Radiance Lifetimes in the Resonance Series of Ar I.

George M. Lawrence
Douglas Advanced Research Laboratories, Huntington Beach, California, 92647
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Radiative lifetimes of the six lowest-energy $J=1$ levels of Ar I have been measured using a pulsed electron technique. The wavelengths and measured lifetimes in nanoseconds are
1066.66, 8.60 ± 0.4; 1048.22, 2.15 ± 0.2; 879.95, 10.1 ± 0.4;
876.06, 3.48 ± 0.2; 869.75, 17.5 ± 2.0; 966.8, 3.0 ± 0.4;
where the error estimates are roughly a factor of 10 larger than the statistical errors. Estimates of branching ratios are made where necessary and f values for the above transitions are given. Lifetimes of cascading levels estimated with a two exponential fit are consistent with known lifetimes of Ar I visible lines. Extrapolation to zero pressure to account for photon entrapment was made for lifetimes enlarged less than 30%.

INTRODUCTION

The radiative lifetime measurements described in this paper are a source of accurate transition probabilities for the first few members of the resonance series of Ar I. Part of the work described here was presented at the 1968 conference on vacuum uv and x-ray spectroscopy.[1] The relevant Ar I energy levels are reviewed by Moore[2] and a partial energy-level diagram is given by Bochkova and Schreyder.[3] Since the ground term of Ar I is $^1S_0$, the only electric dipole transitions to the ground state are from the $^1P_1^\circ$ components of excited states. The spin-orbit interaction in the excited states is sufficiently large to establish intermediate coupling, and all of the $J=1$ levels of the ns and nd configurations will contain such a component. Thus all the $J=1$, ns, and nd levels make transitions to the ground state. An early observation and classification[4] of these transitions was made using an electron "beam."

In this work, an electron beam in low-pressure argon is used for excitation, yielding the spectrum shown in Fig. 1. The time decay of photon emission is recorded electronically after a nsec cutoff of the excitation, and mean lifetimes and error estimates are determined from the decay curves with the aid of an iterative computer program called FRANTIC.[5] Such methods are quite standard in nuclear research[6,7] and are being applied in the measurement of atomic and molecular radiative lifetimes.[8,9] The major complications, to be discussed, are resonance photon entrapment and cascading.

The only previous work on the transition probabilities under study here is on the lines from the $4s$ levels. That work will be mentioned at the end of this paper.

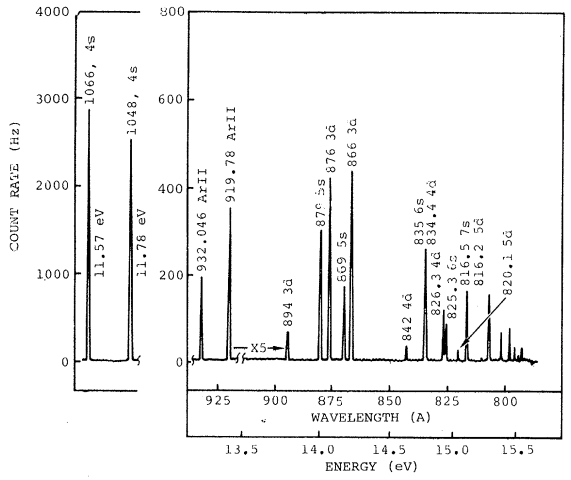

FIG. 1. Photoelectrically recorded spectrum of Ar. Source pressure is one micron; electron energy is 50 V.

EXPERIMENTAL METHOD

A 60-V electron pulse is generated in argon at pressures around 10^{-4} Torr. The source (Fig. 2) is a diode with a tungsten wire cathode which is pulsed to about − 55 V with respect to the hollow anode. Dimensions have been made small to minimize problems due to entrapment of the resonance photons and to reduce the effect of space charge.

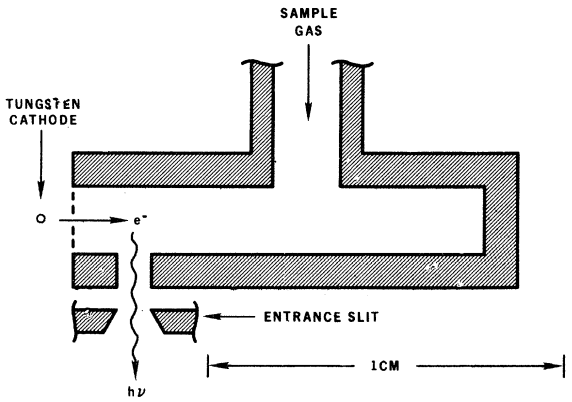

FIG. 2. Pulsed electron, hollow anode source.

