Radiative lifetimes in Rh I and in Ta I

S. Salih, D. W. Duquette, and J. E. Lawler
Department of Physics, University of Wisconsin—Madison, Madison, Wisconsin 53706
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Radiative lifetimes of 22 levels in Rh I and of 35 levels in Ta I are reported. The lifetimes are measured with the use of time-resolved laser-induced fluorescence on an atomic beam. The Rh I lifetimes resolve the discrepancy between the spectroscopically determined solar abundance of Rh and the abundance of Rh determined from chondritic meteorites.

We report the first direct radiative lifetime measurements in neutral rhodium (Rh I) and in neutral tantalum (Ta I). Accurate radiative lifetimes of excited levels in neutral and singly ionized refractory metals are of widespread interest. Lifetimes, combined with accurate branching ratios, provide oscillator strengths (f values). In addition to the intrinsic interest in radiative lifetimes, there are numerous applications that require accurate f values. (i) The limited accuracy of available f values is an important source of uncertainty in the solar and stellar abundances of many chemical elements.[1] (ii) Refractory metals sputtered from the walls of plasma confinement devices cause cooling of the plasma. The atoms are sputtered predominantly as neutrals. Laser-induced fluorescence is used to study the plasma-wall interactions.[2] Absolute metal-atom densities can be determined this way if accurate f values are available. (iii) Some methods in analytical chemistry require accurate f values.[3]

The solar abundance of Rh is determined with the use of 7 lines in Rh I.[4,5] The solar abundance of Rh is in disagreement with a solar-system abundance determined from chondritic meteorites.[1,6] Accurate (5%) radiative lifetimes for the upper levels of 6 of the 7 lines are reported in this paper. Our lifetime measurements provide revised f values that resolve the discrepancy.

A number of methods exist for determining radiative lifetimes. The beam-foil method is the only reliable method for highly ionized atoms. Although the beam-foil method is used for neutral atoms, difficulties are encountered in applying it to heavy atoms in low stages of ionization.[7] The Hanle effect is useful if a suitable gas-phase sample or atomic beam can be produced. Pulsed-excitation time-resolved emission techniques are also useful if a gas-phase sample can be produced. The scarcity of measurements in refractory metals is due to the difficulty of obtaining gas-phase samples in a collision-free environment.

The pioneering study of Corliss and Bozman is the only source of f values in many refractory metals.[8] The values reported are based on absolute emission measurements using intense arcs. Experience in applying the data to solar-abundance determinations casts doubt on their accuracy.[6] The Corliss and Bozman monograph remains a useful source of branching ratios, because branching ratios are not affected by excitation-dependent errors. Accurate experimental radiative lifetimes may be combined with Corliss and Bozman's branching ratios to determine improved f values.

We recently developed an atomic beam source for refractory metals. This source has been used successfully with Rh, Ta, Nb, Mo, W, Zr, and Al.[9–12] The Rh I and Ta I lifetimes are measured using time-resolved laser-induced fluorescence on an atomic beam. Reference 12 contains a detailed description of the experimental apparatus including a drawing of the source showing materials and dimensions. We omit all discussion of the apparatus in this article.

Radiative lifetimes of 22 levels in 8 terms of Rh I are reported in Table I. Radiative lifetimes of 35 levels of Ta I are reported in Table II. Each lifetime represents the mean of 10 or more measurements. The standard deviations of the distributions are typically 5% or less. Figure 1(a) is a decay curve generated by exciting the $z\,^2D_{3/2}$ level of Ta I using laser radiation at 481.28 nm. Figure 1(b) is a semilogarithmic plot of the fluorescence signal. The mean lifetime of this level is 685 ns. The decay curve of Fig. 1 has a high signal-to-noise ratio; decay curves from shorter-lived levels generally have even higher signal-to-noise ratios.

