JANUARY 15, 1939 PHYSICAL REVIEW VOLUME 55

The Infra-Red Spectrum and Molecular Constants of Carbon Monoxide

S. E. Whitcomb and R. T. Lagemann
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

(Received November 28, 1938)

The fundamental and first overtone bands of carbon monoxide have been measured under high resolution and the lines in the positive and negative branches in both bands have been fitted to formulae of the form

$$\nu = a + bm + cm^2 + dm^3.$$

The molecular constants ν_0, I_0, B and C as defined by Colby depend directly on the constants a, b, c, d and have been determined from these measurements. Their values are

$$\nu_0 = 2168.48 \text{ cm}^{-1}, \quad I_0 = 1.429 \times 10^{-39} \text{ g cm}^2, \quad B = 1.38 \times 10^{-6}, \quad C = 6.202.$$

The constants used in electronic work, as defined by Jevons, have also been computed and are in close agreement with previous results.

THE vibration-rotation spectrum of carbon monoxide was originally investigated in this laboratory by Lowry,[1] who was able to obtain only the doublet structure of the fundamental band. More recently, however, the spectrum of CO has been remeasured by Snow and Rideal[2] who were able to resolve partially, at least, both the fundamental and harmonic bands. It has now been found possible to completely resolve this band system into its fine structure and to measure the frequency positions of the lines in both the fundamental and the harmonic. For these measurements a prism-grating spectrometer of a conventional design with a two-meter collimating mirror was available. Echelette gratings of 3600 and 4800 lines to the inch ruled by Wood were used in the first order. The carbon monoxide gas was prepared by passing formic acid vapor over phosphoric pentoxide and then passing the resulting carbon monoxide gas through a liquid-air trap. Glass cells fitted with polished rocksalt windows were used to contain the gas during the investigation. In the case of the fundamental the cell was seven cm long and for the harmonic the cell was 19 cm in length. They were filled to atmospheric pressure for measurement on both bands. In the region of the fundamental the slit widths were equivalent to 0.7 cm^{-1} and galvanometer deflection readings were taken every 0.6 cm^{-1}. In the region of the harmonic the slit widths were equivalent to

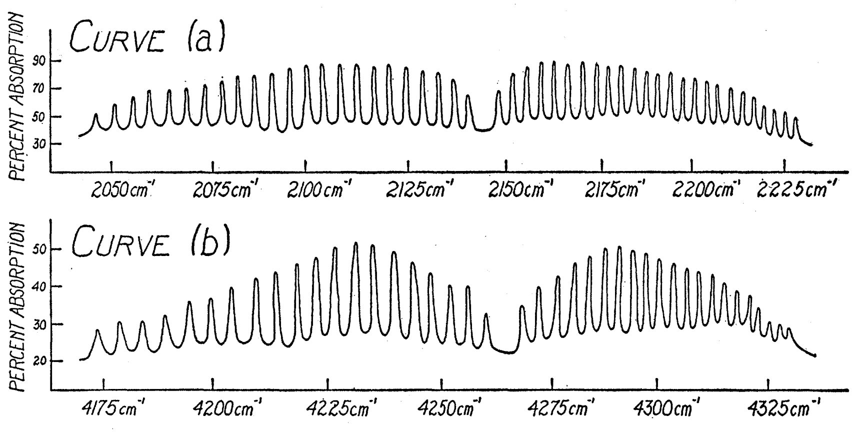

FIG. 1. Absorption plotted against frequency. Curve (a) fundamental band with center at 4.66μ. Curve (b) harmonic band with center at 2.34μ.

---

[1] E. F. Lowry, J. Opt. Soc. Am. **8**, 647 (1924).

[2] C. P. Snow and E. K. Rideal, Proc. Roy. Soc. **A125**, 462 (1929).

