DECEMBER, 1926 PHYSICAL REVIEW VOLUME 28

THE BAND SPECTRA OF CARBON MONOXIDE

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Abstract

All of the numerous band spectra formerly attributed to carbon are due probably to carbon compounds. A majority of those analyzed are now definitely known to be due to carbon monoxide, as a result of the intercorrelation of the various systems and the correlation of one of these systems, the fourth positive group of carbon, with the known absorption spectrum of CO.

The known band spectra of neutral carbon monoxide comprise the fourth positive group of carbon, the Ångström CO bands, the Cameron bands, and the third positive group of carbon,—this latter group having been shown by Duffendack and Fox to comprise in reality two different systems. The relation of these various systems is indicated in Fig. 1 and Table I. The band systems of ionized carbon monoxide,—i.e., the comet-tail bands, the first negative group of carbon, and the Baldet-Johnson combination bands,—are also shown in this figure.

The fourth positive group of carbon, as analyzed by the writer, comprises the former group of that name, and also Lyman's fifth positive group, and practically all the remaining unassigned bands found by Lyman in the ultraviolet spectrum of carbon monoxide. Full details of this analysis are given, and the results are tabulated in Table II and in Fig. 2. The bands found by Leifson in the absorption spectrum of cold carbon monoxide form a selected portion of this system, proving that it is the "resonance" system of CO. The system is also quantitatively related to the known infra-red absorption bands of CO in the manner demanded by the quantum theory. The general intensity distribution is in agreement with Franck's mechanical theory, as extended by Condon. The vibrational data obtained from this system have been used by Birge and Sponer to calculate the heat of dissociation of CO.

The Ångström CO bands have as a final state the initial state of the fourth group, and this relation permits a definite assignment of vibrational quantum numbers for the Ångström bands. Recent work by Jassé on the fine structure of these bands is in agreement with this assignment. All of the measurements on the heads of the Ångström bands are collected in Table III and are compared with the calculated values. A puzzling discrepancy in one of the vibrational energy intervals is noted and discussed.

The Cameron bands and the third positive group of carbon have been found by Johnson to have the same relation as the above two systems, and the Cameron bands form a second "resonance" system for CO. They have recently been found in absorption, by Hopfield. The common electronic level of these two systems is probably triple, although the bands of each system have either five-fold or six-fold heads. The various relations are discussed in detail, and equations are given in all cases.

Recent work indicates that the electronic energy levels of molecules are similar to those found in atoms, and an assumed octet structure for CO suggests its correlation with Mg. The actual details of this correlation are given, but no attempt is made to discuss critically the underlying theory. The levels for CO are shown to be either single or triple, and the only two levels belonging to the same term sequence are found to fit a Rydberg formula with the known correct limit.

INTRODUCTION

ON PAGES 226–234 of Vol. V of Kayser's "Handbuch der Spectroscopie," and on pages 131–147 of Vol. VII, part 1, there are listed the various band spectra assumed due to carbon or its compounds. It would appear at the present time that none of these spectra are due to the molecule of carbon, and it is doubtful if such a molecule (diatomic) exists. The violet and red cyanogen bands are almost certainly due to the molecule CN,[1] and the so-called C+H bands to the molecule CH.[2] The Swan bands are probably due to C_2H_2, but this is still very uncertain.[3] The group of Deslandres and d'Azambuja,[4] and the second negative group of Deslandres and d'Azambuja[4] are so incompletely known that it is not possible as yet to give even an empirical analysis. The high pressure CO bands of Fowler[5] and the triplet bands of Merton and Johnson[6] can be analyzed and reasonably certain quantum assignments made.[7] The chemical origin of these four systems is however not known with certainty. All of the remaining band systems listed under *carbon* in the Handbuch, as well as others discovered quite recently, are definitely known to be due to CO or CO^+, and form the subject of this paper.

Until very recently it was impossible to give the exact chemical origin of practically any band system, even of those most exhaustively investigated. The long controversy concerning the Swan bands[3,8] is a case in point. The striking advance made within the past year or two rests mainly upon the discovery of two related facts, (1) the identity of numerical constants in certain different band systems, proving that all the systems thus related must be due to the same chemical molecule, (2) the discovery of at least *one* of these related systems in absorption in the cold (or fairly cool) vapor of some known molecule. A further criterion, which in many cases is sufficient for the identification, is the evaluation of the moment of inertia of the molecule. This last is the deciding factor in assigning the C+H bands to CH, and the Swan bands to some sym-

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[1] Birge, Phys. Rev. **23**, 294 (1924); Mulliken, Nature **114**, 858 (1924); Freundlich and Hochheim, Zeits. f. Physik **26**, 102 (1924); Holst and Oosterhuis, K. Akad. Amster. Proc. **23**, 727 (1921); and Kayser VII, pp. 131–135.

[2] Kratzer, Zeits. f. Physik. **23**, 298 (1924), and Chap. IV, Sections 7 and 8, Report of the National Research Council on "Molecular Spectra in Gases" (in press). This last reference will be referred to as "Report."

[3] Shea and Birge, Phys. Rev. **27**, 245 (1926), and Johnson, Nature **116**, 539, Oct. 10 (1925).

[4] Deslandres and d'Azambuja, Compt. rendus **140**, 917 (1905).

[5] A. Fowler, M. N. Roy. Ast. Soc. **70**, 484 (1910).

[6] Merton and Johnson, Proc. Roy. Soc. **103A**, 383 (1923).

[7] Birge, Nature **116**, 170, Aug. 1 (1925).

[8] Watts, Phil. Mag. (6) **28**, 117 (1914), and Kayser VII, pp. 139–141.

metrical molecule of approximately the mass of acetylene. In certain cases the measured isotopic effect has made it possible to discriminate between two molecules as possible emitters of the bands. Still further methods of identification have been used, but they are less direct than those just mentioned.

In the present paper we are concerned primarily with the relations between the various bands forming a system, evaluating the vibrational energy levels of the system, and between the various systems, evaluating the electronic energy levels of the molecule. A rather detailed account of the quantum theory of band spectra is given in the Report of the National Research Council on "Molecular Spectra in Gases" (in press), and no attempt at repetition will be made here.

THE SPECTRA OF NEUTRAL CARBON MONOXIDE

The first step in the establishment of the system of energy levels of CO was made by the writer,[9] as a result of the quantum analysis of the extensive set of bands in the ultra-violet, usually attributed to CO.[10] A small portion of this system had been called by Deslandres[11] the "fourth positive group of carbon," and a small part of the remaining bands had been called by Lyman[12] the "fifth positive group of carbon." On completion of the analysis, the writer found that the $n''=0$ progression of this new system appeared on Leifson's[13] absorption spectrum of CO. This definitely established the lower (n'') level as the normal level of the CO molecule. At the same time it was found that the upper (n') level of the new system was also the lower level of the Ångström CO bands, thereby proving that these latter bands were due to neutral CO, as commonly assumed, and also evaluating three electronic energy levels of CO. This work has been briefly reported,[9] and the theoretical interpretation of the results has been given in another short article.[14]

Later, R. C. Johnson[15] found it possible to obtain a similar correlation of the third positive group of carbon with the newly discovered Cameron bands.[16] By using the writer's results for the fourth positive group, Johnson was able to show that the Cameron bands had the same final level. Hence these two additional systems are due to CO, and the band

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[9] Birge, Nature **117**, 229, Feb. 13 (1926).

[10] Lyman, Spectroscopy of the Extreme Ultra-violet, pp. 84 and 114.

[11] Deslandres, Compt. rendus. **106**, 842 (1888), and Ann. chim. et phys. (6) **15**, 5 (1888). The second reference contains a drawing of the system.

[12] Lyman, Proc. Amer. Acad. Arts **45**, 315 (1909).

[13] Leifson, Astrophys. J. **63**, 73 (1926).

[14] Birge, Nature **117**, 300, Feb. 27 (1926).

[15] Johnson, Nature **117**, 376, Mar. 13 (1926).

