The Spectra of Columbium V and Molybdenum VI

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The Rb I-like spectra of columbium and molybdenum have been excited in a vacuum spark and photographed with a vacuum spectrograph. Identifications of lines corresponding to the transitions $5s\ ^2S-5p\ ^2P$, $5p\ ^2P-5d\ ^2D$, $5p\ ^2P-6s\ ^2S$, $4d\ ^2D-5p\ ^2P$, and $4d\ ^2D-4f\ ^2F$ for Cb V and Mo VI have been facilitated by extrapolation from the corresponding lines in the spectra of the four preceding elements in the Rb I-like isoelectronic sequence. The relative term values $4d\ ^2D$, $5s\ ^2S$, $5p\ ^2P$, $4f\ ^2F$, $5d\ ^2D$, and $6s\ ^2S$ have been determined. Absolute term values have been approximately fixed by extrapolating $\nu^{\frac{1}{2}}$ for the terms of the sequence in such a way as to maintain the validity of the irregular doublet law and they have been compared with those obtained by applying the Rydberg formula to the ^2S and ^2D terms, and with those found by extrapolating values of the quantum defects for the ^2S and ^2P terms.

THE spectra of only the first four elements in the Rb I-like isoelectronic sequence have heretofore been identified. Fowler[1] and Paschen-Götze[2] give the classified lines and terms of Rb I and Sr II. The identifications of the spectra of Y III and Zr IV are due to Gibbs and White,[3] to Bowen and Millikan,[4] and to Kiess and Lang.[5] In this report the sequence has been extended to include the spectra of Cb V and Mo VI.

The spectra of Cb V and Mo VI were excited in the vacuum spark between solid metal electrodes and photographed with a vacuum spectrograph containing a concave grating of 150 cm radius of curvature and ruled with 15,000 lines per inch. The dispersion was about 11.3A per mm. The vacuum spark between aluminum electrodes furnished the standard lines, either those of aluminum itself or those of oxygen and nitrogen brought out in the discharge.

The lowest term in each of these spectra is $4d\ ^2D_{1\frac{1}{2}}$, as was anticipated by an almost linear extrapolation from the square roots of the terms of the preceding members of the sequence.

A fair estimate of the separation of the $5p\ ^2P$ terms was obtained from Sommerfeld's law for regular doublets rising from non-penetrating orbits. The doublet separation is given by the equation,

$$\Delta\nu = R\alpha^2(Z-s)^4/n^3l(l+1).$$

The screening constant s was found by extrapolating from the values of s for the preceding members of the sequence (Fig. 1).

A linear extrapolation of the wave numbers in this sequence for the transition $5s\ ^2S_{\frac{1}{2}}-5p\ ^2P_{\frac{1}{2}}$ (irregular doublet law) gave reliable evidence as to the approximate wave-lengths of the $^2S-{}^2P$ lines. This information, together with that obtained from the regular doublet law for the ^2P interval made the identification of these two lines quite unambiguous. Further confirmation of the correctness of this interval was obtained from the identification of combinations with other levels. The identification of other lines was facilitated by the linear extrapolation of radiated wave numbers (Fig. 3) and by the use of extrapolations from the Moseley diagram (Fig. 2).

Tables I and II give the experimental data and classifications.

The diagram (Fig. 2) containing the plot of $\nu^{\frac{1}{2}}$ against atomic number was so drawn that the

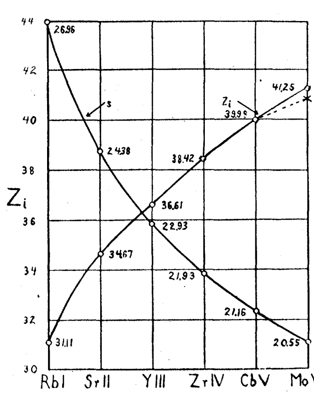

FIG. 1. Z_i and s curves.

[1] Fowler, Report on Series in Line Spectra, pp. 103–105, 131, 132 (1922).
[2] Paschen-Götze, Seriengesetze der Linienspektren, pp. 61–63, 89 (1922).
[3] Gibbs and White, Nat. Ac. Sci. Proc. **12**, 551 (1926).
[4] Bowen and Millikan, Phys. Rev. **28**, 923 (1926).
[5] Kiess and Lang, Bur. Standards J. Research **5**, 305 (1930).

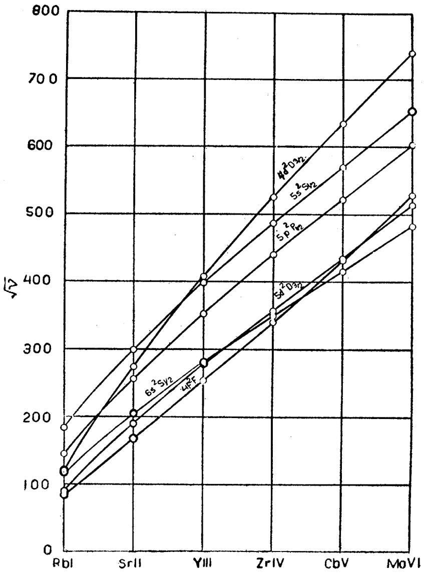

FIG. 2. Moseley diagram.

