# Mean life of the $4s\ ^2S_{1/2}$ resonance level in Al I

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The mean life of the $4s\ ^2S_{1/2}$ resonance level in Al I has been measured at seven different vapor densities using a tunable dye laser for excitation and a method of delayed coincidence for detection. The lifetime values, obtained by exciting the level with radiation at the resonance wavelength of 3944.01 Å and observing its decay by means of the transition at 3961.52 Å, increase with increasing vapor density. This vapor-density dependence was interpreted as being due to the imprisonment of the 3962-Å radiation. Imprisonment theory at low densities was applied to the experimental data to yield the following results: $\tau_0 = 6.78 \pm 0.06$ ns, $f_{3944} = 0.115 \pm 0.001$, and $f_{3962} = 0.116 \pm 0.001$. Experimental and theoretical results of other workers are presented for comparison with the results of the present work.

## INTRODUCTION

With the advent of tunable lasers, highly precise determinations of atomic mean lives have become a reality. A tuned laser permits the selective excitation of a level of interest, thus eliminating the population by cascading often obtained with nonselective sources of excitation. Currently, several groups of workers are active in carrying out high-precision lifetime determinations with lasers.[1-6] The present work gives the results of such a determination involving the $4s\ ^2S_{1/2}$ (25 347.756 $cm^{-1}$) resonance level in Al I.

## EXPERIMENTAL METHOD

The lifetime measurements of the present work were achieved using a previously described method of delayed coincidence for detection[7] and a tuned pulsed dye laser for excitation. In this method atoms in the vapor state are excited by the laser pulses, and the decay times of individual events are measured by a time-to-pulse-height converter and accumulated in a pulse-height analyzer. A system time calibration of $1.75 \pm 0.01$ ns per analyzer channel was used in the measurements to be reported here. In obtaining these measurements, the technique of crossed beams was utilized. This technique involves an exciting beam incident perpendicularly upon a beam of atoms, with light from the decay of an excited state viewed normally to the plane of the beams.

The aluminum atoms in the vapor state were obtained in a diffuse beam from a Knudsen effusion oven, which has a tantalum or tungsten cell as its central element. This high-temperature source has been used to produce beams of silver and uranium atoms[8,9] and has been described in detail in an earlier report.[7] In the initial attempt to achieve an aluminum atomic beam, the vaporous metal was found to attack the tantalum lid of the effusion cell clogging the orifice in the lid. X-ray analysis performed in conjunction with a scanning electron microscope established that "*SV*" impervious yttria-stabilized zirconia was unaffected by aluminum vapor. In the present experiment tungsten cells with such zirconia liners and lids were used successfully to produce beams of aluminum atoms. The sample of aluminum used was National Bureau of Standards Standard Reference Material 44a, which has been used to establish a freezing-point standard and is 99.9% pure with respect to the presence of other metals.

The measurements of the mean life of the $4s\ ^2S_{1/2}$ level were obtained by exciting the level with laser light at 3944.006 Å, corresponding to the resonance transition $3\ ^2P_{1/2} \rightarrow 4\ ^2S_{1/2}$, and observing at 3961.520 Å the decay to the upper level of the doublet ground state $4\ ^2S_{1/2} \rightarrow 3\ ^2P_{3/2}$. By utilizing separate wavelengths for excitation and detection the background from the exciting radiation is kept low. Since the $3\ ^2P_{3/2}$ level is only 112.061 $cm^{-1}$ above the zero ground state, it will be appreciably populated at the temperatures of 1500–1700 K used here to vaporize aluminum. Thus, the measured lifetimes will be lengthened by imprisonment of the 3962-Å radiation, and this effect must be taken into account in arriving at the natural (zero vapor density) mean life. The correction for imprisonment was made using a previously described method applicable at low optical densities.[10,11] In this method the natural mean life is determined from the $y$ intercept of a straight-line fit to a linear plot of the measured mean lives versus the absorption coefficients at the center of the Doppler-broadened spectral line.

The pulsed dye laser used was of the Hänsch configuration[12] and had a bandwidth calculated to be in the range 0.05–0.1 Å at 3944 Å.[12-14] It was pumped by a nitrogen laser with a pulse width of 8-ns full

 

width at half maximum and a peak power of 0.65 MW. The runs were carried out with a monochromator slit setting of 1 mm, representing a bandpass of 16 Å. A Corning-type 7-59 glass filter was used to reduce the scattered background light from the aluminum oven. The seven experimental runs made yielded values for the lifetime of 6.86, 6.80, 6.77, 6.86, 6.89, 7.36, and 7.51 ns at temperatures of 1474, 1485, 1492, 1570, 1618, 1734, and 1743 K, respectively. The natural mean life must now be derived from this set of temperature dependent measurements.

