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## UNIVERSITY OF MISSOURI AT ROLLA

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A Study of the Molecular Emission and of the Life Times of  
the Metastable States in the Afterglow Spectrum of a Mercury Discharge

by Bruce M. Whitcomb a candidate for the degree  
of M.S. in Physics

and find that in form and content it is worthy to submit to the  
examination committee.

Richard Anderson

1st Reader

June 14, 1967  
Date

Don P. Hopkins

2nd Reader

June 16, 1967  
Date

I concur with the above approval

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June 27, 1967  
Date

(to be appointed by the Dean, Graduate School)



A STUDY OF THE MOLECULAR EMISSION AND OF THE  
LIFE TIMES OF THE METASTABLE STATES IN THE  
AFTERGLOW SPECTRUM OF A MERCURY DISCHARGE

BY

BRUCE M. WHITCOMB — , 943 —

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An Abstract of a

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submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN PHYSICS

Rolla, Missouri

June, 1967

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## ABSTRACT

Two methods of studying the spectrum in the early afterglow of a pure mercury sample are discussed. Using a time-sampling technique, information about the intensity of the spectrum as a function of time in the afterglow can be obtained. The intensities of two molecular bands, centered at 3350A and 4850A, are studied. The method of formation of the diatomic mercury molecule and the emission of radiation in the two bands are shown to be density dependent. Mechanisms are presented which explain both the molecular formation and the radiation in the two bands.

In an absorption study, the half-lives of the metastable and resonance states of mercury are measured. The half-lives indicate that there is a depopulation mechanism of the  $6^3P_2$  state at all atom densities and that there is a definite depopulation mechanism of the  $6^3P_0$  state at the very high densities. The depopulation of the  $6^3P_2$  state is shown to be related to an ionization process which is the cause of the enhancement in the intensity of the line spectra. The depopulation mechanism for the  $6^3P_0$  state is the formation of the mercury molecule which occurs with increasing frequency at higher atom densities.

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## LIST OF FIGURES

Figures	Page
1. Block diagram of apparatus used in time-sampling technique. . . . .	28
2. Block diagram of apparatus used in absorption study. . . . .	32
3. Optical system used in absorption study shown with principal light rays in dotted lines. . . . .	34
4. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 428°K. . . . .	37
5. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 443°K. . . . .	38
6. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 468°K. . . . .	39
7. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 488°K. . . . .	40
8. Energy level diagram of mercury. . . . .	41
9. Mercury vapor density as a function of temperature	53



## LIST OF PLATES

Plate	Page
1. Experimental cell on vacuum system. . . . .	26
2. Experimental apparatus for time- sampling technique. . . . .	30
3. Experimental apparatus for absorption study. . .	35

## LIST OF TABLES

Table	Page
I. Half-life of the $6^1P_1$ , $6^3P_2$ , $6^3P_1$ , and $6^3P_0$ states as a function of temperature. . . . .	45

## I. INTRODUCTION

A. Historical Survey. Interest in the structure of light, as it was termed, must have begun with curiosity about such natural phenomena as rainbows. It was not until 1637 when Descartes <sup>1</sup> observed an analogy with a prism that the frequently observed phenomenon of the rainbow was even partially explained. The explanation that a rainbow is caused by the same principle as that by which a prism works was insufficient. In 1660, Marci showed that once white light was dispersed into its colors, no further dispersion of those colors was possible. By this means, it was discovered that there was nothing more basic than the various colors and that they were not combinations of something more fundamental. In 1672, Newton <sup>2</sup> explained how white light is composed of the many colors. He showed experimentally that once it had been dispersed, white light could be reformed from the many colors by means of a second prism.

It was known by this time that light is composed of various combinations of colors. However, there was no adequate explanation for the source of any of these various colors until 1752. Melvil <sup>1</sup> saw that some metals produced spectra consisting of discrete lines of different colors instead of the continuous spectra which had theretofore been known. Further, Melvil recognized the significance of these lines, that the lines occurred at different positions of the

spectrum for different elements, and that this variance should provide a means of identifying the elements. Still, there was no explanation as to what caused the discreteness of the line spectra which had been observed. The Bohr-Sommerfeld orbital model of the atom provided the interpretation. The inward transitions of electrons from one energy level to another of the atom were such that the energy lost in an inward transition was equal to the energy of a photon of a particular wavelength.

After the fundamental concepts of atomic structure were established, specifically that each wavelength of a line spectrum corresponds to a particular electron transition, it became of interest to discover what transitions were prominent in each element, and then to try to fit a theory to them. Most early work in this regard was done in static situations. Often it was an attempt to find new lines of the spectrum of an element or of a compound and then to discover to what transition the particular line corresponded. Such studies were done on active discharges, ones which were continuously being excited. Such work did not give answers to many of the problems which were of interest since they were incapable of demonstrating how a gas, once excited, may once again become neutral.

B. Early Afterglow Studies on Mercury. In an attempt to discover the answer to this problem with respect to mercury,

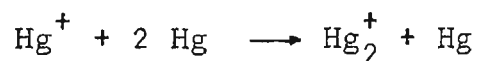
Child<sup>3</sup> was one of several investigators who used various ingenious methods to produce a mechanical delay mechanism by which they could observe the spectrum at short times after the excitation of the discharge had been turned off. Using a 60 cycle per second unidirectional pulsating current, Child operated a mercury arc. The light from the arc was passed through a slit in a disc which rotated synchronously with the current source to the arc. The intensity of the light was then measured as it passed through the slit by means of a photometer. Attached to the disc was a brush contact by which the instantaneous value of the current could be measured. Thus, Child was able to measure the intensity of the light from the arc as a function of the current passing through the arc. The minimum of the intensity of the light was not observed to occur at the minimum of the current, but at about 500 microseconds after that instant. He also observed that there was more yellow radiation at the minimum than there was at other previous times.

In general, the work of Child is typical of the early attempts which were made to study the afterglow spectrum of mercury. The means which were available to vary the time after the source of excitation was shut off were necessarily coarse, and often mechanical. As a result, accurate, quantitative measurements could not be made. In order to obtain more quantitatively correct data, more sophisticated techniques were needed.

Among the more recent experiments which have been performed, Dandurand and Holt<sup>4</sup> studied the mechanisms by which electrons may be removed from the afterglow of a mercury discharge. They were able to measure the electron density by measuring the frequency shift of a microwave resonant cavity. Simultaneously, they measured the light intensity as a function of time in the afterglow of the discharge by using a time-sampling technique. Their time-sampling technique involved using a photomultiplier into which a gated pulse is fed at a known time after the source for the discharge had been shut off. They were able to observe the intensity of the light at some variable time in the afterglow. By using optical band pass filters, they were able to observe the variation of intensity of a region of the spectrum with both time and temperature. They found that at low temperatures and pressures, ambipolar diffusion of electrons was the principal mechanism governing decays. At higher temperatures and pressures they observed that metastable atoms and molecular systems complicated any analysis. They also noted that there was an enhancement in the intensity of the spectral region passed by the filters at some time after the discharge was shut off.

In a manner similar to that used by Dandurand and Holt, Biondi<sup>5</sup> has conducted extensive studies on the decay mechanisms of the electron density in both pure mercury and mercury-helium atmospheres. He, too, found that at low mercury

pressures, ambipolar diffusion was the predominating decay mechanism. He showed that the interaction between an atom and an ion is of no consequence, resulting only in charge transfer. At higher temperatures, he found that the electron ambipolar diffusion was insufficient to explain the experimental decay curves. It was necessary to insert a volume loss term. Biondi proposed two possible interpretations of this added term. One was that electrons might attach themselves to mercury atoms, forming negative mercury ions. This interpretation is sufficient if the concentration of negative ions is small. The other interpretation was that the term may result from conversion of atomic ions to molecular ions. However, despite his own preference for the latter explanation, Biondi was unable to verify experimentally that this was the correct interpretation. At still higher temperatures, he found that a three-body interaction



became of importance. Having formed molecular ions, he showed that electron recombination with these ions correctly explained the electron decay curves which were obtained.

Biondi also noted that the collision of two metastable atoms could produce a ground state atom and an ionized atom. He also observed an enhancement in the electron density at about 200 microseconds after the active discharge was shut off.

C. Stepp and Anderson's Study on Mercury. In another recent work, Stepp and Anderson <sup>6</sup> have studied the mechanisms involved in the early afterglow spectrum of a mercury discharge. They used a pulsed direct current to excite a commercial mercury-argon lamp. Using a time-sampling technique, they observed the decay of certain mercury lines in the discharge. They observed an initially rapid decay in intensity, then an enhancement, and finally another slower decay. It was at that time postulated that the main processes governing the initial decay were spontaneous radiative decay, whereas at later times in the decay, other multiple mechanisms became important. In a later work by the same authors,<sup>7</sup> a pulsed radio-frequency coil wrapped around the experimental cell was used as the source of excitation of a pure mercury sample. Using a recording technique involving the direct readout of data on an oscilloscope, the enhancements of pure mercury lines were observed. Their explanation of this effect was based on the interaction between excited and metastable atoms.

D. Early Absorption Studies. In addition to studies of the emission spectrum, ever since 1802 when Wollaston <sup>1</sup> discovered dark lines in the observed solar spectrum (which were rediscovered by Fraunhofer in 1814), absorptions have been of interest. However, it was not until 1849, when Foucault saw bright lines in the same places of the spectrum as dark lines had been previously observed, that a connection was



made between the absorption of the light and some sort of a resonance effect. As in the case of emission studies, much work was done on the absorption of various lines in the mercury spectrum. It is only the more recent works which are of more than historical interest.

Using two direct current mercury lamps and observing the light from one as it passed through the other, Kenty<sup>8</sup> measured the absorption of the light by the second lamp. He maintained both lamps at the same discharge conditions by carefully controlling the current through each, and assumed that if the same current were flowing, then each would be at the same temperature. He actually measured the absorption by turning off the source of the absorbed light briefly. He studied the effect of various currents and of temperature on the observed absorption. He found that at currents of about 100 ma diffusion became a decay process secondary to quenching collisions between metastable atoms and electrons. He also observed that the 5461A ( $6^3P_2$ ) line was absorbed more than the 4047A ( $6^3P_0$ ) line.

Using a direct readout on an oscilloscope in which both the emission tube and the absorbing cell are pulsed, though at different rates, Shoda, Yokoyama, and Kuroda<sup>9</sup> studied the decay phenomena of metastable atoms in mercury-argon discharges. It was shown that the lifetime of the metastable atoms in the afterglow depends on the current which is developed during the active discharge; but for any given cur-

rent, the per cent of absorption decays exponentially with time. It is assumed, then, that this is directly indicative that the metastable population also decays exponentially with time. In a later publication, using a slight variation of the apparatus used before, the same authors<sup>10</sup> observed the variation of the lifetimes of the metastable and resonant states with temperature. It was shown that the  $6^3P_0$  state does exhibit an increased lifetime, whereas the  $6^3P_2$  state does not, as the temperature is raised. This effect was thought to be due to a quenching collision between the  $6^3P_1$  and  $6^1S_0$  states and hence a replenishment of the  $6^3P_0$  metastable state from the  $6^3P_1$  resonant state.

Using the same apparatus that he and others had reported on before, Yokoyama<sup>11</sup> concluded that the lifetime of the metastable states is dependent upon the intensity during the active discharge of the source of the excitation. He noted that the absorption of the 4047A line (terminating in the  $6^3P_0$  state) exhibits a maximum at a current of 4.5 ma in his experiment. The 5460A line (terminating in the  $6^3P_2$  state) showed no similar effect; instead, the absorption increased with current until it asymptotically approached a constant value. He also observed that the initial decay of the 5460A line during the afterglow is not as fast as the exponential decay at later times. Later,<sup>12</sup> he measured actual populations of the triplet  $6^3P$  states. He showed that the population of the  $6^3P_2$  metastable state was less than that of the  $6^3P_0$  state by a factor of two.

