Lifetime of the $6s6p\ ^1P_1$ State of Mercury

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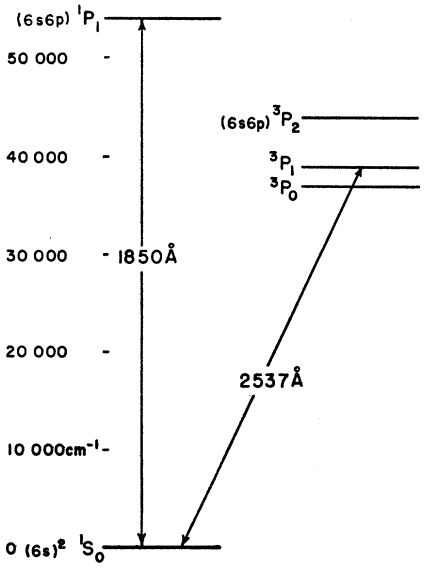
The lifetime of the $6s6p\ ^1P_1$ state of mercury has been determined by the zero-field level-crossing technique (Hanle effect) to be $\tau=(1.31\pm0.08)\times10^{-9}$ sec. This result yields a value of $f=1.18$ for the oscillator strength of the 1850-Å line. From this lifetime result and other experimental data we have calculated the intermediate coupling coefficients for the mixing of the $6s6p\ ^3P_1$ and $^1P_1$ states by three different methods. All three methods are in good agreement.

INTRODUCTION

THE measurement of the lifetime of the $(6s6p)\ ^1P_1$ state of mercury provides a good test of the theory of intermediate coupling in sp configurations since the intermediate coupling coefficients can be determined independently from the following three different experimental results[1]; (1) the $^3P_{2,1,0}$, $^1P_1$ fine structure, (2) the g_J value of the $^3P_1$ state, and (3) the lifetimes of the $^1P_1$ and $^3P_1$ states. All of the required experimental values are known accurately except the lifetime of the $^1P_1$ state for which there is considerable disagreement among the previous results.[2] It is interesting to note that although the lifetime of the $^3P_1$ state has been measured a number of times and is known quite accurately, the most recent previous determination of the $^1P_1$ state lifetime was in 1933.[2]

The use of the zero-field level-crossing technique (Hanle effect) to measure the lifetime of the first excited $^1P_1$ state of the Group II elements has been described in detail in several previous papers.[3] We present here, therefore, only a brief description of the method, and those details which pertain to the present experiment on mercury. In Fig. 1 is shown the energy levels of the ground- and the lowest excited-state configuration of mercury. In Fig. 2 is shown a schematic diagram of the apparatus. Briefly, the experimental method is as follows: incident 1850-Å resonance radiation is scattered by a sample of mercury atoms contained in a cell or in an atomic beam. The radiation scattered at 90° to the incident light direction is detected as a function of a static magnetic field applied to the scattering atoms in a direction perpendicular to the incident and observing directions. From the half-width of the Lorentzian-shaped zero-field level-crossing signal, the lifetime of the $^1P_1$ state is determined.



GROUND AND LOWEST EXCITED STATE OF Hg

FIG. 1. Ground- and lowest-excited-state levels of the neutral mercury atom.

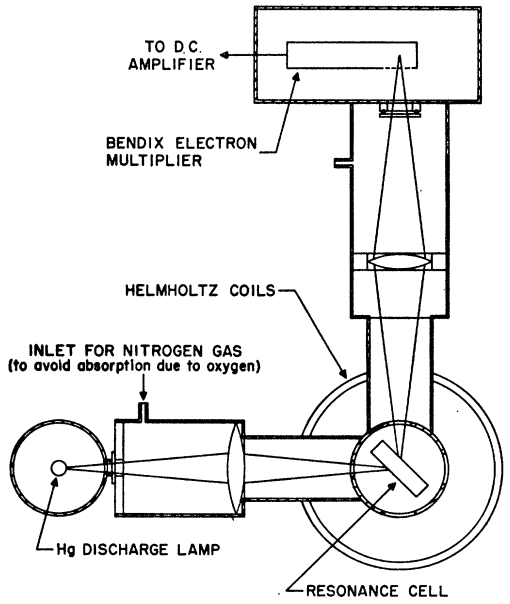


FIG. 2. Schematic diagram of the apparatus. A horizontal section through the center of the apparatus is shown.