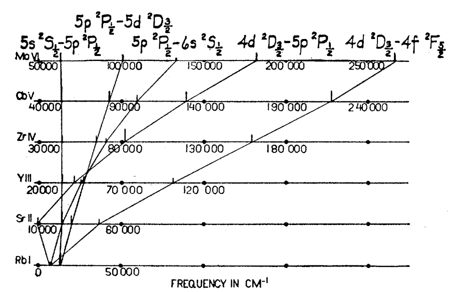

FIG. 3. Linear progression of radiated wave numbers with atomic number.

difference between $(^2S_{\frac{1}{2}})^{\frac{1}{2}}$ and $(^2P_{\frac{1}{2}})^{\frac{1}{2}}$ is nearly constant for the various elements. This is a consequence of the irregular doublet law. Of course, the ordinate interval between the two curves must be such that the term intervals themselves are in harmony with the radiated wave number as determined by the analysis of the spectrum. From the values of $\nu^{\frac{1}{2}}$ found in this way absolute term values can be estimated. Table III gives the numerical values of $(^2S_{\frac{1}{2}})^{\frac{1}{2}}$ and $(^2P_{\frac{1}{2}})^{\frac{1}{2}}$ as plotted in Fig. 2. Other values of $\nu^{\frac{1}{2}}$ plotted in this diagram for these two spectra were obtained by utilizing the relative term values given in Tables V and VI. The resulting curves are satisfactorily consistent.

Another method yielding approximate absolute term values is that of extrapolating a curve

TABLE I. *Classified lines of Cb V.*

Int.	λ(A)	ν(cm⁻¹)	Δν	Classification
10	1877.34	53,266.9	3605.2	$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2}}$
10	1758.33	56,872.1		$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2}}$
4	1267.60	78,889.2	547.1	$5p\ ^2P_{1\frac{1}{2}} - 5d\ ^2D_{1\frac{1}{2}}$
10	1258.87	79,436.3	3604.8	$5p\ ^2P_{1\frac{1}{2}} - 5d\ ^2D_{2\frac{1}{2}}$
7	1212.21	82,494.0		$5p\ ^2P_{\frac{1}{2}} - 5d\ ^2D_{1\frac{1}{2}}$
5	1044.90	95,702.9	3600.0	$5p\ ^2P_{1\frac{1}{2}} - 6s\ ^2S_{\frac{1}{2}}$
4	1007.02	99,302.9		$5p\ ^2P_{\frac{1}{2}} - 6s\ ^2S_{\frac{1}{2}}$
8	774.02	129,196		$4d\ ^2D_{1\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2}}$
8	763.77	130,929	3604 1871	$4d\ ^2D_{2\frac{1}{2}} - 5p\ ^2P_{1\frac{1}{2}}$
6	753.01	132,800		$4d\ ^2D_{1\frac{1}{2}} - 5p\ ^2P_{1\frac{1}{2}}$
8	468.32	213,529	1733	$4d\ ^2D_{2\frac{1}{2}} - 4f\ ^2F_{3\frac{1}{2}}$
8	464.55	215,262		$4d\ ^2D_{1\frac{1}{2}} - 4f\ ^2F_{2\frac{1}{2}}$

TABLE II. *Classified lines of Mo VI.*

Int.	λ(A)	ν(cm⁻¹)	Δν	Classification
9	1595.45	62,678.2	4925.0	$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2}}$
10	1479.22	67,603.2		$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P_{1\frac{1}{2}}$
4	1047.20	95,492.7	768.2	$5p\ ^2P_{1\frac{1}{2}} - 5d\ ^2D_{1\frac{1}{2}}$
12	1038.65	96,278.9	4927	$5p\ ^2P_{1\frac{1}{2}} - 5d\ ^2D_{2\frac{1}{2}}$
10	995.82	100,420		$5p\ ^2P_{\frac{1}{2}} - 5d\ ^2D_{1\frac{1}{2}}$
6	790.75	126,462	4927	$5p\ ^2P_{1\frac{1}{2}} - 6s\ ^2S_{\frac{1}{2}}$
3	761.10	131,389		$5p\ ^2P_{\frac{1}{2}} - 6s\ ^2S_{\frac{1}{2}}$
15	548.21	182,412		$4d\ ^2D_{1\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2}}$
30	541.24	184,761	4938 2589	$4d\ ^2D_{2\frac{1}{2}} - 5p\ ^2P_{1\frac{1}{2}}$
8	533.76	187,350		$4d\ ^2D_{1\frac{1}{2}} - 5p\ ^2P_{1\frac{1}{2}}$
9	376.98	265,266	2185	$4d\ ^2D_{2\frac{1}{2}} - 4f\ ^2F_{3\frac{1}{2}}$
9	373.90	267,451		$4d\ ^2D_{1\frac{1}{2}} - 4f\ ^2F_{2\frac{1}{2}}$

