THE STARK EFFECT IN SILVER

by

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SUMMARY

The Stark effect for arc lines of silver clustered round the diffuse series members $5^2P_{1/2} - 6^2D_{3/2}$, $5^2P_{3/2} - 6^2D_{3/2}$ and $5^2P_{3/2} - 6^2D_{5/2}$ has been examined in detail with fields up to 50,000 volts per centimeter. The observation of several previously unreported line components appear to complete the analysis of the groups investigated and to correct the interpretations of earlier experiments.

The initial 7^2P, 6^2D, and 4^2F terms have nearly the same effective quantum number and this is used with hydrogen perturbation terms connecting states of equal n to give theoretical displacements in rather good agreement with experiment. In a high field approximation, the high and low J-value terms of the initial states are associated with line groups which have independent displacements and may even cross each other. One such crossing has been observed. The low J set of terms provides patterns which are different from the 'normal' patterns because of their doublet nature.

A slight improvement is realized with the use of weak-field interaction terms, the main revelation being the close agreement with experiment which is found in both high or low field considerations.

The calculated intensities are in good qualitative agreement with those observed.

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I. INTRODUCTION

This thesis deals primarily with observations of the Stark effect on a rather uncommon arrangement of neighbouring doublet terms in the arc spectrum of silver. The aim of the research was to resolve the inconsistencies existent in earlier investigations and to provide an extension to the apparently incomplete experimental data. This was essential to any understanding of the part played by the electron spin in determining the Stark patterns. The new data has made possible the realization of this objective since the new components appear to complete the analysis for the groups concerned.

The doublet terms are all near the unresolved $4^2F_{5/2,\ 7/2}$ doublet with an effective quantum number very slightly less than an integral 4, and are categorized into the two groups of $7^2P_{1/2}$, $6^2D_{3/2}$, $4^2F_{5/2}$ terms and $7^2P_{3/2}$, $6^2D_{5/2}$, $4^2F_{7/2}$ terms. The perturbations on these six terms are displayed in Lo Surdo photographs of the line groups around the normal spectrum lines at $\lambda\lambda$ 4055.48 ($5^2P_{1/2} - 6^2D_{3/2}$), 4212.82 ($5^2P_{3/2} - 6^2D_{3/2}$), and 4210.96 ($5^2P_{3/2} - 6^2D_{5/2}$).

On the basis of a few simple ideas, it has been possible to understand the departure from normal Stark patterns as displayed by the first group of terms (lower J values), and to calculate the displacements and intensities of all lines with a rather surprising precision.

Under the high field conditions (which clearly exist for the majority of the interactions), it is assumed that the electron spin, now represented by the quantum number M_S, is aligned along the direction of the electric field by the magnetic field due to the component M_L of the orbital angular momentum such that M_S continues to oppose M_L in the lower J configurations while M_S and M_L have the same direction in the terms of higher J values. Consequently the initial perturbed states break up into two completely independent sets of interacting terms, those with the high J value of each doublet and those having the low J values. Each group of terms can then be treated in the usual manner for a singlet system.

Since it is indicated that the initial terms are approximately hydrogenic in nature, the displacements are calculated by using the hydrogen matrix components of the dipole moment connecting two states of equal n. That the approximations made are very good is shown by the fact that in all cases the calculated displacements are within a fraction of a reciprocal centimeter from the observed values.

Owing to a background arising from foreign gases used for the excitation of the silver lines, it has thus far been found impossible to make significant measurements of the intensities. The calculated intensities are based on the theoretical displacements and the appropriate intensity factors representing the Zeeman components in the multiplet spectrum. The calculated intensities are, at least, in very good qualitative agreement with those observed.

II. HISTORICAL BACKGROUND

Since Stark[1] first discovered the effect named in his honor, a great number of investigations into the effect of an electric field on the spectra of many elements have been carried out.

Of these many elements, the atomic spectrum of hydrogen has received the most thorough analysis, both experimentally and theoretically. The wave-mechanical treatments of the Stark effect in hydrogen, given independently by Schlapp[2] and Rojansky[3], and including the relativity-spin fine structure, are regarded as giving the complete theory and good agreement with limited experimental detail - including the first, second, and third order effects. These complete treatments superseded the very early theories for hydrogen by Epstein[4] and Schwarzschild[5] in terms of quantized orbits, and by Epstein[6] and Schrodinger[7] using the perturbation theory in quantum mechanics - all of which seemed to give the correct first order effect; but through neglect of relativity-spin, failed to establish the connections between fine structure and Stark effect first described by Kramers[8].

Second only to hydrogen in the completeness of its analysis, is the Stark effect in the helium spectrum. Foster[9] investigated the effect on several line groups of parhelium and orthohelium and succeeded in not only establishing the normal Stark effect line patterns of the different series lines, but also in applying the perturbation theory in quantum matrix mechanics to give the line displacements and intensities in very good agreement with experiment.

For the remaining elements the investigations have been largely of an experimental nature only, with the exception of some quantum mechanical attempts at treatment of the one-valence-electron spectra of the alkali atoms.

The first research into the effect of an electric field on the arc spectrum of silver was carried out by Takamine[10] in 1919. He observed the line displacements for the members of the chief sharp and diffuse series of lines in the spectral region $\lambda\lambda$ 3680 - 4670 at fields up to 56 kilovolts per centimeter, and noted similarities with the effect in helium as evidenced by the relatively complex structure appearing round members of the normal diffuse series, the uni-directional displacements of the sharp series lines, and the appearance of what he termed 'detached components' near the diffuse series lines. Since a complete classification of the silver spectrum terms was not available then, Takamine could not assign series notation to the new detached lines that he observed. In the π- and σ -images of the line groups around the normal diffuse series lines at $\lambda\lambda$ 4055, and 4210 - 4212 he observed a total of 2 and 3, 3 and 4, line components respectively.

Further work on silver, at much higher field strengths in the range of 140 to 220 kilovolts per centimeter as developed in an arc discharge, was done in 1924 by Nagaoka and Suguira[11]. Their investigation did not reveal any components not observed by Takamine and served only to give displacement measurements at a higher field for several of Takamine's components.

The most complete analysis of the components appearing in silver was that given by Fujioka and Nakamura[12] in 1927, where they attempted to classify the components observed by themselves and Takamine in the light of Fowler's[13] recent classification of the terms in the silver spectrum. Their experiments did not reveal so much detail in the π- and σ -images of the groups at $\lambda\lambda$ 4055, 4212 - 4210 as Takamine had found. Insofar as the number of components found, their classification of the detached components noted by Takamine as originating in initial ^2F and ^2P states was correct. However it was now obvious that the total number of components observed seemed too few for a complete analysis on the basis of Kramers' association of the line components in the Stark effect with the fine structure levels in an atom and Foster's work on the line patterns in the helium spectrum.

The remaining investigation into the effect in silver is that due to Snyder[14] (1929) on the $\lambda\lambda$ 4055 and 4210 - 4212 groups, in which he found a total of only 2 and 3 components in the π- and σ-images respectively of both line groups. His resultant classification was in radical contrast to that of Fujioka and Nakamura, and introduced confusion by way of an F term near the ^2D level which gives rise to the 4210 line, a G term near the ^2D level giving rise to the 4055 line, as well as discounting the existence of any components in the 4210 - 4212 group as originating from an F term near the ^2D level which is the initial state for the normal 4212 line.

The many inconsistencies and apparent lack of completeness existent in the Stark effect in silver was closely paralleled in the analyses of the terms in the normal spectrum of silver, until Shenstone[15] performed a careful and complete classification of the spectrum in 1940. Previous to this very valuable work, term classifications of the silver spectrum in the region of the 6^2D levels not only gave different values for the separation of the 6^2D doublet, but disagreed widely on the positioning of the unresolved 4^2F term. As given by Fowler and by Bacher and Goudsmit[16], the 4^2F term is below both 6^2D levels in an energy level diagram, while Fujioka and Nakamura place it between the 6^2D levels and closer to the lower of these, as does Shenstone. Again, the separation of this unresolved doublet term from the ^2D doublet terms in reciprocal centimeters is not the same for any of the above four level schemes.

To clarify the notation and values used in the present work, it is not amiss to mention here that the relative positions of the 4^2F and 6^2D terms were found to agree with the classifications of Fujioka and Nakamura, while the absolute separations of the terms were in very good agreement with the values given by Shenstone. Consequently the classification and separation of the terms used in the analysis are taken from Shenstone.