[1] A. Lurio, M. Mandel, and R. Novick, Phys. Rev. **126**, 1758 (1962).
[2] See footnotes in Table II.
[3] A. Landman and R. Novick, Phys. Rev. **134**, A56 (1964); A. Lurio and R. Novick, *ibid.* **134**, A608 (1964); A. Lurio, R. L. DeZafra, and R. Goshen, *ibid.* **134**, A1197 (1964); A. Lurio, *ibid.* **136**, A376 (1964).

APPARATUS

The mercury resonance lamp used in the experiment was supplied by Englehard Hanovia, Inc.[4] It was a shortened version of their type 93 A-1 low-pressure ozone producing lamp, which when operated on 60 cycles/sec at 3000 V produced a very stable discharge. In order to optimize the resonantly scattered 1850-Å line, the lamp was cooled as shown in Fig. 3. Nitrogen gas which was precooled by passage through liquid nitrogen was flowed through the cooling coils surrounding the lamp. Dow Corning type 550 silicone oil filled the lower part of the cooling jacket and maintained the lower third of the discharge lamp at about $-20°$C by means of conduction through the silicone oil. This temperature was found to yield the largest scattering from the mercury atoms. The reduced lamp temperature in addition to optimizing the 1850-Å radiation, also greatly reduced the intensity of the 2537-Å line. A later modification which proved useful was the provision for applying a magnetic field parallel to the axis of the capilliary discharge lamp (see Fig. 3). A permanent magnet, which could be removed, provided a field at the lamp of from 400 to 1150 G by means of aluminum spacers between the permanent magnet and the poles. The use of this magnetic field will be discussed in the next section. The stray field produced by this magnet at the scattering atoms when in the direction opposed to the earth's field was 1.5 G. This field was taken into account in evaluating the data.

The detector for the 1850-Å radiation was a Bendix parallel-plate electron multiplier with a brass input dynode. The photoelectric efficiency of this surface is very much greater for 1850-Å radiation than for 2537-Å radiation and this fact led to the choice of an electron multiplier rather than a photomultiplier for the detector. The electron multiplier operating with a gain of about 10^7, and with a 10^6-Ω anode resistor had a dark current of less than 10 μV, which corresponds to an equivalent cathode current of less than 16 electrons/sec.

All lenses and windows were made of ultraviolet silica. It was found necessary to flush nitrogen through all optical paths between the light source and the detector since 1850-Å radiation is strongly absorbed by oxygen. This fact provided an easy way to distinguish how much 1850-Å compared to 2537-Å radiation is being detected. In our experiment, the substitution of nitrogen for air in the optical paths increased the scattered light signal by about 10 times. The magnetic field at the scattering atoms was provided by a Helmholtz coil which produced 48.9 G/A. It was calibrated by proton resonance.

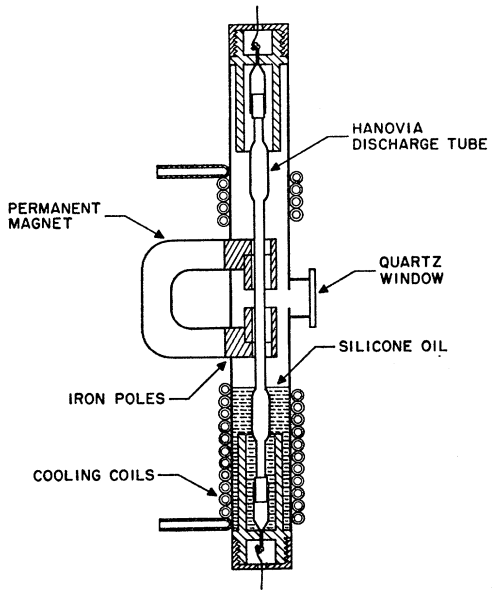


FIG. 3. Cross-section view through lamp and its housing.

