

# Pure Rotational Spectra of SO: Rare Isotopomers in the 80-GHz to 1.1-THz Region

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Pure rotational spectra of rare isotopomers of sulfur monoxide, SO, have been recorded with the Cologne Terahertz Spectrometer, Germany, and the millimeter- and submillimeter-wave spectrometer at Nobeyama, Japan. In total, 176 new transitions have been measured in the  $X^3\Sigma^-$  electronic ground state, including the first laboratory detection of the rare isotopomer  $^{36}\text{SO}$ . New lines are also reported for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  in their vibrational ground states, and for  $^{33}\text{SO}$  and  $\text{S}^{18}\text{O}$  in the first excited vibrational state. A simultaneous fit of 451 transitions has led to an improved set of isotopically invariant parameters for rotation and fine structure. Hyperfine structure constants for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  have been obtained also from the global fit, including first values for the magnetic nuclear spin–rotation interaction. These are compared to other molecules. The isotopically invariant parameters allow precise frequency predictions for the submillimeter-wave region far beyond 1 THz for all SO isotopomers, of importance to astrophysical applications. © 1996 Academic Press, Inc.

## 1. INTRODUCTION

Based on an early work of Dunham (1), vibrational and isotopic invariant expansions of molecular constants have become a useful method to analyze pure rotational spectra of diatomic species. To deal with open-shell molecules as well as species with noticeable nuclear momenta, isotopically invariant parameters have also been introduced for fine and hyperfine interactions (2–6). From a practical point of view, the interest on this approach lies in its potential to support studies of excited vibrational states and searches of so far undiscovered isotopomers. The increased resolution and sensitivity of millimeter- and submillimeter-wave spectroscopy achieved in recent years allows a better judgment of the applicability of the isotopically invariant expansion method.

Sulfur monoxide, SO, serves as a good candidate for this kind of investigation, since oxygen and sulfur provide three and four stable isotopes, respectively. The molecule also provides a good example for the significance of rotational spectra of rare isotopomers in astrochemistry.

Owing to the high cosmic abundance of sulfur, a number of molecules, ions, and radicals which contain sulfur have been found in interstellar media by astronomical observations in the millimeter- and submillimeter-wave range. Since isotopic shifts

in rotational spectra are generally large enough to discriminate the individual line positions from each other in radioastronomy, observations of the rotational spectra for isotopic substituted species can provide important *in situ* information on the isotopic ratios in interstellar sources. In the case of sulfur, the neutron-richest isotope,  $^{36}\text{S}$ , is considered to originate from the layer just outside of the neutronized stellar cores in the deep interior of massive stars. Therefore, extensive searches for the weak rotational spectra of the  $^{36}\text{S}$  containing species are of significant importance for the investigation of the origin of neutron-rich nuclei in the universe.

In previous spectroscopic studies, rotational spectra of  $^{36}\text{S}$  containing closed-shell molecules have been reported for OCS (7), CS (8), and  $\text{H}_2\text{S}$  (9). For open-shell molecules, however, no spectroscopic data for  $^{36}\text{S}$  containing isotopomers have been published. This is due to the short lifetime of most radicals and the low terrestrial abundance of  $^{36}\text{S}$  of only 0.02% (10). On the other hand, quite a lot of experimental data have been acquired for the more abundant isotopomers of SO in the ground electronic state  $X^3\Sigma^-$  (11–17). Among them, the works of Bogey *et al.* (16) and Tiemann (17) showed the breakdown of the Born–Oppenheimer approximation and, following an earlier work of Watson (18), they reported Dunham coefficients for SO for the first time. More recently, the measurements on SO were expanded into the terahertz region by laser sideband spectroscopy (19) and frequency stabilized backward wave oscillators (BWOs) as used at the Cologne Terahertz Spectrometer (20).

In this paper, we report the detection of  $^{36}\text{SO}$  together with measurements of the main and rare isotopomers  $^{32}\text{SO}$ ,

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**TABLE 1**  
**Newly Observed Transitions for  $^{32}\text{SO}$ ,  $^{34}\text{SO}$ , and  $\text{S}^{18}\text{O}$**

$N'$	$J'$	$\leftarrow$	$N''$	$J''$	$v$	$\nu_{exp}^a$ [MHz]	o-c <sup>b</sup> [kHz]	$\nu_{exp}$ [MHz]	o-c [kHz]	$\nu_{exp}$ [MHz]	o-c [kHz]
						$^{32}\text{SO}$		$^{34}\text{SO}$		$\text{S}^{18}\text{O}$	
3	3	$\leftarrow$	2	2	0					119 573.695(50) <sup>c</sup>	25
4	5	$\leftarrow$	3	4	0					166 285.324(50) <sup>c</sup>	9
14	13	$\leftarrow$	13	12	0	601 258.460(30)	6				
14	14	$\leftarrow$	13	13	0	602 293.026(30)	-4				
14	15	$\leftarrow$	13	14	0	603 021.653(30)	2	591 279.803(50)	-12		
15	14	$\leftarrow$	14	13	0	644 378.918(30)	2	631 742.131(50)	6	596 498.005(100)	29
15	15	$\leftarrow$	14	14	0	645 254.933(30)	-6	632 647.840(50)	-5	597 491.609(100)	8
15	16	$\leftarrow$	14	15	0	645 875.924(30)	2	633 293.153(50)	7	598 208.861(100)	10
16	15	$\leftarrow$	15	14	0	687 457.694(30)	-8	673 986.183(50)	0	636 414.555(100)	16
16	16	$\leftarrow$	15	15	0	688 204.630(30)	-6	674 759.674(50)	-7	637 266.718(100)	22
16	17	$\leftarrow$	15	16	0	688 735.700(30)	4	675 312.868(50)	9	637 885.291(100)	-6
17	16	$\leftarrow$	16	15	0			716 194.543(50)	0	676 295.292(100)	1
17	17	$\leftarrow$	16	16	0			716 858.991(50)	-3	677 030.619(100)	-7
17	18	$\leftarrow$	16	17	0			717 334.402(50)	-11	677 565.887(100)	-14
18	17	$\leftarrow$	17	16	0					716 144.872(100)	-5
18	18	$\leftarrow$	17	17	0					716 782.675(100)	-17
18	19	$\leftarrow$	17	18	0					717 246.935(100)	-19
24	23	$\leftarrow$	23	23	0	885 840.855(50) <sup>c</sup>	-4				
21	20	$\leftarrow$	20	19	0	902 381.964(50) <sup>c</sup>	1	884 739.149(100) <sup>c</sup>	9		
21	21	$\leftarrow$	20	20	0	902 741.419(50) <sup>c</sup>	2	885 115.378(100) <sup>c</sup>	6		
21	22	$\leftarrow$	20	21	0	902 986.582(50) <sup>c</sup>	-3	885 375.535(100) <sup>c</sup>	-9		
24	23	$\leftarrow$	23	22	0	1 031 028.249(50) <sup>c</sup>	15				
24	24	$\leftarrow$	23	23	0	1 031 264.804(50) <sup>c</sup>	13				
24	25	$\leftarrow$	23	24	0	1 031 412.213(50) <sup>c</sup>	-4				
25	24	$\leftarrow$	24	23	0			1 052 890.640(100) <sup>c</sup>	12		
25	25	$\leftarrow$	24	24	0			1 053 108.752(100) <sup>c</sup>	4		
25	26	$\leftarrow$	24	25	0			1 053 242.480(100) <sup>c</sup>	-37		
26	25	$\leftarrow$	25	24	0					1 034 063.202(100) <sup>c</sup>	-15
26	26	$\leftarrow$	25	25	0					1 034 288.312(100) <sup>c</sup>	-44
14	13	$\leftarrow$	13	12	1	596 416.207(50)	5				
14	14	$\leftarrow$	13	13	1	597 478.046(50)	-8				
14	15	$\leftarrow$	13	14	1	598 227.116(50)	0				
15	14	$\leftarrow$	14	13	1	639 196.285(50)	-4	626 710.045(100)	11	591 877.644(200)	-40
15	15	$\leftarrow$	14	14	1	640 096.003(50)	-1	627 639.653(100)	-6	592 895.687(200)	-114
15	16	$\leftarrow$	14	15	1	640 734.943(50)	6	628 303.123(100)	13	593 631.679(200)	-82
16	15	$\leftarrow$	15	14	1	681 934.065(50)	-8				
16	16	$\leftarrow$	15	15	1	682 701.745(50)	8			632 364.507(200)	28
16	17	$\leftarrow$	15	16	1	683 248.652(50)	5	669 986.799(100)	0	632 999.603(200)	-49
17	16	$\leftarrow$	16	15	1			710 500.095(100)	19		
17	17	$\leftarrow$	16	16	1			711 182.945(100)	-32		
17	18	$\leftarrow$	16	17	1			711 672.637(100)	-2		
18	17	$\leftarrow$	17	16	1					710 612.904(200)	-47
18	18	$\leftarrow$	17	17	1					711 267.487(200)	-97
21	20	$\leftarrow$	20	19	1	895 147.597(100) <sup>c</sup>	23				
21	21	$\leftarrow$	20	20	1	895 518.650(100) <sup>c</sup>	24				
21	22	$\leftarrow$	20	21	1	895 772.875(100) <sup>c</sup>	21				
24	23	$\leftarrow$	23	22	1	1 022 764.839(100) <sup>c</sup>	-3				
24	24	$\leftarrow$	23	23	1	1 023 010.022(100) <sup>c</sup>	0				
24	25	$\leftarrow$	23	24	1	1 023 164.143(100) <sup>c</sup>	-10				
25	24	$\leftarrow$	24	23	1			1 044 535.108(150) <sup>c</sup>	-41		
25	25	$\leftarrow$	24	24	1			1 044 761.236(150) <sup>c</sup>	-13		
25	26	$\leftarrow$	24	25	1			1 044 901.163(150) <sup>c</sup>	-65		
14	13	$\leftarrow$	13	12	2	591 585.069(70)	12				
14	14	$\leftarrow$	13	13	2	592 675.152(70)	-1				
14	15	$\leftarrow$	13	14	2	593 445.386(70)	12				
15	14	$\leftarrow$	14	13	2	634 025.739(70)	4				
15	15	$\leftarrow$	14	14	2	634 949.003(70)	-4				
15	16	$\leftarrow$	14	15	2	635 607.551(70)	-3				

