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THE M-SERIES ABSORPTION SPECTRA OF METALLIC PLATINUM AND GOLD

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Abstract

The M-absorption spectra of metallic platinum (78) and gold (79) have been investigated by the use of a vacuum spectrograph. Five discontinuities were found for platinum at 5.711A (M_1), 5.506A (M_2), 4.677A (M_3), 4.085A (M_4), and 3.742A (M_5). For gold four were found at 5.506A (M_1), 5.315A (M_2), 4.501A (M_3) and 3.603A (M_5). No M_4 discontinuity was found for gold and the M_4 for platinum was very faint. The $(\nu/R)^{1/2}$ values for the experimentally determined edges compare very favorably with the values predicted by the use of absorption and emission data from the L-series except in the case of M_1 and M_2 where an unmistakable deviation, previously reported by other investigators on other elements, appears to be confirmed. No measurable shift in the position of any of the discontinuities due to a change in valence of four, in the case of the platinum atom, was observed. No "white line" absorption was observed at any of the discontinuities.

Introduction

The work of Rogers[1] on the x-ray M-absorption spectra of osmium (76), iridium (77), and platinum (78) revealed a systematic discrepancy between the actual positions of the M_1 and M_2 discontinuities and those predicted by Bohr and Coster[2] and by Sommerfeld[3] by the use of emission and absorption data from the L-series.

Rogers' results were in agreement with those previously reported by Zumstein[4] in his work on tungsten. Rogers and Zumstein found that the M_1 and M_2 absorption discontinuities occurred at frequencies greater than those predicted, indicating a somewhat tighter binding of the electrons in these levels than was to be expected from the application of the combination principle to the L-emission and absorption data as mentioned above.

The existence of a chemical influence upon the positions of the M discontinuities, due to the state of combination of the atoms composing the absorbing screen, has been suggested[1] as a possible partial explanation of the results observed. The work of a number of authors[5] has definitely established

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[1] R. A. Rogers, Phys. Rev. **30**, 747 (1927).

[2] Siegbahn "Spectroscopy of X-Rays" Eng. pp. 184–5.

[3] Sommerfeld "Atombau—" 4th Ger. ed. pp. 304–5.

[4] R. V. Zumstein, Phys. Rev. **25**, 747 (1925).

[5] J. Bergengren, Zeits. f. Physik **3**, 247 (1920); Comptes rendus **171**, 624 (1920).
A. Lindh. Comptes rendus **172**, 1175 (1921); Zeits. f. Physik **6**, 303 (1921); Comptes rendus **175**, 25 (1922); Ark. f. Mat., Astr. och Fys. **18**, Nr. **14**, (1924); Zeits. f. Physik **31**, 210 (1925).
K. Chamberlain, Nature **114**, 500 (1924); Phys. Rev. **26**, 525 (1925).
D. Coster, Zeits. f. Physik **25**, 83 (1924).

the existence of such an effect in the K-absorption of lighter atoms. The effect has not been reported for the absorption discontinuities of heavier atoms.

Since the investigations of Rogers and Zumstein were made with a compound of the element in question as the absorbing material, it seemed that the "chemical effect" explanation was at least possible. The work here reported was undertaken for the purpose of testing this point by the use of absorption screens made of the pure element.

Platinum was chosen from the elements investigated by Rogers because it seemed to be better suited to the proposed production of absorption screens of the pure element. The method proposed was the evaporation of the metal in a vacuum and its condensation upon a base that would be transparent to the comparatively long and easily absorbed x-radiation to be used in this work.

