SEPTEMBER 15, 1931 PHYSICAL REVIEW VOLUME 38

THE *M*-SERIES ABSORPTION SPECTRUM OF TANTALUM

By Charles A. Whitmer
The State University of Iowa

(Received August 3, 1931)

Abstract

The *M*-series absorption spectrum of tantalum (73) has been investigated, with a vacuum spectrograph of the Siegbahn type. The absorption screens were metallic tantalum, prepared by an evaporation process. Spectrograms were obtained for three absorption limits at 5.64A (M_{III}), 6.773A (M_{IV}), and 6.997A (M_{V}). When the experimental ν/R values are compared to values calculated from *L*-absorption and emission data, the experimental values for M_{IV} and M_{V} show a displacement toward higher frequencies and the M_{III} limit a displacement toward lower frequencies. These discrepancies are in agreement with those found by several other investigators in the region from W(74) to Au(79). The M_{III} limit has the appearance of a white line, and M_{IV} and M_{V} are diffuse in character. The possibility of an explanation of these discrepancies on the basis of transitions to levels in the periphery of the atom is suggested.

Introduction

THE measurements of the *M*-absorption limits of the heavier elements are of particular interest, not only because of the contribution of additional information on the values of the energy levels, but also because the experimental values obtained for the M_{II}, M_{III}, M_{IV}, and M_{V} edges from Au(79) to W(74) do not agree within experimental error with the values calculated from *L*-emission and absorption data. The discrepancy in M_{IV} and M_{V} was first noted by Zumstein in this laboratory.[1] Zumstein measured all five of the *M*-limits of tungsten. Following Zumstein, Rogers[2] investigated the *M*-absorption of platinum, iridium, and osmium. Johnson[3] repeated Roger's measurements on platinum, using the pure metal as absorber, and in addition measured M_{I}, M_{III}, M_{IV} and M_{V} of gold. In addition to the above work, which has been done in this laboratory, an article by E. Lindberg[4] reported measurements on the M_{III}, M_{IV} and M_{V} edges of Ur, Th, Bi, Pb, Tl, Hg, Au, Pt, and W.

The results of these investigators show that in the case of M_{IV} and M_{V} for all the elements from Au(79) to W(74), the experimentally determined wavelengths are systematically shorter than the corresponding calculated values, while for the M_{II} and M_{III} limits the experimentally determined wavelengths are longer than the calculated values.* The experimental wave-

---

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

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

[3] A. J. M. Johnson, Phys. Rev. **34**, 1106 (1929).

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

* The calculated values referred to here are taken from the International Critical Tables Vol. VI, p. 35. They are evidently computed from the following relations:

$M_{\text{I}} = L_{\text{III}} - Ll$
$M_{\text{I}} = L_{\text{II}} - L\eta$
$M_{\text{II}} = L_{\text{I}} - L\beta_4$
$M_{\text{III}} = L_{\text{I}} - L\beta_3$
$M_{\text{IV}} = L_{\text{II}} - L\beta_1$
$M_{\text{IV}} = L_{\text{III}} - L\alpha_2$
$M_{\text{V}} = L_{\text{III}} - L\alpha_1$

lengths for M_{I} are all slightly shorter than the corresponding calculated values, although the discrepancy for this limit is of the order of the experimental error.

An adequate theory has not been developed to explain these discrepancies. Johnson[3] concluded from his work with metallic gold and platinum that the cause of the shift of values, at least for these elements, did not lie in the chemical state of the absorbing material.

The purpose of this research was to extend these investigations to an additional element whose atomic number is less than that of tungsten. Tantalum was chosen because it can be obtained in a chemically pure and uncombined state, thus enabling a check to be made on the effect of chemical combination. Moreover, the experimental difficulties in working in long wave-length regions made it desirable to choose an element whose atomic number was as large as possible. Finally, the fact that tantalum can be obtained either in a thin foil or in wire form suggested the possibility of preparing absorption screens directly from the foil, or from the wire by an evaporation process.

