THE MICROWAVE SPECTRA OF ISOTOPIC MOLECULES OF SULPHUR DIOXIDE

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Summary

Some new lines in the spectra of $^{34}$SO$_2$ and $^{33}$SO$_2$ have been measured and accounted for in terms of a semi-rigid rotor model with centrifugal distortion coefficients derived from Kivelson’s (1954) published figures for $^{33}$SO$_2$, and rotational constants obtained from the measurements.

The hyperfine structure of the $^{33}$SO$_2$ 1,1→2,1 transition has been analysed and found to agree with the quadrupole coupling constants of Bird and Townes (1954).

I. INTRODUCTION

The microwave spectrum of the asymmetric rotor sulphur dioxide has been the subject of investigation of a number of workers (Cable and Smith 1951; Sirvetz 1951; Kivelson 1954; Wertheimer and Clouard 1957) since the first rotational constants were reported by Dailey, Golden, and Wilson (1947). The early work neglected the effects of centrifugal distortion, which were shown by Sirvetz (1951) to be important in accounting for the observed spectrum. Kivelson (1954), by making use of a combination of microwave and infra-red data, has accurately fitted the microwave spectrum, obtaining at the same time a precise estimate of the molecular force constants. In the present work some new lines of the isotopic molecules $^{33}$SO$_2$ and $^{34}$SO$_2$, in addition to those found by Bird and Townes (1954), are reported and accounted for in terms of a semi-rigid model with centrifugal distortion coefficients calculated from Kivelson’s force constants for $^{33}$SO$_2$.

II. EXPERIMENTAL

All measurements were made with a Stark-modulated spectroscope, the essential features of which have been described by Posener (1957). For the stronger lines 5 kc/s square-wave modulation was used, but the greater sensitivity of the 105 kc/s square-wave system was required for some of the weaker ones. Commercial grade sulphur dioxide was used and was consequently unenriched in $^{33}$S, $^{34}$S (natural abundance: $^{33}$S, 0.74 per cent.; $^{34}$S, 4.2 per cent.). The resulting low intensity of the $^{33}$SO$_2$ transitions necessitated the use of very narrow detector bandwidths (down to 0.01 c/s) with a.f.c. locking of the klystron frequency between harmonics of the laboratory frequency standard. In all frequency measurements small corrections for the time delay introduced by the finite detector bandwidths (Smith 1955) were made. The absorption cells could be cooled by dry ice either for enhancing the intensity or for identifying transitions.

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III. $^{34}$SULPHUR DIOXIDE

The rotational constants of $^{34}$SO$_2$ may be estimated roughly from those of $^{32}$SO$_2$ by assuming the same molecular dimensions in evaluating the principal moments of inertia $I_a$, $I_b$ about axes in the plane of the molecule, and the same inertia defect (Dailey, Golden, and Wilson 1947) to give $I_c$. These constants may then be used (neglecting distortion) to estimate line frequencies. Bird and Townes (1954) used this technique for finding two lines of $^{34}$SO$_2$ ($5_{04} \leftarrow 3_{13}$ 31,011·19 Mc/s; $5_{24} \leftarrow 6_{15}$ 17,970·42 Mc/s). The same method has been used here to predict the $1_{11} \leftarrow 2_{02}$ transition at 10,550 Mc/s, which was subsequently measured and identified by its Stark effect at 10,547·91 ± 0·02 Mc/s.

The knowledge of these three transitions enables an accurate set of rotational constants to be calculated but for the effects of centrifugal distortion. The shifts in line frequencies due to distortion in $^{32}$SO$_2$ (Kivelson 1954) are quite small (<100 Mc/s) compared with the line frequencies and consequently need not be known to high precision. In view of the success in the prediction of line frequencies by assuming the molecular structure to be undisturbed by the isotopic substitution, it was concluded that the centrifugal distortion could be calculated with good accuracy using Kivelson's $^{32}$SO$_2$ force constants and structural parameters. Further examination shows that the four independent distortion constants $\tau_{aaaa}$, $\tau_{bbbb}$, $\tau_{aabb}$, $\tau_{abab}$ ($C_{2v}$ symmetry) for the various isotopic molecules may be simply related on this basis using expressions quoted by Kivelson (1954) for the $\tau$'s in terms of the force constants. The following interrelations are obtained:

$$
\begin{align*}
\tau_{aaaa}^3 &= (a^{34}/a^{32})^2 \tau_{aaaa}, \\
\tau_{bbbb}^3 &= (b^{34}/b^{32})^2 \tau_{bbbb}, \\
\tau_{aabb}^3 &= (a^{34}b^{34}/a^{32}b^{32}) \tau_{aabb}, \\
\tau_{abab}^3 &= (a^{34}b^{34}/a^{32}b^{32})^2 \left(\frac{M_0 + M_s^{34}}{2M_0 + M_s^{34}}\right) \left(\frac{M_s^{32}}{M_s^{34}}\right) \left(\frac{1+2(M_0/M_s^{32})\sin^2 \theta}{1+2(M_0/M_s^{34})\sin^2 \theta}\right)^2 \tau_{abab}^3 \quad (1d)
\end{align*}
$$

