

# Calibration Tables Covering the 1460- to 1550-cm<sup>-1</sup> Region from Heterodyne Frequency Measurements on the $\nu_3$ Bands of <sup>12</sup>CS<sub>2</sub> and <sup>13</sup>CS<sub>2</sub>

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Heterodyne frequency measurements have been made on the  $\nu_3$  band of both <sup>12</sup>CS<sub>2</sub> and <sup>13</sup>CS<sub>2</sub> near 1500 cm<sup>-1</sup>. The data were fitted and new molecular constants determined. Values for the constants and newly calculated frequency calibration tables are presented. The calibration tables cover the range from 1460 to 1550 cm<sup>-1</sup>. © 1988 Academic Press, Inc.

## INTRODUCTION

Over the past several years heterodyne frequency measurements and the analysis of the infrared spectrum of the linear triatomic molecules, OCS and N<sub>2</sub>O, have constituted a major part of a continuing project at the NBS Boulder and NBS Gaithersburg Labs to provide accurate frequency calibration tables in the region from 0 to 3000 cm<sup>-1</sup> (1, 2). Although much of the region is now covered (as Fig. 1 indicates), there are several gaps in the coverage provided by these two molecules. Of immediate interest is the gap centered at 1500 cm<sup>-1</sup>. The  $\nu_3$  bands of the normal isotope of carbon disulfide (CS<sub>2</sub>) and of the carbon-13 substituted species have the potential to provide good frequency calibration points in the region from 1460 to 1550 cm<sup>-1</sup>. This is a very strong absorption band so the lines of <sup>13</sup>CS<sub>2</sub> can easily be observed in natural abundance.

Tunable diode lasers (TDL) or Fourier transform spectrometers (FTS) have been used in several recent studies of the  $\nu_3$  band of CS<sub>2</sub> (3-5). Those studies contain a wealth of information on the many hot band transitions that are present at room temperature and on the various sulfur isotopic species that are easily seen in natural abundance.

We report here the results of the first measurements of CS<sub>2</sub> using frequency measurement techniques. These heterodyne frequency measurements were designed to

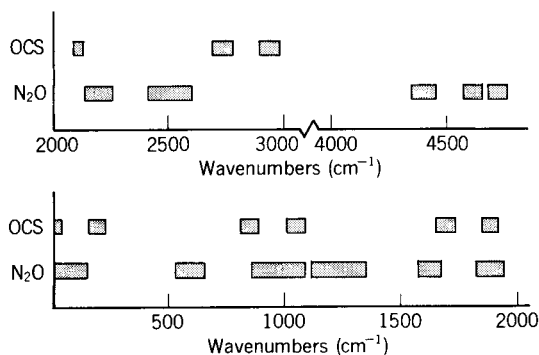


FIG. 1. Calibration standards available from frequency measurements. Coverage afforded by OCS and N<sub>2</sub>O in the 0- to 3000-cm<sup>-1</sup> region.

provide reliable frequency calibration data from 1460 to 1550 cm<sup>-1</sup> by concentrating on measuring the strongest band of <sup>12</sup>CS<sub>2</sub> and <sup>13</sup>CS<sub>2</sub>, the 00<sup>0</sup>1-00<sup>0</sup>0 band in each case. This report outlines our heterodyne measurement techniques and results, includes the new constants resulting from fitting these measurements, and presents tables of transition frequencies calculated from those constants.

#### EXPERIMENTAL DETAILS

The objective of the heterodyne frequency measurements was to refer the measurements of carbon disulfide frequencies to the carbon dioxide laser frequency standards. The technique we have developed requires the use of a liquid nitrogen-cooled, flowing-gas carbon monoxide laser as a transfer oscillator. Each CS<sub>2</sub> frequency determination consists of two nearly simultaneous frequency measurements. In one measurement, the frequency of a CO laser transfer oscillator (local oscillator) is determined relative to CO<sub>2</sub> laser frequency standards. In the second measurement, the frequency difference between a tunable diode laser, which is locked to a particular CS<sub>2</sub> transition, and the lasing frequency of the transfer oscillator is determined. A brief description of the measurements and the definitions of the characters in Table I follow (see Refs. (1, 2) for a detailed description).

