

# Heterodyne frequency measurements with a tunable diode laser-CO<sub>2</sub> laser spectrometer: spectroscopic reference frequencies in the 9.5- $\mu$ m band of carbonyl sulfide

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The frequencies of twelve carbonyl sulfide absorption lines near 9.5  $\mu$ m have been measured by means of a heterodyne frequency measuring technique, which uses a frequency stabilized CO<sub>2</sub> laser and a tunable diode laser. The diode laser was locked to the peak of each OCS absorption line by means of a first derivative frequency lock procedure. In addition to lines in the 02<sup>00</sup>-00<sup>00</sup> band, measurements also include some nearby OCS hot band features as well as lines in isotopically enriched samples of OC<sup>34</sup>S, O<sup>13</sup>CS, and <sup>18</sup>OCS. These measurements are part of an effort to provide frequency standards for the calibration of tunable IR laser devices.

## I. Introduction

The advent of tunable diode lasers<sup>1-4</sup> (TDL) and color center lasers<sup>5</sup> within the last few years has led to a resurgence in IR spectroscopy in the 2-30- $\mu$ m region. These devices permit one to obtain Doppler limited spectra with relative ease. Complex spectra of heavy molecules have been observed with a resolution that was previously not possible. Presently the accuracy of such measurements has not kept pace with the resolution, and a 0.005-cm<sup>-1</sup> value for uncertainty in the line position is not uncommon.<sup>6,7</sup> While standards do exist (for part of the region of interest) in the form of the CO<sub>2</sub> and the CO lasers, a vast majority of the laboratories with some 200 TDL spectrometers<sup>8</sup> have neither access to these lasers nor the heterodyne apparatus to use them, as is evident by the relatively small number of laboratories reporting TDL heterodyne measurements.<sup>9-12</sup> This paper describes our initial effort to satisfy partially an increasing demand<sup>13-16</sup> for absorption frequency standards by the users of tunable laser devices.

Good frequency calibration standards for tunable laser systems should satisfy the following criteria: (1) absorption lines (rather than laser or emission lines) will be used; (2) the calibration substance must be convenient, i.e., must be easily obtained and easily handled;

(3) there must be at least one calibration point every 0.5 cm<sup>-1</sup> (additionally, several nearby spectral features to help identify the calibration line would be extremely valuable); (4) the lines must be well resolved and free of accuracy limiting fine structure; and (5) each line must either be measured accurately or else calculated reliably and accurately. Although no single calibrant can fulfill these requirements over the entire spectral range, the requirements can be easily fulfilled in selected spectral regions by such linear molecules as OCS and N<sub>2</sub>O. The present efforts to generate a table of standards involve carbonyl sulfide.

Carbonyl sulfide is easily obtained and can be handled in any gas handling apparatus without special precautions. It does not attack normal IR absorption cells or IR windows. The 02<sup>00</sup>-00<sup>00</sup> band of interest in this paper has primary features about 0.4 cm<sup>-1</sup> apart. The spectral lines of OCS are well resolved and do not break up into hyperfine components even when studied with microwave resolution (resolution of 100 kHz). In order to satisfy the fifth criterion, it is necessary to make frequency measurements of sufficient accuracy such that the 0.002-cm<sup>-1</sup> uncertainty on the OCS line position<sup>17</sup> in the 02<sup>00</sup>-00<sup>00</sup> band can be reduced to the 0.0003-0.0001-cm<sup>-1</sup> range.

Realizing a sufficient number of frequency measurements is somewhat simplified due to the existence of a wealth of very accurate microwave measurements of the rotational constants for OCS.<sup>18-20</sup> For a linear molecule such as OCS (ignoring for the sake of brevity the effect of vibrational angular momentum), the IR frequencies can be accurately predicted using the equation

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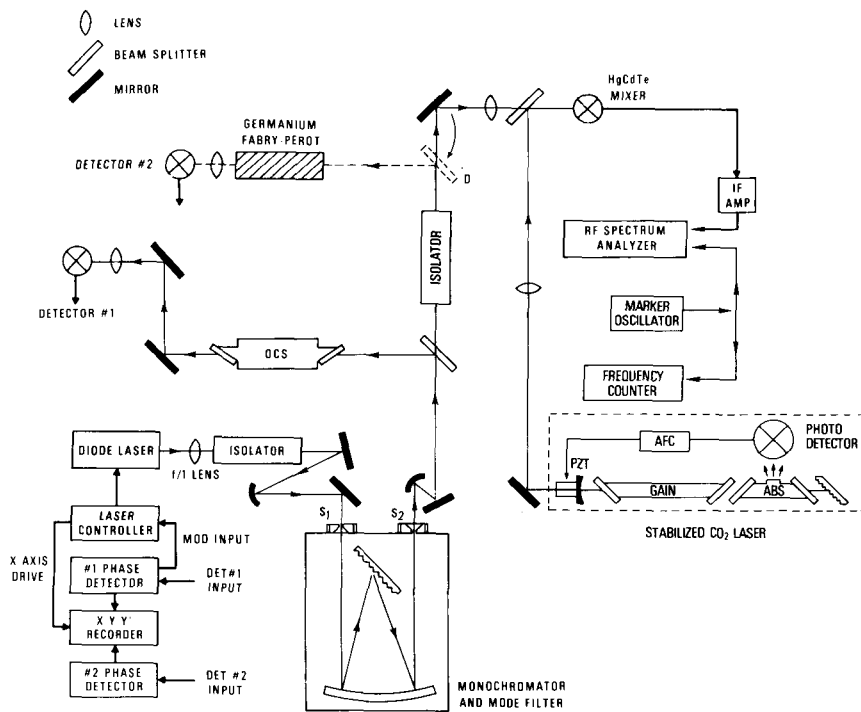


