The Microwave Spectrum and Rotational Structure of the $^{1}\Delta$ and $^{8}\Sigma$ Electronic States of Sulfur Monoxide

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The spectrum of $^{1}\Delta$ and $^{8}\Sigma$ SO has been studied in the millimeter and submillimeter region of the microwave spectrum. This expanded spectral coverage has made possible the measurement of twenty-two previously unobserved transitions, several of which are necessary for an accurate calculation of the energy levels. As a result, it is now possible to calculate the rotational transitions between energy levels for which $J < 10$ in both the ground $^{8}\Sigma$ electronic state and the excited $^{1}\Delta$ electronic state to an accuracy comparable to that of the microwave measurements themselves ($\lesssim 1$ MHz). Among the molecular constants calculated are; for the $^{1}\Delta$ state: $B_0 = 21.295.405$ MHz, $D_0 = 0.0350$ MHz, $\omega_0 = 1108$ cm$^{-1}$, and $r_0 = 1.4920$ Å; and for the $^{8}\Sigma$ state: $B_0 = 21.523.561$ MHz, $D_0 = 0.03399$ MHz, $\alpha_0 = 158.254.387$ MHz, $\gamma_0 = -168.342$ MHz, $\rho_0 = 0.305$ MHz, $r_0 = 1.4840$ Å, $B_0 = 21.609.552$ MHz, $\alpha_0 = 157.779.2$ MHz, and $r_0 = 1.4811$ Å.

I. INTRODUCTION

Microwave spectroscopy has traditionally been the study of the ground state of stable molecular species because of the small Boltzmann population of excited states at room temperature. However, a number of studies have been reported in excited vibrational states that have either low excitation energies or that have been populated at elevated temperatures (I). Although excited electronic states lie at energies that have no significant thermal population and are not ordinarily studied by microwave absorption techniques, a small population can be produced in the metastable $^{1}\Delta$ state of the unstable molecular species SO by means of a reaction between the products of a discharge in oxygen and small, sulfur containing molecules (2). In this paper are reported the measurements of a number of transitions of SO both in its $^{1}\Delta$ excited electronic state and in its $^{8}\Sigma$ ground electronic state. Like O$_2$, SO has a $\ldots (\pi)^2$ ground state electron configuration which can result in three molecular states, $b^{8}\Sigma^+$, $a^{1}\Delta$, and $X^{8}\Sigma^-$. These have electronic term values of $10.509.97$ cm$^{-1}$, $\sim 6350$ cm$^{-1}$, and $0.0$ cm$^{-1}$, respectively.

The lowest rotational transition in the $^{1}\Delta$ electronic state of SO is $N = 2 \rightarrow 3$ at 128 GHz. This transition has been observed by Saito in a Stark-modulation spectrometer and represents the first example of microwave absorption spectroscopy in an excited electronic state (J). In this paper we report the observation of this and three more rotational transitions in the 100–300 GHz region and the calculation of the rotational constants from these data. The low field Zeeman effect has also been observed and is shown to be consistent with that predicted for a $^{1}\Delta$ electronic state, thereby further confirming the assignment.

