

The Rotational Spectra, Hyperfine Interactions, and  $^{17}\text{O}$  Magnetic Shieldings  
of  $^{17}\text{O}^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ , and  $^{17}\text{OS}^{16}\text{O}$ .

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## ABSTRACT

Measurements of the rotational spectra of  $^{17}\text{O}^{16}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$  have been extended to allow determination of a complete set of sextic centrifugal distortion constants for both molecules. A near degeneracy of the  $3_{12}$  and  $4_{04}$  levels of  $^{17}\text{O}^{16}\text{O}^{16}\text{O}$  causes strong perturbations of the hyperfine patterns, gives rise to perturbation allowed  $\Delta J = 2$  transitions, and provides for an accurate determination of  $\chi_{ab}$ . This has allowed the determination of the angle between principal axis of the quadrupole tensor and the O-O bond. The  $^{17}\text{O}$  spin-rotation interactions of  $^{17}\text{O}^{16}\text{O}$  have been measured for comparison with the corresponding values in  $\text{O}_3$  and improved values of the quadrupole coupling have been obtained. Paramagnetic shielding and chemical shifts for  $^{17}\text{O}$  have been calculated from the spin-rotation constants for both compounds.

## INTRODUCTION

A preliminary account of work in this laboratory on the  $^{17}\text{O}$  ozones (1) reported the rotational and quartic centrifugal distortion constants as well as the diagonal elements of the nuclear quadrupole and spin-rotation coupling tensors. Because of ozone's prominence in the Earth's atmospheric spectrum the earlier measurements have been extended to considerably higher  $J$  and  $K_a$  transitions. The parameters derived from fitting these new measurements provide an adequate basis for predicting the contribution of these species to the atmospheric millimeter and submillimeter spectrum. Since the measurements described in this paper were completed, Rinsland, et al., (2) have reported improved rotational constants for the  $^{17}\text{O}$  ozones based on a combined fit of the data in Ref. (1) and their measurements of the high resolution spectra of the  $\nu_2$  bands of both molecules.

Perturbations in the hyperfine patterns of  $^{17}\text{O } 1^6_1 6^0$  which were not reported in the previous paper have been analyzed. These have been shown to be due to  $\chi_{ab}$  mixing of the nearly degenerate  $3_{12}$  and  $4_{04}$  states. As a result, the orientation of the principal axes of the nuclear quadrupole coupling tensor has been precisely determined. A number of transitions in  $^{17}\text{O } 1^6_1 6^0$  were measured at higher resolution than in earlier work (3,4) and a number of additional transitions were observed in order to determine and compare the  $^{17}\text{O}$  spin-rotation interactions with those of  $^{16}\text{O } 1^6_1 6^0$ . These have approximately the same relative size compared to those of  $^{16}\text{O}$  as do the molecular  $g$  values. (5-7) The spin-rotation constants are used to calculate the paramagnetic shielding and chemical shifts for  $^{17}\text{O}$ .

## EXPERIMENTAL

The experimental details, including the Stark modulated spectrometer, 7%  $^{17}\text{O}$  enriched sample, and sample handling were the same as those described in Ref. (1) except for the

measurements above 300 GHz for which tone burst modulation (8) was used. Small quantities of  $^{17}\text{O}^{16}\text{O}$  were made by allowing portions of the enriched ozone sample to react with solid sulfur. The sulfur dioxide required refreshing every 10-15 minutes because of oxygen exchange with adsorbed water in the waveguide.

In the reported measurements, the quoted uncertainties are estimates based on possible contributions to the error. The uncertainties reflect not only a large range of line strengths but also the varying degree of difficulty in determining line positions in complex hyperfine multiplets.

### MECHANICAL CONSTANTS

Although the number of independent measurements that determine the mechanical constants is relatively small, it was found to be sufficient to determine rotational and up to sextic centrifugal distortion constants for both ozone species. The data are also sufficient for the prediction of the  $^{17}\text{O}$  ozone atmospheric millimeter spectra to the accuracy required by current observational instruments (9). The fitted data are listed in Tables 1 and 2 along with observed minus calculated frequencies based on the derived parameters in Table 3. The parameters refer to the standard Watson A reduction Hamiltonian and P representation (10) with the quadrupole and spin-rotation terms fitted simultaneously (11). The  $^{17}\text{O}$  parameters are perfectly consistent with those of the  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ ,  $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ , and normal ozone for which more data are available and also with high resolution infrared results of Rinsland, et al, (2,12-14). Calculated spectra based on these data are available in computer accessible form (15). Those calculations contain assumptions about higher order parameters not determinable by the data presented here and are continually revised as additional data affecting the higher order parameters become available. Consequently, the parameters presented here will not exactly reproduce the cataloged frequencies for transitions which require

long extrapolations in quantum number.

