

Laser Spectroscopy of Carbon Monoxide: A Frequency Reference for the Far Infrared

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Abstract—The rotational spectrum of carbon monoxide ($^{12}\text{C}^{16}\text{O}$) in the far infrared has been accurately measured. Calculated CO rotational frequencies derived from a least-squares fit to these data are given for the range $J'' = 0$ to 45 and are accurate to ≤ 10 kHz (2σ) for $J'' \leq 28$. These frequencies form the most accurate far infrared frequency reference reported to date.

I. INTRODUCTION

WE have measured the far infrared (FIR), rotational spectrum of $^{12}\text{C}^{16}\text{O}$ in its $X^1\Sigma^+(v=0)$ ground state with an accuracy approximately 10 times greater than that reported previously [1]. The 2σ error limits (95% confidence interval) of the calculated transition frequencies derived from a least-squares fit to the observed spectrum (combined with low frequency measurements of the first five rotational transitions by other workers [1]–[4]) are less than or equal to 10 kHz over the frequency range $0.1 \leq \nu \leq 3.5$ THz. These error limits correspond to an accuracy of about 5 parts in 10^9 . CO is a stable and relatively inert molecule ideally suited for use as a frequency reference for the far infrared region. The calculated values provided here will be useful for accurate frequency calibration of high resolution, far infrared spectrometers in the laboratory as well as for radioastronomical investigations of CO.

II. EXPERIMENTAL METHOD

The rotational spectrum of CO was measured in absorption by tunable far infrared (TuFIR) spectroscopy. The experimental configuration and method have been described in greater detail elsewhere [5]. Briefly, far infrared radiation is generated in a metal-insulator-metal (MIM) diode by the nonlinear mixing of mid infrared radiation from two CO_2 lasers with frequencies ν_1 and ν_2 . Adding sidebands of frequency ν_μ from a microwave synthesizer generates two tunable FIR frequencies: $|\nu_1 - \nu_2| \pm \nu_\mu$. With a choice of about 5000 pairs of $^{12}\text{C}^{16}\text{O}_2$ laser frequencies [6], all FIR frequencies as high as 5 THz can

be generated. One of the two CO_2 lasers is frequency stabilized by locking it directly to a saturation dip in the $4.3\text{-}\mu\text{m}$ CO_2 fluorescence signal from a reference cell placed in the beam path [7]. The other CO_2 laser is offset locked to a third CO_2 laser that is frequency stabilized in the same manner as the first laser.

The spectrum of CO was recorded as a first derivative by frequency-modulating one of the two CO_2 lasers at 1 kHz, passing the synthesized FIR radiation through a cell containing high purity CO, and detecting the absorption signal with a lock-in amplifier. The spectral linewidth is limited by Doppler broadening (at 2 THz, the full width at half maximum is 6 MHz). Each spectral line shape was fitted by least squares using five adjustable parameters: the transition frequency and intensity, the Gaussian and Lorentzian linewidths, and the spectrometer baseline.

III. FAR INFRARED REFERENCE FREQUENCIES

A typical example of a CO transition is illustrated in Fig. 1. 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 [1]–[4].

The rotational energy level expression for a diatomic molecule in a $^1\Sigma^+$ state is written [8]

$$E(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + LJ^4(J+1)^4 \quad (1)$$

The rotational transitions were fitted to (1) using a weighted least-squares fitting program, and values for the four molecular constants were obtained. The derived rotational constants are: $B = 57\,635.968\,26(12)$ MHz, $D = 0.183\,505\,52(46)$ MHz, $H = 1.724\,9(59) \times 10^{-7}$ MHz, and $L = -3.1(23) \times 10^{-13}$ MHz, where the 1σ uncertainties of the last digits are indicated in parentheses.

In Table I we list the calculated rotational frequencies for CO in the range $J'' = 0$ to 45, along with the 1σ standard errors of these frequencies. The 95% confidence limits correspond to 2.05σ . It should be noted that the standard errors of the calculated frequencies which lie to higher frequency of the last observed transition ($J = 38 \leftarrow 37$ at 4.34 THz) are likely to be underestimates of the true uncertainties. The uncertainties of these extrapolated values (in contrast to interpolated values) are underestimated by the least-squares fit because the molecular en-

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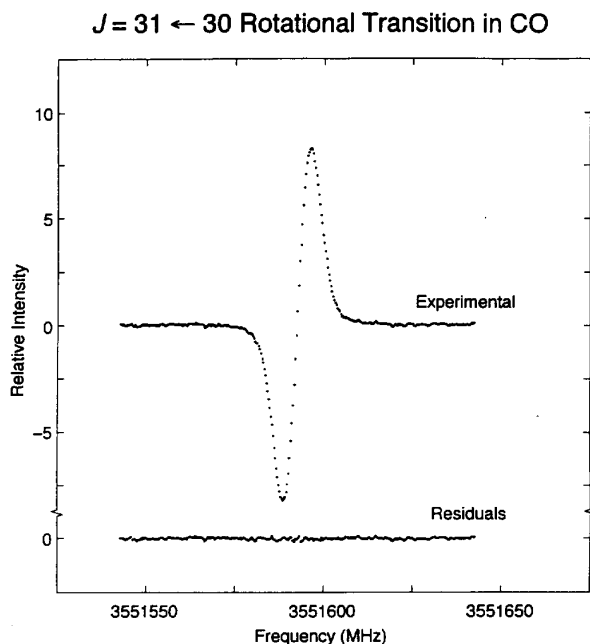


Fig. 1. The upper trace displays the observed $J = 31 \leftarrow 30$ rotational transition in the ground state of CO. The lower trace displays the residuals obtained from a least-squares fit to the observed line shape.

ergy level expression given in (1) is inadequate for levels of higher J . Essentially, the additional term $MJ^5(J+1)^5$ term is required to properly model such high- J levels, but the presently measured transitions are not sensitive to this term. We also list in Table I the observed-minus-calculated frequencies of the data, along with the estimated measurement uncertainties. The data were weighted in the fit by the square of the inverse of these estimated uncertainties. Fig. 2 displays a graph of the fitted residuals plotted as a function of the transition frequencies.