<sup>a</sup> Estimated experimental uncertainties are given in parentheses.

<sup>b</sup> Observed minus calculated values.

<sup>c</sup> Improved frequencies from Ref. (20). See text.

<sup>d</sup> Overlapped lines.

TABLE 1—Continued

$N'$	$J'$	$\leftarrow$	$N''$	$J''$	$v$	$\nu_{exp}$ [MHz]	O-C [kHz]	$\nu_{exp}$ [MHz]	O-C [kHz]	$\nu_{exp}$ [MHz]	O-C [kHz]
$^{32}\text{SO}$						$^{34}\text{SO}$					
16	15	$\leftarrow$	15	14	2			663 272.648(150)	27		
16	16	$\leftarrow$	15	15	2	677 212.636(70)	-1	664 088.864(500) <sup>d</sup>	112		
16	17	$\leftarrow$	15	16	2	677 775.997(70)	1	664 674.618(150)	14		
17	16	$\leftarrow$	16	15	2			704 818.998(150)	-17		
17	17	$\leftarrow$	16	16	2			705 520.969(500) <sup>d</sup>	-91		
17	18	$\leftarrow$	16	17	2			706 025.519(150)	17		
21	20	$\leftarrow$	20	19	2	887 930.822(150) <sup>c</sup>	18				
21	21	$\leftarrow$	20	20	2	888 313.977(150) <sup>c</sup>	31				
$^{32}\text{SO}$											
$v = 3$						$v = 4$		$v = 5$			
15	14	$\leftarrow$	14	13		628 866.801(100)	34	623 718.835(130)	11	618 581.251(170)	-17
15	15	$\leftarrow$	14	14		629 816.485(100)	-34	624 694.993(130)	-50	619 585.043(170)	30
15	16	$\leftarrow$	14	15		630 493.378(100)	-17	625 392.008(130)	-5		
16	15	$\leftarrow$	15	14		670 925.377(100)	0	665 439.166(130)	-47	659 964.323(170)	16
16	16	$\leftarrow$	15	15		671 736.894(100)	12	666 273.976(130)	36	660 823.206(170)	0
16	17	$\leftarrow$	15	16		672 317.313(100)	-18	666 872.147(130)	-21	661 439.971(170)	18
17	16	$\leftarrow$	16	15		712 946.767(100)	7	707 121.848(130)	10	701 309.014(170)	-16
17	17	$\leftarrow$	16	16		713 644.214(100)	12	707 839.825(130)	37	702 048.341(170)	-5
17	18	$\leftarrow$	16	17		714 143.219(100)	-10	708 354.590(130)	-33	702 579.641(170)	-17
21	21	$\leftarrow$	20	20		881 126.799(150) <sup>c</sup>	19				
21	22	$\leftarrow$	20	21		881 400.318(150) <sup>c</sup>	36				
$v = 6$						$v = 7$					
15	14	$\leftarrow$	14	13		613 453.407(200)	21				
15	15	$\leftarrow$	14	14		614 485.732(200)	-60	609 396.697(250)	27		
15	16	$\leftarrow$	14	15		615 225.489(200)	14				
16	16	$\leftarrow$	15	15				649 955.498(250)	-72		
16	17	$\leftarrow$	15	16				650 611.817(250)	16		
17	16	$\leftarrow$	16	15		695 507.548(200)	-5				
17	17	$\leftarrow$	16	16		696 269.194(200)	42				
17	18	$\leftarrow$	16	17		696 817.666(200)	5				

$^{33}\text{SO}$ ,  $^{34}\text{SO}$ ,  $\text{S}^{18}\text{O}$ , and  $\text{S}^{17}\text{O}$  in several vibrational levels belonging to the  $X^3\Sigma^-$  electronic ground state. The hyperfine structure for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  has been reanalyzed, yielding for the first time the magnetic nuclear spin-rotation interaction constants for both  $^{33}\text{S}$  and  $^{17}\text{O}$  nuclei. A new set of mass-independent parameters obtained from a simultaneous fit will be given. The results of the hyperfine structure analysis are compared with the data from other works.

## 2. EXPERIMENTAL

A description of the Cologne Terahertz Spectrometer has been given in the recent literature; see, e.g., Winnewisser *et al.* (21) or Belov *et al.* (22). The essential parts are the high frequency backward wave oscillators (BWOs), supplied by the ISTOK Research and Production Co. (Fryazino near Moscow). The BWOs are frequency and phase stabilized by mixing the output radiation with the harmonics of a 78-

118-GHz synthesizer, supplied by the Institute of Electronic Measurement, KVARZ (Nizhnii Novgorod, Russia). The synthesizer uses a 5 MHz signal from a rubidium frequency standard as external reference. Furthermore, the BWO radiation is frequency modulated and the absorption signal is detected digitally at  $2f$ , after recording it with a liquid helium cooled, magnetically tuned InSb hot-electron bolometer. The resulting lineshape is in the second derivative form.

