The Mean Life of the 7^3S_1 State of Mercury from Polarization Measurements on the Visible Triplet

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Fluorescence of the visible triplet lines of mercury (4047, 4358, 5461) was obtained by exciting a mixture of mercury vapor and a small amount of nitrogen by radiation from a quartz mercury arc. The fluorescence was observed at right angles to the exciting light beam and the polarization of each line, isolated by suitable filters, was measured by the method of crossed Wollaston prisms. Measurements in zero magnetic field (polarized excitation) gave 88.2 percent for 4047, −65.5 for 4358, and 14.55 for 5461, compared to theoretical values (broad line excitation) of 84.7, −67.0, and 8.7 percent, respectively. Measurements were then made of the polarization as a function of a magnetic field applied in the observation direction and the mean life of the 7^3S_1 state calculated from the data. The mean life of this state as measured by 4047 and 4358 was $0.8\pm0.1\times10^{-8}$ sec. at about 3.0 mm nitrogen pressure. The mean life as measured by the line 5461 was about $0.6\pm0.1\times10^{-8}$ sec. The collision cross section for the 7^3S_1 state against nitrogen was measured by measuring the polarization of 4358 at a field of 3 gauss and varying nitrogen pressures, giving the result $\sigma_q{}^2=1.3\times10^{-16}\,\mathrm{cm}^2$.

Introduction

Several attempts have been made to measure the mean life of the 7^3S_1 state of mercury by various methods. This state gives rise to the lines of the visible triplet (4047, 4358 and 5461) and experiments have been performed on the three lines which give a measure of the mean life of the 7^3S_1 state. One would expect theoretically that, as a result of measurements on each of the three lines, the value obtained for the mean life of the upper state should be a constant and not depend on the line used for the measurement. In two experiments which have been performed to date, the results have not been in agreement with the expectation. For example, Randall,[1] using a resonance lamp with electrical cut-off, found the mean life of the 7^3S_1 state to be 5.75×10^{-8} sec., when measured by 4047 and 4358, and 2.37×10^{-7} sec. when measured by 5461. A similar result was found by Richter,[2] who measured the polarization of the three lines obtained as fluorescence when a mixture of mercury vapor and nitrogen was irradiated by light from a mercury arc. By measuring the rotation of the plane of polarization of each line caused by the application of a small magnetic field in the direction of observation Richter calculated the following values of τ as measured by the three lines: from 4047, 0.5×10^{-8} sec.; from 4358, 0.6×10^{-8} sec.; and from 5461, 2.2×10^{-8} sec. Mitchell[3] has pointed out certain mistakes in Richter's calculations mainly arising from erroneous theoretical considerations. Since neither Richter nor Randall obtained results that could be accounted for on the basis of any reasonable theoretical assumptions and since the authors felt that improvements on Richter's method could be made, they undertook the following investigation.

Apparatus and Method of Measurement

The method used is similar to that of Richter and consists of optically exciting mercury vapor in the presence of a few millimeters of nitrogen with light from a quartz mercury arc lamp. Mercury atoms in a resonance tube absorb the line 2537 from the arc, thereby reaching the 6^3P_1 state. On collision with nitrogen molecules some mercury atoms are transferred to the 6^3P_0 state from which they may reach the 7^3S_1 state by absorption of the line 4047 from the arc. The fluorescence of the visible triplet occurs when mercury atoms in the 7^3S_1 state revert to the $6^3P_{0,1,2}$ states. If the direction of observation of the fluorescence is at right angles to that of the exciting beam, and if the resonance tube is situated in a region of zero magnetic field, the fluorescence lines will be polarized. The applica-

[1] R. H. Randall, Phys. Rev. **35**, 1161 (1930).

[2] E. F. Richter, Ann. d. Physik **7**, 293 (1930); **17**, 463 (1933).

[3] A. C. G. Mitchell, Phys. Rev. **43**, 887 (1933). Hereafter referred to as II.

