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LIFETIME MEASUREMENTS OF EXCITED STATES IN SOME
GROUP II METALS

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PART I

INTRODUCTION

Knowledge of transition probabilities is vital in order to make any sort of quantitative study of the radiation processes of atoms and molecules. There are a number of different ways of obtaining these transition probabilities, but each of the older methods has had some disadvantages inherent to it and often there is considerable disagreement among the results from these different methods. One of the more accurate ways of measuring the transition probability, especially for low lying states, is to measure directly the radiative lifetime, which is just the reciprocal of the total transition probability from a given state. A very powerful technique for measuring lifetimes using a bright hollow cathode source and a delayed coincidence analysis has been developed here at the University of Oklahoma and employed to measure lifetimes of various gases [see Holzberlein⁽¹⁾ and Johnson⁽²⁾]. Holzberlein had early felt that the inherent design of the source he invented, termed by us the invertron, would lend itself quite well after some adaptation to use with metallic vapors rather than just gases. There is only very limited experimental data available for most metals on transition probabilities of excited states, except for transitions from excited states directly to the ground state, hereafter referred to as principal transitions. The invertron is best suited for measuring these higher, subsidiary-type transitions. Due to

these considerations it was decided to attempt the necessary modifications on the system to allow work with metal vapors. The metals studied and reported upon in this work are magnesium and cadmium, with a few cursory results given for barium. Transition probabilities yield oscillator strengths which in the case of metals are of interest to astrophysicists, since they are utilized in calculations which determine from observation the abundance of these metals in the sun and other stars. Certain transitions in the cadmium ion are of interest also, since they can be utilized with helium to form a Penning laser.

In the next section we discuss the basic relations and concepts needed and summarize the various methods of obtaining transition probabilities. This is followed by a description of the experimental method and account of the development of the modifications used at various times. Finally the results of this work are given and compared with results of other methods.

PART II

METHODS FOR OBTAINING TRANSITION PROBABILITIES

CHAPTER I

GENERAL BACKGROUND

There are many good references which discuss transition probabilities, so we shall not attempt to list them here. A very useful treatment is given in the book by Griem⁽³⁾. Also a very concise treatment and description of the various methods of obtaining transition probabilities, together with a table of conversion factors between transition probabilities, oscillator strengths, and line strengths is presented in the Bureau of Standards work of Wiese^(4,5) *et al.* Probably the best all around set of references is the bibliography by Miles and Wiese⁽⁶⁾.

The modern concepts of transition probabilities were first introduced in 1916 by Einstein⁽⁷⁾. If there are N_k atoms per cubic centimeter in an excited state k , then a certain part of these will transfer to a state i lower in energy with simultaneous emission of a photon carrying away the extra energy. The energy of the photon determines the frequency and wavelength of the observed emitted light by the well known relation:

$$E = h\nu \tag{2.1}$$

If there are N_k atoms per cubic centimeter in excited state k , then $N_k A_{ki}$ atoms per cubic centimeter per second will "decay" to lower state i , where A_{ki} is the probability of spontaneous emission. There are also probabilities for stimulated emission and absorption, but these are generally unimportant compared to A_{ki} , and will not be considered further.

Many theoretical results are presented in terms of the absorption oscillator strength, f_{ik} . The use of this factor originated in an attempt to compare the quantum concept of Einstein with a classical one. Ladenburg⁽⁸⁾ equated the total emission and absorption of a spectral line for both types of theories, and introduced the factor f_{ik} to obtain the equivalent number of classical oscillators $N = N_i f_{ik}$. Then the following relation is derived:

$$f_{ik} = \frac{m_e c}{8\pi^2 e^2} \frac{g_k}{g_i} \lambda^2 A_{ki} = 1.499 \cdot 10^{-16} \lambda^2 \frac{g_k}{g_i} A_{ki} \quad (2.2)$$

and conversely

$$A_{ki} = \frac{6.670 \times 10^{15}}{\lambda^2} \frac{g_i}{g_k} f_{ik}, \quad (2.3)$$

where g_i and g_k are the statistical weights of the lower and upper states, respectively. The statistical weight g is related to the total angular momentum quantum number J by $g = 2J+1$. There is also a rarely used quantity called the emission oscillator strength f_{ki} . It is related to the absorption oscillator strength by $g_i f_{ik} = g_k f_{ki}$.

There is also an often used quantity called the line strength S ($S_{ik} = S_{ki} = S$) introduced by Condon and Shortley⁽⁹⁾, which is just the

quantum mechanical dipole matrix element squared: $S = \sum_{ik} |(i|\vec{p}|k)|^2$.

This is derived to be:

$$S = \frac{3h}{64\pi^4} g_k \lambda^3 A_{ki} = 4.935 \times 10^{-19} g_k \lambda^3 A_{ki} . \quad (2.4)$$

One can thus write the transition probability as:

$$A_{ki} = \frac{1}{g_k} \frac{64\pi^4 \nu^3}{3hc^3} S . \quad (2.5)$$

We shall now mention the relation of the transition probability to the lifetime of an excited state. The lifetime is simply the rate of decay of atoms out of an excited state. Since there are likely to be several lower lying states, transitions to each of these are possible, We define a total transition probability $A_k \equiv \sum_i A_{ki}$ from excited state k to all lower states. Then if there are N_k atoms in the excited state k :

$$\dot{N}_k = -N_k A_k . \quad (2.6)$$

If we write N_k^0 as the number of atoms in state k at time $t = 0$ then Eq. (2.6) gives:

$$N_k(t) = N_k^0 e^{-A_k t} \equiv N_k^0 e^{-t/\tau_k} . \quad (2.7)$$

Thus we see the time constant or lifetime of decay is given by:

$$\tau_k = 1/A_k = \frac{1}{\sum_i A_{ki}} . \quad (2.8)$$

The lifetime given in these last two equations is also affected by other terms such as atom-atom and atom-wall collisional de-excitation, absorption, induced emission, and feeding from other higher energy terms, a process known as cascading. The work was usually carried out under conditions such that, except for cascading, these effects would be negligible. Our data analysis technique enables us to consider cascade effects directly, as will be seen later.

It is seen that line strength, oscillator strength, and transition probability can be used more or less interchangeably, while lifetime refers to a total summed quantity. If there is only one lower state to which a transition is possible, then the lifetime is indeed just the reciprocal of the transition probability. If, on the other hand, several possibilities exist, we must have information on all other possible transitions in order to obtain the transition probability of primary interest from the lifetime. If we are interested in the transition $k \rightarrow j$, but there also exists transitions $\sum_i (k \rightarrow i)$, then we can define a branching ratio b_{kj} as:

$$b_{kj} \equiv \frac{A_{kj}}{\sum_i A_{ki}} . \quad (2.9)$$

Then

$$\tau_k = \frac{b_{kj}}{A_{kj}} . \quad (2.10)$$

Hence if we can calculate or otherwise determine b_{kj} , the lifetime yields the transition probability of interest. Fortunately in many cases either j is the only lower state and $b_{kj} = 1$ or else the

transition of primary interest has a much higher frequency than the others, so that by Eq. (2.5) the frequency cubed factor will cause its transition probability to be so large compared to the others that again b_{kj} will essentially be one. Finally, we can often approximate b_{kj} adequately by using results from theoretical calculations, as has been done extensively in this work. We shall now briefly review the most important methods of obtaining transition probabilities, both from theory and experiment.

CHAPTER II

THEORETICAL METHODS

Let us first briefly mention some of the theoretical methods commonly used. The squared dipole matrix element known as the line strength S is often separated and written as [e.g., Griem⁽³⁾]:

$$\begin{aligned} S[\ell^V(\alpha_1 S_1 L_1) n' \ell' SLJ; \ell^V(\alpha_1 S_1 L_1) n'' \ell'' SL' J'] \\ = S(L) S(M) (a_0 e)^2 \sigma^2 . \end{aligned} \quad (2.11)$$

S is expressed in terms of atomic units squared, $(a_0 e)^2$. It is written in terms of the usual quantum numbers, with small letters referring to the active electron, capitals to total atomic quantum numbers. $S(L)$ and $S(M)$ are called relative line strength and relative multiplet strength. These matrix elements have been worked out for various cases and tabulated in terms of standard Racah and $3j$ and $6j$ coefficients in a number of places. σ^2 is the square of the radial matrix element,

$$\sigma^2 = \frac{1}{4\ell_{>}^2 - 1} \left(\int R_{n'\ell'}(r) R_{n''\ell''}(r) r dr \right)^2 , \quad (2.12)$$

where $\ell_{>}$ is the larger of ℓ' or ℓ'' , $R_{n\ell}(r)$ are normalized radial wave functions of the active electrons times r .

Coulomb Approximation

In order to calculate line strengths we must know σ^2 . The radial wave functions satisfy the radial Schroedinger Equation:

$$\frac{d^2R}{dr^2} - [2V + \frac{\ell(\ell+1)}{r^2} + E_{n\ell}]R = 0 \quad (2.13)$$

at suitable boundary conditions for $r \rightarrow 0$ and $r \rightarrow \infty$ and under normalization $\int R_{n\ell}^2 dr = 1$. $E_{n\ell}$ is the energy parameter and V the effective potential acting on the jumping electron. Exact solutions for Eq. (2.13) exist only when V is hydrogenic; however, Bates and Damgaard⁽¹⁰⁾ showed that often only the region of r where V is within about one per cent of its asymptotic Coulomb hydrogenic form ($V \sim -z/r$, $z=1$ for neutrals, 2 for first ionized, etc.) contributes a significant amount to Eq. (2.12). Their method is to replace Eq. (2.13) by:

$$\frac{d^2R}{dr^2} + [\frac{2z}{r} - \frac{\ell(\ell+1)}{r^2} - E_{n\ell}]R = 0 \quad , \quad (2.14)$$

which has hydrogenic solutions. The necessary matrix elements have been found and presented in tabular form for several types of transitions. This so-called Coulomb approximation method has been one of the most widely used theoretical approaches to obtaining transition probabilities. The method is capable of quite accurate results for one electron spectra, or for more complex spectra with the active electron in a shell by itself. Results are not so good in many cases where there are equivalent electrons in the same shell, since this method is not really valid in those cases. In Appendix A we present

a simple program used in connection with Griem's⁽³⁾ tables to calculate Coulomb approximation transition probabilities.

Self Consistent Field

Another widely used approach is the self consistent field wave function or Hartree-Fock method described by Hartree⁽¹¹⁾ and Fock⁽¹²⁾. One obtains a self consistent solution of the Schroedinger equation by using charge distributions whose densities are proportional to the square of the wave functions for two or more electrons to form equivalent potentials. Approximate wave functions are used in the potential term and an iteration used to produce better wave functions. Exchange, spin-orbit, spin-spin, and configuration mixing can also be considered. For systems with the active electron in a shell by itself the method works well; however, with equivalent electrons extensive mixing must be carried out, which can run into difficult problems.

Nuclear Charge Expansion

The nuclear charge expansion method, where one expands the Hamiltonian in terms of inverse powers of the nuclear charge and carries out perturbation and mixing calculations, is only suitable for ionized species. It has been discussed earlier by the author in his Special Subject Examination,⁽¹³⁾ and will not be further mentioned.

Thomas Fermi Approach

One final method should be mentioned which has been used by Warner to do extensive calculations of oscillator strengths for several metals. It is referred to as the scaled Thomas Fermi approach. The

electrons of an atom are treated statistically to obtain a wave function, and the Coulomb field is retained for large r . Configuration mixing is considered on a limited basis. Details of the method are given by Warner⁽¹⁴⁾ and Stewart and Rotenberg⁽¹⁵⁾. The method often gives quite good results, although it runs into problems with extensive configuration mixing.

CHAPTER III

EXPERIMENTAL METHODS

Now we shall turn to an outline of some of the more important experimental techniques of obtaining transition probabilities. The first broad category we mention is that of emission measurements in an arc or plasma.

Emission

The intensity of a spectral line is given by:

$$I_{ki} = \frac{1}{4\pi} A_{ki} N_k h\nu_{ik} \quad . \quad (2.15)$$

Thus A_{ki} can be determined from I_{ki} if N_k is somehow known. N_k will be merely a function of temperature and total density if one is assured of local thermodynamic equilibrium, and thus can make use of the Boltzmann relation. By utilizing line broadening measurements or knowledge of intensity and other known transition probabilities one can then obtain N_k . The earliest experiments of this type were done in low current arcs in air. In order to avoid self absorption, very minute traces of the element to be studied were mixed in the electrodes producing the arc. The low concentration and lack of homogeneous mixing of the element with the electrode material make determination of N_k nearly impossible, so measurements of absolute transition probabilities were largely prohibited. Also no attempt was made to account for

the spatial inhomogeneity of the arc temperature, which would cause lines of high excitation potential to be emitted from different areas and at a different temperature than transitions of lower excitation potential. These facts cause this method to be capable of only preliminary, rather than highly accurate transition probabilities. Later experiments have been conducted in stabilized arcs and plasma fronts in shock tubes. Homogeneity is much better across a shock front, but of course critical time resolution is needed for this transitory phenomena. Various techniques are used to stabilize arcs, and very small apertures used, so that one is essentially looking at a homogeneous region of the arc. If an arc plasma is produced which contains more than one element, the ratio of mixture of these elements varies radially due to radial diffusion currents. This is known as demixing, and can be quite difficult to correct. Some corrections have been devised for self absorption, but these measurements are prone to larger error than those of other transitions. This last method is generally capable of fairly accurate results. To sum up, failure of local thermodynamic equilibrium, self absorption of a line, inhomogeneity of the source, demixing in the arc if more than one element is present, and other properties can contribute a fairly great amount of uncertainty in the results. Our experience in the course of this work has led us to believe that generally results obtained from the crude arc method are probably not so reliable as those obtained otherwise.

Absorption

A method in many ways similar and with the same inherent causes of error is the absorption method. If one defines the absorption

transition probability as

$$B_{ik} = \frac{\lambda^3 g_k}{8\pi h g_i} A_{ki} , \quad (2.16)$$

and $A(\nu)$ as the energy absorption at frequency ν , the total energy absorption for a homogeneous, optically thin (no self absorption) column, length ℓ , is:

$$A_L = \int_{-\infty}^{\infty} A(\nu) d\nu = \frac{1}{4\pi} B_{ik} N_i h\nu U(\nu) \ell . \quad (2.17)$$

Here $U(\nu)$ is the energy density of the continuum source radiation field. If we define an "equivalent width" of a line in absorption, W_L , and define it in terms of incident intensity $I(\nu) = (c/4\pi)U(\nu)$ and absorption A_L , then

$$W_L \equiv \frac{A_L}{I(\nu)} = \frac{h\nu}{c} B_{ik} N_i \ell . \quad (2.18)$$

Converting to wavelength and oscillator strength Eq. (2.18) becomes:

$$W_L = \int_{-\infty}^{\infty} W(\lambda) d\lambda = \frac{\pi e^2}{m_e c^2} \lambda^2 N_i f_{ik} \ell , \quad (2.19)$$

where $W(\lambda)$ is the absorption per unit wavelength interval, which is, for the case of an optically thin column,

$$W(\lambda) = \frac{I(\lambda) - I'(\lambda)}{I(\lambda)} . \quad (2.20)$$

$I(\lambda)$ is the incident intensity at wavelength λ and $I'(\lambda)$ the intensity after going through the absorption column. W_L in astrophysics is an

important quantity which represents the width of totally absorbed continuous spectrum equivalent to the area absorbed by the line.

In the laboratory one measures $W(\lambda)$ and again determines N_i to get f_{ik} from Eq. (2.19). It is necessary to heat the sample tube quite hot, as in a King furnace, to obtain significant absorption from a continuum light source sent through the column. The method runs into the same difficulties as before in determining N_i , plus being dependent on a good continuous background light source. Use of a flash lamp or carbon arc for example, can lead to inclusion of weak lines in the supposed continuum, with serious error.

One can also make interesting determinations of oscillator strengths using this same technique but observing the absorbed line profiles in the sun. Lambert and Warner⁽¹⁶⁾ have carefully studied certain transitions of magnesium and other metals in the sun and, using the above technique and fairly reliable and consistent oscillator strengths for these transitions, determined the abundance of these elements in the sun. Then they reverse the procedure, and use the same equations with the newly calculated abundances to generate oscillator strengths for many of the other transitions. These are referred to as "astrophysical" oscillator strengths. The idea is not yet wholly successful, but is interesting.

Anomalous Dispersion

Another famous way of getting oscillator strengths is by measurement of anomalous dispersion. It is known from quantum theory [Korff and Breit⁽¹⁷⁾] that the index of refraction in the vicinity of an isolated absorption line varies thusly:

$$n-1 = \frac{e^2 N_i f_{ik}}{4\pi m_e c^2} \frac{\lambda_0^3}{\lambda - \lambda_0} \left(1 - \frac{N_k g_i}{N_i g_k}\right) . \quad (2.21)$$

Ordinarily, we assume there are many more ground or lower state than higher excited state particles, hence neglect the term $N_k g_i / N_i g_k$. One again assumes equilibrium and obtains N_i from the Boltzmann relation, so this gives f_{ik} if n is measured a small distance $\lambda - \lambda_0$ from the line center. The most used technique for measuring anomalous dispersion is the "hook" method of Rozhdestvenskii used extensively by Penkin⁽¹⁸⁾. Essentially what is done is to make use of a Jamin-Mach interferometer with a tube of gas to be investigated in one arm, and an empty compensating tube in the other. This produces a series of fringes along the continuum, with a perpendicular sharp break wherever a spectral absorption occurs. By introducing a compensating plate in one arm to create a much larger path difference, one causes the fringes to be tilted in a direction opposite to that created by the line in the region of anomalous dispersion. This forms a maxima and minima for each line, the so called "hooks". A relation between the spacing of these hooks and the oscillator strength can be arrived at as follows.

