Millimeter Wave Rotational Transitions of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ and $^{16}\mathrm{O}^{13}\mathrm{C}^{32}\mathrm{S}$

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Rotational transitions of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ and $^{16}\mathrm{O}^{13}\mathrm{C}^{32}\mathrm{S}$ in the ground vibrational state and of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ in several excited states have been accurately measured in the millimeter wave region for a minimum of four different J values. The analysis of the measured frequencies leads to rotational constants for the following vibrational states:

$0\ 0^0\ 0$ of $^{16}\mathrm{O}^{13}\mathrm{C}^{32}\mathrm{S}$ and
$0\ 0^0\ 0$, $0\ 1^{1c}\ 0$, $0\ 1^{1d}\ 0$, $0\ 2^0\ 0$, $0\ 2^{2c}\ 0$, $0\ 2^{2d}\ 0$,
$0\ 0^0\ 1$ of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$.

Since the two components of the $0\ 2^2\ 0$ transitions were resolved, an analysis of the l-type resonance was carried out and the interval $0\ 2^2\ 0 - 0\ 2^0\ 0$ has been determined to be $-4.63(10)\ \mathrm{cm}^{-1}$. The result is in good agreement with the presently available determination of this level from vibrational spectra.

Introduction

Although the ground state rotational transitions of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ have been measured to high J with great accuracy [1, 2], the only previous accurate measurements of the excited vibrational states all fall below 65 GHz [3]. Millimeter wave measurements have only been carried out for one transition of $^{18}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ and $^{16}\mathrm{O}^{13}\mathrm{C}^{32}\mathrm{S}$ in various vibrational states and for the ground state of $^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}$ [4].

We report here transitions in the ground state of both $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ and $^{16}\mathrm{O}^{13}\mathrm{C}^{32}\mathrm{S}$ as well as transitions in the lowest vibrational states of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$. The measurements were made at room temperature with samples of OCS having the natural isotopic abundances. All of the transitions were measured with the millimeter wave spectrometer described in Ref. [5], which uses a free space cell and a small computer for data acquisition and signal averaging. The measurements were originally undertaken to check the operation of our frequency measuring system in the millimeter wave region.

Table 1. Rotational transitions of $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ in the ground vibrational state.

J'	$\leftarrow J''$	obs. freq. [a] this work MHz	obs. – calc. [b] kHz	obs. freq. Winton and Gordy [2] MHz
2	1	24325.9300	1.8	
5	4	60814.2697	–4.2	
6	5	72976.7962	11.2	
7	6	85139.1208	12.2	
8	7	97301.2123	–1.3	
9	8	109463.0574	–11.2	109463.063
10	9	121624.6555	13.1	121624.638
11	10	133785.9063	2.5	133785.900
12	11	145946.8340	12.5	145946.821
13	12	158107.3676	3.3	158107.360
14	13	170267.5074	6.5	170267.494
15	14	182427.2114	11.2	182427.198
16	15	194586.4276	–3.1	194586.433
17	16	206745.1870	25.6	206745.161
18	17	218903.3743	13.3	
19	18	231061.0220	23.9	
20	19	243218.0743	32.6	243218.040
21	20	255374.4571	–3.2	255374.461
22	21	267530.2387	15.8	
23	22	279685.3176	19.6	
24	23	291839.6860	31.4	
25	24	303993.2421	–19.1	

[a] Estimated experimental accuracy is ±15 kHz for frequencies up to 200 GHz and ±30 kHz for those over 200 GHz.
[b] Calculated values were obtained using the constants given in Table 4.

Data and Results

In Table 1 the ground state transitions measured for $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ are listed. Half of these frequencies have also been measured by Winton and Gordy using the saturation dip technique [2]. In all but two cases the present measurements fall within 17 kHz of the saturation dip values; the largest difference is 34 kHz. We thus feel justified in giving the estimated errors as shown, 15 kHz for measurements below

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200 GHz and 30 kHz above 200 GHz (these measurements were carried out before recent improvements in the measuring accuracy of the spectrometer [6]).