III. EXPERIMENTAL APPARATUS

1. Discharge Tube.

Discharge Tube. The discharge tube, of the Lo Surdo type as modified by Foster,[8] is best described with reference to Figure 1 on Page 8.

The elements of the tube are contained in a pyrex-glass envelope of 34 centimeters total length. The aluminum anode (A) is suspended in the upper portion of the tube, this portion including practically all (the positive column) of the length of the discharge and being of relatively large volume in order to assist in maintaining pressure fluctuations at a minimum. Easy access to the anode, for purposes of cleaning or alteration, is provided by the large ground-glass joint (J).

The high electric fields obtained in a Lo Surdo tube are established in the very short cathode dark space immediately above the surface of the cathode and consequently it is this portion of the tube which is of major interest and which requires the utmost care in constructional details.

The silver cathode (C), which fits snugly into a cylindrical plug of lavite (L), has a very highly polished surface and is slightly reduced in diameter at the top so as to leave an annular space about 0.25 mm. wide between the cathode and surrounding lavite wall. This space is designed to prevent breakdown of the electric field by keeping the cathode from coming into contact with the sputtered cathode metal which collects on the lavite walls. That present-day designs of Lo Surdo tubes have an increased lifetime and more dependable operation is mainly due to the use of lavite with its numerous advantages. When in the unfired state, the lavite is soft and easily machined to the required specifications. A slit (S), of width (0.25 - 0.40 mm.) sufficient to fill the spectrograph with light, and of length (3.5 - 4.0 mm.) sufficient to include slightly more than the length of the dark space, is cut through the wall of the lavite

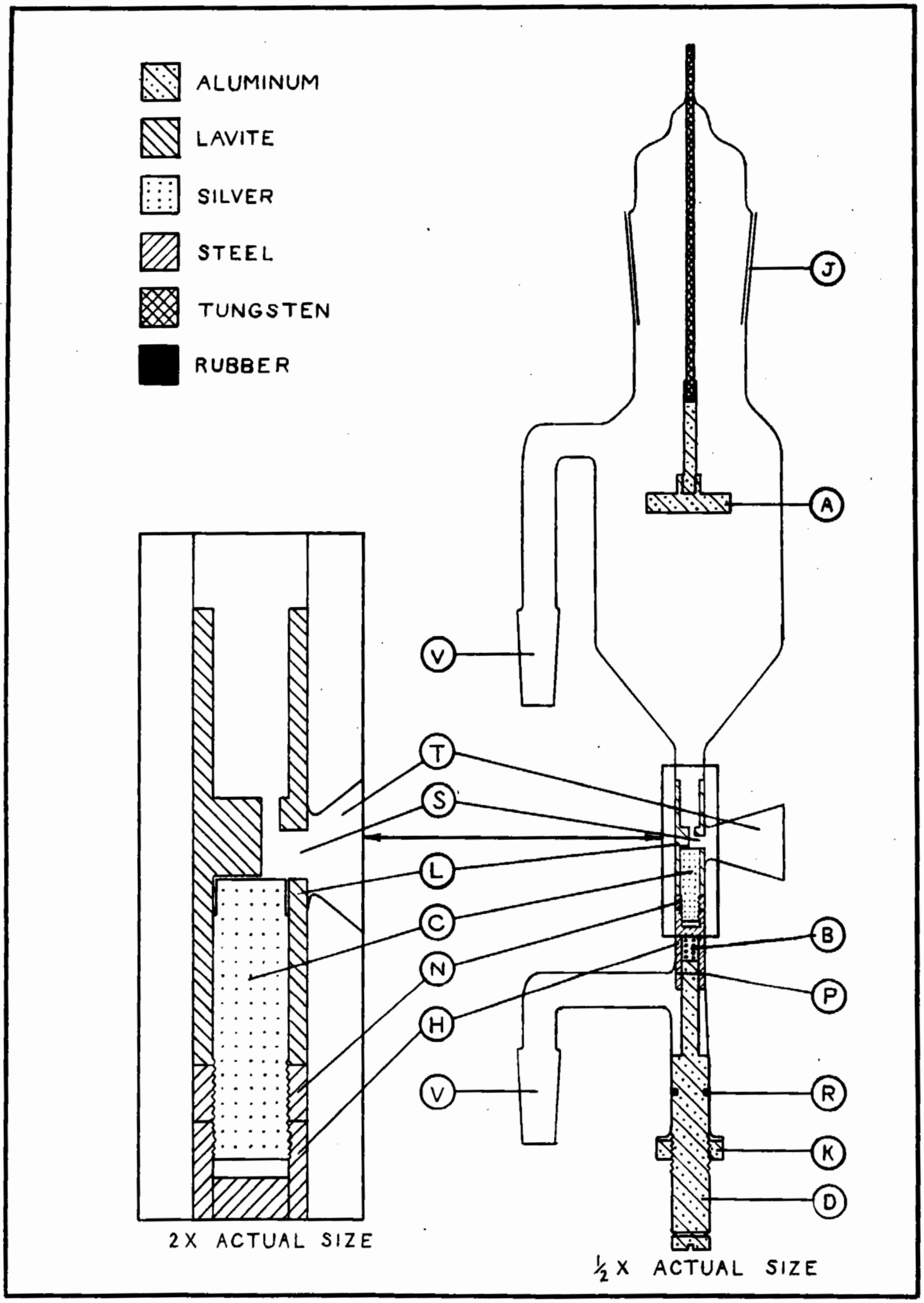


FIG. 1. LO SURDO TUBE

and the light from this slit is the source of light for the experiment. The vertical hole through the lavite, which collimates the discharge, is drilled off the vertical axis of the lavite plug. Thus new portions of the cathode surface may be exposed by a rotation of the cathode. The lavite, after having been prepared and carefully polished, is fired at 1000 - 1100^{o}C, whereupon it becomes very hard and is an exceptionally good insulator. It is then sealed in the tube, a very good seal being possible because of the closeness of the coefficients of thermal expansion of pyrex-glass and lavite. This seal prevents the discharge from by-passing the main discharge track. A side-tube (T) allows passage of the light from the slit to the spectrograph.

The cathode threads into a steel holder (H) and is locked into position with the lock-nut (N), which abutts against the lower end of the lavite and thereby holds the cathode surface a fixed distance back from the lavite. The holder is attached to the aluminum supporting rod (D) by means of the steel spring (B) and the steel pin (P), which combine to give the entire supporting system a small degree of flexibility to compensate for any bending of the glass tubing away from a vertical axis. The lower end of the supporting rod carries an O-Ring (R) to complete the vacuum sealing of the tube and is also threaded to take a knurled nut (K) which rests against the lower rim of the tube envelope and thereby allows the entire cathode-supporting system and cathode to be drawn back by known amounts if so desired. The cathode is grounded with a lead attached to the end of the supporting rod and, as mentioned before, can be rotated simply by turning this rod.

The tube is attached to the vacuum system by means of the two ground-glass joints (V) which allow the tube to be rotated about a vertical axis. Horizontal and vertical motion of the tube are also provided for by sylphon bellows incorporated into the arms connecting the tube to the main body of the vacuum system.

2. Spectrograph. The spectrograph used in this research is of the multiple-prism type and is a modification of the one designed by Foster[17] for investigations of the Stark effect in the visible spectrum range. The design is such as to provide the major requirements for a fine Stark effect analysis: high dispersion and resolving power, a reasonably "fast" optical system, and a rigid mounting for long exposures.

As used in the present investigation, the spectrograph comprises a train of five "coated" flint-glass prisms with faces 2.25 inches high by 4.0 inches wide, and two achromatic lenses of 45 inches focal length and 3 inches aperture as the collimator and camera lenses.

The light passing through the lavite slit is focused on the spectrograph slit by a condensing system of two achromatic lenses, the first lens being placed at its focal distance from the lavite slit and the second at its focal distance from the slit of the spectrograph. Since in the transverse Stark effect, the radiation emitted by atoms affected by the electric field is plane-polarized either parallel or perpendicular to the direction of the field, a Wollaston prism is placed between the two condensing lenses so as to separate the beam of light from the source into its two component beams - one of each polarization. The second condensing lens thus focuses two separated images of the lavite slit on the spectrograph slit, each image being magnified 3X because of the choice of the focal lengths of the condensing lenses. Hereafter the parallel and perpendicular polarizations will be denoted by the usual shortened notation of π- and σ-polarizations respectively.

