Perturbations in the Barium I Spectrum.

By G. O. Langstroth, Ph.D., 1851 Exhibition Scholar, Rijks Universiteit, Utrecht, Holland.

(Communicated by O. W. Richardson, F.R.S.—Received May 23, 1933.)

Quantum mechanics predicts that mutual interactions occur between adjacent spectral terms of the same \( j \) value arising from similar (odd or even) electron configurations. These interactions affect both the series term values and the intensities of transitions from the involved levels, and the normal multiplet intensity formulae* no longer hold. Theoretically, one expects that when such perturbations occur, the intensity\(^f\) sum of each enlarged \( j \) group of the transition array for all the interacting configurations should be invariant,\(^\dagger\) i.e., equal to the theoretical sum which is obtained if the intensities in each multiplet be calculated separately for isolated LS coupling. These theoretical sums depend on uncalculated parameters (concerned with the radial functions) which connect the intensities in one multiplet with those of another arising from a different electron configuration, and which must be determined from the experimental data. The adjustment is easily made, however, if there exist transitions in each multiplet which are perturbed very slightly or not at all.

It has been possible to identify the interacting terms which influence the intensities of the first three multiplets of the diffuse and of the fundamental series in the Ba I spectrum, and to show that for the most part, the experimental results confirm the theoretical prediction that each enlarged \( j \) group intensity sum should be invariant. Three striking exceptions occur, but they have an explanation other than a failure of the theory. This agreement is highly encouraging in view of the fact that the perturbations are in some instances several times the normal line intensity. For the present, no attempt has been made to calculate the perturbation to be expected in individual lines. The spin-orbit interaction matrices, for example, can be determined,\(^\S\) but owing to the fact that the parent electron configurations are not known for

---

† The experimental intensities with the \( v^4 \) and excitation corrections applied.
Perturbations in Barium I Spectrum.

all the perturbing terms, calculations which would give a more detailed test of theory, are at present impracticable.*

The group of mutually perturbed multiplets† in the diffuse series consists of transitions to the 23P (6s6p) levels from 43D (6s6d), 53D (6s7d), 63D (6s8d), 33P (6p2), 3D (5d7s), and an unclassified level qk at 6688.1 cm. The 43D and 63D transitions are only slightly perturbed. In the fundamental series it consists of transitions to the 33D (6s5d) levels from 53F (6s5f), 3F (5d7p), a 3F term at 4561.6, 4750.5, and 4969.3 cm. , and 43F (6s4f), and 63F (6s6f). While the term value perturbations are felt in the latter two terms the intensities of transitions from them show no initial term perturbations large enough to be apparent.

The perturbations in the fundamental series term values are relatively large and all members of the term series are affected. This can only occur if the interactions are of electrostatic origin.§ For reasons to be discussed later, it is believed that the interactions in the diffuse perturbation group are of magnetic origin.

It is a general thing in both perturbation groups that the weakest multiplets show the largest percentage intensity perturbations as required by theory. Configurations with two excited electrons appear to be more sensitive to perturbations than those with one electron in the ground state. There is definite evidence that the 33D3 level is perturbed, although no adjacent terms capable of interacting with it are known. It may be connected with the circumstances determining the normal state of the atom (— 5s2 5p66s2).

A very striking point in the intensity analysis is the manner in which it enables us to understand certain apparently anomalous lines in the spectrum. A weak multiplet may, by perturbation, have one (or more) of its lines intensified until it becomes strong compared to other lines in the spectrum, while its remaining lines are so weak as to escape notice. Several such “fragments” must be considered in the present instance. Naturally their j values are not

* The writer is aware of only one case in which the results of such calculations have been compared with experiment (Kast, ‘Z. Physik,’ vol. 79, p. 731 (1932)). In this case (Sr spectrum) only two terms were involved and the perturbations were not so large as one might wish, in view of the magnitude of the experimental error. There was agreement within the experimental error.

† This will be referred to as a “perturbation group.”

‡ Russell and Saunders, ‘Astrophys. J.,’ vol. 61, p. 39 (1925). The usual (e.g., Fowler’s) term values have been increased by 3 units in accordance with Shenstone and Russell’s suggestion, ‘Phys. Rev.,’ vol. 39, p. 415 (1932).

known uniquely from their combining properties, but only as one of two or three. It has been possible from the intensity analysis to assign them \( j \) values without ambiguity, to show the source of their "borrowed" intensity, and to indicate what their intensities would be if unperturbed. Moreover, from similar considerations it has been possible to identify a line hitherto unclassified, whose intensity is for the most part the result of the same general process. These examples serve to illustrate how such data can be used to further our knowledge and understanding of the more irregular spectral lines.

A generalized Ritz equation, derived by perturbation theory,* has had remarkable success in describing perturbed term value series,† in the form

\[
\nu_n = \frac{R}{(n + \mu + \alpha \nu_n + \sum_k \beta_k / \nu_n - \nu_k)^2}
\]

where \( \beta_k \) is a "perturbation constant," which is a measure of the interaction of the term \( \nu_n \) with some other at \( \nu_k \). \( R, \mu, \) and \( \alpha \) are constants, and \( n \) is the series order number. The very elegant graphical method of determining the constants, given by Shenstone and Russell, does not, however, permit one to find small \( \beta_k \)'s, although if \( \nu_n - \nu_k \) is small, the perturbation effect may be appreciable. Neglect of a small \( \beta_k \) term in an analysis may produce a material discrepancy between the calculated and observed values for a particular level while those immediately before and after show good agreement. This type of "isolated" discrepancy is well illustrated in the fundamental series, and is satisfactorily accounted for by the above explanation. The constants for the \( nF_4, 3, 2 \) series are given.

2. Procedure.

The following procedure was adopted in identifying the interacting terms and comparing experiment with theory. Fortunately, the barium spectrum is well known and only very weak lines have not had their initial and final term values assigned. Moreover, as pointed out later in this paper, it is sufficient to consider only the triplet systems.

A multiplet is chosen which exhibits departures from the normal relative intensity values, e.g., \( 2^3P - 5^3D \). From an examination of all known term values in the standard tables‡ it is possible to pick out all terms, of the same

---

† Shenstone and Russell, loc. cit.
Perturbations in Barium I Spectrum.

kind (odd or even) as the chosen initial term, which lie within a few hundred cm$^{-1}$ from it. The intensities of the transitions from these levels to the final levels (2$^3$P) are then determined. In the present instance, other important transitions from the initial levels do not occur.

In order to test if all the interacting configurations have been considered, the sum rule for the final levels is applied. When the final levels are unperturbed it is sufficient that the intensity sums of transitions to them be in the ratio of their statistical weights. It has been pointed out by Bartlett* that if some of the initial levels arise from configurations containing equivalent electrons, allowance must be made for those terms excluded by the operation of Pauli's equivalence principle. In the present work, the sums are still in the ratios of the statistical weights after such corrections have been made. If the sum rule is found not to hold, the discrepancies may be attributed to failure to include all perturbing initial levels, or to perturbations in the final levels. If the latter is so, it can readily be seen from a comparison of the intensities of the chosen multiplet (with the known initial term perturbations removed), and the intensities in other multiplets of the same series which are not strongly perturbed in the initial levels. If, however, it is the former, it is necessary to extend the measurements to include other transitions from initial levels lying at a greater distance from the chosen multiplet initial levels, or to look for unidentified lines which have sufficient intensity to affect the sums.

When the measurements are complete, a transition array for all the perturbing configurations is drawn up, and the parameters which connect the theoretical intensities of one multiplet with those of another from a different electron configuration are adjusted. The guiding principle is to seek for certain unperturbed or slightly perturbed transitions, which are sufficient to fix the theoretical intensities for most multiplets. The remaining "complete" multiplets can be given rough values from consideration of their intensities in general. One can then without ambiguity assign to definite enlarged $j$ groups those "fragments" of multiplets (whose initial $j$ values are not uniquely known), from consideration of the surplus or deficit of the experimental intensity in each group. This is possible because the fragments in the present case are strong and consist mostly of "borrowed" intensity. The roughly adjusted parameters can then be finally determined, thus making possible the comparison of each enlarged $j$ group sum with the theoretically predicted value, and the determination of the intensity perturbations in the individual lines.

