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Interpretation of the Third Spectrum of Gold (Au III)*

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A revision of the analysis of the Au III spectrum is presented. Of 9 energy levels considered doubtful on the basis of a recent theoretical treatment, 6 are found to be real and 3 have been rejected as incorrect. Three new energy levels have also been found in agreement with theoretical predictions.

Key Words: Corrections to analysis of Au III, gold, spectrum of Au III, third spectrum.

The analysis of the structure of the third spectrum of gold was published in 1960.[1] Recently, Shadmi[2] published the corresponding theoretical interpretation and some discrepancies between both papers justify the present comments.

In our 1960 paper we reported 17 even levels of the Au^{++} ion and 43 odd ones. In order to make them easily identifiable we labeled the even levels with *LS* symbols, pointing out that this coupling scheme did not apply, but was used only as a simple means of identification. Many of the odd levels were identified only by numbers, indicating that the *LS* designation was still more doubtful.

In his theoretical paper, Shadmi interprets the levels by the use of the *jj*-coupling scheme. When theory predicts a dominant *LS* character of the even levels, it is in good agreement with the experimental results, as is also the case as regards the value of the levels. Among the odd levels the situation is quite different. The largest component in *LS* coupling deduced theoretically does not always agree with the experimental designation, which is not surprising; but the theoretical results seem to indicate, also, that some of the experimental levels are incorrect. This result is worth discussing in detail.

Table 1 contains some of the data in table 6 of Shadmi's paper, and the symbols in column 4 have the following meanings:

A dash indicates experimental levels which have such large deviations from the theoretical ones that they are subject to rejection by Shadmi. A question mark indicates doubtful levels.

In this table the results of a new revision of the experimental data are also included, and the following comments are appropriate to each particular level. The levels designated 5°, 18°, and 33°, are rejected as incorrect, since the assumed combinations that were supporting them can now be considered as only numerical coincidences.

The levels 8° and 36° could be considered doubtful because they are based on only one combination. Nevertheless, only two lines are theoretically predicted as combinations of these two levels having $J=11/2$ with the known even ones. We may point out also, that the combinations $a^4F_{9/2}-8°_{11/2}$ and $a^2G_{9/2}-36°_{11/2}$ are expected to be strong. The lines chosen to identify these levels are the only two intense unclassified lines in the appropriate regions. An unsuccessful search has been made to see whether any of the already classified lines would give levels in better agreement with the theoretical predictions. We conclude, therefore, that these levels can be considered correct from the experimental point of view.

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[1] L. Iglesias, J. Res. NBS **64 A** (Phys. and Chem.) No. 6, 481 (1960).
[2] Y. Shadmi, J. Res. NBS **69 A** (Phys. and Chem.) No. 6, 511 (1965).

TABLE 1. *Doubtful levels of* Au III ($5d^8$ 6p *configuration*)

Exper. desig.	J	Level	(Shadmi)	Present situation	Theoretical value	O−C
5°	1/2	98559.1	−	Incorrect	− − −	
8°	11/2	102993.7	?	Probably good	102069	925
18°	1/2	113749.9	+?	Incorrect	− − −	
19°	1/2	113764.9	−	Good	113664	101
20°	7/2	115339.9	−	Good, $J=9/2$	115091	249
24°	3/2	116892.1	?	Good	115987	905
33°	9/2	123508.8?	−	Incorrect	− − −	
34°	3/2	125767.0	−	Good, $J=5/2$	125580	188
36°	11/2	127467.0?	?	Probably good	127104	363
42°	5/2	133058.9	−	Good, $J=3/2$	133181	−122

The level 24° is clearly correct. It is one of the levels giving a large number of combinations. From 12 lines theoretically possible 10 have been observed experimentally. One needs to assume too great a chance for fortuitous coincidences to be able to discard it. If this were done, several intense lines would remain without alternative explanation.

The levels 20°, 34°, and 42° are also correct, but the J-values have to be changed to agree with the theoretical predictions. It was very difficult to assign a J value of 9/2 to the level 20° since there are no even levels having $J=11/2$. By admitting that the assumed transition $a\,^2F_{5/2}-20°$ was just a coincidence, the level can be accepted as having $J=9/2$.

By assuming that the transition $a\,^2P_{1/2}$–34° leads to a fortuitous coincidence, the level 34° combines only with levels of $J=3/2$ or 5/2. The J-value can, therefore, be changed to 5/2 as is done in table 1.

The level 42° is real. Its J-value can be changed to 3/2, since it combines only with levels having $J=5/2$ and 3/2.

The level 19° is also correct but the alternative level 18°, has to be rejected.

As a further result of the present revision three new levels, designated 46°, 47°, and 48° have been found. They correspond to theoretical predicted levels, as shown in table 2.

TABLE 2. *New levels of* Au III ($5d^8\,6p$)

Desig.	J	Dominant *LS* character	Level observed	Level calculated	O−C
46°	1/2	61% (^{3}P)^{4}P	108183.2	108293	−110
47°	7/2	48% (^{1}D)^{2}F	134891.1	135014	−123
48°	1/2	45% (^{1}D)^{2}P	137705.7	137443	263

TABLE 3. *New classified lines of* Au III

λ vac. (Å)	Int.	ν (cm^{-1})	Combination
799.928	50	125011.2	$a\,^2D_{3/2}-48°$
1207.264	10	82831.5	$a\,^2F_{5/2}-47°$
1259.81	2 H	79377.0	$a\,^2P_{1/2}-48°$
1297.486	3	77072.1	$a\,^2G_{9/2}-47°$
1310.488	5	76307.5	$a\,^2G_{7/2}-47°$
1350.715	50	74034.9	$a\,^2P_{3/2}-48°$
1415.487	80	70647.1	$b\,^2D_{5/2}-47°$
1717.820 [a]	300	58213.3	$a\,^4P_{3/2}-46°$
1850.149	80	54049.7	$b\,^2D_{3/2}-46°$
2005.764	30	49856.3	$a\,^2P_{1/2}-46°$

[a] The classification $a\,^4F_{3/2}-z\,^4D^\circ_{1/2}$ assigned to this line in our first paper is not valid.

Table 3 contains the lines classified as combinations of these new levels.

The lines $\lambda=1540.258$ Å, $\lambda=1580.277$ Å, and $\lambda=1996.853$ Å previously classified with unreal levels are now left unclassified.

Finally, we wish to emphasize that the interpretation of this spectrum gives a new and good example of fruitful cooperation of the theoretical spectroscopists in the interpretation of our experimental results.

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