[16] Cameron, Phil. Mag. **1**, 405 (1926).

spectra evaluate two more electronic levels. The theoretical interpretation of the new levels was made immediately by Dr. R. S. Mulliken and by the writer, and is given by Johnson.[17] Recently Duffendack and Fox[18] have found that the third positive group is really the superposition of two systems, and the new system, called the 3A bands, has the same

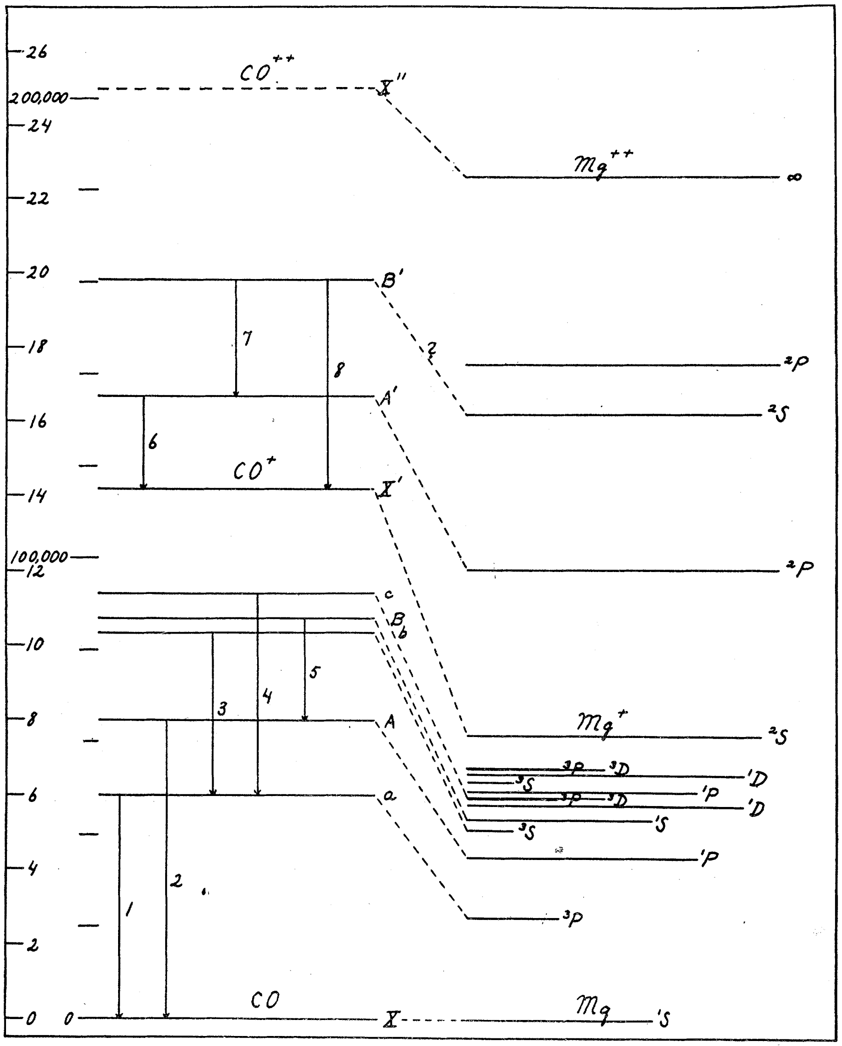

Fig. 1. Electronic energy levels for CO, CO^+, Mg and Mg^+. 1, Cameron CO bands; 2, fourth positive group of carbon; 3, third positive group of carbon; 4, 3A bands of third positive group; 5, Ångström bands of CO; 6, comet-tail bands; 7, combination bands of Baldet-Johnson; 8, first negative group of carbon.

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[17] Johnson, Nature **118,** 50, July 10 (1926).

[18] Duffendack and Fox, Nature **118,** 12, July 3 (1926).

final (lower) level as the other, but a different initial level. This initial level thus constitutes a new, sixth, electronic energy level for CO. All of these relations are shown on Fig. 1, which gives also the electronic levels for CO^+.[19] The scale on the left gives both wave numbers (cm^{-1}) and volts, the former running from zero to 200,000, the latter from zero to 26. (One volt $= 8100$ cm^{-1} approx.) The exact values for the various levels are given in columns 3 and 4 of Table I, and these are discussed in detail later. The separation of any two levels is given by the frequency of the origin of the 0–0 band of the system due to the transition between these two levels. In some cases the fine structure of the bands is not yet known, and the frequency of the head of the 0–0 band is used in the diagram.

Table I

Energy levels of carbon monoxide

1	2	3 cm^{-1}	4 volts	5 term	6 D	7 ω^n
X	^1S	0	0	114,966	0.9767	2149.7
a	^3P	48,426.3 to 48,529.9	5.981 to 5.994	66,540 to 66,436	1.2839 to 1.2849	1724.8
A	^1P	64,737	7.995	50,229	1.4777	1497.3
b	^3S	83,817	10.352	31,149	1.8765	(2214)
B	^1S	86,894	10.732	28,072	1.9766	2158
c	?	92,086	11.374	22,880	2.1894	
X'	^2S	114,966	14.200			2197.0
A'	^2P	135,312 135,438	16.713 16.728			1550.5
B'	^2S	160,604	19.837			1697.8

The Spectra of Ionized Carbon Monoxide

Three systems of bands are almost certainly due to CO^+,—the first negative group of carbon, the comet-tail bands, and the Baldet-Johnson "combination" bands. The writer[7] showed definitely that the first two systems had the same final state, and therefore were due to the same molecule, thus confirming the experimental evidence.[20] Blackburn[21] independently reached the same conclusion. Then Mulliken,[22] Mecke,[23] and the writer[24] independently noted that the new bands measured by

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[19] A more complete diagram, showing also the vibrational levels, has been published by Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[20] Lemon, Proc. Nat. Acad. Sci. **11**, 41 (1925).

[21] Blackburn, Phys. Rev. **25**, 888 (1925).

[22] Mulliken, Phys. Rev. **26**, 561 (1925).

[23] Mecke, Naturwiss. **13**, 698 (1925).

[24] Birge, Nature **116**, 207, Aug. 8 (1925).

Johnson[25] (a few of which had previously been observed by Baldet[26]) formed a new system having for its initial state the initial state of the first negative group of carbon, and for its final state, the initial state of the comet-tail bands. The importance of such a relation was emphasized by the writer,[24] and it is to be hoped that fine structure measurements of these new bands will soon be available.

The conclusion that all three systems are due to CO^+ is based on the fact that all experimental evidence points to the comet-tail bands as being due to some form of CO,[27] while the first negative group of carbon is, as the name indicates,[28] presumably due to a positive ion. Additional relations found by Birge and Sponer,[19] between the molecular constants of CO and CO^+, assuming the above conclusions, form confirmatory evidence.

We now proceed to a more detailed discussion of the various systems of neutral carbon monoxide, considering in particular the new ultra-violet system which includes the old fourth positive group of carbon, and may conveniently be given that designation. Details regarding the spectra of ionized CO will be given in a separate paper.

THE FOURTH POSITIVE GROUP OF CARBON

(*a*) EXPERIMENTAL

The fourth positive group of carbon, as measured by Deslandres,[11] consisted of 42 bands, extending from λ2631 to λ2045. The bands are degraded to the red, not to the violet as stated on page 233 of Kayser, Vol. V. Deslandres gives also the relative intensity of the various bands, and Hof[29] later used Deslandres' measurements, but gave another list of intensities for 28 of these bands. Bair,[30] in 1920, measured 22 bands lying between λ2262 and λ1946, but again with small dispersion (probable error several tenths of an Angstrom). Meanwhile Lyman[12] had found, in agreement with Schumann's earlier work, that nearly all vacuum tubes showed a set of bands in the extreme ultra-violet, due evidently to an impurity. The evidence indicated that this was carbon monoxide.

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[25] Johnson, Proc. Roy. Soc. **108A,** 343 (1925).

[26] Baldet, Compt. rendus. **178,** 1525 (1924). See also Baldet, Nature **116,** 360, Sept. 5 (1925) and Johnson, Nature **116,** 539, Oct. 10 (1925) as to experimental priority.

[27] See references (5), (6), (26) and (20).

[28] A negative group is one predominantly strong near the negative electrode of the discharge. See Blackburn, Proc. Nat. Acad. Sci. **11,** 28 (1925) for the quantum analysis of this system.

[29] Hof, "Untersuchung über die Spektren von Kohlenoxyd und Kohlensäure," Dissertation, Basel (1914).