1 This work was supported by the National Science Foundation, Grant No. GP-34580, and by the Army Research Office, Grant No. DAHCO4 74 G 0034.
\[ ^3\Sigma \text{SO has been extensively studied in the spectral region longer than about 2 mm and}
\[ \text{these results have been critically reviewed for astrophysical purposes (4). However,}
\[ \text{there are a number of weak transitions around 1 mm which are necessary for the direct}
\[ \text{calculation of the electronic spin-spin interaction constant} \lambda. \text{These transitions have}
\[ \text{been predicted from the indirect information contained in the previously observed}
\[ \text{lines (4), but these predictions differ from the observed frequencies reported in this}
\[ \text{work. We report in addition to these transitions a number of other previously unob-
\[ \text{served lines and the analyses of these data.}
\[ \]
\[ \text{For both} ^1\Delta \text{and} ^3\Sigma \text{SO it is now possible to calculate the rotational spectrum to the}
\[ \text{order of the expected uncertainty of microwave measurements} (\leq 1 \text{ MHz}) \text{and the}
\[ \text{redundancy and variety of lines in the data sets make possible accurate calculation of}
\[ \text{the uncertainties in each of the predicted transition frequencies.}
\[ \]
\[ \text{II. THEORY}
\[ \]
\[ \text{The theory of diatomic molecules which are not in} ^3\Sigma \text{ electronic states has been dis-
\[ \text{cussed by a number of authors (1-2, 5-9). Hund has classified these states according to}
\[ \text{limiting cases of the coupling of the several angular momenta that characterize the}
\[ \text{molecular system (5). Molecules in} ^1\Delta \text{ states conform closely to Hund’s case (a), which}
\[ \text{is shown in Fig. 1 for singlet states. For the} ^1\Delta \text{ state:}
\[ \]
\[ \Sigma = 0
\[ \Lambda = \Omega = 2
\[ \mathbf{J} = \mathbf{N} = \mathbf{A} + \mathbf{R}
\[ \]
with $B_{\text{eff}} = B_0 + 8D_0$ and $D_{\text{eff}} = D_0$. Although this is of the same form as the expression for the transition frequencies of $^1\Sigma$ molecules, the difference between $B_{\text{eff}}$ and $B_0$ must be considered in the calculation of any molecular parameters.

The Zeeman effects for molecules in the $^1\Delta$ state are, however, dramatically different from those of molecules in the $^1\Sigma$ state because of the large magnetic dipole moment associated with the electronic orbital angular momentum. From the vector coupling scheme for Hund’s case (a) shown in Fig. 1, it can be seen that in the $^1\Delta$ state $\mu_J$, the component of the magnetic field along $J$ produced by the electronic orbital motion, is given by

$$\mu_J = -\beta \mathbf{J} J / [J(J+1)]^\frac{3}{2}$$

and

$$g_J = \Lambda^2 / [J(J+1)]$$

where $\beta$ is the Bohr magneton. For small magnetic fields, the Zeeman energy is then simply given by

$$E_{\text{Hz}} = g_J \beta \mathbf{H} \mu_J.$$  

The calculation of the rotational energy levels for $^3\Sigma$ SO is substantially more complex both because the effects of electronic orbital and spin angular momenta must be considered and because $^3\Sigma$ SO represents a molecule intermediate between Hund’s cases (a) and (b).

It is convenient to use Hund’s case (b), shown in Fig. 2 for a $^3\Sigma$ state, as the basis for the calculation of matrix elements for $^3\Sigma$ SO. In this basis

$$J = N + S$$

where $J$ is the total angular momentum, $N$ is the angular momentum of the molecular frame, and $S$ is spin angular momentum of the electrons. If the effects due to centrifugal distortion are temporarily neglected, the Hamiltonian for $^3\Sigma$ SO can be written as

$$\mathcal{H} = B \mathbf{N}^2 + \frac{3}{2} \lambda (3S_z^2 - S^2) + \gamma \mathbf{N} \cdot \mathbf{S}$$

where the terms represent rotational kinetic, electron spin–spin, and spin–rotation energy, respectively. The matrix elements of these interactions have been calculated by numerous authors (8, 9, 11). The effects of centrifugal distortion on these matrix
elements can be included through the following expansions

\[ B = B_0 + D_N (N + 1), \]  
\[ \gamma = \gamma_0 + \delta_N (N + 1), \]  
\[ \lambda = \lambda_0 + \rho_N (N + 1), \]

for matrix elements diagonal in \( N \), and

\[ \lambda = \lambda_0 + \rho_N (J^2 + J + 1) \]

for matrix elements for which \( N = J \pm 1 \). Diagonalization of the Hamiltonian matrix which results gives the energy levels and transition frequencies for \( ^2 \Sigma \) SO.

