Heterodyne and FTS Measurements on the OCS Hot Bands near 1890 cm⁻¹*

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New infrared heterodyne frequency measurements are reported for carbonyl sulfide (OCS) near 1890 cm⁻¹. By combining these heterodyne measurements with microwave measurements reported in the literature and with new Fourier transform spectrometer measurements, we have determined rovibrational constants for the states involved in the following transitions: 02^01–00^00, $02^{2e}1$–00^00, 03^11–01^10, 02^02–00^01, 04^01–02^00, 04^21–02^20, and 02^01–00^00 ($^{16}O^{12}C^{34}S$). New FTS measurements have also been made on the 03^12–01^11 band of the normal isotope, the 02^01–00^00 band of $^{16}O^{13}C^{32}S$, and the 03^11–01^10 band of $^{16}O^{12}C^{34}S$. The present frequency measurements have also been combined with other frequency measurements, reported earlier, to determine frequencies for the 02^02–00^00 transitions near 2730 cm⁻¹ and the 04^01–00^00 transitions near 2940 cm⁻¹. A separate set of measurements was made to determine the pressure shift of the transitions in the 02^00–00^00 band of OCS. The shift is quite small, on the order of -0.4 ± 1.5 kHz/Pa (-0.05 ± 0.2 MHz/Torr). © 1988 Academic Press, Inc.

INTRODUCTION

In an earlier paper (*1*) we reported heterodyne frequency measurements on the 02^01–00^00 band[1] of carbonyl sulfide (OCS) near 1885 cm⁻¹. Those frequency measurements were intended to form the basis for tables for infrared frequency calibration in the region 1866 to 1919 cm⁻¹. In the present paper we have extended the heterodyne measurements to include a number of hot bands in that same frequency region and also to include the 02^01–00^00 band of $^{16}O^{12}C^{34}S$ which is present in 4.8% abundance in a normal sample.

These measurements provide a denser comb of frequency calibration points for the region 1840 to 1925 cm⁻¹. More importantly, they also provide frequency measurements of certain energy levels from which it is possible to calculate accurate frequency

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[1] The vibrational numbering system adopted by the IAU-IUPAP joint commission on spectroscopy (*2*) is used throughout this paper. This convention agrees with Refs. (*3, 4*) but most other papers use a notation that interchanges ν_1 and ν_3.

calibration tables for higher frequency regions where we are unable to make direct heterodyne measurements.

The pressure shift for the 02^00–00^00 band of OCS near 1050 cm^{-1} was the subject of a separate set of measurements. The pressure shifts for several gases, CO (5), N_2O (6), and HCl (7), seem to indicate that the self-induced pressure shift in the absorption line frequencies is small if the dipole moment is small. This expectation was verified in an earlier attempt to measure the pressure shift of the 00^01–00^00 band of OCS (8). The shift was determined to be 0.8 ± 3.8 kHz/Pa (0.1 ± 0.5 MHz/Torr). Since some of the present heterodyne measurements were made at pressures as high as 1200 Pa (9 Torr) and since some laboratories may prefer to use small path lengths and high pressures for the calibration gas, it is important to know the value of the pressure-induced shift in the absorption line frequencies and we have reinvestigated this problem. We verified that the shift is small enough to be unimportant for most applications.

EXPERIMENTAL DETAILS

The heterodyne frequency measurements were made by using a CO laser as a local oscillator whose frequency was measured against combination frequencies of two stabilized CO_2 lasers. A MIM diode was used to synthesize the CO_2 combination frequencies and also to generate the difference frequency with the CO laser. In a separate measurement that was made at the same time, a diode laser was locked to the OCS absorption line and the frequency difference between the diode laser and the CO laser was generated in a HgCdTe mixer and measured on a frequency analyzer. This is the same technique that was developed earlier in our Boulder laboratory and described more thoroughly in Refs. (1, 8, 9).

The present measurements use a 1.7-m absorption cell with OCS pressures ranging from 130 to 1200 Pa (1.0 to 9.0 Torr). In most of the measurements the cell was heated to about 90°C.

The heterodyne measurements are given in Table I where the column labeled Obs. − Calc. shows the deviations from the frequencies calculated from the constants given in Tables II and III.

Most of the uncertainties given in Table I are essentially one-tenth of the tunable diode laser jitter linewidth. A few lines were incompletely resolved and were given larger uncertainties (ranging from 20 to 40 MHz) to allow for the effect of such blending.

The heterodyne frequency measurements were also supplemented by the addition of Fourier transform spectrometer (FTS) measurements made with an apodized resolution of 0.004 cm^{-1}. These measurements were internally calibrated by means of the heterodyne frequency measurements reported in Table I and also those given in Ref. (1). The FTS measurements were made on the NBS (Gaithersburg) BOMEM DA3.002 Fourier transform interferometric spectrometer.[2] OCS at a pressure of 380 Pa (2.9 Torr) was used in a 1.2-m absorption tube of which a 52-cm segment was heated to about 200°C.

