# The Submillimeter Wave Spectrum of $^{32}S^{16}O_2$ , $^{32}S^{16}O_2(\nu_2)$ , and $^{34}S^{16}O_2^1$

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Extensive new measurements in the region 400-1000 GHz have been made on  $^{32}S^{16}O_2$ .  $^{32}S^{16}O_2(\nu_2)$ , and  $^{34}S^{16}O_2$ . These measurements represent almost a threefold extension in the frequency region for which high-resolution microwave data are available. These data have been combined with the previously available microwave data for this analysis. The results, when extrapolated into the far infrared, compare favorably with recent results obtained from high-resolution FIR spectroscopy. © 1985 Academic Press, Inc.

#### I. INTRODUCTION

Sulfur dioxide has been the object of many spectroscopic studies. Lovas (1) has noted that more than 3000 lines, including lines in excited states and isotopic species, have been observed in the microwave region. On the basis of these data, he reanalyzed many of the spectra in order to provide both improved spectral constants and "complete" spectral maps for this important and pervasive species. More recently, Sattler et al. (2) have combined these data with the results of a diode laser study of  $\nu_1$  to calculate new spectroscopic constants.

Carlotti et al. (3) have recorded and analyzed a very-high-resolution (0.004 cm<sup>-1</sup>) FIR spectrum in the region 8–90 cm<sup>-1</sup>. In that work 1500 lines were assigned to the ground vibrational state of  ${}^{32}S^{16}O_2$ . Of these, 1061 were retained and used along with the existing microwave data as the basis for a centrifugal distortion analysis. A large number of the remaining unassigned lines are presumably due to the  ${}^{34}S^{16}O_2$  ground state or the  ${}^{32}S^{16}O_2$  bending mode. Carlotti et al. point out that the previous analyses (1, 2), when extrapolated to predict the frequencies of the highest  $K_a$  lines, differ from their FIR observations by 0.01 cm<sup>-1</sup>.

In this work we have extended the microwave data set into the region between 450 and 1000 GHz for the ground and first excited vibrational states of  $^{32}S^{16}O_2$  and for the ground state of  $^{34}S^{16}O_2$ . These lines contain substantial new information

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 $TABLE\ I$   $^{32}S^{16}O_{2}\ Ground\ State\ Transition\ Frequencies\ (MHz)$ 