For the most part an arc with carbon electrodes cored with a mixture of KCl and BaCl₂ was used as a source. This arc in air gives too much background for an accurate determination of relative intensities because of the presence of oxide bands. When operated in nitrogen, however, this difficulty disappears. In general arc currents of about 3.5 amperes were used. Owing to the interference of certain potassium lines this source could not be used for measurements of the 2⁢3P — 4⁢3D multiplet, but an arc cored with LiCl and BaCl₂ in air was found to be satisfactory. Special precautions had to be taken in photographing the 2⁢3P — 6⁢3D and the 3⁢3D — 6⁢3F multiplets, for when the arc was operated under the usual conditions, their lines were so broadened as to have almost the appearance of bands. This broadening increased with the arc current and was worse with low concentrations of BaCl₂. By increasing the concentration of the BaCl₂ and running the arc at the lowest current at which it would operate (about 0.8 amps.), it was possible to obtain sharp lines. The broadening is thought to be due to a Stark effect caused by the fields of charged particles in the arc. The fact that it depends on the arc current and apparently on the ionization potential of the coring material supports this view.

The coring material (KCl) usually contained only 1% BaCl₂ by weight, which corresponds to about 0.2% of barium atoms. Since no change in the relative intensities within strong multiplets occurred when the concentration of BaCl₂ was increased to several times this amount, the effects of self-absorption were taken to be negligible. The final levels lie at approximately 13,000 and 9000 cm⁻¹ above the ground level. Results of test measurements are contained in the data.

A standard Hilger El quartz spectrograph with a dispersion of about 10 Å/mm. at λ3800 was used. Intensity blackening marks were put on each plate by means of a step slit and a standard lamp whose intensity wave-length distribution was known as a function of the current. Exposure times for the barium spectrum and the intensity marks were made equal. For measurements below λ4000 Å, quartz optics and a quartz standard lamp were used.

The blackening measurements were made on a Moll microphotometer. The intensities were determined from these in the usual way.* Corrections for the background were made when it was present by subtracting the intensity of the background from the intensity of the line plus the background. In the few experiments in which overlapping lines occurred, their intensity curves

* Ornstein, Moll and Burger, "Objektive Spektralphotometrie" (Vieweg), 1932.
Perturbations in Barium I Spectrum.

were determined from their photometer curves on a special apparatus,* and these were analysed to give the separate intensities in the usual way.*

The strongest lines of strontium and calcium were faintly present on most plates, owing to impurities in the arc carbons and coring. The sodium D lines were also present. Special care was taken to prevent blends from passing unnoticed, not only by reference to standard wave-length tables, but by comparison with a special control plate. This plate was obtained by photographing the spectrum of an arc cored with KCl and SrCl₂ in the ratio 3:1, which mixture is almost certain to contain all the impurities present in the KCl — BaCl₂ coring. One spectrum on the control plate was strongly overexposed, so that if there was a possibility of any blends occurring in the barium lines to be measured, it was immediately indicated, in "matching" the plate with the control plate. Such blends were very rare, and when present are noted in the data.

In order to measure arc temperatures, which determine the populations in the initial levels (Boltzmann distribution), photographs were taken of the spectrum of an arc cored with powdered carbon and the 1% BaCl₂ — KCl mixture in equal parts. The relative intensities of the bandheads of the 0 → 0, 1 → 1, 2 → 2, and 3 → 3, CN bands at λ3884 were measured and from these the arc temperatures were determined.† The transition probabilities of the lines of \( ^3 \text{P} → ^3 \text{P}' \)) were then calculated by applying the \( v^4 \) and excitation corrections to their intensities measured in the same exposures. The arc temperature for any plate could then be determined from measurement of the intensities of two or more lines of \( ^3 \text{P} → ^3 \text{P}' \) and calculation from their known transition probabilities.

It should be stressed that a specially prepared source is necessary to obtain a primary standard of temperature measurement. Temperatures found from the intensities of the CN bands on the usual plates cannot be used, since the CN bands and the Ba lines are radiated from different parts of the arc. For example, for one plate the temperature found from the CN bands on it was 5700° K, while that determined from \( ^3 \text{P} → ^3 \text{P}' \) was 3600° K. With the specially prepared source in which the coring contains a large percentage of powdered carbon, however, it is believed that no serious error is made in assuming that the temperatures at which the CN bands and the Ba lines are emitted, are identical.

‡ For the nomenclature used in this paper, see Table I.
Two primary temperature determinations were made. The first gave three values which differed from the mean by less than 130° K, while in the second, the maximum variation from the mean was 250° K. The largest temperature correction was about 30% \(2^3P - 3^3P'\).

The experimental error in individual intensity determinations is less than 8%. Since it is more important to know accurately the intensities within the multiplets than it is to know the relative intensity of one multiplet to another, more determinations have been made for the former.

4. Results.

In this section are included the results of (a) the identification of the interacting terms by the procedure outlined in section 2; (b) the intensity measurements in the diffuse series group; (c) the intensity measurements in the fundamental series group; (d) measurements of the triplet singlet ratios in the fundamental series; and (e) a term value analysis of the fundamental series using two perturbing terms.

(a) Fig. 1. Interacting terms lying near \(5^3\)D and \(5^3\)F. The \(4^3\)D and \(6^3\)D, and the \(4^3\)F and \(6^3\)F levels have been omitted in the diagram, although intensities of transitions from the former indicate slight perturbations in the initial levels. For (a), (b), (c), etc., see Table I.
Perturbations in Barium I Spectrum.

Table I.—Term Values for the Interacting Terms.*

<table>
<thead>
<tr>
<th>A.</th>
<th>Symbol.†</th>
<th>Shortened Symbol.</th>
<th>j = 0.</th>
<th>j = 1.</th>
<th>j = 2.</th>
<th>j = 3.</th>
<th>j = 4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5 sD (6s7d)</td>
<td>5 sD</td>
<td>—</td>
<td>6323·1</td>
<td>6270·3</td>
<td>6247·2</td>
<td>—</td>
</tr>
<tr>
<td>b</td>
<td>3 P (6p²)</td>
<td>3 P’</td>
<td>7538·6</td>
<td>7208·9</td>
<td>6415·8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>c</td>
<td>4D (5d7s)</td>
<td>3D”</td>
<td>—</td>
<td>6098·5</td>
<td>5832·0</td>
<td>5403·4</td>
<td>—</td>
</tr>
<tr>
<td>d</td>
<td>12.5</td>
<td>q</td>
<td>—</td>
<td>—</td>
<td>6688·1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>e</td>
<td>5 F (6s5f)</td>
<td>5 F</td>
<td>—</td>
<td>—</td>
<td>4637·6</td>
<td>4613·4</td>
<td>4508·3</td>
</tr>
<tr>
<td>f</td>
<td>4 F (5d7p)</td>
<td></td>
<td></td>
<td>3 F’</td>
<td>—</td>
<td>—</td>
<td>5797·3</td>
</tr>
<tr>
<td>g</td>
<td>4 F (6s4f)</td>
<td></td>
<td></td>
<td>3 F”</td>
<td>—</td>
<td>—</td>
<td>4969·3</td>
</tr>
<tr>
<td>h</td>
<td>4 F (6s6f)</td>
<td></td>
<td></td>
<td>3 F</td>
<td>—</td>
<td>—</td>
<td>7429·8</td>
</tr>
<tr>
<td>i</td>
<td>6 F (6s6f)</td>
<td></td>
<td></td>
<td>6 F</td>
<td>—</td>
<td>—</td>
<td>3216·8</td>
</tr>
</tbody>
</table>

A.—Denotes the symbols used in fig.1.

* The usual values (e.g., Fowler’s) have been increased by three units in accordance with Shenstone and Russell’s suggestion (loc. cit.).

† As given in Bacher and Goudsmit’s “Atomic Energy States.”

‡ j value assigned from the data of this paper.

§ Found and classified from the data of this paper. It is probably a level of the term to which \( q_k \) belongs. If so, both are \(^2\)P levels.

|| Found by Shenstone and Russell and assigned to \(^5\)d\(^7\)p.