Fig. 1. Block diagram of a TDL spectrometer with capabilities for heterodyne frequency measurements. This arrangement permits locking a liquid helium cooled TDL to some absorption feature of the OCS molecule and then making frequency measurements relative to a stabilized CO<sub>2</sub> laser. Use as a conventional TDL spectrometer is facilitated by inserting a chopper in front of S<sub>1</sub> and moving the upper mirror to the dashed position for interpolation with the Fabry-Perot fringes.

$$\nu = \nu_0 + B'(J \pm 1)(J \pm 1 + 1) - D'(J \pm 1)^2(J \pm 1 + 1)^2 + B''J(J + 1) + D''J^2(J + 1)^2, \quad (1)$$

where  $J$  is the quantum number of rotational angular momentum for the lower state, and the  $+$  sign is taken for  $\Delta J = +1$  transitions, while the  $-$  sign is for  $\Delta J = -1$  transitions. Microwave measurements give very accurate values for  $B'$  and  $B''$ , the rotational constants for the upper and lower states, respectively. The ground state centrifugal distortion term  $D''$  and certain upper state  $D'$  terms have also been determined from microwave measurements, although some improvement would be helpful. In order to determine accurate values for the frequencies of all the calibration lines in a given band, it is necessary in principle to measure accurately only a few lines in order to determine the values of the remaining poorly determined terms in Eq. (1). A measurement of these few lines is the objective of these experiments.

## II. Experimental Method

The spectrometer used for the measurement of the OCS frequencies is diagramed in Fig. 1. The PbSnTe tunable diode laser is housed in a liquid helium Dewar that can accommodate three such lasers. A translatable stage facilitates positioning of one of the three lasers on the optic axis. A laser control module (LCM), which supplies current to the laser, has capabilities for slow sweep, several internal modulation options, and an external modulation capability from dc to 10 kHz. The Dewar, laser, and laser control module are all commercially available. The radiation from the diode was collimated by a 5-cm  $f/1$  ZnS polycrystalline lens. Off-axis parabolic mirrors were used to focus the TDL radiation on the entrance slit ( $S_1$ ) of the monochromator and recollimate the beam after it emerged from

the exit slit ( $S_2$ ). The 0.8-m monochromator was an  $f/10.7$  Ebert-Fastie with a 150-line/mm grating. Removable 150- $\mu$ m slits were used in line identification measurements. For general use, the entrance slit was replaced with an aperture (which was blackened and shaped to reduce fringes due to slit reflections feeding back to the TDL), and another slit, typically 500  $\mu$ m or greater, was used on the output. Isolators, consisting of 20-cm long attenuator cells (0–30 dB) with variable pressure of ethyl ether, were also inserted to ameliorate the troublesome fringe problem resulting from feedback to the TDL. Isolation (3 dB) in the alternate leg was added by the OCS cell when the TDL frequency coincided with a strong OCS transition.

A ZnSe beam splitter was used to divide the post monochromator collimated radiation. One beam was directed through a 50-cm long cell containing OCS and focused onto a PbSnTe photovoltaic detector. The other beam was sent through a 12.5-cm  $f/5$  Ge focusing lens and mixed with the reference CO<sub>2</sub> laser beam in a HgCdTe detector/mixer having a 200-MHz bandwidth. The detector was followed by a broadband IF amplifier (0.1–1200 MHz) with 25-dB gain. The output of the amplifier was fed to a spectrum analyzer, and the frequency of the beat signal was measured with a marker oscillator and frequency counter.

