Radiative lifetimes in Nb I

D. W. Duquette and J. E. Lawler
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
(Received 13 January 1982)

The lifetimes of 50 levels in Nb I are measured with the use of time-resolved laser-induced fluorescence on a Nb atomic beam. We describe the hollow-cathode atomic-beam source in detail. The source is capable of producing an atomic beam, which is rich in metastables, of most metallic elements including the highly refractory metals.

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 uncertainty of solar and stellar abundances of many chemical elements is due to the limited accuracy of available f values.[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]

A number of methods exist for determining radiative lifetimes. The beam-foil method is the only reliable method for highly ionized atoms, but it is less suited to neutral or singly ionized atoms. Curtis discusses the difficulties in applying the beam-foil method to heavy atoms in low stages of ionization.[4] 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 line strengths in many refractory metals.[5] The values reported are based on absolute emission measurements on intense arcs. Experience in applying the data to solar abundance determinations casts doubt on their accuracy.[6]

In this article we describe a novel atomic-beam source for refractory metals and we use it to measure radiative lifetimes in Nb I. This source has been used successfully with Nb, Mo, W, Zr, and Al.[7–9]

Figure 1 is a schematic of the atomic-beam source. The hollow-cathode beam source is based on a low-pressure, large bore hollow cathode developed for Doppler-free spectroscopy.[10] The hollow cathode is modified for use as a beam source by closing one end of the cathode except for a 1.0-mm-diam opening. The opening is flared outward at an angle of 45° to serve as a nozzle for forming an uncollimated atomic beam. Argon, the sputtering gas, is continuously fed into the hollow-cathode discharge. A 6-in. 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 argon pressure in the discharge is typically 0.3 Torr at low current, resulting in a scattering chamber pressure of approximately 1.0×10^{-4} Torr. The discharge current is continuously variable from zero to 200 mA. The Nb atomic-beam intensity on axis is 1.8×10^{14} atoms/(sec sr) at 180 mA of discharge current. The source intensity is measured by weighing a Nb film deposited on a glass substrate, and dividing the mass by the operation time and the solid angle of the substrate. We assume every incident atom sticks to the substrate. The atomic beam is rich in atoms in low-lying metastable states, hence we have flexibility in the choice of transitions to be excited. We study transitions to the ground level as well as transitions connected to metastable levels.

Figure 2 is a schematic of the experiment. The atomic beam is crossed by a pulsed dye laser beam 1 cm from the nozzle. Several sets of light baffles are located inside of the Brewster windows which pass the laser beam into and out of the scattering chamber. The dye laser is pumped by a N_2 laser. The N_2 laser produces a 0.5-MW pulse of 337.1-nm radiation with a 5-nsec (FWHM) duration.[11] The

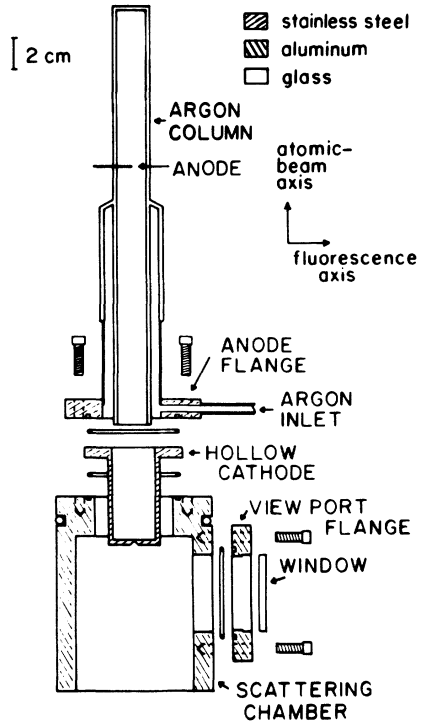

FIG. 1. Exploded view of atomic-beam source. Plane of the figure is normal to the laser beam axis. Materials and dimensions of the source are indicated. Cathode is lined with 0.25-mm-thick Nb.

dye laser, which is tunable from 360 to 900 nm, produces a pulse with a 3-nsec (FWHM) duration.[12] The dye laser pulse begins and ends very abruptly as the dye crosses threshold; it provides impulse excitation to levels with lifetimes longer than a few nanoseconds. The dye laser has a sufficiently narrow bandwidth, 1 cm^{-1}, to isolate a single fine-structure level. Therefore the observed fluorescence is not complicated by cascade from higher levels.

