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A Study of the Spectra of Columbium and Molybdenum in the Extreme Ultraviolet

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The spectra of columbium and molybdenum in the range 100–1000A have been investigated. Spectrograms were obtained with a three-meter grazing incidence vacuum spectrograph having a dispersion of 1.0A/mm at 500A. The lines of Cb V and Mo VI previously reported have been remeasured. Attempts to find higher members of the series $4d-np$ and $4d-nf$ have proved fruitless except for the transition $4d-6p$ in Mo VI, for which tentative identification is given. Six low levels of Cb VI and Mo VII have been identified by extrapolation of frequencies in the Kr sequence. Some of the classifications are supported by considerations from theory. By applying a Rydberg formula to the transitions $4p^6-4p^55s$ and $4p^6-4p^56s$, the absolute value of the ground level of Cb VI is estimated to be 829,750 cm^{-1} and that of Mo VII is estimated to be 1,020,460 cm^{-1}.

The Br sequence has been extended to Cb VII and Mo VIII. The separations of the ground doublets were predicted by use of the regular doublet law. Forty-one lines of Cb VII and forty-two lines of Mo VIII have been identified by extrapolation of frequencies and application of the regular doublet law. These lines arise from transitions between the ground doublet arising from $4s^24p^5$ and the configurations $4s4p^6$, $4s^24p^44d$, and $4s^24p^45s$. The absolute values of the ${}^2P^\circ{}_{3/2}$ ground levels of Cb VII and Mo VIII are estimated to be 1,005,000 cm^{-1} and 1,235,000 cm^{-1}, respectively.

Results of an approximate calculation of the energy levels of the configuration p^4s in intermediate coupling are given and are compared with the observed levels in Cb VII and Mo VIII. The order of J-values is, with one exception, the same for the calculated levels as for the observed levels. The two sets of levels agree roughly, although the observed levels are more intimately mixed than the calculated levels.

INTRODUCTION

THE spectra of columbium have previously been investigated through Cb V and those of molybdenum through Mo VI (with the exception of Mo III).[1] In the present study, some of the low lying levels of higher stages of ionization of these metals are identified on the basis of extrapolations along isoelectronic sequences.

EXPERIMENTAL

The spectrograms upon which this investigation is based were obtained with the three-meter grazing incidence vacuum spectrograph at the Ohio State University; they cover the range 100–1000A. A condensed spark between electrodes of columbium or molybdenum wires in carbon and in copper was used to excite the spectra. Different stages of ionization were distinguished by varying the capacity from 0.1 to 1.8 μf, and by varying the inductance in the circuit. Exposures of two to four hours were made on Ilford Q-II plates. Standard wave-lengths in carbon, nitrogen, and oxygen were taken from the table of Boyce and Robinson;[2] those in copper were taken from the table of Kruger and Cooper.[3] A supplementary spectrogram of the copper spectrum was taken for the purpose of identifying copper lines not published in the table of Kruger and Cooper. It is estimated that the wave-lengths given below are accurate to 0.01A.

THE SPECTRA OF CB V AND MO VI

Classifications in these spectra isoelectronic with Rb I were given by Trawick;[4] Table I summarizes the measurements made on the classified lines lying in the range of the present instrument. The lines $4d\,{}^2D_{5/2}-4f\,{}^2F^\circ$ have now been resolved. The agreement between the present measurements and those of Trawick is quite satisfactory except for the multiplet $4d-4f$ in Mo VI; the present measurements place the $4f$ levels about 400 cm^{-1} lower than their position according to Trawick. Attempts to find higher members of the series $4d-np$ and $4d-nf$ by extrapolation of the quantum defects of the np and nf levels proved fruitless except for the transition $4d-6p$ in Mo VI, for which tentative identification is given in Table I.

Table II gives the relative values of the levels in these spectra, measured from $4d\,{}^2D_{3/2}$.

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[1] W. F. Meggers, J Opt. Soc. Am. **36**, 435 (1946).

[2] J. C. Boyce and H. A. Robinson, J. Opt. Soc. Am. **26**, 133 (1936).

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[4] M. W. Trawick, Phys. Rev. **46**, 63 (1934).