First assume coordinate y in the direction parallel to the slit and λ parallel to the fringes, in the direction of changing wavelength (perpendicular to y) as in Fig. 1. With nothing in the gas absorption tube and no plate present, we have fringes where ay is some multiple m' of λ , as for any interferometer:

$$ay = m' \lambda . \quad (2.22)$$

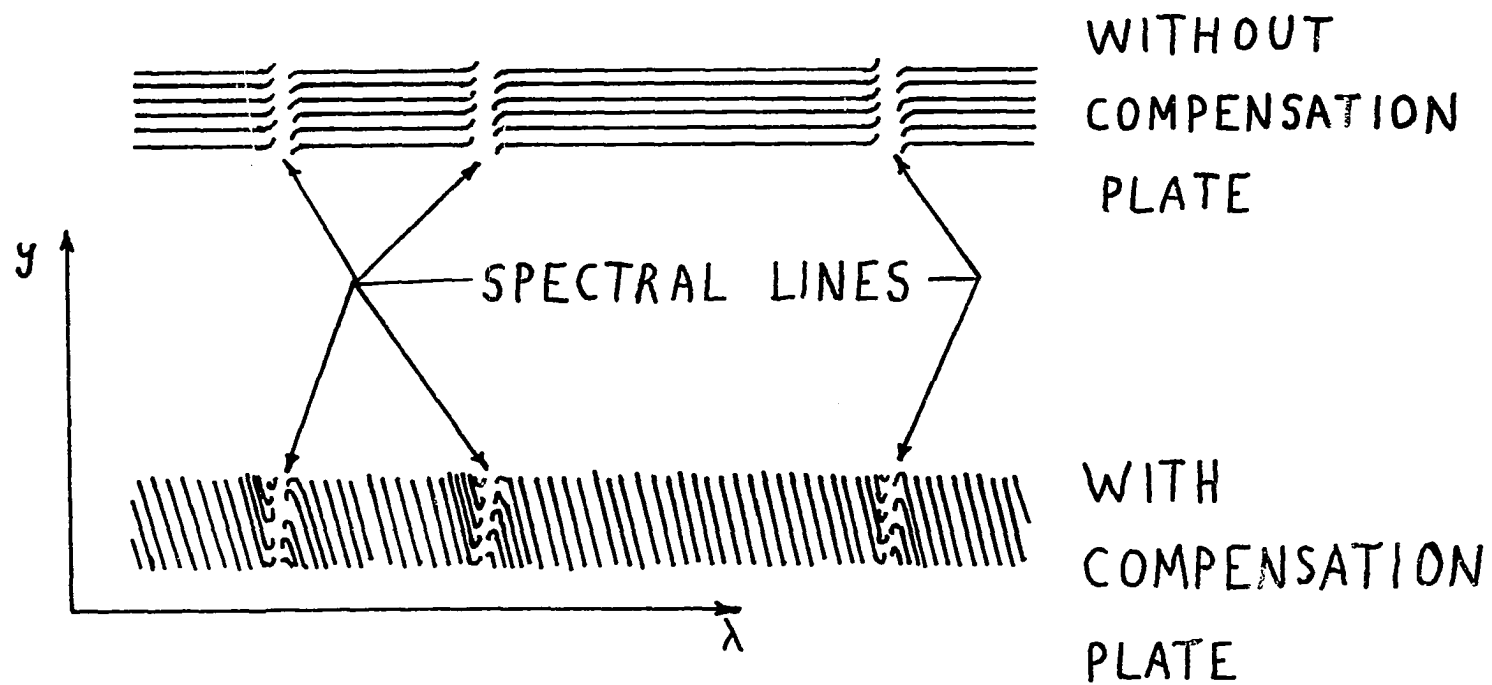


Figure 1. Anomalous Dispersion Pattern with and without Compensation Plate Using "Hook" Method.

Now if gas is added in one arm and a compensating plate in the other, these change the path difference to:

$$ay - (n-1)\ell + (n'-1)\ell' = m\lambda \quad , \quad (2.23)$$

where n is the index of refraction of the gas, n' the index of refraction of the plate, ℓ the absorption gas column length, and ℓ' the plate thickness. The fringes are now spaced differently, of order m . Now if we follow one given fringe along λ , it goes through a maxima and minima at a spectral line, so this gives $(dy/d\lambda)_{\max} = (dy/d\lambda)_{\min} = 0$. Differentiating Eq. (2.23) with respect to λ :

$$a \frac{dy}{d\lambda} - \ell \frac{dn}{d\lambda} + \ell' \frac{dn'}{d\lambda} = m$$

or at the extreme:

$$-\ell \frac{dn}{d\lambda} = m - \ell' \frac{dn'}{d\lambda} \equiv K \quad . \quad (2.24)$$

Differentiate Eq. (2.21) with respect to λ and use Eq. (2.24), along with the fact that $\lambda_{\max} - \lambda_0 = \lambda_{\min} - \lambda_0 = \frac{\lambda_{\max} - \lambda_{\min}}{2}$ and the assumption that $dn'/d\lambda = \text{constant}$ over the small wavelength range of the line:

$$N_{if_{ik}} = \frac{\pi m_e c^2 K}{e^2 \ell} \frac{(\lambda_{\max} - \lambda_{\min})^2}{\lambda_0^3} \quad . \quad (2.25)$$

Now the plate path difference $(n'-1)\ell'$ is much greater than that of the gas $(n-1)\ell$, so in place of Eq. (2.23) we have:

$$ay + (n'-1)\ell' - m\lambda \approx 0 \quad .$$

Consider the variation of m with λ for constant y :

$$\ell' dn' - m d\lambda - \lambda dm = 0$$

or

$$\lambda dm + (m - \ell' \frac{dn'}{d\lambda}) d\lambda = 0 \quad . \quad (2.26)$$

Using Eqs. (2.24) and (2.26), we see that $\lambda dm + K d\lambda = 0$ or for experimental purposes, write:

$$\lambda \Delta m = -K \Delta \lambda \quad . \quad (2.27)$$

Experimentally, K is determined by going along y (perpendicular to spectral lines) and counting the number of fringes Δm in a given spectral interval $\Delta \lambda$. This, and a measurement of $\lambda_{\max} - \lambda_{\min}$ in Eq. (2.25), give a determination of $N_i f_{ik}$, which yields relative oscillator strengths with several per cent accuracy. The necessary determination of N_i , as in emission experiments, is often uncertain, so that this type of measurement is most useful for obtaining relative oscillator strengths and normalizing them to some other absolute measurement.

Delayed Coincidence

The last overall category of methods used in obtaining transition probabilities is that of lifetimes. We have already discussed the relation of transition probabilities to lifetimes. There are several widely used techniques of making these measurements. The first is known as the delayed coincidence method and is the one employed by the author, so discussion of this method will be deferred to a later chapter. Other workers have used this technique with an electron gun, rather than an invertron, to supply source excitation.

Phase Shift

Another method is that of phase shift. Here one modulates the excitation light source or excitation electron beam with a continuous sine wave, frequency ω . One then sees scattered radiation at frequency ω , but with the phase angle θ shifted as $\tan\theta = \omega\tau$. By using sensitive lock in amplifiers one can measure this phase shift and obtain the lifetime τ , as has been done by Demtroder⁽¹⁹⁾ and by Lawrence and Savage⁽²⁰⁾.

Beam Foil

An accelerated ion beam from a Van de Graff generator has been used by Bashkin⁽²¹⁾ *et al.* to get lifetimes. A several million volt ion beam is passed through a thin carbon film. Collisions excite and further ionize the beam. By measuring the intensity as a function of distance behind the foil, and knowing the beam velocity, one gets the radiative lifetime. This method is very useful for studying lifetimes of highly ionized species, but is limited in utility for neutral atom studies.

Hanle Effect

The Hanle effect or zero-filled level crossing technique has been used by Lurio^(22,23) to measure resonance transition lifetimes. Classically what happens is as follows. An atomic beam is excited with incident light along the x axis, polarized in the y direction (see Fig. 2). A constant magnetic field H is applied in the z direction, and scattered radiation is observed along the y axis. With $H = 0$, the electric dipole oscillator states are excited and reradiate

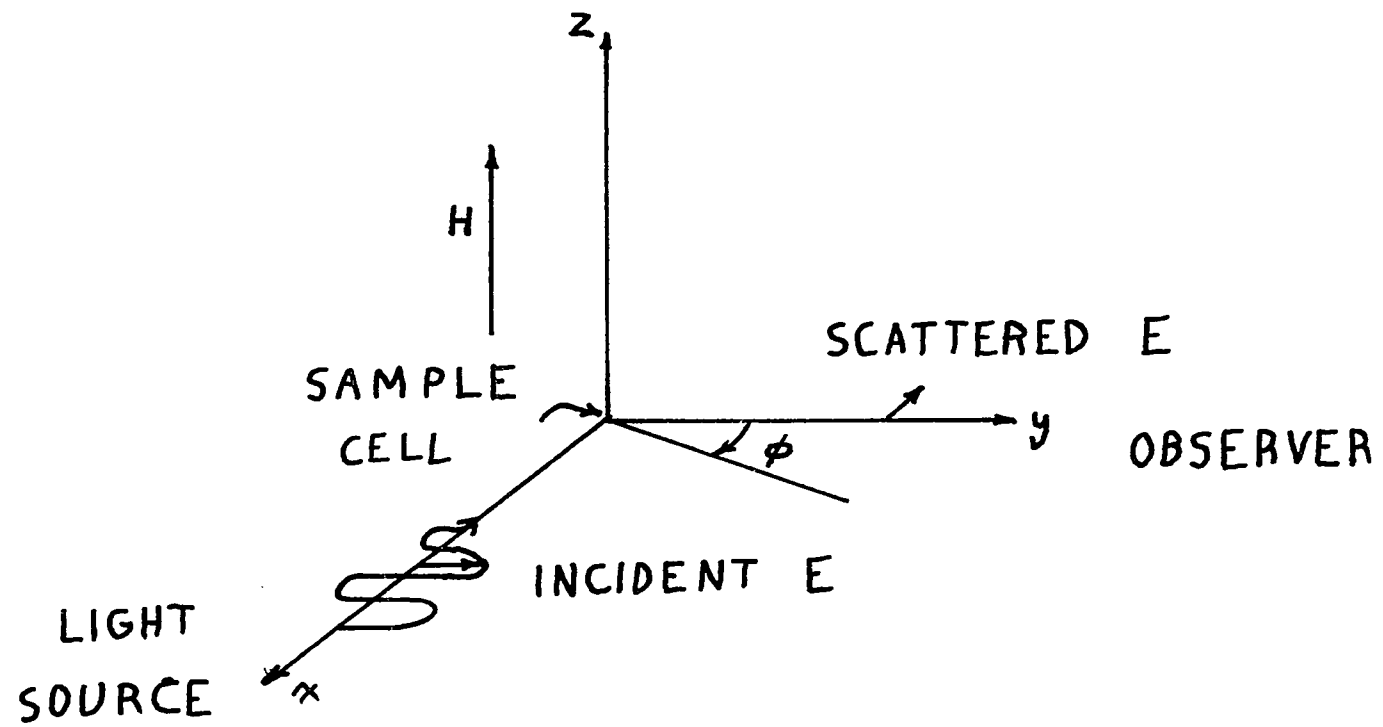


Figure 2. Experimental Setup for Hanle Effect Measurement.

in a dipole pattern, with amplitude damped according to radiative decay:

$$I(\phi, t) = e^{-t/\tau} \sin^2 \phi . \quad (2.28)$$

When H is applied, the dipoles process about z with Larmor frequency $\omega_L = \gamma H$ until they reradiate. γ is the gyromagnetic ratio, $\gamma = 2\pi g_L \mu_O / h$, where μ_O is the Bohr magneton and g_L the electron Landé g factor. So now

$$I(t) = e^{-t/\tau} \sin^2(\omega_L t) . \quad (2.29)$$

Integrating time to infinity and using $\omega_L = \gamma H$, one finds:

$$I = \frac{1}{2} \left[1 - \frac{(1/\tau)^2}{(1/\tau)^2 + 4\gamma^2 H^2} \right] . \quad (2.30)$$

So if one observes along y for a long time at various given values of H , one sees the intensity is an inverted Lorentzian with respect to H . In practice this Lorentzian is measured for several H values of a given line to obtain the profile accurately. Then the halfwidth occurs where $1/\tau = 2\gamma H_{1/2}$, or

$$\tau = \frac{h}{4\pi g_L \mu_O H_{1/2}} \quad (2.31)$$

yielding the lifetime. This method is capable of high accuracy, but is limited to resonance transitions.

There are also other less used methods, such as those where one measures the natural line width to obtain the lifetime, but they are not generally as powerful as the previously described methods. We will now turn to a description of our experiment.

PART III

DETAILS OF THE HOLZBERLEIN-JOHNSON EXPERIMENTAL SYSTEM

Much of the initial theory of the original invertron is discussed by Holzberlein⁽¹⁾ and later developments are treated by Johnson⁽²⁾, so the reader is referred to these works for discussion of detailed aspects of the experiment.

CHAPTER I

VACUUM SYSTEM

Figure 3 shows a diagram of the vacuum system, which was constructed of pyrex glass pipe tubing, various components being assembled using Viton O-rings. Apiezon N stopcock grease was used and all stopcocks were pumpable-bore high vacuum types. All traps were of the liquid nitrogen variety. The system could be pumped down to about 10^{-7} torr. It was pumped by a water cooled mercury diffusion pump, with a liquid nitrogen cold trap to prevent mercury from entering the system. Trap A was used only as a purification trap when refilling a gas bottle. Trap B kept mercury from getting into the system out of the McLeod gauge and Trap C was positioned directly behind the invertron to trap any vapors coming off from it. A Pirani gauge, McLeod gauge, and ionization gauge were available for gas pressure determinations. The window of the invertron was rough pumped by a second small mechanical

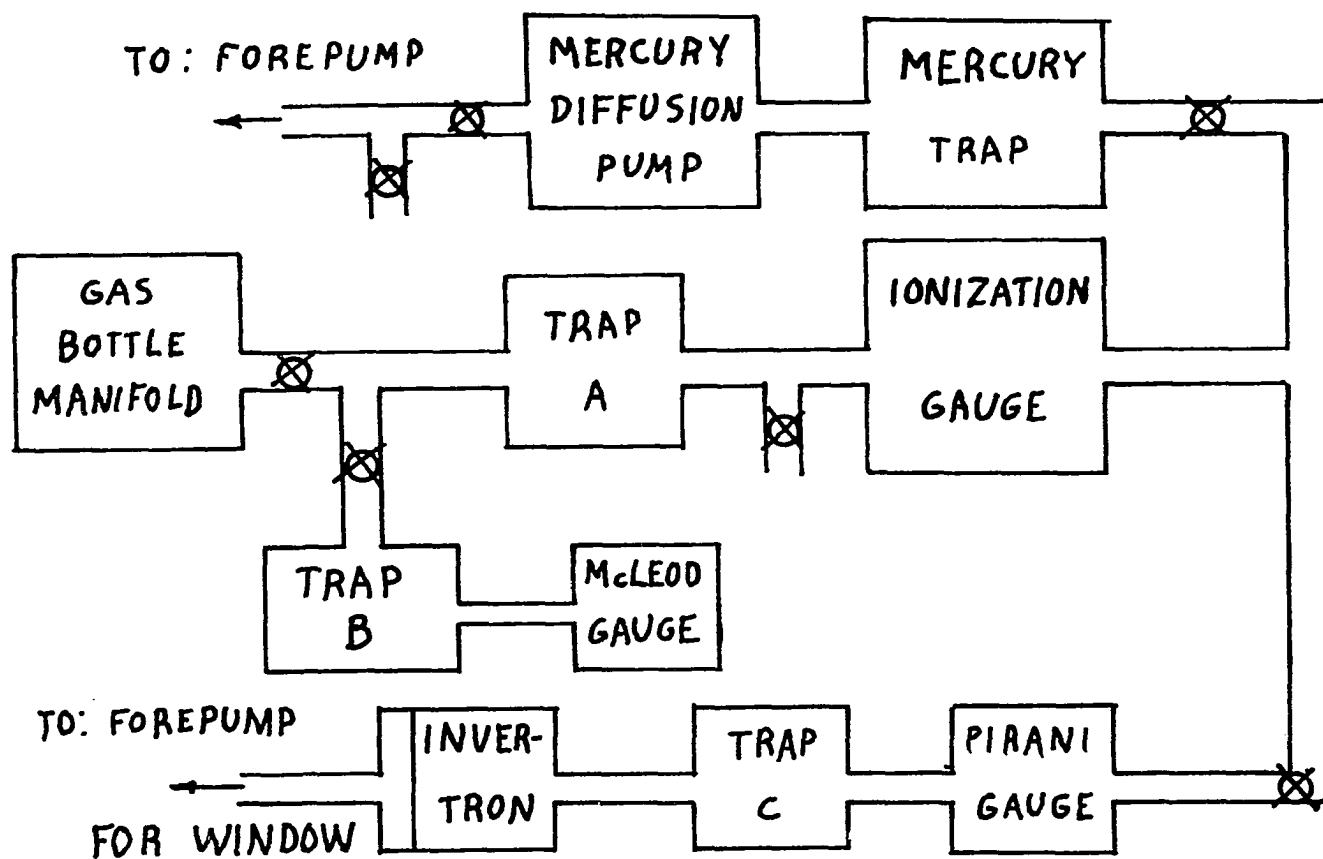


Figure 3. Block Diagram of Vacuum System.

pump entirely separate from the main vacuum system. It was not necessary to maintain a high vacuum on this window. There was also a manifold of gas bottles with which helium, hydrogen, nitrogen, or neon gas could be introduced into the system at will. This was necessary, since a gas is much more convenient to work with while trouble shooting the system or breaking in a new cathode. Also there were cases which will be discussed later when a gas was necessary in addition to the metal vapor.

CHAPTER II

OPTICAL SYSTEM AND DETECTORS

Figure 4 shows a diagram of the optical system generally used. The envelope of the invertron and all optics were quartz in order to allow passage of near ultraviolet radiation. Lens A was a long lens of about 1 m focal length. Lens B was a short focus quartz lens of about 4 inches focal length. The mirror was necessary, due to the vertical configuration of the invertron, to get the light into the monochromator which was placed on a shelf above the apparatus. The lenses and mirror were arranged so as to focus the entire hollow interior of the cathode onto the monochromator grating. A front surface mirror was used to avoid possible absorption of the ultraviolet by mirror glass. The filter was used to eliminate second order radiation in the monochromator when working at wavelengths longer than about 5000 Å. A Corning #3-73, which cuts off at wavelengths less than 4200 Å, was used.

