# THE M-SERIES X-RAY ABSORPTION SPECTRA OF OSMIUM, IRIDIUM, AND PLATINUM

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### Abstract

Using a metal x-ray tube and vacuum spectrometer of the Siegbahn type, the absorption spectra of osmium (76), iridium (77), and platinum (78) have been investigated from 3.5A to 7A. Spectrograms have been obtained showing five discontinuities for osmium at 6.194A ($M_1$), 5.975A ($M_2$), 5.027A ($M_3$), 4.412A ($M_4$), and 4.037A ($M_5$); four for iridium at 5.961A ($M_1$), 5.754A ($M_2$), 4.851A ($M_3$), and 4.270A ($M_4$); four for platinum at 5.736A ($M_1$), 5.541A ($M_2$), 4.674A ($M_3$), and 3.738A ($M_5$). Discontinuities corresponding to an $M_5$ level for iridium and an $M_4$ level for platinum were not obtained. The results are shown to be consistent with those of other investigators for tungsten and bismuth. Comparison between experimental values of $(\nu/R)^{1/2}$ and those computed by Bohr and Coster and Sommerfeld reveals some disagreement, the probable cause for which is discussed. Two types of absorption discontinuities were found on the spectrograms—"limits" separating regions of unequal darkening and "white line" absorption. Although, for each element, the same absorbing screen was used throughout, the first two discontinuities, corresponding to $M_1$ and $M_2$, for each element appeared as "limits" while the discontinuities $M_3$, $M_4$, and $M_5$ appeared as "white lines." Photometric curves are shown in support of this conclusion. Attention is called to the bearing of the phenomenon on the theory of "white lines." No evidence was found of a component on the short wave-length side of $M_3$ as was reported by Zumstein for tungsten.

## Introduction

THE extension of our knowledge of absorption limits to include the elements osmium, iridium, and platinum is especially important, aside from its value as a contribution to the field of atomic structure, in view of the disagreement with computed values of the experimentally determined limits for tungsten and of the possibility of an additional unpredicted limit, $M'_3$, both of which were reported by Zumstein.[1]

Osmium, iridium, and platinum were chosen principally for the following reasons: (1) their proximity to tungsten in the periodic table, (2) the need of experimental data for elements between tungsten and bismuth, and (3) the slight experimental advantages over elements of less atomic number on account of shorter wave-lengths.

It was proposed to obtain spectrograms showing as many as possible of the $M$-series absorption limits, to determine their variation in wave-length from predicted values, and to investigate for all limits, particularly $M_3$, the presence of any components near the principal discontinuity.

## Experimental

A vacuum spectrograph of the Siegbahn type was used in the investigation. This apparatus, with a few improvements, was the same as that employed

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

by Zumstein[1] in his investigation of tungsten. The voltage on the tube was always kept sufficiently low to exclude the possibility of any second order radiation obscuring the detail of the first order. The range of voltage supplied by the transformer was between 2000 and 5000 volts. No rectifying device was necessary as the tube was self-rectifying at these low voltages. The filament was a 15 mil tungsten wire placed about 3 mm from the copper target.

The slit was covered by a very thin membrane upon which was deposited a thin coat of carbon obtained from a kerosene flame. The membrane was made from a solution of celluloid in amyl acetate. A single droplet when allowed to fall on the surface of water formed a film from two to four inches in diameter. This was lifted and dried on a circular wire frame, then mounted over the slit with an ordinary household cement. This type of window was much thinner than the collodion and lampblack window used by Zumstein. The time of exposure for the continuous spectrum was thereby reduced from twelve hours to approximately one hour. Extreme care was required in operating the tube to prevent destruction of the window.

The absorption screens were made by dissolving compounds of the elements under investigation, soluble in ether, in a mixture of flexible collodion and ether, and then pouring on to a glass plate to dry. During exposures the screen was mounted midway between the slit and the crystal.