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[2] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

TABLE I

Heterodyne Frequency Measurements for OCS in the 5.3-μm Region

CO laser $P_{v''}(J'')$	OCS Transition Band[a]	Rot.	Measured Freq. MHz	Obs.-Calc. MHz	CO laser $P_{v''}(J'')$	OCS Transition Band[a]	Rot.	Measured Freq. MHz	Obs.-Calc. MHz
$P_9(15)$	D	P(55)	55484981.5(100)[b]	10.9	$P_8(12)$	E	R(21)	56613092.8(120)	1.2
$P_9(13)$	D	P(34)	55727828.1(100)	2.1		B	P(8)	56614218.2(120)	-5.0
$P_9(19)$	E	P(51)	55754952.8(60)	3.4		C	P(8)	56614487.1(120)	-11.3
$P_8(18)$	E	P(40)	55881343.1(90)	0.2		G,H	P(6)	56615207.0(120)	-34.8
	D	P(21)	55881589.4(70)	-1.3	$P_7(18)$	E	R(23)	56637097.0(80)	-7.1
$P_8(17)$	B	P(58)	56000991.4(100)	-0.7		B	P(6)	56638641.6(300)	15.3
	D	P(11)	56001251.1(100)	-5.9		C	P(6)	56638744.5(200)	-7.4
	F	P(54)	56007893.8(80)	6.8		D	R(40)	56640158.6(120)	3.9
	E	P(29)	56009092.1(150)	-5.0	$P_7(17)$	F	R(7)	56761434.0(200)	12.9
$P_8(16)$	E	P(19)	56126183.5(100)	6.0		D	R(50)	56766752.6(150)	7.0
	C	P(49)	56126694.0(80)	1.3		B	R(4)	56772578.9(60)	-1.4
	F	P(44)	56127605.0(50)	1.3		C	R(4)	56772847.1(60)	1.3
	H	P(46)	56128346.7(60)	4.1		F	R(8)	56773603.5(80)	4.0
$P_8(15)$	F	P(34)	56248736.7(60)	4.5		G,H	R(6)	56773918.2(80)	6.1
	H	P(36)	56249754.1(60)	-4.7	$P_7(16)$	G,H	R(15)	56883782.4(100)	3.2
$P_8(14)$	B	P(28)	56369492.0(200)	0.8		B	R(14)	56893945.0(70)	-2.5
	F	P(24)	56370671.3(150)	2.4		D	R(60)	56895093.3(400)	17.9
	G	P(26)	56371205.8(300)	20.4		F	R(18)	56895292.1(200)	-8.5
	H	P(26)	56371436.8(150)	10.4		C	R(14)	56895757.3(200)	4.0
	C	P(28)	56374232.6(80)	13.7		G,H	R(16)	56895977.5(400)	-6.6
$P_8(13)$	D	R(28)	56490095.7(80)	-7.0	$P_7(15)$	B	R(24)	57014898.5(150)	-9.0
	B	P(18)	56492005.5(100)	-0.6		F	R(28)	57017035.1(100)	-3.8
	F	P(14)	56492912.0(100)	6.8	$P_7(14)$	C	R(33)	57131856.3(100)	6.8
	G,H	P(16)	56493271.0(300)	13.4		E	R(64)	57137040.8(120)	-4.9
	C	P(18)	56493861.2(100)	25.0	$P_6(20)$	B	R(35)	57147493.1(100)	-1.7
$P_7(19)$	B	P(16)	56516461.2(80)	-14.0		F	R(39)	57151473.8(200)	2.1
	G,H	P(14)	56517654.1(80)	4.1	$P_6(19)$	F	R(49)	57274716.8(60)	-14.3
	C	P(16)	56517891.6(80)	4.9		B	R(46)	57279619.6(70)	-7.9
					$P_6(18)$	C	R(54)	57396711.5(100)	-1.0
						B	R(56)	57399428.5(100)	-1.4

a) The band designation (for the normal isotope unless otherwise indicated) is as follows:
B = $03^1e_1 - 01^1e_0$, and C = $03^1f_1 - 01^1f_0$, D = $02^02 - 00^01$, E = $02^01 - 00^00$ (for $^{16}O^{12}C^{34}S$),
F = $04^01 - 02^00$, G = $04^2e_1 - 02^2e_0$, and H = $04^2f_1 - 02^2f_0$.
b) The uncertainty in the last digits is given in parentheses for the heterodyne measurements;
for example, 9428.5(100) means 9428.5±10.0.

TABLE II

Band Centers or Level Differences in Wavenumbers (cm⁻¹)[a] for OCS

BAND	ν_0 this work	ν_0 Ref.(12,17)	ν_0 Ref.(19)
02^01-00^00	1892.23056(9)[b]	1892.23053(5)	1892.23029(13)
02^21-00^00	1886.94796(12)[c]	1886.94755(20)	---
03^11-01^10	1891.70031(10)	1891.70021(10)	---
03^31-01^10	[1881.91855][d]	1881.91852(80)	---
04^01-02^00	1890.10457(23)	1890.10619(33)	1890.10427(27)
04^21-02^20	1890.92359(22)	1890.92424(35)	1890.92337(15)
04^41-02^20	[1877.27955][d]	1877.27955(247)	---
02^00-02^20	[5.74941][d]	5.74941(6)	---
04^01-00^01	2937.14667(40)	2937.14824(33)	---
02^02-00^01	1872.43212(19)	1872.43214(58)	1872.43212(30)
02^02-00^00	2731.39904(19)	2731.39908(56)	---
02^22-00^00	[2726.56498][d]	2726.56498(93)	---
03^12-01^11	1872.80142(16)[c]	1872.80174(118)	---
03^32-01^11	[1863.95659][d]	1863.95659(233)	---
$^{16}O^{12}C^{34}S$			
02^01-00^00	1879.65261(14)	1879.65269(11)	---
02^21-00^00	[1874.73883][e]	1874.73883(40)	---
03^11-01^10	1879.07208(19)[c]	1879.07191(30)	---
03^31-01^10	[1869.93874][e]	1869.93874(130)	---
$^{16}O^{13}C^{32}S$			
02^01-00^00	1857.03310(10)[c]	1857.03314(10)	---
02^21-00^00	[1851.62005][e]	1851.62005(430)	---

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.
c) Band center determined from FTS measurements.
d) Fixed at the value given by Ref. (12).
e) Fixed at the value given by Ref. (17).

