New Lines and Terms in the Arc and First Spark Spectra of Molybdenum: Mo I and Mo II

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The spectrum of molybdenum, as excited in a hollow cathode discharge, has been photographed from 540A to 10,830A. The resonance triplet of Mo II, $^6S-{}^6P^0$, has been found, thus locating the lowest term, the $^6S_{5/2}$, at 11,783.70 cm^{-1} below the previously known lowest level, the $^6D_{1/2}$. Some 20 new lines have been classified and 7 new levels established. Two new multiplets, the $^6D-{}^6P^0$ and the $^6D-{}^6D^0$, have been arranged. Catalán's list of classified Mo I lines has been extended to include 36 additional lines. These lines were classified from levels previously determined by Catalán.

THE complete configuration of electrons for atomic molybdenum is $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 4d^5\, 5s$. The lowest state[1] of singly ionized molybdenum is $4d^5\ {}^6S_{5/2}$ which is the limit for the $4d^5\ ms\ {}^5S$ and ^7S term of Mo I. Excitation of one of the five d electrons to an s state gives the configuration $4d^4\ 5s$ with the low terms $4d^4(^5D)5s\ {}^4D$ and ^6D, while excitation of one d electron to a p state gives the configuration $4d^4(^5D)5p$ with the terms $^4P^0$, $^4D^0$, $^4F^0$, $^6P^0$, $^6D^0$ and $^6F^0$.

The first classifications in the Mo II spectrum were made by Meggers and Kiess.[2] Their investigation yielded five multiplets: $^4D-{}^4P^0$, $^4D-{}^4D^0$, $^4D-{}^4F^0$, $^6D-{}^6D^0$ and $^6D-{}^6F^0$, probably transitions between states of the low d^45s and d^45p configurations. The first, third and fifth multiplets mentioned above, as also the $^6D^0{}_{3/2}$ and $^6D^0{}_{1/2}$ terms of the fourth multiplet, were verified by Wilhelmy's[3] Zeeman-effect data. Wilhelmy also found a $^6D-{}^6P^0{}_{3/2}$ triad but was unable to complete the multiplet.

EXPERIMENTAL

The spectroscopic source used in this research was the hollow cathode discharge in an atmosphere of helium. The processes of excitation in this discharge are due to reactions between the neutral or metastable atoms of the metal and the metastable or ionized rare gas atoms.[4] Since the energy of ionization of helium is 198,308 cm^{-1}, and that of the lowest metastable state of molybdenum,[5] a^5S, is 46,432 cm^{-1}, the maximum energy available for the excitation of the Mo II spectrum is 151,876 cm^{-1} (659A). The source of power for the discharge was a d.c. generator operating to give 1500 volts. The discharge was run at 0.5 amp. and with about 9 mm pressure of helium. A molybdenum cathode was used.

The spectrum of the discharge was photographed from 540A to 10,830A. The region of wave-lengths shorter than 2078A was photographed with a concave grating vacuum spectrograph.[6] The grating (1 m radius, 14,400 lines per inch) gave a dispersion of about 17A/mm. Lines due to impurities in the discharge served as standards in the vacuum region. The region from 2078A–2506A was photographed with a Zeiss "Qu 24" quartz prism spectrograph, while for the region 2300A–4415A a Hilger E2 quartz prism spectrograph was used. The region of wave-lengths longer than 4415A was photographed with a Hilger E1 glass prism spectrograph. Iron arc comparison spectra were placed

TABLE I. *The resonance triplet $^6S-{}^6P^0$, together with two transitions from the $^6D^0$ levels. Intensities were taken from the lines on the vacuum plate. These lines also appeared on the spark plate, with the exception of the line 1972.15, which was out of its range.*

$4d^4\,5p$	$^6P_{7/2}{}^0$	693.81	$^6P_{5/2}{}^0$	568.03	$^6P_{3/2}{}^0$	$^6D_{7/2}{}^0$	127.74	$^6D_{5/2}{}^0$
$4d^5\,{}^6S_{5/2}$	50302.60(3) (1987.969) vac.		49608.79(3) (2015.118)		49040.76(4) (2038.462)	50706.08(1) (1972.15) vac.		50578.34(1) (1977.131) vac

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TABLE II. *The $^6D-^6P^0$ and $^6D-^6D^0$ multiplets of molybdenum.*

