

## Absolute Frequency Measurements of the 2-0 Band of CO at 2.3 $\mu\text{m}$ ; Calibration Standard Frequencies from High Resolution Color Center Laser Spectroscopy

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The absolute frequencies of 20 lines of the 2-0 band of CO near  $4260\text{ cm}^{-1}$  have been measured by heterodyne frequency measurement techniques. Eleven of the lines were measured by saturated absorption techniques which produced linewidths of about 3 MHz. New rovibrational constants have been fitted to these measurements. A table of calculated transition frequencies is given with estimated absolute uncertainties as small as  $0.0000023\text{ cm}^{-1}$  (70 kHz) near the band center. The pressure shifts of three lines have been measured and fall in the range from  $-0.9$  to  $-3\text{ kHz/Pa}$  ( $-122$  to  $-400\text{ kHz/Torr}$ ). It is suggested that the generally accepted frequencies of the 1-0 band of CO should be lowered by 7 MHz.

### INTRODUCTION

The absolute frequencies of the 2-0 vibration-rotation band of  $^{12}\text{C}^{16}\text{O}$  have been used for many years as wavelength or frequency standards for the calibration of infrared instruments (1-5). Over the years the absolute accuracies of the measurements of the CO bands have undergone many stages of refinement (6-11).

In 1973 Guelachvili (9) used a high resolution Fourier transform spectrometer (FTS) to measure the 2-0 band of CO against the krypton wavelength standard to obtain a reported accuracy of  $\pm 1.3 \times 10^{-4}\text{ cm}^{-1}$  (3.9 MHz). Because of this high reported accuracy, these values have become a standard for the calibration of other spectra.

Later Guelachvili measured the 1-0 band of CO using the 2-0 band for calibration (12). Since the 1-0 band is a more strongly absorbing band, it is more commonly used for calibration, but one should remember that the 1-0 band frequencies are based on the measurements of the 2-0 band. Quite recently Guelachvili has measured the CO<sub>2</sub> laser frequencies using the 1-0 band of CO for calibration (13). Since the CO<sub>2</sub> laser frequencies have been calibrated quite accurately against the cesium frequency standard (14), this measurement was considered to be a check on the accuracy

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of the CO standard frequencies. However, the accuracy of that comparison was only about  $\pm 3$  MHz for the CO<sub>2</sub> lines near  $1050\text{ cm}^{-1}$ . This uncertainty translates to an accuracy check on the CO 2–0 band near  $4260\text{ cm}^{-1}$  of about  $\pm 12$  MHz.

Since almost all high resolution measurements now being made are ultimately referred to the 2–0 band measurement of Guelachvili, it is important that these CO transition frequencies be independently confirmed. In light of the new definition of the meter in terms of the cesium frequency standard (15), which is likely to take place in a short time, it is particularly important to have accurate frequency measurements of the 2–0 and 1–0 bands of CO.

In the present work the absolute frequencies of 20 lines of the  $^{12}\text{C}^{16}\text{O}$  2–0 band were measured with a tunable color center laser. In these measurements the color center laser was locked to the center of the CO line, and its frequency was measured by heterodyning in a metal–insulator–metal (MIM) diode with appropriate harmonics of two well-characterized CO<sub>2</sub> lasers. Measurements were made on lines from *P*(29) to *R*(35). Eleven of the transitions nearest the band center were measured with the color center laser locked to the saturated absorption dip in CO, which was observed by monitoring the fluorescence. For many of the saturated measurements the absolute accuracy of the determination of the line center was estimated to be about  $\pm 3 \times 10^{-6}\text{ cm}^{-1}$  ( $\pm 100$  kHz).

#### EXPERIMENTAL TECHNIQUE

A broadly tunable color center laser was used to detect and saturate the CO transitions. The laser has been briefly described elsewhere (16, 17); we note here that it was tunable from  $4100$  to  $4900\text{ cm}^{-1}$ , with cw single mode powers ranging from 10 mW at these extremes to 200 mW near the peak of the tuning curve. The laser frequency was actively stabilized by locking the laser to a passive optical resonator which produced a residual linewidth of less than 10 kHz.

