## High Series Terms in the Arc Spectrum of Mercury

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The spectrum of luminous mercury vapor drawn into a low pressure chamber was found to have the series lines developed to high members. Wave-length measurements of these higher members in the singlet and triplet diffuse and sharp series were made. The  ${}^{3}S_{1}$  terms developed to m = 20 show that this series follows a Ritz formula accurately. The <sup>1</sup>S<sub>0</sub> series and especially the <sup>1</sup> and <sup>3</sup>D series also follow a Ritz formula with definite indications of slight perturbations near the end of the series.

N the basis of the perturbation theory of wave mechanics R. M. Langer<sup>1</sup> deduced an equation to represent the series of optical terms for atoms containing more than one optical electron. The equation of the form

$$\nu_n = R / [n + \sum_{0}^{\infty} p_{in} / (\nu_i - \nu_n)]^2 = R(n^*)^2, \quad (1)$$

where  $p_{in}$  is a function of the probability of transition between  $\nu_n$  and the observable spectroscopic terms  $v_i$ , reduces to a simple Ritz formula

$$\nu_n = R/(n + \mu + \alpha \nu_n)^2 = R/(n^*)^2,$$
 (2)

when the effect of the perturbing  $\nu_i$  terms becomes negligible.

For cases where the atom has two optical electrons, an electron configuration may arise which does not belong to the particular series considered, but which has an energy value nearly equivalent with one of the terms of the series. In that case a perturbation effect will be observed and the equation for the terms will be given by

$$\nu_n = R/(n + \mu + \alpha \nu_n + \beta/(\nu_i - \nu_n))^2 = R/(n^*)^2.$$
 (3)

Such an equation has been used by Shenstone and Russell<sup>2</sup> for the study of the series in Ca I, Ba I, Al II, Cu I and Hg I. In the last named element the  ${}^{1}P_{1}{}^{0}$  series is perturbed by a term around 5368 and can fairly well be represented by the last equation. The  ${}^{3}P^{0}$  terms also show some perturbation especially in the case of  ${}^{3}P_{2}{}^{0}$ . The authors leave open the question as to whether the  ${}^{3}S$  and  ${}^{3}D$  series of Hg I will fit a simple Ritz formula or whether these are affected by some term near the end of the series. The simplest method of determining whether a series follows exactly Eq. (2) is to see whether the plot of  $n^* - n$  against  $\nu$  gives a straight line. This line can also yield the limit of the series. Using the values of the wave-lengths of the  ${}^{3}S$  and  ${}^{3}D$ series measured by Dingle<sup>3</sup> and Buisson<sup>4</sup> and the values of the limits of these series as given by Fowler,<sup>5</sup> Shenstone and Russell find that the plot of the  ${}^{3}S$  and  ${}^{3}D$  terms departs from a straight line near the end of the series. Such a departure may sometimes not be indicative of a true perturbation, but rather of inaccuracies either in the limit assignment or in the measurements of the higher members of the series. The term values of these higher members are below 500 cm<sup>-1</sup> and the value of  $n^* - n$  is changed by about 0.015 for an error of 1 cm<sup>-1</sup>. Some attempts to change the value of the limit were made by the author with slight success. However, it was felt that the measurement of the wave-lengths of the lines which was dependent on a comparison spectrum of iron placed below the spectrum of mercury may be slightly in error. In the region of 2500A an error of 0.06A introduces an error of  $1 \text{ cm}^{-1}$  in the term value.

At the suggestion of Professor Shenstone, I undertook to extend the  ${}^{3}S$  and  ${}^{3}D$  series to still higher members and to improve the accuracy of the measured wave-lengths.

## Apparatus

It was shown by Lord Rayleigh<sup>6</sup> that the higher members of the diffuse series of mercury are broadened by the Stark effect produced on

<sup>&</sup>lt;sup>1</sup> R. M. Langer, Phys. Rev. 35, 649 (1930).

<sup>&</sup>lt;sup>2</sup> A. G. Shenstone and H. N. Russell, Phys. Rev. 39, 415 (1932).

<sup>&</sup>lt;sup>3</sup> H. Dingle, Proc. Roy. Soc. **A100**, 167 (1921). <sup>4</sup> H. Buisson, C. R. **178**, 1270 (1924).

<sup>&</sup>lt;sup>5</sup> A. Fowler, *Report on Series in Line Spectra*, 1922.
<sup>6</sup> Rayleigh, Proc. Roy. Soc. A112, 14 (1926).