The investigation of gold was undertaken for the reason that it lies next to platinum in the periodic classification and can be obtained in sheets thin enough for use in the absorption screens. Edges obtained by the use of such screens would certainly be free from effects due to chemical combination. For this reason results in comparative agreement with those found for platinum by the use of the evaporated metal screens should tend to confirm belief in the reliability of such results. The M-absorption spectrum of gold has never been investigated to the knowledge of the author.*

EXPERIMENTAL

The vacuum spectrograph used has been described by both Zumstein[4] and Rogers.[1] Its operation in this work differed in minor details only. The slit-window separating the metal x-ray tube from the spectrometer chamber was made of goldbeaters skin rendered opaque to ordinary light by a thin coating of lamp black. This type of window, though somewhat less transparent to the x-radiation than the collodion windows used previously, was much stronger. The increased absorbing power of the slit-window was more than offset by the marked increase in intensity of the x-radiation from the metal tube due to the removal of all mercury vapor by the use of a liquid-air trap.

The crystals used were very fine specimens of gypsum ($CaSO_4 \cdot 2H_2O$). Note has been made of their peculiar behavior in an appendix.

The production of uniform platinum absorption screens of the required thickness was the most difficult part of the present problem. The method of finely ground metal suspended in collodion having failed[1] the only other methods that seemed to promise success were the use of very thin foils or the deposition of the metal upon an appropriate base by cathodic sputtering or by evaporation. After unsuccessful attempts to secure platinum foil of

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Franck u. Kuhn, Ziets. f. Physik **43**, 3/4 May (1927)

O. Stelling, Zeits. f. Anorg. Chem. **131**, 48 (1923); Zeits. f. Phys. Chen. 117, 161 (1925).

S. Aoyama K. Kimura. Y. Nishina. Zeits. f. Physik **44**, 810 (1927).

* See note appended.

the desired thickness, the method of evaporation was chosen. The problem of obtaining a suitable base upon which such deposition could be made was finally solved by the use of very thin glass. These bases were prepared by blowing large thin bubbles of soft sodium glass. It was easily possible to find pieces of these bubbles sufficiently flat and of thicknesses of the order of 10^{-4} cm. Such sheets were quite transparent to the rays, were not very seriously affected by proximity to a white-hot platinum filament in vacuum, and with care could be mounted upon pasteboard frames for use in the spectrometer.

The evaporation chamber was very simple in construction. It consisted of a three-litre bell-jar mounted on a brass base. The junction of the jar and base was ground to fit and made vacuum-tight by the use of beeswax melted around the outside of the joint by gently heating the parts with a flame. The use of a harder wax was prohibited by the impossibility of heating the heavy bell-jar sufficiently to melt the wax without cracking the jar.

The filament was made by coiling a platinum wire 0.010 in. in diameter about the shank of a number 60 twist drill. The filament was then suspended horizontally about five or six millimeters above a water-cooled copper table upon which the deposit base was held by two small drops of collodion-amyl-acetate solution.

The evaporation chamber was evacuated by means of a Cenco Hyvac oil pump and a diffusion pump operating through a liquid-air trap.

With the platinum filament operating at temperatures only slightly below the melting point visible deposits could be obtained in from eight to ten minutes. Satisfactory screens for the production of the desired absorption edges were obtained by evaporation of from three to twenty hours depending of course upon the depositing conditions and the discontinuity for which the screen was to be used. The deposits thus obtained were very smooth and had a metallic lustre. In order to try to test the films thus deposited for purity an especially heavy deposit was made on a portion of a microscope slide from which it was dissolved with aqua regia for chemical analysis. Due to the small weight of the sample (less than 0.01 gram) only slightly more than 80 percent of the weight was recovered as platinum. It is felt that the films were much more pure than this single attempt at analysis indicated.

The wave-lengths of the discontinuities here reported are regarded as accurate to within ±0.005A excepting the wave-length of the M_2 absorptions. On account of their diffuse character these edges are harder to measure with accuracy. They are regarded as accurate to at least ±0.008A or slightly more than one-tenth of one percent.