#### *Measurements of Doppler Limited Spectra*

For Doppler limited spectra, the laser frequency was dithered 6 MHz peak-to-peak over the peak of the absorption feature, and a first derivative signal was used. The modulation frequency was 10 kHz, which was near the unity gain frequency of the stabilizing servo; hence, the servo did not significantly reduce the modulation. Figure 1(a) shows the schematic diagram for observing and measuring the Doppler limited transition frequency. A small portion of the color center laser beam (5 mW) was sent through a 2-m cell filled to 670 Pa (5 Torr). The transmitted radiation was monitored with a room temperature InAs detector. The detector output was demodulated in a phase-sensitive detector (PSD), and the subsequent PSD output was used to control the length of a passive optical cavity to which the color center laser frequency was locked. Thus, the color center laser frequency was effectively locked to the peak of the CO absorption line.

For each CO line a potential systematic error can occur because of offsets arising from background slope. These offsets are ubiquitous, arising from intracavity tuning elements, frequency dependences of the laser power, interference effects, etc. We found it impossible to entirely eliminate these effects in spite of attempts with ratio

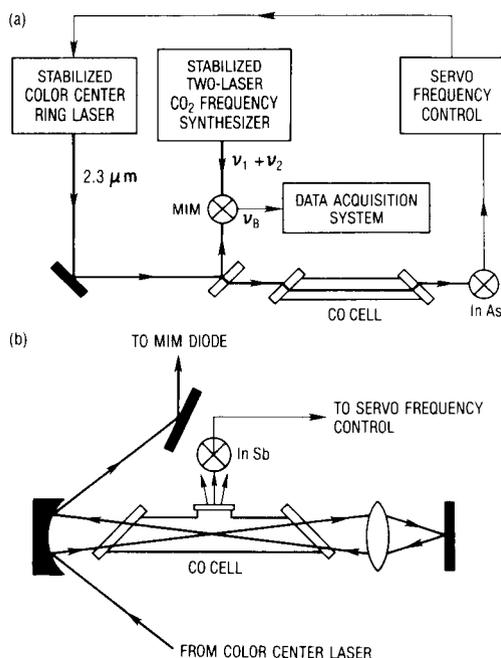


FIG. 1. Block diagram of scheme for heterodyne frequency measurements of the CO 2-0 band. (a) Doppler limited measurements. (b) Saturated absorption measurements.

and difference schemes. Hence, prior to each measurement, the derivative signal was carefully centered about zero with the offset adjustment of the PSD. In general, five independent measurements were made of each line. Figure 2(a) shows a typical Doppler limited signal and several traces of the background slope obtained when the CO was removed from the cell. As is evident in Fig. 2(a), the signal-to-noise ratio ( $S/N$ ) was about 100 to 1, which for a Doppler width of about 300 MHz allowed the center of the line (the zero crossing) to be determined to within about  $\pm 3$  MHz. Unfortunately, the background offsets often were of magnitudes larger than the noise, and hence our line center measurements were limited by how well we could zero these offsets rather than by the  $S/N$ . The uncertainties, which ranged from  $\pm 8$  to  $\pm 20$  MHz, represent our best estimates of the errors in this adjustment. Since the offset error was probably different in magnitude and in sign for each CO transition we expect that the offset errors will appear as random errors in the least squares fit of the data.

The major portion of the color center laser beam was reflected from a beam splitter and directed onto a W-Ni MIM point contact diode. Coincident on the diode were about 200 mW of CO<sub>2</sub> laser radiations from two stabilized <sup>12</sup>C<sup>16</sup>O<sub>2</sub> lasers. The two CO<sub>2</sub> laser frequencies  $\nu_1$  and  $\nu_2$  were chosen such that the harmonic combination  $3\nu_1 + \nu_2$  or  $2\nu_1 + 2\nu_2$  was approximately equal to the desired CO frequency (within 2 GHz). The difference  $\nu_B$  between the color center laser frequency and the synthesized frequency from the CO<sub>2</sub> lasers appeared as an rf beat on the point contact diode. The beat signal was amplified and displayed on an rf spectrum analyzer. In some cases, a stabilized X-band klystron frequency  $\nu_{\mu w}$  was also mixed in the diode with