Absorption screens containing the pure powdered metals held in suspension in a collodion film did not give the absorption discontinuities. The explanation is apparently the following. There is an optimum thickness for the best photographic impression of the absorption limit. This optimum must be fairly general over the screen and cannot be imitated by relatively thick absorbing particles separated by spaces having no absorber. Neither of these areas give the absorption limit and hence both would not. In short, the optimum thickness is not a mean thickness but a uniform one.

The power input of the tube was approximately 1 kva. The width of the slit was 0.2 mm. The crystal used was gypsum (optical selenite). Exposures for only the continuous spectrum and emission lines required from one to three hours. For absorption photographs, continuous exposures of from one to two days were required. Imperial Eclipse Tropical plates were used throughout.

All measurements of absorption limits were made with reference to two or more known emission lines. The wave-lengths of the reference lines were taken from Siegbahn's "Spectroscopy of X-Rays."[2]

Distances on the plates were measured by a low power micrometer comparator focused on the long wave-length edge of both emission lines and absorption limits. A simple interpolation formula was used in computing the wave-length. Lack of sharpness of the edges rendered a more complicated method of determination impractical.

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[2] Siegbahn, Spectroscopy of X-rays, English translation, 1925, Tables 7, 14, and 15, pages 105–125.

## RESULTS

Spectrograms were obtained showing five absorption discontinuities for osmium, four for iridium, and four for platinum. These results are given in Tables I, II, and III. The columns therein are respectively as follows:

### TABLE I

*Osmium M-series absorption spectrum.*

| Limit | Plate | Screen | Reference Lines | Wave-length | Mean |
|---|---|---|---|---|---|
| $M_1$ | 1 | $OsO_4$ | $WM\alpha$, $WM\beta$, $PK\alpha$ | 6.194A | |
| $M_1$ | 2 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 6.193 | |
| $M_1$ | 3 | " | $PK\alpha$, $PK\beta$ | 6.195 | 6.194A |
| $M_1$ | 4 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 6.195 | |
| $M_1$ | 5 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 6.193 | |
| $M_2$ | 1 | " | $WM\alpha$, $PK\alpha$, $WM\beta$ | 5.972 | |
| $M_2$ | 2 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 5.976 | 5.975 |
| $M_2$ | 3 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 5.976 | |
| $M_2$ | 4 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 5.977 | |
| $M_3$ | 1 | " | $PbM\alpha$, $PbM\beta$, $SK_A$ | 5.027 | |
| $M_3$ | 2 | " | $SK_A$ | 5.025 | |
| $M_3$ | 3 | " | $PbM\beta$, $SK_A$ | 5.029 | |
| $M_3$ | 4 | " | $PbM\beta$, $SK_A$ | 5.028 | 5.027 |
| $M_3$ | 5 | " | $BiM\alpha$, $BiM\beta$, $SK_A$ $BiM\gamma$, $SK\alpha$ | 5.026 | |
| $M_3$ | 6 | " | $SK\alpha$, $PbM\alpha$, $PbM\beta$, $BiM\alpha$ | 5.026 | |
| $M_3$ | 7 | " | $PbM\alpha$, $PbM\beta$, $BiM\alpha$, $BiM\beta$, $ClK\alpha$, $SK_A$ | 5.027 | |
| $M_4$ | 1 | " | $AgL\alpha$, $AgL\beta$ | 4.412 | |
| $M_4$ | 2 | " | $AgL\alpha$, $AgL\beta$ | 4.411 | 4.412 |
| $M_4$ | 3 | " | $AgL\alpha$, $AgL\beta$ | 4.414 | |
| $M_5$ | 1 | " | $AgL\alpha$, $AgL\beta$ | 4.035 | |
| $M_5$ | 2 | " | $AgL\alpha$, $AgL\beta$ | 4.039 | 4.037 |
| $M_5$ | 3 | " | $AgL\alpha$, $AgL\beta$ | 4.038 | |