FIG. 1. Diagram of apparatus.

the excited atoms by the electric fields of neighboring ions. This broadening makes it difficult to see many members of the series in the light from an ordinary arc, and only by leading the luminous vapor into a more highly evacuated field free space are the higher series members observable.

The apparatus used (shown in Fig. 1) makes use of this fact. A quartz tube Q was sealed at the top by a water-cooled steel plug which was attached with picein. A steel rod R, 10 cm long, was attached to the rod and carried at its lower end the steel anode A. This anode fitting closely to the quartz tube had a conical hollow below and a slit 1.5 cm long, 3 mm wide and 4 mm deep. Liquid mercury collecting over the anode could flow down through a groove cut in its edge. The cathode was a column of mercury C, whose level was a few cm below the anode and was held in place by barometric pressure. Luminous vapor from the mercury arc between A and C diffused through the slit in A into the low pressure chamber which was connected to a Cenco pump attached to the tube in the plug. In this region the luminous vapor showed the series line of the arc spectrum developed to very high members. The P. D. across the arc was about 30 volts and the current used about 10-12 amp. The light from the luminous vapor which formed a vertical column about 5 mm wide and 2 cm deep was examined with a Hilger E 1 quartz spectrograph. The slit of the spectrograph was about 6 inches from the edge of the column and the light from the full depth of the column at its lower end was utilized. The angle subtended at the slit by the source was large enough to fill the collimating lens completely with light. Photographs were taken on Eastman Process Plates and exposures lasted 15 to 30 hours. A check was kept on the temperature of the room and only those plates were used which were taken during a period of comparative constancy of the barometric pressure, a precaution necessary for long exposures. Plates sensitized with Eastman ultraviolet sensitizer were sometimes used in the region of 2200A but it was found that although they intensified many of the strong lines they were not an improvement over the Process plates for the weak members at the end of the series.

The determination of wave-lengths from a comparison spectrum placed alongside the observed one has received some critical consideration lately. The moving of a Hartman diaphragm over the slit of a spectrograph has been known at times to produce a shift of the lines. Moreover it would be difficult to place an iron arc exactly in the position which the mercury vapor occupied and any displacement from this position causes a shift of the lines as was brought out by Stockbarger and Burns.<sup>7</sup> It was therefore attempted to introduce at least some of the comparison lines into the luminous column itself. Attempts to get iron lines were made by spraying colloidal iron into the beam or arc and by using an electrolytically prepared mercury-iron amalgam as cathode but although in the arc itself the iron spectrum was fully developed none of the iron lines were present in the light of the luminous vapor in B. Greater success was attained with copper. A copper mercury amalgam was floated on top of the mercury column and almost all the lines of the arc spectrum of copper were registered in the light from the vapor column in the time required to bring out the higher series members in the mercury spectrum. (In the space between A and C both the arc and spark lines of copper appeared.) A diaphragm was placed in front of the spectroscope slit. It was mounted on a

<sup>&</sup>lt;sup>7</sup> D. C. Stockbarger and L. Burns, J. Opt. Soc. 23, 379 (1933).

TABLE I.