[4] Englehard Hanovia, Inc., 100 Chestnut Street, Newark 4, New Jersey.

EXPERIMENTAL PROCEDURE

All preliminary measurements were done by scattering unpolarized resonance radiation from an atomic beam of natural mercury. Although the incident and outgoing light directions were visually set to be orthogonal, before each run the lenses were slightly adjusted to make the level crossing signal symmetric about zero gauss (the 1.5 G stray field was taken into account in this procedure). A run consists of observing the scattered radiation as the magnetic field was varied from 400 G in one direction (up) to 400 G in the opposite direction (down). A difficulty which appeared immediately was the following: The scattered light intensity which should have an inverted Lorentzian shape, instead of leveling out at high magnetic fields (i.e., for $H>150$ G the intensity should only rise about 8%), continued to slowly rise as much as 25% on increasing the field from 150 to 400 G. It was thought that this might be caused by self-reversal in the lamp since, if the lamp is self-reversed, as the magnetic field at the scatterers is increased, the $\Delta m=\pm 1$ Zeeman levels scan a higher intensity part of the lamp's intensity profile. After some preliminary tests seemed to confirm this idea, the lamp was modified to permit the application of up to about 1150 G parallel to the axis of the discharge tube. The field applied to the lamp and the field applied to the scatterers were along the same direction. The use of a magnetic field at the lamp both increased the level crossing signal and essentially eliminated the anomalous rise of the level crossing signal at high fields. This improvement was independent of the magnetic field from about 800 to 1500 G. Our explanation of this effect is as follows: The π line emitted by the lamp is unaffected by the magnetic field and will continue to be self-reversed. The σ lines are each displaced from their zero-field position by about 1600 Mc/sec (for 1150 G).

These σ lines which are self-reversed at the center of their shifted positions now add to give a relatively flat profile at the unshifted position.

An exact profile calculation requires a knowledge of the zero-magnetic-field profile and this is complicated by the isotope shifts in the natural mercury mixture used in the lamp.

The final data was taken with a 40-mg sample containing 84.7% Hg^{202} and 92.45% even mercury isotopes. In addition to scattering from an atomic beam of the enriched isotope, data was also taken by scattering from a quartz cell containing the enriched isotope. A typical curve of the atomic beam scattering is shown in Fig. 4. The data was analyzed by plotting the experimental curves against a family of Lorentzian-shaped curves calculated from the equation

$$I=1-\left[1+\tau^2\left(\frac{2g_J\mu_0 H}{\hbar}\right)^2\right]^{-1} \qquad (1)$$

for different values of τ. In order to normalize the experimental curves one must know the asymptotic value of the scattered intensity for large fields. This was obtained from an approximate value of the lifetime and the data taken for H greater than 100 G.

LIFETIME RESULTS AND DISCUSSIONS

The preliminary data taken with natural mercury yielded a lifetime for the $^1P_1$ state of $\tau=(1.2\pm0.1)\times10^{-9}$ sec. The data taken with the enriched Hg^{202} isotope gave a value of $\tau=(1.31\pm0.08)\times10^{-9}$ sec. The difference between these two results is consistent with the fact that the odd isotopes have a smaller g value than the even isotopes. A similar effect has been reported by Anderson for xenon.[5] The effect of multiple scattering narrowing was observed as the density of the scattering atoms was increased. Most of the data were taken at mercury vapor pressures of $1\text{–}3\times10^{-7}$ Torr and

