INTENSITY MEASUREMENTS IN THE ARC SPECTRUM OF THALLIUM

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(Received October 28, 1931)

Abstract

Intensity ratios for the doublets of the principal series, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$, were measured by the photographic method, using a Pfund arc with silver poles. For $m=4$, 5, 6, 7, the values obtained for $\overline{a_1^2}/\overline{a_2^2}$ were 4.4, 6.6, 6.0, 5.2, deviating substantially from the prediction of the sum rule, and showing the effect discovered by Sambursky in the principal series of the alkalies. Separation of results according to arc currents of 2 amp. and 4 amp. showed no effect due to this factor. For the doublet $m=4$, the ratio obtained with a copper arc was 2.5. The relative intensities of the stronger components ($2s-mp_{1\frac{1}{2}}$), for values of $m=4$, 5, 6, 7, 8, were found to be 850, 82, 17.5, 3.2, and 1, respectively.

THE investigations of intensities in the doublet series of the alkali arc spectra carried out by Sambursky and others have revealed several interesting properties. It was therefore of interest to examine the doublet spectrum of a metal of the third group.

Measurements of the ratios for the principal doublets of the thallium arc spectrum were first made by O. U. Vonwiller,[1] at Utrecht, in 1929, but insufficient data were obtained for comparison with previous work. During 1930 the examination of the principal series was continued in Sydney.

The photographic methods introduced by Ornstein, and developed by him and his co-workers at Utrecht, were employed with very slight modifications, necessitated, in the case of one or two doublets, by the difficulty of obtaining suitable photographs. A Hilger spectrograph, of constant deviation type, was used with Ilford Special Rapid Panchromatic plates, which were found suitable for the whole of the range covered, *viz.*, 6700–4750A. By using the varying slit method, twelve exposures to continuous spectra were made on each plate in order to provide density marks, the source being a tungsten filament lamp previously calibrated by Mr. D. Vermeulen, of the Physical Laboratory, Utrecht University.

Preliminary observations on the second doublet of the series were made with a Pfund arc having copper poles. The presence of copper lines almost coincident with the components of the fourth doublet, (5109–5136A), made other means of producing the spectrum desirable. Attempts to excite the spectrum in an electrically heated discharge tube were unsuccessful owing to the sublimation of the metal on the walls of the tube. In nickel, monel metal, and carbon (cored with the chloride), the lines are so numerous that identification is too difficult to give reasonable certainty that the thallium lines, if

[1] O. U. Vonwiller, Phys. Rev. **35**, 802 (1930).

present, are unobscured by a background due to the material forming the poles. Spectra were finally obtained by using a Pfund arc with silver poles, all desired lines being free of any background.

At the expense of some loss of intensity, the illumination was so arranged that the region of the arc used was variable at will by means of diaphragms, light from each point falling uniformly onto the slit of the spectrograph.

No members of the series beyond the sixth were observed in any photographs and measurements could only be made as far as the fifth member (4891–4906A). For the doublets in the red and yellow exposures of a few seconds were sufficient but with those in the green and blue the intensity is so much less that half an hour is necessary. In such exposures the effect of continuous spectrum was greatly increased but this was found to be of advantage in giv ng more definite corrections for the rough ratios.

The combined results are given in Table I, the ratio given being that of the component of shorter wave-length ($2s-mp_{1\frac{1}{2}}$), to that of longer wave-length, ($2s-mp_{\frac{1}{2}}$). The value $\overline{a_1^2}/\overline{a_2^2}$ is obtained from I_1/I_2 by multiplying by the factor $(\lambda_2/\lambda_1)^4$, a_1, a_2, being the amplitudes of the virtual oscillators given by the equation $I=a^2\nu^4$. It will be seen that there is definite evidence of a maximum ratio occurring at the third member of the series. This is in accord with the observations of Sambursky[2] on the doublet spectra of the alkalies.

TABLE I. *Principal series doublets, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$.*

m	Wave-lengths	No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Average error	Probable* error
4	6549–6713A	7	4.9	4.4	0.8	0.3
		†9	2.8	2.5	0.5	0.2
5	5528–5583A	19	6.9	6.6	1.0	0.25
6	5109–5136A	22	6.1	6.0	1.0	0.2
7	4891–4906A	21	5.25	5.2	0.9	0.2

† Copper arc.
* Probable errors calculated with Peter's approximation formula

$$\text{P.E.}=\frac{0.8453\ \Sigma(+v)}{n(n-1)^{1/2}.}$$

Included in the table is the additional value obtained for the second member by use of an arc having copper poles. The difference between the two values, 4.4 and 2.5, is very much greater than the error considered possible in the mean results and presumably is to be attributed to different conditions (temperature, etc.) in the arc with different poles. On the other hand, Vonwiller obtained 4.5 for the ratio by using copper poles and currents of the same order as in this work, a result in good agreement with the value obtained here with silver poles.