The  $^{17}\text{O}^{16}\text{O}$  study was undertaken primarily to determine the  $^{17}\text{O}$  nuclear spin-rotation interaction for comparison with  $^{17}\text{O}^{16}\text{O}^{16}\text{O}$ . A large number of lines had been previously measured and assigned by Van Riel and Steenbeekkers (3). These have also been listed by Lovas (4). Most of the older measurements were used directly but with some additional assignments of hyperfine components based on this study. Several transitions were remeasured and some new measurements made as required for determination of the spin-rotation interactions. Additional measurements were made at higher frequency to remove some correlations among the sextic constants. The new measurements are listed in Table 4. Since the mechanical constants were not the primary objective of this study and since only a limited amount of sample was available, the higher frequency measurements were not extensive. As a result, it was necessary to fix three of the sextic constants to those of normal  $\text{SO}_2$ . These parameters are taken from Afferty, et al. (16) Higher order terms were fixed to those in Ref. (16) as well. The parameters derived from a fit to all the available data are given in Table 3. The calculated parameters are consistent with those listed in Ref. (16) for the normal species. A table of all the line assignments, frequencies and observed-calculated frequencies has been deposited in the editorial office of this journal and is available on request from the authors.

#### HYPERFINE INTERACTIONS

The hyperfine constants to be discussed in this section have been listed in Table 3 along with the other parameters derived from the fit of the spectra. Note that the sign convention for the  $C$ 's is the opposite of that used for the  $M$ 's of Ref. 1.

The quadrupole coupling tensor at the end oxygen in  $^{17}\text{O}^{16}\text{O}^{16}\text{O}$  has a large  $\chi_{ab}$  component. This produces strong mixing of the  $4_{04}$  and  $3_{12}$  levels which in the absence of nuclear

effects would be only 9.47 MHz apart. Both frequency shifts and perturbation allowed transitions are observed. The  $5_{15} - 3_{12}$   $P^{\circ} = 13/2 - 11/2$  line is only about 16 times weaker than the corresponding component of the allowed  $5_{15} - 4_{04}$  transition. Several hyperfine components of the  $5_{15} - 3_{12}$  transition have been observed as has the  $\alpha$ -dipole allowed, but normally extremely weak  $4_{04} - 3_{03}$ ,  $P^{\circ} = 11/2 - 11/2$  transition.

Because  $\chi_{ab}$  is quite well determined the angle between the principal axes of the quadrupole tensor and the O-O bond can also be determined. This angle is  $2.4 (4)^{\circ}$  using the structure of  $O_3$  given by Tanaka and Morino (17). The orientation is such that the quadrupole principal axis nearest the O-O bond makes a smaller angle with the line between the non-bonded oxygens than does the bond. Since the angle in the ground vibrational state is about the same as the equilibrium angle, the difference in angle determined in this work is probably real. In Ref. 1 the elements of the diagonalized quadrupole tensor were calculated subject to the condition that the a principal quadrupole axis lay along the O-O bond. It is now found that  $\chi_{\alpha\alpha} = -14.00$  and  $\chi_{\beta\beta} = 8.44$  MHz where the  $\alpha$  axis is the one nearly along the O-O bond

For  $SO_2$  the quadrupole coupling has been more precisely measured than in the earlier work (3). The small differences in the result presented here may be due to the inclusion of spin-rotation effects in this analysis. Although  $\chi_{ab}$  is expected to be relatively large, there are no near degeneracies in  $^{17}O^{32}S^{16}O$  among the levels included in the present data set which cause sufficient perturbations for  $\chi_{ab}$  to be determined by these measurements.

The diagonal components of the spin-rotation tensors for both  $^{17}O^{16}O^{16}O$  and  $^{16}O^{17}O^{16}O$  are within experimental uncertainty of those reported in Ref.(1).  $(C_{ab} + C_{ba})/2$  of  $^{17}O^{16}O^{16}O$  which is in principle determinable because of the near degeneracy of the  $4_{04}$  and  $3_{12}$  levels, is too small to be determined within its own magnitude by the data. It has been left in the

fit to ascertain its effect on other parameters which which it is slightly correlated and to give a more realistic evaluation of their uncertainties.

The ground electronic state of ozone shows considerable paramagnetic character due to mixing with low lying excited states. The paramagnetic contribution to the nuclear shielding apparently had been difficult to determine from *ab initio* calculations. Schindler and Kutzelnigg (18) using the SCF-IGLO method obtained poor agreement with the chemical shifts measured by Solomon et. al. (19) and showed that their calculation was remarkably sensitive to the assumed geometry. The calculation did show, however that the shielding was paramagnetic and highly anisotropic. More recently Kutzelnigg, et al., (20) reported results using a multiconfigurational generalization of IGLO which gives much better agreement with the experimental results of Ref.(19).