Although a molecule in a pure \( ^2 \Sigma \) state has no first-order spin–orbit coupling, this interaction makes a significant contribution to the spectra of molecules whose states can be characterized as primarily \( ^2 \Sigma \) but which also contain an admixture of other higher electronic states. It has been shown that this second-order effect has the same form as that of the spin–spin term explicitly included in the Hamiltonian of Eq. (7) \( (12) \). As a result, the value of \( \lambda \) calculated from the spectrum of \( ^2 \Sigma \) SO consists of two parts

\[ \lambda = \lambda^{(1)} + \lambda^{(2)} \]

where \( \lambda^{(1)} \) is the first-order spin–spin contribution and \( \lambda^{(2)} \) is the second-order contribution discussed above. Similarly, the spin–rotation constant \( \gamma \) can be expressed as a sum of a direct first-order contribution and a second-order term as

\[ \gamma = \gamma^{(1)} + \gamma^{(2)}. \]

As a result, some means must be used to separate these spectroscopically equivalent, but fundamentally different, effects before experimental values of \( \lambda \) and \( \gamma \) are used for the calculation of molecular parameters.

III. EXPERIMENTAL METHOD

Both wide spectral coverage and good sensitivity are required in order to observe all of the transitions which are required for a complete and accurate characterization of the rotational spectrum of \( ^1 \Delta \) and \( ^2 \Sigma \) SO. The lines near 300 GHz which are necessary for the direct calculation of \( \lambda \) for \( ^2 \Sigma \) SO are on the order of 100 times weaker than the lines previously reported for \( ^2 \Sigma \) SO and the \( ^1 \Delta \) lines are another 10–100 times weaker because of the small population in the excited electronic state.

The millimeter and submillimeter energy necessary for this work was produced by harmonic generation from phase-locked klystrons in the 40–60 GHz region. This energy was transmitted by quasi-optical techniques through a free space absorption cell and detected by an InSb photoconducting detector at 1.6 K. A solenoid is wrapped coaxially around this cell and used both for ac magnetic modulation of the molecular species at 12 kHz and for the measurement of the dc Zeeman effect. Although this solenoid is not exactly uniform because of the many inlet and outlet ports of the cell, no line broadening is observed for dc fields which produce Zeeman splittings of 100 linewidths. The weak \( ^1 \Delta \) lines were detected by a phase-sensitive detector operating at 24 kHz.
The free space cell, shown in Fig. 3, is 1 meter long, 10 cm in diameter, and lined with teflon to retard chemical reactions on the cell walls. The oxygen discharge was produced directly beneath the cell (B) by a 100 W microwave discharge at about 3 GHz. H$_2$S or OCS was admitted near the ends of the cell (A) and allowed to react inside the cell with the oxygen discharge products. The reaction products were evacuated (C) by a 4-inch diffusion pump, backed by a Welch 1397B forepump.

$^1\Delta$ SO is produced by the reaction of the discharge products of O$_2$ with small sulfur containing molecules such as H$_2$S or OCS [2]. The O atoms produced by the discharge react with H$_2$S or OCS to form $\Sigma$ SO which in turn reacts with $^1\Delta$ O$_2$ to form $^3\Delta$ SO. Since the electronic transition $a^1\Delta-X^3\Sigma^-$ is forbidden, a small, but significant population of $^1\Delta$ SO molecules results. Optimum conditions for the production of $^1\Delta$ SO in the cell are about a total oxygen pressure of 0.1 Torr and a H$_2$S pressure of 0.01 Torr. These conditions correspond to those which produce a maximum in the bright blue fluorescence that results from this reaction. The optical spectrum of this fluorescence has been reported by Colin [13]. Optimum conditions for the production of $^3\Sigma$ SO are approximately the same.

IV. RESULTS

A. $^1\Delta$ Electronic State

The observed frequencies for the rotational transitions of SO in the $^1\Delta$ electronic state are shown in Table I along with transition frequencies calculated from the rotational constants of Table II. The fit of the observed spectrum to the simple relation of Eq. (2) is within expected experimental uncertainties. Figure 4 shows the $N = 5 \rightarrow 6$ transition at 256 GHz. As predicted theoretically, this line shows no evidence of $^1\Delta$ electronic splitting.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Frequency (MHz)</th>
<th>Calculated Frequency (MHz)</th>
<th>Difference Obs. - Calc. (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 - 1</td>
<td>125,770.416</td>
<td>125,720.344</td>
<td>0.168</td>
</tr>
<tr>
<td>3 - 2</td>
<td>170,158.667</td>
<td>170,158.623</td>
<td>0.044</td>
</tr>
<tr>
<td>4 - 3</td>
<td>212,439.117</td>
<td>212,439.064</td>
<td>0.053</td>
</tr>
<tr>
<td>5 - 4</td>
<td>255,618.037</td>
<td>255,618.017</td>
<td>0.020</td>
</tr>
</tbody>
</table>
\[ \omega_c = (4B_0^3/D_0)^{1/2}. \]  