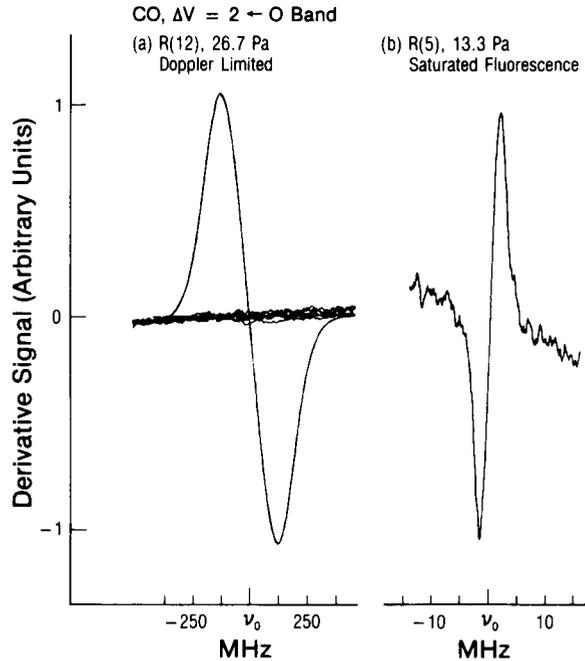


FIG. 2. Comparison of derivative signals from (a) Doppler limited and (b) saturated absorption measurements. Linewidth is about 100 times narrower for the saturated absorption signal. Several traces of the background slope, which were obtained by removing the CO from the cell, are shown in (a).

the color center laser and CO<sub>2</sub> laser radiations to bring the beat frequency within the passband of our amplifiers. Each beat signal, typically with 10–20 dB *S/N*, was averaged for 30 sec along with frequency markers on both sides of the beat signal generated from a stable frequency synthesizer. The averaged signal was plotted for later analysis.

Knowledge of the CO<sub>2</sub> laser frequencies, which are accurate to about two parts in 10<sup>10</sup>, and of the beat frequency permitted the determination of the absolute frequency of the CO transitions. Thus,

$$\nu_{\text{CO}} = l\nu_1 + m\nu_2 \pm \nu_{\mu\nu} \pm \nu_B \quad (1)$$

where *l* and *m* are the harmonic numbers of the two CO<sub>2</sub> lasers. Table I summarizes the results of the Doppler limited CO 2–0 band frequency measurements and the estimated uncertainties.

#### *Saturated Absorption Measurements*

For the saturated absorption measurements, it proved necessary to observe the CO transitions in fluorescence. The experimental apparatus is shown schematically in Fig. 1(b). The color center laser output (generally 30 to 80 mW) was reflected off a 2-m radius-of-curvature mirror to form a focused beam with a 1-mm-diameter waist inside the sample cell. The sample cell was 20 cm long and had a side port covered

TABLE I

Absolute frequency measurements of the 2-0 band of carbon monoxide at 2.3  $\mu\text{m}$ .

Doppler Limited Measurements				
2-0 Band Transition	Pressure (kPa)	Frequency (MHz)	Uncertainty (MHz)	Obs.-Calc. (MHz)
R(35)	0.67 <sup>a</sup>	130 431 270.7	20	0.6
R(33)	0.67 <sup>a</sup>	130 355 118.8	12	-0.5
R(32)	0.67 <sup>a</sup>	130 313 665.3	15	-4.9
R(30)	0.67 <sup>a</sup>	130 224 044.6	10	-1.6
R(29)	0.67	130 175 877.9	10	-2.2
R(27)	0.67	130 072 858.5	9	-2.8
P(23)	0.80	124 540 126.2	8	1.8
P(27)	0.67	123 878 869.0	8	3.5
P(29)	0.80	123 536 339.6	15	2.3
Saturated Absorption Measurements				
2-0 Band Transition	Pressure (Pa)	Frequency (MHz)	Uncertainty (MHz)	Obs.-Calc. (MHz)
R(25)	20	129 960 956.8	2.0	0.61
R(24)	20	129 901 682.27	1.0	0.09
R(20)	20	129 642 545.006	0.25	0.082
R(12)	20	129 019 381.761	0.07	-0.043
R( 5)	20	128 360 848.969	0.07	0.140
R( 0)	20	127 826 623.353	0.15	-0.030
P( 1)	20	127 598 179.703	0.08	-0.096
P( 3)	20	127 361 358.494	0.10	-0.042
P( 6)	20	126 990 495.584	0.08	0.002
P(12)	20	126 192 933.997	0.40	0.016
P(18)	20	125 321 717.312	0.20	-0.046