†† This term has been assigned to \(^5\)d\(^7\)p in Bacher and Goudsmit’s book, but Shenstone and Russell’s more recent assignment has been adopted.

** These terms are included for completeness, although transitions from them show no apparent intensity perturbation due to the group of levels about \(^5\)s\(^2\)F.

(b) In Tables II to VII are given the results of the intensity measurements within the multiplets. Table VIII contains the averaged results from which the relative intensity of one multiplet to that of another was calculated. All values for the intensities have had the \( v^4 \) and excitation corrections applied.

Table II.—\(^2\)3P — \(^5\)sD.

<table>
<thead>
<tr>
<th>( \Delta j )</th>
<th>Conc./( \lambda )</th>
<th>( 3 \to 2 )</th>
<th>( 2 \to 1 )</th>
<th>( 1 \to 2 )</th>
<th>( 1 \to 1 )</th>
<th>( 1 \to 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4489-00</td>
<td>4493-66</td>
<td>4323-63</td>
<td>—</td>
<td>4332-96</td>
<td>4264-43</td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>1</td>
<td>48·0</td>
<td>28·2</td>
<td>10·2</td>
<td>—</td>
<td>6·35</td>
</tr>
<tr>
<td>1</td>
<td>47·8</td>
<td>27·5</td>
<td>10·7</td>
<td>—</td>
<td>6·70</td>
<td>7·30</td>
</tr>
<tr>
<td>1</td>
<td>47·6</td>
<td>28·7</td>
<td>10·2</td>
<td>—</td>
<td>6·41</td>
<td>7·04</td>
</tr>
<tr>
<td>1</td>
<td>47·6</td>
<td>29·0</td>
<td>9·95</td>
<td>—</td>
<td>6·38</td>
<td>7·04</td>
</tr>
<tr>
<td>1</td>
<td>48·3</td>
<td>27·5</td>
<td>9·98</td>
<td>—</td>
<td>6·78</td>
<td>7·40</td>
</tr>
<tr>
<td>1</td>
<td>48·1</td>
<td>27·7</td>
<td>10·2</td>
<td>—</td>
<td>6·30</td>
<td>7·65</td>
</tr>
<tr>
<td>1</td>
<td>46·5</td>
<td>28·0</td>
<td>10·7</td>
<td>—</td>
<td>6·98</td>
<td>7·75</td>
</tr>
<tr>
<td>1</td>
<td>45·5</td>
<td>29·6</td>
<td>11·0</td>
<td>—</td>
<td>7·37</td>
<td>7·13</td>
</tr>
<tr>
<td>1</td>
<td>44·8</td>
<td>29·3</td>
<td>11·2</td>
<td>—</td>
<td>7·90</td>
<td>7·63</td>
</tr>
<tr>
<td>10</td>
<td>48·2</td>
<td>26·0</td>
<td>11·1</td>
<td>—</td>
<td>6·98</td>
<td>7·60</td>
</tr>
<tr>
<td>Average 10%</td>
<td>46·5</td>
<td>27·7</td>
<td>11·2</td>
<td>—</td>
<td>6·99</td>
<td>7·69</td>
</tr>
<tr>
<td>Average 1 %</td>
<td>47·4</td>
<td>28·3</td>
<td>10·4</td>
<td>—</td>
<td>6·66</td>
<td>7·34</td>
</tr>
<tr>
<td>Theory</td>
<td>46·7</td>
<td>8·36</td>
<td>25·0</td>
<td>0·56</td>
<td>8·36</td>
<td>11·1</td>
</tr>
</tbody>
</table>
Table III. — $^{2}3P - 3\,^{3}P'$.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$\Delta j$</th>
<th>Conc./(\lambda)</th>
<th>$2 \rightarrow 2$</th>
<th>$2 \rightarrow 1$</th>
<th>$1 \rightarrow 2$</th>
<th>$1 \rightarrow 1$</th>
<th>$1 \rightarrow 0$</th>
<th>$0 \rightarrow 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>°</td>
<td>%</td>
<td></td>
<td>4523·24</td>
<td>4435·37</td>
<td>4691·63</td>
<td>4505·94</td>
<td>4431·91</td>
<td>4573·38</td>
</tr>
<tr>
<td>4700</td>
<td>1</td>
<td>18·5</td>
<td>12·0</td>
<td>26·1</td>
<td>12·6</td>
<td>17·4</td>
<td>13·6</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>1</td>
<td>19·3</td>
<td>11·5</td>
<td>23·7</td>
<td>13·8</td>
<td>17·7</td>
<td>14·0</td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>1</td>
<td>19·0</td>
<td>11·4</td>
<td>25·5</td>
<td>13·1</td>
<td>17·7</td>
<td>13·3</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>1</td>
<td>18·2</td>
<td>11·8</td>
<td>24·2</td>
<td>12·9</td>
<td>19·5</td>
<td>13·4</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>1</td>
<td>18·0</td>
<td>12·8</td>
<td>24·8</td>
<td>12·7</td>
<td>19·7</td>
<td>12·4</td>
<td></td>
</tr>
<tr>
<td>3700</td>
<td>10</td>
<td>18·2</td>
<td>12·2</td>
<td>23·4</td>
<td>13·5</td>
<td>19·8</td>
<td>12·9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Average)</td>
<td></td>
<td>18·6</td>
<td>11·9</td>
<td>26·0</td>
<td>13·2</td>
<td>16·6</td>
<td>13·5</td>
</tr>
<tr>
<td>Average 1%</td>
<td></td>
<td></td>
<td>18·5</td>
<td>12·0</td>
<td>24·6</td>
<td>13·1</td>
<td>18·6</td>
<td>13·3</td>
</tr>
<tr>
<td>Theory*</td>
<td></td>
<td></td>
<td>65·9</td>
<td>22·0</td>
<td>22·0</td>
<td>13·2</td>
<td>17·6</td>
<td>17·6</td>
</tr>
</tbody>
</table>

* For the reasons for this adjustment, see the discussion.

Table IV. — $^{2}3P - 3\,^{3}D''$.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$\Delta j$</th>
<th>Conc./(\lambda)</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 2$</th>
<th>$2 \rightarrow 1$</th>
<th>$1 \rightarrow 2$</th>
<th>$1 \rightarrow 1$</th>
<th>$1 \rightarrow 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>°</td>
<td>%</td>
<td></td>
<td>4325·11</td>
<td>4406·83</td>
<td>4242·61</td>
<td>—</td>
<td>4291·16</td>
<td>4223·96</td>
</tr>
<tr>
<td>3700</td>
<td>10</td>
<td>19·4</td>
<td>25·3</td>
<td>15·8</td>
<td>—</td>
<td>20·1</td>
<td>19·2</td>
<td></td>
</tr>
<tr>
<td>3700</td>
<td>10</td>
<td>19·4</td>
<td>24·3</td>
<td>15·8</td>
<td>—</td>
<td>20·1</td>
<td>19·5</td>
<td></td>
</tr>
<tr>
<td>3500</td>
<td>10</td>
<td>19·1</td>
<td>25·1</td>
<td>14·9</td>
<td>—</td>
<td>20·7</td>
<td>19·9</td>
<td></td>
</tr>
<tr>
<td>3900</td>
<td>10</td>
<td>19·4</td>
<td>24·5</td>
<td>15·3</td>
<td>—</td>
<td>19·6</td>
<td>21·2</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>19·3</td>
<td>24·8</td>
<td>15·5</td>
<td>—</td>
<td>20·1</td>
<td>20·0</td>
</tr>
<tr>
<td>Theory</td>
<td></td>
<td></td>
<td>19·3</td>
<td>3·5</td>
<td>10·4</td>
<td>—</td>
<td>3·5</td>
<td>4·6</td>
</tr>
</tbody>
</table>