Somewhat more recently, Koedam and Kruithof<sup>13</sup> used a mechanical chopper to interrupt the light which would be absorbed by the experimental cell. Since both lamps were run continuously, they were able to carefully control the discharge conditions. Thus, they were assured that any variations in their observations were real and were not due to change in the discharge conditions between pulses. With this, they observed the variation of the transmission of the  $6^3P$  triplet of lines as a function of temperature, and found that the amount of absorption increased with increasing temperature. They found that the  $6^3P_1$  population varied strongly with changing temperature, and that up to about 343°K the population of the  $6^3P_{2,0}$  states varied, but at that temperature the change in population became less.

By considering that metastable atoms may be destroyed by any of three mechanisms, and by considering also the imprisonment of the resonant radiation, Phelps<sup>14</sup> showed that the observed dependence of the lifetime of the lower metastable state of neon on gas density and size of the absorption cell could be explained. The three mechanisms which he considered were diffusion to the walls of the cell, excitation to the nearest radiating state in collisions with neutral atoms, and three-body collisions involving two neutral atoms. He conducted experiments by passing the light from a pulsed neon emission cell through an absorption cell. Using a time-sampling technique, he studied the change in

the absorption of the lines indicative of metastable states with time and pressure. The theory which he developed to explain his results will be referred to in more detail later, and will be explained further at that time.

Using the same technique which they had previously reported, Shoda and Yokoyama<sup>15</sup> verified the temperature dependence of the imprisonment of the 2537A line by observing the absorption of the 4359A line. In a still more recent publication,<sup>16</sup> these authors have studied the variation of the decay time of this same resonance state with temperature and with varying argon pressures in the experimental cell.

E. Mercury Molecular Spectra. Another type of experiment which can be performed using absorption techniques gives information concerning the existence of mercury molecular ions in the afterglow of a discharge. Holstein, Alpert, and McCoubrey<sup>17</sup> studied this problem using a monochromatic 2537A light to excite a mercury vapor. Using an oscilloscope to display the intensity of the light as a function of time in the afterglow, they were able to observe the decay of the radiation from the cell after the exciting source had been shut off. They observed band fluorescence at densities of about  $10^{16}$  atom/cc. and above, and observed as a result a composite trace on the oscilloscope. From that trace, two decay processes were discernible, the shorter of which was associated with resonance radiation, the longer with molecu-

lar fluorescence. This result, they confirmed by reducing the resonance radiation by means of filters. Further, they observed that the ratio of intensities  $\frac{I(4850\text{\AA})}{I(3350\text{\AA})}$  increased with increasing temperature.

McCoubrey<sup>18</sup> summarized the work which had been done and the results which had been obtained in a paper in 1951. Basically, at that time the following results had been observed. The ratio of intensity of the visible band (4850Å) to that of the ultraviolet band (3350Å) was shown to be proportional to the square of the density. Both bands were known to decay according to a curve which was characterized by two time constants. The longer of them had been studied quite extensively and was found to obey a relationship of the type  $1/\tau = A/N + B + CN^2$ . The interpretation which was attached to this data was that incident 2537Å radiation creates  $6^3P_1$  atoms which upon collision are converted to the  $6^3P_0$  metastable state. The metastable atoms then combine chemically with normal mercury atoms to form  $Hg_2$ . This state decays both spontaneously by the emission of the ultraviolet band and by collision-induced radiation of the visible band.

In a more recent publication, McCoubrey<sup>19</sup> has studied a similar problem. Using a time-sampling technique, he observed the intensity of the band radiation centered at 4850Å and 3350Å in the afterglow of the discharge and its variation with both time and mercury pressure. He observed long decay

times, indicating that diffusion loss was a dominant mode of decay. Other experimental results indicated that since both bands were observed to decay simultaneously, there was a common source of their excitations. Further, since complex decays were observed, a "parent-daughter" process evidently existed. Finally, the observed density variation of the lifetimes strongly indicated that collision destruction processes affected both excitations. Based on these observations, a consistent theory was developed which adequately explains the experimental results which he obtained. Since this theory will be discussed later, it will not be amplified at this time.

Matland and McCoubrey<sup>20</sup> have extended the work which was previously mentioned. Using optical pumping techniques, they measured the decay time in the late afterglow for the band radiation. They found that it decreases from about 70 msec. to about 19 msec. as the temperature varies from 380°K to 580°K respectively. They found, too, that the diffusion coefficient varies as  $T^{1/2}$  when the temperature is expressed in degrees Kelvin. The three-body collision induced radiation rate was found to be unchanged with temperature.

Later, the same authors<sup>21</sup> studied specifically the very late afterglow using the same apparatus as before. In this study, they were interested in times late enough that the population of metastable atoms would be insignificant, and that only excited molecules might remain. At these late

times, they found a single decay slope. In this same study, they showed that metastable molecules are destroyed upon diffusion to the walls.

Of the experiments which have been described in the literature and which have been mentioned here, only McCoubrey's work was done at temperatures in excess of  $423^{\circ}\text{K}$ . The majority of the experiments were performed at much lower temperatures and pressures and often the experiments were done at room temperature ( $300^{\circ}\text{K}$ ). Further, as was pointed out by Dandurand and Holt,<sup>4</sup> any detailed description of the mechanisms which are active in the afterglow of a mercury discharge are severely complicated by the presence of metastable atoms.

## II. THEORY

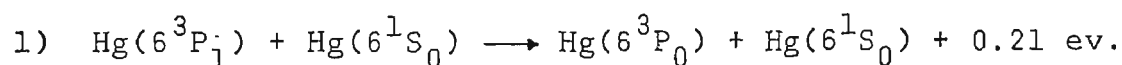
A. Molecular Emission. When a mercury vapor is excited, it radiates in addition to the line spectrum associated with the element, a band spectrum whose intensity is strongly dependent upon the density of the mercury vapor. The band spectrum consists of three main components, centered at 4850A, 3350A, and 2650A. The first two of these, in the visible and near-ultraviolet regions are the only ones which the equipment used in the present experiment was capable of detecting. The band at 2650A is of considerably less intensity than the other two bands and is associated with the fluorescence. However, since this band is of no immediate concern to either the theory or the experiment, it will not be considered further.

The theory which will be presented to partially explain the results which were obtained in these experiments is similar to that proposed by McCoubrey.<sup>19</sup> In order to justify certain assumptions which will be made, certain of McCoubrey's experimental results will be cited. It has been observed that there is a relatively long lifetime associated with the mercury fluorescence. This suggests that diffusion might be an important feature in the mercury decay. This assumption is further substantiated by investigations using different sized cells, which have demonstrated a dependence of the lifetime on the enclosure size. If the bands centered at



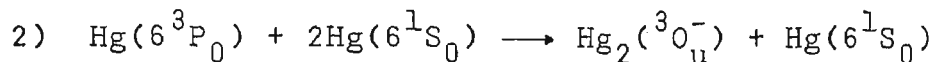
4850A and 3350A had their origins in different excited molecular reservoirs, it would be expected that their lifetimes would be different. Instead, it was observed that the two bands decay simultaneously. This suggests that they have their origins in a common reservoir of molecular excitation. Further, it has been observed that both bands undergo complex decays with which two exponentials are associated. This is characteristic of "parent-daughter" processes in which one decay feeds another. There is an increase in the rate of the decay of the molecular bands as the vapor pressure is increased. This demonstrates that collisional destruction processes affect the life of both molecular states. Finally, it has been shown that the intensity of the entire band structure is strongly density dependent.

If it is assumed that initially there is a fairly random population of the states, depending upon the degeneracies of the various states, then after some time, the  $6^3P_1$  state will be depopulated to the metastable state  $6^3P_0$  by a reaction of the form:



The presence in the afterglow of the metastable  $6^3P_0$  state has been observed<sup>9</sup> and it is known that metastable atoms may be created by the collision quenching of the  $6^3P_1$  state as in equation 1. The metastable atoms may then be converted to metastable diatomic molecules by three-body collisions

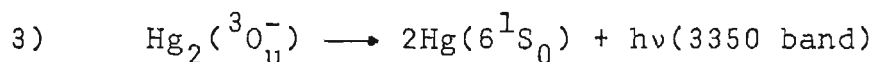
of the form:



It will be shown that these diatomic molecules are the reservoir from which both molecular bands originate.

In this reaction, it is considered that an atom in the  $6^1\text{S}_0$  state collides with a metastable atom in the  $6^3\text{P}_0$  state. While these atoms are in close association, a third atom in the  $6^1\text{S}_0$  ground state collides with the pair, taking away enough energy to stabilize the system in a vibrational state of the molecular electronic  $^3\text{O}_u^-$  configuration.

It is then proposed that the 3350A band arises from spontaneous radiation by the metastable molecules in the form of:



It is thought that this radiation might be emitted despite the fact that the molecule is metastable. If this is the case, the metastability must be broken down by some internal mechanism, perhaps by a gyroscopic disturbance of the electronic motions arising from a nuclear rotation.

Further, it is proposed that the 4850A band arises from an alternate mode of decay of this same molecular state. This must be assumed to account for the simultaneous decay of the two bands. This mode of decay is thought to be col-

lision induced, of the form:



The participation of two normal mercury atoms in this reaction is necessary to explain the dependence of the ratio of the intensities of the two bands upon the square of the density. Further, this explains the effect of the higher densities of the lifetimes.

Whether the reactions given in equations 3 and 4 are actually simple or involve intermediate steps is not clear. If there are intermediate steps involved, they must be very short in duration compared to the lifetimes of the two states. If this were not the case, they could be detected by careful investigation of the decays.

A more complete mathematical description of the processes involved in the decay of both the metastable atomic and molecular states is presented in the paper by McCoubrey.<sup>19</sup> There it is shown that the metastable population must obey a rate equation of the form:

$$5) \quad \frac{\partial m}{\partial t} = D_m \nabla^2 m - C_m N^2 m$$

Here,  $m$  is the density of the metastable  $6^3\text{P}_0$  atoms,  $D_m$  is the diffusion coefficient of these metastable atoms, and  $C_m$  is a constant of proportionality. Further, the first term on the right of the equation corresponds to atoms lost by diffusion, and the second term corresponds to collisional

destruction which creates the metastable molecule as in equation 2.

Further, it may be shown that the molecular population must obey a rate equation of the form:

$$6) \quad \frac{\partial M}{\partial t} = D_M \nabla^2 M - BM - C_M N^2 M + C_m N^2 m$$

Here,  $M$  is the density of the metastable  ${}^3O_u^-$  molecules,  $D_M$  is the diffusion coefficient of these molecules, and  $B$  and  $C_M$  are factors of proportionality. In equation 6, the first term on the right corresponds to molecules lost by diffusion; the second, to those lost by spontaneous radiative decay as described in equation 3. The third term allows for losses by collisionally induced radiation, as in equation 4. Finally, the last term is a source term corresponding to those molecules formed by three-body collisions.

It is shown further <sup>19</sup> that solutions to the rate equations 5 and 6 are given by:

$$7) \quad m(r,t) = m_0(r) \exp(-t/\tau')$$

and

$$8) \quad M(t) = \frac{\text{constant}}{\tau - \tau'} \left[ \tau \exp(-t/\tau) - \tau' \exp(-t/\tau') \right]$$

In obtaining each of these solutions, it was assumed that only the fundamental modes of decay predominate.

