Resonance Irradiation of Mercury Vapor in Nitrogen

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A study has been made of phenomena related to the metastable 6^3P_0 mercury atom appearing in a cell which contains nitrogen and saturated mercury vapor at 22°C and is irradiated with 2537 A ($6^1S_0-6^3P_1$) resonance emission from a cool mercury arc. Various phenomena reported individually by many investigators are observed simultaneously and with improved techniques so that coherent correlations can be drawn and new conclusions developed. The relative 6^3P_0 population produced from 6^3P_1 atoms by inelastic collision is measured by self-absorption of 4047 A ($6^3P_0-7^3S_1$); its dependence upon 2537 A intensity is linear and its dependence upon nitrogen pressure is given by theory. The 6^3P_1 population is quenched by nitrogen. With conditions of high gas purity it is possible to produce large currents of heavy ions, the probable mechanism being a three-body collision between 6^3P_0, 6^3P_1, and N_2 to form a highly excited molecule, which becomes ionized in a subsequent step. The ion formation is a volume process, varying with the second power of the 2537 A intensity. The continuum intensity near 4850 A is linear with 2537 A intensity and shows a pressure dependence consistent with molecular formation in a three-body collision between 6^3P_0, 6^1S_0, and N_2. Mean lifetimes of metastable population, ion formation, and continuum intensity are measured as a function of pressure of nitrogen. They are found to differ distinctly, being generally larger in the order named. At high irradiation intensity an ion current of 405 μa was observed, leading to a prediction that several percent of the mercury atoms could be in the metastable state.

INTRODUCTION

MERCURY atoms in the 6^3P_0 metastable state and phenomena associated with them have been the subject of many investigations.[1–3] Both electronic and resonance excitation have been used to produce high concentrations of these excited atoms. In the latter method, atoms raised to the 6^3P_1 state by 2537 A resonance radiation are transferred to the 6^3P_0 state in collisions of the second kind (see Fig. 1). Certain gases, particularly nitrogen, are very efficient in effecting this transition, the process having been studied early by Klumb and Pringsheim[4] and recently in detail by Matland.[5] Theories have predicted that approximately one out of every few hundred mercury atoms can be in the metastable state.[6–8] Foote[6] has predicted that as high as one out of every thirty-six could be in this state. Until the present work, high concentrations have not been experimentally measured. Buehl[9] did succeed in measuring metastable concentrations, but he used electronic excitation from which only very small concentrations were attainable.

The long mean life of mercury atoms in the 6^3P_0 state (of the order of milliseconds) has been measured by many workers.[6,7,10–16] Development of a rigorous theory predicting the mean life as a function of the pressure of nitrogen is complicated by diffusion of resonance radiation, transitions to the 6^3P_1 state and to the ground state, collision broadening, and wall effects. Nevertheless, semiquantitative theories have been able to predict the manner in which both the population of metastables and the mean life of this state vary as a function of the pressure of gas which is responsible for producing large populations of metastables.[12–14]

The population of the 6^3P_1 state in the presence of such a gas has likewise been frequently investigated.[4,17–24] It has been definitely established that the number of 6^3P_1 atoms is decreased with increasing nitrogen pressure. Collisions of the second kind producing 6^3P_0 atoms are chiefly responsible for this decrease. By the inverse of this transition, in decay the 6^3P_1 population decreases at the same rate as the 6^3P_0 population.[12,13,15]

The several continuous spectra in mercury discharges arise from molecular forms of mercury, although many of the assignments of molecular states are still somewhat in doubt. Certain of the continua have been observed in mercury vapor excited by resonance radiation, those near 4850 A, 3350 A, and 2537 A being most prominent. Their intensities are proportional to the intensity of the 2537 A source[25,26]; all three have been variously reported to have long decay times.[27] The continuum near 4850 A is probably basically due to the molecular combination of a 6^3P_0 atom with a 6^1S_0 atom, although evidence to the contrary has been offered.[25,28]

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McCoubrey[29] has offered a detailed description of the emission process from this excited molecule in collision with two 6^1S_0 atoms. The presence of nitrogen makes possible the observance of the 4850 A band with resonance excitation at room temperature.[25,30]

Steubing[31] determined that ions were present in mercury vapor excited by 2537 A radiation. The most likely source of ionization energy is that available from a 6^3P_0 atom and a 6^3P_1 atom, which on combining lead to an ionized molecule. Using mass spectrograph techniques, Arnot and Millegan[32] have shown the ionization potential of the Hg_2 molecule to be 9.58 ev. Since the combined energy of the 6^3P_0 (4.67 ev) and 6^3P_1 (4.89 ev) atoms plus the heat of formation is 9.62 ev, the above mechanism is energetically possible. A combination of two 6^3P_0 atoms would fail to provide the ionization energy for the molecule, although subsequent thermal ionization of this molecule by an electron of about 0.2 ev is a possibility. Not even two 6^3P_1 atoms could furnish the 10.38 ev needed to ionize an atom, and the time constants of decay here reported discount the occurrence of ionization in a single collision process. Recent work by Biondi[33,34] with rare gases shows that collisions of two metastable atoms can produce atomic ions. In the case of resonance-excited mercury, however, the populated metastable levels lie well below half the the atomic ionization limit, and the molecular ion is therefore favored.

Other mechanisms of ion formation not related to the 6^3P_0 atom have also been postulated.[32,35] In a recent study, Biberman[36] attempts to show that this ion is not formed in the volume of the gas, but is due to electrons ejected from the electrodes by 6^3P_0 atoms. While it has been definitely established that 6^3P_0 atoms do eject electrons in collisions at the surface of a conductor,[37,38] numerous investigations, including the present one, have shown that the ions are formed in the volume of the vapor.[39–43]

Most of the phenomena relating to the metastable 6^3P_0 atom have in the past been studied individually. Consequently, much of the data presented could not be completely interpreted, or interpretations were based upon assumptions which were not substantially supported by experiments of others. It is the purpose of this work to present simultaneous correlations of many of these phenomena, leading to new information and a better understanding of the processes involved.

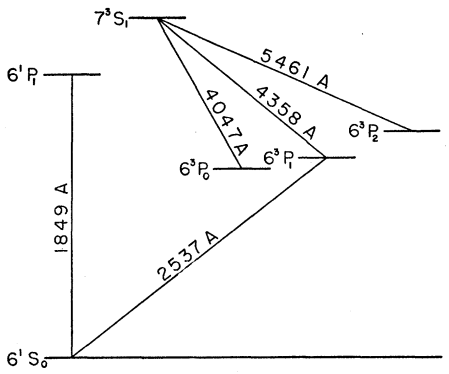

FIG. 1. Energy levels of mercury.