(a) Room temperature pressure. Cell was heated to enhance signal.

by a sapphire window for observing fluorescence. The pressure in the cell was 20 Pa for all measurements. The existing beam was returned to the cell via a lens-mirror combination ("cat's eye reflector"), which caused the reflected beam to refocus and cross at the site of the first focus. The crossing angle could be adjusted by the beam separation on the lens and was adjusted to be as small as possible without causing feedback instabilities in the color center laser. This angle was approximately  $0.7^\circ$ . The saturating beam was recollimated after leaving the sample cell by the 2-m mirror and was directed by a small pick-off mirror to the MIM point contact diode for frequency measurement.

Because the 2-0 band of CO is extremely weak, fluorescence from this band was obscured by the small but unavoidable scattering of laser radiation from the Brewster windows of the sample cell. We chose instead to observe the much stronger fluorescence signal from the 2-1 and 1-0 bands at 4.6  $\mu\text{m}$ . A liquid nitrogen cooled InSb detector with a suitable passband filter was used to observe this fluorescence.

The saturated absorption dip was only observed when the intensity at the crossed beam region in the sample cell surpassed several watts per square centimeter, which was accomplished by focusing the color center laser beam. The need for this relatively

high intensity arose from the large difference between the natural lifetime of the CO excited state ( $\sim 30$  msec) and the collision limited rotational lifetime ( $\sim 25$  nsec  $\cdot$  Torr). The relatively high collision rate tends to "wash out" any holes developed in the equilibrium distribution within a natural lifetime; hence, a high optical pumping rate is necessary to observe saturation effects.

In our case, the CO pressure was adjusted to optimize the  $S/N$ . The fluorescence signal increased with pressure; however, the saturation parameter decreased with pressure. With the intensity available from the focused color center laser beam, we found empirically that 20 Pa gave the best  $S/N$ .

Figure 2(b) shows an example of the saturated absorption signal from the  $R(5)$  transition. The linewidth, as determined from the peaks of the derivative signal, is 2.9 MHz. This linewidth is due almost entirely to the crossing angle  $\theta$  of the two saturating beams as given by the formula

$$\Delta\nu \cong \theta \frac{u}{\lambda}$$

where  $u$  is the most probable velocity of the molecules and  $\lambda$  is the radiation wavelength. Pressure broadening and time-of-flight broadening both contribute about 600 kHz in quadrature with the angle broadening linewidth and, hence, are negligible compared to the crossing angle linewidth.

The saturated absorption dip was observed by dithering the laser 2 MHz peak-to-peak and observing the first derivative spectrum in a manner exactly as described above for the Doppler limited spectra. The 150-Hz modulation frequency was slower than before because of the long excited state lifetime of CO. In CO, collisions have only a small effect on the vibrational deexcitation rate; hence, the fluorescence signals have an  $\sim 30$ -msec lifetime. The 150-Hz rate was chosen as a compromise to give the best  $S/N$ . Lower frequencies had larger fluorescence signals, but were accompanied by large  $1/f$  noise from the detector and preamplifiers. Table I summarizes the results of the saturated absorption frequency measurements and the estimated uncertainties.

#### *Pressure Shift Measurements*

Pressure shifts were measured on both Doppler limited and saturated absorption spectra. Neither technique gave satisfactory signal-to-noise ratios for the pressure limits used. We only report these pressure shift measurements to lend support to the equally unsatisfactory measurements already reported by others (18-21).

