Submillimeter-Wave Rotational Spectra of SO Isotopomers in the Electronic States $a^1\Delta$ and $b^1\Sigma^+$

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Pure rotational transitions of the sulfur monoxide isotopomers $^{32}S\,^{16}O$, $^{34}S\,^{16}O$, and $^{32}S\,^{18}O$ were measured in different vibrational states of the electronic states $a^1\Delta$ and $b^1\Sigma^+$ with the Cologne terahertz spectrometer in the submillimeter-wave region between 300 and 1070 GHz. The new lines were analyzed together with previous results from the literature in a global fit yielding isotopically invariant rotational parameters for both states. The measurements reported here allowed for the first time the determination of the parameters U_{01}^S and U_{01}^O to correct for the breakdown of the Born–Oppenheimer approximation analogously to the $X^3\Sigma^-$ state. Precise equilibrium bond lengths r_e are given for all states concerned. © 1997 Academic Press

1. INTRODUCTION

In contrast to the $^3\Sigma^-$ ground state of SO, for which a large data set on isotopomers and excited vibrational states is available from the literature (see, e.g., (*1, 2*) and references therein), the $a^1\Delta$ and $b^1\Sigma^+$ electronic states at energies of 5 879.2 (*3*) and 10 509.97 cm^{-1} (*4*), respectively, have not been investigated by high resolution spectroscopy to a great extent.

For the $a^1\Delta$ state, Saito (*5*) reported the first measurement of a rotational transition ($N = 3 \leftarrow 2$) and later Clark and De Lucia (*6*) published further measurements up to 255 GHz. Cazzoli *et al.* (*7*) reported frequencies of three rotational transitions between 680 and 1274 GHz using a FIR sideband laser spectrometer reaching a frequency accuracy of 500 kHz, whereas Klaus *et al.* (*8*) measured two lines in the THz region by use of phase-stabilized backward wave oscillators (BWOs). Recently Bogey *et al.* (*2*) investigated the spectrum of $^{32}S\,^{16}O$ in highly excited vibrational states up to $v = 13$ in the submillimeter-wave range using BWOs and two methods for the production of SO: laser photolysis of Cl_2SO with time-dependent detection and electric discharge of SO_2 in argon.

For the $b^1\Sigma^+$ state, pure rotational spectra were measured for the first time by Yamamoto (*9*), who used results from $b^1\Sigma^+—X^3\Sigma^-$ emission experiments (*4, 10*) to predict the spectrum in the millimeter-wave region. He observed $^{32}S\,^{16}O$ up to the vibrational state $v = 8$ and

$^{34}S\,^{16}O$ in the $v = 0$ and 1 states. Bogey *et al.* (*2*) extended these measurements for $^{32}S\,^{16}O$ up to 921 GHz and up to the $v = 11$ state.

Thus far, no laboratory observations have been reported for ^{34}SO or $S\,^{18}O$ in the $a^1\Delta$ state and for $S\,^{18}O$ in the $b^1\Sigma^+$ state. These investigations were carried out in the current work with the aim of completing the isotopically invariant analysis to yield a deviation from the Born–Oppenheimer approximation, analogously to the results on the $X^3\Sigma^-$ state (*11, 12*). The equilibrium structure, expressed by the equilibrium bond distance r_e, could be evaluated for all isotopomers measured in the two electronic states.

2. EXPERIMENT

The Cologne terahertz spectrometer uses phase-stabilized BWOs in the frequency range between 53 GHz and at present 1300 GHz. The BWOs are supplied by the ISTOK Research and Production Company at Fryazino near Moscow. The stabilization is achieved by mixing the BWO output radiation with the harmonics of a low frequency synthesizer (78 to 118 GHz) supplied by the Institute of Electronic Measurement, KVARZ (Nizhnii Novgorod, Russia). Other details concerning the experimental setup are given in Refs. (*13, 14*).