EXPERIMENTAL PROCEDURE

Resonance Cell

A resonance cell was designed to study the population of 6^3P_0 atoms by absorption of 4047 A radiation, to observe emission spectra from mercury vapor excited by 2537 A radiation, and to measure ion formation in the volume of the vapor. A schematic diagram of this cell along with auxiliary equipment is shown in Fig. 2. Commercial germicidal glass tubing of 2.5 cm diameter, which transmits approximately 65% of the 2537 A radiation and a negligible amount of 1850 A, was used for the walls of the cell; flat Pyrex windows were sealed at each end. Two plane-parallel platinum electrodes, 23 cm long and 2.2 cm wide, were placed lengthwide in the germicidal glass tube with separation of 0.465 ± 0.025 cm. Platinum, having a work function 0.8 volt greater that the excitation energy of the 6^3P_0 atom, was used as electrode material to minimize the ejection of electrons by photons and by metastables. However, at low pressures of N_2 a small current of ejected electrons was observed, indicating a lowering of the work function by impurities, presumably mercury.

In use this cell was shielded optically (and electrically) to allow 2537 A radiation to pass laterally through the region between the electrodes. For absorption studies, radiation from the 4047 A source passed between the electrodes parallel to the axis of the cell.

Gas Generator

Several investigators have shown the need for nitrogen of high purity when employing this gas to produce large quantities of metastable atoms.[44–46] Spectroscopic

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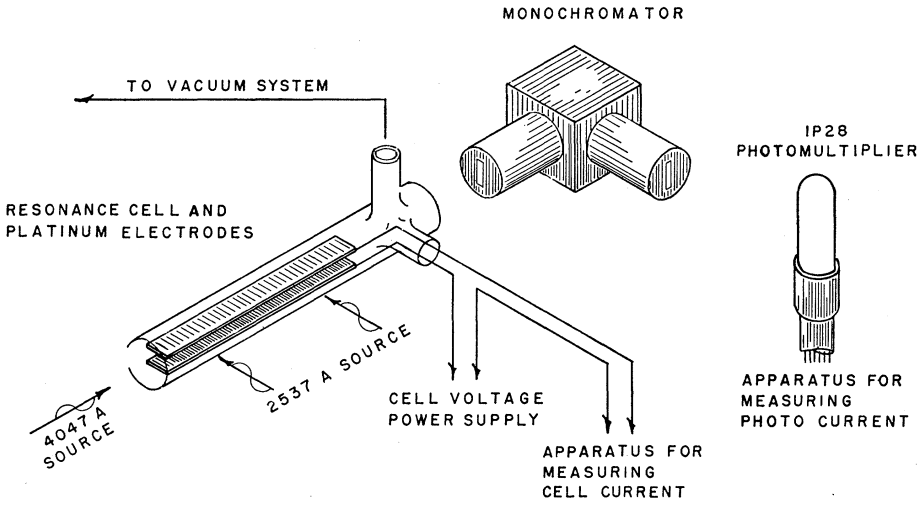

FIG. 2. Resonance cell for absorption and ionization studies.

traces of hydrogen and oxygen severely quench atoms in the 6^3P_0 state. Although water molecules have been shown to enhance the 6^3P_0 population, they may also be dissociated by 2537 A quanta, with the result that as H_2 and O_2 are accumulated, 6^3P_0 atoms are strongly quenched. Thus the N_2 to be used had to be free of H_2, O_2, and H_2O at least.

Nitrogen was prepared by the explosion of sodium azide in the generator shown in Fig. 3. The chief impurity anticipated in this process was H_2O vapor appearing originally as water of crystallization in the NaN_3 crystals. Interaction of this H_2O with free Na would give rise to free H_2. The generator system employed hot copper and copper oxide at 450°C to remove O_2 and H_2 respectively. Phosphorus pentoxide served to remove H_2O vapor, and the liquid air trap removed any volatile vapors as well as H_2O.

Prior to the explosion of the NaN_3, three bottles for collecting N_2 were pumped at a pressure less than 5×10^{-6} mm and baked at 450°C for 8 hours, after which time the open branch of each bottle was sealed off. The Cu and CuO at 525°C and the NaN_3 at 200°C were baked for 6 hours. The NaN_3 was then exploded with a cool torch. Nitrogen was then circulated for 48 hours over the P_2O_5 and hot Cu and CuO, and through the liquid air trap. Break-off tips in the other branch of the N_2 bottles were broken and the bottles sealed off after they had filled with N_2. With this preparation complete a bottle of N_2 could be sealed on the system designed for studying metastable atoms and N_2 admitted at the desired time by fracturing the remaining break-off tip.

The exceptionally large ion currents which were produced using this nitrogen and the constancy of this current when irradiated for extended periods with 2537 A radiation testify to its high purity. This high purity was achieved only after extended trials.

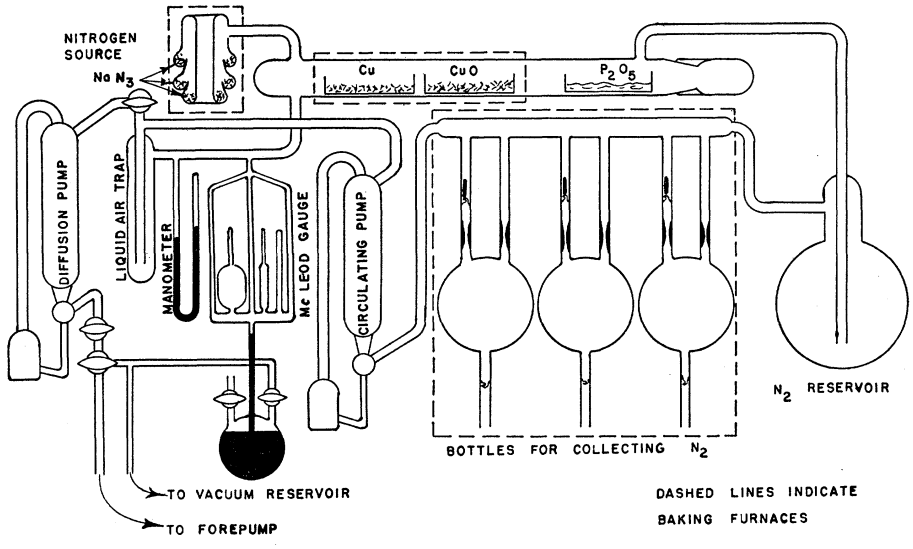

FIG. 3. Nitrogen generator.

