MEAN LIVES OF LINES OF MERCURY TRIPLET $2^3P_{012}-2^3S_1$

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Abstract

The mean life of each of three lines coming from the same upper level in the mercury atom has been measured. The triplet $2^3P_{012}-2^3S_1$ was excited by electron impact under conditions involving negligible ionization and concentration of excited atoms. The method was that previously described by Webb, in which high frequency voltages are applied in phase to the excitation and detecting systems. The lines were excited in a sealed-off tube with mercury pressures between 0.004 and 0.03 mm. The exciting voltage was less than ten volts. The excitation was such that there was no appreciable concentration in the $2P$ states. A specially designed potassium-hydride photoelectric cell was used as the detecting system. Optical filters were used to isolate the line measured. The results agree with the assumption that the radiation decays exponentially after impact. For the lines λ4047 and λ4358 the lives were found to be the same within the experimental error (0.75 percent) viz. $\tau=5.75\times10^{-8}$ secs. The value for λ5461 was four times greater, $\tau=2.37\times10^{-7}$ secs. The agreement between the lives of λ4047 and λ4358 supports the quantum assumption that lines coming from the same level in the atom have the same life. Collins has found that under certain exciting conditions the fine-structure of λ5461 is anomalous as compared to λλ4047 and 4358. It is suggested that the longer life found for λ5461 may be explained by considering the fine structure of the 2^3S_1 level. The results are then consistent with the above assumption.

Introduction

FROM the relation between the mean life, τ_n, of an excited atomic state and the Einstein probabilities for transitions to all possible lower states,

$$\tau_n = \left(\sum_m A_m^n \right)^{-1}$$

it is generally assumed that all spectral lines originating in the same upper level in the atom have the same life.[1] Direct experimental evidence on this point is scarce.

While Kerschbaum[2] has measured τ for a number of spectral lines, using Wien's canal-ray method, and has found equal lives for lines originating in the same upper level, in agreement with the Einstein assumptions, he also found, in general, equal lives for *all* the arc lines of any one element. This last is hardly to be expected, as Maxwell[3] has pointed out, since the sum of the transition probabilities, upon which the lives depend, is not necessarily the same for every level in the atom.

The present investigation was undertaken to test further the validity of the Einstein assumptions by measuring the mean lives of each of several

[1] Pauli, Handbuch der Physik, V. 23, p. 11.
[2] H. Kerschbaum, Ann. d. Physik **83,** 287 (1927).
[3] L. R. Maxwell, Phys. Rev. **34,** 199 (1929).

lines coming from the same upper level, but under simpler excitation conditions than obtained in Kerschbaum's measurements. The lines were excited by simple electron impact at voltages below ionization. The mercury $2^3P_{012}-2^3S_1$ triplet, λλ5461, 4358 and 4047, was chosen because the intensity of the lines and their wide wave-length separation favored the application of the particular method of measurement used. Since levels higher than the 2^3S_1 were not excited to any appreciable extent, the conditions were less complicated than where high voltage excitation is used, as in Wien's canal-ray method. Voltage and pressure conditions were such as to make it unlikely that absorption and re-emission played any part in the persistence of the radiation.

Method

The method of measurement employed was a modification of that previously used in this laboratory.[4] The excitation was produced by electron impact excited by alternating voltages in such a way that there was excitation during only the positive half cycle. A voltage of the same frequency and phase was applied to a photoelectric detecting system, so that only radiation reaching the photoelectric surface in the positive half cycle was effective; during the negative half cycle the photoelectrons were held in the surface. As the frequency was increased, the total excitation being held constant, the photoelectric current decreased, owing to the persistence of the radiation, some of which then reached the photoelectric surface in the negative half cycle. From the form of the curve, the value of the mean life τ of the radiation was calculated, assuming that radiation excited at the time $t=0$ falls off acording to the law e^{-kt}.

Apparatus

The details of the apparatus are shown in Fig. 1. The excitation was produced in an evacuated vessel of Pyrex, containing electrodes C, G, G' and O. The hot cathode C, for which we are indebted to Dr. A. W. Hull of the General Electric Company, was equipotential, consisting of an oxide-coated nickel cylinder with an internal tungsten heater. Electrodes G and G', comprising the accelerating system, were in the form of two concentric cylinders of 1.6 mm mesh nickel gauze, with a difference in radius of 2.0 mm. For most of the measurements grids G and G' were connected together just outside the cell and used as a single electrode which we shall call GG'. The outer cylindrical electrode O, of sheet nickel, had a window covered with gauze to allow the passage of the radiation.