| Transition                                 | Observed   | 0-C    | Transition   | Observed   | 0-C    |
|--|------------|--------|--|------------|--------|
| 6 6 0 <sup>- 5</sup> 5 1                   | 676484.398 | -0.011 | 4013 27-4112 30  | 475196.476 | -0.061 |
| 8 6 2 7 5 3                                | 714779.583 | 0.055  | 40 <sub>14</sub> 26 <sup>-41</sup> 13 29                       | 573977.528 | 0.060  |
| 9 7 3 8 6 2                                | 835294.838 | -0.062 | 42 7 35 -42 6 36   | 614113.682 | 0.065  |
| 11 6 6 <sup>-10</sup> 5 5                  | 772188.250 | 0.163  | 41 <sub>13</sub> 29 <sup>-42</sup> 12 30                       | 455809.962 | -0.106 |
| 11 7 5 <sup>-10</sup> 6 4                  | 873600.726 | 0.155  | <sup>42</sup> 14 28 <sup>-43</sup> 13 31                       | 535433.877 | 0.022  |
| 12 7 5 <sup>-11</sup> 6 6                  | 892745.905 | -0.367 | <sup>43</sup> <sub>14</sub> 30 <sup>-44</sup> <sub>13</sub> 31 | 516132.728 | -0.063 |
| 13 <sub>5</sub> 9 <sup>-12</sup> 4 8       | 708392.542 | 0.091  | <sup>43</sup> 15 29 <sup>-44</sup> 14 30                       | 614155.815 | 0.057  |
| 14 6 8 <sup>-13</sup> 5 9                  | 829477.953 | 0.044  | 45 3 43 <sup>-45</sup> 2 44                                    | 684929.069 | 0.157  |
| 14 8 6-15 7 9                              | 476621.547 | 0.012  | 45 6 40 <sup>-45</sup> 5 41                                    | 565066.230 | -0.073 |
| 17 <sub>10</sub> 8 <sup>-18</sup> 9 9      | 619888.424 | 0.047  | 46 1 45 <sup>-46</sup> 0 46                                    | 766701.520 | -0.074 |
| 19 5 15 <sup>-18</sup> 4 14                | 820150.008 | -0.105 | 46 3 43-46 2 44  | 616525.732 | -0.126 |
| 20 6 14 <sup>-19</sup> 5 15                | 943211.537 | -0.121 | 46 4 42 - 45 5 41  | 768497.921 | 0.046  |
| 20 9 11 <sup>-21</sup> 8 14                | 461875.905 | 0.004  | 45 <sub>14</sub> 32 <sup>-46</sup> 13 33                       | 477466.179 | -0.038 |
| 23 6 18 <sup>-23</sup> 5 19                | 556959.853 | -0.065 | 45 <sub>16</sub> 30 <sup>-46</sup> 15 31                       | 672850.752 | -0.014 |
| 22 <sub>12</sub> 10 <sup>-23</sup> 11 13   | 722704.871 | 0.007  | 45 <sub>17</sub> 29 <sup>-46</sup> 16 30                       | 768898.313 | -0.006 |
| 29 3 27 - 28 2 26                          | 616472.410 | 0.101  | 47 1 47 46 0 46  | 834688.628 | -0.005 |