Some of the measurements presented here have been carried out in the millimeter-wave region, where the synthesizer mentioned above and a second one for the frequency region 118 to 178 GHz have been used.

After precise readjustment of the rubidium atomic clock, providing now a short term accuracy of  $\leq 10^{-11}$ , the accuracy of SO frequencies measured in the previous work (20) has been improved. The remeasured line positions are quoted in Tables 1 and 3 together with the newly measured transitions. The precision of the frequency measurements for strong, well

**TABLE 2**  
**Observed and Calculated Rotational Transitions for  $^{36}\text{SO}$  ( $E''$ )**  
**Represents the Energy of the Lower State in  $\text{cm}^{-1}$ )**

$N'$	$J'$	$\leftarrow$	$N''$	$J''$	$\nu$	$\Delta\nu^a$	$E''$	$\text{o-c}^b$
					[MHz]	[MHz]	[ $\text{cm}^{-1}$ ]	[kHz]
$^{36}\text{SO}$								
2	1	$\leftarrow$	1	1	(12 071.729) <sup>c</sup>	0.011	10.55	
0	1	$\leftarrow$	1	0	(29 382.582) <sup>c</sup>	0.011	0.00	
3	2	$\leftarrow$	2	2	(33 678.013) <sup>c</sup>	0.000	13.32	
1	2	$\leftarrow$	0	1	(61 301.584) <sup>c</sup>	0.015	0.98	
4	3	$\leftarrow$	3	3	(61 738.029) <sup>c</sup>	0.041	17.47	
2	2	$\leftarrow$	1	1	(82 911.729) <sup>c</sup>	0.003	10.55	
5	4	$\leftarrow$	4	4	(93 913.196) <sup>c</sup>	0.054	23.00	
2	3	$\leftarrow$	1	2	(96 299.900) <sup>c</sup>	0.015	3.03	
3	2	$\leftarrow$	2	1	104 518.103	0.150	10.95	90
3	3	$\leftarrow$	2	2	(124 365.706) <sup>c</sup>	0.004	13.32	
6	5	$\leftarrow$	5	5	(128 712.765) <sup>c</sup>	0.065	29.91	
3	4	$\leftarrow$	2	3	133 634.530	0.070	6.24	0
4	3	$\leftarrow$	3	2	(152 425.722) <sup>c</sup>	0.016	14.44	
7	6	$\leftarrow$	6	6	(165 230.765) <sup>c</sup>	0.075	38.21	
4	4	$\leftarrow$	3	3	165 817.447	0.070	17.47	28
4	5	$\leftarrow$	3	4	172 456.746	0.070	10.70	-6
5	4	$\leftarrow$	4	3	(197 992.587) <sup>c</sup>	0.015	19.53	
8	7	$\leftarrow$	7	7	(202 911.619) <sup>c</sup>	0.083	47.89	
5	5	$\leftarrow$	4	4	(207 266.113) <sup>c</sup>	0.008	23.00	
5	6	$\leftarrow$	4	5	(212 181.590) <sup>c</sup>	0.012	16.45	
2	1	$\leftarrow$	1	2	(237 718.078) <sup>c</sup>	0.217	3.03	
9	8	$\leftarrow$	8	8	(241 405.974) <sup>c</sup>	0.090	58.95	
6	5	$\leftarrow$	5	4	(242 065.822) <sup>c</sup>	0.014	26.13	
3	2	$\leftarrow$	2	3	(245 936.192) <sup>c</sup>	0.189	6.24	
6	6	$\leftarrow$	5	5	248 711.094 <sup>d</sup>	0.080	29.91	61
6	7	$\leftarrow$	5	6	252 457.101 <sup>d</sup>	0.080	23.53	45
4	3	$\leftarrow$	3	4	(264 727.383) <sup>c</sup>	0.164	10.70	
10	9	$\leftarrow$	9	9	(280 486.416) <sup>c</sup>	0.097	71.39	
7	6	$\leftarrow$	6	5	(285 228.893) <sup>c</sup>	0.014	34.20	
1	1	$\leftarrow$	0	1	(286 947.933) <sup>c</sup>	0.242	0.98	
8	7	$\leftarrow$	7	6	327 832.165 <sup>d</sup>	0.080	43.72	-113
8	8	$\leftarrow$	7	7	331 586.516 <sup>d</sup>	0.080	47.89	-14
8	9	$\leftarrow$	7	8	333 917.730 <sup>d</sup>	0.080	41.72	-51
9	8	$\leftarrow$	8	7	370 080.878 <sup>d</sup>	0.080	54.65	-7
9	9	$\leftarrow$	8	8	373 015.582 <sup>d</sup>	0.080	58.95	-16
9	10	$\leftarrow$	8	9	374 904.949 <sup>d</sup>	0.080	52.86	-2
14	13	$\leftarrow$	13	12	578 945.254	0.100	130.35	40
14	14	$\leftarrow$	13	13	580 043.964	0.100	134.97	33
14	15	$\leftarrow$	13	14	580 824.178	0.100	129.11	20
15	14	$\leftarrow$	14	13	620 487.887	0.100	149.66	-23
15	15	$\leftarrow$	14	14	621 420.920	0.100	154.32	10
15	16	$\leftarrow$	14	15	622 088.506	0.100	148.49	1
16	17	$\leftarrow$	15	16	663 360.049	0.100	169.24	31
17	16	$\leftarrow$	16	15	703 453.755	0.100	192.44	21
17	17	$\leftarrow$	16	16	704 140.138	0.100	197.16	-2
17	18	$\leftarrow$	16	17	704 634.089	0.100	191.36	-23
22	21	$\leftarrow$	21	20	910 357.889	0.150	323.57	-37
22	22	$\leftarrow$	21	21	910 700.365	0.150	328.38	-11
22	23	$\leftarrow$	21	22	910 935.825	0.150	322.65	4
23	22	$\leftarrow$	22	21	951 665.872	0.150	353.94	32
23	23	$\leftarrow$	22	22	951 965.616	0.150	358.76	9
23	24	$\leftarrow$	22	23	952 167.277	0.150	353.04	143

<sup>a</sup> For calculated frequencies one standard deviation and for experimental frequencies the estimated uncertainties are given.

<sup>b</sup> Observed minus calculated values.

<sup>c</sup> Frequencies calculated from parameters in Table 4.

<sup>d</sup> Transitions recorded with the submillimeter-wave spectrometer in Nobeyama, Japan.

isolated, and Doppler-limited lines is estimated to be  $\pm 5$  kHz, which was checked by CO measurements (22). The accuracy for the discharge measurements is estimated more cautiously

as quoted in Tables 1–3 by taking into consideration the larger noise levels and the higher pressures in the discharge.

The SO radical has been produced in a dc discharge of  $\text{H}_2\text{S}$  and  $\text{O}_2$  with partial pressures of about 10 and 40 mTorr, respectively, and a discharge current of about 100 mA. All spectra have been taken in natural abundance of the precursor gases, except for  $\text{S}^{17}\text{O}$ , for which we used an oxygen sample with 10% enrichment of  $^{16}\text{O}^{17}\text{O}$ . The experimental results are summarized in Table 1 for  $^{32}\text{SO}$ ,  $^{34}\text{SO}$ , and  $\text{S}^{18}\text{O}$ , in Table 2 for  $^{36}\text{SO}$ , and, finally, in Table 3 for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$ . The experimental uncertainties have been estimated according to the obtained signal-to-noise ratios. Figures 1 and 2 display a few spectra recorded with the Cologne Terahertz Spectrometer.