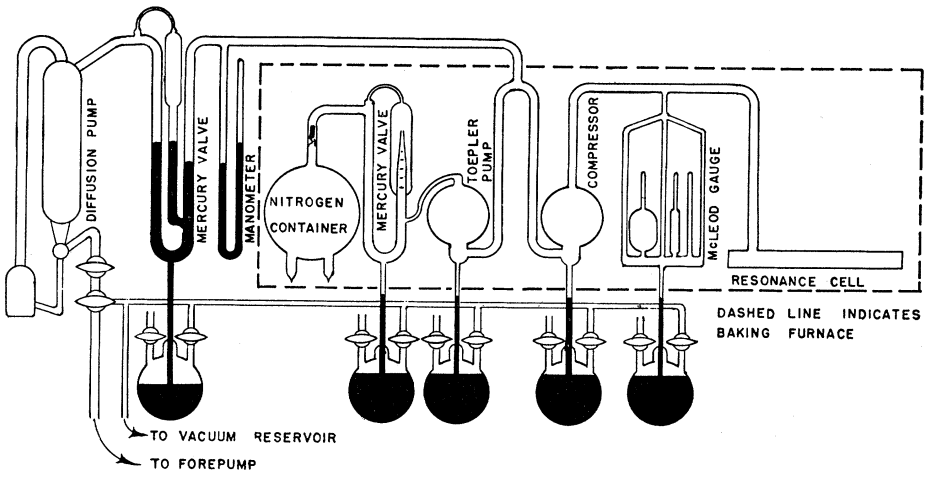

FIG. 4. Plan of apparatus.

Vacuum System

The vacuum system for the resonance cell, shown schematically in Fig. 4, used a mercury diffusion pump and a mechanical backing pump. Stopcocks were excluded from the system on the high vacuum side. Two mercury valves controlled by a vacuum reservoir were used to isolate different portions of the system. The mercury vapor concentration was set by saturation at 22°C room temperature throughout all experiments. In these studies the system was designed to permit a given sample of N_2 to be used for studying all the different phenomena. A Toepler pump was used to transfer N_2 from the storage container to the resonance cell and back. To attain highest pressures, a mercury "compressor" just preceding the resonance cell was used.

In assembling the system and purifying the mercury, great care was taken to prevent contamination. After a bottle of nitrogen was attached to the system, that portion enclosed in the dotted line in Fig. 4 was baked at 300°C for 12 hours with the pumps operating. At the conclusion of the baking, the valve to the diffusion pump was closed, and the system was observed to maintain a McLeod gauge pressure of less than 5×10^{-6} mm for 24 hours.

Light Sources

Light sources used for resonance excitation must operate at low temperatures to have narrow emission line widths and low self-reversal. The first source of 2537 A consisted of a pair of 15-watt commercial germicidal lamps, one on each side of the resonance cell. These were operated on direct current with resistive ballasts, and polarities could be reversed to prevent the "pumping" of mercury to the negative end. In a second type of source the same lamps were excited by 35-megacycle Hartley oscillators. A keying circuit could provide square wave pulses of light at the rate of 30 cps. The decay time of these square wave pulses was measured to be 0.2 millisecond.

For a source of 4047 A a Pyrex tube of $\frac{5}{8}$-in. diameter and 18-in. length, having a plane Pyrex window sealed on one end, was baked and filled with a drop of mercury and a few mm of argon. When excited by one of the rf oscillators and viewed end on, it was a small but intense source of 4047 A radiation. All sources were electrically shielded and air cooled and could be made to operate at constant intensity ($\pm1\%$) for periods of a few hours.

Measurement of 4850 A Continuum

The 4850 A continuum was studied by two methods. In both of these a Corning 9863 ultraviolet filter was

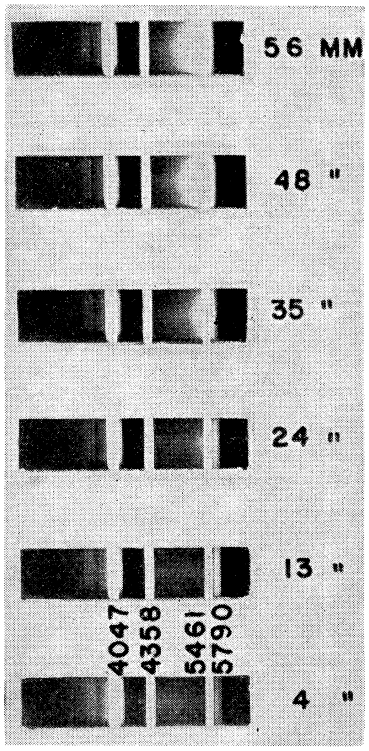

FIG. 5. Spectra of resonance cell, showing 4850 A continuum. Nitrogen pressures are labeled.

placed between the 2537 A source and the resonance cell to exclude almost all visible radiation from the source. In the first method, two Wratten filters, 8 *K*-2 and 47 *C*-5 were used with a 1P28 photomultiplier. This combination permitted only the light from the center of the 4850 A continuum to pass to the photocell.

Also, a small spectrograph was devised from a Bausch and Lomb direct vision spectroscope and placed at the end of the resonance cell to view the region between the electrodes for qualitative studies. Spectrograms were usually taken with a wide slit, using Kodak Super Ortho Press film and exposures of several hours. Figure 5 shows spectrograms of the radiation from the resonance cell at various nitrogen pressures. The exposure times are increased at the low pressures. The spectral sensitivity of the film causes the peak of the green continuum to be shifted toward the red end of the spectrum. The resonance cell emission lines are discussed in a later section.

Measurement of Resonance Cell Current

Steady-state resonance cell currents were measured with either a microammeter or a galvanometer, and periodically varying currents were measured by oscilloscope. A variable power supply was used to apply a voltage across the platinum electrodes. For a given nitrogen pressure and constant 2537 A radiation there was a pleateau region of collection voltage, where all ions being formed were drawn to the electrodes without appreciable recombination, diffusion, or additional ionization by collision. The current at this saturation voltage is thus proportional to the rate at which ions are formed, and consequently the cell current will frequently be referred to as the rate of ion formation.

Measurement of 2537 A Radiation

Only relative measurements of the 2537 A radiation intensity were made. Three methods were used: monochromator and photomultiplier; calibrated neutral screens; and a combination of filters, ultraviolet sensitive phosphor, and photomultiplier. In the first of these methods, a 1P28 photomultiplier was used in conjunction with a Bausch and Lomb quartz monochromator set to transmit the 2537 A line.

Neutral screens were made, using parallel black nylon monofilament threads, uniformly separated and mounted on a special frame. When used, the threads of the screens were parallel to the resonance cell and the 2537 A sources. Varying degrees of transmission were provided by different thread size and spacing. Six screens, having transmission values varying in steps from 18 to 88% were constructed and calibrated.

