THE DIFFERENT CHARACTER OF SPECTRUM LINES BELONGING TO THE SAME SERIES

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It has been generally assumed that the spectrum lines belonging to the same series are similar in character and in behavior under varying experimental conditions. Indeed the similarity in sharpness or diffuseness, or in the direction of unsymmetrical widening, has been a valuable aid in the detection of series relationships in spectra. If, for example, the strong lines of a series were unsymmetrically widened toward the red, the continuation of the series would be looked for in lines widened in the same direction, the widening becoming greater as the higher members were reached. It is therefore of considerable importance to note that there is at least one well-authenticated series in which the character of the lines changes in the course of the series. This is the first subordinate "triplet" series of barium whose lines are given in Table I, column 4. In this series the first members ($\lambda\lambda$ 5819, 5800, 5777, 5536, 5519, 5424), consisting of a triplet and satellites, are all unsymmetrically widened toward the red; the second members $(\lambda\lambda 4493, 4489, 4333, 4323, 4264)$ and probably all succeeding are, on the contrary, unsymmetrically widened toward the violet. This is so surprising and important that it is necessary before proceeding farther to make quite sure of our facts. First, there can be little doubt that the first members do really belong to the same series as the higher members; they fit into a formula of the usual type and have the full complement of satellites analogous to the higher members and to the first subordinate series of calcium and strontium. Secondly, the character of the lines seems equally Although previous investigators of the barium spectrum have not noted the character of the first members of the first subordinate series, the reversals of these lines are in my photographs very eccentrically placed on the violet side of the emission line, indicating unsymmetrical widening toward the red. The character

of the second members is obvious and is given by Kayser and Runge as unsymmetrical toward the violet. There is also the evidence of the displacement at the negative pole compared with the center of the arc. I have previously shown that lines are displaced at the negative pole in the direction of their greater widening. Investigating the displacement of the barium lines, I find that all the first members of the first subordinate series are displaced to the red (λ 5536.07 is interfered with by an adjacent line), and all the second members to the violet; this is complete confirmation of their opposite character.

It is interesting to examine also the analogous first subordinate series of calcium and strontium. Of the calcium series the first members are in the infra-red and their character is not known; the second members are quite symmetrical so far as can be judged from the symmetry of their reversals and from the smallness of their displacements at the negative pole of the arc,3 but the higher members are unsymmetrical toward the violet4 according to Kayser and Runge⁵ and Eder and Valenta.⁶ The calcium series is therefore not so extreme a case as that of barium but is still a noteworthy exception to the general run of series. The strontium series is, on the other hand, quite normal if we exclude the infra-red lines whose character is not known. I find that the second members have their reversals slightly eccentrically placed to the red side of their emission lines and that they are displaced to the violet at the negative pole of the arc. These facts indicate that they are unsymmetrical toward the violet and therefore uniform with the higher members whose character has already been observed.7

- ¹ Kayser, Handbuch der Spectroscopie, 5.
- ² Royds, Kodaikanal Observatory Bulletin, No. XL.
- 3 Ibid.

- 5 Handbuch der Spectroscopie, 5.
- ⁶ Royds, Kodaikanal Observatory Bulletin, No. XL.
- 7 Kayser, op. cit., 6.

⁴ Saunders (Astrophysical Journal, 32, 153, 1910) gives the third members as unsymmetrical toward the red. This is probably a mistake. The photograph of Crew and McCauley of the arc in air (Astrophysical Journal, 39, 29, 1914) shows them to be unsymmetrical toward the violet in agreement with Eder and Valenta's observation of the spark lines and mine of the arc lines.

In brief, the higher members of the first subordinate "triplet" series of calcium, strontium, and barium are unsymmetrical toward the violet; the first members of the barium series are unsymmetrical toward the red, the second members of the calcium series are symmetrical, while the second members of the strontium series are already unsymmetrical toward the violet.

For convenience of reference I have collected in Table I the lines of the first subordinate "triplet" series of calcium, barium, and strontium.

The chief purpose of the present paper is to point out the importance of determining the pressure-shifts of the first subordinate series of calcium and barium, in which, as we have seen, the character of the lines changes. The interest in these first subordinate series lies in the question whether their lines unsymmetrical toward the violet are, like those of iron, displaced by pressure to the violet, i.e., in the contrary direction to the other lines although belonging to the same series. St. John and Miss Ware, as well as Fabry and Buisson, have shown that the iron lines which widen unsymmetrically toward the violet undergo large displacements to the violet with increased pressure, and Gale and Adams have confirmed this,2 while those which widen unsymmetrically toward the red undergo large displacements to the red. At present the only evidence available on the point is the difference in the wave-lengths of the calcium arc in air (Holtz3) and in vacuo (Crew and Mc-Cauley⁴). These differences, which are given in Table I, while they should be accepted with some reserve, show that the lines unsymmetrical toward the violet are displaced to the violet by pressure, and the symmetrical lines of the same series, as was found previously by Humphreys, to the red. It has not been doubted until recently⁵ that, as discovered by Humphreys, the pressure displacement $\delta \lambda / \lambda$ was constant for all lines belonging to the same series, and this fact has been recommended for the detection of

¹ Astrophysical Journal, 36, 14, 1912; 31, 111, 1910.