Measurements were made with two arc currents, namely, 2 amp. and 4 amp. Table II shows the results obtained for each value of the current. It will be seen that the differences are well within the limits of error and it may therefore be assumed that absorption has a negligible effect.

[2] S. Sambursky, Zeits. f. Physik **49**, 731 (1928).

TABLE II. *Principal series doublets, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$.*

m	Wavelength	Arc current = 2 amp.					Arc current = 4 amp.				
		No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Avg. err.	Prob. err.	No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Avg. err.	Prob. err.
4	6549–6713A	3	4.3	3.9	0.5	0.3	5	5.4	4.9	0.7	0.35
5	5528–5583A	8	7.0	6.7	1.0	0.35	11	6.9	6.6	1.0	0.25
6	5109–5136A	11	6.0	5.9	0.8	0.2	11	6.15	6.0	1.0	0.25
7	4891–4906A	10	5.2	5.2	1.0	0.3	11	5.3	5.3	0.8	0.2

The average errors are high, but are not entirely due to the inaccuracy of measurement. The range of variation in each series of results obtained for the four doublets was about 50 percent of the mean value. However, the sets of values (about six), obtained from each plate were usually consistent to within 25 percent, there being noticeable changes from plate to plate. A recalculation of the results obtained for one doublet ($m=6$), showed that the photometry was accurate to within less than 10 percent. Apart from errors which may be involved in exposure and development, the large variation in results is to be attributed to changing conditions in the arc over which there is no direct control.

Since the material was at hand a calculation was made of the relative intensities of the stronger components of the doublets, $(2s-mp_{1\frac{1}{2}})$, from the second to the sixth members. Table III shows the results, the ratios given in column 4 being those of lines in adjacent doublets. In the fifth column the

TABLE III. *Relative intensities of stronger components, $2s-mp_{1\frac{1}{2}}$.*

m	Line	No. of obs.	Mean $I/_mI_{m+1}$	Mean $\overline{a^2}_m/\overline{a^2}_{m+1}$	Average error	Probable error	Ratio $\overline{a^2}_m/\overline{a^2}_{m=8}$
4	6549A	9	5.25	10.3	2.8	0.8	850
5	5528A	13	3.4	4.65	1.0	0.25	82
6	5109A	17	4.65	5.5	1.4	0.35	17.5
7	4891A	7	2.85	3.2	0.5	0.15	3.2
8	4768A						1
Weaker components							
6	5136A	12	3.6	4.3	1.3	0.35	
7	4906A						

ratios are given in terms of the mean squared amplitudes of the virtual oscillators. The errors in columns 6 and 7 refer to the numbers in column 5. In the last column are given the ratios of the mean squared amplitudes for each line to that for λ4768A. The logarithms of these last values have been plotted against m and are shown in Fig. 1. As with the doublet ratios no appreciable variation was found with change of arc current.

The mean of twelve observations of the relative intensities of the weaker components ($2s-mp_{1\frac{1}{2}}$), for $m=6$ and 7 has been used with the data given in Table I to provide an extra result for $m=6$.

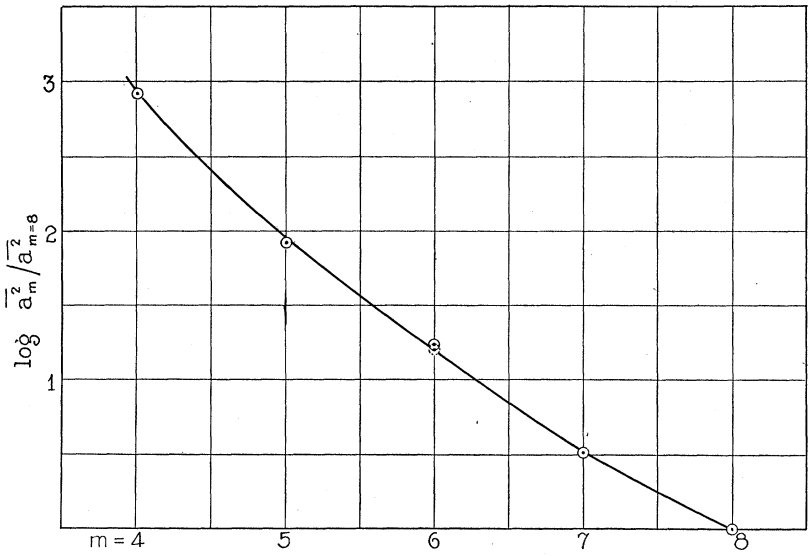

Fig. 1.

In conclusion we wish to express our thanks to the Cancer Research Department of the University of Sydney for the facilities granted in the use of the Moll microphotometer and especially to Professor O. U. Vonwiller for his help and advice in the carrying out of this work.