CLASSIFICATIONS IN THE SPECTRA OF CB VI AND MO VII

The spectra of the ions isoelectronic with neutral krypton have not been extensively studied. An analysis of the spectrum of Kr I was given by Meggers, de Bruin, and Humphreys[5] and supplemented by Meggers and Humphreys.[6] The spectrum of Rb II was analyzed by Laporte, Miller, and Sawyer.[7] No identifications have been made in the spectra of Sr III, Y IV, or Zr V. Therefore, some of the classifications proposed below for the low levels of Cb VI and Mo VII are regarded as subject to revision.

The starting point for the classification given here was the observation of the resonance lines $4p^6-4p^55s$ in Mo VII. These form a very striking pair near 200A, where there are no other strong lines, so that their identification was readily established. Interpolation of frequencies according to the method of Bowen and Millikan[8] then revealed a corresponding pair in Cb. These identifications are supported by considerations from the theory,[9] according to which we should expect the ratio of the separation of the two levels from $4p^5ns$ with $J=1$ to the separation of the two levels from $4p^5$ to be approximately constant through the sequence. Similar considerations led to the identification of the transition $4p^6-4p^56s$.

Table III shows the classifications made in the spectra of Cb VI and Mo VII by extrapolation of frequencies.

TABLE I. Classified lines of Cb V and Mo VI.

Rel. int.	λ_{vac}(A)	ν(cm^{-1})	Transition
		Cb V	
150	774.017	129196	$4d\,^2D_{3/2}-5p\,^2P^\circ_{1/2}$
300	763.752	130933	$4d\,^2D_{5/2}-5p\,^2P^\circ_{3/2}$
50	753.011	132800	$4d\,^2D_{3/2}-5p\,^2P^\circ_{3/2}$
25	468.627	213389	$4d\,^2D_{5/2}-4f\,^2F^\circ_{5/2}$
150	468.325	213525	$4d\,^2D_{5/2}-4f\,^2F^\circ_{7/2}$
100	464.555	215260	$4d\,^2D_{3/2}-4f\,^2F^\circ_{5/2}$
		Mo VI	
25	790.639	126480	$5p\,^2P^\circ_{3/2}-6s\,^2S_{1/2}$
15	760.997	131407	$5p\,^2P^\circ_{1/2}-6s\,^2S_{1/2}$
500	548.234	182404	$4d\,^2D_{3/2}-5p\,^2P^\circ_{1/2}$
1000	541.282	184747	$4d\,^2D_{5/2}-5p\,^2P^\circ_{3/2}$
150	533.820	187329	$4d\,^2D_{3/2}-5p\,^2P^\circ_{3/2}$
75	378.118	264469	$4d\,^2D_{5/2}-4f\,^2F^\circ_{5/2}$
400	377.540	264873	$4d\,^2D_{5/2}-4f\,^2F^\circ_{7/2}$
250	374.472	267043	$4d\,^2D_{3/2}-4f\,^2F^\circ_{5/2}$
150	298.358	335168	$4d\,^2D_{5/2}-6p\,^2P^\circ_{3/2}$(?)
100	297.326	336331	$4d\,^2D_{3/2}-6p\,^2P^\circ_{1/2}$(?)
15	296.087	337739	$4d\,^2D_{3/2}-6p\,^2P^\circ_{3/2}$(?)

TABLE II. Relative term values for Cb V and Mo VI.

Level	Rel. value (cm^{-1})	Level	Rel. value (cm^{-1})
Cb V		Mo VI	
$4d\,^2D_{3/2}$	0	$4d\,^2D_{3/2}$	0
$4d\,^2D_{5/2}$	1869	$4d\,^2D_{5/2}$	2578
$5p\,^2P^\circ_{1/2}$	129196	$5p\,^2P^\circ_{1/2}$	182404
$5p\,^2P^\circ_{3/2}$	132800	$5p\,^2P^\circ_{3/2}$	187329
$4f\,^2F^\circ_{5/2}$	215260	$4f\,^2F^\circ_{5/2}$	267043
$4f\,^2F^\circ_{7/2}$	215394	$4f\,^2F^\circ_{7/2}$	267451
		$6s\,^2S_{1/2}$	313810
		$6p\,^2P^\circ_{1/2}$(?)	336331
		$6p\,^2P^\circ_{3/2}$(?)	337739

TABLE III. Classified lines of Cb VI and Mo VII.

