

Millimeter spectrum and molecular constants of silicon monoxide*

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A new high-temperature millimeter-wave microwave spectrometer has been constructed and used to measure a wide range of vibrational and rotational states of silicon monoxide. This work results in accurate rest frequencies for all of the interstellar SiO maser transitions that have been observed as well as accurate measurements or predictions of all transitions that are likely to be of astrophysical interest. In addition, the Dunham spectral and potential constants are calculated for the three major isotopic species. For $^{28}\text{Si}^{16}\text{O}$: $Y_{01} = 21\,787.453(11)$ MHz, $Y_{11} = -151.026(11)$ MHz, $Y_{21} = 70.5(24)$ kHz, $Y_{02} = -29.38(13)$ kHz, $a_0 = 5.390(22) \times 10^5$ cm $^{-1}$, $a_1 = -2.9899(41)$, $a_2 = 5.7(7)$, $a_3 = -9.0(5)$. The calculated equilibrium parameters for $^{28}\text{Si}^{16}\text{O}$ are $B_e = 21\,787.5(10)$ MHz, $\omega_e = 1252.(3)$ cm $^{-1}$, $\omega_e x_e = 5.96(71)$ cm $^{-1}$, and $r_e = 1.509\,73(4)$ Å.

INTRODUCTION

In 1968, Törring¹ reported the laboratory measurement of the $J=0 \rightarrow 1$ rotational transitions of $^{28}\text{Si}^{16}\text{O}$ in the 43-GHz region for four vibrational states, $v=0, 1, 2, 3$. Meanwhile, a maser signal at 86 243 MHz, observed by radioastronomers² in the nebular source Orion A, has been assigned to the $J=2 \rightarrow 1$, $v=1$ transition of $^{28}\text{Si}^{16}\text{O}$ by Lovas and Johnson³ from a theoretical prediction of the frequency based on Törring's measurement of the $J=0 \rightarrow 1$ transition. Since that time, SiO maser emission lines corresponding to the transitions $v=1$, $J=1 \rightarrow 0$; $v=1$, $J=2 \rightarrow 1$; $v=1$, $J=3 \rightarrow 2$; and $v=2$, $J=1 \rightarrow 0$ have been observed in 20 astronomical sources.⁴

With the present work, direct laboratory measurements have been made of the frequencies of all of the transitions which give rise to the important maser signals from outer space, and measurements of the rotational spectrum of $^{28}\text{Si}^{16}\text{O}$ are extended to 303 926.96 GHz. These measurements, shown in Table I, include seven rotational transitions of $^{28}\text{Si}^{16}\text{O}$ in five vibrational states. They allow precise evaluation of the centrifugal distortion effects which influence all rotational and vibrational constants of the molecule and which cannot be evaluated from the $J=0 \rightarrow 1$ transition alone. These constants make possible the accurate prediction of all transitions that are likely to be of astrophysical interest. Figure 1 shows the laboratory, real-time oscilloscope display of the most commonly observed astrophysical maser, the $J=2 \rightarrow 1$, $v=1$ transition.

EXPERIMENT

A sufficient concentration of silicon monoxide vapor for microwave absorption measurements was produced by the heating of a homogeneous

mixture of silicon and silicon dioxide to 1350°C in a high-temperature reaction chamber which also served as the microwave absorption cell. This combination of reaction chamber and absorption cell consisted of a Mullite MV30 ceramic tube (9 × 45 cm) concentrically positioned inside a cold-rolled steel pipe (25 × 105 cm) which was connected to a pumping line. For the purpose of mechanical support and thermal insulation, the volume between the ceramic tube and the outer steel jacket was filled with A.P. Green G-26 insulating firebricks. The heating element was constructed from ten graphite welding rods which were electrically connected in series and equally spaced around the inside of the Mullite tube.