The transit time of an argon atom across the source is about 2μ sec. Physically, the source is similar to one illustrated by Hesser.[10]

The photon-decay curves produced by the electron pulses are recorded with a system consisting of a time-to-amplitude converter, followed by a pulse-height analyzer. The system used in this work uses a coincidence preselection of events to allow repetition rates to 10 MHz. The detected photon rate varies from ~10/sec (background limited) to 20 kHz (analyzer process time limited). A random-pulse source, a crystal-time base, and a scaler are used to calibrate each and every channel width to better than 1%. The calibration is remade every three decay curves and has been cross checked with a precision delay line.

An EH model 120D pulse generator with the anodes of the output tubes paralleled provides a 60-V pulse to the cathode with a fall time of about 2 nsec. The excitation drops sharply to zero as the cathode voltage goes below threshold for the level under study, and the photon rate is assumed to decay freely after this point in time.

The wavelength desired is selected by a McPherson model 225 monochromator.[11]

The photon flux at the exit of the monochromator is detected by an Amperex 56P17 multiplier[12] with the first dynode used as the cathode upon which a layer of CsI is vacuum deposited to improve the quantum efficiency.[13]

A more detailed description of the apparatus must await the results of modifications to improve the time resolution. In order to determine what the system decay time is, a fast transition, Ne II 461, was measured and yielded a mean decay time (reciprocal log slope) of 0.7 nsec, cascade free. The radiative lifetime of this transition has been calculated[14] to be 0.03 nsec, and an experimental upper bound[15] of 0.2 nsec has been obtained with the phase-shift technique. Thus the instrumental response can be described as a 0.7-nsec decay and is not a limiting factor in the determination of the lifetimes reported here.

Decay curves were made at various pressures (0.1–10 μ) electron voltages (15–55 V) emission-limited electron currents (0.1–10 mA) repetition rates (2–5 MHz) and time-channel widths (0.35–0.7 nsec). Lifetimes obtained from these decay curves had statistical error estimates on the order of 1 to 2% and no significant variations in lifetime were caused by variation in the above parameters except pressure.

DATA ANALYSIS, CASCADING

The problem of cascading, present with electron excitation, is ideally solved by operating with electron energy below the threshold of the cascading levels.[9] Experimentally, however, one loses two or more orders of magnitude in signal intensity compared with uncontrolled excitation. Fortunately resonance lines usually have a simple cascade pattern which can be handled with a two exponential component model. Let us examine the cascade analysis with an example.

A typical decay curve is shown in Fig. 3 for λ = 1048.22 Å. The excitation pulse full width at half-maximum is 6 nsec, the average spacing between channels is 0.60 nsec, and the count in the channels is ~10 000 near the peak, giving a statistical uncertainty of ~1% per point. The two straight lines in Fig. 3, obtained from FRANTIC, represent a "main" lifetime $\tau = 2.27 \pm 0.03$ nsec and an effective cascade lifetime $T = 34 \pm 0.5$ nsec. The sum of these two exponential components forms a statistically viable fit to the data points (for the record length used) according to a χ-square test. The reader, however, will note that data points for time delays greater than 47 nsec are not describable in terms of the 34-nsec decay. Thus one must determine the effect of using different record lengths in the fitting process. This effect is examined in Fig. 4, where the END FIT time of Fig. 3 is varied. The value of T obtained from the fit is sensitive to the length-of-time record used in the fit, which shows that the cascade is a mixture of lifetimes. The value of τ, however, is relatively

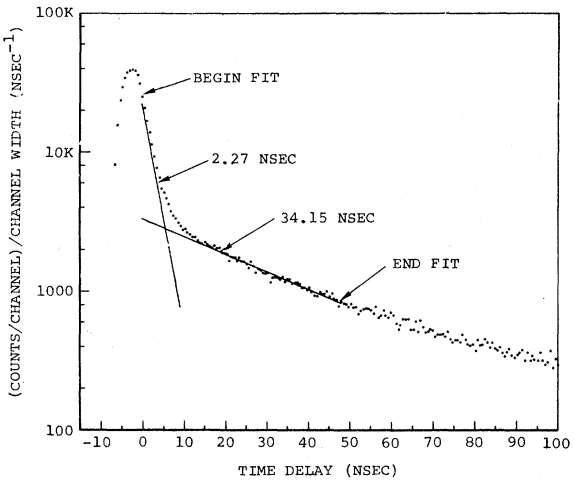

FIG. 3. Decay curve for λ1048.22 Å. The data points were accumulated in 20 min. The straight lines represent the fit by FRANTIC with a record length of 48 nsec.