First to be outlined is the measurement of the transfer oscillator frequency relative to the standard CO<sub>2</sub> laser frequencies. By the use of two stabilized CO<sub>2</sub> lasers, a microwave oscillator, and a metal-insulator-metal (MIM) diode to mix the frequencies, we synthesize a frequency,  $\nu_s$ , given by

$$\nu_s = l\nu_1 + m\nu_2 + n\nu_{Mw},$$

where  $\nu_1$  and  $\nu_2$  are the frequencies of the CO<sub>2</sub> laser standards and  $\nu_{Mw}$  is a microwave frequency. The quantities  $l$ ,  $m$ , and  $n$  are integers which are allowed both positive and negative values. The synthesized  $\nu_s$  signals generally become weaker as the mixing order,  $[1 + |l| + |m| + |n|]$ , increases. The objective of this experiment is to synthesize frequencies in the 43.8 to 46.5 THz region. In an effort to keep the mixing order (more particularly,  $[|l| + |m|]$ ) low, we have been constrained to use the highest

TABLE I  
Heterodyne Frequency Measurements on Carbon Disulfide

Synthesis Scheme			Transfer Oscillator		Carbon Disulfide		
$l \times T(\nu_1)^a$	$+ m \times T(\nu_2)^a$	$+ n \times \nu_{\text{fer}} + \nu_{B1}$	CO Trans. P $\nu^n$ (J $''$ )	Freq., MHz	Trans. & $\nu_{B2}$	Frequency, MHz	O. - C., MHz
$3 \times^8 R_{II}(10)$	$- 2 \times^3 P_I(10)$	$+ 2 \times 9000 + 725.8$	P25(13)	43855934.8 <sup>b</sup>	$^{13}\text{CS}_2$ P(82) +827.9	43856762.7(30) <sup>c</sup>	0.5
$3 \times^8 R_{II}(16)$	$- 2 \times^3 P_I(6)$	$- 2 \times 10500 + 904.4$	P25(12)	43957232.4	P(72) -3827.7	43953404.7(30)	-0.1
$3 \times^8 R_{II}(18)$	$- 2 \times^3 P_I(12)$	$- 1 \times 10000 + 966.8$	P24(15)	44372051.8	P(22) -3619.8	44375671.6(30)	-2.0
$3 \times^8 R_{II}(16)$	$- 2 \times^3 P_I(16)$	$- 0 + 991.8$	P24(14)	44476365.2	P(8) -751.6	44475613.6(20)	0.3
$3 \times^8 R_{II}(16)$	$- 2 \times^3 P_I(20)$	$- 0 - 746.1$	P24(12)	44682033.9	R(24) -2729.7	44679304.2(30)	1.1
$3 \times^8 R_{II}(20)$	$- 2 \times^3 P_I(18)$	$- 1 \times 10000 - 234.5$	P24(11)	44783379.9	R(44) -2516.8	44780863.1(30)	1.1
$3 \times^8 R_{II}(18)$	$- 2 \times^3 P_I(22)$	$- 1 \times 12000 - 952.4$	P24(10)	44883726.3	R(68) -2917.5	44880808.8(50)	-2.6
$3 \times^8 R_{II}(20)$	$- 2 \times^3 P_I(22)$	$- 2 \times 10000 - 294.1$	P24(9)	44983071.0	R(102) -1817.5	44981253.5(30)	0.0
$3 \times^8 R_{II}(20)$	$- 2 \times^3 P_I(22)$	$- 2 \times 10000 - 294.1$	P24(9)	44983071.0	$^{12}\text{CS}_2$ P(116) +3894.3	44986965.3(20)	0.9
$3 \times^8 R_{II}(22)$	$- 2 \times^3 P_I(22)$	$- 1 \times 11500 - 832.7$	P23(15)	45095970.6	P(106) +3132.6	45099103.2(50)	2.3
$3 \times^8 R_{II}(26)$	$- 2 \times^3 P_I(24)$	$- 1 \times 10000 - 496.0$	P23(12)	45409085.8	P(76) +1282.4	45410368.2(30)	0.1
$3 \times^8 R_{II}(30)$	$- 2 \times^3 P_I(28)$	$- 2 \times 11000 + 563.5$	P23(8)	45812635.1	P(30) +1340.7	45813975.8(40)	-2.5
$3 \times^8 R_{II}(34)$	$- 2 \times^3 P_I(26)$	$+ 1 \times 12000 + 769.8$	P22(14)	45928609.7	P(14) +4723.3	45933333.0(20)	-1.1
$3 \times^8 R_{II}(30)$	$- 2 \times^3 P_I(32)$	$- 2 \times 10500 - 575.5$	P22(13)	46034027.1	R(0) +1295.2	46035322.3(30)	0.2
$3 \times^2 P_I(34)$	$- 1 \times^8 R_{II}(30)$	$- 2 \times 9000 - 299.0$	P21(16)	46442404.9	R(88) -3407.1	46438997.8(70)	5.2

<sup>a</sup>The left superscript indicates the CO<sub>2</sub> isotope; 8 indicates  $^{12}\text{C}^{18}\text{O}_2$  and 3 is for  $^{13}\text{C}^{16}\text{O}_2$ .

