THE ZEEMAN EFFECT IN THE ANGSTROM CO BANDS. II

By F. H. Crawford

Abstract

This paper is a continuation of the work previously reported in this Journal (Phys. Rev. **30**, 438 (1927)). *Experimental Improvements.* The former source for the CO spectrum has been replaced by a Pyrex *discharge tube* placed longitudinally in the field. By special construction and the use of a forced-draft cooling system it has been possible to increase the intensity of the source about fourfold and to eliminate impurity bands previously the source of much trouble. *Field strengths* were determined from the Zeeman triplet (five-halves normal) of the W λ4660 line. This pattern could be obtained with great sharpness from a brass-tungsten intermittent arc operating in the open air and was standardized against Zn lines in vacuo. Its magnitude between 15000 and 28000 gauss was proportional to the field within ±0.4 percent. The Hg lines λ4047 and 4358 were used as field standards in later parts of the work. *Results.* Observations of the Zeeman effect have been extended from the bands at λλ5610, 5198 and 4835 to include λλ4511 and 4394. Measurements on thirty patterns with M (the ordinal number of the line in a branch) $=1$, for fields from 18000 to 36000 gauss, have shown the widths of the Zeeman patterns to be proportional to the field strengths to within 2 percent, the estimated accuracy of measurement. The weighted average of the pattern widths for $M=1$ is 97.7 percent $\Delta\nu_n$ and $M=2$, 66.3 percent $\Delta\nu_n$, where $\Delta\nu_n$ is the normal Lorentz triplet half-width. The quantum mechanics predicts 100 percent $\Delta\nu_n$ and 66.7 percent $\Delta\nu_n$ for these widths respectively as against 88.9 percent and 64 percent on the old quantum theory. Thirteen out of the possible eighteen patterns predicted for the first two lines of the $P, Q,$ and R branches have been resolved and measured and found to agree with predictions within the error of measurement. The intensity asymmetries reported previously and later treated theoretically by Kronig (Phys. Rev. **31**, 195 (1928)) have been found wherever comparison in both high and low fields was possible to behave qualitatively (though *not quantitatively*) as Kronig's calculations predict. Eight isolated lines ($M=23$ to $M=35$) in four bands have been found which show anomalously large Zeeman effects. Three (and possibly four) new bands have been observed which from their behavior in the magnetic field must belong to the Angstrom group. Their analysis is reserved for another paper.

I. General

In a previous paper[1] a theoretical account of and experimental results for the Zeeman effect in three of the Angstrom bands of carbon-monoxide are given. As was there pointed out the qualitative features of the Zeeman effect in band lines as predicted by the conventional quantum theory[2] and the quantum mechanics[3] are the same. Each predicts that the Zeeman pattern for electronic transitions of the type $^1S \rightarrow {}^1P$ (to which type these

[1] E. C. Kemble, R. S. Mulliken and F. H. Crawford, Phys. Rev. **30**, 438 (1928). This will hereafter be referred to as Part I.

[2] E. C. Kemble, Phys. Rev. **27**, 799A (1926); "Molecular Spectra in Gases," National Research Council Bulletin 57, Chap. VII; H. A. Karmers and W. Pauli, Jr., Zeits. f. Physik **13**, 35 (1923).

[3] J. H. Van Vleck, Phys. Rev. **28**, 980 (1926); D. M. Dennison, Phys. Rev. **28**, 318 (1926).

bands belong[4]) will be symmetrical about the position of the original line, will be of the same magnitude for corresponding lines in different branches and will be of the greatest magnitude for the first line in a branch. The patterns will then decrease uniformly in size with the serial number M of the line in the branch, the number of components in each pattern being $(2M+1)$. As a matter of fact the total pattern-width, $\Delta\nu$, in cm^{-1} is

$$\Delta\nu = \frac{2}{(M+1+1/4M)} \cdot \Delta\nu_n \tag{1}$$

on the old theory, and

$$\Delta\nu = \frac{2}{(M+1)} \Delta\nu_n \tag{2}$$

on the quantum mechanics.[4a] Here as before $\Delta\nu_n$ is the half-width of the normal Zeeman triplet. From these it appears that the predictions for $M>2$ differ by one percent or less and hence are incapable of experimental differentiation. For $M=1$ the results, however, differ by 11.1 percent and for $M=2$ by 2.7 percent. Consequently although there is no doubt about the fundamentally greater soundness of the quantum-mechanics treatment it seemed highly desirable to discover which was in closer agreement with experimental facts. In Part I the small number of good plates available gave average values falling midway between the two predictions. The results of recent measurements on some thirty Zeeman patterns of lines with $M=1$ fall distinctly nearer the value calculated from (2) [as do those for $M=2$, though the number of trustworthy measurements for the latter case is only 3.]

In Part I likewise theoretical *intensities*[5] of the components in the Zeeman patterns were given and were found to agree in general with the visually estimated intensities in the resolved patterns and with the general size and appearance of the patterns for the higher lines where complete resolution was not possible. There remained nevertheless certain small but distinct departures from the theoretical intensities for the P and Q line patterns (see Part I, page 453) which were later shown by Kronig,[6] to be due to the perturbing action of the high magnetic fields. The very satisfactory agreement of the predicted perturbations with the observed intensities and the

[4] R. S. Mulliken, Phys. Rev. **28,** 482 (1926).