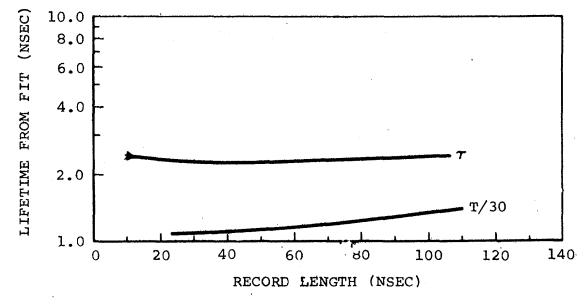

FIG. 4. Variation of main lifetime (τ) and effective cascade lifetime (T) with record length used in a two-parameter fit. Record length can be correlated with the time axis of Fig. 3. With record lengths shorter than the curves shown, a two-parameter fit is not obtained by FRANTIC. Best fit is obtained for a record length of 48 nsec.

insensitive to the record length used. The value of T obtained is a weighted average of all the long-lived cascading states involved. The cascading into the 4s levels is, for example, largely due to the 4p levels which have lifetimes known to be in the neighborhood of 30 nsec but will also contain some components with larger lifetimes. In some cases, three exponential components were better than two. But in all cases the third component has small amplitude, affecting the τ component less than the τ error estimate, and had a large error estimate itself. As an example to indicate this type of behavior, a three-component fit with a 95-nsec record length was made to the data of Fig. 3 and yielded lifetimes of 2.22 ± 0.03, 25 ± 3, and 110 ± 50 nsec. The amplitudes at time zero for these components were 25388 ± 288, 2988 ± 262, and 605 ± 327, respectively.

As an overall system check, H_2 was used as a sample gas, the lifetime of Lyman α (H I 1216.7 Å) was measured with the above technique, and the result of the three decay curves, using three-parameter fits, is 1.58 ± 0.08 nsec. This compares favorably with the theoretical, field free, lifetime of the 2p level which is 1.60 nsec.

The error estimates quoted thus far are provided by FRANTIC and are calculated from the *a priori* standard deviation of each data point. This is computed from the uncertainty in the channel widths, ΔT, and from the uncertainty in the count in each channel ($\sqrt{N}$). In addition to these purely statistical errors, a standard deviation of 1/2% of each count was included to allow for systematic calibration errors. FRANTIC calculates statistical weights W_i from each of the standard deviations σ_i, $W_i = 1/\sigma_i^2$, and carries out a weighted least-squares fit. The estimated standard deviations in the parameters (lifetimes, amplitudes) are obtained from the diagonal elements of the inverse of the least-squares matrix.

PRESSURE DEPENDENCE

The existing theories[16] for resonant-photon entrapment are strictly applicable only to idealized source geometries. However, for low enough optical densities and neglecting polarization effects, the theories reduce to $\tau' = \tau_0 \exp(k_0 L B)$ where τ' is the observed lifetime, τ_0 is the natural (zero pressure) lifetime, k_0 is the absorption coefficient at the center of the Doppler line profile, L is a characteristic dimension of the source, and B is the branching ratio $A\tau_0$. Figure 5 illustrates this variation for part of the data. Least-square, straight-line fits were made to the $\ln\tau'$-versus-pressure points. The zero-pressure intercepts are the lifetimes reported in Table I. Using standard formulas,[17] one can show that the slopes of the lines in Fig. 5 should be proportional to $\lambda^3 B^2/\tau_0$ for a line of wavelength λ. The normalized slopes listed in Table I are the observed slopes (in arbitrary units) multiplied by $Q = \tau_0/\lambda^3 B^2$ and nominally should be constant. This correction factor Q varies a factor of 13 from smallest to largest and is adequate to bring the normalized slopes within ~30% of each other. The reason for the relatively low slopes on the 1048 and 1067 lines is not known. The absolute magnitude of the normalized slope yields a value of 1.5 mm for L.

