

Heterodyne Frequency and Fourier Transform Spectroscopy Measurements on OCS near 1700 cm^{-1}

J. S. WELLS AND M. D. VANEK

Time and Frequency Division, National Institute of Standards and Technology,¹ Boulder, Colorado 80303

AND

A. G. MAKI

*Molecular Spectroscopy Division, National Institute of Standards and Technology,¹
Gaithersburg, Maryland 80899*

Heterodyne frequency measurements are given for carbonyl sulfide (OCS) in the 1700 cm^{-1} region. The measurements were combined with Fourier transform spectroscopy measurements of the same bands and with other measurements in the literature (microwave, submillimeter wave, and other infrared measurements) in a least-squares fit. The combined data and fit result in improved frequency calibration values for the 1700 cm^{-1} region and also allow one to determine calibration values for the $00^0_3-00^0_0$ band near 2550 cm^{-1} from application of the Ritz principle.

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Heterodyne frequency and Fourier transform spectroscopy (FTS) measurements have been made on the $00^0_2-00^0_0$, $01^1_2-01^1_0$, and $00^0_3-00^0_1$ bands² of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ (carbonyl sulfide), and the $00^0_2-00^0_0$ band of $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ and $^{16}\text{O}^{13}\text{C}^{32}\text{S}$ between 1650 and 1736 cm^{-1} . These measurements have been combined with earlier heterodyne measurements (2, 3) to determine the best constants to calculate the frequencies of the transitions in the 1700 and 2550 cm^{-1} regions for the purpose of calibration standards.

The present heterodyne measurements used the measurement techniques described in earlier papers on OCS (4) and N_2O (5). The measurements were all referred (by means of a CO laser transfer oscillator) to well characterized CO_2 lasers used as frequency standards. The CO_2 frequencies given by Petersen *et al.* (6) and Bradley *et al.* (7) were used. The FTS measurements were made with a resolution of 0.005 cm^{-1} and were calibrated by means of the OCS transitions for which there were heterodyne measurements.

A 1.7-m-long absorption cell and pressures ranging from 133 to 667 Pa (1 to 5 Torr) were used for the heterodyne measurements. The cell was heated to 100°C for the measurements of some high J ($J > 70$) transitions. A path length of 1 m and an

¹ Formerly National Bureau of Standards.

² The vibrational numbering system adopted by the IAU-IUPAP joint commission on spectroscopy (1) is used throughout this paper. Most other authors use a notation that interchanges ν_1 and ν_3 .