The SO radical was produced in a dc discharge of H_2S and O_2. For the measurements in the $a^1\Delta$ state, the exper-

TABLE 1

Newly Observed Rotational Transitions of SO Isotopomers in the $a^1\Delta$ State

J'	$\leftarrow$	J''	v	ν_{exp} [MHz]	$\Delta\nu_{exp}$ [MHz]	O−C [MHz]
				^{32}SO		
7	$\leftarrow$	6	0	298 091.531	0.100	0.036
14	$\leftarrow$	13	0	595 894.568	0.050	0.015
15	$\leftarrow$	14	0	638 397.464	0.100	−0.010
21	$\leftarrow$	20	0	893 120.432	0.100	−0.060[a]
24	$\leftarrow$	23	0	1 020 253.808	0.500	−0.920[a,b]
25	$\leftarrow$	24	0	1 062 593.528	0.100	0.019
14	$\leftarrow$	13	1	590 819.261	0.050	−0.031
15	$\leftarrow$	14	1	632 959.522	0.050	−0.037
16	$\leftarrow$	15	1	675 087.175	0.050	−0.004
14	$\leftarrow$	13	2	585 746.404	0.050	0.015
15	$\leftarrow$	14	2	627 524.174	0.050	0.011
16	$\leftarrow$	15	2	669 289.246	0.050	−0.014
17	$\leftarrow$	16	2	711 040.786	0.050	−0.048
14	$\leftarrow$	13	3	580 674.766	0.100	0.013
16	$\leftarrow$	15	3	663 492.730	0.100	−0.040
17	$\leftarrow$	16	3	704 881.838	0.100	−0.030
14	$\leftarrow$	13	4	575 603.177	0.100	0.003
16	$\leftarrow$	15	4	657 696.273	0.100	−0.045
17	$\leftarrow$	16	4	698 722.965	0.100	0.037
15	$\leftarrow$	14	5	611 220.706	0.150	−0.016
16	$\leftarrow$	15	5	651 898.398	0.150	0.035
17	$\leftarrow$	16	6	686 398.256	0.300	−0.121
17	$\leftarrow$	16	7	680 228.925	0.300	−0.007
				^{34}SO		
15	$\leftarrow$	14	0	625 926.215	0.100	0.002
16	$\leftarrow$	15	0	667 587.833	0.100	0.037
17	$\leftarrow$	16	0	709 236.440	0.100	0.001
15	$\leftarrow$	14	1	620 647.293	0.200	−0.024
16	$\leftarrow$	15	1	661 956.694	0.200	−0.132
				S^{18}O		
15	$\leftarrow$	14	0	591 148.527	0.100	0.010
17	$\leftarrow$	16	0	669 837.606	0.100	0.000
17	$\leftarrow$	16	1	664 347.515	0.150	−0.045
16	$\leftarrow$	15	2	620 167.332	0.200	0.078
17	$\leftarrow$	16	3	653 373.812	0.300	−0.062

[a]Already reported in Ref. (*1*).
[b]Disturbed line. Not included in the fit.

TABLE 2

Isotopically Invariant Parameters for $a^1\Delta$ SO in Comparison to Earlier Works

Parameter	This Work	Bogey et al. (*2*)[a]	Klaus et al. (*8*)	Unit
U_{01}^e	228 003.260 (14)[b]	228 003.236 (20)[b]	228 003.262 (44)[b]	MHz u
U_{01}^{BO}	228 033.30[c] (14)			MHz u
U_{01}^S	7.98 (20)			MHz u
U_{01}^O	22.06 (12)			MHz u
U_{11}	−6 312.911 (46)	−6 312.785 (66)	−6 313.60 (17)	MHz u$^{3/2}$
U_{21}	7.761 (56)	7.620 (83)	8.84 (21)	MHz u^2
U_{31}	−1.914 (34)	−1.848 (52)	−2.714	MHz u$^{5/2}$
U_{41}	−0.1670 (93)	−0.1830 (45)		MHz u^3
U_{51}	−0.01419 (90)	−0.0127 (15)		MHz u$^{7/2}$
U_{02}	−3.97749 (32)	−3.97720 (45)	−3.9708 (25)	MHz u^2
U_{03}	−0.0000249 (29)	−0.0000261 (48)	−0.000132 (25)	MHz u^3
U_{12}	−0.02759 (50)	−0.02839 (67)	−0.290 (51)	MHz u$^{5/2}$
U_{22}	−0.00157 (38)	−0.00103 (50)		MHz u^3
U_{32}	−0.000752 (81)	−0.00084 (10)		MHz u$^{7/2}$
Δ_{01}^S	−2.040[c] (51)			
Δ_{01}^O	−2.820[c] (15)			