The use of two lenses for the condensing system offers two advantages over the use of only one, the chief of these being a minimum of chromatic variation introduced in the two polarized images because the light incident on the Wollaston prism is very nearly parallel over the range of wavelengths used. The two lenses also provide for a constant image magnification of the order of 3X while requiring motion of the first lens only to focus the source of light.

The intensities of the two polarizations, as received at the photographic plate, are enhanced by the use of two quartz wedges placed at the spectrograph slit. The Wollaston prism, while separating the two polarized beams, makes the incident angles of the light in the two images on the spectrograph slit such that the light comprising each image does not completely fall within the limiting cone in which light will be received by the collimator lens. The angles of the two wedges, which are identical geometrically, are such that when they are placed at the slit of the spectrograph the light of both images is refracted back towards the axis of the spectrograph, thereby increasing the amount of light accepted by the collimator lens from each image. The wedge used for the σ-image is of fused quartz and thus enhances the intensity of this image only as mentioned, but the use of crystal quartz for the wedge in the case of the π-image makes possible a further increase in the intensity of this image. This further possible enhancement comes about from the fact that the two plane-polarized beams of light are incident on the dispersing prisms of the spectrograph at angles very near to the polarizing angle, with the result that the light forming the σ-image is mainly refracted while a considerable percentage of the light in the π-polarization is lost by reflection. The crystal quartz wedge rotates the plane of vibration of the electric vector in the π-polarization through an angle near 90°, thereby permitting the light forming the π-images to pass through the dispersing prisms as 'σ' polarization with consequent low reflective losses.

The camera plate-holder can be rotated about a vertical axis to bring most of the spectral lines on the plate into good focus at the same time, and can also be raised or lowered for purposes of taking several exposures on one plate.

Plate II, Page 13, shows the entire experimental arrangement with the spectrograph in its normal position, while the condensing system can be seen in the close-up of Plate I.

3. Vacuum System. The evacuation of the discharge tube is accomplished by a mercury diffusion pump backed by a mechanical forepump. The mechanical pump can be turned out of the system upon completion of evacuation, and the tube filled with the desired mixture of gases from reservoirs of He and H_2 contained in the vacuum line, or with air trapped in the 3 liter ballast volume. The pressure attained in evacuation is read from a tilting McLeod gauge in the system, this gauge also providing for measurement of the gas pressure to which the tube is filled.

A charcoal trap immersed in liquid nitrogen is also included in the vacuum line and aids both in evacuation of the tube and (except when air is used) in maintaining the purity of the gases in the discharge tube.

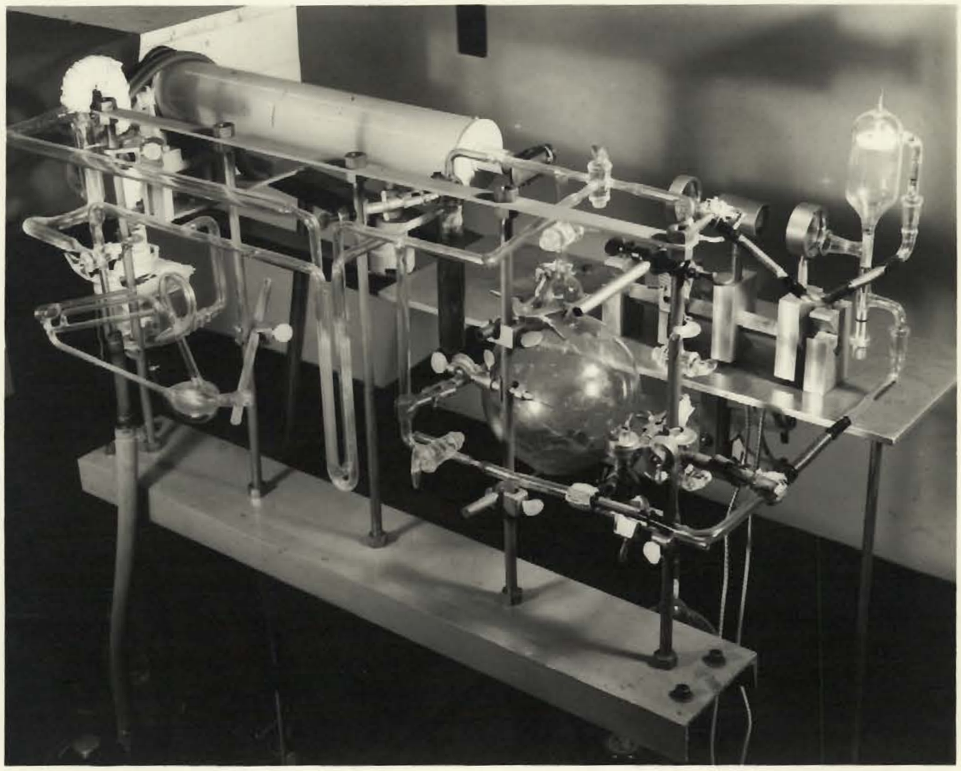


PLATE I - VACUUM SYSTEM AND OPTICAL CONDENSING SYSTEM

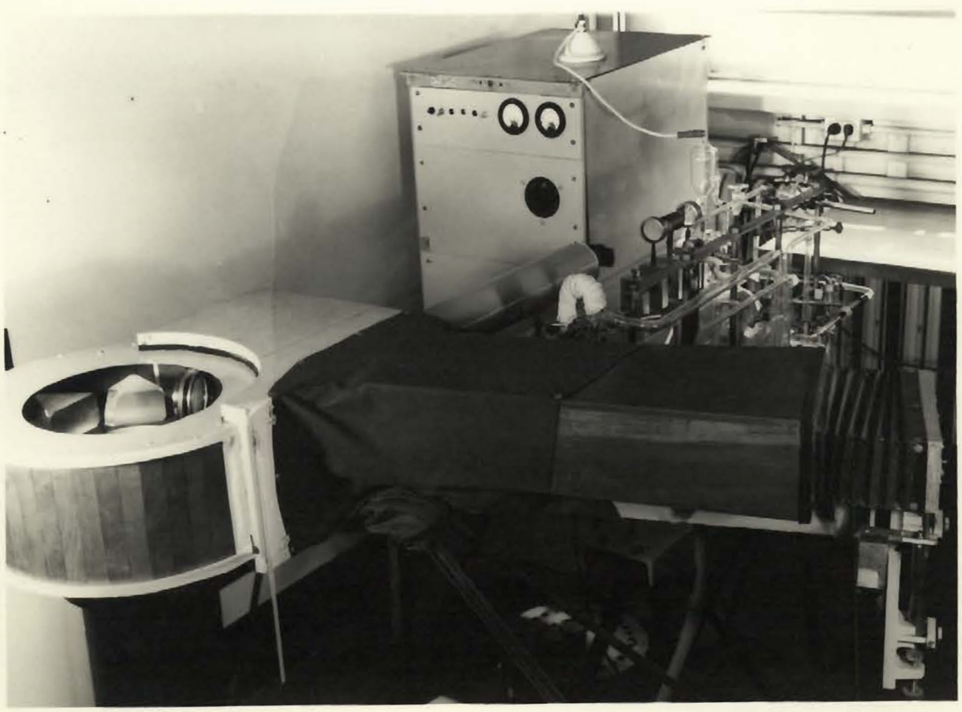


PLATE II - EXPERIMENTAL ARRANGEMENT

The mercury pump is designed to operate at pressures of a few millimeters of mercury and can therefore be used to provide a continuous circulation of the gases through the discharge tube and the charcoal trap.

The vacuum system is shown in Plate I.

4. Power Supply. The D.C. power supply is designed to supply a maximum of 50 milliamperes at 20,000 volts. 120 volt-60 cycle alternating current is supplied to the primary of a high voltage transformer through a controlling Variac. Full-wave rectification of the output of the transformer is supplied by two 8020 high-vacuum rectifier tubes, the ripple voltage being reduced by a single-stage choke-input filter. A bleeder resistance of 800,000 ohms provides continuous current through the inductance for normal operation. In the range of voltages used, the percentage ripple voltage is of the order of one-third of one percent.