<sup>b</sup>We estimate that the CO freq. represents the center of the transition to within 3 MHz.

The uncertainty as a transfer oscillator is 0.2 MHz and is included in the CS<sub>2</sub> uncertainty.

<sup>c</sup>The uncertainty in the last digits is given in parentheses.

band of frequencies for the  $\nu_1$  laser transition (the  $R_{II}$  band of the  $^{18}\text{O}^{12}\text{C}^{18}\text{O}$ ), and the lowest band of frequencies for the  $\nu_2$  transitions (the  $P_I$  band of  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ ). While other combinations ( $l = 4$  and  $m = -2$ , for example) will work to synthesize some of the frequencies, a choice of  $l = 3$  and  $m = -2$  will permit synthesis of most of the frequencies needed without the inconvenience of changing to different CO<sub>2</sub> lasers. The various  $n$  values selected were restricted to 0,  $\pm 1$ , and  $\pm 2$ , and a single  $X$ -band klystron sufficed for the microwave requirements. The difference between the synthesized frequency,  $\nu_s$ , and the transfer oscillator frequency,  $\nu_{\text{fer}}$ , was a beatnote,  $\nu_{B1}$ , which was measured with respect to an rf synthesizer. The frequency of the transfer oscillator was then

$$\nu_{\text{CO}} = \nu_{\text{fer}} = \nu_s \pm \nu_{B1}.$$

The second part of the procedure was a difference frequency measurement between the CO laser transfer oscillator and a TDL whose frequency was locked to the carbon

disulfide transition of interest. These measurements and the apparatus are described in detail in Refs. (1, 2). The frequency of the CS<sub>2</sub> transition was then

$$\nu_{\text{SCS}} = \nu_{\text{xfer}} \pm \nu_{\text{B2}},$$

where the beat frequency,  $\nu_{\text{B2}}$ , was observed on a microwave spectrum analyzer and measured with a marker oscillator whose frequency was counted. The measurements are given in Table I, which, for each carbon disulfide frequency measurement, lists the CO<sub>2</sub> laser transitions which oscillate at the frequencies  $\nu_1$  and  $\nu_2$ , the microwave frequency, the two beatnote frequencies, and the values for the CO and CS<sub>2</sub> frequencies.

As indicated by the O. - C. (observed - calculated) column in Table I, the fit is equal to our best previous work. This is due to two factors which are improved over some of our other recent work. First, the absorption lines were quite strong and permitted good signal-to-noise ratios for the lock signal. Perhaps even more important was the relatively narrow jitter linewidth of the TDL used for these measurements (compared to TDLs available for our last work (6)).

A 1.7-m cell was used for the measurements and pressures were all on the order of 10 Pa (0.08 Torr) or less. The carbon disulfide sample used was enriched in carbon-13 to provide an equal mixture of both carbon isotopes.

#### FITTING AND ANALYSIS

Like carbon dioxide, carbon disulfide has only even values of  $J$  allowed in the ground state because the two equivalent sulfur atoms have zero spin. Because of its symmetry it also lacks a dipole moment and thus has no microwave transitions that could accurately determine the ground state rotational constants. In this analysis we have used the usual term value equations to determine the energy levels and transitions for CS<sub>2</sub> as follows:

$$E'(J) = \nu_0 + B'J(J+1) - D'[J(J+1)]^2 + H'[J(J+1)]^3 \dots, \quad (1)$$

$$E''(J) = B_0J(J+1) - D_0[J(J+1)]^2 + H_0[J(J+1)]^3 \dots, \quad (2)$$

TABLE II  
Rovibrational Constants (in cm<sup>-1</sup>) for CS<sub>2</sub>

	<sup>12</sup> CS <sub>2</sub>	<sup>13</sup> CS <sub>2</sub>
$\nu_0(00^01-00^00)$	1535.35623(10) <sup>a</sup>	1485.33123(9)
$\Delta B(00^01-00^00) \times 10^3$	-0.712774(34)	-0.685911(65)
$\Delta D(00^01-00^00) \times 10^8$	0.000218(188)	-0.000047(680)
$B_0$	0.10912606(62)	0.10912954(49)
$D_0 \times 10^8$	1.1758(23)	1.1756(35)

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

and

$$\nu_{\text{obs}} = E'(J') - E''(J''). \quad (3)$$

We were not able to determine a value for the  $H$  terms so Eqs. (1) and (2) were truncated after the quartic centrifugal distortion term,  $D$ .