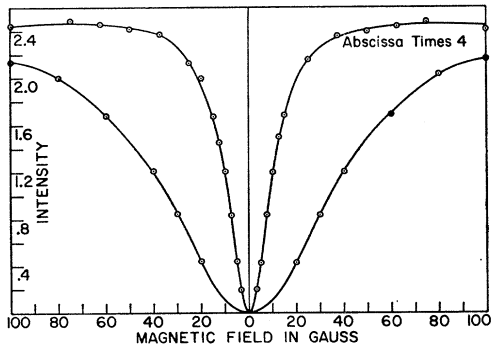


FIG. 4. Hanle-effect line shape for the 1850-Å line. The zero of the ordinate is chosen to be the scattered intensity at zero magnetic field.

[5] D. K. Anderson, Phys. Rev. **137**, A21 (1965).

TABLE I. g_J values for the $^1P_1$ and $^3P_1$ states.

$g_J(^3P_1)$	1.486118(16)	Smith[a]
$g_J(^3P_1)$	1.486094(8)	Kohler and Thaddeus[b]
$g_J(^1P_1)$	1.019(6)	Green and Loring[c]
$g_J(^1P_1)$	1.0218(88)	Van Kleef and Fred[d]

[a] W. W. Smith, Phys. Rev. **137**, A330 (1965).
[b] R. Kohler and P. Thaddeus, Phys. Rev. **134**, A1204 (1964).
[c] J. B. Green and R. A. Loring, Phys. Rev. **46**, 888 (1934).
[d] Th. A. M. Van Kleef and M. Fred, Physica **29**, 389 (1963).

the coherence time was extrapolated to its zero-pressure value which introduced a correction of 3%.

From Eq. (1) we note that the level crossing signal depends on the product g_JH. In Table I are given the measured values of g_J for the $^1P_1$ and $^3P_1$ state. We have used the average result $g_J(^1P_1)=1.020\pm0.007$ in analyzing our data. Within experimental error the g_J for the $^1P_1$ and $^3P_1$ states satisfy the g sum rule. In Table II are given our value and previous values for the lifetime of the $^1P_1$ state. The agreement between our result and Wolfsohn's is excellent which is very pleasing since of the earlier results Wolfsohn's is expected to be most reliable.

With our result for the lifetime of the $6s6p\ ^1P_1$ state we obtain a value $f=1.18$ for the oscillator strength of the 1850-Å line. This is to be compared with the Bates and Damgaard prediction of 1.48.[6]

We may now proceed to our objective, mentioned in the Introduction, the calculation of the intermediate coupling coefficients by the three different methods. In line 1, Table III are given the intermediate coupling coefficients c_1 and c_2 (also α and β) obtained from the $^3P_{2,1,0}$, $^1P_1$ fine structure by the method of Wolfe.[7]

In line 2 are given the coefficients calculated from the deviation of the $^3P_1$ state g_J value from its value for pure Russell-Saunders coupling. The $g_J{}^0$ values for pure

TABLE II. Lifetime of the $^1P_1$ and $^3P_1$ states.

Quantity	Lifetime (sec)	Author
$\tau(^1P_1)$	0.3×10^{-9}	Garrett[a]
	1.6×10^{-9}	Ladenburg and Wolfsohn[b]
	1.30×10^{-9}	Wolfsohn[c]
	1.31×10^{-9}	Present work
$\tau(^3P_1)$	1.14×10^{-7}	Ladenburg and Wolfsohn[b]
	1.15×10^{-7}	Kaul[d]
	1.18×10^{-7}	Barrat[e]
	1.14×10^{-7}	Schuler[f]

[a] P. H. Garrett, Phys. Rev. **40**, 779 (1932).
[b] R. Ladenburg and G. Wolfsohn, Z. Physik **63**, 616 (1930).
[c] G. Wolfsohn, Z. Phys. **83**, 234 (1933).
[d] R. D. Kaul, thesis, Case Institute of Technology, Cleveland, Ohio, 1963 (unpublished).
[e] J. P. Barrat, J. Phys. Radium **20**, 541, 633, 657 (1959).
[f] C. J. Schuler, Quarterly Progress Report, No. 64, 1964, Massachusetts Institute of Technology, Research Laboratory for Electronics, Cambridge, Massachusetts (unpublished).