[4a] Eqs. (1) and (2) here correspond to Eqs. (6) and (7) in Part I (page 443). Unfortunately Eq. (6) is incorrectly printed both there and in Fig. 6 (page 455). The quantity to be added to $(M+1)$ in the denominator of Eq. (6) is $1/4M$ and *not* $M/4$.

[5] The intensity of the components in a Zeeman pattern were found by combining the formulas deduced for line spectra from the summation rule by Kronig [R. deL. Kronig, Zeits. f. Physik **31,** 885 (1925)] and Hönl [H. Hönl, Zeits. f. Physik **31,** 340 (1925)] with those deduced by Hönl and London [H. Hönl and F. London, Naturwiss. **13,** 756 (1925); Zeits. f. Physik **33,** 803 (1925)] for the relative intensities of the unperturbed lines. These combination formulas are in harmony with those obtained by Dennison (see footnote 3) from the matrix mechanics. Obviously these formulas are strictly valid only for small fields as Kronig later showed (footnote 6).

[6] R. deL. Kronig, Phys. Rev. **31,** 195 (1928).

disappearance of the effect at lower fields will be discussed in detail in the sequel.

The interpretation of the photographs on which the conclusions of Part I are based was in many cases rendered difficult by the faintness of the early lines and the presence of a faint background of impurity lines. Due to the lengths of exposure required (15 to 40 hours) a no-field comparison photograph was taken with only one set of plates. Consequently the positive interpretation of the results necessitated very minute examination and careful comparison of all of the plates. Every line appearing near the head of each band was measured on every available plate, the intensity of each line being estimated visually, and the results thus collected were compared with the data from the no-field exposure. By this laborious process it was possible to distinguish impurity lines from Zeeman effect components by the fact that they were either (1) not present regularly on all of the plates, or (2) were characteristically different in physical appearance from Zeeman components about which there was no doubt, or (3) showed at most only a broadening in the field with no relative displacement in different fields. Results obtained from later photographs, where, due to greater intensity, entirely different modes of excitation, and elimination of many impurity lines (bands!) these sources of ambiguity have been pretty largely removed, have not in any case been in disagreement with the conclusions arrived at in Part I.

The general questions which earlier work left unsettled or in a state such that more evidence was desirable were the following: 1 The proportionality of pattern-width to field strength, 2 The nature of the patterns for the lines $R(1)$, $R(2)$, and $Q(2)$, 3 The behavior of the perturbed intensities with different fields and 4 The nature and occurence of the anomalously large Zeeman patterns in higher lines ($M>23$ usually). In addition it was hoped to extend the observations to the other strong bands ($\lambda\lambda$4511, 4394 and 4123) of the Angstrom group where previously impurities had rendered observation quite impossible.

II. Experimental Details and Improvements

For all of these questions greater intensity and the elimination of as many impurity lines as possible were seen to be quite necessary. Since 30-hour exposures with the Back vacuum box[7] gave only the first order with usable intensity, it seemed inadvisable by prolonging the time to obtain a higher order photograph (quite aside from the physical strain of tending the apparatus over such protracted intervals, unavoidable temperature fluctuations—due to sudden changes in the weather—and the cumulative effect of small jars and vibrations in the building seemed to place a practical limit on the length of exposure.). Actually a 45-hour run with the Back box gave poorer results than some of the shorter ones. Hence it was decided that other methods must be devised which would be more suitable for exciting

[7] See Part I, page 445.

gaseous molecular spectra than the Back box with high-tension electrodes. (This type of source was designed primarily for exciting metallic lines and for such is probably unequalled. For gaseous spectra, however, the discharge spreads through too great a volume to be very brilliant.).

Giving up the Back box necessitated two things—first, a new source where the discharge was sufficiently confined to give greater intensity than before and second, another method of determining the field strength.

Excitation of the CO spectrum. The requirements for the new source were two and these were mutually somewhat conflicting. It was necessary to obtain a great increase in photographic intensity and at the same time effect a reduction in the undesired band spectra excited. The attainment of the first requirement was limited in practise by the necessity of keeping down the mean effective temperature in the discharge since high temperatures favor the production of the lines of high rotational quantum number (j''-value)[8] as against the earlier lines in the branch.[9] The attainment of the second requirement was limited by the practicable limits of chemical purification of the carbon-dioxide and the appearance after long exposures

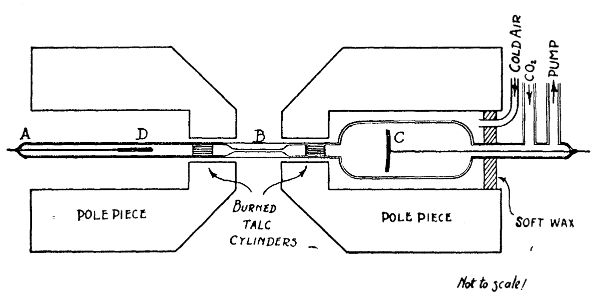

Fig. 1. Discharge tube in magnet.

of a background of very fine lines. These extended from the mass of ultraviolet bands of Deslandres and d'Azambuya to the limits of photographic sensitivity of the plates in the red. The enormous number and closeness of the lines, (often 10 or 15 per Angstrom) together with no very obvious structural regularities suggest that the CO_2 molecule is possibly the origin. Attempts to test this by using CO for the discharge rather than CO_2 were not decisive.