The saturated absorption measurement used the  $R(12)$  transition at three different pressures: 6.7, 13.3, and 26.7 Pa. The pressures were measured with a calibrated capacitance manometer, and the frequencies were measured as described before. The resulting pressure shift was  $-3 \pm 2$  kHz/Pa ( $-400 \pm 250$  kHz/Torr), where the uncertainty is our 95% confidence interval estimate.

Higher pressures could be used for Doppler limited measurements, and this technique was used to measure the pressure shift of the  $R(0)$  and  $R(24)$  lines. For both lines, however, the low pressure (20 Pa) measurements were from saturated absorption spectra. Figure 3 shows the data for  $R(24)$  for which the pressure shift was  $-1.6 \pm 0.5$  kHz/Pa ( $-210 \pm 60$  kHz/Torr). The measurements for  $R(0)$  only extended

to a pressure of 2.7 kPa (20 Torr), and the pressure shift for  $R(0)$  was determined to be  $-0.9 \pm 0.6$  kHz/Pa ( $-122 \pm 80$  kHz/Torr).

These measurements are only significant for showing the sign and the order of magnitude of the shift. The uncertainties are so large that it is not possible to say whether or not the shift is the same for all  $J$  values.

#### ANALYSIS OF THE FREQUENCY MEASUREMENTS

There are now quite a few measurements on various bands of CO with a high degree of precision and, in many cases, a high degree of accuracy as well. We have tried to fit the available data in a number of different ways, but after much consideration we believe that the best way to obtain a list of calculated frequencies and uncertainties for the 2-0 band is to use constants obtained from an analysis which uses only frequency measurements that have been made on the two vibrational states directly involved. That is to say, we have used only the present frequency measurements of the 2-0 transitions and the microwave and millimeterwave measurements of the rotational transitions in the  $v = 0$  and  $v = 2$  states (22, 23).

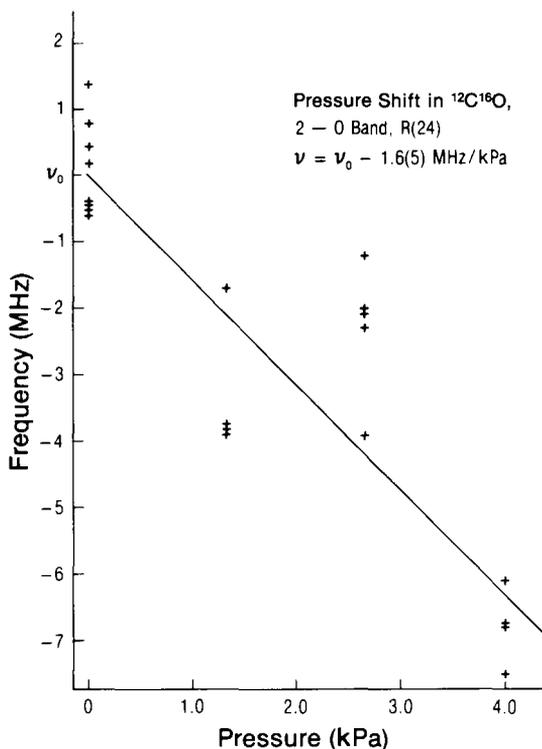


FIG. 3. Pressure shift in  $^{12}\text{C}^{16}\text{O}$ , 2-0 band,  $R(24)$ . Low pressure (20 Pa) points are from saturated absorption spectra; the rest are Doppler limited. The 20 Pa points were weighted by a factor of five over the higher pressure points in the least-squares fit to reflect the increased accuracy of the saturated measurements. The pressure shift is  $-1.6(5)$  MHz/kPa where the uncertainty is the 95% confidence interval estimate.

Although combination-differences formed from the FTS measurements of Guelachvili (9) and of Mantz and Maillard (10) might improve the centrifugal distortion constants for the 2-0 band, we preferred not to use any data involving wavelength measurements. Besides, the data of Guelachvili would not contribute very much since it extends only to  $J = 26$ . On the other hand, the data of Mantz and Maillard go to very high  $J$  values but are taken from flame spectra with the gas at atmospheric pressure and, therefore, are subject to pressure shifts which may or may not be significant.

