mated energies, selection rules, likely weakness of many not-forbidden transitions (especially, perhaps, two-electron jumps), etc., readers can draw their own conclusions.

The ultraviolet fluorescence spectrum of I_2 which follows excitation to the D electron level has already been discussed. No similar spectrum has been found in any of the other halogens X_2

or XY, except in IBr.[17] The IBr fluorescence resembles that of I_2, except that it does not follow excitation to the D state of IBr, which is not yet known (cf. end of section 9), but presumably (cf. Cordes[3]) to energy levels belonging to $\sigma^2\pi^4\pi^3\sigma^X$, II (cf. section 6).

[17] F. W. Loomis and A. J. Allen, Phys. Rev. **33**, 639 (1929) obtained IBr and I_2 fluorescence by λ1849 excitation, but obtained none in Br_2, ICl, or BrCl.

Rotational and Vibrational Structure of the Fourth Positive Bands of Carbon Monoxide

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The rotational structure of twelve of the fourth positive bands of CO ($A\,^1\Pi - X\,^1\Sigma$) has been measured and analyzed. The analyses of two bands are given. The values obtained for the rotational constants of the normal state are $B_0 = 1.9170$ cm^{-1}, $\alpha = 0.01738$ cm^{-1}. This is in disagreement with the result of infrared band measurements, which give $B_0 = 1.84$. The data obtained on the excited $A\,^1\Pi$ state are in complete agreement with the results of Angstrom

($B\,^1\Sigma - A\,^1\Pi$) band studies. The higher value of B_0 for the normal state is verified by measurement of the 0−0 band of the ultraviolet system $B\,^1\Sigma - X\,^1\Sigma$. The recently reported predissociation of the B state is also observed in this band. New measurements are given of the fourth positive band heads below 2270A. A formula is given to represent all the known band heads, and from this a formula for band origins is obtained.

INTRODUCTION

THE carbon monoxide spectrum is one of the most exhaustively studied of all molecular spectra. Nevertheless, no rotational analyses have been reported of bands involving the normal state of the molecule. Most of these lie in the far ultraviolet region.

The most important of the ultraviolet band systems is the fourth positive ($A\,^1\Pi - X\,^1\Sigma$). About 140 band heads have been identified, extending from about 1300 to 2600A. The upper state of this system is the lower state of the well-known Angstrom band system ($B\,^1\Sigma - A\,^1\Pi$). The vibrational analysis is given by Birge,[1] and more recent band head measurements have been reported by Headrick and Fox,[2] and by Estey.[3] The object of this paper is to report rotational analyses of a number of these bands, and more accurate band head measurements.

EXPERIMENTAL

The present work is based on a spectrogram taken by Professor H. D. Smyth with the two-meter vacuum spectrograph at Massachusetts Institute of Technology.[4] The source used was a hollow cathode discharge in flowing CO_2. The original object was to search for CO_2 emission bands, but none were found in this region.

The plate covers the region from 0 to about 2475A with a dispersion of 4.2A/mm. It shows about 65 heads of the fourth positive system of CO. Many of the bands are quite intense and well resolved except in the immediate neighborhood of the heads. There are also present on the plate a number of the first negative bands of CO$^+$, six of the ultraviolet bands of CO reported by Hopfield and Birge,[5] and atomic lines due to C, O, N, and Ni.

The measurements of the plate were converted to wave-lengths by use of a dispersion table for

[1] Birge, Phys. Rev. **28**, 1157 (1926).
[2] Headrick and Fox, Phys. Rev. **35**, 1033 (1930).
[3] Estey, Phys. Rev. **35**, 309 (1930).

[4] Compton and Boyce, Rev. Sci. Inst. **5**, 218 (1934).
[5] Hopfield and Birge, Phys. Rev. **29**, 922 (1927).