Following Flygare (21) and Flygare and Goodisman (22) and combining the fundamental constants in their equations, the diagonal components of the paramagnetic shielding tensor are given by

$$\sigma_{aa}^p = 1.212 \times 10^9 \frac{C_{aa}}{A} - 14.09 \sum_{\alpha} \frac{Z_{\alpha}(r_{\alpha}^2 - a_{\alpha}^2)}{r_{\alpha}^3}$$

where  $\sigma$  is in parts per million, the  $Z_{\alpha}$  are the atomic numbers of other nuclei, and the distances and coordinates are measured from the atom in question and given in Angstroms. The other components are obtained by cyclic permutation  $a$ ,  $b$ , and  $c$ . The average diamagnetic contribution is

$$\sigma_{ave}^d = \sigma^d(\text{free atom}) - 9.39 \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}}$$

where  $\sigma^d(\text{free atom})$  is taken to be 395.1 ppm for  $^{17}\text{O}$  (23). The diamagnetic shieldings calculated in this way are essentially the same as those calculated by Ray and Parr (24) for both oxygens. Rothenberg and Schaefer (25) have calculated the individual components of the diamagnetic shielding tensors for ozone. Those values may be used to estimate the

individual components of the total shielding tensors. Their average diamagnetic shieldings are also quite close to those calculated here. The average shielding can be determined without any knowledge of the molecular structure by combining the above equations to give

$$\sigma_{avc} = \sigma^d(\text{free atom}) + 4.040 \times 10^9 \left( \frac{C_{aa}}{A} + \frac{C_{bb}}{B} + \frac{C_{cc}}{C} \right).$$

As a point of reference, the above equation gives  $\sigma_{avc}$  for  $^{17}\text{O}$  in water as 357 ppm with spin-rotation constants taken from Helminger and DeLucia (26). This is essentially identical with an equilibrium value derived by applying the vibrational correction of Fowler and Raynes (27) to the measured gas phase value of 344 ppm (28).

Table 5 gives the diagonal paramagnetic shielding tensor elements, total shielding and chemical shift from liquid water. The absolute shielding of  $^{17}\text{O}$  in liquid water is taken as 307.8 ppm (28). The quoted uncertainties include only the 1 u uncertainty of the spin rotation constants. Correlations among the individual uncertainties are included in the calculation of the average shielding uncertainty. The spin-rotation constants measured in this work are quite consistent with the chemical shifts of Solomon et al., (19) and with a highly paramagnetic, anisotropic shielding tensor. The recent calculations of Kutzelnigg, et al., (20) give absolute shieldings which also agree well with the present results.

For  $^{17}\text{O}^{16}\text{O}$  the diagonal components of the spin-rotation tensor have been determined for the first time. These have also been used to calculate the paramagnetic shielding tensor and total shielding. The calculated chemical shift is again in good agreement with the experimental value (29) as seen in Table 5. Rothenberg and Schaefer (30) and Gierke and Flygare (31) have calculated the diamagnetic shielding tensors for  $^{17}\text{O}$  in sulfur dioxide. The total shielding calculated by vanWüllen and Kutzelnigg (32) is in good agreement with both the direct measurement of the chemical shift and the result derived here.

It is interesting to compare the  $^{17}\text{O}$  spin-rotation interaction in  $\text{SO}_2$  with that in the



asymmetrically substituted  $\text{O}_3$ . For a planar molecule the quantity

$$\frac{g_{aa}}{A} - 1 = \frac{g_{bb}}{B} - \frac{g_{cc}}{C},$$

where the  $g_{ii}$ 's are components of the molecular  $g$  tensor, is independent of origin (32) and may be compared with a similar expression for the  $C_{ii}$ 's. For ozone, both quantities are about 3.3 times as great as the corresponding values for  $\text{SO}_2$  (5-7). This is consistent with the fact that the lowest lying excited electronic states of  $\text{SO}_2$  are almost 3 times as high as the lowest state of ozone (33).

### CONCLUSION

Measurements of the rotational spectra of the  $^{16}\text{O}$ - $^{17}\text{O}$  substituted ozones and sulfur dioxide have been extended, yielding improved mechanical and hyperfine parameters. The ozone results increase the data base for the atmospheric spectrum. The hyperfine parameters provide useful references for comparison with theoretical calculations of the electronic structure of these fundamental molecules.

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### REFERENCES

1. E. A. Cohen and H. M. Pickett, *J. Mol. Struct.* **7** (1983) 97.

2. C. P. Rinsland, M. A. H. Smith, V. Malathy Devi, A. Perrin, J.-M. Flaud, and C. Camy-Peyret, *J. Mol. Spectrosc.* 49 (1991) 474.
3. R. Van Riet and G. Steenbeckeliers, *Acad. Roy. Belg. Mémoires*, 36 (1965) 1.
4. F. J. Lovas, *J. Phys. Chem. Ref. Data*, 7 (1978) 1445.
5. J. Pochan, R. Stone, and W. H. Flygare, *J. Chem. Phys.* 51(1969) 4278.
6. A. W. Ellenbrook and A. Dymanus, *Chem. Phys. Lett.* 42 (1976) 303.
7. W. L. Meerts, S. Stolte, and A. Dymanus, *Chem. Phys.* 19 (1977) 467.
8. H. M. Pickett, *Appl. Opt.*, 19 (1980) 2745.
9. J. W. Waters, *Atmospheric Remote Sensing by Microwave Radiometry*, M. A. Janssen, Editor, John Wiley & Sons, Inc. 1993, Chapter 8.
10. J. K. G. Watson, *J. Mol. Spectrosc.*, 65 (1977) 123.
11. H. M. Pickett, *J. Mol. Spectrosc.*, 148 (1991) 371.
12. J.-M. Flaud, C. Camy-Peyret, C. P. Rinsland, and H. A. H. Smith, *J. Mol. Spectrosc.* 118(1986) 334.
13. J.-M. Flaud, C. Camy-Peyret, A. Perrin, C. P. Rinsland, and M. A. H. Smith, *J. Mol. Spectrosc.* 118 (1986) 345.
14. H. M. Pickett, E. A. Cohen, and J. S. Margolis, *J. Mol. Spectrosc.* 110 (1985) 186.
15. H. M. Pickett, R. L. Poynter and E. A. Cohen, *JPL Pub. 80-23, Version 3*, (1992).  
The 1992 version is available on magnetic tape from the National Space Science Data Center, Goddard Space Flight Center, Greenbelt, MD. Instructions for obtaining more recent updates may be obtained from the authors.

