

ACCURATE FAR-INFRARED ROTATIONAL FREQUENCIES OF CARBON MONOXIDE¹

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ABSTRACT

High-resolution measurements of the pure rotational absorption spectrum of CO in its ground state are reported for the range $J'' = 5-37$. A least-squares fit to this data set, augmented by previous microwave measurements of the $J'' = 0-4$ rotational transitions by other workers, determined the following accurate values for the molecular constants (1σ errors of the last digits in parentheses): $B_0 = 57635.96826(12)$ MHz, $D_0 = 0.18350552(46)$ MHz, $H_0 = 1.7249(59) \times 10^{-7}$ MHz, and $L_0 = -3.1(23) \times 10^{-13}$ MHz. A table of calculated CO rotational frequencies is given for the range $J'' = 0-45$; these frequencies are accurate to ≤ 10 kHz (2σ) for $J'' \leq 28$.

Subject headings: line: identification — molecular data — molecular processes

1. INTRODUCTION

The first interstellar detection of carbon monoxide was made in 1970 by Wilson, Jefferts, & Penzias (1970). They identified the $J = 1 \rightarrow 0$ pure rotational transition at 2.6 mm in the Orion Molecular Cloud. Carbon monoxide was the source of both the first submillimeter and the first far-infrared molecular emission lines observed in the interstellar medium (also in Orion): Phillips et al. (1977) detected the $J = 3 \rightarrow 2$ transition at 870 μm , and Watson et al. (1980) detected the $J = 21 \rightarrow 20$ and $22 \rightarrow 21$ transitions near 120 μm . Later, Watson, et al. (1985) observed CO transitions as high in J as $34 \rightarrow 33$ ($\lambda = 77.06 \mu\text{m}$) in Orion. Recent high-resolution, radio (heterodyne) detections of the $J = 17 \rightarrow 16$ (Boreiko, Betz, & Zmuidzinas 1989) and $22 \rightarrow 21$ (Boreiko & Betz 1989) transitions in Orion have illuminated the role of shock processes in the formation of molecular material. Clearly, accurate laboratory measurements of CO spectra are an important complement to these astrophysical observations.

In this paper we report the measurement of the far-infrared, pure rotational spectrum of CO in its $X^1\Sigma^+$ ($v = 0$) ground state with an accuracy approximately 10 times greater than that reported previously (Nolt et al. 1987). The 2σ error limits (95% confidence interval) of the calculated transition frequencies derived from a least-squares fit to the observed spectrum are less than or equal to 10 kHz in the range $J'' = 0-28$; these error limits correspond to an accuracy of about 5 parts in 10^9 . The calculated values of the CO transition frequencies will be useful for astrophysical measurements, as well as for accurate frequency calibration of high-resolution, far-infrared spectrometers in the laboratory.

2. EXPERIMENTAL

The pure rotational spectrum of CO was measured in absorption by tunable far-infrared (TuFIR) spectroscopy. The experimental configuration and method have been described in detail elsewhere (Zink et al. 1990), but a brief description follows. Far-infrared (FIR) radiation is generated by the nonlinear mixing of radiation from two $^{12}\text{C}^{16}\text{O}_2$ lasers (with fre-

quencies ν_1 and ν_{II}) in a metal-insulator-metal (MIM) diode. Tunability of the FIR radiation is provided by adding sidebands (of frequency ν_μ) from a microwave frequency synthesizer. The synthesized FIR radiation is composed of two tunable frequencies: $(\nu_1 - \nu_{II}) \pm \nu_\mu$. The microwave frequency ν_μ is in the range of 5-20 GHz, so that each FIR sideband can be tuned continuously over 15 GHz, leaving only a 10 GHz gap centered about the CO_2 difference frequency. With a choice of about 5000 pairs of CO_2 laser frequencies, all FIR frequencies as high as 5 THz can be generated. One of the two CO_2 lasers (ν_1 or ν_{II}) is frequency stabilized by locking it directly to a saturation dip in the 4.3 μm CO_2 fluorescence signal from a reference cell placed in the beam path (Freed & Javan 1970). The other CO_2 laser (ν_{II} or ν_1) is offset-locked to a third CO_2 laser which is frequency stabilized in the same manner as the first laser.

High-purity carbon monoxide was contained in a 4 m long, 12 mm diameter copper tube with 75 μm thick polypropylene windows at each end. The CO pressure was kept at less than 4 Pa (30 mTorr) on the strong lines in order to prevent significant absorption of the FIR radiation in the cell, which would have degraded the line shape; for the weak high- J lines, we increased the CO pressure to as much as ~ 130 Pa (1 Torr). For the highest frequency line that we measured ($J = 38 \leftarrow 37$), we initiated a 250 mA DC discharge in the carbon monoxide. This increased the signal strength by a factor of 2 by raising the rotational temperature of the gas.

