# Submillimeter Microwave Spectrum and Spectroscopic Constants of the OCS Molecule[1]

## Less Abundant Isotopic Species of the Molecule

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Microwave spectra of the molecules $^{16}O^{13}C^{34}S$, $^{17}O^{12}C^{32}S$, $^{16}O^{12}C^{36}S$, $^{18}O^{12}C^{34}S$, $^{16}O^{13}C^{33}S$ in their natural abundances were investigated within the range 280–510 GHz. Rotational and centrifugal distortion constants are determined for the molecules in each vibrational state observed. For the first three molecules some constants of the vibrational–rotational interaction are also obtained.

## INTRODUCTION

OCS is one of the most extensively studied molecules in microwave spectroscopy. The dipole moment and rotational frequencies of some isotopic species of this molecule in various vibrational states have been well investigated (*1–3*). The precisely measured rotational spectrum of OCS serves as a natural etalon for various measurements and equipment calibrations (see, for example, Ref. (*4*)) in the centimeter range. However, in view of newer developments in the submillimeter wavelength region there is a need to extend measurements on the spectrum of this molecule to shorter wavelengths. Our investigation of the submillimeter wave spectrum of OCS in the broad frequency interval permitted us to determine more accurate values of the spectroscopic constants and to obtain, for the first time, a number of constants for the vibrational states of several of its isotopic species. In all, we have measured about 500 frequencies of the OCS rotational transitions with absorption coefficients $\gamma \geq 10^{-7}$ cm$^{-1}$ belonging to 10 isotopic species of the molecule occurring in their natural abundances. This paper is the first to report some of these investigations, and it is devoted to discussion of the rotational spectra of the isotopic species the natural abundances of which are less than 0.05%.

## EXPERIMENTAL DETAILS

The absorption spectrum of OCS was investigated at room temperature by using a RAD spectrometer. The experimental procedure and the RAD spectrometer

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TABLE I

Experimental Frequencies of Rotational Transitions of Less Abundant Isotopic Species of OCS in Different Vibrational States

| $v_1 v_2^{|1|\tau} v_3$ $\tau = c,d$ | Transition $J+1 \longrightarrow J$ | Exp. Frequency* MHz | δ corr. KHz | Exp.-Calc. KHz |
|---|---|---|---|---|
| | | $^{16}O^{13}C^{34}S$ | | |
| 00°0 | 2 - 1 | 23 646.888(10)[a] | | - 5 |
| | 3 - 2 | 35 470.264(20)[b] | | - 1 |
| | 26 - 25 | 307 323.084(14) | | - 12 |
| | 27 - 26 | 319 136.136(14) | | 7 |
| | 28 - 27 | 330 948.367(14) | | 6 |
| | 29 - 28 | 342 759.767(14) | 1 | 7 |
| | 30 - 29 | 354 570.303(14) | - 1 | 4 |
| | 31 - 30 | 366 379.949(14) | | 4 |
| | 32 - 31 | 378 188.654(14) | 166 | - 17 |
| | 41 - 40 | 484 420.860(14) | | 4 |
| | 42 - 41 | 496 218.736(14) | | - 2 |
| 01$^{1c}$0 | 2 - 1 | 23 673.410(60)[a] | | - 39 |
| | 26 - 25 | 307 667.194(56)[b] | | - 14 |
| | 27 - 26 | 319 493.404(56) | - 1 | 19 |
| | 28 - 27 | 331 318.757(56) | | 7 |
| | 29 - 28 | 343 143.281(56) | | 9 |
| | 30 - 29 | 354 966.954(56) | | 33 |
| | 31 - 30 | 366 789.633(56) | - 13 | - 34 |
| | 32 - 31 | 378 611.460(56) | | - 20 |
| | 41 - 40 | 484 960.860(56) | - 1 | 4 |
| 01$^{1d}$0 | 2 - 1 | 23 698.200(60)[a] | | - 68 |
| | 25 - 24 | 296 150.275(56)[b] | | 35 |
| | 27 - 26 | 319 828.159(56) | - 1 | 28 |
| | 28 - 27 | 331 665.863(56) | | - 6 |
| | 29 - 28 | 343 502.784(56) | | 22 |
| | 30 - 29 | 355 338.752(56) | | - 27 |
| | 31 - 30 | 367 173.873(56) | | - 18 |
| | 32 - 31 | 379 008.036(56) | - 4 | - 31 |
| | 41 - 40 | 485 468.525(56) | - 4 | - 30 |
| | 42 - 41 | 497 291.750(56) | - 59 | 38 |
| | | $^{17}O^{12}C^{32}S$ | | |
| 00°0 | 26 - 25 | 305 865.796(15)[b] | | - 21 |
| | 28 - 27 | 329 379.320(15) | 11 | 14 |
| | 29 - 28 | 341 134.861(15) | 14 | 16 |
| | 30 - 29 | 352 889.533(15) | 11 | - 8 |
| | 32 - 31 | 376 396.286(15) | - 1 | - 1 |
| | 41 - 40 | 482 127.255(15) | | 7 |
| | 42 - 41 | 493 869.554(15) | | - 7 |

