

## Wavelength Measurements of $^{13}\text{C}^{16}\text{O}$ Laser Transitions

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Wavelength measurements of 160  $^{13}\text{C}^{16}\text{O}$  laser lines in the range from 1500 to 1900  $\text{cm}^{-1}$  have been made with a conventional grating spectrometer. The accuracy of the measurements is about  $\pm 0.003 \text{ cm}^{-1}$ . Although more precise measurements of these lines will ultimately be made using microwave beating techniques, the present results should be of interest for the determination of improved molecular constants for CO and especially for the various spectroscopic applications of the CO laser.

### I. INTRODUCTION

Several workers have made wavelength measurements of carbon monoxide ( $^{12}\text{C}^{16}\text{O}$ ) laser lines (1-5) using conventional infrared grating spectrometers. The most accurate and complete study is that of Roh and Rao (5), who used a liquid nitrogen cooled, Q-switched laser and observed emission ranging from the 4-3 ( $v' \rightarrow v''$ ) band ( $\sim 2000 \text{ cm}^{-1}$ ) to the 37-36 band ( $\sim 1200 \text{ cm}^{-1}$ ). In this paper, we describe similar measurements of the output of a  $^{13}\text{C}^{16}\text{O}$  laser in the range 1900-1500  $\text{cm}^{-1}$ .

Wavelength measurements of the carbon monoxide laser spectrum yield a more detailed knowledge of the molecular constants of CO, and may be used to derive accurate potential energy functions (6). More importantly, however, an accurate knowledge of the CO laser line positions is essential for its use in spectroscopic applications such as laser Stark (7) and laser Zeeman (8, 9) spectroscopy, and the direct detection of pollutant gases by their absorption of laser radiation (10). For many of these applications, the new set of laser lines provided by isotopically substituted carbon monoxide should be particularly useful.

It has been shown by Sokoloff *et al.* (11) that the absolute frequencies of CO laser lines can be measured directly by harmonic mixing techniques. More recently Eng *et al.* (12) have determined the frequencies of several  $^{12}\text{C}^{16}\text{O}$  lines and one  $^{13}\text{C}^{16}\text{O}$  line and Riccius *et al.* (13) have determined the frequencies of one  $^{12}\text{C}^{16}\text{O}$  line and one  $^{13}\text{C}^{16}\text{O}$  line. Despite the fact that these techniques will ultimately provide the most precise frequencies, we felt that it would be useful to make wavelength measurements at this time since the difficulties of measuring frequencies in the THz range will probably delay the appearance of a comprehensive list of accurate frequencies for some time.

### II. EXPERIMENTAL

The practicability of an isotopic CO laser has been brought about by the recent development of sealed-off carbon monoxide lasers by Freed (14), and by Seguin, Tulip,

<sup>1</sup> N.R.C.C. Summer Student, 1973.

and White (15). Our laser is similar to those in Refs. (14) and (15), and has been described previously (7). No difficulty was encountered in operating the laser<sup>2</sup> with <sup>13</sup>C<sup>16</sup>O, and output powers were comparable to those obtained with ordinary research grade <sup>12</sup>C<sup>16</sup>O. A typical gas mixture was 0.5 Torr CO, 1.0 Torr N<sub>2</sub>, 1.5 Torr Xe, and 8 Torr He. The laser discharge tube was cooled to about -78°C.

The measurements were made using the vacuum infrared spectrometer originally described by Douglas and Sharma (16). This instrument has a focal length of 2 m, and its optical layout is similar to the symmetric Czerny-Turner pattern, except that the collimating mirrors are off-axis paraboloids. Recently, various modifications have been made to the spectrometer in order to improve its performance, and it seems appropriate to describe some of these here.

The original grating drive motor has been replaced by a SLO-SYN stepping motor located inside the vacuum tank. The advantage of this type of motor is that there are no brushes and it can therefore operate reliably at any pressure. The main disadvantage, that of stepwise operation, has been largely overcome by supplying the motor windings with triangular waveforms. The two required triangular waveforms, phase shifted 90° with respect to each other, are generated digitally with 32 steps in each ramp. In this way the rate of angular rotation of the shaft is smoothed to within ±0.2° and we have, in effect, a 'stepless' stepping motor drive. The motor drives the lead screw, which rotates the grating, through a 4:1 reduction gear and its position is recorded on a 6 digit up-down counter. At the fastest speed the motor can drive the nut from one end of the lead screw to the other in about 20 minutes. The speed is switch selectable in a binary sequence with 14 steps, and is locked to the 60 Hz line frequency.