The spectrum was recorded as a first derivative by frequency modulating one of the two CO_2 lasers at 1 kHz (with a typical frequency width of 2 MHz) and detecting the absorption signal with a lock-in amplifier. A time constant of 300 ms was used on the lock-in amplifier, and the spectrum was recorded by computer as the average of two scans, one in each direction. The scan width varied from 30 to 100 MHz, and we collected 320 data points in each direction. Additional scans were averaged for the weakest lines to improve the signal-to-noise ratio.

The spectrum of each rotational line was fitted by least squares using a computer program written by Chance (Chance et al. 1991). The program employed five adjustable parameters to fit the spectral line shapes: the transition frequency and intensity, the Gaussian and Lorentzian line widths, and the spectrometer baseline.

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3. DATA ANALYSIS

We recorded spectra of 26 pure rotational lines of CO from $J = 6 \leftarrow 5$ at 0.69 THz to $38 \leftarrow 37$ at 4.34 THz. A typical example of a CO transition is illustrated in the upper trace of Figure 1, which displays the $J = 31 \leftarrow 30$ transition. The signal-to-noise ratio for this spectrum is ~ 75 ; overall, the signal-to-noise ratio of an up-and-down averaged scan varied from ~ 400 for the strongest lines to ~ 3 for the weakest. The lower trace of Figure 1 displays the residuals obtained by subtracting a least-squares fit to the line shape from the experimental values; the flatness of this trace at the line center indicates a satisfactory fit.

In addition to our 26 measured rotational transitions, we included in the data set low-frequency measurements of rotational transitions from $J'' = 0-4$ which have been made by other workers (Rosenblum, Nethercot, & Townes 1958; Helminger, De Lucia, & Gordy 1970; Nolt et al. 1987; Belov, Tretyakov, & Suenram 1991). For some of these five lines, more than one measurement have been reported; in these cases either the most accurate value or an average of two equally accurate values was used in the least-squares fitting.

The rotational energy level expression for a diatomic molecule in a $^1\Sigma^+$ state is written (Townes & Schawlow 1975):

$$E(J) = B_0 J(J+1) - D_0 J^2(J+1)^2 + H_0 J^3(J+1)^3 + L_0 J^4(J+1)^4, \quad (1)$$

where the subscripts on the molecular constants denote the $v = 0$ level. The rotational transitions were fitted to equation (1) using a weighted least-squares fitting program, and values for the four molecular constants were obtained. The derived rotational constants and their 1σ uncertainties are listed in Table 1 along with the values determined by Nolt et al. (1987) in a previous TuFIR experiment conducted in our laboratory at NIST. The fitted values of the first three constants are in agreement at the 2σ level, but our new values are considerably more accurate. Nolt et al. (1987) were not able to determine the fourth rotational constant L_0 , but our data set is sensitive to this parameter: the magnitude of L_0 is 1.3 times greater than its 1σ standard error, and the variance of the least-squares fit decreased by 3% when we varied L_0 in the fitting.

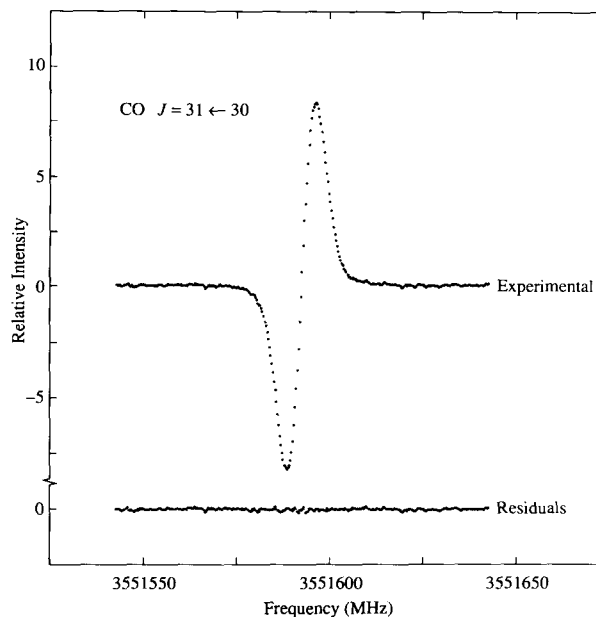


FIG. 1.—The upper trace displays the observed $J = 31 \leftarrow 30$ rotational transition in the ground state of CO. The lower trace displays the residuals obtained from a least-squares fit to the observed line shape.