The CO<sub>2</sub> laser was stabilized to a saturated absorption dip in CO<sub>2</sub> (observed in fluorescence).<sup>21</sup> This laser was similar to those used in previous IR frequency synthesis experiments.<sup>22</sup> The estimated absolute fractional frequency uncertainty for the CO<sub>2</sub> laser is about  $1 \times 10^{-9}$ , which is negligible compared with other errors in these experiments. A 0.633- $\mu$ m He-Ne laser was used to align the optical elements so that both the TDL and CO<sub>2</sub> laser had a common optic axis over a

length several meters past the NaCl beam splitter. The CO<sub>2</sub> laser was focused onto the detector with a 40-cm focal length lens positioned to produce a beam waist at the mixer element. We estimate the CO<sub>2</sub> laser power at the detector to be about 1 mW. Figure 2(a) shows the rectified signals from both the CO<sub>2</sub> laser and TDL radiation. These levels, along with a negative 0.6-V bias on the detector, give rise to the beat note shown in Fig. 2(b), which has a width of about 2 MHz. The width of the beat note increased considerably at higher TDL currents, thereby limiting the range over which useful measurements could be made.

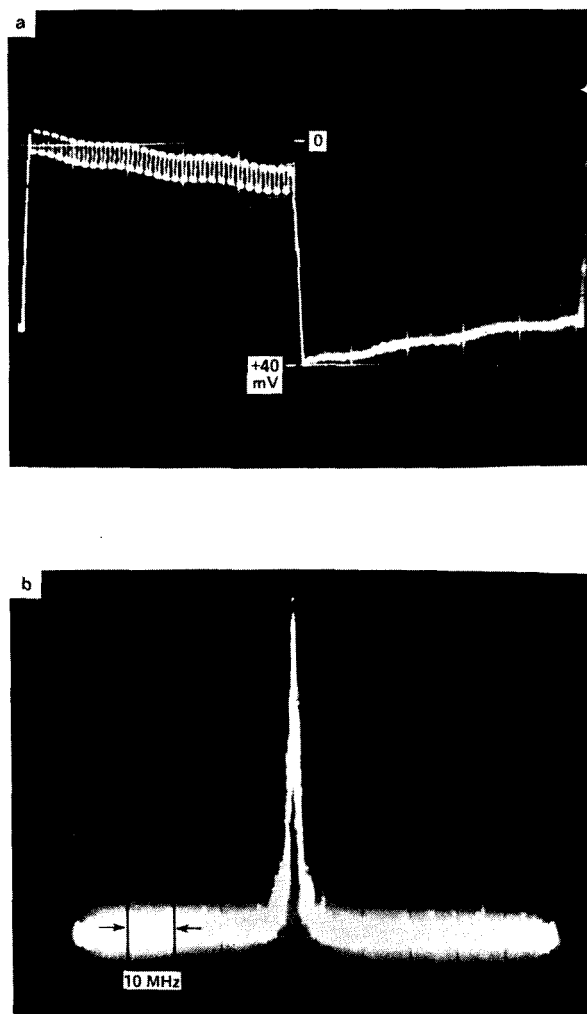


Fig. 2. (a) Rectified signals from tunable diode laser and CO<sub>2</sub> laser radiation. The detector was connected directly to the scope, which was adjusted to a 10-mV/division display. The lower frequency 40-mV chopped signal is due to the CO<sub>2</sub> laser. Detector nonlinearity is evidenced by the TDL signal, which drops from nearly 5 mV with the CO<sub>2</sub> laser off to about 1 mV with the CO<sub>2</sub> laser on. (b) Beat note between TDL [near *P*(41) of the OCS molecule] and the *P*(36) line of the CO<sub>2</sub> laser. The TDL current was about -0.69 A, just slightly above threshold. The center frequency is 530 MHz, and the dispersion is 10 MHz/cm. Other spectrum analyzer parameters are linear display, 300-kHz bandwidth, and 10-msec/cm sweep rate.

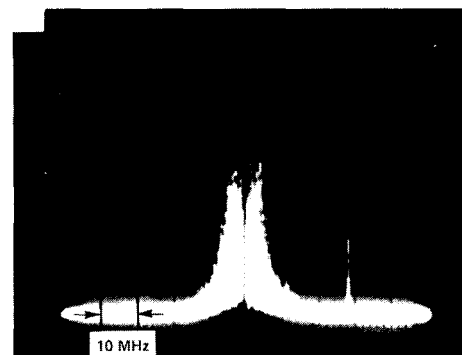
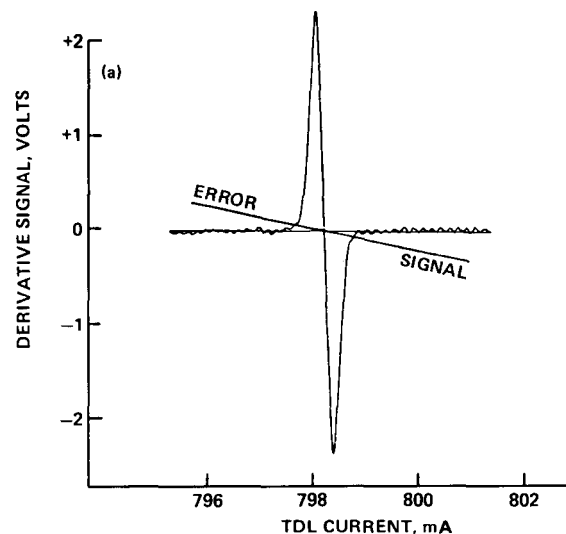


