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THE ABSORPTION SPECTRUM OF TIN VAPOR IN THE ULTRAVIOLET

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ABSTRACT

Spectrum of tin.—(1) *Arc spectrum.* The spectrum of a 25 ampere arc was measured between 2170 and 1950A and 12 new lines observed. (2) *Absorption spectrum of tin vapor, 6000 to 2000A.* The tin was heated in a small carbon tube to about 1600°C and 53 absorption lines were observed, of which 38 are new. (3) *Frequency differences.* The results in general support the table of frequency differences given by McLennan, Young and McLay, lines from the normal state X_6 and X_5 showing strong absorption, those from X_4 medium absorption, those from X_2 only faint absorption and those from X_1 no absorption. A new table containing some changes and additions is given, using a different notation, which includes nearly all the arc lines. While the numerical relationships of the energy diagram are now well known, the nature of the terms involved has not yet been determined.

Although the number of lines in the tin arc spectrum is not large, the study of the spectrum from the series viewpoint has made very slow progress. A large percentage of the arc lines are readily reversed (especially with a current of 25 amperes) but their distribution is apparently irregular. One cannot by inspection recognize triplets or doublets. It frequently happens that the absorption spectrum of the vapor of an element furnishes a valuable clue to the relationships between the lines. Grotrian[1] has found four lines to be absorbed by tin vapor. McLennan, Young and McLay[2] have extended this number to 16.

The present experiments were undertaken using the methods that were employed in the study of manganese vapor.[3] Between 6000A and 2000A, 53 absorption lines were observed. If the absorption spectrum is photographed with the vapor at the highest temperature (about 1600°C), the intensities of the absorption lines fall quite naturally into three classes, very faint (*f*), medium (*m*) and the strongest absorption lines (*S*). One would expect that the strong absorption lines are due to atoms in the normal state while the very faint lines indicate atoms in excited states.

Table I contains the wave-lengths of all the known lines of the arc spectrum of tin below 6000A together with their frequencies. From

[1] W. Grotrian, Zeits. f. Physik **18**, 169 (1923).
[2] McLennan, Young and McLay, Trans. Roy. Soc. Can. Sec. III, 57 (1924).
[3] Zumstein, Phys. Rev. **26**, 765 (1925).

6000 to 2190A Arnolds'[4] values of the wave-lengths are used. The intensities are as given by Kayser and Runge. Between 2190 and 1950A, the wave-lengths are my own values. The intensities are rough visual estimates of the spectrum of a 50 ampere arc. The maximum error of my measurements appears to be .1A above 2020A and .2A below 2020A. These values may be compared with the measurements of McLennan, Young and McLay[2] who first called attention to the important group of tin arc lines in this region. With a few exceptions, the agreement is very good. Two of their lines are resolved into doublets and 12 new lines are added to their list. Below 1950A the wave-lengths are those found by McLennan, Young and McLay as reversals of a tin arc in an

TABLE I

Tin arc spectrum

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
5631.69	17751.7	5	—	V
4524.740	22094.54	5	—	V
11.30	22160.4	2	—	—
4077.73	24516.5	1	—	—
3801.031	26301.21	4R	f	IV
3655.78	27345.5	3	—	V
3330.596	30016.04	6	*f*	IV
3262.338	30644.06	5R	*f*	IV
23.574	31012.54	1	—	—
18.690	31059.60	3	—	V
3175.039	31486.61	5R	*S*	III
41.823	31819.47	3	—	V
3067.76	32587.62	2	—	—
34.116	32948.96	6R	*S*	—
32.783	32963.45	3R	—	V
09.138	33222.46	6R	*S*	II
2913.542	34312.47	4R	—	V
2863.320	34914.29	6R	*S*	I
50.618	35069.84	4R	*f*	IV
39.985	35201.13	8R	*S*	III
13.582	35531.08	3R	*f*	IV
12.566	35544.28	3	—	V
2790.187	35829.35	2	—	—
89.323	35840.45	1	—	—
87.936	35858.26	4R	—	V
85.027	35896.15	3R	*f*	IV
79.814	35963.03	4R	*f*	IV
61.784	36197.82	4	—	—
06.504	36937.10	7R	*S*	II
2661.245	37565.23	4R	*S*	II
36.988	37910.76	3u	—	V
32.6	37974.		—	V
23.5	38105.		—	V
21.7	38132.		—	V
20.6	38148.		—	—
14.177	38241.55	1	—	—
2599.4	38459.		—	V
94.431	38532.59	4R	*f*	IV
71.598	38874.70	5R	*f*	IV