* Exp. Freq. = Meas. Freg. − $\delta_{corr}$.

[a] Ref. (1, 3).

[b] The present paper.

were described in Refs. (5, 6). Figure 1 shows a part of the survey record of the OCS spectrum. The weak lines were identified using graphical techniques. The gas pressure in the absorption cell amounted to 0.5–1 Torr. Within the limits of experimental accuracy line shifts due to pressure were not observed (i.e., they were less than 20 kHz/Torr). However, the influence of the wings of one line on the location of intensity maxima of the other lines may be important. Therefore, all the measured transition frequencies were corrected by the method given in the Appendix. The values of these corrections to the measured frequencies and transition frequencies after corrections (which we call experimental transition frequencies) are given in Table I. One can see from Table I that these corrections are of appreciable value for only a few lines.

TABLE I—(Continued)

| $v_1 v_2^{|l|} v_3$ τ=c,d | Transition J+1 → J | Exp.Frequency MHz | δ corr. KHz | Exp.-Calc. KHz |
|---|---|---|---|---|
| $01^{1c}0$ | 26 – 25 | 306 247.240(75)[b] |  | 1 |
|  | 27 – 26 | 318 018.823(75) | –116 | –126 |
|  | 29 – 28 | 341 559.928(75) | 15 | –26 |
|  | 30 – 29 | 353 329.275(75) | 154 | 86 |
|  | 31 – 30 | 365 097.619(75) | 22 | 80 |
|  | 41 – 40 | 482 725.930(75) |  | –2 |
|  | 42 – 41 | 494 482.591(75) |  | –20 |
| $01^{1d}0$ | 26 – 25 | 306 558.613(75)[b] |  | 127 |
|  | 27 – 26 | 318 342.196(75) | –1 | 66 |
|  | 28 – 27 | 330 124.965(75) | –40 | –9 |
|  | 29 – 28 | 341 907.004(75) |  | 17 |
|  | 31 – 30 | 365 468.173(75) | 46 | –234 |
|  | 41 – 40 | 483 215.708(75) | 9 | 60 |
|  | 42 – 41 | 494 984.167(75) |  | –12 |

$^{16}O^{12}C^{36}S$

| $v_1 v_2^{|l|} v_3$ τ=c,d | Transition J+1 → J | Exp.Frequency MHz | δ corr. KHz | Exp.-Calc. KHz |
|---|---|---|---|---|
| $00^00$ | 2 – 1 | 23 198.670(100)[a] |  | –60 |
|  | 26 – 25 | 301 500.440(23)[b] |  | 32 |
|  | 27 – 26 | 313 089.766(23) |  | –7 |
|  | 29 – 28 | 336 266.167(23) | –2 | 4 |
|  | 30 – 29 | 347 853.124(23) |  | –7 |
|  | 31 – 30 | 359 439.229(23) |  | –14 |
|  | 32 – 31 | 371 024.458(23) | 5 | –13 |
|  | 41 – 40 | 475 247.016(23) | –4 | 5 |
|  | 42 – 41 | 486 821.828(23) | –145 | 2 |
| $01^{1c}0$ | 29 – 28 | 336 681.724(180)[b] | –2 | 114 |
|  | 30 – 29 | 348 282.628(180) | –8 | –163 |
|  | 32 – 31 | 371 482.571(180) |  | 49 |

$^{18}O^{12}C^{34}S$

| $v_1 v_2^{|l|} v_3$ τ=c,d | Transition J+1 → J | Exp.Frequency MHz | δ corr. KHz | Exp.-Calc. KHz |
|---|---|---|---|---|
| $00^00$ | 2 – 1 | 22 239.850(20)[a] |  | 16 |
|  | 28 – 27 | 311 263.546(31)[b] | –1 | 29 |
|  | 29 – 28 | 322 372.953(31) |  | 8 |
|  | 31 – 30 | 344 589.534(31) |  | 11 |
|  | 32 – 31 | 355 696.609(31) | 3 | –13 |
|  | 33 – 32 | 366 802.869(31) | –4 | –24 |
|  | 34 – 33 | 377 908.295(31) | –4 | –15 |
|  | 43 – 42 | 477 814.385(31) |  | 1 |
|  | 44 – 43 | 488 909.795(31) | –2 | –47 |
|  | 45 – 44 | 500 004.214(31) | –63 | 52 |