	23	$p_{2^0} - m^3 S_1$		231	$P_{1^0} - m^3 S_1$		281	$p_{0^0} - m^3 S_1$		Ave.			$\mu - \alpha \nu$		
<i>m</i>	λ	ν	$m^3S_1$	λ	ν	$m^{3}S_{1}$	λ	ν	$m^{3}S_{1}$	$m^3S_1$	<i>n</i> *— <i>n</i>	αν =	=(n*-n) <sub>ca</sub>	le. <sup>v</sup> cale.	$\nu_{\rm obs}$ . $-\nu_{\rm calc}$ .
$\begin{array}{r} 2\\ 3\\ 4\\ 5\\ 6\\ 7\\ 8\\ 9\\ 10\\ 11\\ 12\\ 13\\ 14\\ 15\\ 16\\ 17\\ 18\\ 10\\ 17\\ 18\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10$	5460.740 C 3341.478 C 2759.704 C 2759.704 C 2674.99 S 2625.24 S 2503.41 S 2551.35 2544.94 2529.53 2524.20 2519.91 2513.43 * 2519.91 2513.43 *	18307.5 29918.3 34173.4 36225.3 37372.5 38080.7 38548.0 38872.2 39106.3 39281.8 39521.1 39604.5 39672.1 39772.9 39772.9 39874.2 39874.2	21833.6 10222.8 5967.7 3915.8 2768.6 2060.4 1593.1 1268.9 1034.8 859.3 618.0 536.6 469.0 413.2 366.9 327.8 366.9	4358.342 C 2893.596 C 2576.290 C 2380.08 2340.589 C 2380.05 2315.21 2297.97 2285.66 2276.54 2269.61 2269.61 2256.44 * 2255.46 * 2255.47 * 2249.28 *	$\begin{array}{c} 22938.1\\ 34548.9\\ 38803.9\\ 40855.7\\ 42003.6\\ 42071.9\\ 43179.3\\ 43503.3\\ 43571.6\\ 43912.7\\ 44046.8\\ 44373.6\\ 44355.5\\ 44405.3\\ 44455.3\\ 44405.6\\ 44440.5\\ 644444.9\end{array}$	$\begin{array}{c} 21833.6\\ 10222.8\\ 5967.8\\ 3916.0\\ 2768.1\\ 12059.8\\ 1592.4\\ 1268.4\\ 1034.1\\ 859.0\\ 724.9\\ 619.9\\ 536.2\\ 468.3\\ 412.4\\ 366.1\\ 326.8 \end{array}$	4046.563 C 2752.775 C 2345.43 22345.43 2224.19 2224.19 2208.24 2196.86 2182.06 * 2182.06 * 2177.08 *	24705.4 36316.2 40571.2 42623.0 43771.1 44478.8 44946.2 45705.2 45505.2 45505.2 45507.9 45813.8 45918.6 46003.8	$\begin{array}{c} 21833.6\\ 10222.8\\ 5967.8\\ 3916.0\\ 2767.9\\ 2060.2\\ 1592.8\\ 1268.2\\ 1033.8\\ 859.1\\ 725.2\\ 620.4\\ 535.2 \end{array}$	$\begin{array}{c} 21833.6\\ 10222.8\\ 5967.8\\ 3915.9\\ 2768.2\\ 2060.1\\ 1592.8\\ 1268.5\\ 1034.2\\ 859.1\\ 620.1\\ 536.2\\ 468.7\\ 412.8\\ 366.5\\ 327.5\\ 327.5\\ \end{array}$	0.24189 .27636 .28814 .29937 .2961 .3982 .3003 .3010 .3020 .3021 .3029 .3059 .3013 .3059 .3013 .3059 .3038 .3038 .3038	0.06030 .02824 .01648 .0108 .0077 .0057 .0044 .0029 .0024 .0029 .0024 .0015 .0013 .0013 .0010 .0010	0.24432 .27639 .28814 .2938 .2970 .2989 .3002 .3011 .3018 .3023 .3026 .3029 .3031 .3033 .3035 .3036 .3037 .3036	$\begin{array}{c} 21783.9\\ 10222.6\\ 5967.8\\ 3915.7\\ 2767.4\\ 2059.7\\ 1592.8\\ 1268.5\\ 1034.0\\ 859.0\\ 725.0\\ 620.1\\ 536.4\\ 448.6\\ 412.8\\ 366.5\\ 327.5$	$\begin{array}{c} 49.7 \\ .2 \\ 0 \\ .3 \\ .4 \\ 0 \\ .2 \\ .4 \\ 0 \\ .2 \\ .1 \\ .1 \\ 0 \\ 0 \\ .1 \\ 0 \\ 0 \\ 0 \\ 1 \end{array}$
20	2507.08 *	39875.0	266.1							266.1	.3074	.0007	.3039	266.2	1

separate support and was not in contact with the slit. In this manner the mercury and copper spectra were exposed to the whole slit except for a narrow strip across the middle. Over this region a subsequent exposure was taken of the light from an arc using an iron anode and copper cathode. This arc was aligned as accurately as possible.

Measurements of the wave-lengths were carried out by using an interpolation formula with the constants and corrections determined from Burns' values of the wave numbers of the copper lines, and by using a linear interpolation between iron lines. Any shift between the mercury and iron lines could be determined by observing the position of the copper lines appearing in the two spectra. The wave-lengths so obtained are probably correct to within 0.01 or 0.02A for lines at 2500A or lower. The accuracy is not as high for the series around 3400A where the dispersion is less.

