

Rotational Spectrum of SO in the Terahertz Region

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The pure rotational spectrum of sulfur monoxide, SO, has been recorded in the $X^3\Sigma$ electronic ground state and $a^1\Delta$ excited electronic state with the Cologne terahertz spectrometer in conjunction with a newly designed dc-discharge cell, covering the frequency range between 880 GHz and 1.05 THz. The expanded spectral coverage allowed us to observe ground state and vibrationally excited rotational transitions as high as $N_J = 25_{26} - 24_{25}$ for SO and the isotopomers $^{34}\text{S}^{16}\text{O}$, $^{33}\text{S}^{16}\text{O}$, and $^{32}\text{S}^{18}\text{O}$ in natural abundance. The vibrational and isotopic dependence of various molecular parameters such as the mass-independent rotational constants U_{ij} , the spin-spin coupling constants L_{ij} , and the spin-rotation constants G_{ij} have been determined. Although these values are in very close agreement with earlier parameters of Bogey *et al.* [*Chem. Phys.* **66**, 99–104 (1982)], it was necessary to include higher order terms in order to achieve a satisfactory fit to the combined data set, consisting of all previous and newly acquired submillimeter-wave lines. On the basis of these data, the rotational spectrum of SO can now be predicted up to about 1.5 THz with a high level of accuracy, which will be important for future astrophysical identifications. © 1994 Academic Press, Inc.

1. INTRODUCTION

It has now been 30 years since the first six spectral transitions of the gaseous free radical sulfur monosulfide, SO, were observed in the millimeter-wave region between 99 and 160 GHz by M. Winnewisser *et al.* (1) at Duke University in Professor W. Gordy's laboratory. These laboratory measurements confirmed that the electronic ground state of SO is $X^3\Sigma$ and yielded for the first time values for the rotational constants B_0 and D_0 as well as the two magnetic coupling constants λ_0 and γ_0 , the spin-spin and spin-rotation coupling constants, respectively. This Duke experiment, in which SO was produced in a 15-MHz RF-discharge directly connected to the "free-space" absorption cell (2), marked the beginning of free radical spectroscopy in the millimeter wave region.

Almost simultaneously, five low-frequency microwave transitions, located between 13 and 70 GHz, were reported by Powell and Lide (3), proving the existence of SO in different discharge arrangements. Since this early pioneering work, a number of important papers based on technical refinements have appeared, greatly expanding the spectral coverage and the sensitivity of laboratory experiments (4–10).

Amano *et al.* (4) and Tiemann (5) expanded the microwave measurements by observing transitions of the ground and first excited vibrational state as well as lines of various isotopomers, leading to improved equilibrium constants. Considerable ex-

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pansion of the ground state millimeter-wave spectrum into the submillimeter-wave region was achieved by Clark and De Lucia (6), with the result that the rotational transitions for the energy levels $J \leq 10$ could accurately be predicted. In addition, several rotational transitions in the $^1\Delta$ electronic excited state were observed (6, 7) following Saito's discovery (8) of the $N = 3-2$ transition at 128 GHz, representing the first microwave transition to be measured in an electronically excited state. Bogey *et al.* (9) and Tiemann (10) measured rotational lines in highly excited vibrational states up to $v = 8$ and determined from a simultaneous fit to all the available data the isotopic shift of the molecular parameters and a breakdown of the Born–Oppenheimer approximation.

Since its first detection in molecular clouds associated with HII regions (11, 12), SO has turned out to be a ubiquitous interstellar molecule under average molecular cloud conditions. In addition, SO and its isotopomers (12–14) are seen in such diverse regions as the cores of dark clouds, e.g., L134N (15), the center of star formation regions (16, 17), far-infrared IRAS sources (18), in the envelopes of oxygen-rich red giants (19), in galactic cirrus clouds (20), and very recently also in the Jovian atmosphere during the comet-crash of Shoemaker-Levy 9. The fact that SO is found in the cores of star forming regions suggests that SO can be excited to very high energies by associated shock waves to observable abundances detectable through submillimeter-wave transitions.

The purpose of the present paper is to provide highly accurate frequency predictions of SO and its most abundant isotopomers, based on new and very precise measurements of the rotational spectrum up to 1 THz. These predictions stem from an analysis of all presently available data. Section 2 gives a short account of the Cologne terahertz spectrometer and the newly designed “free-space” discharge cell. In Section 3, a few comments are made on the Hamiltonian used, followed by the experimental measurements and a brief discussion of the quality of the fit to the extended Hamiltonian. After a brief discussion, Section 5 presents a short account of the astrophysical implications.

2. EXPERIMENTAL CONSIDERATIONS

The SO measurements presented here are part of an effort devoted to generate, observe, and analyze the spectra of astrophysically relevant radicals in the terahertz region. In the course of this program, we have observed in addition to SO the terahertz rotational spectra of CN and CCH. The spectra of the latter two species will be reported elsewhere.