A small prism monochromator has been placed after the exit slit to separate the grating orders. The prism table accommodates two CaF<sub>2</sub> prisms of different dispersions and, in addition, a plane mirror so that a filter can be used instead of a prism. Any one of a number of detectors can be mounted on this unit; for the present work, a liquid helium cooled Ge:Cu detector was used.

In normal operation, infrared radiation passes through the center of the slits and visible radiation from a calibration source enters the spectrometer just above the center of the entrance slit and leaves just below the center of the exit slit. This light is diverted to a photomultiplier before passing through the order separating monochromator. At the beginning and end of each run a system of mirrors illuminates that portion of the slit normally used for infrared radiation with light from the calibrating source and directs light from the center of the exit slit to a second photomultiplier. In this way the 'optical' shift caused by the infrared and calibration beams following different paths through the spectrometer can be measured and later used in the calibration.

The infrared radiation is modulated by a small tuning fork chopper located inside the vacuum tank directly in front of the entrance slit. A chopping frequency of 800 Hz was used for this work, but other frequencies are available. The calibration radiation is separately modulated by a 210 Hz chopper, and the resulting electrical signals from the two radiation detectors are synchronously detected with conventional lock-in amplifiers. The outputs of these amplifiers are measured by digital voltmeters which also serve as analog to digital converters. The digitized values of the voltages, together with an

<sup>2</sup> The <sup>13</sup>C enriched carbon monoxide gas was supplied by Merck, Sharpe and Dohme Ltd., and has an isotopic purity of 90%.

identification character, are written on magnetic tape at a rate which can be varied from 1 to 5 per second. The interface electronics are controlled by a clock which is phase locked to the 60 Hz line so that the grating drive motor and the data recording are effectively locked together. The spectrum is recorded as two large arrays of numbers, each pair of numbers also being associated with an identification character. One of the arrays contains the calibration spectrum; the beginning and end of the other also contains calibration spectra (in order to measure the optical shift as mentioned above) while the central portion contains the unknown spectrum. The change from calibration in both channels to calibration in one and unknown in the other is signaled by a change in the identification character, and this may also be used to mark special features in the spectrum as they are recorded. The magnetic tapes are read into an IBM 360/67 computer and processed by a program which finds and measures lines according to methods described by Steinhaus *et al.* (17). Briefly, a first pass through the data is made in order to determine the background. Then, regions of the spectrum which differ significantly from the background are digitally smoothed and both first and second derivatives found. Small regions which contain only one line are finally isolated by criteria based on the first and second derivatives and the points within these regions fitted to a polynomial in order to find the line peak. As well as finding the peak positions of the lines the program also returns the log relative intensity (corresponding to the peak position) and, if desired, the width of the line and a factor defining the asymmetry of the line (provided that these quantities can be measured).

The present spectra were taken in the third and fourth orders of a 72 line/mm grating blazed for 25  $\mu\text{m}$ , and the calibration source was a thorium electrodeless lamp (18). Since our laser is designed for single line operation by means of an intracavity grating, it was necessary to readjust the laser continually as a spectrum was being recorded. This procedure was greatly facilitated by first performing a survey during which the location of each laser line was measured both in terms of spectrometer grating position and laser grating position.

### III. RESULTS

Despite the fact that our method of measurement attempts to correct for shifts between the unknown and calibration channels, past experience has shown that, while relative wavenumbers are usually good to about  $\pm 0.003 \text{ cm}^{-1}$ , absolute wavenumbers cannot be relied on to better than about  $\pm 0.01 \text{ cm}^{-1}$ . However, as mentioned in the introduction, the absolute frequencies of two  $^{13}\text{C}^{16}\text{O}$  lines have recently been measured with high accuracy and we have used these two measurements to correct our wavenumbers for a small absolute error. We proceeded as follows.

The  $^{13}\text{C}^{16}\text{O}$  lines were measured as described in the previous section using Thorium lines as wavelength standards. Most of the measurements are averages of two or three separate observations. No difficulties were encountered in assigning the observed lines since previously determined constants for  $^{12}\text{C}^{16}\text{O}$  (5), modified by simple isotope relations (19), predicted the line positions to within  $0.03 \text{ cm}^{-1}$ .