The rotational constants for the ground state were obtained by fitting the observed frequencies to the expression

$$\nu = 2\,B_0(J+1) - 4\,D_0(J+1)^3 + 2\,H_0(J+1)^3\,(3\,J^2+6\,J+4)\,. \qquad (1)$$

The constants for each of the other states considered here were obtained using the expression

$$\nu = 2\,B_\mathrm{v}(J+1) - 4\,D_\mathrm{v}(J+1)\,[\,(J+1)^2 - l^2\,]\,. \qquad (2)$$

We fit simultaneously, with weighting inversely proportional to the estimated errors, all reliable ground state data for $^{16}O^{12}C^{32}S$ as reviewed by Maki[7]. These data include the Winton and Gordy measurements[2], and our measurements as given in Table 1 for those transitions not measured by Winton and Gordy. The slight difference between the constants obtained here and in Ref. [7] is due to different estimates of the experimental errors of our measurements.

Transitions measured for the ground state of $^{16}O^{13}C^{32}S$ are given together with those of Maki and Johnson[4] in Table 2. The rotational constants for this molecule given in Table 4 were found from a weighted fit of all six of these frequencies.

The newly measured excited state transitions of $^{16}O^{12}C^{32}S$ are listed in Table 3, and the effective rotational constants obtained for each state from these measurements alone are listed in Table 4.

Table 2. Rotational transitions of $^{16}O^{13}C^{32}S$ in the ground vibrational state.

$J' \leftarrow J''$		Observed frequency MHz	obs. − calc. kHz
2	1	24247.668 (10) [a]	9.2
3	2	36371.390 (30) [a]	−20.3
7	6	84865.166 (15) [b]	−3.0
10	9	121233.301 (15) [b, a]	−3.8
14	13	169719.648 (15) [b]	6.5
15	14	181840.209 (15) [b]	−3.9

[a] From Ref. [4]. [b] Present work.

Table 3. Rotational transitions of $^{16}O^{12}C^{32}S$ in excited vibrational states.

$J' \leftarrow J''$		v_1	v_2^l	v_3	Observed frequency [a] MHz	obs. − calc. [b] kHz
7	6	0	0^0	1	84885.188	5
		0	1^{1c}	0	85242.800	2
		0	1^{1d}	0	85331.824	−9
		0	2^0	0	85401.177	7
		0	2^{2c}	0	85433.833	−5
		0	2^{2d}	0	85434.156	6
10	9	0	0^0	1	121261.832	−8
		0	1^{1c}	0	121772.716	−9
		0	1^{1d}	0	121899.928	9
		0	2^0	0	121999.429	−6
		0	2^{2c}	0	122045.138	5
		0	2^{2d}	0	122046.037	−6
14	13	0	0^0	1	169759.449	10
		0	1^{1c}	0	170474.706	7
		0	1^{1d}	0	170652.759	−14
		0	2^0	0	170793.315	−1
		0	2^{2c}	0	170854.734	0
		0	2^{2d}	0	170857.232	−3
15	14	0	0^0	1	181882.798	−6
		0	1^{1c}	0	182649.161	1
		0	1^{1d}	0	182839.968	14
		0	2^0	0	182990.933	−2
		0	2^{2c}	0	183055.908	−1
		0	2^{2d}	0	183058.987	3
20	19	0	1^{1c}	0	243513.679	−2
		0	1^{1d}	0	243768.075	−2

[a] Estimated experimental accuracy is ±15 kHz for frequencies up to 200 GHz and ±30 kHz for those over 200 GHz.

[b] Calculated values were obtained using the constants given in Table 4.

Isotopic species	Vibrational state			B_v / MHz	D_v / kHz	H_v / Hz×10^4
$^{16}O^{12}C^{32}S$	0	0^0	0	6081.492475 (81)	1.301777 (90)	−0.25 (14) [b]
	0	0^0	1	6063.35748 (70)	1.3274 (18)	— [c]
	0	1^{1c}	0	6088.89837 (28)	1.32374 (47)	— [c]
	0	1^{1d}	0	6095.25802 (54)	1.32344 (93)	— [c]
	0	2^0	0	6100.19105 (46)	1.0964 (12)	— [c]
	0	2^{2c}	0	6102.55846 (33)	1.5720 (9)	— [c]
	0	2^{2d}	0	6102.56019 (44)	1.3440 (12)	— [c]
$^{16}O^{13}C^{32}S$	0	0^0	0	6061.92510 (59)	1.2993 (16)	— [d]

Table 4.
Rotational constants [a] determined for $^{16}O^{12}C^{32}S$ and $^{16}O^{13}C^{32}S$.

[a] Errors shown are standard deviations.

[b] Data from present work and frequencies listed in Ref. [7] were used.

[c] Data from present work only were used.

[d] Data from present work and from Ref. [4] were used.