Rel int.	λ_{vac}(A)	ν(cm^{-1})	Transition
		Cb VI	
250	325.795	306941	$4p^6\,p_0-4p^54d\,d_2^\circ$
250	248.724	402052	$4p^6\,p_0-4p^55s\,s_4^\circ$
400	238.176	419858	$4p^6\,p_0-4p^55s\,s_2^\circ$
25	180.548	553869	$4p^6\,p_0-4p^55d\,d_5^\circ$(?)
125	177.552	563215	$4p^6\,p_0-4p^55d\,d_2^\circ$(?)
100	170.180	587613	$4p^6\,p_0-4p^56s\,s_4^\circ$
75	164.977	606145	$4p^6\,p_0-4p^56s\,s_2^\circ$
		Mo VII	
200	286.294	349291	$4p^6\,p_0-4p^54d\,d_2^\circ$
500	207.774	481292	$4p^6\,p_0-4p^55s\,s_4^\circ$
800	198.839	502919	$4p^6\,p_0-4p^55s\,s_2^\circ$
75	149.639	668275	$4p^6\,p_0-4p^55d\,d_2^\circ$(?)
150	140.955	709446	$4p^6\,p_0-4p^56s\,s_4^\circ$
50	136.675	731663	$4p^6\,p_0-4p^56s\,s_2^\circ$

The first column gives relative intensities estimated visually; the other columns indicate wave-lengths, frequencies, and transitions, respectively. The notation used for levels is adapted from that used by Meggers, de Bruin, and Humphreys[5] for Kr I. The classifications in the transitions $4p^6-4p^54d$ and $4p^6-4p^55d$ rest upon a correlation of levels of the $4p^54d$ and $4p^55d$ configurations in Rb II[7] with those in Kr I,[6] and may be open to some question. Since the relative energy values are identical with the radiated frequencies, they are not repeated.

An estimate of the absolute values of the ground levels in Cb VI and Mo VII has been made by applying a Rydberg formula to the frequencies $4p^6\,p_0-4p^55s\,s_4^0$ and $4p^6\,p_0-4p^56s\,s_4^0$. The p_0 level of Cb VI is found to be 829,750 cm^{-1} below the $^2P^\circ_{3/2}$ level of Cb VII and the p_0 level of Mo VII to be 1,020,460 cm^{-1} below the $^2P^\circ_{3/2}$ level of Mo VIII. These values correspond to ionization potentials of 103 v and 127 v for Cb VI and Mo VII, respectively.

CLASSIFICATIONS IN THE SPECTRA OF CB VII AND MO VIII

These ions are isoelectronic with bromine. They have an inverted doublet ground state arising from $4s^24p^5$.

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[8] I. S. Bowen and R. A. Millikan, Phys. Rev. **26**, 313 (1925).

[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (The Cambridge University Press, New York, 1935), p. 271.

TABLE IV. Classified lines of Cb VII.

Rel. int.	λ_{vac}(A)	ν(cm^{-1})	Transition
150	517.281	193319	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s4p^6\,{}^2S_{\frac{1}{2}}$
300w	470.590	212499	$4s^24p^5\,{}^2P^\circ_{3/2}-4s4p^6\,{}^2S_{\frac{1}{2}}$
75	386.819	258519	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$
200	378.901	263914	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^4D'_{\frac{1}{2}}$
75	369.197	270858	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{5/2}$
150	360.099	277701	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$
35	353.240	283094	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{\frac{1}{2}}$
10	325.386	307327	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^4P'_{\frac{1}{2}}$
35	320.527	311986	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$
20	316.043	316413	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$
25	312.010	320503	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')4d\,{}^2P'_{\frac{1}{2}\text{ or }3/2}$
25	306.274	326505	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{\frac{1}{2}}$
150	301.960	331170	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$
150	297.984	335588	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$
35	297.556	336071	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{5/2}$
100	294.390	339686	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2P'_{\frac{1}{2}\text{ or }3/2}$
100	286.276	349314	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2D'_{5/2}$
150	274.219	364672	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2F'_{5/2}$
100	265.293	376942	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$
50	263.417	379626	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1D')4d\,{}^2P'_{3/2}$
250	262.453	381021	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2D'_{5/2}$
100	261.434	382516	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1D')4d\,{}^2P'_{\frac{1}{2}}$
75	257.498	388353	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1S')4d\,{}^2D'_{3/2}$
25	252.448	396121	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$
150w	251.973	396868	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$
25	250.737	398824	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2P'_{3/2}$
25h	248.944	401697	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2P'_{\frac{1}{2}}$
250	247.979	403260	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')4d\,{}^2D'_{5/2}$
35	245.620	407133	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')5s\,{}^4P'_{\frac{1}{2}}$
25h	245.368	407551	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')4d\,{}^2D'_{3/2}$
50	240.351	416058	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$
15	234.576	426301	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^4P'_{\frac{1}{2}}$
100	234.260	426876	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$
150	227.463	439632	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^3P')5s\,{}^2P'_{\frac{1}{2}}$
200	224.737	444964	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$
300	224.182	446066	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$
500	219.746	455071	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')5s\,{}^2D'_{5/2}$
300	217.945	458831	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^2P'_{\frac{1}{2}}$
400	215.444	464157	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$
200	205.182	487372	$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}-4s^24p^4({}^1S')5s\,{}^2S'_{\frac{1}{2}}$
100	197.415	506547	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')5s\,{}^2S'_{\frac{1}{2}}$