16. W. J. Lafferty, G. T. Fraser, A. S. Pine, J.-M. Flaud, C. Camy-Peyret, V. Dana, J.-Y. Mandin, A. Barbe, J. J. Plateaux, and S. Bouazza, *J. Mol. Spectrosc.*, **154** (1992) 51.
17. T. Tanaka and Y. Morino, *J. Mol. Spectrosc.*, **33** (1970) 538.
18. M. Schindler and W. Kutzelnigg, *Mol Phys.*, **48** (1983) 781.
19. I. J. Solomon, J. N. Keith, A. J. Kacmarek, and J. H. Itatley, *J. Am. Chem. Soc.*, **90** (1968) 5408.
20. W. Kutzelnigg, Ch van Wüllen, U. Fleischer, R. Franke, and T. v. Mourik, *Nuclear Magnetic Shieldings and Molecular Structure*, J. A. Tossell (ed.), Kluwer Academic Publishers, Dordrecht, 1993, p. 141.
21. W. H. Flygare, *J. Chem. Phys.*, **41** (1964) 793.
22. W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, **49** (1968) 3122.
23. G. Malli and C. Froese, *Int. J. Quantum. Chem.*, **1** (1967) 95.
24. N. H. Ray and R. G. Parr, *J. Chem. Phys.*, **73** (1980) 1334.
25. S. Rothenberg and H. F. Schaefer III, *Mol. Phys.*, **21** (1971) 317.
26. F. Helminger and F. C. De Lucia, *J. Mol. Spectrosc.*, **56** (1975) 138.
27. J. W. Fowler and W. H. Raynes, *Mol. Phys.*, **43** (1981) 65.
28. R. E. Wasylishen, S. Mooibroek, and J. B. Macdonald, *J. Chem. Phys.*, **81** (1984) 1057.
29. B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.*, **A269** (1962) 469.
30. S. Rothenberg and H. F. Schaefer III, *J. Chem. Phys.*, **53** (1970) 3014.

31. '1'. D.Gierke and W. 11. Flygare, J. Am.Chem.Soc., **94** (1972) 7277.
32. Ch. van Wüllen and W. Kutzelnigg, Chem.Phys.Lett., 205 (1993) 563.
33. w. 11. Flygare, Chem.Rev., 74 (1974) 653.
34. G.Herzberg, Molecular Spectra and Molecular Structure (111. Electronic Spectra of Polyatomic Molecules), Van NostradReinhold Co., New York,1966,pp. 604-605,

Table 1. Fit teci  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$  Rotational Transitions

