INTENSITIES IN THE STARK EFFECT OF HELIUM: II

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ABSTRACT

The intensities of the new spectral lines appearing in an electric field may be calculated from the quantum theory of perturbations. To apply the method to helium we consider the helium atom a perturbed hydrogen atom. Calculations are given here for a number of helium lines whose intensities have previously been measured. Measurements of the intensities of the groups $2S-nM$ and $2s-nm$ for $n=4$, 5, 6, and $M=S$, P, D, etc. are given and compared with the calculated intensities. The theory gives intensities of the correct order of magnitude and gives the variation with field approximately correctly but large deviations from the experimental values appear in all groups.

SINCE the previous communication[1] on this subject was written, Heisenberg and Foster have worked out a method of calculating the displacements and intensities of the lines in the spectrum emitted by helium in the presence of an electric field which should give valid results at all fields.[2] In a paper to appear shortly Foster gives calculations of the wave-lengths of these lines and compares them with the results of his measurements.[3] In this paper the results of calculations made by this method are given for the intensities of all lines on which measurements were reported in the previous paper. In addition new measurements of the intensities of lines lying in the violet portion of the helium spectrum are given.

Calculation of the intensities. In order to make the calculation we regard the helium atom as a perturbed hydrogenlike atom. The recent work of Heisenberg[4] on the helium spectrum shows that we may treat the orthohelium and parhelium spectra separately; each can be regarded as the spectrum emitted by a single electron, moving in a central field of force which differs slightly from a Coulomb field. To determine the effect of an external field on the helium atom we must determine the perturbation of a hydrogen atom by the two fields, an internal field, which we may attribute to the doubly charged nucleus and the interaction of the two electrons, and the external field which we apply.[4a] All we need know about the internal field (if we calculate the perturbation only to a first approximation) are the deviations of the empirically known helium terms from the corresponding hydrogen terms. We carry out the perturbation calculation by the method

[1] Dewey, Phys. Rev. **28**, 1108 (1926).

[2] Calculations for small fields are given by Unsold, Ann. d. Physik **82**, 355 (1927).

[3] Foster, Phys. Rev. **23**, 667 (1924); Proc. Roy. Soc. **A114**, 47 (1927).

[4] Heisenberg, Zeits. f. Physik **38**, 441 (1924), **39**, 499 (1926).

[4a] A corresponding calculation on the basis of the earliest methods of the quantum theory was given by Kramers, Zeits. f. Physik **3**, 199 (1920), and by Becker, *ibid*, **9**, 332 (1922).

given by Born, Heisenberg and Jordan[5] for the case in which the unperturbed system is degenerate. We try to find[6] the matrix **S** such that

$$\mathbf{W}=\mathbf{S}^{-1}\mathbf{H}(\mathrm{p}_0,\mathrm{q}_0)\mathbf{S} \tag{1}$$

is a diagonal matrix

$$\mathrm{q}=\mathbf{S}^{-1}\mathrm{q}_0\mathbf{S} \tag{2}$$

where $W(n,n)$ represents the change of the total energy by the perturbation, $W(n,m)$ is zero when n is not equal to m, **H** is the mean value of the perturbing energy, taken over the unperturbed system, q the coordinate of the electron in a given direction. The subscripts 0 refer to the unperturbed system. The necessary equation is

$$\det\left|W\delta(r,s)-H(r,s)\right|=0 \tag{3}$$

where r and s refer to the rows and columns of the determinant. In the case we are considering

$$\mathbf{H}=\mathbf{H}'+\mathbf{H}''$$

where $\mathbf{H}'$ refers to the inner and $\mathbf{H}''$ to the outer field.