## RESULTS

To determine the term values of the states  $6sms^3S$  the three sharp series were measured and the average of the term values was obtained. The wave-lengths and wave numbers of the lines are given in Table I.

The term values can be calculated by subtracting from the limits  $2^{3}P_{2}^{0}$ ,  $2^{3}P_{1}^{0}$  and  $2^{3}P_{0}^{0}$ . If one uses the limits given by Fowler and calculates from a Rydberg table the value of  $n^{*}-n$ for each of the terms one obtains the curve A for the plot of  $n^{*}-n$  against  $\nu$  which reaches a value of 0.415 for the term  $20^3S_1$ . This departure from a straight line is difficult to explain on the basis of a perturbing term and is more probably due to an error in the value assigned to the limit. It was found that if the values of  $2^3P_{0, 1, 2}$  were increased by 2.8 cm<sup>-1</sup> the plot for the  ${}^3S_1$  terms is a straight line with variations no greater than the experimental error except for the first term. The same effect was found for the diffuse series. If Fowler's value of  $2^3P_2^0$  were used the values of  $n^*-n$  rose from -0.047 at  $6^3D_3$  to +0.23 at  $26^3D_3$ , whereas if the limit was increased by 2.8 the terms more nearly followed a Ritz formula.

In the following tables therefore the values of the  $2^3P^0$  terms are set at

## $2^{3}P_{2^{0}} = 40141.1, 2^{3}P_{1^{0}} = 44771.7, 2^{3}P_{0^{0}} = 46539.0.$

Table I contains the terms  $m^3S_1$  calculated from these limits. In column 11 is given the values of  $n^* - n$  obtained from a Rydberg table prepared by Miss J. MacInnes at Princeton. The next three columns are steps used in calculating the term value that would exactly fit a Ritz formula taken for two of the terms. The values of the slope of the line  $\alpha$  and the intercept  $\mu$  were calculated for the best straight line through the plotted points. The last column gives the difference between the observed and calculated term values.

The wave-lengths of the first few lines in each series are taken from Cardaun's<sup>8</sup> or Stiles'<sup>9</sup> measurements and are marked C or S. The other lines

<sup>&</sup>lt;sup>8</sup> L. Cardaun, Zeits. f. Wiss. Phot. 14, 56, 89 (1914).

<sup>&</sup>lt;sup>9</sup> H. Stiles, Astrophys. J. 30, 48 (1909).

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m	2³Ι λ	$D_{2^0} - m^3 D_1$	$m^3D_1$	2³ <i>I</i> λ	$p_{1^0} - m^3 D_1$	$m^3D_1$	2³Ι λ	$P_{0}^{0}-m^{3}D_{1}$	$m^3D_1$	Ave. <i>m</i> <sup>3</sup> <i>D</i> <sub>1</sub>	Calc. $m^3D_1$	$v_{\rm obs.} - v_{\rm calc.}$
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19	3662.878 C 3025.617 S 2805.33 2699.81 * 2640.65 * 2603.42 *	27293.2 33041.5 35636.0 37028.7 37858.2 38399.6	12847.9 7099.6 4505.1 3112.4 2282.9 1741.5	3131.546 C 2653.681 C 2482.721 C 2399.76 2352.65 * 2323.21 *	31923.9 37672.3 40266.2 41658.2 42492.2 43030.6	$\begin{array}{c} 12847.8\\ 7099.4\\ 4505.5\\ 3113.5\\ 2279.5\\ 1741.1 \end{array}$	2967.278 C 2334.771 C 2378.31 2302.06 2238.71 2231.55 2213.36 2200.58 2191.25 2184.21 2178.75 2174.49 2170.98 * 2163.87 * 2163.87 * 2162.23 *	$\begin{array}{r} 33691.1\\ 39439.4\\ 42033.8\\ 43426.0\\ 44259.4\\ 44797.9\\ 45166.1\\ 45428.3\\ 45621.8\\ 45883.4\\ 45973.4\\ 46047.6\\ 46108.4\\ 46157.8\\ 46198.9\\ 46234.0\\ \end{array}$	$\begin{array}{c} 12847.9\\ 7099.6\\ 4505.2\\ 3113.0\\ 2279.6\\ 1741.1\\ 1372.9\\ 1110.7\\ 917.2\\ 655.6\\ 565.6\\ 491.4\\ 430.6\\ 381.2\\ 340.1\\ 305.0 \end{array}$	$\begin{array}{c} 12847.9\\7099.5\\4505.3\\3113.1\\2279.6\\1741.1\\1372.9\\1110.7\\917.2\\770.2\\655.6\\565.6\\491.4\\430.6\\381.2\\340.1\\305.0\end{array}$	$\begin{array}{c} 12837.9\\ 7099.1\\ 4505.3\\ 3113.0\\ 2279.4\\ 1741.1\\ 1373.1\\ 1110.7\\ 916.9\\ 769.7\\ 655.3\\ 564.7\\ 491.6\\ 431.8\\ 381.9\\ 340.9\\ 305.9 \end{array}$	$ \begin{array}{r} 10.0 \\ .4 \\ 0 \\ .1 \\ .2 \\ 0 \\ -  0.2 \\ 0 \\ .4 \\ .5 \\ .3 \\ .9 \\ -  .2 \\ -  1.2 \\ -  .7 \\ -  .6 \\ -  .9 \\ \end{array} $