High-resolution scanning spectroscopy in the terahertz region has been achieved with microwave accuracy by frequency and phase stabilization of high-frequency backward wave oscillators, BWOs, supplied by the ISTOK Research and Production Co. located in Fryazino, near Moscow. The high-frequency beam of the BWO power output was coupled into a newly constructed dc-discharge cell by an off-axis parabolic mirror. Otherwise, the arrangement of the Cologne terahertz spectrometer corresponds to the schematic diagram shown by Winnewisser *et al.* (21).

The frequency measurements in the low-frequency region between 118 and 178 GHz were carried out by a frequency synthesizer supplied by the Institute of Electronic Measurements, KVARZ, Nizhnii Novgorod, Russia. This frequency region was used to optimize the radical production before the terahertz beam was directed through the absorption cell.

A new "free-space" absorption cell, 2 m in length and 10 cm in diameter, was used to produce SO in a dc-discharge of O₂ and H₂S without buffer gas. Stable operational conditions and optimal signal were obtained at total pressures of about 60 μ bar and currents between 100 and 150 mA. For ¹ Δ SO the same values were determined. The integration time constant was set to 30 msec, but even for ³³SO, with a relative abundance of 0.75%, only a few averaging scans were necessary to obtain a good signal-to-noise ratio. The measurement accuracy in the terahertz region is estimated to be about 100 kHz for unblended lines, and the sensitivity under optimal conditions may reach 10⁻⁶ cm⁻¹. Figures 1–3 show some selected rotational transitions of SO and its isotopomers.

3. HAMILTONIAN

The electronic ground state of SO is $X^3\Sigma$. Thus, besides the rovibrational energies, the rotational spectrum is also characterized by a fine structure arising from spin–spin and spin–rotation interactions. The latter, also called spin-doubling, is caused by perturbing excited electronic Π states. In general, the spin–spin contribution is more dominant than the spin–rotation interaction and is due to the interaction of the magnetic moments associated with the two unpaired electrons. For ³³S and ¹⁷O nuclei, magnetic dipole and electric quadrupole hyperfine interactions have to be considered also. We briefly summarize the matrix elements accounting for all these effects. Since we intend to apply them to a diatomic molecule, we prefer to express them in terms of isotopically invariant parameters, following earlier discussions given by Watson (22), Tiemann (10), Ryzlewicz *et al.* (23), and Bogey *et al.* (9, 24, 25).

For a diatomic molecule, the rovibrational matrix elements are most conveniently expressed by Dunham-type series involving isotopically invariant parameters U_{ij} :

$$\begin{aligned} \langle N'J'F; v | H_{\text{Rot}} | NJF; v \rangle \\ = \delta_{N'N} \delta_{J'J} \sum_{i,j=0}^{\infty} \mu^{-(i/2+j)} U_{ij} (v + 1/2)^i [N(N+1) - \Lambda^2]^j. \end{aligned} \quad (1)$$

Here μ is the reduced mass in a.u. The most precise values for atomic masses are provided by the IUPAC database (26). Equation (1) will need to be slightly modified if a breakdown of the Born–Oppenheimer has to be taken into account (e.g. see Ref. (22)). This occurs for the SO molecule as detected by Tiemann (10) and Bogey *et al.* (9). The rotational constant U_{01} should be replaced by the expression (10, 24)

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

where A and B refer to the isotopes A and B of the nuclei 1 and 2, respectively, and M_A^0 and M_B^0 are the atomic masses in the reference isotopomer, here ³²S¹⁶O. U_{01}^A and U_{01}^B carry the corrections to the Born–Oppenheimer approximation; their conversion to Watson's Δ_{01} constants is given by (10)

$$\Delta_{01}^A = - \frac{M_A^0}{m_e (U_{01}^e + U_{01}^A + U_{01}^B)} U_{01}^A \quad (3)$$

and analogously for Δ_{01}^B .