TABLE I. *1—1 band, 1560.133A.*

J	R(J)	Q(J)	P(J)	R(J) -Q(J)	Q(J+1) -P(J +1)	R(J) -Q(J +1)	Q(J) -P(J+1)
0							
1							
2							
3							
4	(64097.1H)						
5							
6			64056.7		22.3		
7	64095.5	64070.6	048.3	24.9	24.8	30.8	30.7
8	093.1	064.7	039.9	28.4	28.5	34.0	34.1
9		059.1a	030.6		31.4		38.2
10	086.2		020.9				
11	082.1		64009.8		38.0		45.7
12		036.4	63998.4b		40.4		49.1
13		027.7	987.3c		44.2		53.3
14	066.6	018.6	974.4	48.0	47.1	57.9	57.0
15	059.1a	64008.7	961.6	50.4	50.6	60.7	60.9
16	052.3	63998.4b	947.8	53.9	53.6	65.0	64.7
17		987.3c	933.7		56.7		68.5
18	035.3	975.5	918.8	59.8	59.9	72.0	72.1
19	026.6	963.3	903.4	63.3	62.8	76.4	75.9
20	016.2	950.2	887.4	66.0	65.8	79.8	79.6
21	64005.2	936.4	870.6	68.8	69.2	82.9	83.3
22	63993.8	922.3	853.1	71.5	71.9	87.0	87.4
23	982.4	906.8	834.9	75.6	75.6	90.7	90.7
24	969.2	891.7	816.1	77.5	78.3	94.4	95.2
25	954.6	874.8	796.5	79.8	83.0	95.8	99.0
26	944.5	858.8	775.8	85.7	87.4	103.7	105.4
27	928.7	840.8	753.4	87.9	87.0	106.5	105.6
28	913.5	822.2	735.2	91.3	89.8	111.2	109.7
29	897.7	802.3	712.5	95.4	94.1	113.6	112.3
30	881.4	784.1	690.0	97.3	96.7	118.0	117.4
31	863.9	763.4	666.7	100.5	99.6	121.2	120.3
32	845.6	742.7	643.1	102.9	103.1	124.6	124.8
33	827.9	721.0	617.9	106.9	105.0	130.0	128.1
34	808.3	697.9	592.9	110.4	110.6	130.6	130.8
35	788.4	677.7	567.1	110.7	112.3	135.7	137.3
36	767.9	652.7	540.4	115.2	115.6	139.4	139.8
37	746.5	628.5	512.9	118.0	118.8	142.5	143.3
38	724.6	604.0	485.2	120.6	122.5	146.0	147.9
39	701.9	578.6	456.1	123.3		149.9	
40		552.0					
41		524.7					
42		497.1					
43		468.4					

H. Position of head calculated from other lines of the band. The head is obscured on the plate.
a, b, c Blends of two lines.