The voltage applied at the tube, and the current drawn by the tube, can be read from a moving-coil voltmeter and an ammeter in the output circuit. If necessary, this voltage is maintained constant by manual operation of the Variac in the primary circuit.

IV. EXPERIMENTAL PROCEDURE AND RESULTS

1. Adjustment of Spectrograph. An iron arc of the Pfund-type was constructed and used for the adjustment and focusing of the spectrograph.

The dispersing prisms were set for minimum deviation of the iron line λ 4132.06 at the geometrical center of the plate, and the camera was focused photographically using a Hartmann diaphragm in the usual manner.

The quartz wedges before the spectrograph slit were adjusted by visual observation of the images received at the camera when the Lo Surdo tube was in operation.

2. Operation of Lo Surdo Tube. The silver atoms for investigation were obtained from the bombardment of the silver cathode by the positive ions of the carrier gases in the tube. The cathode was drawn back from the lavite by 0.25 - 0.33 millimeters, and for steady operation of the tube it was found that the strict requirements of cleanliness and high polish of the cathode and lavite surfaces were also applicable to the condition of the anode. A small conical pit, with a diameter the order of that of the collimating hole in the lavite and a depth of the order of one millimeter, is formed in the cathode during a normal exposure. This necessitates a rotation of the cathode after one or two exposures, but it is a remarkable feature of the tubes that while this pit is being formed during an exposure, with undoubtedly a consequent alteration of the equipotential lines, there is no noticeable shift of the electric field as seen on a good quality photographic plate.

The operating lifetime of the tubes was generally limited by the sputtered silver either collecting on the lavite walls and coming into contact with the cathode, thereby breaking-down the electric field, or collecting in the lavite slit and thus cutting off the light.

The tubes were filled with a mixture of helium and air, or helium and hydrogen, to total pressures ranging from 2.2 to 4.2 millimeters of mercury. If the partial pressures of the hydrogen and air were respectively greater than 30 or 40 percent of the total pressure of the mixture, the tubes became rather highly conducting and quite unstable. Both mixtures were used since each offered an advantage not possessed by the other. The helium-hydrogen mixture yielded plates on which fewer foreign lines appeared in the neighborhood of the silver line groups to be measured, while the use of the air excited the silver spectrum to greater brightness. When air was used, the cathode glow in the tube was a bright green in color and the silver lines were visually observable at the camera.

Three different diameters (1.5, 2.0 and 2.8 millimeters) of the collimating hole in the lavite were used, the intermediate value being most used as the best compromise between the high field - weak intensity and low field - strong intensity relations obtained with the smaller and larger diameters respectively.

The applied voltage on the tubes ranged from 4.0 to 6.5 kilovolts and seldom fluctuated by more than two per cent, while the currents drawn were between 2.0 and 6.0 milliamperes. The voltage-current characteristics were largely dependent upon the diameter of the lavite hole and the proportion of the gases present.

Exposures vaired from ten minutes to two hours and the normal lifetime of a tube was usually of the order of four or five exposures.

3. Measurement of Plates. A total of 29 photographs of the spectral region between $\lambda\lambda$ 4000 - 4600 were taken on Eastman Kodak Type II-O Spectroscopic Plates. Of this total, three plates best combining the features of sharp focus, maximum resolution, suitable intensities and steady fields, were used for accurate measurement of the displacements of the silver line components. Several plates, while not of a sufficiently high quality for accurate measurement, yielded much valuable qualitative information. One such plate, taken with a considerably higher field than normal, gave visual confirmation of an interesting result indicated by both the experiment and theory, and will be mentioned in the following chapter.

The plates were measured on a Gaertner travelling-microscope comparator which has a least count of 0.001 millimeters. The comparator was first checked and found to be free of periodic error within the limits of experimental error. Errors due to backlash in the instrument and to systematic error of the observer were avoided by always travelling in the same direction when making any one set of measurements, and by making a total of four settings, two in each direction of microscope travel, on each line.

Dispersion curves, in units of reciprocal centimeters per millimeter of plate, were drawn for each plate measured, noting that for the small regions over which the dispersion was needed, the effect of line curvature was within experimental error and the dispersions were linear within experimental error, which was of the order of one-tenth of one per cent for the plates. As taken from one plate, the dispersions were 25.96, 21.90, 18.57 and 17.14 cm.$^{-1}$/mm. at H_γ, λ 4210.96, H_δ and λ 4055.48 respectively. The lines on the plates used as standard lines for the dispersion determinations, were the lines of the secondary hydrogen spectrum measured by Gale, Monk and Lee,[18] and the mercury and helium lines as listed in the M.I.T. Wavelength Tables. Conversion of the wavelengths of all lines into reciprocal centimeters was done with the most recent and thorough determination of the refractive index of air as given by Barrell and Sears.[19]

The field strengths were accurately determined from the measured displacements of the lines H_γ and H_δ appearing on the plates. The presence of these two lines, widely separated on the plates, made possible the elimination of error often encountered in the measurement of Lo Surdo plates due to chromatic variation along the plate (as discussed by Iskida and Tamura[20]) and enabled the setting of the plates such that all measurements were made at one field strength.

4. Experimental Results. The absolute wavelengths of the members of the second group of chief diffuse series lines in the silver spectrum are given by Shenstone and the M.I.T. Wavelength tables as $\lambda\lambda$ 4212.817, 4210.960, 4055.476, and $\lambda\lambda$ 4212.68, 4210.936, 4055.264 respectively. The differences, particularly for $\lambda\lambda$ 4212 and 4055, are considerably larger than the limits of experimental error attainable with the present spectrographic equipment and consequently the wavelengths of the two strongest lines were measured on a good quality plate, using the wavelengths of the secondary hydrogen lines on the plate as sufficiently accurate standards. The measurements, with probable error, gave λ4210.947 $\pm$ 0.010 and λ4055.479 $\pm$ 0.013 - in very close agreement with Shenstone.

On another plate the ratio of the measured separation of $\lambda\lambda$4210-4212 to that of λ4210 and the line suspected as originating in the unresolved

4^2F level yielded a value of 1.21, which was within probable experimental error of the figure 1.19 obtained using Shenstone's tabulated wavelengths.

Still further close agreement with Shenstone was revealed in the wavelengths of the $5^2P_{3/2} - 7^2P_{3/2}$ and $5^2P_{1/2} - 7^2P_{1/2}$ combination lines, calculated from the term classifications as λ4227.46 and λ4082.25, and measured in very low fields to be λ4227.41 and λ4082.5 respectively.

As a result of these very good experimental agreements, Shenstone's analysis of the silver spectrum was used in this research. The term classified in his analysis as 4^2F in reality consists of both the 4^2F levels lying very close together, this being clearly shown by the fact that five Stark line components originate from the 4^2F position at zero field - a pattern impossible of production by one of the levels alone. This is one of the few cases in atomic spectra where the Stark effect is most useful as a tool for term analysis.

The measurements of the displacements of the silver line components are recorded in Table I. Mean deviations of the readings lie in the range from 0.05 to 0.20 cm.$^{-1}$, with the majority having a mean deviation around 0.10 cm.$^{-1}$ Excluding two measurements made on the $5^2P_{3/2} - 7^2P_{3/2}$ line, measurements at seven field strengths were made for each of the π- and σ-images of the three line groups. The fields given are the mean values of the fields determined at H_γ and H_δ and should be good to the order of one-half to two per cent, being particularly good for the groups of lines at $\lambda\lambda$4210 - 4212 which lie about midway between the two hydrogen lines.

