Journal of Research of the National Bureau of Standards Vol. 61, No. 1, July 1958 Research Paper 2883

Emission Spectrum of Carbon Monoxide From 2.3 to 2.5 Microns[1]

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The 2–0, 3–1, 4–2, 5–3, and 6–4 emission bands of carbon monoxide have been measured in the region from 4000 to 4360 cm^{-1} with a grating spectrometer. A 10,000 line per inch grating used in the second order resolved lines separated by 0.08 cm^{-1}. Several sets of measurements were made on the 2–0 band and the molecular constants were calculated. The constants in cm^{-1} are $B_0=1.922511\pm0.000025$ $D_0=6.13\pm0.02\times10^{-6}$. Using these values and the B_0 from 1–0 band in conjunction with the microwave constant a new determination of the speed of light is obtained, $c=299{,}794\ \pm3$ kilometers per second.

1. Introduction

The vibrational-rotational spectrum of carbon monoxide in emission was first measured in the infrared region in 1951 [1].[2] The observations were made on the harmonic band in the region from 4000 to 4360 cm^{-1}. Due to the high temperature of the flame the 2–0, 3–1, 4–2, and 5–3 transitions were observed. Recently Goldberg and Muller [2] have measured the absorption spectrum of carbon monoxide in the solar spectrum and have observed rotational lines with J values up to 75.

Other bands of carbon monoxide have also been measured. Herzberg and Rao [3] have measured the 4–0 band of CO in absorption in the near infrared, and the fundamental band at 4.67 μ has been measured by Plyler, Blaine, and Tidwell [4]. More recently 33 lines of the 2–0 band of CO have been measured by Rank and his co-workers [5]. From each set of measurements the various workers have calculated a set of molecular constants for the CO molecule and the results of different authors [2, 4, 5] are in close agreement.

Since the earlier measurements were made on the harmonic band of CO, improvements in detectors and infrared spectrometers permit more accurate measurements to be made. The bands in the 4000 to 4360 cm^{-1} region have been remeasured and this paper gives the results which have been obtained.

2. Experimental Method and Results

The emission from carbon monoxide in the 2.3-μ region was produced in two ways. First, a tube containing CO was placed in the coil of a hf oscillator. (The use of a hf oscillator for the production of molecular spectra has been previously studied by Wilkinson, Ford, and Price [6].) The pressure of the CO was 6 cm and a small flow of fresh gas was maintained. A spectrum of high intensity was observed showing transitions up to 11–9. The intensity of the rotational lines, however, varied with the pressure and the current through the oscillator coil and it was felt that more precise measurements of the lines could be made of the spectrum from a flame.

Second, the CO spectrum was observed in emission from an oxyacetylene flame. The gases were premixed and were slightly rich in fuel. The burning took place in a welding torch and a section of the flame about 2 in. above the inner cone was focused on the front slit of the spectrometer. The radiation falling on the slit was increased by reflections of mirrors around the flame [7]. A grating spectrometer with a collimating mirror of one-meter focal length and a grating of 10,000 lines/in. was used for resolving the bands. The spectrum was observed in the first and second orders, the second order giving higher resolution. Emission lines separated by 0.08 cm^{-1} were partially resolved.

The observed spectrum (4000 to 4360 cm^{-1}) includes the transitions 2–0, 3–1, 4–2, 5–3, 6–4, and 7–5. Because of the overlapping of the lines from the different transitions, precise measurements were made on the bands arising from the three lowest transitions. In figure 1 are shown the band heads and some of the rotational lines for the 2–0, 3–1, 4–2, 5–3, and 6–4 transitions. The intensity of the rotational lines with the same J values of the 2–0 and the 3–1 is about equal. In the other transitions the intensity is lower. In order to obtain sizeable deflections it was necessary to increase the amplifier gain for the other transitions; the noise level was the greatest for the 6–4 band.