Although the rotational constants obtained here are effective constants for the ground vibrational state rather than equilibrium constants, the differences between the two sets of constants should be compared to the experimental uncertainty in \( D_0 \). The result of this calculation is shown in Table II. This same technique produces a value for \( \omega_c \) for \( \Sigma \) SO which differs from the measured optical value by only 0.5%.

Also included in Table II is the value of \( r_0 \), calculated from the relation

\[ r_0(\text{Å}) = [505 \text{ 376}/B_0(\text{MHz})\mu(\text{amu})]^1/2. \]  

The uncertainty listed reflects only the uncertainty in \( B_0 \) and neither the uncertainty in Planck’s constant nor in model errors associated with the calculation of \( B_0 \). The latter are expected to be small because \( D_0 \) is included in Eq. (2) and \( B_0 \) rather than \( B_{\text{eff}} \) was used for this calculation.

In the absence of external fields the \( \Delta \) spectrum reported here is indistinguishable from that of a \( \Sigma \) diatomic molecule except for the absence of the \( N = 0 \rightarrow 1 \) and \( N = 1 \rightarrow 2 \) transitions. As a further check of the assignment of this spectrum to \( \Delta \) SO, the small field Zeeman effect of the \( N = 2 \rightarrow 3 \) transition was recorded and found to agree with the \( g_J \) values predicted for \( J = 2 \) and \( J = 3 \) of \( 3/2 \) and \( 3 \), respectively, to about 3%. This agreement is comparable to the calibration uncertainty of our magnetic field.
Table III. Microwave Spectrum of $^{32}$S$^{16}$O in the $^2\Sigma$ Ground Vibrational State

