UCRL-17414

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Submitted to the Journal of the Optical Society of America

UCRL-17414
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

MEASUREMENT OF LIFETIMES OF EXCITED STATES OF Na, Tl, In, Ga, Cu, Ag, Pb, AND Bi BY THE PHASE SHIFT METHOD.

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February 1967

Measurement of Lifetimes of Excited States of Na, Tl, In, Ga, Cu, Ag, Pb, and Bi by the Phase Shift Method.

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Lifetimes of thirteen upper states of optical resonance transitions in selected metal atoms have been measured using the phase shift method. Data were taken over a range of at least twelve in fluorescence intensity to allow the effects of radiation entrapment and exciting light scattering to be taken into account. The following results were obtained: Na 3p $^2P^o$ 16.2 nsec, Tl 7s $^2S_{1/2}$ 7.65 nsec, Tl 6d $^2D_{3/2}$ 6.9 nsec, In 6s $^2S_{1/2}$ 7.5 nsec, In 5d $^2D_{3/2}$ 7.9 nsec, In 5d $^2D_{5/2}$ 7.9 nsec, Ga 5s $^2S_{1/2}$ 7.6 nsec, Ga 4d ^2D 7.7 nsec, Cu 4p $^2P^o$ 7.2 nsec, Ag 5p $^2P^o_{3/2}$ 6.7 nsec, Ag 5p $^2P^o_{1/2}$ 7.5 nsec, Pb 7s $^3P^o_1$ 6.05 nsec, and Bi 7s $^4P_{1/2}$ 5.9 nsec. Estimated absolute accuracies vary between 3 and 7 percent.

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Introduction

It is only in the last several years, with the development of vapor density independent techniques of atomic transition probability measurement, that more than a few experimentally determined transition probabilities with accuracies of 10% or better have been available. The older literature on atomic transition probabilities[1] is full of widely divergent and inaccurate results. This situation is best illustrated by the important volume on transition probabilities by Corliss and Bozman[2] which was published in 1962. They chose only eighteen experimental absolute f-values as reliable enough for use as a basis for normalization factors. Since then all but three of the numbers have been redetermined by methods which should be reliable to 10%. Examination of the values Corliss and Bozman used shows that only those f-values they selected for the resonance transitions of the alkali metals agree to within 10% with the best numbers available as of fall 1966.

The currently popular methods which produce vapor density independent results are level-crossing,[3] optical-double-resonance,[3] and the phase-shift technique.[4] Under favorable circumstances and when used properly they are capable of generating lifetimes with better than 10% absolute accuracy. The commonly used vapor density dependent techniques of transition probability measurement are the hook method,[5] the atomic beam method,[6] the method of magneto-rotation,[7] the absorption tube method,[8] and the emission arc method.[2] They all

reflect the 10% or greater uncertainties in the best available vapor pressure data[9] or contain serious sources of error if a direct vapor density determination is involved.

For the work described in this paper, the state being studied is optically excited with intensity modulated light. The phase shift between the exciting and fluorescent light, $\Delta\phi$, is related to the lifetime, τ, by the relation $\tan \Delta\phi = \omega\tau$, where ω is the radial modulation frequency. The phase-shift apparatus and experimental procedures have been described in a previous paper.[10] Only differences in experimental procedure and apparatus will be discussed here.

Apparatus and Procedure

The phase-shift apparatus has previously been used for the measurement of the lifetimes of the first excited states of the alkali metals.[10] The alkali metal atoms were contained in heated pyrex cells. All of the lifetimes reported in this paper were measured while the metal atoms were in an atomic beam. For Na a quartz crucible was used while all of the other elements were vaporized from carbon crucibles. In all cases 0.002 inch tantalum foil heating elements were used. A residual gas pressure of about 5×10^{-5} torr was maintained in the atomic beam chamber.

During the course of several Ag runs a marked sluggishness in the variation of fluorescence intensity with change in furnace heating power was observed. This was attributed to the melting or solidifying of the Ag metal in the crucible. Assuming fluorescent intensities to

be proportional to Ag beam densities and using the melting point where the vapor pressure of Ag is roughly 0.003 torr to relate the fluorescent intensity to the Ag vapor pressure inside the crucible one concludes that a typical run went from crucible pressures of about 2.5×10^{-4} torr (limit of detectability of fluorescence) to roughly 1.2×10^{-2} torr (beginning of entrapment of resonance light in the beam). This corresponds to a range of Ag atom density in the beam of from about 10^8 to 6×10^9 per cc. These numbers, when scaled by appropriate f-value and doppler width ratios, should be typical of all the metals studied. It should be noted that the mean free path of a fluoresced photon in an atomic beam, with a total opening angle of 40° and a direction of photon travel perpendicular to both the mean motion of the beam and the exciting light, will be about ten times less than in the atomic gas at thermal equilibrium at the same temperature and density.

The photomultiplier, which viewed the fluorescent light from the atomic beam, faced perpendicular to and was set back 14 cm from the path of the exciting light. A 7.5 cm focal length quartz lens, with a 6.4 cm diameter, was placed in the vacuum chamber to focus fluorescent light from the atomic beam onto the photocathode and thus extend the accessible fluorescence intensity range when low light level was a problem.

