The Millimeter Wave Rotational Spectra of Carbonyl Sulfide

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The following rotational spectra of carbonyl sulfide have been accurately remeasured with a beam-absorption spectrometer:

$^{16}O^{12}C^{32}S$ in the vibrational ground state and in the vibrational state $0\,1^1\,0$.

$^{16}O^{12}C^{34}S$ in the vibrational ground state.

The ground state spectra of the following isotopic species have been measured with a video spectrometer:

$^{17}O^{12}C^{32}S$, $^{18}O^{12}C^{32}S$, $^{16}O^{13}C^{32}S$, $^{16}O^{12}C^{33}S$, $^{16}O^{12}C^{36}S$, and $^{16}O^{13}C^{34}S$.

Our measurements have enabled us to improve the molecular constants notably for these cases.

In order to test the performances of our molecular beam spectrometer we carried out a procedure which is normal amongst microwave spectrocopists, namely we measured lines of OCS. During these experiments it became clear that existing measurements were insufficiently accurate for our purposes. Since OCS is a molecule of fundamental importance in molecular spectroscopy as well as in astrophysics we have accurately remeasured its millimeter-wave spectrum.

All isotopic species have been measured in natural abundance. The most intense lines have been observed with a molecular beam spectrometer. This spectrometer has been described elsewhere [1, 2]. High resolution is obtained by using a molecular beam perpendicular to the direction of propagation of the microwave radiation. This spectrometer allows a reduction of the Doppler broadening by a factor of sixty the experimental line width at 73 GHz is about 2 kHz (HWHM) for the $J = 5 \rightarrow 6$ line. The accuracy of the measurements is between 1 and 5 kHz depending of the S/N ratio and the line width. The other lines have been measured with a cooled video spectrometer using the same superheterodyne detection scheme as in the beam spectrometer.

The measurements and their estimated uncertainties are listed in Tables 1 to 7. The expressions used

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Table 1. Observed $J + 1 \leftarrow J$ transitions of $^{16}O^{12}C^{32}S$ in the ground vibrational state.

J.	Observed Frequency in MHZ (estimated uncertainty)	Obs.-Calc. Frequency in kHZ	Reference or Method[a]
0	12 162 9790 (10)	0.0	5
1	24 325.9270 (10)	0.2	6
2	36 488.8128 (20)	0.7	7
3	48 651.6043 (10)	0.6	P.I. Beam
4	60 814.270 (15)	−0.7	8
5	72 976.7794 (10)	−1.5	P.I. Beam
6	85 139.121 (20)	16.8	8
7	97 301.2085 (2)	0.0	9
8	109 463.063 (5)	−0.1	10
9	121 624.638 (5)	1.4	10
10	133 785.900 (5)	2.2	10
11	145 946.812 (2)	−3.4	P.I. Beam
12	158 107.360 (5)	1.9	10
13	170 267.494 (5)	−0.9	10
14	182 427.1956 (20)	1.3	P.I. Beam
15	194 586.433 (10)	7.7	10
16	206 745.161 (5)	4.6	10
17	218 903.3565 (20)	−0.1	P.I. Beam
18	231 060.983 (10)	−11.8	P.I. Video
19	243 218.040 (5)	1.1	10
20	255 374.461 (10)	2.4	10
21	267 530.239 (30)	16.4	8
22	279 685.318 (30)	18.9	8
23	291 839.673 (30)	16.2	11
24	303 993.242 (30)	−22.9	11
25	316 146.063 (30)	−29.3	P.I. Video
27	340 449.2 (20)	−78.9	12
29	364 748.960 (30)	− 6.2	11
31	389 041. (4)	−3905.2	12

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Table 1. (continued)

J.	Observed Frequency in MHZ (estimated uncertainty)	Obs.-Cal.c Frequency in kHZ	Reference cr Method[a]
32	401 191.388 (30)	− 0.2	11
35	437 624.562 (30)	27.4	11
38	474 047.560 (30)	3.9	11
39	486 184.2 (30)	−1967.3	13
41	510 457.3 (30)	−2308.9	13
57	704 437.052 (60)	−54.9	14
58	716 546.559 (60)	−58.3	14
65	801 259.782 (60)	1.4	14
66	813 353.706 (60)	51.0	14

[a] P.I. = present investigation, see text for details.

Table 2. Observed $J + 1 \leftarrow J$ transitions of $^{16}O^{12}C^{32}S$ in the vibrational state 0 1^1 0 (lower level first).