[30] Bair, Astrophys. J. **52,** 301 (1920).

He measured the wave-lengths of 100 bands, stretching from λ2068 to λ1335.[31] The bands are gradually fading out at this latter point, probably due to general absorption of some kind, and it seems apparent at the present time that the system runs further toward the short wave-lengths.

It is evident that the first two bands measured by Lyman (λλ2068.4 and 2047.0) are identical with the last two measured by Deslandres (λλ2066.8 and 2045.6) and that therefore all of the bands observed by Deslandres and by Lyman may be closely related. Very recently Duncan[32] has measured 14 of the strongest bands between λ2338 and λ2040. Duncan, however, as the writer[9] has pointed out, did not recognize these bands as a portion of the fourth positive group of carbon, and called them a seventh positive group of nitrogen.

A comparison of all available data seems to indicate that it is necessary to raise Deslandres' wave-lengths (in air) by 1.0A, in order to bring them into agreement with those of Bair and Duncan. These wave-lengths, reduced to vacuum then agree fairly well with those of Lyman (in vacuum) in the overlapping portion. The set of wave-lengths adopted in the present work and listed in Table II then consists essentially of Lyman's measurements for the wave-lengths *in vacuum* in the region λ2068 to λ1335, and of Deslandres' measurements, raised by 1.0A, for the wave-lengths *in air* in the region λ2632 to λ2090. In the reduction to vacuum, Kayser's "Tabelle der Schwingungszahlen" has been used. With the present experimental errors, the distinction between the Rowland and the I. A. system may be ignored.

The intensities, as given in column 3, are due to Lyman and to Deslandres, respectively. Because of the great extent of the system, these are not even qualitatively comparable, except for closely adjacent bands. Lyman marks a few strong bands as double, indicated by "*d*" in the intensity column and in Fig. 2. All the bands of this system are presumably double headed, due to a Q branch, as in the case of the Ångström CO bands. These two systems, according to the present theoretical interpretation to be discussed later, should have a similar fine structure.

Bair gives bands at λ2188 and λ2107.7, not listed by Deslandres. Duncan gives one of these (at λ2107.1), and also a band at λ2209.0 not listed by any other investigator. Of these three bands, only λ2107.1 finds a place in the system, as analyzed below. Other bands (or lines) not apparently belonging in the system are mentioned later.

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[31] A photograph of the portion of this system between λ1335 and λ1880 is published by Lyman in Astrophys. J. **23,** 181 (1906) (1, Plate XI), and in Memoirs Amer. Acad. Arts **13,** 125 (1906) (Plate VII).

[32] Duncan, Astrophys. J. **62,** 155 (1925).

(*b*) QUANTUM ANALYSIS

Deslandres has arranged the bands of nearly all his systems in sets called progressions. The quantum theory of band spectra has shown that these progressions consist of bands with a common lower (final) vibra-

TABLE II

Fourth positive group of carbon

1 λ	2 ν_{vac} (cm^{-1})	3 I	4 $n'-n''$	5 $O-C$ (cm^{-1})	1 λ	2 ν_{vac} (cm^{-1})	3 I	4 $n'-n''$	5 $O-C$ (cm^{-1})
2632.55	37,974.5	4	11–22	−1	2068.4	48,346.5	8	4–11	+7
2600.0	38,450.0	6	10–21	−3	2047.0	48,852.0	8	3–10	+5
2569.2	38,911.0	4	9–20	+9	2035.1	49,137.6	4	6–12	+6
			5–17?	−7	2031.7	49,219.9	1	9–14?	+11
2557.8	39,084.4	2	12–22	+8	2026.4	49,348.6	7	2–9	+5
2539.7	39,362.9	4	8–19	+10	2012.6	49,687.0	8	5–11	+5
2525.1	39,590.5	4	11–21	+12	2007.2	49,820.6	5	1–8	−11
2511.8	39,800.1	6	7–18	+6	1991.0	50,226.0	1	4–10	+3
2493.7	40,089.0	4	10–20	+17	1970.1	50,758.8	8	3–9	+4
2485.2	40,226.1	4	6–17	−2	1953.0	51,203.3	5		
2464.3	40,583.7	4	9–19	+28	1951.7	51.237.4	5		
2459.8	40,641.4	2	5–16	−7	1950.4	51,271.5	4	2–8	−6
2436.0	41,038.4	8	8–18	+6	1933.6	51,717.0	2	5–10?	−48
			4–15?	−24	1931.5	51,773.2	6	1–7	−18
2426.0	41,207.6	6	11–20	±0	1918.2	52,132.2	7	4–9	±0
2408.4	41,508.7	8	7–17	+10	1914.0	52,246.6	1	0–6?	−49
2395.0	41,740.9	6	10–19	+15				7–11?	−16
2382.5	41,959.9	8	6–16	+4	1898.0	52,687.0	10	3–8	−2
2365.8	42,256.1	6	9–18	+12	1891.2	52,876.5	6	6–10	+3
2357.3	42,408.4	4	5–15	+4	1878.5	52,234.0	10d	2–7	−3
2338.7	42,745.7	6	8–17	+9	1870.3	53,467.4	3	5–9	−7
2333.5	42,840.9	2	4–14	−1	1859.6	53,775.0	10d	1–6	−1
			11–19	−20	1849.4	54,071.6	4	4–8	+7
2312.4	43,231.8	8	7–16	+3	1846.7	54,150.6	2	7–10	+5
2310.7	43.263.6	4	3–13	−10	1841.3	54,309.5	8	0–5	+3
2302.7	43,413.9	2	10–18	+8	1837.2	54.430.7	1		
2287.2	43,708.1	8	6–15	−4	1830.1	54,641.8	9	3–7	−6
			2–12?	+13	1825.7	54,773.5	7	6–9	−8
2274.5	43,952.1	4	9–17	+10	1811.0	55,218.1	10d	2–6	−4
			12–19?	−14	1804.9	55,404.7	8	5–8	−2
2262.6	44,183.2	4	5–14	−3	1801.9	55,497.0	2		
2247.7	44,476.1	4	8–16	+8	1792.6	55,784.9	10d	1–5	−1
2238.8	44,652.9	4	4–13	+3	1785.1	56,019.3	6	4–7	−5
2221.7	44,996.5	8	7–15	+11	1774.9	56,341.2	8d	0–4	±0
2216.3	45,106.2	6	3–12	±0	1747.3	57,231.2	7	2–5	−1
			10–17	−5	1743.5	57,355.9	3	5–7	−11
2209.0	45,255.2	1			1729.5	57,820.2	8d	1–4	−1
2196.9	45,504.4	8	6–14	+11	1723.9	58.008.0	6	4–6	−2
2195.0	45,543.8	6	2–11	−8	1712.2	58,404.4	7	0–3	+2
2189.1	45,668.6	2	9–16	−3	1705.3	58,640.7	6	3–5	−1
2188	45,689				1698.8	58,865.1	1		
2173.3	45,998.5	8	5–13	+6	1688.5	59,224.2	1	2–4?	−43
			1–10?	+8	1685.3	59,336.6	1	5–6	−14
2162.6	46,226.1	8	8–15	+3	1669.9	59,883.8	6	1–3	+2
2150.9	46,477.5	8	4–12	−5	1666.7	59,998.8	1	4–5	−20
2137.5	46,768.8	6	7–14	+3	1653.3	60,485.1	4	0–2	−3
2128.8	46,959.9	2	3–11	−4	1648.2	60,672.2	5	3–4	−6
2113.7	47,295.4	8	6–13	−5				6–6?	+13
2107.1	47,443.5	2	2–10	+8	1630.3	61,338.4	6	2–3	+10
			9–15?	+15				5–5	−23
2090.3	47,824.7	8	5–12	±0	1629.6	61,364.7	3		

TABLE II (*continued*)