B. Theory of Absorption. There are two types of information

which may be extracted from absorption experiments. First, information may be obtained dealing with the population of various states. If the experiment is properly set up, the variation in these populations with time in an afterglow may be studied. Second, an absorption coefficient for the gas under investigation may be determined. The theory developed in this section is contained in the book by Mitchell and Zemansky.<sup>22</sup>

If  $I_0$  is the intensity of the parallel rays of incident light having a frequency lying in the range between  $\nu$  and  $\nu + d\nu$ , then it is known that after the light emerges from an absorption cell, the final intensity,  $I$ , will be somewhat less than  $I_0$ . A quantity called the fractional absorption,  $A$ , is defined as:

$$1) \quad A = \frac{I_0 - I}{I_0}$$

It is of interest to investigate this quantity.

It is known that if the intensity of the beam is observed as it passes through the cell, at a distance  $x$  after it enters, the intensity is given by

$$2) \quad I(x) = I_0 \exp(-k_\nu x)$$

where  $k_\nu$  is the absorption coefficient of the gas for frequency  $\nu$ . It is shown in reference 22 that if only thermal motions of the atoms in the gas are taken into consideration,

the absorption coefficient may be expressed as

$$3) \quad k = k_0 \exp(-\omega^2)$$

where

$$4) \quad \omega = \frac{2(\nu - \nu_0)}{\Delta \nu_D} \sqrt{\ln 2}$$

where  $\Delta \nu_D$  is the Doppler breadth and  $\nu_0$  is the center frequency of the absorption line. When Doppler broadening alone is present,  $k_0$  is the maximum absorption coefficient and is given by

$$5) \quad k_0 = \frac{2}{\Delta \nu_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda_0^2}{8\pi} \frac{g_2}{g_1} A_{2 \rightarrow 1} N$$

where  $\lambda_0$  is the wavelength corresponding to the central frequency of the absorption line,  $g_1$  and  $g_2$  are the statistical weights (or degeneracies) of the states 1 and 2 respectively,  $N$  is the number of atoms per  $\text{cm}^3$  in state 1 (the lower state), and  $A_{2 \rightarrow 1}$  is the Einstein spontaneous transition probability from state 2 to state 1.

It is now possible to calculate the fractional absorption directly. In general neither the vapor pressure nor the thickness of the emitting layer is known accurately, so it is necessary to use an empirical expression for the frequency distribution of the radiation emitted from the incident light source. A conventional expression for the source emission line frequency dependence is given by

$$6) \quad I_{\nu} = I_{\nu_0} \exp \left| -(\omega/\alpha)^2 \right|$$

where  $I_{\nu_0}$  is the intensity at the center of the line and

$$7) \quad \alpha = \frac{\text{emission line breadth}}{\text{absorption line breadth}}$$

A value of  $\alpha$  equal to unity implies that the incident line has the same shape and breadth as does the absorption coefficient of the gas in the absorption cell. A value of  $\alpha$  greater than unity represents an incident line of the same shape, but with greater breadth than that of the absorbing gas. In the case of a lamp with a thin emitting layer, equation 6 very accurately represents the emitted radiation. In this case,  $\alpha$  is given by the square root of the ratio of the absolute temperature of the emitting gas to the absorbing gas. The incident beam intensity from the source is then given by

$$8) \quad I_0 = \int_0^{\infty} I_{\nu} d\nu$$

The fractional absorption can now be written:

$$A = 1 - \frac{I(l)}{I_0}$$

$$A = 1 - \exp(-k_{\nu}l)$$

$$A = \frac{\int_0^{\infty} I_{\nu} [1 - \exp(-k_{\nu}l)] d\nu}{\int_0^{\infty} I_{\nu} d\nu}$$

$$9) \quad A = \frac{\int_{-\infty}^{\infty} \exp[-(\omega/\alpha)^2] \{1 - \exp[-k_0 l \exp(-\omega^2)]\} d\omega}{\int_{-\infty}^{\infty} \exp[-(\omega/\alpha)^2] d\omega}$$

where  $l$  is the total length of the absorption cell. Equation 9 may be reduced to the form:

$$10) \quad A = \frac{k_0 l}{\sqrt{1+\alpha^2}} - \frac{(k_0 l)^2}{2! \sqrt{1+2\alpha^2}} + \dots + \frac{(-1)^n (k_0 l)^n}{n! \sqrt{1+n\alpha^2}} + \dots$$

Except very early in the afterglow, under usual experimental conditions it is known that the concentration of metastable atoms may be assumed to decay exponentially with time. This is represented by the relation

$$11) \quad M(t) = M_0 \exp(-t/\tau)$$

where  $M_0$  is the concentration of metastable atoms at the initial stage of the decay after the excitation is terminated and  $\tau$  is the decay time of the state.

If the previous theory is now applied specifically to metastable states, and if  $\alpha$  and  $k_0 l$  are each small, then equations 5, 10, and 11 may be combined and rewritten as:

$$A = k_0 l$$

$$A = \frac{2}{\Delta v_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda_0^2}{8\pi} \frac{g_2}{g_1} A_{2 \rightarrow 1} M_0$$

$$12) \quad A(t) = \left\{ \frac{2}{\Delta v_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda_0^2}{8\pi} \frac{g_2}{g_1} A_{2 \rightarrow 1} M_0 \right\} \exp(-t/\tau)$$

$$13) \quad A(t) = C \exp(-t/\tau)$$

If the natural logarithm of each side of equation 13 is taken, the fractional absorption becomes

$$14) \quad \ln A(t) = -t/\tau + \ln C$$



Hence, the decay time  $\tau$  of the state may be measured by observing the variation in the fractional absorption as a function of time in the afterglow of the discharge.

If instead of using equation 13, equation 12 had been grouped as:

$$A(t) = \left\{ \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda_0^2}{8\pi} \frac{g_2}{g_1} A_{2 \rightarrow 1} \right\} M_0 \exp(-t/\tau)$$

then by taking the natural logarithm of each side of this equation, there results an expression:

$$15) \quad \ln A(t) = -\frac{t}{\tau} + \ln M_0 + \ln \left\{ \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda_0^2}{8\pi} \frac{g_2}{g_1} A_{2 \rightarrow 1} \right\}$$

If the temperature is accurately known, then all the terms in the parentheses are known for any gas and for a particular frequency. Then, since these terms are constant in time, it may be seen in equation 15 that it should be possible to find the actual population of the metastable state at the time of the shut off.

### III. EXPERIMENTAL PROCEDURE

A. Introduction to the Experiment. The present experiments are an extension of the work done by Edward E. Stepp<sup>23</sup> which was presented in a Ph.D. dissertation in June, 1965. It was felt that there were certain variations which could be made in Stepp's experimental method which could increase knowledge about mercury discharges. The present thesis describes two such experiments: the first is an emission study, the second an absorption study.

Stepp's work was done by observing the decay in intensity of several atomic lines in the early afterglow spectrum of an active mercury discharge using an oscilloscope. The first experiment which is presented in this thesis is a confirmation of Stepp's results, but the data were collected in a way that not only the existence and decay of the lines of the spectrum could be studied, but also the variation of the band structure with both temperature and time could be investigated.

The results of the first experiment indicated that an absorption study could contribute further data which would be of considerable interest in attempting to explain the data which had been previously obtained. Such data would give information concerning the population of the metastable levels of mercury and their variation with time and temperature in the afterglow. Hence, the light from a mercury va-

por discharge cell was shone through the experimental cell. By making proper intensity measurements, the absorption of the light by the excited vapor in the experimental cell could be observed during the early afterglow of an active discharge.

B. Preparation of the Experimental Cell. The experimental cell was a Pyrex cylinder 300 mm long and 46 mm in inside diameter. It had a 5 mm diameter side arm which was used to connect the cell to a vacuum system. Two electrodes, one 25 mm from each end, consisting of a circular loop 35 mm in diameter of nickel wire were fused through two parallel side-arms on the walls of the cell and oriented concentric to the cell. The vacuum system consisted of a rotary forepump, phosphorus pentoxide trap, and an oil diffusion pump. The pressure was measured with an ion gauge trapped on each side by cold fingers containing dry ice and acetone. The cell was outgassed at a pressure of about  $2 \times 10^{-6}$  mm of mercury and at a temperature of about 673°K. The cell on the vacuum system is shown in Plate 1 while it is being outgassed. A small amount of triply distilled mercury was distilled into the cell. After the cell was removed from the vacuum system, the 5 mm diameter appendage was used as a mercury reservoir. The tank coil for a 28.5 megacycle radio-frequency (hereafter, r-f) source was placed around the cell. Both the coil and the cell were then placed in the oven which had two pyrex windows located along the axis of the cell.

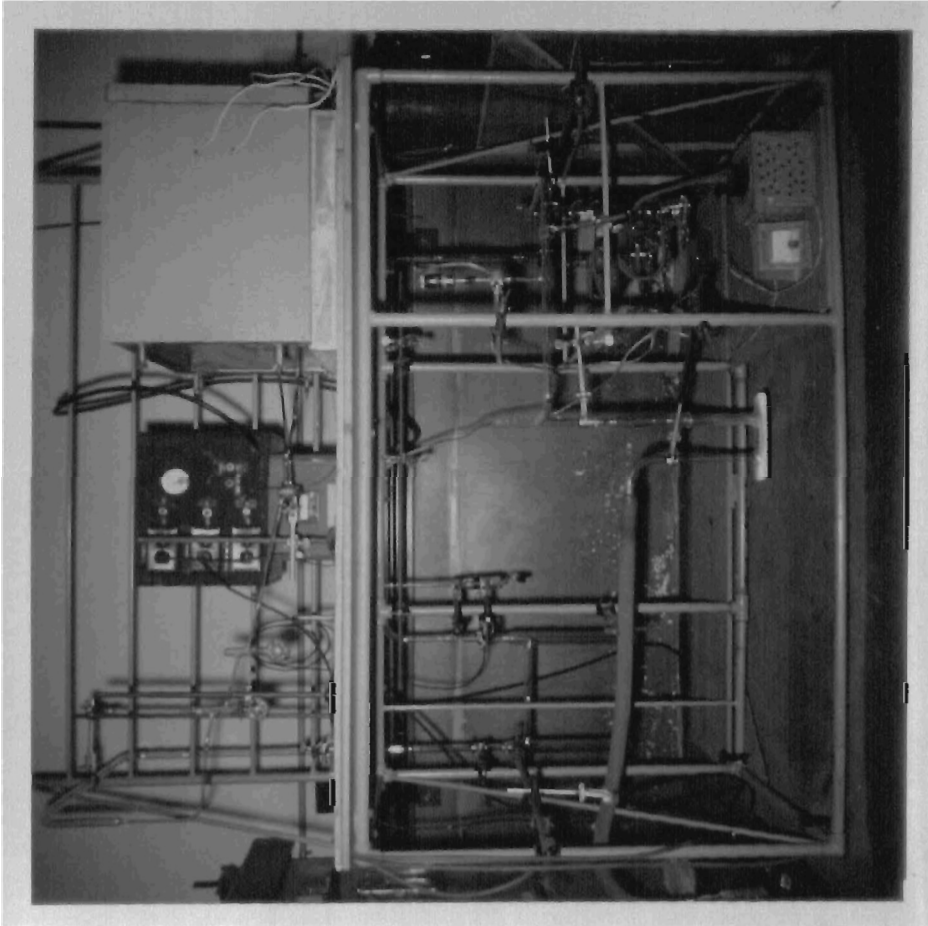


Plate 1. Experimental cell on vacuum system.