All other levels, except one, are formed by the addition of a valence electron to the configuration $4s^24p^4$ of the ion. The other level comes from $4s4p^6$. Most of the expected even levels from $4s^24p^44d$, $4s4p^6$, and $4s^24p^45s$ of Cb VII and Mo VIII have been identified in this investigation from their combinations with the ground doublet. It has not been possible to identify any combinations between these levels and higher odd levels, although some of them are expected to lie within the range covered.

The spectra of Br I,[10] Kr II,[11] Rb III,[12] Sr IV,[12] Y V,[13] and Zr VI[13] have been previously investigated. The screening constant in the regular doublet law was extrapolated from the results of these investigations. The doublet separation of the ground levels of Cb VII was then predicted to be about 19,100 cm^{-1}, and found experimentally to be 19,185 cm^{-1}. That for Mo VIII was predicted and found to be 23,280 cm^{-1}.

Table IV gives the lines classified in Cb VII, and Table VI gives those classified in Mo VIII, showing estimated relative intensity, wave-length, frequency, and transition. The symbols used in the intensity columns are those used in the M.I.T. wave-length tables.[14] For the sake of consistency, the L−S notation employed in previously reported classifications in this sequence has been retained, although it is no longer significant to use any quantum number except J. This has been indicated by using primed symbols. No levels of $J=5/2$ were identified in Rb III and Sr IV, therefore the levels of $J=5/2$ in the present paper are subject to some question. The assignments of $4s^24p^4({}^3P')5s\,{}^4P'_{\frac{1}{2}}$ and $4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$ are not certain. The levels $4s^24p^4({}^1S')4d\,{}^2D'_{3/2,\,5/2}$ were not found in Br I nor in Rb III or Sr IV; the assignments given here are extrapolations from Y V and Zr VI. They are open to question since these levels might be expected to be separated from the levels $4s^24p^4({}^1D')4d\,{}^2D'$ by approximately the separation of the levels $4s^24p^4\,{}^1S'$ and $4s^24p^4\,{}^1D'$ of the ion, as is the case with $4s^24p^4({}^1S')5s\,{}^2S'$ and $4s^24p^4({}^1D')5s\,{}^2D'$. This would place the transition $4s^24p^5\,{}^2P-4s^24p^4({}^1S')4d\,{}^2D'$ at shorter wave-length; no acceptable substitute assignment was found. Therefore, the assignments given in Tables IV and VI are retained for the present. The line $4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2F'_{5/2}$ could not be definitely established in either spectrum. Only one $4s^24p^4({}^3P')4d\,{}^2P'$ level can be identified, since there is serious doubt of the validity of the assignments in Y V and Zr VI. The J value can only be specified as $\frac{1}{2}$ or 3/2. The data indicate several possibilities for a

Table V. Relative energy level values for Cb VII.