² Ibid., 37, 301, 1013.

³ Zeitschrift für wissenschaftliche Photographie, 12, 101, 1913.

⁴ Astrophysical Journal, 39, 29, 1914.

⁵ Swaim, *ibid*., **40**, 137, 1914.

TABLE I
THE FIRST SUBORDINATE "TRIPLET" SERIES OF CALCIUM, STRONTIUM, AND BARIUM

Order in Series	CALC	IUM	Strontium	BARIUM	
	λ	λ(Arc in Air) -λ(Arc in Vacuo)‡	λ	λ	
First members.	[19916.0 19864.6 19777.4 19507.1 19452.9 19310.6		30110.7 29225.9 27356.2 26915.4 26024.5	\[\begin{array}{c} \\ 5819.21 & (ur) \\ 5800.48 & (ur) \\ 5777.84 & (ur) \\ 5536.07 & (ur) \\ 5519.37 & (ur) \\ 5424.82 & (ur) \end{array} \]	
$\left.\begin{array}{c} \text{Second} \\ \text{members} \dots \end{array}\right\}$	4456.81 (s) 4456.08 (s) 4454.97 (s) 4435.86 (s) 4435.13 (s) 4425.61	+0.011 + .018 + .016 + .009 + .016 + .021	\[\begin{array}{ll} 4971.85 & (uv) \\ 4968.11 & (uv) \\ 4962.45 & (uv) \\ 4872.66 & (uv) \\ 4832.23 & (uv) \end{array} \]	{4493.82 (uv) 4489.50 (uv) 44333.04 (uv) 4323.15 (uv) 4264.45 (uv)	
Third members.	3645.14* 3644.86 (uv)† 3644.50 (uv)† 3631.10 (uv) 3630.83 (uv)† 3624.15 (uv)†	003 + .003 015 010 001	4033.25 4032.51 (uv) 4030.45 (uv) 3970.15 (u) 3969.42 3940.91 (uv)	4087.53 (u) 4084.94 (u) 3947.6 (u) 3945.6 (u)	
Fourth members	3362.42* 3362.27* 3361.92 (uv) 3350.50* 3350.22 (uv) 3344.49 (uv)	014 010 017	3705.88 (u) 3653.90 (u) 3653.32 (u) 3629.15 (u)	3895.2 (u) 3767.5 (u)	
Fifth members.	3226.26* 3225.74 (uv) 3215.46* 3215.15 (uv) 3209.68 (uv)	021 019 038	3547.92 (u) 3499.40 (u) 3477.33 (u)	3787 (u)	
Sixth members.	3151.41* 3150.85 (u) 3141.29* 3140.91 (u) 3136.09 (u)	030 062 -0.135	3457.70 (u) 3411.62 (u) 3390.09 (u)		
Seventh members	3101.87 (u)		3400.39 (u)		

⁽s) denotes symmetrical, (ur) unsymmetrically widened toward the red, (uv) unsymmetrically widened toward the violet, and (u) hazy or diffuse. Those given in italic are new observations; those in roman type are as recorded by other observers.

^{*}Wave-lengths in the arc in vacuo by Crew and McCauley reduced to Rowland's scale.

 $[\]dagger$ These lines are given by Saunders as unsymmetrical toward the red, probably by mistake. See footnote on p. 155.

[‡] Taken from Crew and McCauley's paper.

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series. Judging from the analogy of the iron lines and from the foregoing results for calcium, however, it appears probable that, so far from being constant, the pressure-shift may even be in opposite directions for different lines of the same series.

This brings up the whole question of the relationship between pressure-shift and series. Humphreys found² that the pressure-shift $(\delta \lambda/\lambda)$ was constant for all the lines of the same series, and that the shifts for the principal, the first and second subordinate series were in the ratio 1:2:4. Although these ratios seem to hold for the majority of cases, about one-third of the total number are exceptions. These exceptions are given in Table II; the mean shifts reduced to λ 4000 at the same pressure for the different series of the same element are quoted from Humphreys' tables. Where data at the same pressure are not available the shift has been calculated from that at a neighboring pressure and is given in parentheses.

TABLE II

EXCEPTIONS TO HUMPHREYS' SERIES LAW

Series	Mean Shift	Ratio	Series	Mean Shift	Ratio
Al First subordinate Second subordinate	50 (40)	1:0.8	Hg{First subordinate Second subordinate.	70 66	1:0.9
Li{Principal	66 (96)	1:1.5	Na{Principal First subordinate*	73 312	1:4.3
Mg First subordinate Second subordinate	35 45	1:1.3			

^{*}By an unfortunate error or misprint, Humphreys has classed the lines $\lambda\lambda$ 5682, 5688 as belonging to the second subordinate series of sodium instead of to the first, making it appear as though they conformed to his law.