All metal parts were pre-outgassed. Before sealing off, the excitation cell was baked for several hours at 450°C, the filament sensitized and a strong arc operated for an hour. Later tests indicated that accumulated gas did not exceed 10^{-4} mm of mercury.

The mercury vapor pressure in the excitation cell was controlled by a mercury well at the bottom, kept in a water-bath whose temperature was

[4] H. W. Webb, Phys. Rev. **24,** 113 (1924); F. G. Slack, Phys. Rev. **28,** 1, (1926); H. W. Webb and H. A. Messenger, Phys. Rev. **33,** 319 (1929).

held constant to 0.1°C. The body of the tube was superheated to about 80°C.

The detecting system, containing electrodes *P*, *H* and *W*, was a specially constructed photoelectric cell placed at a distance of 8 cm from the excitation cell. The potassium-covered electrode *P* was a nickel cylinder, supported on a long re-entrant glass tube to increase the electrical leakage path. Surrounding *P* was a cylindrical nickel gauze electrode *H*. Against the walls was a third cylindrical grid, which in addition to removing the photoelectrons quickly, served as a flashing electrode in forming the sensitive potassium-hydride surface. During the flashing process electrode *H* was slid to one end of the cell, allowing a more uniform discharge between *W* and *P* and preventing the formation of a light sensitive surface on *H*.

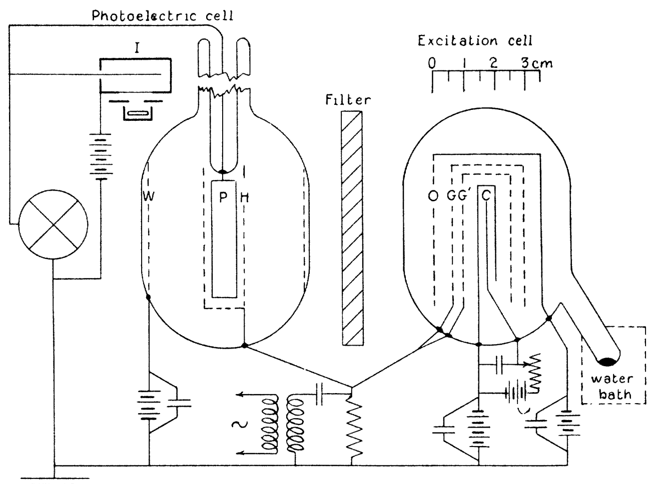

Fig. 1. Schematic diagram of apparatus and electrical circuits.

The metal parts were pre-outgassed and the cell which was of Pyrex, was baked out before distilling in the potassium. The hydrogen necessary for the flashing process was thoroughly pumped out before sealing off. The gas pressure in the cell after sealing off was below 10^{-4} mm mercury.

An electric heater on the electrometer lead prevented internal electrical leakage due to the formation of a film of potassium. Occasionally, after standing, a strong reverse photoelectric current from the grid *H* was found, due probably to a thin potassium film. This effect soon disappeared, however, after exposure to the heat of the excitation cell.

Corning glass filters were used between the excitation cell and the photoelectric cell to isolate each of the three lines; filters nos. G 555-Q and G 34-Y for λ5461; nos. G585-L and G-38 for λ4358; and nos. G586-A and G38-L for λ4047.

Photographs of a mercury arc taken through the filter for λ5461 and for λ4358, made certain that under the conditions of excitation of this experiment, the transmission of one filter for either of the other two lines, or for any other line likely to be excited, was less than 1 percent of the transmission for the desired line. The radiation transmitted by the filter for λ4047 also included the line λ4078, but was otherwise monochromatic. White[5] and Crozier[6] have found that under excitation conditions similar to those of this experiment, λ4078 was considerably weaker than λ4047. A study of the results of the present investigation showed that the presence of the small quantity of λ4078 did not affect the measurement of the life of λ4047.