A $\frac{1}{2}$ -meter, 16 Å/mm Jarrell-Ash Ebert mounting monochromator was used for most of the work reported on here. It was desirable to measure lifetimes of each member of a given triplet, so the resolution obtainable by the $\frac{1}{2}$ m was most desirable. In some of the earlier experimentation, and for the measurement of λ 8806 3^1D magnesium line, a

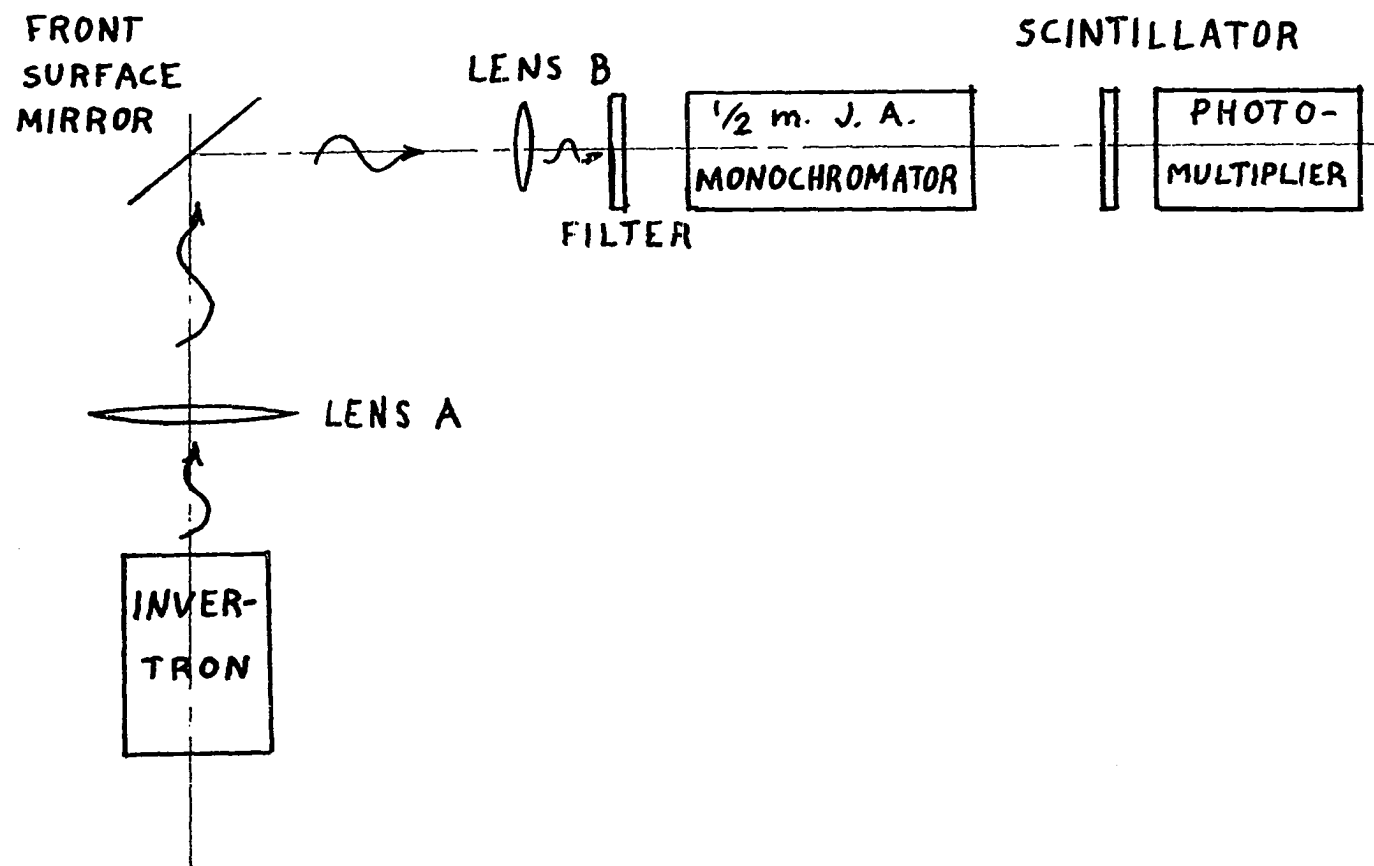


Figure 4. Diagram of Optical System.

32 Å/mm $\frac{1}{4}$ -m Jarrell-Ash instrument was used. For the 3^1D measurement, the setup was essentially as in Fig. 4, except a Spectrolab #85 broadband interference filter (8000-12,300 Å response) was used and an adjustable iris placed in front of the monochromator. For the other $\frac{1}{4}$ -m work, the mirror and Lenses A and B were eliminated and the monochromator was mounted on an adjustable frame directly over the invertron window and about one inch above it. Pilot B scintillator was used in front of the photomultiplier tube for measurements of wavelength less than 3500 Å because usually a glass enveloped photomultiplier was being used. This was a plastic scintillator which was cut to fit directly in front of the photomultiplier window inside the metal tube housing and shielding.

Most of the work was carried out using an RCA 8575 photomultiplier with a commercial base and preamplifier discriminator. This tube is quoted as having a bialkali response. It is a fast (2.7 nsec) rise photomultiplier having a gain suitable for photon counting. Some measurements were also made with an RCA 7746 S-11 response tube with focusing dynode. A home made tunnel diode amplifier built by R. T. Thompson was used in connection with this photomultiplier. Results were essentially the same as with the 8575, and since its circuitry was somewhat more convenient to use, the 8575 was employed for most of the work. It was found advantageous to wrap the 8575 case with copper tubing and pump an ice water bath through the tubing. This action lessened the background noise counts by a very large percentage.

Finally, the 3^1D measurement was made with an RCA 7102 photomultiplier with an S-1 response. This tube was cooled with liquid nitrogen

and used with the tunnel diode circuit in a manner similar to that discussed with the 7746. All the above mentioned tubes had glass envelopes, and thus were limited to visible response. In earlier experimentation an EMI 9558 with quartz envelope and S-20 response was used. This tube had sufficient amplification for our purposes, but its venetian blind dynode structure limited its response time to about 10 nsec, and it was found to be unsuitable for measuring lifetimes in the range in which we worked. Thus all measurements in the near ultraviolet were made with the use of Pilot B scintillator. Figure 5 shows the spectral response of the various photomultipliers used.

The $\frac{1}{4}$ -meter monochromator had a series of fixed entrance and exit slits of various widths, and the $\frac{1}{2}$ meter was equipped with adjustable slits. A drive was built for either unit which could be used to scan spectra. The $\frac{1}{2}$ meter instrument had a 4500 Å blaze grating, and the $\frac{1}{4}$ meter grating was blazed at 12,000 Å.

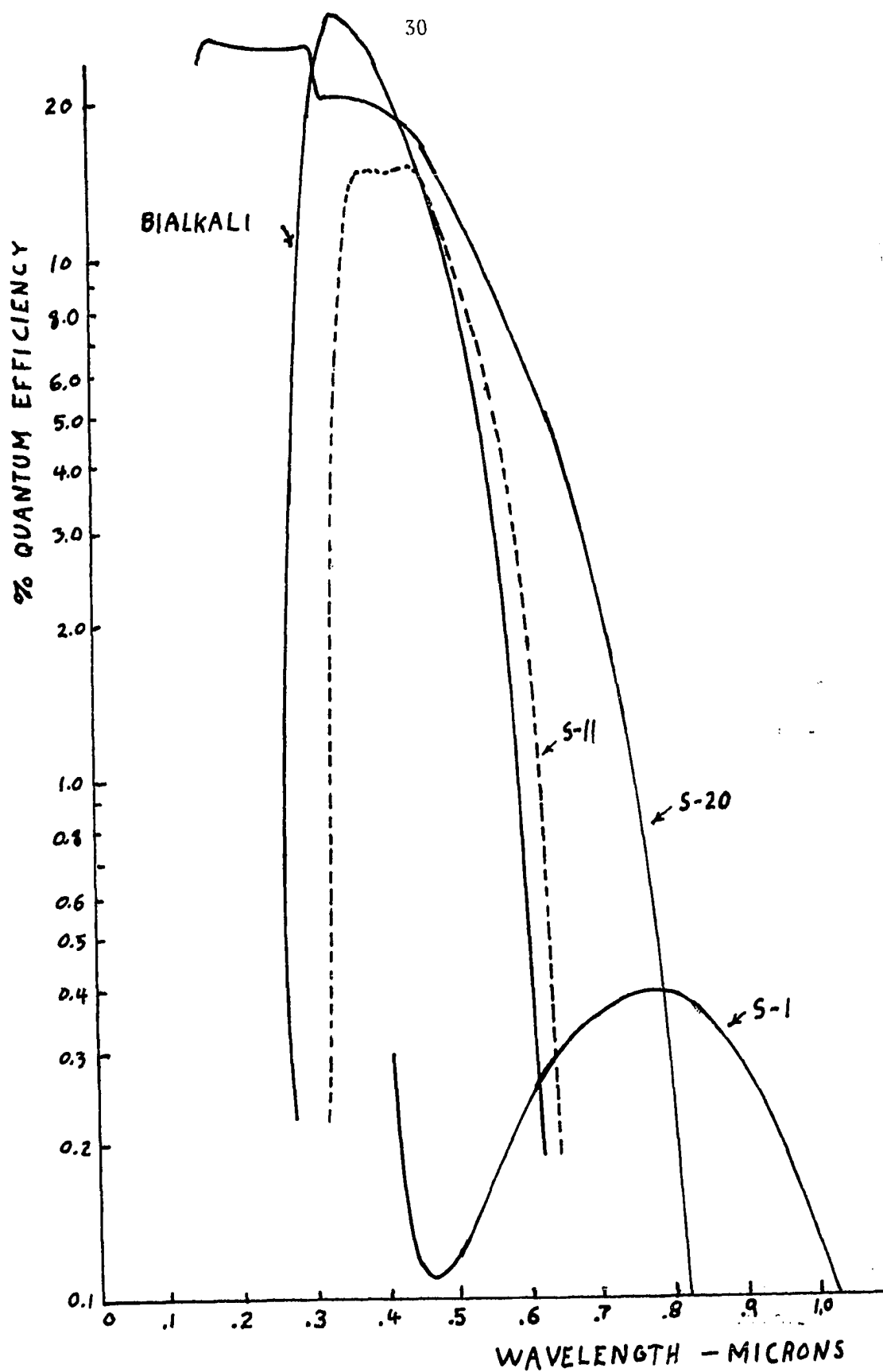


Figure 5. Spectral Response of Photomultipliers.

CHAPTER III

ELECTRON EXCITATION PULSER

The invertron causes atomic excitation and ionization by accelerating a beam of electrons into the target gas. In order to do this, a pulse must be applied to the invertron. The pulse should be of up to 100 or 150 volts into low (15 ohms) impedance, of several tens to several hundreds of nanoseconds duration, and have a fall time of two or three nanoseconds. The best technique found so far for producing this pulse is to discharge one end of an open energized coaxial delay line through its characteristic impedance, utilizing a 2D21 thyatron switch. The theory of this method is given by Lewis and Wells⁽²⁴⁾. A physically interesting development adapted from Millman and Taub⁽²⁵⁾ will be presented here.

Figure 6a shows the equivalent circuit which we will consider first. Let us assume that before time $t = 0$ that switch S1 is closed and S2 is open. The line will be charged up to voltage V across R_1 , so the line current is $i(t < 0) = V/R_1$. Now at $t = 0$, S1 opens and S2 closes simultaneously. The line voltage now changes to $V_{in} = V'$. The current through R_2 is given by $i'(t=0) = V'/R_2$, and we can easily see from Fig. 6a that $i'(t=0) = -i(t=0)$, the delay line current. Thus $i(t=0) = -V'/R_2$. Now as a function of time a voltage step ΔV will be propagated down the delay line, where $\Delta V = V' - V$. This corresponds

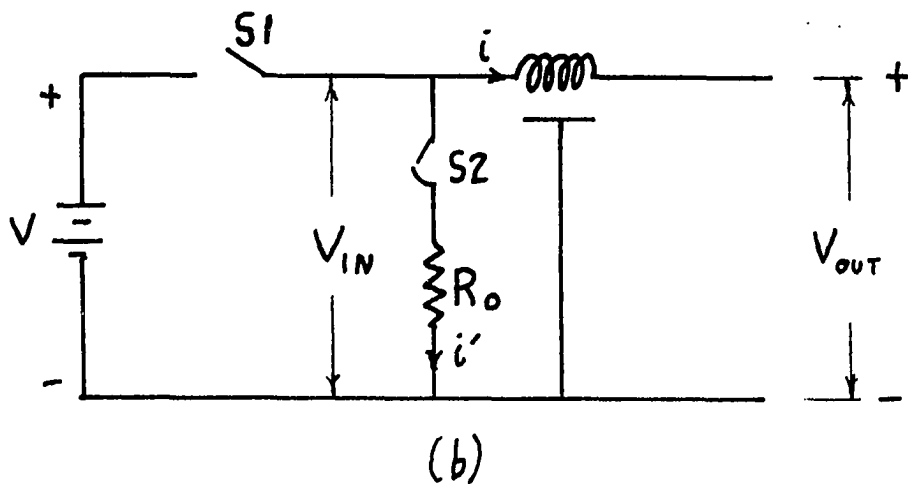
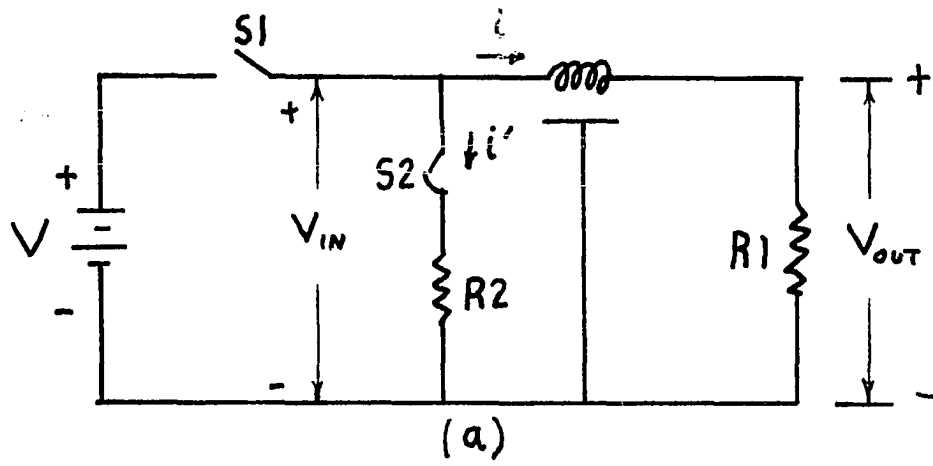


Figure 6. Equivalent Delay Line Circuits.

to a current step $\Delta i = i(t=0) - i(t<0)$. Thus $\Delta i = -V'/R_2 - V/R_1$. Now it can be shown [Lewis and Wells⁽²⁴⁾] that the ratio of voltage to current for a wave traveling down a transmission line is equal to the characteristic impedance R_0 of the line. Thus we get:

$$\Delta V = R_0 \Delta i = R_0 \left(-\frac{V'}{R_2} - \frac{V}{R_1} \right) \quad (3.1)$$

Rewriting:

$$\frac{\Delta V}{V} = -\frac{R_2/R_1 + 1}{R_2/R_0 + 1} \quad (3.2)$$

We have here assumed a lossless line. Now consider the specific case of Fig. 6b. Here $R_2 = R_0$ and $R_1 = \infty$. We will also assume a reflection coefficient of one (complete reflection) at an open ended transmission line, and a reflection coefficient of zero (complete absorption) at a line end terminated in the characteristic impedance. Then Eq. (3.2) gives:

$$\frac{\Delta V}{V} = -\frac{0+1}{1+1} = -\frac{1}{2} \quad .$$

Thus the total voltage V' at $t = 0$ is $V' = \Delta V + V = V/2$. The discontinuity $\Delta V = -V/2$ starts at the input and propagates down the line discharging it to $V/2$ as it goes. At the end of the line, after time t_d which it took to get down the line, it reflects back from the open circuit and discharges the remaining $V/2$ as it goes, completing the cycle and being absorbed at $2 t_d$. Thus the result across the characteristic load R_0 is a pulse of amplitude $V/2$, where V is the voltage to which the delay line is originally charged, and duration $2 t_d$, where t_d is the time delay one way of the delay line.

Now let us describe how the theory is actually applied. The transmission line used is 3/4 inch Phelps-Dodge coaxial cable. Several different lengths are available and have been measured by the author and Johnson, and are listed by Johnson⁽²⁾. Because of this a number of different excitation pulse widths are available, a condition which, as we shall see later, is desirable. The initial charging to V is accomplished by a large 0-3000 volt power supply. In reality, switch S_1 is not actually a switch, but a charging resistor much larger ($\sim 50\text{-}100\text{K } \Omega$) than the R_0 of the cable. Switch S_2 is a 2D21 thyatron. In actual operation the thyatron is open, allowing the cable to be charged through the charging resistor. When the thyatron fires, closing S_2 , the impedance of the charging resistor at S_1 is so much greater than the 50Ω impedance of the cable that it is open circuit as far as the cable is concerned, allowing a square wave discharge as described above.