Fig. 3. (a) The derivative signal as the TDL was swept through an OCS line is displayed as a function of TDL current. The residual fringes on this signal are difficult to eliminate and are included in the error limit for our measurements. Zero voltage and an error voltage when lock loop is closed are also indicated. The lock point for the frequency measurements is the intersection of these three lines. (b) Beat note (linear display) between TDL, which is locked to a carbonyl sulfide line, and the *P*(32) line of the CO<sub>2</sub> laser. The center frequency is 507 MHz, and the dispersion is 10 MHz/cm. The dark void in the center of the beat note is due to a marker oscillator which is simultaneously fed to a counter for an accurate frequency determination. The 10-MHz linewidth of the beat note is due primarily to the frequency modulation used for the first derivative locking signal.

A set procedure for the measurements started with a real-time display of the spectrum on the oscilloscope. After identifying the OCS line to be measured, the monochromator was then roughly adjusted to shape the transmitted signal on the oscilloscope such that it was nearly flat over the region of the transition. A chopper was inserted in front of *S*<sub>1</sub>, and the signal was phase detected and displayed on the recorder as the current was slowly swept. The monochromator was then finely adjusted to flatten the transmitted signal on both sides of the OCS transition. (This procedure and a first derivative lock were used in lieu of a third derivative lock.)

The chopper was then removed, and the spectral feature was again observed on the scope. The  $f/1$  lens in front of the diode was readjusted (and the ethyl ether pressure in the cells increased if necessary) to minimize any feedback fringe distortion on or near the line. Recorder display was resumed, and a phase sensitive detector reference signal was used to frequency modulate the TDL as the current was slowly swept. This 10-mV 3.5-kHz signal produced a 10-MHz frequency modulation for our particular TDL at currents a few hundred mA above threshold. The 10 MHz was chosen as a trade off of beat frequency linewidth (narrowness) for fringe discrimination and lock stability.

The preceding steps were taken in order to insure an acceptable lock of the TDL to an OCS line frequency. One goal, which was not always met, was to have a ratio of OCS line derivative amplitude (signal) to fringe derivative amplitude (noise) of 50:1. A SNR of 50:1 should permit the location of the center of the 50-MHz Doppler-broadened line to within 1 MHz. A second goal was to have the average of the derivative signal on either side of the OCS line coincide with zero volts. Both goals were satisfied by the derivative of the OCS line displayed in Fig. 3(a). The derivative signal in proper phase was then applied to the modulation input along with the 3.5-kHz signal, and the TDL was locked to the line center to within the limits of our present capabilities. Figure 3(b) shows a beat note between the locked TDL and the CO<sub>2</sub> reference laser.

After verifying the CO<sub>2</sub> laser lock, a marker oscillator was tuned to the center of the beat note and simultaneously fed to a frequency counter in order to measure the TDL-CO<sub>2</sub> laser difference frequency. The last step is needed because the beat notes observed thus far do not have sufficient SNR reliably to drive a frequency counter.

The measurements were made with pressures between 40 Pa and 133 Pa (0.3 Torr and 1.0 Torr) in a 50-cm absorption cell. In addition to an isotopically normal sample of carbonyl sulfide, three isotopically enriched samples were used containing 86% OC<sup>34</sup>S, 64% O<sup>13</sup>CS, and 98% <sup>18</sup>OCS, respectively. Many lines of the

isotopically rare species could be seen in the spectrum of the isotopically normal sample at higher pressures, but the enriched samples were needed to make accurate measurements.

### III. Results and Discussion

Table I gives the measurements obtained in this work. The transitions were identified in the following way. Diode laser spectra were measured from about 0.1 cm<sup>-1</sup> below the CO<sub>2</sub> laser transition to about 0.1 cm<sup>-1</sup> above it. The observed spectra were then compared with the spectrum calculated from the ro-vibronic constants given in various references.<sup>17-20,23-28</sup> Although there were at first a few uncertainties in the assignments, the uncertainties were usually resolved by observing the relative intensities of the lines, by scanning the diode laser even farther from the CO<sub>2</sub> laser line, or by less ambiguous assignments made elsewhere in the band. In all cases a refit of the present heterodyne measurements with other diode measurements made in our laboratory and with data reported in the appropriate references<sup>18-20,23-25</sup> resulted in an internally consistent fit and yielded ro-vibronic constants close to previously determined values.