The inner field can be regarded as a field of central symmetry, as it does not change the selection rule for the azimuthal quantum number. Its mean value, taken over the unperturbed motion, is directly given by the term values ν_r of the helium atom; if ν_0 is the term value of the corresponding hydrogen term, we get

$$\begin{aligned} H'(r,s)&=h(\nu_0-\nu_r) \qquad \text{for } r=s \\ &=0 \qquad\qquad\qquad \text{for } r\neq s \end{aligned}$$

The outer field F gives rise to a term eqF in the potential energy, its time-mean value is given by the coordinate of the "electric center" in the direction of the field. The matrix elements of eqF are calculated by Pauli[7]:

$$H''(r,r-1)=(3/2)a_0eF\left[(n^2-r^2)(r^2-m^2)/(4r^2-1)\right]^{1/2}$$

$$H''(r,r+1)=(3/2)a_0eF\left\{\left[n^2-(r+1)^2\right]\left[(r+1)^2-m^2\right]/\left[4(r+1)^2-1\right]\right\}^{1/2}$$

$$H''(r,s)=0 \text{ for } r\neq s\pm 1$$

where a_0 is the hydrogen radius, e the charge on the electron, n the principal quantum number, m the magnetic quantum number and F the electric field. To carry through the numerical calculation we consider the atom initially exposed to a very weak external magnetic field which removes the degeneracy with respect to the magnetic quantum number m. The system is then degenerate only with respect to the azimuthal quantum number and we may

[5] Born, Heisenberg and Jordan, Zeits. f. Physik **35**, 557 (1926). For a shorter account of the quantum theory of perturbations see Heisenberg, Math. Ann. **95**, 683 (1926).

[6] For details of the following calculations see J. S. Foster, Proc. Roy. Soc. (in press).

[7] W. Pauli, Zeits. f. Physik **36**, 336 (1927), Eqs. (60) and (66).

apply Eq. (3) to solve for W. If we insert the values of H in the determinant and insert for W its value $h(\nu_0-\nu)$, where ν is the frequency of the displaced helium term, and replace $\nu_0-\nu$ by x and $\nu_0-\nu_r$ by λ_r we obtain the determinant

$$\begin{vmatrix} h(x-\lambda_r) & \frac{3a_0 eF}{2}\left(\frac{[n^2-(r+1)^2]\,[(r+1)^2-m]}{4(r+1)^2-1}\right)^{1/2} & 0 & \cdots \\ \frac{3a_0 eF}{2}\left(\frac{[n^2-(r+1)^2]\,[(r+1)^2-m^2]}{4(r+1)^2-1}\right)^{1/2} & h(x-\lambda_{r+1}) & \frac{3a_0 eF}{2}\left(\frac{[n^2-(r+2)^2]\,[(r+2)^2-m^2]}{4(r+2)^2-1}\right)^{1/2} & \cdots \\ 0 & \frac{3a_0 eF}{2}\left(\frac{[n^2-(r+2)^2]\,[(r+2)^2-m^2]}{4(r+2)^2-1}\right)^{1/2} & h(x-\lambda_{r+2}) & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}=0 \qquad (5)$$

The subscripts refer to azimuthal quantum numbers. The λ's for the s, p and d terms are taken from Paschen's tables, for the higher terms they are calculated from the formulae of Waller.[8] The determinant has $n-m$ roots which give the displacements of the $n-m$ terms which have the quantum numbers n and m for which we have set up the determinant. Since the lower state will be practically undisturbed at any field obtainable in the laboratory the displacements of the terms of the upper state are the same as the displacements of the lines.

Having solved for the W's we can insert them in the determinant and regard it as a system of linear equations in the S's. We may write Eq. (2) in the form

$$q(r,u)=\sum_s\sum_t \tilde{S}^*(r,s)q_0(s,t)S(t,u) \qquad (6)$$

where $\tilde{S}^*$ indicates the transposed conjugate form of S. Since the final state is undisturbed

$$S(t,u)=\begin{cases} 1 \text{ for } t=u \\ 0 \text{ for } t\neq u. \end{cases}$$

Also

$$q_0(s,t)=0 \text{ for } s\neq t\pm 1$$

On solving (1) for the S's we obtain $n-m$ S's for each value of x which we insert in the equation, one corresponding to each index (azimuthal quantum number) appearing in the equation. Using the azimuthal quantum number as the second index of S and the number of the root x to which it corresponds as the first, Eq. (6) reduces to

$$q(k,l)=S(k,l-1)q_0(l,l-1)+S(k,l+1)q_0(l,l+1) \qquad (7)$$

where k is the azimuthal quantum number of the initial state and l of the final state. For instance

$$q(2P-4F)=S(4F,4S)q_0(2P-4S)+S(4F,4D)q_0(2P-4D)$$

[8] Waller, Zeits. f. Physik **38**, 635 (1926).