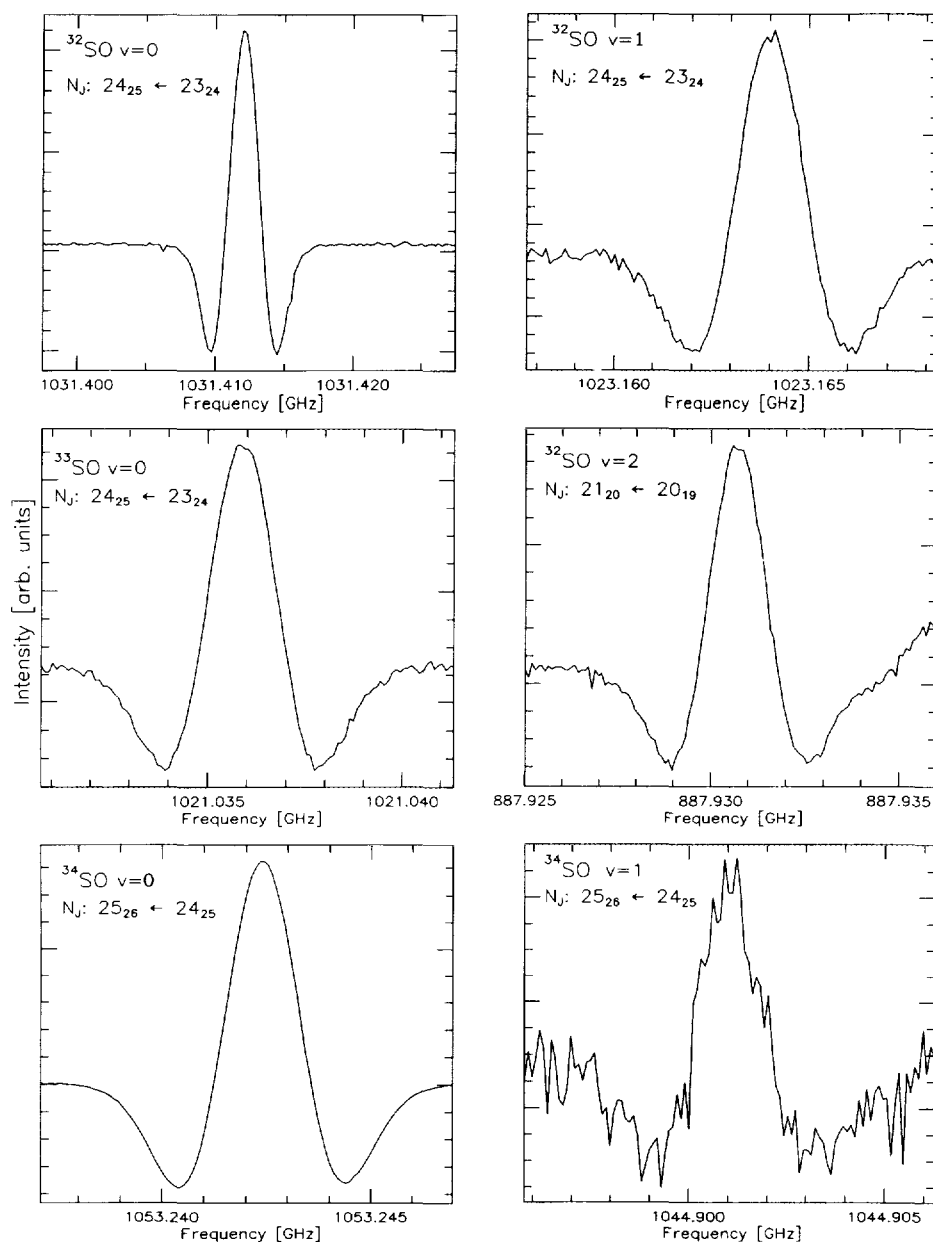


FIG. 1. Several high- N rotational terahertz transitions of SO and its isotopomers in the $X^3\Sigma$ vibrational ground state and excited vibrational states. The lineshape is second derivative and the stepwidth is 90 kHz. For ^{33}SO , the hyperfine splitting is not resolved.

For the spin-rotation interaction, a Dunham-type expansion in terms of mass-independent parameters G_{ij} has been given by Ryzlewicz *et al.* (23) and subsequently been used by Bogey *et al.* (24, 25). Using the mass-independent formalism, the matrix elements for the spin-doubling become

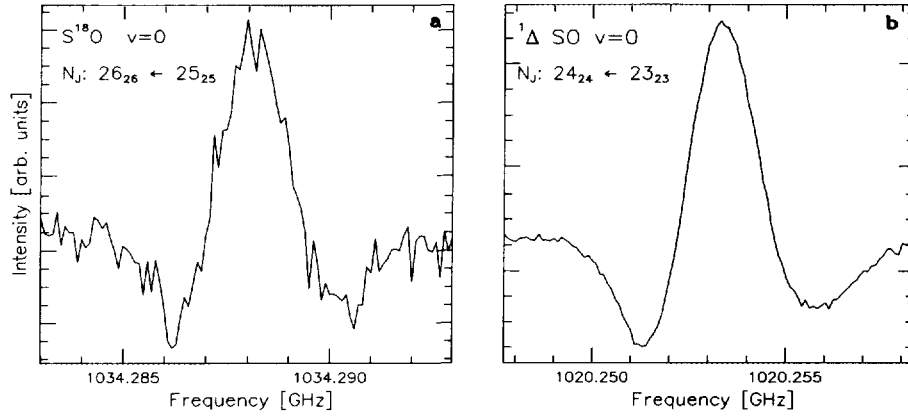


FIG. 2. (a) Observed spectra for the $S^{18}O$ isotopomer in the $X^3\Sigma$ vibrational ground state. Here signal averaging was employed. (b) Transition of SO in $a^1\Delta$ vibrational ground state. The line intensity is roughly the same as that for ^{33}SO in Fig. 1.