TABLE II. *4—10 band, 1990.890A.*

J	R(J)	Q(J)	P(J)	R(J) -Q(J)	Q(J+1) -P(J +1)	R(J) -Q(J +1)	Q(J) -P(J+1)
0							
1					6.0		
2		50216.4a	50210.4f		8.7		10.2
3		214.9	206.2		12.4		14.6
4		212.7b	200.3g		15.0		17.3
5	50228.8H	210.4f	195.4	18.4	17.8	21.6	21.0
6	228.8	207.2	189.4	21.6	20.8	25.0	24.2
7	228.3	203.8c	183.0	24.5	24.1	28.0	27.6
8		200.3g	176.2		27.3		31.6
9	226.4	196.0	168.7	30.4	30.9	35.3	35.8
10	224.6	191.1	160.2h	33.5	33.3	38.8	38.6
11	222.0	185.8	152.5i	36.2	36.1	41.8	41.7
12	219.3	180.2d	144.1j	39.1	39.2	45.5	45.6
13	216.4a	173.8e	134.6	42.6	42.3	49.2	48.9
14	212.7b	167.2	124.9	45.5	45.3	52.5	52.3
15	207.9	160.2h	114.9	47.7	48.2	55.4	55.9
16	203.8c	152.5i	104.3	51.3	50.9	59.7	59.3
17*	198.8	144.1j	093.2	54.7	54.1	63.0	62.4
18	193.2	135.8	081.7	57.4	57.2	66.3	66.1
19	186.8	126.9	069.7	59.9	60.0	69.5	69.6
20	180.2d	117.3	057.3	62.9	63.2	72.8	73.1
21	173.8e	107.4	044.2	66.4	66.3	76.8	76.7
22		097.0	030.7		69.6		80.2
23	158.0	086.4	016.8	71.6	72.2	83.6	84.0
24	149.5	074.6	50002.4	74.9	75.0	86.8	86.9
25	140.6	062.7	49987.7	77.9	77.9	90.4	90.4
26	131.1	050.2	972.3	80.9	81.0	93.8	93.9
27	121.2	037.3	956.3	83.9			97.3
28	110.7		940.0		86.8	100.6	
29	099.8	50010.1	923.3	89.7	89.7	104.0	104.0
30	088.6	49995.8	906.1	92.8	93.0	107.6	107.8
31	076.4	981.0	888.0	95.4		110.9	
32		965.5					
33		949.7					
34		933.6					
35		916.3					
36		898.8					
37		880.9					

a, b, c etc. Blends of two lines.

the spectrograph. A graphical correction was applied to these results, using Edlén's[6] measurements of the C, O and N lines as standards. This amounted at most to 0.01A.

ROTATIONAL ANALYSIS

The rotational structure of twelve of the fourth positive bands has been measured and analyzed. The bands chosen include all values of the lower vibrational quantum number from 1 to 10. The structure consists of single P, Q and R branches, to be expected from a $^1\Pi \rightarrow {}^1\Sigma$ transition, the R branches forming the heads. The P and Q branches are about equally strong, and the R branch considerably weaker in the region where the lines are well resolved. In most bands, from 50 to 100 lines can be identified. In the neighborhood of the origins and heads,

which are quite close together, the structure is practically unresolved.

The analyses of two of the bands are given in Tables I and II, together with the combination differences

and

$$R(J) - Q(J) = Q(J+1) - P(J+1)$$
$$R(J) - Q(J+1) = Q(J) - P(J+1), \qquad (1)$$

which give the separations of the rotational levels of the upper and lower states, respectively. These equalities are strictly valid only if the Λ-type doubling of the $^1\Pi$ state is negligible. From studies of the Angstrom bands[7,8,9] this is known to be the case for the A state of CO, except where the state is perturbed. Actually the equations are satisfied to within about 0.5 cm⁻¹ in most cases where lines are not blended except in these perturbed regions.

Since the band lines are not traced with certainty to J values lower than about 10, there

[6] Edlén, Zeits. f. Physik **85**, 85 (1933).

[7] Hulthén, Ann. d. Physik **71**, 41 (1923).
[8] Johnson and Asundi, Proc. Roy. Soc. **A123**, 560 (1929).
[9] Rosenthal and Jenkins, Proc. Nat. Acad. Sci. **15**, 896 (1929).

might be some question about the assignment of quantum numbers. The quantum numbers have been assigned in every case so as to make the combination differences for the upper state agree with those for the lower state of the Angstrom band which involves the same vibration level. All the lines near the origins of the Angstrom bands are resolved, and the numbering is certain. With the quantum numbers as assigned, the combination differences (Eq. (1)) also satisfy the condition that when plotted as a function of J they should extrapolate to 0 at $J = -1$.

It is well known that perturbations are observed in the lines of the Angstrom bands. These have been studied by Rosenthal and Jenkins,[9] and found to be due to the A state. Since this is the upper state of the fourth positive system, the same perturbations should be observed in these bands. The quantum numbers of the displaced lines are easily predicted from the data of Rosenthal and Jenkins. The appropriate displacements are observed in all cases. This is shown, for instance, by the inequality of the combination differences in Table I in the neighborhood of $J = 25$, and their deviations from a smooth curve. The displaced lines are $R(25)$, $Q(24)$ and $P(27)$. The measurements are not sufficiently accurate to make a careful study of the perturbations, such as Rosenthal and Jenkins have given.