MAKI ET AL.

TABLE III

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

vib. state	B_v	$D_v \times 10^8$	$H_v \times 10^{15}$	$q_v \times 10^4$	$q_{vJ} \times 10^{10}$	$q_{vJJ} \times 10^{15}$
00^00	[0.2028567410][a](8)	[4.340899](295)	[-2.88](46)	---	---	---
02^01	0.2029534767(207)[b]	4.5553(80)	---	2.2247(94)	2.378(153)	---
02^21	0.2030482354(142)	4.6397(82)	---	---	---	---
03^11	0.2032590893(176)	4.60037(55)	---	2.183537(138)	1.5279(260)	---
03^31	0.203428162(120)	4.7596(68)	---	---	---	---
01^10	[0.2032098310](15)	[4.411267](270)	[-2.34](45)	[2.12193977](49)	[1.4358](49)	[0.81](24)
04^01	0.203437524(245)	4.0302(102)	-305.0(115)	2.12839(108)	-0.961(203)	[1.01](59)
04^21	0.203568903(139)	4.6631(36)	[-2.74](67)	---	---	---
04^41	[0.20379995](37)	4.617(145)	[-2.73](67)	---	---	---
02^00	[0.203480504]	[4.42327]	[-2.73]	[2.0863804]	[0.6694]	[1.02]
02^20	[0.203559482]	[4.48283]	[-2.73]	---	---	---
02^02	0.202414947(86)	4.852(121)	---	2.492(112)	[1.4355](88)	---
02^22	[0.20252316](41)	[4.8047](8)	---	---	---	---
00^01	[0.202251858]	[4.434758]	[2.1381]	---	---	---
03^12	0.20274466(34)	4.7495(141)	---	2.30214(57)	[1.9]	---
03^32	[0.202936096]	[4.90]	---	---	---	---
01^11	[0.20265714]	[4.54]	---	[2.285]	[3.14]	---
$^{16}O^{12}C^{34}S$						
00^00	[0.1978980341](34)	[4.14052](70)	---	---	---	---
02^01	0.197995441(112)	[4.3400]	---	2.1127(26)	[2.378]	---
02^21	[0.1980796]	[4.4167]	---	---	---	---
03^11	0.198297123(266)	4.3833(75)	---	2.083317(373)	[1.53]	---
03^31	[0.1984492]	[4.55]	---	---	---	---
01^10	[0.1982425371]	[4.20332]	---	[2.0243347]	[1.3132]	---
$^{16}O^{13}C^{32}S$						
00^00	[0.2022040195]	[4.32925]	---	---	---	---
02^01	0.202261707(179)	[4.58]	---	2.3403(58)	[2.378]	---
02^21	[0.202367186]	[4.65888]	---	---	---	---

a) The values given in square brackets were either fixed or included in the fit but with the value
   and uncertainty reported in the literature.
b) The uncertainty in the last digits (twice the standard error) is given in parentheses.

The FTC measurements were primarily intended to improve the accuracy of the various rotational constants used in the fit and are too extensive to report here although a copy may be obtained from the authors. The extent of the FTS measurements is shown in Table IV along with the root mean square (rms) deviations obtained from the least-squares fit that produced the constants given in Tables II and III.

The pressure shift measurements were made on the 02^00–00^00 band of OCS, which has lines conveniently close to the CO_2 laser transitions. Three OCS transitions, $R(3)$,

TABLE IV

Summary of the Present FTS Measurements on OCS

BAND	$P(J)_{max}$	$R(J)_{max}$	Transitions	RMS Dev. (cm^{-1})
$02^01 - 00^00$	101	106	191	0.0001
$02^{2e}1 - 00^00$	83	92	58	0.0003
$03^11 - 01^10$	94	100	337	0.0002
$02^02 - 00^01$	78	73	116	0.0002
$04^01 - 02^00$	76	81	112	0.0003
$04^21 - 02^20$	76	83	192	0.0003
$03^12 - 01^11$	51	50	92	0.0003
$^{16}O^{12}C^{34}S$				
$02^01 - 00^00$	72	73	103	0.0002
$03^11 - 01^10$	61	55	104	0.0003
$^{16}O^{13}C^{32}S$				
$02^01 - 00^00$	64	22	73	0.0003

$P(30)$, and $P(53)$, were chosen for measurement because they are close to CO_2 laser transitions and represent a wide range of J values. The technique used for these measurements consisted of locking the diode laser to the peak of the absorption line and measuring the frequency difference between the diode frequency and the CO_2 laser frequency as described in Refs. (10, 11). In order to accurately locate the center of the absorption line it is necessary to take into account any small residual slope in the background. If there is any slope to the background, then the zero value for the first derivative will not be the line center. Compensating for the background slope is more difficult for broad lines and ultimately is the limitation on the accuracy of the present measurements. The pressure shifts were obtained from measurements at pressures on the order of 40, 2700, and 4700 Pa (0.3, 20, and 35 Torr). Even at a pressure of 20 Torr, the linewidth is about 100 times the value of the pressure shift.

ANALYSIS OF THE MEASUREMENTS

The line assignments were based on the line positions calculated from the constants given by Fayt et al. (12). The high-resolution FTS spectrum was also used to verify the assignments. It is sometimes difficult to be certain of the assignment when only small portions of the spectrum are observed as is usually the case with diode laser measurements. The complete spectrum given by the FTS measurements was useful in showing that lines assigned to the same vibrational transition are indeed part of the same subband in the spectrum.