$$\langle N'J'F; v | H_{SR} | NJF; v \rangle = \delta_{N'N} \delta_{J'J} (1/2) [J(J+1) - N(N+1) - 2] \\ \times \sum_{i,j=0}^{\infty} \mu^{-(i/2+j+1)} G_{ij}(v+1/2)^i [N(N+1)]^j. \quad (4)$$

For SO, the triplet splitting caused by the spin-spin interaction is, for low N rotational quantum numbers, almost equal to the separation of the adjacent rotational levels

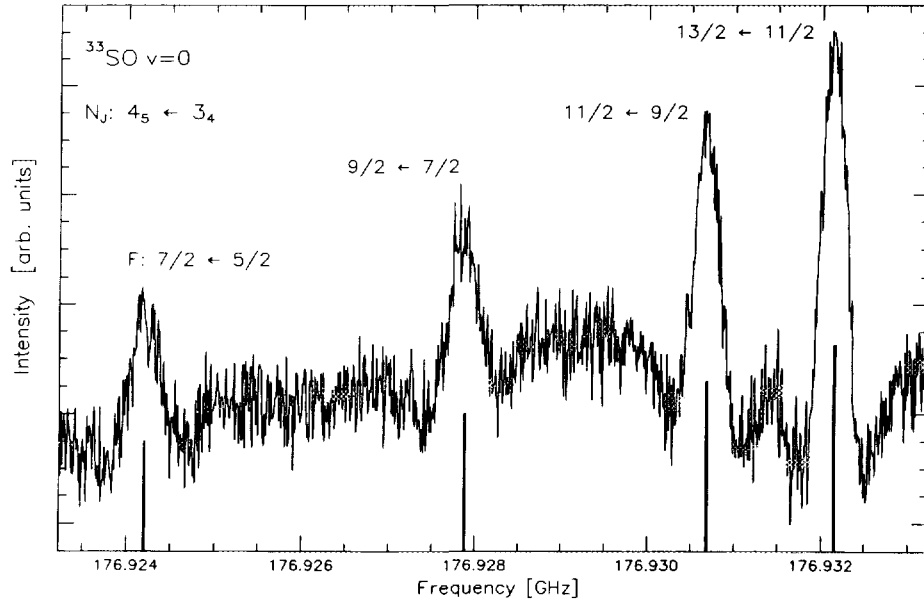


FIG. 3. Resolved hyperfine components of ^{33}SO at 176 GHz recorded with the KVARZ synthesizer. Sticks mark the calculated line positions and relative intensities. This 10-MHz scan was recorded with a stepwidth of 10 kHz.

and therefore of dominating influence on the observed spectra. The appropriate matrix elements for a given vibrational state can be taken from the literature (27). In order to fit several vibrational states simultaneously, we adopt here an expansion similar to the ones in Eqs. (1) and (4) for the matrix elements:

$$\begin{aligned} \langle N'J'F; v | H_{SS} | NJF; v \rangle &= \delta_{N'N} \delta_{J'J} (2/3) \sqrt{30} (-1)^{N+J+1+N'} \sqrt{(2N'+1)(2N+1)} \\ &\times \left\{ \begin{matrix} J & 1 & N' \\ 2 & N & 1 \end{matrix} \right\} \left\{ \begin{matrix} N' & 2 & N \\ 0 & 0 & 0 \end{matrix} \right\} \times (1/2) \sum_{i,j=0}^{\infty} \mu^{-(i/2+j)} L_{ij}(v+1/2)^i \\ &\times \{ [N'(N'+1)]^j + [N(N+1)]^j \}. \quad (5) \end{aligned}$$

The L_{ij} terms are isotopically invariant parameters of the Dunham-type expansion. To reproduce the isotopic dependence of the spin-spin interaction fully, we follow Tiemann (10) in employing Eq. (1) and replacing the U_{01} parameters by the appropriate L_{00} .

Hyperfine structure (hfs) constitutes the smallest contribution that has to be considered here. For SO, it applies to the nuclei ^{33}S (spin $I = \frac{3}{2}$) and ^{17}O ($I = \frac{5}{2}$). The hfs can also be expanded in terms of isotopically invariant parameters (23, 28). However, since presently the ^{33}SO $v = 0$ transitions are the only measured exhibiting hfs splittings, in fact only three constants have to be considered, namely, b_F , and t , representing the magnetic Fermi-contact and nuclear spin-spin interactions (27), and eQq , for the electric quadrupole hfs.

