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LIFETIMES, BRANCHING RATIOS AND TRANSITION PROBABILITIES IN MOLYBDENUM I

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Abstract—The radiative lifetimes of 14 excited levels in Mo I have been measured by time-resolved laser fluorescence spectroscopy. Emission branching ratios for the decay of these levels have been measured to determine absolute transition probabilities for 135 lines in the wavelength range 2600–6800 Å. The transition probabilities are compared with earlier values. Erroneous J assignments in the literature are corrected.

INTRODUCTION

An attempt to use recently published Mo I transition probabilities to find excited level populations in a molybdenum spectral light source revealed several deficiencies in the published values.[1] The paper by Whaling *et al.*[2] suffers from misclassified levels and incomplete branching ratios, and it includes only lines with upper level energy $E_{ex} \leqslant 41$ kK. The paper by Schnehage *et al.*[3] includes lines from levels at higher energy but their large uncertainties ($\pm$10–30%) are underestimated.

We have corrected these deficiencies by measuring the radiative lifetimes of 14 levels in Mo I with excitation energies up to 55 kK and by measuring the branching ratios for the decay of these levels to find absolute transition probabilities for the decay channels. We have also corrected the level classification errors in Whaling *et al.* and present the corrected transition probabilities. Some of the lines we have measured in emission have been measured in absorption by Schnehage *et al.* and we compare the results of the two different methods.

LIFETIME MEASUREMENTS

The Mo lifetimes are measured using time-resolved laser fluorescence spectroscopy on a Mo atomic beam. The apparatus is a greatly improved version of that used by Duquette *et al.* 4 years ago in work on Mo.[4]

Figure 1 is a schematic of the lifetime experiment. The N_2 laser pumped dye laser produces 50 kW of tunable radiation in a 3 ns duration pulse with a bandwidth of 0.2 cm^{-1}. The dye laser improvements since earlier work on Mo include the substitution of a prismatic beam expander for the telescopic beam expander and the addition of a dye laser amplifier. These improvements resulted in a five fold reduction in dye laser bandwidth, a dramatic reduction of broadband amplified spontaneous emission, an increase in dye laser conversion efficiency, and considerable improvement in output beam quality. The performance of the dye laser is now sufficiently high to use both KDP (potassium dihydrogen phosphate) and less efficient KB5 (potassium pentaborate) frequency doublers.

Reference [5] contains a detailed description of the atomic beam apparatus including a drawing of the source showing materials and dimension. The beam source is based on a low pressure, large bore hollow cathode discharge. The hollow cathode is used as a beam source by sealing one end

*Guest Observer, Kitt Peak National Observatory, operated by AURA, Inc., under contract with the National Science Foundation.

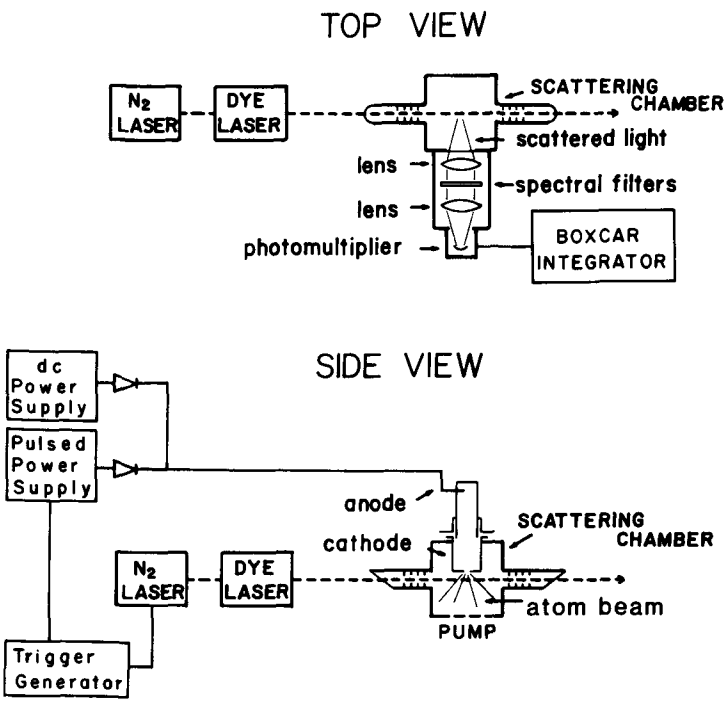

Fig. 1. Schematic of the lifetime experiment.