The atomic beam was collimated to a total opening angle of about 40 degrees. Light baffles were used about the atomic beam and in front of the fluorescence photomultiplier so that light emitted by

the glowing heating element had to scatter off at least two surfaces before it could reach the photocathode. The inside of the vacuum chamber was blackened to further reduce light scattering. The entrance and exit window ports for the exciting light were set back in 10.5 cm deep side arms to minimize the amount of exciting light which could reach the photocathode by scattering off the entrance and exit windows (the latter was a large Wood's horn).

The exciting light phase was measured by swinging a piece of frosted glass directly above the crucible orifice and in front of the photomultiplier so that the exciting light was diffusely reflected onto the photocathode. The frosted glass was mounted above a beam shutter which blocked the atomic beam while the exciting light phase was being determined. Before each run the phase of the exciting light as read off the frosted glass plate was carefully checked against the phase read off a dilute $Al(OH)_3$ scattering sol.

The lifetime of the Na ^2P state was measured as a consistency check to see if lifetimes measured from the atomic beam agreed with those measured while the metal vapor was at equilibrium in a sealed cell.[10] In the work with sealed cells it was clear that the use of a dilute scattering sol would exactly reproduce the fluorescent geometry. This was important because the transit time of electrons through a photomultiplier can vary by several nsec depending upon where on the photocathode they are ejected.[11] The use of a dilute sol to scatter the exciting light in the atomic beam lifetime work reported here did not exactly reproduce the fluorescent geometry as the density

of scattering particles in the sol was uniform throughout the sol while the density of atoms in the illuminated portion of the atomic beam was greatest in the region directly above the crucible orifice and decreased monotonically as a function of distance away from that region. The agreement of the Na ^2P state lifetime measurements in the atomic beam (16.2 nsec) with those in a sealed cell (16.1 nsec)[10] to within less than the random experimental uncertainly indicated that the inability of the uniform scattering sol to exactly reproduce the fluorescent geometry was not an important source of systematic error.

If the frosted glass plate had slight deposits of metal on it, which were often undetectable to the eye, it would scatter some parts of the exciting light beam more efficiently than others and thus not give the same exciting light phase as the sol. This was because the phase of the exciting light varied by about 10 degrees over its cross section even after careful alignment and focusing of the light modulator. If the light modulator was out of alignment, the variation of the phase of the exciting light across its cross section was much greater and the exciting light phase would not be the same in going from the sol to the frosted glass plate. After proper alignment of the modulator and with the frosted glass plate clean the two phase readings would agree to within the sensitivity of the phase meter (0.2 degrees or 0.1 nsec).

Atomic Resonance Lamps

Except for Na where an Osram lamp was used, all the resonance lamps were made of well out-gassed quartz tubing 8 mm O.D., 6 mm I.D., and about 5 cm long. They were excited by micro-waves at 2,450 Mc by a 100 watt diathermy unit using a type 'A' antenna.

A simple heater was used for the Cu, Ag, Tl, Bi and Pb lamps. The lamp slipped smoothly into a piece of 9 mm I.D. quartz wrapped uniformly with #28 Nichrome wire. The lamp and heater were then fitted inside a 18 mm I.D. outer quartz jacket to reduce convection currents and improve the heating efficiency.

The Cu, Ag, and Bi lamps contained a small amount of distilled iodide of the element and about 1 torr of Argon. In, Ga, and Pb iodide lamps made in the above manner were unstable and showed severe self-reversal of the strong resonance lines. This is because the In, Ga, and Pb iodides are sufficiently volatile that the heating of the lamp by the micro-wave power causes a high density of halide vapor which leads to a high density of electrons which causes instability and a high density of atoms leading to self-reversal of the resonance lines. The Tl lamp contained a small amount of distilled Tl and about 1 torr of Argon. This was found to work better than a halide lamp.

The following procedure was developed to allow introduction of such a small amount of In, Ga, and Pb iodide into the lamp that it could completely vaporize without interfering with the stability and useful brightness of the lamp. A small piece of metal (undistilled) was placed in the unsealed lamp. Iodine in contact with a temperature bath

provided 0.03 torr of I_2 pressure (about 2.2×10^{-9} moles) in the case of In and Ga and 0.22 torr for Pb. One torr of Argon was added and the lamp sealed off. The metal was left undistilled so that no appreciable formation of iodide would occur before the lamp was sealed off and thus the total amount of iodide formed in the lamp was closely controlled. Excitation with micro-waves and mild heating then caused the formation of the iodide.

The Pb lamp ran best with slight heating, the In lamp with no heating, and the Ga lamp with air cooling. In all cases the micro-wave power level and the amount of heating or cooling was adjusted until maximum fluorescence was produced at constant atomic beam density. A properly operating resonance lamp was characterized by a marked weakening or disappearance of the molecular halide and Argon features with respect to the atomic emission lines. The Na Osram lamp was run by a square wave generator to minimize low frequency ripple.

The atomic beam had a total opening angle of about 40 degrees so its effective doppler width was about 1/3 of that of atoms in thermal equilibrium at the crucible temperature. Thus maximizing the fluorescent light produced meant that the lamps were emitting reasonably sharp unself-reversed lines. Tests made with Tl using 3776Å and Cu using unresolved 3247 and 3274Å showed that atomic beams of high densities, corresponding to severe radiation entrapment, could absorb up to 1/3 of the exciting resonance lines.