The small lines appearing between the strong lines from R30 to R45 in each band arise from the band folding back on itself; these lines are part of the R branch extending up to about $J=68$. The high J values are almost superimposed on the lower J's in the 2–0 transition, but in the 3–1, 4–2, and 5–3 transitions the high J lines are well separated from the stronger lines in the region R30 to R45.

Some of the low-intensity lines observed in the 3–1 region are the R3 to R6 lines of the 2–0 band. Their low intensity shows that very few of the molecules in the flame exist in the lower rotational states. On figure 1 are given the identifications of the different lines. Precise measurements were made on the 2–0, 3–1, and 4–2 bands. When the lines of the different series overlapped they were not measured. In order to have a more complete set of measurements of the 2–0 band the lines from R20

[1] This work was supported by the Geophysics Research Directorate, Air Force. Cambridge Research Center.
[2] Figures in brackets indicate the literature references at the end of this paper.

to P20 were measured in absorption. The calculated and observed wave numbers of the 2–0, 3–1, and 4–2 bands are given in table 1.

3. Discussion of Results

The molecular constants of CO have been calculated from measurements of the 4–0, 2–0, and 1–0 bands by several observers [1, 2, 3, 4, 5]. In most cases the constants determined by Goldberg and Muller; Plyler, Blaine, and Tidwell; and Rank agree within the probable error given by the authors.

The line positions measured in the 2–0 band have been used to calculate B_0, D_0 and ν_0 by the equation,

$$\nu=\nu_0+(B_2+B_0)m+(B_2-B_0-D_2+D_0)m^2-2(D_2+D_0)m^3-(D_2-D_0)m^4.$$

TABLE 1. *Observed frequencies* (cm^{-1}) *and deviations from calculated values of* CO *lines from emission measurements*