TABLE I
Heterodyne Measurements on OCS near 1700 cm⁻¹

Transfer Oscillator CO Trans. Pv ⁿ (J ⁿ)	Carbonyl Sulfide		
	Trans. ^a	Frequency MHz	Obs. - Calc. MHz
P17(15)	P(78)E	49488266.7(200) ^b	-2.6
P17(13)	P(65)E	49708361.8(50)	0.8
P16(19)	P(76)B	49773465.4(300)	-5.9
P17(12)	P(80)F	49819241.4(200)	7.7
P17(12)	P(73)B	49825200.8(50)	-1.3
P17(11)	P(67)C	49929960.4(50)	-0.9
P17(11)	P(51)E	49931791.0(50)	-1.1
P16(17)	P(85)A	49998816.2(100)	4.2
P16(17)	P(61)D	49999475.5(90)	0.6
P16(14)	P(39)D	50347398.4(50)	-2.0
P16(12)	P(24)D	50563908.0(200)	0.0
P16(12)	P(52)A	50564525.8(30)	0.3
P16(12)	P(34)F	50565605.5(100)	2.4
P16(12)	P(5)E	50567619.9(100)	4.6
P16(12)	P(25)B	50568164.9(50)	0.4
P16(12)	P(25)C	50568423.5(50)	-3.5
P16(11)	P(17)B,C	50676729.5(150)	-5.0
P16(11)	P(26)F	50679663.3(80)	-1.2
P15(17)	P(12)B,C	50742338.6(60)	0.9
P15(17)	P(21)F	50748608.2(80)	5.1
P15(17)	P(10)D	50750887.1(30)	1.9
P15(14)	R(44)E	51087031.1(50)	-2.1
P15(14)	R(16)B	51089542.7(40)	-2.8
P15(14)	R(16)C	51090060.7(50)	1.8
P15(14)	P(16)A	51090402.1(120)	2.1
P15(14)	R(18)D	51091675.4(150)	-4.6
P15(13)	R(26)C	51196971.4(60)	-2.0
P15(13)	R(58)E	51199695.8(60)	3.8
P15(13)	R(15)F	51202495.5(60)	2.1
P15(13)	R(29)D	51204381.2(30)	-1.1
P15(13)	R(27)B	51206151.0(80)	-3.7
P15(12)	R(38)B	51314334.1(60)	-0.7
P15(12)	R(38)C	51316312.6(60)	-5.6
P15(12)	R(41)D	51316789.1(60)	0.1
P14(18)	R(44)B	51369747.4(40)	0.5
P14(18)	R(44)C	51372281.2(40)	3.3
P14(16)	R(58)F	51603367.7(90)	2.5
P14(16)	R(27)A	51604457.8(60)	1.3
P14(16)	R(73)C	51606832.2(60)	6.1
P14(16)	R(74)B	51607782.9(80)	13.0
P14(15)	R(39)A	51719760.0(60)	1.5
P14(14)	R(52)A	51832373.1(60)	-3.0
P14(13)	R(68)A	51953123.5(90)	-7.4
P14(12)	R(86)A	52064897.1(90)	-1.9

^a The bands are defined as follows: A = 00⁰2-00⁰0, B = 01¹e2-01¹e0, C = 01¹f2-01¹f0, and D = 00⁰3-00⁰1, all for the normal isotope. E and F are the 00²2 - 00⁰0 transitions for OC³⁴S and O¹³CS respectively.

^b The uncertainty in the last digits is given in parentheses.

OCS pressure of 385 Pa (2.9 Torr) were used for the FTS measurements. The FTS measurements were made with the cell heated to about 100°C.

The transitions measured by heterodyne techniques are given in Table I. The assignments were based on the calculated transition frequencies given by the constants reported by Fayt *et al.* (8).

TABLE II

Band Centers Determined from Heterodyne Measurements on OCS

Transition	ν_0 this work (cm^{-1}) ^a	ν_0 Ref. (8,15) (cm^{-1})	ν_0 Ref. (16) (cm^{-1})
$^{16}\text{O}^{12}\text{C}^{32}\text{S}$			
00 ⁰ 2-00 ⁰ 0	1710.97625(9) ^b	1710.97640(3)	1710.97622(42)
01 ¹ 2-01 ¹ 0	1697.60663(10)	1697.60593(44)	1697.60642(26)
00 ⁰ 3-00 ⁰ 1	1697.02429(13)	1697.02398(66)	1697.02446(26)
$^{16}\text{O}^{12}\text{C}^{34}\text{S}$			
00 ⁰ 2-00 ⁰ 0	1688.75687(13)	1688.75691(18)	---
$^{16}\text{O}^{13}\text{C}^{32}\text{S}$			
00 ⁰ 2-00 ⁰ 0	1701.79097(15)	1701.79104(16)	---

- a) In this paper the conversion from frequency to wavenumber units used the defining value of $c=299792458$ m/s.
 b) The uncertainty (twice the standard error) in the last digits is given in parentheses.