1 λ	2 ν_{vac} (cm^{-1})	3 I	4 $n'-n''$	5 $O-C$ (cm^{-1})
1623.4	61,599.1	1	10–8?	− 2
1615.1	61,915.7	2	7–6 1–2?	−16 −52
1611.7	62,046.3	3	4–4	− 8
1603.3	62,371.4	1	9–7?	−19
1597.4	62,601.7	3	0–1	+ 2
1596.1	62,652.7	1	6–5 3–3?	−15 −75
1576.5	63,431.6	4	2–2 5–4?	+18 −65
1559.3	64,131.3	5	1–1 4–3	+51 +16
1545.1	64,720.7	3	0–0 6–4	−16 +17
1542.2	64,842.4	5	3–2	+17
1534.2	65,180	2	8–5	− 1
1527.6	65,462	3	5–3	+ 5
1526.0	65,531	2	2–1 10–6?	+ 5 −14
1520.4	65,772	1	12–7	−24
1515.7	65,976	3	7–4	− 1
1510.7	66,194	2	1–0 4–2	−23 − 8
1506.8	66,366	2	9–5	−19
1497.8	66,764	3	6–3	− 1
1493.8	66,943	3	3–1	+ 7
1488.0	67,204	2	8–4	−12
1480.9	67,526	2	5–2	−17
1478.0	67,659	2	2–0	− 4
1475.4	67,778	1	12–6	− 2
1473.0	67,889	1	14–7	− 5
1463.7	68,320	3	4–1	+ 7
1452.4	68,851	3	6–2 13–6	± 0 + 4
1447.0	69,108	1	3–0	+34
1443.7	69,266	1	8–3	−11
1438.7	69,507	1		
1435.6	69,657	2	5–1	+ 2
1426.1	70,121	3	7–2	− 3
1419.0	70,472	2	4–0 9–3	+22 − 9
1414.0	70,721	1	11–4	− 4
1411.4	70,852	1	13–5	− 5
1409.0	70,972	2	6–1	+ 9
1405.5	71,149	1		
1404.0	71,225	1		
1401.1	71,372	2	8–2	+ 9
1395.7	71,649	2	10–3	− 2
1392.2	71,829	1	5–0 12–4	+37 + 3
1386.4	72,129	1		
1384.4	72,233	1	7–1	− 3
1378.1	72,564	2	9–2	− 3
1374.1	72,775	2	11–3	−11
1371.8	72,897	2	13–4	+ 5
1368.0	73,099	1	6–0	− 1
1361.3	73,459	2	8–1	−16
1356.1	73,741	2	10–2	+ 4
1353.6	73,877	1	12–3	−10
1343.0	74,460	1	7–0?	+85
1339.0	74,683	1	9–1	+ 4
1335.0	74,906	1	11–2	+34

tional level, (here designated n' progressions), or of a common upper (initial) level, (here designated n'' progressions). It is further found that Deslandres' n *usually* refers to the lower level, so that his first progressions, [$f(n)$], are usually n'' progressions, while his second progressions [$f(p)$] are usually n' progressions.[33] There are however exceptions, as in the case of the first positive group of nitrogen. If the "origin" of each band, as defined by the quantum theory, is used, the various first or the various second progressions should differ only in the constant term. It is however ordinarily necessary at the present time to use data for the heads, and therefore the various first or second progressions are not quite identical, although the variations may easily be less than the experimental error.

In the case of this fourth group of carbon, Deslandres arranged the bands in five progressions, designated I to V, but the numerical relations, on this interpretation, are quite unusual, as the writer[7] has noted. Later

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[33] The numbering of n' and n'' is quite different from that of n and p, and always runs in the opposite direction.

the thought occurred that in this one case, Deslandres' progressions were probably actually sequences, i.e., sets of bands having a common value of $n''-n'$, and usually much more closely spaced than the bands of a progression. With this new interpretation, it was possible to obtain progressions having the expected relations. Now Lyman[12] had arranged 28 bands out of the 100 measured by him in six series (designated VI to XI) similar to those formed by Deslandres. He called these 28 bands the "fifth positive group of carbon." An extrapolation of the new progressions, as arranged by the writer, led directly to the bands of this fifth group, and showed that Lyman's progressions also were actually sequences. Further extrapolation resulted in the identification of practically all the remaining bands as parts of one great system which it seems best to designate as the fourth positive group of carbon. The true quantum designations ($n'-n''$), giving the upper and lower vibrational quantum numbers respectively, appear in column 4 of Table II. As can be seen, only a dozen bands remain unassigned. These latter include the two *strong* bands λλ1953.0 and 1951.7. These two bands I have however found on one of Professor Hopfield's spectrograms, and are, I believe, really a double *line*, of unknown origin. All of the remaining unassigned bands are extremely weak, with the exception of λ1801.9 (2), and λ1629.6 (3), and all *may* be lines.

On the other hand, many of the measured heads seem to represent the blending of two or more bands. Such matters can best be discussed by considering the general intensity distribution of the system, as shown in Fig. 2. In this $n'n''$ diagram merely the intensities are listed. When a band is believed to be the superposition of two, it is starred. The details may be obtained from Table II. The broken line in Fig. 2 marks the division of Deslandres' and Lyman's data. The distribution of intensity shown in this figure is now known to be typical of a fairly large change in the moment of inertia accompanying the emission of the bands.[34] Condon,[35] in his extension of Franck's[36] mechanical explanation of the intensity distribution, has obtained a satisfactory quantitative agreement for this particular system. The expected symmetry of the distribution indicates however that the true relative intensity of the bands near the short wave-length limit is greater than shown, and that the system runs still further to the shorter wave-lengths.

Because of the relatively large general experimental errors, and the many blended bands, it is difficult to obtain a trustworthy formula for

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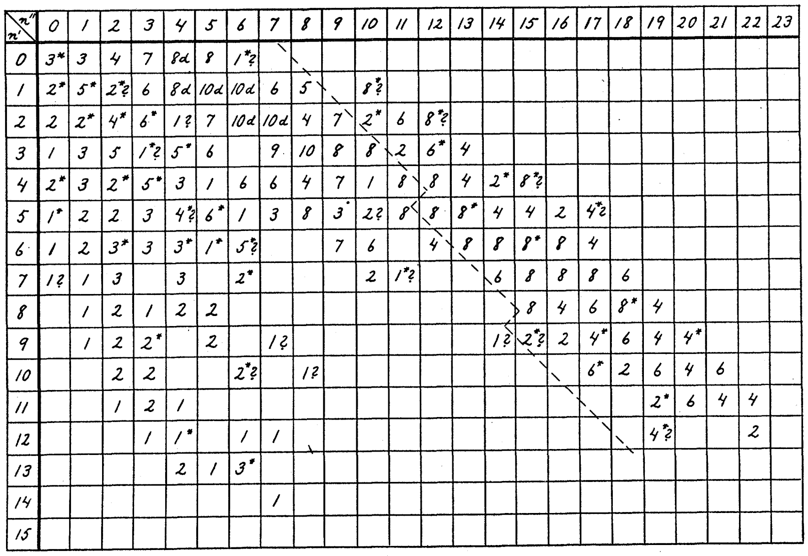
[34] See "Report," Chap. IV, Section 4, for detailed discussion.

[35] Condon, Phys. Rev. **27**, 640 (A) (1926). Detailed article in Phys. Rev. **28**, (1926).

[36] Franck, Trans. Faraday Soc. **21**, Part 3 (1925).

this band system. That previously published by the writer[9] was based upon an analysis of the frequency *differences* of the successive bands in the progressions, since there was no certainty that the absolute wavelengths of the various investigators were consistent. A more searching examination of this question, made recently, indicates that all of the wave-lengths listed in Table II are consistent within the limits of experimental error, and that it is possible to obtain a simple formula giving no noticeable trend in the residuals. This formula, which differs slightly from that previously published, is[37]



n' \ n''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
0	3*	3	4	7	8d	8	1*?																	
1	2*	5*	2*?	6	8d	10d	10d	6	5		8*?													
2	2	2*	4*	6*	1?	7	10d	10d	4	7	2*	6	8*?											
3	1	3	5	1*?	5*	6		9	10	8	8	2	6*	4										
4	2*	3	2*	5*	3	1	6	6	4	7	1	8	8	4	2*	8*?								
5	1*	2	2	3	4*?	6*	1	3	8	3	2?	8	8	8*	4	4	2	4*?						
6	1	2	3*	3	3*	1*	5*?			7	6		4	8	8	8*	8	4						
7	1?	1	3		3		2*				2	1*?			6	8	8	8	6					
8		1	2	1	2	2										8	4	6	8*	4				
9		1	2	2*		2		1?							1?	2*?	2	4*	6	4	4*			
10			2	2			2*?		1?									6*	2	6	4	6		
11			1	2	1															2*	6	4	4	
12				1	1*		1	1												4*?			2	
13					2	1	3*																	
14								1																
15																								

Fig. 2. Distribution of intensity in the fourth positive group of carbon. Starred numbers refer to blended bands, as given in Table II.

$$\nu = 64,737 + (1497.28n' - 17.24n'^2) - (2149.74n'' - 12.703n''^2) \qquad (1)$$

The residuals for every band of the system, calculated according to this revised formula, are listed in column 5 of Table II. Some of these are rather large, but in a majority of such cases the error is obviously due to the difficulties of measurement caused by overlapping bands. In a few cases there seems to be an actual error of setting. The writer hopes to obtain in the near future better data for this system, and to examine all apparent discrepancies.