Most of the measurements were made with beat frequency widths of 10 MHz (determined by the amplitude of the frequency modulation needed to lock the diode laser to the peak of the absorption line). In such cases repeated measurements (sometimes made by different observers) gave results that always had an rms deviation of less than 1 MHz and often less than 0.5 MHz. Such measurements were assigned an uncertainty of  $\pm 2$  MHz to allow for possible systematic errors. Possible sources of error that could affect the TDL lock to the OCS line include a small slope of the absorption line background, the pulling effect of feedback fringes, and a residual zero offset from the phase sensitive detector. A nonuniform amplitude vs frequency response of the detector/mixer altered the shape of the beat note and caused measurements to be discarded in two instances. Possible asymmetries in the beat note due to nonlinear tuning of the TDL have also been considered. As indicated

Table I. Frequencies of Some Carbonyl Sulfide Absorption Lines Measured by the Heterodyne Technique

Molecular species	Vibrational transition	Rot. trans.	Freq. diff. OCS-CO <sub>2</sub> (MHz)	OCS freq. (MHz)	CO <sub>2</sub> laser trans.	CO <sub>2</sub> freq. (MHz) <sup>a</sup>
<sup>16</sup> O <sup>12</sup> C <sup>32</sup> S	02 <sup>00</sup> -00 <sup>00</sup>	P(41)	-485.6 $\pm$ 2.0	30 922 429.8	P(36)	30 922 915.42
	02 <sup>00</sup> -00 <sup>00</sup>	P(30)	-1512.6 $\pm$ 2.0	31 041 205.5	P(32)	31 042 718.06
	02 <sup>00</sup> -00 <sup>00</sup>	P(5) <sup>b</sup>	129.3 $\pm$ 2.0	31 329 090.8	P(22)	31 328 961.49
	02 <sup>00</sup> -00 <sup>00</sup>	R(3) <sup>b</sup>	499.6 $\pm$ 2.0	31 438 559.8	P(18)	31 438 060.17
<sup>16</sup> O <sup>12</sup> C <sup>34</sup> S	03 <sup>1e0</sup> -01 <sup>1e0</sup>	P(20) <sup>b</sup>	-832.3 $\pm$ 2.0	31 328 129.2	P(22)	31 328 961.49
	02 <sup>00</sup> -00 <sup>00</sup>	P(31)	-982.7 $\pm$ 2.0	30 982 208.0	P(34)	30 983 190.75
	03 <sup>1f0</sup> -01 <sup>1f0</sup>	P(48)	507.2 $\pm$ 2.0	30 983 698.0	P(34)	30 983 190.75
<sup>16</sup> O <sup>13</sup> C <sup>32</sup> S	03 <sup>1f0</sup> -01 <sup>1f0</sup>	R(26)	48.3 $\pm$ 2.0	30 983 239.1	P(34)	30 983 190.75
	03 <sup>1e0</sup> -01 <sup>1e0</sup>	R(31)	-147.1 $\pm$ 2.0	31 042 571.0	P(32)	31 042 718.06
<sup>18</sup> O <sup>12</sup> C <sup>32</sup> S	02 <sup>00</sup> -00 <sup>00</sup>	P(2)	-510.8 $\pm$ 2.0	31 042 207.3	P(32)	31 042 718.06
	03 <sup>1f0</sup> -01 <sup>1f0</sup>	P(18)	1066.6 $\pm$ 2.0	31 043 784.7	P(32)	31 042 718.06
	03 <sup>1e0</sup> -01 <sup>1e0</sup>	P(18)	-370.7 $\pm$ 2.0	31 042 347.4	P(32)	31 042 718.06

<sup>a</sup> See Ref. 22.

<sup>b</sup> A thermal impedance [0.010-in. (0.254-mm) stainless steel shim] was inserted between the TDL and the helium cold surface to obtain a narrower laser line at lower current.

previously, the above error sources were minimized, and the uncertainties given in Table I are estimated to represent one standard deviation ( $1\sigma$ ).

A few of the lines measured in this work are quite far from the frequencies predicted.<sup>23</sup> Refitting the data indicates, however, that the discrepancies are not due to errors in the band centers determined in that work.<sup>23</sup> The new data indicate the band centers need be shifted by less than 12 MHz from the previous values. A more complete analysis containing results of additional diode laser measurements will be given in a later communication.

Table II gives the recommended frequencies (and wave numbers) of the absorption lines of the 02<sup>0</sup>-00<sup>0</sup> band of <sup>16</sup>O<sup>12</sup>C<sup>32</sup>S. This table is designed to be used for the calibration of tunable laser devices in this spectral region. Table III gives the constants used to calculate the transitions given in Table II. The constants were determined by combining the present measurements on *P*(41), *P*(30), *P*(5), and *R*(3) with the microwave measurements<sup>18,19</sup> and with the results of the laser Stark resonance measurements.<sup>23</sup> These data were used in a least-squares fit with each datum weighted by the inverse square of the cited uncertainty. In the case

Table II. Wave Numbers, Frequencies, and Intensities of Spectral Lines of the 02<sup>0</sup>-00<sup>0</sup> Band of OCS from 1025 cm<sup>-1</sup> to 1074 cm<sup>-1</sup>