All of the transitions reported in this paper involve energy levels that are perturbed by l-type resonance. The most noticeable effect of this resonance is an unusually large change (from the ground state values) in the effective centrifugal distortion constants, D_v and H_v, and the relatively large splitting of the doublets of the $l = 2$ levels. In this analysis we have taken into account the effects of this l-type resonance by using the appropriate matrix elements as described in Ref. (13). This brings the effective centrifugal distortion constants much closer to the ground state values and has the correct functional form thus allowing more accurate fitting of the measurements.

For OCS there is also a weak Fermi resonance that couples the levels v_1, v_2, l, v_3 and v_1, $v_2 - 2$, l, $v_3 + 1$. This resonance gives rise to small changes in the effective values of q_v and D_v but is weak enough to be ignored in this analysis without affecting the accuracy of the fits.

To avoid any uncertainty in the interpretation of the constants given in Tables II and III, we repeat here the equations used in the present analysis.

The observed transitions were calculated using

$$\nu_{obs} = E(v, J, l)' - E(v, J, l)'',$$

where the energy levels were given by the solutions to the appropriate secular determinants which had the form

$$\begin{vmatrix} E_1^0 \, (l = v_2) - \lambda & W_{12} & 0 & 0 & \cdots \\ W_{21} & E_2^0 \, (l = v_2 - 2) - \lambda & W_{23} & 0 & \cdots \\ 0 & W_{32} & E_3^0 \, (l = v_2 - 4) - \lambda & & \cdots \\ & \cdots & & & \cdots \\ & \cdots & & E_i^0 \, (l = -v_2) - \lambda \end{vmatrix}$$

$$= 0, \quad (1)$$

where

$$E^0 = G + B_v J(J + 1) - D_v[J(J + 1) - l^2]^2 + H_v[J(J + 1) - l^2]^3 \qquad (2)$$

and

$$W_{ij} = W_{ji} = \langle v, l | H | v, l - 2 \rangle$$

$$= \tfrac{1}{4} q \{ [v_2 + l][v_2 - l + 2][J(J + 1) - l(l - 1)][J(J + 1) - (l - 1)(l - 2)] \}^{1/2}, \quad (3)$$

where, for all W_{ij} below the diagonal, l is the value of the vibrational angular momentum for the column in which W_{ij} appears and $l - 2$ is the value for the row. The l-doubling constant used in Eq. (3) has the form

$$q = q_v - q_{vJ} J(J + 1) + q_{vJJ}[J(J + 1)]^2. \qquad (4)$$

In this paper we have used the definition

$$\nu_0 = G' - G''.$$

Unlike Ref. (13), Eq. (1) does not include any $\Delta l = 4$ matrix elements because they are not significant for the present analysis. For those levels with $v_2 = 0$, Eq. (2) alone was used to calculate the energy levels.

In order to obtain the most accurate constants possible for the various vibrational levels involved in the present measurements, we have combined in least-square fits the present measurements with microwave measurements reported in the literature. All measurements were weighted by the inverse square of their estimated uncertainty.

The FTS measurements were fit with band centers different from those used in heterodyne measurements in order to allow for any residual calibration errors. The band centers reported in Table II are, of course, those resulting from the heterodyne measurements, except where noted. In the least-squares fits the heterodyne measurements were assigned the uncertainties indicated in Table I and the FTS measurements were given uncertainties approximately equal to the rms deviation of the FTS measurements.

For all of the bands studied in this paper the lower state constants have been quite accurately reported from other measurements and liberal use was made of whatever data were available. In some cases the data taken from the literature were given the uncertainties cited in the literature and were included as data to be fit in the least-squares analysis. This procedure was followed in order to obtain the variance–co-variance matrix that took into account the uncertainties in those parameters. This variance–covariance matrix was then used to calculate the uncertainties in the transitions calculated for Tables V, VI, and VII. In the remainder of this section the data used to analyze each band are described.

The 02^01-00^00 and 02^21-00^00 Bands

Because of the availability of the new FTS measurements on this band we have reanalyzed the heterodyne measurements of the 02^01-00^00 band previously reported in Ref. (1). The present FTS measurements also include 58 transitions of the $02^{2e}1-00^00$ band, which borrows intensity from the 02^01-00^00 band through the l-type resonance. These normally forbidden transitions were only observed at high J values, J

> 41. Three other heterodyne measurements involving the 02^01–00^01 transitions were taken from Ref. (*14*) along with other diode laser measurements reported there and involving the 02^01 level. Also included in the least-squares fit were the microwave transitions for the 02^01 and 02^21 states (*15*). The constants for the other states were fixed at the values given in earlier papers (*8, 14*). The ground state constants were taken from Jolma *et al.* (*16*) and were included in the fit as data with uncertainties given by their reported standard errors.

The 03^11–01^10 Band

The present analysis includes the microwave measurements on both the 03^11 and 03^31 states (*15*) and the FTS and heterodyne measurements. The constants for the lower state were well determined by Jolma *et al.* (*16*) and were included in the fit as independent measurements with their estimated uncertainties. The vibrational energy for the 03^31 state was also necessary to calculate the *l*-type resonance effect and was taken from the work of Fayt *et al.* (*12*).

The 02^02–00^01 Band

For the analysis of the 02^02–00^01 band it was necessary to use the constants given by Fayt *et al.* (*12*) for the $02^{2/2}$ state in order to calculate the effect of the *l*-type resonance. The constants for the lower state were taken from Ref. (*8*).