A set of molecular constants were then obtained for  $^{13}\text{C}^{16}\text{O}$  by fitting the observed data to the usual term value expression

$$T(v, J) = \sum_{l,j} Y_{l,j} (v + \frac{1}{2})^l [J(J + 1)]^j, \quad (1)$$

where  $v$  and  $J$  are the vibrational and rotational quantum numbers and  $Y_{l,j}$  are the Dunham coefficients. Also included in the fit was a microwave measurement of the  $^{13}\text{C}^{16}\text{O}$  pure rotation  $R(0)$  transition by Rosenblum, Nethercot, and Townes (20), and measurements of 76 emission lines of the 1-0, 2-1, and 3-2 bands of  $^{13}\text{C}^{16}\text{O}$  observed in natural abundance in an electrical discharge by Telfair and Pliva (21). The microwave measurement was weighted by a factor of  $10^7$  relative to the infrared measurements in the fit.

The constants obtained in this way were used to predict the two lines which have recently been measured by Eng *et al.* (12) and by Riccius *et al.* (13). It was found that our measurements had to be increased by  $0.005_0 \text{ cm}^{-1}$  for the 7-6  $P(18)$  line and by  $0.006_0 \text{ cm}^{-1}$  for the 7-6  $P(19)$  line. Accordingly, we added  $0.005_0$  to all our original measurements and repeated the fit. This time the accurate frequencies of the two lines mentioned above were included with a weight of 20.

The measured positions of the 160 observed lines are given in Table I (note that these measurements include the small correction of  $0.005_0 \text{ cm}^{-1}$ ). The constants obtained

TABLE I  
WAVENUMBERS ( $\text{cm}^{-1}$ ) OF  $^{13}\text{C}^{16}\text{O}$  LASER TRANSITIONS

TRANSITION	OBSERVED	CALCULATED	TRANSITION	OBSERVED	CALCULATED
7-6 P(16)	1885.626	.624	11-10 P(20) <sup>b</sup>		1772.861
P(17)	1881.637	.639	P(21) <sup>b</sup>		1768.887
P(18)	1877.625 <sup>a</sup>	.625	P(22)	1764.871	.883
P(19)	1873.579 <sup>a</sup>	.580			
8-7 P(12)	1876.727	.723	12-11 P(08)	1793.804	.804
P(13)	1872.896	.894	P(09)	1790.229	.231
P(14) <sup>b</sup>		1869.035	P(10)	1786.632	.627
P(15)	1865.146	.144	P(11)	1782.988	.992
P(16)	1861.224	.223	P(12) <sup>b</sup>	1779.326	.325
P(17)	1857.273	.272	P(13)		1775.627
P(18)	1853.289	.290	P(14) <sup>b</sup>	1771.894	.898
P(19)	1849.279	.278	P(15)		1768.139
			P(16)	1764.341	.349
9-8 P(10)	1859.760	.762	P(17) <sup>b</sup>	1760.526	.528
P(11)	1856.031	.028	P(18)		1756.677
P(12)	1852.264	.263	P(19) <sup>b</sup>	1752.785	.796
P(13)	1848.473	.467	P(20)		1748.884
P(14) <sup>b</sup>		1844.640	P(21)	1744.941	.943
P(15)	1840.789	.783			
P(16)	1836.892	.894	13-12 P(08)	1769.509	.512
P(17)	1832.979	.976	P(09)	1765.967	.971
P(18)	1829.019	.026	P(10)	1762.396	.400
P(19) <sup>b</sup>		1825.047	P(11)	1758.789	.797
P(20)	1821.036	.037	P(12) <sup>b</sup>	1755.162	.163
P(21)	1816.989	.998	P(13)		1751.498
			P(14)	1747.800	.802
10-9 P(09)	1838.980	.979	P(15)	1744.076	.075
P(10)	1835.313	.309	P(16)	1740.314	.318
P(11)	1831.610	.608	P(17)	1736.528	.530
P(12)	1827.879	.876	P(18)	1732.716	.711
P(13)	1824.109	.113	P(19)	1728.860	.863
P(14)	1820.322	.319	P(20)	1724.980	.984
P(15)	1816.490	.494	P(21)	1721.076	.076
P(16)	1812.641	.638			
P(17)	1808.750	.752	14-13 P(08)	1745.292	.296
P(18)	1804.836	.835	P(09)	1741.786	.788
P(19)	1800.888	.889	P(10) <sup>b</sup>	1738.251	.250
			P(11) <sup>b</sup>		1734.679
			P(12)	1731.077	.078
11-10 P(08)	1818.171	.173	P(13)	1727.446	.446
P(09)	1814.565	.568	P(14)	1723.777	.782
P(10)	1810.932	.931	P(15)	1720.088	.088
P(11)	1807.265	.262	P(16)	1716.365	.364
P(12)	1803.561	.563	P(17)	1712.606	.608
P(13)	1799.836	.832	P(18)	1708.823	.823
P(14)	1796.069	.071	P(19)	1705.009	.007
P(15)	1792.283	.279			
P(16)	1788.453	.456	15-14 P(07)	1724.593	.601
P(17) <sup>b</sup>	1784.599	.602	P(08) <sup>b</sup>	1721.259	.158
P(18)		1780.719	P(09)		1717.683
P(19)	1776.800	.805	P(10)	1714.176	.177