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[37] The old formula is $64,721 + (1499.28n' - 17.24n'^2) - (2147.74n'' - 12.703n''^2)$. The changes were made of exactly two units merely for convenience. The probable error in the constants 2149.74 and 1497.28 is several tenths of a unit.

An important point in connection with Eq. (1) is the fact that the vibrational energy of both the initial and the final state can be represented by a second degree equation, (i.e., that the $\omega^n : n$ curve giving the frequency of vibration as a function of n is strictly linear). Considering the large range of values of n as shown in Fig. 2, this is a surprising result. More accurate data may show that the $\omega^n : n$ curves deviate slightly from linearity, but the deviation, if it exists, must be very small. It can scarcely change the value of the heat of dissociation D, as calculated by Birge and Sponer,[19] by an appreciable amount. The new value of D given by Eq. (1) is only 0.02 volts greater than the older value.

The most important result of the quantum analysis of this band system was the discovery that the n' progression for $n''=0$ was identical with the bands found by Leifson[13] in the absorption spectrum of cold carbon monoxide. Leifson's measured values average 1.3 ± 0.2A higher than the theoretical values given by Eq. (1). But Leifson's setting is on the center of the narrow, fairly symmetrical double band characteristic of low temperature (like the infra-red bands) while the equation applies to the violet edge (head) of the high temperature band. The discrepancy is therefore in the correct direction and apparently of the expected amount. Leifson's measured absorption bands begin at $0-0$ and run to $11-0$, being limited only by the transparency of his fluorite window, while Lyman's emission bands run only to $7-0$. Leifson's last band at $\lambda 1264.6$ is therefore an extension of the system to the shorter wave-lengths. His bands should occupy the first column of Fig. 2, but are not shown.

This correlation of Leifson's data with that of Lyman proves beyond question that the general quantum arrangement shown in Fig. 2 is correct, and also proves that these bands are due to neutral carbon monoxide and that the lower electronic state of this system is the normal state of the molecule. The basis for the complete set of energy levels of CO was thus established, as discussed by the writer,[9] and reviewed in the introduction of the present paper.

If the present interpretation is correct, the lower vibrational levels of the fourth positive group are merely those levels which are concerned with the vibration-rotation bands of the near infra-red. Three such bands are known ($1-0$, $2-0$, and $3-0$) at 4.67μ, 2.35μ, and 1.573μ, as measured by Schaefer and Thomas.[38] Using Eq. (1), we *calculate* for these bands the values 4.679μ, 2.354μ, and 1.578μ. This is the first molecule for which the available data make possible a correlation of electronic bands in the visible and ultra-violet with vibration-rotation

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[38] Schaefer and Thomas, Zeits. f. Physik. **12**, 330 (1923).

bands in the near infra-red. The above *quantitative* agreement is a real confirmation of the general quantum interpretation of band structure.

THE ÅNGSTRÖM CO BANDS

A further result of the above analysis of the fourth positive group was the discovery that the Ångström CO bands could be so interpreted as to have as a lower level, the upper level of this system. There can scarcely be any doubt as to the validity of this conclusion, but because of one puzzling irregularity a rather detailed discussion seems advisable.

The older data for the Ångström CO bands are listed on pp. 227–8 of Kayser, Vol. V. These bands, degraded to the violet, were originally measured by Ångström and Thalén,[39] who recorded 29 band heads between λ6854 and λ4123. Seven of them were labelled as an "*a*" series, and except for the last one (λ4209), these bands are now interpreted as constituting the n'' progression for $n'=0$. Seven other bands were labelled "*b*" bands, and these constitute the n'' progression for $n'=1$. It is very doubtful if any of the remaining heads are anything more than accidental clusters of lines. This is evident from the photograph given in Konen "Atlas der Emissionsspektren," No. 269 and 279[40] where only

TABLE III

Ångström bands of CO

1	2	3	4	5	6	7	8	9
$n'-n''$	ν_{calc}	Loos	Hulthén	M. S. P.	Jassé	Watts	A. & T.	*I*.
0–0	22,156.6	+5.8			+6.2	+6.2	+8.7	4
0–1	20,676.6	−1.0	−1.3			−0.7	+1.0	4
0–2	19,231.0	+1.2	+1.2			+1.2	+0.7	5
0–3	17,819.9	+0.3	±0.0	+3.6		+0.2	+4.3	5
0–4	16,443.3			−1.9		+2.8	+1.4	4
0–5	15,101.2			−0.3			−7.2	3
0–6	13,793.6			+3.3				
1–0	24,237.6	+8.2			+6.4	+8.6	−44.8	3
1–1	22,757.6	−0.5	−1.1			−0.5	−12.4	3
1–2	21,312.0						−33.7	2
1–3	19,900.9						+28.6	2
1–4	18,524.3						−6.8	3
1–5	17,182.2						+0.2	3
1–6	15,874.6						−5.2	2
2–0	26,164.6							
2–1	24,684.6							
2–2	23,239.0						+3.3	1
2–3	21,827.9						−6.1	1
2–4	20,451.3							
2–5	19,109.2							
2–6	17,801.6							

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[39] Ångström and Thalén, Nova acta Reg. Soc. sc. Upsal. (**3**), 9 (1875).

[40] The scale on 279 should be shifted 100A to the right.

the *a* and *b* bands appear, and from the fact that no subsequent investigator has measured any but these *a* and *b* bands. However, in Table III, the possible bands 2–2 and 2–3 of the $n'=2$ progression are listed, and are used in deriving the constants of Eq. (3) ahead. Watts and Wilkinson[41] later measured five of the *a* bands, and two of the *b* bands. Their measurements agree well with those of subsequent investigators, and show that the Ångström and Thalén wave-lengths should be raised 1.5A. This change has been made in obtaining the figures of Table III. The first fine structure analysis was made by Loos,[42] who incidentally measured with great accuracy the heads of the bands later given by Watts and Wilkinson, with the exception of λ6079 (0–4). All of these measurements are in the Rowland system, and are listed in Kayser's Handbuch.

Hulthén[43] made the first quantum analysis of these bands,—in fact this work constitutes the first accurate verification of the combination principle as applied to band spectra, and is consequently of the highest importance. His measurements give data for the heads and also for the origins of the four bands λλ5610, 5198, 4835, and 4393. His assignment of quantum numbers (n and p) was however incorrect, the true n' and n'' being given by

$$n'=n-2, \qquad n''=p+1 \tag{2}$$

Hulthén stated that the strong *a* band λ4511 had a different structure from the others, and hence did not belong to the system. This exclusion carries with it the strong *b* band λ4123. But very recently Jassé[44] has shown that the λ4511 band *does* have a structure similar to the others (a singlet P, Q, and R branch), but has in addition extra branches called P' and R'. The writer[45] finds that the moment of inertia calculated from the P and R branches of the λ4511 band (the 0–0 band) is entirely consistent with the value obtained from Hulthén's data. The extra P' and R' branches yield an "origin" identical with that for the usual branches, but a moment of inertia about $\frac{3}{4}$ as large. The origin and interpretation of these additional branches is as yet entirely a mystery and it may be the case that they are spurious.

Jassé analyzed also the λ4123 (1–0) band, and the moment of inertia evaluated from this band also agrees with Hulthén's data. It therefore seems evident that these two bands form a part of the system. Both of them are however displaced 6 to 8 wave numbers from the expected

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[41] Watts and Wilkinson, Phil. Mag. (6) **12**, 581 (1906).