Apparatus and Experimental Procedure

The Siegbahn type vacuum spectrograph used in this investigation has been described by both Zumstein[1] and Rogers.[2] It was altered in only a few minor details. The mercury vapor from the diffusion pump and occluded vapors from the walls of the metal tube were removed from the tube by a liquid air trap. The removal of the vapors decreased the sputtering of the filament markedly, and rendered the occurrence of gaseous discharges less likely, so that a steady operation of the tube could be had at 100 milliamperes over long periods of time.

The crystal used was gypsum. Imperial Eclipse dry plates manufactured by the Imperial Dry Plate Co., Cricklewood, London, produced spectrograms of excellent contrast. The time of exposure ranged from 10 to 40 hours. Tube voltages ranged from 2000 to 5000 volts; the tube voltage was kept low enough at all times to prevent masking of the absorption limits by second order general radiation. In order to obtain spectrograms of the M_{IV} and M_{V} edges it was necessary to substitute for the usual tungsten filament one of molybdenum, for the sputtered tungsten on the target produced the relatively intense W$M\alpha$ and W$M\beta$ emission lines, which masked the M_{V} and M_{IV} limits respectively. Although the W$M\alpha$ line appeared faintly on some of the spectrograms, it was weak enough not to mask the M_{V} edge, and was thus useful as a reference line. The operation of the molybdenum filament was quite satisfactory, although it did not last nearly as long as the tungsten filament.

An attempt was made to prepare absorption screens by thinning tantalum foil with hydrofluoric acid, but a screen of sufficient thinness could not be obtained. The screens used were prepared by evaporating the tantalum from an incandescent filament in a high vacuum. The evaporated metal was deposited on a base prepared by blowing large bubbles of soft sodium glass, from which a flat piece free from strain can be selected. The thickness of the glass based used was of the order of 10^{-4} centimeters, and transmitted approximately 75 percent of the incident radiation.

The evaporator was similar to that used by Johnson. It consisted of a bell-jar, evacuated by a two-stage mercury diffusion pump. In the bell-jar two filaments in parallel were supported horizontally two centimeters above a table which supported the glass base on which the tantalum was deposited. At first this table was water cooled, but it was found that the water-cooled surface on one side and the hot filament on the other created strains in the glass which caused it to shatter. The best table was found to be of sheet iron set loosely on the water-cooled bell-jar base. Enough cooling was obtained by conduction to keep the glass from melting, yet without causing it to warp. After the deposition of the metal the screen was cemented to a metal frame. The same screens were used for all the limits measured; the thinner screens produced more distinct spectrograms for the M_{IV} and M_{V} edges. Screens of sufficient thickness were obtained in from one to two hours of evaporation; it is estimated that their thickness ranged from 10^{-4} to 10^{-5} centimeters.

The measurement of the wave-length of the edges was accomplished by reference to several known emission lines.* It can be shown by a Taylor's expansion of Bragg's law that, to a second approximation,

$$\Delta\lambda = \frac{d}{\gamma}\left(\cos\theta - \frac{\Delta s}{4}\sin\theta\right)\Delta s, \tag{1}$$

where d is the grating constant of the crystal, r the radius of the focal circle, θ the angle between the crystal face and the incident beam, and Δs the distance between the known emission line and the absorption limit. Δs was measured with a low-powered traveling microscope, and the corresponding $\Delta\lambda$ calculated from (1). θ is obtained from Bragg's law, using the wave-length value of the known emission line. The advantage of this method of interpolation lies in the fact that it is accurate over the entire length of the spectrogram, a distance of about two centimeters.

Tests of formula (1) on identified emission lines gave results accurate within 0.003A. The chief error in this method of measurement arises in setting the cross-hairs of the microscope on the diffuse absorption limits. The average error in this setting was less than 0.015 centimeters, which corresponds to approximately 0.007A. The total error has been estimated to be not greater than ±0.010A.

RESULTS

Spectrograms were obtained for the M_{III}, M_{IV}, and M_{V} limits of tantalum. The mean value of the measurements on the individual plates are tabulated in Table I, and these values are averaged to give the final mean value for the absorption limit. In Table II are listed the wave-lengths of the lines used for reference in accordance with the method of interpolation described above.