Table V. — $^{2}3P \pm q_k$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$k \rightarrow 2$</th>
<th>$k \rightarrow 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./(\lambda)</td>
<td>4579·67</td>
<td>4402·55</td>
</tr>
<tr>
<td>° %</td>
<td>75·0</td>
<td>25·3</td>
</tr>
<tr>
<td>0·5</td>
<td>71·8</td>
<td>28·4</td>
</tr>
<tr>
<td>1·0</td>
<td>75·2</td>
<td>24·9</td>
</tr>
<tr>
<td>Average</td>
<td>73·9</td>
<td>26·2</td>
</tr>
</tbody>
</table>
Table VI.—$^{2}{}^{3}\text{P} - ^{4}{}^{3}\text{D}$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 2$</th>
<th>$2 \rightarrow 1$</th>
<th>$1 \rightarrow 2$</th>
<th>$1 \rightarrow 1^*$</th>
<th>$1 \rightarrow 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./(\lambda)</td>
<td>5777·70</td>
<td>5800·30</td>
<td>5519·12</td>
<td>5818·91</td>
<td>5535·93</td>
<td>5425·55</td>
</tr>
<tr>
<td>(%)</td>
<td>48·6</td>
<td>7·32</td>
<td>24·0</td>
<td>—</td>
<td>—</td>
<td>9·28</td>
</tr>
<tr>
<td>0·9</td>
<td>49·6</td>
<td>8·33</td>
<td>22·3</td>
<td>—</td>
<td>—</td>
<td>8·92</td>
</tr>
<tr>
<td>0·9</td>
<td>48·6</td>
<td>8·40</td>
<td>22·7</td>
<td>—</td>
<td>—</td>
<td>9·80</td>
</tr>
<tr>
<td>0·9</td>
<td>49·6</td>
<td>8·80</td>
<td>22·0</td>
<td>—</td>
<td>—</td>
<td>9·50</td>
</tr>
<tr>
<td>0·9</td>
<td>49·0</td>
<td>7·58</td>
<td>23·1</td>
<td>—</td>
<td>—</td>
<td>9·70</td>
</tr>
<tr>
<td>0·9</td>
<td>48·7</td>
<td>7·11</td>
<td>23·8</td>
<td>—</td>
<td>—</td>
<td>9·92</td>
</tr>
<tr>
<td>0·9</td>
<td>46·8</td>
<td>7·20</td>
<td>23·9</td>
<td>—</td>
<td>—</td>
<td>10·8</td>
</tr>
<tr>
<td>0·9</td>
<td>48·0</td>
<td>8·66</td>
<td>24·2</td>
<td>—</td>
<td>—</td>
<td>9·28</td>
</tr>
<tr>
<td>0·9</td>
<td>48·6</td>
<td>—</td>
<td>22·9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Average</td>
<td>48·6</td>
<td>7·92</td>
<td>23·2</td>
<td>0·56</td>
<td>8·36</td>
<td>11·1</td>
</tr>
<tr>
<td>Theory</td>
<td>46·7</td>
<td>8·36</td>
<td>25·0</td>
<td>0·56</td>
<td>8·36</td>
<td>11·1</td>
</tr>
</tbody>
</table>

* This line is blended with a very strong principal series lines at \(\lambda\) 5535·53.

Table VII.—$^{2}{}^{3}\text{P} - ^{6}{}^{3}\text{D}$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 2^*$</th>
<th>$2 \rightarrow 1^*$</th>
<th>$1 \rightarrow 2$</th>
<th>$1 \rightarrow 1$</th>
<th>$1 \rightarrow 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./(\lambda)</td>
<td>4084·87</td>
<td>4087·31</td>
<td>3945·61</td>
<td>—</td>
<td>3947·51</td>
<td>3890·57</td>
</tr>
<tr>
<td>(%)</td>
<td>—</td>
<td>—</td>
<td>22·1</td>
<td>—</td>
<td>11·0</td>
<td>12·0</td>
</tr>
<tr>
<td>50</td>
<td>—</td>
<td>—</td>
<td>22·0</td>
<td>—</td>
<td>10·2</td>
<td>11·4</td>
</tr>
<tr>
<td>50</td>
<td>48·1</td>
<td>22·5</td>
<td>—</td>
<td>10·1</td>
<td>10·9</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>48·1</td>
<td>—</td>
<td>22·3</td>
<td>—</td>
<td>10·4</td>
<td>11·6</td>
</tr>
<tr>
<td>50</td>
<td>48·1</td>
<td>—</td>
<td>21·6</td>
<td>—</td>
<td>11·1</td>
<td>13·1</td>
</tr>
<tr>
<td>50</td>
<td>48·1</td>
<td>—</td>
<td>22·6</td>
<td>—</td>
<td>10·2</td>
<td>11·2</td>
</tr>
<tr>
<td>Average</td>
<td>48·2</td>
<td>22·2</td>
<td>—</td>
<td>10·5</td>
<td>11·7</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>46·7</td>
<td>8·36</td>
<td>25·0</td>
<td>0·56</td>
<td>8·36</td>
<td>11·1</td>
</tr>
</tbody>
</table>

† A blend with the sharp series line \(\lambda\) 4087·31.

As previously stated, this multiplet showed Stark broadening if precautions were not taken to prevent it. As a check on the above maximum blackening measurements the areas under the intensity curves found with the Wouda apparatus were measured and compared. The results, as follows, confirm the above measurements. For : \(\lambda3946: \lambda3948\) the m.b. measurements gave

Table VIII.—Relative Intensities of the Various Multiplets.

<table>
<thead>
<tr>
<th>$^{2}{}^{3}\text{P}_2 - ^{5}{}^{3}\text{D}_2$</th>
<th>$^{2}{}^{3}\text{P}_1 - ^{3}{}^{3}\text{P}'_2$</th>
<th>$^{2}{}^{3}\text{P}_2 - ^{3}{}^{3}\text{P}'_2$</th>
<th>$^{2}{}^{3}\text{P}_2 - ^{3}{}^{3}\text{D}'_2$</th>
<th>$^{2}{}^{3}\text{P}_1 - ^{3}{}^{3}\text{P}'_1$</th>
<th>$^{2}{}^{3}\text{P}_1 - ^{3}{}^{3}\text{D}'_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^{3}\text{P}_1 - g_Z$</td>
<td>$2^{3}\text{P}_2 - g_Z$</td>
<td>$2^{3}\text{P}_2 - 5^{3}\text{D}_2$</td>
<td>$2^{3}\text{P}_1 - 5^{3}\text{D}_2$</td>
<td>$2^{3}\text{P}_1 - 4^{3}\text{D}_2$</td>
<td>$2^{3}\text{P}_1 - 6^{3}\text{D}_2$</td>
</tr>
<tr>
<td>0·60</td>
<td>0·77</td>
<td>0·86</td>
<td>0·35</td>
<td>0·45</td>
<td></td>
</tr>
</tbody>
</table>
in two instances \(22.3 : 10.3\) and \(22.4 : 10.1\), while for the same two instances the area measurements gave the ratios \(22.0 : 10.2\), and \(22.3 : 10.4\).

These results are the averages for several determinations. From them, it is possible to calculate the intensities of all the measured lines in the same units, so that they can be compared. The above values have had the \(v^4\) and excitation corrections applied. This table has been used in drawing up Table XVII of the discussion, section 5.

(c) In Tables IX to XIII are given the results of intensity measurements within the multiplets. Table XIV contains the averaged results from which the relative intensity of one multiplet to that of another was calculated. All values for intensities have had \(v^4\) and excitation corrections applied.