Transition <sup>a</sup>	Freq./MHz <sup>b</sup>	AC	Transition	Freq./MHz	$\Delta$	Transition	Freq./MHz	A
50 <sub>8,42</sub> - 51 <sub>7,45</sub>	26674.375(1.50)	-74	2 7 <sub>2,25</sub> - 26 <sub>3,23</sub>			4 <sub>1,3</sub> - 4 <sub>0,4</sub>		
46 <sub>6,40</sub> - 45 <sub>7,39</sub>	32056.580(70)	-24	25-24	670.50	.794(50) 81	6-7	978 75.726(50)	3
18 <sub>2,16</sub> - 19 <sub>1,19</sub>			30-29,25-25	670.51	172(20) -23	4-3,5-4,3-2	97876.568(50)	50
20-21,1 9-20,18-19	32202.730(100)	-42	2% 2S,27-25,28-27	67051.689(50)	-1	4-4,5-5,6-6,6-5	97877.235(50)	3 3
17-18	32203.370(100)	-64	13 <sub>3,11</sub> - 14 <sub>2,12</sub>			3-4	97878.570(50)	2 3
7-22	32203.830(100)	-86	16-17,11-12	71393.7.50(20)	-27	2-3,7-6	97878.798(50)	-46
36 <sub>6,30</sub> - 37 <sub>5,33</sub>	33340.684(50)	-11	15-16,12-13	71397.246(50)	.53	6 <sub>1,15</sub> - 6 <sub>0,15</sub>		
334,30 - 32 <sub>5,27</sub>	35476.737(70)	-27	14-15,13-14	71397.400(100)	5	8-8,7-7,6-6	107369.271(50)	39
12 <sub>2,10</sub> - 13 <sub>1,13</sub>			6 <sub>0,5</sub> - 5 <sub>1,5</sub>			9-9,5-5	107369.698(50)	-5
13-14	35634.868(40)	18	8-7,7-6,6-5	71478.349(30)	35	9-8,4-5	107371.062(70)	15
12-13,14-15	35635.0.5.5(40)	-2	5-4	71478	.657(50) 6	24 <sub>2,22</sub> - 25 <sub>1,25</sub>		
11-12	3663.5 ..57.5(20)	15	9-8,4-3	71479.080(30)	2 3	24-25,25-26,26-27	113474 .?64(60)	-111
15-16	3653.5.800(20)	2	8 <sub>2,6</sub> - 9 <sub>1,9</sub>			23-24	113475.614(60)	30
10-11	36536.278(40)	-22	10-11,9-10,8-9	83612.158(30)	-4	27-28	113476.160(60)	34
1 <sub>1,1</sub> - 2 <sub>0,2</sub>			11-12,7-8	83612.646(50)	17	22-23	113476 .80S(60)	50
2-1	38747.308(30)	2	6-7	83613.162(100)	18	1 <sub>1,1</sub> - 0 <sub>0,0</sub>		
2-2	38748.377(70)	-20	35 <sub>4,32</sub> - 34 <sub>5,29</sub>	85249.704(50)	-65	4-3,2-3	114125 .522(30)	16
4-5	38748.607(20)	-3	14 <sub>3,11</sub> - 15 <sub>2,14</sub>	85428.374(50)	-5.4	3-3	114128 .452(30)	10
2-3	38749.619(50)	5	34 <sub>6,28</sub> - 35 <sub>5,31</sub>	86789.708(100)	69	31 <sub>3,29</sub> - 30 <sub>4,26</sub>	114538.184(40)	68
4-4	38750.238(50)	28	2 6 <sub>3,23</sub> - 25 <sub>4,22</sub>	87991.220(50)	-2.7	6 <sub>2,4</sub> - 7 <sub>1,7</sub>		
3-2	38750.438(100)	1	12 <sub>1,11</sub> - 11 <sub>2,10</sub>			6-7,7-8,8-9,9-10	1171.58.680(70)	100
3-3	38751.6.51(30)	-3	13-12,12-1 1	90140.886(30)	10	26 <sub>5,21</sub> - 27 <sub>4,24</sub>	11?224.338(80)	20
3-4	387.52.08.5(30)	-9	14-13,11-10	90141.106(30)	-30	8 <sub>1,7</sub> - 8 <sub>0,8</sub>		
4 0 <sub>5</sub> , 3 <sub>5</sub> - 39 <sub>6,34</sub>	65721.214(40)	32	15-14,10-9	90141.6.51(30)	-30	10-10,9-9,8-8,	121253.826(50)	-10
			48 <sub>6,42</sub> - 47 <sub>7,41</sub>	90976.778(70)	-25	7-7,11-11	121254.306(50)	-77
			2 <sub>1,1</sub> - 2 <sub>0,2</sub>			22 <sub>3,19</sub> - 22 <sub>2,20</sub>	358631.720(60)	6
			4-5	92151	.513(50) -12	20 <sub>1,19</sub> - 19 <sub>2,18</sub>	3714.50.694(69)	-15
			3-2,2-1	92151.957(50)	-36	26 <sub>1,25</sub> - 26 <sub>0,25</sub>	488137 .12S(60)	-17
			5-5,4-3,3-3,4-4	92152.800(70)	-91	34 <sub>4,30</sub> - 34 <sub>3,31</sub>	492001.240(80)	O
			3-A	92153.637(100)	15	20 <sub>4,16</sub> - 20 <sub>3,17</sub>	611043.960(100)	53
			5-4,2-3,1-2	92154.315(70)	0			

a. F -L  $\frac{1}{2}$  designates F assignments of resolvable features.

b. Numbers in ( ) are experimental uncertainties in kHz.

c. Obs.-calc./kHz. Intensity weighted average for blends.