---

* In addition, the sharp K-absorption edge of Si, from the absorption in the glass base, which appeared on the spectrograms of Ta M_{IV} and M_{V}, was very convenient for reference. The wave-length of this edge was taken from a paper by G. B. Deodhar, Nature, May 24, 1930.

TABLE I. *Tantalum M-series absorption.*

Limit	Screen number	Plate number	Reference lines	Wave-length	Mean wave-length	Mean ν/R
M_{III}	17	177	Pb$M\alpha$, Au$M\alpha$, Au$M\beta$	5.648A		
M_{III}	19	181	Pb$M\alpha$	5.643		
M_{III}	17	182	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$ Mo$L\alpha$, Mo$L\beta$	5.651		
M_{III}	22	183	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$ Mo$L\alpha$, Mo$L\beta$	5.646		
M_{III}	18	185	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$	5.643	5.647A	161.35
M_{IV}	17	190	Si K-absorption limit, Si$K\alpha$	6.768		
M_{IV}	17	191	Si K-absorption limit, Si$K\alpha$	6.766		
M_{IV}	17	192	Si K-absorption limit, Si$K\alpha$	6.769		
M_{IV}	23	199	Si K-absorption limit, Si$K\alpha$, W$M\alpha$, Sn$L\beta$	6.777		
M_{IV}	17	202	W$M\alpha$, Sn$L\beta$	6.781		
M_{IV}	17	203	Si K-absorption limit, Si$K\alpha$	6.775	6.773	134.54
M_V	17	190	Si K-absorption limit, Si$K\alpha$	6.992		
M_V	17	191	Si K-absorption limit, Si$K\alpha$	6.994		
M_V	17	192	Si K-absorption limit, Si$K\alpha$, W$M\alpha$	6.998		
M_V	23	199	Si K-absorption limit, Si$K\alpha$, Sn$L\alpha$, W$M\alpha$, Sn$L\beta$	6.994		
M_V	17	202	Si K-absorption limit, Si$K\alpha$	7.003		
M_V	17	203	Si K-absorption limit, Si$K\alpha$	6.997	6.997	130.24

TABLE II. *Wave-lengths of reference lines.*

Sn$L\alpha$	7.184	(second order)	Au$M\alpha$	5.827
Si$K\alpha$	7.109		Pt$M\beta$	5.820
W$M\alpha$	6.973		Au$M\beta$	5.611
Sn$L\beta$	6.756	(second order)	Mo$L\alpha$	5.394
SiK-abs.	6.705		Pb$M\alpha$	5.273
Pt$M\alpha$	6.041		Mo$L\beta$	5.166

DISCUSSION

The M_{II} edge of tantalum was masked by the K-absorption of the sulphur in the gypsum crystal and consequently was not observed. Attempts at obtaining the M_I edge were unsuccessful, due, in all probability, to the fact that this edge is least intense of the M-limits and consequently requires a screen with a thickness very near the optimum in order to be detected. That there is an optimum thickness has been shown by Sandström,[5] who has derived for it the expression

$$d = \frac{\log \mu_2 - \log \mu_1}{\mu_2 - \mu_1},$$

where μ_1 and μ_2 are the absorption coefficients on the long and short wave-length sides of an absorption limit respectively.

The M_{III} edge had the appearance of a single white line, the short wave-length side being very nearly, if not quite, as sharp as the long wave-length

---

[5] A. Sandström, Zeits. f. Physik **65**, 632 (1930).

side. Such a white line absorption was also observed by Rogers[2] for the M_{I}, M_{II}, and M_{III} limits of Os(76), Ir(77), and Pt(78). Johnson[3] did not observe such a white line structure for PtM_{I} and M_{III}, and Lindberg[4] makes no mention of it in his article.

The M_{IV} and M_{V} limits were of the true edge type, and were rather diffuse in character.