Two thermocouples were placed in the oven, one on the top and the other on the bottom, in order to monitor the temperature. A temperature gradient of only  $282^{\circ}\text{K}$  was found in this manner under operating conditions. The oven was placed in a screen cage to limit the r-f noise which was found to interfere with the electronic equipment used in the experiment.

C. Time Sampling Experimental Technique. The r-f source induced an intense mercury discharge in the cell. This discharge was turned on and off at a frequency of 60 cycles per second. The decay time of the r-f source was of the order of a few microseconds. The lines emitted in the afterglow of the discharge were separated with a Bausch and Lomb 500 mm quartz grating monochromator and detected with an RCA 931A photomultiplier. The current pulses whose amplitudes were proportional to the light intensity were passed into a Keithley model 610B electrometer. An average of these pulses was observed and the electrometer's 1 ma output was used as the source for a Heathkit Model EUW - 20A Servo-recorder. As the monochromator was scanned from 3000A to 6000A at a constant rate, a trace of the spectrum at a particular time in the decay and a set temperature was recorded.

Figure 1 is a block diagram of the electronics apparatus which was used.

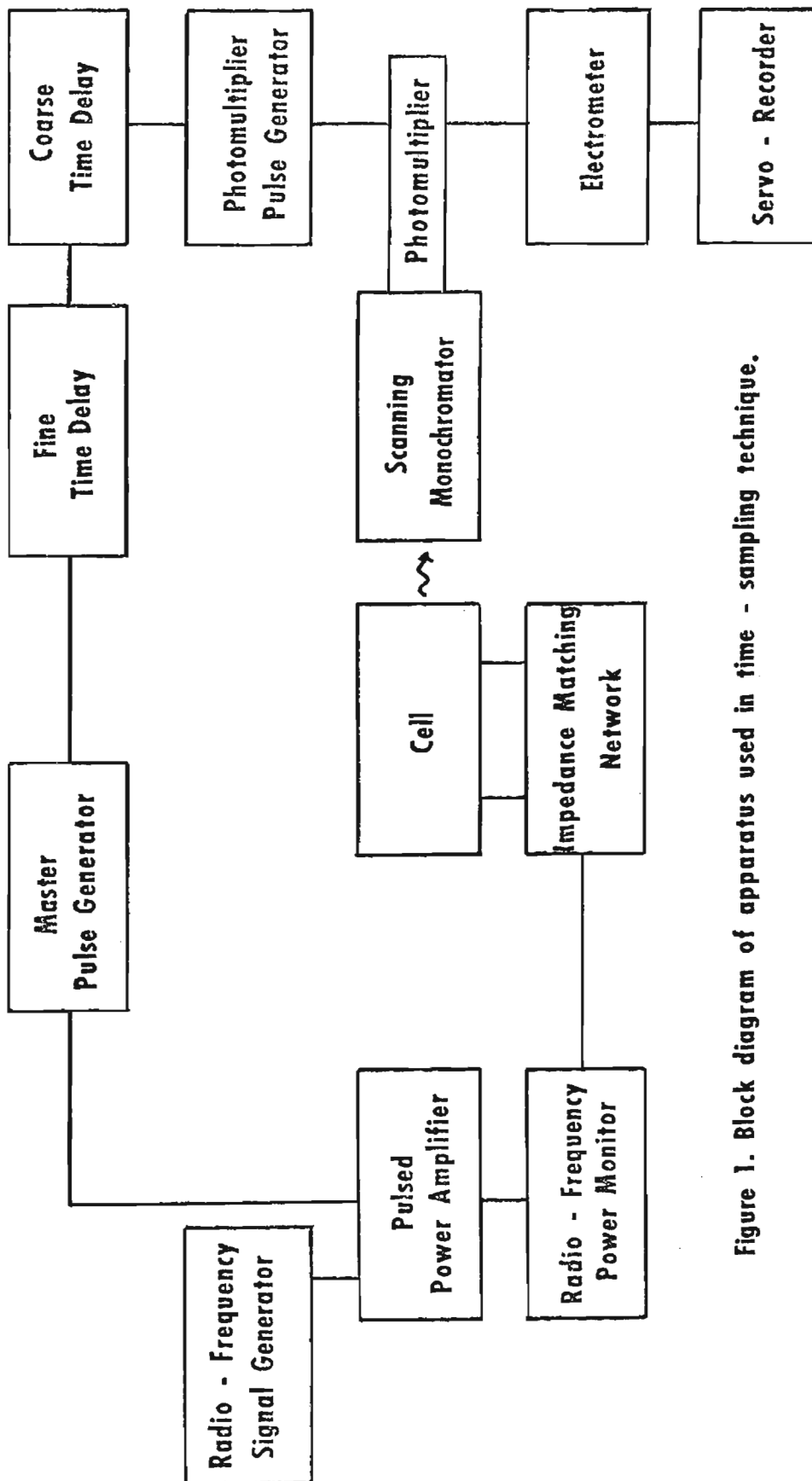


Figure 1. Block diagram of apparatus used in time - sampling technique.

The master pulse generator supplied a pulse at the rate of 60 cps which was subsequently used for two purposes.

One output of the pulse generator, after being subjected to a 12.8 microsecond delay within the generator, was fed to the pulsed r-f amplifier. The pulse controlled a thyatron which turned on and off the power amplifier. An r-f signal was continuously supplied to the same amplifier from a Heathkit Transmitter, Model HX - 11. The amplified, pulsed r-f signal was then passed through a Reflected Power Meter (Heathkit Model HM - 11) and through an impedance matching network to the tank coil which was wrapped around the cell. The r-f signal which reached the cell was pulsed on and off at 60 cps. The actual time periods of the pulsed discharge were 12 milliseconds on and 4 milliseconds off. The power fed into the tank coil was kept as constant as possible throughout the experiment.

The other output from the master pulse generator was subjected to no internal time delay, but instead was passed through two variable time delay units. First, the pulse was sent through a commercial delay unit, purchased from the Denver Research Institute Electronics Division, which was continuously variable from 5 to 190 microseconds. Then it was sent through a coarse delay which was capable of more than a 4 millisecond delay in increments of about 50 microseconds. This delayed pulse was then used as the trigger for a high voltage pulse generator which was used to turn

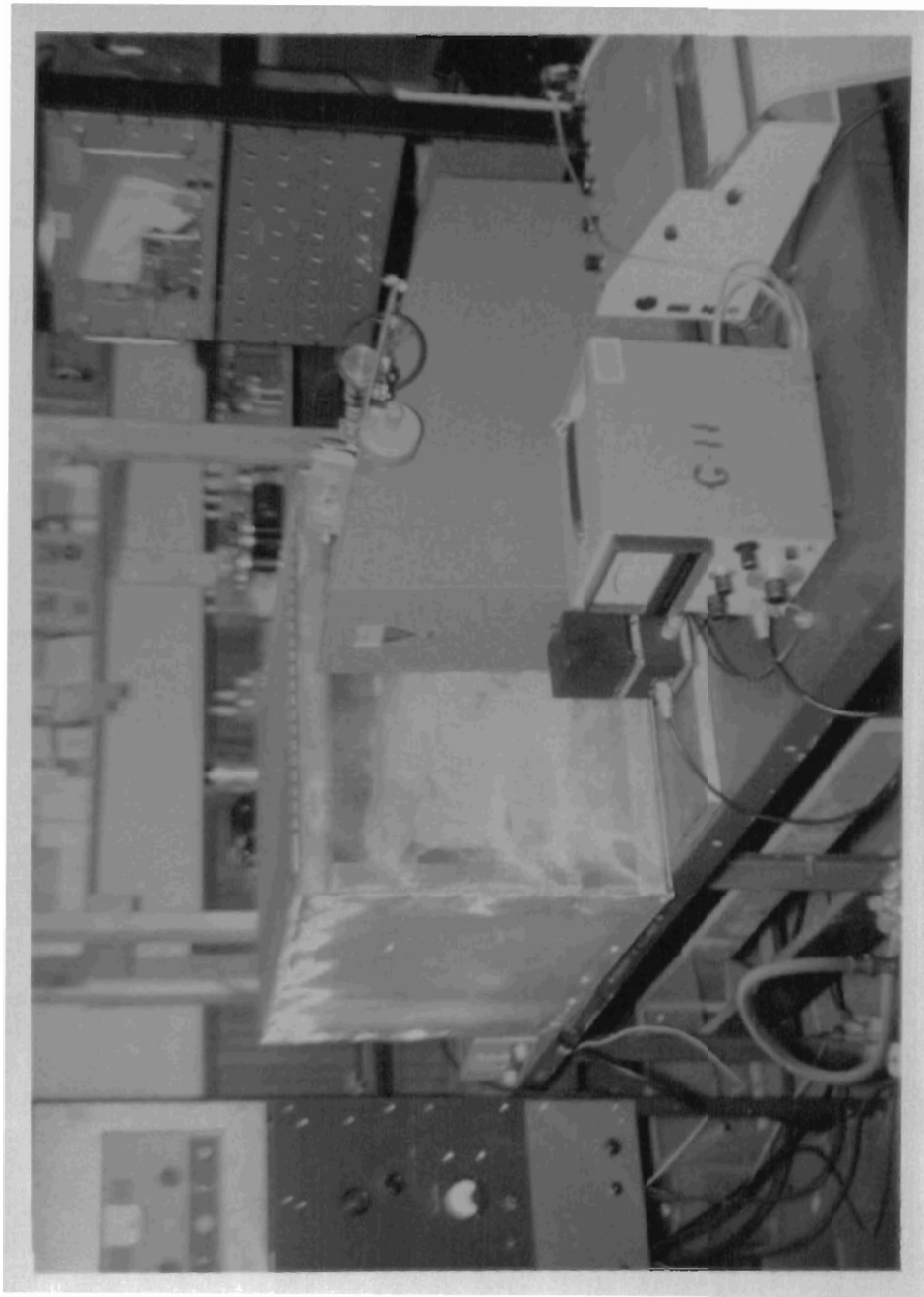


Plate 2. Experimental apparatus for time-sampling technique.



on the photomultiplier. This pulse was about 1000 volts in amplitude and its half width was about 0.3 microseconds. This pulse, as a result of the delay circuitry, could be made to occur 12.8 microseconds before the discharge was turned off and could be set at any time after the termination of the discharge until 4 milliseconds. Applying this delayed pulse to the photomultiplier the intensity of the discharge could be observed at any desired time after the r-f source was shut off. The complete experimental apparatus is shown in Plate 2.

D. Absorption Study Equipment. As may be seen by referring to Figure 2, a block diagram of the absorption experiment, the only major differences between this experiment and that previously described were in the existence of an external mercury lamp, which was used as a source, and in the completely different detection system. The cell used in this experiment was the same as that used previously. It was changed only in the repositioning of the thermocouples so that for this experiment there were four. The thermocouples were placed so that there was one on the top of the cell, one on the reservoir, and one each at the end windows of the cell.