TABLE I (continued)

TRANSITION	OBSERVED	CALCULATED	TRANSITION	OBSERVED	CALCULATED
15-14 P(11)	1710.641	.639	19-18 P(07)	1628.706	.703
P(12)	1707.067	.071	P(08)	1625.389	-.391
P(13) <sup>b</sup>	1703.468	.471	P(09)	1622.048	-.047
P(14) <sup>b</sup>		1699.841	P(10)	1618.676	.672
P(15) <sup>b</sup>		1696.179	P(11)	1615.267	-.265
P(16)	1692.485	.487	P(12)	1611.826	.827
P(17) <sup>b</sup>	1688.764	.765	P(13)	1608.356	-.358
P(18)		1685.012	P(14)	1604.858	-.859
P(19)	1681.225	.222	P(15)	1601.326	-.328
P(20)	1677.407	.416	P(16)	1597.767	-.767
P(21)	1673.565	-.573	P(17) <sup>b</sup>	1594.176	.176
			P(18)		1590.554
			P(19)	1586.906	.902
16-15 P(08)	1697.090	.099	20-19 P(07)	1604.921	.926
P(09) <sup>b</sup>	1693.654	.656	P(08)	1601.642	-.646
P(10)		1690.183	P(09)	1598.335	-.335
P(11) <sup>b</sup>	1686.674	.678	P(10)	1594.995	.992
P(12)		1683.142	P(11)	1591.610	-.618
P(13)	1679.575	.575	P(12)	1588.214	-.213
P(14)	1675.977	.977	P(13)	1584.777	.777
P(15)	1672.349	.348	P(14)	1581.310	.310
P(16)	1668.691	.689	P(15)	1577.813	.812
P(17)	1665.005	1664.999	P(16)	1574.280	.284
P(18)	1661.287	.279	P(17)	1570.726	.725
P(19)	1657.532	.529	P(18)	1567.131	.136
17-16 P(07)	1676.491	.494	21-20 P(08)	1577.981	.980
P(08) <sup>b</sup>	1673.112	.117	P(09)	1574.699	.701
P(09)		1669.707	P(10)	1571.389	.391
P(10) <sup>b</sup>	1666.270	.267	P(11)	1568.048	.050
P(11)		1662.795	P(12) <sup>b</sup>		1564.678
P(12)	1659.293	.292	P(13) <sup>b</sup>	1561.272	.274
P(13) <sup>b</sup>	1655.761	.757	P(14) <sup>b</sup>		1557.840
P(14)		1652.192	P(15) <sup>b</sup>		1554.375
P(15)	1648.601	.596	P(16)	1550.875	.879
P(16)	1644.971	.970	P(17)	1547.354	.353
P(17) <sup>b</sup>	1641.313	.313			
P(18)		1637.625	22-21 P(09)	1551.141	.146
P(19)	1633.910	.908	P(10)	1547.868	.869
			P(11)	1544.560	.560
18-17 P(08) <sup>b</sup>	1649.216	.214	P(12)	1541.219	.221
P(09)		1645.838	P(13)	1537.849	.850
P(10)	1642.431	.430	P(14)	1534.446	.448
P(11) <sup>b</sup>	1638.994	.990	P(15)	1531.014	.016
P(12)		1635.520	P(16) <sup>b</sup>		1527.553
P(13)	1632.019	.018	P(17)	1524.063	-.060
P(14)	1628.487	.486			
P(15)	1624.926	.923	23-22 P(10) <sup>b</sup>	1524.423	.423
P(16)	1621.331	-.329	P(11) <sup>b</sup>		1521.148
P(17)	1617.707	.705	P(12) <sup>b</sup>		1517.841
P(18)	1614.052	.050	P(13)	1514.502	.503
P(19)	1610.366	.365	P(14)	1511.134	-.134

<sup>a</sup>These are the two transitions whose frequencies have been accurately measured (12,13) to be 1877.6250 cm<sup>-1</sup> and 1873.5800 cm<sup>-1</sup>, respectively.