Level	Rel. value (cm^{-1})	Level	Rel. value (cm^{-1})
$4s^24p^5\,{}^2P^\circ_{3/2}$	0	$4s^24p^4({}^1D')4d\,{}^2D'_{5/2}$	381021
$4s^24p^5\,{}^2P^\circ_{\frac{1}{2}}$	19185	$4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$	396124
$4s4p^6\,{}^2S_{\frac{1}{2}}$	212501	$4s^24p^4({}^1D')4d\,{}^2P'_{3/2}$	398817
$4s^24p^4({}^3P')4d\,{}^4D'_{5/2}$	270858	$4s^24p^4({}^1D')4d\,{}^2P'_{\frac{1}{2}}$(?)	401699
$4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$	277702	$4s^24p^4({}^1S')4d\,{}^2D'_{5/2}$(?)	403260
$4s^24p^4({}^3P')4d\,{}^4D'_{\frac{1}{2}}$	283097	$4s^24p^1({}^1S')4d\,{}^2D'_{3/2}$(?)	407544
$4s^24p^4({}^3P')4d\,{}^4P'_{\frac{1}{2}}$	326509	$4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$(?)	416055
$4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$	331170	$4s^24p^4({}^3P')5s\,{}^4P'_{\frac{1}{2}}$	426310
$4s^24p^4({}^3P')4d\,{}^4P'_{5/2}$	336071	$4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$	446064
$4s^24p^4({}^3P')4d\,{}^2P'_{\frac{1}{2}\text{ or }3/2}$	339687	$4s^24p^4({}^3P')5s\,{}^2P'_{\frac{1}{2}}$	458824
$4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$	335593	$4s^24p^4({}^1D')5s\,{}^2D'_{5/2}$	455071
$4s^24p^4({}^3P')4d\,{}^2D'_{5/2}$	349314	$4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$	464153
$4s^24p^4({}^3P')4d\,{}^2F'_{5/2}$	364672	$4s^24p^4({}^1S')5s\,{}^2S'_{\frac{1}{2}}$	506552

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[14] *Massachusetts Institute of Technology Wavelength Tables* (George R. Harrison, Editor) (John Wiley and Sons, Inc., New York, 1939), p. 429.

second ${}^2P'$ level, but there are no criteria for predicting its position. The $4s^24p^4({}^3P')4d\,{}^4F'$ levels were not found in Cb VII; their combinations in Mo VIII are quite faint.

The relative values of the energy levels measured from $4s^24p^5\,{}^2P^\circ_{3/2}$ are given for Cb VII and Mo VIII in Table V and Table VII, respectively. An estimate of the absolute values of the ground levels may be made by extrapolating Moseley diagrams, keeping them parallel and at the same time making the difference of the squares of their ordinates equal to observed frequencies. This extrapolation has been made with $4s^24p^5\,{}^2P^\circ_{3/2}$, $4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$ and $4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$. It is estimated that $4s^24p^5\,{}^2P^\circ_{3/2}$ of Cb VII is 1,005,000 cm^{-1} below the ionization limit and $4s^24p^5\,{}^2P^\circ_{3/2}$ of Mo VIII is 1,235,000 cm^{-1} below the corresponding limit. The ionization potentials are approximately 125 v for Cb VII and 153 v for Mo VIII.

TABLE VI. Classified lines of Mo VIII.

