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NEW MEASUREMENTS IN THE FOURTH POSITIVE CO BANDS

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ABSTRACT

That part of the fourth positive system of CO lying between 1970A and 2800A has been remeasured together with sixteen bands not previously observed. An equation for the band heads is given, the constants of which yield the values $D'=12.00$ volts, $D''=11.17$ volts for the heat of dissociation.

Modifications in values of frequency have been small, while those of intensity have been rather large. Some discrepancies have been removed. Revision of intensity estimates permits a far more accurate comparison than previously with Condon's theory of intensity distribution and shows the superiority of Morse's $U(r)$ function. Using this function, the distribution of intensity among the bands of the fourth positive system agrees perfectly with Snow and Rideal's value of the moment of inertia for the normal state, $I_0''=15.0\times10^{-40}$ g cm^2.

The quantum assignment of Asundi's infra-red electronic bands has been revised.

INTRODUCTION

THE fourth positive band system of CO, which extends at least from 2800A to 1300A, has never been completely measured by any one investigator. The work on this system prior to 1926 is fully described by Birge.[1] His paper analyzes data taken by Deslandres (42 bands), Bair (22 bands), Duncan (14 bands), Lyman (100 bands), and Leifson (12 bands), all under low dispersion. Subsequent to 1926 papers have appeared on the energy levels of CO,[2,3] the mode of dissociation,[4] CO in active nitrogen,[5] the isotope effect,[6] and a series of papers on the structure of the various systems.[7,8,9,10]

The initial vibrational levels of this system are the same as the final levels of the Angstrom bands and of the new bands analyzed by Herzberg,[7] and Johnson and Asundi,[8] while the final levels are the same as those of the Cameron bands and several absorption systems. These relationships are shown in Fig. 1, which diagrams the electronic energy levels for neutral CO. In addition to the bands just mentioned there are shown the third

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[1] Birge, Phys. Rev. **28**, 1157 (1926).
[2] Hopfield and Birge, Phys. Rev. **29**, 922 (1927).
[3] Duffendack and Fox, Astrophys. J. **65**, 214 (1927).
[4] Hogness and Harkness, Phys. Rev. **32**, 936 (1928).
[5] Knauss, Phys. Rev. **32**, 417 (1928).
[6] Birge, Phys. Rev. **34**, 379 (1929).
[7] Herzberg, Zeits. f. Physik **52**, 815 (1929).
[8] Johnson and Asundi, Proc. Roy. Soc. **A123**, 560 (1929).
[9] Asundi, Proc. Roy. Soc. **A124**, 277 (1929).
[10] Asundi, Nature **123**, 47 (1929).

positive and the three A systems. Asundi[9] has contributed two other new systems, the five B and an unnamed system in the near infra-red. The absorption and emission systems described by Hopfield and Birge are also shown.

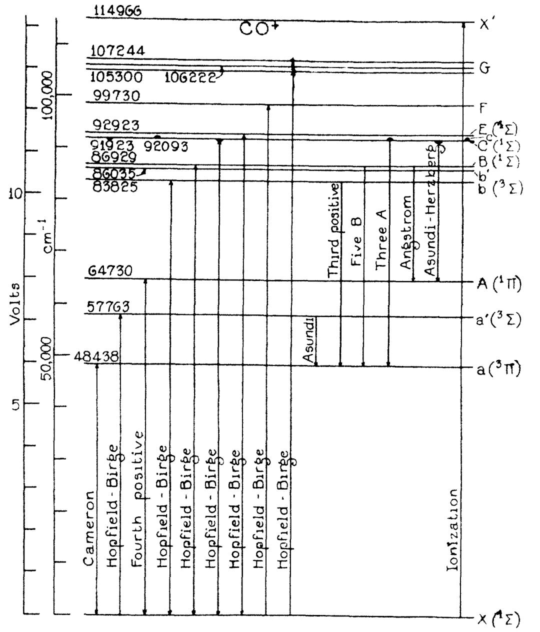

Fig. 1. Energy level diagram for neutral CO.

Asundi's vibrational analysis[11] of the infra-red system requires revision with respect to the initial state. The upper electronic level is at 57763 cm^{-1} (Birge, private communication) rather than at 58927, and the most recent value[12] for ω_0' is 1173 cm^{-1}. This yields the equation for the infra-red bands

$$\nu = 9325 + (1173n' - 9n'^2) - (1726.5n'' - 14.4n''^2).$$

Accordingly the initial quantum numbering must be increased by one unit and the band called 1, 0 by Asundi is really the 2, 0 band.