| 31 <sub>2 30</sub> -30 <sub>1 29</sub>     | 576042.056 | -0.052 | 46 <sub>14</sub> 32 <sup>-47</sup> 13 35                       | 458098.193 | -0.048 |
| 30 <sub>11</sub> 19 <sup>-31</sup> 10 22   | 469422.343 | -0.036 | 48 4 44 <sup>-48</sup> 3 45                                    | 530380.695 | -0.065 |
| 30 <sub>12</sub> 18 <sup>-31</sup> 11 21   | 569102.784 | 0.105  | 48 7 41 -48 6 42   | 555750.334 | 0.027  |
| 33 <sub>14</sub> 20 <sup>-34</sup> 13 21   | 708381.145 | 0.014  | 48 8 40 -48 7 41   | 718681.046 | 0.056  |
| 35 2 34 <sup>-35</sup> 1 35                | 571383.123 | 0.081  | 49 5 45 - 49 4 46  | 619796.181 | -0.002 |
| 35 1 35 <sup>-34</sup> 0 34                | 624344.489 | -0.137 | 50 4 46 <sup>-50</sup> 3 47                                    | 580132.501 | 0.068  |
| 35 <sub>12 24</sub> -36 <sub>11 25</sub>   | 472520.782 | 0.080  | 50 7 43 -50 6 44   | 529606.882 | -0.034 |
| 35 <sub>13</sub> 23 <sup>-36</sup> 12 24   | 571775.154 | -0.075 | 50 6 44 - 49 7 43  | 461410.201 | 0.03   |
| 35 <sub>14</sub> 22 <sup>-36</sup> 13 23   | 670047.199 | 0.084  | 52 5 47 <sup>-52</sup> 4 48                                    | 464664.644 | 0.05   |
| 37 2 36 <sup>-37</sup> 1 37                | 606896.446 | -0.046 | 54 5 49 <sup>-54</sup> 4 50                                    | 515421.659 | -0.00  |
| 37 3 35 <sup>-36</sup> 2 34                | 709510.677 | -0.096 | 54 7 47 <sup>-54</sup> 6 48                                    | 476625.543 | 0.02   |
| 38 1 37 <sup>-38</sup> 0 38                | 624108.138 | 0.032  | 56 5 51 <sup>-56</sup> 4 52                                    | 568464.595 | -0.03  |
| 37 <sub>13</sub> 25 <sup>-38</sup> 12 26   | 533208.786 | -0.091 | 56 7 49 <sup>-56</sup> 6 50                                    | 455093.098 | -0.02  |
| 13 25 12 26<br>40 2 38 <sup>-40</sup> 1 39 | 590076.669 | 0.024  | 55 <sub>16</sub> 40 <sup>-56</sup> 15 41                       | 480838.305 | -0.00  |
| 40 0 40 <sup>-39</sup> 1 39                | 712010.554 | 0.056  | 57 7 51 <sup>-57</sup> 6 52                                    | 667419.837 | -0.08  |
| 41 5 37 <sup>-41</sup> 4 38                | 517100.099 | -0.008 | 56 <sub>16</sub> 40 <sup>-57</sup> 15 43                       | 461546.356 | -0.04  |
| 5 37 4 38<br>41 3 39 <sup>-40</sup> 2 38   | 771258.296 | 0.094  | 58 5 53 -58 4 54   | 621617.968 | 0.06   |
| 3 39 2 38                                  |            |        | 57 <sub>16</sub> 42 <sup>-58</sup> 15 43                       | 442234.475 | -0.06  |