	$^6D_{1/2}$	250.70	$^6D_{3/2}$	383.15	$^6D_{5/2}$	482.90	$^6D_{7/2}$	560.46	$^6D_{9/2}$
$^6P_{7/2}{}^0$					37885.24(5) (2638.765)	483.07	37402.17(5) (2672.848)	560.50	36841.67(2) (2713.515)
693.65					693.84		693.61		
$^6P_{5/2}{}^0$			37574.66(5) (2660.578)	383.26	37191.40(5) (2687.997)	482.84	36708.56(3) (2723.355)		
568.03			568.05		568.05				
$^6P_{3/2}{}^0$	37257.33(4) (2683.240)	250.72	37006.61(4) (2701.420)	383.26	36623.35(2) (2729.692)				
	$^6D_{1/2}$	250.70	$^6D_{3/2}$	383.15	$^6D_{5/2}$	482.90	$^6D_{7/2}$	560.46	$^6D_{9/2}$
$^6D_{9/2}{}^0$							36580.53(1) (2732.887)	560.40	36020.13(7) (2775.408)
−1224.55							−1224.59		−1224.51
$^6D_{7/2}{}^0$					———		37805.12(5) (2644.357)	560.48	37244.64(6) (2684.153)
127.99							128.19		
$^6D_{5/2}{}^0$			38543.37(4) (2593.705)		———		37676.93(4) (2653.355)		
385.62									
$^6D_{3/2}{}^0$	38408.61(2) (2602.806)		———		37774.63(4) (2646.491)				
242.57	242.57								
$^6D_{1/2}{}^0$	38166.04(2) (2619.348)	250.76	37915.28(3) (2636.674)						

on all plates throughout the quartz and glass regions.

In addition the spectrum from a 35,000-volt condensed-spark in air, covering the region 1944A–2200A, was photographed with a Bausch and Lomb quartz prism spectrograph. Copper and silver spark spectra were placed on these plates for comparison.

TABLE III. *New energy levels.*

CONFIGURATION	SYMBOL	J	TERM VALUE	$\Delta\nu$
$4d^5$	^6S	5/2	−11783.70	
$4d^4(^5D)5p$	$^6P^0$	3/2	37257.28[1]	
				568.03
		5/2	37825.31	
				693.65
		7/2	38518.96[2]	
$4d^4(^5D)5p$	$^6D^0$	5/2	38793.87	
				127.99
		7/2	38921.86[2]	
				−1224.55
		9/2	37697.31	

[1] Level given by Wilhelmy.
[2] Levels given by Meggers and Kiess, but differently assigned.

DATA AND CLASSIFICATION

In the absence of extensive Zeeman-effect data, the discovery of the $4d^5\ ^6S$ term, with transitions to $4d^4(^5D)5p\ ^6P^0$ and $^6D^0$, offers the best possibility for verification of these terms. Comparison with the Cr II spectrum indicated that these transitions should lie near 2000A. To bring out the $^6S-^6P^0$ and $^6S-^6D^0$ lines more strongly relative to the rest of the spectrum than in the hollow cathode discharge, a condensed spark plate was made in the region 2200A−1940A. Only a few lines having wave-lengths less than 2050A appeared on this plate, of which the three strongest form a $^6S-^6P^0$ resonance triplet, involving the $^6S-^6P_{3/2}{}^0$ term of Wilhelmy. A weaker line

TABLE IV. *Classified lines of* Mo II. *The letter n in column one indicates a new line. The symbols in column one have the following meaning: P—M. Puhlmann, Zeits. f. Wiss. Phot.* **17**, *7–131 (1917–1918); H—G. R. Harrison, M.I.T. Wave-length Tables (1939); E—F. Exner and E. Haschek, Tabellen der Bogenspektra (1911); S—new observation.*