Table I.

Summary of Experimental Parameters

Element	Wavelength in Å	Wavelength Isolation Filters	Photomultiplier	Range of $1 + \frac{I_f}{I_s}$ Free of Entrapment
Na	5890 5896	Interference filter 100 Å band pass	RCA 7265	60
Tl	3776	Wratten #39	RCA 7265	400
Tl	2768	Nickel-cobalt sulfate solution	Amperex 56UVP	12
In	4101 4511	Corning #0-52 Wratten #39	Amperex 56UVP	50
In	3256 3259 3039	Schott UG11	Amperex 56UVP	30
In	3256 3259	Schott UG11	RCA 7264	
Ga	4033 4172	Wratten #39	RCA 7264	40
Ga	2874 2944	Nickel-cobalt sulphate solution Corning #9-59	Amperex 56UVP	15
Cu	3247 3274	Schott UG11	Amperex 56UVP	16
Ag	3281 3383	Schott UG11	RCA 7264	16
Ag	3383	Schott UG11 Crown Glass lens	RCA 7264	7
Pb	2833	Nickel sulphate solution	Amperex 56UVP	50
Bi	3068	Schott UG11	Amperex 56UVP	25

Analysis and Results

Table I gives the wavelength isolation filters and photomultipliers used along with the range of $(1 + I_f/I_s)$, where I_f is the fluorescent intensity and I_s the scattered light intensity, over which lifetimes could be measured before the onset of more than a 2% lengthening of the measured lifetime due to radiation entrapment.

Figure 1 shows the atomic energy levels of interest for all of the atoms studied. Figure 2 shows a plot of τ_m against $(1 + I_f/I_s)$ for the Tl $^2S_{1/2}$ state. Figure 3 shows a similar plot for data taken on the Ag $(0.9\ \tau\ ^2P_{1/2} + 0.1\ \tau\ ^2P_{3/2})$ measurement. These two plots show the largest and smallest range of $(1 + I_f/I_s)$, 400 in the case of the Tl $^2S_{1/2}$ state and only 7 in the case of the Ag $(0.9\ \tau\ ^2P_{1/2} + 0.1\ \tau\ ^2P_{3/2})$ measurement, which were observed before the onset of radiation entrapment lengthening of the measured lifetime.

The lifetimes measured in this work along with their estimated errors are given in the third column of Table II. The error estimates are the sum of 0.1 nsec for systematic error and the estimated uncertainty in fitting the experimental data to the theoretical curve[10] for the unentrapped region as given by

$$\tau_m = \tau\left\{1 - \frac{1}{\frac{I_f \cos \Delta\phi}{I_s} + 1}\right\} . \qquad (1)$$

According to this relation the measured lifetime τ_m varies from zero, pure scattered exciting light, to τ, the true lifetime, as I_f/I_s increases from zero to at least 200.

Table II. Lifetimes for States of Eight Elements

Element	State	τ nsec	Other Measurements in nsec. phase shift	level crossings	atomic beam	hook	absorption tube	misc.
Na	$3p\ ^2P^o$	16.2 ± 0.3	16.1 ± 0.3[a] 15.9 ± 0.4[b]	16.3 ± 0.5[c]				16.1 ± 0.8[d]
Tl	$7s\ ^2S_{1/2}$	7.65 ± 0.2	8.7 ± 0.3[e]	7.6 ± 0.2[f]	8.1 ± 0.8[g'']	8.25 ± 0.6[h]		
Tl	$6d\ ^2D_{3/2}$	6.9 ± 0.4		6.2 ± 1.0[f] 5.2 ± 0.8[i]	6.65 ± 1.0[g'']	6.9 ± 0.5[h]		
In	$6s\ ^2S_{1/2}$	7.5 ± 0.3	8.5 ± 0.1[b]		8.35 ± 1.2[g]	6.3 ± 0.8[h]		
In	$5d\ ^2D_{3/2}$	7.9 ± 0.5			8.55 ± 0.9[g]	6.35 ± 0.8[h]		
In	$5d\ ^2D_{5/2}$	7.9 ± 0.5			9.9 ± 1.5[g]	6.4 ± 0.8[h]		
Ga	$5s\ ^2S_{1/2}$	7.6 ± 0.4	9.9 ± 0.2[e]		11.4 ± 1.7[g]	6.4 ± 2.4[j]		
Ga	$4d\ ^2D$	7.7 ± 0.3*			9.7 ± 1.4[g*]	6.6 ± 2.4[j*]		
Cu	$4p\ ^2P^o$	7.2 ± 0.3		7.2 ± 0.7[k] 7.0[l]	7.4 ± 0.7[m]	5.0 ± 0.8[n+]	6.5 ± 1.0[p+]	
Ag	$5p\ ^2P^o_{3/2}$	6.7 ± 0.4		7.4 ± 0.7[k] 6.7[l]	7.2 ± 0.7[g]	6.4 ± 0.7[q]	7.0 ± 0.8[o]	
Ag	$5p\ ^2P^o_{1/2}$	7.5 ± 0.4			8.0 ± 0.8[g]	7.0 ± 0.8[q]	8.75 ± 1.0[o]	
Pb	$7s\ ^3P^o_1$	6.05 ± 0.3		5.75 ± 0.2[r]	4.2 ± 1.0[s-]	5.2 ± 0.6[t]		
Bi	$7s\ ^4P_{1/2}$	5.9 ± 0.2						$5.3\ ^{+2.3}_{-1.7}$[u'] 8.9 ± 1.8[v']

Sodium

The hook method results of Kvater[12] indicate that the lifetimes of the $^2P_{1/2}$ and $^2P_{3/2}$ states are equal to better than 1%, so no attempt was made to separate the two D-lines.