[4] Arnolds, Zeits. f. wiss. Photographie **13**, 322 (1914).

TABLE I—continued

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
58.056	39080.47	4r	—	V
46.552	39257.00	5R	*S*	I
31.122	39496.31	4r	—	V
23.912	39609.13	3R	*f*	IV
10.9	39815.		—	—
2497.724	40024.39	2	—	V
96.768	40039.70	2	—	—
95.722	40056.50	5R	*f*	IV
91.71	40121.0	2r	—	V
83.389	40255.42	5R	*S*	III
55.250	40716.73	3	*f*	III
2433.473	41081.01	2	—	—
29.490	41148.41	6R	*S*	III
21.690	41280.93	6R	*f*	IV
08.143	41513.13	4R	*f*	IV
2380.742	41990.90	3R	*m*	II
68.217	42212.94	1	—	—
57.88	42398.0	1	—	IV
54.840	42452.73	6R	*S*	II
34.799	42817.09	5R	*S*	II
17.21	43142.1	6R	*f*	IV
2286.65	43718.5	4R	*m*	III
82.222	43803.32	3	—	IV
68.902	44060.53	6R	*S*	III
67.160	44094.37	4R	*f*	IV
51.12	44408.9	4R	*f*	IV
46.02	44509.7	6R	*S*	I
31.68	44795.3	4R	*m*	III
11.0	45214.	2R	—	IV
09.60	45242.9	6R	*m*	III
2199.29	45454.9	6R	*S*	II
94.42	45555.8	5R	*m*	III
71.21	46042.8	3R	—	IV
66.72	46137.4	1R	—	—
51.37	46467.3	3R	*f*	III
48.71	46524.8	3R	*m*	IV
48.44	46530.6	3R	*f*	II
47.81	46544.3	1R	—	IV
41.34	46684.9	2R	—	IV
40.65	46700.0	2R	*f*	III
23.61	47074.8	1R	—	IV
21.25	47126.9	2R	*f*	IV
18.51	47187.6	1R	—	IV
13.97	47289.4	3R	*S*	II
00.83	47585.1	4R	*m*	III
2098.77	47631.8	1R	—	IV
96.19	47690.4	4R	*f*	IV
94.20	47735.7	2R	*m*	III
93.77	47745.5	1R	—	—
92.41	47776.5	1R	—	IV
91.58	47795.4	3R	*S*	III
85.60	47933.4	1R	—	IV
84.19	47964.9	1R	—	IV
80.51	48049.7	2R	*f*	IV or III
74.75	48183.0	1R	—	—
72.86	48226.9	6R	*S*	I
68.47	48329.3	4R	*m*	III
63.95	48435.1	2R	*m*	II
61.42	48494.7	1R	*m*	IV
59.56	48538.5	1R	*f*	IV
2058.28	48569.0	2R	—	IV
54.05	48670.1	2R	—	IV
40.85	48983.4	3R	*m*	I