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed frequency (MHz)</th>
<th>Calculated frequency (estimated uncertainty)</th>
<th>Obs. - Cal. (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J, N - J', N'</td>
<td>Obs.</td>
<td>Cal.</td>
<td></td>
</tr>
<tr>
<td>1, 0 - 1, 0</td>
<td>30 001.560$^{a,c}$</td>
<td>30 001.523 (± 0.010)</td>
<td>0.057</td>
</tr>
<tr>
<td>2, 1 - 2, 1</td>
<td>66 931.480$^{a-d}$</td>
<td>66 931.488 (± 0.020)</td>
<td>0.162</td>
</tr>
<tr>
<td>3, 2 - 3, 2</td>
<td>286 340.207$^{a}$</td>
<td>286 340.131 (± 0.046)</td>
<td>0.076</td>
</tr>
<tr>
<td>4, 3 - 4, 3</td>
<td>99 199.880$^{b,d}$</td>
<td>99 199.917 (± 0.056)</td>
<td>0.001</td>
</tr>
<tr>
<td>5, 4 - 5, 4</td>
<td>86 093.940$^{b,d}$</td>
<td>86 093.769 (± 0.018)</td>
<td>0.029</td>
</tr>
<tr>
<td>6, 5 - 6, 5</td>
<td>329 385.477$^{c}$</td>
<td>329 385.486 (± 0.048)</td>
<td>0.009</td>
</tr>
<tr>
<td>7, 6 - 7, 6</td>
<td>339 502.444$^{e}$</td>
<td>339 502.463 (± 0.047)</td>
<td>0.019</td>
</tr>
<tr>
<td>8, 7 - 8, 7</td>
<td>13 043.700$^{a,c}$</td>
<td>13 043.682 (± 0.008)</td>
<td>0.002</td>
</tr>
<tr>
<td>9, 8 - 9, 8</td>
<td>236 452.325 (± 0.044)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 9 - 10, 9</td>
<td>138 178.609$^{a}$</td>
<td>138 178.645 (± 0.030)</td>
<td>0.006</td>
</tr>
<tr>
<td>11, 10 - 11, 10</td>
<td>129 138.923$^{d}$</td>
<td>129 138.915 (± 0.024)</td>
<td>0.008</td>
</tr>
<tr>
<td>12, 11 - 12, 11</td>
<td>127 025.215$^{d}$</td>
<td>127 025.226 (± 0.026)</td>
<td>0.006</td>
</tr>
<tr>
<td>13, 12 - 13, 12</td>
<td>339 341.459$^{g}$</td>
<td>339 341.511 (± 0.054)</td>
<td>0.002</td>
</tr>
<tr>
<td>14, 13 - 14, 13</td>
<td>35 201.820$^{a,c}$</td>
<td>35 201.988 (± 0.018)</td>
<td>0.005</td>
</tr>
<tr>
<td>15, 14 - 15, 14</td>
<td>244 494.604 (± 0.056)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16, 15 - 16, 15</td>
<td>178 605.403$^{c}$</td>
<td>178 605.367 (± 0.034)</td>
<td>0.003</td>
</tr>
<tr>
<td>17, 16 - 17, 16</td>
<td>172 181.406$^{b}$</td>
<td>172 181.414 (± 0.024)</td>
<td>0.006</td>
</tr>
<tr>
<td>18, 17 - 18, 17</td>
<td>158 971.800$^{b}$</td>
<td>158 971.861 (± 0.036)</td>
<td>0.005</td>
</tr>
<tr>
<td>19, 18 - 19, 18</td>
<td>66 034.949$^{a,c}$</td>
<td>66 035.025 (± 0.028)</td>
<td>0.053</td>
</tr>
<tr>
<td>20, 19 - 20, 19</td>
<td>257 197.890 (± 0.082)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21, 20 - 21, 20</td>
<td>35 344.279 (± 0.075)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22, 21 - 22, 21</td>
<td>219 945.442$^{a}$</td>
<td>219 945.398 (± 0.024)</td>
<td>0.004</td>
</tr>
<tr>
<td>23, 22 - 23, 22</td>
<td>215 220.653$^{e}$</td>
<td>215 220.649 (± 0.028)</td>
<td>0.004</td>
</tr>
<tr>
<td>24, 23 - 24, 23</td>
<td>206 176.005$^{c}$</td>
<td>206 176.033 (± 0.028)</td>
<td>0.002</td>
</tr>
<tr>
<td>25, 24 - 25, 24</td>
<td>100 029.640$^{a}$</td>
<td>100 029.644 (± 0.034)</td>
<td>0.004</td>
</tr>
<tr>
<td>26, 25 - 26, 25</td>
<td>294 768.556 (± 0.113)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table III. (continued)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed frequency (MHz)</th>
<th>Calculated frequency (estimated uncertainty)</th>
<th>Obs. - Cal. (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5 - 5, 5</td>
<td>409 639.862 (± 0.108)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6, 5 - 6, 5</td>
<td>261 843.984$^{g}$</td>
<td>261 843.716 (± 0.034)</td>
<td>0.032</td>
</tr>
<tr>
<td>7, 5 - 7, 5</td>
<td>250 255.007 (± 0.030)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8, 5 - 8, 5</td>
<td>251 825.770$^{a}$</td>
<td>251 825.746 (± 0.026)</td>
<td>0.024</td>
</tr>
<tr>
<td>9, 6 - 9, 6</td>
<td>156 414.709$^{c}$</td>
<td>156 414.709 (± 0.040)</td>
<td>0.004</td>
</tr>
<tr>
<td>10, 7 - 10, 7</td>
<td>326 644.794 (± 0.142)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11, 8 - 11, 8</td>
<td>448 265.911 (± 0.140)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12, 9 - 12, 9</td>
<td>174 082.424 (± 0.048)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13, 10 - 13, 10</td>
<td>361 351.179 (± 0.174)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14, 11 - 14, 11</td>
<td>487 706.195 (± 0.190)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15, 12 - 15, 12</td>
<td>346 528.521 (± 0.048)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16, 13 - 16, 13</td>
<td>294 314.612 (± 0.052)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17, 14 - 17, 14</td>
<td>246 714.658 (± 0.036)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18, 15 - 18, 15</td>
<td>246 357.017 (± 0.062)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19, 16 - 19, 16</td>
<td>391 367.417 (± 0.020)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20, 17 - 20, 17</td>
<td>527 914.054 (± 0.204)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21, 18 - 21, 18</td>
<td>384 527.085 (± 0.068)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22, 19 - 22, 19</td>
<td>254 573.477 (± 0.088)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23, 20 - 23, 20</td>
<td>367 328.661 (± 0.080)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24, 21 - 24, 21</td>
<td>435 986.040 (± 0.204)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25, 22 - 25, 22</td>
<td>286 711.434 (± 0.034)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26, 23 - 26, 23</td>
<td>488 110.448 (± 0.104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27, 24 - 27, 24</td>
<td>295 555.273 (± 0.126)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
B. $^3\Sigma$ Electronic State