Thallium

The Tl and argon electrodeless discharge lamp emitted at least ten times more fluorescence producing light at 2767Å than did a Tl Osram lamp with a special quartz jacket.

While studying the $^2S_{1/2}$ state lifetime with a 7265 photomultiplier a lengthening in measured lifetime of the order of one nsec was observed when the fluorescence was viewed at 5350Å instead of at the excitation wavelength 3776Å.[13] The effect was attributed to variation in electron transit time between the photocathode and the first dynode with different incident photon energies. As expected, the transit time difference was found to be proportional to the reciprocal of the photocathode-to-first-dynode voltage.

Indium

The $^2P_{3/2}$ state lies only 0.27 ev above the ground state (see Figure 1) and so had a population of about 15% at the temperatures needed to produce the atomic beam. This meant that the $^2D_{5/2}$ state was being excited as well as the $^2D_{3/2}$ state when only a Schott UG-11 wavelength selection filter was used. However the S-11 spectral response of the RCA 7264 tubes falls sharply between 3256Å and 3039Å.

It was found that the ratio of fluorescent light at 3039Å to that at 3256 and 3259Å was 1/8 as seen by the 7264 tube while it was 1/0.8 as seen by the Amperex 56UVP with its U spectral response. The relative intensity measurements were made using a 1/4-meter Farrand Ultra-Violet Visible Grating Monochrometer with a 100Å band pass. The same phase shift was obtained for both tubes indicating that the lifetimes of the $^2D_{3/2}$ and $^2D_{5/2}$ states are equal. In this analysis the ratio I_{3039}/I_{3259} was taken to be 4.5 from averages of the relative f-values for the two transitions taken from Lawrence et al.[14] and from Penkin and Shabanova.[15]

In the case of the $^2S_{1/2}$ state both the fluorescent and exciting light had the same intensity ratio for I_{4511}/I_{4101} so there was no problem from the wavelength effect on photomultiplier transit time. Using an interference filter to eliminate 4511Å in the exciting light while viewing about an equal mixture of 4101 and 4511Å in fluorescence with an Amperex 56UVP caused at most a 0.1 nsec lengthening of the observed lifetime. The wavelength effect decreases markedly with increasing photon energy and was not a problem while making measurements on the ^2D states.

Gallium

The $^2P_{3/2}$ state lies only 0.10 ev above the $^2P_{1/2}$ ground state (see Figure 1). At the temperatures used to produce the Ga atomic beam (~1500°K) both states were about equally populated. Relative intensity measurements on the fluorescent light at 2874Å and 2944Å

indicated that the measured lifetime was an equally weighted average of the lifetimes of the $^2D_{3/2}$ and $^2D_{5/2}$ states. The exciting and fluorescent light had roughly the same wavelength composition for both the $^2S_{1/2}$ and ^2D state measurements. Measurement of ^2D state lifetime with and without a Corning #9-53 cut-off filter in the exciting light beam produced no change in lifetime thus indicating that the presence of small amounts of light of wavelength shorter than 2800Å, which could excite the 6s $^2S_{1/2}$ state, was not a problem.

Copper

A branching ratio of 0.985 for both $^2P_{3/2}$ - $^2S_{1/2}$ and $^2P_{1/2}$ - $^2S_{1/2}$ transitions was computed using an average of the results of Riemann[16] and of Corliss and Bozman.[2] The hook method relative f-values for the two transitions obtained by Ostrovskii and Penkin[17] then predict equality of the two upper state lifetimes to within experimental uncertainties. Therefore no attempt was made to separate the two resonance lines during the lifetime measurements.

Silver

The fluorescence intensity ratio seen by the RCA 7264 tube through a Schott UG-11 filter was $I_{3383}/I_{3281} = 2/3$ when the lamp was set to produce maximum fluorescence. A lifetime measured under these conditions was then resolved in the following way: $0.4\ \tau\ ^2P_{1/2} + 0.6\ \tau\ ^2P_{3/2} =$ 7.0 nsec. A crown glass lens was found which transmitted 3383Å but attenuated 3281Å quite strongly. With this lens in the system a

lifetime was measured which was determined to be $0.9\ \tau\ ^2P_{1/2} + 0.1\ \tau\ ^2P_{3/2} = 7.4$ nsec. The two equations yield a lifetime of 6.7 nsec for the $^2P_{3/2}$ state and 7.5 nsec for the $^2P_{1/2}$ state.

Lead

The 2833Å line was observed in fluorescence over an entrapment free range of $(1 + I_f/I_s)$ of 50. Since the branching ratio for the 2833Å line is only 0.27,[18] only about 1/3 of the fluorescent photons were used.