$^{16}O^{13}C^{33}S$

| $v_1 v_2^{|l|} v_3$ τ=c,d | Transition J+1 → J | Exp.Frequency MHz | δ corr. KHz | Exp.-Calc. KHz |
|---|---|---|---|---|
| $00^00$ | 25 – 24 | 299 149.115(32) |  | 67 |
|  | 26 – 25 | 311 108.302(32) |  | 6 |
|  | 27 – 26 | 323 066.735(32) |  | –19 |
|  | 29 – 28 | 346 981.153(32) |  | –26 |
|  | 30 – 29 | 358 937.067(32) |  | –18 |
|  | 31 – 30 | 370 892.057(32) |  | –22 |
|  | 40 – 39 | 478 441.044(32) |  | 38 |
|  | 41 – 40 | 490 385.178(32) |  | –38 |
|  | 42 – 41 | 502 328.195(32) |  | 15 |

## PROCESSING OF EXPERIMENTAL DATA

The experimental rotational transition frequencies were treated as follows:

1. Each vibrational state of every isotopic species of the molecule was analyzed in the framework of the model

$$F(J) = B_{eff}[J(J + 1) - l^2] - D_{eff}[J(J + 1) - l^2]^2 \qquad (1)$$

Here $J$ is the quantum number of the total angular momentum of the molecule, $l$ is the quantum number of the vibrational angular momentum, and $B_{eff}$ and $D_{eff}$
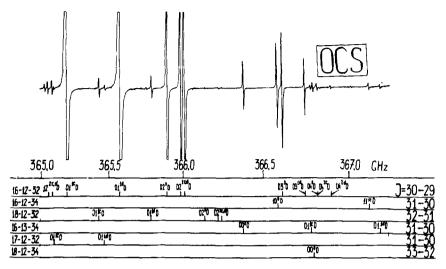
FIG. 1. A part of the record of the submillimeter spectrum of OCS obtained by a RAD spectrometer at room temperature, natural isotopic abundances with gas pressure of 0.5 Torr in a cell of length 13 cm. The response from spectral lines was recorded as the derivatives of the absorption profile. Identifications of the lines are shown in the figure.

are the effective rotational and centrifugal distortion constants. Our measurements were combined with the data given in Refs. ($1, 3$). The values obtained for the effective constants and their correlation coefficient matrix are given in Table II and the differences between experimental and calculated values are shown in Table I. The effect of a higher-order distortion constant ($\sim H_{\text{eff}}$) was found to be negligible in the fitting of experimental data. However, this is not a sufficient reason for excluding it. The problem is that after exclusion of parameter $H_{\text{eff}}$ refinements of parameters strongly correlated with it, $B_{\text{eff}}$ and $D_{\text{eff}}$, do not always have the proper physical meaning. In fact, if we vary slightly the value of the parameter $H_{\text{eff}}$ near the zero value, then parameters $B_{\text{eff}}$ and $D_{\text{eff}}$ would be also varied. For preserving the physical meaning of these refined constants the unknown value of the excluded parameter $H_{\text{eff}}$ should not exceed some limiting value, in order to maintain the values of constants $B_{\text{eff}}$ and $D_{\text{eff}}$ within their new error limits (see Ref. ($7$)). The obtained upper limits of $H_{\text{eff}}$ are given in Table II for different vibrational states.

2. The rotational spectra of isotopic species $^{16}O^{13}C^{34}S$, $^{17}O^{12}C^{32}S$, and $^{16}O^{12}C^{36}S$ were treated in all observed vibrational states simultaneously by taking account of the effects of resonances. The diagonal elements of the energy matrix of resonantly interacting vibrational–rotational states were introduced in a manner similar to that in Ref. ($6$). Account was taken of "$l$ resonance" by using the non-diagonal matrix element.[2]

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[2] The given matrix element differs from that used in Ref. ($6$) by term (3a). Term (3a) seems to us to be more logical compared to its analog used in Ref. ($6$): $q = q_v + q_J J(J + 1) + q_{JJ} J^2 (J + 1)^2$. Naturally, the constants involved in expression (3a) and its analog are related to each other by simple linear relations.