[a]Values converted to isotopically invariant parameters.
[b]Values in brackets: 1σ.
[c]Derived value.

TABLE 3

Newly Observed Rotational Transitions of SO Isotopomers in the $b^1\Sigma^+$ State

J'	$\leftarrow$	J''	v	ν_{exp} [MHz]	$\Delta\nu_{exp}$ [MHz]	O−C [MHz]
				^{32}SO		
14	$\leftarrow$	13	0	586 743.790	0.050	0.008
15	$\leftarrow$	14	0	628 590.549	0.050	0.007
16	$\leftarrow$	15	0	670 424.153	0.050	−0.007
25	$\leftarrow$	24	0	1 046 190.489	0.100	−0.058
14	$\leftarrow$	13	1	581 389.420	0.050	−0.064
15	$\leftarrow$	14	1	622 853.555	0.050	−0.001
16	$\leftarrow$	15	1	664 304.411	0.050	−0.027
22	$\leftarrow$	21	1	912 683.360	0.100	−0.029[a]
23	$\leftarrow$	22	1	954 017.265	0.100	−0.005
				S^{18}O		
15	$\leftarrow$	14	0	582 076.989	0.050	0.018
16	$\leftarrow$	15	0	620 820.049	0.050	0.008
17	$\leftarrow$	16	0	659 551.099	0.050	0.003
18	$\leftarrow$	17	0	698 269.375	0.050	−0.011
15	$\leftarrow$	14	1	576 966.816	0.150	−0.140

[a]This transition was measured by Bogey et al. (*2*) at 912 683.377 MHz.