J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in kHZ	Reference or Method[a]
1	24 355.580 (40)	24.6	15
	24 381.000 (40)	− 1.0	
2	36 533.38 (20)	126.0	15
	36 571.360 (60)	−62.0	
3	48 710.80 (40)	−57.4	16
	48 761.55 (40)	−197.6	
4	60 888.35 (10)	15.9	15
	60 951.94 (10)	− 6.1	
5	73 065.6522 (20)	− 0.3	P.I. Beam
	73 141.9854 (20)	− 0.1	
6	85 242.800 (30)	19.3	8
	85 331.824 (30)	−10.1	
7	97 419.688 (2)	0.9	P.I. Beam
	97 521.462 (2)	1.8	
9	121 772.716 (15)	8.2	8
	121 899.928 (20)	10.6	
10	133 948.772 (20)	13.2	P.I. Video
	134 088.701 (20)	16.0	
11	146 124.4576 (30)	− 3.7	P.I. Beam
	146 277.1016 (20)	− 1.2	
12	158 299.775 (20)	− 8.5	P.I. Video
	158 465.105 (30)	−34.0	
13	170 474.706 (20)	12.2	8
	170 652.759 (30)	− 2.9	
14	182 649.161 (20)	0.4	8
	182 839.968 (30)	28.5	
15	194 823.155 (20)	2.8	P.I. Video
	195 026.626 (20)	−14.2	
16	206 996.665 (30)	28.2	P.I. Video
	207 212.831 (30)	− 1.2	
17	219 169.586 (5)	3.3	P.I. Beam
	219 398.483 (5)	− 0.6	
18	231 341.980 (30)	21.3	P.I. Video
	231 583.546 (30)	−16.7	
19	243 513.679 (60)	−53.1	8
	243 768.075 (60)	37.4	
24	304 362.450 (20)	−11.7	P.I. Video
	304 680.229 (20)	− 8.0	
25	316 529.955 (30)	− 3.1	P.I. Video
	316 860.462 (30)	42.8	

[a] P.I. = Present investigation.

Table 3. Observed $J + 1 \leftarrow J$ transitions of $^{16}O^{12}C^{34}S$ in the ground vibrational state.

J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in kHZ	Reference or Method[a]
0	11 865.712 (60)	49.4	17
1	23 731.302 (15)	6.6	18
2	35 596.910 (60)	41.4	18
3	47 462.3518 (20)	− 0.6	P.I. Beam
5	71 192.9380 (50)	5.1	P.I. Beam
9	118 651.680 (80)	−30.5	18
10	130 515.730 (20)	− 4.6	P.I. Video
11	142 379.4297 (30)	− 1.3	P.I. Beam
12	154 242.780 (20)	10.1	P.I. Video
13	166 105.750 (20)	25.4	19
15	189 830.28 (20)	−59.9	19
16	201 691.979 (30)	24.0	P.I. Video
17	213 553.061 (30)	1.1	P.I. Video
18	225 413.638 (30)	9.6	P.I. Video
19	237 273.635 (30)	4.4	P.I. Video
22	272 849.959 (30)	15.2	P.I. Video
23	284 707.29 (40)	−94.3	19
24	296 564.160 (50)	50.2	P.I. Video
25	308 420.102 (30)	11.5	P.I. Video
26	320 275.260 (30)	−36.7	P.I. Video

[a] P.I. = Present investigation.

Table 4. Observed $J + 1 \leftarrow J$ transitions of $^{16}O^{13}C^{32}S$ in the ground vibrational state.

J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in MHZ	Reference[a]
1	24 247.668 (20)	14.3	18
2	36 371.390 (30)	−12.7	18
5	72 741.967 (20)	2.5	P.I.
6	84 865.166 (20)	13.1	8
7	96 988.1211 (30)	− 2.1	P.I. Beam
9	121 233.301 (20)	15.7	8
10	133 355.416 (20)	1.3	P.I.
11	145 477.197 (20)	− 4.5	P.I.
12	157 598.625 (20)	10.4	P.I.
13	169 719.648 (30)	25.2	8
14	181 840.209 (20)	14.1	8
15	193 960.289 (20)	−10.9	P.I.
16	206 079.955 (60)	48.5	P.I.
17	218 198.998 (30)	14.2	P.I.
18	230 317.527 (30)	26.8	P.I.
24	303 015.090 (30)	7.8	P.I.
25	315 128.774 (30)	−28.4	P.I.

[a] P.I. = Present investigation, video measurement unless otherwise stated.

Table 5. Observed $J+1 \leftarrow J$ transitions of $^{16}O^{12}C^{33}S$ in the ground vibrational state.

J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in kHZ	Reference[a]
1	24 019.633 (30)[b]	12.2	20; 21
3	48 038.86 (40)[b]	−137.8	16; 21
5	72 057.836 (30)[b]	−51.1	P.I.
10	132 101.384 (30)	7.2	P.I.
11	144 109.240 (30)	49.1	P.I.
12	156 116.627 (30)	−12.2	P.I.
15	192 136.475 (30)	−10.0	P.I.
16	204 142.140 (30)	−25.7	P.I.
17	216 147.359 (30)	30.9	P.I.
18	228 151.943 (30)	1.0	P.I.
19	240 155.961 (30)	−15.8	P.I.
24	300 166.419 (30)	21.2	P.I.
25	312 166.302 (30)	−16.0	P.I.

[a] P.I. = Present investigation.
[b] unperturbed frequency.

Table 6. Observed $J+1 \leftarrow J$ transitions of $^{18}O^{12}C^{32}S$ in the ground vibrational state.