The 04^01–02^00 and 04^21–02^20 Bands

The lower state constants given by Jolma *et al.* (*16*) were used in the analysis. The constants for the 04^41 state were taken from the tables given by Fayt *et al.* (*12*).

While fitting these bands we observed that a very large and negative H term was needed for the 04^01 state even though we thought that correcting for the *l*-type resonance should have resulted in a small H term. On the other hand the 04^21 state was easily fit with no need for an H term any different from the ground state value. This must be due to a vibrational interaction between the 04^01 and 10^01 levels which are separated by 19 cm^{-1}. This interaction will be very weak, but will manifest itself in the higher order centrifugal distortion constants because the difference in the rotational constants for the two states causes them to separate more at higher J values and thus diminish the resonance interaction.

Hunt *et al.* (*4*) and Klebsch *et al.* (*3*) both noted that the 10^01 level has unusually large H terms, as well as an L term according to Ref. (*4*). We believe this confirms the significance of the coupling of these two levels especially since the H terms are of opposite sign for the two bands. This interaction was included in the work of Fayt *et al.* (*12*) and has been attributed in part to a potential function term of the form k_{22221} although the normal Fermi resonance complicates the interpretation. This is the same resonance interaction term that couples the ν_1 and $4\nu_2$ bands.

The 03^12–01^11 Band

No heterodyne measurements were made on this band. All of the constants for these states shown in square brackets in Tables II and III were taken from Ref. (*12*),

with the exception of $D(03^32)$ which was set at a value 0.15×10^{-8} cm^{-1} greater than $D(03^12)$ in order to agree with the difference found for the 03^11 and 03^31 states.

The 02^01–00^00 Band of $^{16}O^{12}C^{34}S$

Since this band was observed in natural abundance in a normal OCS sample, the intensity of the $02^{2e}1$–00^00 band was too weak to be seen in our spectrum. The ground state constants and their uncertainties were taken from the work of Jolma et al. (16) and were included in the fit, while the data for the 02^21 state were fixed at the values given by Lahaye et al. (17) for the $02^{2f}1$ state. The l-type resonance constant, q_v, was highly correlated with the centrifugal distortion constant $D(02^01)$. Consequently, the centrifugal distortion constant was fixed at a value 0.08×10^{-8} cm^{-1} smaller than that of $D(02^21)$ in order to agree with the difference observed for the normal isotopic species. The higher order term, q_{vJ}, was fixed at the value found for this band for the normal isotope.

The 03^11–01^10 Band of $^{16}O^{12}C^{34}S$

No heterodyne measurements were made on this band. The lower state constants were taken from Jolma et al. (16). The upper state constants were estimated from the tables given by Lahaye et al. (17). We assumed that $D(03^31)$ was larger than $D(00^00)$ by about 0.4×10^{-8} cm^{-1}, as was found for the normal isotope, and q_{vJ} was assumed to be the same as for the normal isotope. Since this band was weak and overlapped in many places, the constants given in Table III are not very accurate and are only useful for calculating the low J line positions.

The 02^01–00^00 Band of $^{16}O^{13}C^{32}S$

No heterodyne measurements were made on this band but it was identified in the FTS measurements and we give the band center determined from our observations in order to compare it with the tables of Lahaye et al. (17). With the exception of B' and q', which were fit along with the band center, both the ground state and the upper state constants were taken from the tables of Ref. (17). The constants for the $02^{2f}1$ state were also taken from Ref. (17). The D' and q'_{vJ} terms were fixed by means of the same criteria as were used for the same band of $^{16}O^{12}C^{34}S$.

RESULTS OF THE PRESSURE SHIFT MEASUREMENTS

In order to minimize the experimental difficulties, the pressure shift measurements were made on the 02^00–00^00 transitions rather than the 02^01–00^00 transitions. The measurement of the low pressure line positions was relatively easy with all measurements having a scatter of 0.5 MHz about the mean value. The results, $R(3)$ = 31 438 557.6 MHz, $P(30)$ = 31 041 205.4 MHz, and $P(53)$ = 30 798 788.9 MHz, agreed with the calculated transition frequencies given by the constants in Ref. (14). The largest deviation was 1.2 MHz.

On the other hand, the high pressure measurements are much less accurate since they are more susceptible to errors due to small irregularities in the background. The resettability of the high pressure measurements was on the order of 1 MHz but

the uncertainty in the effect of the irregular background on the location of the true line center was more like 3 to 5 MHz although it depended on the quality of the diode mode.