## CORRECTION FOR IMPRISONMENT

At the low optical densities used here, the theories of resonant photon imprisonment give[10,11]

$$\tau_m = \tau_0(1 + ak_0LB_r)\,, \tag{1}$$

where $\tau_m$ is the measured lifetime, $\tau_0$ is the natural (zero vapor density) lifetime, $a$ is a constant determined by the geometry of the source and exciting beams, $k_0$ is the absorption coefficient at the center of the Doppler-broadened resonance line, $L$ is a characteristic dimension of the source, and $B_r$ is the branching ratio of the resonance transition. Although some information is available on the values of $L$ and $a$ for this source,[15] knowledge of these parameters will not be needed in the analysis to be carried out here of fitting Eq. (1) to a linear plot of the experimental data. The absorption coefficient is given by the expression

$$k_0 = \frac{\lambda_0^3 n}{8\pi}\frac{g_2}{g_1}\frac{A_r}{v_0\sqrt{\pi}}. \tag{2}$$

Here, $\lambda_0$ is the wavelength at the line center, $v_0$ is the most probable thermal speed of an atom in the beam, $n$ is the particle density of atoms in the ground state, $A_r$ is the probability per unit time for emission of a quantum of resonance radiation by an isolated atom, and $g_2$ and $g_1$ are the statistical weights of the resonance and ground levels, respectively.

From Eq. (1) we see that for a given experimental geometry the measured lifetime is a function only of $k_0$. From Eq. (2) we see that $k_0$ varies directly with $n$ and inversely with $v_0$. Referring to Ramsey[16] and Klose,[9] we find that $v_0$ is proportional to $p'/T$, where $p'$ is the pressure inside the cell and $T$ is the absolute temperature. Thus, since $p'$ is itself dependent on $T$, consolidating the temperature dependent quantities gives $\tau_m$ as a function of $p'T^{-3/2}$. This result has been derived for the case of all the atoms of the beam in the zero ground state. For aluminum the ground term is a doublet with a splitting of 112.061 $cm^{-1}$. As has been mentioned above, the 112 $cm^{-1}$ level is the lower level of the 3962-Å transition, which was used to observe the decay, and since it was appreciably populated at the temperatures used, imprisonment of the 3962-Å radiation took place. Thus, in correcting for imprisonment here, $n_{112}$, the density of particles in the 112-$cm^{-1}$ state, replaces $n$. Assuming that $n = n_0 + n_{112}$ and making use of the expression

$$n_{112}/n_0 = g_{112}/g_0\ \exp[-(\epsilon_{112} - \epsilon_0)/kT]\,,$$

we can determine $b_{112}$, the fraction of particles in the 112-$cm^{-1}$ state. Since $n_{112} = b_{112}n$, the complete temperature dependence of $\tau_m$ is combined in the product $b_{112}p'T^{-3/2}$, and this quantity will be the independent variable in the linear plot according to Eq. (1).

Brightness temperatures were measured by sighting an optical pyrometer through a 7056 glass window on the aperture in the lid of the cell. After the brightness temperatures were corrected for reflections at the window surfaces,[17] the true temperatures were obtained by correcting for the nonblackbody character of the glowing cell. The blackbody corrections were carried out using normal spectral emittances for zirconia given by Touloukian and DeWitt[18] and the Gouffé expression for the emittance of a cavity given by Moore.[19] The values of $p'$ for the different temperatures were then obtained from the critically evaluated vapor pressure data for aluminum given by Hultgren *et al.*[20]

## RESULTS

Figure 1 presents the straight line least-squares fit to the plot of $\tau_m$ vs $b_{112}p'T^{-3/2}$. The fit was

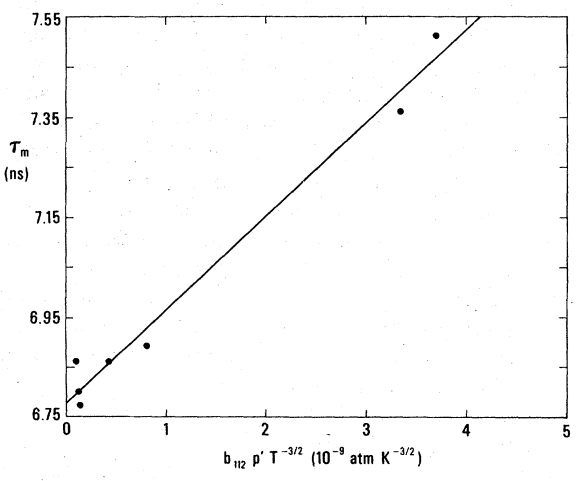


FIG. 1. Plot of $\tau_m$ vs $b_{112}p'\ T^{-3/2}$ showing the effect of radiation imprisonment at low particle densities for the $3p\ ^2P_{3/2}$-$4s\ ^2S_{1/2}$ (3961.520 Å) transition in AlI. A least-squares analysis was used to obtain the straight-line fit to the data.

