Radiative lifetimes in W I using a novel atomic-beam source

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The first direct radiative lifetime measurements in W I are described. Radiative lifetimes of 15 levels from the $5d^46s(a\,^6D)6p(z\,^7D^0)$, $5d^46s(a\,^6D)6p(z\,^5F^0)$, $5d^5(a\,^6S)6p(z\,^7P^0)$, and $5d^46s(a\,^6D)6p(z\,^5P^0)$ terms are reported with an accuracy of ±5%. The lifetimes are measured using time-resolved laser-induced fluorescence and a novel atomic-beam source. This novel hollow cathode effusive beam source produces an intense beam of ground-state W atoms and metastable W atoms.

Accurate radiative lifetimes of excited levels in neutral or singly ionized refractory elements are of interest for several reasons. Radiative lifetimes combined with branching ratios determined from emission measurements, provide accurate absolute oscillator strengths (f values). Solar abundance determinations of chemical elements are in many cases limited by the accuracy of available f values.[1] Heavy refractory elements, sputtered from the wall of confinement devices, cause radiative cooling of thermonuclear plasmas. Spectroscopic diagnostics, such as laser-induced fluorescence, are used to study the sputtering of wall materials.[2] Atoms are sputtered from the walls predominantly as neutrals. Accurate f values are needed if absolute measurements of sputtered atom densities are to be made using laser-induced fluorescence. Radiative lifetimes and f values of neutral and singly ionized refractory elements are also of intrinsic interest.

Radiative lifetime measurements of refractory elements can be performed using the Hanle effect or pulsed-excitation time-resolved emission techniques, if a suitable gas-phase sample of the element can be produced in a collision-free environment. The relative scarcity of such measurements is due to the difficulty of producing gas-phase samples of refractory elements. Beam-foil techniques are enormously useful in measuring radiative lifetimes of highly ionized heavy elements, but are not well suited to measuring radiative lifetimes of heavy elements in low stages of ionization.[3]

In this Communication we describe a novel atomic-beam source for refractory metals, and an application of this source in measuring some radiative lifetimes of W I. The source is an effusive beam source employing a hollow cathode discharge to produce W vapor. The density of W atoms in the ground state and in metastable states 1.0 cm from the nozzle of this source is sufficient so that a laser-induced fluorescence decay curve can be displayed directly on an oscilloscope.

The hollow cathode effusive beam source is based on a low-pressure (≤0.25-Torr), large-bore (2.7-cm) hollow cathode developed for Doppler-free spectroscopy. This device has been described in substantial detail elsewhere.[4] The hollow cathode is modified for use as a beam source by closing one end of the cathode except for a 1-mm-diam nozzle, and by providing a continuous source of the sputtering gas Ar. The hollow cathode is operated at a current of 20 to 200 mA. The uncollimated W beam emerges from the nozzle into a scattering chamber pumped by a 6-in. diffusion pump. The background Ar pressure in the scattering chamber when the hollow cathode is operating is approximately 10^{-4} Torr. The W beam is crossed by a pulsed dye-laser beam 1.0 cm from the nozzle. The W beam, the dye-laser beam, and the axis of the fluorescence detection system are mutually orthogonal. Several sets of light baffles are necessary to minimize scattered laser light. They are located before and after the Brewster windows that pass the dye-laser beam into and out of the scattering chamber.

Figure 1 is a schematic of the experiment. A

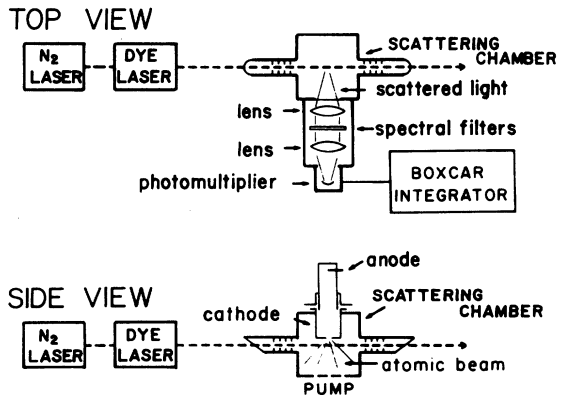

FIG. 1. Schematic of the experiment.

pulsed dye laser, pumped by a N_2 laser, is used in this investigation. The N_2 laser produces a 0.5-MW pulse of 337.1-nm radiation of 5-ns full width at half maximum (FWHM) duration.[5] The dye laser produces a pulse of tunable radiation (360–900 nm) of 3-ns (FWHM) duration.[6] The dye laser provides impulse excitation to levels with lifetimes longer than a few nanoseconds. The dye-laser bandwidth, 1 cm^{-1}, is sufficient to isolate a single fine-structure level. Thus, the fluorescence decay signal is not complicated by cascade from higher excited levels.

The W I levels studied in this investigation are excited from the $5d^4 6s^2(a\ ^5D)$ levels and the $5d^5(a\ ^6S)6s(a\ ^7S_3)$ level using dye-laser radiation at the appropriate wavelength between 360 and 530 nm. The $a\ ^5D_4$ level is 6219 cm^{-1} above the ground level. We have observed W atoms in metastable levels more than 18000 cm^{-1} above the ground level. There is a sufficient density of these higher-lying metastables in the beam so that a laser-induced fluorescence decay curve can be readily detected.