The observations on the line components originating from initial 6^2D and 4^2F states revealed totals of 4 σ-components and 2 π-components at λ4055, and of 10 σ-components and 7π-components at $\lambda\lambda$4212 - 4210 taken as one large group. Of the four previous investigators, Takamine had

TABLE I EXPERIMENTAL DISPLACEMENTS

	λ 4055 Group π $6D_{3/2}$	λ 4055 Group π $4F_{5/2}$	λ 4055 Group σ $6D_{3/2}$		λ 4055 Group σ $4F_{5/2}$		λ 4212 Group π $6D_{3/2}$	λ 4212 Group π $4F_{5/2}$	λ 4212 Group σ $6D_{3/2}$		λ 4212 Group σ $4F_{5/2}$		λ 4210 Group π $7P_{3/2}$	λ 4210 Group π $6D_{5/2}$		λ 4210 Group π $4F_{7/2}$	λ 4210 Group σ $6D_{5/2}$			λ 4210 Group σ $4F_{7/2}$	
M_J	±1/2	±1/2	±1/2	±3/2	±1/2	±3/2	±3/2	±1/2, 3/2	±1/2	±3/2	±1/2	±3/2	±1/2,3/2	±1/2	±3/2	±1/2,3/2	±1/2	±3/2	±5/2	±1/2,3/2	±5/2
F																					
6.2	-1.37	+3.38					-1.42	+2.69								-9.69					
9.9	-2.03	3.75					-2.21	3.21								10.09					
12.1				-2.38		+4.18															-10.02
18.2				-4.40	+7.23	5.90			-5.22								+3.08		+1.71	-11.89	11.03
24.1				-5.43	8.80	7.37			-6.73		+8.68						5.17		3.05	12.83	11.93
24.8	-6.79	9.28					-5.96							+5.12		13.29					
27.9	-8.05	10.55					-6.86							6.28		14.63					
29.2													-93.76								
29.9	-8.33	10.66					-7.10							6.83		14.47					
30.0			-8.62	-7.28	11.12	8.87			-8.74	-7.00	11.13	+8.67					7.07		4.90	14.20	
32.7			-9.24	-7.87	11.84	9.74			-9.68		11.74	9.22					7.94		5.03	14.96	
33.3													-94.12								
43.1				10.25	16.00	12.30						12.33					12.39	10.75	7.05	17.95	16.43
46.8	12.85	16.51					11.38							13.98	12.43	18.94					
47.8			13.32	11.50	17.55	13.67						13.19					14.55	13.05	8.39	18.79	17.46
49.6	13.84	18.07					12.04							15.43	13.61	19.31					

reported the largest number of line components, the true existence of some components being questioned by later observers. His observations were of 3 σ - and 2 π-components at λ4055 and of 4 σ - and 3 π-components at $\lambda\lambda$ 4210-4212. The present experiment thus included eleven previously unreported line components in the overall sum of twenty-three components observed.

Leaving the assignment of the M_J values of the initial perturbed states from which the line components arise and the association of the components with the correct normal 4^2F level until a full discussion of the results in the following chapter, certain guiding facts to the interpretation of the observed line patterns may be noted from the table of results.

The displacements are given in cm.$^{-1}$ (with a negative sign meaning a displacement of the line component towards the red) and are classified into three groups about the normal diffuse series lines, the displacements of the components in each group being measured from the position of the normal line in that group. No measurements are listed for a component where a good measurement was rendered impossible by the presence of foreign lines or too low a component intensity.

The displacements listed under $4^2F_{7/2}$, $M_J = \pm 1/2, 3/2$, were for the center of gravity of a pair of very close components. That this line was in fact double was clearly indicated on the plates, being very nearly resolved on the better plates and always having the order of twice the line width of another component running very close to it and coming from the same normal level. For some of the remaining components the displacements at lower fields were also for the centers of gravity of a pair of components not resolved on the plate, such readings being indicated in the table.

The line components of the λ 4210 and λ 4055 groups were in general considerably more intense than those of the λ 4212 group, such that a more complete set of measurements could be made for the former two groups.

Measurements of the displacement of the $5^2P_{3/2} - 7^2P_{3/2}$ line were made at two field strengths in the π-image, the line $5^2P_{1/2} - 7^2P_{1/2}$ being insufficiently intense to be capable of good measurement of what was obviously a small displacement towards the red.

V. DISCUSSION AND THEORETICAL INTERPRETATION OF RESULTS

<u>1. Discussion of Observed Results</u>. For the interpretation of the observed Stark patterns it was first assumed that any displacements of the final 5^2P states were neglig ibly small. This would mean that the Stark line components on the photographic plate form a direct picture of the perturbations of the initial levels and that such a picture would be a complete representation of all the initial perturbed levels, provided transitions take place from all of these levels. The validity of this basic assumption would require equal displacements in the same direction for the line components originating from the normal positions of the $\lambda 4212$ and $\lambda 4055$ diffuse series lines, since these components represent the same initial perturbed states. That this was so, within the limits of experimental error, can be seen at once by an examination of Table I or from a composite plot of the totality of measurements made for the two line patterns. The data reveals two perturbed levels arising from the normal $6^2D_{3/2}$ level, and since M_J is the only quantity to retain its status as an accurate quantum number in the presence of an electric field, these two levels can be correctly assigned M_J values of $\pm 1/2$ and $\pm 3/2$.

From the perturbation theory of the Stark effect, matrix components of the electric moment connecting two unperturbed states give rise to the familiar 'repulsive' effect of terms on one another. The general conditions for the existence of such matrix components are that the two states be of opposite parity, have J values which are equal or differ by unity, and have equal components M_J of the total angular momentum.

Considering only the close 6^2D doublet terms and the unresolved 4^2F terms lying between them, there could only be interaction terms connecting the $4^2F_{5/2}$ level with both D levels and the $4^2F_{7/2}$ level with the $6^2D_{5/2}$. This means that the perturbed levels of the normal $4^2F_{7/2}$ level must be represented by components which come from the zero-field 4^2F position and are displaced to longer wavelengths. The three observed components could thus be assigned the M_J values of $\pm 1/2$, $\pm 3/2$, $\pm 5/2$. The $M_J = \pm 7/2$ level is not observed because of the ΔM_J selection rule. On the basis of the theory this state, having the highest possible M_J, is not perturbed. Similarly the three line components coming from the position of the normal $\lambda 4210$ line represent the perturbed states, characterized by $M_J = \pm 1/2$, $\pm 3/2$ and $\pm 5/2$, of the normal $6^2D_{5/2}$ level. This leaves only two remaining line components, displaced toward shorter wavelengths. These definitely represent perturbed states of the $4^2F_{5/2}$ level and, from the magnitude of their displacements and the polarizations, must be correctly denoted by $M_J = \pm 1/2$ and $\pm 3/2$. This would appear to complete the picture of the displacements of the perturbed levels for the four normal terms, with the possible exception of a level having $M_J = \pm 5/2$ associated with the normal $4^2F_{5/2}$ term.

This assignment of the perturbed energy levels is completely confirmed by the theoretical treatment given in the following section. The absence of the transition from the $M_J = \pm 5/2$ level of the $4^2F_{5/2}$ term is found to be due to the essential degeneracy of the 4^2F doublet.

Figure 5 depicts the displacements of the energy levels of the terms investigated, and shows the transitions which take place to give rise to the displaced line components on the photographic plate.

As discovered by Foster in the parhelium spectrum, the 'normal' Stark patterns (written as the ratio of π- to σ- components) in strong fields, for transitions from initial P, D and F levels to a final P level, were 2/2, 2/3 and 2/3 respectively. In the present investigation, the displacements of the Stark components coming from the initial $4^2F_{5/2}$ and $6^2D_{3/2}$ levels are linear with the field from very near the zero-field position, while those from the initial $4^2F_{7/2}$ and $6^2D_{5/2}$ terms exhibit a quadratic effect in fields up to the order of 15 kilovolts per centimeter, after which the displacements become very nearly linear with field strength. Thus for the range of fields used in the research, the close 4^2F and 6^2D terms were for the most part subjected to a strong field. However, while the line patterns associated with the $6^2D_{5/2}$ and $4^2F_{7/2}$ levels were observed to be 'normal', those associated with the lower J-value $6^2D_{3/2}$ and $4^2F_{5/2}$ levels lack a sufficient number of components for a 'normal' pattern. The existence of simplified patterns for the low J-value $6^2D_{3/2}$ and $7^2P_{1/2}$ levels is due to their doublet character and can be directly seen from the ΔM_J selection rule. As has already been mentioned, the reduced number of components from the $4^2F_{5/2}$ level is simply explained by the theory.

An interesting case of two levels crossing one another was observed on a plate taken with higher fields than were usually obtained. The field at which this occurs is of the order of 65 kilovolts per centimeter.