The matrix elements are

$$\begin{aligned} \langle N'J'F; v=0 | H_{\text{HFS}} | NJF; v=0 \rangle &= -t\sqrt{30} \times (-1)^{J+J'+F+N'} \left\{ \begin{matrix} F & J' & I \\ 1 & I & J \end{matrix} \right\} \left\{ \begin{matrix} S & S & 1 \\ N' & N & 2 \\ J' & J & 1 \end{matrix} \right\} \left\{ \begin{matrix} N' & 2 & N \\ 0 & 0 & 0 \end{matrix} \right\} \\ &\times \sqrt{I(I+1)(2I+1)S(S+1)(2S+1)(2J+1)(2J'+1)(2N+1)(2N'+1)} \\ &+ b_F \delta_{N'N} (-1)^{J+J'+F+S+N+J+1} \left\{ \begin{matrix} F & J' & I \\ 1 & I & J \end{matrix} \right\} \left\{ \begin{matrix} S & J' & N \\ J & S & 1 \end{matrix} \right\} \\ &\times \sqrt{I(I+1)(2I+1)S(S+1)(2S+1)(2J+1)(2J'+1)} \\ &+ \frac{1}{4} eQq (-1)^{J+J'+F+S+N+J'+2+N'} \left\{ \begin{matrix} F & J' & I \\ 2 & I & J \end{matrix} \right\} \left\{ \begin{matrix} N' & J' & S \\ J & N & 2 \end{matrix} \right\} \left\{ \begin{matrix} N' & 2 & N \\ 0 & 0 & 0 \end{matrix} \right\} \\ &\times \sqrt{\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)}} (2J+1)(2J'+1)(2N+1)(2N'+1). \quad (6) \end{aligned}$$

Concerning the excited $^1\Delta$ state, for which only the main isotopomer $^{32}\text{S}^{16}\text{O}$ has been observed, the Hamiltonian simplifies considerably since spin-doubling and spin-spin interaction are of no importance. The Λ -doubling has not been resolved in the experiment and thus remains of no consequence. The same holds for the hyperfine interactions because all available experimental data concern $^{32}\text{S}^{16}\text{O}$, with both nuclear spins zero. Thus, all observable effects are already described by Eq. (1).

4. DISCUSSION

The newly observed $^3\Sigma$ transitions, shown in Table I, have been fitted for all isotopomers simultaneously together with all available data in the literature to yield the

TABLE I
All New Measured Lines of $X^3\Sigma$ SO

N'	J'	\leftarrow	N''	J''	ν	ν_{exp}	$\Delta\nu_{exp}$	obs.-calc.
$^{32}\text{S}^{16}\text{O}$								
24	23		23	23	0	885 840.735	0.100	-0.005
21	20		20	19	0	902 381.845	0.100	-0.018
21	21		20	20	0	902 741.303	0.100	-0.011
21	22		20	21	0	902 986.470	0.100	-0.010
24	23		23	22	0	1 031 028.107	0.100	0.007
24	24		23	23	0	1 031 264.663	0.100	0.010
24	25		23	24	0	1 031 412.068	0.100	-0.009
21	20		20	19	1	895 147.482	0.100	-0.016
21	21		20	20	1	895 518.535	0.100	-0.036
21	22		20	21	1	895 772.761	0.100	-0.025
24	23		23	22	1	1 022 764.699	0.100	0.028
24	24		23	23	1	1 023 009.882	0.100	0.009
24	25		23	24	1	1 023 164.003	0.100	0.016
21	20		20	19	2	887 930.707	0.150	-0.034
21	21		20	20	2	888 313.862	0.150	-0.030
21	21		20	20	3	881 126.684	0.150	-0.004
21	22		20	21	3	881 400.203	0.150	-0.014
$^{34}\text{S}^{16}\text{O}$								
21	20		20	19	0	884 739.034	0.100	-0.004
21	21		20	20	0	885 115.263	0.100	-0.004
21	22		20	21	0	885 375.420	0.100	-0.018
25	24		24	23	0	1 052 890.500	0.100	0.016
25	25		24	24	0	1 053 108.612	0.100	0.013
25	26		24	25	0	1 053 242.365	0.100	-0.001
25	24		24	23	1	1 044 534.968	0.150	0.027
25	25		24	24	1	1 044 761.096	0.150	0.033
25	26		24	25	1	1 044 901.023	0.150	-0.002
$^{32}\text{S}^{18}\text{O}$								
3	3		2	2	0	119 573.675 ^(a)	0.050	-0.001
4	5		3	4	0	166 285.304	0.050	-0.020
26	25		25	24	0	1 034 063.062	0.100	-0.030
26	26		25	25	0	1 034 288.172	0.100	-0.054

(a) Already measured by Tiemann (5) with lower accuracy.

isotopically invariant parameters shown in Table II. The comparison to the values reported by Bogey *et al.* (9) shows good agreement; the new data have mainly contributed to determine higher order terms of the expansions involved in Eqs. (1), (4) and (5). In the overall fit, the hyperfine constants for the ^{33}S nucleus have also been determined. Table III shows that they agree very well with the previous values determined by Amano *et al.* (4).