Several types of discharge tubes were tried including quartz tubes having the capillary perpendicular to the field. In all cases the heavy current required soon ruptured the walls or at least rendered them quite opaque. Consequently a Pyrex tube placed along the axis of the magnet was eventually resorted to. A great number of various designs were used of which that in Fig. 1 was the most successful. This figure shows the tube in place in the magnet.

[8] In these bands the M-value of the line and the final rotational quantum number, j'' (in the quantum mechanics) are the same.

[9] See R. S. Mulliken, Phys. Rev. **29,** 411 (1927).

The following points regarding the design and operation of the tube are to be noted:

1. The seals for the electrode are placed as far from the discharge end of the electrode as possible (10 to 15 cm is usually sufficient). This prevents the softening of the seal and development of slow leaks.[10] 2. Use of fine capillary at *B* (Fig. 2). Thermometer capillary of internal bore 0.3 to 0.5 mm gave the most brilliant discharge. 3. Use of massive tungsten electrode at *C* having large surface area. This minimized the oxidation so troublesome when a single heavy wire was used. The oxide so formed diffused slowly down the tube and deposited in the capillary rendering its walls fairly opaque after a few hours operation. 4. Placing perforated cylinders of talc on either side of capillary to catch small amounts of oxide diffusing from electrode. These cylinders of talc were bored longitudinally with 8 or 10 half millimeter holes and baked at 950°C for 5 hours or so before being placed in the discharge tube. They acted as effective traps for the tungsten oxide without increasing too greatly the resistance of the tube to the discharge. The tube could be run continuously for 40 hours before it was necessary to cut out the capillary and replace it with a fresh one.[11] 5. Cooling of tube by air blast. When the maximum discharge from a half kilowatt transformer was sent through the tube—confined in its small hole in the magnet—the glass usually softened at some point or other in 10 or 15 minutes. When, however, a blast of cool air was blown continuously through the annular space around the tube this was entirely prevented.

This source is at least 4 times as intense photographically as the one described in Part I (page 445), requires less attention during operation and gives a spectrum almost entirely free from N_2 bands (minute leaks in the Back box made it difficult to keep small amounts of air out of the discharge). Of course, since the capillary was horizontal and the slit of the grating vertical it was necessary to rotate the image of the former through 90°. This was accomplished in the well-known way by using a large-faced 45° prism between the focussing lens and the slit, the plane of the largest face being parallel to the optic axis of the lens, the 90°-edge of the prism lying in a vertical plane and making an angle of 45° with the slit of the grating.

Field-strength determinations. The monumental work of Back and Landé of the Zeeman effect in line spectra necessitated, of course, the development of a method and technique for measuring fields of all sizes with high precision. All requirements seemed to be met by the vacuum arc between wobbling zinc electrodes developed by them[12] and used previously by us (cf Part I, 447). There appeared, however, to be no obvious way of adapting such a vacuum metallic arc to the magnet set up for use with a glass discharge tube.

[10] It is quite necessary to prevent all access of air since the nitrogen band spectrum is excited so strongly in this type of tube that in 5 minutes it can ruin a 24-hour CO photograph.

[11] This was very important since it was quite necessary not to disturb the optical system until both the exposure without field (10 hours or so) and that with field (25 to 30 hours) had been completed.

[12] Cf. Back and Landé, Zeemaneffekt u. Multiplettstruktur, page 124.

Preliminary experiments with a self-interrupting arc[13]—see Fig. 2—showed that this would be suitable at least for high fields. The device is placed between the poles of the electromagnet and a current of 3 to 8 amperes sent through in such a direction that the ponderomotive force acting on the arm A causes it to turn (upward) on a pivot at O, thus drawing the current out into a momentary arc at B. The weight of A then causes it to drop, and the process is repeated. In order to obtain the zinc triplet (λλ4680, 4722, 4810) with sufficient intensity, it is necessary to connect a capacity (5 to 20 microfarads) across the gap. But under these circumstances the lines are diffuse and quite unsuited for accurate measurement. If now a large inductance (10 to 30 millihenrys) is connected in series with the capacity, the lines are greatly sharpened.[14] By varying current, capacity inductance and frequency of interruption (by adjusting the counterpoise C—Fig. 2) the lines could be obtained sufficiently sharply for the field to be determined to less than a percent (from second order photographs). This method was not, however, entirely satisfactory, due to the rapid burning away of the brass with the consequent forming of a crater of oxide on the lower electrode. After the arc had run for 10 minutes, the lines were much less sharp than when first started.