The fluorescence detection system consists of two $f/1$ lenses with spectral filters between them, followed by a RCA 1P28A photomultiplier. In this initial investigation only low-lying, odd-parity levels of W are studied. Thus, only a minimum of spectral filtering, provided by Corning dye filters, is necessary to prevent the observation of cascade fluorescence involving lower levels. The bias resistors for the 1P28A photomultiplier are bypassed with capacitors to ensure good linearity at large peak currents. No loss of linearity for peak photomultiplier currents less than 20 mA is detectable. A single photon spike, with a 2-ns (FWHM) duration, represents the impulse response function of the photomultiplier. Although the fluorescence decay curves from short-lived levels can be displayed directly on an oscilloscope, some averaging is helpful in improving the signal-to-noise ratios. A P.A.R. model 165-162 scanning boxcar integrator with a 300-MHz bandwidth and a 2-ns aperture duration is used.

Figure 2(a) is a typical fluorescence decay curve. The lower trace of Fig. 2(a) is the fluorescence signal observed by tuning the dye laser to the W I transition at 505.33 nm. The dye laser excites atoms from the a^5D_1 level at 1670 cm^{-1} to the $z\ ^7D_1^0$ level at 21 454 cm^{-1}. The upper trace is the signal observed by tuning the dye laser slightly away from 505.33 nm. The base line (upper trace) is not perfectly flat, owing to residual ratio-frequency interference reaching the detection circuitry despite extensive shielding. The background signal due to light from the hollow cathode is negligible. The base line, although not quite flat, is very reproducible. Figure 2(b) is a semilogarithmic plot of the difference between the two traces of Fig. 2(a). The radiative lifetime determined from this scan is 277.5 ns. The average of this measurement and 12 additional measurements is 274.8 ns with a

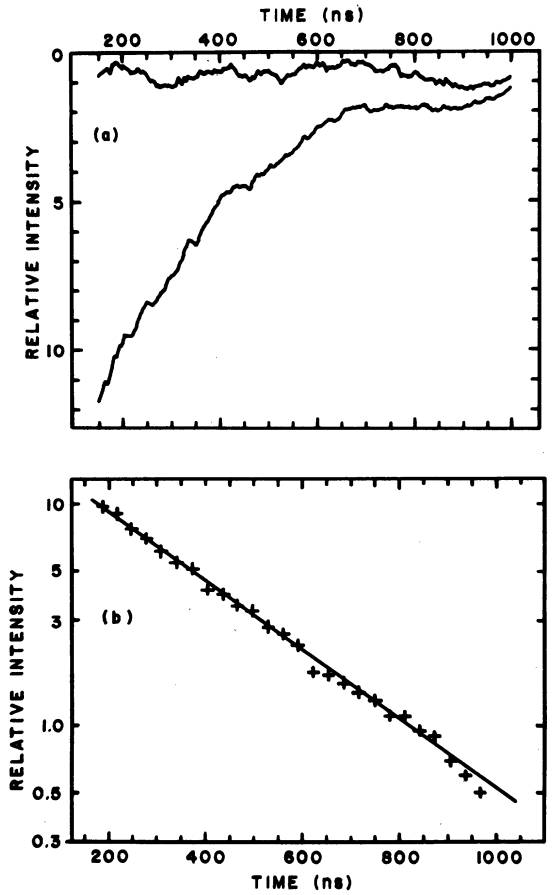

FIG. 2. (a) Time-resolved laser-induced fluorescence signal. The lower trace is the signal observed with the dye laser tuned to the W I transition at 505.33 nm. The upper trace is the signal observed with the dye laser tuned slightly off the transition. (b) Fluorescence signal on a semilogarithmic plot.

standard deviation for the distribution of ±10.6 ns.

Each radiative lifetime determined in this investigation is a mean of approximately 12 fluorescence decay curves. The standard deviation of the distribution is typically ±5%. We have investigated several potential sources of systematic error and concluded that such errors are less than 5%. The overall uncertainty of the radiative lifetimes determined in this investigation is ±5%.

The possibility of errors due to radiation trapping is greatest for levels with short lifetimes. The fluorescence signal is particularly strong from the $z\ ^5P_3^0$ level ($\tau = 59.1$ ns). The density of W atoms in the beam is varied by changing the hollow cathode current. The fluorescence signal, and hence the density of atoms in the beam, is observed to decrease by a factor of 10 as the hollow cathode current is decreased from 180 to 40 mA. The observed lifetime of the $z\ ^5P_3^0$ level is independent of discharge current from

180 to 40 mA. Thus we conclude that errors due to radiation trapping are less than 5%. The possibility of errors due to collisional quenching is considered remote due to the low, 10^{-4} Torr, Ar pressure in the scattering chamber. Nevertheless, we vary the background Ar pressure by a factor of 2 when studying levels with long lifetimes. No changes in the observed lifetimes result. Error due to precession of polarized atoms in stray magnetic fields, of order 0.05 G, is negligible.