Extensive checks and precautions insure that our lifetimes are free from common systematic errors at the 5% level. We have searched for evidence of radiation trapping, but have not detected it even on the very strong Mo and Al resonance lines.[9,12] The absence of radiation trapping is consistent with the measured atomic beam intensity of $\sim 10^{14}$ atoms/s sr. We search for evidence of collisional quenching by throttling the diffusion pump to increase the scattering chamber pressure to 8×10^{-4} Torr and by remeasuring the lifetime of the long-lived $z\,^2D_{3/2}$ level of Ta I. Collisional quenching is not observed at the 5% level in the case of the $z\,^2D_{3/2}$ level with a 685-ns lifetime, or previously in the case of W I and

TABLE I. Radiative lifetimes in Rh I.

Level		Energy (cm^{-1})	Lifetimes (ns) This experiment (±5%)	Ref. 8 (+100%, −50%)
$4d^8(^3F)5p$	$z\,^4D_{7/2}$	27075	10.6	25.8
	$z\,^4D_{5/2}$	28860	10.4	12.0
	$z\,^4D_{3/2}$	30397	10.2	6.7
	$z\,^4D_{1/2}$	31147	10.1	6.1
$4d^8(^3F)5p$	$z\,^4G_{9/2}$	28543	10.1	11.8
	$z\,^4G_{7/2}$	31102	8.6	7.2
$4d^8(^3F)5p$	$z\,^4F_{9/2}$	29431	9.2	12.3
	$z\,^4F_{7/2}$	29866	9.5	9.7
	$z\,^4F_{5/2}$	31475	9.0	6.2
	$z\,^4F_{3/2}$	32277	8.7	5.0
$4d^8(^3F)5p$	$z\,^2G_{9/2}$	31614	8.2	9.2
	$z\,^2G_{7/2}$	33044	9.2	7.0
$4d^8(^3F)5p$	$z\,^2F_{7/2}$	32004	8.7	6.6
	$z\,^2F_{5/2}$	33946	7.3	5.1
$4d^8(^3F)5p$	$z\,^2D_{5/2}$	32046	8.1	5.1
	$z\,^2D_{3/2}$	33867	7.0	4.6
$4d^8(^3P)5p$	$z\,^4P_{5/2}$	35334	12.0	6.5
	$z\,^4P_{3/2}$	35404	9.8	5.5
	$z\,^4P_{1/2}$	35670	12.2	7.8
$4d^8(^3P)5p$	$y\,^4D_{7/2}$	36787	11.3	6.2
	$y\,^4D_{1/2}$	38474	17.1	7.2
Unclassified	$J=\frac{5}{2}$	39127	16.0	6.6

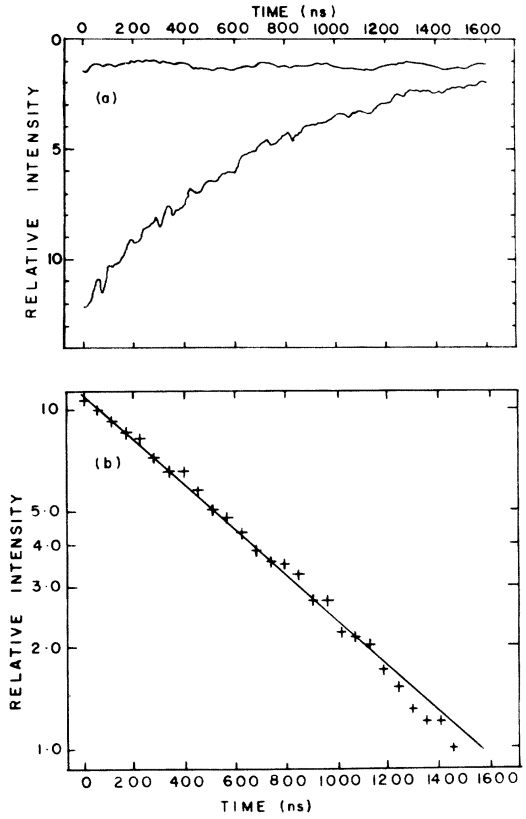

FIG. 1. (a) Time-resolved laser-induced fluorescence signal. The lower trace is the photomultiplier signal observed with the dye laser turned to the Ta I transition at 481.28 nm. The upper trace is the signal observed with the dye laser tuned slightly off the transition. (b) Semilogarithmic plot of the difference between the signal observed with the dye laser tuned to the transition and the signal observed with the dye laser tuned slightly off the transition. The solid line corresponds to a lifetime of 657 ns.