Bismuth

Useful Bi beams were produced at crucible temperatures of around 900°K. At this temperature about 40% of the beam was Bi_2 molecules.[9] The Bismuth iodide resonance lamp did not emit any detectable Bi_2 radiation and there are no Bi_2 lines in the vicinity of the 3068Å atomic Bi resonance line so the presence of Bi_2 molecules in the beam had no effect on the atomic lifetime measurements.

Discussion

In many cases the "other measurements" given in the last six columns of Table II have been derived from reported absolute f-values using the following relations:

$$f_{mn} = 1.499\lambda^2_{mn}\ A_{mn}\ g_m/g_n$$

$$\tau_m = 1/\sum_n A_{mn}$$

where λ_{mn} is the wavelength of the transition in cm, g_m and g_n the statistical weights of the upper and lower states respectively, and A_{mn} the transition probability in sec^{-1}.

The error estimates for the hook and absorption tube methods were computed on the basis of the uncertainty estimates given for the vapor pressure data by Hultgren et al.[9] These uncertainties in all cases far exceeded the reported experimental scatter.

A discussion of the data in Table II will be given only for those cases where special comment or explanation is necessary.

Sodium

The lifetime listed under misc. in Table II was obtained by Weingeroff[19] using a version of the method of magneto-rotation which was vapor density independent.

Thallium

We found in the course of work on the $^2S_{1/2}$ state with a 7265 photomultiplier that lifetimes measured using λ3776 for excitation and viewing only λ5350 in fluorescence (see Figure 1) gave lifetimes which were roughly 1 nsec too long due to the variation in electron transit time between photocathode and first dynode with incident photon energy. Demtroder[20,21] indicates that he also viewed the fluorescence at λ5350 while exciting the $^2S_{1/2}$ state with λ3776 and that further lifetime work at Bonn has produced a lifetime in agreement with the number reported from our experiment.

In the case of the $^2D_{3/2}$ state the two $\Delta m = 2$ high field level crossings can not be resolved. This leads to a dependence of the level crossing results on exciting lamp profile[3,22] and a large uncertainty in the $^2D_{3/2}$ state lifetime as determined by level crossings. Gallagher and Lurio[3] based the absolute f-values given in Table I of their paper on hook method relative f-values reduced to an absolute scale using their value for the 7s $^2S_{1/2}$ state lifetime and an average of their value and that of Kvater[23] for the transition probability ratio $A(7\ ^2S_{1/2} - 6\ ^2P_{3/2})/A\ (7\ ^2S_{1/2} - 6\ ^2P_{1/2})$. They used the hook method ratio of 0.461 reported by Prokof'ev and Filippov[24] for $\frac{f3776}{f2768}$. N. P. Penkin[25] feels that the work of Prokof'ev and Filippov[24] contains a systematic error due to using a prism spectrograph and that the value $\frac{f3776}{f2768} = 0.427 \pm 0.003$[15] measured using a grating spectrograph is more reliable. The ratio $\frac{f3776}{f2768} = 0.445$ reported by Penkin[26] is merely the average of the ratios from references 24 and 15. If the n $^2D_{3/2}$ - 6 $^2P_{1/2}$ numbers in Table I of Gallagher and Lurio's[3] paper are adjusted to the best hook method $\frac{f3776}{f2768}$ ratio[15] a lifetime of 6.3 ± 0.5 nsec for the 6d $^2D_{3/2}$ state is obtained in better agreement with the direct level-crossing values[3,22] than with the results of this experiment.

Gallium

Demtroder,[20] who also used the phase shift method, reports a lifetime of 9.9 nsec for the $^2S_{1/2}$ state. He, however, estimates that his lifetime may be 6% long because the limited sensitivity of his equipment may have made lifetime measurements at Gallium densities low enough to eliminate radiation trapping effects impossible.

The lack of agreement with the atomic beam method[14] values $\tau\ ^2S_{1/2}$ 11.4 nsec and $\tau\ ^2D$ 9.8 nsec may be due to the Ga beam's failure to form a pure Ga deposit on the micro-balance pan but rather one which was augmented by absorption or gettering of residual gas in the vacuum chamber thus leading to calculated Ga beam densities which were too large and f-values which were erroniously small as has been observed in the case of Cu.[27]

Copper

The Nf values reported by King and Stockbarger[8] and by Ostrovskii and Penkin[17] were combined with the latest vapor pressure data on Copper given by Hultgren et al.[9] to recalculate absolute f-values. King and Stockbarger,[8] Ostrovskii and Penkin,[17] and Ashenfelter[27] measured only f-values for the resonance transitions at λλ3247 and 3274. An average of the emission arc results of Corliss and Bozman[2] and Riemann[16] gives a branching ratio of 0.015 for transitions to the low lying ^2D states (see Figure 1). Therefore a branching ratio of 0.985 was used to convert their reported resonance transition f-value to a lifetime. Ashenfelter's[27] f-values of 0.427 for the 3247Å transition and 0.206 for the 3274Å transition differ by more than quoted uncertainties from those given by Bell et al.[6] who used the same atomic beam method. Ashenfelter placed a heating coil around the micro-balance pan which was used to monitor the atomic beam density. This apparently reduced the amount of residual gas from the vacuum chamber which was trapped on the micro-balance pan thus leading to a lower deposit rate and a larger f-value. Also Ashenfelter's residual vacuum pressure was about ten times less than that of Bell et al.[6]

Lead

The 7s $^3P_1^o$ state can decay to five lower states (see Figure 1). The results of Corliss and Bozman[2] set the branching ratio to the $^1D_2$ and $^1S_0$ states at less than 0.01 and in converting the atomic beam and hook method f-values for λλ2833, 3640 and 4058 to a $^3P_1^o$ state lifetime it was neglected. The f-value of 0.23 for the 2833Å resonance transition obtained by Bell and King[28] was combined with the branching ratio for that transition of 0.27 given by Saloman and Happer[18] in calculating the atomic beam lifetime given in Table II.