### TABLE II

*Iridium M-series absorption spectrum.*

| Limit | Plate | Screen | Reference Lines | Wave-length | Mean |
|---|---|---|---|---|---|
| $M_1$ | 1 | $IrCl_3$ | $PK\alpha$, $PK\beta$ | 5.965A | |
| $M_1$ | 2 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 5.961 | 5.961A |
| $M_1$ | 3 | " | $PK\alpha$, $HgM\alpha$ | 5.958 | |
| $M_2$ | 1 | " | $PK\alpha$, $PK\beta$ | 5.750 | |
| $M_2$ | 2 | " | $PK\alpha$, $PK\beta$, $HgM\alpha$ | 5.753 | 5.754 |
| $M_2$ | 3 | " | $PK\alpha$, $HgM\alpha$ | 5.760 | |
| $M_3$ | 1 | " | $SK\alpha$, $PbM\alpha$, $PbM\beta$, $ClK\alpha$ | 4.849 | |
| $M_3$ | 2 | " | $SK\alpha$, $PbM\alpha$, $PbM\beta$, $SK_A$, $ClK_\alpha$ | 4.850 | |
| $M_3$ | 3 | " | $SK\alpha$, $PbM\alpha$, $BiM\alpha$, $PbM\beta$, $SK_A$ | 4.851 | 4.851 |
| $M_3$ | 4 | " | $PbM\alpha$, $BiM\alpha$, $PbM\beta$, $BiM\beta$, $SK_A$ | 4.853 | |
| $M_4$ | 1 | " | $CdL\alpha$, $CdL\beta$ | 4.275 | 4.270 |
| $M_4$ | 2 | " | $CdL\alpha$, $CdL\beta$ | 4.265 | |

TABLE III

*Platinum M-series absorption spectrum.*

| Limit | Plate | Screen | Reference Lines | Wave-length | Mean |
|---|---|---|---|---|---|
| $M_1$ | 1 | PtCl$_4$ | $PK\alpha$, HgM$\alpha$, $PK\beta$ | 5.738A | |
| $M_1$ | 2 | " | $PK\alpha$, HgM$\alpha$ | 5.738 | 5.736A |
| $M_1$ | 3 | " | $PK\alpha$, $PK\beta$, HgM$\alpha$ | 5.733 | |
| $M_1$ | 4 | " | $PK\alpha$, $PK\beta$, HgM$\alpha$ | 5.734 | |
| $M_2$ | 1 | " | $PK\alpha$, HgM$\alpha$ | 5.544 | |
| $M_2$ | 2 | " | $PK\alpha$, $PK\beta$, HgM$\alpha$ | 5.534 | 5.541 |
| $M_2$ | 3 | " | $PK\alpha$, $PK\beta$, HgM$\alpha$ | 5.545 | |
| $M_3$ | 1 | " | BiM$\alpha$, SK$_A$, BiM$\beta$, BiM$\gamma$ | 4.673 | |
| $M_3$ | 2 | " | BiM$\alpha$, BiM$\beta$, BiM$\gamma$, SK$_A$ | 4.674 | |
| $M_3$ | 3 | " | BiM$\alpha$, PbM$\beta$, BiM$\gamma$, BiM$\beta$, ClK$\alpha$ | 4.675 | 4.674 |
| $M_3$ | 4 | " | BiM$\alpha$, BiM$\beta$, PbM$\beta$, SK$_A$, BiM$\gamma$, ClK$_A$ | 4.676 | |
| $M_5$ | 1 | " | AgL$\alpha$, AgL$\beta$ | 3.738 | 3.738 |
| $M_5$ | 2 | " | AgL$\alpha$, AgL$\beta$ | 3.739 | |

first, the symbols of the discontinuities, $M_1$, $M_2$, $M_3$, $M_4$, and $M_5$ in the order of decreasing wave-length; second, the plate number; third, the compound used in preparing the absorption screen; fourth, the reference lines used in measuring the wave-length of each absorption limit; fifth, the average results for each plate, obtained from repeated measurements, of the wave-length of the absorption limit; sixth, the mean value for each discontinuity of the wave-length of all the plates measured.