where $a$, $b$, $c$ are rotational constants,

$$
\begin{align*}
M_0 &= \text{mass of } ^{16}\text{O atom}, \\
M_s^{32,34} &= \text{mass of } ^{32,34}\text{S, } ^{34}\text{S atoms}, \\
20 &= \text{S–O–S angle,} \\
&= 119·536° \text{ (Kivelson 1954).}
\end{align*}
$$

The remaining non-zero $\tau$'s may then be derived (Kivelson and Wilson 1953):

$$
\begin{align*}
\tau_{cccc} &= (c/b)^4 \tau_{bbbb} + (c/a)^4 \tau_{aaaa} + 2(c/a^2b^2)\tau_{aabb}, \quad (2a) \\
\tau_{bbcc} &= (c/b)^2 \tau_{bbbb} + (c/a)^2 \tau_{aabb}, \quad (2b) \\
\tau_{acc} &= (c/a)^3 \tau_{aaaa} + (c/b)^2 \tau_{aabb}, \quad (2c)
\end{align*}
$$

In this way the distortion coefficients listed in Table 1 were obtained. The same number of figures is retained for the $\tau$'s as was quoted by Kivelson but it must not be assumed in either case that they are all significant.
The usual $D_J$, $D_{JK}$, etc. (Nielsen 1951) were found from the $\tau$'s and used to set up the energy matrices. A set of rotational constants for $^{34}$SO$_2$ was then found which fitted the three known lines $1_{11} \leftrightarrow 2_{02}$; $4_{04} \leftrightarrow 3_{13}$; $5_{34} \leftrightarrow 6_{15}$. In these and other calculations the reduced energy was calculated by the continued fraction method (King, Hainer, and Cross 1943) modified (Posener 1953) where

### Table 1

**Distortion Coefficients of Sulphur Dioxide Molecules**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\tau_{aaa}$ (Mc/s)</th>
<th>$\tau_{bbb}$ (Mc/s)</th>
<th>$\tau_{aabb}$ (Mc/s)</th>
<th>$\tau_{abab}$ (Mc/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{34}$SO$_2$</td>
<td>-9.8098</td>
<td>-0.039696</td>
<td>0.41170</td>
<td>-0.053203</td>
</tr>
<tr>
<td>$^{34}$SO$_2$</td>
<td>-9.2413</td>
<td>-0.039698</td>
<td>0.39690</td>
<td>-0.052739</td>
</tr>
<tr>
<td>$^{35}$SO$_2$</td>
<td>-9.5143</td>
<td>-0.039697</td>
<td>0.40546</td>
<td>-0.052966</td>
</tr>
</tbody>
</table>

* Kivelson (1954), "combined infra-red and microwave" results.

required to include the $H_{K,K\pm4}$ elements introduced by centrifugal distortion. The number of iterations required was reduced by the procedure of Posener (1956) for improving the convergence. The evaluation of any small changes of the rotational constants $a$, $b$, $c$ is conveniently carried out using the variables $\alpha=(a+c)/2$, $\beta=(a-c)/2$, and $\kappa$ the asymmetry parameter, together with the rigid rotor relations for the derivatives of the energy levels $W_{J\kappa}$:

$$
\begin{align*}
\frac{\partial W_{J\kappa}}{\partial \alpha} &= J(J+1), & \text{(3a)} \\
\frac{\partial W_{J\kappa}}{\partial \beta} &= E_{J\kappa}(\chi), & \text{(3b)} \\
\frac{\partial W_{J\kappa}}{\partial \kappa} &= \beta dE_{J\kappa}(\chi)/d\kappa, & \text{(3c)}
\end{align*}
$$

where $E_{J\kappa}$ is the reduced energy. $dE_{J\kappa}/d\kappa$ may in some cases be evaluated analytically, but otherwise may be estimated adequately for this purpose by differentiation of the fourth-order expansion of King, Hainer, and Cross (1943) for $E_{J\kappa}$ in terms of the alternative asymmetry parameter $\delta=(\kappa+1)/2$,

$$
\frac{dE_{J\kappa}}{d\kappa} = \frac{1}{2}dE_{J\kappa}/d\delta. \quad \text{(4)}
$$

The constants obtained in this manner are:

$$
\begin{align*}
\alpha &= 58,991 \cdot 27 \text{ Mc/s}, \\
\beta &= 10,318 \cdot 42 \text{ Mc/s}, \\
\gamma &= 8,761 \cdot 42 \text{ Mc/s},
\end{align*}
$$

(5)

together with the distortion coefficients of Table 1. These constants were then used to predict a number of $^{34}$SO$_2$ transitions which were later found and measured, and the results are listed in Table 2.