and make possible very accurate calculations throughout the millimeter, submillimeter, and well into the FIR.

## II. EXPERIMENTAL DETAILS

We have previously discussed the experimental techniques that we have developed for use in the millimeter and submillimeter spectral region (4-6). Briefly, a klystron, phase-locked to a frequency synthesized from an oscillator referenced to WWVB, is

TABLE II

Rotational Constants of Sulfur Dioxide (MHz)

| Constant                              | <sup>16</sup> s <sup>32</sup> o <sub>2</sub> |                   | 16 s 34 o <sub>2</sub> |       | <sup>16</sup> s <sup>32</sup> 0 <sub>2</sub> |        |
|---------------------------------------|--|-------------------|------------------------|-------|--|--------|
| Constant                              | v <sub>2</sub> =0                            |                   | v <sub>2</sub> =0      |       | v <sub>2</sub> =1                            |        |
| A                                     | 60778.5522ª                                  | (26) <sup>b</sup> | 5 89 91 .1 85 9        | (98)  | 61954.8239                                   | (71)   |
| В                                     | 10318.0722                                   | (4)               | 10318.5100             | (8)   | 10320.3975                                   | (12)   |
| С                                     | 8799.7023                                    | (4)               | 8761.3026              | (8)   | 8783.8567                                    | (11)   |
| $\Delta_{\mathbf{J}}(\cdot 10^{3})$   | 6.610013                                     | (289)             | 6.56857                | (74)  | 6.627049                                     | (1215) |
| $\Delta_{JK}(\cdot 10^1)$             | -1.169588                                    | (33)              | -1.11650               | (9)   | -1.220432                                    | (85)   |
| Δ <sub>K</sub> (·10 <sup>0</sup> )    | 2.5904328                                    | (553)             | 2.440125               | (92)  | 2.872636                                     | (174)  |
| d <sub>T</sub> (·10 <sup>3</sup> )    | 1.701045                                     | (46)              | 1.722141               | (140) | 1.711139                                     | (85)   |
| d <sub>K</sub> (·10 <sup>2</sup> )    | 2.53531                                      | (64)              | 2.4627                 | (5)   | 3.10147                                      | (192)  |
| H <sub>J</sub> ( · 10 <sup>8</sup> )  | 1.0645                                       | (63)              | 1.109                  | (19)  | 1.1766                                       | (482)  |
| H <sub>JK</sub> (·10 <sup>8</sup> )   | 2.522  | (260)             | 1.95                   | (85)  | 13.58  | (107)  |
| H <sub>KJ</sub> ( • 10 <sup>5</sup> ) | -1.93691                                     | (158)             | -1.7856                | (83)  | -2.2394                                      | (91)   |
| H <sub>K</sub> (·10 <sup>4</sup> )    | 3.71799                                      | (580)             | 3.37059                | (839) | 4.62598                                      | (2054  |
| h <sub>T</sub> (·10 <sup>9</sup> )    | 5.4326                                       | (172)             | 5.394                  | (52)  | 5.5284                                       | (693)  |
| h <sub>JK</sub> (·10 <sup>8</sup> )   | -1.09  | (32)              |                        |       | -3.79  | (127)  |
| h <sub>K</sub> (·10 <sup>5</sup> )    | 1.6673                                       | (107)             | 1.559                  | (35)  | 2.2723                                       | (470)  |
| $L_{T}(\cdot 10^{13})$                |  |                   |                        |       | -1.63  | (60)   |
| LKKJ ( · 10 9)                        | 4.1512                                       | (357)             | 3.305                  | (283) | 4.685  | (342)  |
| L <sub>K</sub> ( • 10 <sup>8</sup> )  | -8.1384                                      | (2467)            | -5.940                 | (301) | 12.728                                       | (1032) |
| P <sub>K</sub> (·10 <sup>11</sup> )   | 1.704  | (305)             |                        |       | 6.511  | (1777) |
| rms                                   | 0.07   | L                 | 0.0                    | 97    | 0.1  | 08     |