When two terms appear in this formula, one of them is in all the cases we shall consider very much larger than the other; for all the lines for which calculations are given in this paper the smaller will be disregarded. That is, for instance:

$$I(2P-4F)=\text{const.}\,[S(4F,4D)q_0(2P-4D)]^2$$

The S's are real and so normalized that

$$\sum_s S(r,s)^2=1$$

Then

$$\sum_r S(r,s)^2=1,$$

which gives a check on the correctness of the calculation. The S's must be calculated for each value of m. The relative intensities of the unperturbed lines which differ only in the magnetic quantum number are determined from the rules given by Kronig[9] and others. In most cases in these experiments the lines which have the same principal and azimuthal quantum numbers are superposed on the plates and their calculated intensities are added. The method of normalizing the S's and of summing superposed lines is equivalent to the assumption made in the calculations from the dispersion theory that the number of atoms in the states nS, nP, nD, etc., is the same. In making the calculations for orthohelium the fine structure was neglected and the calculations made as if the terms were single. This should not introduce appreciable error, since we can regard the fine structure as a perturbation of negligible magnitude.

Experimental Method

The experimental arrangement was as described in the previous paper except for certain minor changes. The operation of the Lo Surdo tube was improved by using a copper cathode with an aluminum end. The aluminum spattered less than molybdenum and the copper served to conduct away the heat. To keep the tube running smoothly it is necessary to keep the cathode below red heat. The tube was made of pyrex glass and a very massive anticathode also of aluminum was used. Instead of direct current generators rectified current from a high-tension transformer was used. A Coolidge tube was connected in series with the apparatus as a resistance. This was found very convenient as current through the filament of the Coolidge tube could be adjusted until the current put through the apparatus was just under the saturation current of the Coolidge tube. This reduced flashing somewhat, and protected the apparatus and transformer from damage in case for any reason the resistance of the Lo Surdo tube fell while it was in operation, so that it was not necessary to watch the apparatus so closely. A Hilger quartz spectrograph, type E, was used, with, as before, Ilford Rapid Chromatic plates, developed for four minutes in Rodinol 1/20 at 18°. The field was

[9] Kronig, Zeits. f. Physik **31,** 885 (1925).

determined from the separation of the lines of the group $2S$–$5M$ by comparison with the calculated separations. As it seemed probable that the displacement of the lines by variations in the field might make the more displaced lines appear weaker on the plates than the less displaced lines a very wide slit was used, 0.06 mm. This corresponds to a wave-length difference of about 0.5A on these plates and should reduce this error to a very small value. The effect of time on the blackening curves was investigated experimentally and found to be negligible. The blackening curves for the longer wave-lengths were taken with a tungsten filament lamp with a quartz plate cemented to one end. As it was found very difficult to obtain intensity enough from such a lamp at wave-lengths below about 3300A, a water cooled Finssen quartz mercury arc such as is used in hospitals was used for the shorter wave-lengths. The variation in intensity was obtained by varying the time of exposure. The lamp did not give a constant emission over short periods, showing irregular variations of periods shorter than a minute, but when all the exposures were long these variations were averaged out and reproducible results were obtained. The light emitted by this lamp was thus very similar to the light emitted by the Lo Surdo tube. At 3450A a blackening curve was taken with this lamp and also with the tungsten filament lamp and it was found that the two curves had the same form. The form of the blackening curves changes fairly rapidly with wave-length in the region in which these measurements were made and this may introduce considerable error into certain of the measurements, particularly into those on the lines of group $2s$–$4m$ (3185A), and to a less extent into the other measurements on the orthohelium lines; for the parhelium lines this error is small. A comparison of the intensities of the least disturbed lines gives the same values for the ratio of the intensities of these lines to within thirty percent for all lines on all exposures, even when the measured intensity of the lines is very different on the different exposures, and the agreement is usually better than this. For the lines in the visible region, whose intensity was given in the previous paper, the agreement was somewhat better, no disagreements larger than twenty percent being observed. As only two exposures were compared to obtain any of the ratios given in this paper the error should never be more than doubled in making this comparison.