In the case of the $8_{17} \leftrightarrow 7_{26}$ line there was initially some ambiguity due to the presence of a weak line at $30,977 \cdot 29 \pm 0.05$ Mc/s. However, by cooling to dry ice temperatures this line was no longer detected, indicating that it arose from more excited levels, probably of $^{35}$SO$_2$. 

The r.m.s. error on each of the measured frequencies of Table 2 is approximately 20 kc/s and the mean deviation from the frequencies computed by the rotational constants (5) together with the distortion coefficients of Table 1 is 120 kc/s, the largest individual deviation being 320 kc/s. The mean deviation for the prediction of new frequencies is 220 kc/s.

Table 2

<table>
<thead>
<tr>
<th>Transition</th>
<th>Predicted Frequency from (5) (Mc/s)</th>
<th>Observed Frequency (Mc/s)</th>
<th>Final Calculated Frequency from (6) (Mc/s)</th>
<th>Shift Due to Distortion (Mc/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111→ 202</td>
<td>10,547·90</td>
<td>10,547·91</td>
<td>10,547·900</td>
<td>- 2·036</td>
</tr>
<tr>
<td>434→ 313</td>
<td>31,011·21</td>
<td>31,011·19</td>
<td>31,011·144</td>
<td>- 0·469</td>
</tr>
<tr>
<td>524→ 618</td>
<td>17,970·40</td>
<td>17,970·42</td>
<td>17,970·491</td>
<td>-20·363</td>
</tr>
<tr>
<td>828→ 919</td>
<td>20,699·43</td>
<td>20,699·30</td>
<td>20,699·247</td>
<td>-12·364</td>
</tr>
<tr>
<td>1038→ 1111</td>
<td>9,650·95</td>
<td>9,650·63</td>
<td>9,650·640</td>
<td>-13·269</td>
</tr>
<tr>
<td>817→ 726</td>
<td>30,975·61</td>
<td>30,975·39</td>
<td>30,975·421</td>
<td>+ 0·304</td>
</tr>
</tbody>
</table>

* Bird and Townes (1954).

To make maximum use of all of the experimental data a least-squares fit was then performed on the six lines to find the best values of \( a, b, c \). Only linear changes in frequency for changes in \( a, b, c \) were taken in view of the smallness of the variations required, and the equations (3), (4) were used for computing the coefficients. For small changes in \( a, b, c \) the distortion shifts from the rigid-rotor frequencies were found to be unaffected, so the final calculations involved the evaluation of rigid-rotor energies only. The least-squares procedure was repeated until no further changes in \( a, b, c \) were indicated. The final results obtained are:

\[
\begin{align*}
  a &= -58,991.212 \text{ Mc/s}, \\
  b &= 10,318.404 \text{ Mc/s}, \\
  c &= 8,761.412 \text{ Mc/s}, \\
\end{align*}
\]

and the calculated frequencies appear in Table 2, where the mean deviation has now been reduced to only 37 kc/s, which is not far in excess of the r.m.s. error on each measurement. The final decimals in (6) are probably not fully significant considering the assumptions involved in the method, but rounding off to two decimals increases the mean deviation to 60 kc/s, indicating at least statistical significance. It will be noted that the differences from the initial set (5) are quite small, namely, \(-58, -16, \) and \(-8 \) kc/s, indicating good reliability for the process leading to the constants (5).

However, the small mean deviation cannot be taken as an estimate of the expected error on new predictions, since only a comparatively small number of lines has been taken and even these are either \( P \) or \( R \) type transitions of low or
moderate $J$. Finally, of course, the predictions cannot very well be better than those of Kivelson for $^{32}$SO$_2$ since the distortion coefficients are derived from his. Kivelson obtained mean deviations of about 200 kc/s and it was decided to test the accuracy of prediction on the previously unobserved $1_{11} \leftarrow 2_{02}$ transition of $^{32}$SO$_2$ calculated to fall at 12,256.14 Mc/s. This line was found at 12,256.64 ± 0.02 Mc/s, showing a discrepancy of 500 kc/s.

**IV. $^{33}$SULPHUR DIOXIDE**

The rotational constants of $^{33}$SO$_2$ were estimated roughly from those of $^{32}$SO$_2$ by the same method as used for $^{34}$SO$_2$ in the previous section. Bird and Townes (1954) have used this method to find the $5_{24} \leftarrow 6_{15}$ and $4_{04} \leftarrow 3_{13}$ transitions of $^{33}$SO$_2$ at 20,605.97 and 30,194.09 Mc/s respectively. The $1_{11} \leftarrow 2_{02}$ line was estimated here as falling near 11,378 Mc/s.