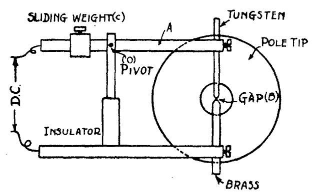

Fig. 2. Self-interrupting arc.

Fortunately there always appeared on the zinc plates an extremely sharp Zeeman triplet, identified as that of the tungsten line at λ4660. The components of this triplet are as sharp as those obtained from a zinc arc in vacuo and in addition, the total width of the triplet is $5\Delta\nu_n$. The accurate proportionality of the pattern of the tungsten line was proved by standardization against zinc patterns in vacuo and held within less than ± 0.4 percent for fields between 15,000 and 28,000 gauss. In later parts of the work a special discharge tube for mercury was made and the patterns of the lines of the spectroscopic triplet λλ4047, 4358 and 5461 were used.[15] The first two lines were obtained in both first and second orders of the grating in a 5 minute exposure and gave values for the field differing from one another by not over 0.3 percent.

III. Results

1. Proportionality of pattern width to field strength. Since the general simplicity and regularity of the CO Angstrom bands gives every reason for supposing that the molecule is very rigid, it appeared desirable to show that the consequent predicted linearity of the Zeeman effect with field was actually observed. In Part I this approximate linearity was established from measurements on the $P(1)$ and $Q(1)$ patterns of λ5610 and λ5198 at fields

[13] Due in principle to Professor H. Crew.

[14] C. R. Helmsalech, **152,** 1007 (1911); **152** 1086 (1911); and many others before and since.

[15] See Gmelin, Ann. d. Physik **29,** 1079 et seq. (1909); Runge and Paschen, Ann. d. Physik (IV) **39,** 897 (1912).

of 36,000 and 25,000 (5 individual measurements). In the course of investigating the other bands of the series, data have been obtained on fields of 28,000 and 19,000 to 21,000 from five different bands and a dozen or so different plates, (all told some 30 individual measurements). These data together with those previously obtained are summarized in Table I where

TABLE I.

Band	Line	Plates used	$\Delta\nu$ observed (cm^{-1})	Average field (gauss)	$\Delta\nu_n$ (cm^{-1})	$\frac{\Delta\nu}{\Delta\nu_n}$ (percent)
λ5610	Q(1)	5	0.887	19,670	0.924	96.0
	Q(1)	1	1.088	24,400	1.147	94.8
	Q(1)	1	1.272	28,050	1.319	96.5
	Q(1)	2	1.546	34,900	1.641	94.2
	P(1)	2	.916	19,880	.934	98.1
	P(1)	1	1.104	24,400	1.147	96.1
	P(1)	1	1.300	28,050	1.319	98.5
	Q(2)	2	.616	19,650	.923	66.7
	Q(2)	1	.853	28,050		64.7
5198	Q(1)	4	.902	19,950	.937	96.2
	Q(1)	1	1.084	24,400	1.147	94.4
	Q(1)	1	1.287	28,050		97.5
4035	Q(1)	3	(.76)	19,300	.907	(84)±10
4511	Q(1)	4	.919	19,780	.929	97.9
	P(1)	2	.962	19,690	.925	104
	R(1)	3	.939	19,800	.930	101
4394	Q(1)	2	.79	19,300	.907	87

the total pattern widths are expressed in percent of $\Delta\nu_n$ as well as in inverse cm for the field in question. In Fig. 3 these pattern widths (expressed in cm^{-1}) are plotted against field strength for $M=1$ and $M=2$. In both cases the upper and lower straight lines represent the predictions respectively of Eq. (2) and (1). While the observed points fall in general somewhat below the upper curve they certainly lie closer to it than to the lower one. In fact the weighted average (weighted only according to actual size of pattern being measured on plate) of all determinations[16], for $M=1$ (expressed in percent of $\Delta\nu_n$) is 97.7 percent ($\pm 2.$ percent) and for $M=2$, 66.3 percent (± 1.4 percent). Eq. (2) and (1) give for $M=1$, 100 percent and 88.9 percent respectively and for $M=2$, 66.7 percent and 64.0 percent respectively. Hence the experimental results are described more satisfactorily by the quantum mechanics (i.e. by Eq. (2) of this paper).[16a]

[16] I have not included in this average the values from the band λ4835. The grating did not seem to be so accurately in focus for this region in the II order. The combination of faintness and lack of focus rendered quantitative measurements untrustworthy.