An Hanovia Type SH mercury vapor lamp was used as the external source. It was powered by a 135 volt D.C. power supply. Light from this source was shone through the experimental cell and the variation of the intensity of the light with time after emerging from the cell was observed. The

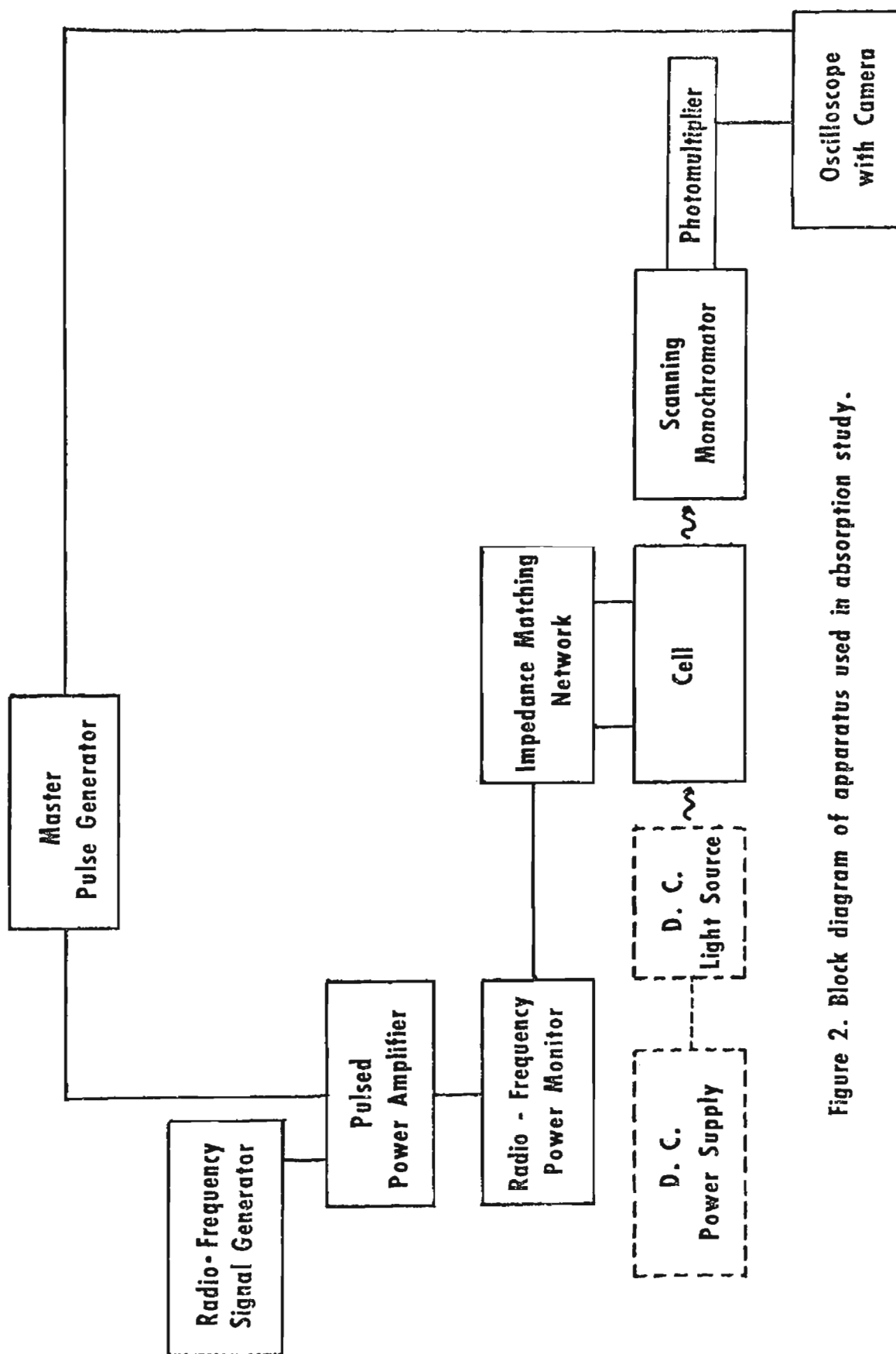


Figure 2. Block diagram of apparatus used in absorption study.

optical system which was used is shown in Figure 3. This system was chosen in an attempt to maximize the light from the source and to minimize the light from the cell which was seen by the monochromator.

The detection system consisted of the same Bausch and Lomb monochromator and an EMI 6256B photomultiplier. The signal from the photomultiplier was displayed on a Tektronix Type 531A Oscilloscope during the first few hundred microseconds after the discharge was shut off, and the trace was photographed. The same pulse which was used to trigger the r-f power amplifier was used to provide a stable trigger for the oscilloscope.

The equipment which was used in this experiment is shown in Plate 3.

In the emission study, using the time sampling technique, data were taken at temperatures from 398°K to 488°K, corresponding to vapor pressures of 1.0 to 29.0 mm of mercury, respectively. In the absorption study, data were taken at temperatures from 333°K to 498°K, corresponding to vapor pressures of 0.055 to 36.0 mm of mercury, respectively. Throughout both experiments, the power level passed into the cell was maintained constant.

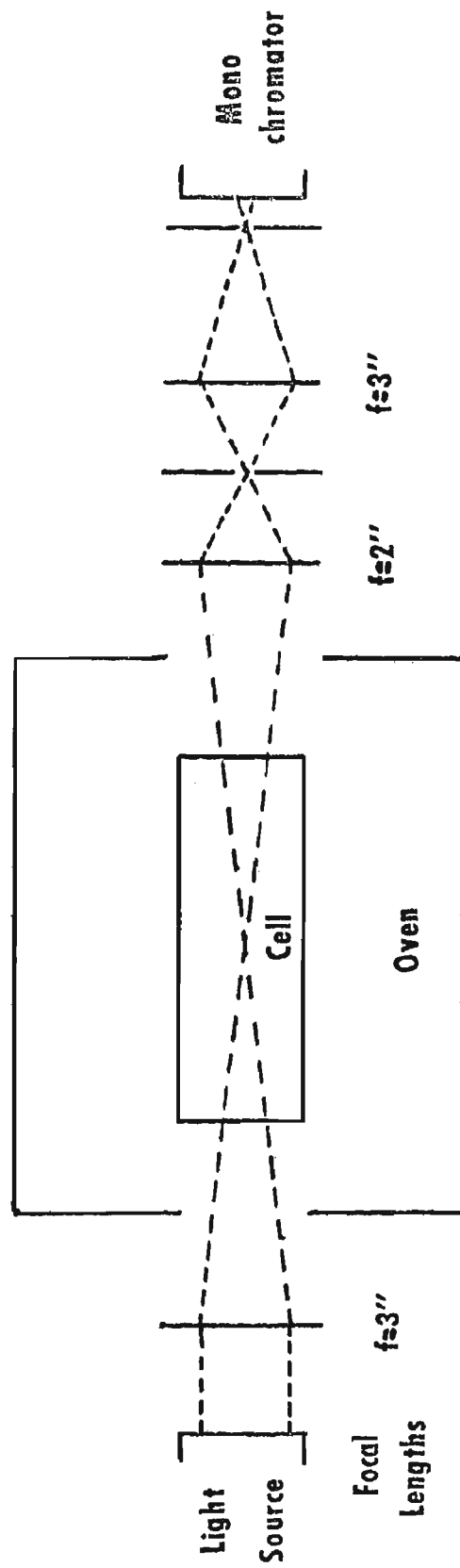


Figure 3. Optical system used in absorption study shown with principal light rays in dotted lines.



Plate 3. Experimental apparatus for absorption study.

## IV. RESULTS AND DISCUSSION

A. Emission Afterglow Results. Figures 4, 5, 6, and 7 exhibit data which are typical of that obtained in the emission study. Although data were taken at five temperatures, 398, 428, 443, 468, and 488°K, it is sufficiently illustrative to show only the results from the last four of these temperatures. Further, data were taken at two delay times in addition to the four shown. Since there was nothing of interest that happened in the last two time periods, the data obtained at these times are also omitted.

Figure 8 is an energy level diagram which shows the lines which are of interest in the emission study. It is included at this time for convenience only, and will be referred to later.

For the molecular bands the data taken at 428°K are devoid of interest beyond a note that there is apparently no molecular formation at this low temperature.

At 443°K, it may be observed that in the very early decay two bands were apparent. The band at 4850A decays within the first 100 microseconds to the point that it is no longer apparent at 115  $\mu$ sec. The band centered at 3350A decays to about half its initial intensity in the first 100  $\mu$ sec. It is still visible at 115  $\mu$ sec., though it is not so pronounced as at the earlier time. Finally, at 220

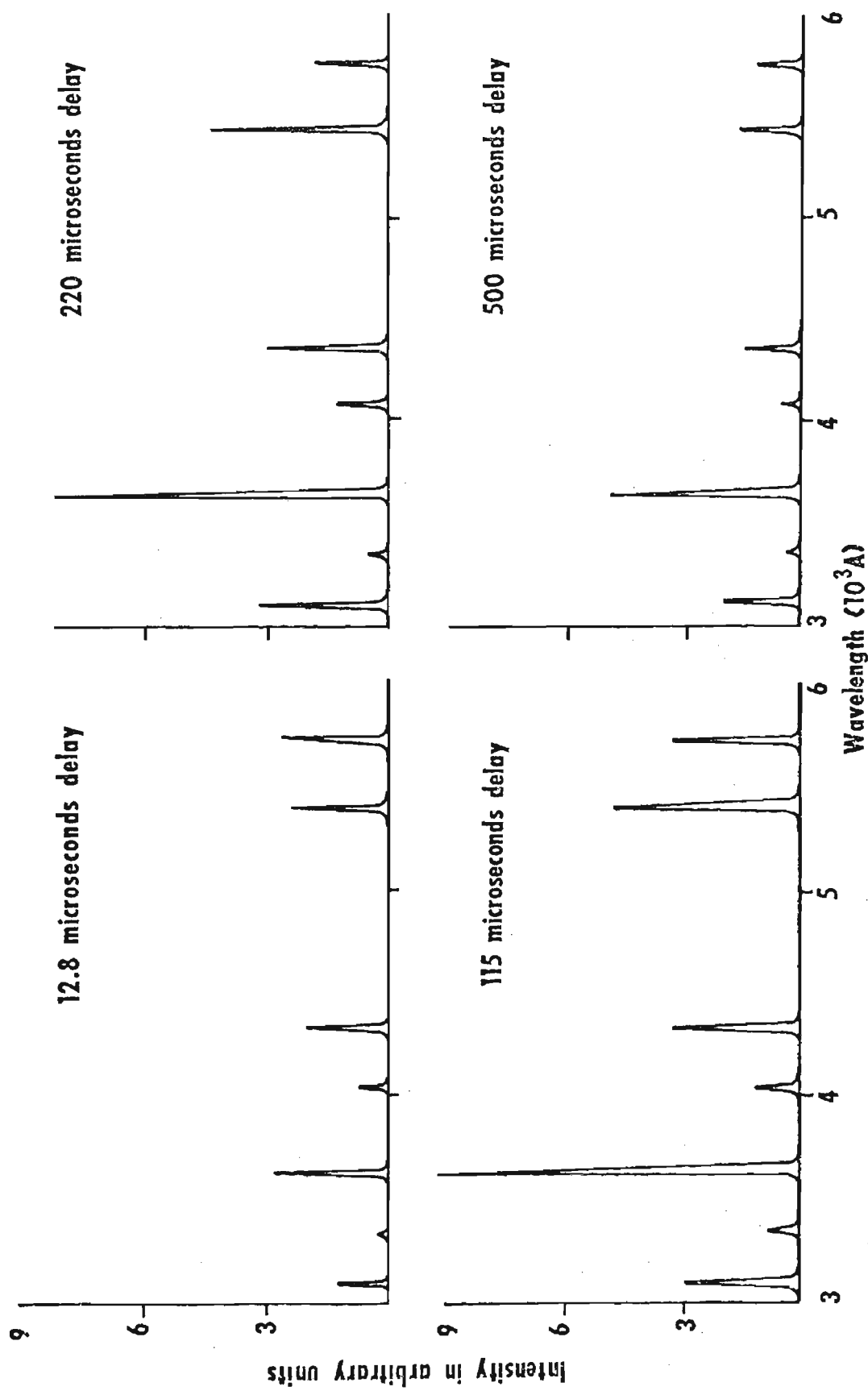


Figure 4. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 428°K.