TABLE I—*Continued*

N'	J'	F'	\leftarrow	N''	J''	F''	ν_{exp}	$\Delta\nu_{exp}$	obs.-calc.
$^{33}\text{S}^{16}\text{O}$ $v = 0$									
3	3	1.5		2	2	0.5	127 825.444	0.050	-0.003
3	3	2.5		2	2	1.5	127 826.341	0.050	0.011
3	3	3.5		2	2	2.5	127 832.048	0.050	0.003
3	3	4.5		2	2	3.5	127 842.538	0.050	-0.012
3	4	2.5		2	3	1.5	136 934.062	0.050	-0.054
3	4	3.5		2	3	2.5	136 939.382	0.050	0.012
3	4	4.5		2	3	3.5	136 943.680	0.050	-0.008
3	4	5.5		2	3	4.5	136 946.184	0.050	-0.013
4	3	3.5		3	2	2.5	157 173.508	0.200	0.112
4	3	2.5		3	2	1.5	157 173.508	0.200	-0.137
4	3	4.5		3	2	3.5	157 179.478	0.050	-0.007
4	3	1.5		3	2	0.5	157 180.432	0.050	0.007
4	4	2.5		3	3	1.5	170 439.124	0.050	-0.054
4	4	3.5		3	3	2.5	170 440.278	0.050	-0.011
4	4	4.5		3	3	3.5	170 443.512	0.050	-0.022
4	4	5.5		3	3	4.5	170 448.469	0.050	-0.027
4	5	3.5		3	4	2.5	176 924.190	0.050	-0.020
4	5	4.5		3	4	3.5	176 927.879	0.050	-0.002
4	5	5.5		3	4	4.5	176 930.684	0.050	-0.018
4	5	6.5		3	4	5.5	176 932.150	0.050	-0.003
21	20	19.5		20	19	18.5	893 280.441	0.200	0.065
21	20	20.5		20	19	19.5			0.036
21	20	18.5		20	19	17.5			-0.054
21	20	21.5		20	19	20.5			-0.109
21	21	19.5		20	20	18.5	893 648.651	0.200	0.157
21	21	20.5		20	20	19.5			0.065
21	21	21.5		20	20	20.5			-0.051
21	21	22.5		20	20	21.5			-0.167
21	22	20.5		20	21	19.5	893 901.630	0.200	0.165
21	22	21.5		20	21	20.5			-0.013
21	22	23.5		20	21	22.5			-0.088
21	22	22.5		20	21	21.5			-0.106
24	23	22.5		23	22	21.5	1 020 638.291	0.200	0.066
24	23	23.5		23	22	22.5			0.040
24	23	21.5		23	22	20.5			-0.020
24	23	24.5		23	22	23.5			-0.073
24	24	22.5		23	23	21.5	1 020 881.961	0.200	0.192
24	24	23.5		23	23	22.5			0.121
24	24	24.5		23	23	23.5			0.032
24	24	25.5		23	23	24.5			-0.056
24	25	23.5		23	24	22.5	1 021 035.850	0.200	0.130
24	25	24.5		23	24	23.5			-0.006
24	25	26.5		23	24	25.5			-0.056
24	25	25.5		23	24	24.5			-0.075

TABLE II

Isotopically Invariant Parameters for the SO Radical Determined in the Present Fit
in Comparison to Values Obtained by Other Authors (9, 10)