A tapered horn combined with a Teflon lens focused the microwave radiation into the reaction chamber and through the vapor above the reactants. The radiation emerging from the reaction zone was then focused onto a sensitive InSb radiation detector operated at 1.6°K. The detected absorption-line signals, after amplification, were displayed on an oscilloscope for the frequency measurements. Description of the millimeter-wave spectrometer and measuring techniques are given in an earlier publication.⁵

DATA AND ANALYSIS

The most accurate formulas for analysis of the rotational spectra of diatomic molecules are provided by Dunham theory.⁶ Dunham solved the Schrödinger wave equation for the diatomic vibrating rotor with a potential function of the form

$$V(\xi) = cha_0\xi^2(1 + a_1\xi + a_2\xi^2 + \dots), \quad (1)$$

where $\xi = (r - r_e)/r_e$, $a_0 = \omega_e^2/4B_e$, and a_1, a_2, \dots are the potential constants. His solution for the rotation-vibration energies is expressed by the

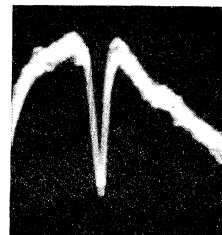
TABLE I. Observed transitions of silicon monoxide.

$J \rightarrow J+1$	v	Measured frequencies (MHz)	Difference from calculated frequencies (MHz)
$^{28}\text{Si}^{16}\text{O}$			
0 → 1	0	43 423.76 ^a	-0.04
	1	43 122.03 ^a	0.00
	2	42 820.48 ^a	-0.06
	3	42 519.34 ^a	0.01
1 → 2	0	86 846.96	0.07
	1	86 243.37	0.02
	2	85 640.46	0.09
2 → 3	0	130 268.61	0.04
	1	129 363.24	-0.02
3 → 4	0	173 688.31	0.16
	1	172 481.15	0.09
	2	171 275.28	0.18
	3	170 070.35	0.07
4 → 5	0	217 104.98	0.09
	1	215 595.95	-0.09
	2	214 088.54	-0.06
	3	212 582.60	0.04
	4	211 077.87	-0.07
5 → 6	0	260 518.02	-0.09
	1	258 707.45	-0.04
6 → 7	0	303 926.96	-0.15
$^{29}\text{Si}^{16}\text{O}$			
0 → 1	0	42 879.82 ^a	0.00
$^{30}\text{Si}^{16}\text{O}$			
0 → 1	0	42 373.34 ^a	0.00

^aReference 1.

series

$$E_{v,J} = h \sum_{l,m} Y_{l,m} (v + \frac{1}{2})^l [J(J+1)]^m, \quad (2)$$

in which the coefficients $Y_{l,m}$ are now known asFIG. 1. Video display of the $J=1 \rightarrow 2$, $v=1$ transition of $^{28}\text{Si}^{16}\text{O}$.

Dunham's constants. Each $Y_{l,m}$ is a function of the molecular parameters $r_e, a_0, a_1, a_2, \dots$ which appear in Eq. (1). In terms of the familiar spectroscopic constants,

$$Y_{10} \approx \omega_e, \quad Y_{01} \approx B_e, \quad Y_{11} \approx -\alpha_e, \quad Y_{21} \approx \gamma_e, \quad (3)$$

$$Y_{20} \approx -\omega_e x_e, \quad Y_{02} \approx -D_e, \quad Y_{12} \approx -\beta_e, \quad Y_{03} \approx H_e.$$

With the selection rules $J \rightarrow J+1$ and $v \rightarrow v$ for pure rotational transitions, Eq. (2) predicts the rotational frequencies to be

$$\nu_{v,J \rightarrow v, J+1} = 2[Y_{01} + Y_{11}(v + \frac{1}{2}) + Y_{21}(v + \frac{1}{2})^2 + \dots](J+1) + 4Y_{02}(J+1)^3 + \dots, \quad (4)$$

where only terms which give a detectable contribution to the spectra reported in this paper are retained. For the less abundant isotopic species the Dunham isotope relation,

$$Y'_{l,m} = (\mu/\mu')^{(l+2m)/2} Y_{l,m}, \quad (5)$$

is accurate to within experimental error for all $Y_{l,m}$ except $Y_{0,1}$. In Eq. (5) μ' denotes the reduced mass of the less abundant species, and the unprimed parameters, $Y_{l,m}$ and μ , refer to the parent species ($^{28}\text{Si}^{16}\text{O}$).

The silicon monoxide microwave spectrum was analyzed by substitution of each measured absorption frequency and the appropriate J and v quantum numbers into Eq. (4). In this manner a

TABLE II. Comparison of molecular constants measured in this work with previous values.