Nb I levels with microsecond lifetimes.[10,12] The absence of collisional quenching is consistent with the scattering chamber pressure of 10^{-4} Torr of Ar. The fluorescence collection system includes a provision for inserting spectral filters. Dye or interference filters are used, when necessary, to insure that only primary fluorescence is detected and not cascade fluorescence involving lower levels. We have analyzed the possibility of errors due to laser-excited atoms leaving the detection region prior to fluorescing. Errors from this effect are smaller than 5% for lifetimes of a microsecond or less.[12]

The bandwidth of the detection electronics is adequate to measure lifetimes as short at 6 ns. The detection bandwidth is verified by measuring the lifetime of the $4s\,^2S_{1/2}$ level of Al which has a well-established lifetime of 6.78 ±0.22 ns.[13] We measure 6.71 ±0.14 ns. Precautions are taken to avoid errors from distortion of the decay curves due to Zeeman quantum beats. Radiative lifetimes less than 500 ns are measured in zero magnetic field (residual field ≤0.02 G). Longer lifetimes are measured in a "high field" of 30 G. The fluorescence decay curve is not complicated by background from the hollow cathode, typically several orders of magnitude less than the peak fluorescence signal, or by electrical noise. The entire detection apparatus is shielded from electrical interference.

We quote overall uncertainties of ±5% on our measurements. The agreement of our recent lifetime measurements in Mo, Zr, and Nb with independent direct lifetime measurements indicates that the ±5% uncertainty is conservative.[9,11–14]

There are no other direct radiative lifetime measurements in Rh I or in Ta I. Our lifetimes are compared in Tables I and II with lifetimes derived from the transition probability data of Corliss and Bozman.[8] These investigators quote an uncertainty of ±0.26 on $\log_{10}(gf)$ values determined from emission intensity measurements on intense arcs. The Corliss and Bozman lifetimes in Tables I and II are determined by summing gA values for all the radiative decay channels tabulated for each level.[8] The lifetimes determined by summing gA values are actually upper limits due to the possibility of strong infrared transitions not observed by Corliss and Bozman. Our life-

TABLE II. Radiative lifetimes in Ta I.

Level	Energy (cm^{-1})	Lifetimes (ns) This experiment (±5%)	Lifetimes (ns) Ref. 8 (+100%, −50%)
$5d^26s^2(a^3F)6p\ z^4D_{1/2}$	18 505	572	2870
$z^4D_{5/2}$	21 168	908[a]	3570
$5d^26s^2(a^3P)6p\ z^2D_{3/2}$	20 772	685[a]	3060
$5d^36s(a^5F)6p\ z^4F_{3/2}$	21 855	449	1130
$z^4F_{5/2}$	23 363	390	853
$5a^36s(a^5F)6p\ z^6F_{7/2}$	26 586	261	531
$z^6F_{9/2}$	27 733	265	508
$z^6F_{11/2}$	30 361	304	500
$5d^36s(a^5F)6p\ z^6D_{3/2}$	24 739	170	402
$z^6D_{5/2}$	26 795	113	254
$z^6D_{7/2}$	27 781	120	305
$z^6D_{9/2}$	28 767	138	444
$5d^36s(a^5F)6p\ y^4D_{1/2}$	25 513	112	340
$y^4D_{3/2}$	26 364	128	308
$y^4D_{5/2}$	28 134	157	260
$5d^36s(a^3P)6p\ z^4P_{3/2}$	26 590	176	395
Unclassified $J=\frac{7}{2}$	26 960	285	577
$\frac{11}{2}$	27 783	379	745
$\frac{3}{2}$	28 689	138	248
$\frac{5}{2}$	28 862	180	309
$\frac{5}{2}$	29 343	97.5	175
$\frac{7}{2}$	29 723	129	137
$5d^36s(a^5P)6p\ y^6D_{3/2}$	30 665	57.9	65.6
$y^6D_{5/2}$	32 487	60.5	88.9
Unclassified $J=\frac{9}{2}$	30 021	238	485
$\frac{7}{2}$	30 591	139	181
$5d^36s(a^5P)6p\ z^4S_{3/2}$	30 895	75.4	91.7
$5d^36s(a^5P)6p\ z^6P_{3/2}$	31 066	54.0	75.2
$z^6P_{5/2}$	31 961	81.7	116
$z^6P_{7/2}$	33 198	63.4	76.3
Unclassified $J=\frac{9}{2}$	31 530	122	103
$\frac{3}{2}$	31 554	97.1	186
$\frac{7}{2}$	31 601	106	162
$\frac{11}{2}$	33 070	175	185
$\frac{9}{2}$	35 498	54.3	