Wavenumber, ( $\sigma$ ) <sup>a</sup> (cm <sup>-1</sup> )	Frequency, ( $\sigma$ ) <sup>a</sup> (MHz)	Transition	Intensity (cm <sup>-2</sup> atm <sup>-1</sup> )	wavenumber, ( $\sigma$ ) <sup>a</sup> (cm <sup>-1</sup> )	Frequency, ( $\sigma$ ) <sup>a</sup> (MHz)	Transition	Intensity (cm <sup>-2</sup> atm <sup>-1</sup> )
1025.03101(48)	30729656.5(145)	P(60)	0.0196	1047.44906(7)	31401732.7(20)	R(0)	0.0124
1025.35562(45)	30739388.2(134)	P(59)	0.0217	1047.85726(7)	31413970.4(20)	R(1)	0.0249
1025.68183(41)	30749167.6(124)	P(58)	0.0240	1048.26672(7)	31426245.5(20)	R(2)	0.0371
1026.00962(38)	30758994.5(115)	P(57)	0.0264	1048.67741(7)	31438558.0(20)	R(3)	0.0493
1026.33897(35)	30768868.4(106)	P(56)	0.0291	1049.08936(7)	31450907.7(20)	R(4)	0.0611
1026.66989(32)	30778789.1(97)	P(55)	0.0319	1049.50255(7)	31463294.8(20)	R(5)	0.0726
1027.00236(30)	30788756.2(89)	P(54)	0.0350	1049.91698(7)	31475719.2(20)	R(6)	0.0838
1027.33637(27)	30798769.6(82)	P(53)	0.0382	1050.33266(7)	31488180.9(20)	R(7)	0.0945
1027.67191(25)	30808828.8(75)	P(52)	0.0416	1050.74958(7)	31500679.9(20)	R(8)	0.1046
1028.00897(23)	30818933.6(68)	P(51)	0.0452	1051.16775(7)	31513216.3(20)	R(9)	0.1143
1028.34754(21)	30829083.7(62)	P(50)	0.0491	1051.58716(7)	31525790.0(20)	R(10)	0.1233
1028.68761(19)	30839278.8(56)	P(49)	0.0531	1052.00782(7)	31538401.1(20)	R(11)	0.1316
1029.02918(17)	30849518.7(51)	P(48)	0.0573	1052.42973(7)	31551049.6(20)	R(12)	0.1393
1029.37223(15)	30859803.1(46)	P(47)	0.0617	1052.85289(7)	31563735.5(20)	R(13)	0.1463
1029.71676(14)	30870131.7(41)	P(46)	0.0663	1053.27730(7)	31576459.0(20)	R(14)	0.1525
1030.06275(12)	30880504.3(37)	P(45)	0.0711	1053.70296(7)	31589219.9(20)	R(15)	0.1580
1030.41020(11)	30890920.5(33)	P(44)	0.0760	1054.12987(7)	31602018.5(20)	R(16)	0.1627
1030.75910(10)	30901380.3(30)	P(43)	0.0811	1054.55804(7)	31614854.6(20)	R(17)	0.1666
1031.10944(9)	30911883.2(27)	P(42)	0.0862	1054.98746(7)	31627728.4(20)	R(18)	0.1698
1031.46121(8)	30922429.1(24)	P(41)	0.0915	1055.41815(7)	31640640.0(20)	R(19)	0.1722
1031.81441(7)	30933017.8(21)	P(40)	0.0968	1055.85009(7)	31653589.4(20)	R(20)	0.1739
1032.16903(7)	30943649.0(20)	P(39)	0.1022	1056.28330(7)	31666576.7(20)	R(21)	0.1748
1032.52505(7)	30954322.4(20)	P(38)	0.1076	1056.71778(7)	31679601.9(20)	R(22)	0.1751
1032.88249(7)	30965037.9(20)	P(37)	0.1130	1057.15352(7)	31692665.2(20)	R(23)	0.1746
1033.24131(7)	30975795.3(20)	P(36)	0.1184	1057.59054(7)	31705766.6(20)	R(24)	0.1735
1033.60153(7)	30986594.3(20)	P(35)	0.1236	1058.02883(7)	31718906.3(20)	R(25)	0.1718
1033.96313(7)	30997434.8(20)	P(34)	0.1287	1058.46840(7)	31732084.3(20)	R(26)	0.1696
1034.32610(7)	31008316.5(20)	P(33)	0.1337	1058.90925(7)	31745300.6(20)	R(27)	0.1668