Since we were able to measure only a small number of transitions by means of heterodyne techniques, we have included other data or constants taken from the literature to ensure the accuracy of interpolating between measurements. The constants obtained from the least-squares fits are given in Table II. In Table II we report values for  $\Delta B = B' - B_0$  and  $\Delta D = D' - D_0$  because they are practically uncorrelated to the ground state constants.

For the analysis of the  $^{12}\text{CS}_2$  transitions we have included in a least-squares fit of the heterodyne measurements, ground state combination differences taken from the FTS measurements of Jolma and Kauppinen (7), the upper state combination differences taken from the TDL measurements of Baeten *et al.* (8), and the TDL measurements of the  $\nu_3$  transitions made by Lindenmayer and Jones (3). The values given by Winther *et al.* (4) for  $B_0$ ,  $D_0$ , and  $D'$  were also included in the fit with the uncertainty given in Ref. (4). In the fitting process, the data of Lindenmayer and Jones were

TABLE III  
Wavenumbers (in  $\text{cm}^{-1}$ ) Calculated for the  $\nu_3$  Band of  $^{13}\text{CS}_2$

P-BRANCH	J''	R-BRANCH	P-BRANCH	J''	R-BRANCH
---	0	1485.54812(09)	1471.00438(10)	56	1495.49568(13)
1484.89334(09) <sup>a</sup>	2	1485.97778(09)	1470.41377(10)	58	1495.77074(13)
1484.44997(09)	4	1486.40194(09)	1469.81773(10)	60	1496.04025(14)
1484.00111(09)	6	1486.82062(09)	1469.21627(10)	62	1496.30421(14)
1483.54677(09)	8	1487.23380(09)	1468.60940(11)	64	1496.56261(15)
1483.08696(09)	10	1487.64148(09)	1467.99711(11)	66	1496.81545(15)
1482.62166(09)	12	1488.04366(09)	1467.37940(11)	68	1497.06272(15)
1482.15090(09)	14	1488.44034(08)	1466.75629(11)	70	1497.30443(15)
1481.67466(09)	16	1488.83152(08)	1466.12777(11)	72	1497.54058(15)
1481.19295(08)	18	1489.21719(08)	1465.49384(11)	74	1497.77115(15)
1480.70578(08)	20	1489.59735(08)	1464.85451(11)	76	1497.99615(15)
1480.21314(08)	22	1489.97200(08)	1464.20978(11)	78	1498.21558(15)
1479.71504(08)	24	1490.34113(08)	1463.55965(12)	80	1498.42943(15)
1479.21148(08)	26	1490.70475(08)	1462.90412(12)	82	1498.63770(15)
1478.70246(08)	28	1491.06286(08)	1462.24320(12)	84	1498.84039(14)
1478.18799(08)	30	1491.41544(08)	1461.57688(13)	86	1499.03750(14)
1477.66806(07)	32	1491.76250(08)	1460.90518(14)	88	1499.22903(14)
1477.14268(07)	34	1492.10404(08)	1460.22808(15)	90	1499.41496(13)
1476.61185(08)	36	1492.44005(08)	---	92	1499.59531(13)
1476.07558(08)	38	1492.77053(09)	---	94	1499.77006(13)
1475.53386(08)	40	1493.09548(09)	---	96	1499.93922(14)
1474.98670(08)	42	1493.41489(10)	---	98	1500.10278(14)
1474.43410(08)	44	1493.72877(10)	---	100	1500.26075(16)
1473.87606(08)	46	1494.03711(10)	---	102	1500.41311(17)
1473.31259(09)	48	1494.33992(11)	---	104	1500.55987(19)
1472.74368(09)	50	1494.63718(11)	---	106	1500.70103(22)
1472.16934(09)	52	1494.92889(12)	---	108	1500.83657(25)
1471.58957(09)	54	1495.21506(12)	---	110	1500.96651(29)

a) The uncertainty (twice the estimated standard error) in the last digits is given in parentheses. In spite of the small uncertainty given by the statistics of the fits, the absolute frequency uncertainty should not be less than  $\pm 0.0001 \text{ cm}^{-1}$  (3 MHz).

allowed to determine a different band center than the present measurements, but the rotational constants were required to be the same for all measurements included in the fit. In our fit, the data of Lindenmayer and Jones gave  $\nu_0 = 1535.35649(20)$ . The data of Refs. (3, 7, 8) were weighted by the inverse square of the root-mean-square (RMS) deviation of each data set.