The data were fit to the usual equations for the energy levels of diatomic molecules:

$$F(v) = G(v) + B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 \quad (2)$$

$$\nu_{\text{obs}} = F(v') - F(v'') \quad (3)$$

and

$$\nu_0 = G(v') - G(v''). \quad (4)$$

In addition to fitting the present heterodyne frequency measurements, we also used the microwave transitions given in Table II. Each of the data points was weighted by the inverse square of the estimated uncertainty of the value. Because of the large uncertainty in the pressure shift, none of the measurements was corrected for the effect of pressure on the frequency of the line center.

The results of three different fits are given in Table III. In fit 1 all seven constants including  $H_2$  and  $H_0$  were determined. In fit 2 the value of  $H_0$  was fixed and the other constants were floated. For fit 3 both  $H_0$  and  $H_2$  were fixed and the remaining five constants were fit.

Fit 1 did not give very accurate values for the  $H$  terms. Consequently, the present heterodyne measurements are adequate for calculating the CO transitions to  $J = 24$  with a high degree of confidence, but for higher  $J$  values the calculated frequencies

TABLE II  
Frequencies of the rotational transitions used in the present analysis.

Frequency (MHz)	Uncertainty (MHz)	Obs.-Calc. <sup>a</sup> (MHz)	J'	J''	V	Ref.
115 271.204	0.01	0.000	1	0	0	22
230 537.974	0.05	-0.029	2	1	0	22
345 795.989	0.10	-0.006	3	2	0	22
461 040.811	0.10	0.037	4	3	0	22
576 267.934	0.10	-0.004	5	4	0	22
691 472.978	0.10	-0.106	6	5	0	22
806 651.719	0.10	-0.090	7	6	0	22
113 172.41	0.06	0.030	1	0	2	23

(a) The column labeled Obs.-Calc. gives the residuals obtained from fit 3.

TABLE III  
 Constants obtained for the 2-0 band of CO.

Constants	Fit 1	Fit 2	Fit 3
$\nu_0$ (MHz)	127 713 450.987(34) <sup>a</sup>	127 713 450.993(33)	127 713 451.003(30)
$B_2$ (MHz)	56 586.558 44(217)	56 586.557 279(1708)	56 586.556 852(1609)
$D_2$ (kHz)	183.4995(192)	183.483 53(611)	183.480 01(420)
$H_2$ (Hz)	0.1968(318)	0.169 34(505)	[0.1653] <sup>b</sup>
$B_0$ (MHz)	57 635.969 60(204)	57 635.968 805(1814)	57 635.968 929(1793)
$D_0$ (kHz)	183.5251(192)	183.508 85(482)	183.508 48(476)
$H_0$ (Hz)	0.2057(364)	[0.1739] <sup>b</sup>	[0.1739] <sup>b</sup>

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

(b) The values of the  $H_\nu$  terms were fixed at the values given by  $Y_{03} = 0.176\ 06$  Hz and  $Y_{13} = -0.004\ 30$  Hz, see text.

are less accurate. This problem presents us with a dilemma. We wish to give the most accurate frequencies possible for as many CO transitions as possible, but to do this the centrifugal distortion constants need to be improved, particularly the  $H$  terms.

One way to do this is to first abandon our resolve to use only frequency measurements and then to use the Dunham expressions (24) and make a nonlinear least-squares fit of many bands to obtain the best Dunham potential constants for CO. This type of fit was used for KF (25) and for SnO (26), and a somewhat different approach was used by Dale *et al.* (27) to fit all the data for CO.

When this procedure was tried, the new heterodyne measurements were so diluted by the overwhelming amount of data on other states that the heterodyne measurements were not fit to the accuracy that was obtained from fit 1. This result was probably due to unrealistically small uncertainties given to some of the data taken from the literature. As a compromise we have used the Dunham potential constants to determine  $Y_{03}$  and  $Y_{13}$  and have used those values to fix the values of  $H_0$  and  $H_2$  in fits 2 and 3. The values of  $Y_{03}$  and  $Y_{13}$  are slightly different from the values given by Dale *et al.* (27) because we used a much smaller data base that covered only representative transitions for low vibrational states and because Dale *et al.* fit the data to the  $Y_{ij}$  constants whereas we fit the data to the  $a_i$  Dunham potential constants.