TABLE I—continued

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
40.53	48990.9	3R	*m*	III
28.56	49280.0	1R	—	IV
27.15	49314.3	2R	*f*	II
20.79	49469.4	1R	*f*	II
15.75	49593.3	2R	*f*	III
07.90	49787.2	2R		II
1994.30	50126.6	2R		I
92.67	50167.6	1R		—
91.14	50206.1	2R		III
83.39	50402.5	3R		III
70.75	50726.0	2R		II
59.60	51014.4	1R		I or II
51.54	51224.8	3R		III or I
47.6	51329.0	1R		II
41.81	51482.2	1		I or IV
32.32	51734.4	1R		III
24.50	51945.3	2		II
12.61	52268.1	1		III
λ(I.vac.)				
11.3	52320	R		III
08.8	52389	R		—
1899.63	52641.8	3		—
97.05	52713.4	1		I
91.1	52879	R		III
85.8	53028	R		I
82.7	53115	R		III
81.4	53152	R		III
73.3	53382	R		II
72.2	53413	R		—
71.1	53444	R		II
65.6	53602	R		II
63.1	53674	R		III
61.3	53726	R		III
60.3	53755	R		III
54.2	53932	R		II
52.0	53996	R		II
48.5	54098	R		—
37.4	54425	R		III
29.1	54672	R		III
23.1	54852	R		II
19.3	54966	R		III
15.6	55078	R		I
13.0	55157	R		I
08.8	55285	R		I
1804.6	55414	R		II
03.2	55457	R		II
1795.7	55688	R		I
92.0	55803	R		I
87.4	55947	R		—
80.4	56167	R		II
79.3	56202	R		II
78.0	56243	R		I
73.4	56389	R		I
72.8	56408	R		II
71.4	56452	R		—
66.8	56599	R		—
65.7	56635	R		—
64.8	56664	R		III
63.6	56702	R		II
61.7	56763	R		—
56.1	56944	R		—

atmosphere of hydrogen, and are a very valuable contribution to our knowledge of the tin arc spectrum. Those lines at which I have observed absorption by the vapor are indicated in column 4, Table I by the letters *f*, *m* or *S* which represent the magnitude of the observed absorption.

On the basis of their own experiments and the work of others (see their paper for complete references) McLennan, Young and McLay give a table of frequency differences. Sponer[5] has recently given a similar table. The faint arc lines reported by Sponer are also included in Table I. These two tables of frequency differences have been used to interpret the absorption experiments. Most of the lines of column X_6 (McLennan, etc. notation) show strong absorption supporting their opinion that these lines represent transitions to the normal state. Strong absorption is also observed for the lines which come from the X_5 state. This is not surprising as X_5 is an excited state differing in frequency from the normal state by only 1692 cm^{-1}. The absorption lines from the X_4 state ($X_6 - X_4 = 3428$ cm^{-1}) are in the medium class. From the X_2 state ($X_6 - X_2 = 8324$ cm^{-1}) only faint absorptions were observed and finally from X_1 ($X_6 - X_1 = 16873$ cm^{-1}) no absorptions were observed. In general, therefore, the intensities of the absorption lines support their table of frequency differences.

One naturally wonders if every tin arc line finds a place in this table or if there are more excited states close to the normal state. Several lines occupy two positions in their table. For example, 35544.3 (using frequency rather than wave-length) represents a transition to both the X_1 and X_3 states. The fact that no absorption was observed for this line shows clearly that the transition is to the X_1 state. 48676 is given as a transition to the normal state. It should therefore be absorbed rather strongly by the vapor. No trace of absorption was found. 41081.1 should be a medium absorption line but absorption was not observed. Proceeding in this manner, a new table of frequency differences has been made and is given in Table II. It is based primarily on the two tables already referred to and contains a few changes and several additions as suggested by the absorption experiments and the new arc lines observed. The X_3 state has been omitted as all the ultraviolet lines can be given other places in the table and also because the two red lines 16558.0 and 16845.3 were not observed reversed or absorbed. As regards notation, X_1 is used for the normal state, X_2 for the first excited state etc. From this list we get the last column of Table I. A line of origin IV is one where the transition is to the X_4 metastable state.

[5] H. Sponer, Zeits. f. Physik 32, 24 (1925).