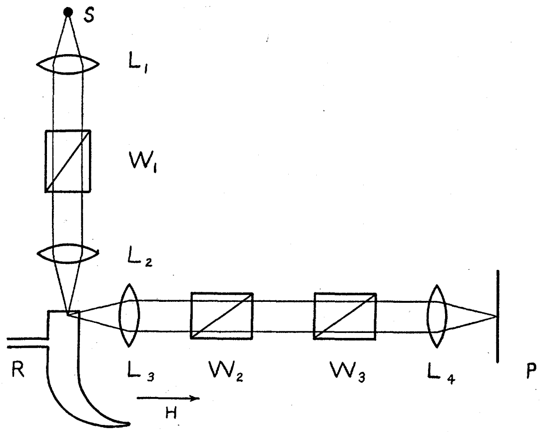

FIG. 1. Diagram of apparatus.

tion of small magnetic fields, applied in the direction of observation, will cause the polarization of the lines to decrease. From these measurements the mean life of the 7^3S_1 state can be calculated.

The light from a water-cooled and magnetically deflected quartz-mercury arc (Fig. 1) was made parallel by the lens L_1 and passed through the Wollaston prism W_1, which was transparent to wave-lengths greater than 2200. The two polarized images of the source were focussed on the resonance tube R, which was surrounded by a shield by means of which one image could be cut out. The resonance tube was made of glass and had a fused quartz window cemented to the front end with picein wax. An all quartz tube could not be used since quartz fluoresces in the blue-green when irradiated with ultraviolet light. The fluorescence light, escaping from a square hole in the shield (about 1 mm on each side), was made parallel by the lens L_3 and sent through the two Wollaston prisms W_2 and W_3. The prism W_2 was fixed while W_3 could be rotated so that its axis could make any desired angle with that of W_2, and the angle could be read to 1 minute with a scale and vernier. The polarized images of the hole were then brought to a focus on the photographic plate P. The various lines were isolated by means of filters[4] placed at the lens L_4. All lenses were of fused quartz.

A large Helmholtz coil placed about the apparatus served to neutralize the earth's field to less than 0.01 gauss. A smaller Helmholtz coil, placed with its axis along the direction of observation, was used to apply known magnetic fields to the resonance tube. This coil was calibrated by the standard inductance method with the help of a Brooks inductometer, so that the field produced by a given current flowing through the coil was known to 0.5 percent.

The nitrogen used in the experiment, made by heating NaN_3, was stored in a flask over metallic sodium. Any desired pressure of nitrogen could be admitted to the apparatus by means of stopcocks. Pressures were read on a McLeod gauge. The pressure of mercury vapor in the apparatus corresponded to the vapor pressure of mercury at room temperature.

The determination of the degree of polarization of any line under given experimental conditions was made photographically by taking four or five exposures and varying the angle made by the Wollaston prism W_3 with respect to W_2 for each exposure. At a certain angle α, two of the images will be of equal intensity, for which conditions the polarization is given by $P = -\cos 2\alpha$. The approximate positions for equal angles was found by taking exposures at angular settings differing by several degrees and examining the plates visually. In the final measurements exposures were made at angle settings one degree apart and the plates run through a recording microphotometer. On the resulting tracing the heights of the two peaks corresponding to the two images were measured. Calling these two heights a and b, a curve was drawn in which $(a-b)/(a+b)$ was plotted against the angle setting, and the position of equal images determined from the curve. Only exposures taken on one plate were used for the determination of a given angle. The zero position of the two Wollastons, i.e., the angle reading for which the principal planes of the two prisms were parallel, was determined to within 5 minutes of arc.

