms [10,49]. Such long lifetimes are difficult to measure, and the experimental error may be underestimated. On the other hand, the *ab initio* values of μ_0 and μ_1 arise from contributions of similar magnitude and varying signs and may be underestimated.

The relative signs of μ_0 and μ_1 are important and must be opposite in order to reproduce the observed line intensities. For PGOPHER, however, the sign of the parameter corresponding to μ_1 , $ft(1,1)$, must be changed (i.e., $ft(1,1) = -\mu_1$) to obtain the correct line intensities. The vibrationally-averaged $a^1\Delta-X^3\Sigma^-$ electric transition dipole moment matrix elements (Table 6) were directly taken from the output of LEVEL and used in PGOPHER. No reliable experimental lifetimes are available for the $a^1\Delta$ state, so no scaling is possible. Note that the selection rules for the magnetic dipole branches are the same as electric dipole rules except that total parity obeys $+\leftrightarrow+$ and $-\leftrightarrow-$ selection rules.

3. Results and discussion

As discussed previously [18], the usual electric dipole selection rules on J ($\Delta J=0, \pm 1$ and $+\leftrightarrow-$ for total parity) [11] result in 9 branches for a $^1\Delta-^3\Sigma^-$ transition: $^oP_{13}$, $^pP_{12}$, $^pQ_{13}$, $^qQ_{12}$, $^qR_{13}$, qP_1 , $^rR_{12}$, rQ_1 and sR_1 [6]. The lines are labeled using the traditional notation, $\Delta^N\Delta J_{F'F''}(J'')$: the left superscript is ΔN ($N = J-S$) written in lower case with o, p, q, r and s corresponding to $\Delta N=-4, -2, 0, 2$ and 4 , respectively; ΔJ in upper case is P, Q and R for $\Delta J=-1, 0$ and 1 , respectively; the right subscript is F'/F'' , in which F' is 1 ($N = J$) for the upper $a^1\Delta$ state and F'' is 1, 2 or 3, for $J = N+1$, $J = N$ and $J = N-1$, respectively; prime and double prime refer to upper and lower energy levels, respectively. The “form” of the branches (ΔN) is a convenient label because near the band ori-

Table 5
Transition dipole vibrational matrix elements for the $b^1\Sigma^+-X^3\Sigma^-$ transition.

Vibrational Band $v'-v''$	$b0^+ - X0^+$ Electric Transition Dipole Moment in 10^{-3} D	$b0^+ - X1$ Electric Transition Dipole Moment in 10^{-3} D	Magnetic Transition Dipole Moment in $10^{-3} \mu_B$
0-0	10.7	-11.9	160
1-0	-0.383	4.09	41.2
2-0	-1.47	-1.22	8.17
0-1	5.34	-1.97	41.38
1-1	8.93	-11.1	149
2-1	-2.01	5.58	57.4
0-2	0.114	-0.397	7.27
1-2	5.74	-2.77	57.9
2-2	7.34	-10.2	137
0-3	-0.847	-0.0478	0.993
1-3	0.144	-0.656	12.9
2-3	5.63	-3.36	69.9
0-4	0.144	0.0176	0.111
1-4	-1.17	-0.101	2.11
2-4	0.0272	-0.918	18.8
0-5	0.172	-0.00751	1.11E-02
1-5	0.147	0.0162	0.274
2-5	-1.29	-0.170	3.55
0-6	-0.141	-0.00598	9.183E-04
1-6	0.330	-0.0133	3.40E-02
2-6	0.268	0.0116	0.532

Table 6
Transition dipole vibrational matrix elements of the $a^1\Delta-X^3\Sigma^-$ ($a2-X1$) transition.

Vibrational Band $v'-v''$	Electric Transition Dipole Moment in 10^{-3} D	Vibrational Band $v'-v''$	Electric Transition Dipole Moment in 10^{-3} D
0-0	1.03	3-3	0.986
1-0	-0.136	4-3	-0.285
2-0	0.0240	5-3	0.0498
3-0	-0.00463	0-4	-0.00366
4-0	-0.00239	1-4	-0.00163
5-0	0.00185	2-4	0.0205
0-1	0.0814	3-4	0.175
1-1	1.02	4-4	0.959
2-1	-0.192	5-4	-0.327
3-1	0.0341	0-5	0.000389
4-1	-0.00957	1-5	-0.00579
5-1	-0.00218	2-5	-0.00474
0-2	0.0152	3-5	0.0198
1-2	0.123	4-5	0.194
2-2	1.01	5-5	0.927
3-2	-0.240	0-6	0.000862
4-2	0.0418	1-6	0.00139
5-2	-0.0139	2-6	-0.00683
0-3	0.000656	3-6	-0.00759
1-3	0.0196	4-6	0.0189
2-3	0.153	5-6	0.209

gin o, p, q, r and s branches are spaced by approximately $-4B$, $-2B$, $0B$, $+2B$, $+4B$ (Fig. 3) with the rotational constant B of about 0.71 cm^{-1} . This is illustrated in Fig. 3 with a Fortrat diagram drawn with cm^{-1} on the x-axis (in contrast to the paper of Bernath et al. [22] that used wavelength). The size of the symbols in Fig. 3 (and Fig. 4 below) is proportional to the line intensity.