Constants	$^{28}\text{Si}^{16}\text{O}$		$^{29}\text{Si}^{16}\text{O}$		$^{30}\text{Si}^{16}\text{O}$	
	This work ^a	Others	This work	Others	This work	Others
Y_{01} (MHz)	21 787.453(11)	21 787.462(25) ^b	21 514.046(13)	21 514.074(25) ^b	21 259.494(13)	21 259.425(25) ^b
Y_{11} (MHz)	-151.026(11)	-151.05(4) ^b	-148.193(11)	-148.22(4) ^b	-145.570(11)	-145.59(4) ^b
Y_{21} (kHz)	70.5(24)	76.(1) ^b	68.7(24)	74.(1) ^b	67.1(24)	72.(1) ^b
Y_{02} (kHz)	-29.38(13)	-29.9(1) ^{b,c}	-28.64(13)	-29.2(1) ^{b,c}	-27.97(13)	-28.5(1) ^{b,c}
B_e (MHz)	21 787.5(10)		21 514.1(10)		21 259.5(10)	
ω_e (cm ⁻¹)	1 252.(3)	1 241.4(1)	1 244.(3)		1 237.(3)	
$\omega_e x_e$ (cm ⁻¹)	5.96(71)	5.9(1)	5.89(71)		5.82(71)	

^aNumbers in parentheses represent one standard deviation.^bReference 1.^cReference 7.

TABLE III. Potential constants and equilibrium bond length for silicon monoxide.

	This work ^a	Ref. 1
a_0	$5.390(22) \times 10^5 \text{ cm}^{-1}$	$5.298(1) \times 10^5 \text{ cm}^{-1}$
a_1	-2.9899(41)	-2.973(2)
a_2	5.7(7)	5.58(10)
a_3	-9.0(5)	-8.32(75)
r_e	1.509 733(40) Å	1.509 732(40) Å

^aErrors are in standard deviation.

set of N simultaneous equations in six unknowns was constructed, where N is the number of experimentally measured frequencies and where the six unknown constants are Y_{01} , Y_{11} , Y_{21} , and Y_{02} for $^{28}\text{Si}^{16}\text{O}$, plus the Y_{01} values for $^{29}\text{Si}^{16}\text{O}$ and $^{30}\text{Si}^{16}\text{O}$. By the method of least squares, this set

of equations was solved for these constants. The vibrational constants Y_{10} and Y_{20} were calculated for each isotopic species by use of the following relations:

$$Y_{10} = (4Y_{01}^3 / -Y_{02})^{1/2} \quad (6)$$

and

$$Y_{20} = \frac{3}{2}Y_{01}(a_2 - \frac{5}{4}a_1^2), \quad (7)$$

where a_1 and a_2 are the Dunham potential constants which appear in Eq. (1).

RESULTS AND COMMENTS

Table II summarizes the results of this analysis and gives a comparison of the rotational, vibrational, and potential constants derived from our measurements with those obtained by others.

TABLE IV. Predicted rotational spectrum of silicon monoxide.