of the cathode except for 1.0 mm dia opening. The opening is flared outward at 45° to serve as a nozzle for forming an uncollimated atomic beam. The hollow cathode and the scattering chamber are at ground potential. Argon, the sputtering gas, is continuously fed into the hollow cathode discharge. A 10 cm diffusion pump is used to pump the scattering chamber. It is sealed from the hollow cathode discharge except for the nozzle and is maintained at a much lower pressure than the discharge. The Ar pressure in the discharge is typically 0.3 Torr. The resulting scattering chamber pressure is approx. 1.0×10^{-4} Torr. The most significant change in the atomic beam apparatus from the earlier experiment on Mo is the addition of the pulsed power supply. The pulsed supply is constructed of a storage capacitor, a triggerable switch, and a pulsed modulator transformer. Steady currents of up to 200 mA were used in the earlier experiment. Current pulses up to 10 A of 5 μs duration are essential to produce useful population in high lying metastable levels (30,000 cm^{-1}). These high lying metastables serve as lower levels for laser excitation to odd parity levels at energies up to 55,000 cm^{-1}. The discharge current is maintained at 30 mA between pulses. The pulsed supply has also been used to produce intense bursts of metal ions.[6]

The experiment includes a trigger generator to provide an adjustable delay between the current pulse to the hollow cathode and the laser pulse. The optimum delay of 25–30 μs is a measure of the time of flight of the Mo atoms from the discharge source to the laser beam. The atomic beam is crossed by the pulsed dye laser beam 1 cm from the nozzle. The fluorescence is detected along an axis orthogonal to the atomic beam and the laser beam. In order to minimize scattered light, several sets of light baffles are arranged along the laser beam axis inside of the Brewster windows that pass the laser beam into and out of the scattering chamber. Fluorescence from the scattering chamber is focused on the photomultiplier by two lenses comprising an $f/1$ system. The bias resistors of the 1P28A photomultiplier are bypassed by capacitors to ensure good linearity at large peak currents. All components are wired for very low overall inductance and fast response. The fluorescence decay curves in earlier work on Mo were displayed on an oscilloscope and recorded photographically. In this work signals from the photomultiplier pass through a delay line for synchronization of electronic components, then to a Princeton Applied Research model 162/163/165 boxcar averaging system. Curves are plotted directly on an X–Y recorder.

Line identification requires extra care in this experiment because rather weak lines from high lying metastable levels were excited. Two lines are used for 13 of the 14 levels. The lifetimes

measured using the two transitions for each level generally agree to within a few percent. The redundancy provides a check on line identification and a test for line coincidence. The lines used are indicated by an "L" next to the wavelength in Table 1.

We quote overall uncertainties of $\pm 5\%$ for the lifetimes. A number of possible systematic errors merit some discussion. Radiation trapping might occur if a level has a strong transition to the ground level or to a low metastable level. All of the levels studied in this work radiate only to metastable levels above 12,000 cm^{-1}, thus radiation trapping is unimportant. Collisional quenching is not a problem because of the low pressure (10^{-4} Torr of Ar) in the scattering chamber. The detection apparatus has sufficient electrical bandwidth to measure lifetimes as short as 3 ns,[6] and thus it is not a limitation. Zeeman quantum beats are avoided by using Helmholtz coils to "zero" the field in the scattering chamber to within 0.020 G. Hyperfine quantum beats are not a likely source of error because the odd isotopes ^{95}Mo and ^{97}Mo have only 15.7 and 9.5% abundances. No effects due to hyperfine quantum beats are observed. The error due to atoms at thermal velocities leaving the observation region of 5 mm width before radiating is completely negligible. Although we are not able to propose a mechanism by which the discharge pulser could produce a systematic error, we performed lifetime measurements on some levels over a wide range of pulsed currents. The observed lifetimes show no dependence on pulsed current. We believe, on the basis of the above precautions and tests, that the 5% uncertainty on the lifetimes is conservative.