TABLE V

Calculated Transition Wavenumbers (cm⁻¹) for the $03^11–01^10$ Band of OCS

P-Branch	J"	R-Branch	P-Branch	J"	R-Branch
---	1E[a]	1892.51235(10)[b]	1877.41846(10)	35E	1906.23524(10)
---	1F	1892.51454(10)	1877.67028(10)	35F	1906.54885(10)
1890.88777(10)	2E	1892.91817(10)	1877.00887(10)	36E	1906.63651(10)
1890.88737(10)	2F	1892.92214(10)	1877.27591(10)	36F	1906.96706(10)
1890.48131(10)	3E	1893.32387(10)	1876.59922(10)	37E	1907.03766(10)
1890.48139(10)	3F	1893.33006(10)	1876.88191(10)	37F	1907.38558(10)
1890.07473(10)	4E	1893.72944(10)	1876.18953(10)	38E	1907.43869(10)
1890.07573(10)	4F	1893.73829(10)	1876.48831(10)	38F	1907.80440(10)
1889.66803(10)	5E	1894.13487(10)	1875.77979(10)	39E	1907.83960(10)
1889.67040(10)	5F	1894.14685(10)	1876.09509(10)	39F	1908.22354(10)
1889.26121(10)	6E	1894.54018(10)	1875.37001(10)	40E	1908.24038(10)
1889.26540(10)	6F	1894.55572(10)	1875.70227(10)	40F	1908.64299(10)
1888.85427(10)	7E	1894.94535(10)	1874.96020(10)	41E	1908.64105(10)
1888.86073(10)	7F	1894.96491(10)	1875.30984(10)	41F	1909.06276(10)
1888.44722(10)	8E	1895.35039(10)	1874.55034(10)	42E	1909.04160(10)
1888.45639(10)	8F	1895.37442(10)	1874.91781(10)	42F	1909.48283(10)
1888.04004(10)	9E	1895.75530(10)	1874.14046(10)	43E	1909.44204(10)
1888.05239(10)	9F	1895.78424(10)	1874.52618(10)	43F	1909.90322(10)
1887.63275(10)	10E	1896.16007(10)	1873.73056(10)	44E	1909.84237(10)
1887.64871(10)	10F	1896.19437(10)	1874.13496(10)	44F	1910.32392(10)
1887.22535(10)	11E	1896.56471(10)	1873.32063(10)	45E	1910.24259(10)
1887.24538(10)	11F	1896.60482(10)	1873.74413(10)	45F	1910.74494(10)
1886.81784(10)	12E	1896.96921(10)	1872.91068(10)	46E	1910.64271(10)
1886.84238(10)	12F	1897.01558(10)	1873.35372(10)	46F	1911.16626(10)
1886.41021(10)	13E	1897.37358(10)	1872.50073(10)	47E	1911.04273(10)
1886.43971(10)	13F	1897.42666(10)	1872.96371(10)	47F	1911.58791(10)
1886.00248(10)	14E	1897.77781(10)	1872.09077(10)	48E	1911.44264(10)
1886.03739(10)	14F	1897.83805(10)	1872.57412(10)	48F	1912.00987(10)
1885.59464(10)	15E	1898.18191(10)	1871.68080(10)	49E	1911.84246(10)
1885.63541(10)	15F	1898.24975(10)	1872.18495(10)	49F	1912.43214(10)
1885.18669(10)	16E	1898.58587(10)	1871.27084(10)	50E	1912.24219(10)
1885.23378(10)	16F	1898.66176(10)	1871.79619(10)	50F	1912.85473(10)
1884.77864(10)	17E	1898.98969(10)	1870.86089(10)	51E	1912.64184(10)
1884.83248(10)	17F	1899.07408(10)	1871.40785(10)	51F	1913.27763(10)
1884.37049(10)	18E	1899.39337(10)	1870.45096(10)	52E	1913.04140(10)
1884.43154(10)	18F	1899.48671(10)	1871.01993(10)	52F	1913.70085(10)
1883.96224(10)	19E	1899.79692(10)	1870.04104(10)	53E	1913.44088(10)
1884.03094(10)	19F	1899.89966(10)	1870.63244(10)	53F	1914.12439(10)
1883.55389(10)	20E	1900.20033(10)	1869.63116(10)	54E	1913.84028(10)
1883.63069(10)	20F	1900.31291(10)	1870.24538(10)	54F	1914.54825(10)
1883.14545(10)	21E	1900.60360(10)	1869.22131(10)	55E	1914.23962(10)
1883.23079(10)	21F	1900.72647(10)	1869.85875(10)	55F	1914.97242(10)
1882.73691(10)	22E	1901.00674(10)	1868.81150(10)	56E	1914.63889(10)
1882.83125(10)	22F	1901.14035(10)	1869.47255(10)	56F	1915.39692(10)
1882.32828(10)	23E	1901.40974(10)	1868.40173(10)	57E	1915.03810(10)
1882.43207(10)	23F	1901.55453(10)	1869.08679(10)	57F	1915.82173(11)
1881.91956(10)	24E	1901.81260(10)	1867.99203(10)	58E	1915.43726(11)
1882.03324(10)	24F	1901.96902(10)	1868.70146(10)	58F	1916.24686(11)
1881.51075(10)	25E	1902.21533(10)	1867.58238(10)	59E	1915.83637(11)
1881.63477(10)	25F	1902.38382(10)	1868.31658(10)	59F	1916.67231(11)
1881.10186(10)	26E	1902.61792(10)	1867.17281(11)	60E	1916.23544(11)
1881.23666(10)	26F	1902.79893(10)	1867.93214(11)	60F	1917.09809(11)
1880.69289(10)	27E	1903.02038(10)	1866.76331(11)	61E	1916.63447(11)
1880.83891(10)	27F	1903.21435(10)	1867.54815(11)	61F	1917.52418(11)
1880.28383(10)	28E	1903.42270(10)	1866.35390(11)	62E	1917.03347(11)
1880.44153(10)	28F	1903.63008(10)	1867.16460(11)	62F	1917.95059(11)
1879.87470(10)	29E	1903.82488(10)	1865.94458(11)	63E	1917.43246(11)
1880.04452(10)	29F	1904.04612(10)	1866.78151(11)	63F	1918.37733(11)
1879.46550(10)	30E	1904.22694(10)	1865.53537(11)	64E	1917.83142(11)
1879.64788(10)	30F	1904.46247(10)	1866.39887(11)	64F	1918.80439(11)
1879.05622(10)	31E	1904.62886(10)	1865.12627(11)	65E	1918.23039(11)
1879.25161(10)	31F	1904.87913(10)	1866.01669(11)	65F	1919.23177(11)
1878.64688(10)	32E	1905.03065(10)	1864.71729(11)	66E	1918.62935(11)
1878.85571(10)	32F	1905.29609(10)	1865.63497(11)	66F	1919.65947(11)
1878.23746(10)	33E	1905.43231(10)	1864.30844(11)	67E	1919.02832(11)
1878.46019(10)	33F	1905.71337(10)	1865.25370(11)	67F	1920.08749(11)
1877.82799(10)	34E	1905.83384(10)	1863.89974(11)	68E	1919.42732(11)
1878.06505(10)	34F	1906.13096(10)	1864.87290(11)	68F	1920.51584(11)

a) The E or F indicates the *e–e* or *f–f* transition, respectively.
b) The estimated uncertainty (twice the standard error) in the last digits is given in parentheses.