The present knowledge of the fourth positive band system is somewhat inaccurate because it has been measured under low dispersion only, and because of a lack of satisfactory wave-length standards in the region which it occupies. Therefore it seemed advisable to remeasure as many bands as could be reached with a quartz spectrograph.

EXPERIMENTAL DETAILS

The CO bands were excited at 0.3 mm pressure in a water-cooled U-shaped discharge tube, the straight portion of which was viewed end on. This straight portion was 23 cm long and 6 mm in diameter. Large iron

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[11] His equation is $\nu = 10489 + (1155n' - 9n'^2) - (1726.5n'' - 14.4n''^2)$.

[12] Mulliken, Phys. Rev. **32,** 186 (1928).

electrodes permitted an input of 1.2 amperes at 2200 volts from a 3 KVA power transformer. Magnesium carbonate in an electrically heated side tube served as a source of CO_2 which later broke down to CO in the discharge. The vapor pressure of CO_2 over magnesium carbonate is constant at constant temperature. In this way fresh gas was provided as rapidly as required by the clean-up of the electrodes.

The pictures were taken on Hilger Schumann plates, or oiled Eastman 40's with a Hilger E 1 quartz spectrograph. This instrument has a dispersion of 3.91A/mm at 2800A and 1.21A/mm at 1970A, the limits of the range covered in this investigation.

Copper arc and spark lines and nickel spark lines as listed by Shenstone[13,14,15] served as standards below 2500A, while in the region above this iron standards as listed in volume VII of Kayser and Konen, "Handbuch der Spektroskopie," were used. The transformations between wave-lengths and wave-numbers were made with the aid of Kayser's "Tabelle der Schwingungszahlen."

RESULTS

The new measurements on the band heads are shown in the following table.

TABLE I. *Fourth positive bands of CO.*

λ(I.A.)	ν(cm⁻¹)	*I*	*n'*, *n''*		O−C
2799.7	35708.2	9	9	22	+ 1.6
2785.4	35890.3	8	4	18	− 4.8
2742.6	36450.7	6	11	23	+14.1
2740.0	36486.0	4	7	20	− 4.0
2712.1	36860.5	4	6	19	− 7.7
			10	22?	−15.8
2698.3	37049.7	6	13	24	− 4.2
2684.0	37247.4	3	5	18	+10.1
2680.8	37291.5	5	9	21	+15.5
2662.9	37541.8	4	12	23	+ 4.6
2661.5	37561.7	4	15	25	+ 3.0
2659.6	37587.9	4	4	17	− 9.6
2630.0	38011.4	6	11	22	± 0.0
2598.3	38474.8	4	10	21	− 1.8
2594.5	38531.5	1	16	25	+10.3
2567.8	38932.8	5	9	20	− 0.1
2556.0	39111.7	3	12	22	− 0.3
2538.6	39379.7	4	8	19	− 0.4
2521.8	39642.7	3	14	23	− 7.9
2509.9	39830.1	8	7	18	+11.8
2492.9	40102.1	8	10	20	− 0.3
2483.8	40248.8	3	6	17	+ 1.3
2463.2	40584.6	10	9	19	+ 0.3
2458.0	40671.5	2	5	16	+ 3.8
2433.9	41057.5	9	8	18	+ 0.5
2424.1	41239.3	5	11	20	+ 1.7
2407.6	41552.0	7	7	17	+ 1.3
2394.2	41754.2	3	10	19	+ 0.3
2393.1	41773.9	4	13	21	− 4.5
2381.6	41975.3	6	6	16	− 0.2
2365.5	42261.9	5	9	18	+ 0.7
2356.5	42422.3	4	5	15	+1.1
2337.9	42760.1	7	8	17	+0.7
2332.5	42860.0	3	4	14	+2.0
2311.5	43249.2	8	7	16	+0.5
2286.1	43728.5	7	6	15	−0.5
2273.9	43963.4	3	9	17	−0.2
2272.3	43994.0	1	12	19	+4.4
2261.7	44200.0	9	5	14	−0.2
2247.2	44486.6	7	8	16	−0.8
2238.3	44663.8	9	4	13	+1.3
2221.5	45001.4	10	7	15	−0.8
2215.8	45115.9	3	3	12	+0.1
2196.8	45506.4	10	6	14	−1.6
2173.0	46004.7	9	5	13	−0.1
2150.2	46492.6	8	4	12	±0.0
2137.0	46779.9	5	7	14	−1.2
2128.3	46971.1	8	3	11	−0.2
2113.1	47309.6	9	6	13	−2.9
2107.2	47440.3	7	2	10	−0.8
			9	15	−3.8
2089.9	47834.0	10	5	12	−0.8
2086.9	47901.5	1	1	9	−0.4
2067.6	48349.4	10	4	11	+1.3
2046.3	48852.9	10	3	10	+0.5
2025.8	49347.8	9	2	9	+0.1
2011.8	49690.6	8	5	11	+0.2
2005.8	49838.2	5	1	8	+4.2
λ(vac.)					
1990.8	50230.9	10	4	10	+1.7
1970.0	50761.7	8	3	9	+2.6

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[13] Shenstone, Phys. Rev. **28,** 449 (1926).