Rel. int.	λ_{vac}(A)	ν(cm^{-1})	Transition
250	474.941	210553	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s4p^6\,{}^2S_{\frac12}$
1000w	427.660	233831	$4s^24p^5\,{}^2P^\circ_{3/2}-4s4p^6\,{}^2S_{\frac12}$
150	348.252	287148	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$
50	337.631	296181	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^4D'_{\frac12}$
200	331.612	301557	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{5/2}$
150	322.152	310412	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$
25	313.033	319453	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4D'_{\frac12}$
150	294.138	339977	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^4P'_{\frac12}$
50	290.111	344696	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^4F'_{3/2}$
25	287.304	348063	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$
250	283.412	352843	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$
200	279.463	357829	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')4d\,{}^2P'_{\frac12\text{ or }3/2}$
50	275.288	363256	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{\frac12}$
20	271.871	367822	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4F'_{5/2}$
25	271.769	367960	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4F'_{3/2}$
100	269.287	371351	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$
150	265.869	376125	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$
150	264.629	377888	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^4P'_{5/2}$
500	262.402	381095	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2P'_{\frac12\text{ or }3/2}$
200	255.637	391179	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2D'_{5/2}$
150	244.263	409395	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')4d\,{}^2F'_{5/2}$
100	237.552	420960	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$
25	236.886	422144	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^1D')4d\,{}^2P'_{3/2}$
75	236.004	423722	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2D'_{5/2}$
250	231.998	431038	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^1S')4d\,{}^2D'_{3/2}$
150h	225.102	444243	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$
75	224.497	445440	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')4d\,{}^2P'_{3/2}$
500	223.270	447888	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')4d\,{}^2D'_{5/2}$
250	220.102	454298	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')4d\,{}^2D'_{3/2}$
50	213.126	469206	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$
25	208.319	480033	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')5s\,{}^4P'_{\frac12}$
100	203.042	492509	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$
100	198.686	503307	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^4P'_{\frac12}$
150	198.351	504157	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$
75	192.283	520067	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^3P')5s\,{}^2P'_{\frac12}$
300	190.243	525644	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$
750	189.602	527421	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$
600	186.376	536550	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')5s\,{}^2D'_{5/2}$
600	184.050	543360	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^3P')5s\,{}^2P'_{\frac12}$
400	182.179	548911	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$
150	174.891	571785	$4s^24p^5\,{}^2P^\circ_{\frac12}-4s^24p^4({}^1S')5s\,{}^2S'_{\frac12}$
100	168.050	595061	$4s^24p^5\,{}^2P^\circ_{3/2}-4s^24p^4({}^1S')5s\,{}^2S'_{\frac12}$

TABLE VII. Relative energy level values for Mo VIII.

Level	Rel. value (cm^{-1})	Level	Rel. value (cm^{-1})
$4s^24p^5\,{}^2P^\circ_{3/2}$	0	$4s^24p^4({}^3P')4d\,{}^2F'_{5/2}$	409395
$4s^24p^5\,{}^2P^\circ_{\frac12}$	23277	$4s^24p^4({}^1D')4d\,{}^2D'_{5/2}$	423722
$4s4p^6\,{}^2S_{\frac12}$	233830	$4s^24p^4({}^1D')4d\,{}^2D'_{3/2}$	444240
$4s^24p^4({}^3P')4d\,{}^4D'_{5/2}$	301557	$4s^24p^4({}^1D')4d\,{}^2P'_{\frac12\text{ or }3/2}$	445430
$4s^24p^4({}^3P')4d\,{}^4D'_{3/2}$	310419	$4s^24p^4({}^1S')4d\,{}^2D'_{5/2}$(?)	447888
$4s^24p^4({}^3P')4d\,{}^4D'_{\frac12}$(?)	319456	$4s^24p^4({}^1S')4d\,{}^2D'_{3/2}$(?)	454307
$4s^24p^4({}^3P')4d\,{}^4P'_{\frac12}$	363255	$4s^24p^4({}^3P')5s\,{}^4P'_{3/2}$(?)	492522
$4s^24p^4({}^3P')4d\,{}^4F'_{5/2}$	367822	$4s^24p^4({}^3P')5s\,{}^4P'_{\frac12}$	503309
$4s^24p^4({}^3P')4d\,{}^4F'_{3/2}$	367967	$4s^24p^4({}^3P')5s\,{}^2P'_{3/2}$	527428
$4s^24p^4({}^3P')4d\,{}^4P'_{3/2}$	371345	$4s^24p^4({}^1D')5s\,{}^2D'_{5/2}$	536550
$4s^24p^4({}^3P')4d\,{}^2D'_{3/2}$	376122	$4s^24p^4({}^3P')5s\,{}^2P'_{\frac12}$	543352
$4s^24p^4({}^3P')4d\,{}^4P'_{5/2}$	377888	$4s^24p^4({}^1D')5s\,{}^2D'_{3/2}$	548916
$4s^24p^4({}^3P')4d\,{}^2P'_{\frac12\text{ or }3/2}$	381102	$4s^24p^4({}^1S')5s\,{}^2S'_{\frac12}$	595062
$4s^24p^4({}^3P')4d\,{}^2D'_{5/2}$	391179		