BRANCHING RATIOS

The emission branching ratio R_{ul} for the decay of level u to level l is

$$R_{ul} = A_{ul} \Big/ \sum_{l'} A_{ul'} = I_{ul} \Big/ \sum_{l'} I_{ul'}, \tag{1}$$

where A_{ul} is the transition probability and I_{ul} the photon intensity (photons/s) for the emission line λ_{ul} and the sum in the denominator includes all transitions by which the level u decays. The I_{ul} were measured on three spectra of a Mo + Ne + Ar hollow cathode source recorded with the 1-m Fourier transform spectrometer (FTS) at the National Solar Observatory, Kitt Peak.[7] These are the same spectra used earlier by Whaling *et al.*;[2] for details of the source, spectrometer parameters, and the calibration of the FTS response, see Ref. [2].

The claim that we have measured all significant transitions that contribute to the sum ΣI_{ul} in equation (1) requires justification. For each upper level, we have computed the wavelength of every transition allowed by ΔJ and parity selection rules to lower levels listed in the AEL.[8] We searched our strongest spectrum for these predicted lines, typically 25–30 lines per level, within our wavelength range of 2300–10,000 Å.The signal/noise ratio of our spectra is such that we can detect branches of 1% strength, and even down to 0.1% when the upper level is abundantly populated in the hollow cathode source. The upper levels were selected with $J \geqslant 5$ so that there would be no allowed transitions with wavelength beyond our 2300 Å limit.

All of our upper levels that have known configuration have a $5p$ excited electron, and in view of their decay patterns, it is clear that the two levels (61°_{5} and 97°_{5}) for which the AEL gives no configuration also have a $5p$ electron. These levels have many strong $5p \rightarrow 5s$ decay channels with $\lambda < 10{,}000$ Å. With no apparent reason why longer wavelength transitions should be favored, we believe that we have missed no significant decay branches by neglecting transitions beyond 10,000 Å. If we have omitted significant decay channels, it is because the lower level in the transition is unknown.

RESULTS AND DISCUSSION

Absolute transition probabilities A_{ul} have been calculated from the emission branching ratio R_{ul} and the upper level lifetime τ_u: $A_{ul} = R_{ul}/\tau_u$. The transition probabilities are listed in the last column of Table 1, where the uncertainty ΔA (in parentheses) is given by $\Delta A/A = [(\Delta R/R)^2 + (\Delta\tau/\tau)^2]^{1/2}$.

Transition probabilities for many lines in Table 1 were measured earlier by Corliss and Bozman;[10] their values are, on average, higher than ours by a factor of ~ 8. More recently, Schnehage *et al.*[3]

have measured by an absorption method 8 lines in Table 1. They compare relative gf-values $gf(\lambda_1)/gf(\lambda_2)$ of two absorption lines from a common lower level, and then measure $gf(\lambda_1)$ in emission (by the same method used in the present work) to find $gf(\lambda_2)$. On average, the transition probabilities measured by this absorption method are higher than the values in Table 1 by a factor 1.9 ± 0.4. Two lines, 3038.36 and 3389.69Å, attributed by Schnehage *et al.* to the upper level t^5F_5, do not appear in our spectra. We find upper limits for the transition probabilities of these lines much lower than the values they report, and it seems likely that Schnehage *et al.* have mistaken impurity lines for these Mo transitions.

Table 1. Molybdenum I level lifetimes, branching ratios, and transition probabilities