Table III contains the 13 previously reported (14–17) transitions of $^3\Sigma$ SO and 19 additional observed transition frequencies. This table also includes the transition frequencies calculated from the constants of Table II. The inclusion in the analysis of the five low frequency transitions originally reported in Ref. (16) and remeasured in Ref. (17) doubles the rms deviation. Since these transitions can be calculated with high accuracy from the remaining data, they have been excluded from the final analysis.

Since the weak transitions near 300 GHz that are necessary for a direct calculation of $\lambda$ are now included in the data set, substantially improved values of the constants which

![Fig. 4. N = 5 → 6 transition of SO $^1\Delta$ at 256 GHz.](image)
relate to the electronic interactions can be calculated. The frequencies of these transitions differ by about 10 MHz from those predicted in the comprehensive review of Ref. (4) which was based on the data previously available. As a result, the transition frequencies calculated from the constants of Table II deviate from those previously published. Table III has therefore been expanded to include predictions of all electric dipole transition frequencies and the uncertainties in these predictions for transitions between levels for which \( J \leq 10 \). These uncertainties are calculated from the relation

\[
\sigma_i^2 = \sum_{ij} \sigma_i \rho_{ij} C_{ij} \]  

(16)

where \( \sigma_i \) is the standard error in the \( i \)th spectral constant, \( \rho_{ij} \) the correlation coefficient matrix, and \( C_i \) the corresponding spectral constant \( (18) \). Since the data set is now representative of all of the types of transitions included in Table III and since the statistical uncertainties have been tested by the removal of measured lines from the analysis, it is felt that these calculation uncertainties are, in fact, representative of the actual uncertainties in the predictions.

Although \( \lambda \) and \( \gamma \) are referred to as the spin–spin and spin–rotation constants, respectively, they also contain contributions from other sources. Kayama and Baird \((18)\) have calculated that the second order contribution \( \lambda^{(2)} \) to \( \lambda \) is, in fact, the major contribution and that the first order spin–spin interaction explicitly included in the Hamiltonian of Eq. (7) accounts for only 17 807 MHz of the total. Similar calculations \((9)\) of the second order contributions \( \gamma^{(2)} \) to \( \gamma \) show that the second order contributions contribute \(-117 \text{ MHz}\) of the \(-168 \text{ MHz}\) total calculated from the experimental results.

Amano, Hirota, and Morino \((16)\) have reported observation of 5 lines of \( ^3\Sigma \text{SO} \) in the \( \nu = 1 \) state and the analysis of these data. Since the resulting constants were determined graphically and without knowledge of the values of several of the higher order \( \nu = 0 \) constants, new spectral constants have been calculated and included in Table III. In this calculation the distortion constants \( D_1 \) and \( \rho_1 \) are fixed at their \( \nu = 0 \) values and \( B_1, \lambda_1, \) and \( \gamma_1 \) are treated as adjustable parameters. Since the changes in these parameters from \( B_0, \lambda_0, \) and \( \gamma_0 \) are of the order of 1\%, and since \( D_1 \) and \( \rho_1 \) make only small contributions to the observed frequencies, this approximation introduces little error into the calculation and is substantially better than the assumption that \( D_1 = \rho_1 = 0 \). Inspection of Table IV, which contains both the experimental and calculated frequencies, shows an rms deviation of only 0.055 MHz.