a. The number of places retained in each constant is required so that the data may be reproduced from the constants.

used to drive a harmonic generator. The output of this generator is focused through the sample cell via quasioptical techniques and detected by an InSb detector operating at 1.5 K. For these experiments the sample cell was a 2-cm-diameter copper tube, 1 m in length.  $SO_2$  was obtained from Matheson in its natural isotopic form and used without further purification.

## III. RESULTS AND ANALYSIS

Sulfur dioxide is a relatively light asymmetric rotor with a large dipole moment and b-type transitions. As such, it has many strong transitions throughout the millimeter, submillimeter, and FIR spectral regions. At microwave resolution essentially all of these transitions are fully resolved. The earlier work, summarized by Lovas, made initial assignments straightforward, and additional transitions were assigned and measured by the usual bootstrap procedure involving cycles of analysis, prediction, and data acquisition. For this analysis we have used the A-reduced form

b. One standard deviation in the units of the last quoted digit.

TABLE III  $^{32}\mathrm{S}^{16}\mathrm{O}_2$  Excited State ( $\nu_2=1$ ) Transition Frequencies (MHz)

| Transition  | Observed       | 0-C    | Transition                               | Obseraved  | 0-C    |
|---|----------------|--------|--|------------|--------|
| 5 5 1 4 0   | 566145.134     | 0.061  | <sup>36</sup> 12 24 <sup>-37</sup> 11 27 | 479303.697 | 0.175  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 689233.752     | -0.043 | 38 6 32 - 38 5 33                        | 502112.611 | 0.044  |
| 7 4 4 6 3 3   | 5 00074.955    | -0.021 | 38 7 31 -38 6 32                         | 650669.285 | -0.045 |
| 8 5 3 7 4 4   | 623516.751     | 0.045  | 37 <sub>12 26</sub> -38 <sub>11 27</sub> | 459902.689 | 0.016  |
| 9 8 2 9 7 3   | 781278.374     | -0.116 | 39 6 34 <sup>-39</sup> 5 35              | 558989.014 | 0.046  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 5 57 402 . 576 | 0.025  | 38 <sub>12 26</sub> -39 <sub>11 29</sub> | 440471.475 | 0.087  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 448399.797     | 0.196  | 40 1 39-40 0 40                          | 671120.142 | -0.100 |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 494110.938     | 0.012  | 40 0 40 - 39 1 39                        | 710903.253 | -0.246 |
| 18 4 14 <sup>-17</sup> 3 15                           | 713588.329     | 0.119  | 41 6 36 <sup>-41</sup> 5 37              | 562245.371 | -0.03  |
| 19 4 16 -18 3 15                                      | 710177.611     | -0.032 | 4013 27-4112 30                          | 503378.478 | -0.05  |
| 19 9 11 -20 8 12                                      | 500891.709     | 0.132  | 42 6 36 <sup>-42</sup> 5 37              | 456211.563 | 0.04   |
| 24 <sub>11</sub> 13 <sup>-25</sup> 10 16              | 609150.513     | -0.244 | 42 4 38 -41 5 37                         | 615767.885 | 0.15   |
| 25 <sub>10</sub> 16 <sup>-26</sup> 9 17               | 487812.889     | 0.027  | 43 <sub>13</sub> 31 <sup>-44</sup> 12 32 | 445196.895 | -0.18  |
| 27 <sub>10 18</sub> -28 9 19                          | 449102.301     | -0.085 | 46 4 42 <sup>-46</sup> 3 43              | 484158.585 | -0.00  |
| 27 <sub>12</sub> 16 <sup>-28</sup> 11 17              | 652819.870     | 0.013  | 46 5 41 -45 6 40                         | 539315.417 | 0.00   |
| 29 7 23 <sup>-29</sup> 6 24                           | 671191.924     | 0.012  | 46 <sub>14</sub> 32 <sup>-47</sup> 13 35 | 488267.235 | 0.01   |
| 30 <sub>1 29</sub> -30 <sub>0 30</sub>                | 486722.159     | 0.016  | 48 4 44 <sup>-48</sup> 3 45              | 535687.713 | -0.02  |
| 30 <sub>11</sub> 19 <sup>-31</sup> 10 22              | 493492.730     | 0.088  | 48 7 41 -48 6 42                         | 571844.400 | 0.03   |
| 32 3 29 <sup>-31</sup> 4 28                           | 445836.923     | -0.004 | 48 <sub>14</sub> 34 <sup>-49</sup> 13 37 | 449498.473 | 0.05   |
| 33 4 30 <sup>-33</sup> 3 31                           | 447699.728     | 0.050  | 50 7 43 -50 6 44                         | 545569.476 | 0.04   |
| 32 <sub>11</sub> 21 <sup>-33</sup> 10 24              | 454735 .779    | 0.022  | 50 6 44 <sup>-49</sup> 7 43              | 443825.123 | 0.03   |
| 35 <sub>2</sub> 34 -35 <sub>1</sub> 35                | 581075.151     | 0.105  | 51 <sub>15</sub> 37 <sup>-52</sup> 14 38 | 492079.448 | -0.09  |
| 2 34 1 35<br>35 5 31 <sup>-35</sup> 4 32              | 482609.669     | 0.007  | 52 <sub>15</sub> 37 <sup>-53</sup> 14 40 | 472743.508 | -0.08  |
| 5 31 4 32<br>35 <sub>12</sub> 24 <sup>-36</sup> 11 25 | 498675.632     | -0.090 | 54 5 49 <sup>-54</sup> 4 50              | 519225.234 | 0.00   |
|   | 498207.084     | 0.012  | 54 7 47 <sup>-54</sup> 6 48              | 491314.556 | -0.05  |
| <sup>37</sup> 4 34 <sup>-37</sup> 3 35                |                |        | 60 7 53 <sup>-60</sup> 6 54              | 445180.832 | 0.01   |

of Watson's Hamiltonian. This is the same choice that we have previously made in our work on light asymmetric rotors (7–9). The exact form, as well as our implementation of it, is detailed in those works. All calculations were done on a Harris H800 computer. The numerically intensive parts of the calculations were done in quadruple precision (96 bit) arithmetic.