AUTHORITY*	λ	I	ν	CLASSIFICATION	$\Delta\nu$	NOTES
n	1972.15	1	50706.1	$4d^5\ ^6S_{5/2} - 4d^45p\ ^6D_{7/2}{}^0$	−0 5	*v*
n	1977.13	1	50578.3	$4d^5\ ^6S_{5/2} - 4d^45p\ ^6D_{5/2}{}^0$	−0.7	*v*
n	1987.969	3	50302.60	$4d^5\ ^6S_{5/2} - 4d^45p\ ^6P_{7/2}{}^0$	+0.06	*v*
S	2015.118	3	49608.79	$4d^5\ ^6S_{5/2} - 4d^45p\ ^6P_{5/2}{}^0$	+0.22	
S	2038.462	4	49040.76	$4d^5\ ^6S_{5/2} - 4d^45p\ ^6P_{3/2}{}^0$	+0.22	
H	2593.705	4	38543.37	$4d^45s\ ^6D_{3/2} - 4d^45p\ ^6D_{5/2}{}^0$	−0.20	
P	2602.806	2	38408.61	$4d^45s\ ^6D_{1/2} - 4d^45p\ ^6D_{3/2}{}^0$	−0.10	*x*
P	2619.348	2	38166.04	$4d^45s\ ^6D_{1/2} - 4d^45p\ ^6D_{1/2}{}^0$	0	*x*
P	2636.674	3	37915.28	$4d^45s\ ^6D_{3/2} - 4d^45p\ ^6D_{1/2}{}^0$	+0.06	
P	2638.765	5	37885.24	$4d^45s\ ^6D_{5/2} - 4d^45p\ ^6P_{7/2}{}^0$	+0.13	*x*
P	2644.357	5	37805.12	$4d^45s\ ^6D_{7/2} - 4d^45p\ ^6D_{7/2}{}^0$	−0.01	
P	2646.491	4	37774.63	$4d^45s\ ^6D_{5/2} - 4d^45p\ ^6D_{3/2}{}^0$	+0.03	*x*
P	2653.355	4	37676.93	$4d^45s\ ^6D_{7/2} - 4d^45p\ ^6D_{5/2}{}^0$	+0.19	
P	2660.578	5	37574.66	$4d^45s\ ^6D_{3/2} - 4d^45p\ ^6P_{5/2}{}^0$	−0.04	
P	2672.848	5	37402.17	$4d^45s\ ^6D_{7/2} - 4d^45p\ ^6P_{7/2}{}^0$	+0.04	
P	2683 240	4	37257.33	$4d^45s\ ^6D_{1/2} - 4d^45p\ ^6P_{3/2}{}^0$	−0.05	*y*
P	2684.153	6	37244.64	$4d^45s\ ^6D_{9/2} - 4d^45p\ ^6D_{7/2}{}^0$	+0.01	
P	2687.997	5	37191.40	$4d^45s\ ^6D_{5/2} - 4d^45p\ ^6P_{5/2}{}^0$	+0.07	
P	2701.420	4	37006.61	$4d^45s\ ^6D_{3/2} - 4d^45p\ ^6P_{3/2}{}^0$	−0.03	*y*
P	2713.515	2	36841.67	$4d^45s\ ^6D_{9/2} - 4d^45p\ ^6P_{7/2}{}^0$	+0.08	
H	2723.355	3	36708.56	$4d^45s\ ^6D_{7/2} - 4d^45p\ ^6P_{5/2}{}^0$	+0.01	He
P	2729.692	2	36623.35	$4d^45s\ ^6D_{5/2} - 4d^45p\ ^6P_{3/2}{}^0$	+0.08	*y*
P	2732.887	.1	36580.53	$4d^45s\ ^6D_{7/2} - 4d^45p\ ^6D_{9/2}{}^0$	+0.03	
P	2775.408	7	36020.13	$4d^45s\ ^6D_{9/2} - 4d^45p\ ^6D_{9/2}{}^0$	−0.03	

* The more accurate grating wave-length measurements of other observers were used for previously reported lines. The intensities are ours. *v* Vacuum wave-length. *x* Classified by Meggers and Kiess. *y* Zeeman effect by Wilhelmy. He Helium line is superposed.

appears to be a ${}^6S-{}^6D_{5/2}{}^0$ transition. These transitions, together with a probable ${}^6S-{}^6D_{7/2}{}^0$ transition from the hollow cathode data, are given in Table I. The ${}^6D_{7/2}{}^0$ was previously assigned as ${}^6D_{9/2}{}^0$ by Meggers and Kiess. The corresponding ${}^6D-{}^6P^0$ multiplet is given in Table II. The intensities and the ${}^6P^0$ intervals fit the theoretical expectations as well as is to be anticipated for an element of this atomic number.

Some changes are necessary in the ${}^6D-{}^6D^0$ multiplet given by Meggers and Kiess, because their ${}^6D_{7/2}{}^0$ level has been reassigned as ${}^6P_{7/2}{}^0$, and because the combination of their ${}^6D_{9/2}{}^0$ term with ${}^6S_{5/2}{}^0$ has led to reassignment of this term as ${}^6D_{7/2}{}^0$. A revised ${}^6D-{}^6D^0$ multiplet is given in Table II. The ${}^6D_{5/2}{}^0$ and ${}^6D_{9/2}{}^0$ terms are new; the ${}^6D_{7/2}{}^0$ term, as noted, is a reassignment. The new and reassigned energy levels are given in Table III. All of the newly classified lines of Mo II are listed in Table IV.