Table III shows the discrepancy between the observed and calculated values of tantalum.* A comparison of the calculated values of the M-limits with the experimental values for the region between Bi(83) and Yb(70), which have been measured by the various experimenters, is shown graphically in Fig. 1, in which $(\nu/R)^{1/2}$ has been plotted against atomic number. The calculated values are taken from the International Critical Tables;** a careful check of the calculations show that they are calculated from experimentally determined L-limits and L-emission lines.

TABLE III. *A comparison of the computed and experimental values of the M-limits of tantalum.*

Limit	λ, exp.	λ, cal.	Δλ	ν/R, exp.	ν/R, cal.	$\Delta\nu/R$
M_{III}	5.647A	5.594A	+0.053A	161.35	162.9	−1.55
M_{IV}	6.773	6.893	−0.120	134.54	132.2	+2.34
M_{V}	6.997	7.130	−0.133	130.24	127.8	+2.44

$\Delta\lambda = \lambda\text{ (exp.)} - \lambda\text{(cal.)}$ $\quad$ $\Delta\nu/R = \nu/R\text{ (exp.)} - \nu/R\text{ (cal.)}$

* See the footnote above regarding the method of calculation.

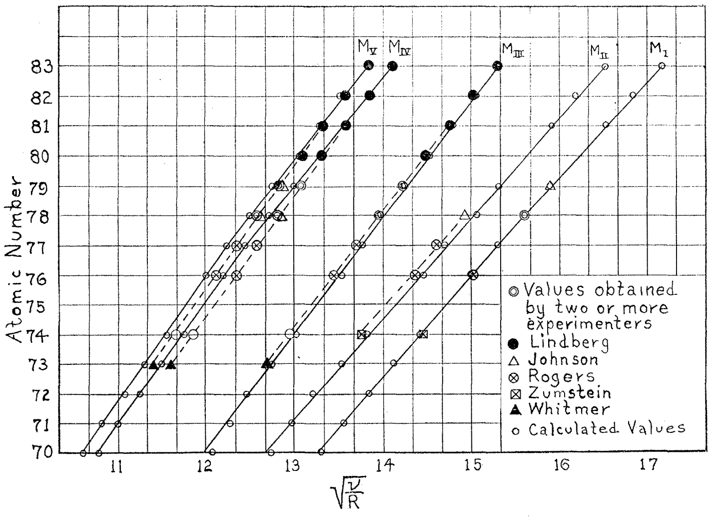

Fig. 1. Values of $(\nu/R)^{\frac{1}{2}}$ plotted against atomic number. Full lines represent values given in the International Critical Tables.

** The computed values for Os(76) and Ir(77) are not given in the International Critical Tables. The values used are taken from an article by Cork, Phys. Rev. **21**, 326 (1923).

The calculated values of $(\nu/R)^{1/2}$ for M_{I}, M_{IV} and M_{V} show a change of slope of the curve at Ir(77), which is not evident in the experimental values for M_{IV} and M_{V}; in the case of M_{I} the experimental points are apparently in good agreement with the calculated curve.

The experimental evidence at hand indicates two possibilities for an explanation of the discrepancies shown in Fig. 1. The observed limit may not correspond to the energy necessary to remove an M electron to infinity. For example, the simultaneous ejection of an M electron and an outer electron by a single quantum would result in a shift of the limit to higher energy levels. Or, the absorbed quantum may remove the M electron to one of the outer permitted levels of the atom.[6] Such an absorption would produce white lines, shifted to lower frequencies than the calculated values, such as has been reported for M_{II} and M_{III} by Rogers, and for TaM_{III} by the writer. Thus the experimental evidence indicates the possibility of an explanation of the discrepancies shown in Fig. 1 by means of transitions to permitted levels in the periphery of the atom.

In conclusion, the writer wishes to express his appreciation to the staff of the Department of Physics of the State University of Iowa for their interest and assistance, and in particular to Professor G. W. Stewart, who suggested and directed this investigation.

---

[6] This suggestion, recently made by Siegbahn, Zeits. f. Physik **67**, 567 (1931) has just come to the attention of the author.