In the determination of the degree of polarization the time of exposure varied from thirty minutes to two and a half hours depending on the

[4] The filters used for the lines were: For 5461, Corning filters No. 351, 2 mm thick and No. 512, 4.39 mm thick; for 4358, Corning filters No. 038, 2.55 mm thick and No. 585, 4.52 mm thick; for 4047, Corning filters No. 585, 4.52 mm thick and No. 305, 3.62 mm thick together with 3 cm of a solution of 2.5 g I_2 in 500 cc CCl_4. For a discussion of these filters see E. J. Bowen, J. Chem. Soc. 2236 (1932).

line being measured, the pressure of nitrogen, and the strength of the depolarizing magnetic field. Frequent exposures were made to test for the presence of scattered light by placing a glass plate between the exciting light source and the resonance tube. Plates showing any trace of scattered light were, of course, discarded.

In all experiments the current through the arc lamp and that through the magnet used to deflect the arc stream was kept constant. The temperature of the water used to cool the arc was measured as it left the cooling chamber and arrangements were made to keep this temperature fairly constant to within about two degrees. Later experiments showed, however, that variations of the temperature of the cooling water from 15°C to 25°C had no measurable effect on the degree of polarization obtained.

Polarization in Zero Field

With a pressure of 3 mm of nitrogen in the resonance tube, the degree of polarization of the three lines was measured in zero magnetic field. For the lines 4358 and 5461 the exciting light was polarized with electric vector vertical while for 4047, on account of the low intensity of this line, unpolarized exciting light was used. The values of the degree of polarization for the line 4047, obtained with unpolarized light, were placed on a basis for comparison with the other lines, which were obtained using polarized excitation, by employing the well-known relation $\bar{P}_0 = P_0/(2-P_0)$, in which $\bar{P}_0$ is the degree of polarization measured with unpolarized exciting light and P_0, that to be expected if the exciting light is polarized with electric vector vertical. The values of the percentage polarization in zero field using polarized excitation (P_0) for the three lines are given in Table I. The theoretical values of the percentage polarization calculated from the known hyperfine structure are given in column 3 of the table. The minus sign before the value for the line 4358 denotes that this line is polarized with its electric vector at right angles to that of the exciting beam.

Table I. *Percentage polarization in zero field with polarized excitation.*

Line	Polarization (percent) P_0 Measured	calculated With hfs	calculated Without hfs	Mean life 7^3S_1 state (sec.)
4047	88.3 ±0.1	84.7	100	0.8×10^{-8}
4358	−65.7 ±0.9	−67.0	−100	0.8×10^{-8}
5461	14.57±0.16	8.6	14.3	0.6×10^{-8}

Polarization in Applied Magnetic Fields

With a nitrogen pressure of 3 mm in the resonance tube the polarization of each line was measured when a magnetic field was applied in the direction of observation. Measurements made for various values of the intensity of magnetic field up to 5 gauss are shown in Fig. 2, in which the percentage polarization $P(H)$ is plotted against the intensity of the magnetic field. In the figure the experimental data are given by the circles (4047), triangles (4358), and squares (5461), while the curves are theoretical ones whose significance will be discussed later. In making the measurements of the percentage polarization in applied fields the same procedure was adopted as in those made in zero field. In order to be sure that no fluctuations in the arc lamp were occurring which might change the value of the percentage polarization obtained, a test exposure was made on every plate. This was accomplished by taking an exposure in zero applied field with the Wollaston set at an angle α for which images of equal intensity had been obtained for the previous experiments in zero field. In the series of experiments represented by the points in Fig. 2, no significant variation in the zero field polarization was observed.

As in the case of the zero field measurements, the results for the line 4047 were obtained using unpolarized excitation. The points shown in Fig. 2 were obtained by computing the degree of

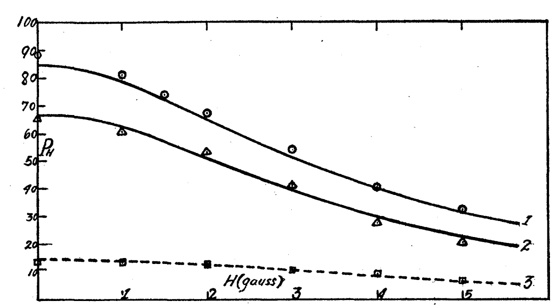

Fig. 2. Percentage polarization as a function of magnetic field. Circles, 4047; triangles, 4358; squares 5461.

polarization which would have occurred had polarized excitation been used. The method of computation given by Breit[5] consisted in multiplying the observed polarization $\bar{P}(H)$, obtained with unpolarized excitation, by $(2-P_0)$ where P_0 is the polarization in zero field obtained from the experimental values given in Table I.