THEORETICAL CONSIDERATIONS

During the consideration of the configuration $4p^45s$ in Cb VII and Mo VIII, an approximate calculation of the energy levels to be expected in intermediate coupling was made, using the matrices of electrostatic energy and spin-orbit interaction given for p^2s by Condon and Shortley. The electrostatic part of the energy matrix is the same for p^4s as for p^2s.[15] The matrix of spin-orbit interaction for p^4s may be obtained from that for p^2s by reversing the sign of the parameter ζ_p.[16] The secular determinant for $J=5/2$ leads to a quadratic equation, while those for $J=3/2$ and for $J=\frac{1}{2}$ yield cubic equations in the energy. As an example, the secular determinant for $J=3/2$ is

$$\begin{vmatrix} F-G-E' & -(\sqrt{3})^{\frac12}/6\,\zeta_p & (15)^{\frac12}/6\,\zeta_p \\ -(\sqrt{3})^{\frac12}/6\,\zeta_p & \begin{matrix}1/3\,\zeta_p-5F\\ -2G-E'\end{matrix} & (5)^{\frac12}/6\,\zeta_p \\ (15)^{\frac12}/6\,\zeta_p & (5)^{\frac12}/6\,\zeta_p & \begin{matrix}-1/3\,\zeta_p-5F\\ +G-E'\end{matrix} \end{vmatrix}=0.$$

In this determinant, E' is written for $E-F_0$.

When this is expanded and powers of G/F higher than the first are neglected, the equation becomes

$$\begin{aligned}(E'/F)^3+(9+2G/F)(E'/F)^2\\ -(75\chi^2/4-15-14G/F-5\chi G/F)(E'/F)\\ -(225\chi^2/4+25-125\chi^3/4+25\chi^2G/F\\ -20G/F+5\chi G/F)=0,\end{aligned}$$

where χ is written for $\zeta_p/5F$. We assume that this

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[15] See reference 9, p. 299. The energies are given on p. 199.

[16] See reference 9, p. 301. The matrix for p^2s is given on p. 268.

equation is of the form

$$(E'/F-x/F+lG/F)(E'/F-y/F+mG/F)\times(E'/F-z/F+nG/F)=0,$$

where x and y are the energy values for the levels of p^4 belonging to $J=2$, while z is the value for the level belonging to $J=1$.

$$x/F=-2-5\chi/4+(9+15\chi/2+225\chi^2/16)^{\frac{1}{2}},$$
$$y/F=-2-5\chi/4-(9+15\chi/2+225\chi^2/16)^{\frac{1}{2}},$$
$$z/F=-5+5\chi/2.$$

Equating coefficients of like powers of G/F, we obtain equations for l, m, and n which yield the solutions

$$l=1/4+(3/4+5\chi/16)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}},$$
$$m=1/4-(3/4+5\chi/16)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}},$$
$$n=3/2.$$

Thus the energy levels are given by

$({}^1D_2')_{J=3/2}$:

$$(E-F_0)/F=-2-5\chi/4+3(1+5\chi/6+25\chi^2/16)^{\frac{1}{2}} -G/F[1/4+(3/4+5\chi/16)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}}],$$

$({}^3P_2')_{J=3/2}$:

$$(E-F_0)/F=-2-5\chi/4-3(1+5\chi/6+25\chi^2/16)^{\frac{1}{2}} -G/F[1/4-(3/4+5\chi/16)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}}],$$

$({}^3P_1)_{J=3/2}$: $(E-F_0)/F=-5+5\chi/2-3G/2F.$

In the same manner, we obtain for $J=5/2$

$({}^1D_2')_{J=5/2}$:

$$(E-F_0)/F=-2-5\chi/4+3(1+5\chi/6+25\chi^2/16)^{\frac{1}{2}} -G/F[3/2-(1/2+5\chi/24)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}}],$$

$({}^3P_2')_{J=5/2}$:

$$(E-F_0)/F=-2-5\chi/4-3(1+5\chi/6+25\chi^2/16)^{\frac{1}{2}} -G/F[3/2+(1/2+5\chi/24)(1+5\chi/6+25\chi^2/16)^{-\frac{1}{2}}].$$

For $J=\frac{1}{2}$, we find

$({}^3P_1)_{J=\frac{1}{2}}$: $(E-F_0)/F=-5+5\chi/2,$

$({}^1S_0')_{J=\frac{1}{2}}$: $(E-F_0)/F=5/2+5\chi/2 +15/2(1-2\chi/3+\chi^2)^{\frac{1}{2}}-G/F,$

$({}^3P_0')_{J=\frac{1}{2}}$: $(E-F_0)/F=5/2+5\chi/2 -15/2(1-2\chi/3+\chi^2)^{\frac{1}{2}}-G/F.$

TABLE VIII. Comparison of relative level values.