<sup>b</sup>Most of the "missing" lines in the observed column lie close to H<sub>2</sub>O absorption lines and were presumably prevented from oscillating by atmospheric water vapour in the laser cavity.

from fitting these lines are given in Table II, and the wavenumbers calculated from the constants are listed in Table I beside the measured values. Because our measurements do not extend beyond the  $v = 23$  vibrational level, we have only included 9 adjustable parameters in the fit; the inclusion of 14 parameters, as used for <sup>12</sup>C<sup>16</sup>O in Ref. (5), lowers the root-mean-square deviation of our fit by only 5%. The deviations between the measured wavenumbers and those calculated from the constants in Table II are illustrated in Fig. 1; the r.m.s. deviation is 0.003 cm<sup>-1</sup>. It should be noted that both of the accurately measured <sup>13</sup>C<sup>16</sup>O lines which were used to fix our wavenumber scale are

TABLE II

MOLECULAR CONSTANTS OF  $^{13}\text{C}^{16}\text{O}$  ( $\text{cm}^{-1}$ )

$Y_{10}$	$\omega_e$	2121.43001	$\pm(112)^a$
$Y_{20}$	$-\omega_e x_e$	-12.697609	$\pm(393)$
$Y_{30}$	$\omega_e y_e$	$8.9690 \times 10^{-3}$	$\pm(458)$
$Y_{40}$	$-\omega_e z_e$	$1.1693 \times 10^{-4}$	$\pm(218)$
$Y_{50}$	$\omega_e^2 a_e$	$-1.3091 \times 10^{-6}$	$\pm(371)$
$Y_{01}$	$B_e$	1.84614841	$\pm(151)$
$Y_{11}$	$-\alpha_e$	$-1.635190 \times 10^{-2}$	$\pm(299)$
$Y_{02}$	$-D_e$	$-5.7205 \times 10^{-6}$	$\pm(313)$
$Y_{12}$	$\beta_e$	$-6.05 \times 10^{-9}$	$\pm(507)$

<sup>a</sup> The quoted errors are the standard deviations, and are right adjusted to the last digits of the constants.

located at the high frequency end of the range of our measurements. Thus there is still the possibility of a small systematic error towards the low frequency end of the range.

#### IV. CONCLUSIONS

As mentioned above, it must be noted that it is now technically feasible (11, 12, 13) to measure carbon monoxide laser lines by "microwave" techniques with far greater precision than is possible with a conventional spectrometer as used in this work. However, it may be some time before comprehensive measurements of the laser emissions from the various CO isotopes are made by the direct measurement of their absolute frequencies. In fact, a technique other than comparison with doubled CO<sub>2</sub> frequencies will have to be used for CO laser lines below  $\sim 1770 \text{ cm}^{-1}$  because of the limited range of the CO<sub>2</sub> laser. In the mean time, the present results should prove useful for the various

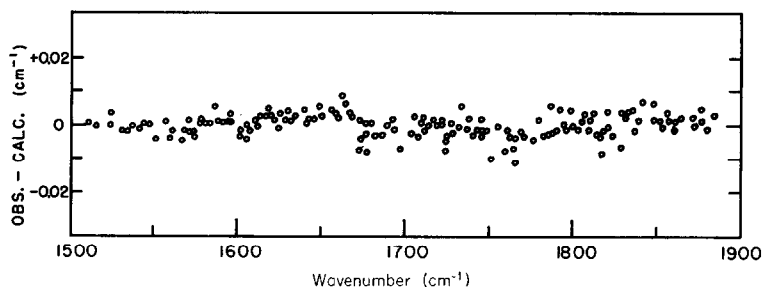


FIG. 1. The deviations between the observed values of the  $^{13}\text{C}^{16}\text{O}$  laser lines and the values calculated from the constants in Table II. The scatter of the data from Ref. (21), also used in the fit, was approximately equal to that shown here.

spectroscopic applications of the CO laser; indeed it was our own interest in laser Stark spectroscopy (7) and infrared-infrared double resonance (22) which prompted this investigation.

## ACKNOWLEDGMENTS

We are grateful to C. A. Harris and M. B. Wadsworth for their assistance in the measurements, to Dr. K. Narahari Rao, to Mr. W. B. Telfair, and to Dr. R. S. Eng for communicating their experimental results prior to publication, and to P. R. Bunker and A. E. Douglas for their critical reading of the manuscript. We also thank H. D. Riccius, K. J. Siemsen, and B. G. Whitford for their precision measurement of a  $^{13}\text{C}^{16}\text{O}$  frequency at our request.

RECEIVED: January 14, 1974

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