The shifts were reduced to λ 4000 by Humphreys on the assumption that the absolute pressure-shifts are proportional to the wavelength. If the shifts are proportional to some other power of the wave-length than the first, some of these exceptions might be brought into line, but on the other hand new ones would be introduced.

¹ Kayser, Handbuch der Spectroscopie, 2, 327, 579.

² Astrophysical Journal, 6, 169, 1897.

Recently Swaim has arrived at entirely different series relationships in studying the pressure-shifts of the zinc lines.¹ He finds that the shifts of the lines in the first subordinate series are *inversely* proportional to the cube of the wave-length, in the second subordinate series *inversely* proportional to the first power of the wave-length, and of non-series lines *directly* proportional to the square of the wave-length. There is therefore no direct relation between the first and second subordinate series.

It seems to me exceedingly probable that all these inconsistencies are due to the existence of a density effect superposed on the true pressure effect. When the arc is placed under pressure there is probably not only an increase in the pressure of the atmosphere surrounding the arc but also an increase in the density of the vapor in the arc owing to a more rapid production of vapor, or other The effect of an increase of density is to displace the unsymmetrical lines in the direction of their greater widening, and by an amount apparently dependent only on the degree of unsymmetrical widening.2 This might explain Swaim's curious results mentioned above. He noted that the amount of displacement under pressure depended on the diffuseness of the line, and, since the series lines he measured are unsymmetrical toward the red, it seems probable that the large displacements to the red he obtained for the higher and more unsymmetrical members of the series are due, at any rate in part, to increased vapor density.

Many of the anomalous results obtained by Duffield in the arc under pressure are also probably due to density effects. Duffield found that when unsymmetrical lines are reversed the displacement of the reversal falls to half of that of the unreversed line, while the reversals of symmetrical lines remain normally displaced.³ Now the unsymmetrical lines are those sensitive to density-shift and it would be expected that at the lower density of the absorption line their displacement would be smaller, while symmetrical lines would be unaffected. He also finds that the displacement of a line may have two alternative values at one and

¹ Astrophysical Journal, 40, 137, 1914.

² Royds, Kodaikanal Observatory Bulletin, No. XL.

³ Phil. Trans. Roy. Soc., A 208, 151, 1908.

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the same pressure.¹ Duffield says: "Whatever the nature of the disturbing cause, Group III and then Group II [of the iron lines] are most susceptible to it." The lines of Group III, all unsymmetrically widened toward the red, are those most susceptible to density-shift, while the lines of Group II, much widened but not unsymmetrically by pressure, have not been sufficiently investigated. He further says: "On the photographs showing abnormal displacements [approximately twice the normal values], the reversals are more numerous and broader than they are on plates giving normal values"; this observation is direct evidence of increased density. I admit, however, that there is no obvious reason why the ratio of the larger displacement to the smaller should be approximately 2:1.

An additional interest for the investigation of the calcium lines under pressure is the question of the behavior of Fowler's series of narrow triplets ($\lambda\lambda$ 4586, 4581, 4578, etc.). According to Moore⁵ the Zeeman effect for these lines is either zero or at least very small, and therefore their pressure displacement would be expected to be small also.⁶ It will, however, not be conclusive if they prove to have large displacements in the *arc* under pressure, since these lines are easily displaced by density.⁷

For the elucidation of the relationship between pressure-shift and series, as well as for the solution of solar problems, it seems essential to isolate the pressure effect from the density effect. The means of doing this are not obvious, and the only hope seems to lie in investigating the furnace spectrum under pressure rather than the arc spectrum, for in the furnace the vapor density, dependent on the rate of production and of disappearance of vapor, is almost certainly influenced by pressure to a much less degree than in the arc. All that we know at present is that since the density effect

¹ Phil. Trans. Roy. Soc., A 209, 216, 1909. ² Ibid.

³ Royds, Kodaikanal Observatory Bulletin, Nos. XXXVIII and XL.

⁴ Duffield, Phil. Trans. Roy. Soc., A 208, 161, 1908.

⁵ Astrophysical Journal, 33, 385, 1911.

⁶ See King, Astrophysical Journal, 31, 433, 1910; and Humphreys, *ibid.*, 23, 233, 1906; 26, 18, 297, 1907; 27, 194, 1908.

⁷ Royds, Kodaikanal Observatory Bulletin, No. XL.

is very small for symmetrical lines, their shifts in the arc under pressure are probably due to the pressure only, but that the shifts of unsymmetrical lines are, partly at least, due to density. Evershed suggests to me that the shift to the violet found in the arc under pressure for certain iron lines may be entirely a density effect, and an observation of Humphreys¹ supports this view. It certainly seems probable that many of the laws of pressure-shifts will be modified, and it is hoped simplified, if experiments can be conducted under conditions of constant vapor density. The elimination of density effects in order to obtain true pressure-shifts is one of the most pressing problems for those interested in the displacements in the sun's spectrum.

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¹ Astrophysical Journal, 31, 459, 1910.