RESULTS

The following tables include the average wave-length results of the plate measurements with the corresponding (ν/R) and $(\nu/R)^{1/2}$ values together with the corresponding data taken from Bohr and Coster's revised tabulations (see Siegbahn "Spectroscopy of X-rays") of the computed values of the M-absorptions for both gold and platinum. In the table of the results on platinum there have been included the values previously reported by R. A. Rogers in his article to which frequent reference has been made.[1]

TABLE I. *Platinum M-series absorption. Wave-lengths of all emission lines used as reference are taken directly from Siegbahn's "Spectroscopy of X-rays."*

Edge	Wave-length	(ν/R)	$(\nu/R)^{1/2}$	Reference lines	Author*
M_1	5.711A	159.6	12.63	Au $M\alpha$; Au $M\beta$; Pb $M\alpha$.	J.
	5.736	158.9	12.60		R.
	5.826	156.4	12.51		B&C.
M_2	5.506	165.5	12.86	Au $M\alpha$; Au $M\beta$; Pb $M\alpha$.	J.
	5.541	164.5	12.83		R.
	5.615	162.3	12.74		B&C.
M_3	4.677	194.8	13.96	Bi $M\alpha$; Bi $M\beta$; Pb $M\alpha$; Pb $M\beta$; Cl $K\alpha$.	J.
	4.674	195.0	13.96		R.
	4.671	195.1	13.97		B&C.
M_4	4.085	223.1	14.94	Th $M\alpha$; Th $M\beta$; K $K\alpha$.	J.
	——	——	——		R.
	4.063	224.3	14.98		B&C.
M_5	3.742	243.5	15.61	Th $M\alpha$; Th $M\beta$; K $K\alpha$.	J.
	3.738	243.8	15.61		R.
	3.744	243.4	15.60		B&C.

* J. = Johnson; R. = Rogers: experimental values.
B&C. = Bohr and Coster: calculated values.

TABLE II. *Gold M-series absorption.*

Edge	Wave-length	(ν/R)	$(\nu/R)^{1/2}$	Reference lines	Author
M_1	5.506A	165.5	12.86	Au $M\alpha$; Au $M\beta$; Mo $L\alpha$; Mo $L\beta$; Bi $M\alpha$; Pb $M\alpha$.	J.
	5.594	163.0	12.77		B&C.
M_2	5.315	171.5	13.09	Same as for M_1	J.
	5.383	169.3	13.01		B&C.
M_3	4.501	202.5	14.23	Bi $M\alpha$; Bi $M\beta$; Pb $M\alpha$; Pb $M\beta$; Cl $K\alpha$; Pb $M\gamma$; Bi $M\gamma$; Th $M\alpha$.	J.
	4.494	202.8	14.25		B&C.
M_4	——	——	——	——	J.
	3.876	235.1	15.33		B&C.
M_5	3.603	252.9	15.90	K $K\alpha$; Th $M\beta$; Th $M\alpha$.	J.
	3.604	252.9	15.90		B&C.

DISCUSSION

The values of the M_1 and M_2 absorption wave-lengths of platinum as measured by the author appear to be such as to indicate a somewhat *tighter* binding of the electrons of these two levels than found by Rogers, being shorter in wave-length than the values reported by him by 0.025A and 0.035A respectively. This apparent difference has no significance for at least two reasons. Rogers used the mercury M_α and M_β lines for reference in making his measurements on these edges. The wave-lengths of these lines as given in Siegbahn are taken from Karcher's measurements,[6] which are found to be on the average about 20XU too high in value by the method of measurement by interpolation using strong neighboring emission lines whose wave-lengths have been measured more accurately by Stenstrom. (Siegbahn "Spectroscopy of X-rays" page 125.) Karcher's M lines, α and β in particular of the elements lead, thallium, gold and platinum also show a corresponding variation of from 0.013A to 0.031A above the values reported by Stenstrom. Thus it would seem that the use of these lines as reference would introduce an error of at least 0.020A in the proper direction to explain the above disagreement. Reduction of the values reported by Rogers by this amount brings the value of the M_1 edge to agreement with the values here reported within the experimental accuracy claimed for these results. The discrepancy of 0.015A remaining between the result here reported for M_2 and that of Rogers can certainly be partly due to the very diffuse character of this edge. Rogers' three reported measurements on this edge differ among themselves by 0.011A.[1] The author's remeasurements of Rogers' original plates have given an average value somewhat shorter than the average reported by him. Careful comparison of the two sets of plates has shown no observable difference in the positions of the M_2 edges.