The last method for measuring the 2537 A intensity used a commercial phosphor (General Electric) having a narrow absorption band in the region of the 2537 A line and emitting between 5200 A and 5750 A, peaking about 5400 A. An ultraviolet filter, Corning 9863, placed between the source and the phosphor, cut out essentially all radiation above 4200 A. A second filter, Wratten 58 *B*-2, placed after the phosphor, transmitted radiation between 4800 A and 6400 A. Only the 2537 A line of the source produced any significant emission from the phosphor. It was only the light from the phosphor that arrived at the photomultiplier. Since the intensity of the emitted light was found to be proportional to the intensity of the 2537 A line, the photomultiplier current was proportional to the latter. This system was used mainly to monitor the 2537 A sources to insure constant intensity.

TABLE I. Absorption constant at various pressures.

Pressure of N_2 in mm	Absorption constant A_0
6.7	0.38
13.6	0.38
20.5	0.37
28.6	0.37
37.4	0.38
55.	0.38

Measurement of 4047 A Absorption

As shown in Fig. 2, radiation from the 4047 A source passed through the resonance cell to the monochromator, set to pass only the full 4047 A line, and then to the photomultiplier. The percent absorption was obtained by dividing the difference between 4047 A intensities with the 2537 A source first off and then on by the 4047 A intensity with the 2537 A source off. When the 2537 A source was operated in a square wave fashion, the absorption of 4047 A radiation varied as a function of time due to the time decay of the 6^3P_0 atoms. In this instance, the oscilloscope pattern of output of the photomultiplier showed the manner in which the absorption varied from its maximum steady state value to zero. To obtain the percent absorption, a synchronous motor was used to drive an interruptor synchronized so as to interrupt the 4047 A beam briefly during the off time of the 2537 A radiation; and from the resulting pattern it was simple to calculate the percent absorption as before.

OBSERVATIONS

Population of 6^3P_0 Atoms

The percent absorption is proportional to the concentration of 6^3P_0 atoms when the concentration is small. To obtain a more widely useful relation between these two quantities, we postulate that the 4047 A radiation is absorbed according to Beer's law and that the 4047 A emission line of the source is broad compared to the absorption line of the metastable atoms of the resonance cell. For this moderate absorption one may approximately represent the intensity distribution in the transmitted line by a broad, flat-topped distribution with a narrow, partly absorbed area at the

center. If the concentration of absorbing atoms is not too large, the absorption line is of fixed form and the absorbed area is simply proportional to $(1-e^{-kN_0})$, where N_0 is the concentration of metastables and k is proportional to the central absorption cross section per atom.

If the observables R and $\bar{R}$ are the total areas of the transmitted line with and without the presence of absorbing metastables, respectively, then the fractional absorption A is

$$A=\frac{\bar{R}-R}{\bar{R}}=\frac{K(1-e^{-kN_0})}{\bar{R}} \quad (1)$$

or,

$$A=A_0(1-e^{-kN_0}),$$

leading to

$$N_0=-\frac{1}{k}\ln\frac{A_0}{A_0-A}. \quad (2)$$

The validity of the above assumed conditions of moderate, narrow absorption can be tested by checking the constancy of A_0 as N_0 is varied by known fractions over the full range of operation. The relative values of N_0 were easily provided by calibrated screens on the 2537 A source and use of the fact that N_0 is proportional to the intensity of the 2537 A. Equation (2) could then be solved for A_0 using known values for N_0 and A. Not only were semilogarithmic plots of Eq. (2) linear, but the value of A_0 at different N_2 pressures remained constant, indicating negligible effects of pressure broadening. The values of A_0 determined for six different pressures of N_2 are shown in Table I. Their constancy justifies the use of Eq. (2) up to $A=24\%$, the highest absorption value used in calculations. The facts that A_0 is considerably less than unity and that A reached only 0.73 even with the very high N_0 present during the production of the 405 μa current, as discussed later, give support to the above assumption of an emission line broader than the absorption line.

This absorption technique was used to measure the relative concentration N_0 of metastables as a function of the nitrogen pressure P in mm at constant 2537 A intensity. These data are given in Fig. 6(A), which shows the experimental points for N_0 *vs* P. Klumb and Pringsheim[4] have discussed the factors affecting N_0 as a function of P. They obtained the expression

$$N_0=MP/(1+aP+bP^2), \quad (3)$$

where M is a convenient scale factor and a and b are constants having physical significance but arbitrary values. If one uses $M=7.8$ and the values $a=0.0143$ and $b=0.00093$, this equation fits the present data very well, as shown by the curve in Fig. 6(A).

A low intensity of 2537 A radiation was used in order to avoid high absorption of 4047 A. The data obtained here are similar to those obtained by other investigators.[4,12,47] Further agreement with the work of others was obtained when it was found impossible to detect any absorption of the 4358 A and 5461 A lines, indicating that the populations of the 6^3P_1 and 6^3P_2 states were small.

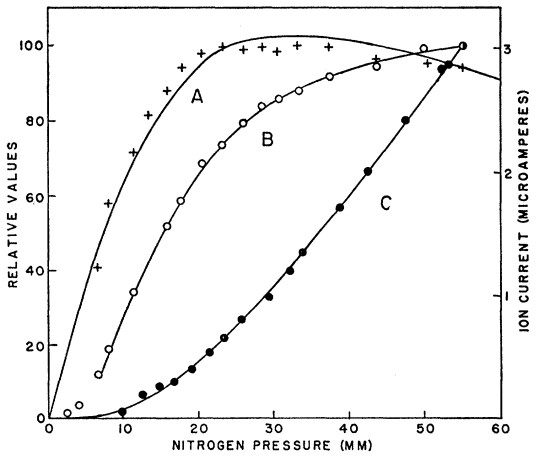

FIG. 6. Pressure dependence of resonance phenomena at constant 2537 A intensity. Curves show fit of theory to experimental points. A: Population of 6^3P_0 atoms. B: Rate of ion formation. C: Intensity of 4850 A continuum.

If the 4047 A absorption source was removed, it was possible to observe line emission excited by double absorption, as illustrated by the spectra of Fig. 5. The 6^3P_0 atoms, derived from resonance-excited 6^3P_1 atoms, were raised to the 7^3S_1 state by the 4047 A radiation which weakly penetrated the ultraviolet filter of the 2537 A source. The lines 5461 A, 4358 A, and (in part) 4047 A come from this excitation. The yellow line is presumably 5790 A from $(6^1P_1-6^3D_1)$, similarly excited by the $(6^3P_0-6^3D_1)$ absorption of 2967 A, which the ultraviolet filter readily transmits. The resonance cell line at 4047 A is due in part to radiation of this wavelength passing through the filter. The 5461 A line was shown not to be caused by such leakage, for the variation of its intensity with N_2 pressure was approximately the same as that of N_0. Because of the overlap of the 4850 A continuum, especially at high pressures, the 5461 A emission was not used for quantitative measurements of N_0.