#### RESULTS AND DISCUSSION

The goal of this work has been to produce the most accurate possible table of calculated frequencies for the  $\nu = 2 \leftarrow 0$  transitions of CO. It is also important to give the best estimate of the uncertainties of the calculated frequencies. Table IV was prepared by using the constants from fit 3 to calculate the frequencies, but the variance-covariance matrix from fit 3 was not used to estimate the uncertainties because it assumed that  $H_0$  and  $H_2$  were well-known quantities. The variance-covariance matrix from fit 1 gives a more conservative estimate of the uncertainties in the  $H_\nu$  terms and the correlation with the other terms and was used to estimate the statistical part of the uncertainties in Table IV.

TABLE IV

Calculated absorption frequencies and wavenumbers for the 2-0 band of CO.

Transition	Frequency <sup>a</sup> (MHz)	Wavenumber <sup>b</sup> (cm <sup>-1</sup> )
P(29)	123 536 337.31(990)	4120.728658(330)
P(28)	123 708 589.32(785)	4126.474366(262)
P(27)	123 878 865.47(614)	4132.154167(205)
P(26)	124 047 161.41(473)	4137.767916(158)
P(25)	124 213 472.79(357)	4143.315466(119)
P(24)	124 377 795.23(264)	4148.796673( 88)
P(23)	124 540 124.37(190)	4154.211390( 63)
P(22)	124 700 455.83(132)	4159.559472( 44)
P(21)	124 858 785.24( 88)	4164.840773( 29)
P(20)	125 015 108.23( 56)	4170.055146( 19)
P(19)	125 169 420.39( 36)	4175.202446( 12)
P(18)	125 321 717.36( 26)	4180.282526( 9)
P(17)	125 471 994.73( 25)	4185.295240( 8)
P(16)	125 620 248.13( 26)	4190.240441( 9)
P(15)	125 766 473.15( 27)	4195.117982( 9)
P(14)	125 910 665.39( 27)	4199.927718( 9)
P(13)	126 052 820.47( 26)	4204.669501( 9)
P(12)	126 192 933.98( 23)	4209.343184( 8)
P(11)	126 331 001.52( 20)	4213.948622( 7)
P(10)	126 467 018.69( 17)	4218.485666( 6)
P( 9)	126 600 981.09( 14)	4222.954171( 5)
P( 8)	126 732 884.30( 11)	4227.353988( 4)
P( 7)	126 862 723.94( 9)	4231.684972( 3)
P( 6)	126 990 495.58( 8)	4235.946976( 3)
P( 5)	127 116 194.83( 7)	4240.139851( 2)
P( 4)	127 239 817.29( 7)	4244.263453( 2)
P( 3)	127 361 358.54( 7)	4248.317632( 2)
P( 2)	127 480 814.18( 8)	4252.302244( 3)
P( 1)	127 598 179.80( 8)	4256.217139( 3)
R( 0)	127 826 623.38( 8)	4263.837197( 3)
R( 1)	127 937 692.53( 8)	4267.542065( 3)
R( 2)	128 046 654.06( 7)	4271.176630( 2)
R( 3)	128 153 503.55( 7)	4274.740746( 2)
R( 4)	128 258 236.60( 7)	4278.234264( 2)
R( 5)	128 360 848.83( 7)	4281.657040( 2)
R( 6)	128 461 335.82( 7)	4285.008925( 2)
R( 7)	128 559 693.19( 8)	4288.289774( 3)
R( 8)	128 655 916.53( 8)	4291.499439( 3)
R( 9)	128 750 001.46( 8)	4294.637774( 3)
R(10)	128 841 943.57( 9)	4297.704633( 3)
R(11)	128 931 738.48( 9)	4300.699869( 3)
R(12)	129 019 381.80( 10)	4303.623335( 3)
R(13)	129 104 869.15( 10)	4306.474886( 3)
R(14)	129 188 196.12( 12)	4309.254375( 4)
R(15)	129 269 358.35( 14)	4311.961655( 5)
R(16)	129 348 351.45( 16)	4314.596582( 5)
R(17)	129 425 171.03( 19)	4317.159007( 6)
R(18)	129 499 812.72( 22)	4319.648786( 7)
R(19)	129 572 272.14( 25)	4322.065772( 8)
R(20)	129 642 544.92( 29)	4324.409820( 10)
R(21)	129 710 626.69( 34)	4326.680783( 11)
R(22)	129 776 513.07( 41)	4328.878516( 14)
R(23)	129 840 199.69( 51)	4331.002873( 17)
R(24)	129 901 682.18( 67)	4333.053708( 22)
R(25)	129 960 956.19( 89)	4335.030876( 30)
R(26)	130 018 017.34(120)	4336.934231( 40)
R(27)	130 072 861.28(162)	4338.763628( 54)
R(28)	130 125 483.64(217)	4340.518921( 72)
R(29)	130 175 880.06(288)	4342.199965( 96)
R(30)	130 224 046.20(376)	4343.806614(125)
R(31)	130 269 977.68(486)	4345.338724(162)
R(32)	130 313 670.17(621)	4346.796148(207)
R(33)	130 355 119.30(785)	4348.178742(262)
R(34)	130 394 320.72(983)	4349.486361(328)
R(35)	130 431 270.09(1220)	4350.718859(407)