2. Theoretical Displacements. The energy shift of a level in an electric field is given by the product of the field and the component of the electric moment of the atom along the field. The conditions for the existence of a matrix component of the electric moment were stated in the preceding section, and if the energy levels and corresponding eigenfunctions of an atom are known, then the matrix components of the electric moment can be calculated

and the perturbation theory applied to give the displacements of the affected energy levels.

Since in the present investigation the 7^2P, 4^2F and 6^2D terms lie very close together and relatively far away from any other possible perturbing terms, the secular equation, formed from the matrix of the perturbed Hamiltonian by including just the rows and columns which refer to these six terms, should permit reasonably accurate calculations of the shifts of the energy levels.

The three pairs of close doublet terms have effective quantum numbers in the range from 3.990 for the $6^2D_{5/2}$ term to 3.941 for the $7^2P_{1/2}$ term, which means that the terms are all very nearly like that of the hydrogen $n = 4$ level. The use of the well-known hydrogen matrix components of the electricmoment connecting two states of equal n and L differing by unity, might thus be expected to yield a good approximation to the actual displacements of the levels, particularly if the effective quantum numbers are used in place of $n = 4$.

As previously noted from experiment, the existence of a so-called strong field seems to be indicated by the displacements of the close 4^2F and 6^2D terms. The usual definition of a strong field in the Stark effect is that such a field exists when the displacements of the levels are large compared to the fine structure separation of the terms.

It is difficult to set an initial value of the experimental field which is to be called "strong", for a field will undoubtedly often be high for one doublet while remaining low for another. Such strong fields mean that the interaction energy between the field and the electron of the atom is greater than the electron spin-orbit interaction. Consequently the magnetic coupling between L and S is broken down and L becomes quantized with respect to the direction of the electric field, and precesses around it. While the electron spin is not affected directly by the electric field, the precession of L produces a net magnetic field along the electric field direction, and it is this field that quantizes the electron spin. Thus in strong fields, $M_J = M_L + M_S$, where M_L and M_S are now both good quantum numbers.

If one now assumes that in the strong electric field the relative orientations of M_L and M_S will remain the same as in the normal level (an assumption which seems physically reasonable), then there will be no interaction between terms for which $\Delta J = 0$, and the original group of six terms will break up into two completely independent sets of interacting terms. One set includes the high J-value term of each doublet and the other set consists of the low J-value terms.

The calculation of the displacements of the levels may now easily be carried out as for a singlet system(9), and involve no determinants larger than the third order. Using the strong-field hydrogen matrix components of the perturbation energy, given by $(n, L-1, M_L | FP | n, L, M_L) = -nkF\sqrt{\frac{(n^2 - L^2)(L^2 - M_L^2)}{4L^2 - 1}}$, the calculated displacements were within a reciprocal centimeter of the observed values.

That the field strengths used in the experiment could not be classed as strong for the 7^2P terms was obvious. It was therefore felt that use of the matrix elements of the electric moment for hydrogenic atoms in weak fields (as given by Rojansky(21)) for the interaction terms between the relatively distant P and D terms, would provide a still better approximation

TABLE II THEORETICAL DISPLACEMENTS

LOW J TERMS ($\lambda\lambda$4212 and 4055)					
Normal level	$7P_{1/2}$	$6D_{3/2}$		$4F_{5/2}$	
M_J of initial state	± 1/2	± 1/2	± 3/2	± 1/2	± 3/2
Polarization in 4212 4055	ps ps	ps ps	ps s	ps ps	ps s
Field in kv./cm. 0	-161.73	0		+1.47	
10	161.84	-2.49	-1.91	4.07	3.38
20	162.12	5.51	4.40	7.37	5.87
30	162.60	8.44	6.92	10.78	8.39
40	163.28	11.27	9.45	14.29	10.92
50	164.16	13.99	11.93	17.89	13.40

HIGH J TERMS (λ4210)								
Normal level	$7P_{3/2}$		$6D_{5/2}$			$4F_{7/2}$		
M_J of initial state	± 1/2	± 3/2	± 1/2	± 3/2	± 5/2	± 1/2	±3/2	±5/2
Polarization in 4210	ps	ps	ps	ps	s	ps	ps	s
Field in kv./cm. 0	-92.70		0			-9.00		
10	92.88	92.82	+1.31	+1.14	+0.67	10.13	10.02	9.67
20	93.45	93.20	4.22	3.72	2.28	12.47	12.22	11.28
30	94.38	93.91	7.78	6.89	4.35	15.10	14.68	13.35
40	95.64	94.70	11.64	10.33	6.61	17.68	17.33	15.61
50	97.31	95.83	15.72	13.96	8.97	20.11	19.83	17.97