[42] Loos, Zeits. wiss. Phot. **1**, 151 (1903).

[43] Hulthén, Ann. d. Physik **71**, 41 (1923).

[44] Jassé, Compt. rendus. **182**, 692 (1926).

[45] "Report," Chap. IV, Section 7, note (g).

position, as indicated by the residuals of Table III, and this displacement is a most surprising fact. It occurs regardless of whether heads or origins are used, and is in fact slightly larger for the latter, as shown later. (Table III uses data for heads.)

The only additional measurements are those of McLennan, Smith, and Peters.[46] These cover only four *a* bands (0–3 to 0–6) but are more accurate than the older Ångström and Thalén measurements and were of real assistance to the writer in verifying the identity of the final state of the Ångström bands with the initial state of the fourth positive group. In Eq. (3) this identity is assumed, the $f(n'')$ being taken arbitrarily as the $f(n')$ of Eq. (1). The residuals listed in Table III indicate that this assumption is entirely justified, with the exception of the strange displacement of the 0–0 and 1–0 bands already noted. In Table III there are given in column 1 the $n'-n''$ assignments, and in column 2 the frequency in vacuum, in the I.A. system for the heads of the bands, calculated from the equation[47]

$$\nu = 22,156.6 + (2158n' - 76n'^2) - (1497.28n'' - 17.2n''^2) \qquad (3)$$

The next six columns give the residuals in cm^{-1} for the data of Loos, Hulthén, McLennan Smith and Peters, Jassé, Watts and Wilkinson, and Ångström and Thalén, respectively. Where necessary the Rowland measurements have been reduced to I.A., and then all to vacuum. The Ångström and Thalén measurements have been raised 1.5A, as stated. The last column gives the intensities according to Ångström and Thalén.

The progression of *a* bands (0–0 to 0–6) differs from the *b* bands (1–0 to 1–6) by 2081 cm^{-1}. This is the only figure for the $f(n')$ that is at all certain. The $f(n')$ given in Eq. (3) is derived from the assumed identity of the 2–2 and 2–3 bands. The true head of the 0–0 band is at 22,162.8 cm^{-1} according to Jassé (instead of 22,156.6 as calculated) and the origin is at 22,172.0. The distance from head to origin is thus 9.2, while for the next four *a* bands, Hulthén measures this same difference as 7.1, 7.3, 7.4, and 7.2. The discrepancy for the 0–0 band is again surprising.

It should be pointed out in this connection that there is no violation of the combination principle in the position of the 0–0 and 1–0 bands, but merely an observed spacing of the two vibrational energy levels $n''=0$ and 1, greater than that obtained by extrapolation of a *linear* $\omega^n : n$ curve. In fact, with the data by Hulthén for the λ4835 (0–1) and

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[46] McLennan, Smith and Peters, Trans. R. S. Canada **19**, 39 (1925).

[47] Mecke (Phys. Zeits. **26**, 217 (1925)) has adopted the same quantum assignments as those given here, and has given as the correct representation of the three *a* band *origins* measured by Hulthén, $\nu = 22,154.6 - (1487.05n'' - 14.85n''^2)$. This formula is however unsatisfactory for the more extensive data used here.

λ4393 (1–1) bands, and by Jassé for the λ4511 (0–0) and λ4123 (1–0) bands, it is possible to test the combination principle, line by line, and to evaluate the frequency of vibration as a function of the nuclear quantum number $m(=j-0.5)$. In this case the frequency of vibration corresponds to $n=\frac{1}{2}$, since the interval is between $n=0$ and 1. The theoretical expression is[48]

$$\omega_m^n=\omega_0{}^n(1-\gamma m^2) \tag{4}$$

and the actual results I find to be

$$\omega'=2081.5(1-1.29\times 10^{-5}m^2) \tag{5}$$

for the initial state, from the data of Hulthén, and 2082.3 into the same parenthesis, from the data of Jassé. There is thus a uniform discrepancy of 0.8 cm^{-1} in the data of the two observers, or else a violation of the combination principle by just this amount. The former alternative is doubtless the correct one. For the final state I obtain

$$\omega''=1488.6(1-2.62\times 10^{-5}m^2) \tag{6}$$

from the 0–1 and 0–0 bands, and 1489.4 into the same parenthesis from the 1–1 and 1–0 bands. The *relative* wave-lengths of *each* investigator are evidently quite accurate, for the average residual calculated from Eq. (5) is less than 0.1 cm^{-1} for each. But in Eq. (6) the residuals are much larger, thus proving that discrepancies really exist between the data of the two observers. It may be noted in conclusion that the 1488.6 (or 1489.4) of Eq. (6) for the final state is to be compared with the expected value of 1480.04 given by Eq. (3), while the 2081.5 (or 2082.3) of Eq. (5) for the initial state is to be compared to 2081.0. Since Eq. (3) refers to the heads, and Eqs. (5) and (6) to the origins, the agreement is very good for the initial state interval. The disagreement for the final state is the surprising fact already noted and constitutes apparently a *vibrational* "perturbation."

THE THIRD POSITIVE GROUP OF CARBON, AND THE CAMERON BANDS

The third positive group of carbon, extending from λ3825 to λ2295, was first measured by Deslandres,[11] and consists of three progressions which must be interpreted[49] as n'' progressions corresponding to $n'=0$, 1, and 4. The measurements are given on page 233 of Kayser vol. V. Wolter[50] later made a partial study of the fine structure, and concluded

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[48] See "Report," Chap. IV, Eq. (51).

[49] See Birge, reference (7), and Johnson, reference (15).

[50] Wolter, Zeits. wiss. Phot. 9, 361 (1911).

that only the progression which we have called $n'=0$ was real. This consists of six bands degraded toward the violet, whose heads, using the data by Wolter, are given by

$$\nu=\nu_e-(1724.78n''-14.47n''^2) \tag{7}$$

where ν_e is six-fold, the six heads of the 0–0 band lying between 35,287.6 cm^{-1} and 35,390.4 cm^{-1}. Each band, in addition to the six-fold head, is characterized by a curious repeated rise and fall of intensity. This appears clearly on Wolter's published photograph of the λ2977 (0–1) band (reproduced also on page 211 of Konen "Das Leuchten der Gase und Dämpfe"). The other two progressions of Deslandres, according to Wolter, are merely chance clusters of lines in one of these secondary intensity maxima. Duffendack and Fox[18] have however recently obtained the so-called $n'=4$ progression at a different critical voltage from the $n'=0$ progression, and they consider it to be the $n'=0$ progression of a *new* system (called 3A). On this interpretation each system consists in all probability merely of the n'' progression for $n'=0$, the 3A system being given by

$$\nu=43{,}556-(1724.78n''-14.47n''^2) \tag{8}$$

where the constant term refers to the least refrangible of the six heads. Since only the $n'=0$ progression of this new system is known, we cannot evaluate the frequency of vibration for the initial state. The same situation is true for the third positive group, if Wolter's conclusion regarding the $n'=1$ progression is correct. Assuming however this progression to exist, the Deslandres[11] data give 2214 cm^{-1} as the single known interval. The value 2264 previously published by the writer[19] (or 2258.5 as given by Johnson[15]) was obtained from the assumed reality of the $n'=4$ progression.

Meanwhile Johnson[15] had given

$$1728.2n-14.6n^2 \tag{9}$$

as the $f(n)$ representing both the final state of this third positive group and the initial state of the newly discovered Cameron[16] bands. Now Deslandres' data for the third positive group, used by Johnson, give

$$1731.25n-15.39n^2 \tag{10}$$

while Cameron's data for his new bands give

$$1727.3n-14.35n^2 \tag{11}$$

but all of these discrepancies are easily within the limits of error.

Moreover, Johnson finds that the Cameron bands have a five-fold head and he gives figures indicating that the separations are the same as those occurring for the third positive group, providing the second head of this latter group is omitted. The situation is however not as simple as this. The theory to be discussed later in the present paper predicts that the common level associated with these two band systems should be triple. If each band has a Q branch, as is to be expected from various considerations, there will be apparently six heads, three of them being the heads of the three Q branches, defining the triple origin, while the other three are the true heads of the bands (turning points of R or P branches). Thus if the six heads are numbered in the direction of degradation of the bands, then in the case of *both* systems, the second, fourth, and sixth heads are the Q branch heads, and the respective separations (defining $4\text{–}2=A$, $6\text{–}4=B$) give the intervals A and B of the triple electronic level, A lying above B, on the energy diagram, Fig. 1. The value of A and of B must be the same for both systems. It is however unnecessary that the other intervals shall be the same. Thus the identity of all intervals, as quoted by Johnson, is if true merely a coincidence, according to the present interpretation.