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

(b) Wavenumber units were obtained by using  $c = 299\,792.458$  km/s.

We estimate that the uncertainty in the CO frequency measurements due to the uncertainty in the CO<sub>2</sub> frequencies amounts to about  $\pm 20$  kHz. That uncertainty has been added in quadrature to the statistically determined uncertainties in the CO frequencies and is included in the uncertainties given in Table IV.

Pressure shift measurements were made on only three lines because the pressure shifts were too small to be accurately measured. Previously at least four papers have reported self-induced pressure shift measurements on CO. The measurements by Bouanich and Brodbeck seem to give the clearest indication of the small  $J$  dependence of the pressure shift for both the  $P$  and  $R$  branches, but their measurements did not extend beyond  $J = 21$ . All measurements are in rough agreement if one assumes that the pressure shift is proportional to  $\Delta v$ . None of the pressure shift measurements made so far is very accurate and none extends beyond  $J = 25$ . For that reason we have not corrected our frequency measurements for the pressure shift, but this neglect will mainly affect the weaker high  $J$  transitions for which pressures greater than 133 Pa (1 Torr) were used.

The uncertainties given in Table IV for the calculated frequencies do not include the uncertainty (or the error) due to the pressure shift for the heterodyne measurements although those uncertainties were within the uncertainties ascribed to the raw data. Since the most strongly weighted low  $J$  measurements were made at a pressure of 20 Pa (0.15 Torr), Table IV should be considered to be appropriate for that pressure.

The band center determined by the new measurements presented here is about 14 MHz lower in frequency than the band center given by Guelachvili (9, 12). This discrepancy is about three times the absolute uncertainty given by Guelachvili and illustrates the difficulty one has in estimating the effect that systematic errors can have on the accuracy of a wavelength measurement. For the present measurements we believe that the pressure shift effect is the dominant source of systematic error.

Doppler limited measurements were also made on the low  $J$  transitions even though those results are not reported in Table I. The Doppler limited measurements all agreed with the saturated absorption measurements to within  $\pm 4$  MHz although the estimated uncertainty was  $\pm 6$  MHz. Consequently, no systematic errors that affected only the Doppler limited measurements were detectable.

The present results for the 2-0 band of CO cast suspicion on the accuracy of the 1-0 band, which was calibrated against the 2-0 band by Guelachvili (12, 28). Since some of the 2-0 band data that were used for that calibration were too high by 14 MHz, it seems reasonable to expect that the 1-0 band measurements may be too high by 7 MHz. This is supported and in fact emphasized by the more recently reported measurements of the 1-0 and 2-1 bands of CO (28), from which the 2-0 center is calculated to be 25 MHz higher than the presently determined value.

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