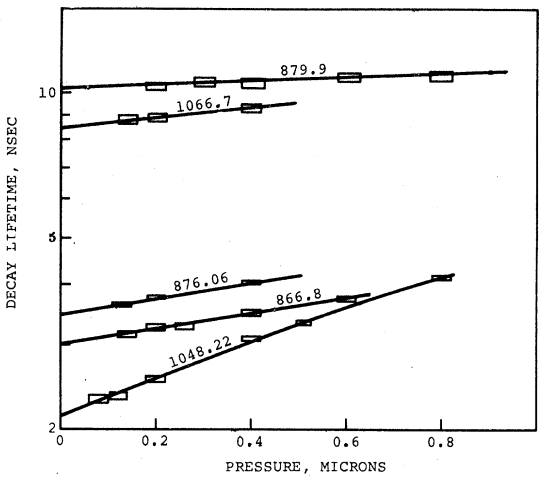

FIG. 5. Pressure extrapolation. Error boxes measure twice the probable error in τ by the estimated uncertainty in relative pressure. This figure represents approximately the first third of the decay curves made.

The lifetimes T of the cascading states did not show pressure-dependence because they do not connect with the ground state.

The quality of the fit was observed to deteriorate for $\tau'/\tau_0 \gtrsim 1.3$. Presumably this is caused by the production of nonexponential decays by the entrapment process.

BRANCHING RATIOS AND CASCADE LIFETIMES

The Bates-Damgaard (BD) Coulomb approximation[18] was applied to several of the transition arrays between excited configurations by assuming LS coupling and using average energies. In this approximation, the transition probabilities for the singlet and triplet arrays are identical so that the introduction of spin-orbit splitting should introduce changes in lifetimes only by wavelength factors. The lifetime of the 4p levels calculated in this manner is 27 nsec which is to be compared with a range of 22.5 to 43.2 nsec calculated using the Coulomb approximation and intermediate coupling.[19] The absolute scale of the latter calculations has received support from the lifetime measurements of Klose.[20]

The lifetimes obtained in the simplified approximation are 4p, 27 nsec; 5s, 54 nsec; 6s, 85 nsec; 5p, 220 nsec ?; 6p, 580 nsec; 3d, 62 nsec; 4d, 340 nsec; and 4f, 45 nsec; neglecting the effect of the transitions to the ground state. The question mark by the 5p lifetime indicates the uncertainty caused by being near a node in the BD tables. These lifetimes are listed as Calc T's in Table I for primary and secondary cascades. Qualitative agreement is obtained with the observed cascade lifetimes T.

THEORETICAL RELATIVE STRENGTHS

Relative transition strengths of the uv lines from

TABLE I. Ar I lifetimes and oscillator strengths.

nl	Wavelength (Å)	Lifetime (nsec)	Branching[a] A (10^6/sec)	f value ($\times 10^3$)	Theory Rel f	Normalized slope	T (nsec)	Calc.[a] T (nsec)
4*s*	1066.66	8.60 ± 0.4	0	59 ± 3	59	32 ± 2	62 ± 15	27, 54, 62
4*s*	1048.22	2.15 ± 0.2	0	228 ± 21	237[b]	32 ± 2	40 ± 10	27, 54, 62
5*s*	879.95	10.1 ± 0.4	18	28 ± 3	28	48 ± 9	150 ± 30	220?, 85, 340
5*s*	869.75	17.5 ± 2.0	18	13 ± 3	21[b]	41 ± 17	120 ± 40	220?, 85, 340
3*d*	876.06	3.48 ± 0.2	16	93 ± 6	93	45 ± 4	90 ± 15	45, 580, 85
3*d*	866.81	3.0 ± 0.4	16	107 ± 15	85[c]	39 ± 4	90 ± 15	45, 580, 85
3*d*	894.31	94 ± 20[d]	...	...	0.3[c]	...	...	45, 580, 85
4*d*	842.81	74 ± 10[d]	...	...	...	...	...	... ...

[a] Estimated with the Coulomb approximation. See text and Ref. 18.
[b] Peterson formula, Ref. 21.
[c] Intermediate coupling.
[d] Presumably dominated by cascading and downward branching. See text.

the *ns* levels can be easily calculated from a formula given by Peterson.[21] Good agreement is obtained for the 4*s* lines but only fair agreement for the 5*s* lines.