TABLE I. *The fundamental band.*

m	OBSERVED ν	COMPUTED ν	DIFFERENCE
+25	2228.16	2227.91	+0.25
+24	2225.31	2225.15	+ .16
+23	2222.33	2222.32	+ .01
+22	2219.48	2219.45	+ .03
+21	2216.45	2216.52	− .07
+20	2213.63	2213.54	+ .09
+19	2210.60	2210.52	+ .08
+18	2207.39	2207.44	− .05
+17	2204.19	2204.31	− .12
+16	2201.06	2201.15	− .09
+15	2197.66	2197.92	− .26
+14	2194.33	2194.67	− .34
+13	2191.15	2191.37	− .22
+12	2187.80	2188.01	− .21
+11	2184.36	2184.61	− .25
+10	2181.30	2181.17	+ .13
+ 9	2177.59	2177.68	− .09
+ 8	2174.17	2174.16	+ .01
+ 7	2170.67	2170.59	+ .08
+ 6	2166.88	2166.98	− .10
+ 5	2163.40	2163.32	+ .08
+ 4	2159.65	2159.63	+ .02
+ 3	2155.78	2155.90	− .12
+ 2	2152.07	2152.14	− .07
+ 1	2148.30	2148.32	− .02
− 1	2140.57	2140.60	− .03
− 2	2136.69	2136.68	+ .01
− 3	2132.86	2132.72	+ .14
− 4	2128.81	2128.73	+ .08
− 5	2124.66	2124.69	− .03
− 6	2120.66	2120.64	+ .02
− 7	2116.54	2116.55	− .01
− 8	2112.55	2112.42	+ .13
− 9	2108.30	2108.26	+ .04
−10	2103.99	2104.07	− .08
−11	2099.82	2099.85	− .03
−12	2095.63	2095.59	+ .04
−13	2091.28	2091.31	− .03
−14	2087.08	2086.99	+ .09
−15	2082.48	2082.66	− .18
−16	2078.32	2078.29	+ .03
−17	2073.90	2073.88	+ .02
−18	2069.50	2069.46	+ .04
−19	2065.07	2065.02	+ .05
−20	2060.70	2060.54	+ .16
−21	2056.46	2056.04	+ .42
−22	2051.80	2051.51	+ .29
−23	2047.26	2046.96	+ .30

1.2 cm^{-1} and values of the percent transmission were obtained at intervals of 0.9 cm^{-1}. The galvanometer deflections were of the order of 100 mm for the fundamental and 200 mm for the harmonic.

Curve (a) Fig. 1, where percent absorption is plotted against frequency, shows the lines of the fundamental band which has its center at 4.66μ. There is no Q branch and the lines of the P and R branches have been fitted to the formula

$$\nu' = 2144.48 \pm 3.865m - 0.01860m^2 \mp 0.0001m^3, \quad (1)$$

where m is the ordinal number of the line counted outward from the center. In Table I are given the observed frequencies of the lines in cm^{-1}, the frequencies as calculated from Eq. (1), and the differences between the observed and calculated values.

The harmonic band, with its center at 2.34μ, is shown in curve (b), Fig. 1. Here again it has been possible to fit the lines in both branches to a formula

$$\nu'' = 4264.96 \pm 3.862m - 0.0353m^2 \mp 0.00004m^3, \quad (2)$$

where m is the ordinal number of the line counted outward from the center. Table II gives the observed frequencies of the lines, the frequencies calculated from Eq. (2), and the

TABLE II. *The harmonic band.*

m	OBSERVED ν	COMPUTED ν	DIFFERENCE
+21	4330.10	4330.12	−0.02
+20	4327.86	4327.76	+ .10
+19	4325.69	4325.33	+ .36
+18	4322.99	4322.81	+ .18
+17	4320.28	4320.21	+ .07
+16	4317.57	4317.55	+ .02
+15	4314.81	4314.81	.00
+14	4311.96	4312.00	− .04
+13	4309.14	4309.11	+ .03
+12	4306.34	4306.15	+ .19
+11	4303.17	4303.12	+ .05
+10	4300.07	4300.01	+ .06
+ 9	4297.06	4296.83	+ .23
+ 8	4293.88	4293.58	+ .30
+ 7	4290.64	4290.25	+ .39
+ 6	4286.96	4286.85	+ .11
+ 5	4283.76	4283.38	+ .38
+ 4	4280.12	4279.85	+ .27
+ 3	4276.41	4276.23	+ 18
+ 2	4272.54	4272.54	.00
+ 1	4268.96	4268.78	+ .18
− 1	4260.95	4261.06	− .11
− 2	4256.90	4257.10	− .20
− 3	4252.86	4253.05	− .19
− 4	4248.93	4248.95	− .02
− 5	4244.79	4244.78	+ .01
− 6	4240.22	4240.53	− .31
− 7	4236.07	4236.21	− .14
− 8	4231.80	4231.82	− .02
− 9	4227.21	4227.37	− .16
−10	4222.68	4222.85	− .17
−11	4218.32	4218.26	+ .06
−12	4213.66	4213.61	+ .05
−13	4209.05	4208.87	+ .18
−14	4204.09	4204.08	+ .01
−15	4199.58	4199.23	+ .35
−16	4194.32	4194.29	+ .03
−17	4189.20	4189.31	− .11
−18	4184.28	4184.23	+ .05
−19	4179.14	4179.11	+ .03
−20	4173.92	4173.92	.00