### Table IX. \(-3^3D - 5^3F.\)

<table>
<thead>
<tr>
<th>(\Delta j)</th>
<th>4 (\rightarrow) 3</th>
<th>3 (\rightarrow) 3</th>
<th>3 (\rightarrow) 2</th>
<th>2 (\rightarrow) 3</th>
<th>2 (\rightarrow) 2*</th>
<th>2 (\rightarrow) 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./(\lambda)</td>
<td>3579.67</td>
<td>3593.20</td>
<td>3544.66</td>
<td>3596.33</td>
<td>3547.70</td>
<td>3524.97</td>
</tr>
<tr>
<td>%</td>
<td>35.0</td>
<td>5.4</td>
<td>32.0</td>
<td>—</td>
<td>4.8</td>
<td>23.0</td>
</tr>
<tr>
<td>1</td>
<td>34.2</td>
<td>6.1</td>
<td>32.3</td>
<td>—</td>
<td>4.8</td>
<td>23.0</td>
</tr>
<tr>
<td>1</td>
<td>33.7</td>
<td>5.9</td>
<td>32.6</td>
<td>—</td>
<td>4.8</td>
<td>23.3</td>
</tr>
<tr>
<td>1</td>
<td>34.0</td>
<td>6.4</td>
<td>31.2</td>
<td>—</td>
<td>5.5</td>
<td>22.8</td>
</tr>
<tr>
<td>1</td>
<td>34.8</td>
<td>7.3</td>
<td>29.8</td>
<td>—</td>
<td>5.9</td>
<td>22.4</td>
</tr>
<tr>
<td>Average</td>
<td>34.4</td>
<td>6.2</td>
<td>31.6</td>
<td>—</td>
<td>5.2</td>
<td>22.9</td>
</tr>
<tr>
<td>Theory</td>
<td>49.0</td>
<td>4.2</td>
<td>33.9</td>
<td>0.12</td>
<td>4.2</td>
<td>22.9</td>
</tr>
</tbody>
</table>

* This may be a blend with a very faint unknown line as shown by matching with the control plate.

### Table X. \(-3^3D - 4^3F.\)

<table>
<thead>
<tr>
<th>(\Delta j)</th>
<th>4 (\rightarrow) 3</th>
<th>3 (\rightarrow) 3</th>
<th>3 (\rightarrow) 2</th>
<th>2 (\rightarrow) 3</th>
<th>2 (\rightarrow) 2*</th>
<th>2 (\rightarrow) 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./(\lambda)</td>
<td>3993.40</td>
<td>3995.66</td>
<td>3935.72</td>
<td>3997.92</td>
<td>3937.88</td>
<td>3909.92</td>
</tr>
<tr>
<td>%</td>
<td>45.8</td>
<td>3.6</td>
<td>28.4</td>
<td>—</td>
<td>3.1</td>
<td>19.0</td>
</tr>
<tr>
<td>1</td>
<td>47.5</td>
<td>3.6</td>
<td>28.1</td>
<td>—</td>
<td>3.0</td>
<td>19.4</td>
</tr>
<tr>
<td>0.2</td>
<td>44.0</td>
<td>(4.4)</td>
<td>28.4</td>
<td>—</td>
<td>(4.0)</td>
<td>18.7</td>
</tr>
<tr>
<td>0.2</td>
<td>47.0</td>
<td>3.9</td>
<td>28.7</td>
<td>—</td>
<td>3.3</td>
<td>18.7</td>
</tr>
<tr>
<td>0.2</td>
<td>44.2</td>
<td>(5.6)</td>
<td>28.2</td>
<td>—</td>
<td>(4.5)</td>
<td>18.7</td>
</tr>
<tr>
<td>0.2</td>
<td>45.0</td>
<td>(2.7)</td>
<td>27.0</td>
<td>—</td>
<td>(2.4)</td>
<td>18.7</td>
</tr>
<tr>
<td>Average</td>
<td>45.6</td>
<td>3.9</td>
<td>28.1</td>
<td>—</td>
<td>3.4</td>
<td>18.9</td>
</tr>
<tr>
<td>Theory</td>
<td>40.5</td>
<td>3.5</td>
<td>28.0</td>
<td>0.10</td>
<td>3.5</td>
<td>18.9</td>
</tr>
</tbody>
</table>

The bracketed values are measurements on weak intensity plates where the plate grain effects are felt in the very weak lines. This accounts for their variations.
Perturbations in Barium I Spectrum.

Table XI.—$3^3D - 6^3F$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$4 \rightarrow 3$</th>
<th>$3 \rightarrow 3$</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 3$</th>
<th>$2 \rightarrow 2$</th>
<th>$2 \rightarrow 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./A.</td>
<td>3420·32</td>
<td>3421·01</td>
<td>3376·98</td>
<td>3421·48</td>
<td>3377·40</td>
<td>3356·80</td>
</tr>
<tr>
<td>Average 50%</td>
<td>46·0</td>
<td>3·6</td>
<td>27·8</td>
<td>1·8</td>
<td>4·3</td>
<td>17·5</td>
</tr>
<tr>
<td>Theory</td>
<td>40·5</td>
<td>3·5</td>
<td>28·0</td>
<td>0·10</td>
<td>3·5</td>
<td>18·9</td>
</tr>
</tbody>
</table>

This multiplet like $2^3P - 6^3D$ showed Stark broadening unless precautions were taken to prevent it. Due to the small splitting of the initial levels, lines ending on each final level were not separated on the photometer curve. In order to obtain maximum blackening measurements of them the composite intensity curves had to be analysed, and separated into their component lines. To provide a check on the work the area under each composite intensity curve corresponding to all transitions to a final level was measured. The intensity ratios for the sum of the transitions to each final level were then

Table XII.—$3^3D - 3^1F$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$4 \rightarrow 3$</th>
<th>$3 \rightarrow 3^*$</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 3^*$</th>
<th>$2 \rightarrow 2^*$</th>
<th>$2 \rightarrow 1^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./A.</td>
<td>3631·7</td>
<td>—</td>
<td>3663·5</td>
<td>—</td>
<td>3701·0</td>
<td>3676·3</td>
</tr>
<tr>
<td>%</td>
<td>88·2</td>
<td>—</td>
<td>12</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>86·5</td>
<td>—</td>
<td>13</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>90·0</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>89·5</td>
<td>—</td>
<td>11</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>89·8</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Average</td>
<td>88·8</td>
<td>—</td>
<td>11</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Do not appear on plates suitably exposed for the measurement of the $4 \rightarrow 3$ and $3 \rightarrow 2$ lines. $4 \rightarrow 3$ was generally compared with $3^2D_3 - 5^2F_4$ at the same time.

Table XIII.—$3^3D - 3^3F''$.

<table>
<thead>
<tr>
<th>$\Delta j$</th>
<th>$4 \rightarrow 3$</th>
<th>$3 \rightarrow 3$</th>
<th>$3 \rightarrow 2$</th>
<th>$2 \rightarrow 3^+$</th>
<th>$2 \rightarrow 2^+$</th>
<th>$2 \rightarrow 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc./A.</td>
<td>3586·50</td>
<td>3610·96</td>
<td>3561·94</td>
<td>3639·72</td>
<td>3589·95</td>
<td>3566·66</td>
</tr>
<tr>
<td>%</td>
<td>33</td>
<td>36</td>
<td>15</td>
<td>—</td>
<td>—</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>33</td>
<td>35</td>
<td>18</td>
<td>—</td>
<td>—</td>
<td>14</td>
</tr>
<tr>
<td>Average</td>
<td>33</td>
<td>36</td>
<td>16</td>
<td>—</td>
<td>—</td>
<td>15</td>
</tr>
</tbody>
</table>

† These lines were too weak to measure. The multiplet intensities are in general, weak, and the background corrections were large. Accordingly the intensities in this table are not as accurate as those in the previous tables.
calculated from the m.b. measurements, and the two sets of values were compared. The area measurements gave the following ratios for the intensities of transitions ending on the $j = 3, 2$ and $1$ levels: $53.7 : 30.8 : 17.3$. The ratios calculated from the analysed lines in Table XI are $51.3 : 32.1 : 17.5$ which is in satisfactory agreement.

Table XIV.—Relative Intensities of the Various Multiplets.

<table>
<thead>
<tr>
<th>$3^2D_3 - 5^2F_4$</th>
<th>$3^2D_1 - 4^2F_2$</th>
<th>$3^2D_3 - 3^2F'_4$</th>
<th>$3^2D_3 - 5^2F_4$</th>
<th>$3^2D_3 - 5^2F_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>0.63</td>
<td>0.12</td>
<td>0.85</td>
<td></td>
</tr>
</tbody>
</table>

This table has been used in drawing up Table XIX in the discussion, section 5.

(d) The intensity of the singlet relative to the total intensity of the corresponding triplet in the fundamental series is given in three instances in Table XV, in the column headed “Ratio.” The singlet series given by Shenstone and Russell (loc. cit.) has been used. $v^4$ and excitation corrections have been applied.

Table XV.—Singlet-Triplet Intensity Ratios (DF Series).