Figure 7 shows the actual circuit diagram of the arrangement used. The thyatron is held off by a negative bias B^- , typically about -75 volts, on the first grid. The other grid is tied to the cathode. The impedance of the thyatron (about 25 ohms) plus that of R_1 , R_2 , and the invertron must be fifty ohms for the system to work well. In actual practice this impedance is often a little less than fifty ohms, since this condition produces the fastest cutoff; however, reflected oscillations or "ringing" will occur if the undertermination is too severe, which can seriously alter the excitation cutoff seen by the invertron. A large ($\sim 100\text{V}$) pulse is applied to the grid of the thyatron by a Tektronix 105 square wave generator. This causes the thyatron

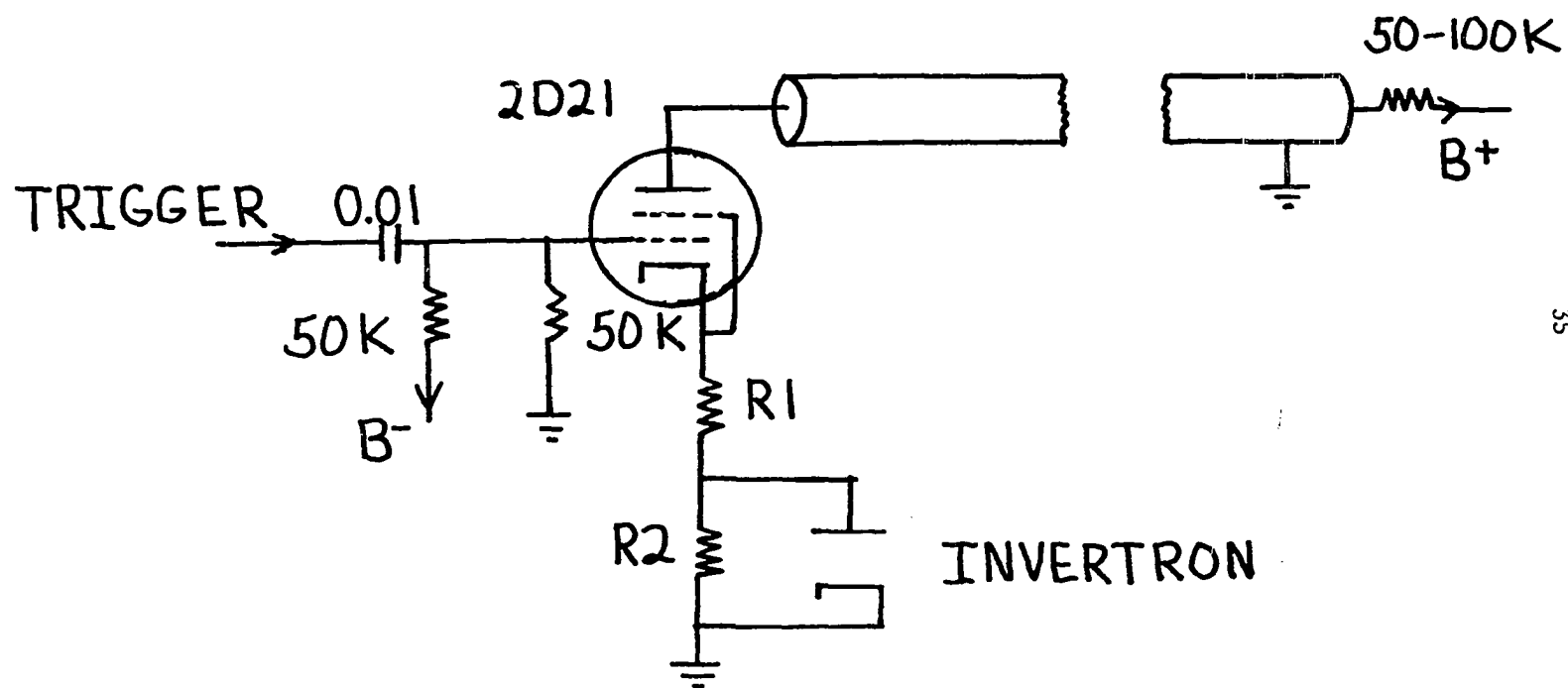


Figure 7. Schematic of Excitation Pulse Generator.

to "fire", go into conduction, until the cable is discharged, at which time the tube will again be open by the negative bias. The cable then recharges through the charging resistor. By changing the frequency of pulses from the square wave generator trigger one controls the repetition rate of firing and recharging of the circuit. One must choose the value of B^+ charging resistor such that the RC charging time of the cable is short enough to allow the cable to be charged up sufficiently between firings, yet have R large enough so that it is an open circuit compared to fifty ohms as far as the voltage step discontinuity is concerned, and a good fast rise and fall square pulse can be formed. Typical firing repetition rates obtainable with this system have been 10-12 khz/sec. for pulse widths of from 20 to 500 nsec in duration, 40 to 180 eV electrons being obtained across the invertron. R1 and R2 are adjusted to obtain suitable impedance and also act as a voltage divider to adjust the voltage of the pulse delivered to the invertron. Cutoffs obtainable with this system are typically 2-3 nsec. One must select the thyatron used with care, and also experimentally adjust the bias and exact trigger frequency for a given 2D21. These tubes differ markedly both in stability and in cutoff time attainable. A break in period for a new tube is necessary, during which one starts with lower voltages, and is gradually able to increase the maximum voltage under which the tube will operate. 2D21 W tubes have given the best results. The tubes are observed to have certain frequency "modes" which are a function of the bias and pulse width (cable length) used. This changes with time. A typical tube may at first operate

best at about 8.5 khz/sec; and as time goes on, its running mode will be seen to increase to about 12 khz/sec before it wears out. A typical thyratron will last from 12-36 hours running time, depending upon the voltage applied. A tube forced to run in a mode other than its "running mode" will be unstable, and will usually be destroyed in a fairly short time. No significant change in the cutoff of a given tube was observed with respect to cable length used.

The above described method of producing an excitation pulse was used nearly all the time; however, for ion and a few other transitions whose lifetimes were expected to be in the ten nanosecond or less region, another method can be used which gives cutoffs of less than half a nanosecond for the excitation pulse. The heart of the device is a mercury wetted relay switch under many atmospheres of hydrogen pressure, which can give almost instantaneous contact and no arcing on making and breaking. The detailed circuitry is described by Johnson⁽²⁾, so only the basic elements will be described here.

Figure 8 shows a diagram of the circuit used. This time a lumped parameter artificial delay line was wound and used for sake of compactness, since the system is not now dependent on its response time, which is markedly inferior to that of a real cable. R1, R2, the 2D21, and the invertron should again provide the characteristic impedance of the delay line, although this is not so important as before. A different power supply was built and utilized for the B^+ ; its schematic is shown in Fig. 9. A regulated 55V supply was built to power the delayed trigger generator; Fig. 10 gives its schematic. The relay is in a

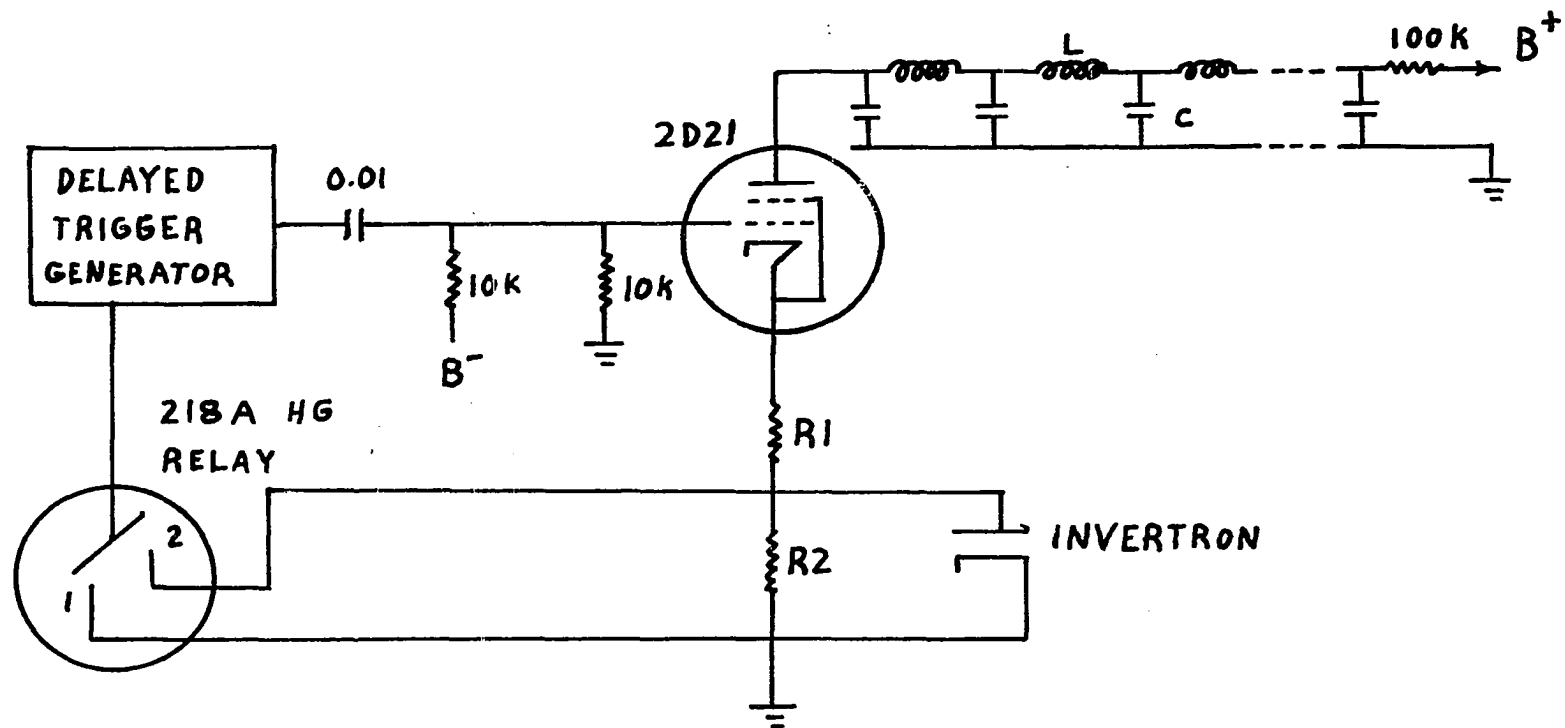


Figure 8. Schematic of Mercury Relay Excitation Pulse Circuit.

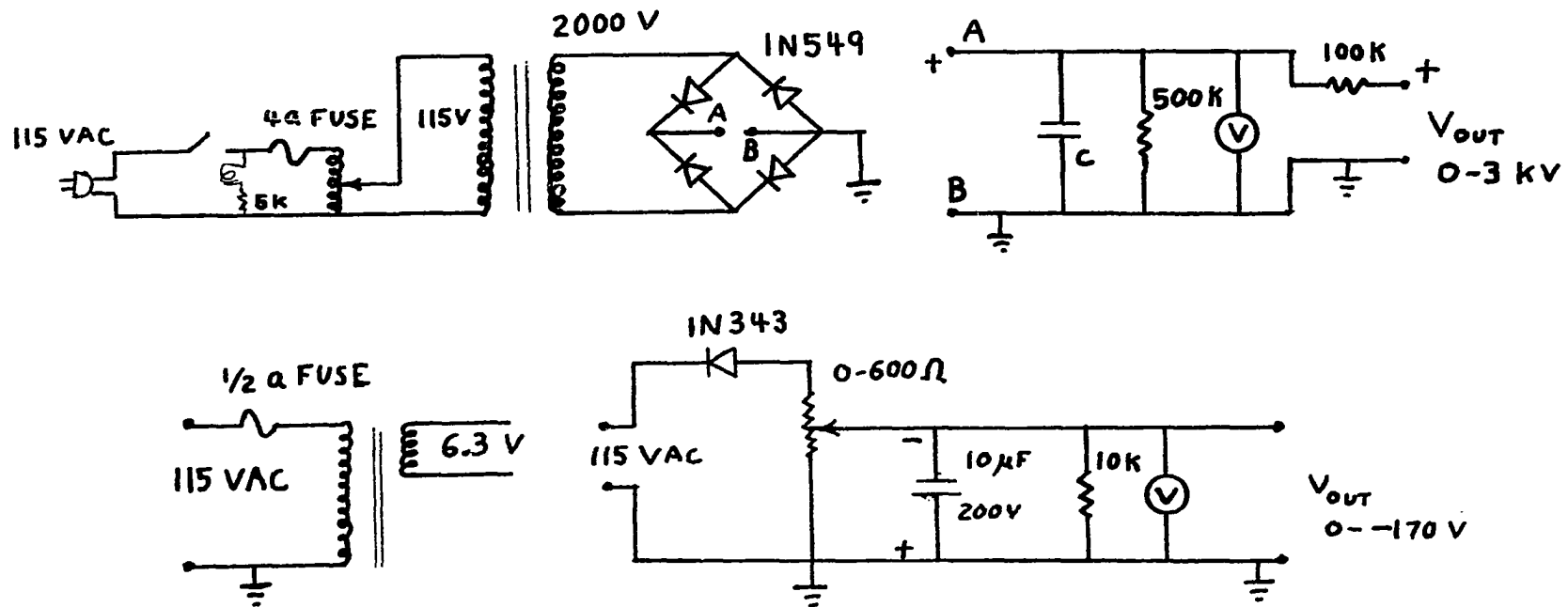


Figure 9. High Voltage Power Supply.

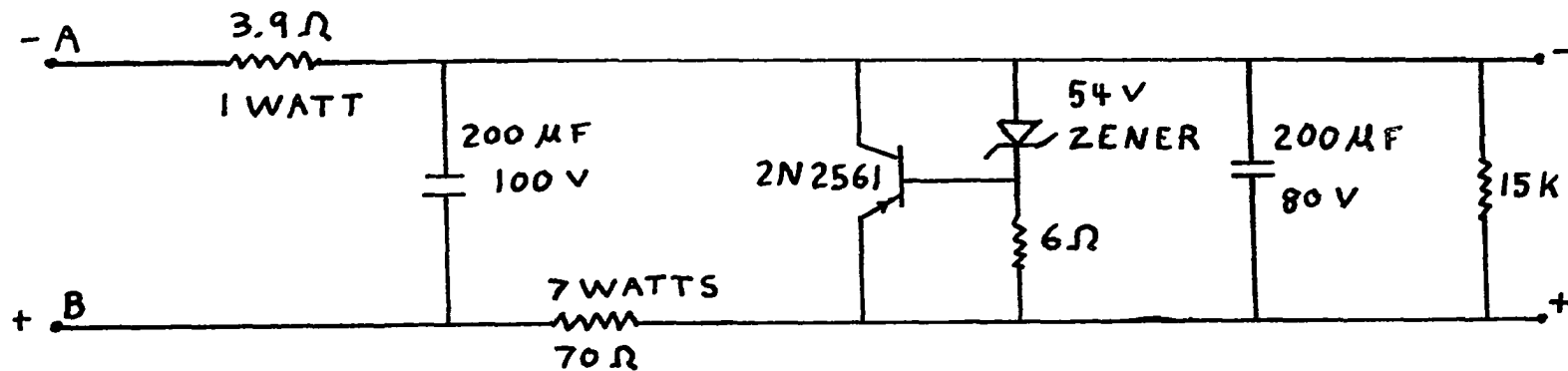
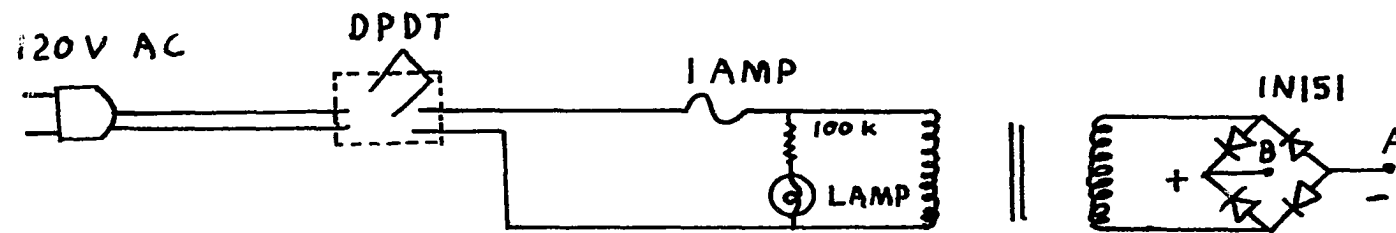


Figure 10. Regulated 54 Volt Power Supply.

field coil driven at 20-30V by a Variac. It can be made to run at 120 Hz/sec, and is tuned with small bar magnets so that contact 1 is made consistently and stably before contact 2. This tuning is important and requires some amount of adjustment.

The 2D21 is initially open, allowing the artificial delay line to charge up as before. Figure 11 shows a time schematic of events as they happen. At time A, pin 1 of the relay makes contact, grounding the delay trigger generator and activating its circuit. After a predetermined delay time to B, the trigger activates and fires the 2D21, allowing a square discharge to form exactly as in the case described previously. The difference here is that the pulse shape (rise and fall) is not nearly so sharp, since an artificial line is being used. We have shown the entire pulse in dotted line as it would appear if it were allowed to discharge and turn off by itself. However, at time C pin 2 of the relay makes contact, grounding the signal or "crowbarring" it. Thereupon the 2D21, negatively biased, reopens and the line is recharged for the next pulse. The time between pin contacts AC is fairly constant, although there is a small amount of jitter which can be minimized by proper magnetic "tuning" of the relay. Of course the pulse width BD is constant, determined by the delay length of the delay line. The trigger activation time AB is continuously variable, so by varying this, one slides the pulse in time through point C, thus effectively regulating the actual pulse width obtained.

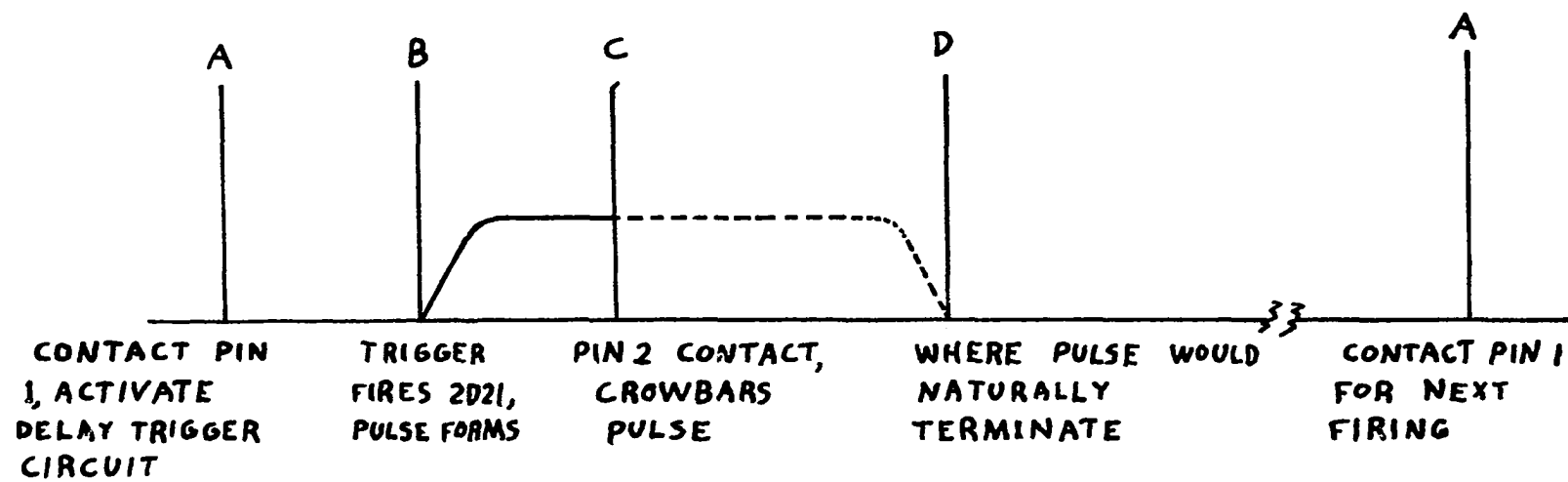


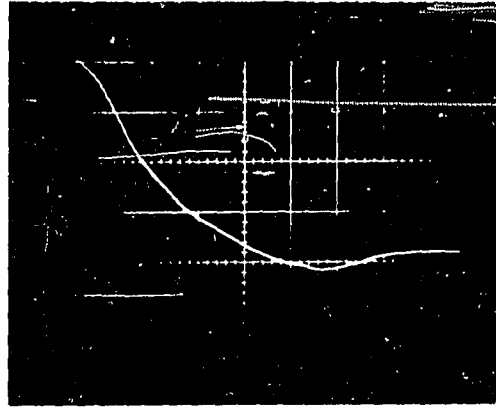
Figure 11. Time Diagram of Mercury Relay Firing Sequence.