Band	2–0				3–1				4–2			
J''	R(J)		P(J)		R(J)		P(J)		R(J)		P(J)	
	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$
0	4263.842	−0.006	--------	--------	4210.91	−0.009	--------	--------	4158.15	0.011	--------	--------
1	4267.548	−.005	4256.226	[a]−0.003	4214.64	.052	--------	--------	--------	--------	--------	--------
2	4271.182	−.005	4252.308	−.006	4218.19	.002	4199.47	−0.019	4165.33	−.008	--------	--------
3	4274.750	−.001	4248.330	.000	--------	--------	4195.52	−.020	--------	--------	--------	--------
4	4278.235	−.010	4244.278	.002	4225.18	.005	--------	--------	--------	--------	--------	--------
5	4281.655	−.012	4240.150	−.002	4228.60	.038	--------	--------	4175.59	−.018	--------	--------
6	4285.013	−.006	4235.952	−.008	4231.89	.011	4183.26	−.015	4178.88	−.009	4130.74	0.000
7	4288.298	−.002	4231.694	−.004	4235.13	.005	4179.05	.002	4182.09	−.010	--------	--------
8	4291.512	.003	4227.371	.004	4238.32	.021	4174.75	−.002	--------	--------	4122.30	.013
9	4294.639	−.008	4222.974	.007	4241.41	.008	4170.38	−.008	4188.29	−.017	--------	--------
10	4297.703	−.011	4218.504	.005	4244.44	.006	4165.95	−.004	4191.28	−.024	4113.56	.001
11	4300.712	.003	4213.962	.000	4247.40	.006	4161.45	−.002	4194.20	−.029	--------	--------
12	4303.614	−.018	4209.356	−.001	--------	--------	4156.91	.028	4197.07	−.013	--------	--------
13	4306.482	−.002	4204.673	−.010	4253.10	.001	4152.26	.017	--------	--------	--------	--------
14	4309.262	−.001	4199.931	−.010	4255.85	.007	4147.56	.023	4202.57	−.003	--------	--------
15	4311.969	−.001	4195.120	−.012	4258.52	.005	4142.80	.038	4205.19	−.020	--------	--------
16	4314.606	.001	4190.234	−.020	4261.12	.005	4137.91	−.010	4207.77	−.005	--------	--------
17	4317.173	.006	4185.302	−.007	4263.64	−.002	4133.02	.011	4210.25	−.017	--------	--------
18	4319.665	.008	4180.286	−.010	4266.10	.003	4128.05	.018	4212.67	−.017	--------	--------
19	4322.085	.011	4175.212	−.004	4268.48	.001	4123.00	.013	4215.02	−.014	--------	--------
20	4324.425	.007	4170.066	−.003	4270.79	.002	4117.89	.016	4217.29	−.018	--------	--------
21	4326.699	.010	4164.852	−.003	4272.03	.006	4112.70	.005	4219.50	−.009	--------	--------
22	4328.878	−.008	4159.564	−.009	4275.18	.002	4107.46	.011	4221.64	.004	--------	--------
23	4331.022	.012	4154.234	.009	4277.28	.004	4102.14	.004	4223.68	−.011	--------	--------
24	4333.057	−.004	4148.817	.007	4279.29	−.001	4096.74	−.016	4225.66	−.011	--------	--------
25	--------	--------	4143.33	.001	4281.21	−.023	4091.30	−.009	4227.58	.002	--------	--------
26	--------	--------	4137.79	.009	--------	--------	4085.76	−.037	4229.42	.008	--------	--------
27	--------	--------	4132.19	.023	--------	--------	--------	--------	4231.17	−.001	--------	--------
28	--------	--------	--------	--------	4286.59	−.026	--------	--------	4232.86	.004	--------	--------
29	--------	--------	4120.74	−.002	--------	--------	--------	--------	4234.47	.003	--------	--------
30	4343.804	−.010	4114.94	.010	4289.83	−.004	--------	--------	--------	--------	--------	--------
31	4345.341	−.005	--------	--------	4291.35	.019	--------	--------	4237.47	.004	--------	--------