The best measurement was for the $P(53)$ line for which the pressure shift was estimated to be -0.4 ± 0.8 kHz/Pa (-0.05 ± 0.10 MHz/Torr). No significant difference could be measured for the pressure shift of any of the three lines. Consequently, we believe the best estimate of the pressure shift is -0.4 ± 1.5 kHz/Pa (-0.05 ± 0.2 MHz/ Torr) for all lines in the 02^00-00^00 band of OCS.

CONCLUSION

In Table V we give the wavenumbers and uncertainties for the hot band transitions, 03^11-01^10, as calculated from the constants given in Tables II and III. The new calculated frequencies for the 02^01-00^00 band do not differ by more than 6 MHz from the previously published values (1). Based on the present measurements two of the authors, Wells and Maki, are developing quite extensive tables of transition frequencies

TABLE VI

Calculated Transition Wavenumbers (cm^{-1}) for the 02^02-00^00 Transitions of OCS

P-Branch	J''	R-Branch	P-Branch	J''	R-Branch
---	0	2731.80387(19)[a]	2713.63522(18)	42	2748.02417(18)
2730.99332(19)	1	2732.20781(19)	2713.19578(18)	43	2748.39285(18)
2730.58673(19)	2	2732.61087(19)	2712.75570(18)	44	2748.76080(18)
2730.17925(19)	3	2733.01305(19)	2712.31497(18)	45	2749.12803(18)
2729.77089(19)	4	2733.41434(19)	2711.87360(18)	46	2749.49455(18)
2729.36166(19)	5	2733.81474(19)	2711.43161(18)	47	2749.86037(18)
2728.95155(19)	6	2734.21426(19)	2710.98901(18)	48	2750.22550(18)
2728.54056(19)	7	2734.61289(19)	2710.54580(18)	49	2750.58994(18)
2728.12870(19)	8	2735.01063(19)	2710.10200(18)	50	2750.95371(18)
2727.71597(19)	9	2735.40749(19)	2709.65763(18)	51	2751.31680(18)
2727.30238(19)	10	2735.80347(19)	2709.21268(18)	52	2751.67925(18)
2726.88791(19)	11	2736.19857(18)	2708.76717(18)	53	2752.04104(18)
2726.47259(19)	12	2736.59278(18)	2708.32111(18)	54	2752.40219(18)
2726.05641(18)	13	2736.98611(18)	2707.87451(18)	55	2752.76271(18)
2725.63937(18)	14	2737.37857(18)	2707.42739(18)	56	2753.12261(19)
2725.22148(18)	15	2737.77015(18)	2706.97976(19)	57	2753.48189(19)
2724.80275(18)	16	2738.16085(18)	2706.53161(19)	58	2753.84057(19)
2724.38316(18)	17	2738.55068(18)	2706.08298(19)	59	2754.19865(19)
2723.96274(18)	18	2738.93964(18)	2705.63386(19)	60	2754.55614(19)
2723.54149(18)	19	2739.32774(18)	2705.18426(19)	61	2754.91305(20)
2723.11940(18)	20	2739.71497(18)	2704.73421(20)	62	2755.26939(20)
2722.69648(18)	21	2740.10134(18)	2704.28370(20)	63	2755.62516(20)
2722.27275(18)	22	2740.48685(18)	2703.83275(20)	64	2755.98038(21)
2721.84819(18)	23	2740.87151(18)	2703.38136(21)	65	2756.33504(21)
2721.42283(18)	24	2741.25532(18)	2702.92955(21)	66	2756.68915(21)
2720.99666(18)	25	2741.63828(18)	2702.47733(21)	67	2757.04273(21)
2720.56970(18)	26	2742.02040(18)	2702.02470(21)	68	2757.39577(21)
2720.14194(18)	27	2742.40168(18)	2701.57167(22)	69	2757.74829(22)
2719.71339(18)	28	2742.78213(18)	2701.11825(22)	70	2758.10028(22)
2719.28406(18)	29	2743.16175(18)	2700.66445(22)	71	2758.45175(22)
2718.85396(18)	30	2743.54055(18)	2700.21027(22)	72	2758.80271(23)
2718.42309(18)	31	2743.91853(18)	2699.75572(23)	73	2759.15315(24)
2717.99147(18)	32	2744.29570(18)	2699.30081(24)	74	2759.50309(27)
2717.55909(18)	33	2744.67207(18)	2698.84554(25)	75	2759.85252(30)
2717.12597(18)	34	2745.04763(18)	2698.38991(27)	76	2760.20143(34)
2716.69211(18)	35	2745.42241(18)	2697.93393(31)	77	2760.54985(40)
2716.25752(18)	36	2745.79639(18)	2697.47761(35)	78	2760.89776(47)
2715.82222(18)	37	2746.16959(18)	2697.02094(41)	79	2761.24516(55)
2715.38620(18)	38	2746.54203(18)	2696.56393(48)	80	2761.59205(65)
2714.94949(18)	39	2746.91369(18)	2696.10658(56)	81	2761.93843(77)
2714.51208(18)	40	2747.28460(18)	2695.64888(66)	82	2762.28430(90)
2714.07398(18)	41	2747.65476(18)	2695.19085(78)	83	---

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

of OCS, in this region as well as other frequency regions, which are available to anyone with a specific request.