The wave-lengths of all reference lines used in the computations are contained in the following table:

TABLE IV

*Wave-lengths of reference lines.*

| | | | | | |
|---|---|---|---|---|---|
| WM$\alpha$ | 6.973A | PbM$\alpha$ | 5.2751A | SK$\alpha$ | 5.3613A |
| WM$\beta$ | 6.745 | PbM$\beta$ | 5.0648 | ClK$\alpha$ | 4.7182 |
| $PK\alpha$ | 6.1417 | SK$_A$ | 4.988 | AgL$\alpha$ | 4.1456 |
| $PK\beta$ | 5.789 | BiM$\alpha$ | 5.1072 | AgL$\beta$ | 3.9266 |
| HgM$\alpha$ | 5.649 | BiM$\beta$ | 4.8993 | CdL$\alpha$ | 3.9478 |
| HgM$\beta$ | 5.439 | BiM$\gamma$ | 4.5238 | CdL$\beta$ | 3.7300 |

## DISCUSSION OF RESULTS

The limitations of the accuracy of the experimental results were determined by the accuracy of the wave-lengths of the emission lines used for reference, by the distance on the plate over which interpolation was made, but mainly by the accuracy with which one is able to focus the cross-hair of the comparator on the edge of the absorption discontinuity.

The first of these may be summarily dismissed since only well established and precisely measured emission lines were used as reference. In the event of any revision of the reference lines, adjustment of the wave-length of the absorption discontinuities can easily be made.

An attempt was always made to choose such lines for reference as would keep the distances on the plate over which interpolation was made well within one centimeter. A check on the inaccuracies due to this cause was made on emission lines. They were found to be insignificant compared to the following source of inaccuracy.

In those cases where the absorption discontinuities were fairly weak or not extremely sharp, some difficulty was experienced in focusing the cross-hair exactly on the edge of the discontinuity. Repeated measurements over many plates on known emission lines and absorption edges together with the agreement obtained from repeated measurements on the absorption discontinuities of the present investigation determined the possible accuracy (0.005A) which is claimed for the results. This represents accuracy to approximately one-tenth of one percent.
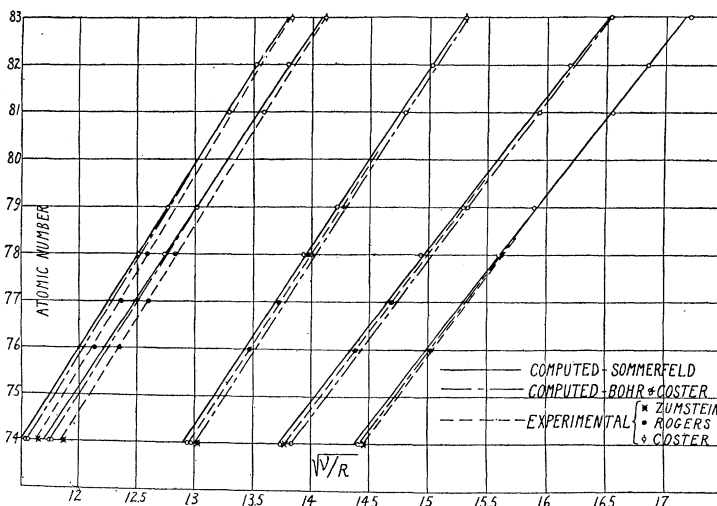


Fig. 1. Relation between the present experimental results and those for tungsten and bismuth.

It is recognized that chemical combination may have some influence on the value of the absorption discontinuities. The valences of the elements in the compounds used in the absorbing screens were: osmium eight, iridium three, and platinum four. To be sure, there is a possibility of reduction of the compounds by the x-ray beam. Investigation of possible chemical effects on the $M$ levels in one of these elements is under investigation at the present time in this laboratory.

In Fig. 1 above are shown graphically the relation of the present experimental results to the corresponding measurements for tungsten[1] and for bismuth[3]; also their relation to the computed values for the $M$ levels as given by Bohr and Coster[4] and Sommerfeld.[5]

[3] D. Coster, Phys. Rev. **19**, 22 (1922).

[4] N. Bohr and D. Coster, Zeits. f. Physik **12**, 347 (1923).

[5] A. Sommerfeld, Atombau etc., 4th Edition, p. 304–305.