In the course of this study of the molybdenum spectrum, a considerable number of lines were observed which appear to be previously unpublished transitions between levels of Mo I given by Catalán.[5] A list of these lines and their classification is given in Table V. The differences between the observed and calculated wave numbers in Tables IV and V is believed to be in all cases within the tolerance of accuracy of the respective measurements and wave-length standards. The authors are indebted to Professor O. Laporte for discussions of these spectra, and to Dr. H. B. Vincent for cooperation in obtaining the condensed spark spectrum with equipment in his laboratory.

TABLE V. *Classified lines of* Mo I. *This list supplements that of Catalán, reference 5. Lines were classified from levels as given by Catalán authorities as in Table IV.*

Authority	λ	I	ν	Classification	$\Delta\nu$	Notes
n	1952.81 (vac.)	1	51209	$a^7S_3 - 49_3{}^0$	+0.80	
n	2026.54 (vac.)	1	49345	$a^7S_3 - 39_2{}^0$	+1.20	
n	2075.05 (vac.)	2	48192	$a^7S_3 - 32_4{}^0$	0	
H	2114.30	0	47281.94	$a^7S_3 - 26_2{}^0$	+0.06	
n	2128.98	0	46956.0	$a^7S_3 - 22_3{}^0$	−0.10	
H	2337.42	0	42969.08	$a^7S_3 - 12_3{}^0$	+0.02	
H	2387.18	0	41877.65	$a^5D_3 - 52_3{}^0$	−0.05	
H	2497.863	0	40022.16	$a^5D_1 - 48_2{}^0$	−0.16	
P	2601.96	1	38421.10	$a^5S_2 - 37_1{}^0$	+0.20	
n	2626.79	0	38057.9	$a^5G_3 - 56_2{}^0$	0	
H	2702.772	0	36988.10	$a^5G_4 - 52_3{}^0$	−0.20	
E	2737.3	1	36521.56	$a^3P_3 - 56_2{}^0$	+0.24	
H	2737.88	1	36513.82	$a^5S_2 - 26_2{}^0$	−0.12	
H	2884.590	0	34656.83	$a^5S_2 - 15_2{}^0$	−0.13	
H	2887.619	0	34620.48	$b^5D_1 - 56_2{}^0$	+0.12	
P	2892.812	3	34558.23	$b^5D_2 - 57_3{}^0$	−0.13	
n	2895.68	2	34524.1	$a^5G_2 - 48_2{}^0$	−0.40	
H	3057.88	3	32692.92	$a^5P_2 - 47_2{}^0$	−0.02	
H	3146.683	1	31770.32	$a^5P_3 - 45_3{}^0$	−0.12	
H	3173.777	0	31499.12	$a^5G_3 - 32_4{}^0$	−0.02	
H	3235.878	0	30894.63	$a^5G_3 - 28_2{}^0$	−0.03	
P	3266.283	1	30607.05	$a^5G_2 - 19_1{}^0$	−0.05	
H	3268.193	0	30589.16	$a^5G_3 - 26_2{}^0$	−0.06	
H	3383.981	3	29542.55	$a^5P_1 - 29_1{}^0$	+0.05	
H	3442.665	0	29039.17	$b^5D_1 - 36_1{}^0$	−0.17	
H	3445.411	2	28955.39	$a^5P_3 - 25_3{}^0$	+0.01	
H	3460.226	1	28891.60	$a^5P_2 - 19_1{}^0$	+0.10	*
P	3475.037	2	28768.47	$a^5P_1 - 19_1{}^0$	+0.13	*
H	3686.575	1	27117.76	$b^5D_1 - 19_1{}^0$	+0.14	*
H	3702.032	0	27004.54	$a^5G_3 - 58_3{}^0$	+0.06	
P	3707.170	2	26967.12	$b^5D_2 - 19_1{}^0$	+0.08	*
H	3885.508	0	25729.40	$a^5G_3 - 10_3{}^0$	+0.10	
E	4006.7	0	24951.17	$b^5D_1 - 14_2{}^0$	−0.37	
H	4078.381	0	24512.64	$a^5P_3 - 11_4{}^0$	+0.06	
H	4222.411	2	23676.46	$a^5P_1 - 9_1{}^0$	+0.14	
H	4981.827	0	20067.37	$b^5D_0 - 3_1{}^0$	−0.17	

* The symbol indicates that Catalán assigned these classifications to the wrong lines because of an arithmetical error of 1000 cm^{-1} in his level $19_1{}^0$.