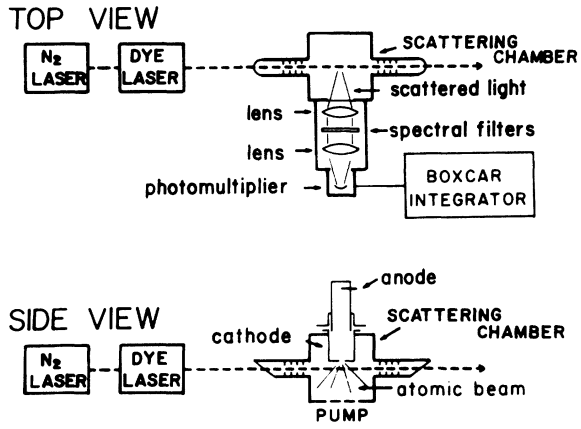

FIG. 2. Schematic of the experiment.

The fluorescence is detected with an RCA 1P28A photomultiplier. The bias resistors of the 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. Light from the scattering chamber is focused on the photomultiplier by two lenses comprising an $f/1$ system. The optical system includes a provision for inserting spectral filters between the lenses. Interference or dye filters are used, when necessary, to block cascade fluorescence involving lower levels. The photomultiplier output signal passes 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.

are reported in Table I. Each value is a mean of ten or more measurements. For 48 levels the standard deviation is less than 5%, while for the two levels with longest lifetimes it is less than 10%. We investigate a number of possible systematic effects, described below, and conclude that these contribute errors of less than 5%.

The possibility of error due to collisional quenching of excited levels was considered remote, *a priori*, because of the very low scattering chamber pressure (10^{-4} Torr). The effect would be most noticeable for levels with long lifetimes, such as the $z^6F_{9/2}$ level with a lifetime of 1.05 μsec $\pm$10%. We vary the scattering chamber pressure by a factor of 5 and detect no dependence of observed lifetime on pressure. We conclude that collisional effects are negligible.

Possible error due to the precession of polarized atoms in stray magnetic fields is avoided by performing zero-field measurements on levels with short lifetimes and high-field measurements on levels with long lifetimes. Three independent, orthogonal sets of Helmholtz coils are used to cancel the earth's magnetic field. The small residual field $\leq$0.02 G could still produce a 10% effect for 1.0-μsec lifetimes, but is not a problem for short lifetimes. A high, 30-G field is generated along the laser beam axis at the center of the scattering chamber when measuring radiative lifetimes over 500 nsec.

The possibility of error due to atoms leaving the observation region before radiating is a concern when measuring the lifetimes of long-lived levels. It is well known that the velocity distribution of sputtered atoms in a hollow-cathode discharge is a thermal distribution at T, the translational temperature of the rare gas. This is illustrated in the

TABLE I. Radiative lifetimes in Nb I.