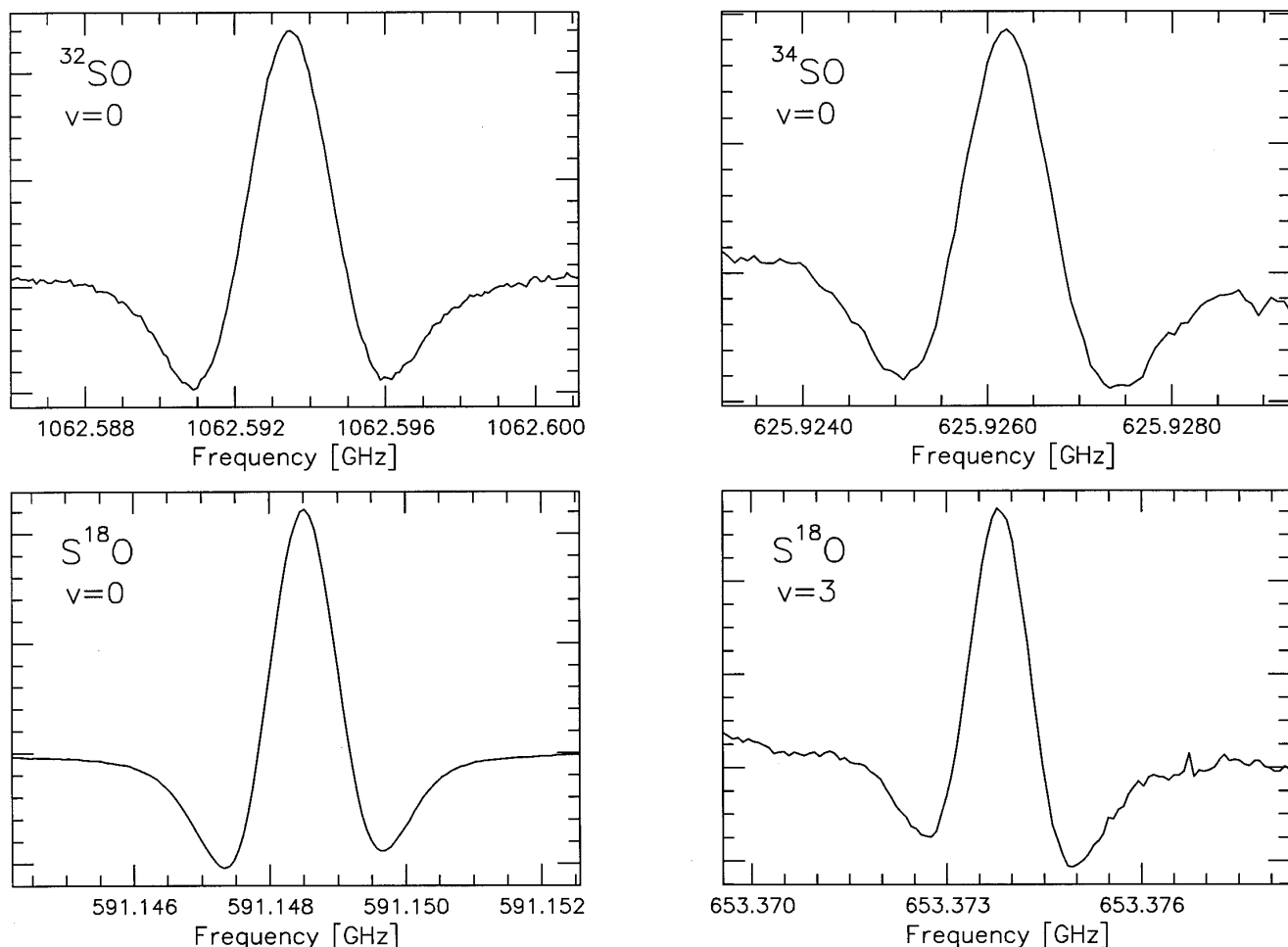**FIG. 1.** Observed transitions of ^{32}SO, ^{34}SO, and S^{18}O in the $a^1\Delta$ state. The lines are recorded in the second derivative from.

imental conditions were similar to those for the $X^3\Sigma^-$ state (*1*), i.e., partial pressures of about 10 and 40 mTorr for H$_2$S and O$_2$, respectively, and a discharge current of about 100 mA. In the case of the $b^1\Sigma^+$ state, the absorption signals were increased by adding helium to the discharge gas and by applying a higher current of 500 mA. This agrees with the experimental findings reported in Ref. (*9*). The spectra of ^{34}SO were observed in natural abundance of ^{34}S, whereas for the S^{18}O measurements the oxygen sample was replaced by an ^{18}O$_2$ sample delivered by MSD Isotopes (Montreal, Canada) with an atomic ^{18}O enrichment of 96.5%.

3. RESULTS AND ANALYSIS

(a) The $a^1\Delta$ State

Since the total electronic spin equals zero in this state, no spin–spin or spin–rotation interaction occurs. A pos-sible Λ-type doubling was not observed. The rotational energy levels are expressed here by an expansion with isotopically invariant coefficients U_{ij} and the various reduced masses μ,

$$E_{vJ} = \sum_{ij}\mu^{-i/2-j}U_{ij}(v + 1/2)^i[J(J + 1) - \Lambda^2]^j, \quad [1]$$

when only a single isotopomer is considered. In the global analysis of the three isotopomers the deviation from the Born–Oppenheimer approximation is taken into account by replacing the U_{01} parameter by (*12*)

$$U_{01} = U_{01}^e + U_{01}^A\left(1 - \frac{M_A^0}{M_A}\right) + U_{01}^B\left(1 - \frac{M_B^0}{M_B}\right), \quad [2]$$