There was always a considerable steady photoelectric current, due to the light from the hot cathode of the excitation cell. This was balanced out by means of a radio-active leak, *I*, Fig. 1, controlled by a variable lead shutter over the opening of the metal box containing the active material.

The filament was heated by an 8 volt storage battery while all other d.c. voltages were furnished by small dry cells. The alternating voltages were supplied by air-core transformers coupled to the 60 cycle lighting circuit

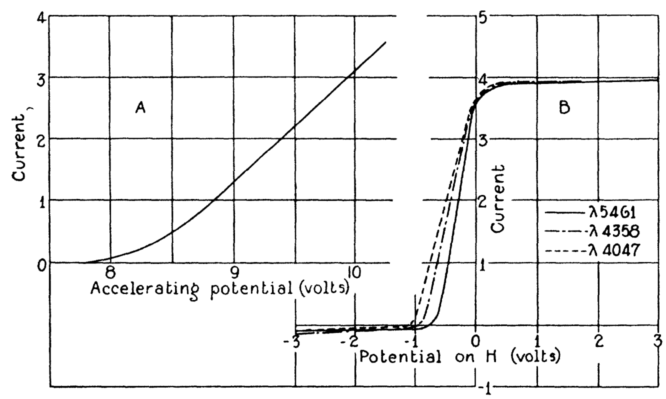

Fig. 2. Curve *A*, a typical excitation curve (λ4358). Curve *B*, photoelectric characteristics.

or to a vacuum-tube oscillator of variable frequency. The voltages were applied to the experimental cells across a nearly non-inductive resistance of about 45 ohms, one end of which was connected directly to the grids *H* and *GG′*. In the case of the high frequencies supplied by the oscillator this resistance formed part of a tuned circuit which helped to insure a pure impressed sine wave. The alternating voltages were measured with a vacuum-tube voltmeter. The frequencies were measured with a wave-meter.

A Compton quadrant electrometer with a sensitivity of about 3000 mm per volt was used to measure the photoelectric current.

Experimental and Results

Fig. 2 shows the steady current characteristics of the exciting and of the detecting systems which it was necessary to know in calculating the lives of the radiations. The excitation curve (*A*) was taken with the filter for λ4358 in place, and shows how the photoelectric current varied with the accelerating voltage between *GG′* and *C*, the voltage between *H* and *P* being held constant. The voltage conditions were $P=0.0$, $H=2.0$, $W=6.0$, $GG'=0.0$, $O=-3.0$, and *C* variable between 0.0 and -10.5 volts.

[5] D. R. White, Phys. Rev. **28**, 1125 (1926).
[6] W. D. Crozier, Phys. Rev. **31**, 800 (1928).

The curve for λ4358 shows that this radiation appeared at about the theoretical voltage 7.7 and that the variation of the photoelectric current was roughly linear for higher voltages up to 10.5 volts. Excitation curves taken with each of the other two filters were found to have exactly the same shape as that shown for λ4358, agreeing with the results of White[5] and Crozier.[6] The line λ4078 should theoretically come in at 7.9 volts. There was, however, no evidence of complexity in the excitation curve found for λ4047, indicating that λ4078 was considerably weaker than λ4047.

The photoelectric characteristics Fig. 2 (*B*) were taken with each of the three filters separately, maintaining a constant voltage between *GG′* and *C*

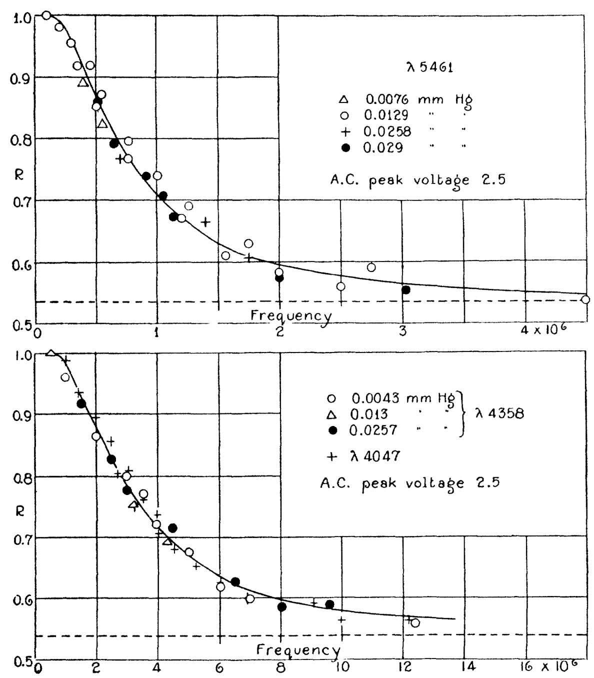

Fig. 3. *R*-frequency curves.