Finally, experiments were performed to show the effect of nitrogen pressure on the degree of polarization. With a magnetic field of 3 gauss applied to the resonance tube, the degree of polarization of the 4358 line was measured at several nitrogen pressures. The results are given in column 2 of Table II. It will be noted that, at

TABLE II. *Percent polarization of the 4358 line at various nitrogen pressures.* H=3 gauss.

N_2 Pressure in mm Hg	Polarization percent $P(H, p)$ Line 4358	$\frac{1}{f(P)}$
2.50	40.19	1.261
3.20	41.20	1.302
3.95	43.35, 42.26 } 42.81	1.368

constant magnetic field, the degree of polarization increased with increasing nitrogen pressure, in agreement with similar experiments performed by Richter. Other experiments showed that the degree of polarization in zero field was independent of the nitrogen pressure over the range examined.

Discussion of Results

(a) The zero field polarization

A comparison of the percentage polarization obtained with that to be expected from the known hyperfine structure of the lines in question shows that for the two lines 4047 and 4358 the agreement is quite good, while for the line 5461 the percentage polarization observed is definitely higher than that expected theoretically. The theoretical calculation[3] was made under the assumption that the exciting source had "broad line characteristics" as far as the 4047 line is concerned, i.e., the intensity at the center of each hyperfine structure component is the same. If the source had "narrow line characteristics" (i.e., the intensity of each component is that which would be given by a source entirely free from self-absorption), the degree of polarization expected should have been much higher.

The high polarization of the 5461 line is not understood at present. Since the 4047 line is the only line absorbed to any appreciable extent by the mercury vapor in the resonance tube, and since the fluorescent lines 4047 and 4358 do not show a degree of polarization too high to be accounted for on the basis of a broad line source, it is probable that the characteristics of the source cannot account for the result obtained in the case of 5461.

The apparatus was carefully checked to be sure that no systematic error of measurement could be operative in making the observed polarization too high. With this object in view the zero position of the two Wollaston prisms was rechecked using the fluorescent line 5461, depolarized by a magnetic field of 20 gauss, as a source, and the results were in agreement with those previously obtained. The resonance tube was observed between crossed Nicol prisms to see if strains might be causing erroneous results, but no strains were found.

It is conceivable that the fluorescence radiation is partially absorbed in getting out of the resonance tube and that this might account for the observed results. The light path through the vapor in our apparatus was less than 5 mm, and a calculation made with the help of the data of Pool and Simmons[6] on the absorption coefficient of the various hyperfine structure components of the 4047 line shows that no appreciable effect can arise from this source.

(b) The mean life of the 7^3S_1 state

The mean life of the 7^3S_1 state may be obtained from curves of the polarization $P(H)$ against the magnetic field as shown in Fig. 2. Provided such a series of points is at hand the mean life may be obtained by fitting the data to the theoretical curve

$$P(H)=\sum_{\alpha}\sum_{\varphi}\frac{P_0(\varphi\alpha)}{1+[(eH/mc)g_{\varphi}(\alpha)\tau]^2}. \qquad (1)$$

[5] G. Breit, Rev. Mod. Phys. **5**, 91 (1933), see p. 124.

[6] M. L. Pool and S. J. Simmons, Phys. Rev. **44**, 997 (1933).