Ion Formation

Ions were observed in the mercury vapor at all pressures of nitrogen with resonance excitation. That these ions were not due to the ejection of photoelectrons from the electrode surfaces was shown by the great reduction in current at low nitrogen pressures, by studies of transients, by the inability of a high intensity iron arc to produce measurable surface emission, and by supplementary experiments consisting of irradiating selected portions of the volume between widely separated electrodes. Characteristic curves of rate of ion

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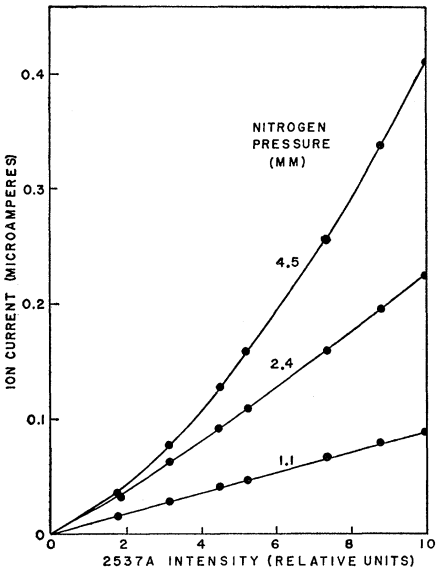

FIG. 7. Dependence of rate of ion formation on the first power of 2537 A intensity at low nitrogen pressures. Curves indicate experimental points.

formation *versus* cell voltage were taken at several nitrogen pressures between 1 and 55 mm. At all pressures plateaus were found to exist, and collection voltages in other measurements were always chosen on these plateaus to insure that negligible ionization by collision was occurring.

As shown in Figs. 7 and 8, the rate of ion formation exhibits a first power dependence upon the 2537 A intensity at a pressure of 1.1 mm. At pressures of 7 mm and higher the rate of ion formation is proportional to the second power of the intensity of the 2537 A radiation.

These results agree with those of other investigators.[41,43,48] At very low pressures metastable atoms, the number of which is proportional to the intensity of the 2537 A radiation, rapidly diffuse to the electrode surface and eject electrons. At higher pressures this process becomes unimportant compared with that involving collisions of two excited atoms within the volume. This process exhibits a square law dependence, and the most likely mechanism is

$$\begin{aligned} &\mathrm{Hg}(6^3P_1)+\mathrm{N_2}\rightarrow \mathrm{Hg}(6^3P_0)+\mathrm{N_2}' \\ &\mathrm{Hg}(6^3P_0)+\mathrm{Hg}(6^3P_1)+\mathrm{N_2}\rightarrow \mathrm{Hg_2}''+\mathrm{N_2} \\ &\mathrm{Hg_2}''\rightarrow \mathrm{Hg_2}^+ + e. \end{aligned} \qquad (4)$$

Evidence in support of the postulated intermediate excited molecule is presented later in connection with studies of decay transients. The possibility suggested by Biondi[34] of single step ionization in a collision of two excited mercury atoms is not contradicted by these decay studies, as the necessary 6^3P_2 atoms would be much more abundant following his electrical excitation than after our resonance absorption.

[48] F. G. Houtermans, Z. Physik **41**, 619 (1927).

The rate of ion formation as a function of N_2 pressure, the 2537 A intensity being constant, is given in Fig. 6(B). The process involving the combination of a 6^3P_0 and a 6^3P_1 atom to form the ion is the only one which adequately explains these data. Since a three-body collision is required to satisfy the conservation of momentum and energy, the current I is proportional to N_0N_1P, where N_1 is the population of 6^3P_1 atoms. Since N_1 was not measured as a function of the pressure of nitrogen, it was assumed that the population varied in the manner described by the Stern-Volmer theory of quenching,[2]

$$N_1=[(N_1)_{P=0}]/(1+cP).$$

Thus

$$I=BN_0P/(1+cP). \qquad (5)$$

Using the values of N_0 given by a smooth curve through the experimental data of Fig. 6(A), and choosing the scale constant $B=0.0595$ and the quenching coefficient $c=0.0384$ mm^{-1}, one obtains a good fit of this equation to the experimental data, as demonstreated by the curve of Fig. 6(B). Close agreement at pressures below 7 mm is not expected, as it has just been shown that the postulated three-body collision process does not predominate in this region. It is seen that at 50 mm N_1 is reduced to 34% of its initial value. This amount of quenching is not inconsistent with other reports. Zemansky's theory[2] predicts a value of 25% at this pressure. Also, Badger[49] determined that the intensity of the scattered 2537 A radiation, while not directly proportional to the 6^3P_1 population, decreased at 50 mm of N_2 to about 30% of its value at zero pressure. The recent quenching cross section given by Matland[5] can be used in calculating an approximate quenching coefficient for the present experiment, following his method appropriate to a long, circular tube. One must use an equivalent radius for our electrode geometry. Using his cross section of 0.4×10^{-16} cm^2 and the extreme choices of equivalent radius as 1.3 cm and 0.23 cm, one finds that our observed value of $c=0.0384$ mm^{-1} is bracketed by the calculated values 0.013 mm^{-1} and 0.13 mm^{-1}, respectively.

The success of this mechanism in explaining the data lends added support to substantiate the hypothesis of Houtermans,[48] Snavely,[50] and Arnot and McEwen,[51] namely, that the ion arises from the combination of an atom in the 6^3P_0 state with one in the 6^3P_1 state in a three-body collision.[52]

[49] R. M. Badger, Z. Physik **55**, 56 (1929).
[50] B. L. Snavely, Phys. Rev. **52**, 174 (1937).
[51] F. L. Arnot and M. B. McEwen, Proc. Roy. Soc. (London) **A165**, 133 (1938).
[52] This theory in its present form fails to explain the reported dependence of ion formation on the third power of the 2537 A intensity at high vapor pressures.[42] However, it has been demonstrated in this work that high concentrations of 6^3P_0 atoms are possible. It is also possible that the cross section of interaction with an excited atom might be much greater than with an unexcited atom. The cubic law could thus conceivably arise at the higher vapor pressures if the 6^3P_0 atoms become so abundant that they commonly act as the third body.

It is well to note here that Houtermans observed a linear relationship between the rate of ion formation and the pressure of argon which was used as a diluent gas. It is fairly well established that argon does not appreciably quench 6^3P_1 atoms. Thus Eq. (5) would reduce to

$$I = BN_0P.$$

But Klumb and Pringsheim, using argon as a diluent gas, found that above 3 mm of argon, N_0 was a constant. Thus above 3 mm of A, I would be proportional to P only, and Houtermans' observations would be quite understandable.