A calculation of the relative oscillator strengths of the 3*d* transitions was made by diagonalizing the spin-orbit matrix[22] and minimizing the deviation from experimental energies with respect to the spin-orbit parameters.[19] The parameters obtained (in cm^{-1}) are $\xi_d = 70$, $\xi_p = -667$, $F_2 = 181$, $G_1 = 131$, and $G_3 = 9.4$. The rms error in the energy fit is 140 cm^{-1}, which is rather large. The relative line strengths obtained are $|\langle 3d,\ ^1P_1 | 3d, J=1\rangle|^2 = 0.475$, 0.523, and 0.0018 for the levels which radiate at 866.8, 876.1, and 894.3 Å, respectively. Corresponding relative f values are listed in Table I. This is in disagreement with the result obtained assuming pair coupling,[23] which predicts equal strengths for the three lines. The relative emission intensities of the weak lines at 894.3 Å (3d) and at 842.8 Å (4d) can be estimated for 50-v electrons from Fig. 1. At 150 v, these "weak" lines are attenuated about an order of magnitude with respect to the other lines in the spectrum. This behavior is consistent with exchange excitation of these (mostly) triplet states.

Unfortunately, the lifetime measurements of the 894.3 and 842.8 Å lines are uninterpretable in terms of f values because of the uncertainties in the branching ratios and cascade lifetimes.

TABLE II. Oscillator strength comparisons for the 4*s* levels.

Wavelength λ	1066.66 Å	1048.22 Å
This Work	0.059 ± 0.003	0.228 ± 0.021
HF;		
Knox, Theory (1) (Ref. 25)	0.052	0.17
Knox, Theory (2) (Ref. 25)	0.049	0.20
Electron impact f sum (Ref. 27)		
Relative (Ref. 28)	0.049	0.181
Lifetime (Ref. 28)	0.024 ± 0.002	...
Collision broadening (Ref. 29)	0.036 ± 0.004	0.275 ± 0.02

ERRORS, COMPARISON, AND DISCUSSION

The errors quoted for the lifetimes in Table I are meant to be limits on the size of the error, and are roughly a factor of 10 larger than the probable error estimates obtained after the pressure extrapolation, starting with FRANTIC'S standard deviations. The largest uncertainty is the effect of cascading on the fit and is estimated from the studies indicated in Fig. 4.

The only data available for comparison are for the 4*s* lines and are assembled in Table II.

The disagreement with the lifetime result of Morack and Fairchild[24] is surprising and is not understood by the author. The Hartree-Fock calculation of Knox[25] should be reasonably accurate as there seem to be no configuration perturbations connected with the 4*s* levels.[26] Electron-energy-loss spectral data given by Geiger[27] and by Chamberlain *et al.*[28] have been combined and seem to give quite accurate values. Stacey and Vaughn[29] measured the resonance broadening of some 4*p*-4*s* lines to determine the 4*s* f values. Their values are quoted in a useful summary given by Wilkinson.[30]

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Radiative Mean-Life Measurements of Some Atomic-Hydrogen Excited States Using Beam-Foil Excitation*

E. L. Chupp, L. W. Dotchin, and D. J. Pegg
Physics Department, University of New Hampshire, Durham, New Hampshire
(Received 8 August 1968)

The beam-foil excitation method has been used to measure the radiative mean lives of the $2p$ and $3p$ states of atomic hydrogen. The results obtained were $(1.60 \pm 0.01) \times 10^{-9}$ sec and $(5.5 \pm 0.2) \times 10^{-9}$ sec, respectively. A study of the results of this experiment has led to the following conclusions: (a) the Lyman-α decay curves are best fitted by the sum of two exponential terms whose characteristic decay times correspond to spontaneous decay of the $2p$ state and repopulation of this state by higher states, (b) the shapes of the Lyman-α decay curves vary with foil thickness, and (c) the ion energy loss in the foils used in this experiment changes with the age of the foil. A review of previous measurements on atomic-hydrogen radiative mean lives is also made and compared with theory.

I. INTRODUCTION

A method of determining the radiative mean lives of excited states of atoms and ions of astrophysical interest has recently been suggested.[1] This technique, which has become known as the beam-foil excitation method, is actually a modern refinement of a method first used by Wien.[2,3] In the present