ROTATIONAL CONSTANTS

The rotation function is assumed to be

$$F(J) = B_v J(J+1) \qquad (2)$$

and accordingly the combination differences are given by

$$\Delta F(J) = F(J+1) - F(J) = 2B(J+1). \qquad (3)$$

This simple form of rotation function seems adequate to represent the data up to about $J = 25$. Beyond this point the perturbations of the upper state cause considerable displacements of the band lines, obscuring the effect of higher power terms in the rotation functions.

The values of B_v'' for the twelve bands are determined by fitting Eq. (3) to the combination differences, up to about $J = 25$, by the method

of least squares. The results are given in Table III. The values of B_v'' are assumed to be related by the equation

$$B_v'' = B_0'' - \alpha'' v''. \qquad (4)$$

TABLE III. Rotational constants of lower state.

Band	B_v(obs.)	B_v(calc.)	O−C
1–1	1.8981		−0.0015
4–1	1.9001	1.8996	+0.0005
7–1	1.9012		+0.0016
2–2	1.8819	1.8822	−0.0003
1–3	1.8634	1.8649	−0.0015
3–4	1.8492	1.8475	+0.0017
3–5	1.8287	1.8301	−0.0014
1–6	1.8130	1.8127	+0.0003
3–7	1.7953	1.7954	−0.0001
3–8	1.7775	1.7780	−0.0005
3–9	1.7610	1.7606	+0.0004
4–10	1.7433	1.7432	+0.0001

The constants of this equation are evaluated by least squares. The results are: $B_0'' = 1.9170$, $\alpha'' = 0.01738$ cm^{-1}. The values of B_v'' calculated from Eq. (4) with these constants are also given in Table III. The residuals are seen to be less than 0.002 in all cases.

The other constants of the normal state of the molecule which follow immediately are:

$I_0 = 1.443 \times 10^{-39}$ g cm^2 $\qquad r_0 = 1.130 \times 10^{-8}$ cm
$I_e = 1.436$ " " $\qquad r_e = 1.127$ " " .

Table IV gives the values of B_v' determined from the present data, compared with their values calculated in the same way from the Angstrom band data. The agreement proves the

TABLE IV. Rotational constants of upper state.

Band	B_v(obs.)	B_v from Angstrom bands
1–1	1.5724	
1–3	1.5706	1.5716
1–6	1.5720	
2–2	1.5502	1.5519
3–4	1.5300	
3–5	1.5280	
3–7	1.5282	1.5297
3–8	1.5276	
3–9	1.5284	
4–1	1.5043	
4–10	1.5047	
7–1	1.4344	

consistency of the analysis and the quantum-number assignments.

COMPARISON WITH OTHER DATA

Asundi[10] has analyzed some of the fourth positive bands of high vibrational quantum number which could be photographed with a 21-ft. grating in air. He obtained $B_{18}''=1.60$, $\alpha''=0.023$. Eq. (4) gives by extrapolation $B_{18}''=1.604$, in good agreement with Asundi's value. His value of α'', however, is somewhat too high.

Snow and Rideal[11] have observed the $1\leftarrow0$, $2\leftarrow0$, and $3\leftarrow0$ vibration-rotation bands of CO in the infrared absorption spectrum. The $1\leftarrow0$ band was well resolved, and they obtained from the separation of the lines $B_0=1.84$. This is in considerable disagreement with the value obtained in the present work, 1.917. Their methods and results have been studied carefully in the hope of finding some explanation of the discrepancy, but none has been found.