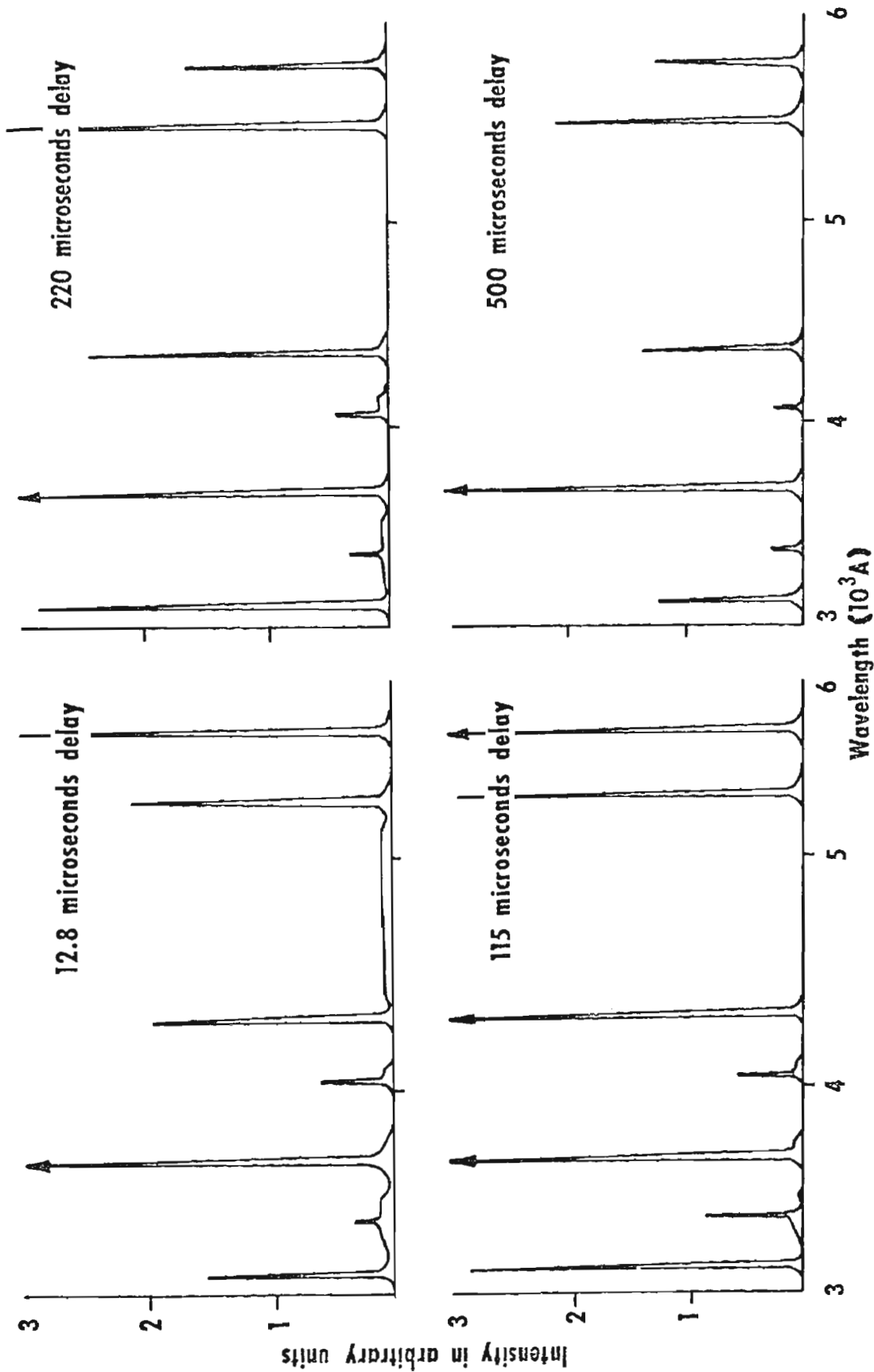


Figure 5. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 443°K.



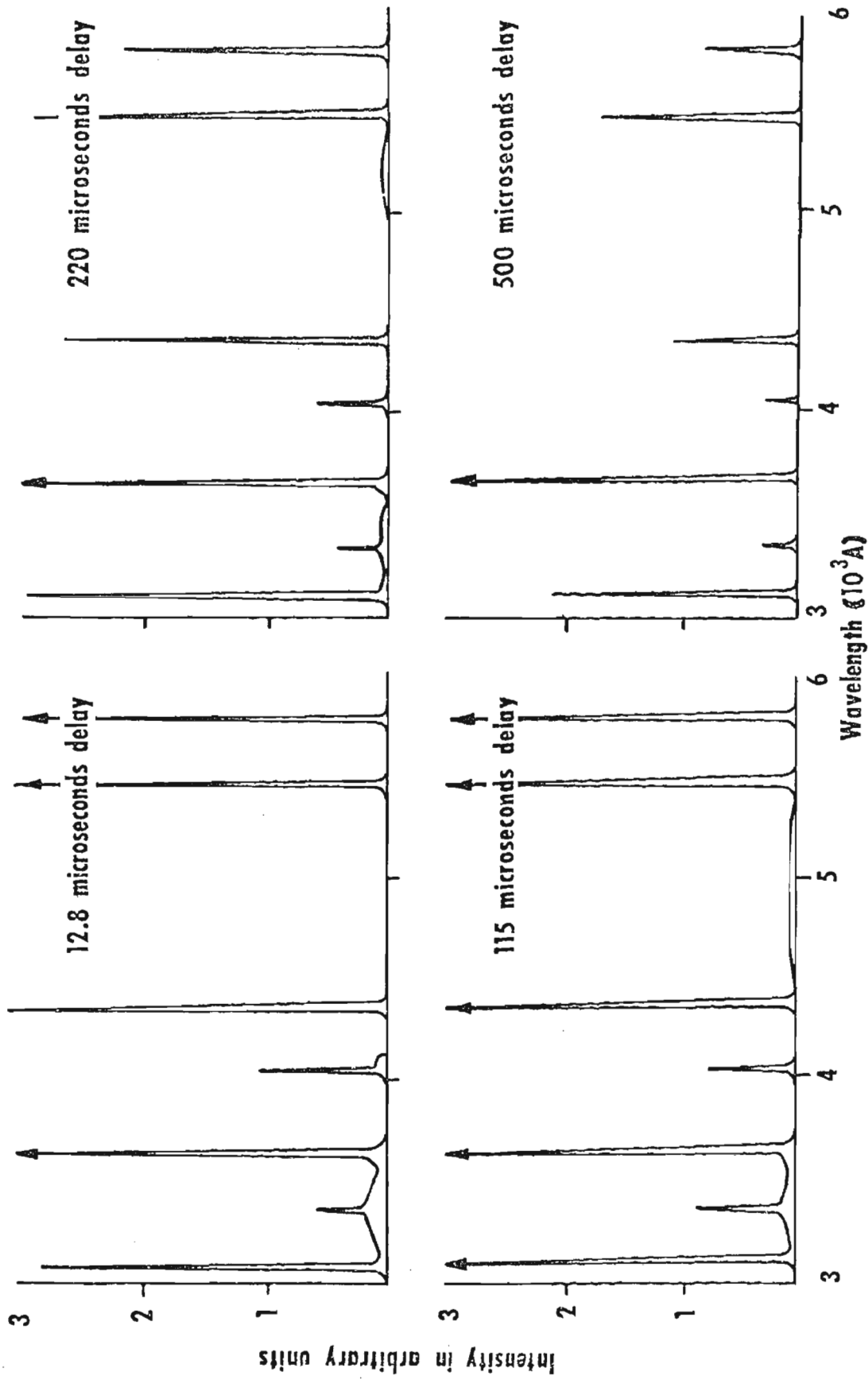


Figure 6. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 468°K.

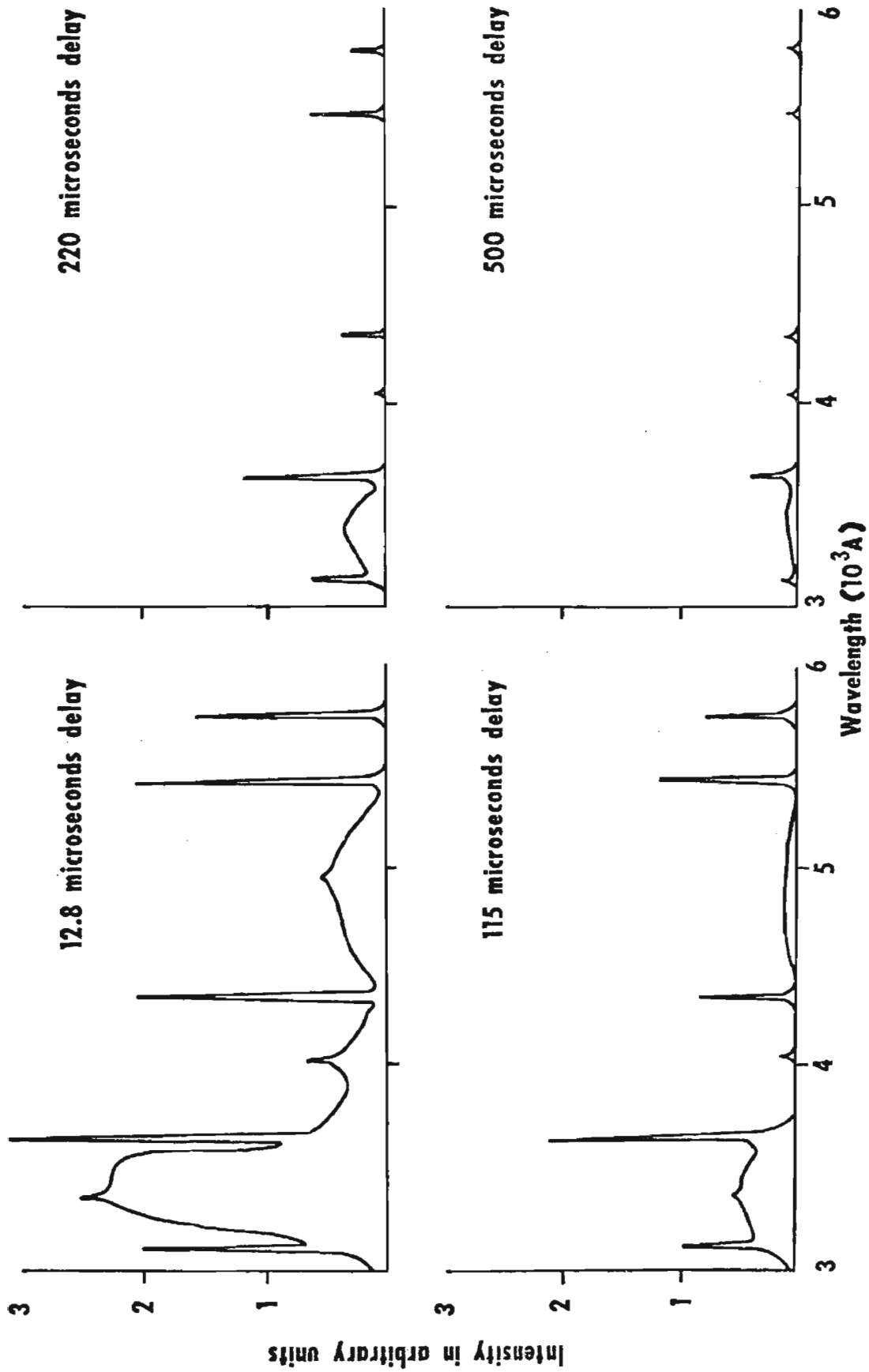


Figure 7. Intensity of the mercury spectrum in the afterglow as a function of wavelength at 488°K.