TABLE II

Effective Rotational and Centrifugal Distortion Constants of Less Abundant Isotopic Species of OCS in Different Vibrational States

| Vibration State | $B_{eff.}$ MHz | $D_{eff.}$ KHz | $R_{B,D}$ | Condition on $\|H_{eff.}\|$, Hz |
|---|---|---|---|---|
| | | $^{16}O^{13}C^{34}S$ | | |
| $00^00$ | 5 911.733 14(21) | 1.237 869(84) | 0.940 | $\leqslant 1.7 \; 10^{-5}$ |
| $01^{1c}0$ | 5 918.369 83(99) | 1.253 88(45) | 0.946 | $\leqslant 1.7 \; 10^{-4}$ |
| $01^{1d}0$ | 5 924.574 59(84) | 1.257 85(34) | 0.939 | $\leqslant 8.9 \; 10^{-5}$ |
| | | $^{17}O^{12}C^{32}S$ | | |
| $00^00$ | 5 883.672 37(26) | 1.211 119(98) | 0.943 | $\leqslant 2.6 \; 10^{-5}$ |
| $01^{1c}0$ | 5 891.027 9(13) | 1.228 05(48) | 0.940 | $\leqslant 1.3 \; 10^{-4}$ |
| $01^{1d}0$ | 5 897.022 4(12) | 1.234 70(47) | 0.936 | $\leqslant 1.3 \; 10^{-4}$ |
| | | $^{16}O^{12}C^{36}S$ | | |
| $00^00$ | 5 799.692 04(37) | 1.188 81(15) | 0.943 | $\leqslant 3.8 \; 10^{-5}$ |
| $01^{1c}0$ | 5 806.879(21) | 1.205(11) | 0.997 | $\leqslant 4.0 \; 10^{-3}$ |
| | | $^{18}O^{12}C^{34}S$ | | |
| $00^00$ | 5 559.967 22(46) | 1.077 88(15) | 0.949 | $\leqslant 3.4 \; 10^{-5}$ |
| | | $^{16}O^{13}C^{33}S$ | | |
| $00^00$ | 5 984.563 25(48) | 1.265 84(18) | 0.942 | $\leqslant 4.9 \; 10^{-5}$ |

$$\langle v_1 v_2^l v_3 J \| v_1 v_2^{l \pm 2} v_3 J \rangle \tag{2}$$

$$= (q/2)\{(v_2 \mp l)(v_2 \pm l + 2)[J(J + 1) - l(l \pm 1)][J(J + 1) - (l \pm 1)(l \pm 2)]\}^{1/2},$$

where

$$q = q_v + q_J[J(J + 1) - (l + 1 \pm 1)^2] + q_{JJ}[J(J + 1) - (l + 1 \pm 1)^2]^2, \tag{3a}$$

$$q_v = q_{(010)} + q_1 v_1 + q_2(v_2 - 1) + q_3 v_3. \tag{3b}$$

Here $q$ is the $l$-type doubling constant; $v_n$ is the vibrational quantum number of the $n$th vibration; and the values $q_J$, $q_{JJ}$, $q_1$, $q_2$, $q_3$ determine a weak dependence of the "$l$-doubling" constant on the vibrational–rotational state. The given set of experimental data is described by the following independent spectroscopic constants: rotational and centrifugal distortion constants of the ground vibrational states $B_0$ and $D_0$; constants involved in the matrix element of "$l$ resonance" $q_{(010)}$ and $q_J$; constants of nonresonant vibrational–rotational interaction $\alpha_2'$ and $\beta_2$, where

$$\alpha_2' = \alpha_2 - \gamma_{11} - 3\gamma_{22} - \gamma_{13} - \gamma_{ll}. \tag{4}$$

The values of these spectroscopic constants and the matrix of their correlation coefficients are presented in Table III.