In the analysis of the transitions for which $v_2 \leq 1$ the term values were given by $T(v, l, J) = G(v, l) + B_v J(J+1) - D_v [J(J+1) - l^2]^2 + H_v [J(J+1) - l^2]^3$, (1) and the band center was given by

$$\nu_0 = G(v', l') - G(v'', l''). \quad (2)$$

When $l = 1$ the l -type doubling was taken into account by substituting for B_v the expression

$$B_v \pm 0.5[q_v - q_{vJ}J(J+1) + q_{vJJ}J^2(J+1)^2],$$

TABLE III

Rotational Constants (in cm^{-1}) Determined for OCS

vib. state	B_v	$D_v \times 10^8$	$H_v \times 10^{15}$
00 ⁰ 0	0.2028567415(10) ^a	4.34106(38)	-2.410(636)
01 ¹ 0 ^b	0.2032098316(32)	4.41146(42)	[-2.410] ^c
00 ⁰ 1	0.202251841(22)	4.4334(19)	[-2.410]
00 ⁰ 2	0.201635357(39)	4.53411(134)	4.85(128)
01 ¹ 2 ^d	0.202091248(57)	4.67880(138)	[-2.410]
00 ⁰ 3	0.201006215(116)	4.6471(61)	16.4(82)
$^{16}\text{O}^{12}\text{C}^{34}\text{S}$			
00 ⁰ 0	0.1978980346(90)	4.1409(18)	---
00 ⁰ 2	0.196706897(94)	4.3028(29)	---
$^{16}\text{O}^{13}\text{C}^{32}\text{S}$			
00 ⁰ 0	[0.2022040195]	[4.32925]	---
00 ⁰ 2	0.20099360(28)	4.5563(139)	---

- a) The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.
 b) The l -type doubling constants for 01¹0 are:
 $q=2.12193973(114) \times 10^{-4}$, $q_J=1.4354(120) \times 10^{-10}$,
 and $q_{JJ}=8.3(54) \times 10^{-16}$
 c) Values given in square brackets were fixed.
 d) The l -type doubling constants for 01¹2 are:
 $q=2.44737(68) \times 10^{-4}$, $q_J=6.048(196) \times 10^{-10}$.

where the value of q_b was assumed to be positive. For OCS, the positive sign is needed for the f levels and the negative sign is needed for the e levels (that is, the f levels are higher in energy than the e levels).

For the analysis of the present measurements we have used a large least-squares fitting program that has been developed to fit all of the infrared and microwave data on OCS to obtain the best constants for all of the energy levels. In this fit each datum was weighted by the inverse square of the uncertainty assigned to it. Care was taken to ensure that the vibrational constants (the ν_0 's) were only determined by heterodyne frequency measurements. That is to say, the FTS measurements were fitted to a different