where M_A^0 and M_B^0 are the atomic masses in the reference isotopomer, here ^{32}S^{16}O, and U_{01}^A and U_{01}^B the effective, isoto-
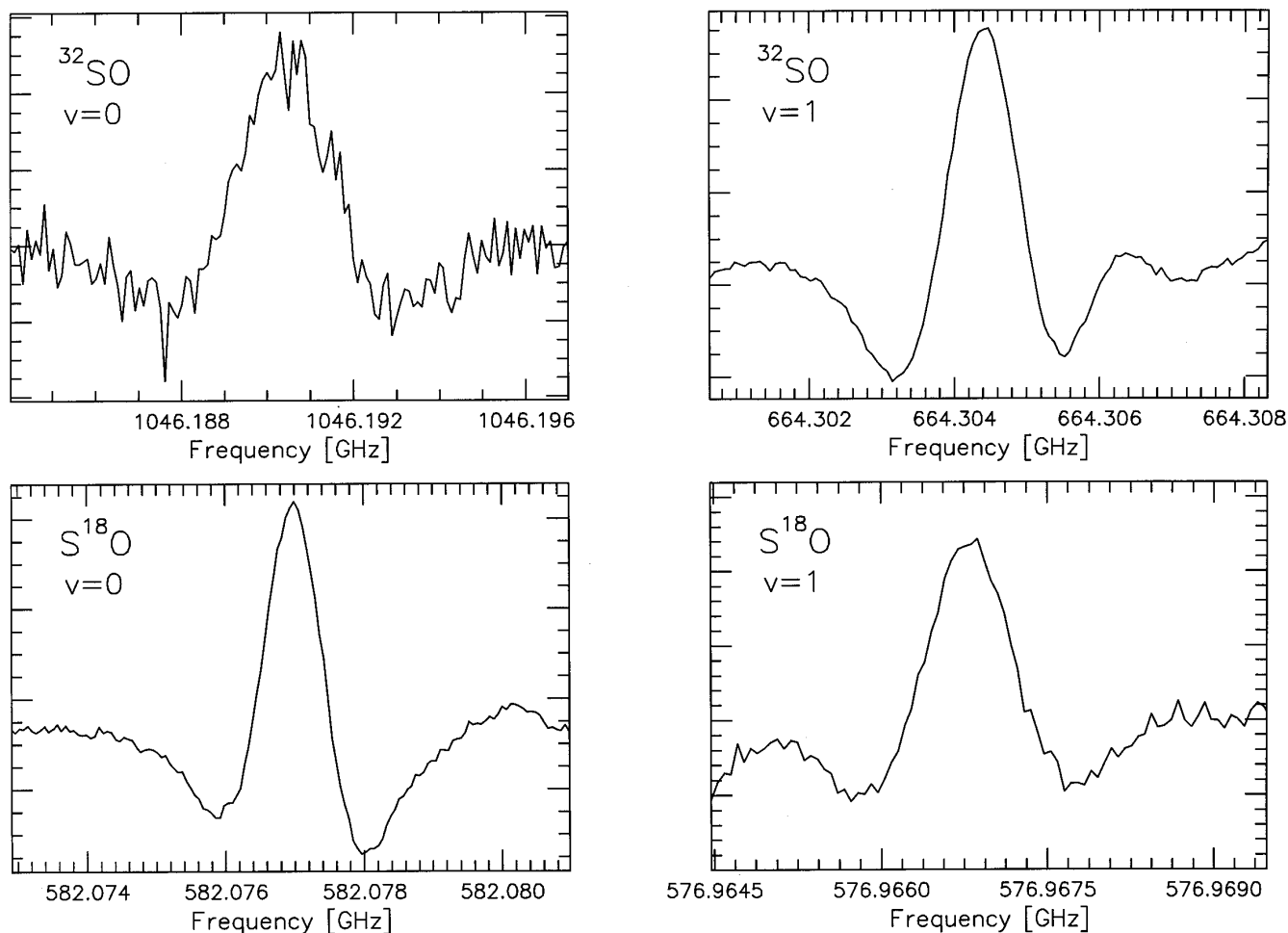
FIG. 2. Observed transitions of ^{32}SO and S^{18}O in the $b^1\Sigma^+$ State.

pically invariant corrections to the Born–Oppenheimer approximation. They are directly related to Watson's Δ_{01} constants (*12, 15*).