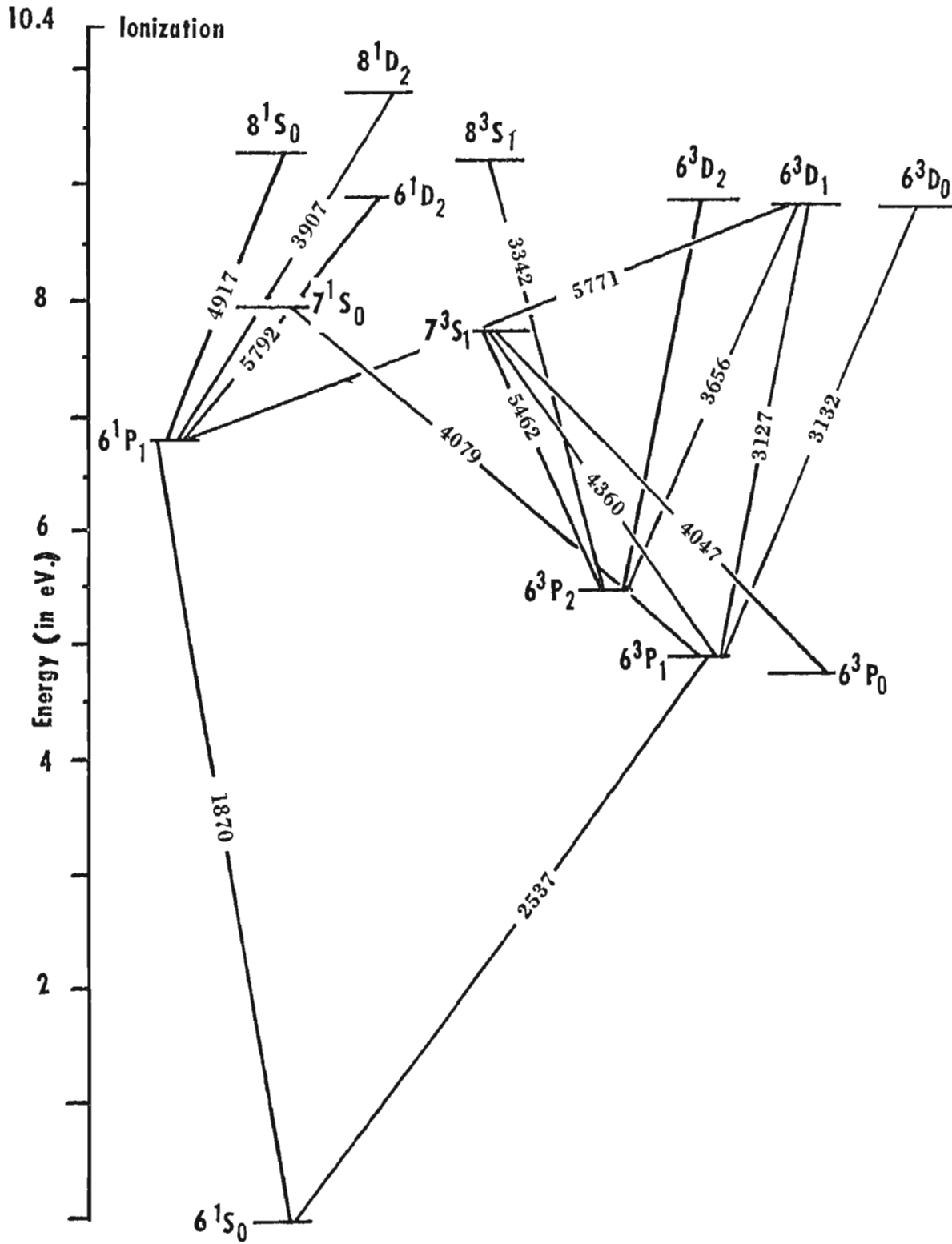


Figure 8. Energy level diagram of mercury.

$\mu\text{sec.}$ , this band is still visible, though its intensity is very greatly reduced from what had been seen earlier; and its profile is also somewhat changed from the earlier shape. Finally, at the last time shown, at 500  $\mu\text{sec.}$ , the band structure has apparently disappeared completely. It might be noted at this point that in the data which were taken at 1050 and 2100  $\mu\text{sec.}$ , there was little change in the overall shape of the spectrum from what is seen at 500  $\mu\text{sec.}$  The only difference lies in the intensities of the lines, and they seem to have decayed in exponential fashion, a fact which will be discussed in some detail later on.

The data which were obtained at 468°K, and which are shown in Figure 6, show little change from those observed at 443°K. The band centered at 3350A has become more pronounced than at 443°K, and it is interesting to notice that there is apparently no band structure at 4850A at this time. The reason for this is not clear, and in fact it seems somewhat doubtful that this is actually the case. It may be seen that in the first 100  $\mu\text{sec.}$ , the 3350A band has decayed by about half its initial value. Further, at 115  $\mu\text{sec.}$  there is band structure apparent at 4850A. This is the major factor contributing to the uncertainty of the earlier spectrum. The data taken at 468°K are similar to that at 443°K and at 220  $\mu\text{sec.}$  for both bands have nearly disappeared. At 500  $\mu\text{sec.}$ , there is no apparent trace of either band.

The data which were obtained at 488°K and which are

shown in Figure 7 deserve careful attention. Obviously the band structures are the predominant features in the spectral profiles; however, there are other changes which are of considerable interest. As before, the band at 3350A is much more intense than the one at 4850A. The band at 4850A decays in the first 100  $\mu$ sec. to about one-fourth of its initial value and after another 100  $\mu$ sec., this band is not observable. The band at 3350A also decays in the first 100  $\mu$ sec. to about one-fourth of its initial value. In the next 100  $\mu$ sec., however, the change in its intensity is much less. It has in the second hundred microseconds decayed by only about two-thirds of its previous intensity. Finally, at 500  $\mu$ sec., the intensity of this band is so feeble that it is barely observable.

Of interest in these profiles also is the change of intensity of the atomic lines. In particular, it is of interest to compare the data taken at 428°K and at 488°K, since the effects, which are apparent, are most strongly noticeable at these temperatures.

Consider first the line spectrum shown in Figure 4. It may be seen, from the data taken at 12.8  $\mu$ sec. and that taken at 115  $\mu$ sec., that the intensities of each of the lines increases. This is the effect which was originally noted in Stepp's thesis<sup>23</sup> and related papers.<sup>7,8</sup> Further, it is this effect which prompted the present studies. In the second hundred microseconds of the decay, the intensities of all

lines, except 3127-32A line, show a decrease in intensity. Further, in the following three hundred microseconds, all lines show a further decrease in intensity. As was noted before, at 1000 and 2000  $\mu$ sec., all lines continue to decrease in intensity. It may also be observed that, since the data was taken at discrete points in the afterglow, it is impossible to determine exactly when the maximum in intensity occurs and what its value is. It has been shown in other experiments<sup>24</sup> that at this temperature the maximum in intensity occurs at about eighty microseconds; but this information is extraneous to the present discussion.

In contrast to these data, if the data of Figure 7 are considered in a similar manner, it may be seen that no such enhancement is apparent. Instead at these times, the intensities appear to decrease. Again it is impossible to be certain whether this is true, or if the enhancement occurs early in the afterglow, and the intensity has decayed by 115  $\mu$ sec. to a value less than the initial value.

Again, other experiments<sup>24</sup> have shown that it is the latter case which prevails. At this temperature, there is an enhancement, although the overall intensity of the line itself is less.

B. Absorption Results in the Afterglow. In Table I, the data which were obtained from an absorption study are presented. The data were collected on three different days,

Table I. Half-life of the  $6^1P_1$ ,  $6^3P_2$ ,  $6^3P_1$ , and  $6^3P_0$  states as a function of temperature.

State:	$6^3P_0$	$6^3P_1$	$6^3P_2$		$6^1P_1$	
Wavelength Observed:	4047	4360	3650	3650 new	5460 new	5790 new
Temperature			Half-life (in microseconds)			
333°K	185	105	45	140	50	90
353	215	90	63	74	75	93
373	205	70	25	112	40	43
393				32		43
398	175	60	70		72	
403	190*	52*	0*		53*	
413	235*	85*	90*	25	57*	44
423	260	85	58		60	
433	160*	60*	28*		57*	
443	225	57	20		45	
453	68	40	40		55	
473	25	20	--		36	
498	--	--	--		49	

The data marked with an asterisk was taken in a supplementary experiment and that indicated as "new" was taken in a still more recent experiment.

and in three totally different experiments, although the experimental conditions were reproduced as carefully as possible. The data taken on the 3650, 4047, 4360, and 5460A lines which are marked with an asterisk were taken in a second experiment, for when the original data were graphed with decay time as a function of temperature, it was found that there was an increase in the decay time at about 413°K, and data had not been originally taken at this temperature. In order to attempt to verify this increase, supplementary data were obtained. It may be seen that these data fairly well reproduce the type of results which were obtained initially. In fact, it was thought that the increase was substantiated. When these data were analyzed, it was thought that it might be interesting to do two further supplementary studies. It may be seen that, in general, the decay-times of the lines at 3650 and 5460A are short. It was thought that more accurate data might be obtained by increasing the sweep speed of the oscilloscope; and if this were done, the data would be more illuminating. Further, when this was done, similar data were taken on the 5790A line. The data taken on these three lines are indicated as "new" since they were taken in a more recent experiment. It may be seen that the values which were obtained in these "new" experiments agree only qualitatively with the values obtained initially. The decay times of the 3650 and 5460A lines are still short when compared to the decay times of the 4047 and 4360A lines. Further, it is seen that the decay time of the 5790A line is



very short compared to any of the other lines. Finally, it should be noted that at least qualitatively the decay times of the 3650 and 5460A lines are similar and this is to be expected since both lines in the absorption study originate from the same ( $6^3P_2$ ) state.

It is obvious from this data that there were certain problems encountered in this study which could not be entirely eliminated. It was stated in the theory of absorption that the light should be shone through the absorption cell in a parallel beam. In these experiments it was not possible to employ parallel light. When parallel light was used, it was found that the light originating from the experimental cell was greater in intensity than was the light from the source. As a result, the light was focused in the manner stated in the experimental procedure. This meant that when the absorption line was studied, the absorption principally at a point was observed rather than the absorption throughout the cell. In the experimental cell there was some liquid mercury. If the distribution of this pool of metallic liquid varied from one experiment to another, it would cause a perturbation of the symmetry of the r-f discharge. If this did happen, then the exact conditions of the discharge could not be reproduced. Hence, the conditions which prevailed in any experiment at the focal point of the absorbed light beam might not be constant; so there might well be some variation in the absorption which was measured. As a result, the actual lifetimes of the various states could

not be accurately measured; however, it is felt that the order of magnitude of the measurements should be correct.

Further, it was stated in the theory, that it is feasible to treat quantitatively only those absorption studies where either natural or Doppler broadening dominates. It was assumed in the experiments that Doppler broadening was the dominant process, for the data were obtained at the center of the spectral lines. This may or may not be a valid assumption at the lower temperatures, and it certainly is not valid at the higher temperatures which were studied. However, it was necessary to make this assumption due to the method which was used to collect data.