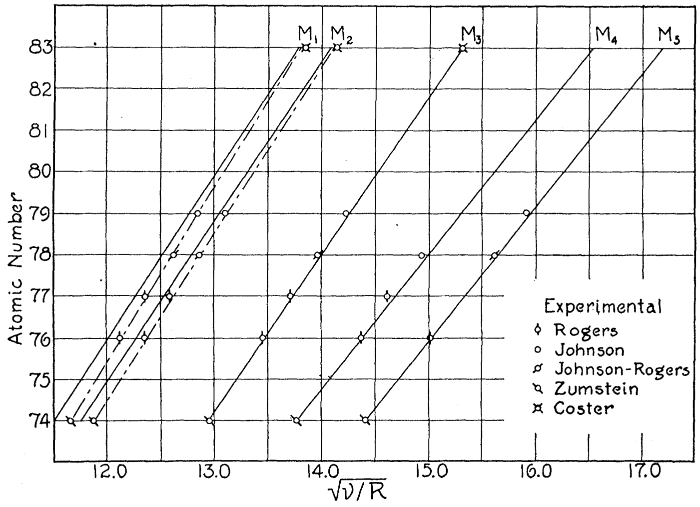

Fig. 1. Values of $(\nu/R)^{1/2}$ plotted against atomic number. Full lines represent the average computed values of both Bohr and Coster and of Sommerfeld.

Such small discrepancies observed between the wave-lengths reported for Pt M_1 and Pt M_2 by Rogers and the author in no way approximate the value of the displacement of the values of $(\nu/R)^{1/2}$ for these two edges toward higher values than those predicted by computation from L-series data.

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[6] J. C. Karcher, Phys. Rev. **15**, 288 (1920).

The positions of the measured values of $(\nu/R)^{1/2}$ plotted against the atomic number for the elements W (74) to Bi (83) are shown in the figure. The solid lines represent the average computed values of both Bohr and Coster[2] and of Sommerfeld.[3] The displacements of the absorption edges on the photographic plates corresponding to the displacements in $(\nu/R)^{1/2}$ values from the average predicted values as shown in the figures are from about 0.18 cm to 0.30 cm. The accuracy of measurement of the positions of these discontinuities as determined by repeated measurements was at least to ± 0.015 cm in the case of the M_2 edge, which is the most diffuse, and at least to ± 0.01 cm for the other edges. The accuracy of such measurements over this region of wave-lengths has been discussed elsewhere[1] and will not be further treated here.

That the predicted positions are subject to the errors of measurement of the L-series phenomena necessary for such computations is recognized. Supposing the errors inherent in such L-series measurements to be as great as the errors admitted for these measurements it can be shown by a simple computation that at most the effect upon the position of an M-discontinuity will not be greater than five times the error of measurement of the edge by the present method. Such an error is apparently out of the question but if it were not it would be insufficient to account for the variation observed.

The variation seems to increase with decreasing atomic number (See Tables I and II) the experimental points falling upon the broken lines, (Fig. 1) which are displaced toward higher frequency values. The calculated and observed values for the elements Bi (83), Th (90), and U (92), the only other elements upon which measurements have been made,[7] agree well within the limits of experimental error.