The frequency predictions were made by employing the previously obtained mass-invariant parameters (*8*). The Born–Oppenheimer correction parameters U_{01}^S and U_{01}^O were taken from the $X^3\Sigma^-$ (*1*) state, leading to accurate predictions for the ^{34}SO and S^{18}O isotopomers.

Table 1 lists the newly observed lines measured in the course of this work. For ^{32}SO 21 lines up to $v = 7$ were observed. The transition $N_J = 21_{21} \leftarrow 20_{20}$ at 893 120.432 MHz[1] was remeasured after adjustment of the frequency reference standard used in the stabilization circuit (see Ref. *1*). When the transition at 1020 GHz ($N_J = 24_{24} \leftarrow 23_{23}$) reported in the previous work (*8*) was remeasured, a disturbance was detected at this frequency, probably

caused by an unknown absorption line. This frequency was not included in the global fit. In total, 10 lines were measured for the isotopomers ^{34}SO and S^{18}O in vibrational states up to $v = 3$. Figure 1 displays a few sample spectra.

All measurements reported in the literature (*2, 6, 7*) were included in the global analysis, in which a total of 95 lines were fitted, the σ of the fit being 36 kHz. The resulting isotopically invariant parameters are shown in Table 2. The agreement with the values from other works (*2, 8*) is good. However, in comparison with these previous results, the accuracy of the present parameters is slightly higher. Bogey *et al.* (*2*) fitted only transitions of the main isotopomer ^{32}S^{16}O; their values given in the table were converted to the U_{ij} parameters. All frequencies from the literature (*2, 6, 7*) are well reproduced within the uncertainties stated in these references.

(b) The $b^1\Sigma^+$ State

The electronic state $b^1\Sigma^+$ exhibits no fine structure in the rotational energy levels, so that, as for the $a^1\Delta$ state,

[1] This improved frequency agrees perfectly with the value of 893 120.434 MHz reported independently by Bogey *et al.* (*2*).

TABLE 4

Isotopically Invariant Parameters for $b^1\Sigma^+$ SO in Comparison to Earlier Works

Para-meter	This Work[a]	Bogey et al. (2)[a,b]	Yamamoto (9)[b,c]	Unit
U_{01}^e	224 580.135 (12)	224 580.108 (15)	224 580.107 (49)	MHz u
U_{01}^{BO}	224 612.568[d] (91)			MHz u
U_{01}^S	8.98 (15)			MHz u
U_{01}^O	23.453 (53)			MHz u
U_{11}	−6 650.788 (49)	−6 650.680 (63)	−6 650.62 (20)	MHz $u^{3/2}$
U_{21}	−5.347 (78)	−5.491 (93)	−5.64 (26)	MHz u^2
U_{31}	−2.473 (56)	−2.386 (63)	−2.22 (15)	MHz $u^{5/2}$
U_{41}	−0.203 (18)	−0.227 (19)	−0.314 (28)	MHz u^3
U_{51}	−0.0178 (20)	−0.0155 (22)		MHz $u^{7/2}$
U_{02}	−4.14018 (29)	−4.14011 (38)	−4.1398 (26)	MHz u^2
U_{03}	−0.0000174 (28)	−0.0000149 (45)		MHz u^3
U_{12}	−0.04806 (53)	−0.04851 (63)	−0.0495 (74)	MHz $u^{5/2}$
U_{22}	−0.00405 (48)	−0.00389 (55)	−0.0049 (32)	MHz u^3
U_{32}	−0.00075 (12)	−0.00074 (15)		MHz $u^{7/2}$
Δ_{01}^S	−2.331[d] (39)		−2.58[d] (98)	
Δ_{01}^O	−3.0444[d] (69)			

[a]Values in brackets: 1σ.
[b]Values converted to isotopically invariant parameters.
[c]Values in brackets: 3σ.
[d]Derived value.