TABLE IV
Wavenumbers (in cm^{-1}) Calculated for the 00^0_3 - 00^0_0 Band of OCS

P-Branch	J"	R-Branch	P-Branch	J"	R-Branch
	0	2556.39320(14) ^a	2535.20739(14)	43	2570.15189(14)
2555.58548(14)	1	2556.79151(14)	2534.64257(14)	44	2570.38893(14)
2555.17606(14)	2	2557.18612(14)	2534.07401(14)	45	2570.62215(14)
2554.76295(14)	3	2557.57702(14)	2533.50174(14)	46	2570.85154(14)
2554.34614(14)	4	2557.96422(14)	2532.92573(14)	47	2571.07710(14)
2553.92563(14)	5	2558.34771(14)	2532.34600(14)	48	2571.29883(14)
2553.50143(14)	6	2558.72749(14)	2531.76254(14)	49	2571.51672(14)
2553.07353(14)	7	2559.10355(14)	2531.17534(14)	50	2571.73077(14)
2552.64193(14)	8	2559.47591(14)	2530.58441(14)	51	2571.94096(14)
2552.20664(14)	9	2559.84456(14)	2529.98974(14)	52	2572.14731(15)
2551.76766(14)	10	2560.20948(14)	2529.39133(14)	53	2572.34980(15)
2551.32498(14)	11	2560.57069(14)	2528.78917(15)	54	2572.54843(15)
2550.87860(14)	12	2560.92819(14)	2528.18328(15)	55	2572.74319(15)
2550.42854(14)	13	2561.28196(14)	2527.57363(15)	56	2572.93408(15)
2549.97478(14)	14	2561.63200(14)	2526.96023(15)	57	2573.12109(16)
2549.51733(14)	15	2561.97832(14)	2526.34308(15)	58	2573.30423(16)
2549.05618(14)	16	2562.32092(14)	2525.72218(16)	59	2573.48347(16)
2548.59134(14)	17	2562.65978(14)	2525.09751(16)	60	2573.65883(17)
2548.12281(14)	18	2562.99491(14)	2524.46909(16)	61	2573.83029(17)
2547.65059(14)	19	2563.32631(14)	2523.83690(17)	62	2573.99786(17)
2547.17467(14)	20	2563.65397(13)	2523.20094(17)	63	2574.16151(17)
2546.69505(14)	21	2563.97789(13)	2522.56121(17)	64	2574.32126(18)
2546.21175(13)	22	2564.29807(13)	2521.91771(17)	65	2574.47709(18)
2545.72474(13)	23	2564.61450(13)	2521.27043(18)	66	2574.62899(18)
2545.23405(13)	24	2564.92718(13)	2520.61938(18)	67	2574.77698(19)
2544.73965(13)	25	2565.23612(13)	2519.96454(18)	68	2574.92102(19)
2544.24156(13)	26	2565.54130(13)	2519.30591(19)	69	2575.06114(20)
2543.73977(13)	27	2565.84272(13)	2518.64350(19)	70	2575.19731(21)
2543.23428(13)	28	2566.14038(13)	2517.97729(20)	71	2575.32953(22)
2542.72510(13)	29	2566.43428(13)	2517.30729(21)	72	2575.45779(24)
2542.21221(13)	30	2566.72442(13)	2516.63349(22)	73	2575.58210(26)
2541.69562(13)	31	2567.01078(14)	2515.95589(24)	74	2575.70245(28)
2541.17533(13)	32	2567.29338(14)	2515.27448(26)	75	2575.81882(31)
2540.65134(14)	33	2567.57219(14)	2514.58926(28)	76	2575.93122(34)
2540.12364(14)	34	2567.84723(14)	2513.90023(31)	77	2576.03963(38)
2539.59223(14)	35	2568.11849(14)	2513.20738(34)	78	2576.14406(43)
2539.05712(14)	36	2568.38595(14)	2512.51072(38)	79	2576.24449(48)
2538.51830(14)	37	2568.64963(14)	2511.81022(43)	80	2576.34093(53)
2537.97577(14)	38	2568.90952(14)	2511.10591(48)	81	2576.43336(60)
2537.42952(14)	39	2569.16560(14)	2510.39776(53)	82	2576.52178(67)
2536.87957(14)	40	2569.41789(14)	2509.68577(60)	83	2576.60619(75)
2536.32589(14)	41	2569.66637(14)	2508.96995(67)	84	2576.68657(84)
2535.76850(14)	42	2569.91104(14)	2508.25029(75)	85	2576.76292(93)

a) The estimated uncertainty (twice the standard error) in the last digits is given in parentheses.

band center than the heterodyne measurements. The constants resulting from this fit are given in Tables II and III. The band centers given in Table II are those given by the heterodyne measurements. Data that were particularly useful in this analysis were taken from Refs. (2, 3, 9-14).

The constants given by this least-squares fit and reported in Tables II and III were used to calculate the transition frequencies for the 00^03-00^00 band reported in Table IV. The variance-covariance matrix given by the least-squares fit was used to determine the uncertainties given in Table IV. We have also measured the 00^03-00^00 band with our FTS spectrometer and found that, at a pressure of 1330 Pa (10 Torr) and a path length of 0.75 m, the strongest lines have a transmission of about 77% at the line center when measured with a resolution of 0.004 cm^{-1} .

The present values for the 00^02-00^00 band centers of the various isotopic species of OCS are in excellent agreement with our earlier (less extensive in J) measurements (3) and as shown in Table II the band centers are also in excellent agreement with those given by Fayt *et al.* (8, 15) and Tanaka *et al.* (16).

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