<table>
<thead>
<tr>
<th>$3^1D - 4^1F$</th>
<th>$3^2D_2 - 4^2F_3$</th>
<th>Ratio.</th>
<th>$3^1D - 5^1F$</th>
<th>$3^2D_2 - 5^2F_3$</th>
<th>Ratio.</th>
<th>$3^1D - 6^1F$</th>
<th>$3^2D_2 - 6^2F_4$</th>
<th>Ratio.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3935.72</td>
<td>3861.91</td>
<td>3544.66</td>
<td>3636.83</td>
<td>3420.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>118</td>
<td>15.9</td>
<td>17.6</td>
<td>9.2</td>
<td>10.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69.2</td>
<td>2.1</td>
<td>3.5</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Blended with the calcium line $\lambda 4283.17$. It was possible to estimate a correction for this from the intensities of the calcium lines at $\lambda 4289$ and $\lambda 4299$, which are of nearly the same intensity as the blended calcium line and which lie near enough to it to make such a procedure feasible. The lower limit of the corrected value is given in Table XV. It is important to know this, for the singlet intensity is too large.

(e) The following term analyses using two perturbing terms have been made for the reasons given in the discussion. Shenstone and Russell’s analyses with one perturbing term are also given.

5. Discussion.

From the results of (b) and (c), section 4, it is possible to draw up transition arrays for the perturbed configurations in the diffuse, and in the fundamental series perturbation groups. This is done in Tables XVII and XIX, in which
the intensities of all measured lines are comparable. Estimated intensities of other lines (adjusted to the same scale to make them comparable with the measured results) have been included in the tables for the purpose of showing that those transitions which have not been measured and which should strictly be considered in a test of the theory, are so weak that they cannot appreciably affect the experimental sums.

Table XVI.—Constants for Langer's Formula for the \( n \, ^3F \) term values.*

<table>
<thead>
<tr>
<th>Author.</th>
<th>S. and R.</th>
<th>Author.</th>
<th>S. and R.</th>
<th>Author.</th>
<th>S. and R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n^F_4 )</td>
<td>( n^F_3 )</td>
<td>( n^F_2 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4900.5</td>
<td>4900.5</td>
<td>5521.2</td>
<td>5521.2</td>
<td>5797.3</td>
<td>5797.3</td>
</tr>
<tr>
<td>4561.6</td>
<td>—</td>
<td>4750.5</td>
<td>—</td>
<td>4969.3</td>
<td>—</td>
</tr>
<tr>
<td>—32.7</td>
<td>—33</td>
<td>—30</td>
<td>—32.3</td>
<td>—26.5</td>
<td>—28</td>
</tr>
<tr>
<td>0.50</td>
<td>—0.40</td>
<td>—</td>
<td>—</td>
<td>—0.38</td>
<td>—</td>
</tr>
<tr>
<td>0.1963</td>
<td>0.1080</td>
<td>0.1965</td>
<td>0.1956</td>
<td>0.1930</td>
<td>0.1934</td>
</tr>
<tr>
<td>( 8 \times 10^{-6} )</td>
<td>( 8 \times 33 \times 10^{-6} )</td>
<td>( 8 \times 00 \times 10^{-6} )</td>
<td>( 8 \times 016 \times 10^{-6} )</td>
<td>( 7 \times 10^{-6} )</td>
<td>( 7 \times 23 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

\( r_1 \) residuals.—|1, (-1); \( \nu_{01}, \nu_{02} \); -1, (-19); -1, (-2); 0, (-1); -3, (-3); -4, (-5); -3, (-3) |
\( r_2 \) residuals.—0, (-1); \( \nu_{01}, \nu_{02} \); 0, (-1); -2, (0); 0, (2); -1, (0); 1, (1); -2, (-2); -2, (-2); -1, (-1); 0, (0). |
\( r_3 \) residuals.—0, (0); \( \nu_{01}, \nu_{02} \); -1, (0); -1, (0); 2, (2); 1, (1); 8, (8); -1, (-1); -1, (-1). |

S. and R. = Shenstone and Russell.

* Usual term values increased by three units.

†Residuals calculated using Shenstone and Russell's constants are given in brackets.

In both transition arrays the triplet intensity sum in each enlarged \( j \) group, theoretically should be "invariant" to at least the degree to which the experimental values are known. For instance, in the diffuse series array (Table XVII), an examination shows that the three known intercombination lines are weak and cannot materially affect the intensity sums, and that strong singlets (singlets of "perturbing" configurations are not known and are therefore extremely weak) have their initial levels at large distances from the nearest "perturbing" terms of like \( j \) value. (1300 cm.\(^{-1}\) for \( 5^1D \).

Following the procedure of section 2, we apply the sum rule for the final levels of the diffuse series perturbation group to test whether all interacting terms have been considered. The intensity sums of the triplet transitions to \( 2^3P_2 \), \( 2^3P_1 \) and \( 2^3P_0 \) (excluding \( 2^3P_1 - q_0 \), which will be dealt with later) are 473, 268 and 90.5, in the ratio 5:1:2:9:0.98. This agrees within the experimental error (3\%) with the ratios of the statistical weights of the final levels, and therefore all important perturbing configurations have been con-
### Initial levels.

<table>
<thead>
<tr>
<th>$j$</th>
<th>$O$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{1}S'$</td>
<td>$^{3}P'$</td>
</tr>
<tr>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(40.0)</td>
<td>(41.2)</td>
</tr>
<tr>
<td>1</td>
<td>$^{3}P$</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(40.0)</td>
<td>(30.0)</td>
</tr>
<tr>
<td>2</td>
<td>$^{3}P$</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(50.0)</td>
<td>(2.0)</td>
</tr>
</tbody>
</table>

The measured intensities are given above the theoretical values for isolated terms in LS coupling which are contained in the round ( ) brackets.

* Initial Configurations.

- $6s7d \rightarrow 5^{1}D$; $5^{3}D$.
- $6p^{2} \rightarrow 5^{1}S'$; $^{1}D'$; $^{3}P'$.
- $5d7s \rightarrow 5^{3}D''$; $^{3}D''$.

+ Final Configuration.

- $6s6p \rightarrow 2^{3}P$; $2^{3}P$.

Considered. Including $2^{3}P_{1} - q_{0}$ gives a ratio somewhat nearer to the ratio 5:3:1. The sum rule still holds if $2^{3}P - 4^{3}D$ and $2^{3}P - 6^{3}D$ are omitted, but since they show slight perturbations in some of their lines for which no other explanation has been found, they have been included in this perturbation group. Two lines in these multiplets are blends and their intensities cannot be measured. However, since appreciable perturbations in these multiplets are rare, and since those which occur are small, the error in the sums introduced by assuming these lines to be of normal intensity is very small. It is also a fortunate fact that both blended lines are weak transitions in their respective multiplets.

The first step in adjusting the parameters which connect the theoretical intensities of one multiplet with those of the others, is to make the theoretical values for $2^{3}P_{2} - 5^{3}D_{3}$ and $2^{3}P_{2} - 5^{3}D''_{3}$ equal to their respective experimental intensities (Table XVII). This adjustment is possible because the separation of $5^{3}D_{3}$ and $5^{3}D''_{3}$ is great, and there are no other perturbing $j = 3$ levels near. It fixes the theoretical intensities for $2^{3}P - 5^{3}D$ and $2^{3}P - 5^{3}D''$, and a consideration of the agreement with theory of the other lines in these multiplets confirms the adjustment. Naturally, the $2^{3}P_{2} - 4^{3}D_{9}$ and $2^{3}P_{2} - 6^{3}D_{4}$ transitions may also be taken as unperturbed so that the theoretical parameters are adjusted for all except $2^{3}P - 3^{3}P'$, and the "fragment" with the initial
Perturbations in Barium I Spectrum.

Seri: Perturbation Group.