Parameter	This work	Bogey et al. ^(a)	Tiemann ^(a)	unit
U_{01}^S	230387.575 (12) ^(b)	230387.620 (26)	230387.6 (18)	MHz amu
U_e^{BO}	230416.923 (73)	230416.20 (30)	230415.80 (37)	MHz amu
U_{01}^S	7.796 (96)	7.23 (22)	7.19 (61)	MHz amu
U_{01}^O	21.553 (82)	21.34 (13)	21.0 (12)	MHz amu
U_{11}	-6001.480 (64)	-6001.73 (14)	-6003 (17)	MHz amu ^{3/2}
U_{21}	25.638 (97)	25.94 (18)		MHz amu ²
U_{31}	-0.867 (48)	-0.954 (63)		MHz amu ^{5/2}
U_{02}	-3.85474 (29)	-3.8525 (11)	3.8527 (33)	MHz amu ²
U_{12}	-0.00624 (26)	-0.00052 ^(c)		MHz amu ^{5/2}
U_{03}	-0.0000046 (31)	-0.0000024 ^(c)		MHz amu ³
G_{00}	-1787.501 (96)	-1787.77 (21)	-1787.59 (23)	MHz amu
G_{10}	-44.95 (64)	-44.07 (77)	-44.5 (15)	MHz amu ^{3/2}
G_{20}	1.47 (77)			MHz amu ²
G_{01}	-0.05966 (94)	-0.0485 (94)	-0.049 (15)	MHz amu ²
L_{00}^S	157795.19 (12)	157795.671 (74)	157795.04 (81)	MHz
L_e^{BO}	157787.64 (25)	157787.77 (62)	157782.25 (54)	MHz
L_{00}^S	-0.40 (36)	-0.53 (43)	-1.09 (20)	MHz
L_{00}^O	-7.15 (20)	-7.37 (43)	-10.62 (69)	MHz
L_{01}	3.2395 (43)	3.255 (13)	3.266 (15)	MHz amu
L_{11}	0.183 (18)	0.150 (42)		MHz amu ^{3/2}
L_{10}	2982.2 (11)	2977.57 (62)	2981.4 (65)	MHz amu ^{1/2}
L_{20}	104.5 (27)	115.7 (12)	116 (11)	MHz amu
L_{30}	21.6 (22)	13.44 (45)		MHz amu ^{3/2}
L_{40}	-2.05 (55)			MHz amu ²
Δ_{01}^S	-1.972 (24) ^(c)	-1.830 (56)	-1.82 (15)	
Δ_{01}^N	-2.727 (10) ^(c)	-2.700 (24)	-2.66 (15)	

(a) Values converted to mass-independent parameters.

(b) Values in brackets: 1σ .

(c) Derived value.

These constants allow us to perform highly accurate frequency predictions higher than 1 THz for the various isotopomers covering a wide range of vibrational states. The predictions are available from the authors upon request. A major improvement in the spectrum with astrophysical relevance has been achieved for ^{33}SO , where the submillimeter-wave spectrum could not be predicted with a high level of confidence on the basis of the only previous analysis by Amano *et al.* (4).

As already pointed out, the analysis of the excited electronic $^1\Delta$ state is straightforward. Our transitions together with all lines reported in the literature (6, 7) are listed in Table IV. A global fit of these data leads to new mass-independent parameters, shown in Table V. Corrections to the Born–Oppenheimer approximation could not be considered, because only $^{32}\text{S}^{16}\text{O}$ has been measured in the microwave region until now and so Eq. (2) is not applicable. Thus, the U_{01} value can be expanded as soon as data on ^{34}SO and S^{18}O become available. In this context, we would like to mention that for Δ states the isotopic dependence of U_{01} is also influenced by small contributions

TABLE III
SO: Hyperfine Structure Parameters (MHz) for the
 ^{33}S Nucleus Determined in the Global Fit

Parameter	This work	Amano et al.
b_F	18.875 (53) ^(a)	18.83 (21)
t	-32.202 (47)	-32.167 (67)
eQq	-16.22 (38)	-15.9 (3)

(a) Values in brackets: 1σ .

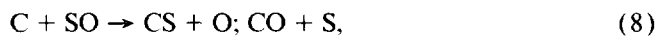
from interactions with Π and Φ states, whereas such interactions do not appear in a Σ state.

5. ASTROPHYSICAL IMPLICATIONS

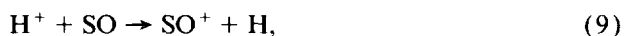
First detected in interstellar space more than 20 years ago, SO is found in a variety of interstellar environments by radioastronomical detection of its rotational spectrum (29). In cool dense interstellar clouds, characterized by a gas temperature of 10 K, a gas density of 10^4 cm^{-3} which is overwhelmingly in the form of H_2 , and little if any penetration of external visible radiation, SO is found to have a fractional abundance with respect to the overall gas density in the neighborhood of $\approx 10^{-9}$ or even greater. In particular, its fractional abundance in the well-studied dense cloud TMC-1 is 5×10^{-9} (30). Gas-phase chemical models are able to reproduce the observed fractional abundance assuming that the molecule is formed predominantly by the neutral-neutral reaction



and destroyed by the reaction



as well as by a variety of ion-molecule reactions such as



although the low temperature rates of the neutral-neutral reactions are not well determined (31).