Level		Energy (cm^{-1})	Lifetime nsec This exp. (±5%)	Lifetime nsec Ref. 5 (+100%, −50%)
$4d^35s(a\ ^5F)5p$	$z\ ^6F_{7/2}$	19917	545[a]	5710
	$z\ ^6F_{9/2}$	20432	1050[a]	12700
$4d^35s(a\ ^5F)5p$	$z\ ^6D_{1/2}$	19624	158	1530
	$z\ ^6D_{3/2}$	19765	161	1770
	$z\ ^6D_{5/2}$	19994	166	1650
	$z\ ^6D_{7/2}$	20316	164	1490
	$z\ ^6D_{9/2}$	20734	154	1500
$4d^35s(a\ ^3F)5p$	$z\ ^4D_{1/2}$	20107	106	901
	$z\ ^4D_{3/2}$	20384	102	1080
	$z\ ^4D_{5/2}$	20838	92.7	1080
	$z\ ^4D_{7/2}$	21512	85.3	895
$4d^4(a\ ^5D)5p$	$z\ ^4P_{1/2}$	22007	53.8	331
	$z\ ^4P_{3/2}$	23007	51.9	346
	$z\ ^4P_{5/2}$	23684	46.6	294
$4d^35s(a\ ^3F)5p$	$z\ ^4G_{5/2}$	22647	146	742
	$z\ ^4G_{7/2}$	23023	132	876
	$z\ ^4G_{9/2}$	23537	128	684
	$z\ ^4G_{11/2}$	24203	126	730
$4d^35s(a\ ^3F)5p$	$z\ ^4F_{3/2}$	23244	44.4	163
	$z\ ^4F_{5/2}$	23574	44.5	178
	$z\ ^4F_{7/2}$	24015	38.6	142
	$z\ ^4F_{9/2}$	24507	35.9	105
$4d^4(a\ ^5D)5p$	$y\ ^6F_{1/2}$	23985	8.5	14.6
	$y\ ^6F_{3/2}$	24165	8.6	16.5
	$y^6F_{5/2}$	24397	8.8	17.8
	$y\ ^6F_{7/2}$	24770	8.5	18.4
	$y\ ^6F_{9/2}$	25200	8.2	16.6
	$y\ ^6F_{11/2}$	25680	7.8	15.3
$4d^4(a\ ^5D)5p$	$z\ ^6P_{3/2}$	24283	46.7	121
	$z\ ^6P_{5/2}$	24543	44.0	102
	$z\ ^6P_{7/2}$	24905	40.6	100
$4d^35s(a\ ^5P)5p$	$y\ ^6D_{1/2}$	25880	62.7	121
	$y\ ^6D_{3/2}$	26067	54.8	185
	$y\ ^6D_{5/2}$	26386	38.9	74.4
	$y\ ^6D_{7/2}$	26832	25.8	60.5
	$y\ ^6D_{9/2}$	27420	15.1	38.3
$4d^4(a\ ^5D)5p$	$y\ ^4F_{3/2}$	25930	47.6	323
	$y\ ^4F_{5/2}$	26061	41.5	120
	$y\ ^4F_{7/2}$	26166	37.9	68.8
	$y\ ^4F_{9/2}$	26440	35.6	101
$4d^4(a\ ^5D)5p$	$x\ ^6D_{1/2}$	26552	8.0	16.0
	$x\ ^6D_{3/2}$	26713	7.3	14.5
	$x\ ^6D_{5/2}$	26983	7.0	17.0
	$x\ ^6D_{7/2}$	27427	7.7	19.1
	$x\ ^6D_{9/2}$	27975	10.8	28.7

TABLE I (*Continued.*)

Level		Energy (cm^{-1})	Lifetime nsec This exp. (±5%)	Ref. 5 (+100%, −50%)
$4d^4(a\,^5D)5p$	$y\,^4D_{1/2}$	26718	14.9	32.6
	$y\,^4D_{3/2}$	26937	22.1	46.5
	$y\,^4D_{7/2}$	27597	31.9	62.5
$4d^4(a\,^3H)5p$	$z\,^2G_{7/2}$	26897	56.2	85.2
	$z\,^2G_{9/2}$	27332	56.7	133

[a] ±10%.

Doppler-limited and Doppler-free spectra of Ref. 10. The rms velocity of Nb atoms from an effusive source is $(4k_BT/M)^{1/2}$ where k_B is Boltzmann's constant and M is the mass of a Nb atom. Although our atomic-beam source is not quite an effusive source, the velocity of Nb atoms in a beam formed by seeding Nb in a high-pressure Ar jet is an upper limit for the rms velocity of Nb atoms in our beam. The upper limit is $(5k_BT/m)^{1/2}$ where m is the mass of an Ar atom.[13] The laser excites a 5 mm length of the atomic beam. The collection lenses image, without magnification, a 7.9-mm length of the atomic beam onto a 7.9-mm-wide photocathode. We conclude, on the basis of reasonable estimates of T, that any error introduced by Nb atoms leaving the observation region is covered by our 10% uncertainty on the longest lifetimes.

The possibility of error due to radiation trapping is investigated for the $x\,^6D_{5/2}$ level in Nb, with a lifetime of 7.0 nsec±5%. If radiation trapping occurs in our system, it would be most easily observed for a short-lived level. The density of Nb atoms in the atomic beam is roughly proportional to the discharge current. Measurements at 50-, 100-, and 150-mA discharge current indicate that the observed lifetime is independent of the Nb density. The fluorescence at 150 mA was nearly enough to saturate the photomultiplier. We conclude that radiation trapping is negligible.

The bandwidth of the detection electronics is a critical consideration when measuring short lifetimes. The $4s\,^2S_{1/2}$ level of Al has a well-established lifetime of 6.78±0.22 nsec.[14] We measure 6.71±0.14 nsec. Thus we conclude that our detection system, a 1P28A photomultiplier, wideband cable delay line (rise time ≤0.1 nsec), and fast boxcar integrator, has sufficient bandwidth to measure lifetimes longer than 6.0 nsec.