[a] ±8%.

TABLE III. Solar abundance of Rh [$\log_{10}A(H)=12$].

Wavelength (nm)	$\log_{10}gf$ Ref. 8	$\log_{10}gf$ Revised	$\log_{10}A$ Ref. 5	$\log_{10}A$ Revised
369.236	−0.24	+0.14	1.43	1.05
350.732	−0.33	−0.42	1.45	1.54
339.682	−0.28	−0.15	1.33	1.20
347.066	+0.02	−0.22	0.97	1.21
358.310	−0.29	−0.16	1.22	1.09
346.204	+0.02	−0.14	1.00	1.16

time measurements indicate a systematic error in Corliss and Bozman transition probabilities for these elements that is dependent on the energy of the upper level. Branching ratios derived from Corliss and Bozman's data are not affected by an "excitation-dependent" error; they are more reliable than absolute transition probabilities. Our radiative lifetimes and Corliss and Bozman's branching ratios can be combined to yield improved transition probabilities for 171 spectral lines of Rh I and 192 spectral lines of Ta I. An improved transition probability for an emission line from one of the levels in Tables I or II may be derived using the relation

$$gA = gA_{\mathrm{CB}}(\tau_{\mathrm{CB}}/\tau_{\mathrm{expt}}) \ , \qquad (1)$$

where gA is the improved transition probability, gA_{CB} is a transition probability from Corliss and Bozman's monograph, τ_{CB} is the lifetime derived from Corliss and Bozman's data, and τ_{expt} is our experimental lifetime. We omit a tabulation of all 363 improved gA values in this article.

In Table III we report revised f values for selected Rh I lines determined using our lifetimes and Corliss and Bozman's branching ratios. We then use the revised f values to adjust the Rh abundance determinations of Aller.[5] The equivalent widths in the solar spectrum of the 6 lines in Table III are not of equal quality and reliability. The equivalent width of the 369-nm line is the best. It is described as a line "for which the blends are unimportant and the location of the continuum is relatively easy to establish."[4] The remaining ones are all described as "lines whose intensities are extremely uncertain because they are either very faint or very seriously blended and because the height of the continuum is also doubtful."[4] A weighted mean of the revised values for $\log_{10}A$ in Table III may range from 1.05 to 1.20 depending on the precise weight factors. The values of $\log_{10}A$ in Table III are in reasonable agreement with the value $\log_{10}A=1.10$ determined from chondritic meteorites.[15]

In summary, we report direct radiative lifetime measurements on 22 levels in Rh I and on 35 levels in Ta I. The lifetimes are measured using time-resolved laser-induced fluorescence on an atomic beam. Improved f values are determined by combining these new lifetimes with branching ratios from the Corliss and Bozman monograph. The improved Rh I f values resolve the discrepancy between the solar abundance of Rh and the abundance of Rh determined from chondritic meteorites.

Kwiatkowski, Zimmerman, Biemont, and Grevesse have measured 13 Rh I lifetimes. They plan to publish in Astron. Astrophys. and their results corroborate ours.

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