TABLE 5

**Comparison of Equilibrium Bond Lengths of SO Isotopomers
in the Electronic States $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$**

	$X^3\Sigma^-$[a]	$a^1\Delta$	$b^1\Sigma^+$	Unit
Δ_{01}^S	−1.9772 (58)	−2.040 (51)	−2.331 (39)	
Δ_{01}^O	−2.7247 (34)	−2.820 (15)	−3.0444 (69)	
r_e^{BO}	1.48098769 (68)	1.48870789 (106)	1.50000115 (93)	10^{-10} m
$r_e(^{32}S^{16}O)$	1.48108202 (64)	1.48880595 (67)	1.50010947 (67)	10^{-10} m
$r_e(^{34}S^{16}O)$	1.48108054 (64)	1.48880441 (68)	1.50010771 (67)	10^{-10} m
$r_e(^{32}S^{18}O)$	1.48107431 (64)	1.48879793 (69)	1.50010075 (67)	10^{-10} m

[a]Taken or calculated from rotational parameters in Ref. (1).

Eqs. [1] and [2] are sufficient to describe the rotational spectrum.

To predict the rotational transitions for the desired isotopomers, the measurements from Yamamoto (*9*) were converted to mass-invariant parameters including the U_{01}^S term. The U_{01}^O parameter was taken from the $X\,^3\Sigma^-$ state (*1*). Subsequently 14 transitions in the vibrational states $v = 0$ and 1 were measured (Table 3). Four of these lines are displayed in Fig. 2.

Together with the measurements presented here, the lines reported by Yamamoto (*9*) and Bogey *et al.* (*2*) were subjected to a global fit ($\sigma = 28$ kHz), resulting in a new set of isotopically invariant parameters (Table 4). Comparison with the previous constants shows that they agree within a tolerance of 2σ, similarly to the $a\,^1\Delta$ state, and that the present analysis based on a larger number of lines (in total 92) yielded more precise values for all parameters. Yamamoto determined the Δ_{01}^S term from his measurements to be $-2.58(98)$ which remains in agreement with the more precise values from our analysis.

4. DISCUSSION

The mass-invariant Born–Oppenheimer equilibrium separation r_e^{BO} and the isotopomerically different bond lengths for the ground and the two excited electronic states are summarized in Table 5. The uncertainties for the various r_e values include the error due to the limited precision of Planck's constant h. Comparison of the r_e values for different isotopomers in a given electronic state clearly shows the deviation of the Born–Oppenheimer approximation. The increase of the r_e values with the change of the electronic state is explained by the different molecular potentials owing to the change of the electron distribution in the $(2\pi)^4(3\pi)^2$ configuration.

The values of the $\Delta_{01}^{S,O}$ parameters are also listed in Table 5. Their absolute values increase when going from the ground to higher electronic states. The $\Delta_{01}^{S,O}$ parameters are effective constants which can explicitly be separated into a Dunham correction and an adiabatic and nonadiabatic contribution (*16*). Since the nonadiabatic term is related to the rotational g-factors which are not currently known for all excited states, a quantitative discussion of the variation of the Born–Oppenheimer corrections cannot be given here. Nevertheless their increase with higher energies can be interpreted in terms of increasing influence of other electronic states.

In conclusion, the new measurements presented here led to improved sets of isotopically invariant parameters for the $a\,^1\Delta$ and $b\,^1\Sigma^+$ states of SO. For the first time the deviations from the Born–Oppenheimer approximation could be determined completely by including new measurements of ^{34}SO and S^{18}O in the analysis. The effective parameters U_{01}^S and U_{01}^O presented here are sufficient to correct for the breakdown of the Born–Oppenheimer approximation. Together with the other rotational parameters they reproduce the measured frequencies and provide accurate frequency predictions in the submillimeter-wave region beyond 1 THz for all isotopomers of SO.

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