For the analysis of the <sup>13</sup>CS<sub>2</sub> data the ground state constants and upper state  $D$  value, given by Winther *et al.* (4), were used with their quoted uncertainty. Upper state combination differences taken from Ref. (9) were also used in the fit, with uncertainties given by the RMS deviation of the data.

## CONCLUSION

The constants given in Table II were used to calculate the transition frequencies given in Table III for the carbon-13 isotope and in Table IV for the most abundant isotope. These tables give the uncertainty in the transitions as determined from the variance-covariance matrix given by the least-squares fits.

One of the potential problems in using this molecule as a calibration reference is the large number of strong lines in the spectrum which belong to hot bands. Refer

TABLE IV  
Wavenumbers (in cm<sup>-1</sup>) Calculated for the  $\nu_3$  Band of <sup>12</sup>CS<sub>2</sub>

P-BRANCH	J''	R-BRANCH	P-BRANCH	J''	R-BRANCH
---	0	1535.57306(10) <sup>a</sup>	1519.14007(09)	62	1546.22041(15)
1534.91830(10)	2	1536.00243(10)	1518.52648(09)	64	1546.47186(15)
1534.47467(10)	4	1536.42610(10)	1517.90727(10)	66	1546.71753(16)
1534.02534(09)	6	1536.84406(10)	1517.28243(10)	68	1546.95743(16)
1533.57032(09)	8	1537.25631(10)	1516.65197(10)	70	1547.19154(16)
1533.10961(09)	10	1537.66285(10)	1516.01588(10)	72	1547.41987(17)
1532.64320(09)	12	1538.06368(10)	1515.37416(10)	74	1547.64242(17)
1532.17110(09)	14	1538.45879(10)	1514.72683(10)	76	1547.85917(18)
1531.69332(09)	16	1538.84818(10)	1514.07389(10)	78	1548.07014(18)
1531.20986(09)	18	1539.23184(10)	1513.41532(10)	80	1548.27532(19)
1530.72071(09)	20	1539.60979(10)	1512.75115(11)	82	1548.47470(19)
1530.22588(09)	22	1539.98200(10)	1512.08136(11)	84	1548.66828(20)
1529.72538(09)	24	1540.34849(10)	1511.40597(11)	86	1548.85607(20)
1529.21920(09)	26	1540.70925(10)	1510.72497(11)	88	1549.03805(20)
1528.70734(09)	28	1541.06428(10)	1510.03837(11)	90	1549.21423(21)
1528.18982(09)	30	1541.41357(10)	1509.34616(11)	92	1549.38461(21)
1527.66663(08)	32	1541.75712(10)	1508.64836(10)	94	1549.54918(21)
1527.13777(08)	34	1542.09494(11)	1507.94496(10)	96	1549.70793(22)
1526.60325(08)	36	1542.42701(11)	1507.23596(10)	98	1549.86088(22)
1526.06307(08)	38	1542.75334(11)	1506.52138(10)	100	1550.00801(22)
1525.51722(08)	40	1543.07392(11)	1505.80120(10)	102	1550.14932(23)
1524.96572(08)	42	1543.38876(11)	1505.07543(10)	104	1550.28481(23)
1524.40857(08)	44	1543.69784(11)	1504.34408(10)	106	1550.41448(23)
1523.84576(08)	46	1544.00117(12)	1503.60714(10)	108	1550.53833(23)
1523.27730(08)	48	1544.29874(12)	1502.86463(10)	110	---
1522.70319(09)	50	1544.59056(12)	1502.11653(10)	112	---
1522.12344(09)	52	1544.87661(13)	1501.36286(10)	114	---
1521.53804(09)	54	1545.15691(13)	1500.60361(11)	116	---
1520.94701(09)	56	1545.43144(13)	1499.83879(11)	118	---
1520.35033(09)	58	1545.70020(14)	1499.06840(12)	120	---
1519.74801(09)	60	1545.96319(14)	1498.29244(13)	122	---

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

to the more complete spectral analyses given for CS<sub>2</sub> in this region (see Refs. (3, 4)) to identify with certainty the calibration features given in this paper.

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