TABLE I. Natural mean life and absolute $f$ values for the $4s\,^2S_{1/2}$ level in Al I.

| Authors | Method | $\tau_0$ (ns) | $f_{3944}$ | $f_{3962}$ |
|---|---|---|---|---|
| Present work | Delayed coincidence with laser excitation | 6.78 ± 0.06 | 0.115 ± 0.001 | 0.116 ± 0.001 |
| Bach[a] | Theory | 7.9 | 0.098 | 0.099 |
| Havey *et al.*[b] | Direct observation with laser excitation | 6.8 ± 0.3 | 0.11 ± 0.01 | 0.12 ± 0.01 |
| Migdalek[c] | Theory | 6.33 | 0.123 | 0.124 |
| Marek and Richter[d] | Phase shift | 6.94 ± 0.35 | 0.112 ± 0.006 | 0.113 ± 0.006 |
| Anderson and Anderson[e] | Theory | 6.86 | 0.114 | 0.114 |
| Smith and Liszt[f] | Phase shift | 6.9 ± 0.7 | 0.11 ± 0.01 | 0.11 ± 0.01 |
| Weiss[g] | Theory | 7.1 | 0.11 | 0.11 |
| Andersen *et al.*[h] | Beam foil | 6.4 ± 0.4 | 0.12 ± 0.01 | 0.12 ± 0.01 |
| Cunningham[i] | Phase shift | 7.05 ± 0.30 | 0.110 ± 0.005 | 0.111 ± 0.005 |
| Gruzdev and Prokof'ev[j] | Theory | 7.1 | 0.11 | 0.11 |
| Penkin and Shabanova[k] | Hook | 5.2 ± 1.4 | 0.15 ± 0.04 | 0.15 ± 0.04 |
| Demtröder[l] | Phase shift | 6.43 ± 0.12 | 0.121 ± 0.002 | 0.122 ± 0.002 |
| Bierman and Lübeck[m] | Theory | 6.0 | 0.13 | 0.13 |

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achieved using the complete least-squares procedure of Gerhold,[21] which fits to uncertainties in both the dependent and independent variables. The natural mean life is obtained from the $y$ intercept and is given in Table I along with other results for comparison.

Sources of systematic error in atomic lifetimes obtained by the present method are time scale calibration, background from stray laser light, collisional deexcitation, and photon pile-up from the occurrence of more than one decay photon per timing interval. Calibration of the time scale was achieved by providing known time delays with accurately measured coaxial cables. The deviation in linearity over a time delay corresponding to 171 channels was less than one channel, and thus an error of 1 in 171 or 0.585% was assigned to the time-scale calibration.

The background from stray laser light was kept low by detecting the decays to the 112-$cm^{-1}$ level at 3962 Å instead of to the zero level at the exciting wavelength of 3944 Å. No contribution to the background from stray laser light was detected in runs without an atomic beam but otherwise identical to the lifetime runs. Collisional deexcitation was found to be insignificant at the temperatures (1500–1700 K) and particle densities ($10^9$–$10^{11}$ $cm^{-3}$) used here. In the worst case the measured lifetime is shortened by ≈0.001%, according to the Stern-Volmer relation.[1,22] Finally, at the low data-collection rates of the present work the criteria of Coates[23] indicate that the corrections for photon pile-up are also negligible.

In determining the error in the natural mean life, the effects of the errors in the quantities in the abscissa of Fig. 1 must also be investigated. Throughout the lifetime runs the measured values of temperature showed a spread of ±2 K. The total errors in the values of $p'$ were obtained by combining the stated errors in the tabulated values[20] with the errors arising from the uncertainties in the measured temperatures. These total errors were found to be approximately 20%. The values at their error limits of the temperatures, pressures, fractions of atoms in the 112-$cm^{-1}$ state, and measured lifetimes were then used in plots similar to Fig. 1 to determine the contribution to the total error. The percentage error assigned to each measured lifetime was determined from the experimental standard deviation of the three measurements at approximately the same value of $b_{112}p'T^{-3/2}$ (see Fig. 1). In this manner the errors in the ordinates and abscissas were found to produce a standard deviation of 0.59% in the natural

mean life. This result was combined with the standard deviation in $\tau_0$ of 0.18% from the least-squares fit of Fig. 1 and the error in the time-scale calibration to yield the total standard deviation in the natural mean life. The total error is the root sum of the squares of the contributions and is given in Table I with the result of the present work.

The values of $f_{3944}$ and $f_{3962}$ given in Table I for the present work were derived from the natural mean life assuming $LS$ coupling. Likewise, $LS$ coupling was assumed in deriving $f$ values from lifetimes or lifetimes from $f$ values for the other results in Table I.

As can be seen from Table I, the experimental determinations of other workers generally agree with the results obtained in the present work. The other recent measurement using laser excitation is in excellent agreement with the present work, and only the early measurements of Penkin and Shabanova and of Demtröder fail to overlap the error limits of the present results. The theoretical values, with one exception, fall within approximately 10% of the present results.

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