A direct observation of the presence of 6^3P_0 atoms in the ion formation process was afforded by decreasing N_0 independently by absorption of 4047 A. One 2537 A source was operated continuously; the other was keyed by a 30-cps square wave, filtered to give only visible wavelengths, and used as the source of 4047 A radiation. The supply of 6^3P_1 atoms was thus held constant, and a small fraction of 6^3P_0 atoms was selectively removed by absorption. A resulting decrease in cell current, which was determined to be less than 0.2%, was clearly observed by oscilloscope. However, to use this method for distinguishing directly between ion processes involving either two 6^3P_0 atoms or one 6^3P_0 and one 6^3P_1, one would need to produce reductions in I of the order of 10%.

An ion current of 405 μa was observed at 50 mm pressure when the 2537 A intensity was temporarily made very large, and the absorption of 4047 A by metastables became 73%. In this experiment and those of other investigators it is reasonable to assume that at least one 6^3P_0 atom is required for every ion. The ratio of population of 6^3P_0 atoms to that of Hg atoms in the ground state N′ is given by

$$N_0/N' \geqq I\tau_0/N'e, \tag{6}$$

where e is the electronic charge, τ_0 is the mean life of the 6^3P_0 state, and I is the cell current of 405 μa. For a temperature of 22°C N′ is 5×10^{13} atoms/cm³ and τ_0 at 55 mm of N_2 is measured (Fig. 13) to be 0.59 millisecond. Substituting these values gives

$$N_0/N' \geqq 1/700. \tag{7}$$

Thus at least 1 out of every 700 mercury atoms was in the 6^3P_0 state.

It is probable, however, that the estimate of one 6^3P_0 atom for every ion formed is conservatively low, for all studies concerning the mechanisms whereby 6^3P_0 atoms decay consider the number contributing to the formation of ions as being negligible. The exponential character of the decay of 6^3P_0 population illustrated in Fig. 10 shows that in decay the disappearance rate must predominantly have terms in the first power of N_0, not the N_0^2 or N_1N_0 terms characteristic of loss by ion formation. It is also apparent that in normal steady state measurements the process of ion formation is not dominant, for both the rate of production of 6^3P_0 atoms and their population are proportional to the 2537 A intensity. It is likely that loss by ion formation is still minor even at the increased intensity of irradiation used to produce the 405 μa current. Moreover, an intense 2537 A arc was not used here to produce this current. Thus it is quite conceivable that under favorable conditions as many as 1 out of every 20 mercury atoms could be in the 6^3P_0 state. The present evidence and its extended implication therefore give an approach to substantiating the theories of Wood and Gaviola[7,8] and of Foote,[6] which have predicted these high concentrations.

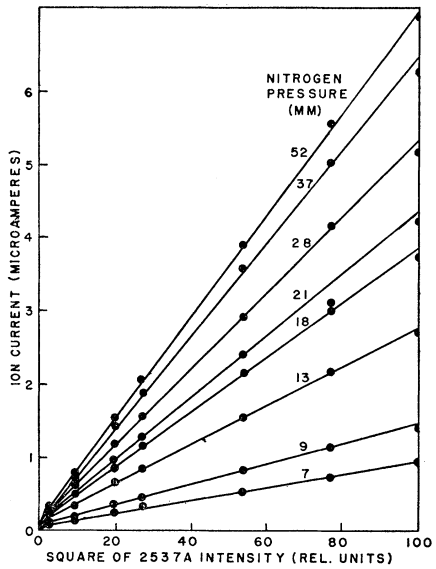

FIG. 8. Dependence of rate of ion formation on the second power of 2537 A intensity at high nitrogen pressures. Curves indicate experimental points.

Continuum at 4850 A

The central region of this 4850 A continuum was isolated by filters previously described and its intensity measured by photomultiplier. The direct proportionality between this intensity and that of the incident 2537 A radiation is shown in Fig. 9 at three nitrogen pressures. Since the population of metastables N_0 is proportional to the 2537 A intensity, these results agree with the following excitation process, leading to the emission of the 4850 A continuum:

$$\begin{aligned} &Hg(6^3P_1)+N_2 \rightarrow Hg(6^3P_0)+N_2' \\ &Hg(6^3P_0)+Hg(6^1S_0)+N_2 \rightarrow Hg_2'+N_2. \end{aligned} \tag{8}$$

Assuming that the population N_g of these excited molecules is proportional in a steady state to the intensity of the 4850 A continuum and that the two main sinks for these molecules are radiation and diffusion to the walls, one equates rates of production and loss and

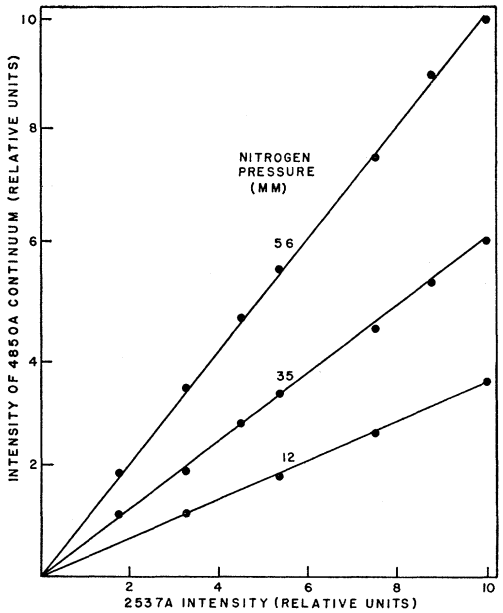

FIG. 9. Linear dependence of 4850 A continuum intensity on 2537 A intensity at three nitrogen pressures.

obtains

$$CN_0P=N_g(1+d/P)$$

or,

$$N_g=CN_0P^2/(P+d), \tag{9}$$

where C and d are constants and P is nitrogen pressure in mm. The dependence of N_0 on P is given independently in Fig. 6(A). The curve passing through the experimental points in Fig. 6(C) illustrates the success with which this equation can be fitted to the data, using $C=0.073$ and $d=155$. A small, constant intensity due to the measured background of glass fluorescence has been subtracted from the observed data.

McCoubrey[29] has shown evidence that in pure mercury vapor at 200°C the continuum is emitted as collision-induced radiation from the excited molecule on striking two ground-state atoms. No such collision process appears called for in the present studies, however, where nitrogen serves as collision particles.

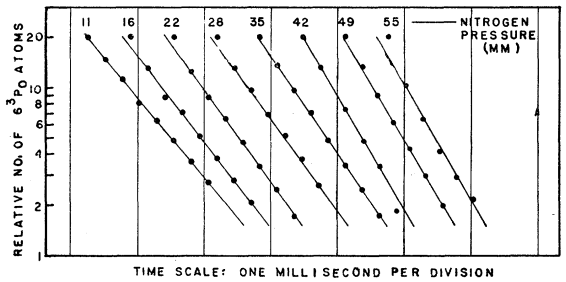

FIG. 10. Semilogarithmic plot showing exponential decay of population of 6^3P_0 atoms at various nitrogen pressures.