Certainly the present investigation shows no shift in the positions of the M_1 and M_2 edges of pure platinum from the positions observed by Rogers using chloroplatinic acid as absorbing material. That the state of chemical combination of the absorption screen exerts no observable effect upon the positions of these edges is further borne out by the observed positions of the corresponding edges for gold. Here there is certainly no valence effect, yet the edges show relatively the same displacements from their predicted positions as do those of the elements observed in which compounds were used as absorbing screens.

A word must be said concerning the nature of the edges observed. With no exception they were of the " edge" type. The "white line" type of absorption reported by Rogers for the M_3 and M_5 discontinuities of platinum was not observed. (He did not observe M_4.) In this research both M_4 and M_5 of platinum were very faint and it cannot be definitely stated that they did not exhibit white lines. M_5 of gold however was very strong and certainly showed no such fine structure. The M_3-absorptions of both platinum and gold were strong and sharp and were certainly of the true edge type. No explanation can be offered at this time for the two different types of edges observed in

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[7] D. Coster, Phys. Rev. **19**, 20 (1922).

the two investigations. It might be suggested, however, that the explanation put forward by Miss Chamberlain[8] have some confirmation here. She has attempted to explain the appearance of white-line phenomena as being due in some manner to the reduction of the chemical compound in the absorption screen by the action of the rays themselves.

Though the errors inherent in the prediction of the M-levels from L-series data are from four to five times greater than the error of actual measurement of these same edges, granting the same accuracy of determination of the L-absorptions as has been claimed for the M-absorption measurements, it seems that the comparatively greater accuracy of measurement possible in the case of the L-series wave-lengths makes the predicted and the measured values of almost exactly equal reliability. We have therefore great confidence in the reality of the displacement of the edges from the positions at which we should expect to find them.

These marked systematic discrepancies apparently cannot be explained upon the basis of errors either of prediction or of measurement, and since the use of the carefully measured L_1-absorption with the appropriate emission line of the L-series results in the prediction of the M_4 and M_5 levels with satisfactory accuracy, while the use of this same edge with the strong sharp lines, which have their origins on the M_1 and M_2 levels, does not result in values sufficiently close to the measured values, it seems possible that the simple application of the combination principle is insufficient in this case. This principle has received such general confirmation from spectroscopic and other sources that we cannot well question its general applicability. We may suggest however that the general truth of the principle as applied to the radiation of characteristic spectral lines involves energy levels whose frequencies *may* not be exactly identical with the frequencies associated with these same "levels" when the atom is being excited by the absorption of incident x-radiation. The usual conceptions of the changes that take place in the absorption and emission of x-radiation leave no room for such possibilities, and yet we have evidence here of a phenomenon that at present is unexplained. We can only say that we regard the measured values as accurate, within the limits assigned to them, and *apparently* the experimental measurements upon which the predictions of these levels have been based are of sufficient accuracy to permit of their use with confidence in the order of accuracy of the results.

The writer wishes to thank the members of the staff of the Department of Physics of the State University of Iowa for their interest and assistance. Thanks are especially due to Dr. G. W. Stewart who suggested and directed this investigation.

NOTE ADDED AUGUST 3, 1929

After the preparation of this article for publication, an article appeared by Ernst Lindberg[9] in which some of the absorption discontinuities here re-

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[8] K. Chamberlain. Phys. Rev. **26**, 525 (1925).

[9] E. Lindberg, Zeits. f. Physik **54**, 632 (1929).

ported have been measured. His values of the M_1 and M_2 absorption wave-lengths for platinum and gold are longer than those reported here by amounts seemingly greater than is permitted by the errors of measurement. His wave-length values nevertheless show the same tendency as those here reported, being unmistakably shorter than those predicted. The following tables show how these new values compare with those reported here and with the computed values.