The $b^1\Sigma^+-X^3\Sigma^-$ transition has 5 electric dipole branches, $^oP_{13}$, $^qQ_{12}$, $^qR_{13}$, pP_1 and sR_1 , illustrated by a Fortrat diagram in Fig. 4. These are $-4B$, $0B$, $0B$, $0B$ and $+4B$ branches, respectively. In addition, there are 4 much weaker magnetic dipole branches, $^pP_{12}$, $^pQ_{13}$, $^rR_{12}$ and rQ_1 , that are not shown in Fig. 4. These branches are $-2B$, $-2B$, $+2B$ and $+2B$ branches, respectively.

The calculated transition dipole moment for the 0-0 band of the $a^1\Delta-X^3\Sigma^-$ transition is 0.00103 D (Table 6). In our previous paper, we used a value of 0.0059 D based on a calculation of Klotz et al. [11]. Xing et al. [21] recently also calculated transition dipole moment functions for the b-X and a-X transitions. From

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

Fig. 4. Fortrat diagram of the 0-0 band of the $b^1\Sigma^+-X^3\Sigma^-$ transition.

their Fig. 3, the values obtained at the equilibrium geometry are -0.0060 D, -0.0005 D, and -0.0005 D for the $b^1\Sigma^+-X^0+$, $b^1\Sigma^+-X^1$ and $a^1\Sigma^+-X^1$ transitions, respectively, and the μ_1/μ_0 ratio is 0.08. These results disagree with our corresponding *ab initio* values of 0.00136 D, -0.00184 D, and 0.00129 D, respectively, and the resulting μ_1/μ_0 ratio is -1.36 . Our ratio has the correct sign and is in reasonable agreement with the experimental 0-0 band value of -1.112 [10]. The poor agreement of the Xing et al. [21] μ_1/μ_0 ratio with experiment casts doubt on the reliability of their results.

The transition dipole matrix element of 0.00103 D for the 0-0 band of the $a^1\Delta-X^3\Sigma^-$ transition converts to an Einstein A_{0-0} value of 0.067 s $^{-1}$, using the equation [50], $A = 3.136 \times 10^{-7} \nu^3 S^2$, in which ν is in cm $^{-1}$ and S (transition moment) is in debye. The A_{0-1} value is 2.19×10^{-4} s $^{-1}$ so the lifetime for $\nu = 0$ $a^1\Delta$ is calculated to be 14.8 s, compared to estimated values of 0.45 s and 0.86 s by Klotz et al. [11] and Xing et al. [21], respectively. As a check, the sum of the Einstein A values for the 5 strong transitions coming from $\nu = 0$, $J = 2$, e parity is 0.0667 s $^{-1}$, in agreement with the value above.

The Einstein A_{0-0} value for the $b^1\Sigma^+-X^3\Sigma^-$ transition is 141 s $^{-1}$, calculated by summing the 7 strongest $A_{J'-J''}$ values for the lines coming from $J'=2$ in the b state for the 0-0 band. Adding the value (9.25 s $^{-1}$) for the 0-1 band calculated in the same way gives a lifetime of 6.6 ms, compared to the observed value of 6.8 ± 0.4 ms [10]. This good agreement is expected because the experimental value is the basis for our intensity scaling described above. This value is also to be compared to the calculated values of 13.8 ms and 78.7 ms by Klotz et al. [11] and Xing et al. [21], respectively.

4. Conclusion

Line lists for the nominally forbidden $b^1\Sigma^+-X^3\Sigma^-$ and $a^1\Delta-X^3\Sigma^-$ transitions of SO have been calculated based on spectroscopic data from the literature for line positions and *ab initio* calculations for line strengths. All possible bands connecting $\nu = 0-2$ in the $b^1\Sigma^+$ state and $\nu = 0-5$ in the $a^1\Delta$ state with $\nu = 0-6$ in the $X^3\Sigma^-$ state are included. Of these bands, the $a^1\Delta-X^3\Sigma^-$ 0-0 band and perhaps the 1-1 band from hot volcanic SO are observable in emission from Io [7], while the $b^1\Sigma^+-X^3\Sigma^-$ 0-0 band may be observable in the future with the James Webb Space Telescope. The line lists are suitable for the analysis of astronomical spectra and are provided as supplementary data. The line lists include quantum numbers, line positions in cm $^{-1}$ and line strengths as Einstein $A_{J'-J''}$ values. Einstein A values can be converted into customary units

such as oscillator strengths using formulas provided in Bernath's book [50].

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.

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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.2021.107772.

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