In Table 2 we list the calculated rotational frequencies for CO in the range $J'' = 0-45$, along with the 1σ standard errors of these frequencies. The 95% confidence limits correspond to 2.05σ . We also list in Table 2 the observed-minus-calculated frequencies of the data, along with the estimated measurement uncertainties. The data were weighted by the square of the inverse of these estimated uncertainties.

For our TuFIR data, the measurement uncertainties arise primarily from two sources. First, although the relative 1σ uncertainties of the $^{12}\text{C}^{16}\text{O}_2$ laser frequencies are about 3 kHz (Petersen, Beaty, & Pollock 1983), we anticipate that the uncertainties in the resettability and stability of our CO_2 lasers are significantly larger. In previous TuFIR experiments in our laboratory, we have estimated this uncertainty as 25 kHz, giving rise to a 35 kHz uncertainty in the FIR frequency ($35 \sim$

TABLE 1
MOLECULAR CONSTANTS FOR CO IN ITS GROUND STATE

Constant	Present Work (in MHz) ^a	Nolt et al. 1987 (in MHz) ^a
B_0	57635.96826(12)	57635.9660(17)
D_0	0.18350552(46)	0.1835053(29)
H_0	$1.7249(59) \times 10^{-7}$	$1.731(7) \times 10^{-7}$
L_0	$-3.1(23) \times 10^{-13}$...

Variance-Covariance Matrix and Correlation Coefficients ^b				
	B_0	D_0	H_0	L_0
B_0	1.3548×10^{-8}	3.6022×10^{-11}	3.4243×10^{-14}	-1.0775×10^{-17}
D_0	0.6711	2.1264×10^{-13}	2.6024×10^{-16}	-9.3713×10^{-20}
H_0	0.4971	0.9536	3.5027×10^{-19}	-1.3391×10^{-22}
L_0	-0.4008	-0.8798	-0.9795	5.3357×10^{-26}

^a Values in parentheses are 1σ standard errors in units of the last quoted digits. For the present work (with 27 degrees of freedom), 95% confidence limits correspond to 2.05σ .

^b Variances (in MHz^2) are on the diagonal, covariances (in MHz^2) are above the diagonal, and the dimensionless correlation coefficients are below the diagonal. Variance of the weighted least-squares fit is 0.98.

TABLE 2
CALCULATED AND OBSERVED ROTATIONAL FREQUENCIES
FOR CO IN ITS GROUND STATE

$J'-J''$	Calculated Frequency (cm ⁻¹) ^a	Calculated Frequency (MHz) ^a	Obs. - Calc. (MHz)	Exper. Uncert. (MHz) ^b
1-0	3.84503344 (1)	115271.202 (<1)	0.002 ^c	0.005
2-1	7.68991997 (2)	230538.001 (<1)	-0.001 ^d	0.001
3-2	11.53451269 (2)	345795.991 (1)	0.000 ^d	0.001
4-3	15.37866472 (3)	461040.770 (1)	-0.001 ^d	0.002
5-4	19.22222917 (3)	576267.933 (1)	-0.011 ^e	0.032
6-5	23.06505918 (4)	691473.078 (1)	0.012	0.012
7-6	26.90700790 (4)	806651.804 (1)	0.002	0.010
8-7	30.74792852 (5)	921799.707 (1)	0.004	0.010
9-8	34.58767424 (5)	1036912.388 (2)	0.015	0.010
10-9	38.42609832 (6)	1151985.447 (2)	0.007	0.011
11-10	42.26305404 (6)	1267014.485 (2)	0.019	0.010
12-11	46.09839471 (7)	1381995.106 (2)	0.004	0.013
13-12	49.93197370 (7)	1496922.913 (2)	0.002	0.012
14-13	53.76364444 (8)	1611793.512 (2)	0.005	0.011
15-14	57.59326039 (9)	1726602.510 (3)
16-15	61.42067509 (10)	1841345.516 (3)	-0.004	0.011
17-16	65.24574211 (11)	1956018.140 (3)	0.002	0.011
18-17	69.06831513 (12)	2070615.996 (3)	0.002	0.014
19-18	72.88824787 (12)	2185134.699 (4)	-0.014	0.013
20-19	76.70539413 (13)	2299569.865 (4)	-0.018	0.010
21-20	80.51960779 (13)	2413917.114 (4)	0.004	0.011
22-21	84.33074281 (13)	2528172.067 (4)	-0.007	0.011
23-22	88.13865324 (13)	2642330.350 (4)
24-23	91.94319322 (13)	2756387.589 (4)	0.001	0.017
25-24	95.74421698 (14)	2870339.415 (4)	-0.001	0.013
26-25	99.54157885 (14)	2984181.460 (4)	0.001	0.014
27-26	103.33513328 (15)	3097909.360 (4)	0.006	0.017
28-27	107.12473479 (16)	3211518.755 (5)
29-28	110.91023803 (17)	3325005.288 (5)
30-29	114.69149779 (18)	3438364.603 (5)	0.015	0.010
31-30	118.46836893 (19)	3551592.352 (6)	0.013	0.010
32-31	122.24070647 (19)	3664684.186 (6)
33-32	126.00836554 (20)	3777635.763 (6)	-0.032	0.016
34-33	129.77120140 (24)	3890442.744 (7)	-0.020	0.013
35-34	133.52906945 (31)	4003100.794 (9)
36-35	137.28182522 (44)	4115605.582 (13)	0.010	0.022
37-36	141.02932439 (64)	4227952.781 (19)
38-37	144.77142279 (93)	4340138.069 (28)	0.055	0.043
39-38	148.50797639 (131)	4452157.127 (39)
40-39	152.23884131 (180)	4564005.644 (54)
41-40	155.96387385 (242)	4675679.310 (73)
42-41	159.68293044 (320)	4787173.822 (96)
43-42	163.39586769 (417)	4898484.880 (125)
44-43	167.10254239 (534)	5009608.192 (160)
45-44	170.80281149 (676)	5120539.469 (203)
46-45	174.49653212 (846)	5231274.428 (254)