TABLE III. *Comparison of the results of Lindberg and of Johnson on the absorption-edge wave-lengths.*

Edge	Calc.	Johnson	Lindberg	Δ_1*	Δ_2*	Δ_3*
Pt M_1	5.826A	5.711A	5.746A	0.115A	0.080A	0.035A
Pt M_2	5.615	5.506	5.544	.109	.071	.038
Pt M_3	4.671	4.677	4.676	−.006	−.005	−.001
Au M_1	5.594	5.506	5.529	.088	.065	.023
Au M_2	5.383	5.315	5.330	.078	.053	.015
Au M_3	4.494	4.501	4.508	−.007	−.014	.007

TABLE IV. *Comparison of* (ν/R) *values.*

Edge	Calc.	Johnson	Lindberg	Δ_1*	Δ_2*	Δ_3*
Pt M_1	156.4	159.6	158.6	3.2	2.2	1.0
Pt M_2	162.3	165.5	164.4	3.2	2.1	1.1
Pt M_3	195.1	194.8	194.9	−.3	−.2	−.1
Au M_1	163.0	165.5	164.8	2.5	1.8	.7
Au M_2	169.3	171.5	171.0	2.2	1.7	.5
Au M_3	202.8	202.5	202.2	−.3	−.6	.3

TABLE V. *Comparison of* (ν/R)$^{1/2}$ *values.*

Edge	Calc.	Johnson	Lindberg	Δ_1*	Δ_2*	Δ_3*
Pt M_1	12.51	12.63	12.59	.12	.08	.04
Pt M_2	12.74	12.86	12.82	.12	.08	.04
Pt M_3	13.97	13.96	13.96	−.01	−.01	.00
Au M_1	12.77	12.86	12.84	.09	.07	.02
Au M_2	13.01	13.09	13.08	.08	.07	.01
Au M_3	14.25	14.23	14.22	−.02	−.03	.01

* Δ_1 = Difference between Johnson and calculated values.
Δ_2 = Difference between Lindberg and calculated values.
Δ_3 = Difference between Johnson and Lindberg values.

The maximum variation between the values given by Lindberg and those of the author above corresponds to a distance on the photographic plate of approximately one-half millimeter. The obvious explanation would seem to be that the gold emission lines, which form part of our reference system for the measurement of Pt M_1 and M_2, are in error. Lindberg has measured these lines[10] and though his reported values are longer by 0.008A for Au M_α and by 0.010A for Au M_β this will only account for one-third of this discrepancy. With the data at hand the reasons for the too large difference between our values is not apparent.

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[10] E. Lindberg, Zeits. f. Physik **50**, 91 (1928).

APPENDIX

Very marked deterioration of the gypsum crystals used in this investigation with respect to their reflecting power for x-rays was noticed after use for certain lengths of time. This deterioration occurred four times during the progress of this work at intervals of several months. The only crystal upon which any data were taken exhibited this peculiarity after having been in vacuum for about eighteen hundred hours during which time it was exposed to x-radiation from a tungsten coated cathode excited by potentials of from four to ten kilovolts for approximately nine hundred hours.

It is suggested that the effect may be due to dehydration of the crystal, possibly due to the exposure of the crystal to the radiation in a partial vacuum; which would be destructive of the crystal arrangement. No visible deterioration of the crystal was observed. It remained clear with no traces of the white powdry appearance usually associated with the dehydration effect caused by heat.

The effect is not confined to the reflecting "surface", for the reflecting power of the face approximately one sixteenth of an inch below the original surface is also very poor, although slightly better than that of the original outside surface. This was tested by simply splitting thin layers from the reflecting surface of the bad crystal and taking photographs with the newly exposed surfaces. No appreciable recovery of reflecting power after several months "rest" under atmospheric conditions was observable. In the article "The Dehydration of Barium Platino-cyanide Crystals under the Action of X-Rays" reported by Trapesnikow[11] it was found that the crystals recovered the lost water of hydration when air was admitted to the vacuum system. No further suggestions can be offered at this time to explain the phenomenon observed. That it occurs there can be no doubt.

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[11] A. Trapesnikow, Zeits. f. Physik **47,** 732–4 (1928).