The SO molecule is found to have a greatly enhanced abundance in selected regions of giant dense interstellar clouds characterized by high temperatures and gas densities due either to heat generated during the formation of a star via gravitational collapse or to heat from the infant star itself. In these so-called star formation regions, even higher temperatures, reaching thousands of K, are sporadically generated by shock waves travelling through the material. The best known such shock source is called the "plateau" source, and is found in the Orion Molecular Cloud, a very well-known and relatively nearby giant interstellar cloud. In the "plateau" source, the fractional abundance of SO increases by more than two orders of magnitude from its background value of 9×10^{-10} to 5×10^{-7} (29). Since the SO is also highly excited, the high-

TABLE IV

¹Δ SO: All Lines Included in the Global Fit

N'	J'	\leftarrow	N''	J''	v	ν_{exp}	$\Delta\nu_{exp}$	obs.-calc.
3	3		2	2	0	127 770.416 ^(a)	0.100 ^(b)	0.133
4	4		3	3	0	170 356.467 ^(a)	0.100 ^(b)	0.007
5	5		4	4	0	212 939.337 ^(a)	0.100 ^(b)	0.058
6	6		5	5	0	255 518.037 ^(a)	0.100 ^(b)	0.138
8	8		7	7	0	340 659.165 ^(c)	0.050	-0.016
9	9		8	8	0	383 220.117 ^(c)	0.050	-0.044
21	21		20	20	0	893 120.312 ^(d)	0.150	0.096
24	24		23	23	0	1 020 253.369 ^(d)	0.150	-0.046
8	8		7	7	1	337 759.315 ^(c)	0.050	0.006
9	9		8	8	1	379 957.766 ^(c)	0.050	0.009
8	8		7	7	2	334 860.867 ^(c)	0.050	-0.006
9	9		8	8	2	376 696.963 ^(c)	0.050	-0.005
8	8		7	7	3	331 963.161 ^(c)	0.050	-0.010
9	9		8	8	3	373 437.007 ^(c)	0.050	0.002
8	8		7	7	4	329 065.541 ^(c)	0.050	0.041
9	9		8	8	4	370 177.054 ^(c)	0.050	-0.024
8	8		7	7	5	326 167.134 ^(c)	0.050	-0.026
9	9		8	8	5	366 916.416 ^(c)	0.050	0.019

(a) Clark et al. (6).

(b) No uncertainty stated in Ref. (6).

(c) Endo et al. (7).

(d) This work.

frequency lines reported here will be excellent tracers of high-temperature SO. A variety of chemical models which include the effects of shock waves have been developed to explain the enhanced abundances of SO and other molecules in shocked sources (32). These shock models have large uncertainties in them and must compete with other models, in which the excitation stems primarily from the radiation of the newly born star, forming what is now known as a “photon-dominated region” or PDR.

The SO molecule has also been detected in the cores of so-called Galactic cirrus interstellar clouds (20). These cores have similar to somewhat lower gas densities than standard dense clouds but, given their small size and their placement inside more diffuse regions of space, they are beset by higher levels of external radiation. We have recently run models to study the SO abundance in such sources and find that, providing the degree of ultraviolet penetration is not too great, the model results can approach the observations, which show fractional abundances in excess of 10^{-9} .

TABLE V

SO: Molecular Constants of the $a^1\Delta$ State Determined in the Present Work in Comparison to Values Obtained by Endo *et al.* (7)

Parameter	This work	Endo <i>et al.</i> ^(a)	unit
U_{01}	228003.262 (44) ^(b)	228003.406 (115) ^(c)	MHz amu
U_{11}	-6313.60 (17)	-6313.512 (480)	MHz amu ^{3/2}
U_{21}	8.84 (21)	8.77 (60)	MHz amu ²
U_{31}	-2.714 (75)	-2.69 (22)	MHz amu ^{5/2}
U_{02}	-3.9708 (25)	-3.9847 (94)	MHz amu ²
U_{12}	-0.0290 (51)	-0.020 (16)	MHz amu ^{5/2}
U_{03}	-0.000132 (25)		MHz amu ³

(a) Values converted to mass-independent parameters.

(b) Values in brackets: 1σ .

(c) Values in brackets: 2.5σ .

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Note Added in Proof. After the submission of this manuscript, we learned that Cazzoli *et al.* (*J. Mol. Spectrosc.* **167**, 468–471, 1994) had reported FIR measurements of ^{32}SO in both the ground electronic state and the $a^1\Delta$ excited state. Their observed transitions between 570 and 1880 GHz obtained by laser sideband spectroscopy agree with our predictions to within the standard error of 500 kHz estimated by Cazzoli *et al.* For three lines at 1031 GHz measured with both techniques, the deviations in frequency are between 150 and 450 kHz.

Furthermore, we have become aware of a recent publication by Yamamoto (*Chem. Phys. Lett.* **212**, 113–117, 1993) in which the rotational spectra of SO and ^{34}SO in the $b^1\Sigma^+$ excited electronic state are reported for the first time.

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