^a Values in parentheses are the 1 σ standard errors of the calculated transitions in units of the last quoted digits. The 95% confidence limits correspond to 2.05 σ .

^b This column lists the estimated 1 σ uncertainty of each observed frequency.

^c Observed value from Rosenblum et al. 1958.

^d Observed value from Belov et al. 1991.

^e Average of observed values from Helminger et al. 1970 and Nolt et al. 1987.

$\sqrt{2} \times 25$). A preliminary least-squares fit to the present CO data using a 35 kHz uncertainty in the FIR frequency produced a variance relative to the experimental uncertainty of 0.13. A relative variance which is much less than 1 implies an overestimate of the experimental uncertainties (Albritton, Schmel-

teckopf, & Zare 1976), so it seems that this estimation of the uncertainty in the FIR frequency was overly pessimistic. A second least-squares fit assuming a 10 kHz uncertainty in the FIR frequency produced a variance of 0.98; thus, this value for the uncertainty was chosen. The CO data recorded here can be regarded as a quantitative measurement of the frequency stability and resettability of our CO₂ lasers. Given the 3 kHz relative uncertainty in the tabulated CO₂ frequencies (Petersen et al. 1983), it appears that the 1 σ frequency uncertainty arising from the locking scheme of our CO₂ lasers is about 6 kHz, because this produces a FIR frequency uncertainty of about 10 kHz. To be explicit, the frequency uncertainty of each laser is the quadrature sum $[(6 \text{ kHz})^2 + (3 \text{ kHz})^2]^{1/2} \sim 7 \text{ kHz}$, and the FIR frequency uncertainty is then $[(7 \text{ kHz})^2 + (7 \text{ kHz})^2]^{1/2} \sim 10 \text{ kHz}$.

A second source of uncertainty is the determination of the line center of each CO transition from the computer fit of its line shape. For all but the weakest lines, these 1 σ uncertainties were less than 10 kHz. The estimated uncertainty of each transition (see Table 2) was calculated as the quadrature sum of the uncertainties in the FIR frequency and the fitted line center.

The estimated experimental uncertainties of the present TuFIR data set are about 10 times smaller than those of the previous TuFIR experiment of Nolt et al. (1987). This increase in precision has been accomplished by two significant improvements in our experimental method. First, we now insert a length scrambler in the FIR radiation path in order to eliminate standing waves (Zink et al. 1991). This flattens the spectrometer baseline and improves our ability to measure the transition line centers.

Second, and most important, we now fit by least squares the spectral line shapes to determine the line centers. For a line with a signal-to-noise ratio of 100 and a line width of 5 MHz, the standard error in the fitted frequency is typically $\sim 5 \text{ kHz}$. Previously in our laboratory, transition line centers were estimated by eye with the aid of a computer display. Nolt et al. (1987) suggested that the uncertainties in these line center estimations ranged from 100 to 200 kHz for strong transitions; therefore, the overall measurement uncertainties were dominated by these estimations of the line centers. In the present method the uncertainty in the FIR frequency is the predominant experimental uncertainty. This significant improvement in the measurement uncertainties of the data is clearly reflected in the standard errors of the calculated frequencies: the present errors are a factor of 10 smaller than those determined by Nolt et al. (1987).

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