The details are as follows. If Wolter's data for the third positive group are used, the five intervals (2–1, 3–2, 4–3, etc.) are 11.86, 17.74, 19.98, 19.93, and 27.77. Johnson, from his own plates, gives 8.8, 27.6, 17.4, 17.8, and 29.6, and there is thus a considerable discrepancy. Cameron's published wave-lengths for the other system yield for the unweighted values of the intervals, 37.53, 18.80, 18.00, and 29.33 cm^{-1}. Johnson, however, using the same data, quotes 37.8, 18.3, 17.2, and 29.8 cm^{-1}. It is evident here that if the Cameron bands also have six-fold heads, it must be the second head which has not been measured. The value of B from the third positive group, using Wolter's data, is 47.70 cm^{-1}, or using Johnson's data is 47.4. Its value from the Cameron bands is 48.13. The agreement is well within the limits of error. The value of A from the third group, using Wolter's data, is 37.72, or using Johnson's data, is 45.0, a wide discrepancy. We cannot obtain this interval from the Cameron bands, since the second head has apparently not been measured. If however the value of A, obtained from the third group, is assumed for the Cameron bands, one can calculate the 1–2 and 2–3 intervals, and the results are more reasonable if Johnson's value of 45.0 is taken.

The above relations are consistent with the theory that we have here a triple electronic level which is common to the third positive group and the Cameron bands. There is however one possible objection. The three intervals 1–2, 3–4, and 5–6, giving the separation of each band head from its origin, while not necessarily the same for the two systems, are normally roughly constant in the same system. But these intervals are 8.8, 17.4, and 29.6 for the third group (Johnson's data), and 10.53, 18.00 and 29.33 for the Cameron bands, on the basis of 45.0 for the A interval. The variation from 8.8 to 29.6 and from 10.5 to 29.3 is quite unusual, but Professor Mulliken (private communication) reports a similar variation for the red CN bands.

It is not possible, from the twelve measured Cameron bands, to give the n'' numbering for this system, for the sequence $n''-n'=1$ is faintly present, but not measured, while the zero sequence is not observed at all. However the six final state intervals actually measured agree with those resulting from the writer's analysis of the fourth positive group so well that Johnson immediately assumed that the two systems had a common final state, and that the Cameron bands thus constituted a second "resonance" system of neutral CO. The actual $f(n'')$ found by Johnson is, in fact,

$$2151.1n''-12.7n''^2 \tag{12}$$

while, using the better data for the fourth group and for the third group, the whole Cameron system should be given by

$$\nu=\nu_e+(1724.78n'-14.47n'^2)-(2149.74n''-12.70n''^2) \tag{13}$$

where ν_e=48,529.9, 48,492.4, 48,473.6, 48,455.6, and 48,426.3. The expected n' progression, for $n''=0$, does not appear on Leifson's absorption plates of carbon monoxide, but this is not necessarily an objection to the above interpretation, since the atmospheric bands of oxygen, for instance, require a considerable quantity of absorbing gas in order to be detected. Moreover, Hopfield (unpublished work) has now found the $n''=0$ progression of Cameron bands in absorption in carbon monoxide.

DISCUSSION

Generalizing previous tentative suggestions by Mulliken and others, the writer[14] has assumed that "the energy levels associated with the valence electrons of molecules agree in all essential aspects with those associated with the valence electrons of atoms." In this same reference the previous evidence on this point is briefly summarized, and some new evidence is presented. Some of the relations just discussed in connection with the spectrum of carbon monoxide form the most significant portion of this new evidence. Taking the above generalization as a basis for action, Mulliken[51] has very recently worked out extensive systematic

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[51] Mulliken, Proc. Nat. Acad. Sci. **12**, 144, 151, 158, and 338 (1926); Phys. Rev. **28**, 481 (1926), Phys. Rev. **28**, 1202, (1926).

relations in band spectra, and has presented the results in a series of remarkable papers. In the present paper there is hardly space to give a detailed critical discussion of these new developments. A brief summary of certain points is however advisable.

It has commonly been assumed that there are two main types of diatomic molecules,—one consisting of loosely bound atoms (low heat of dissociation) and the other of firmly bound atoms (high heat of dissociation). It has been thought that the first type consisted merely of two atoms held together by mutual polarization effects (secondary, or van der Waals forces), the quantization of the various electronic orbits being identical with that of the two atoms when entirely separate. It should be possible to separate such a molecule continuously (adiabatically) into its constituent atoms, not only by electron impact, but also by absorption of light. In the case of iodine this latter process is actually observed in the n' progression of bands which runs to a definite head at 20,020 cm^{-1}. Dymond[52] has proved that this point corresponds to dissociation of the molecule.

On the other hand, it has been supposed that in the case of firmly bound molecules like O_2, N_2, CO, etc., certain electrons are in quantum orbits different from those in the atoms. Such orbits may possibly encircle both nuclei. On such a basis, Mulliken adopted the Lewis-Langmuir idea of octets in the N_2, CO, and NO molecules. On this interpretation, each of these molecules has four K electrons (each atom with its usual two), while the remaining electrons are arranged in some sort of a group of eight, with two (for N_2 and CO) or three (for NO) extra electrons. These extra electrons are assumed more loosely bound and hence may be termed the valence electrons of the molecule. On such an assumption N_2 and CO may be correlated with the two-valent atom Mg, since this has two K electrons, a group of eight L electrons, and two valence electrons. Similarly NO is correlated with Al.

Now it has been shown that the character of the spectral formulas known to hold true for atoms (Rydberg, Ritz etc.) is due to the essentially constant penetration of an electron into a cluster of electronic charges, in a series of orbits of the same angular momentum (k) but varying total momentum (n). If the electronic orbits in molecules are quantized in a manner at all similar to those in atoms, we should therefore expect that the spacing of the electronic energy levels associated with the loose-bound ("valence") electrons in molecules should follow at least approximately the same law as is found in the case of atoms. Previous work by

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[52] Dymond, Zeits. f. Physik **34**, 553 (1925).

Mulliken, Mecke, and Hulthén has shown that the molecular levels have a multiplicity quite similar to that found in atoms. The very recent work of Mulliken has been devoted mainly to assigning an inner quantum number j_s to each electronic energy level of the molecule, using precisely the same values as for the "corresponding" atom, on Sommerfeld's interpretation, and then correlating each j_s with the observed fine structure of the accompanying bands. This correlation, which has been very successful, gives a new basis for the correctness of the j_s values which it is not possible to obtain from a study of atomic structure.

The preceding sections of this paper give the experimental data necessary for the construction of a series of electronic energy levels for CO. To be accurate one should use in each case the origin of the 0–0 band. This however is unknown, except for the Ångström bands. For the sake of consistency we therefore in all cases use the head of the 0–0 band. The difference is immaterial for the present discussion. Beginning then with the normal state of the molecule (level X of Fig. 1) as the zero energy level, the initial state of the fourth positive group (level A of Fig. 1) is, by Eq. (1), 64,737 cm^{-1} (=7.995 volts[53]) while the initial state of the Cameron bands (level a) is, by Eq. (13) 48,426.3 to 48,529.9 cm^{-1} (=5.981 to 5.994 volts). Then from Eq. (3) the initial level of the Ångström bands (level B) is 86,894 cm^{-1} (10.732 volts), while from Eqs. (7) and (13), the best value for the initial state of the third positive group (level b) is 83,817.1 cm^{-1} (=10.352 volts). Finally, from Eqs. (8) and (13) we obtain 92,086 cm^{-1} (=11.374 volts) for the initial state of the new 3A bands of Duffendack and Fox[18] (level c). All of these values are listed in columns 3 and 4 of Table I.