TABLE II.

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m	λ 231	$D_{2^{0}} - m^{3}D_{2}$	$m^3D_2$	23Η	$P_{1^{0}} - m^{3}D_{2}$	$m^3D_2$	2 <sup>1</sup> ] λ	$P_1 - m^3 D_2$	$m^3D_2$	Ave. $m^3D_2$	Calc. $m^3D_2$	$\nu_{\rm obs.} - \nu_{\rm cale.}$
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23	3654.833 C 3023.470 C 2804.44 2699.36 2640.15 * 2603.20 * 2578.59 * 2561.33 *	27353.3 330657.2 35647.2 37035.0 37865.5 38402.9 38769.3 39030.6	12787.8 7076.1 4493.9 3106.1 2275.6 1738.2 1371.8 1110.5	3125.663 C 2652.042 C 2482.008 C 2399.35 2352.41 2323.03 2289.62 2279.51 2271.90 2266.02 2261.36 2257.63 2257.63 2252.05 * 2254.94 * 2244.28 * 2244.28 * 2244.28 *	$\begin{array}{c} 31984.0\\ 37695.6\\ 40277.8\\ 41665.3\\ 42496.5\\ 4303.9\\ 43400.1\\ 43651.9\\ 43655.5\\ 44002.4\\ 44364.2\\ 44364.2\\ 44430.2\\ 44430.2\\ 44430.2\\ 44431.9\\ 44430.2\\ 44431.9\\ 44467.4\\ 44543.8\\ 44563.6\\ \end{array}$	$\begin{array}{c} 12787.7\\ 7076.1\\ 4493.9\\ 3106.4\\ 2275.2\\ 1737.8\\ 1371.6\\ 1109.8\\ 916.2\\ 769.3\\ 655.2\\ 5564.2\\ 491.3\\ 381.5\\ 339.8\\ 304.8\\ 304.8\\ 274.3\\ 249.1\\ 227.9\\ 208.1\\ \end{array}$	5769.60 C 4339.233 C 3901.899 C 3701.46 3591.01 3523.02 3478.04 3446.64 *	17327.4 23039.1 25621.4 27008.7 27839.4 28376.6 28743.7 29005.5	12787.8 7076.1 4493.8 3106.5 2275.8 1738.6 1371.5 1109.7	$\begin{array}{c} 12787.8\\ 7076.1\\ 4493.9\\ 3106.3\\ 2275.4\\ 1738.2\\ 1371.6\\ 1109.9\\ 916.2\\ 769.3\\ 655.2\\ 564.2\\ 491.3\\ 431.5\\ 381.5\\ 339.8\\ 304.8\\ 274.3\\ 249.1\\ 227.9\\ 208.1 \end{array}$	$\begin{array}{r} 12772.8\\ 7075.4\\ 4493.9\\ 3106.7\\ 2275.4\\ 1738.3\\ 1371.3\\ 915.7\\ 768.9\\ 654.7\\ 564.2\\ 491.2\\ 491.2\\ 491.2\\ 382.1\\ 382.1\\ 382.1\\ 326.7\\ 275.8\\ 2250.1\\ 227.8\\ 208.4 \end{array}$	$ \begin{array}{r} 15.0 \\ .7 \\ 0 \\4 \\ 0 \\1 \\ .5 \\ .6 \\ .5 \\ .4 \\ .5 \\ 0 \\ .1 \\ 0 \\6 \\9 \\9 \\9 \\1.5 \\ - 1.0 \\3 \\ \end{array} $

are newly measured and those marked with an asterisk have not previously been reported in the literature.