Upper level Energy lifetime	Lower level	λ (Å)	Branch ratio (%)	Trans. prob. (10^6 s^{-1})
z5Go6	a5G6	4381.63	93.0 (2)	29.1 (9)
39600 cm^{-1}	a5G5	4381.76	1.14 (3)	0.36 (2)
32 (1) ns*	a3G5	5475.89	2.57 (5)	0.80 (3)
	a3H6	6765.63	0.27 (2)	0.085 (6)
	a5F5	7300.19	3.0 (1)	0.94 (5)
z3Ho5	a5D4	3339.40	0.07 (2)	0.04 (1)
42283 cm^{-1}	a5G4	3915.01	0.23 (2)	0.12 (1)
18.7 (9) ns	a5G6	3920.57	0.12 (1)	0.064 (7)
	a5G5	3920.67	0.10 (1)	0.053 (8)
	b5D4	4518.44	1.20 (3)	0.64 (6)
	a3G4	L4731.42	79 (1)	42 (2)
	a3G5	4774.20	2.0 (1)	1.07 (8)
	a3F4	5327.10	1.75 (5)	0.94 (5)
	a3H5	L5610.89	9.40 (9)	5.0 (3)
	a5F5	6104.19	0.14 (2)	0.07 (1)
	a5F4	6138.58	0.73 (4)	0.39 (3)
	a1G4	6389.07	1.25 (4)	0.67 (4)
	b3G4	6691.06	0.68 (6)	0.36 (4)
	b3G5	6867.89	0.20 (2)	0.11 (1)
	b3F4	6886.32	3.3 (1)	1.8 (1)
z3Ho6	a5G6	3911.10	1.0 (1)	0.55 (6)
42345 cm^{-1}	a5G5	3911.20	0.19 (2)	0.10 (1)
18.3 (9) ns	a3G5	L4760.16	85 (1)	46 (2)
	a3H5	5591.51	0.56 (2)	0.31 (2)
	a3H6	L5705.69	7.3 (2)	4.0 (2)
	a3I7	5984.09	0.21 (2)	0.11 (1)
	a5F5	6081.26	0.58 (3)	0.32 (2)
	b3G5	6838.88	5.3 (1)	2.9 (2)
x5Fo5	a5D4	L3229.80	57 (1)	14.6 (8)
43299 cm^{-1}	a5G4	3765.22	8.7 (2)	2.2 (1)
38.9 (19) ns	a5G6	3770.36	3.0 (1)	0.77 (4)
	a5G5	3770.46	12.1 (4)	3.1 (2)
	a3G4	4514.38	1.35 (9)	0.35 (3)
	a3G5	L4553.30	2.5 (3)	0.64 (7)
	a3F4	5053.55	1.42 (9)	0.36 (3)
	a3H4	5206.12	0.63 (9)	0.16 (2)
	a3H5	5308.24	0.56 (4)	0.14 (1)
	a3H6	5411.04	0.59 (5)	0.15 (1)
	c5D4	5602.73	7.7 (5)	2.0 (2)
	a5F5	5747.68	2.5 (1)	0.64 (5)
	a5F4	5778.16	1.45 (9)	0.37 (3)
	a1G4	5999.57	0.32 (5)	0.08 (1)
z3Go5	a5G6	3680.61	24.9 (8)	10.0(6)
43946 cm^{-1}	a5G5	L3680.70	72.5 (3)	29 (1)
24.9 (12) ns	a3G5	4423.05	1.25 (9)	0.50 (4)
	a5F5	L5541.68	1.09 (5)	0.44 (3)
z5Io5	a5G4	L3624.45	87 (2)	52 (3)
44330 cm^{-1}	a5G5	3629.31	12 (1)	7.2 (8)
16.6 (8) ns	a3G4	4313.52	0.62 (6)	0.37 (4)
y5Go6	a5G6	L3233.14	89 (1)	63 (3)
47705 cm^{-1}	a5G5	3233.21	6.1 (2)	4.3 (3)
14.0 (7) ns	a3H5	4301.91	0.86 (7)	0.61 (6)
	a3H6	4369.17	0.35 (4)	0.25 (3)
	a3I6	4512.23	1.10 (9)	0.79 (9)
	a5F5	L4586.06	2.0 (7)	1.4 (1)
x5Go5	a5G4	L3070.90	15.1 (9)	26 (2)
49302 cm^{-1}	a5G6	3074.33	4.8 (2)	8.1 (4)
5.9 (3) ns	a5G5	L3074.39	75 (1)	127 (6)
	b5D4	3430.25	1.7 (3)	2.9 (5)
	a3H5	4025.23	0.4 (1)	0.7 (1)
	a3I6	4208.80	0.36 (6)	0.6 (1)
	a5F5	4272.96	1.0 (2)	1.7 (3)
	a5F4	4289.78	1.2 (2)	2.0 (3)