Bismuth

Corliss and Bozman[2] report the $^4P_{1/2}$ to $^2D_{3/2}$ branching ratio as 0.026. They list nothing for the $^4P_{1/2}$ to $^2P_{1/2}$ branching ratio (see Figure 1) but it can be assumed to be less than 0.01. The f-value given by Lvov[29] for the 3068Å line was converted to a lifetime for the $^4P_{1/2}$ state by assuming its branching ratio to be 0.97.

The method for determining the absolute f-value of a transition described by Rice and Ragone[30] is correct only if the transition being studied is the only one depopulating the upper state. For a general transition they need the branching ratio for the transition in order to obtain the upper state lifetime and the absolute f-value of the transition. In the definition of the integrated absorption S, and in equations (7) and (12), of Rice and Ragone's paper,[30] the lifetime τ should be replaced by 1/A where A is the transition probability for

the specific transition being observed. Use of the branching ratio 0.97 instead of 1.00 for the 3068Å line changes Rice and Ragone's $^4P_{1/2}$ state lifetime from 5.4 to 5.3 nsec.

Comparison of the results of this work with other phase shift results, shown in column 4 of Table II, indicates agreement only in the case of Na.[31] For Tl[20] and Ga[20] the differences have already been discussed. The work on the In $^2S_{1/2}$ state by Hulpke et al.[31] was done over a range of beam densities and the lifetime obtained by extrapolation to zero beam density so there should be no error due to radiation entrapment. Furthermore the lifetimes of Hulpke et al.[31] for Ca, Sr, and Ba all agree with the latest level crossing results[32,33] to better than 10%. Therefore the difference between the In $^2S_{1/2}$ state lifetime reported by Hulpke et al. and that of this work remains unexplained.

The most striking aspect of the comparison data in Table II is that in all cases where the method of level crossing gives an unambiguous result (Na $^2P^o$ [34], Tl $^2S_{1/2}$ [3], Cu $^2P^o_{3/2}$ [35,36], Ag $^2P^o_{3/2}$ [35,36], and Pb $^3P^o_1$ [18] but not Tl $^2D_{3/2}$ [3,22]) there is agreement with the results of this experiment to within 10% or better.

The comparison, in Table II, of atomic beam method lifetimes with the results of this experiment doesn't always show agreement to within quoted uncertainties. For Ag $^2P^o_{3/2}$ and $^2P^o_{1/2}$ [14], Tl $^2S_{1/2}$ and $^2D_{3/2}$ [14], Cu $^2P^o$ [27], and In $^2S_{1/2}$ and $^2D_{3/2}$ [14] the agreement is within 10%. While for Pb $^3P^o_1$ [28], Ga $^2S_{1/2}$ and ^2D [14], and In $^2D_{5/2}$ [14] the differences range from 16 to 40%. The case of Cr should be noted here.

The recent level crossing results of Bucka et al.[37] differ by about 25% from the atomic beam values of Lawrence et al.[14] Thus it seems that although in many cases the atomic beam method will give transition probabilities accurate to 10%, it does not at present seem possible to predict beforehand for which elements this will be true. Therefore the atomic beam method can not be considered to be a priori reliable to 10% as can the level crossing technique and the phase shift method.

Examination of the hook and absorption tube results, in Table II, shows the Tl[15], Ga [38], Ag [39,40], Cu[8] (absorption tube), and Pb[41] lifetimes to agree with the results of this experiment to within estimated uncertainties in the vapor pressure data. The lack of agreement for the In[15] lifetimes may indicate unestimated inaccuracies in the vapor pressure data and for the Cu[17] (hook method) the failure in attainment of equilibrium vapor pressures under the conditions of the experiment.

Acknowledgment

This work was performed under the auspices of the United States Atomic Energy Commission.

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Key to Table II.

a. Link (1966)[10]

b. Hulpke, Paul and Paul (1964)[31]

c. Markova and Chaika (1964)[34]

d. Weingeroff (1931)[19]

e. Demtröder (1962)[20]

f. Gallagher and Lurio (1964)[3]

g. Lawrence, Link, and King (1965)[14]

h. Penkin and Shabanova (1963)[15]

i. Gough and Series (1965)[22]

j. Penkin and Shabanova (1965)[38]

k. Levin and Budick (1966)[35]

l. Bucka, Ney and Heppka (1966)[36]

m. Ashenfelter (1965)[27]

n. Ostrovskii and Penkin (1957)[17]

o. Moise (1966)[40]

p. King and Stockbarger (1940)[8]

q. Penkin and Slavenas (1963)[39]

r. Soloman and Happer (1966)[18]

s. Bell and King (1961)[28]

t. Penkin and Slavenas (1963)[41]

u. Rice and Ragone (1965)[30]

v. Lvov (1965)[29]

* $\frac{1}{2}(\tau\ ^2D_{3/2} + \tau\ ^2D_{5/2})$

Key - continued

+ $(\frac{2}{3}\tau\ ^2P_{3/2} + \frac{1}{3}\tau\ ^2P_{1/2})$ revised using latest vapor pressure data.