A dedicated laboratory search for the  $^{36}\text{SO}$  species has been conducted in parallel at the facilities of Nobeyama Radio Observatory. The apparatus used was a direct absorption millimeter- and submillimeter-wave spectrometer. Details of the experimental setup will be described elsewhere. Briefly, it consists of a phase-locked Gunn oscillator with a Schottky diode tripler and quadrupler, a 1-m-long Pyrex cell, and a helium-cooled InSb detector. Frequency modulation of the Gunn oscillator is employed for the  $2f$  phase sensitive detection, by using an analog Lock-in amplifier.

The  $^{36}\text{SO}$  isotopomer was generated in a dc discharge in a gas mixture of 50 mTorr  $\text{O}_2$  and 10 mTorr OCS. The discharge current was  $\sim 200$  mA. When bright blue color was observed in the stably discharged gas, the spectrum of  $\text{S}^{18}\text{O}$  ( $X^3\Sigma^-$ ;  $v=0$ )  $N_J = 9_{10} \leftarrow 8_9$  transition was recorded at 360.638 GHz. After optimization of the experimental conditions for the  $\text{S}^{18}\text{O}$  spectral line, one could readily observe the weak paramagnetic spectrum in the 252–370 GHz region, easily assigned to the series of rotational transitions for  $^{36}\text{SO}$  in the ground vibronic state. Typical linewidths observed were  $\sim 1$  MHz. Figure 3 shows the spectrum of the  $N_J = 9_8 \leftarrow 8_7$  transition for  $^{36}\text{SO}$ . In the present experimental setting, the value of the peak frequency is different by  $\sim 100$  kHz, owing to the integration time constant (300 msec) for the Lock-in amplifier. Therefore, the center frequencies of the spectrum were measured by conducting both ascending and descending frequency scans, then averaged to determine precise transition frequencies.

### 3. HAMILTONIAN

The Hamiltonian for SO in the  $X^3\Sigma^-$  electronic ground state is

$$H = H_{\text{Rotation}} + H_{\text{Spin-Spin}} + H_{\text{Spin-Rotation}} + H_{\text{Hyperfine}} \quad [1]$$

The matrix elements for rotation and the fine structure have been given in Ref. (20). Here we restrict the discussion to the hyperfine structure (hfs) which for SO has to be considered for the  $^{33}\text{S}$  and  $^{17}\text{O}$  nuclei with spins  $I = \frac{3}{2}$  and  $I = \frac{5}{2}$ , respectively. Isotopically invariant expansions for the hfs constants have been introduced (2–6). Since

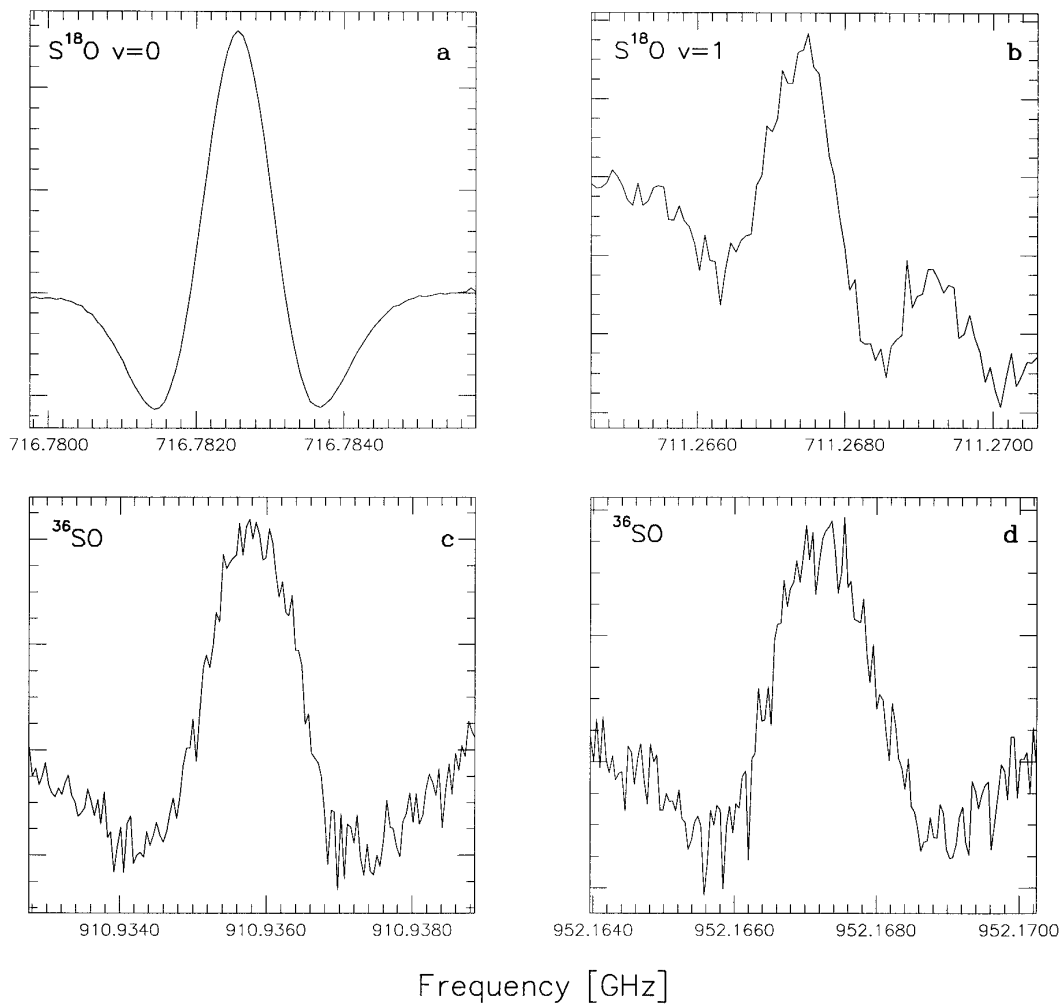
TABLE 3  
Observed Transitions in MHz for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$