ULTRAVIOLET BANDS OF HOPFIELD AND BIRGE

In view of this disagreement between the infrared results and the present ones, it is interesting to have independent evidence from other electronic bands. There appear on the plate six of the ultraviolet CO bands reported by Hopfield and Birge.[5] They are:

Transition		λ	ν
B—X	0–0	1150.52	86917.3
"	0–1	1179.59	84775.2
"	0–2	1209.80	82658.3
C—X	0–0	1087.86	91923.6
"	0–1	1113.89	89775.9
E—X	0–0	1077.10	92841.9

All these bands appear similar in structure, consisting of P and R branches lying entirely on opposite sides of the origins. The line structure is very fine, and practically unresolved in most cases.

The B–X system connects the upper state of the Angstrom system with the lower state of the fourth positive. The present value of the rotational constants for the normal (X) state can therefore be used, together with the constants of the B state found from the Angstrom band analysis, to predict the structure of the

bands of the B–X system. This prediction has been made for the $0-0$ band ($B_0'=1.943$, $B_0''=1.917$), and compared with measurements of the R branch of this band, which is completely resolved on the plate in both the first and second orders. The prediction is accurate for the first 25 lines. Beyond this point there is a slight divergence due to higher power terms in the rotation functions. If the infrared value $B_0''=1.84$ were used instead of the present value, $B'-B''$ would be about four times as large, and an entirely different type of band would be expected.

A striking feature of this band is the sudden decrease in intensity of the lines of the R branch after $R(36)$. The behavior of the P branch is not observed, since it is obscured by atomic lines. This is the same effect as has recently been reported by Coster and Brons,[12] who observed it in the 0-1 Angstrom band. They interpret it as predissociation of the B state. The decrease in intensity in the present case is greater than they observed, amounting almost to complete termination of the structure, but otherwise the observations are identical.

BAND HEAD MEASUREMENTS AND VIBRATIONAL CONSTANTS

New measurements have been made of the fourth positive band heads below 2270A. They are given in Table V. The intensity figures are taken from the paper of Headrick and Fox,[2] and represent densitometer measurements.

In order to represent these band heads together with those of longer wave-length measured by Estey,[3] it has been found necessary to use a slightly more complicated equation than is usually given. The equation is:

$$\nu_h(v', v'') = 64{,}756.3 + (1497.49v' - 17.1841v'^2)$$
$$- (2155.61v'' - 13.2843v''^2 + 0.012v''^3)$$
$$- 0.0804v'v''. \quad (5)$$

The $O-C$ column of Table V is determined from this equation. Most of Estey's measurements show residuals of the same order of magnitude. A few of them, however, are not well represented either by his own equation or the present one.

[10] Asundi, Proc. Roy. Soc. A124, 277 (1929).
[11] Snow and Rideal, Proc. Roy. Soc. A125, 462 (1929).

[12] Coster and Brons, Nature 133, 140 (1934); Physica 1, 155 (1934).