Effects of Large Voltage

Large changes in collection voltage caused noticeable effects, which will be reported for a pressure of 55 mm. The absorption of 4047 A decreased from 22.9 to 22.2% as the voltage changed from 0 to 400 volts, while the intensity of the 4850 A continuum increased linearly from 83 to 100%. The ion current, reaching the knee of the plateau region at about 40 volts, increased linearly from 90 to 100% between 40 and 400 volts.

Time-Dependent Transients

If the source of 2537 A is operated steadily and the collecting voltage is switched on and off as a square wave, one observes characteristic transients in the cell current. An oscillographic study of the ion pulse shape after the collecting voltage is turned on shows a linear decrease of ion density from the recombination-limited, free-field value to the steady value limited by the rate of production. To assume linearity of slope, it was necessary to avoid high ion densities, where appreciable recombination introduced curvature. In agreement with the processes involved, the latter steady value was proportional to the second power of the 2537 A intensity, and the former initial value was proportional to the first power. While the resonance cell was not designed with a uniform field E for accurate mobility measurements, the heavy ion mobility was measured to be 2.2 ± 0.2 cm^2/volt sec over the observed range of E/P from 3.0 to 6.6 volts/cm mm. Mitchell and Ridler[53] have determined the mobility of Hg^+ in nitrogen to be 2.20, while for Hg_2^+ they give the theoretical value of 1.50 with the comment that it may be too high. Thus, the observed mobility in the resonance cell would somewhat favor the atomic ion. However, energy considerations and the work of many investigators require that the Hg_2^+ form be given preference over the Hg^+ form. The presence of positive ions in the volume of the resonance cell, as shown in these transients, discounts Biberman's contention that currents produced by resonance excitation are due only to ejection of electrons by metastables.

If the 2537 A source is keyed on and off as a square wave, additional information can be gained from observing the decay transients of the 6^3P_0 atom population, the cell current, and the 4850 A continuum. For the first named transients, the 4047 A source was operated steadily, and for the second, a constant collecting voltage was supplied. These decays are all essentially exponential, having lifetimes τ_0, τ_i, and τ_g, respectively. The switching time of the optical excitation and the collection time of the ions were both very rapid compared to the decay times observed. The results of the decay observations of these three quantities are graphed in Figs. 10, 11, 12, and 13. All decay curves commence at the end of the 2537 A radiation.

[53] J. H. Mitchell and K. Ridler, Proc. Roy. Soc. (London) A146, 911 (1934).

The lifetime τ_0 of the 6^3P_0 state as a function of pressure of nitrogen has been the subject of many investigations. It is well established that the decay is essentially exponential,[14] and we may write the time dependent concentration as

$$n_0=N_0e^{-\beta t}. \tag{10}$$

Samson has considered the diffusion of resonance radiation and the quenching of and radiation from 6^3P_1 and 6^3P_0 states in arriving at the following expression, which fits his experimental measurements:

$$\beta=\frac{1}{\tau_0}=\frac{f}{P}+\frac{gP+hP^2}{P+m}, \tag{11}$$

where f, g, h, and m are constants depending on the temperature and geometry of the resonance cell. The maximum lifetime of about 3 milliseconds observed by Samson in a cell whose dimensions exceeded 2 cm is reasonably matched by the value of about 0.9 millisecond in the present cell, whose smaller dimensions

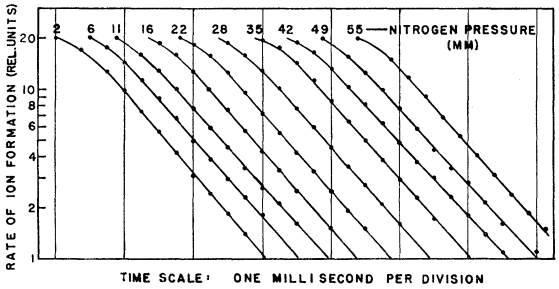

FIG. 11. Semilogarithmic plot showing exponential decay of rate of ion formation at various nitrogen pressures.

would enhance the loss by diffusion. The expected decrease of τ_0 with sufficiently large pressures is also observed.

One may refer to the observed cell current as the rate of ion formation because the transit time of the collected ions was always less than 5% of the current decay time. After about 0.5 millisecond the transients in Fig. 11 show a simple exponential decay, of lifetime τ_i, following a slower decay during the first few tenths of a millisecond. It is at once clear that since τ_i is greater than $\tau_0/2$ and in fact is slightly greater than τ_0, as shown in Fig. 13, then the ion cannot arise directly from the collision of two excited atoms and a third body. An intermediate excited molecule may be formed, whose lifetime is approximately τ_i and which then produces an ion by a subsequent process of unspecified nature, not involving excited atoms. The electronic state of this postulated molecule and the cause of its surprisingly long lifetime remain undetermined.

The decay of the concentration n of these highly excited molecules follows the equation

$$dn=\alpha n_0n_1dt-\mu ndt, \tag{12}$$

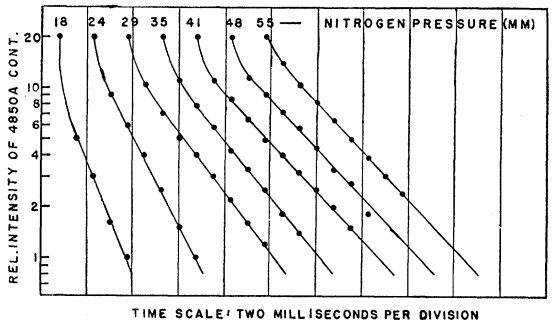

FIG. 12. Semilogarithmic plot showing exponential decay of intensity of 4850 A continuum at various nitrogen pressures.

where the constants α and μ refer respectively to molecule formation by three-body collision and to loss by ion formation and diffusion. Since in decay 6^3P_0 atoms are the source of 6^3P_1 atoms, each then decays as $e^{-\beta t}$, giving

$$dn=\alpha N_0N_1e^{-2\beta t}dt-\mu ndt. \tag{13}$$

The solution for this equation is

$$n=\frac{\alpha N_0N_1}{(2\beta-\mu)}(2\beta e^{-\mu t}-\mu e^{-2\beta t}), \tag{14}$$

which has an initial slope of zero and which asymptotically approaches a simple exponential decay of lifetime $1/\mu$. The decay curves of Fig. 11 fit this analysis. As an independent check on Eq. (14), one may make a rough calculation of $\tau_0=1/\mu$ based on Eq. (14) and the small differences between these decay curves and their asymptotes. The values of τ_0 thus obtained range from 0.6±0.2 to 0.5±0.2 millisecond over the full pressure range and are in fair agreement with the τ_0 values in Fig. 13(A) as measured directly for the 6^3P_0 atoms.