The constants would not be improved by including the data of Ref. [3], since the accuracy of the present frequencies is greater. The vibrational state 001 is the first excited state of the lower frequency stretching mode, following the notation of Reference [7]. In addition to the effective constants we have given in Table 5 the constants obtained by averaging the frequencies of the symmetric and antisymmetric components of the rotational *l*-type doublets, $01^{1c}0$ and $01^{1d}0$, for each *J*.

Table 5. Constants [a] determined for the states $0\,1^1\,0$ and $0\,2^{0,2}\,0$ of $^{16}O^{12}C^{32}S$.

Vibrational state	Constant	Value
$0\ \ 1^1\ \ 0$	B_v / MHz	6092.07820(21)
	D_v / MHz	1.32359(36)
$0\ \ 2^{0,2}\ \ 0$	B_v / MHz	6100.19117(54)
	D_v / MHz	1.3375(5)
	γ_{ll} / MHz	0.59227(19)
	ϱ / kHz	0.0131(13)
	q_2 / MHz	6.272 [b]
	$4g$ / cm^{-1}	−4.63(10) [c]

[a] Errors given are standard deviations.

[b] Average of values given in Ref. [7] for $v_2=1$ and $v_2=3$.

[c] Error indicates range found by setting $\varrho=0$ or slightly varying q_2.

The vibrational interval 02^00-02^20 was obtained by fitting the rotational transitions of the three components of the $2\,\nu_2$ state to frequency expressions which consider the *l*-type resonance but neglect the effect of the Fermi resonances in which the 02^00 level is involved. Details of the analysis procedure may be found in Reference [8]. The frequency expressions used are

$$\begin{aligned}\nu_a &= 2(J+1)B_v - 4(J+1)^3 D_v \\ &\qquad + 2(J+1)\Delta_2^{(1)} - \tfrac{1}{2}\varrho_t f',\\ \nu_s^{\pm} &= 2(J+1)B_v - 4(J+1)^3 D_v + 2(J+1)\tfrac{1}{2}\Delta_2^{(1)} \\ &\quad + \tfrac{1}{4}\varrho_t f' \pm \tfrac{1}{2}\{[\Delta_2 + \tfrac{1}{2}\varrho_t f(f-2)]^2 \\ &\qquad + 4 q_t^2 f(f-2)\}^{1/2}_{J+1} \\ &\quad \mp \tfrac{1}{2}\{[\Delta_2 + \tfrac{1}{2}\varrho_t f(f-2)]^2 + 4 q_t^2 f(f-2)\}^{1/2}_J,\end{aligned} \tag{3}$$

where

$$f = J(J+1) \quad \text{and} \quad \begin{aligned} f' &= [f(f-2)]_{J+1} - [f(f-2)]_J \\ &= -4(J+1) + 4(J+1)^3 \end{aligned} \tag{4}$$

and

$$\begin{aligned} E_2 - E_0 = \Delta_2 &= \Delta_2^{(0)} + \Delta_2^{(1)} J(J+1) \\ &= 4[g_{l_t l_t} - 4 D_v - B_v - 4\gamma_{l_t l_t}] \\ &\quad + 4[\gamma_{l_t l_t} + 2 D_v] J(J+1)\,. \end{aligned} \tag{5}$$

The expressions for ν_a, ν_s^- and ν_s^+ apply to the frequencies for $02^{2d}0$, $02^{2c}0$ and 02^00 respectively. For a triatomic molecule the constants to be determined may be represented in the simpler notation γ_{ll}, ϱ and g. The values obtained for these three constants and given in Table 5 must of course be considered as effective values, since all are influenced by the Fermi resonances.

From the observed value of the 02^00 energy level [9] and the value of the 02^20 energy level calculated by Morino and Nakagawa [10] we find that the interval 02^20-02^00 may be given by $-4.8\ \text{cm}^{-1}$. More recently Fayt [11] has arrived at the value $-5.105(40)\ \text{cm}^{-1}$ for this interval, for which we obtained $-4.63(10)\ \text{cm}^{-1}$. The Fermi resonance largely determines the vibrational interval, since the anharmonic contribution to g is only on the order of $0.02\ \text{cm}^{-1}$ (Ref. [11]), but *l*-type resonance dominates the effects on centrifugal distortion of these levels. The discrepancy between our value and that calculated by Fayt may be attributed to the *J*-dependent effects of the Fermi resonance.

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