The plot of the weighted average of the term values of the  ${}^{3}S_{1}$  series against their values of  $n^{*}-n$  is shown in the graph. The points are on a straight line showing that the series follows a Ritz formula within the limits of the experimental error. This Ritz equation for the  ${}^{3}S_{1}$  terms is

$$\nu = R/[n+0.3046-2.762\times 10^{-6}\nu]^2$$

and as is often found the residual  $\nu_{obs.} - \nu_{calc.}$  is large for the first term.

The measurements of the diffuse series cannot be carried out with as great an accuracy as the sharp series due to the diffuse character of the higher series lines. The  ${}^{3}D_{1}$  series was determined to m = 19 from the  ${}^{3}P_{0}{}^{0} - m^{3}D_{1}$  lines although some of the first few terms were also obtained from the lines in the  ${}^{3}P_{1}{}^{0} - m^{3}D_{1}$  and the  ${}^{2}{}^{3}P_{2}{}^{0} - m^{3}D_{1}$  series. Table II gives the wave-lengths, wave numbers and term values for the  ${}^{3}D_{1}$  series. The last two columns give the calculated values on the basis of a Ritz formula and the difference between the observed and calculated term values. The constants of the Ritz equation  $\nu = R/(n + \mu + \alpha \nu)^{2}$ were  $\mu = -0.0585$  and  $\alpha = -1.390 \times 10^{-6}$ .

The  ${}^{3}D_{2}$  series has been extended by nine new terms to m=23. The terms up to m=10 were determined also with the aid of  $2{}^{3}P_{2}{}^{0}-m{}^{3}D_{2}$  lines and measurement of the  $2{}^{1}P_{1}-m{}^{3}D_{2}$  series, the  $2{}^{1}P_{1}$  term being also corrected by 2.8 cm<sup>-1</sup> and set at 30,115.2 cm<sup>-1</sup>. These are given in Table III and the constants used for the cal-

TABLE IV.

	23	$P_{2^0} - m^3 D_3$		0.1	
m	λ	ν	$m^{3}D_{3}$	Calc. $m^{\circ}D_{3}$	$\nu_{\rm obs.} - \nu_{\rm calc.}$
3	3650.146 C	27388.4	12752.7	12744.6	8.1
4	3021.499 C	33086.5	7054.6	7054.6	0
5	2803.48	35659.5	4481.6	4481.5	.1
6	2698.83	37042.2	3098.9	3098.9	0
7	2639.80	37870.4	2270.7	2270.4	.3
8	2602.97	38406.2	1734.9	1735.3	4
9	2578.39	38772.3	1368.8	1368.8	0
10	2561.15	39033.3	1107.8	1107.4	.4
11	2548.53	39226.6	914.5	914.3	.2
12	2539.07	39372.7	768.4	767.8	4
13	2531.72	39486.9	654.2	654.8	6
14	2525.94	39577.3	563.8	563.5	.3
15	2521.27	39650.6	490.5	490.7	2
16	2517.49	39710.1	431.0	431.1	1
17	2514.37	39759.4	381.7	381.7	0
18	2511.76	39800.6	340.5	340.4	.1
19	2509.54	39836.0	305.1	305.4	3
20	2507.64	39866.2	274.9	275.6	7
21	2506.08	39890.9	250.2	249.9	.3
22	2504.71*	39912.7	228.4	227.7	.7
23	2503.46 *	39932.6	208.5	208.3	.2
24	2502.35 *	39950.4	190.7	191.2	5
25	2501.47 *	39964.4	176.7	176.2	.5
26	2500.57 *	39978.8	162.3	162.9	6
				1	

culated term value are  $\mu = -0.0529$  and  $\alpha = -1.247 \times 10^{-6}$ .

Table IV gives the series  $m^3D_3$  to m = 26, the constants of the Ritz equation being  $\mu = -0.0440$  and  $\alpha = -1.695 \times 10^{-6}$ .