$N'$	$J'$	$F'$	$\leftarrow$	$N''$	$J''$	$F''$	$\nu_{exp}$	$\Delta\nu_{exp}$	$\text{o-c}^a$	$N'$	$J'$	$F'$	$\leftarrow$	$N''$	$J''$	$F''$	$\nu_{exp}$	$\Delta\nu_{exp}$	$\text{o-c}$
$^{33}\text{SO } v = 0$										14	15		$\leftarrow$	13	14		592 242.919 <sup>c</sup>	0.150	10
2	3	1.5	$\leftarrow$	1	2	0.5	98 474.602	0.030	-13	15	14		$\leftarrow$	14	13		632 754.999 <sup>c</sup>	0.150	-6
2	3	2.5	$\leftarrow$	1	2	1.5	98 482.302	0.030	25	15	15		$\leftarrow$	14	14		633 670.384 <sup>c</sup>	0.150	36
2	3	3.5	$\leftarrow$	1	2	2.5	98 489.232	0.030	-4	16	15		$\leftarrow$	14	15		634 322.140 <sup>c</sup>	0.150	48
2	3	4.5	$\leftarrow$	1	2	3.5	98 493.642	0.030	-12	16	16		$\leftarrow$	15	14		675 067.381 <sup>c</sup>	0.150	-39
3	3	1.5	$\leftarrow$	2	2	0.5	127 825.464 <sup>b</sup>	0.030	-10	16	17		$\leftarrow$	15	15		675 849.042 <sup>c</sup>	0.150	-20
3	3	2.5	$\leftarrow$	2	2	1.5	127 826.361 <sup>b</sup>	0.030	-11				$\leftarrow$	15	16		676 407.599 <sup>c</sup>	0.150	-23
3	3	3.5	$\leftarrow$	2	2	2.5	127 832.080 <sup>b</sup>	0.030	7	$\text{S}^{17}\text{O}$									
3	3	4.5	$\leftarrow$	2	2	3.5	127 842.532 <sup>b</sup>	0.030	-4	1	2	4.5	$\leftarrow$	0	1	3.5	61 161.150 <sup>e</sup>	0.070	23
3	4	2.5	$\leftarrow$	2	3	1.5	136 934.082 <sup>b</sup>	0.030	-19	1	2	3.5	$\leftarrow$	0	1	2.5	61 169.750 <sup>e</sup>	0.070	46
3	4	3.5	$\leftarrow$	2	3	2.5	136 939.357 <sup>b</sup>	0.030	-1	1	2	2.5	$\leftarrow$	0	1	1.5	61 179.900 <sup>e</sup>	0.070	37
3	4	4.5	$\leftarrow$	2	3	3.5	136 943.672 <sup>b</sup>	0.030	-6	1	2	1.5	$\leftarrow$	0	1	1.5	61 222.900 <sup>e</sup>	0.070	82
3	4	5.5	$\leftarrow$	2	3	4.5	136 946.194 <sup>b</sup>	0.030	-3	1	2	2.5	$\leftarrow$	0	1	2.5	61 229.400 <sup>e</sup>	0.070	67
4	3	3.5	$\leftarrow$	3	2	2.5	157 173.538 <sup>b</sup>	0.030	1	1	2	3.5	$\leftarrow$	0	1	3.5	61 236.900 <sup>e</sup>	0.070	-22
4	3	2.5	$\leftarrow$	3	2	1.5	157 173.538 <sup>b</sup>	0.030	1	2	2	4.5	$\leftarrow$	1	1	3.5	82 701.284 <sup>f</sup>	0.100	-44
4	3	4.5	$\leftarrow$	3	2	3.5	157 179.508 <sup>b</sup>	0.030	12	2	2	3.5	$\leftarrow$	1	1	2.5	82 724.355 <sup>f</sup>	0.100	22
4	3	1.5	$\leftarrow$	3	2	0.5	157 180.462 <sup>b</sup>	0.030	29	2	2	2.5	$\leftarrow$	1	1	1.5	82 740.850 <sup>e</sup>	0.070	-69
4	4	2.5	$\leftarrow$	3	3	1.5	170 439.157 <sup>b</sup>	0.030	-21	2	3	5.5	$\leftarrow$	1	2	4.5	96 085.277 <sup>f</sup>	0.050	7
4	4	3.5	$\leftarrow$	3	3	2.5	170 440.310 <sup>b</sup>	0.030	9	2	3	4.5	$\leftarrow$	1	2	3.5	96 089.308 <sup>f</sup>	0.050	10
4	4	4.5	$\leftarrow$	3	3	3.5	170 443.547 <sup>b</sup>	0.030	3	2	3	3.5	$\leftarrow$	1	2	2.5	96 095.507 <sup>f</sup>	0.050	4
4	4	5.5	$\leftarrow$	3	3	4.5	170 448.497 <sup>b</sup>	0.030	3	2	3	2.5	$\leftarrow$	1	2	1.5	96 104.056	0.100	-23
4	5	3.5	$\leftarrow$	3	4	2.5	176 924.181 <sup>b</sup>	0.030	-8	3	2	2.5	$\leftarrow$	2	1	2.5	104 188.870	0.100	64
4	5	4.5	$\leftarrow$	3	4	3.5	176 927.863 <sup>b</sup>	0.030	-3	3	2	4.5	$\leftarrow$	2	1	3.5	104 247.339 <sup>f</sup>	0.150	-113
4	5	5.5	$\leftarrow$	3	4	4.5	176 930.673 <sup>b</sup>	0.030	-21	3	2	3.5	$\leftarrow$	2	1	2.5	104 261.987 <sup>f</sup>	0.050	-7
4	5	6.5	$\leftarrow$	3	4	5.5	176 932.140 <sup>b</sup>	0.030	-17	3	2	2.5	$\leftarrow$	2	1	1.5	104 267.416	0.050	4
6	5	5.5	$\leftarrow$	5	4	4.5	249 159.167	0.150	-104	3	3	5.5	$\leftarrow$	2	2	4.5	124 059.785 <sup>f</sup>	0.050	-5
6	5	4.5	$\leftarrow$	5	4	3.5	249 159.167	0.150	-104	3	3	2.5	$\leftarrow$	2	2	2.5	124 064.777	0.050	12
6	5	6.5	$\leftarrow$	5	4	5.5	249 160.501	0.070	20	3	3	4.5	$\leftarrow$	2	2	3.5	124 066.562 <sup>f</sup>	0.050	-4
6	5	3.5	$\leftarrow$	5	4	2.5	249 162.273	0.070	34	3	3	1.5	$\leftarrow$	2	2	1.5	124 069.812	0.050	26
6	6	4.5	$\leftarrow$	5	5	3.5	255 649.354	0.070	-36	3	3	3.5	$\leftarrow$	2	2	2.5	124 071.440 <sup>f</sup>	0.050	-2
6	6	5.5	$\leftarrow$	5	5	4.5	255 649.354	0.070	-36	3	3	2.5	$\leftarrow$	2	2	1.5	124 074.425 <sup>f</sup>	0.050	-2
6	6	6.5	$\leftarrow$	5	5	5.5	255 651.184	0.070	-2	3	4	6.5	$\leftarrow$	2	3	5.5	133 331.248 <sup>f</sup>	0.050	1
6	6	7.5	$\leftarrow$	5	5	6.5	255 653.034	0.070	-9	3	4	5.5	$\leftarrow$	2	3	4.5	133 332.980 <sup>f</sup>	0.150	142
6	7	5.5	$\leftarrow$	5	6	4.5	259 280.331	0.070	4	3	4	4.5	$\leftarrow$	2	3	3.5	133 336.349 <sup>f</sup>	0.050	-2
6	7	6.5	$\leftarrow$	5	6	5.5	259 282.276	0.070	-30	3	4	3.5	$\leftarrow$	2	3	2.5	133 341.853 <sup>f</sup>	0.100	-19
6	7	7.5	$\leftarrow$	5	6	6.5	259 284.027	0.100	47	3	4	2.5	$\leftarrow$	2	3	1.5	133 349.435 <sup>f</sup>	0.050	-23
6	7	8.5	$\leftarrow$	5	6	7.5	259 284.027	0.100	47	3	4	1.5	$\leftarrow$	2	3	0.5	133 359.250 <sup>e</sup>	0.070	113
7	6	6.5	$\leftarrow$	6	5	5.5	293 458.847	0.100	-28	4	3	2.5	$\leftarrow$	3	2	1.5	152 028.987 <sup>f</sup>	0.100	38
7	6	5.5	$\leftarrow$	6	5	4.5	293 458.847	0.100	-28	4	3	5.5	$\leftarrow$	3	2	4.5	152 033.447 <sup>f</sup>	0.050	8
7	6	7.5	$\leftarrow$	6	5	6.5	293 459.704	0.100	-36	4	3	3.5	$\leftarrow$	3	2	2.5	152 034.745 <sup>f</sup>	0.050	29
7	6	4.5	$\leftarrow$	6	5	3.5	293 460.996	0.100	88	4	3	4.5	$\leftarrow$	3	2	3.5	152 036.266 <sup>f</sup>	0.050	31
14	13		$\leftarrow$	13	12		595 169.817 <sup>c</sup>	0.100	9	4	4	5.5	$\leftarrow$	3	3	5.5	165 404.865	0.020	-23
14	14		$\leftarrow$	13	13		596 221.884 <sup>c</sup>	0.100	3	4	4	4.5	$\leftarrow$	3	3	4.5	165 409.639	0.050	-14
14	15		$\leftarrow$	13	14		596 964.649 <sup>c</sup>	0.500 <sup>d</sup>	70	4	4	6.5	$\leftarrow$	3	3	5.5	165 413.112 <sup>f</sup>	0.050	6
15	14		$\leftarrow$	14	13		637 859.779 <sup>c</sup>	0.100	-8	4	4	5.5	$\leftarrow$	3	3	4.5	165 416.228 <sup>f</sup>	0.050	1
15	15		$\leftarrow$	14	14		638 751.307 <sup>c</sup>	0.100	-22	4	4	4.5	$\leftarrow$	3	3	3.5	165 418.524 <sup>f</sup>	0.050	-21
15	16		$\leftarrow$	14	15		639 385.040 <sup>c</sup>	0.100	20	4	4	3.5	$\leftarrow$	3	3	2.5	165 420.091	0.020	-10
16	15		$\leftarrow$	15	14		680 508.004 <sup>c</sup>	0.100	2	4	4	2.5	$\leftarrow$	3	3	1.5	165 420.969 <sup>f</sup>	0.050	13
16	16		$\leftarrow$	15	15		681 268.779 <sup>c</sup>	0.100	-31	4	4	1.5	$\leftarrow$	3	3	0.5	165 420.969 <sup>f</sup>	0.050	13
16	17		$\leftarrow$	15	16		681 811.450 <sup>c</sup>	0.100	27	4	5	7.5	$\leftarrow$	3	4	6.5	172 057.836 <sup>f</sup>	0.100	7
21	20		$\leftarrow$	20	19		893 280.556 <sup>b,c</sup>	0.100	-5	4	5	6.5	$\leftarrow$	3	4	5.5	172 058.256 <sup>f</sup>	0.100	20
21	21		$\leftarrow$	20	20		893 648.765 <sup>b,c</sup>	0.100	3	4	5	5.5	$\leftarrow$	3	4	4.5	172 060.201 <sup>f</sup>	0.050	-21
21	22		$\leftarrow$	20	21		893 901.745 <sup>b,c</sup>	0.100	-6	4	5	4.5	$\leftarrow$	3	4	3.5	172 063.812 <sup>f</sup>	0.050	-23
24	23		$\leftarrow$	23	22		1 020 638.431 <sup>b,c</sup>	0.100	7	4	5	3.5	$\leftarrow$	3	4	2.5	172 069.087	0.050	-22
24	24		$\leftarrow$	23	23		1 020 882.045 <sup>b,c</sup>	0.100	12	4	5	2.5	$\leftarrow$	3	4	1.5	172 076.026	0.100	-41
24	25		$\leftarrow$	23	24		1 021 035.990 <sup>b,c</sup>	0.100	-7	4	5	4.5	$\leftarrow$	3	4	4.5	172 120.834	0.100	-52
$^{33}\text{SO } v = 1$										14	13		$\leftarrow$	13	12		577 539.104	0.500 <sup>c,e</sup>	152
14	13		$\leftarrow$	13	12		590 400.232 <sup>c</sup>	0.150	33	14	15		$\leftarrow$	13	14		579 423.053	0.500 <sup>c,e</sup>	-250
14	14		$\leftarrow$	13	13		591 479.836 <sup>c</sup>	0.500 <sup>d</sup>	175	15	16		$\leftarrow$	14	15		620 587.307	0.500 <sup>c,e</sup>	-154