1034.69045(7)	31019239.2(20)	P(32)	0.1384	1059.35139(7)	31758555.6(20)	R(28)	0.1635
1035.05615(7)	31030202.8(20)	P(31)	0.1429	1059.79481(7)	31771849.2(20)	R(29)	0.1598
1035.42322(7)	31041207.1(20)	P(30)	0.1471	1060.23953(7)	31785181.5(20)	R(30)	0.1556
1035.79163(7)	31052251.8(20)	P(29)	0.1509	1060.68555(7)	31798552.7(20)	R(31)	0.1512
1036.16139(7)	31063336.9(20)	P(28)	0.1544	1061.13288(7)	31811963.0(20)	R(32)	0.1464
1036.53248(7)	31074462.1(20)	P(27)	0.1574	1061.58149(7)	31825412.3(20)	R(33)	0.1414
1036.90491(7)	31085627.3(20)	P(26)	0.1600	1062.03142(7)	31838901.0(20)	R(34)	0.1361
1037.27867(7)	31096832.3(20)	P(25)	0.1620	1062.48267(7)	31852429.1(20)	R(35)	0.1307
1037.65376(7)	31108077.0(20)	P(24)	0.1634	1062.93524(7)	31865996.7(20)	R(36)	0.1251
1038.03016(7)	31119361.2(20)	P(23)	0.1643	1063.38913(7)	31879604.1(20)	R(37)	0.1195
1038.40787(7)	31130684.7(20)	P(22)	0.1645	1063.84435(7)	31893251.4(21)	R(38)	0.1138
1038.78689(7)	31142047.5(20)	P(21)	0.1641	1064.30091(8)	31906938.7(24)	R(39)	0.1081
1039.16722(7)	31153449.4(20)	P(20)	0.1630	1064.75881(9)	31920666.2(27)	R(40)	0.1024
1039.54884(7)	31164890.3(20)	P(19)	0.1611	1065.21806(10)	31934434.1(30)	R(41)	0.0968
1039.93176(7)	31176369.9(20)	P(18)	0.1586	1065.67866(11)	31948242.6(33)	R(42)	0.0913
1040.31598(7)	31187888.3(20)	P(17)	0.1552	1066.14062(12)	31962091.8(37)	R(43)	0.0856
1040.70148(7)	31199445.4(20)	P(16)	0.1512	1066.60395(14)	31975981.9(41)	R(44)	0.0805
1041.08826(7)	31211040.8(20)	P(15)	0.1463	1067.06864(15)	31989913.1(46)	R(45)	0.0753
1041.47632(7)	31222674.7(20)	P(14)	0.1407	1067.53472(17)	32003885.7(51)	R(46)	0.0703
1041.86567(7)	31234346.9(20)	P(13)	0.1344	1068.00218(19)	32017899.8(56)	R(47)	0.0654
1042.25628(7)	31246057.3(20)	P(12)	0.1274	1068.47103(21)	32031955.6(62)	R(48)	0.0608
1042.64817(7)	31257805.7(20)	P(11)	0.1196	1068.94128(23)	32046053.3(68)	R(49)	0.0563
1043.04132(7)	31269592.2(20)	P(10)	0.1112	1069.41293(25)	32060193.2(75)	R(50)	0.0521
1043.43574(7)	31281416.6(20)	P(9)	0.1021	1069.88600(27)	32074375.4(82)	R(51)	0.0480
1043.83142(7)	31293278.8(20)	P(8)	0.0924	1070.36049(30)	32088600.3(89)	R(52)	0.0442
1044.22837(7)	31305178.3(20)	P(7)	0.0822	1070.83641(32)	32102868.0(97)	R(53)	0.0405
1044.62657(7)	31317116.7(20)	P(6)	0.0714	1071.31377(35)	32117178.7(106)	R(54)	0.0371
1045.02603(7)	31329092.1(20)	P(5)	0.0603	1071.79257(38)	32131532.8(115)	R(55)	0.0339
1045.42674(7)	31341105.1(20)	P(4)	0.0487	1072.27282(41)	32145930.4(124)	R(56)	0.0309
1045.82870(7)	31353155.7(20)	P(3)	0.0368	1072.75453(45)	32160371.8(134)	R(57)	0.0281
1046.23192(7)	31365243.8(20)	P(2)	0.0247	1073.23771(48)	32174857.3(145)	R(58)	0.0255
1046.63638(7)	31377369.3(20)	P(1)	0.0124	1073.72238(52)	32189387.1(156)	R(59)	0.0231
				1074.20853(56)	32203961.4(168)	R(60)	0.0209