Results

Parhelium lines. In Table I the calculated values of the intensities of the parhelium lines of the fourth group are given, together with the measured values, which are repeated from the previous paper for comparison with the calculation. The measured and calculated values of the intensities are so arranged as to add up to 100 for the entire group under consideration. The line $2S$–$4S$ was not observed. In Fig. 1 the calculated intensities of the lines of group $2S$–$5M$ are represented by solid lines and the points represent the measured intensities of these lines. The square of the field is used as abscissa and the relative intensity of the line as ordinate. The dotted lines are the straight lines which best represent the experimental data. The line

TABLE I

The calculated and measured intensities of the parhelium lines of the fourth group.

Field kv/cm	2P−4P ∥	2P−4P ⊥	2P−4D ∥	2P−4D ⊥	2P−4F ∥	2P−4F ⊥	2S−4P ∥	2S−4P ⊥	2S−4D ∥	2S−4D ⊥	2S−4F ∥	2S−4F ⊥
14.2 calc.	1.7	0.65	77	79	22	20	98	99	1.4	1.0	0.69	0.47
obs.	2.3	.86	77	77	23	22	96	96	2.5	2.0	1.0	1.7
16.2 calc.	2.1	0.79	74	77	23	22	97	98	1.7	1.3	0.89	0.77
obs.	2.3	.85	72	76	26	23	95	95	2.7	2.5	2.0	2.3
18.6 calc.	2.6	0.98	72	74	25	25	97	97	2.1	1.6	1.2	1.0
obs.	3.3	1.3	63	64	34	35	94	94	3.3	3.0	3.1	2.9
19.8 calc.	3.0	1.1	72	73	26	26	96	97	2.3	1.7	1.4	1.2
obs.	3.3	1.2	63	64	34	35	93	95	3.4	2.7	3.2	2.8
24.3 calc.	4.6	1.8	69	69	27	30	94	96	3.2	2.3	2.3	2.0
obs.	7.4	3.0	66	61	27	36	91	93	4.5	3.6	4.2	3.2

$2S$–$5S$ was always observed as a totally parallel polarized line. Its intensity is not given as the line is superposed on the group $2s$–$8m$. In Fig. 2 the lines represent the calculated values of the intensities of the lines of group $2P$–$5M$

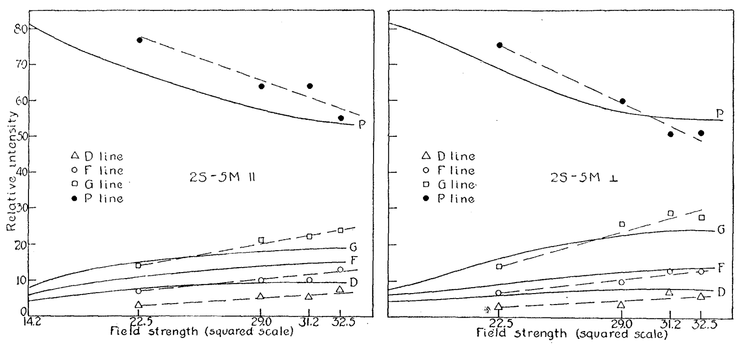

Fig. 1. Calculated and measured intensities of the lines of the group $2S-5M$.

and the points represent the measured values, which are taken from the data given in the previous paper. In Fig. 3 the intensities of the lines of the groups $2P$–$6M$ and $2S$–$6M$ are represented as in the previous paper, the intensities of the parallel components being given by lines above and the intensities of the perpendicular components by lines below the base line. The experimental values for the former group are taken from the first paper and for the latter are new.