Table 1—*continued*

Upper level Energy lifetime	Lower level	λ (Å)	Branch ratio (%)	Trans. prob. (10^6 s^{-1})
y3Io6	a5G6	3065.05	35 (1)	29 (2)
49400 cm^{-1}	a5G5	3065.11	4.7 (5)	3.9 (4)
12.0 (6) ns	a3H5	L4009.35	6.5 (2)	5.4 (3)
	a3H6	4067.71	1.6 (6)	1.3 (1)
	a3I5	L4185.82	47 (1)	39 (2)
	a3I6	4191.43	0.84 (7)	0.70 (7)
	a3I7	4207.26	1.3 (1)	1.1 (1)
	a5F5	4255.06	0.5 (1)	0.4 (1)
	b3H5	5148.25	0.5 (1)	0.4 (1)
	b1I6	5580.12	0.8 (1)	0.7 (1)
x5Go6	a5G6	L3064.28	68.2 (7)	83 (4)
49409 cm^{-1}	a5G5	3064.34	7.2 (3)	8.7 (6)
8.2 (4) ns	a3G5	3562.09	4.3 (2)	5.2 (4)
	a3H5	4008.03	1.2 (1)	1.5 (1)
	a3H6	L4066.36	4.0 (3)	4.9 (4)
	a3I5	4184.39	2.0 (3)	2.4 (4)
	a3I6	4190.00	5.2 (3)	6.3 (5)
	a3I7	4205.82	5.1 (3)	6.2 (5)
	a5F5	4253.59	1.3 (2)	1.6 (2)
	b3G5	4610.87	0.7 (1)	0.9 (1)
	b3H5	5146.08	0.3 (1)	0.4 (1)
t5Fo5	a5D4	L2679.86	75 (7)	167 (17)
49651 cm^{-1}	a5G6	3041.71	16 (2)	36 (4)
4.5 (2) ns	a5G5	3041.77	0.81 (9)	1.8 (4)
	a3G5	3531.62	0.5 (1)	1.1 (3)
	a3F4	3825.32	1.6 (2)	3.6 (6)
	a3H4	3912.11	0.5 (1)	1.1 (3)
	c5D4	L4131.90	4.0 (5)	9 (2)
	a5F5	4210.21	0.4 (1)	0.9 (2)
	a5F4	4226.54	0.3 (1)	0.7 (2)
	b3G4	4481.29	0.31 (6)	0.7 (1)
	b3G5	4559.94	0.26 (7)	0.6 (1)
z3Ko7	a3I6	L4042.87	14 (1)	9.5 (7)
50277 cm^{-1}	a3I7	4057.59	9.0 (2)	6.1 (3)
14.7 (7) ns	a1I6	L4536.80	72 (1)	49 (2)
	b3H6	4958.01	1.2 (1)	0.82 (8)
	b1I6	5319.87	3.7 (1)	2.5 (2)
59o5	a3G4	L3192.79	22 (1)	19 (1)
52465 cm^{-1}	a3F4	3453.38	5.6 (3)	4.8 (3)
11.7 (6) ns	a3H5	3570.45	10.3 (5)	8.9 (6)
	a3H6	3616.67	1.7 (2)	1.5 (2)
	a3I5	3709.74	2.5 (3)	2.1 (2)
	a5F5	3764.02	3.8 (2)	3.2 (3)
	a1G4	3870.44	13.1 (4)	11.3 (7)
	b3G4	3979.22	7.4 (3)	6.3 (4)
	b3G5	4041.12	5.0 (2)	4.3 (3)
	b3H5	L4446.43	22.2 (6)	19 (1)
	b3H6	4472.56	3.0 (2)	2.6 (2)
	c3G4	4770.84	0.5 (1)	0.4 (1)
	c3H5	5695.35	2.5 (3)	2.1 (3)
	c3H6	5662.48	1.06 (9)	0.91 (9)
61o5	a3G4	3172.33	2.2 (2)	1.8 (2)
52667 cm^{-1}	a3G5	L3191.51	6.9 (3)	5.6 (4)
12.2 (6) ns	a3F4	3429.46	0.9 (1)	0.8 (1)
	a3H4	3499.05	2.1 (2)	1.7 (2)
	a3H5	3544.89	4.3 (2)	3.5 (2)
	a3H6	3590.44	1.5 (1)	1.24 (9)
	c5D4	3673.85	3.5 (2)	2.9 (2)
	a5F5	3735.62	19.2 (3)	15.7 (7)
	a5F4	3748.47	45 (1)	37 (2)
	b3G4	3947.50	3.6 (2)	3.0 (2)
	b3H5	L4406.85	6.5 (2)	5.3 (3)
	c3H6	5598.48	1.7 (2)	1.4 (2)
	c3H5	5630.59	2.2 (5)	1.8 (4)
97o6	a3G5	2958.01	3.9 (4)	5.3 (6)
55140 cm^{-1}	a3H5	L3259.15	27.5 (5)	37 (2)
7.4 (4) ns	a3I6	3378.45	28.0 (5)	38 (2)
	a3I7	3388.73	4.5 (4)	6.1 (7)
	b3G5	3646.86	4.1 (3)	5.6 (5)
	b3H5	L3973.75	27.3 (7)	37 (2)
	b3H6	3994.61	1.3 (2)	1.8 (3)
	c3H5	4942.34	3.3 (2)	4.4 (3)