Table 2. Fitted  $^{17}\text{O}^{16}\text{O}$  Rotational Transitions

Transition <sup>a</sup>	Freq./MHz <sup>b</sup>	$\Delta^c$	Transition	Freq./MHz	'A	Transition	Freq./MHz	A
23 <sub>2,22</sub> - 22 <sub>3,19</sub>			1 <sub>1,0</sub> - 1 <sub>0,1</sub>			1 <sub>1</sub> , ) - 0 <sub>0,0</sub>		
21-20	29355.91 O(5O) 34		3 2	93975.1 12(30)	7	4 3,2-3	116992.148(30)	74
26 25	29356.445(70) -6		3 4	93975.789(30)	36	3 3	116094.939(30)	51
22-21	2935 6.750(100) 0		4 4	93976.221(30)	17	5 <sub>2,4</sub> - 6 <sub>1,5</sub>		
2524,2423,2322	29357.305(30) -21		2-2	93976.762(50)	-18	8 9,3 4	118008.014(30)	-3
4 2 <sub>5,38</sub> - 4 <sub>1,6</sub>	35 29812.902(50) -3		4 3	93977.524(30)	-1	4 5	118009.200(50)	27
467 <sub>,39</sub> - 47 <sub>6,42</sub>	30361 .165( 80) 2		2-3	93978.738(30)	-11	7-8.5 G, G-7	118009.989(100)	-49
23 <sub>4,20</sub> - 24 <sub>3,21</sub>	31250.725(100) -30		2 <sub>1</sub> , ] - 2 <sub>0,2</sub>			80,8 -- 7 <sub>1,7</sub>		
18 <sub>3,15</sub> - 19 <sub>2,18</sub>			4 5	95434.664(30)	14	9 8,87 ,10-9	1 19558.037(30)	-9
21-22,17-18	31287.275(50) -17		3 2,4 3	95435 .43 6(50)	60	7-G	119558.630(100)	-66
16-17	31287.767(70) -50		4 4	95435.829(50)	3	11-10	II 9559.222(30)	-5
1819,19,20,20,21	31286 .843 ( 20 ) 4		3 4,5-5	95436.513(30)	-6	8 <sub>1,7</sub> - 8 <sub>,,8</sub>		
35 <sub>4,32</sub> - 34 <sub>5,29</sub>	31833.172(30) - 1		5- 4,1-2-3	95437.766(70)	-25	9 9	121870.568(30)	19
14 <sub>2</sub> , 12 - 15 <sub>1,15</sub>			8 <sub>2,6</sub> - 9 <sub>1,9</sub>			10 10,8 8	121870.952(30)	23
15 16	31 866,220(50) -14		9-10	96308.648(50)	5	7-7	121871.864(30)	27
14 15	31866.600(50) -36		8 9,10 11	96309.012(30)	-9	11-11	121872.358(30)	27
16 17	31 866.900(50) -13		7-8	96309.993(50)	-60	6-6	121873.072(30)	22
13 14	31867.910(50) -6		11-12	96310.382(50)	45	17 <sub>4,14</sub> - 18 <sub>3,15</sub>	202627.122(50)	20
17-18	31868.890(50) -2		6-7	96311 .312(100)	-26	5 <sub>1,5</sub> - 40,4		
12-13	31869.870(50) -10		3 <sub>1,2</sub> - 3 <sub>0,3</sub>			3 2	204860.830(30)	-7
263,23- 25 <sub>4,22</sub>			5-6	97 655.526(50)	18	8 7,4 3	204861 .680( 30) -20	
26-25	32586.623(50) 21		4-3	97655.895(90)	31	5 4,7- 6	204862.630(30)	-14
26 <sub>3,23</sub> - 25 <sub>4,22</sub>			3 2	97656.090(100)	14	6 5,5 5	204863.391(30)	-25
27-26,25 24,2827	32586 .867 (50) -12		4,4 5,5- 4,5-5	97656 .543 ( 30 )	4	5 <sub>1,5</sub> - 3 <sub>1,2</sub>		
29 28>24 23	32587.430(50) -8		6-6	97656.999(50)	20	32	204870.610(90)	-83
37334- 38 <sub>2,37</sub>			3 4	97657.460(100)	-6	7-G	204871 .896( 60) -28	
36-37	33328 .750(1 50) 36		2-2	97657.740(100)	5	4-3	204872.444(150)	-60
40-41	33329.560(150) -22		6-5	97658.109(60)	17	5-4	204873.510(150)	-120
35 36	33330.780(150) -18		2-3	97658.496(60)	13	151, ]4--150,]5		
11], ]0- 10 <sub>2,9</sub>			1-1	97658.821(100)	51	16-16,15- 15,17-17	205498.794(60)	-25
12-11	35002.191(30) 4		1-2	97659.336(60)	-8	14"14	205499.910(30)	-1
11-10	35002.344(30) -7		40,4 -30,3			18-18	205500.873(30)	12
13 12	35002.666(20) 2		6-6	97666 .33?(30)	-14	13 13	205501 .623( 30) 9	
10-9	35003 .010(20) -5		4 <sub>1,3</sub> - 4 <sub>0,4</sub>			11 <sub>0,11</sub> - 10 <sub>1,10</sub>		
14 13	35003.942(30) 8		5 G,4 3,5- 4,6-6	100674.986(80)	81	11-10,13 12,12-1]	205601.709(30)	-12
9-8	35004 .062(30) 14		5 5, G-5	100675.605(120)	56	14 13,9 8	205602.726(30)	5
5 <sub>0,5</sub> - 4 <sub>1,4</sub>			3 2,44	100675.965(120)	24	17 <sub>4,13</sub> - 18 <sub>3,16</sub>	209090.150(60)	-10
6-5	35705.303(30) 2		7-7	100676 .650(200)	-219	343,31- 34 <sub>2,32</sub>	368193.132(80)	-4
7-G	35705.593(20) 16		2-2	00677.420(120)	-2	152,14 -- 15 <sub>1,15</sub>		
54	35705.721(30) -26		2-3	00678.000(150)	1	16 16,15 15,17-]7	368655.408(100)	15
4-3	35706 .57](20) 12		5 <sub>1,4</sub> - 5 <sub>0,5</sub>			18 18	368656.632(120)	-43
87	35707.012(20) 9		7-7,6,6,5 5	04541 .987(100)	-87	13-13	368657.436(100)	5 3
3 2	35707.446(20) -1		8 8,4 4	04543.211(100)	-62	1 8 <sub>5,14</sub> - 19 <sub>4,15</sub>	369244.566(60)	12
20 <sub>2,18</sub> - 19 <sub>3,17</sub>			7 <sub>2,5</sub> - 8 <sub>1,8</sub>			18 <sub>5,13</sub> - 19 <sub>4,16</sub>	369598.482(60)	-15
21-20,20 19	93172.382(40) 18		7-8,9 10,8 9	112630.575(70)	15	27 <sub>1,26</sub> - 27 <sub>0,27</sub>		
22-21,19 18	93172.799(40) -5		7 <sub>1,6</sub> - 7 <sub>0,7</sub>			2828,27,27,2929	488819 .308(100)	6
18 17,23 22	93173.678(40) -24		8 8	115065.642(150)	-88	19 <sub>3,17</sub> - 19 <sub>2,18</sub>	4907] 4, {}04(100)	10
			7-7,9 9	115066.032(30)	-5 8	10 <sub>2,9</sub> - 9 <sub>1,8</sub>		
			6-G	115067.010(1,50)	-14	13 12,8.7	491965.672(160)	-52
			10 10	1 15067.343(30)	-64			
			5-5	1 15068 .164 ( 30 ) 9				