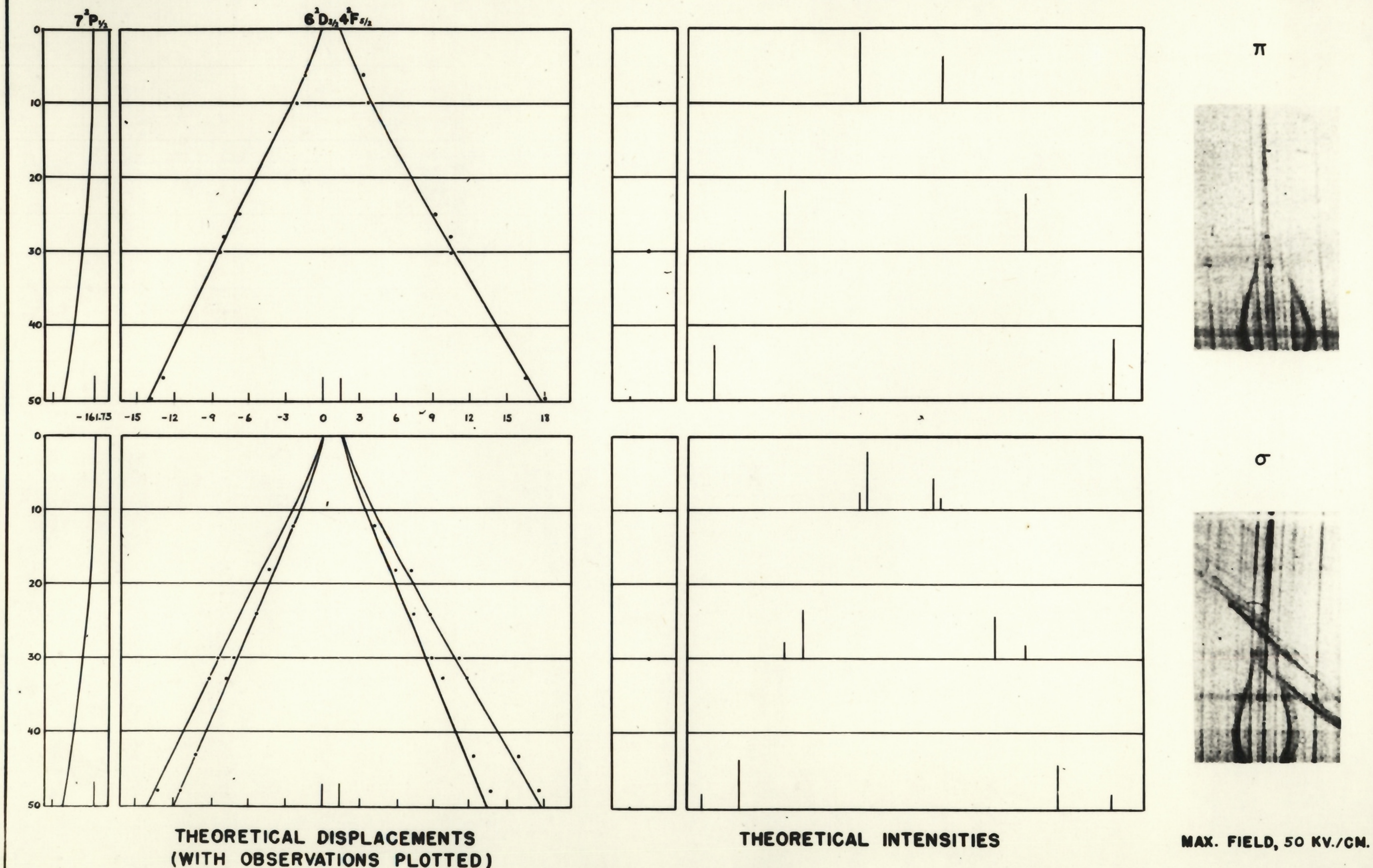
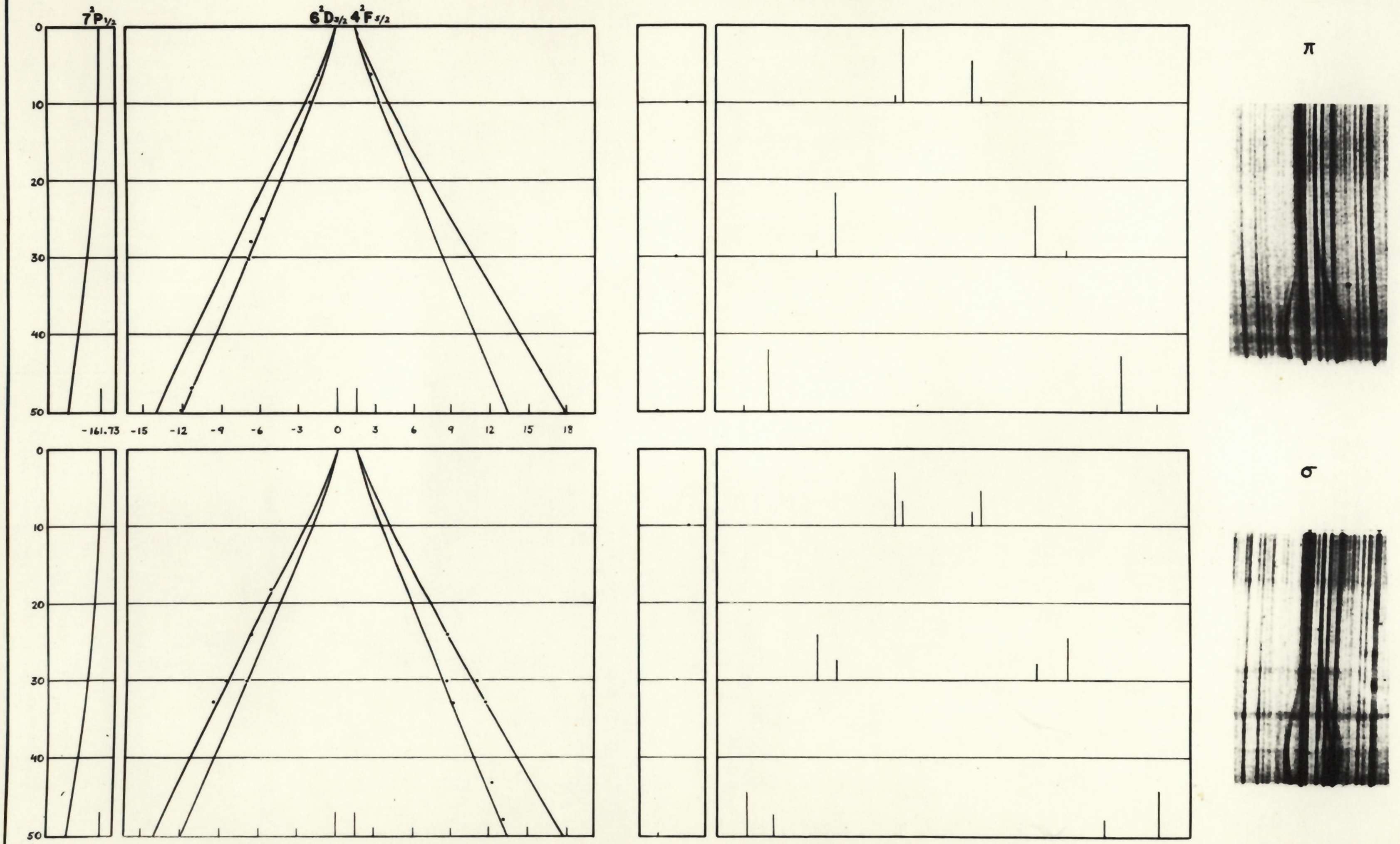


FIG. 2 4055 GROUP



THEORETICAL DISPLACEMENTS
(WITH OBSERVATIONS PLOTTED)

THEORETICAL INTENSITIES

MAX. FIELD, 50 KV./CM.