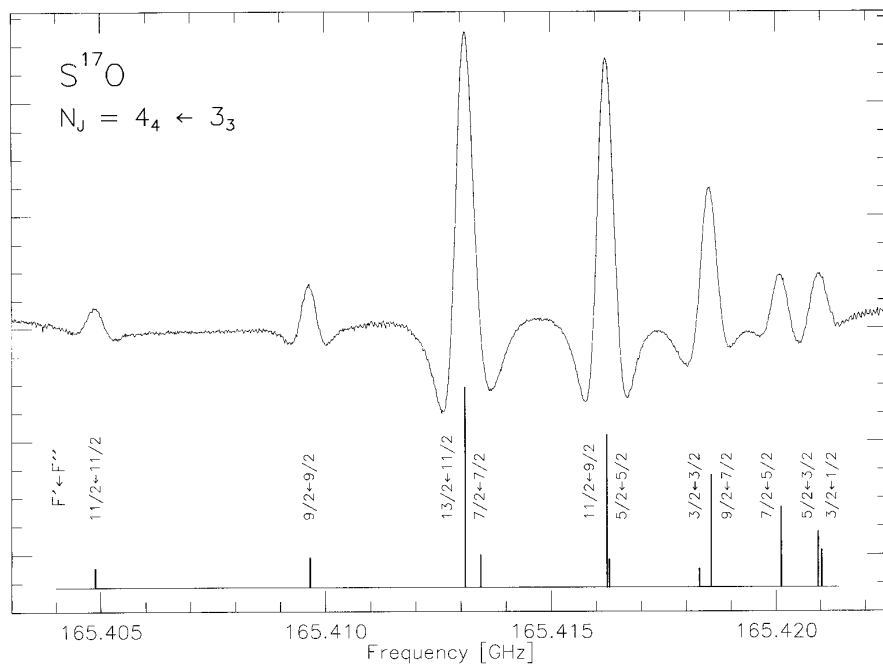
<sup>a</sup> Observed minus calculated values in kHz.<sup>b</sup> Improved frequencies from Ref. (20).<sup>c</sup> For unresolved hfs splitting the  $F' \leftarrow F''$  values are omitted. See text.<sup>d</sup> Overlapped lines.<sup>e</sup> Frequencies taken from Ref. (15).<sup>f</sup> Remeasured frequencies from Ref. (15).<sup>g</sup> Lines partly resolved.

the hfs of  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  has been resolved only for the vibrational ground states and a rotational dependence has not been determined, it is sufficient here to deal with the

constants  $t$ ,  $b_F$ , and  $eQq$ , representing nuclear spin-spin, magnetic Fermi contact, and electric quadrupole interactions. In addition to these contributions, the weak mag-



**FIG. 1.** SO lines recorded with the Cologne terahertz spectrometer. (a) The  $N_J = 18_{18} \leftarrow 17_{17}$  transition of  $S^{18}O$  in  $v = 0$  and (b) the same transition in  $v = 1$ . (c) and (d) display recordings of the  $N_J = 22_{23} \leftarrow 21_{22}$  and  $23_{24} \leftarrow 22_{23}$  transitions of  $^{36}SO$ , respectively. Spectrum (d) consists of 140 points with 45 kHz step size and 953 msec integration time/point.