TABLE III. *Values used in applying the irregular doublet law to the* $^2S_{\frac{1}{2}}$ *and* $^2P_{\frac{1}{2}}$ *terms.*

	$(5s\ ^2S_{\frac{1}{2}})^{\frac{1}{2}}$	$(5p\ ^2P_{\frac{1}{2}})^{\frac{1}{2}}$	$(5s\ ^2S_{\frac{1}{2}})^{\frac{1}{2}} - (5p\ ^2P_{\frac{1}{2}})^{\frac{1}{2}}$
Rb I	183.546	145.293	38.253
Sr II	298.249	255.416	42.833
Y III	397.269	351.978	45.291
Zr IV	485.602	438.282	47.320
Cb V	569.64	520.79	48.85
Mo VI	651.5	601.5	50.0

drawn by plotting the values of the quantum defect $(n-n^*)$ for the ^2S and ^2P terms of the sequence against atomic numbers.

The absolute term values of the $5d\ ^2D_{1\frac{1}{2}}$ levels for both spectra found by applying the Rydberg formula to relative term values for both S and D terms are somewhat larger than those obtained from the irregular doublet law, Fig. 2.

The absolute term values for the lowest D levels found by different methods are shown in Table IV. The numbers in the parentheses are the values obtained after correcting the $5s\ ^2S_{\frac{1}{2}}$ terms as obtained from the Rydberg formula by an amount consistent with that found necessary for the other elements of the sequence in which absolute term values can be computed from a three term formula. The absolute term values obtained from the extrapolation of $\nu^{\frac{1}{2}}$ are considered the most reliable. This opinion is well supported by a result obtained from the Landé doublet formula for penetrating orbits,

$$\Delta\nu = R\alpha^2 z^2 Z_i^2/n^{*3}l(l+1).$$

Using the observed $\Delta\nu$'s for the ^2P interval and the n^*'s computed from the preferred $^2P_{\frac{1}{2}}$ values, one obtains values of Z_i which, when plotted against the atomic numbers, give a smooth curve[6] (Fig. 1). If one regards the smoothness of the Z_i curve as essential, its extrapolation from member to member in the sequence furnishes a fairly sensitive check on the term value. For example, if the value of the $^2P_{\frac{1}{2}}$ term for Mo VI is increased by 5000 cm^{-1}, i.e., by about 1 percent, one obtains the value of Z_i marked by the cross in Fig. 1.

Tables V and VI give the term values of Cb V and Mo VI, respectively, relative to $4d\ ^2D_{1\frac{1}{2}}$,

TABLE IV. *Absolute term values of 4d $^2D_{1\frac{1}{2}}$ obtained by different methods.*

	Rydberg formula From S terms	Rydberg formula From D terms	$\nu^{\frac{1}{2}}$ extrapolation	$n-n^*$ extrapolation
Cb V	413,400 (404,900)	433,700	400,000	396,000
Mo VI	562,000 (550,000)	590,000	543,600	515,000

[6] Gibbs and White, Phys. Rev. **33**, 157 (1929). The values of Z_i for Y III and Zr IV have been recomputed from the most recent data.

TABLE V. *Term values for Cb V.*

Term	Relative term values	$\Delta\nu$	Approximate absolute term values
$4d\ ^2D_{1\frac{1}{2}}$	0		400,000
		1871	
$4d\ ^2D_{2\frac{1}{2}}$	1,871		398,129
$5s\ ^2S_{\frac{1}{2}}$	75,929		324,071
$5p\ ^2P_{\frac{1}{2}}$	129,196		270,804
		3605	
$5p\ ^2P_{1\frac{1}{2}}$	132,801		267,199
$5d\ ^2D_{1\frac{1}{2}}$	211,690		188,310
		547	
$5d\ ^2D_{2\frac{1}{2}}$	212,237		187,763
$4f\ ^2F_{2\frac{1}{2}}$	215,262		184,738
		138	
$4f\ ^2F_{3\frac{1}{2}}$	215,400		184,600
$6s\ ^2S_{\frac{1}{2}}$	228,500		171,500

TABLE VI. *Term values for Mo VI.*

Term	Relative term values	$\Delta\nu$	Approximate absolute term values
$4d\ ^2D_{1\frac{1}{2}}$	0		543,600
		2589	
$4d\ ^2D_{2\frac{1}{2}}$	2,589		541,011
$5s\ ^2S_{\frac{1}{2}}$	119,739		423,861
$5p\ ^2P_{\frac{1}{2}}$	182,417		361,183
		4928	
$5p\ ^2P_{1\frac{1}{2}}$	187,345		356,255
$4f\ ^2F_{2\frac{1}{2}}$	267,451		276,149
		404	
$4f\ ^2F_{3\frac{1}{2}}$	267,855		275,745
$5d\ ^2D_{1\frac{1}{2}}$	282,837		260,763
		787	
$5d\ ^2D_{2\frac{1}{2}}$	283,624		259,976
$6s\ ^2S_{\frac{1}{2}}$	313,807		229,793

and the absolute term values as evaluated from the irregular doublet law.

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