FIG. 3 4212 GROUP

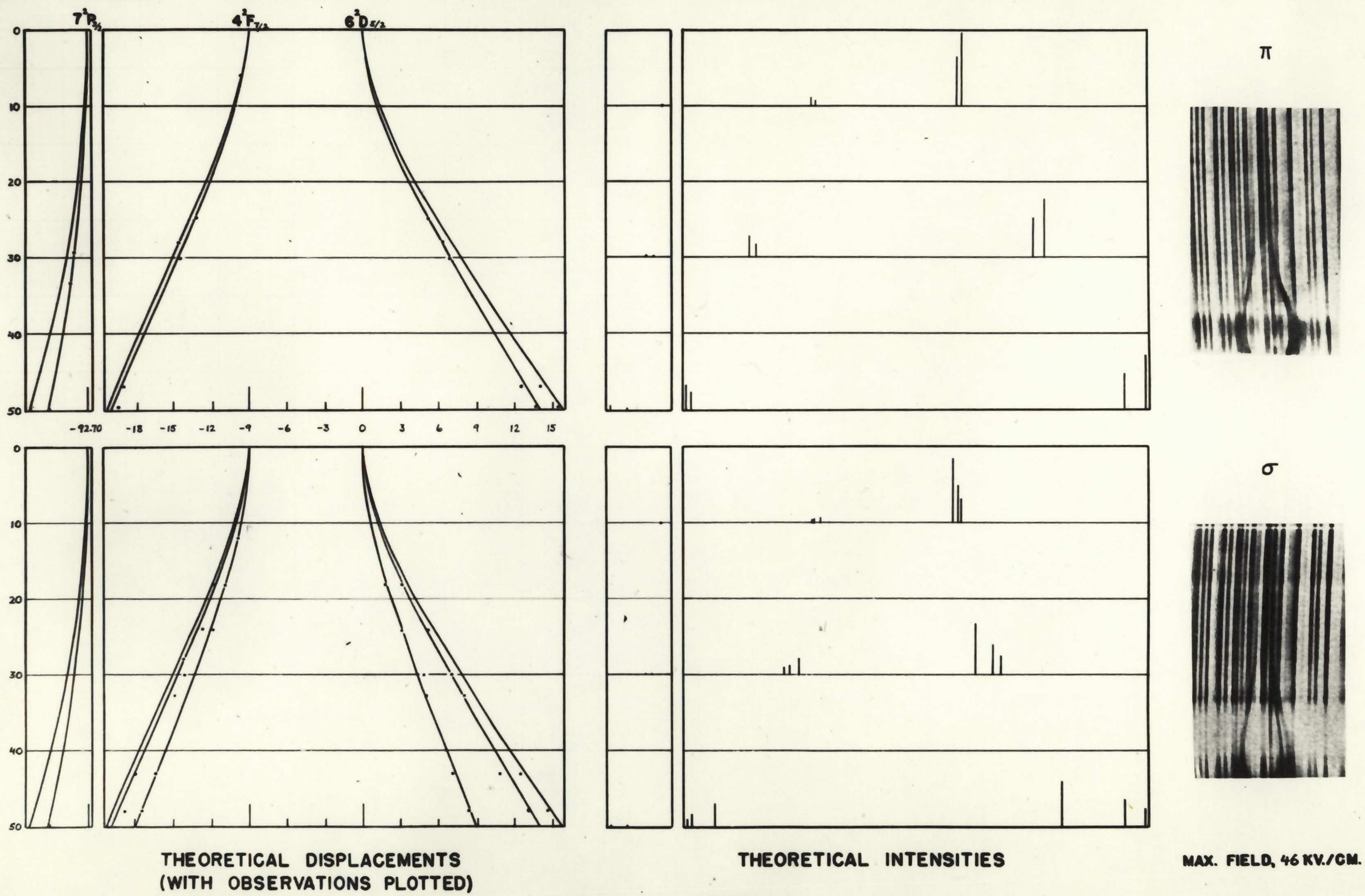


FIG. 4 4210 GROUP

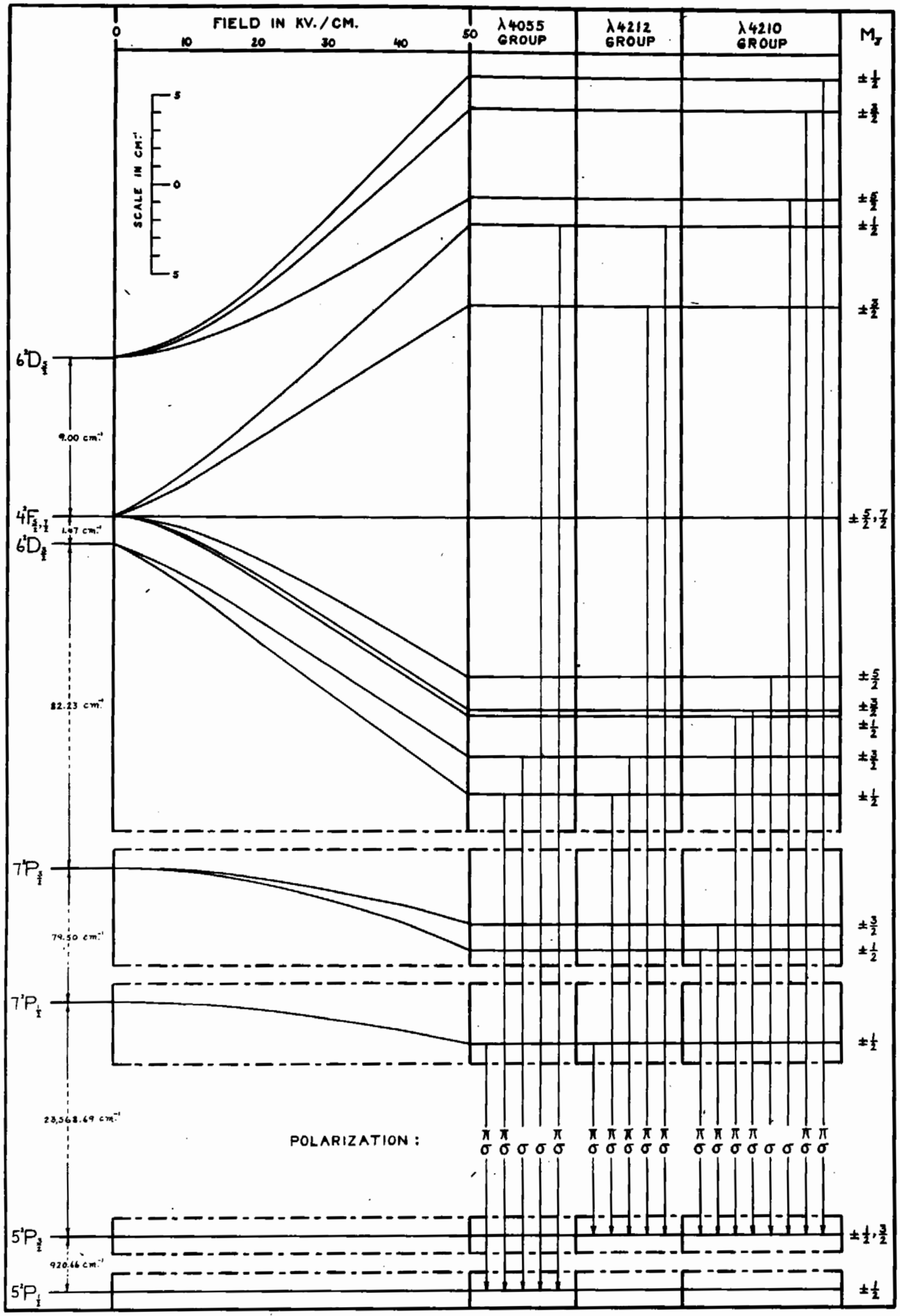


FIG. 5 ENERGY LEVELS AND TRANSITIONS

to the correct displacements. The final calculations, as given in Table II, were made in this approximation and showed an improvement of a fraction of a reciprocal centimeter in the levels concerned.

The good agreement between the calculated and observed displacements is graphically shown in Figures 2, 3 and 4. In a great many of the cases the difference between the observed and calculated displacements is within the limits of experimental error and it is never greater than 0.5 cm^{-1}.

From the diagrams it is therefore seen that, with the exception of the π-component in λ4212 which originates in the $M_J = \pm 1/2$ level of the normal $6^2D_{3/2}$ level, observations have been made of all the Stark component lines.

The $M_J = \pm 5/2$ level from the normal $4^2F_{5/2}$ level does of course exist, but being the only M_J of this value in the low J group, it is not perturbed. Hence while a transition from this level would be allowed in the σ-image of the λ4212 group, it would have zero intensity.

The crossing of two components as observed on one plate is fully supported by the theory, which shows that if the theoretical displacement diagrams were extended to higher fields, the $M_J = \pm 1/2$ component of the $4^2F_{5/2}$ level would cross the $M_J = \pm 5/2$ component of the $6^2D_{5/2}$ level in the vicinity of 64 kilovolts per centimeter.

3. Theoretical Intensities. The procedure followed for the calculation of the relative intensities of the Stark line components is as described in detail by Foster.(9)

Since the perturbations of the final states are negligible, the intensity of each polarized Stark component can be given, to a close approximation, as a fraction of the intensity of a Zeeman component line with the same initial M_J value as the Stark line. The fractional part of any one particular Zeeman component line is given by the S^2 terms, which connect the perturbed states with the unperturbed states from which normal transitions occur in the spectrum. These S^2 terms are found from the determinants which give the displacements of the initial perturbed levels and are normalized through the condition $\sum_x (S_{Dx})^2 = 1$. This means that each new component of the $5^2P - 4^2F$ and $5^2P - 7^2P$ lines will grow in intensity at the expense of the appropriate Zeeman pair (with initial $\pm M_J$) in the original D line and that the total intensity, apart from details of excitation, will remain constant at all fields.

The relative intensities are given in Table III, and are all expressed in terms of the weakest pair of Zeeman lines for the three diffuse lines. The table thus allows direct comparison of the intensities of components on a plate, without the necessity of any conversion factors for the three line groups. The intensities are graphically represented in Figures 2, 3, and 4. The fields are chosen to permit comparison with the experiments. Owing to the wide range of intensities, different scales have been used in the graphs, so that direct comparison of the intensities for two different line groups should be made with the table.

The intensities are in good qualitative agreement with observation and point out why the components of the λ4212 group are so difficult to obtain, and why it is difficult to get any one particular plate to show all the detail around the $\lambda\lambda$4210 - 4212.

TABLE III

4055 Group

		$D_{3/2}$		$F_{5/2}$		$P_{1/2}$
$\lvert M_J\rvert =$		1/2	3/2	3/2	1/2	1/2
σ	F = 10	6.03	19.2	10.8	3.96	0.005
	F = 30	5.14	16.44	13.56	4.82	0.053
	F = 50	4.77	15.93	14.1	5.05	0.22
π	F = 10	24.12			15.84	0.02
	F = 30	20.56			19.27	0.21
	F = 50	19.08			20.22	0.89

4212 Group

		$P_{1/2}$	$D_{3/2}$		$F_{5/2}$	
$\lvert M_J\rvert =$		1/2	1/2	3/2	1/2	3/2
σ	F = 10	.0035	4.22	1.92	2.77	1.08
	F = 30	.015	3.59	1.64	3.36	1.36
	F = 50	.155	3.34	1.59	3.53	1.41
π	F = 10	.0005	0.603	5.76	0.396	3.24
	F = 30	.002	0.514	4.93	0.432	4.07
	F = 50	.022	0.477	4.77	0.505	4.23

4210 Group

		$P_{3/2}$		$F_{7/2}$			$D_{5/2}$		
$\lvert M_J\rvert =$		1/2	3/2	1/2	3/2	5/2	5/2	3/2	1/2
σ	F = 10	.13	.13	7.13	9.89	11.70	168.3	98.03	64.8
	F = 30	1.30	1.51	18.79	27.76	44.28	135.72	78.41	51.91
	F = 50	3.36	3.53	20.99	33.21	59.94	120.06	71.31	47.21
π	F = 10	.39	.17	21.38	13.19			130.71	194.40
	F = 30	3.89	2.02	56.38	37.01			104.54	155.74
	F = 50	10.09	4.71	62.96	44.28			95.083	141.63

THEORETICAL RELATIVE INTENSITIES

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