**FIG. 2.** The observed hyperfine pattern of the  $N_J = 4_4 \leftarrow 3_3$  rotational transition of  $S^{17}O$  recorded with the KVARZ synthesizer at Cologne. The appropriate  $F' \leftarrow F''$  values are given. Bold sticks mark the calculated frequencies and relative intensities.

netic interaction of the nuclear spin with the rotation of the molecular frame described by the constant  $C_7$  has been

determined in the analysis. The hfs matrix elements for both  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  then become

$$\begin{aligned}
 \langle N'J'F; v=0 | H_{\text{Hyperfine}} | NJF; v=0 \rangle = & -t\sqrt{30}(-1)^{I+J'+F+N'} \left\{ \begin{matrix} F & J' & I \\ 1 & I & J \end{matrix} \right\} \left\{ \begin{matrix} S & S & 1 \\ N' & N & 2 \\ J' & J & 1 \end{matrix} \right\} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} \\
 & \times \sqrt{I(I+1)(2I+1)S(S+1)(2S+1)(2J+1)(2J'+1)(2N+1)(2N'+1)} + b_F \delta_{N'N} (-1)^{I+J'+F+S+N+J+1} \\
 & \times \left\{ \begin{matrix} F & J' & I \\ 1 & I & J \end{matrix} \right\} \left\{ \begin{matrix} S & J' & N \\ J & S & 1 \end{matrix} \right\} \times \sqrt{I(I+1)(2I+1)S(S+1)(2S+1)(2J+1)(2J'+1)} \\
 & + \frac{1}{4} eQq (-1)^{I+J'+F+S+N+J'+2+N'} \left\{ \begin{matrix} F & J' & I \\ 2 & I & J \end{matrix} \right\} \left\{ \begin{matrix} N' & J' & S \\ J & N & 2 \end{matrix} \right\} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} \\
 & \times \sqrt{\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)}} (2J+1)(2J'+1)(2N+1)(2N'+1) + C_I \delta_{N'N} (-1)^{I+J'+F+S+N+J'+1} \\
 & \times \left\{ \begin{matrix} F & J' & I \\ 1 & I & J \end{matrix} \right\} \left\{ \begin{matrix} N & J' & S \\ J & N & 1 \end{matrix} \right\} \times \sqrt{(2J'+1)(2J+1)N(2N+1)I(I+1)(2I+1)}. \quad [2]
 \end{aligned}$$

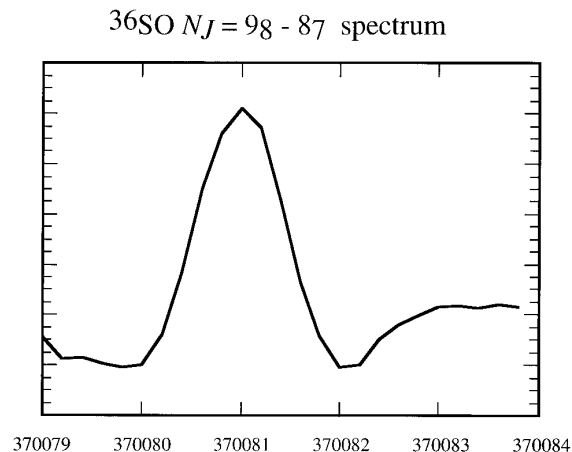
#### 4. ANALYSIS AND DISCUSSION

Together with the lines from the literature and the 176 new lines reported here, a total of 451 transitions for SO in the electronic ground state have been subjected to a simultaneous fit, weighted proportional to the inverse square of their experimental uncertainties. For nonresolved hyperfine splittings we followed Rudolph (23) and entered the sum of their intensity-weighted average as calculated frequencies into the fit.

The sideband laser measurements from Cazzoli *et al.* (19) have not been included because of their large experimental uncertainties (500 kHz estimated standard error). In cases where a comparison between the different experimental methods is possible, the sideband laser frequencies deviate up to 900 kHz from the BWO measurements. For  $\text{S}^{17}\text{O}$ , the lines higher than 82 GHz from (15) have been remeasured and used in the fit together with 12 so far not reported transitions and the lower frequency data from (15).

The capability of the global-fit method used can be seen by how well the  $^{36}\text{SO}$  transitions could be predicted by using our previously published mass-invariant parameters (20): all undisturbed lines with a good S/N ratio deviated less than 75 kHz from that prediction over the whole frequency range. The new, improved constants are listed in Table 4. The comparison with the results from earlier works (16, 20) shows good agreement. Small deviations appear from the fact that (i) frequencies given in (20) have been slightly corrected, (ii) a considerably larger number of transitions has been included, and (iii) higher order terms of the rotation

parameters  $U_{ij}$ , the spin-spin parameters  $L_{ij}$ , and the spin-rotation parameters  $G_{ij}$  have been fitted here, in order to achieve the best agreement between the observed and the calculated (o-c) frequencies. The resulting  $\sigma$  value of the fit was 29 kHz. The lines from literature are well reproduced by our calculated frequencies. It should be mentioned that



**FIG. 3.** The observed spectrum of the  $N_J = 9_8 \leftarrow 8_7$  transition of  $^{36}\text{SO}$  (descending scan) measured at Nobeyama. The lineshape is second derivative, and the peak frequency for the spectrum is 370 080.99 MHz. Note that the value of the peak frequency is  $\sim 100$  kHz higher than the appropriate transition frequency listed in Table 2, because of the time constant for PSD circuit (see text). Step width for measured frequency is 200 kHz, and the integration time for each step is 150 msec. The number of data points is 25.

TABLE 4  
Isotopically Invariant Parameters for the SO Radical

Parameter	This work	Ref. (20)	Ref. (16) <sup>a</sup>	unit
$U_{01}^e$	230387.5604 (52) <sup>b</sup>	230387.575 (12) <sup>b</sup>	230387.620 (26) <sup>b</sup>	MHz amu
$U_{01}^{BO}$	230416.909 <sup>c</sup> (21)	230416.923 <sup>c</sup> (73)	230416.20 <sup>c</sup> (30)	MHz amu
$U_{01}^S$	7.817 (23)	7.796 (96)	7.23 (22)	MHz amu
$U_{01}^O$	21.532 (27)	21.553 (82)	21.34 (13)	MHz amu
$U_{11}$	-6001.429 (36)	-6001.480 (64)	-6001.73 (14)	MHz amu <sup>3/2</sup>
$U_{21}$	25.462 (75)	25.638 (97)	25.94 (18)	MHz amu <sup>2</sup>
$U_{31}$	-0.591 (56)	-0.867 (48)	-0.954 (63)	MHz amu <sup>5/2</sup>
$U_{41}$	-0.118 (14)			MHz amu <sup>3</sup>
$U_{02}$	-3.85373 (13)	-3.85474 (29)	-3.8525 (11)	MHz amu <sup>2</sup>
$U_{03}$	-0.0000126 (14)	-0.0000046 (31)	-0.0000024 <sup>c</sup>	MHz amu <sup>3</sup>
$U_{12}$	-0.00859 (39)	-0.00624 (26)	-0.00052 <sup>c</sup>	MHz amu <sup>5/2</sup>
$U_{13}$	0.0000299 (46)			MHz amu <sup>7/2</sup>
$L_{00}^e$	157795.534 (68)	157795.19 (12)	157795.671 (74)	MHz
$L_{00}^{BO}$	157787.76 <sup>c</sup> (16)	157787.64 <sup>c</sup> (25)	157787.77 <sup>c</sup> (62)	MHz
$L_{00}^S$	-0.57 (24)	-0.40 (36)	-0.53 (43)	MHz
$L_{00}^O$	-7.20 (13)	-7.15 (20)	-7.37 (43)	MHz
$L_{01}$	3.2443 (20)	3.2395 (43)	3.255 (13)	MHz amu
$L_{10}$	2978.67 (64)	2982.2 (11)	2977.57 (62)	MHz amu <sup>1/2</sup>
$L_{20}$	114.5 (16)	104.5 (27)	115.7 (12)	MHz amu
$L_{30}$	12.0 (13)	21.6 (22)	13.44 (45)	MHz amu <sup>3/2</sup>
$L_{40}$	0.78 (31)	-2.05 (55)		MHz amu <sup>2</sup>
$L_{11}$	0.149 (12)	0.183 (18)	0.150 (42)	MHz amu <sup>3/2</sup>
$L_{21}$	0.0314 (78)			MHz amu <sup>2</sup>
$G_{00}$	-1787.423 (37)	-1787.501 (96)	-1787.77 (21)	MHz amu
$G_{10}$	-45.67 (21)	-44.95 (64)	-44.07 (77)	MHz amu <sup>3/2</sup>
$G_{20}$	2.21 (15)	1.47 (77)		MHz amu <sup>2</sup>
$G_{01}$	-0.05895 (40)	-0.05966 (94)	-0.0485 (94)	MHz amu <sup>2</sup>
$\Delta_{01}^S$	-1.9772 <sup>c</sup> (58)	-1.972 <sup>c</sup> (24)	-1.830 (56)	
$\Delta_{01}^O$	-2.7247 <sup>c</sup> (34)	-2.727 <sup>c</sup> (10)	-2.700 (24)	