32	4346.810	.007	4103.12	.010	4292.75	−.003	--------	--------	4238.86	.007	--------	--------
33	4348.193	.007	4097.09	−.012	4294.10	−.001	--------	--------	--------	--------	--------	--------
34	4349.494	.001	--------	--------	4295.36	−.013	--------	--------	--------	--------	--------	--------
35	4350.726	.000	4084.88	−.010	4296.57	−.001	--------	--------	4242.58	.014	--------	--------
36	4351.889	.006	--------	--------	--------	--------	--------	--------	4243.66	.007	--------	--------
37	4352.966	.002	--------	--------	4298.75	.010	--------	--------	4244.67	.005	--------	--------
38	4353.965	−.006	--------	--------	4299.72	.009	--------	--------	4245.60	−.001	--------	--------
39	4354.902	.001	--------	--------	--------	--------	--------	--------	4246.46	−.001	--------	--------
40	4355.762	.006	--------	--------	4301.42	−.006	--------	--------	4247.25	.004	--------	--------
41	4356.542	.008	--------	--------	4302.16	−.010	--------	--------	4247.96	.005	--------	--------
42	4357.241	.004	--------	--------	4302.82	−.017	--------	--------	4248.60	.013	--------	--------
43	4357.862	−.001	--------	--------	4303.41	−.018	--------	--------	4249.15	.007	--------	--------
44	4358.411	−.002	--------	--------	4303.92	−.023	--------	--------	4249.63	.007	--------	--------
45	4358.885	−.001	--------	--------	4304.36	−.021	--------	--------	4250.03	.004	--------	--------
46	4359.293	.010	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
47	--------	--------	--------	--------	4305.04	.013	--------	--------	--------	--------	--------	--------
[b] 48	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
55	4359.367	−.006	--------	--------	--------	--------	--------	--------	4249.82	.006	--------	--------
56	4358.984	−.010	--------	--------	--------	--------	--------	--------	4249.36	−.005	--------	--------
57	4358.528	−.009	--------	--------	--------	--------	--------	--------	4248.84	.003	--------	--------
58	4357.996	−.005	--------	--------	4303.01	−.032	--------	--------	--------	--------	--------	--------
59	4357.395	.008	--------	--------	4302.37	−.022	--------	--------	--------	--------	--------	--------
60	4356.691	−.003	--------	--------	4301.65	−.014	--------	--------	4246.78	−.004	--------	--------
61	4355.922	.000	--------	--------	--------	--------	--------	--------	4245.94	−.002	--------	--------
62	4355.063	−.008	--------	--------	4299.96	−.011	--------	--------	4245.03	.009	--------	--------
63	4354.144	.004	--------	--------	4299.01	.004	--------	--------	4244.02	−.001	--------	--------
64	4353.146	.015	--------	--------	4297.93	−.031	--------	--------	4242.96	.019	--------	--------
65	4352.057	.016	--------	--------	4296.83	−.007	--------	--------	4241.79	.008	--------	--------
66	4350.885	.013	--------	--------	4295.62	−.013	--------	--------	4240.55	.007	--------	--------
67	--------	--------	--------	--------	4294.33	−.019	--------	--------	4239.24	.016	--------	--------
68	--------	--------	--------	--------	4292.97	−.015	--------	--------	--------	--------	--------	--------