[16a] It should be pointed out that on the quantum mechanics high fields produce a *second order* perturbation in the energy levels (and hence pattern widths) which is associated with a *first order* perturbation in the transition probabilities (and hence intensities of components). The latter effect is that calculated by Kronig and found to agree qualitatively with observation. It is possible that the tendency for the patterns for $M=1$ to depart more from 100

2. *Nature of patterns for lines R(1), R(2) and Q(2).* As a result of the increased intensity and reduction of impurities it has been possible to resolve and measure 13 out of the possible 18 characteristic patterns predicted for the six lines, $P(1)$, $Q(1)$, $R(1)$, $P(2)$, $Q(2)$ and $R(2)$ [counting no polarization, parallel polarization and perpendicular polarization as 3 separate cases (see Fig. 1, Part I, page 444).] The other five patterns, viz. $\sigma \cdot \pi R(2)$, $\sigma \cdot R(2)$, $\pi \cdot R(2)$, $\sigma \cdot Q(2)$ and $\sigma \cdot \pi P(2)$, had in each case the calculated over-all width and the expected intensity distribution. (Here as before σ refers to the part

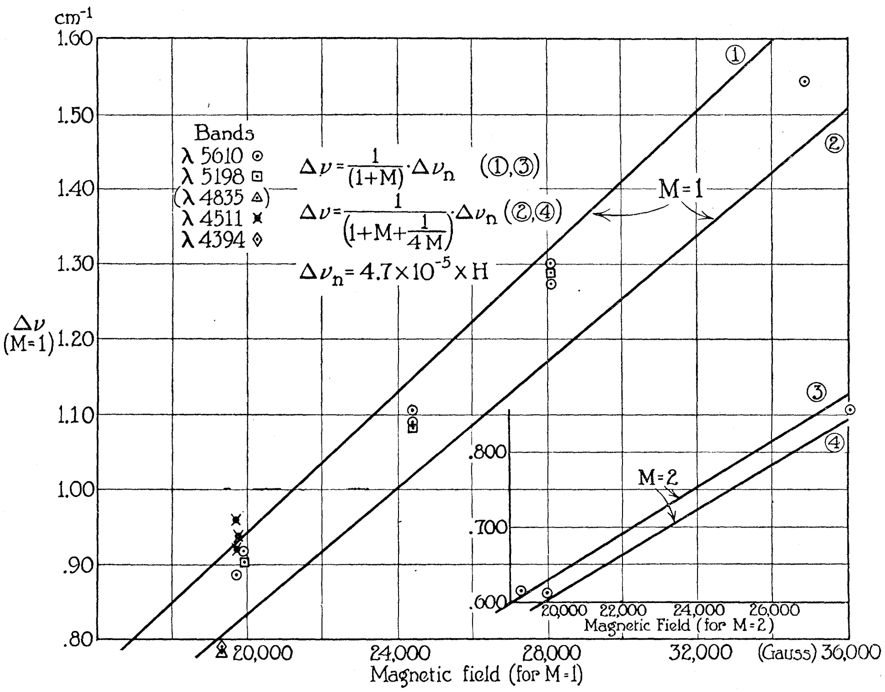

Fig. 3. The observed widths of Zeeman patterns (in cm^{-1}) are plotted against field strength for the cases of $M=1$ and $M=2$ from the data of Table I. Most of the points represent the average of measurements on from two to five different plates. The measurements for $M=2$ were made only on patterns actually resolved and represented the widths between the extreme components of the quintette patterns. In general the measurements on the Q lines of $\lambda 5610$ are the most trustworthy.

of the pattern observed in perpendicular polarization, π that observed in parallel polarization and $\sigma \cdot \pi$ when no polarizing prism was used.) In particular the $\sigma \cdot \pi R(2)$ patterns were uniformly broad bands showing *no* tendency

percent $\Delta \nu_n$ at *high fields* than at low fields is due to the existence of this second order effect. Two accurate measurements on $Q(1)$ at $H=35,000$ give a width of 94.2 percent $\Delta \nu_n$ against 98 percent for the patterns measured around 20,000 gauss. Many more measurements at the high field, however, would be required before this could be taken as definitely ascertained.

to lightness in the center as previously reported from one plate. This has been confirmed on four plates.

The $R(1)$ pattern has been obtained on four (and possible five) plates and as was expected had the same general appearance in both polarizations.

The resolution of the $Q(2)$ line into its quintette patterns was definitely obtained on two recent plates (λ5610 band). On the λ5610 plate on which this pattern was previously found to be resolved the intensity was so small that there was always the bare possibility that the line identified as the $\pi Q(2)_{+1}$ component might have been simply part of the very faint fringe usually found near the edge of a strong line (in this case $P(9)$, a line about 15 times as intense as the above Zeeman component). Resolution of the pattern for both parallel polarization and no polarization definitely removes this doubt (particularly when taken along with the quantitative agreement of the size of the pattern with the prediction for the lower field).

The higher lines ($M>2$) have been re-examined and as previously reported confirm all details of the theory. In particular the "Q-doublets" (parallel polarization) on second order photographs have been traced as far as $Q(14)$ for λ5610, $Q(11)$ for λ5194, $Q(10)$ for λ4835 and $Q(11)$ for λ4511.