[14] Shenstone, Phys. Rev. **29,** 380 (1927).

[15] Shenstone, Phys. Rev. **30,** 255 (1927).

The assignment of vibrational quantum numbers (n', n'') is substantially that given by Birge. A few bands given by him were not measured because of overlapping by other bands. Otherwise, all bands given by Birge, as well as many new bands, have been measured and quantum numbers assigned.

The new measures on fifty-eight bands yield the equation[16]

$$\nu = 64729.60 + (1497.63\, n' - 17.262\, n'^2) - (2149.08\, n'' - 12.761\, n''^2).$$

The column headed "O−C" in Table I lists the observed minus calculated values of the band heads as calculated from this equation. Unfortunately it was possible to measure bands of relatively large quantum numbers only. For this reason the equation written above probably does not express the origin of the system and the bands near it as well as the former equation[16] does, although for the region represented by the bands of Table I the new equation is probably the better.

The plates showed clearly the presence of a single P, Q, and R branch in each band. The bands degrade to the red. Although they were unresolved at the origin and it was impossible to determine how many lines were missing, there is no reason to doubt the correctness of the assumption that these bands result from a $^1\Pi$ to $^1\Sigma$ transition.

Discussion

Accuracy in our present methods of evaluating the heat of dissociation of a molecule from data on vibrational energy levels depends on our ability to extrapolate to $\omega_n = 0$ the $\omega_n : n$ curve. Fortunately in many cases including this one the $\omega_n : n$ curve is nearly linear over the known range, which facilitates extrapolation. The data in this paper, being more accurate and extensive, yield a more reliable extrapolation and provide a more certain value of the heat of dissociation than that previously reported.[17] The heat of dissociation of a CO molecule in the normal state, as now determined, is 11.17 volts. To raise a CO molecule to the $^1\Pi$ level and dissociate it there requires 12.00 volts.

The large extent of the fourth positive system affords both opportunity and difficulty in discussing vibrational intensity relations. Table I gives, under the heading "I", simple visual estimates of intensity, allowing as well as possible for overlapping bands and for large variations in plate sensitiveness over the range considered. Fig. 2 shows in a graphical manner the intensities of the observed bands. The diameters of the circles are proportional to the intensities of the corresponding bands.

A theory has been given by Condon[18] which predicts, from a knowledge of certain band constants including the moment of inertia, which bands of a system will be the most intense. A $U(r)$ curve (potential energy as a function of r) is drawn for each of the two electronic states involved. Such a curve

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[16] The next most recent equation (I.C.T. Vol. 5, p. 412) is $\nu = 64765 + (1499.0n' - 17.24n'^2) - (2154.7n'' - 12.70n''^2)$. $D = 11.2$ volts.

[17] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[18] Condon, Phys. Rev. **28**, 1182 (1926).

shows the extremes between which a molecule with a given amount of energy can vibrate. Condon's theory is based on the assumption that the molecule spends most of its time in an extreme position and that as a consequence the transitions between the extreme positions are the most probable. Since the $U(r)$ curve represents these extremes, transitions drawn between the upper and lower of two $U(r)$ curves of a molecule are according to the theory the most probable, and on an n', n'' diagram (cf. Fig. 2) they fall on a smooth curve roughly parabolic in form with the vertex near the origin of the system. If the constants and the function on which the $U(r)$ curves are based are correct, then the theoretical intensity distribution curve should pass through the most intense bands observed. The $U(r)$ function used by Condon in developing his theory is a power series, and for computing purposes the polynomial composed of the first three terms is used. In the particular case of the CO molecule this polynomial is satisfactory only over a very small range of r near r_0. An intensity curve using $I_0''=14.9$ appears in Condon's paper.[18] This curve fits near the origin, but for quantum numbers higher than $n''=10$ the upper branch becomes concave upward while the trend of the bands in this region is concave downward.