There are experimental data available for the molecule $^{16}O^{12}C^{36}S$ in the ground and excited vibration state $01^{1c}0$ only. Therefore, to describe the spectrum

TABLE III

Rotational and Centrifugal Distortion Constants and Vibrational–Rotational Interaction
Constants of Less Abundant Isotopic Species of OCS

| | | | $^{16}O^{13}C^{34}S$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| $B_0$ | /MHz | 5 911.733 12(21) | 1 | | | | | |
| $\alpha'_2$ | /MHz | −9.739 084(68) | 0.309 | 1 | | | | |
| $D_0$ | /KHz | 1.237 867(84) | 0.940 | 0.290 | 1 | | | |
| $\beta_2$ | /Hz | −18.00(29) | 0.270 | 0.941 | 0.287 | 1 | | |
| $q(010)$/MHz | | 3.102 39(65) | 0.000 | 0.154 | 0.000 | 0.205 | 1 | |
| $q_J$ | /Hz | −1.98(28) | 0.000 | −0.204 | 0.000 | −0.273 | −0.942 | 1 |
| | | | $^{17}O^{12}C^{32}S$ | | | | | |
| $B_0$ | /MHz | 5 883.672 34(25) | 1 | | | | | |
| $\alpha'_2$ | /MHz | −10.353 54(95) | 0.269 | 1 | | | | |
| $D_0$ | /KHz | 1.211 109(97) | 0.842 | 0.254 | 1 | | | |
| $\beta_2$ | /Hz | −20.46(35) | 0.258 | 0.938 | 0.273 | 1 | | |
| $q(010)$/MHz | | 2.998 00(91) | 0.000 | −0.041 | 0.000 | −0.021 | 1 | |
| $q_J$ | /Hz | −3.51(34) | 0.000 | 0.021 | 0.000 | 0.009 | −0.937 | 1 |
| | | | $^{16}O^{12}C^{36}S$ | | | | | |
| $B_0$ | /MHz | 5 799.692 04(37) | 1 | | | | | |
| $\alpha''_2$ | /Mhz | −7.187(21) | 0.018 | 1 | | | | |
| $D_0$ | /KHz | 1.188 8(15) | 0.943 | 0.017 | 1 | | | |
| $\beta'_2$ | /Hz | −16(11) | 0.012 | 0.997 | 0.013 | 1 | | |

of this molecule, it is sufficient to have four independent spectroscopic constants:
rotational and centrifugal constants in the ground vibrational states $B_0$ and $D_0$
and vibrational–rotational interaction constants $\alpha''_2$ and $\beta'_2$, where $\alpha''_2 = \alpha'_2$
$- q_{(010)}$, $\beta'_2 = \beta_2 - q_J$. The values of these spectroscopic constants and their
correlation coefficient matrix are presented in Table III.

APPENDIX

Influence of the wings of neighboring lines on the position of line center has
been taken into account as follows. Our measurements and those given in
Ref. (1) were treated (without corrections) in the framework of the ordinary
model of the linear molecule described by Eq. (1). The obtained constants were
then used to calculate the spectrum of the molecule (frequencies and intensities
of lines)—in the region of measurements. The required values of vibrational
energies were taken from Ref. (8) or were calculated. The values of the dipole
moments of the molecule were used from Ref. (1). The case of those isotopic
combinations for which dipole moments were not measured was assumed to be
equivalent to that of $^{16}O^{12}C^{32}S$ in the ground vibrational state. The abundances
of isotopic species of the molecules were calculated on the basis of the data on
abundances of the elements given in Ref. (9). The profile of the absorption line
was assumed to be Lorentzian. The absorption line half-widths were determined
experimentally in each experimental run using a small number of lines and the

averaged value of linewidth was used in the calculations. The corrections to the frequencies of the lines were then calculated by using the iteration method of minimizing the function:

$$\varphi = \frac{1}{1 + \epsilon^2} + \sum_{k=1}^{N} \frac{\eta_k}{1 + (\epsilon - \delta_k)^2} \, , \qquad (A1)$$

where

$$\epsilon = \frac{\nu - \nu_0^{(0)}}{\Delta\nu} \, , \qquad \delta_k = \frac{\nu_0^{(0)} - \nu_0^{(k)}}{\Delta\nu} \, , \qquad \eta_k = \gamma^{(k)}/\gamma^{(0)}. \qquad (A2)$$

Here $\Delta\nu$ is the line half-width, $\nu_0^{(k)}$ is the position of the center of the "unshifted" $k$th absorption line, $\gamma^{(k)}$ is the absorption coefficient of the $k$th line. Expression (A1) represents the sum of Lorentz profiles of $N + 1$ absorption lines of different intensities and equal half-widths. In this expression only those lines were taken into account for which the shift at the frequency $\nu_0^{(0)}$ amounted to more than one-tenth of the measurement error. The accidentally coinciding unresolved lines were omitted. The criterion of resolution of line used in the computer program corresponded to the condition that the maximum value of the frequency derivative of the line profile exceed the value of the frequency derivative from the wing of the neighboring line. Roughly this condition may be written as

$$\eta/\delta^3 \leqslant 0.28. \qquad (A3)$$

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