3. Intensity perturbations for Zeeman components. In Part I the fact that the "Q-doublets" (parallel polarization) and presumably[17] the "P-doublets" (perpendicular polarization) were unsymmetrical in intensity was particularly emphasized. According to the simple theory, the intensities as well as the displacements should be symmetrical in parallel and perpendicular polarization whereas actually in parallel polarization the components of the Q patterns are more intense on the low-frequency side (i.e. on the side towards the band head). Recently Kronig[18] has shown on the basis of the quantum mechanics that this is precisely what is to be expected at high fields and that the intensity relations contained in Eqs. 8A to 10B inclusive (Part I, page 444) are in reality strictly true only for the limiting case of zero field strength. Kronig calculates the perturbative effect of the field on the normal transition probabilities for transitions from the upper magnetically insensitive state, ^1S, to the lower magnetically subdivided state, ^1P. He finds to a first approximation that the relative changes in the normal intensities (i.e., those calculated for the limiting case of $H=0$) are directly proportional to the field strength and are of such a nature that the decrease in intensity for a given Zeeman component on one side of the undisplaced line is added to the original intensity of the symmetrically situated component on the other side of the line. Thus, if j[19] and r are final rotational and magnetic quantum numbers respectively and I' and I'' are moments of inertia characteristic of the ^1S and ^1P, electronic states of the molecule, the expression giving the *relative change* in the intensity of a Zeeman component

[17] Only $P(1)$ could be observed due to the presence of so many other lines.

[18] R. de L. Kronig, Phys. Rev. **31**, 195 (1928).

[19] This is a rotational quantum number in the new mechanics and for the case in hand is $\frac{1}{2}$ unit lower than those in which the formulas of Part I are expressed.

of a line of the Q branch (for which ordinal number, M, of line is numerically equal to the value of j) in parallel polarization is:

$$\epsilon_z(l'jr\ ;\ l''jr)=\frac{8\pi^2\mu_1 I''H}{h^2}\,\frac{(j^2-1)(j^2-r^2)}{j^2(2j-1)(2j+1)r}+\frac{j(j+2)[(j+1)^2-r^2]}{(j+1)^2(2j+1)(2j+3)r} \tag{3}$$

(Here the subscript z refers to the direction of the magnetic field, H.) In this expression μ_1 is the value of the Bohr magneton $eh/m4\pi$. The coefficient can conveniently be written as $K\Delta\nu_n$, where $\Delta\nu_n$ is the normal Zeeman half-width for field H and K is 0.635. Now we see that for negative r's the expression is negative, and for positive r's, positive.[20] In other words, the low-frequency components have their relative intensities increased, while the high-frequency ones have theirs decreased. Moreover, as j gets larger and larger, the effect tends to vanish.

The expression for the P branch in parallel polarization is:

$$\epsilon_z(l'jr\ ;\ l_1''j+1r)=-\frac{8\pi^2\mu_1 I''H}{h^2}\,\frac{r}{(j+1)^2} \tag{4}$$

where the transition to negative r's refers as before to the components on the low-frequency side of the pattern. But here ϵ is negative, so the intensity *decreases*. Hence the behavior of the P patterns should be opposite that of the "Q-doublets." As a matter of fact, the two effects are not just the reverse of one another, since the relative weakening of the P components is greater than for the Q components except for the first line in the branch. In Fig. 4 I have drawn the theoretical Zeeman intensity patterns for the first two lines of the P and Q branches for perturbing fields of $H=0$ (when the intensities are symmetrical), of $H=20{,}000$ and of $H=35{,}000$ gauss, using Eqs. (3) and (4) and the others given by Kronig. [For convenience all of the pattern *widths* are drawn to the same scale (otherwise the pattern for $H=0$ would have zero width).] The values of the field given in Fig. 4 are the ones used in computing the perturbed intensities.]

A detailed comparison with the plates has shown that the intensities behave in general as expected, the asymmetries becoming less for small fields. In all cases, of course, the effects are small changes in the intensities of already weak lines and consequently too much cannot be expected from a visual observation. In the case of the R lines the predicted effect is small even for high fields. Since R lines were resolved only for low fields any lack of symmetry would be still smaller and hence beyond observation.

P lines. For the $P(1)$ line no effect is predicted for *either* polarization. Actually the low frequency component seems to be less intense than the high frequency one on several plates (λ5610) both at $H=20{,}000$ and $H=24{,}400$ gauss. This result is probably not a real contradiction with theory

[20] In Part I the opposite convention was used, i.e., positive r's corresponded to high frequency components and negative r's to low frequency components. No confusion need arise if intensities are computed properly from Kronig's expression and diagrams labeled in terms of *our* notation.

but is to be assigned to "weakening" [due to the immediate proximity of the strong line $P(7)$] of the low frequency component in development since in λ5198 where both components are equally distant from a strong line no such lack of symmetry is observed even for $H=35{,}000$ gauss. For the $P(2)$ line in parallel polarization the theory predicts that at $H=35{,}000$ the low frequency member of the narrow triplet (see Figs. 4 and 5) should be only about one half the intensity of the other two components of the pattern. This accounts in part at least for its non-appearance in the reproduction of Fig. 5. At lower fields while the pattern was not resolved it was at least