Table I shows the transitions measured in this work for the ground vibrational state of  ${}^{32}S^{16}O_2$  and Table II shows the constants derived from our analysis. Also included in our analysis is the earlier microwave data as compiled by Lovas. The constants retained in the analysis were selected by means of the criteria we have discussed previously (7-9). As usual, several different combinations are about equally acceptable for fitting the data. It is gratifying, however, that the extrapolations of calculated frequencies well into the FIR are relatively insensitive to the details of these choices. Also shown in Table II is the rms deviation of the fit, 0.070 MHz (2 × 10<sup>-6</sup> cm<sup>-1</sup>). Table III shows the transitions measured in this work for the first bending state ( $\nu_2$ ) of  ${}^{32}S^{16}O_2$  and the fit of the analysis to these data. The  $51_{4.48}$ -

TABLE IV  ${}^{34}S^{16}O_2$  Ground State Transition Frequencies (MHz)

| Transition                              | Observed   | 0-C    | Transition   | Observed   | 0-С    |
|---|------------|--------|--|------------|--------|
| 5 4 2 4 3 1                             | 441174.032 | -0.027 | <sup>37</sup> 1 37 <sup>-36</sup> 0 36   | 656549.496 | -0.133 |
| 6 5 2 5 4 1                             | 558717.549 | 0.050  | <sup>38</sup> <sub>3</sub> <sub>35</sub> <sup>-38</sup> <sub>2</sub> <sub>36</sub> | 448811.048 | 0.032  |
| 6 6 0 5 1                               | 656900.713 | -0.026 | <sup>38</sup> 6 32 <sup>-38</sup> 5 33   | 459535.911 | 0.085  |
| 7 7 0 6 1                               | 773885.720 | -0.083 | 38 7 31 <sup>-38</sup> 6 32  | 608339.153 | 0.036  |
| 9 5 5 8 4 4                             | 615985.529 | 0.105  | 38 4 34 <sup>-37</sup> 5 33  | 501920.146 | -0.053 |
| 9 6 4 8 5 3                             | 714223.701 | -0.113 | <sup>37</sup> 13 25 <sup>-38</sup> 12 26   | 490960.031 | -0.050 |
| 9 7 3-10 6 4                            | 449079.357 | 0.044  | 40 1 39-40 0 40  | 658797.517 | 0.059  |
| 5 7-10 4 6                              | 654069.881 | -0.085 | 40 3 37 -40 2 38   | 495286.969 | -0.060 |
| 4 4 10 <sup>-13</sup> 3 11              | 613338.148 | -0.010 | 40 7 33 -40 6 34   | 597519.231 | -0.208 |
| 4 5 9 <sup>-13</sup> 4 10               | 711021.060 | 0.126  | <sup>39</sup> 14 26 <sup>-40</sup> 13 27   | 547779.682 | 0.177  |
| .6 4 12 <sup>-15</sup> 3 13             | 652652.865 | 0.046  | 42 4 38 -41 5 37   | 652745.791 | 0.095  |
| .7 5 13 <sup>-16</sup> 4 12             | 766772.835 | -0.061 | 43 6 38 - 43 5 39  | 542257.673 | -0.084 |
| 8 3 15 <sup>-17</sup> 2 16              | 648737.597 | 0.053  | 43 7 37 -43 6 38   | 612670.968 | 0.136  |
| 7 9 9 18 8 10                           | 490539.553 | -0.011 | <sup>42</sup> 14 28 <sup>-43</sup> 13 31   | 489942.961 | -0.115 |
| 9 11 -20 8 12                           | 452062.461 | 0.032  | 44 4 40 -44 3 41   | 447981.198 | 0.012  |
| 5 1 25 -24 0 24                         | 447275.249 | -0.007 | 45 6 40 <sup>-45</sup> 5 41  | 553329.138 | -0.039 |
| <sup>4</sup> 10 14 <sup>-25</sup> 9 17  | 452796.567 | 0.122  | 46 4 42 - 46 3 43  | 498409.999 | 0.008  |
| 8 0 28 27 1 27                          | 498995.036 | 0.045  | 46 7 39-46 6 40  | 542984.626 | -0.071 |
| 0 1 29-30 0 30                          | 479152.273 | 0.046  | 48 4 44 - 48 3 45  | 548333.613 | -0.016 |
| 9 <sub>12 18</sub> -30 <sub>11 19</sub> | 549370.664 | -0.107 | 48 7 41 -48 6 42   | 517525.470 | 0.122  |
| <sup>0</sup> 12 18 <sup>-31</sup> 11 21 | 530119.754 | 0.127  | 47 <sub>15</sub> 33 <sup>-48</sup> 14 34   | 488516.151 | -0.062 |
| <sup>2</sup> 12 20 <sup>-33</sup> 11 23 | 491549.487 | 0.007  | 50 7 43 <sup>-50</sup> 6 44  | 490440.474 | -0.082 |
| 4 1 33 - 34 0 34                        | 551699.871 | 0.068  | 49 <sub>15</sub> 35 <sup>-50</sup> 14 36   | 449884.155 | 0.060  |
| 4 0 34 <sup>-33</sup> 1 33              | 604080.004 | -0.008 | 52 7 45 <sup>-52</sup> 6 46  | 464237.845 | 0.270  |
| 4 <sub>13 21</sub> -35 <sub>12 24</sub> | 548807.215 | -0.088 | 54 7 47 54 6 48  | 441872.643 | -0.205 |
| 6 6 30 <sup>-36</sup> 5 31              | 480055.437 | 0.075  | 56 7 49 -55 8 48   | 500228.123 | 0.022  |
| <sup>7</sup> 2 36 <sup>-37</sup> 1 37   | 605924.403 | -0.152 | 1 49 5 48  |            |        |