Of the 53 absorption lines observed, 52 fit in Table II and in general with the approriate intensities. A glance at column 5, Table I, shows

TABLE II

Frequency differences—tin arc

X_5V	X_4IV	X_3III	X_2II	X_1I
8549.5	5185.5	1735.9	1692.	(Normal state)
17751.7	26301.21	31486.61	33222.46	34914.29
	30016.04	35201.13	36937.10	
22094.54	30644.06		37565.23	39257.00
	35069.84	40255.42	41990.90	
	35531.08	40716.73	42452.73	
27345.5	35896.15		42817.09	44509.7
	35963.03	41148.41		
	38532.59	43718.5	45454.9	
	38874.70	44060.53		
31059.60	39609.13	44795.3	46530.6	48226.9
	40056.50	45252.9		
31819.47		45555.8	47289.4	48983.4
	41280.93	46467.3		
32963.45	41513.13	46700.0	48435.1	50126.6
	42398.0	47585.1	49314.3	(51014.4)
		47735.7	49469.4	
		47795.4		(51224.8)
34312.47		(48049.7)	49787.2	(51482.2)
	43142.1	48329.3		
	43803.32	48990.9	50726.0	
35544.28	44094.37		(51014.4)	52713.4
35858.26	44408.9	49593.3	51329	53028
		50206.1	51945.3	
	45214	50402.5		
	46042.2	(51224.8)		
37910.76			53382	55078
37974	46524.8		53444	
	46544.3	51234.4		55157
38105		51842		
38132	46684.9		53602	55285
38459			53932	
	47074.8	52268.1	53996	55688
	47126.9	52320		
	47187.6			55803
39080.47	47631.8			56243
	47690.4	52879		
	47776.5			56389
	47933.4	53115	54852	
	47964.9	53152		
39496.31	(48049.7)			
	48494.7	53674	55414?	
40024.39	48569.0	53755		
	48538.5	53726	55457?	
40121.0	48670.1			
		54425	56167	
	49280		56202	
		54672	56408	
		54966	56702	
	(51482.2)	56664		

Lines in parentheses occur in two places.

that the lines of the arc spectrum (below λ5600) which do not find a place in the frequency difference list are as a rule the faint emission lines given only by Arnolds. It seems therefore very probable that some of these do not belong to the tin arc spectrum. Out of 40 lines observed by McLennan, Young and McLay in the Schumann region, only 9 are not classified. We have therefore considerable confidence in Table II and do not consider it probable that there are metastable states between X_1 and X_5. If the value of the X_1 term (59158) as given by McLennan, etc., is correct, then we can calculate the values of all the other terms. The problem of determining the nature of the individual terms is one of considerable difficulty and I have made practically no advance in that direction beyond a few general observations.

The vacant spaces in Table II are largely to be attributed to the selection principle of the inner quantum number. It is also certain that the 5 terms X_1, X_2, X_3, X_4 and X_5 do not at all belong to one system (for example quintet *d*) as there are terms which combine with all 5 and we would have a contradiction to the selection principle for inner quantum numbers. We should expect singlet, triplet, quintet, etc., systems for tin. If there are *p* terms among $X_1, \ldots\ldots X_5$ then by the interval rule the ratios of the separations would be 3/2 for quintets and 2/1 for triplets. We note that $(X_3-X_4)/(X_3-X_1)=3/2$. The very strong absorption line 3034.116 which could not be placed in Table II is one of the strongest absorption lines. It represents a transition to X_1, X_2 or X_3 and may be a combination between a quintet *d* term with inner quantum number 4 and *p* terms of the same system. This would explain the lack of other combinations with the particular term involved. Since we have two systems present it is to be expected that all lines which involve transitions to the X_4 term will be faint absorption lines if both terms are in the same system and may even not be observed as an absorption line if the terms belong to different systems and the dispersion of the spectroscope is not large enough. The lines from the X_1, X_2 and X_3 states while usually observed as strong absorption lines may be faint where we have an intercombination between two systems. In conclusion it may be said that the numerical relationship of the energy diagram for the tin arc spectrum are very well known; the nature of the terms involved, however, is practically unknown.

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