and varying the voltage between *H* and *P*. The ordinates are proportional to the photoelectric currents in each case and have been reduced to the same saturation current for comparison. The voltage conditions for the curves shown were $GG' = 0.0$, $C = -9.0$, $O = -3.0$, $P = 0.0$, and *H* variable between -3.0 and 3.0 volts. The three curves show that for these wave-lengths the cell was practically unidirectional and that a change of only a volt in the potential on *H* was sufficient to produce saturation. The shift in the stopping voltage is the only marked variation of the photoelectric characteristic with wave-length.

The curves from which the lives of the radiations were determined were obtained by applying alternating voltages, of the same peak value and phase, to *GG′* and *H* simultaneously and measuring the photoelectric current at different frequencies. The curves in Fig. 3 are typical of those obtained.

The abscissas are the frequencies. The ordinates are proportional to the photoelectric currents and represent in each case the ratio R of the current obtained with a high frequency to that obtained with a low frequency, 60 cycles, for which the effect of the persistence of the radiation was negligible. The ratio R was used instead of the actual photoelectric current to avoid error due to changes in the sensitivity of the photoelectric cell.

The d.c. voltage conditions for the curves shown were $GG' = 0.0$, $C = -7.5$, $O = -3.0$, $P = 0.0$, $H = 0.0$ and $W = 6.0$. The peak value of the alternating voltage applied to GG' and H was 2.5, so that the accelerating voltage varied between 5 and 10 volts. Measurements were taken at several different pressures, varying between 0.004 and 0.03 mm of mercury, as indicated in the figure. In the case of λ4047 the different pressures are not specified on the graph, for the sake of clearness, but the points for this line were taken over the same pressure range as for λ4358. Pressures below 0.004 mm in the case of $\lambda\lambda$4047 and 4358, and below 0.007 mm in the case of λ5461, could not be used since there was then insufficient energy to give a measurable photoelectric current, while with pressures much above 0.03 mm trouble was experienced with the arc striking.

It is important for this method of measurement that the impressed alternating voltages be of approximately sine form. The tests for wave-form described in earlier papers, were made for each frequency and indicated that up to the highest frequency it was possible to use, 1.2×10^7 cycles, no error was introduced due to faulty wave-form.

The solid lines shown with the experimental points in Fig. 3 were calculated in a manner similar to that discussed in earlier papers. It was assumed that the radiation excited at any time $t = 0$ falls off according to the exponential law e^{-kt}. Since the excitation was approximately linear with the voltage, the excitation during the positive half cycle approximated the form of the positive half of a sine curve. Also the photoelectric cell was nearly unidirectional and saturated quickly with a reversal of the voltage. It was therefore possible to find a simple approximate analytic expression for R as a function of the frequency f

$$R = \frac{K^2 + 2\pi^2 f^2}{K^2 + 4\pi^2 f^2}\,.$$

To this approximate expression certain correction terms, amounting to about 10 percent had to be added to take care of the fact that the photoelectric cell did not saturate instantaneously with a reversal of the voltage, and also the fact that excitation did not begin immediately with positive values of the alternating voltage. Since these correction terms were complicated and involved quantities determined empirically from the excitation and photoelectric characteristics, they are of no special interest here. With very high frequencies R approached a limiting value determined by the photoelectric characteristics and the amplitude of the applied alternating voltages. This is shown in Fig. 3 (a) and (b) by a horizontal dotted line.