 $50_{545}$ , which was measured at 42615.90 MHz in an earlier experiment (1), is inconsistent with the prediction from our analysis of 42614.65 (10) and was not included in the final fit. Table II shows the constants which resulted. A similar analysis has been carried out on  $^{34}S^{16}O_2$ . The data and the fit to it are shown in Table IV and the results of the analysis in Table II. It would have been possible to observe hundreds more transitions for inclusion in each of these analyses. However, we selected only those transitions necessary to provide the experimental basis for our calculations. Our statistical calculations and experimental checks show that these additional lines would add little new information, most being predictable to <0.1 MHz.

The variation among the three constant sets shown in Table II is well behaved. As expected, the isotopic substitution of sulfur leaves the value of B essentially unchanged (10). Constants associated with the  $P_z^{2n}$  expansion are slightly smaller in

TABLE V

Comparison Among FIR Observation, Fit to the FIR Data Set, and Predictions Based upon Microwave Analysis (MHz)

| Transition            | observed              | ₽ <u>-</u> 6 | Prediction   |
|-----------------------|-----------------------|--------------|--------------|
| 24(22 2) - 24(21 3)   | 2110.818              | -13          | 2110.803( 7) |
| 26(22 4) - 26(21 5)   | 2111.246              | 4            | 2111.213( 7) |
| 27(22 6) - 27(21 7)   | 2111.454              | -2           | 2111.428( 7) |
| 28(22 6) - 28(21 7)   | 2111.665              | -12          | 2111.649( 7) |
| 29(22 8) - 29(21 9)   | 2111.907              | 3            | 2111.875( 7) |
| 30(22 8) - 30(21 9)   | 2112.112 <sup>b</sup> | -23          | 2112.108( 7) |
| 31(22 10) - 31(21 11) | 2112.361              | -12          | 2112.346( 7) |
| 35(22 14) - 35(21 15) | 2113.358 <sup>b</sup> | -19          | 2113.350( 7) |
| 38(22 16) - 38(21 17) | 2114.150 <sup>b</sup> | -26          | 2114.151( 7) |
| 39(22 18) - 39(21 19) | 2114.439              | -12          | 2114.426( 7) |
| 41(22 20) - 41(21 21) | 2114.979 <sup>b</sup> | -31          | 2114.985( 7) |
| 42(22 20) - 42(21 21) | 2115.275 <sup>b</sup> | -19          | 2115.269( 7) |
| 46(22 24) - 46(21 25) | 2116.431 <sup>b</sup> | -22          | 2116.430( 7) |
| 26(23 3) - 26(22 4)   | 2200.943              | 0            | 2200.901(12) |
| 28(23 5) - 28(22 6)   | 2201.396              | -5           | 2201.359(12) |
| 29(23 7) - 29(22 8)   | 2201.619 <sup>b</sup> | -21          | 2201.599(13) |
| 30(23 7) - 30(22 8)   | 2201.868              | -17          | 2201.845(13) |
| 31(23 9) - 31(22 10)  | 2202.123              | -14          | 2202.097(13) |
| 32(23 9) - 32(22 10)  | 2202.375 <sup>b</sup> | -20          | 2202.355(13) |
| 38(23 15) - 38(22 16) | 2204.073 <sup>b</sup> | 14           | 2204.020(13) |
| 27(24 4) - 27(23 5)   | 2289.871              | 5            | 2289.806(22  |
| 30(24 6) - 30(23 7)   | 2290.622              | 4            | 2290.559(22) |
| 31(24 8) - 31(23 9)   | 2290.894              | 12           | 2290.824(22) |
| 32(24 8) - 32(23 9)   | 2291.151              | -1           | 2291.096(22) |
| 36(24 12) - 36(23 13) | 2292.303              | 1            | 2292.247(22) |