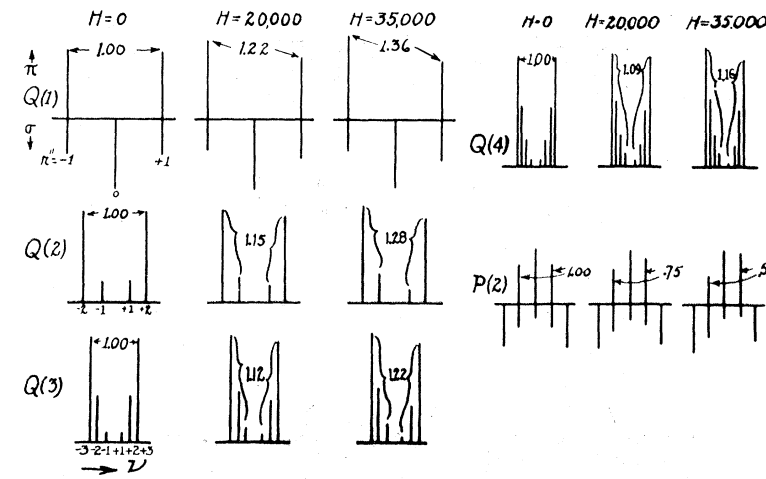

Fig. 4. Theoretical intensities of Zeeman patterns according to Kronig. Here the intensities are plotted for perturbing fields of 0, 20,000 and 35,000 gauss (where for convenience the pattern *widths* for a given M value are drawn to the same scale) for lines $Q(1)$, $Q(2)$, $Q(3)$, $Q(4)$ and $P(2)$. Components polarized $\|$ (π) to the field are drawn upward and those polarized perpendicularly (σ) are drawn downward. The number written in each pattern is the ratio of the sums of the intensities of the low frequency components to the sum of the intensities of the high frequency components for that pattern. Where the individual components thus added are too close together to be resolved on the photograph these ratios are approximately the intensity ratios for the observed doublet-like pattern.

more nearly symmetrical about the undisplaced position of the original line.[20a]

Q lines. In the case of the Q lines observation is easier and the qualitative results more satisfactory. In parallel polarization theory predicts greater intensity for the low frequency components. The asymmetry should be greatest for $M=1$ and decrease gradually for larger M. At $H=35{,}000$ both members of the $Q(1)$ doublet can be observed in only one band. In this case the high frequency component is undoubtedly weaker though this may be in large part caused by the immediate nearness of the strong line $P(9)$. The asymmetry gradually decreases however with M and is not observable for

[20a] In perpendicular polarization the $P(2)$ pattern has its low frequency edge too close to the (now broad) pattern of the $P(6)$ line to be clearly resolved from it.

$M>7$. At $H=20{,}000$ it is very small for $Q(1)$ and cannot be detected (visually) beyond $M=3$ or 4. In perpendicular polarization the unresolved lines are mere broad bands for $M>2$. For $M=1$ the outside components are too faint to show in the weak high-field photographs while at $H=20{,}000$ the pattern is practically symmetrical. The theory thus predicts no effects which are not *qualitatively* in close agreement with observations. As to the quantitative results, however, the theory seems to predict that the asymmetry should increase rather more slowly with field than it actually does. Thus for the highest fields (35,000) if we take the case of $\pi \cdot Q(3)$ and simply

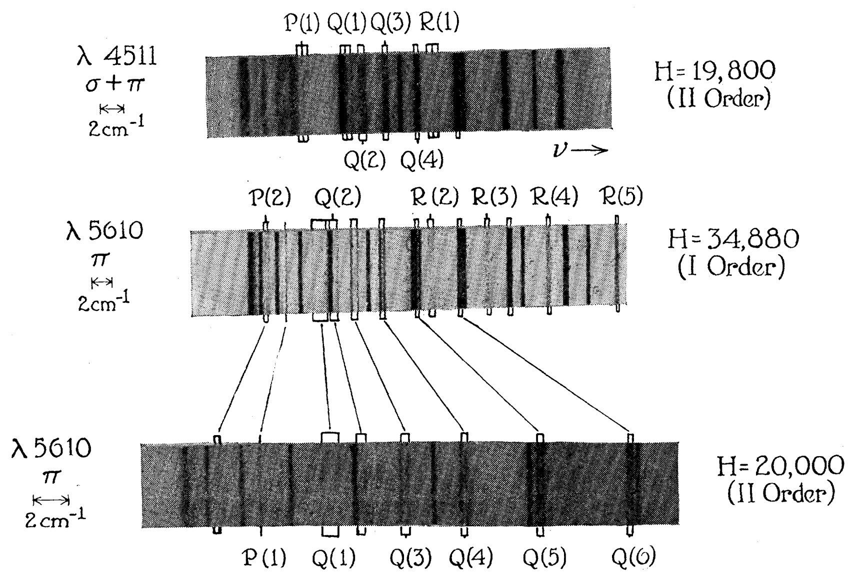

Fig. 5. The upper photograph shows an enlargement (from a second order plate) of the head of the λ4511 band showing in particular the two high frequency components of the $P(1)$ triplets and the very faint $R(1)$ triplet. In the second photograph is a portion of the λ5610 band (first order plate and $\|$ polarization). Here the asymmetry of the Q-"doublets" [particularly $Q(3)$ and $Q(4)$] is to be noted and compared with the near symmetry in the lower photograph which represents the same band in $\|$ polarization at a *lower field*. At $H=34{,}880$ gauss the two high frequency components only of the $\pi \cdot P(2)$ patterns are visible. At the lower field the pattern is not resolved but on the plate looks too wide to be the unresolved pattern of less than three components (compare with the theoretical patterns in Fig. 4).