a. b. c. See footnotes to Table 1.

Table 3. Molecular Parameters/M Hz.

Parameter	160170160 <sup>a</sup>	1701601760	17O <sup>32</sup> S <sup>16</sup> O
<i>A</i>	102351.0412 (110) <sup>a</sup>	105490.9498(57)	59883.72105(260)
<i>B</i>	13351.08549(137)	12951.27723(79)	10008.21211(89)
<i>C</i>	11781.72001(143)	11508.02902(73)	8555.13498(63)
$\Delta_J$	0.01352001(259)	0.0128607(38)	0.0062292(114)
$\Delta_{JK}$	-0.046972(63)	- 0.056338(75)	--0.112678(194)
<i>AK</i>	5.84916(83)	6.22091 (83)	2.51274(66)
$\delta_J$	0.00214023(65)	0.00194524(40)	0.00158936(137)
$\delta_K$	0.094969(95)	0.092027(103)	0.023996(58)
$\Phi_J$	0.1203 (192)x10 <sup>-7</sup>	0.547(234) x 10 <sup>-8</sup>	0.1643 (204)x10 <sup>-7</sup>
$\Phi_{JK}$	-0.196(199) × 10 <sup>-6</sup>	-0.217(169) x10 <sup>-6</sup>	<b>0.397 × 10<sup>-7</sup></b> <sup>b</sup>
$\Phi_{KJ}$	--0.463(32) x 10 <sup>-4</sup>	-0.5255 (19 6)x10 <sup>-4</sup>	--0.1950 (137) x10 <sup>-4</sup>
$\Phi_K$	0.000982(56)	0.001116(32)	0.0003674(145)
$\phi_J$	0.464(90) x 10 <sup>-8</sup>	0.452 (58)x10 <sup>-8</sup>	0.714 (92)x10 <sup>-8</sup>
$\phi_{JK}$	- 0.384(272)x 10 <sup>-6</sup>	- 0.236(197)x 10 <sup>-6</sup>	- <b>0.114 × 10<sup>-7</sup></b> <sup>b</sup>
$\phi_K$	0.736(147)x10 <sup>-4</sup>	0.743 (125)x10 <sup>-4</sup>	0.167 x10 <sup>-5</sup> <sup>b</sup>
$\chi_{aa}$	--8.481(75)	- 6.473(92)	- 1.105(69)
$\chi_{bb}$	7.524(49)	10.911(53)	5.569(25)
$\chi_{cc}$	<b>0.958(81)</b>	- 4.438(M)	--4.463(59)
$\chi_{ab}$		13.695(236)	
<i>C<sub>aa</sub></i>	-0.1716(133)	- 0.2572(86)	--0.0484 (34) <sup>a</sup>
<i>C<sub>bb</sub></i>	--0.0087(4 1)	- 0.01788(232)	- 0.00503(309)
<i>C<sub>cc</sub></i>	-0.0023(37)	-0.00403(235)	-0.00152(274)
$(C_{ab} + C_{ba})/2$		0.0087(1 13)	

a. Numbers in parentheses are approximately 1 $\sigma$  uncertainties.

b. Fixed to value in Reference 16.