The spectrum of $^{33}$SO$_2$ is complicated by the hyperfine splitting due to the quadrupole moment of the $^{33}$S nucleus ($I = \frac{3}{2}$) but Bird and Townes in their analysis of the $4_{04} \leftarrow 3_{13}$ transition deduced quadrupole coupling constants $\chi_{aa} = -1.7 \pm 0.2$ Mc/s, $\chi_{bb} = 25.71 \pm 0.03$ Mc/s. Fortunately, both the centrifugal distortion and the quadrupole splittings are small and each may be considered independently as a perturbation of a rigid rotor. Using these quadrupole coupling constants the splitting of the $1_{11} \leftarrow 2_{02}$ transition has been calculated by the usual first-order formula (Bragg and Golden 1949) and is shown in Figure 1. The initial approximation to $\chi$ gives sufficient accuracy for estimating this splitting and $dE(\chi)/d\chi$ may be found from the analytical forms of $E(\chi)$. The expected transitions give rise to what is essentially a triplet having intensities in the ratio 1 : 3 : 2.

A reasonable value of 20 Mc/s per mm for the line-breadth parameter gave an estimated absorption coefficient of approximately $3.5 \times 10^{-9}$ cm$^{-1}$ for the strongest (central) component with natural abundance of $^{33}$S. Accordingly narrow detector bandwidths with klystron frequency stabilization, and in some runs dry ice cooling of the absorption cell was necessary to provide adequate sensitivity.
The triplet structure was subsequently confirmed, with measured peaks at $11,368.002 \pm 0.015$, $11,373.286 \pm 0.015$, and $11,379.825 \pm 0.015$ Mc/s (r.m.s. errors). After allowing for the effects of the several transitions contributing to each component of the triplet, these results were found to be in good agreement with the coupling constants of Bird and Townes (1954) together with an unsplit frequency of $11,374.581 \pm 0.015$ Mc/s. Unfortunately $^{33}\text{SO}_2$ is close to the symmetric rotor limit and $\chi_{aa}$, $\chi_{bb}$ could not both be accurately determined from this transition. However, it was possible to estimate $\chi_{bb} - 0.514 \chi_{aa} = 26.64 \pm 0.05$ Mc/s, which compares well with $26.58 \pm 0.1$ Mc/s derived from Bird and Townes's figures.

Centrifugal distortion constants obtained from those of $^{32}\text{SO}_2$ are listed in Table 1. A set of rotational constants was then obtained which accounted for the three known transition frequencies ($1_{11} \rightarrow 2_{02}$; $4_{04} \rightarrow 3_{13}$; $5_{24} \rightarrow 6_{15}$) including effects of centrifugal distortion as was done to obtain the constants (5) for $^{34}\text{SO}_2$. The constants are:

$$
\begin{align*}
   a &= 59,856.49 \text{ Mc/s}, \\
   b &= 10,318.20 \text{ Mc/s}, \\
   c &= 8,780.23 \text{ Mc/s},
\end{align*}
$$

and the results are summarized in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>$^{33}\text{SO}_2$ Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transition</strong></td>
</tr>
<tr>
<td>$1_{11} \rightarrow 2_{02}$</td>
</tr>
<tr>
<td>$4_{04} \rightarrow 3_{13}$</td>
</tr>
<tr>
<td>$5_{24} \rightarrow 6_{15}$</td>
</tr>
</tbody>
</table>

* Bird and Townes (1954).

V. DISCUSSION OF RESULTS

It has been shown that a good account of the $^{34}\text{SO}_2$ spectrum is possible using centrifugal distortion coefficients derived from those of $^{32}\text{SO}_2$. Pierce (1956) also has found a similar technique useful in accounting for the spectrum of $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ using the force constants of $^{16}\text{O}_3$. These results suggest that the procedure may also be applied to isotopic species of other molecules, but it must be remembered that the simplicity of the interrelations both in the present work and in the work of Pierce is a consequence of the $C_2v$ symmetry of the molecules.

The method has also been applied to $^{33}\text{SO}_2$ using the same quantum transitions as were initially used for estimating the rotational constants (5) of $^{34}\text{SO}_2$. Although no further transitions of $^{33}\text{SO}_2$ have been observed, a similar accuracy of prediction would be expected from the constants (7) as was obtained...
from the constants (5) for $^{34}\text{SO}_2$. However, the necessity for caution is demonstrated by the comparatively poor fit of the $1_{11}\leftarrow 2_{02}$ transition of $^{33}\text{SO}_2$ to Kivelson’s (1954) original figures.

The hyperfine structure of the $1_{11}\leftarrow 2_{02}$ transition of $^{33}\text{SO}_2$ has been analysed and found to be in complete accord with the published coupling constants of Bird and Townes (1954).

VI. ACKNOWLEDGMENT

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VII. REFERENCES