J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in kHZ	Reference
1	22 819.404 (20)	11.4	18
2	34 229.045 (30)	24.1	18
5	68 457.288 (30)	−19.8	P.I.
6	79 866.446 (20)	− 0.9	P.I.
10	125 500.890 (50)	61.6	18
11	136 908.755 (30)	10.8	P.I.
12	148 316.344 (30)	10.3	P.I.
13	159 723.574 (20)	4.0	P.I.
16	193 942.886 (30)	− 0.5	P.I.
17	205 348.392 (30)	−45.4	P.I.
18	216 753.488 (30)	−10.9	P.I.
19	228 158.026 (30)	−18.0	P.I.
20	239 562.039 (30)	− 6.5	P.I.
23	273 770.554 (30)	38.1	P.I.
25	296 572.970 (30)	23.7	P.I.
26	307 973.113 (30)	− 1.9	P.I.
27	319 372.529 (30)	−20.6	P.I.

[a] P.I. = Present investigation.

to fit the experimental frequencies are:

$$\nu = 2B(J+1) - 4D(J+1)^3 + H(J+1)^3[(J+2)^3 - J^3]$$

for the ground state of $^{16}O^{12}C^{32}S$ and

$$\nu = 2B(J+1) - 4D(J+1)[(J+1)^2 - l^2]$$

for the other spectra.

Table 7. Observed $J+1 \leftarrow J$ transitions for less abundant isotopes of OCS in the ground vibrational state.

Isotopic specis	J	Obs. Frequency in MHZ (Est. Uncertainty)	Obs.-Calc. Frequency in kHZ	Reference[a]
$^{16}O^{13}C^{34}S$	1	23 646.888 (30)	0.9	18
	2	35 470.264 (30)	7.2	18
	5	70 939.706 (30)	−10.2	P.I.
	10	130 051.552 (30)	8.3	P.I.
	12	153 694.203 (30)	− 4.1	P.I.
$^{17}O^{12}C^{32}S$	1	23 534.660 (30)	5.4	3; 21
	5	70 603.022 (30)	−11.8	P.I.
	10	129 434.380 (30)	14.4	P.I.
	12	152 964.856 (30)	− 7.6	P.I.
$^{16}O^{12}C^{36}S$	1	23 198.67 (10)	−62.3	22
	5	69 595.285 (30)	2.3	P.I.
	10	127 586.900 (30)	0.0	P.I.
	12	150 781.547 (30)	− 0.2	P.I.
$^{18}O^{12}C^{34}S$	1	22 239.850 (20)	7.1	18
	6	77 838.092 (30)	− 1.3	P.I.
	11	133 431.819 (30)	− 2.2	P.I.
	13	155 667.324 (30)	1.5	P.I.

[a] P.I. = Present investigation.

Table 8. Molecular constants for carbonyl sulfide[a].

Molecule	Vibrational state		B (MHZ)	D (kHZ)	Number of lines used in the fit
$^{16}O^{12}C^{32}S$[b]	$0\,0^0\,0$		6081.492106 (12)	1.301 367 (50)	38
	$0\,1^1\,0$	c	6088.896782 (63)	1.320 15 (14)	20
		d	6095.258200 (66)	1.324 89 (16)	20
$^{16}O^{12}C^{34}S$	$0\,0^0\,0$		5932.833775 (88)	1.241 26 (18)	20
$^{16}O^{13}C^{32}S$	$0\,0^0\,0$		6061.92381 (13)	1.297 73 (25)	17
$^{16}O^{12}C^{33}S$	$0\,0^0\,0$		6004.91536 (57)	1.269 92 (61)	13
$^{18}O^{12}C^{32}S$	$0\,0^0\,0$		5704.85720 (37)	1.132 63 (34)	17
$^{16}O^{13}C^{34}S$	$0\,0^0\,0$		5911.73162 (71)	1.2307 (25)	5
$^{17}O^{12}C^{32}S$	$0\,0^0\,0$		5883.6733 (13)	1.2111 (46)	4
$^{16}O^{12}C^{36}S$	$0\,0^0\,0$		5799.6926 (12)	1.1903 (44)	4
$^{18}O^{12}C^{34}S$	$0\,0^0\,0$		5559.96933 (45)	1.0768 (14)	4

[a] The errors shown in parentheses are in units of the last digit and are one standard error.
[b] For $^{16}O^{12}C^{32}S$ $H = -8.34 \pm 0.88 \times 10^{-5}$ HZ

For each spectrum, a weighted least-squares fitting of the observed transitions was carried out. All the reliable data as reviewed by Lovas [3] are included in the fit. They are also listed in Tables 1 to 7. The calculation of the standardized residuals:

$$t(\Delta\nu_i) = \Delta\nu_i / \sqrt{s^2/w_i - \sigma_i^2}$$

which should follow a Students t distribution was

of a great utility in checking the accuracy of each individual line [4].

The derived molecular constants are reported in Table 8. They are in good agreement with those obtained previously [3], but the accuracy is better. For some isotopic species the centrifugal distortion constant is determined for the first time.

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