differences between the observed and calculated values.

Since the last two constants in each of the Eqs. (1) and (2) are not known very accurately, the first two numerical constants in each case have been used to determine the molecular constants ν_0, I_0, r_0, B and C as defined by Colby.[3] The numerical values of these constants are

$$\begin{array}{ll} \nu_0=2168.48\ \mathrm{cm}^{-1}, & I_0=1.429\times10^{-39}\ \mathrm{g\ cm}^2, \\ B=1.38\times10^{-6}, & C=6.202. \\ r_0=1.124\times10^{-8}\ \mathrm{cm}, & \end{array}$$

For convenience the molecular constants as defined by Jevons[4] have also been computed and are given below.

$$\begin{array}{ll} \omega_e=2168.48\ \mathrm{cm}^{-1}, & B_e=1.9543, \\ x_e=5.534\times10^{-3}, & B_0=1.9453, \\ x_e\omega_e=12.00\ \mathrm{cm}^{-1}, & B_1=1.9232, \\ I_0=1.425 & B_2=1.9134, \\ \quad\times10^{-39}\ \mathrm{g\ cm}^2, & D_e=-6.349 \\ r_0=1.122\times10^{-8}\ \mathrm{cm}, & \quad\times10^{-6}\ \mathrm{cm}^{-1}. \end{array}$$

The values of I_0 and ν_0 as here determined are seen to be in good agreement within the approximation used in the two definitions of the constants. As would be expected, the values of B_v decrease with increasing vibrational quantum number. In Table III a comparison is made with the previously determined values of the moment of inertia and the internuclear distance. The value of I_0 as here determined is seen to be less than previous values from infra-red work, but is in very close agreement with electronic band results. This new value is probably more nearly correct because of the excellent resolution obtained and because of the more precise energy formula used.

TABLE III. *Comparison of the values of the moment of inertia and the internuclear distance here determined with values previously obtained.*

	I_0(g cm^2)	r_0(cm)
Average* of classical doublet separation	1.48×10^{-39}	1.15×10^{-8}
Asundi** from electronic bands	1.38×10^{-39}	1.104×10^{-8}
Gerö, Herzberg and Schmid† from electronic bands	1.438×10^{-39}	1.128×10^{-8}
Snow and Rideal‡ from fundamental fine structure	1.50×10^{-39}	1.15×10^{-8}
Present determination from fine structure of both bands	1.429×10^{-39}	1.124×10^{-8}

* E. F. Lowry, reference 1; W. Burmeister, Verh. d. D. Phys. Ges. **15**, 589 (1913); C. Schaefer and B. Phillips, Zeits. f. Physik **36**, 399 (1926).

** R. K. Asundi, Proc. Roy. Soc. **A124**, 277 (1929).

† L. Gerö, G. Herzberg and R. Schmid, Phys. Rev. **52**, 467 (1937).

‡ C. P. Snow and E. K. Rideal, Proc. Roy. Soc. **A125**, 462 (1929).

In conclusion we wish to acknowledge a grant from the National Research Council which aided in securing the gratings used and to express our appreciation to Dr. H. H. Nielsen for valuable help in both the experimental work and the analysis.

---

[3] W. F. Colby, Phys. Rev. **34**, 53 (1929).

[4] W. Jevons, *Report on Band Spectra of Diatomic Molecules* (University Press, Cambridge), p. 39.