The delay line constructed gave a pulse up to 12 microseconds in duration, with cutoff width variable from zero to full pulse width. In practice, due to relay jitter, it was impractical to run with a pulse width of less than about 750 nsec. Voltages obtained on the invertron were the same as before. The big advantage of this system over the one described earlier is that cutoffs of less than half a nanosecond were attainable. However, the electronic complexity of the system, its limitation to fairly wide excitation pulses, and worst of all, its limited repetition rate of 120 Hz/sec all combine to make it very inconvenient to use except for a few of the fastest transitions. A narrower pulse is desirable to avoid exciting long lived cascade states.

Figure 12 shows traces obtained of the cutoffs of the two systems, using a Type 1S1 Tektronix sampling scope. The top two photos are of the real cable pulser cutoff, the loads referring to the impedance of the invertron. The improvement in cutoff is due to undertermination resulting when the invertron is at a typical load impedance. The cutoff is about 3 nsec. The crowbar cutoff of the mercury relay system is independent of the load impedance. It was about 0.5 nsec.

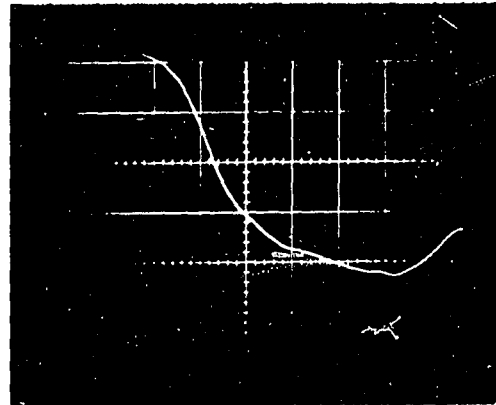
CUTOFFS
COAX PULSER
NO LOAD

2 nsec/cm.



12 OHM LOAD

2 nsec/cm.



Hg RELAY

NO LOAD

0.2 nsec/cm.

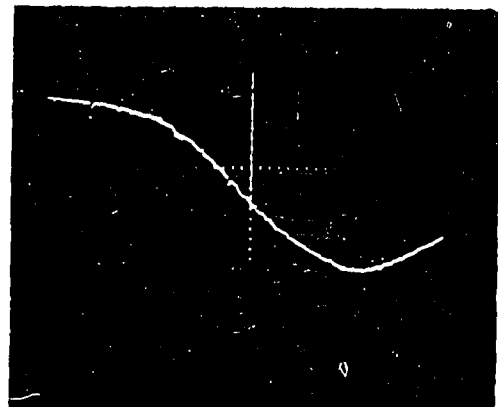


Figure 12. Cutoffs of Coaxial and Hg Relay Pulsers.

CHAPTER IV

FIRST MODIFIED INVERTRON

In the earliest days of our work it was thought perhaps one could use a metallic molecule with the ordinary gas invertron described by Holzberlein⁽¹⁾ and Johnson⁽²⁾. The molecule would dissociate upon electron bombardment and contact with the hot cathode, releasing trace amounts of the metal atom for study. Klose has used such a technique at the Bureau of Standards, using iron carbonyl to obtain iron atoms for study. A chloromethyl substituted silane compound of high vapor pressure was available to us, so we constructed a port on the vacuum system through which small amounts of the vapor could be admitted to the system. As expected the chlorine immediately poisoned the cathode. The difficulty of controlling these often dangerous metal substituted compounds and the small amount of metal atoms yielded in proportion to the amount of other unwanted species present made us determine to devise a suitable technique whereby metal vapor could be introduced directly into the system.

Figure 13 shows the first modifications tried in order to accomplish this. First we shall outline the basic invertron itself. It consists of a hollow nickel cylinder about three inches long and $\frac{1}{4}$ inch thick with a center hole diameter of about two centimeters acting

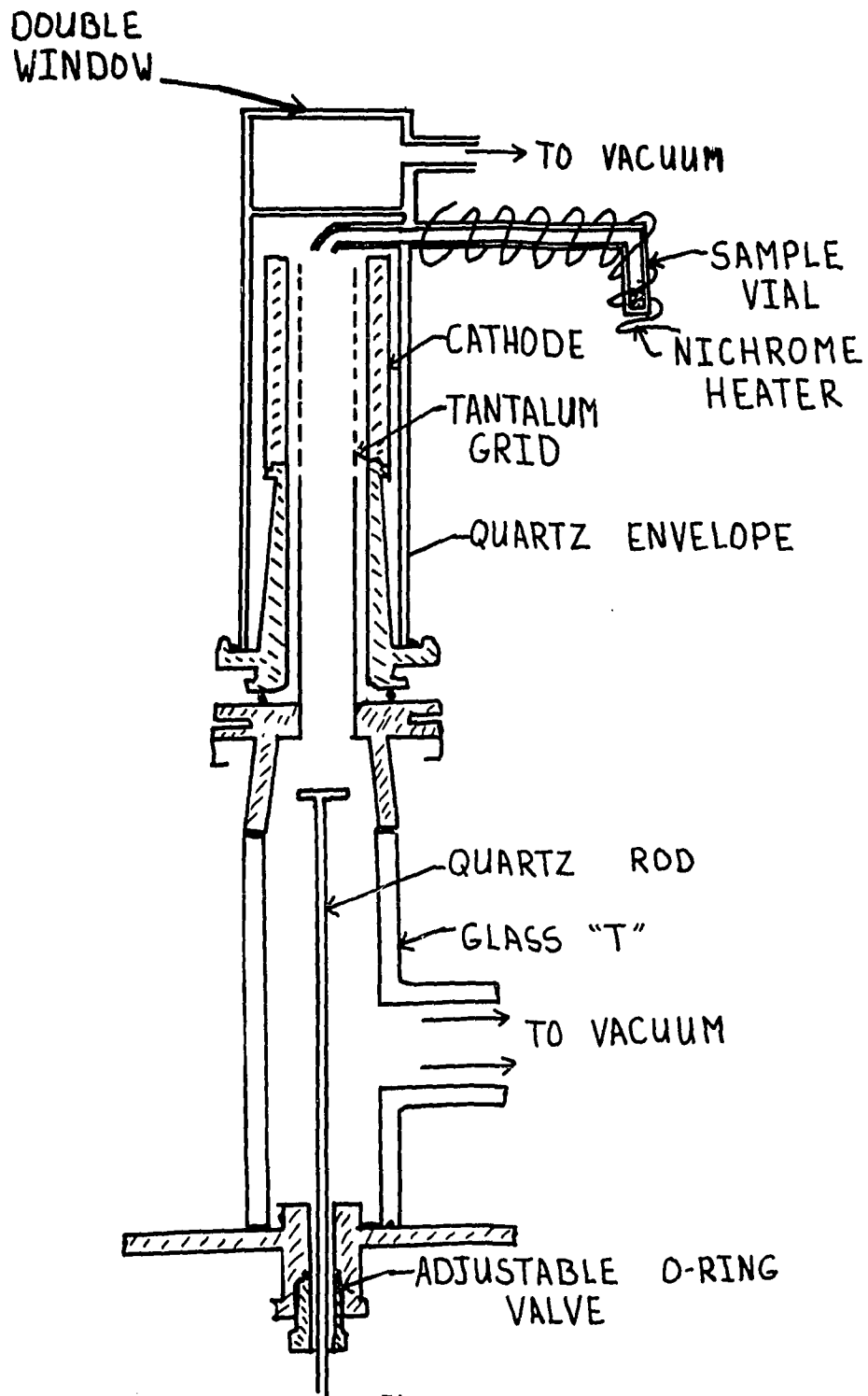


Figure 13. First Modified Invertron.

as cathode, and a tantalum wire circular grid concentric to the cathode and about 2 millimeters interior from it as the anode. The cathode is inductively heated by a one kilowatt Thermonic induction heater, generally to about 800-900° C, as measured by an optical pyrometer. The cylinder is painted with a commercial barium cathode coating material which liberates a large amount of electrons when an accelerating voltage is applied. The cathode is attached to a stainless steel mount, which is water cooled below. As has been well described earlier by others, the excitation pulse is applied to the grid, the cathode being at ground. This causes many electrons to be accelerated inward from the cathode toward the center, causing ionization and excitation of the gas particles present. At first the electrons are repelled due to space charge, but as some ions are formed they neutralize some of the space charge and allow penetration of the electron "beam". Currents in the ten ampere range are possible for the device. The square excitation pulse terminates in a couple of nanoseconds, and we monitor the decay of the excited electrons to lower energy states by measuring the decrease of light intensity as a function of time. How this is done will be discussed later.

We now come to the first set of modifications shown by Fig. 13. First a double evacuated quartz window was added. It was felt that perhaps with vacuum insulation, radiation from the hot cathode would keep the inner window hot enough to prevent metal vapor from condensing out upon it and causing it to become opaque or "darken". Also a side arm vial and nozzle of quartz were added. Chips of the metal

were placed in the vial, and the vial and arm were wound right up to the envelope with layers of asbestos and nichrome wire. The nichrome was attached to a large variac. By adjusting the variac one could control heating of the arm and thus send small controllable amounts of metal vapor through the nozzle into the excitation chamber. The nozzle aimed away from the window and helped protect it from the metal. It was also decided that since this was such an open system the metal vapor would quickly pass out of the cathode region and condense. To avoid this, the following device was added. A $\frac{1}{4}$ inch piece of quartz rod had a one centimeter diameter disc formed on one end of it. This disk would just fit up into the tantalum sleeve support, and when inserted up toward the hot cathode, the radiation from the cathode would heat it sufficiently so that the metal vapor, rather than condensing on it, would be partially trapped in this region. This rod was also to be adjustable; it could be pulled out of the invertron for pumping down purposes. To accomplish this a plate was bolted onto a glass tee with an O-ring seal. In this plate was a threaded plug designed to tighten on a small O-ring which just fit the quartz rod. The quartz rod was kept well greased with silicon stopcock grease. The plug could be loosened slightly and the rod moved up or down into or out of the system while maintaining good vacuum. The plug could be tightened to hold the rod in any given position. One had to be certain the plug was kept tight, or the rod would be pushed right up into the grid by atmospheric pressure.

This model of invertron was used for some time in the early part of our experiments on magnesium, but it worked only fairly well. For one thing, the nozzle blocked part of the optical axis, cutting down the observed intensity somewhat. Also the magnesium vapor tended to condense somewhat in the nozzle and side arm and block it off. Also in order to obtain sufficient ionization and penetration of the electron wave, it was found to be advisable to run with a background gas such as helium present. This system was also rather difficult to clean and reload new samples into. Probably the worst fault, however, is that hot magnesium in any quantity tends to attack quartz, especially at seals. This caused the side arm to actually break off after some hours of run time, a condition obviously unsatisfactory! With these problems in mind we changed the system again somewhat.

CHAPTER V

CURRENT MODIFIED INVERTRON

Figure 14 shows the invertron as it was used for most of the data taken in this work. The double evacuated window is maintained, but the side arm has been done away with. The quartz disc was replaced by first a small cup and then larger cups into which the sample metal chips were placed. Larger cups were necessary to hold more sample and allow longer run times between refilling. The cup was still of a diameter which would just fit up into the invertron, and was about one inch tall. By raising the cup up toward the hot cathode, the metal sample becomes heated and vaporizes. The first time this was attempted the inner window, now unprotected by the nozzle, darkened rather quickly. The envelope was shortened so that the inner window was closer to the cathode, but some darkening still occurred. Finally a third window, composed of sapphire to lessen the chances of reactive darkening with hot metal vapors, was placed on top of the hot cathode in direct thermal contact. This seemed to solve the darkening problem quite nicely. Also there was a problem of shorting out the grid to cathode after a short time of running. The metal vapor was condensing down in the space between the stainless cathode mount and the tantalum grid sleeve. When a sufficient amount of the metal built up it shorted

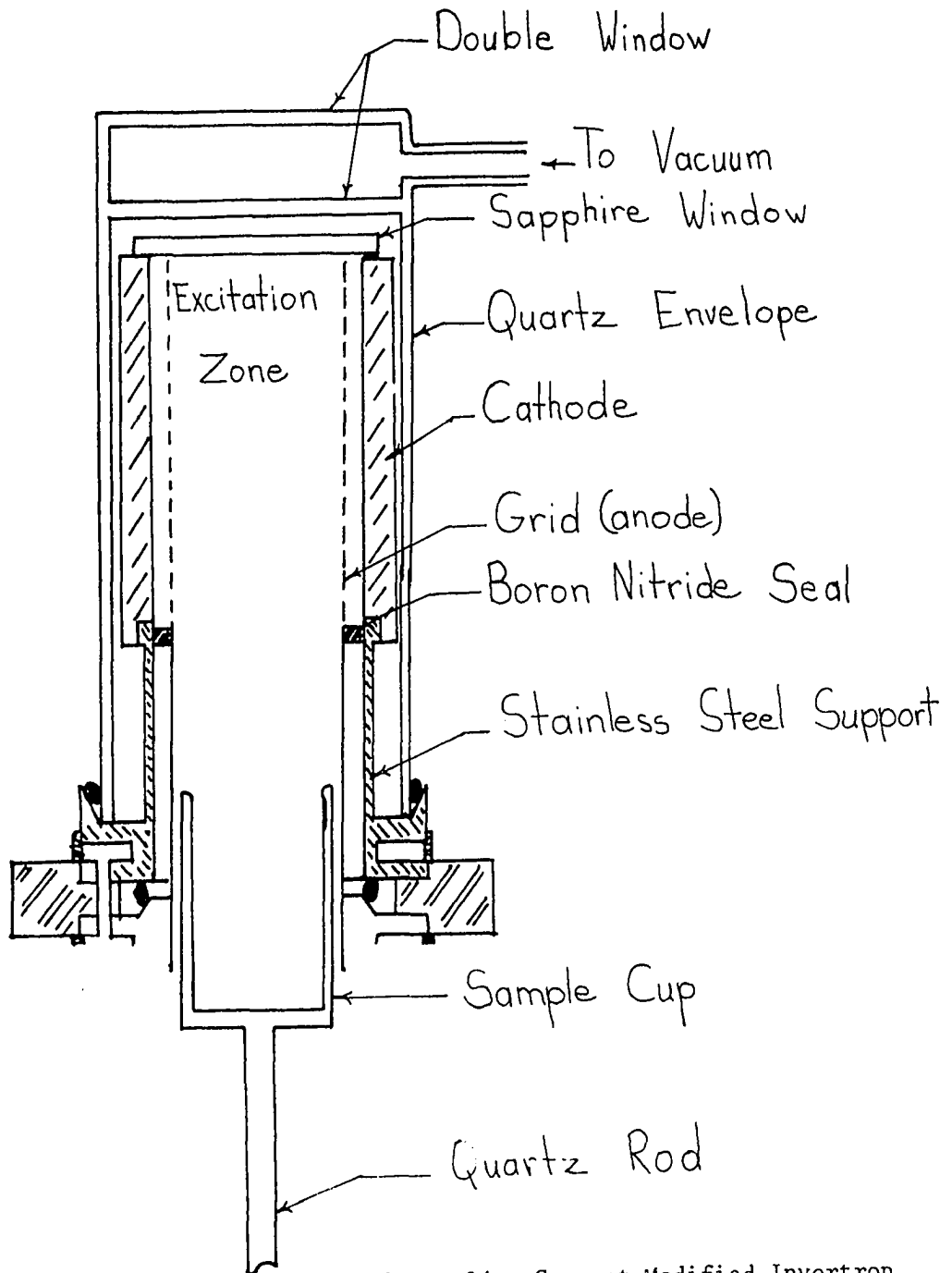


Figure 14. Current Modified Invertron.

these two elements together. This condition was corrected as shown by sealing off the cathode-grid space with boron nitride. A paste form of boron nitride was inserted into the space. It was found to be best to fire this with a torch, then refill and fire again. In this way the cracks which developed upon reaching high temperature were filled so as not to leak metal vapor down into the inner space area. Some amount of leakage was inevitable, and the system eventually shorted out and had to be dismantled and cleaned, but not until after many hours of running time elapsed.