With atomic number as ordinates and $(\nu/R)^{1/2}$ as abscissas, the maximum deviation from a linear relationship between the various experimental results was approximately five volts. One may therefore conclude that the linear relation in this region is thereby established. This shows excellent agreement between the present results and those of the other investigators whose values are shown on the curve above, and adds credence to the belief in the reliability of the experimental determinations.

In making comparison of the experimental values of $(\nu/R)^{1/2}$ with the computed values, it must be recalled that the computations of Bohr and Coster[4] and of Sommerfeld[5] necessarily assume one or more absorption discontinuities whence, by the principle of combination of emission lines and absorption discontinuities, other levels are calculated. For the elements here represented the $L_1$ level has, with one exception, been used as the absorption limit on which the computations are based. The literature is not clear as to the specific measurements used by Bohr and Coster and Sommerfeld in making the computations. However, it has generally been possible, by reversing the computation process, to identify the emission lines and absorption limits, their wave-lengths, and observer. For bismuth, the $M_1$, $M_2$, and $M_3$ values contained in both tables are Coster's experimental values. From them the values for $M_4$ and $M_5$ of bismuth have been computed.

A very small error in the wave-length of the $L_1$ limit produces a relatively large error in the computed $M$ levels. Assuming the same percent of error in the $L_1$ measurements as has been allowed for the $M$ levels, the error thereby introduced in the computed $M$ levels is between four and five times that in the direct experimental measurements. Furthermore, this takes into account no error whatsoever in the case of the $L$ and $M$ emission lines used in connection with the absorption limit for computing the $M$ levels. Granting the probability of more exact measurement of emission lines than of absorption limits, yet the same relative error in the shorter wave-length emission lines as in our reference lines would introduce more error in the computed than in the directly measured results. The direct measurements are believed reliable to the accuracy stated. For these reasons, therefore, the experimental values of the $M$ levels should be considered much more nearly correct than the computed ones.

The results seem quite definitely to offer at least partial evidence of a systematic error in the $L_1$ levels. However, there also seems to be shown an increasing accuracy in the $L_1$ levels with increasing atomic number. This cannot be accounted for as yet. Neither can all measurements and computations be completely reconciled. One possible explanation of a portion of the discrepancies may lie in the fact that compounds and not free metal atoms were used in the absorbing screens.

Two types of absorption discontinuities were found on the spectrograms— "white line" absorption and "limits" separating regions of unequal darkening.

$M_1$ and $M_2$, the former in particular, appeared as limits. The $M_1$ limit appeared less sharp than $M_2$ but much more pronounced probably because

the $M_1$ absorption continues with little diminution over the region where the $M_2$ absorption occurs.

On the other hand, $M_3$, $M_4$, and $M_5$ so far as here measured were distinctly of the "line" type for each of the elements. The short wave-length edge was very nearly if not exactly as sharp as the long wave-length edge. Five of the seven absorptions obtained among these levels gave conclusive evidence of this fact. The other two were too faint to warrant definite conclusion.

In order to investigate the reliability of the conclusion regarding the appearance of the $M_3$, $M_4$, and $M_5$ absorptions as "line" absorptions, photometric curves were made of some of the best plates of which a representative collection is shown in Fig. 2.
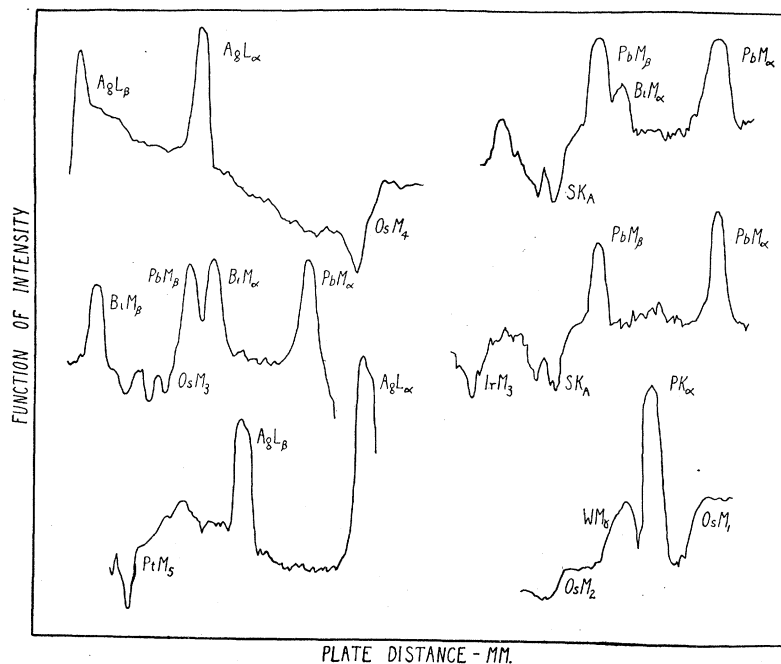