Now in order to compare the law of spacing of electronic energy levels in molecules with that found in atoms, we need the "term" value of the various energy levels. This in turn requires a knowledge of the ionization potential of the molecule. Fortunately carbon monoxide is one of the very few molecules for which a fairly accurate value is known, the best direct measurements giving 14.1 and 14.3 volts[54] while from Duncan's measurement of the excitation potential of the first negative group of carbon,[55] one obtains 14.2±0.3 volts (=114,966 cm^{-1}). Each "term" is then obtained from $114{,}966-x$, where x is the cm^{-1} value of the level as previously listed. These values are given in column 5 of Table I. The *denominator* of each term is given by $D=\sqrt{\nu/R}$ where ν is the term

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[53] 1 volt = 8096.2 cm^{-1}, according to recent data. See Birge, Science, **64**, 180 (1926).

[54] See page 123, Report by Compton and Mohler on "Critical Potentials."

[55] See Birge, reference (9).

value and $R = 109{,}678$ cm^{-1}. The results are listed in column 6, Table I. In the simple Rydberg formula the denominators differ by unity. The denominators first obtained by the writer,[14] for the levels X, A, and B, have the values 0.98 ± 0.02, 1.48 ± 0.10, and 1.98 ± 0.15, assuming 0.3 volts probable error in the ionization potential value.

By comparison with the term scheme of Mg (see Fig. 1) this immediately suggested that the true designations are $1\ {}^1S$, $1\ {}^1P$, and $2\ {}^1S$, using the nomenclature of Russell and Saunders. The Ångström CO bands consist merely of three branches (P, Q, and R) of strictly single lines. In this respect they correspond to the "single-line" series of atomic spectra, and by analogy we may conclude that the two levels concerned with this system also are single. This is in agreement with the designations just given. Similarly we may *predict* that the fourth positive group of carbon also will be found to consist of P, Q, and R branch bands, with the individual lines strictly single.

By similar analogy with Mg, it is probable that the new a and b levels of Johnson[15] are respectively ${}^3P$ and ${}^3S$ levels. This was noticed immediately by Mulliken and by the writer, as noted in the introduction. The evidence concerning the multiplicity of the a level has already been discussed, and we may assume provisionally that it is triple, even though there is still some uncertainty as to this. On this assumption, the triplet separations are approximately 45 and 48 cm^{-1} (A and B of the previous discussion) as compared to 41 and 20 for the corresponding level in Mg. In the case of N_2, the writer has interpreted the first positive group in such a way as to give 20 and 40 for the corresponding intervals, i.e., the molecular level is "inverted." Until this nitrogen system has been actually analyzed in respect to its fine structure, such a conclusion[56] must be regarded as merely tentative.

The assumption that the initial level of the Cameron bands is triple, while the initial level of the fourth positive group is single,—the common final level of both systems being single,—may be the explanation of the faintness of the Cameron bands in emission,[16] and the failure until recently to get them in absorption. For, as Professor H. N. Russell has reminded the writer, transitions between levels of varying multiplicity are very improbable in the case of light atoms, although quite the reverse is true for heavy atoms. Now CO is a molecule composed of two relatively light atoms, and if the same rule applies to molecules, the relation is quite as expected.

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[56] Based on the spacing of the strong first, second, and fourth heads of the first positive group of nitrogen. It may be noted that Hund, in his important paper on the structure of molecules (Zeits. f. Physik **36**, 657 (1926)) predicts that the multiple levels in molecules should be *equidistant*.

The b level is apparently single, as it should be. Because of the crowding together of the levels, near the ionization potential, it is not possible to identify the new c level of Duffendack and Fox[18] with any certainty. Johnson has suggested that it is another ^3P level. The denominators (1.28 and 2.19) do not however favor this assumption and by comparison with Mg, it seems more likely that it is a ^3D level. (Compare Fig. 1, where these analogies with Mg are indicated by broken lines.) By making such an identification, all of the transitions for neutral CO obey the selective principle ($\Delta k = \pm 1$) of line spectra. This rule is apparently violated in certain molecules (CN, NO, and certainly BO and CO^+), but we do not know yet whether such violations are the exception or not, and I think it is at least significant that in the case of CO, where the analogy with a given atom is fairly complete, the rule is obeyed. The same situation is true in the case of the helium molecule, according to the analysis of Mulliken[57], but here we have undoubtedly merely two slightly distorted helium atoms, and might expect the atomic laws to apply. On the other hand, Hund's[56] theoretical analysis indicates that in molecules the transitions $\Delta k = 0, \pm 1$, are allowed.

In the case of CO^+, the analogy with Mg^+ is very good, as far as the multiplicity is concerned.[58] The A' level of Fig. 1 is double, with spacing 126 cm^{-1}, compared to 91.5 for the first ^2P level of Mg^+, while the X' and B' (^2S) levels are single, if as Blackburn[28] believes, the lines of the first negative group of carbon are strictly single. If the B' level is ^2S and if the Rydberg formula is true, the ionization potential of CO^+ is only 10.7 volts, placing this level at 24.9 volts on the Fig. 1 diagram (level X''). This point will be considered more at length in a separate paper on CO^+.

The energy levels for CO^+, plotted in Fig. 1, and given in Table I, are evaluated from the constants previously published by the writer.[7] In this case, values are known for the true origins of the comet-tail bands ($\nu_e = 20{,}472$ and $20{,}346$ cm^{-1}) and of the first negative group of carbon ($\nu_e = 45{,}638$ cm^{-1}) and these have been used for the calculation. Table I contains finally, in column 7, the frequency of vibration, ω^n, for each of the electronic levels of CO and CO^+. It was at first believed that the relative values of ω^n could be used as a criterion for the identity of the various states. Thus all S states, in molecules like CO, have

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[57] Mulliken, Proc. Nat. Acad. Sci. **12,** 158 (1926).

[58] See Birge[14] and contained references.

roughly the same value of ω'', while the P states have a smaller value. If this were a general rule, it should furnish valuable evidence regarding molecular structure, as was pointed out by the writer.[14] Recent work by Jenkins, Barton and Mulliken[59] on NO seems to indicate however that such a criterion is quite untrustworthy, and hence the theoretical conclusions based on it must likewise be uncertain.

CONCLUSION

The present paper has been concerned primarily with the experimental data for the band spectra of carbon monoxide. By a suitable analysis of these data, the general energy level scheme of Fig. 1 and Table I has been obtained. There can be no question as to the qualitative correctness of this scheme. The actual energy values of the various levels may be in error as follows. For the levels a, A, b, B, and c, of neutral CO, the error arises from the use of the head of a band in place of the origin, but the entire discrepancy for any level is probably less than 100 cm^{-1}. The relative position of the levels of CO^+, since these are given in terms of the true origins, is very accurate. On the other hand, the energy value of level X', and hence of all the CO^+ levels relative to the CO levels is uncertain to possibly 0.3 volts (2430 cm^{-1}), and the "term" values of the CO levels have the same uncertainty.

The energy scheme is thus established, but the correlation of the various levels with levels of the Mg atom is of course still a pure assumption. This correlation has been merely sketched in the present paper, with no attempt at critical discussion.

Note added in proof. Duffendack and Fox (Science **64,** 277, Sept. 17 (1926)) have recently obtained from data on excitation potentials striking confirmation of the quantum analysis of the CO and CO^+ band systems made previously by Birge[7,9,24] and Johnson.[17] The 0–0 band of the third positive group is emitted at a minimum voltage of 10.2, compared to 10.35 volts for level b, as given in Table I. Similarly levels B, c, A' and B' are placed at 10.7, 11.1, 16.9 and 20.0 volts, compared to the values 10.73, 11.37, 16.72 and 19.84 volts, of Table I. The only discrepancy is in the case of the combination bands of CO^+, which Duffendack and Fox find at 22.9 volts, compared to the calculated value of 19.84 volts. As a result they assume that these bands are due to a transition from a higher (C') level to the B' level, instead of from B' to A', and they remark "This system contains so few bands that its

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[59] Mulliken, private communication.

relation to others can not be determined with certainty by analysis." This, however, is apparently not the case. There are six bands in the system and each fits unambiguously into the $B'-A'$ transition.

Still more recently, Ann B. Hepburn (Nov. 1926 meeting, Amer. Phys. Soc.) has obtained, in a similar way, data in complete agreement with the values in Table I, *including* the combination bands of CO^+.

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