It is obvious from the figures that the disagreement between theory and experiment is much larger than the experimental error. On the other hand the theory in every case gives the correct order of magnitude for the intensity and an approximately correct value for the polarization of the lines and predicts correctly which lines increase in relative intensity, which decrease and which go through a maximum as we increase the field. We obtain a qualitative but not a quantitative agreement between theory and experiment. A comparison of Fig. 1 with Fig. 2 and of the two groups whose intensities are given in Fig. 4 with each other shows that the deviations are very similar for the groups of lines which have the same sets of initial states. This suggests that the assumption that the probability of exciting

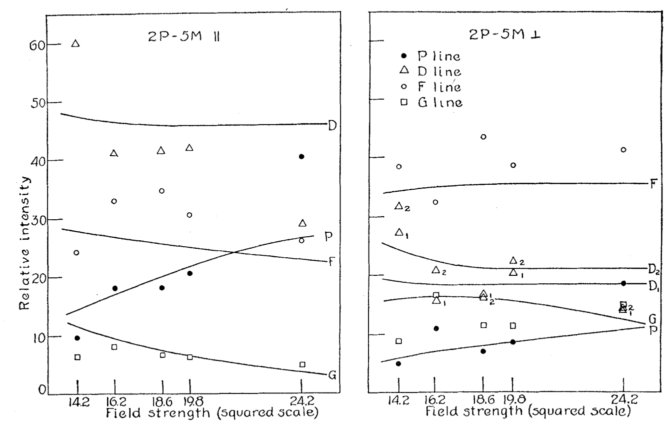

Fig. 2. Calculated and measured intensities of the lines of the group $2P-5M$.

the states nP, nD, nF, etc., is the same may not be warranted and that at least a part of the deviation may be due to differences in the number of atoms excited to the different states. In the fourth group, where the deviations are smaller compared to the experimental error, the deviations are not the same for the lines which have the same initial but different final states. In comparing the figures one should bear in mind that the intensity of the parallel components of the lines of group $2S-nM$ depends on the S's for the states where the magnetic quantum number m is 0, and the number of atoms excited to each of these states. The intensity of the perpendicular components of the lines of this group depends on the S's for m equal to one, and the intensities of the parallel components of the lines of group $2P-nM$ depend on both sets of S's. The intensity of the perpendicular components of the lines of the latter group depends largely on the S's for m equal to two. Because of the method of normalizing the S's and of expressing the measured values any deviation of a strong line causes an inverse deviation of all the other lines. The closeness with which the deviation of a line with a given initial and final state is repeated by the deviation of the line with the same initial but a different final state makes it unlikely that the deviation is due to experimental error.

Orthohelium lines. In Table II are given the calculated intensities of the groups of lines $2p$–$4m$ and $2s$–$4m$ and the measured values for the former group are repeated from the earlier paper and measured values given for the latter group. In Table III the same data is given for the fifth group. The measured and calculated values for the group $2p$–$6m$ are plotted for three

TABLE II

The calculated and measured intensities of orthohelium lines of the fourth group.

Field kv/cm	2p−4p ∥	2p−4p ⊥	2p−4d ∥	2p−4d ⊥	2p−4f ∥	2p−4f ⊥
14.2 calc.	0.072	0.028	85	86	15	14
obs.	.15	.07	86	89	14	11
16.2 calc.	0.099	0.037	81	84	19	16
obs.	.20		85	88	15	12
18.6 calc.	0.12	0.048	79	82	21	18
obs.	.23	.15	83	88	17	12
19.8 calc.	0.13	0.054	78	81	22	19
obs.	.25	.15	80	84	20	16
24.3 calc.	0.19		73		27	
obs.	.35		75		25	

	2s−4s ∥	2s−4d ∥	2s−4d ⊥	2s−4f ∥	2s−4f ⊥
22.5 calc.	0.01		0.12		0.02
obs.			.003		
29.0 calc.	0.02	0.26	0.20	0.06	0.04
obs.	.001	.01	.005	.002	.001

TABLE III

Calculated and measured intensities of orthohelium lines of the fifth group.