By trial, a value of K was found such that the calculated curve best fitted the experimental points. The agreement was such as to justify the assumption of an exponential decay. For $\lambda 5461$, K was found to be 4.23×10^6 secs.$^{-1}$; the mean life of the radiation, τ, was then $1/K$ or 2.37×10^{-7} secs. The same K was found for $\lambda 4358$ and for $\lambda 4047$, viz. 1.74×10^7 secs.$^{-1}$, giving a mean life for each of these lines of 5.75×10^{-8} secs. The life of $\lambda 5461$ was therefore closely four times that of $\lambda\lambda 4358$ and 4047.

The precision of measurement for τ was about 4 percent. In order to see how closely the lives of $\lambda 4358$ and $\lambda 4047$ agreed, a fixed frequency of 3×10^6 cycles was used and a large number of alternate measurements of R were taken by simply interchanging the filters, the electrical conditions remaining the same. The same value of R was found for both lines to within the experimental error 0.75 percent, indicating the same value of K for the two lines to within that precision.

Measurements were taken using a peak value for the alternating voltage of 1.1 instead of 2.5. This resulted in a slightly different form for the calculated $R-$ frequency curve. The experimental points lay on the calculated curve, however, and the values of K which best fitted the data agreed in every case with those found using a peak voltage of 2.5, to within the experimental error.

Using Corning glass filter no. G-586-AW, measurements were made on the mean life of another group of lines, which included the singlet $2^3P_1-3^1D_2$, $\lambda 3663$, and the triplet $2^3P_1-3^3D_{123}$, $\lambda\lambda 3650$, 3654 and 3662. These lines could not be separated optically and the life measured was for the composite radiation. It was found impossible to obtain a complete R-frequency curve, since the radiation was apparently short-lived and it was necessary to go to very high frequencies before the photoelectric current began to decrease. Enough of the curve was obtained from which to estimate a value for the mean life of the radiation of 2.4×10^{-8} secs., certain to within 10 percent. The curve was too incomplete, however, to be able to determine whether there were different lives for the different components of the radiation.

Discussion

There was some question as to the purity of the radiation reaching the photoelectric cell when using the filter for $\lambda 4047$. The theoretical voltages at which $\lambda 4047$ and $\lambda 4078$ come in are 7.7 and 7.9 respectively. Both White[5] and Crozier,[6] however, found no appreciable intensity for $\lambda 4078$ under 8.4 volts. From a study of their voltage-intensity curves for these lines, the change in the peak value of the alternating voltage from 1.1 to 2.5 volts which changed the peak of the excitation voltage from 8.6 to 10.0 volts, would be expected to increase the average intensity of $\lambda 4078$, as compared to that of $\lambda 4047$, several times. If the intensity of $\lambda 4078$ were comparable to that of $\lambda 4047$, a change in the peak voltage should result in different R-frequency curves, providing the life of $\lambda 4078$ were appreciably different from that of $\lambda 4047$. No such change was noted, indicating either that the intensity of $\lambda 4078$ was too low to give a measurable photoelectric current; or that if $\lambda 4078$ were present to any considerable extent, its life was very nearly that of λ4047. In either case the measured life must be approximately the true life of λ4047.

A study of the results for all three lines, λλ5461, 4358 and 4047, leads to the conclusion that the results were not affected by absorption and re-emission of the radiation, but that the lives measured are actually those of the single atomic processes. It has been shown that for λ2537 these absorption and re-emission processes play an important part in the persistence of the radiation emitted by excited mercury vapor, even down to pressures of 0.0002 mm of mercury.[7] It is also known that under certain conditions large concentrations of excited atoms in the 2^3P_1 and the metastable 2^3P_0 state exist in the vapor and considerable absorption of λ4358 and λ4047 results.[8] The subsequent re-emission of all three lines, λλ4047, 4358 and 5461 by atoms so excited to the 2^3S_1 level would cause persistence of the radiation in the vapor, beyond the mean life of the single atomic processes.

That such absorption processes did not occur to any measurable extent in the present experiment is evident from the fact that no change in the mean life resulted from varying the pressure and the exciting alternating voltages. Increasing the pressure should increase the concentration of atoms excited to the 2^3P_1 and 2^3P_0 states and as a consequence there should be greater persistence of the lines under study, if absorption processes were playing a part. The concentration of atoms in the 2^3P_1 and 2^3P_0 states would also be greater when the peak voltage of 2.5 was used than with the peak voltage of 1.1, since in the former case the population in these states would be augmented by the return of electrons from upper states excited by the higher accelerating voltages.