*Lifetime value from Whaling *et al.*[2]

L: laser excitation line in lifetime experiment.

The lifetime of the $z^5G^\circ_6$ level at 39,600 K is taken from Ref. [2], where the authors identify the level at 39,600 K as $z^5H^\circ_7$, following the identification in the AEL. They consequently failed to measure decay channels to levels with $J = 5$, and their transition probabilities for lines from this upper level are wrong. This error was immediately apparent when Brault and Faires[1] used the incorrect transition probabilities to compute level populations in their spectral light source, an inductively coupled plasma (ICP) in argon containing a trace of $Mo(CO)_6$. Brault[11] has measured the energy of this level to be 39,599.9915 K and determined that the J-value must be 6 from the strong transitions to $J = 5$ levels. With this corrected J-value, we find the branching ratios listed in Table 1 and, with the radiative lifetime from Ref. [2], the absolute transition probabilities.

The AEL places the level $z^5G^\circ_6$ at 39,522.19 K. This level apparently originated with Meggers *et al.*[9] who classified the line at 4396.65 Å as $a^5G_6 - z^5G^\circ_6$. Precise wavelengths[11] measured with the FTS give no indication of a level at 39,522.19 K. The classification of the 4396.65 Å line is unknown.

We find a similar error in the level labeled 97° at 55,139.74 K in the AEL. A J-value of 5 is assigned to this level in the AEL; we believe it should be 6. Brault[11] has measured the energy of this level to be 55,139.6951 K. Both the hollow-cathode and the ICP spectra show a line at 29,501.129 ± 0.005 K which we attribute to a transition from 97° to a $^3I_7$, the only known Mo I level with $J = 7$ and even parity, with predicted wavenumber 29,501.1291 K based on the Brault's new level energies. The assignment $J = 6$ is consistent with the observed population[1] of this level in the ICP source where the level populations are in approximate thermodynamic equilibrium. It is also consistent with the fact that neither the hollow cathode nor the ICP spectra show transitions from this level to any of the nineteen $J = 4$ even-parity levels in our spectral range.

As a final test of the $J = 6$ assignment for level 97°, we performed a spectrally resolved laser-induced fluorescence experiment in a Mo hollow-cathode discharge. Level 97° was selectively populated with the dye laser. Prompt fluorescent signals with appropriate relative strength were observed at 3388.73 Å and also at the wavelengths corresponding to transitions to the even-parity levels with $J = 5$ and 6. No fluorescence to levels with $J = 4$ was observed. Although collisional mixing in the discharge is a possibility, the evidence indicates that λ3388.73 is the transition from level 97° to the a^3I_7 level. We conclude that level 97° must have $J = 6$.

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