Field kv/cm	2p−5p ∥	2p−5p ⊥	2p−5d ∥	2p−5d ⊥	2p−5f ∥	2p−5f ⊥	2p−5g ∥	2p−5g ⊥
14.2 calc.	0.6	0.25	39	42	35	41	25	17
obs.	1.2	.67	46	47	35	35	19	17
16.2 calc.	0.8	0.33	38	39	35	41	26	20
obs.			31	36	49	45	20	18
18.6 calc.	1.1	0.45	36	36	36	39	27	24
obs.	1.4	1.2	33	33	42	46	23	20
19.8 calc.	1.2	0.51	35	35	36	39	28	25
obs.	1.3	1.0	32	35	44	47	23	18
24.3 calc.	1.7	0.70	32	35	36	39	29	25
obs.	2.8	2.3	25	29	55	55	17	13

	2s−5s ∥	2s−5p ∥	2s−5p ⊥	2s−5d ∥	2s−5d ⊥	2s−5f ∥	2s−5f ⊥	2s−5g ∥	2s−5g ⊥
22.5 calc.	0.07	98	98	0.8	0.7	0.7	0.6	0.4	0.3
obs.		99	100	.25	.15	.25	.17	$<.1$	$<.1$
29.0 calc.	0.11	96	97	1.3	1.2	1.2	0.9	1.0	0.6
obs.	.12	99	100	.27	.17	.29	.18	$<.1$	0.05

of the fields for which data were given in Fig. 4 and measurements of $2s$–$6m$ are given together with the calculated intensities in Table IV. Fig. 4 gives the measured intensity of the lines of group $2p$–$7m$ at three fields higher

TABLE IV

The calculated and measured intensities of the lines of the group 2s−6m.

Field kv/cm	2s−6s ∥	2s−6p ∥	2s−6p ⊥	2s−6d ∥	2s−6d ⊥	2s−6f ∥	2s−6f ⊥	2s−6g ∥	2s−6g ⊥	2s−6h ∥	2s−6h ⊥
22.5 calc.	0.7	87		5.2		3.2		3.0		1.1	
obs.		95		2.4		1.5		1.2		<.6	
29.0 calc.	1.2	78	83	8.6	7.0	5.9	4.8	4.3	3.2	2.5	1.8
obs.	.7	93	96	2.4	1.2	4.2	1.8	.75	.5	<.3	<.2

than those for which the intensities in this group were given in the previous paper and corrects an *erratum* in the intensities of this group at 19.8 kv/cm given in that paper. No calculations were made for this group as they would be extremely laborious and sufficient data has already been given to show