Tables VI and VII give the wavenumbers calculated for the 02^{0}2–00^{0}0 and 04^{0}1–00^{0}0 bands, respectively. In addition to the frequency measurements given here, these tables are also based on the constants for the 00^{0}1–00^{0}0 and 02^{0}0–00^{0}0 bands given in Ref. (8) and Refs. (14, 16), respectively. Although these are quite weak bands, they provide well-determined frequency calibration data in the region 2700 to 3000 cm^{-1} where such data are needed. In order to measure these two bands one must use a pressure–path length product of about 5 kPa · m (18).

One source of systematic error for the weaker transitions may come from the pressure shift. We have tried to measure the pressure shift and believe it is smaller than 2 kHz/Pa. The largest effect of such a shift on the present measurements will be about 2 MHz for the weakest lines. We are not even certain of the sign of the shift.

The rotational dependence of the frequency shift was too small to be measured. This attempt to measure the pressure shift is in agreement with an earlier measurement on the R(29) line of the 00^{0}1–00^{0}0 band (8) which found a shift of 0.8 ± 3.8 kHz/Pa.

The present values for the band centers are in excellent agreement with those given by Fayt et al. (12). The largest deviations are for the 04^{0}1 and 04^{2}1 levels which are about 0.001 cm^{-1} lower than the values given in Ref. (12). All other deviations are

TABLE VII

Calculated Transition Wavenumbers (cm^{-1}) for the 04^{0}1–00^{0}0 Band of OCS

P-Branch	J"	R-Branch	P-Branch	J"	R-Branch
---	0	2937.55349(23)[a]	2925.50856(18)	30	2950.32512(18)
2936.74091(23)	1	2937.96153(23)	2925.14152(18)	31	2950.77155(18)
2936.33636(23)	2	2938.37073(23)	2924.77603(18)	32	2951.21950(18)
2935.93297(23)	3	2938.78109(23)	2924.41210(18)	33	2951.66899(18)
2935.53075(23)	4	2939.19261(22)	2924.04976(18)	34	2952.12005(18)
2935.12970(23)	5	2939.60531(22)	2923.68903(18)	35	2952.57271(18)
2934.72983(22)	6	2940.01917(22)	2923.32994(18)	36	2953.02698(18)
2934.33113(22)	7	2940.43421(22)	2922.97252(18)	37	2953.48289(18)
2933.93362(22)	8	2940.85043(22)	2922.61679(18)	38	2953.94046(18)
2933.53730(22)	9	2941.26783(21)	2922.26278(18)	39	2954.39973(18)
2933.14217(22)	10	2941.68643(21)	2921.91051(18)	40	2954.86072(18)
2932.74825(21)	11	2942.10622(21)	2921.56002(18)	41	2955.32345(18)
2932.35555(21)	12	2942.52722(21)	2921.21133(18)	42	2955.78795(18)
2931.96407(21)	13	2942.94944(20)	2920.86447(18)	43	2956.25424(18)
2931.57382(21)	14	2943.37288(20)	2920.51948(18)	44	2956.72236(18)
2931.18481(20)	15	2943.79756(20)	2920.17636(18)	45	2957.19233(18)
2930.79706(20)	16	2944.22348(19)	2919.83517(18)	46	2957.66417(18)
2930.41058(20)	17	2944.65066(19)	2919.49591(18)	47	2958.13792(18)
2930.02538(19)	18	2945.07911(19)	2919.15863(18)	48	2958.61359(18)
2929.64147(19)	19	2945.50884(19)	2918.82335(18)	49	2959.09122(18)
2929.25887(19)	20	2945.93987(19)	2918.49010(18)	50	2959.57082(17)
2928.87759(19)	21	2946.37222(18)	2918.15891(18)	51	2960.05243(17)
2928.49765(19)	22	2946.80589(18)	2917.82979(17)	52	2960.53606(17)
2928.11907(18)	23	2947.24090(18)	2917.50279(17)	53	2961.02174(16)
2927.74187(18)	24	2947.67727(18)	2917.17792(17)	54	2961.50950(16)
2927.36605(18)	25	2948.11502(18)	2916.85522(16)	55	2961.99934(16)
2926.99165(18)	26	2948.55417(18)	2916.53470(16)	56	2962.49131(16)
2926.61868(18)	27	2948.99473(18)	2916.21639(16)	57	2962.98540(16)
2926.24716(18)	28	2949.43673(18)	2915.90031(16)	58	2963.48165(16)
2925.87711(18)	29	2949.88018(18)	2915.58649(16)	59	2963.98007(16)

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

within the assigned uncertainties. The rotational constants are also in agreement with Fayt *et al.* (*12*) when one remembers that Ref. (*12*) gives effective constants without allowing for the *l*-type resonance. There is also very good agreement with the work of Tanaka *et al.* (*19*) even though their work depended on the accuracy of the CO laser frequencies that they used and which they did not measure independently, as we have.

As can be seen in Table II, the present measurements also agree quite well with the band centers given by Lahaye *et al.* (*17*) for $^{16}O^{13}C^{32}S$ and $^{16}O^{12}C^{34}S$. We believe the present measurements confirm the accuracy of the tables of constants given by Refs. (*12, 17*) for various isotopic species of OCS.

ACKNOWLEDGMENTS

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