A further test for effects due to absorption was made by varying the voltage on the outer electrode O in the excitation cell between the limits -8.0 and 0.0 volts. This had the result of increasing the total number of excited atoms produced in the positive half cycle, as O was made less negative, and this change should have increased the probability of any quantum of radiation being absorbed by an excited atom before escaping from the vapor. Again, some of the curves were taken with the two accelerating grids, G and G' connected together; for other curves only the inner grid served as an accelerating grid, the outer of the pair being connected to the electrode O. This change also affected the total concentration of excited atoms and should therefore have affected any persistence due to absorption.

The lives measured were, however, found to be independent of any of these pressure or voltage changes, indicating that they are the true mean lives of the corresponding single atomic processes.

The results show identical lives for λλ4047 and 4358. This is strong evidence in support of the assumption that lines coming from the same upper level in the atom have the same life. While the fact that λ5461 was found to have quite a different life than the other two lines may be interpreted as evidence that the Einstein relation is not valid, it is believed that a much more reasonable explanation will be found in the fine-structure of the lines.

[7] H. W. Webb and H. A. Messenger, Phys. Rev. **33**, 319 (1929).

[8] C. Füchtbauer, Phys. Zeits. **21**, 635 (1920); R. W. Wood, Proc. Roy. Soc. **A106**, 679, (1924), Phil. Mag. **50**, 774 (1925), Phil. Mag. **4**, 406 (1927).

These fine-structure components have been carefully studied. Under the conditions obtaining in a strong arc λ5461 has at least twelve distinct components; λ4358 at least twenty; and λ4047 at least nine. Ruark[9] has proposed a fine-structure energy level scheme which supposes a triple fine structure for the 2^3S_1 level as well as a triple fine structure for each of the $2P$ levels, and which accounts for about $\frac{2}{3}$ of the components found in the arc. Some experiments of Collins,[10] however, have shown that the fine structure of these lines is much simpler when the lines are optically excited than in the strong arc. He excited the lines in a resonance tube placed next to a mercury arc. Atoms were excited to the 2^3S_1 level by the successive absorption of λ2537 and λ4358. About half the components found in a strong arc appeared in the case of λλ4358 and 4047, while only *one* of the many arc components of λ5461 appeared. When nitrogen was introduced into the resonance tube little change was noted in the fine structures of λλ4358 and 4047, but to the single component of λ5461 was added one other equally strong component.

These results indicate a certain anomalous character for λ5461 as compared to the other two lines. It suggests that under certain excitation conditions, quite different upper fine-structure levels may be involved in the case of λ5461 than in the case of λλ4047 and 4358, and that the lives measured in the present investigation may therefore be the lives characteristic of these different sub-levels. It is, however, not possible to say whether a single one of these sub-levels is involved in the case of each of the lines or whether the result, in each case, is the average life of lines coming from a group of sub-levels. The precision of the method is such that if a radiation were made up of two components of about equal intensity, the complexity could be detected if their lives differed by more than 30 percent. Again, if there were two components of widely different lives, the complexity could be detected as long as the intensity of one component was not less than 10 percent that of the other. Since there was no evidence of complexity from the curves, it was concluded either that one fine-structure component predominated in the case of each of the three lines, or that if several strong components were excited in each case, they had about equal lives.

A study of the fine structure of these lines under conditions of excitation somewhat similar to those of this investigation is being undertaken in this laboratory.

It is interesting to note that Wien,[11] using his canal-ray method, found a value for the mean life of λ4358 of 1.82×10^{-8} secs. No explanation can be offered for the difference between the value of the mean life found here and Wien's result. It should be pointed out, however, that the type of excitation was quite different for the two experiments, Wien using high voltages, while here the exciting voltage was always below ionization.

The author wishes to express his thanks to Professor H. W. Webb, who suggested this problem, for his continued help and advice throughout the experiment.

[9] A. E. Ruark, Phil. Mag. **1,** 977 (1926).
[10] E. H. Collins, Phys. Rev. **32,** 753 (1928).
[11] W. Wien, Ann. d. Physik **73,** 483 (1924).