The use of this method has been discussed in detail in II. Curves 1 and 2 of Fig. 2 were obtained from Eq. (1) using the hyperfine structure values of $P_0(\varphi\alpha)$, the correct values of $g_\varphi(\alpha)$ for the various hyperfine states of 7^3S_1 and a value of $\tau = 0.8 \times 10^{-8}$ sec. Curve 3 was obtained using $\tau = 0.6 \times 10^{-8}$ sec. and not taking into account hyperfine structure.

It was pointed out in II that, while P_0 is quite sensitive to the hyperfine structure of the line in question and also to the nature of the source, the value of the mean life obtained from a curve of $P(H)$ against P_0 is quite insensitive to these factors. This is especially true in the case of mercury where most of the light comes from the isotopes of even atomic weight. If, now, $P(H)/P_0$ is plotted against H discrepancies in the values of P_0 cancel out and a value of τ can be obtained. Fig. 3 shows curves of $P(H)/P_0$ against H for the line 4047. Curves 1, 2 and 3 are drawn for mean lives of 0.7, 0.8 and 0.9×10^{-8}, respectively, under the assumption that there is no hyperfine structure. The dotted curve is obtained when hyperfine structure is considered for the mean life $\tau = 0.8 \times 10^{-8}$ sec. With this method of calculation the mean life of the 7^3S_1 state, obtained from the observations on the three lines 4047, 4358 and 5461, measured at a nitrogen pressure of 3 mm, is 0.8×10^{-8}, 0.8×10^{-8} and 0.6×10^{-8} sec., respectively, to within about 10 percent.

The results for the mean life of the 7^3S_1 state seem to be the same whether measured by the line 4047 or 4358. The value for the mean life obtained from the measurements on the 5461 line appears to be smaller than that measured by the other two lines by about 25 percent. This discrepancy would seem to lie outside of the experimental error of this investigation. The discrepancy is, however, not very great and in view of the anomalous value obtained for the percentage polarization of 5461 in zero field, the three results for the mean life may be considered to be essentially the same. There is no evidence from this investigation that the mean life as measured by 5461 is four times as large as that measured by the other two lines, as has been reported in the other two investigations.

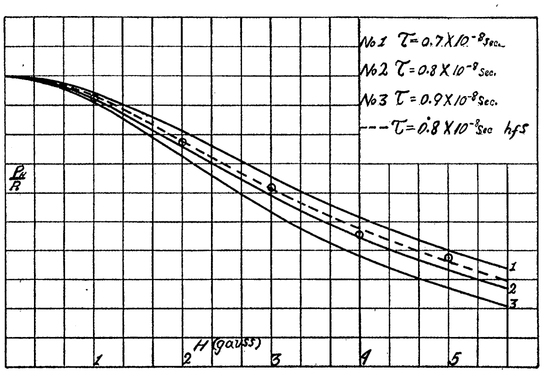

FIG. 3. $P(H)/P_0$ as a function of magnetic field.

(c) The effect of nitrogen on observed values of $P(H)$. Collision cross section

It was found in the above experiments that $P(H)$ at a given value of the magnetic field increases with increasing nitrogen pressure. This may be explained by letting the mercury atom in the 7^3S_1 state be represented by a damped classical oscillator of mean life τ. The oscillator will precess in the magnetic field H. If there were no foreign gas present to disturb the oscillator, the amplitude of the oscillator should decrease to $1/e$ of its original value in a time τ, and the plane of the oscillation should be rotated through an angle φ calculated from the Larmor precession velocity. The net result of this process is that the polarization observed, $P(H)$, should be given by

$$P(H) = P_0/\{1 + [(eH/mc)g\tau]^2\}, \qquad (2)$$

which is similar to (1). If, now, nitrogen is present it may quench the mercury atom in the 7^3S_1 state. The result of collisions of nitrogen with the classical oscillator in a magnetic field would be to damp the amplitude of oscillation before the oscillator had a chance to precess very far. A calculation, similar to that made by Turner[7] for the quenching of resonance radiation, shows that a formula similar to (2) may be used provided τ is replaced by $\tau T/(\tau + T)$, where T is the time between collisions, and provided that nitrogen has no effect on the polarization in zero field.