Table 4. Newly Measured  $^{17}\text{O}^{32}\text{S}^{16}\text{O}$  Rotational Transitions

Transition <sup>a</sup>	Freq./MHz <sup>b</sup>	A' Transition	Freq./MHz	A Transition	Freq./MHz	$\Delta$
$1_{1,0} - 1_{0,1}$		$15_{2,13} - 14_{3,12}$		$10_{1,9} - 10_{0,10}$		
3-2,3-4	5132.5484(20)	33 16-15,15-14,17-16,14-13	67628.068(60)	3 11-11,10-10,12-12	101069.310(60)	142
4-4	51326.393(20)	3 9 18-17,13-12	<b>6762 S.770(30)</b>	-14 9-9	<b>101069.783(120)</b>	<b>-92</b>
A-3	51326.584(30)	9		8-S,13-13	101070.563(60)	-97
2-2	51326.815(60)	18 $1_{1,1} - 0_{0,0}$				
2-3	<b>.51327 .148(20)</b>	<b>11</b> 2-3	6843.5901(8)	-5 80,8 -71,7		
		4-3	58435.253(5)	-4 9-8,8-7,10-9	112675.726(30)	-18
$5_{2,3} - 6_{1,6}$		3-3	68437.512(5)	<b>-2 7-6,11 -10,6-5</b>	112576.306(90)	16
6-7	57102.660(.50)	24				
7-8,5-6	<b>57102.839(50)</b>	-41 $6_{0,6} - 5_{1,5}$		$11_{1,10} - 11_{0,11}$		
		7-6	69712.273(50)	4 12-12,11-11,13-13	113069.875(90)	189
$4_{1,3} - 4_{0,4}$		6-S,8-7	69712.423(30)	<b>-1 4</b> 10-10	113070.377(90)	-15
5-4,5-5,5-6,6-7,6-6 .5-5	.5 8250.156(30)	-17 54	69712.912(40)	1.5 14-14, 9-9	113071.137(90)	-98
4-3,4,4,4-5	58250.520(50)	0 9-8	59713.087(15)	S		
3-2,3-3,7-7,3-4,7-6	582.51.161(30)	8 4-3	69713.332(30)	1 $4_{1,4} - 3_{0,3}$		
				2-1,2-2	117654.103(120)	-31
$5_{1,4} - 5_{0,5}$		$9_{3,6} - 10_{2,9}$	71201.527(30)	<b>14</b> 7-6,3-2,3-3	117664.584(60)	29
6-5,6-6,6-7,7-7,5-4,5-5,5-6	62362.869(30)	-8		4-3,3-3,6-6,6-5,5-4,5-5	117665.444(60)	65
4-3,4-4,4-5,8-8	62363.501(30)	12 $9_{1,8} - 9_{0,9}$				
3-3,3-4	62364.340(100)	S $10-10,9-9,11-11$	90569.036(30)	17 $3_{2,2} - 2_{1,1}$		
		12-12	90570.240(100)	<b>-73</b> 5-5,5-5,3-2,2-2	20.5282.731(90)	1
$6_{1,5} - 6_{0,6}$		$7_{0,7} - 6_{1,6}$		4-3,3-3,5-4,4-4	20.5283.748(90)	23
7-7	67538.217(50)	-2 4				
5-5,8-8	<del>67539</del> 8.497(10)	-2 $8-7,9-8,7-6$	91162.403(30)	50 $3_{3,1} - 2_{2,0}$	30534.069(90)	41
5-5	.155(10)	1 5-5,10-9,5-4	91162.998(60)	15 $3_{3,0} - 2_{2,1}$	308.55.5.799(90)	64
9-9	67539.480(10)	2				
4-4	67.539 .59(10)	-4		12 <sub>6,7} - 13<sub>5,8}</sub></sub>	312792.971(90)	16
				12 <sub>5,6} - 13<sub>5,9}</sub></sub>	21970.51027(90)	1

a. b. c. See footnotes to Table 1.



**Table 5. Calculated  $^{17}\text{O}$  Paramagnetic Shielding, Absolute Total Shielding, and Derived Chemical Shifts Relative to  $\text{H}_2^{17}\text{O}$  in ppm.**

$G$	$(C_{gg}/G) \times 10^6$	$\sigma_{gg}^p$	$\sigma_{ca}$	$\sigma_{\text{IGLO}}$	$\delta_{ca}$	$\delta_{obs}$
$^{16}\text{O}^{17}\text{O}^{16}\text{O}$						
<i>A</i>	-1.677(130)	2080(160)				
<i>B</i>	-0.653(310)	-919(370)				
<i>C</i>	-0.194(320)	-412(380)				
average		-1137(240)	-658	-625 <sup>a</sup>	-932	-1032 <sup>b</sup>
$^{17}\text{O}^{16}\text{O}^{16}\text{O}$						
<i>A</i>	-2.438(82)	-2979(100)				
<i>B</i>	-1.381(180)	1789(220)				
<i>c</i>	-0.350(200)	-564(250)				
average		-1777(170)	-1152	-1289 <sup>a</sup>	-1597	-1598 <sup>b</sup>
$^{17}\text{O}^{32}\text{S}^{16}\text{O}$						
<i>A</i>	-0.8082(570)	-1020(70)				
<i>B</i>	-0.5036(3100)	772(370)				
<i>C</i>	-0.1777(3200)	-419(390)				
average		737(240)	-206	-234 <sup>c</sup>	-514	-513 <sup>d</sup>

a. Reference 20. b. Reference 19. c. Reference 32. d. Reference 29.