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P</td>
<td>2P'</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5D</td>
<td>6D</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

- Denotes a line expected but not found and therefore extremely weak.
- Denotes a line forbidden by the \( j \) selection rule, or an intercombination which is not found.
- \[ \text{Estimated intensity.} \]
- \( \text{Denotes a line too weak to appear on the plate under the ordinary conditions of measurement.} \)
- \( \text{Small theoretical intensities which are estimated in the discussion.} \)
- \( \text{Since the triplet sums are expected to be invariant, we are not directly concerned with these lines.} \)

level \( q_k \). A rough adjustment can be made for the parameter of \( 2 \, ^3P - 3 \, ^3P' \) (actually \( 2 \, ^3P_1 - 3 \, ^3P'_{0} \) was made equal in theory and experiment). A comparison of the theoretical and experimental intensity sums in each enlarged \( j \) group can then be made, omitting the strong transitions from \( q_k \), the level of unknown \( j \) value. It is found that in \( J_2^2 \) and \( J_1^2 \), the experimental deficits are about 96 and 37, while in \( J_2^1 \) and \( J_1^1 \) there are surpluses of 2 or 3. Since we expect that the transitions from \( q_k \) are lines of a weak multiplet greatly strengthened by "borrowed" intensity, it is at once obvious that the only place these transitions can fit is in \( J_2^2 \) and \( J_1^2 \). This fixes the \( j \) value of \( q_k \) without ambiguity. The parameter of \( 2 \, ^3P - 3 \, ^3P' \) is then finally adjusted by making the theoretical intensity sum in \( J_1^2 \) equal to the experimental sum, and calculating in this way the theoretical value for \( 2 \, ^3P_1 - 3 \, ^3P'_{1} \). This fixes the intensities for this multiplet and completes the adjustment of the parameters.

It now remains to compare the theoretical and experimental intensity sums in each enlarged \( j \) group. The experimental sum \( J_1^0 \) shows a deficit of 25%. This group contains only \( 2 \, ^3P_1 - 3 \, ^3P'_{0} \) and there are no known transitions from adjacent levels capable of perturbing it. If its intensity has been "loaned," then the line which has "borrowed" it must be included in the array. A careful examination of my plates showed only one line in this
region at \( \lambda 4600 \), for which the initial and final levels were not known, and which had sufficient intensity to account for this behaviour. All other lines were either identified, and if so it was known that they could not perturb, or were so faint that they could not account for the discrepancy in the \( J_1^0 \) sum. If \( \lambda 4600 \) belongs in \( J_1^0 \), its initial level is at 7654 cm\(^{-1}\), which is just 118 cm\(^{-1}\) from \( 3^3P_0 \) so that a large perturbation is practically certain. Moreover, it is in a reasonable position for the \( j = 0 \) level of the term to which \( q_k \) belongs. On this evidence, it is believed that \( \lambda 4600 \) is \( 2^3P_1 - q_0 \) and has been inserted as such in the tables. It follows that \( q_k \) and \( q_0 \) are \( 3^3P_2 \) and \( 3^3P_0 \) levels.

It is now possible to test the theory by comparing the theoretical and experimental sums in each enlarged \( j \) group. The results are given in the following table:

Table XVIII.—Comparison of Theoretical and Experimental \( j \) Group Sums (Diffuse series).

<table>
<thead>
<tr>
<th>Enlarged ( j ) Group</th>
<th>Experiment.</th>
<th>Theory.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_2^3 )</td>
<td>224</td>
<td>218</td>
</tr>
<tr>
<td>( J_3^3 )</td>
<td>193</td>
<td>189 + s</td>
</tr>
<tr>
<td>( J_1^2 )</td>
<td>166</td>
<td>167 + r</td>
</tr>
<tr>
<td>( J_4^1 )</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>( J_2^1 )</td>
<td>72</td>
<td>69</td>
</tr>
<tr>
<td>( J_4^1 )</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>( J_1^0 )</td>
<td>38.5 (+ 3)</td>
<td>40 + t</td>
</tr>
</tbody>
</table>

Examination of the table shows that the intensities of the transitions from \( q_k \) and \( q_0 \) if unperturbed (i.e., \( s, r, t \)) are very small, being less than the error in the \( j \) group sums. This was just what was expected in order to account for the absence (extreme weakness) of the other lines of the multiplet. The sources of the borrowed intensity are apparent from Table XVII. Table XVIII shows the agreement with theory to be surprisingly good in view of the complicated nature and of the magnitude of the perturbations. In all except one case (\( J_2^1 \)) there is agreement within the error of measurement (3\%).

The general procedure of section 2 is also followed in the fundamental series group. Here, however, the sum rule for the \( 3^3D_2, 3^3D_3 \) and \( 3^3D_1 \) final levels gives the ratio 8·0 : 5·0 : 3·0, when all the measured triplet transitions are included. The \( 3^3D - 4^3F \) and \( 3^3D - 6^3F \) multiplets do not show any appreciable perturbation which can be attributed to the levels which perturb \( 5^3F \). The sum rule for the final levels applied separately to the transitions
from $4^3\text{F}, 6^3\text{F},$ and $5^3\text{F}$ levels with the known initial term perturbations removed, gives respectively the ratios, $7 \cdot 9 : 5 \cdot 0 : 3 \cdot 0, 8 \cdot 5 : 5 \cdot 0 : 3 \cdot 0$ and $8 \cdot 5 : 5 \cdot 3 : 2 \cdot 9$.

The fact that these ratios are similar shows that none of the perturbing terms considered is responsible for the excess of intensity of transitions to $3^3\text{D}_3$. If it were due to other unconsidered initial levels they would have to be situated similarly for each term in order to produce similar perturbations in each multiplet. No levels capable of doing this are known. Moreover, when the theoretical parameters are adjusted, as in Table XIX, the $J_3^4, J_3^3$ and $J_3^2$ intensity sums all show a surplus of experimental intensity. These circumstances can only arise from a perturbation in the final levels, although no adjacent terms capable of causing such perturbations are known. Because transitions to the $3^3\text{D}_2$ and $3^3\text{D}_1$ levels appear to be normal, it is thought that the perturbation is in the $3^3\text{D}_3$ level. That the $3^3\text{D}_2$ and $3^3\text{D}_1$ levels should be each perturbed in exactly the right manner to make them appear relatively normal, is a coincidence that appears highly improbable. The adjustment of the parameters in Table IX has been made accordingly.

There is no apparent reason why the $3^3\text{D}_3$ level should be perturbed. The interval ratio for the $3^3\text{D}$ term is greater than $3 : 2$ instead of less as it should be if the perturbation were due to a repulsion from terms higher in the energy diagram. It may be connected with the fact that in building up the Ba atom two $6s$ electrons are added to the Xe configuration, while the first $5d$ electron is not added until the next element La.

Examination of Table XX shows that there is agreement with the theory within the experimental error of measurement for all transitions not involving the $3^3\text{D}_3$ level. The latter $j$ groups show in all cases a surplus of experimental intensity. It is not, however, a true disagreement with theory but rather is due to the effect of unconsidered factors, as has been pointed out. The source of the intensity “borrowed” by $3^3\text{D}_3 - 3^3\text{F}'_4$ is obviously $3^3\text{D}_3 - 5^3\text{F}_4$ and when this is “restored” the former has an intensity comparable with the other lines of its multiplet (see Table XIX).

A very elegant graphical method for determining the constants in Langer's equation for the term values has been given by Shenstone and Russell. The observed quantum defects multiplied by $(\nu_n - \nu_0)$, the separation of the “perturbed” and “perturbing” levels, are plotted against $\nu_n$ for all the levels of a series, and the perturbation constant $\beta_0$ is given by the intercept of $\nu_n = \nu_0$ with this curve. This enables one to find $\beta_0$ when it is large but not when it is very small, owing to the small scale necessary, and to the errors inherent in graphical methods. It is possible, however, for the perturbation...
Table XIX.—Fundamental Levels.

<table>
<thead>
<tr>
<th>$j$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$3P'$</td>
<td>$1P'$</td>
<td>$3P'$</td>
</tr>
<tr>
<td>1</td>
<td>$33D$</td>
<td>[1]</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>$33D$</td>
<td>[2]</td>
<td>[0·2]</td>
</tr>
<tr>
<td>3</td>
<td>$33D$</td>
<td>[0·3]</td>
<td>[1·5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The measured intensities are given above the theoretical values for isolated LS coupling which are contained round ( ) brackets.

* Initial Configurations.