a) The uncertainty (one standard deviation) in the last digit is given in parenthesis. See text for explanation.

Table III. Ro-Vibrational Constants and Variance-Covariance Matrix for the 02<sup>0</sup>0-00<sup>0</sup>0 Transitions of <sup>16</sup>O<sup>12</sup>C<sup>32</sup>S

Constant	Value, MHz	Value, cm <sup>-1</sup>			
$\nu_0$	31 389 532.3(8) <sup>a</sup>	1047.04209			
$B'$	6 100.19078(34)	0.203480462			
$D'$	0.001 09553(69)	$3.6543 \times 10^{-8}$			
$B''$	6 081.492516(62)	0.20285675			
$D''$	0.001 301937(13)	$4.34279 \times 10^{-8}$			
Variance-covariance matrix (in units of MHz <sup>2</sup> )					
	$\nu_0$	$B'$	$D'$	$B''$	$D''$
$\nu_0$	0.588 951	$8.944 449 \times 10^{-5}$	$2.791 705 \times 10^{-7}$	$8.745 916 \times 10^{-7}$	$1.008 042 \times 10^{-10}$
$B'$		$1.167 756 \times 10^{-7}$	$1.916 400 \times 10^{-10}$	$-6.244 748 \times 10^{-10}$	$-4.970 268 \times 10^{-14}$
$D'$			$4.702 130 \times 10^{-13}$	$-1.864 777 \times 10^{-12}$	$-1.508 793 \times 10^{-16}$
$B''$				$3.858 123 \times 10^{-9}$	$5.283 937 \times 10^{-13}$
$D''$					$1.625 743 \times 10^{-16}$

<sup>a</sup> The uncertainty in the band center is placed at  $\pm 2$  MHz in order to reflect possible systematic error in these measurements.

of the laser Stark results, the reported band center was used as input to the least-squares fit, but the uncertainty was taken to be  $\pm 10$  MHz in order to allow for systematic errors, which would not have appeared in the reported statistical analysis of the data. The band center was also lowered to 31 359 542.8-MHz to allow for the slightly different laser frequencies used in the present analysis.

The variance-covariance matrix determined from this least-squares fit was used in calculating the uncertainties given for the frequencies in Table II. The variance-covariance matrix is also given in Table III. The uncertainties determined by the variance-covariance matrix have been doubled because our experience has been that the statistically estimated standard deviation is usually too small. We regard the uncertainties given in Table II as equivalent to one standard deviation. Although the uncertainties were slightly less than 2 MHz from  $P(39)$  to  $R(37)$ , a lower limit of  $\pm 2$  MHz has been set on the uncertainties given in Table II in order to allow for systematic errors in our measurements.

The data were analyzed using the usual equations similar to Eq. (1). The sextic terms  $H_v$  were not used in fitting the data since it has been shown<sup>18</sup> that they cannot be determined with useful accuracy even though the microwave measurements extend to  $J = 67$  for the ground state. The use of an expansion that goes to higher order than the data warrant will usually result in both extrapolated and interpolated frequencies that are less accurate than those obtained from a lower order expansion.

The last column of Table II gives the estimated intensity of each transition. The intensities were calculated for a temperature of 295 K by using the equation

$$S = C\nu R^2 Q_V^{-1} Q_R^{-1} N_i |m| \exp(-E''/kT), \quad (2)$$

where  $\nu$  is the frequency of the transition (in  $\text{cm}^{-1}$ ),  $R$  is the transition moment (in debyes),  $Q_V$  and  $Q_R$  are the partition functions for vibration and rotation, respectively,  $N_i$  is the isotopic concentration of the sample (i.e., 0.9325 for <sup>16</sup>O<sup>12</sup>C<sup>32</sup>S in normal abundance),  $E''$  is the energy of the lower state with respect to the ground state, and  $m = J'$  for  $\Delta J = +1$  transitions and  $m = -J''$

for  $\Delta J = -1$  transitions. The constant  $C$  includes Loschmidt's number and several other factors that result in an integrated line intensity given in the usual spectroscopic units of  $\text{cm}^{-2} \text{atm}^{-1}$  (i.e.,  $C = 10.3546$  at 295 K).

Foord and Whiffen<sup>29</sup> measured a transition moment of  $|R| = 0.0372$  D from the integrated intensity of the unresolved  $2\nu_2$  band. However, the intensities given in Table II are based on  $|R| = 0.0386$  D ( $0.129 \times 10^{-30}$  Cm), a value that gives calculated line intensities for  $P(30)$  and  $P(41)$  in better agreement with the intensities observed in the present work.

To calculate the absorption at the peak of a non-pressure broadened line, one must use the usual equations

$$\% \text{ transmission} = \frac{I \times 100}{I_0} = 100 \exp(-KLP), \quad (3)$$

$$K = \frac{S}{\pi b_D} \left[ \frac{\ln 2}{\pi} \right]^{1/2} \quad (4)$$

where  $S$  is the integrated line intensity taken from the last column of Table II,  $b_D$  is the Doppler width (half of the linewidth at half of the intensity, in  $\text{cm}^{-1}$ ),  $L$  is the absorption path length (in cm), and  $p$  is the partial pressure of the carbonyl sulfide (in atmospheres).

In using Table II one should remember that the absolute intensities are not known very accurately although the relative intensities are quite reliable, at least for lines that are not spectrally far apart.

Plans for similar experiments in the near future include measurements in the 10<sup>0</sup>0-00<sup>0</sup>0 band of OCS at 11  $\mu\text{m}$  with respect to the <sup>13</sup>C<sup>16</sup>O<sub>2</sub> laser and, then, measurements of the 20<sup>0</sup>0-00<sup>0</sup>0 OCS band at 6  $\mu\text{m}$  with respect to a CO laser. It is anticipated that our frequency difference range will be expanded by using the detector in the varactor<sup>30</sup> mode.

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