This system had been found to work quite nicely with metals of fairly high vapor pressure such as magnesium and cadmium. A number of other metals are also accessible to it. The inner cathode region now forms a fairly good oven, although it is not yet a completely closed system. It is no longer necessary to use a background gas in most cases; in fact, generally one pumps on the system all the time while metal vapor is being used. The system is not a closed one, which makes absolute determination of the vapor pressure of the metal practically impossible. However the system does reach dynamic equilibrium in pressure, and the position of the cup toward the cathode gives a very sensitive control of the vapor pressure. It is possible to determine relative pressures because the loading of the excitation pulse is a very sensitive indicator of this. Since some ionization of the vapor is necessary to neutralize space charge and allow the wave of electrons to flow, the amount of current drawn is very much a function of the amount of vapor present. Because we are dealing with metals, their low

ionization potential is in our favor, since only small amounts of metal vapor are necessary to provide sufficient ionization. The procedure followed was to make lifetime measurements of a spectral line at very little loading shown by the excitation pulse voltage curve, some with intermediate loading, and some where the pulse was fairly heavily loaded. In no case of excited states did we notice any pressure dependence of the lifetime. The only transitions which showed pressure effects were resonance transitions to ground state; for the most part these were left for other methods of measurement. By knowing the temperature of the cathode and consulting closed system vapor pressure versus temperature curves, one can get rough upper bound vapor pressures for a given position of the sample rod. By observing where a sample melts as it is very slowly raised toward the hot cathode and marking this position on the rod, a rough temperature calibration can be obtained. Also some comparisons were made of the excitation pulse loading between metal and known pressures of gases such as neon. From these considerations we can safely say the vapor pressures in the system never exceeded ten microns while measurements were made, and were usually considerably less.

A few rudimentary calculations will reassure us of the negligible effect of collisional depopulation at these pressures. Assume an ideal gas, temperature 1100° K , at 10 microns Hg pressure, which is certainly higher than that actually encountered. The mean Maxwellian velocity is given by

$$\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2} . \quad (3.3)$$

This gives a velocity of 3.1×10^4 cm/sec for magnesium and 1.4×10^4 cm/sec for cadmium. Now using Loschmidt's number, 10 microns at 1100° K implies $N = 26.9 \times 10^{18} \times \frac{0.01}{760} \times \frac{1100}{273} = 1.4 \times 10^{15}$ atoms/cm³. The mean free path is given by:

$$\lambda = \frac{1}{\sqrt{2}\pi ND^2} \quad (3.4)$$

for an elastic sphere model, where N is no.atoms/cm³ and D is the atomic diameter. Taking approximate values of D for cadmium and magnesium from values for similar weight atoms given in McDaniel⁽²⁶⁾ of 3×10^{-8} cm for magnesium and 5×10^{-8} cm for cadmium, Eq. (3.4) yields $\lambda = 0.18$ cm for magnesium and 0.063 cm for cadmium. This represents a time between collisions of $T = \lambda/\bar{v}$ equal 5.7 microsec for magnesium and 4.3 micro-seconds for cadmium. This is over an order of magnitude greater than the lifetimes considered in this work and so can be neglected.

The usual procedure was as follows. First metal chips were prepared and cleaned with acetone. The system was suitably cleaned. The cathode was painted with a well mixed solution of cathode coating material, and placed on the system. The chips were loaded into the sample cup. Before the cathode was put in position the boron nitride was inserted and fired as described earlier. The envelope was then sealed on and the system outgassed several hours. The cathode is then activated as described by Holzberlein⁽¹⁾, by slowly raising the cathode temperature while pumping and applying an excitation pulse to the cathode. This process required about an hour. One must make certain the metal cup is down far enough to prevent metal from vaporizing until

desired. Once activated, the electronics and optics of the system were adjusted so they were properly functioning with a substitute gas such as helium. Once everything was working properly the gas was pumped out and the cup raised slowly toward the hot cathode. One must be cautious at this point. The liquid nitrogen trap should be in place below the invertron. The cup had to be raised ever so slowly because the metal chips tend to outgas vigorously, and a close watch had to be kept upon the pressure. Once the chips are hot enough they complete outgassing and the observed pressure quickly falls to minimal. At this point one watches the excitation pulse monitor scope while raising the sample cup slowly. Once the metal vaporizes the curve immediately loads down. The cup should then be withdrawn to the minimum intensity practical for the transition being studied. The sample rod provides a very sensitive control on the vapor pressure, and must be raised slightly ever so often to compensate for the decrease of metal in the cup. For both magnesium and cadmium it was not necessary to melt the chips as the sublimation vapor pressure was more than enough. We did on occasion melt cadmium however, to obtain a temperature versus cup position reference. The cadmium vapor pressure passes a discontinuity here; it increases until melting, whereupon it shows a fairly sizeable decrease, as monitored by the intensity of a given transition. Now that we have discussed the invertron and associated electronics we shall consider the data acquisition equipment.

CHAPTER VI

DATA ACQUISITION TECHNIQUE

The various means of acquiring data have been discussed previously by Johnson⁽²⁾ and Copeland⁽²⁷⁾, so we will outline the method here but not present detailed circuitry.

Figure 15 is a block diagram of the entire system. The data acquisition system consists of an Ortec preamp and photomultiplier base, Ortec NIM bin, discriminator, and Time-to-Pulse Height Converter, Nuclear Data 256 channel Model 1100 analyzer, and Canberra rate meter, with Teletype readout and paper tape punch.

The system works as follows. An excitation pulse is produced by the delay line as described earlier. A small part of this pulse is differentiated to be used as a trigger. When the pulse cuts off, the differentiator produces a negative spike which activated the time-to-pulse height converter (TPHC). The photomultiplier, preamp, and discriminator circuits are designed to produce a similar negative pulse upon detecting photons from the invertron. The TPHC is turned on by the differentiated trigger and stopped by the first photoelectron pulse from the photomultiplier. The TPHC converts this time to a voltage level and sends it to the pulse height analyzer, where it is stored. The cycle is then repeated. In this way a statistical record of the

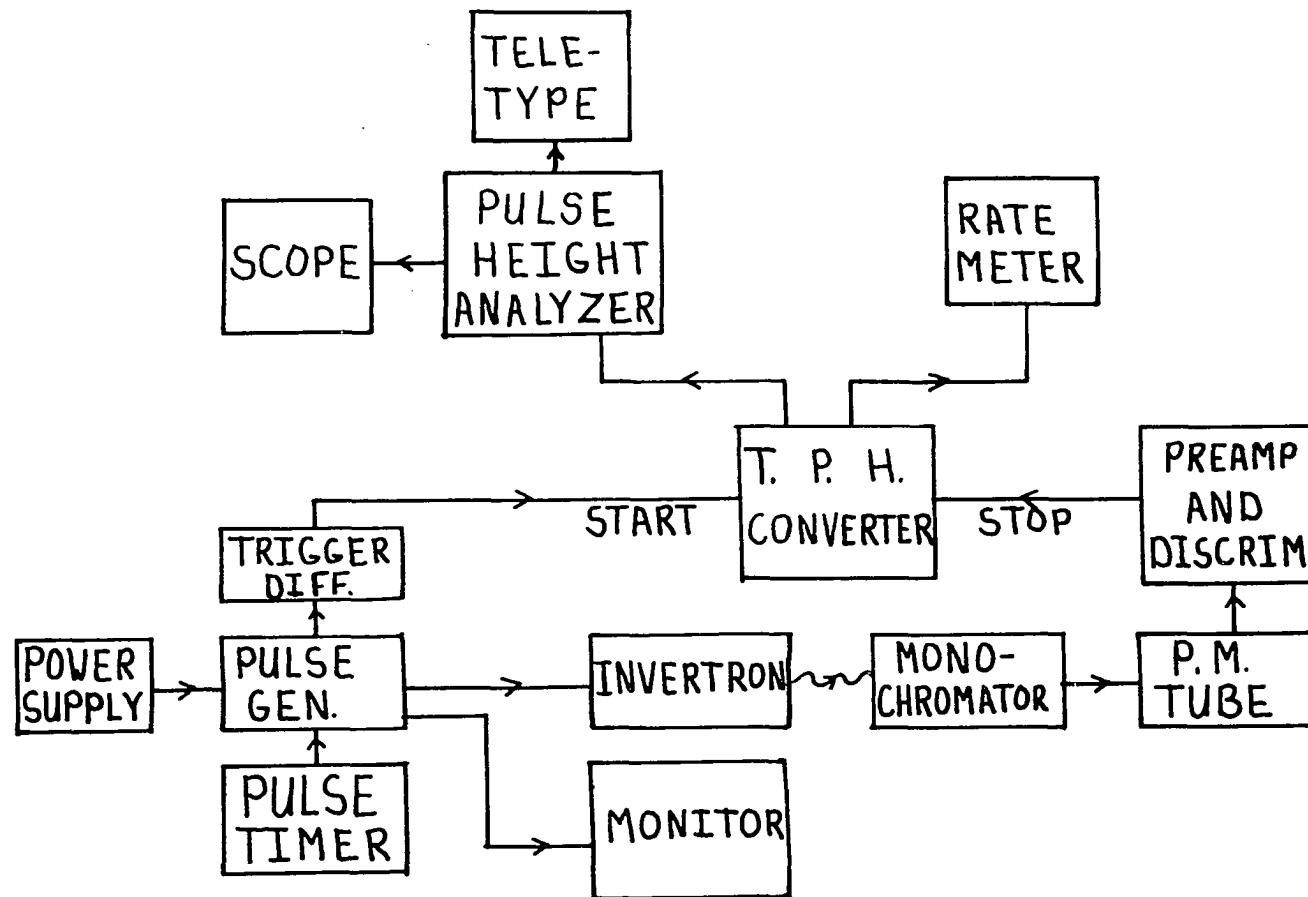


Figure 15. Block Diagram of Lifetime System.

intensity decay is acquired. If no photon is detected within a predetermined length of time the TPHC resets without registering any count on the pulse height analyzer. A signal is sent to a ratemeter simultaneously with the one to the pulse height analyzer. By knowing the pulse repetition rate (the maximum possible counting rate) and the actual count rate recorded by the rate meter, one can determine the per cent of maximum count rate. This quantity must be kept to less than ten per cent in order to avoid statistical distortion of the decay curve due to inclusion of multiple photon counts being counted simultaneously as only one count. This means limiting the overall light intensity, controlled either by the excitation pulse voltage, the vapor pressure, or the monochromator slit width. In actual practice we generally kept the per cent count rate to less than five per cent to be safe.

It was generally found that about eight to ten thousand counts in the initial channels of the analyzer were optimum for getting accurate statistics, though of course this also depends on the case one is actually dealing with. A typical acquisition time per measurement was from twenty to forty-five minutes, depending on the intensity. Once the curve was acquired it was displayed upon a scope for examination and read out on a Teletype and punched paper tape for later analysis. Figure 16 shows a typical pair of curves. The first is a magnesium transition, λ 4058, which is $8^1D \rightarrow 3^1P$; and the second is magnesium λ 5528, $4^1D \rightarrow 3^1P$.

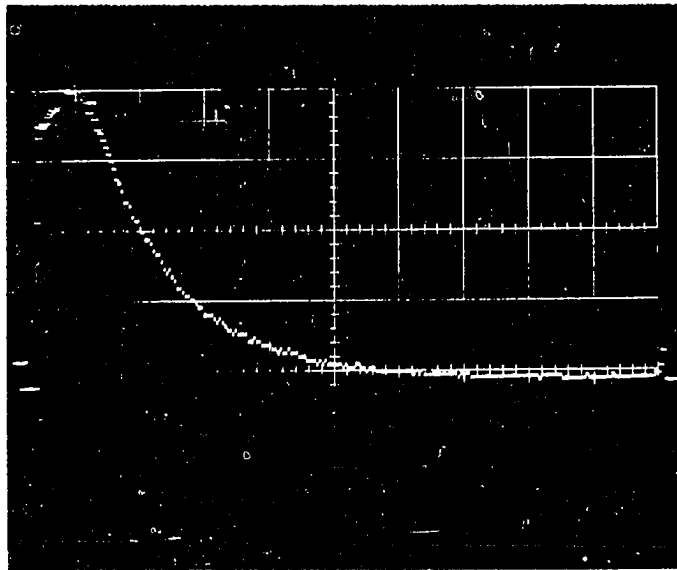
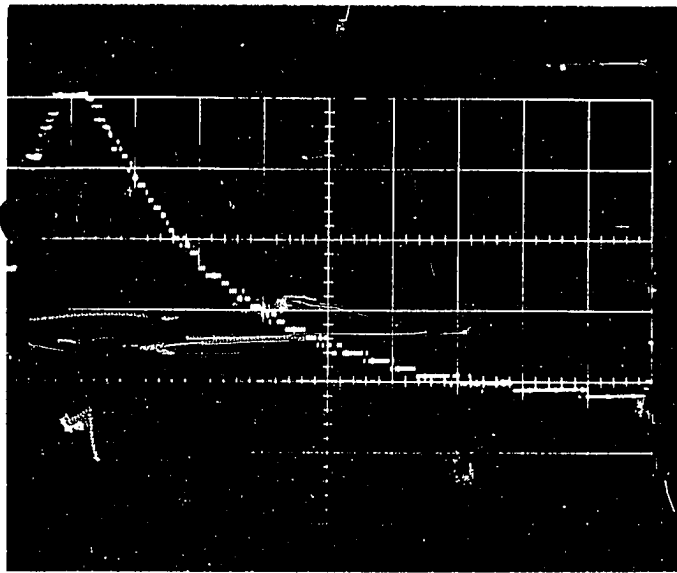


Figure 16. Typical Decay Curves for Mg, λ 4058 8^1D and λ 5528 4^1D .

The method of time calibration should be mentioned briefly. It consists merely of inserting the differentiated trigger pulse simultaneously into the start of the TPHC and one end of a length of RG58 50 ohm coaxial cable. The other end of the cable is connected to the TPHC stop, so one obtains in the analyzer many counts in the one channel which corresponds to the time delay of the length of cable. By doing this with several lengths of cable each of whose time delay length is accurately known and applying a least squares fit to the points, one obtains an excellent time calibration. The lengths of cable were measured by inserting a sine wave signal simultaneously into one channel of a scope and one end of the cable being measured. The other end of the cable was hooked to the other input of the scope, and by adjusting the signals so they were the same amplitude and adding them, nulls were obtained as one scanned through frequency. The reciprocal of the time delay of the cable is equal to the difference between any two consecutive frequency nodes as shown below. Upon adjusting both primary and delayed phase shifted signals to the same amplitude and adding one has:

$$y = K \sin \omega t + K \sin (\omega t + \theta_d) , \quad (3.5)$$

where ω is the frequency and θ_d is the time delay phase shift.

$\theta_d = \omega \tau_d$ where τ_d is the time delay of the cable. Using the identity $\sin x + \sin y = 2 \sin \frac{1}{2}(x+y) \cos \frac{1}{2}(x-y)$ Eq. (3.5) becomes:

$$y = 2K \sin(\omega t + \theta_d/2) \cos \theta_d/2 . \quad (3.6)$$

A mode occurs when $\theta_d/2 = (2n-1)\pi/2$ $n = 1, 2, 3, \dots$. Thus two consecutive frequency nodes have a spacing of

$$\frac{\omega_2 - \omega_1}{2} \tau_d = \pi = \frac{\Delta\omega}{2} \tau_d \quad (3.7)$$

Now $\Delta\omega = 2\pi\Delta\nu$, so:

$$\Delta\nu = 1/\tau_d \quad (3.8)$$

Equation (3.8) was applied to each cable several times and averaged as frequencies from less than 1 MHz to almost 100 MHz were applied. The frequency at each node was accurately measured with a Hewlett-Packard 524D/515A counter, good to one part in 10^6 . Some cables were measured this way by the author and Johnson, and later re-measured, and new cables added, by Copeland and Bradshaw. The lengths of all cables are listed by Copeland⁽²⁷⁾.

The timing calibration obtained in this way should be accurate to better than one per cent. Linearity of the TPHC on all ranges except 50 nsec was checked and appeared also to be better than one per cent.

Before leaving the subject of data acquisition it should be mentioned that there are other simpler techniques of data acquisition, but they are not nearly so precise as the one described above, and do not lend themselves to computer analysis of the data. These methods are (1) simple photograph of the direct photomultiplier trace immediately after excitation cutoff, and (2) photograph of statistically averaged photomultiplier trace on 1S1 sampling scope immediately after excitation cutoff. These photos can then be placed upon a calibrated

exponential function synthesizer for analysis of decay parameters. A serious difficulty is the dependence of the results upon the scope timing calibration. Also the signals are often just too noisy to be analyzed, especially for low intensity transitions. These two techniques are discussed in detail by Holzberlein⁽¹⁾ and Johnson⁽²⁾. They were used by the author in early experimentation while system and techniques were being developed, but yielded no useful data.

CHAPTER VII

SPECTROGRAPHIC STUDIES

It was always deemed necessary to make spectrograms of the light from the invertron in order to study just what transitions were present, their intensities and possible impurities present. In fact a very important discovery was made in this way, quite by accident. Upon investigating some impurity lines appearing in a magnesium spectrogram, it was discovered these were barium lines. Since the cathode coating material contains barium, and both barium and magnesium are second period metal atoms with consequent similar chemistries, it is surmised that the magnesium atoms hitting the hot cathode sometimes displace barium atoms. Many of them must pick up excitation energy in the process, because more barium ion lines are seen in respect to neutrals than for magnesium, the metal being introduced directly.

Several methods of taking spectra have been devised and used in the course of the experiment. The monochromators used either had interval drives, or small motors with suitable switches and gears were assembled and mounted on them to provide constant, controllable rate scan of wavelength. The simplest method was then to simply turn on the system, then set the monochromator slits fairly narrow for good resolution and begin scanning. The photomultiplier output was then

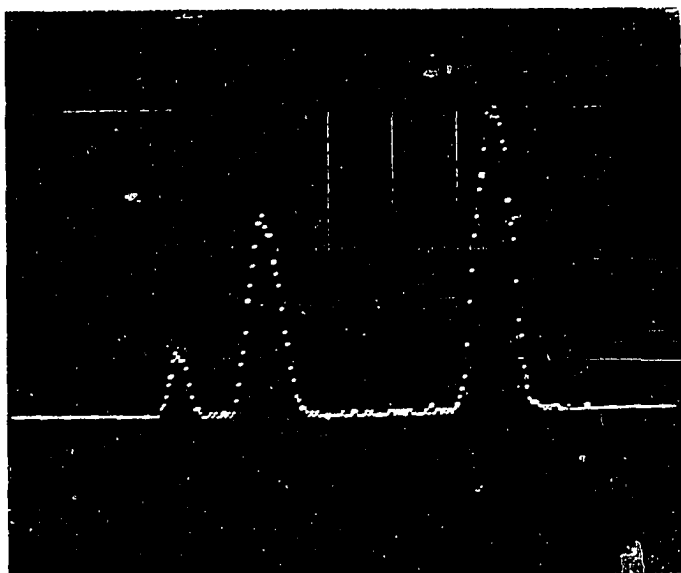
applied to a moving chart recorder, which resulted in a fairly noisy but useable spectrum. The next method devised is described in detail by Copeland⁽²⁷⁾. This system was designed to be used with the photon counting equipment, yet take advantage of a 1024 channel memory Nuclear Data Enhancetron. The system was turned on and monochromator set scanning. The photon counting signal was taken from the rate meter and run to the Enhancetron, which was in a multiscaling mode. (This is a mode of operation in which one channel accepts all counts for a given time, then the next channel, and so on). In this way a closely spaced histogram of the spectrum is built up; the more intense the line, of course, the more counts placed in each channel of the transition, giving a good indication of relative intensities. The Enhancetron was then read out onto a chart recorder for permanent recording.