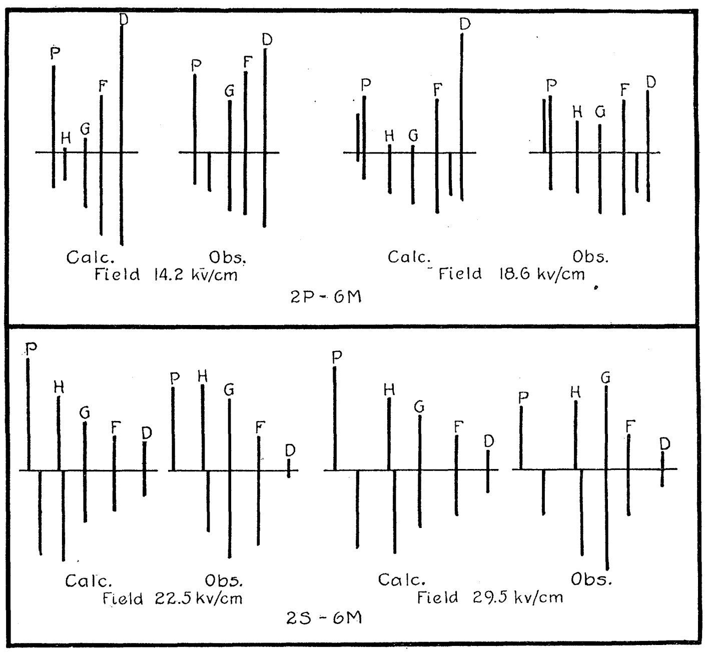

Fig. 3. Calculated and measured intensities of parhelium lines of the sixth group.

what agreement can be expected between the theory as applied here and experiment.

The deviation of the measured intensities of the orthohelium lines from the calculated intensities is considerably larger than for the parhelium lines. Particularly in the groups with the final state 2*s* the deviations are very large. The polarization of the weak lines does not agree with that given by the theory[10] and the deviations can not be regarded as depending only on the initial state. The deviations are in the same direction for lines with the same initial and different final state but are much larger for those with the final

[10] Cf. Table III of the previous communication.

state $2s$. The lines which represent large changes of azimuthal quantum number in the s groups appear with very slight intensity, the theoretical values being much larger. The experimental uncertainty is larger for these groups than for any others but should not be large as long as the weak lines are compared with each other. The deviations, however, are as large when this is done as when the intensity of the strong line is compared with that of a weak line. In the seventh group the total disappearance of the parallel component of the d line is interesting. This has been previously reported

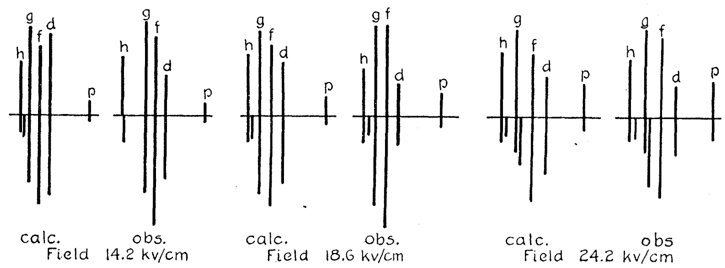

Fig. 4. Calculated and measured intensities of the lines of the group $2p-6m$.

by Foster. The theory predicts that the parallel component of a line with final state P will almost entirely disappear when the line is so displaced as have the same wave-length as the undisplaced P line. It will in general reappear when it is further displaced, as the line $2P$–$6H$ does. According to Foster's measurements the line $2p$–$7d$ crosses the position of the undisplaced p line at a field of about twenty kilovolts per centimeter, the field at which it is no longer observed. This line does not reappear at the fields which are used in our experiment; at a field of twenty-nine kilovolts per centimeter

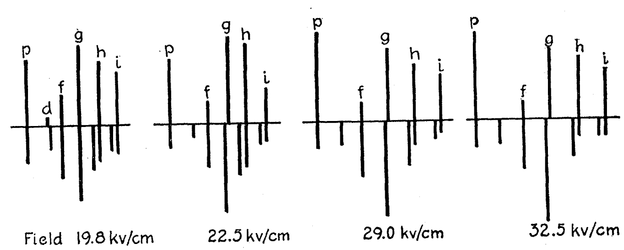

Fig. 5. Measured intensities of the lines of the group $2p-7m$.

it has an intensity of less than one one-thousandth the intensity of the whole group.

Conclusions

Calculations from the quantum theory of perturbations on the assumptions used here and to this approximation give only approximate values for the intensities of the new lines appearing in the Stark effect. The deviations are such as to suggest that they are partly due to differences in the number of atoms excited to different states of almost the same energy. Apparently, factors come into play in the case of orthohelium other than those which influence the parhelium lines. No explanation of the deviations suggests itself. They may be due to the influence of the atoms on each other, which is here entirely neglected, and to the fact that we have neglected higher approximations of the theory in making the calculations.

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