[a] Lines from R20 to P20 measured in absorption. [b] No measurements were taken for J''=48 through 54.

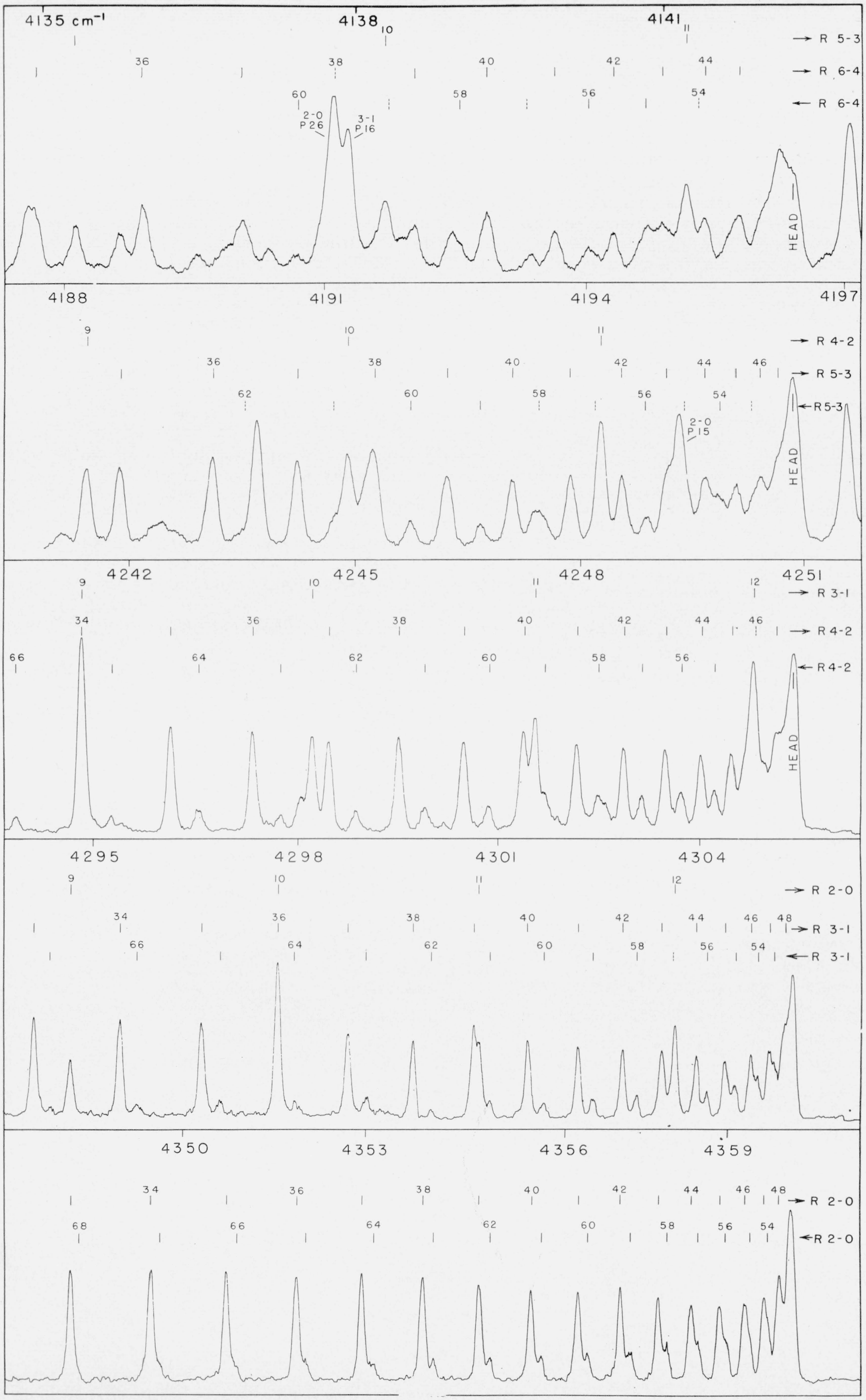

FIGURE 1.

Emission spectrum of carbon monoxide in the overtone region.

The 2–0, 3–1, 4–2, 5–3, and 6–4 band heads can be seen at the high frequency side of each trace.

The constants were calculated both with and without the m^4 term. Only very small differences occurred in ν_0, B_0, and D_0 when the fourth power term was omitted. Since D_2—D_0 is about 2×10^{-9} cm^{-1}, the contribution of this term for $J=20$ is approximately 0.001 cm^{-1} which is about one-fourth the experimental error in the measurements of the lines. Sixty-five lines of the 2–0 band were used in the calculation. They extended from R46 to P24 (see table 1). The constants obtained, in cm^{-1}, were

$$\nu_0=4260.069 \pm0.001$$

$$B_0=1.922511 \pm0.000028$$

$$D_0=6.13 \pm0.022\times10^{-6}.$$

The constants B_0 and D_0 had been previously calculated from measurements of the 1–0 band [8] and found to be

$$B_0=1.922523 \pm0.000025$$

$$D_0=6.26 \pm0.17\times10^{-6}.$$

The standard deviations were first reported but the uncertainty is now given as probable error. The values of B_0 from the two bands fall within the error of measurements. A better value of B_0 can be obtained by combining [8] the two B_0's determined by analyses of the 1–0 and 2–0 bands, which gives the result,

$$B_0=1.922517 \pm0.000019,$$

the uncertainty again being the probable error.

The central value of D_0 as determined from an analysis of the 2–0 band is in better agreement with the recent value of $D_0=6.131\times10^{-6}$ obtained by Gordy from the microwave spectrum [9], and the value of $D_0=6.117\times10^{-6}$ from a measurement of the 2–0 by Rank et al. [5] than was the earlier determination from the 1–0 band.

There are now two determinations for B_0 which give an average value of 1.922517 ± 0.000019. This value of B_0 is in excellent agreement with the values obtained by Rank et al. [5],

$$B_0=1.922519\pm0.000013$$

and

$$B_0=1.922521\pm0.0000035.$$

The first value was obtained from the least squares treatment of 13 Δ_2F'' values from the measurements, and the second value was the result of using a calculated value for the constant D_0 and including only the 8 largest Δ_2F'' values in the least squares treatment. Rank et al. [5] have calculated the velocity of light using the second B_0 given above and from $B_0=57{,}635.965 \pm0.005$ Mc determined from the rotational spectrum. The result is $c=299{,}793.7 \pm0.7$ km/sec. On using the same value of B_0 from microwave measurements and the average value from our infrared measurements, the speed of light is determined as $c=299{,}794 \pm3$ km/sec in excellent agreement with previous determinations by this method. The central value is somewhat higher than the best value given by Bearden and Thomsen [10], 299,792.8 and also that given by Cohen, DuMond et al. [11], 299,793.0; however both of their values are within the probable error of this determination.

In conclusion, the authors thank Carroll Dannemiller for doing the least squares calculations on the Bureau's electronic computer.

4. References

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WASHINGTON, February 5, 1958.