The method we most commonly use is simply to set the analyzer in the multiscaling mode rather than pulse-height analysis mode. This is essentially the same acquisition technique as that just described, except here we are limited to 256 channels and a maximum acquisition dwell time of 0.8 sec/channel. This is sufficient for most cases, however. The main advantage is that now the output is punched onto paper tape, and a time share computer plotting routine has been written which takes the data and plots the spectrogram out on teletype, eliminating the need to use a chart recorder.

This technique can provide relatively good quality spectrograms. Also by selecting the range accepted by the TPHC, one has time resolved spectra, e.g., if the maximum range is set to 400 nsec, all

light emitted more than 400 nsec after excitation cutoff will be excluded from the spectrogram. Figure 17 shows a couple of examples of fairly highly resolved spectra. These are magnesium triplets. The first is λ 3829, 3832, 3838 $3^3D \rightarrow 3^3P_{0,1,2}$. The second is λ 5167, 5172, 5183 $4^3S \rightarrow 3^3P_{0,1,2}$. Let us now describe the theory and analysis of results gathered in the experiment.

(a)



(b)

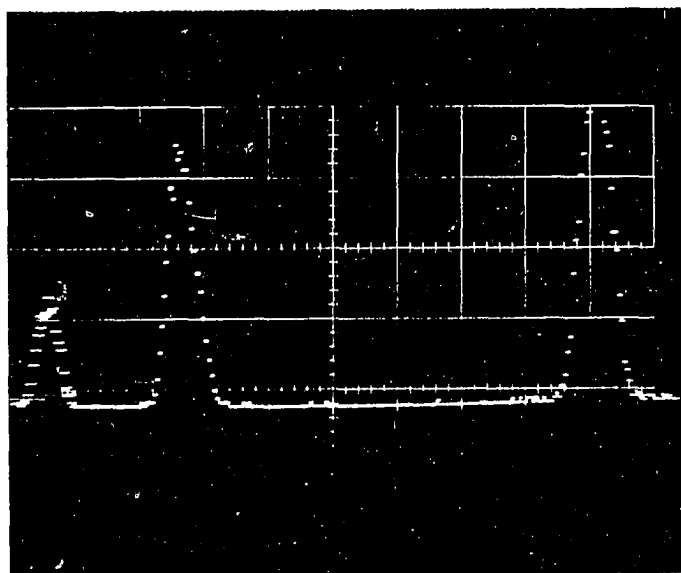


Figure 17. Spectra of Mg Triplets: $3^3D \rightarrow 3^3P$ and $4^3S \rightarrow 3^3P$.
 a) 3829, 3832, 3838 Å; b) 5167, 5172, 5183 Å

CHAPTER VIII

DATA ANALYSIS

We have already mentioned that in the early stages some data was taken using direct view methods and analysis carried out with a comparison curve generator. This data was not of a quality to be considered useful, hence these methods of analysis will not be discussed here. For a full treatment see Johnson⁽²⁾.

Let us discuss now just what sort of intensity curve we expect to see. In Part II, Chapter III, we had

$$I_{ki} = \frac{1}{4\pi} A_{ki} N_k h\nu_{ik} , \quad (2.15)$$

so essentially if we know A_{ki} , which we get from the lifetime measurement, and $h\nu_{ik}$ from the wavelength, $I_{ki}(t)$ is essentially determined by $N_k(t)$. For a single one level transition we found this to be given by:

$$N_k(t) = N_k^0 e^{-t/\tau_k} . \quad (2.7)$$

In real life things are much more complicated than this. We have already mentioned that absorption, stimulated emission, and collisional and wall collisional depopulation can all affect the intensity curve; however, the experiment is designed to keep these factors small enough to neglect. The one big factor we cannot ignore is the effect of

repopulation of a state from transitions into this state from other higher energy states, referred to as cascade. Also, whenever the excitation source is on before cutoff, we have production into the state given by the electron collision excitation cross section and beam current: $N_g Q_{ji}/eA$ where Q_j is the cross section for excitation from ground to the j^{th} excited state, i is the beam current, A the beam area, and e the electronic charge. The number of atoms in ground state in this experiment is so great compared to those excited that we ignore collision excitation contributions from excited states to higher states. Also we can therefore easily derive N_g , the number of atoms in ground state, from the pressure. Many of these terms will cancel however.

If we then consider two levels, j above i , the general population rate equations for all transitions into and out of these levels from states above and below are:

$$\dot{N}_j = N_g Q_{ji} \frac{i}{eA} + \sum_{\ell=j+1}^L N_{\ell} A_{\ell j} - N_j \sum_{\ell=1}^i A_{j\ell} , \quad (3.9)$$

$$\dot{N}_i = N_g Q_{ji} \frac{i}{eA} + \sum_{\ell=j}^L N_{\ell} A_{\ell i} - N_i \sum_{\ell=1}^{i-1} A_{i\ell} . \quad (3.10)$$

Here L is the uppermost limit excited, in our case an infinite limit since the excitation electron energies exceed the ionization potential. The first term describes electron beam excitation, the second is population from cascades, and the third is spontaneous emission from the state. After cutoff we eliminate the first term and the equations have solutions of the form:

$$N_j = \sum_{\ell=j+1}^L C_{\ell} e^{-A_{\ell} t} + C_j e^{-A_j t} \quad (3.11)$$

and

$$N_i = \sum_{\ell=j}^L D_{\ell} e^{-A_{\ell} t} + D_i e^{-A_i t}, \quad (3.12)$$

where

$$A_{\ell} = \sum_{m=1}^{\ell-1} A_{\ell m} \quad A_i = \sum_{\ell=1}^{i-1} A_{i\ell} \quad A_j = \sum_{\ell=1}^i A_{j\ell}.$$

In other words if we have n cascade contributions, we see an $n+1$ exponential sum decay curve. These equations of course are very difficult to handle. Of much more interest is the case where we have only, say, one primary cascade contribution state j , we are measuring state i , and there are several lower states. We can now solve for the amplitude coefficients. The rate equations are:

$$\begin{aligned} \dot{N}_j &= -N_j A_j \\ \dot{N}_i &= N_j A_{ji} - N_i A_i \end{aligned} \quad (3.13)$$

where

$$A_j = \sum_{\ell=1}^i A_{j\ell} \quad A_i = \sum_{\ell=1}^{i-1} A_{i\ell}.$$

Equations (3.13) have solutions:

$$\begin{aligned} N_j &= N_j^0 e^{-A_j t} \\ N_i &= \frac{A_{ji} N_j^0}{A_i - A_j} e^{-A_j t} + \left(N_i^0 - \frac{A_{ji} N_j^0}{A_i - A_j} \right) e^{-A_i t} \end{aligned} \quad (3.14)$$

where N_i^0 and N_j^0 are the initial populations of these states at the time of excitation cutoff.

Now one can evaluate the coefficients in terms of initial excitation parameters. Generally in the experiment one has an excitation pulse applied for longer than the lifetimes involved so that the population rates in the atoms come to equilibrium. In this stage the rates of change $\dot{N}_j = \dot{N}_i = 0$. So by looking at the rate equations with excitation on and setting the $\dot{N}$ terms to zero, we can solve for N_i^0 and N_j^0 in terms of excitation parameters. These will of course be the initial values of N_i^0 and N_j^0 at time of cutoff. The equilibrium rate equations are:

$$\begin{aligned} N_g \frac{i}{eA} Q_j - N_j^0 A_{ji} &= 0 \\ N_g \frac{i}{eA} Q_i + N_j^0 A_{ji} - N_i^0 A_{ij} &= 0 \end{aligned} \quad (3.15)$$

This gives:

$$N_j^0 = \frac{N_g \frac{i}{eA} Q_j}{A_{ji}} \quad \text{and} \quad N_i^0 = \frac{N_g \frac{i}{eA} (Q_i A_{ji} + Q_j A_{ji})}{A_{ij} A_{ji}} .$$

So finally what intensity do we see as a function of time after cut-off? Looking at some given transition out of i to any lower state h and using $I_{ih} = h\nu_{ih} N_i A_{ih}$ we get from Eq. (3.14):

$$\begin{aligned} I_{ih} = N_g \frac{i}{eA} h\nu_{ih} A_{ih} \frac{A_{ji} Q_j}{(A_i - A_j) A_j} e^{-A_j t} + N_g \frac{i}{eA} h\nu_{ih} A_{ih} \left(\frac{Q_i A_{ji} + Q_j A_{ji}}{A_j A_i} \right. \\ \left. - \frac{Q_j A_{ji}}{(A_i - A_j) A_j} \right) e^{-A_i t} \end{aligned} \quad (3.16)$$

or

$$I_{ih} = \alpha e^{-t/\tau_j} + \beta e^{-t/\tau_k} .$$

As Copeland⁽²⁷⁾ has discussed, it is interesting to look at the ratio of amplitude coefficients β/α . If one does this the beam parameters cancel and one obtains:

$$\beta/\alpha + 1 = \frac{(A_j Q_i + Q_j A_{ji})(A_i - A_j)}{A_i Q_j A_{ji}} = \frac{(1/\tau_j Q_i + Q_j A_{ji})(1/\tau_i - 1/\tau_j)}{1/\tau_i Q_j A_{ji}} \quad (3.17)$$

This could be of interest because experimentally one measures τ_i , τ_j , α , and β , so if any two of A_{ji} , Q_i , or Q_j are known the third is determined.

Equation (3.16) predicts the form of the two exponential decay which will be observed. There are of course many interesting different adjustments of coefficients of amplitude possible. We will consider a few of them here.

For quick ease in comparison let us postulate Q_i equal to Q_j and factor it out. Then the two factors which determine the relative amplitudes of the two coefficients are

$$\frac{A_{ji}}{(A_i - A_j)A_j} = \alpha' \text{ for the cascade and } \frac{A_j + A_{ji}}{A_i A_j} - \frac{A_{ji}}{(A_i - A_j)A_j} = \beta'$$

for the primary lifetime. First consider the often seen case where the cascade lifetime is much greater than that of the primary. Let us say that the primary has $A_i = 10^8/\text{sec}$, the cascade $10^7/\text{sec}$, and the branching ratio for the cascade $A_{ji}/A_j = 1:10$ so $A_{ji} = 10^6$. Then the cascade coefficient $\alpha' = 10^{-9}$ and primary $\beta' = 10^{-8}$. Thus the cascade decay having a lifetime of 100 nsec will have an amplitude

only one tenth that of the primary. This is an often encountered case in the experiment. Another case sometimes encountered is that of two, say, fairly highly excited states which are quite close together. The v^3 factor of Eq. (2.5), being small, causes the transition probability of the upper state cascading to the lower one to be small, yet because there are several lower lying states, both may have fairly short lifetimes. If we have a cascade lifetime of $1/A_j = 30$ nsec, primary lifetime of $1/A_i = 10$ nsec, and transition probability of cascade A_{ji} only equal 10^7 , $\alpha'=\beta'=5 \times 10^{-9}$. So for this case the amplitude of the cascade exponential appears as large as that of the primary lifetime. Since their lifetimes do not differ by too much, this type of curve can be difficult to analyze. If one pushes a little further in this direction a curve can even be obtained where the slower lived cascade has a greater amplitude coefficient than the faster primary lifetime, a case which has been observed experimentally.

As it turns out experimentally, there is usually a primary cascade source plus a composite of long lived background cascades and noise which appear to contribute a background constant. Thus the type of curve usually encountered experimentally is:

$$I = \alpha e^{-t/\tau_1} + \beta e^{-t/\tau_2} + \gamma$$

where γ is the background constant. There have been a few cases where three exponentials from a two-cascade fed transition were seen:

$$I = \alpha e^{-t/\tau_1} + \beta e^{-t/\tau_2} + \gamma e^{-t/\tau_3} + \delta$$

but these are rare. Even in these cases whether a two exponential or three exponential analysis was carried out made little difference in the resulting primary lifetime.

Figure 18 shows an experimental plot of $\ln I$ versus time (channel number) for $3^3D \rightarrow 3^3P$ transition in magnesium. This is a large amplitude primary decay curve with a small background cascade. This type of curve gives very precise results. Figure 19 is a different case, that of $4^3S \rightarrow 3^3P$ in magnesium. This is a case where the cascade amplitude is larger than that of the primary lifetime, making analysis quite difficult. This curve can be fit to three exponentials.

How does one proceed with the analysis? Originally much of the data was analyzed by a graphical technique. By averaging about five points at a time and fitting a straight line to the end of the cascade part of the data curve at the far right one could obtain a fair estimate of the cascade lifetime. First a background constant had to be estimated and subtracted off the data. This was usually done by measuring background noise with the monochromator slits covered. By fitting a straight line to the "tail" of the cascade and measuring the slope, one can estimate its lifetime. This line is produced all the way to the left. Now by subtracting this line's value off from the remaining fast exponential decay, a second straight line of steeper slope is obtained. The slope of this line yields the primary decay lifetime. This method is fairly crude, and is almost impossible to carry out to any degree of accuracy in the case of equal amplitude primary and cascade, or of three exponential curves. Also it is very difficult to

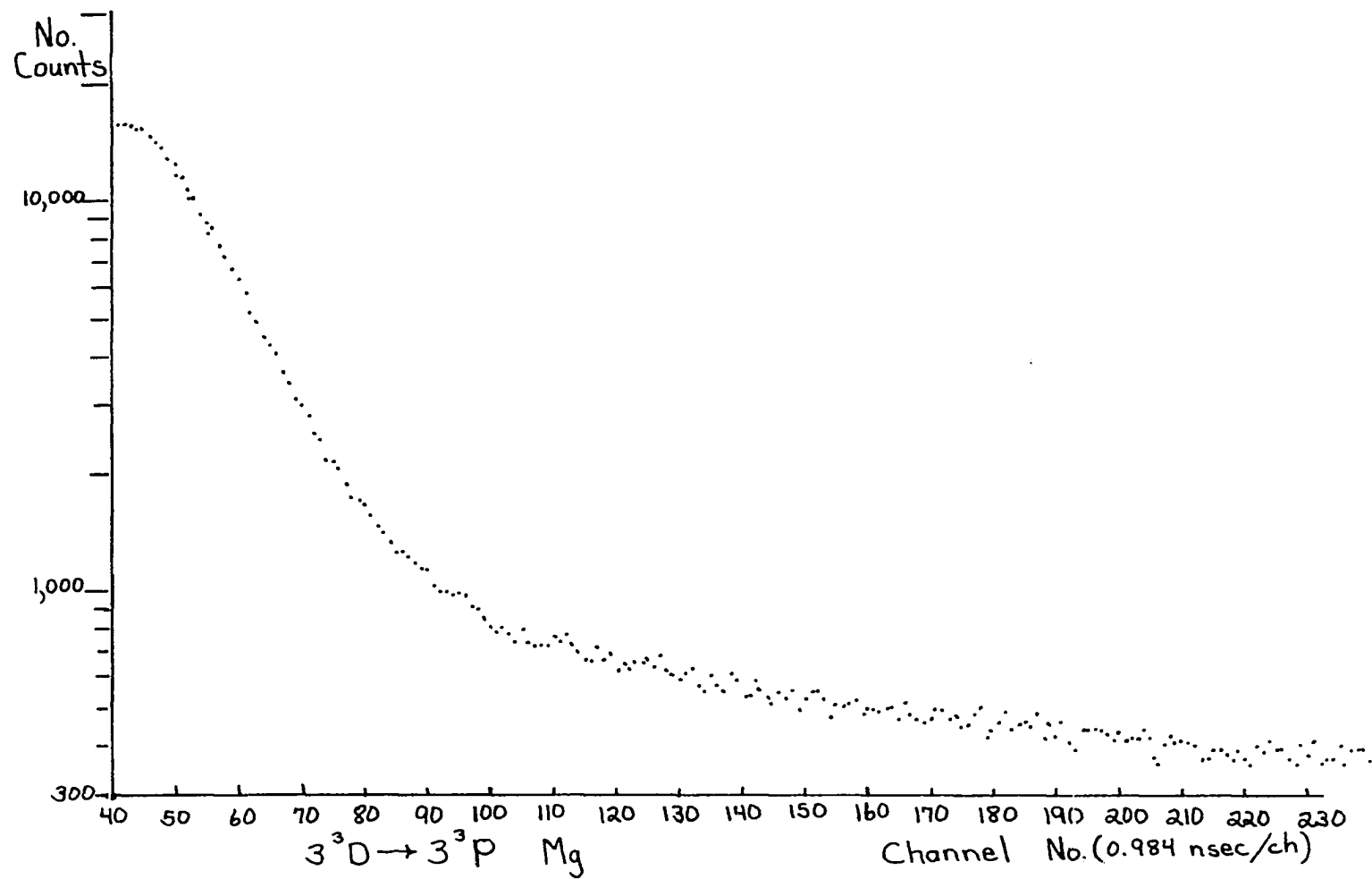


Figure 18. Two Exponential Decay Curve.