The plots of the term values against  $n^* - n$  for the  ${}^{3}D_{1, 2, 3}$  series are shown in Fig. 2. The points for the high terms are seen to fall off the straight line representing the Ritz equation more often than in the case of  ${}^{3}S_{1}$  series. The decreased accuracy in the wave-lengths of the diffuse lines is not sufficient, however, to account for these deviations. At about 800  $cm^{-1}$  there is a dip in the curve with a subsequent rise at about 500 cm<sup>-1</sup>. The reality of these small deviations is confirmed by the fact that the separate series are calculated from lines in quite different parts of the spectrum. The deviations are small and they occur in each of the component 3D series at about the same place. There is no obvious cause for such a perturbation.

Measurements were also carried out on the  $2^{1}P_{1}-m^{1}S_{0}$  and the  $2^{3}P_{1}^{0}-m^{1}S_{0}$  series. The wave-lengths, wave numbers and term values are collected in Table V which also contains the calculated term values on the basis of a Ritz formula. The small difference between observed and



FIG. 2. Plot of  $n^* - n$  for the terms of the S and D series.

m	λ	$2^{1}P_{1} - m^{1}S_{0}$	$m^1S_0$	λ	$2^{3}P_{1^{0}} - m^{1}S_{0}$	$m^1S_0$	Ave. $m^1S_0$	Calc. $m^1S_0$	$\nu_{\rm obs.} - \nu_{\rm calc}$
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	$\begin{array}{c} 10139.75\\ 4916.036\ C\\ 4108.082\ C\\ 3801.665\ S\\ 3558.73\ *\\ 3502.00\ *\\ 3436.15\ *\\ 3436.15\ *\\ 3436.15\ *\\ 3436.78\ *\\ 3371.73\ *\\ 3365.49\ *\\ \end{array}$	9859.5 20335.9 24335.4 26296.8 28091.9 28547.0 28864.1 20094.0 29265.9 29397.5 29500.7 29582.3 20649.9 29704.8	$\begin{array}{c} 20255.7\\ 9779.3\\ 5779.8\\ 3818.4\\ 2023.3\\ 1568.2\\ 1251.1\\ 1021.2\\ 849.3\\ 717.7\\ 614.5\\ 532.9\\ 465.3\\ 410.4\\ \end{array}$	4077.828 C 2856.938 C 2563.88 2441.10 2376.77 * 2338.55 * 2313.88 * 2297.03 *	24516.0 34992.3 38991.8 40952.6 42061.0 42748.5 43204.1 43521.0	20255.7 9779.4 5779.9 3819.1 2710.7 2023.2 1567.6 1250.7	$\begin{array}{c} 20255.7\\ 9779.3\\ 5779.8\\ 3819.1\\ .2710.7\\ 2023.3\\ 1567.9\\ 1250.9\\ 1021.2\\ 849.3\\ 717.7\\ 614.5\\ 532.9\\ 465.3\\ 410.4 \end{array}$	$\begin{array}{c} 20201.4\\ 9778.8\\ 5779.8\\ 3819.5\\ 2710.3\\ 2023.3\\ 1558.2\\ 1250.9\\ 1021.2\\ 849.3\\ 717.7\\ 614.2\\ 531.6\\ 464.7\\ 409.7 \end{array}$	$54.3 \\ .5 \\4 \\ .4 \\3 \\ 0 \\ 0 \\ 0 \\ .3 \\ 1.3 \\ .6 \\ .7 $

TABLE V.

TABLE VI.