Transition $v \quad J \rightarrow J'$	$^{28}\text{Si}^{16}\text{O}$		$^{29}\text{Si}^{16}\text{O}$		$^{30}\text{Si}^{16}\text{O}$	
	Predicted frequency	Uncertainty	Predicted frequency	Uncertainty	Predicted frequency	Uncertainty
0 0 → 1	43 423.798	0.015	42 879.820	0.025	42 373.340	0.025
1 0 → 1	43 122.027	0.015	42 583.710	0.028	42 082.469	0.028
2 0 → 1	42 820.539	0.015	42 287.874	0.030	41 791.866	0.030
3 0 → 1	42 519.332	0.015	41 992.314	0.030	41 501.531	0.030
4 0 → 1	42 218.407	0.026	41 697.028	0.035	41 211.465	0.034
5 0 → 1	41 917.764	0.052	41 402.018	0.053	40 921.667	0.052
0 1 → 2	86 846.891	0.028	85 758.953	0.050	84 746.009	0.050
1 1 → 2	86 243.350	0.020	85 166.732	0.056	84 164.266	0.056
2 1 → 2	85 640.373	0.022	84 575.061	0.060	83 583.060	0.060
3 1 → 2	85 037.959	0.025	83 983.940	0.060	83 002.391	0.060
4 1 → 2	84 436.110	0.052	83 393.369	0.070	82 422.259	0.069
5 1 → 2	83 834.824	0.103	82 803.348	0.106	81 842.663	0.103
0 2 → 3	130 268.574	0.037	128 636.710	0.076	127 117.335	0.076
1 2 → 3	129 363.262	0.027	127 748.379	0.085	126 244.721	0.085
2 2 → 3	128 458.796	0.030	126 860.873	0.092	125 372.912	0.092
3 2 → 3	127 555.176	0.034	125 974.192	0.092	124 501.908	0.092
4 2 → 3	126 652.402	0.075	125 088.335	0.105	123 631.710	0.104
5 2 → 3	125 750.473	0.153	124 203.303	0.158	122 762.317	0.154
0 3 → 4	173 688.142	0.046	171 512.406	0.104	169 486.647	0.104
1 3 → 4	172 481.060	0.035	170 327.964	0.118	168 323.162	0.117
2 3 → 4	171 275.105	0.041	169 144.623	0.127	167 160.750	0.127
3 3 → 4	170 070.278	0.045	167 962.381	0.126	165 999.411	0.126
4 3 → 4	168 866.579	0.098	166 781.239	0.142	164 839.147	0.140
5 3 → 4	167 664.008	0.202	165 601.196	0.210	163 679.957	0.205
0 4 → 5	217 104.891	0.058	214 385.351	0.138	211 853.275	0.137
1 4 → 5	215 596.037	0.052	212 904.800	0.157	210 398.918	0.156
2 4 → 5	214 088.594	0.061	211 425.623	0.168	208 945.902	0.167
3 4 → 5	212 582.560	0.062	209 947.820	0.166	207 494.230	0.165
4 4 → 5	211 077.936	0.122	208 471.392	0.183	206 043.899	0.181
5 4 → 5	209 574.722	0.249	206 996.339	0.264	204 594.912	0.258
0 5 → 6	260 518.114	0.084	257 254.860	0.181	254 216.546	0.180
1 5 → 6	258 707.489	0.086	255 478.198	0.206	252 471.317	0.204
2 5 → 6	256 898.557	0.095	253 703.185	0.219	250 727.699	0.217
3 5 → 6	255 091.317	0.094	251 929.823	0.216	248 985.692	0.214
4 5 → 6	253 285.768	0.152	250 158.109	0.232	247 245.296	0.228
5 5 → 6	251 481.912	0.298	248 388.046	0.322	245 506.510	0.315

Törring¹ could not determine the effects of centrifugal distortion from his microwave measurements alone; but, by combining his accurate measurements of the $J=0 \rightarrow 1$ transition with the earlier measurements of the vibrational spectra of SiO by Lagerqvist and Uhler,⁷ he was able to make corrections for these effects in his derived constants. We believe that the vibrational constant ω_e , which we have derived entirely from microwave measurements (see Table II), is more accurate than the values obtained more directly from vibrational spectra. The inclusion of Törring's frequencies for the $J=0 \rightarrow 1$ transitions with our results did not alter the constants derived from our results alone. We conclude that his measurements are at least as accurate as ours.

Table III gives the Dunham potential constants a_0, a_1, a_2, a_3 which were calculated from the $Y_{l,m}$'s of Table II. The Y_{12} constant, which is necessary for the computation of the constants a_2 and a_3 but not recorded in Table II, was found

to be zero within the limits of experimental error. A contribution to the uncertainty in the a_4 from a calculated upper limit for Y_{12} is included in our estimates of the uncertainty in the a_4 . This contribution, as well as other contributions, was neglected in Törring's uncertainties. Although our listed uncertainties are somewhat larger than those quoted for previous work, our a_i values are, in fact, substantially more accurate. The values for B_e which appear in Table II were obtained from Y_{01} by application of the Dunham correction. The wobble-stretch correction is zero to within experimental error, but a calculated upper limit on it is included in the uncertainty.⁵

Table IV shows a set of predictions of all transitions that appear to be of possible astrophysical interest as well as the uncertainties in these predictions. For the higher v, J states, these predictions are comparable in accuracy with the experimental observations, but at low v, J they are substantially better.

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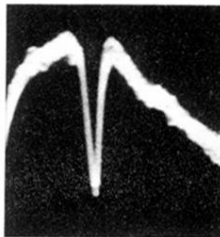


FIG. 1. Video display of the $J=1 \rightarrow 2, v=1$ transition of $^{28}\text{Si}^{16}\text{O}$.