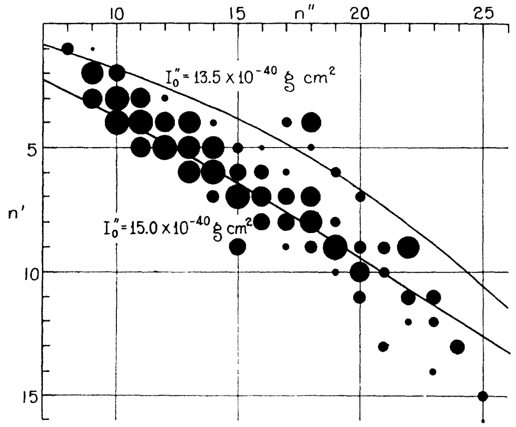

Fig. 2. Intensities of band heads. The intensity of each band as listed in Table I is proportional to the diameter of the corresponding circle on the n', n'' diagram. Intensity distribution curves based on Morse's $U(r)$ function are plotted for two values of I_0''. The observed distribution of band intensities agrees with $I_0''=15.0\times10^{-40}$ g cm^2.

Fortunately another form of $U(r)$ function is available[19] which has the following properties: (a) when r is zero, U is very large, (b) when r is r_0, U is at its only minimum, (c) when r is very large, U is asymptotic to D, the heat of dissociation, and (d) when the quantum theory is applied, the function yields the correct expression for the vibrational energy levels. This function is given by the expression

$$U=A+De^{-2a(r-r_0)}-2De^{-a(r-r_0)},$$

where A is the constant which moves the entire curve up or down on the energy scale, D is the heat of dissociation, $a=0.2454(M\omega_0x)^{1/2}$, where M is

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[19] Morse, Phys. Rev. **34**, 57 (1929).

the reduced mass in terms of the atomic weights; and r and r_0 are nuclear separations, the latter corresponding to the special case of zero vibrational energy.

Theoretical intensity curves are drawn on Fig. 2 corresponding to $U(r)$ curves computed from the following constants:

	A	D	a	r_0
Initial	97500	32500	2.67	1.24
Final	91394	91394	2.29	1.09
	91394	91394	2.29	1.15

Curves corresponding to two values of the moment of inertia ($I_0''=15.0\times 10^{-40}$ g cm^2, giving $r_0''=1.15$A, and $I_0''=13.5\times 10^{-40}$, givirg $r_0''=1.09$) appear on Fig. 2 because at the time the figure was first drawn Snow and Rideal's paper[20] giving $I_0''=15.0\times 10^{-40}$ had not appeared and it seemed probable that the lower value of I_0'' was about right.[9,21] The intensity curve corresponding to the lower value of the moment of inertia does not fit the observed bands very well, while the intensity curve corresponding to the larger value is an excellent fit, especially in the center of the diagram. For low quantum numbers the fit is really better than the figure would indicate because bands observed by others with a vacuum spectrograph are not shown since the diagram shows only the data of the author.

The intensity distribution among the bands of the fourth positive system is very distinct evidence in favor of the larger value of the moment of inertia if we assume that the $U(r)$ function given above is essentially correct. The evidence strongly favors this assumption and the intensity distribution can therefore be taken as good evidence from the electronic bands for the correctness of the infra-red value of the moment of inertia for the normal state. This represents a new and useful check on the value of this constant.

Babcock[22] has estimated the prevalence of O^{16} relative to O^{18} as 1250:1. If we assume that C^{12} has an atomic weight 12.000 and that C^{12} and C^{13} are the only factors influencing the atomic weight (12.003) of carbon,[23] then they are prevalent in the ratio of 333:1. This calculation shows, in harmony with the experimental findings of King and Birge[24] that $C^{13}O^{16}$ is much more prevalent than $C^{12}O^{18}$ or $C^{13}O^{18}$. Therefore the calculated positions of several favorably located band heads of the $C^{13}O^{16}$ molecule have been examined on a heavily exposed plate, but no isotopic heads have been found. This does not cast doubt on the isotopic heads reported by Birge on the fourth positive absorption plates taken by Hopfield, but merely goes to show that absorption spectra show these faint bands more readily than do emission spectra.

I wish to express my appreciation for the advice and assistance of Professor R. S. Mulliken.

[20] Snow and Rideal, Proc. Roy. Soc. **A125,** 462 (1929).

[21] Lowry, J.O.S.A. & R.S.I. **8,** 647 (1924). A numerical error appears in this paper (Lowry, private communication) and a recalculation of Lowry's data by the writer gives $I_0=13.0\times 10^{-40}$ g cm^2.

[22] Babcock, Phys. Rev. **34,** 540 (1929).

[23] Birge, Phys. Rev. Sup. **1,** 1 (1929).

[24] King and Birge, Phys. Rev. **34,** 376 (1929).