The decay of the 4850 A continuum shows a lifetime τ_g which increases greatly with pressure and reaches a value 3 to 5 times that of τ_0 and τ_i. See Fig. 13. Since

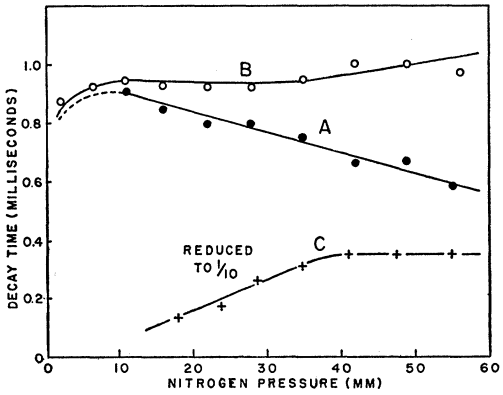

FIG. 13. Decay times of resonance cell phenomena at various nitrogen pressures. A: Population of 6^3P_0 atoms. B: Rate of ion formation. C: Intensity of 4850 A continuum.

τ_0 is independent of collecting voltage from 0 to 400 volts, ionic recombination cannot be the source of this excitation. The initial rapid decay shown in Fig. 12 is the result of fluorescence of the glass tube. The excited molecular state responsible for this continuum, presumably formed from the combination of 6^3P_0 and 6^1S_0 atoms, is clearly not the same as the shorter-lived state from which the ions are derived.

SUMMARY

A study has been made of phenomena related to the metastable 6^3P_0 mercury atom appearing in a resonance cell containing mercury vapor and nitrogen and irradiated with 2537 A from a cool mercury arc. The chief objective was to observe coherently the variety of phenomena reported individually by many investigators and, when possible, to use improved techniques to provide new data and consistent interpretations. Those studies which were a repetition of the work of other investigators gave in general excellent agreement; some of the results of this work point to correct solutions where contradictory results have existed in the past.

Quenching of the 6^3P_1 state.—The only feasible mechanism for the formation of the ion required that the 6^3P_1 state be quenched in a manner very similar to that described by the Stern-Volmer formula. The quenching at 55 mm of N_2 was approximately 66%.

The 6^3P_0 atom.—A method for measuring relative populations of the 6^3P_0 atom is described, which uses the self-absorption of the 4047 A line. This technique was checked and used in the absorption range up to 24% and at pressures as high as 55 mm. The population varies as the first power of the 2537 A intensity. Some of the work of other investigators which disagrees with this relation may be explained by the theory of Gaviola, which concludes that at high intensities the metastable population is proportional to the square root of the intensity. The population was also measured as a function of nitrogen pressure, and the results agreed satisfactorily with the theory of Klumb and Pringsheim. The decay constant of the metastable atoms was studied as a function of pressure, and the results were consistent with the theory of Samson.

The 4850 A continuum.—Additional evidence is presented to show that the molecule responsible for the continuum around 4850 A is formed according to the mechanism

$$\mathrm{Hg}(6^3P_1)+\mathrm{N_2}\rightarrow \mathrm{Hg}(6^3P_0)+\mathrm{N_2}'$$
$$\mathrm{Hg}(6^3P_0)+\mathrm{Hg}(6^1S_0)+\mathrm{N_2}\rightarrow \mathrm{Hg_2}'+\mathrm{N_2}.$$

This conclusion is based upon the observations that the intensity of the continuum varies as the first power of the 2537 A radiation, and secondly, that this mechanism explains the manner in which the intensity varies with nitrogen pressure. The mean lifetime for this emission in decay is several times longer than the decay time of the 6^3P_0 atoms or of the rate of ion production.

The resonance cell ion.—The ion originally discovered by Steubing was found in this experiment to exhibit the characteristics reported by numerous observers. The rate at which this ion was produced is dependent on the second power of the 2537 A intensity. Despite the insistence of Biberman that the ion is produced at the surface of the electrodes, the present work definitely confirms Rouse and Giddings' conclusions that the ions are formed in the volume of the gas. It is concluded that the probable mechanism for the formation of the ion is

$$\mathrm{Hg}(6^3P_1)+\mathrm{Hg}(6^3P_0)+\mathrm{N_2}\rightarrow \mathrm{Hg_2}''+\mathrm{N_2}$$
$$\mathrm{Hg_2}''\rightarrow \mathrm{Hg_2}^+ + e.$$

This mechanism requires a three-body collision of a 6^3P_1 atom and a 6^3P_0 atom with a N_2 molecule to form a highly excited mercury molecule; this molecule is then ionized in a process that is not completely understood. The observation that the decay time of the rate of ion formation is greater than the decay time of the 6^3P_0 state requires that the molecule be formed in an intermediate step prior to its ionization.

The dependence of this ion upon the population of 6^3P_0 atoms was directly demonstrated when it was shown that the ionization rate was decreased when the metastable population was selectively reduced by absorption of 4047 A radiation. The 4047 A intensity was only sufficient to demonstrate the effect; much greater intensities would be needed to distinguish between molecule formation by 6^3P_0 and 6^3P_0 and by 6^3P_1 and 6^3P_0.

From the study of the number of 6^3P_0 atoms required for the formation of the highest ion currents measured, it is concluded that certainly 1 out of every 700 mercury atoms was in the 6^3P_0 state, and that reasonable arguments could place the true value one or two orders of magnitude higher. This offers support to theories which have predicted such high concentrations.

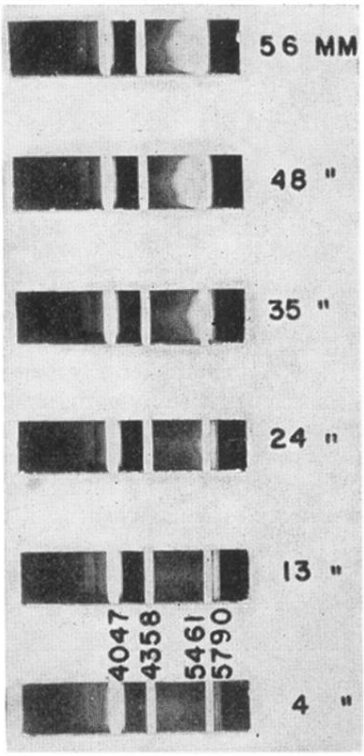

FIG. 5. Spectra of resonance cell, showing 4850 A continuum. Nitrogen pressures are labeled.