- f(2833) combined with branching ratio of 0.27 from Soloman and Happer[18]

' Assuming branching ratio of 0.97 for λ 3067.

" f(3776) and f(2768) combined with $\frac{f(3776)}{f(5350)}$ and $\frac{f(3529)}{f(2768)}$ ratios from Penkin and Shabanova[38]

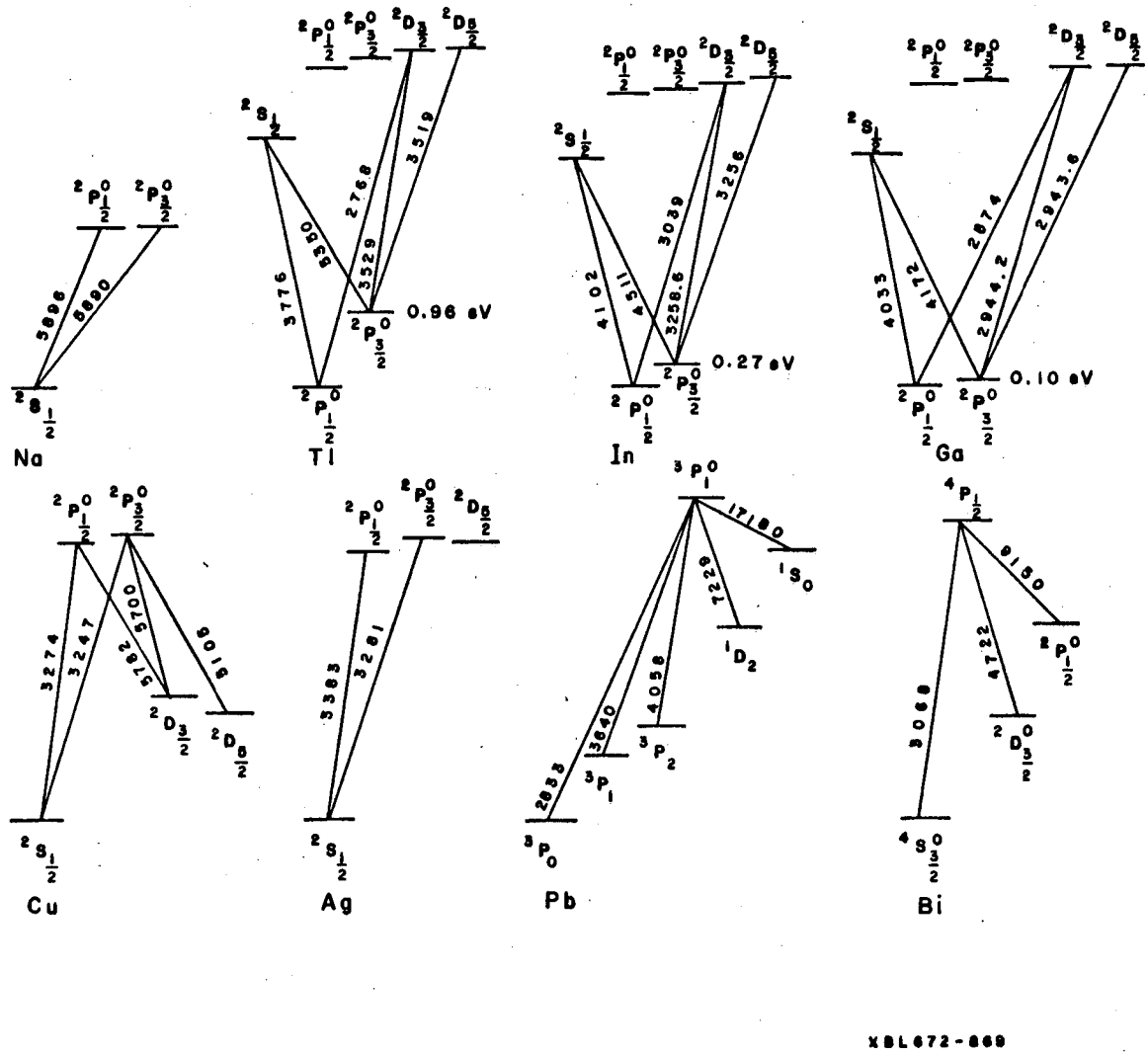

Figure 1. Atomic energy levels and transition wavelengths, given in Å, for all the states studied. The energy level spacings are drawn to scale. The $^2P_{1/2}$ to $^2P_{3/2}$ level spacing is given in electron volts for Ga, In and Tl.