Fig. 2. Photometric curves showing the $M_3$, $M_4$, and $M_5$ absorptions.

Each of these curves represents the graphical average of three separate curves taken from different places on the plates. For purposes of comparison, one curve is given of the $K$-absorption due to sulphur in the crystal showing the "white line" absorption on the long wave-length side. For contrast, one curve is shown of osmium $M_1$ and $M_2$ which are distinctly of the "limit" type.

Because of the fact that the microphotometer available did not have particularly high resolving power, the edges of some of the absorptions and emission lines as well were not particularly sharp, so much so in fact that measurements on the wave-length from these photometric curves were not considered reliable. The conclusion regarding "line" absorptions, however, was fully substantiated.

The experimental verification of the existence of "white lines" is a matter of no little importance. Attention should be called to the fact that there must be a significant fundamental difference between "limits" and "white lines" in that the outer levels $M_1$ and $M_2$ are the former while the inner levels $M_3$, $M_4$, and $M_5$ are the latter. This fact must have some bearing on the theory of "white lines." Evidently the law of absorption for $M_3$, $M_4$, and $M_5$ is different from that for $M_1$ and $M_2$.

The failure of the earlier work on x-ray absorption spectra to show absorption lines (Fraunhofer lines) was explained upon the consideration that an electron cannot jump from an inner level to a level farther away from the nucleus since, in general, there is no vacant place to which it may go. Kossel, however, pointed out that this explanation should not apply to the peripheral levels. Subsequently, many cases have been mentioned in which continuous x-ray spectra have shown white lines.

In response to the report of Coster[6] on the complicated structure of the $K$-absorption edges of titanium, vanadium, chromium, and manganese and the $L_{III}$ absorption edges of tin, antimony, tellurium, and iodine, Miss Chamberlain[7] offered the explanation, supported by experimental investigation, that the white line found on the long wave-length side of the absorption edge for the more highly oxidized compound was due to reduction of a portion of the compound to the free metal.

The presence in this investigation of absorption "lines" for some of the levels and of "limits" for other levels of the same series while, for each element, the same absorbing screen was used for all five levels has not found a satisfactory explanation.

The absence of $Ir M_5$ and $Pt M_4$ should not be interpreted as evidence of their non-existence; particularly so since $Ir M_4$ and $Pt M_5$ were obtained. It must be recalled that the only emission lines which are attributed to transitions involving the $M_5$ level are the $l$ and $\eta$ lines of the $L$-series, both of which are weak. The $M_4$ level is involved in transitions yielding $L_{\beta_4}$ and one component of $K_{\beta_1}$. While it, too, is expected to be fairly weak yet it should be obtainable. For all the $M_4$ and $M_5$ discontinuities, experimental conditions, particularly in regard to the thickness of the absorbing screen, are very critical. It is therefore very difficult to obtain them.

No evidence was found of a component near any of the principal absorption discontinuities.

In conclusion, the writer wishes to express his appreciation to the members of the staff of the Department of Physics of the State University of Iowa for their interest and assistance, and especially to Professor G. W. Stewart who suggested the problem and under whose direction the work has been carried on.

Physics Laboratory,
University of Iowa,
June 10, 1927.

[6] D. Coster, Zeits. f. Physik (July 2, 1924).
[7] K. Chamberlain, Phys. Rev. 26, p. 525 (1925).