a. Uncertainties in units of last quoted place.

 $^{34}\mathrm{S}^{16}\mathrm{O}_2$  and somewhat larger in  $^{32}\mathrm{S}^{16}\mathrm{O}_2$  ( $\nu_2=1$ ). The former results from the increased moment of inertia due to  $^{34}\mathrm{S}$  and the latter from the change in vibrational averaging. Some, if not most, of the reduction in  $L_K$  for  $^{34}\mathrm{S}^{16}\mathrm{O}_2$  is due to the constraint of  $P_K$  to zero in that analysis.

## IV. DISCUSSION

It is difficult to compare, on the basis of spectral constants, our results with other studies because of the differences in Hamiltonians, data sets, and weighting schemes. It is perhaps more useful to compare the energy levels calculated from them. The most difficult lines for our analysis to predict are the highest  $K_a$  lines that could be

b. Lines considered to be blends (derivations greater than 18 MHz).

observed in the FIR experiment. Table V shows a comparison among the observed FIR frequencies, the frequencies calculated from a fit to the FIR lines, and the predictions calculated from our microwave analysis. All lines considered by Carlotti et al. to be blended are marked with a "b." In that analysis (with one exception at low J) all lines with a deviation greater than 18 MHz are considered to be blended and the remainder unblended. This effectively sets an upper limit of 18 MHz on the deviation of lines included in their analysis and makes it difficult for us to estimate the uncertainty in observed frequencies for their weak lines. We note that our calculations actually better predict those lines excluded from the FIR fit as blends because all of them are observed to be systematically lower than the FIR fit, as are our predictions. From these considerations we conclude, for the transitions that are most difficult to calculate by extrapolation from the microwave analysis, that the errors in these calculations are comparable to the uncertainties in the experimental line positions. Furthermore, for the large majority of thermally populated transitions the microwave analysis predicts line positions to better than 1 MHz, and for many, to better than 0.1 MHz.

Although the data sets for  $^{32}S^{16}O_2(\nu_2)$  and  $^{34}S^{16}O_2$  are not as extensive as those of  $^{32}S^{16}O_2$ , they are similar in information content. The ground and excited state constants for the abundant species should, to within an additive constant, predict the  $\nu_2$  infrared band with high accuracy. These constants should also make the assignment of the remaining lines in the FIR spectrum straightforward.

These (or any of several logical subsets) are available via telephone modem from the H800 by use of very simple programs (virtually any terminal or resident terminal program capable of down-loading files). Interested parties should contact FCD for telephone numbers and passwords.

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