add the intensities of the (unresolved and very close) components on the low frequency side and compare this with the sum for the high frequency side we obtain a theoretical ratio of about 1.22: 1.00. Actually, visual estimation gives a ratio of at least 2:1, if not more (see Fig. 5, λ5610). A similar situation holds for $\pi \cdot Q(4)$ and to a less extent for $\pi \cdot Q(5)$. At present a new densitometer is in process of adjustment and will be used to determine these ratios objectively.[21]

[21] It is possible that the above discrepancy is traceable to the assumption in Kronig's calculations that perturbative terms in H^2 are negligible, whereas this is not necessarily so for very high fields.

4 *Irregular Zeeman effects in higher lines.* In addition to the regular effects produced by the magnetic field in these bands, there are a number of very complex and apparently rather irregular effects confined entirely to lines of large M value. Before it will be possible to attempt any theoretical interpretation of these facts, it will be necessary to make an extended study of the ordinary rotational perturbations present in the Angstrom bands. The magnetic effects in general are confined to isolated lines, or at most to groups of two successive lines in a given branch. They consist essentially of broadening and of splitting of the lines into doublets, in some cases broad and fuzzy and in others very sharp. The size of these patterns is in general of the same order of magnitude as that of the early lines, but in some cases may be nearly twice as great. Usually only two or three such sensitive lines are observed in each band, and these may or may not belong to the same branch. In almost all cases, however, they occur at or near the points in the bands at which large rotational perturbations occur. It seems possible that a systematic correlation of the Zeeman effects and the rotational perturbations may throw light on the origin of the latter, though at the present time the observations show so little regularity that I simply append in Table II a list of the bands and the sensitive lines in each.

TABLE II. *Sensitive lines.*

Band	Sensitive lines
λ5610	$Q(28)$ [Others also- probably]
5198	$P(25)$ $P(26)$ $P(34)$ $P(35)$
4835	$Q(23)$ ($Q24$)
4511	$Q(25)$ [Probably several others]

5 *New bands and analysis of λ4511 band.* In the course of this work a great variety of discharges through CO and CO_2 have been used and on certain of the photographs three or four new bands (always faint) have been discovered. From their simple three-branch nature and their behavior in the magnetic field they can fairly definitely be assigned to the Angstrom system. It is hoped in another paper to give an analysis of these bands together with that of the very important band (0,0) at λ4511. Previous attempts on the latter band have either been unsuccessful[22] or have led to an analysis which Zeeman photographs show in part to be incorrect.[23] This band seems definitely to have more than 3 branches though the extra ones are fragmentary and weak.

In conclusion the author wishes to express his appreciation of the interest in this work taken by Professors R. S. Mulliken and E. C. Kemble and in particular to signify his obligation to the Milton Fund of Harvard University for a generous grant used for experimental expenses.

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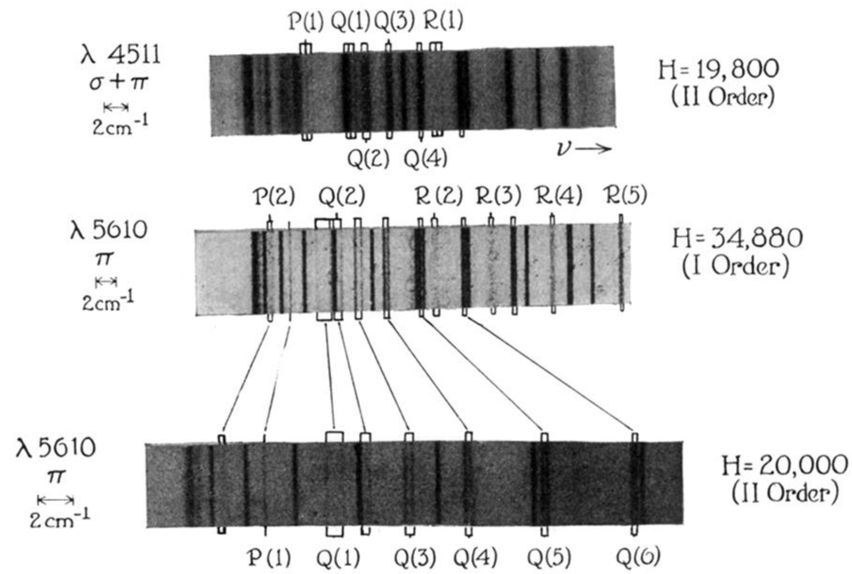
HARVARD UNIVERSITY,
December 10, 1928.

[22] E. Hulthén, Thesis, Lund (1923).
[23] Jasse, Compt. Rend. **182,** 692 (1926).



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