As a result of the above problems, it is felt that only qualitative conclusions may be drawn. The energy level corresponding to the absorption of the 3650 and 5460A lines, the  $6^3P_2$  state, has a half-life of approximately 60 microseconds. Those levels corresponding to the 4047 and 4360A lines, the  $6^3P_0$  and  $6^3P_1$  states respectively, have half-lives of approximately 175 microseconds, except at the very high temperatures. Finally, the level corresponding to the 5790A line, the  $6^1P_1$  state, has a very short half-life on the order of 30 microseconds.

C. Results of an Experiment by Aubrecht.<sup>24</sup> It was mentioned earlier from these experiments, it was impossible to observe the enhancement to any degree of accuracy beyond noting its

existence; that is, it is impossible to determine when the peak of the enhancement occurs and how intense it is. For this reason, there was one set of experiments which dealt specifically with observing the enhancement, and its variation with temperature and input power. These experiments were done by Aubrecht,<sup>24</sup> and because they are of some significance to this discussion, the results will be briefly outlined here.

It was observed that the amount of enhancement changes drastically with temperature. At 333°K, no enhancement was observed and the decay was a simple exponential. At 433°K, a very pronounced enhancement was apparent. This enhancement may be characterized by the superposition of three exponential decays. Finally, in the decays at 498°K, there was no apparent initial decrease in the intensity. Instead, the enhancement effect seems to dominate. It is thought that there is still a very rapid initial decrease, however; and it may not have been observed by the instruments.

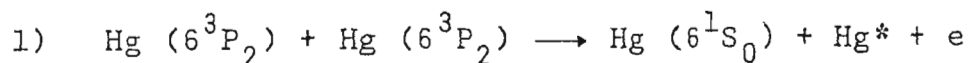
In the experiments which were performed by Aubrecht, there was a variation in power at each temperature; however, the results from this particular study are of no consequence here. Only those results which were obtained at very nearly the same power level as used in this experiment are cited.

It was shown that the lines which exhibited the greatest enhancement are the 5771, 3650, 3342, and 3130A lines.

It may be noted that these lines all originate on  $6^3D$  levels, except the 3342A line which originates from the  $8^1S_1$  level. Further, the 3650 and 3130A lines showed greater enhancement than did the 5771A line and the lines at 4047 and 4079A exhibited only a slight enhancement.

It was observed that those lines which originate on lower energy levels, whether they originate from singlet or triplet states, do not show an appreciable enhancement. On the other hand, the lines originating from higher lying states do show enhancement. It is also interesting to observe that for those lines which are intercombination lines, no large enhancement occurs. On the other hand, the lines which are not intercombination lines do show an enhancement, although the enhancements of these lines in some cases are such that their intensities are never greater than in the active discharge. In general, then, it could be concluded that the enhancement is greatest for those lines originating from the high lying states, above 8.8 ev. This is true whether the lines originate from S or D states.

In the theory which was developed by Aubrecht, the enhancement in intensity of the mercury atomic lines was produced by ionizing collisions between metastable mercury atoms of the form:



It may be seen by reference to Figure 8 that it is only meta-

stable atoms in the  $6^3P_2$  state which are capable of ionizing collisions of this form, for the energies of either of the other  $6^3P$  states are too small for this process. Further, it was assumed that the resonance state  $6^1P_1$  was not involved in this process and this assumption was later confirmed by the absorption study.

As was previously mentioned, the intensity of the atomic radiation can be described by the superposition of three decaying exponential functions of the form:

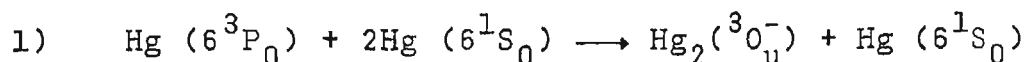
$$2) \quad I(t) = A \exp(-\alpha t) - B \exp(-\beta t) + C \exp(-\gamma t)$$

It was shown that such a function does adequately describe the enhancement effect. Based on this functional description, the enhancement is explained by the following three mechanisms. The initial steep decay is produced predominantly by volume electron-ion recombination. The enhancement is then caused by electron production as in equation 1. The final decay is caused by electron-ion recombination whose decay time is controlled by the rate of electron ambipolar diffusion to the container walls.

## V. CONCLUSIONS

The variation with temperature of the band structures may best be explained by reference to Figure 9. From this graph of mercury vapor density as a function of temperature, it may be seen that at a temperature of about 423°K, the density begins to increase rapidly. At the two lower temperatures which were considered in the experiment, 398°K and 428°K, the density is still relatively low. However, at 443°K the density has increased, and at the higher temperatures, 468°K and 488°K, the density is very much higher than before.

The mechanism which was presented in the theory for the formation of metastable diatomic molecules involves a three-body collision of the form:



Since the number of such collisions which may occur depends upon the density of mercury atoms, the intensity of the band structure should show a strong dependence upon density.

This is what was observed.

Further, it was stated in the theory that the molecular bands at 3350A and 4850A radiate by different mechanisms, although both are dependent upon the formation of the  $\text{Hg}_2(3^1\text{O}_u^-)$  metastable molecular state. The two mechanisms which were stated are:

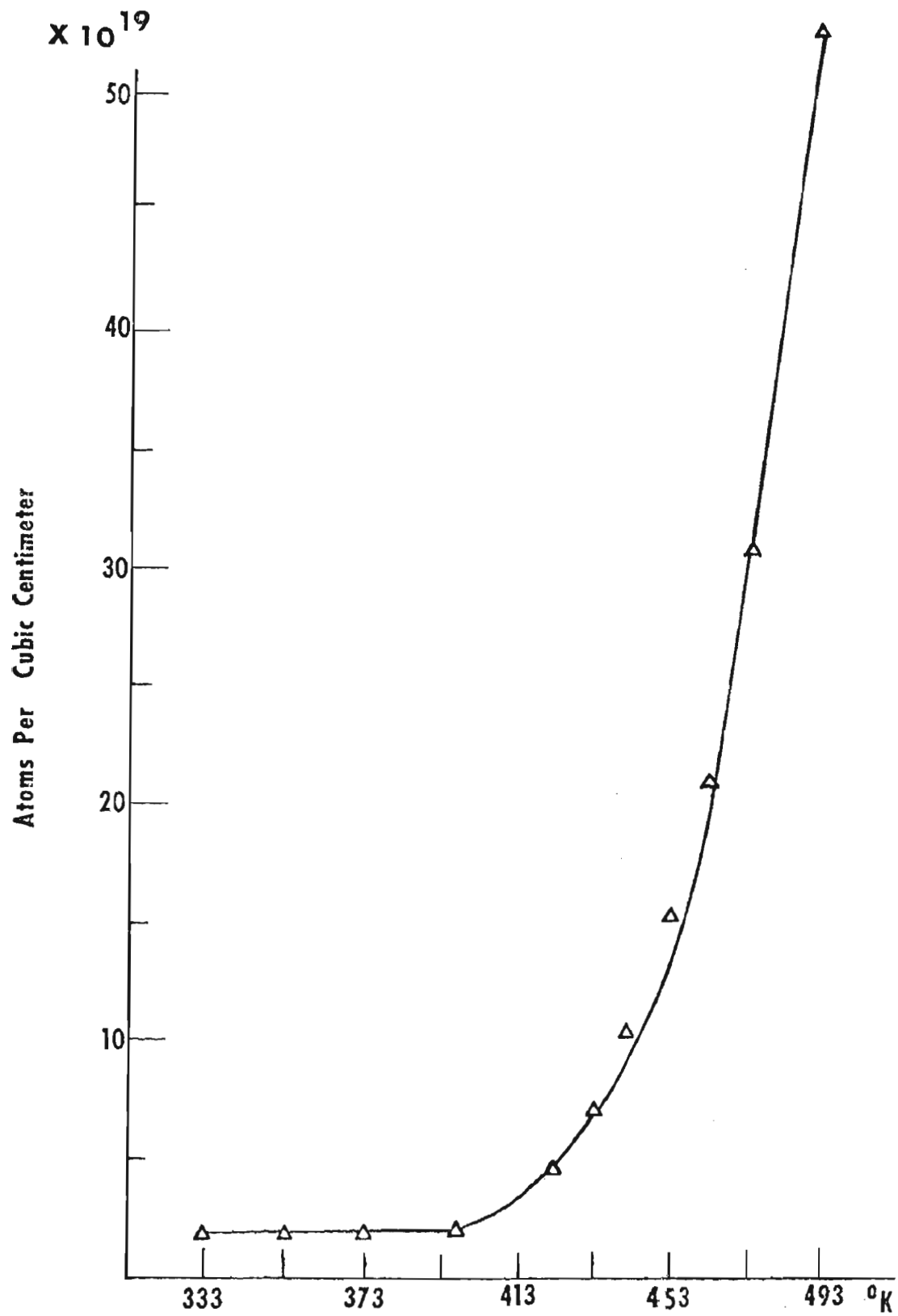
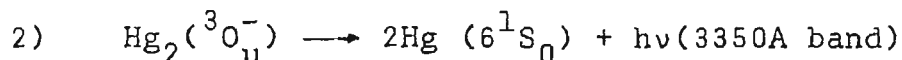


Figure 9. Mercury vapor density as a function of temperature.



and



The radiation of the 3350A band as shown in equation 2 is dependent upon the existence of the diatomic molecule. The radiation of the 4850A band, however, is dependent upon another three-body collision, this involving the diatomic molecule and two ground state atoms. Both of these radiation mechanisms depend upon the density in that they both require the previous formation of the diatomic molecule by a three-body collision. However, the radiation of the 4850A band is again dependent upon the density for its radiation is dependent upon another three-body collision. Hence, it is expected from the theory that the band at 3350A should be more strongly radiated at the lower densities and that the 4850A band should show a stronger density dependence than does the 3350A band.

The results which were obtained in these experiments verify this theory. The 3350A band increased in intensity with temperature and density. The 4850A band is apparent only at high densities, and it increases in intensity with increasing density. The mechanisms which are stated in equations 1, 2, and 3 explain the observed experimental results.

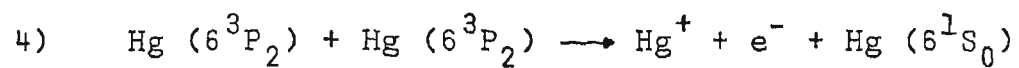
It was noted that at high temperatures the half-life of



the  $6^3P_0$  state decreases radically. Since the population of this state decreases with temperature, there must be a density dependent process which depopulates this state. The mechanism of equation 1 which provides for the formation of the diatomic molecules depends upon the destruction of an atom in the  $6^3P_0$  state. Hence, the short lifetime for this state which is seen at high temperatures may be explained by the depopulation process of equation 1, which itself is density dependent. Hence, the short lifetime of this metastable state indicates that the mechanism of equation 1 is correct.

It was shown by Aubrecht <sup>24</sup> that the enhancement effect which was observed in both his and this author's experiments could be explained on the basis of ion producing metastable collisions. In the absorption study, the four energy levels which could be involved in this process were studied. It was shown that the metastable  $6^3P_0$  state and the resonant  $6^3P_1$  state both have long lifetimes and are apparently not involved in the enhancement. It was also shown that the resonant  $6^1P_1$  state has a very short lifetime, much too short to be involved in the enhancement. It was shown by the investigation of both of the absorption lines of the metastable  $6^3P_2$  state that the lifetime is shorter than might normally be anticipated. This state has a half-life on the order of 60 microseconds. The enhancement occurs at a time on the order of 50 to 100 microseconds into the afterglow. Thus, it is concluded that the  $6^3P_2$  state is directly involved in the enhancement effect.

This conclusion is sufficient to substantiate the proposed mechanism of ionization:



With this mechanism, the enhancement effect can be explained as stated by Aubrecht, and as outlined in the Results and Discussion.

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## VITA

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