	21	$P_1 - m^1 D_2$		23F	$D_{2^0} - m^1 D_2$		23F	$P_{10} - m^1 D_2$				
т	λ	ν	$m^1D_2$	λ	ν	$m^1D_2$	λ	ν	$m^1D_2$	Ave. $m^1D_2$	Calc. $m^1D_2$	$\nu_{\rm obs}, -\nu_{\rm calc}.$
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	$\begin{array}{c} 5790.66 \\ c\\ 4347.500 \\ c\\ 3906.399 \\ c\\ 3704.217 \\ c\\ 3592.74 \\ 3524.27 \\ 3424.26 \\ s\\ 3447.27 \\ 3424.26 \\ s\\ 3406.99 \\ s\\ 3393.71 \\ s\\ 3333.30 \\ s\\ 3333.30 \\ s\\ 33374.93 \\ s\\ 3362.71 \\ s\\ 3357.69 \\ s\end{array}$	$\begin{array}{c} 17264.4\\ 22995.3\\ 25591.9\\ 26988.6\\ 27826.0\\ 28366.6\\ 28736.4\\ 29000.1\\ 29195.0\\ 29343.0\\ 29343.0\\ 29457.8\\ 29548.5\\ 29621.8\\ 29621.8\\ 29621.8\\ 29621.8\\ 29621.8\\ 29729.4\\ 29773.8\\ \end{array}$	$\begin{array}{c} 12850.8\\ 7119.9\\ 4523.3\\ 3126.6\\ 2289.2\\ 1748.6\\ 1378.8\\ 1115.1\\ 920.2\\ 772.2\\ 657.4\\ 556.7\\ 493.4\\ 433.8\\ 385.8\\ 385.8\\ 341.4 \end{array}$	3663.276 C 3027.483 C 2806.74 2700.80 2641.08 2603.82 2579.01 2561.61 *	27290.2 33021.2 35618.0 37015.1 37852.0 38393.7 38763.0 39026.3	$\begin{array}{c} 12850.9\\7119.9\\4523.1\\3126.0\\2289.1\\1747.4\\1378.1\\1114.8\end{array}$	3131.837 C 2655.127 C 2483.829 C 2400.51 2353.18 * 2323.56 * 2303.78 * 2289.88 *	31920.9 37651.8 40248.4 41645.1 42482.7 43024.1 43393.6 43656.9	12850.8 7119.9 4523.3 3126.6 2289.0 1747.6 1378.1 1114.8	$\begin{array}{c} 12850.8\\7119.9\\4523.2\\3126.4\\2289.1\\1747.9\\1378.3\\1114.9\\920.2\\772.2\\657.4\\566.7\\493.4\\433.8\\385.8\\341.4\end{array}$	$\begin{array}{c} 12763.8\\ 7114.0\\ 4523.2\\ 3126.5\\ 2289.1\\ 1747.9\\ 1378.3\\ 1114.4\\ 919.8\\ 772.0\\ 657.2\\ 566.1\\ 492.8\\ 432.9\\ 383.2\\ 384.6 \end{array}$	$\begin{array}{c} 87.0\\ 5.9\\ 0\\ - & .1\\ 0\\ 0\\ 0\\ .5\\ .4\\ .2\\ .2\\ .6\\ .6\\ .9\\ 2.6\\ - & .2\end{array}$

calculated values, as well as the plot shown in Fig. 2, indicates that the  ${}^{1}S_{0}$  terms can well be represented by a Ritz formula. The constants are  $\mu = 0.3679$  and  $\alpha = -1.835 \times 10^{-6}$ .

The  ${}^{1}D_{2}$  terms were obtained by measuring the  ${}^{21}P_{1}-m{}^{1}D_{2}$ ,  ${}^{2^{3}}P_{2}{}^{0}-m{}^{1}D_{2}$  and  ${}^{2^{3}}P_{1}{}^{0}-m{}^{1}D_{2}$  series. These are collected in Table VI. The attempt to fit these values to a Ritz equation again showed deviations of the order of those found in the  ${}^{3}D$  series. The straight line through the  ${}^{1}D_{2}$  terms has a positive slope and misses the first term by a considerable amount. It is difficult to put the line through the second term without getting the other points all off. The Ritz equation which best fits the set of terms has constants  $\mu = 0.9218$  and  $\alpha = 8.071 \times 10^{-7}$ .

The list below contains a number of lines, not belonging to the sharp or diffuse series, which were measured in the course of the work. Some of these lines have not been identified and in every case the intensity of the line was weak.

2478.64	40332.5	$2^{3}P_{1}^{0}-5^{3}F_{2}^{0}$
2402.48	41610.9	•. •
2401.19	41633.3	
2397.80	41692.1	$2^{3}P_{1}^{0}-6^{3}F_{2}^{0}$
2384.92	41917.4	
2380.72	41991.2	
2376.20	42071.2	•
2375.29	42087.2	
2374.62	42099.2	$2^{3}P_{0}^{0} - 5^{3}F_{2}^{0}$
2351.56	42512.0	$2^{3}P_{1}^{0} - 7^{3}F_{2}^{0}$
2322.52	43043.5	$2^{3}P_{1}^{0} - 8^{3}F_{2}^{0}$
2300.30	43439.2	$2^{0}P_{0}^{0} - 0^{0}P_{2}^{0}$
4400.94	44010.2	$2^{-1} 0^{-1} 0^{-1} 0^{-1} 1^{-2}$

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