If the polarization at a given magnetic field and pressure of nitrogen, $P(H, p)$ be measured as a function of the nitrogen pressure and the quantity

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[7] L. A. Turner, Phys. Rev. 23, 464 (1924).

$$\frac{1}{f(P)}=\left(\frac{1-P(H,p)/P_0}{P(H,p)/P_0}\right)^{-\frac{1}{2}}$$

be plotted against the pressure p, a straight line should result whose intercept is $mc/eHg\tau$ and whose slope, $(A\sigma_q^2/g)(mc/eH)$, where σ_q^2 is the quenching cross section and

$$A=2666.6\left(\frac{2\pi N}{kT}\cdot\frac{m_1+m_2}{m_1m_2}\right)^{\frac{1}{2}}.$$

If the values of $1/f(P)$ for the experiments on the line 4358 taken from Table II are plotted against the corresponding nitrogen pressures a straight line results which gives a value of $\tau=0.88\times10^{-8}$ sec. and of $\sigma_q^2=1.3\times10^{-16}$ cm^2. This result must be taken as only an approximation to σ_q^2 and τ, since in the theoretical treatment hyperfine structure was not considered. The experiments were performed, however, at such a magnetic field ($H=3$ gauss) that the value of $P(H)/P_0$, calculated on the basis of hyperfine structure, is not essentially different from that calculated neglecting hyperfine structure.

Finally, it must be emphasized that, in the experiments in which the mean life of the 7^3S_1 state was measured by observations on the three fluorescent lines, $\tau T/(\tau+T)$ was measured and not τ. Since, however, the nitrogen pressure was kept constant at 3 mm in these experiments, a short calculation shows that the values of the true mean life as measured by the three lines should have the same relation to each other as do the values given in Table I.

In conclusion, the authors wish to acknowledge their indebtedness to Dr. R. L. Garman, of the Chemistry Department of the Washington Square College who kindly made the intensity measurements with the microphotometer.

A Calculation of Mass Scattering Coefficients

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By means of graphical integration, the mass scattering coefficients of the substances carbon, aluminum, iron, tin and gold have been calculated over the wave-length range $\lambda=0.4$A to 1.1A. The results show: (1) the mass coefficients obtained agree reasonably well with those obtained experimentally by Coade, Mertz, Hewlett, Statz and Allen; (2) the mass scattering coefficients may be expressed by the relation, $\sigma/\rho=0.0230Z^{1.16}\lambda$, over a wave-length range $\lambda=0.4$A to 1.1A and upwards from atomic number 12; (3) the part of the scattering coefficient due to incoherent scattering averages 20 percent lower than that value expressed by the Dirac or the Klein-Nishina formula.

Introduction

EXPERIMENTAL values of the mass scattering coefficients of x-rays have been determined for a number of elements directly by Coade,[1] Mertz,[2] Statz[3] and Hewlett[4] and indirectly by Allen.[5] As yet no satisfactory theoretical calculations have been made that agree with the experimental values. It was the purpose of this study to calculate the value of these coefficients from the existing accurate knowledge of the intensity of x-rays, as a function of the scattering angle, scattered by gases and powdered crystals.

Method

The intensity of x-rays scattered by a single electron is given by the classical theory[6] as

$$I_{sc}=I_0(e^4/2m^2c^4R^2)(1+\cos^2\theta),$$

[1] E. H. Coade, Phys. Rev. **36**, 1109 (1930).
[2] P. Mertz, Phys. Rev. **28**, 891 (1926).
[3] Statz, Zeits. f. Physik **11**, 304 (1922).
[4] Hewlett, Phys. Rev. **20**, 688 (1922).
[5] Allen, Bull. Am. Phys. Soc. **8**, Nos. 5, 6.

[6] J. J. Thomson, *Conduction of Electricity Through Gases*, 3rd Ed., p. 321.