Level	Cb Calculated value (cm^{-1})	Cb Observed value (cm^{-1})	Mo Calculated value (cm^{-1})	Mo Observed value (cm^{-1})
$({}^1S_0')_{J=\frac{1}{2}}$	506552	506552	595062	595062
$({}^1D_2')_{J=3/2}$	464153	464153	548916	548916
$({}^1D_2')_{J=5/2}$	464116	455071	547474	536550
$({}^3P_0')_{J=\frac{1}{2}}$	442188	426310	522838	503309
$({}^3P_1)_{J=\frac{1}{2}}$	446282	458824	534164	543352
$({}^3P_1)_{J=3/2}$	446064	446064	527428	527428
$({}^3P_2')_{J=3/2}$	423444	416055	507565	492522
$({}^3P_2')_{J=5/2}$	423127		497768	

The variation of $\chi^{\frac{1}{3}}$ with Z is approximately linear along an isoelectronic sequence.[17] Using this relation with the data of Table VII of the paper by Robinson and Shortley,[17] we estimate χ to be 0.97 for Cb and 1.13 for Mo. Putting these values in the above equations, we obtain the following expressions for the energy values in the form $(E-F_0)/F$:

Level	Cb	Mo
$({}^1D_2')_{J=5/2}$	$2.21-1.11\,G/F$	$2.53-1.13\,G/F$
$({}^3P_2')_{J=5/2}$	$-8.65-1.89\,G/F$	$-9.35-1.87\,G/F$
$({}^1D_2')_{J=3/2}$	$2.21-0.83\,G/F$	$2.53-0.81\,G/F$
$({}^3P_1)_{J=3/2}$	$-2.57-1.50\,G/F$	$-2.18-1.50\,G/F$
$({}^3P_2')_{J=3/2}$	$-8.65+0.33\,G/F$	$-9.35+0.31\,G/F$
$({}^1S_0')_{J=\frac{1}{2}}$	$13.48-1.00\,G/F$	$14.57-1.00\,G/F$
$({}^3P_1)_{J=\frac{1}{2}}$	-2.57	-2.18
$({}^3P_0')_{J=\frac{1}{2}}$	$-3.62-1.00\,G/F$	$-3.93-1.00\,G/F$

With the exception of the inversion of $({}^1D_2')_{J=5/2}$ and $({}^3P_1)_{J=\frac{1}{2}}$, the order of levels predicted by the above considerations is the same as that observed experimentally. Furthermore, the predictions of the theory agree roughly with the observed positions of the levels. Since the energy differences between levels are functions of the parameters F and G, two observed differences may be used to calculate F and G and the other intervals calculated. For this purpose, the intervals chosen were that between $({}^1S_0')_{J=\frac{1}{2}}$ and $({}^1D_2')_{J=3/2}$ and that between $({}^1S_0')_{J=\frac{1}{2}}$ and $({}^3P_1)_{J=3/2}$. For Cb, one obtains the equations

$$11.27F-0.17G=42399\text{ cm}^{-1},$$
$$16.05F+0.50G=60488\text{ cm}^{-1}$$

from which $F=3764$ cm^{-1}, $G=142$ cm^{-1}. For Mo, the equations are

$$12.04F-0.19G=46146\text{ cm}^{-1},$$
$$16.75F+0.50G=67634\text{ cm}^{-1}$$

from which $F=3904$ cm^{-1}, $G=4494$ cm^{-1}. Using these parameters in the remaining expressions for energy intervals, we obtain the values given in the first and third columns of Table VIII for the relative level values. The observed values are given in the second and fourth columns.

Although the calculated and observed values are roughly equal, the observed levels are more intimately mixed than the calculated levels.

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[17] H. A. Robinson and G. H. Shortley, Phys. Rev. **52**, 720 (1937).