$6s5f \rightarrow 53F$; $53F$, $5d7p \rightarrow ^3(P', D', F')$; $^3(P', D', F')$.

† Final Configuration.

$6s5d \rightarrow 31D$; $33D$.

The term $\beta_0/\nu_n - \nu_0$ to be appreciable even if $\beta_0$ is very small, i.e., if $(\nu_n - \nu_0)$ is also small. Under these circumstances neglect of the small $\beta_0$ term leads to poor agreement with experiment for the level near $\nu_0$, but does not appreciably affect the agreement for other levels of the series. Such a case occurs in the fundamental series which has been analysed by Shenstone and Russell using one perturbing term. The analysis in Table XVI is given to point out how a large "isolated" discrepancy in the calculated values may be explained; $53F_4$ is an example, and the corrected value is given; $93F_2$ is possibly another example of the same thing. The corrections involve the recalculation of the constants for all three series $nF_4$, $nF_3$ and $nF_2$. The
Perturbations in Barium I Spectrum.

<table>
<thead>
<tr>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4^1F</td>
<td>5^1F</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>118</td>
<td>15.9</td>
</tr>
<tr>
<td>(78)</td>
<td>(21.3)</td>
</tr>
<tr>
<td>u</td>
<td>v</td>
</tr>
<tr>
<td>a</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- \(a\) denotes a line expected but not found and therefore very weak.
- Denotes line forbidden by \(j\) selection rule, or an intercombination line which is not found.
- \(u\) denotes a line too weak to appear on a plate under ordinary conditions of measurement.
- \(v\) denotes line expected but not found.
- \(a\) denotes line possibly weak.
- \(v\) denotes line forbidden by \(j\) selection rule.
- \(v\) denotes line which is not found.
- \(v\) denotes line too weak.

Small \(\beta_0\)'s were found by trial and error, but the trials can be made so that the approximations converge rapidly to give the best agreement with experiment. Langer's formula may be expected to hold only so long as the perturbation is small compared to the distance between the perturbed and perturbing levels; the ratio of the latter to the former is about 3:1 for this. This is apparently within the region of validity, for the formula describes the term value series surprisingly well.

I have found the perturbation constants in Langer's formula by the graphical method, for the terms which perturb the diffuse series intensities. They are all very small if not zero, so that the interactions which affect the intensities, do not affect the series term values to any extent. Since the main term value perturbations in the diffuse series near 2800 cm.\(^{-1}\) and 1400 cm.\(^{-1}\) (probably \(5d4f\)) are due to terms whose precise values are not known, no analysis has been made.

It is possible to draw some conclusions from the data concerning the nature of the interactions in the diffuse, and in the fundamental series groups. Shortley (loc. cit.) has pointed out that magnetic interaction between two configurations can only occur if the \(n\) value of at least one electron in each is the same. The interactions in the fundamental series are then obviously of electrostatic origin, for terms arising from \(5d4p\) (and the other unknown

\[\text{VOL. CXLIII.—A.} \]
configuration) interact with terms arising from the \(6snp\) configurations, and perturb the whole series of term values.

On the other hand, in the diffuse group the term values series show little effect of interaction with the terms which perturb the intensities. Moreover, it appears to be a general thing that perturbations of electrostatic origin occur only between terms of the same \(L\) and \(S\), as well as \(J\) value, for Russell and Saunders coupling. This rules out the possibility of the interaction being electrostatic. An examination of the electron configurations involved (Table I) shows that all terms, including \(4^3D\) and \(6^3D\), are capable of interacting magnetically with some other term in the perturbation group. It is therefore believed that the interactions are of magnetic origin.

The following observations have been made. While the term value perturbations due to the \(3^F\) (and \(3^F'\)) levels are strongly felt both in \(4^3F\) and \(6^3F\), the intensity perturbations due to them in the corresponding multiplets do not appear to be appreciable. As shown by the behaviour of the doubly excited configuration terms in the diffuse series group, intensities of transitions from terms of this type appear to be more sensitive to perturbations than those from terms of singly excited configurations. The weakest multiplets show the largest percentage intensity perturbations as required by theory, as reference to Tables XVII or XIX shows.

The following circumstances may, however, provide the correct explanation. Randall has found the combination \(4^3D - 4^3F\) with some intensity in the infra-red, but I have not been able to find in his papers* any reference to a line at \(\lambda 15,375\) where \(4^4D - 4^4F\) is expected. It may be that if the intensity sum of \(3^3D - 4^3F\) and \(4^3D - 4^3F\) (for example) were compared with the

intensity of $3^1D - 4^1F$, which has no corresponding strong transition $4^1D - 4^1F$, the expected result would be obtained.

In conclusion, I wish to express my thanks to Professor L. S. Ornstein for discussion, and for many suggestions. I am also indebted to Mr. G. G. Zaalberg for assistance in carrying out some of the experimental work, and to the Royal Commission for the Exhibition of 1851 for the award of a scholarship.

**Summary.**

(1) It has been possible to show that the large departures from the normal intensities which occur in certain barium multiplets are due to interactions of "overlapping" electron configurations, and to identify the mutually perturbed terms.

(2) The method by which this is done is described. The intensity measurements include transitions to the $2^3P$ levels from $4^3D$, $5^3D$, $6^3D$, $3^3P'$ and a level at 6688·1 cm.$^{-1}$ and to the $3^3D$ levels from $4^3F$, $5^3F$, $6^3F$, $3^3F'$ and $3^3F''$, which form the two perturbation groups. For the nomenclature, see Table I.

(3) The ratio of the singlet to the total triplet intensity has been obtained for the first three members of the fundamental series.

(4) An arc in nitrogen was used, for the most part, as a source. Special precautions were taken to render the effects of self-absorption negligible, and tests were made to show that this was so.

(5) The multiplets arising from $6^3D$ and $6^3F$ showed pronounced Stark broadening under ordinary conditions of arc current and BaCl$_2$ concentration. The method used to obtain suitable conditions is described.

(6) A method of measuring the arc temperature which corresponded to the temperature of the region from which the barium lines were emitted is given.

(7) The intensity sum of each enlarged $j$ group in the transition array for each perturbation group usually agrees with the theoretically predicted sum. Where this is not so, it is shown that other factors enter, so that the discrepancies are not "real" disagreements with the theory.

(8) Examples of how such measurements can be used to assign definite $j$ values, and to classify certain "irregular" lines, are given. The presence of certain "fragments" of multiplets is explained.

(9) The perturbations in the diffuse series are probably of magnetic origin, while those in the fundamental series are certainly of electrostatic origin.

(10) There is definite evidence that the $3^3D_3$ level is perturbed, but no explanation has been found.

x 2
(11) An explanation is offered of the occurrence of certain "isolated" disagreements in term value analyses by Langer's formula. An example is furnished in the fundamental series analysis which has been made for two "perturbing" terms.

(12) The ratio of the singlet intensity to that of the corresponding triplet in the fundamental series is too large. An explanation is offered.

(13) Some general observations on the perturbations are made.

Interference Due to Walls of a Wind-Tunnel.

By L. Rosenhead, Ph.D., Professor of Applied Mathematics, The University, Liverpool; Fellow of St. John's College, Cambridge.

(Communicated by H. G. Glauert, F.R.S.—Received May 23, 1933.)

1. Introduction.

This paper arose out of a discussion with Mr. Glauert on the validity of certain results on wind-tunnel interference given in a recent paper by Theodorsen,* and I am greatly indebted to him for several very valuable suggestions. In his paper Theodorsen investigated, on the lines of the approximate theory laid down by Glauert,† the interference factors due to rectangular tunnels in the following five conditions: (1) tunnel entirely enclosed; (2) free jet; (3) horizontal boundaries only, the vertical sides being free surfaces; (4) vertical boundaries only, the horizontal sides being free surfaces; (5) bottom boundary only, the remaining sides being free surfaces. Apart from one or two minor errors, Theodorsen's paper has to face a more serious objection on the score that the approximate method employed is not always valid. This objection to the approximate method was raised rather briefly in a previous paper,‡ but at that time all the cases discussed, using the approximate method, were those due to Glauert, and they were such that the approximate method did not come into conflict with the exact theory. The more complicated

---