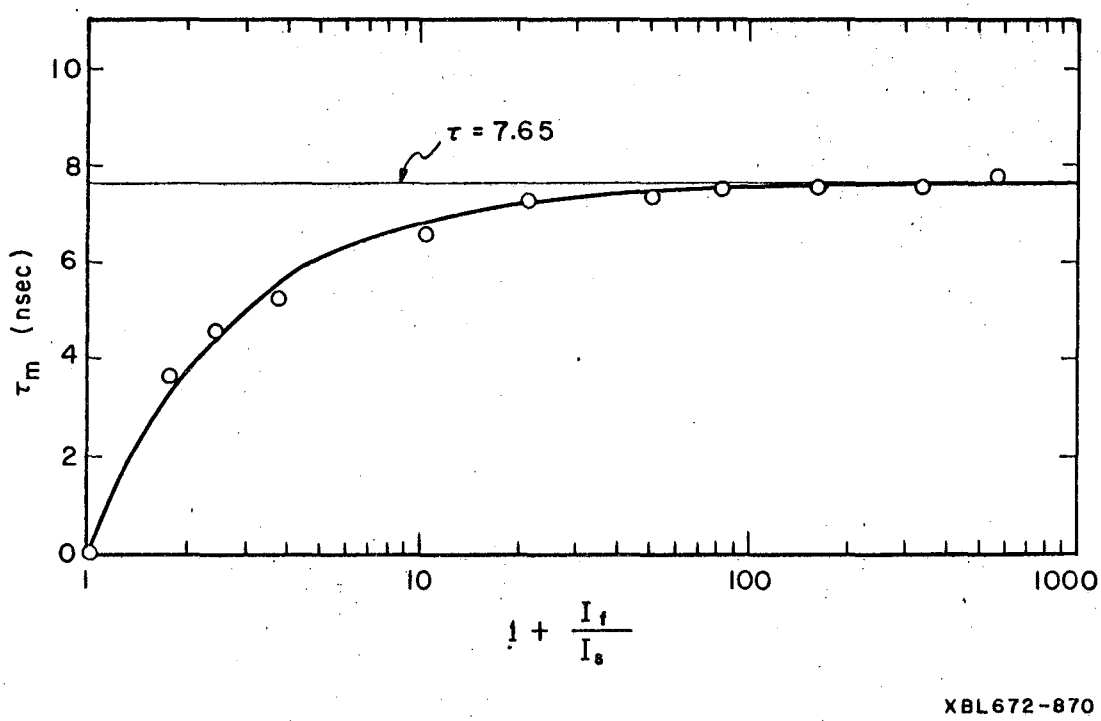

Figure 2. Experimental τ_m values for the 7s $^2S_{1/2}$ state of Tl. The solid curve is calculated using Eq. (1) and a true lifetime, τ, of 7.65 nsec. Entrapment starts where $(1 + I_f/I_s) \simeq 500$.

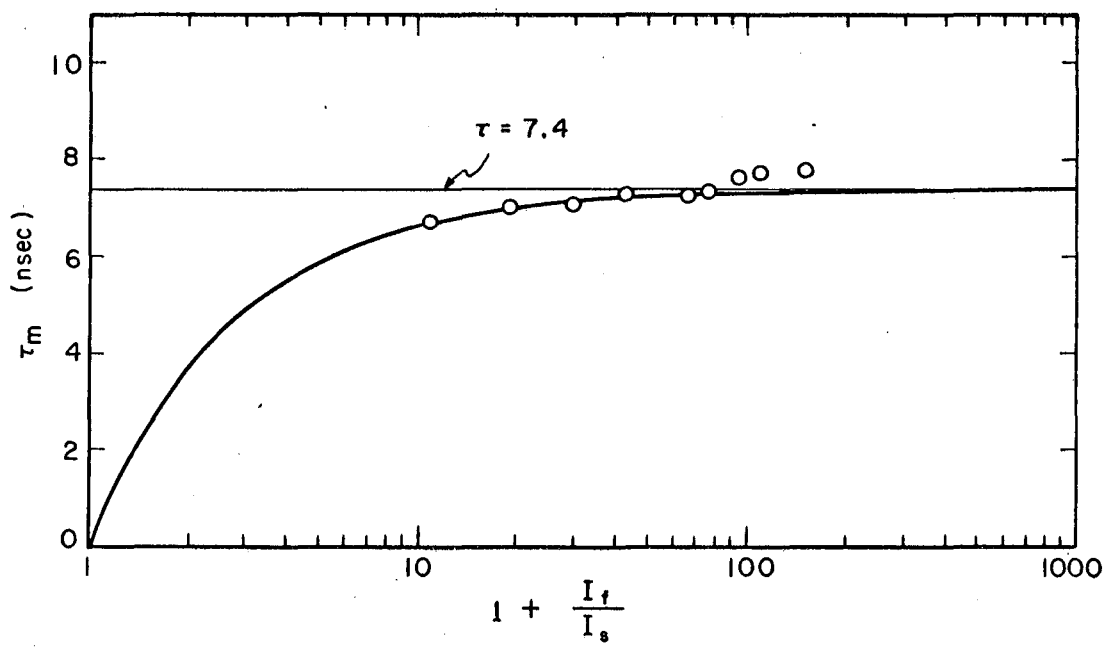

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Figure 3. Experimental τ_m values for the Ag ($0.9\ \tau\ ^2P_{1/2} + 0.1\ \tau\ ^2P_{3/2}$) measurement (see text). The solid curve is calculated using Eq. (1) and a true lifetime, τ, of 7.4 nsec. Entrapment starts where $(1 + I_f/I_s) \simeq 80$.

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