TABLE V. *Band heads.*

λ	ν cm⁻¹	Int.	v′−v″	O−C	λ	ν cm⁻¹	Int.	v′−v″	O−C
2262.42	44200.4	0.1	5–14	−0.4	1712.19	58404.7	3.9	0–3	−4.0
2238.98	44663.3	0.1	4–13	+0.4	1705.16	58645.7	3.1	3–5	+0.2
2150.87	46492.8	0.3	4–12	+0.5	1704.30	58675.2	1.5	6–7	−1.5
2128.97	46971.1	0.3	3–11	0.0	1669.68	59891.8	3.9	1–3	+3.0
2107.88	47441.0	0.3	2–10	−0.3	1653.02	60495.5	6.0	0–2	−2.6
2090.58	47833.7	0.5	5–12	−0.5	1647.90	60683.4	4.0	3–4	+0.9
2068.35	48347.8	0.7	4–11	+0.3	1630.40	61334.6	6.9	2–3	+0.1
2047.00	48852.1	0.5	3–10	+0.1	1629.61	61364.4	2.0	5–5	−0.3
2035.00	49140.0	0.7	6–12	−1.7	1611.26	62063.3	3.1	4–4	+3.9
2026.44	49347.5	1.4	2–9	−0.4	1597.14	62611.8	6.9	0–1	−2.2
2012.52	49688.9	0.7	5–11	−0.6	1595.60	62672.4	1.6	6–5	−0.4
2006.56	49836.7	0.4	1–8	+1.5	1576.67	63425.0	7.1	2–2	+0.9
1990.89	50228.8	1.6	4–10	+0.4	(1560.14)	(64096.9)*	6.0	1–1	+2.7
1970.08	50759.3	2.8	3–9	+0.6	1559.47	64124.4	5.0	4–3	+1.7
1950.07	51280.2	2.6	2–8	−0.2	1542.34	64836.4	6.9	3–2	+1.0
1939.12	51569.9	0.5	5–10	−0.6	1527.52	65465.5	4.0	5–3	+0.1
1930.70	51794.8	3.0	1–7	+1.2	1525.75	65541.6	5.3	2–1	+1.6
1918.08	52135.4	1.4	4–9	+0.2	1509.66	66240.0	5.0	1–0	+3.4
1897.83	52691.6	4.0	3–8	+0.2	1493.60	66952.3	6.0	3–1	+0.7
1878.33	53238.9	6.1	2–7	−0.1	1477.48	67682.9	3.0	2–0	+0.4
1859.41	53780.4	4.8	1–6	+2.3	(1463.47)	(68330.8)*	6.0	4–1	+2.1
1841.47	54304.6	1.3	0–5	−4.3	1452.17	68862.5	4.9	6–2	−0.9
1829.81	54650.6	4.0	3–7	+0.6	1447.27	69095.4	1.0	3–0	+1.3
1825.38	54783.1	0.8	6–9	−2.0	1435.28	69672.9	6.4	5–1	+1.5
1810.82	55223.8	7.6	2–6	+0.3	1425.78	70137.2 ·	4.7	7–2	−0.2
1804.74	55409.8	1.9	5–8	−0.3	1418.91	70476.6	1.0	4–0	+5.3
1792.38	55791.7	7.5	1–5	+2.9	1408.86	70979.6	4.8	6–1	−0.2
1774.90	56341.3	3.4	0–4	−4.3	1401.02	71376.5	2.5	8–2	−0.5
1747.20	57234.4	3.8	2–5	+0.1	1391.97	71813.8	0.5	5–0	−0.4
1743.12	57368.4	0.7	5–7	−0.5	1384.00	72254.2	2.7	7–1	+0.4
1729.25	57828.7	6.1	1–4	+3.0	1377.75	72582.3	1.5	9–2	+0.1
1723.79	58011.9	2.2	4–6	+0.5	1355.84	73755.0	0.4	10–2	+2.0

* Band heads obscured on the plate. Position calculated from the rotational analysis.

In Eq. (5), the coefficient of v''^2 is appreciably larger than the value 12.7 which is usually given. This is due in part to the use of a cubic term, though even if this term is neglected a value of about 13.10 seems necessary to represent the data.

By use of the B's and α's found in the rotational analysis, an equation may be found for the band origins.[13] It is:

$$\nu_0(v', v'') = 64{,}746.5 + (1498.36v' - 17.2505v'^2) - (2156.05v'' - 13.2600v''^2 + 0.012v''^3). \quad (6)$$

[13] Jevons, *Report on Band Spectra of Diatomic Molecules,* p. 54, *et seq.*

The fundamental vibration constants of the normal state may be found by writing this equation as a function of $(v+\frac{1}{2})$. They are:

$$\omega_e = 2169.32 \qquad \omega_e x_e = 13.2780 \qquad \omega_e y_e = 0.012.$$

For the A state, $T_e = 65{,}075.2$ cm⁻¹. It is believed that these values, as well as those derived from the rotational data, are somewhat more accurate than those previously obtained for the normal state of the CO molecule.

In conclusion, the author wishes to express his appreciation to Professor H. D. Smyth for suggesting and supervising this work.