<sup>a</sup> Values converted to isotopically invariant parameters.  
<sup>b</sup> Values in brackets:  $1\sigma$ .  
<sup>c</sup> Derived value.

the o-c values (see Tables 1–3) for strong lines are less than 10 kHz and even for the faintest lines they do not exceed 50 kHz in most cases.

The hfs constants for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  shown in Table 5 have also been determined in the global fit. In general they agree with previously published values. The small deviations of the present  $^{33}\text{SO}$  values to the previous are explained by point (i) mentioned above and the fact that the additional constant  $C_I$  has been fitted here.

The nuclear spin–rotation parameters  $C_I$  for both nuclei are determined for the first time in this paper. Since data on  $^{17}\text{O}$ , as well as  $^{33}\text{S}$ , nuclear spin–rotation interaction are quite rare, this is worth a brief discussion. Townes and Schawlow (24) first mentioned that the interaction with excited electronic states mainly contributes to the magnetic nuclear spin–rotation interaction for nuclei other than hydro-

gen. Resuming their discussion, Saleck (25, 26) has found, from an inspection of this interaction in molecules containing  $^{14}\text{N}$ ,  $^{17}\text{O}$ , or  $^{33}\text{S}$  nuclei, that in linear molecules the ratio

$$\tilde{C}_I = \frac{C_I I}{B\mu_I/\mu_N}$$

[ 3 ]

is approximately constant for nuclei of the second period, independent of the chemical surrounding, whereas for third period nuclei this does not hold. Since the  $C_I$  are related to the radial distribution of the valence electrons, this was interpreted as a sign that atoms of the second period do not strongly change the radial distribution of the orbitals in different bonds, whereas for third-period atoms, the presence of  $d$  orbitals leads by hybridization to a change of that radial



distribution, depending on the chemical surrounding. Table 6 shows that the  $\tilde{C}_I$  for the  $^{17}\text{O}$  nucleus in SO is smaller than expected by this picture; however, it is poorly determined so that within  $3\sigma$  it does not contradict the mentioned picture. A higher accuracy or further data on other  $^{17}\text{O}$  containing molecules is needed to verify these previous findings. For the  $^{33}\text{S}$  nucleus, the  $\tilde{C}_I$  value is far better determined, but here, a close agreement with other molecules is not necessarily expected. For SO, we find it to be about 30% larger than in CS and five times larger than in OCS.

## 5. CONCLUSION

The new measurements presented in this work have led to an improved set of isotopically invariant parameters for the SO radical. The analysis of the hyperfine structure included the weak magnetic nuclear spin-rotation interaction for  $^{33}\text{SO}$  and  $\text{S}^{17}\text{O}$  for the first time. The isotopically invariant parameters allow not only precise predictions into higher frequency regions for all measured isotopomers, but also the discovery of previously not detected isotopic species is straightforward. This has been demonstrated by reporting the first measurements for the rare  $^{36}\text{SO}$  isotopomer, for which accurate line positions have been predicted on the basis of previously published mass-independent parameters (20). Thus, together with recent work on other species like  $\text{MgCl}$  (4),  $\text{CN}$  (3, 5),  $\text{HBr}$  (6), and  $\text{NS}$  (32), this method is confirmed to provide a powerful and efficient tool to analyze and predict high-resolution rotational spectra of diatomic molecules and radicals.

During the completion of this manuscript we became aware of the first interstellar detection of a  $^{36}\text{S}$ -bearing molecule. Mauersberger *et al.* (33) observed the  $J = 2-1$  and  $3-2$  transitions of  $\text{C}^{36}\text{S}$  in several galactic sources. This detection encourages us to search also for other  $^{36}\text{S}$ -bearing species. For  $^{36}\text{SO}$ , frequency predictions for the millimeter-wave region are included in Table 2. Calculated line positions for higher frequencies and other isotopomers of SO are available from the authors upon request.

**TABLE 5**  
Hyperfine Structure Constants for the  $^{33}\text{S}$  and  $^{17}\text{O}$  Nuclei  
Determined in the Global Fit in Comparison to Earlier Works

Isoto- pomer	$b_F$ [MHz]	$t$ [MHz]	$eQq$ [MHz]	$C_I$ [kHz]	Ref.
$^{33}\text{SO}$	18.884 (18) <sup>a</sup> 18.875 (53) 18.83 (21)	-32.080 (20) -32.202 (47) -32.167 (67)	-16.02 (12) -16.22 (38) -15.9 (3)	15.8 (29)	here (20) (13)
$\text{S}^{17}\text{O}$	-39.783 (11) -39.85 (5)	31.780 (16) 31.83 (3)	-3.614 (60) -3.5 (2)	-4.4 (15)	here (15)

<sup>a</sup>Values in brackets:  $1\sigma$ .

<sup>a</sup>Values in brackets:  $1\sigma$ .

**TABLE 6**  
Compilation of Electric Quadrupole and Nuclear Magnetic  
Spin-Rotation Constants for  $^{33}\text{S}$  and  $^{17}\text{O}$  in Different Linear Molecules

Molecule	Nucleus	$eQq$ [MHz]	$C_I$ [kHz]	$\tilde{C}_I \cdot 10^7$	Ref.
CO	$^{17}\text{O}$	-4.377 (56)	-30.4 (12)	7.14 (28)	(27)
$\text{O}^{17}\text{O}$	$^{17}\text{O}$	-8.3 (3)			(28)
OCS	$^{17}\text{O}$	-1.333 (22)	-3.3 (13)	7.40 (299)	(29)
OH	$^{17}\text{O}$	-1.92			(30)
NO	$^{17}\text{O}$	-1.30 (4)	-28.1 (25)	7.50 (67)	(26)
SO	$^{17}\text{O}$	-3.627 (61)	-4.4 (15)	2.8 (10)	here
CS	$^{33}\text{S}$	12.833 (36)	13.4 (38)	12.9 (36)	(8)
OCS	$^{33}\text{S}$	-29.1184 (12)	0.87 (5)	3.38 (19)	(31)
SO	$^{33}\text{S}$	-16.02 (12)	15.8 (29)	17.2 (31)	here

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*Note added in proof:* Very recently Bogey *et al.* have submitted a manuscript about  $^{32}\text{S}^{16}\text{O}$  to *J. Mol. Spectrosc.* They reported measurements of rotational transitions in very high excited vibrational states for the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  electronic states. These data agree well with the frequencies reported here, also for the excited electronic states, for which the new results obtained in Cologne will be presented elsewhere.

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