Radiative lifetimes of the $z\,^7D^0$, $z\,^5F^0$, $z\,^7P^0$, and $z\,^5P^0$ levels of W I are reported in Table I. The radiative lifetimes of the $z\,^7D^0$ levels are of particular interest because absorption lines from the $a\,^5D$ term to the $z\,^7D^0$ term are used to measure the solar abundance of W. There are no other direct radiative lifetime measurements in W I. Our measurements are compared in Table I with transition probability data from the pioneering work of Corliss and Bozman.[7] These investigators quote an uncertainty of ± 0.26 on $\log_{10}(gf)$ values determined from emission intensity measurements on thermalized arcs. The lifetimes listed under Corliss and Bozman in Table I are determined by summing gA values for all the radiative decay channels tabulated for each level.[7] 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. However, selection rules indicate that most infrared transition rates from the levels in Table I should be negligible in comparison to visible and ultraviolet transition rates. Improved f values for individual transitions can be determined by combining our lifetime measurements with branching ratios from emission intensity measurements.[7,8] Consider the $z\,^7P^0_3$ level at 27 488 cm^{-1}. This level decays via the 407.44-nm transition to the $a\,^7S_3$ level at 2951 cm^{-1}, via the 413.75-nm transition to the $a\,^5D_2$ level at 3326 cm^{-1}, and via the 470.04-nm transition to the $a\,^5D_4$ level at 6219 cm^{-1}. Corliss and Bozman determined gA values of 0.95×10^8 s^{-1} for the 407.44-nm transition, 0.11×10^8 s^{-1} for the 413.75-nm transition, and 0.010×10^8 s^{-1} for the 470.04-nm transition. Only the uncertainty of ± 0.12 in $\log_{10}(gf)$ due to the intensity measurement need be included when using Corliss and Bozman's data to determine a branching ratio. All systematic uncertainties associated with the density of W atoms in the arc, the electron temperature in the arc, the partition function, and the absolute intensity measurement are eliminated. The branching ratio for the 407.44-nm transition is 0.89 ($\pm 5\%$). This branching ratio can be combined with our lifetime measurement of 85.6 ns ($\pm 5\%$) for the $z\,^7P^0_3$ level to determine an improved gA of 0.73×10^8 s^{-1} ($\pm 7\%$) for the 407.44-nm transition. The corresponding gf is 0.181 ($\pm 7\%$).

Although the radiative lifetimes determined in this investigation have a much smaller uncertainty than those determined from the transition probabilities of Corliss and Bozman, the agreement is encouraging. The Corliss and Bozman monograph is widely used as a source of line-strength data. It is worth noting,

TABLE I. Radiative lifetimes of W I levels.

Level		Energy (cm^{-1})	Lifetime (ns) this expt. ($\pm 5\%$)	Ref. 7 ($+100\%$, -50%)
$5d^46s(a\,^6D)6p$	$(z\,^7D^0_1)$	21 454	275	494
	$(z\,^7D^0_2)$	23 965	250	282
	$(z\,^7D^0_3)$	26 189	161	153
	$(z\,^7D^0_4)$	28 797	194	150
	$(z\,^7D^0_5)$	29 773	695	510
$5d^46s(a\,^6D)6p$	$(z\,^5F^0_1)$	25 984	820	491
	$(z\,^5F^0_2)$	27 663	182	134
	$(z\,^5F^0_3)$	29 139	257	135
	$(z\,^5F^0_4)$	31 433	479	205
$5d^5(a\,^6S)6p$	$(z\,^7P^0_2)$	26 230	76.1	78
	$(z\,^7P^0_3)$	27 488	85.6	65
	$(z\,^7P^0_4)$	27 890	63.1	49
$5d^46s(a\,^6D)6p$	$(z\,^5P^0_1)$	28 199	132	69
	$(z\,^5P^0_2)$	29 393	80.4	51
	$(z\,^5P^0_3)$	30 587	59.1	40

however, that the differences between the two sets of lifetimes in Table I are not random. The differences show a definite trend with the energy of the level. Radiative lifetimes of low-lying levels are shorter than predicted by the line-strength data of Ref. 7. Radiative lifetimes of higher-lying levels are longer than predicted by the line-strength data of Ref. 7. The trend suggests that line strengths of Corliss and Bozman for transitions connected to very highly excited levels of W I and for transitions in W II may be far too large. This hypothesis is supported by relative transition probability measurements in a shock tube.[8] The matter deserves further study.

In summary radiative lifetimes of 15 levels of W I are reported with an accuracy of ±5%. The radiative lifetimes can be combined with branching ratios determined from emission measurements to produce improved f values for many transitions in W I. The radiative lifetimes are measured using time-resolved laser-induced fluorescence and a novel atomic-beam source. The atomic-beam source is an effusive beam source employing a hollow cathode to generate metal vapor. In the future we plan to measure many additional radiative lifetimes in neutral and singly ionized refractory elements.

Lastly, we note that the refractory metal beam source described in this Communication has additional applications in atomic spectroscopy and atomic physics.

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