Our 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 [6], we believe that the uncertainty in the resettability and stability of our CO_2 lasers is significantly larger. We estimate this combined uncertainty as 7 kHz, giving rise to a 10 kHz uncertainty in the FIR frequency ($10 \sim \sqrt{2} \times 7$). Our least-squares fit to the CO data assuming this uncertainty in the FIR frequency produced a variance relative to the experimental uncertainty of 0.98. Since a relative variance of 1 implies an appropriate estimate of the experimental uncertainties [9], it appears that our estimation of the uncertainty in the FIR frequency is correct.

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 1σ uncertainties were less than 10 kHz. The estimated uncertainty of each transition (see Table I) was calculated as the quadrature sum of the uncertainties in the FIR frequency and the fitted line center.

TABLE I
CALCULATED AND OBSERVED ROTATIONAL FREQUENCIES FOR $^{12}\text{C}^{16}\text{O}$ IN ITS
 $X^1\Sigma^+(v=0)$ GROUND STATE

$J'-J''$	Calculated Frequency (MHz) ^a	Observed-Calculated (MHz)	Exper. Uncert. (MHz) ^b
1-0	115 271.202 (<1)	0.002 ^c	0.005
2-1	230 538.001 (<1)	-0.001 ^d	0.001
3-2	345 795.991 (1)	0.000 ^d	0.001
4-3	461 040.770 (1)	-0.001 ^d	0.002
5-4	576 257.933 (1)	-0.011 ^e	0.032
6-5	691 473.078 (1)	0.012	0.012
7-6	806 651.804 (1)	0.002	0.010
8-7	921 799.707 (1)	0.004	0.010
9-8	1 036 912.388 (2)	0.015	0.010
10-9	1 151 985.447 (2)	0.007	0.011
11-10	1 267 014.485 (2)	0.019	0.010
12-11	1 381 995.106 (2)	0.004	0.013
13-12	1 496 922.913 (2)	0.002	0.012
14-13	1 611 793.512 (2)	0.005	0.011
15-14	1 726 602.510 (3)
16-15	1 841 345.516 (3)	-0.004	0.011
17-16	1 956 018.140 (3)	0.002	0.011
18-17	2 070 615.996 (3)	0.002	0.014
19-18	2 185 134.699 (4)	-0.014	0.013
20-19	2 299 569.865 (4)	-0.018	0.010
21-20	2 413 917.114 (4)	0.004	0.011
22-21	2 528 172.067 (4)	-0.007	0.011
23-22	2 642 330.350 (4)
24-23	2 756 387.589 (4)	0.001	0.017
25-24	2 870 339.415 (4)	-0.001	0.013
26-25	2 984 181.460 (4)	0.001	0.014
27-26	3 097 909.360 (4)	0.006	0.017
28-27	3 211 518.755 (5)
29-28	3 325 005.288 (5)
30-29	3 438 364.603 (5)	0.015	0.010
31-30	3 551 592.352 (6)	0.013	0.010
32-31	3 664 684.186 (6)
33-32	3 777 635.763 (6)	-0.032	0.016
34-33	3 890 442.744 (7)	-0.020	0.013
35-34	4 003 100.794 (9)
36-35	4 115 605.582 (13)	0.010	0.022
37-36	4 227 952.781 (19)
38-37	4 340 138.069 (28)	0.055	0.043
39-38	4 452 157.127 (39)
40-39	4 564 005.644 (54)
41-40	4 675 679.310 (73)
42-41	4 787 173.822 (96)
43-42	4 898 484.880 (125)
44-43	5 009 608.192 (160)
45-44	5 120 539.469 (203)
46-45	5 231 274.428 (254)

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

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

^cObserved value from [2].

^dObserved value from [3].

^eAverage of observed values from [1] and [4].

IV. CONCLUSION

The estimated experimental uncertainties of the present TuFIR data set are about 10 times smaller than those of Nolt *et al.* [1], resulting in calculated frequencies of the transitions which are an order of magnitude more accurate. This new, comprehensive set of $^{12}\text{C}^{16}\text{O}$ frequencies will be useful as a frequency reference for the far infrared.

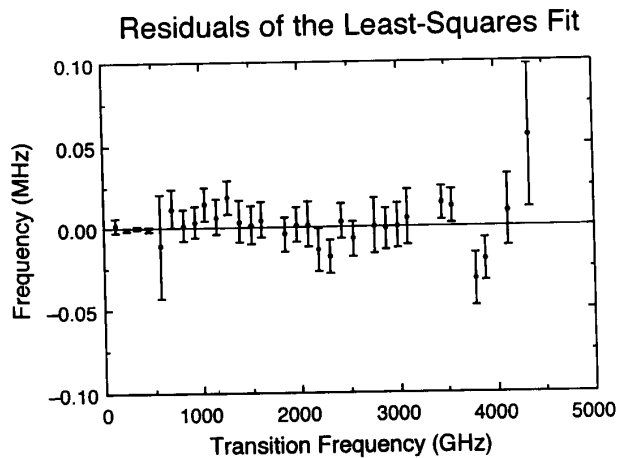


Fig. 2. Plot of the fitted residuals (observed-calculated) versus the transition frequencies. The error bars on each point denote the estimated experimental uncertainty of the transition frequency.

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