[6] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) **A242**, 101 (1949).
[7] H. Wolfe, Phys. Rev. **41**, 443 (1932); G. Breit and L. A. Wills, *ibid.* **44**, 470 (1933).

TABLE III. Intermediate coupling coefficients.

Methods	c_1	c_2	α	β
Fine structure	0.4412	0.8974	0.9874	−0.1582
$^3P_1$ state g_J value	0.4278	0.9038	0.9850	−0.1725
Lifetime ratio	0.4289	0.9033	0.9852	−0.1714
Pure LS coupling	0.5774	0.8165	1	0

Russell-Saunders coupling are related to the values in intermediate coupling by the expression[1]

$$g_J(^3P_1)=\alpha^2[g_J{}^0(^3P_1)]+\beta^2[g_J{}^0(^1P_1)], \quad (2)$$

where α and β are related to the coupling coefficients c_1 and c_2, and we have taken $g_J{}^0(^3P_1)=1.50096$ and $g_J{}^0(^1P_1)=0.99980$. These values for $g_J{}^0$ include an estimate of −200 ppm for relativistic and diamagnetic corrections. This estimate is obtained as follows: $g_J(^3P_2)=1.50099(10)$. The difference between this value and the theoretical value $g_J=1.501156$ is 170 ppm. From a treatment of the relativistic and diamagnetic corrections similar to the treatment of Abragam and Van Vleck for oxygen,[8] we can show that the corrections to both the $^3P_1$ and the $^1P_1$ g_J values are almost the same and are slightly larger than the correction to the $g_J(^3P_2)$. Hence we make the estimate of -200 ± 40 ppm for the corrections.

In line 3, we have used the $^1P_1$ state lifetime together with the $^3P_1$ state lifetime to calculate the coupling coefficients from the equations

$$\frac{\beta^2}{\alpha^2}=\frac{\tau(^1P_1)}{\tau(^3P_1)}\frac{\lambda^3(^3P_1-{}^1S_0)}{\lambda^3(^1P_1-{}^1S_0)},$$

$$\alpha^2+\beta^2=1.$$

We have taken an average value $\tau=(1.145\pm0.02)\times10^{-7}$ sec for the lifetime of the $^3P_1$ state.

The agreement between all three methods is good and the agreement between the methods of lines 2 and 3 is excellent. This is expected, since the fine structure is more sensitive to configuration interaction than are g_J values or the lifetime ratio.

[8] A. Abragam and J. H. Van Vleck, Phys. Rev. **92**, 1448 (1953).

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Wave Functions and Transition Probabilities in Scaled Thomas-Fermi Ion Potentials*

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A semiempirical method for computing atomic and ionic wave functions is described. The method uses a one-electron potential obtained from a scaled Thomas-Fermi ionic charge distribution. The scale factors are chosen to make the one-electron binding energies agree with experimental ionization potentials. A number of oscillator strengths have been evaluated and are found to agree well with results of alternative methods of calculation. The method has a wider range of applicability than that of Bates and Damgaard, and calculations are much shorter than those using the self-consistent-field methods.

I. INTRODUCTION

WE consider in this paper an approximate and rapid method for obtaining radial wave functions in many-electron atoms and ions. Our main goal in this work is the calculation of electric-dipole transition probabilities ("oscillator strengths"), although other applications (collision cross sections, spin-orbit parameters, Slater integrals, etc.) suggest themselves. In applications such as opacity calculations, which require many hundreds of wave functions for transition probabilities, speed of computation becomes an important consideration. Our particular concern, therefore, is to evaluate wave functions via some method which circumvents the lengthy "self-consistent-field"

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