The fluorescence decay curve is not greatly 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, except for the two longest lifetimes which have a ±10% uncertainty. The agreement of our recent lifetime measurements in Zr with independent direct lifetime measurements indicates that the ±5% uncertainty is conservative.[9,14]

There are no other direct radiative lifetime measurements in Nb I. Our lifetimes are compared in Table I and Fig. 3 with lifetimes derived from the transition probability data of Corliss and Bozman.[5] 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 Table I and Fig. 3 are determined by summing gA values for all the radiative decay channels tabulated for each level.[5] The life-

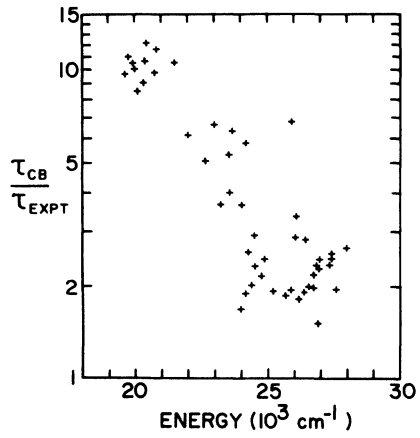

FIG. 3. Semilog plot of the ratio of the lifetime derived from Corliss and Bozman's gA values to our measured lifetime vs the energy of the upper level.

times determined by summing gA values are actually upper limits due to the possibility of strong infrared transitions not observed by Corliss and Bozman. The comparison of Fig. 3 suggests a large systematic error in Corliss and Bozman's transition probabilities that is strongly 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 hundreds of Nb I lines.

Transitions connected to the $y\,^6F$ multiplet are used to study the solar abundance of Nb.[15] Determinations based on Corliss and Bozman's f values yield an abundance that is significantly higher than the observed Nb abundance in carbonaceous chondritic meteorites.[6] Our results indicate that the actual f values are larger. This will reduce the discrepancy.

In summary, we report radiative lifetimes for 50 levels in Nb I. The lifetimes are measured using time-resolved laser-induced fluorescence on a Nb atomic beam. The atomic-beam source is described in detail. We suggest the source has additional applications in atomic physics and spectroscopy.

ACKNOWLEDGMENTS

This research is supported by the Wisconsin Alumni Research Foundation and by the Atlantic Richfield Grant of Research Corporation.

[1]J. E. Ross and L. H. Aller, Science 191, 1223 (1976).
[2]W. R. Husinsky, P. W. King, and J. B. Roberto, Bull. Am. Phys. Soc. 25, 977 (1980).
[3]D. W. Golightly, A. F. Dorrzapf, Jr., and C. P. Thomas, Spectrochim. Acta B 32, 313 (1977).
[4]L. J. Curtis, in *Beam Foil Spectroscopy,* edited by S. Bashkin (Springer, Berlin, 1976), p. 63.
[5]C. H. Corliss and W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements,* Natl. Bur. Stand. (U.S.) Monogr. 53 (U.S. G.P.O., Washington, D.C., 1962).
[6]E. Biemont and N. Grevesse, Phys. Scr. 16, 39 (1977).
[7]D. W. Duquette, S. Salih, and J. E. Lawler, Phys. Lett. 83A, 214 (1981).
[8]D. W. Duquette, S. Salih, and J. E. Lawler, Phys. Rev. A 24, 2847 (1981).
[9]D. W. Duquette, S. Salih, and J. E. Lawler, Phys. Rev. A (in press).
[10]J. E. Lawler, A. Siegel, B. Couillaud, and T. W. Hansch, J. Appl. Phys. 52, 4375 (1981).
[11]W. A. Fitzsimmons, L. W. Anderson, C. E. Riedhauser, and J. M. Vrtilek, IEEE J. Quantum Electron. QE-12, 624 (1976).
[12]J. E. Lawler, W. A. Fitzsimmons, and L. W. Anderson, Appl. Opt. 15, 1083 (1976).
[13]James B. Anderson, in *Molecular Beams and Low Density Gas Dynamics,* edited by P. Wegener (Dekker, New York, 1974).
[14]P. Hannaford and R. M. Lowe, J. Phys. B 14, L5 (1981).
[15]Ö. Hauge and N. H. Youssef, Sol. Phys. 41, 67 (1975).