### Table IV. Observed and Calculated Frequencies

<table>
<thead>
<tr>
<th>( J, L ) = ( J', N )</th>
<th>( \text{Observed} )</th>
<th>( \text{Calculated} )</th>
<th>( \text{Observed} - \text{Calculated} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MHz)</td>
<td>(MHz)</td>
<td>(MHz)</td>
<td></td>
</tr>
<tr>
<td>1, 0 = 0, 0</td>
<td>24 419.46</td>
<td>24 419.515</td>
<td>0.042</td>
</tr>
<tr>
<td>2, 1 = 1, 0</td>
<td>62 612.145</td>
<td>62 612.077</td>
<td>0.067</td>
</tr>
<tr>
<td>3, 2 = 2, 1</td>
<td>12 756.278</td>
<td>12 756.778</td>
<td>0.476</td>
</tr>
<tr>
<td>4, 3 = 3, 2</td>
<td>18 510.420</td>
<td>18 510.378</td>
<td>0.042</td>
</tr>
<tr>
<td>5, 4 = 4, 3</td>
<td>24 495.617</td>
<td>24 495.183</td>
<td>0.034</td>
</tr>
</tbody>
</table>

a. Overlapped with line of \(^3\Sigma \text{PO}\).
b. Not included in list.
Comments should be made about the uncertainties in the \( v = 1 \) constants of Table II. The listed uncertainties in \( B_1, \lambda_1, \) and \( \gamma_1 \) assume a 1\% uncertainty in the estimated values of \( D_1 \) and \( \rho_1 \). The uncertainties which result are larger than those calculated from the simple expression of Eq. (16) and the assumption that \( D_1 \) and \( \rho_1 \) are exactly known. This is especially true if \( D_1 \) and \( \rho_1 \) are assumed to be zero. It is assumptions of this type that have led to underestimates in the uncertainties both in predicted line frequencies and spectral constants in previous analyses of SO.

The equilibrium constants are calculated from the relations

\[
B_v = B_o - \alpha(v + \frac{1}{2}), \\
\lambda_v = \lambda_o - \alpha(\gamma(v + \frac{1}{2}),
\]

with higher order (\( \gamma \)) vibrational expansion constants constrained to zero. The uncertainties in these equilibrium constants are calculated from the uncertainties in the spectral constants in the \( v = 0 \) and \( v = 1 \) states. It is to be expected that the higher order terms are not zero to the accuracy of these constants. It should therefore be remembered that these uncertainties are valid only in the context of Eq. (17).

Table II also contains the values of \( r_b, r_l, \) and \( r_s \) calculated from \( B_b, B_l, \) and \( B_s \) and Eq. (15). The listed uncertainties reflect only the contributions from the uncertainties in the corresponding \( B \)'s.

V. CONCLUSIONS

The electronic, vibrational, and in some cases rotational structure of free radicals have long been studied by optical techniques (7). Although a number of species have now been observed by microwave and other high resolution techniques, the number of species for which enough microwave data has been acquired to simply characterize the rotational energy levels to within microwave accuracy is still small. This is especially true for molecules in excited electronic states for which, to our knowledge, \( \Delta \) SO now represents the only example.

The studies presented here show directly that both wide spectral coverage and good sensitivity are necessary to achieve this goal for \( \Delta \) and \( \Sigma \) SO. These requirements are, in fact, rather general because many of the most common and important free radical species have large rotational and effective electronic interaction constants which cause many important transitions to fall outside the centimeter wavelength region. It is felt that the experimental procedures described in this paper can therefore make significant and, in many cases, indispensable contributions to the study of unstable free radical species.

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REFERENCES

6. R. S. Mulliken, Rev. Mod. Phys. 2, 60 (1930); 3, 89 (1931).