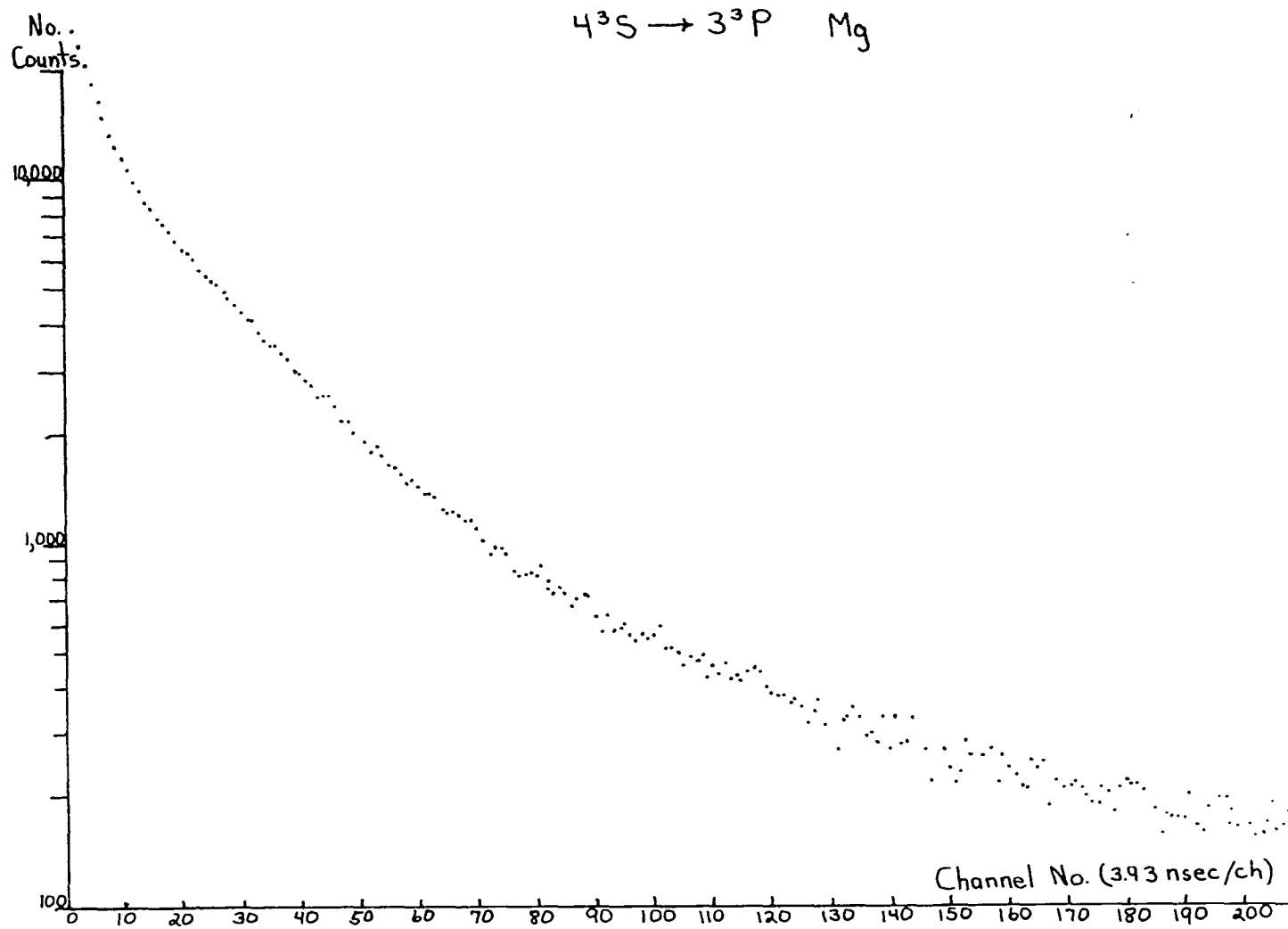


Figure 19. Three Exponential Decay Curve.

accurately estimate the background constant, and finally, very time consuming. For these reasons, a scheme of computerized analysis was developed. Mr. Richard Thompson is primarily responsible for the production and debugging of these programs, and will describe them in detail in his dissertation. We will describe them here only briefly. All data reported in this work has been analyzed in this way.

The first program to be run on the data is termed FPLOTT. This simply plots a graph of $\ln(\text{intensity})$ vs. channel, which is necessary in order to carry out the detailed analysis. The program is also adaptable to plotting spectra in conjunction with the method mentioned earlier. One then gets a plot of $\ln(\text{intensity})$ vs. wavelength.

The second program, called RICH, is a linear regression fitting routine, and is used for preliminary results only. It essentially carries out analytically the graphical procedure described above, though in a more sophisticated manner. The straight lines are analytically fit to the data points via a least squares method, and a statistical linearity of fit parameter is monitored. The program varies the value of background constant until the linearity parameter is maximized, having also determined the number of points in the tail to fit by checking the linearity. After this is done it and the constant are subtracted off the primary exponential, which is then fit. Now the time delays and channels filled by the timing calibration procedure have also been input, and the program determines the timing calibration nsec/channel. It then reads out values of lifetimes and amplitude coefficients for the primary decay curve, cascade, and constant. A plot routine similar to one which

will be described below is also available, but not always needed. This program yields results which are more accurate than those obtained by hand, but still somewhat crude in many cases, as tests have shown. Hence a very sophisticated routine is used for the final calculation.

The main data analysis routine, termed LASL, is a nonlinear numerical iterative analysis, the basic algorithm of which is given by Marquardt⁽²⁸⁾. One inputs initial guesses of the lifetime, amplitude, and constant factors obtained from RICH, together with appropriate weighting functions if desired. The program outputs final results of the lifetimes, amplitudes, and constant, together with their standard deviations and other statistical diagnostic factors. One then obtains a multi-line plot of the results. A plot of the raw data minus the calculated cascade minus the calculated constant shows the resulting primary decay. The data minus the primary decay minus the constant indicates the cascade decay. The data minus all three, the primary and cascade and constant, linearly scaled, gives a good indication of validity of the constant, since this should be zero. Each of these lines should be straight if the calculated fit were proper and the analysis was started and ended with good data. These curves are very sensitive to the properness of fit, and if there is a small amount of a third exponential present on a curve which was analyzed as two exponential, a marked deviation in linearity of these curves will be evident. This is also true in case one starts data analysis too soon, before excitation cutoff is complete. Many tests have been run on this program wherein one generates tests cases of data of known amplitude and lifetimes, one, two, or three exponential plus background constant, and

superimposes random noise on the curve in order to generate test data identical to the type actually obtained in the experiment. The analysis program can be run on the test data and its results compared with the known values of the decay parameters. In every case the proper answers are obtained. In very difficult cases where one tries to fit too many exponentials to the data the program simply will not converge to a solution. It does not give erroneous results. Figures 20 and 21 are plots after analysis of the data in Figs. 18 and 19. This concludes the discussion of the experimental method.

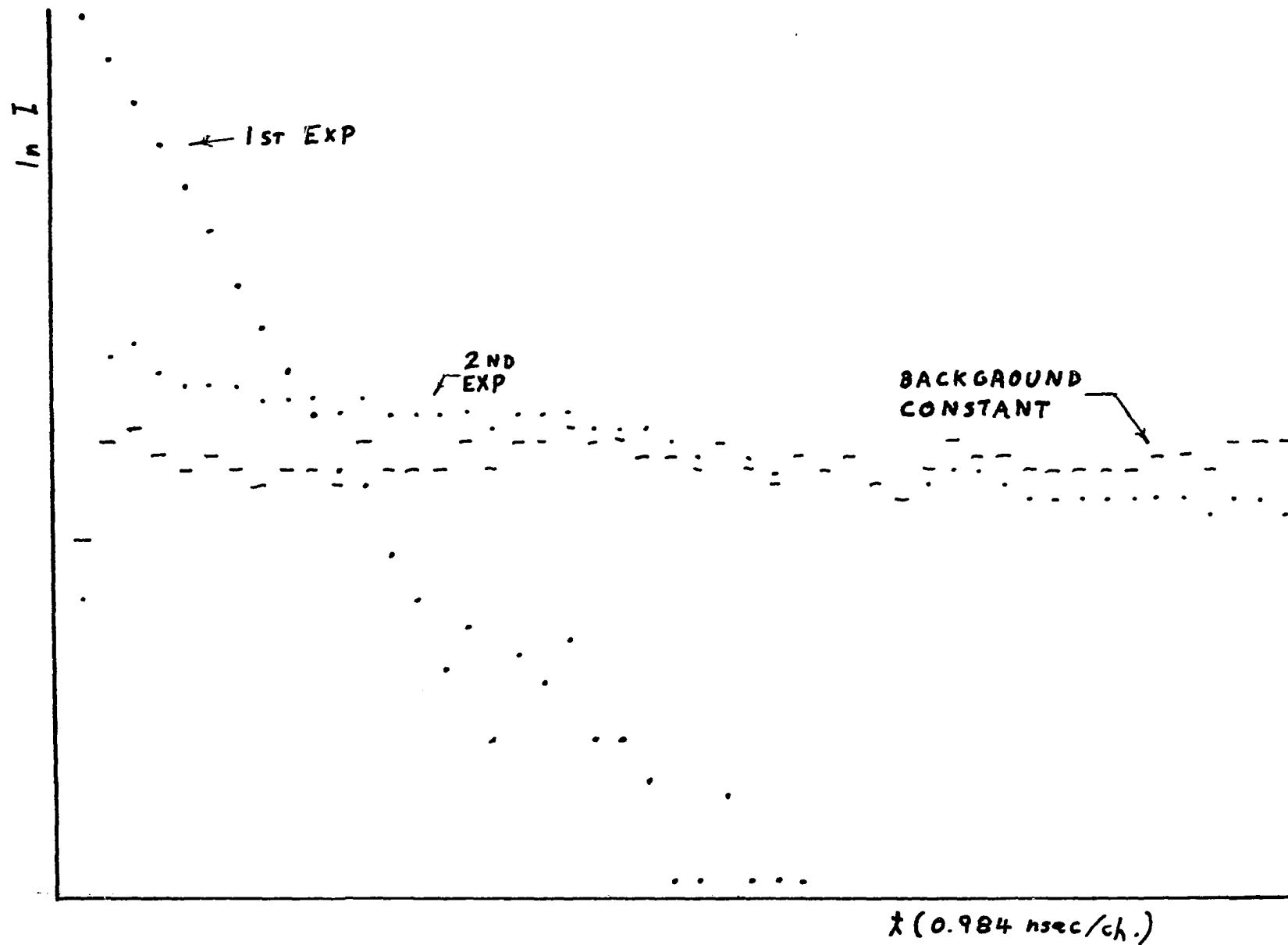


Figure 20. Analyzed Output Plot of $3^3\text{D} \rightarrow 3^3\text{P}$ Mg.

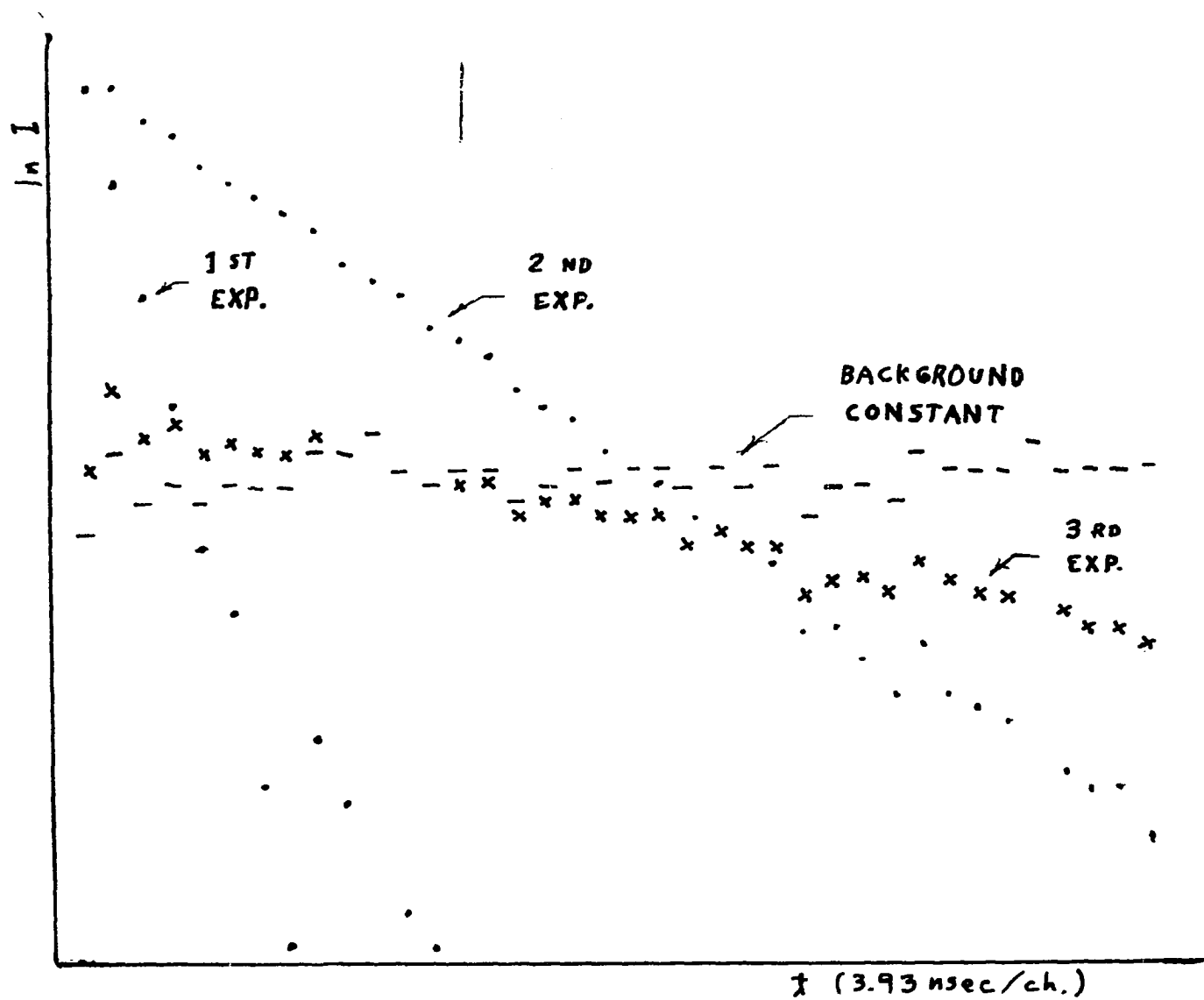


Figure 21. Analyzed Output Plot of $4^3S \rightarrow 3^3P$ Mg.

PART IV

EXPERIMENTAL RESULTS

CHAPTER I

MAGNESIUM

Previous Work

We shall now turn to a discussion of the results obtained. For reference we have included energy level diagrams of all elements and their ions which were studied in Appendix B.

There have been very few actual measurements of lifetimes or oscillator strengths of the excited states of magnesium. Most of the experimental work has consisted of phase shift measurements of the resonance transitions. For this reason, and from the importance of these results to astrophysicists for abundance studies, it was deemed desirable to make direct lifetime measurements of as many as possible of the excited states of the various spectral series in magnesium.

The principal earlier experimental work in magnesium consists of measurements of the resonance lines by Lurio⁽²⁹⁾ and Smith and Gallagher⁽³⁰⁾, utilizing Hanle effect lifetime measurements; and measurement of relative oscillator strengths of a number of excited states by Kersten and Ornstein⁽³¹⁾ using emission intensity measurements and

Penkin and Shabanova⁽³²⁾ using the "hook" or anomalous dispersion method. There is also an atomic beam measurement by Karstensen and Schramm⁽³³⁾ of the 4^1D term lifetime. Our own technique is not as well suited to measure resonance transitions because of imprisonment, but by virtue of the high light intensity available, it is ideal for measuring all the other excited transitions. The work Kersten and Ornstein⁽³¹⁾ and Penkin and Shabanova⁽³²⁾ yields only relative results, and must somehow be normalized to an absolute scale. For this reason it is especially important to have absolute measurements like the present ones. The transition probability tables of Corliss and Bozman⁽³⁴⁾, derived from spectral line intensity studies, suffer from lack of local thermodynamic equilibrium and arc demixing problems, and are quite unsuitable for accurate absolute oscillator strength and transition probability measurements.

On the theoretical side, much detailed work has been done for magnesium. Self consistent field calculations have been carried out by Weiss⁽³⁵⁾, Trefftz⁽³⁶⁾, and Zare⁽³⁷⁾, and include various amounts of configuration mixing. Warner^(38,39) has done a calculation with configuration mixing using a scaled Thomas Fermi method and has tabulated the absolute oscillator strengths obtained for 627 lines of magnesium. Lambert and Warner⁽¹⁶⁾ list some oscillator strengths derived from solar abundance studies, as noted in Part II.

Probably one of the more complete references for transition probabilities with which we can compare our values is that of Wiese, Smith, and Miles⁽⁵⁾ of the National Bureau of Standards. They have

taken averages of the results of Lurio⁽²⁹⁾, Smith and Gallagher⁽³⁰⁾, Kersten and Ornstein⁽³¹⁾, Penkin and Shabanova⁽³²⁾, Weiss⁽³⁵⁾, Trefftz⁽³⁶⁾, and Zare.⁽³⁷⁾

Results

The results of our measurements are shown in Tables 1 and 2, where we have given our results plus or minus the standard deviation of the measurements of each line. Using the relations

$$1/\tau_k = \sum_i A_{ki} \quad (2.8)$$

and

$$A_{ki} = \frac{6.67 \times 10^{15}}{\lambda^2} \frac{g_i}{g_k} f_{ik} \quad (2.3)$$

we have for sake of comparison computed lifetimes of states resulting from the transition probabilities and oscillator strengths given by Wiese *et al.*⁽⁵⁾, Corliss and Bozman⁽³⁴⁾, Warner^(38,39), and Lambert and Warner⁽¹⁶⁾. An asterisk denotes that the theory of Warner⁽³⁸⁾ was used to add in estimates of probabilities for transition to higher excited states than that of the primary transition. We estimate our experimental accuracy to be of the order of our standard deviations. The estimated uncertainties of Wiese *et al.*⁽⁵⁾ are listed as percentages in parentheses after the value.

In Table 3 we present our data converted to transition probabilities using the data of Warner⁽³⁸⁾ as mentioned above where denoted by an asterisk and the abundance data of Lambert and Warner⁽¹⁶⁾ where denoted by + to subtract higher transition probability. We have used these results to plot $(n^*)^3 f$ vs. n^* in Fig. 22.

Table 1. Lifetimes Measured in Mg Triplets Compared with Lifetimes Calculated from the Work of Others.

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)	τ (nsec) (6)	τ (nsec) (7)	τ (nsec) (8)
5178	$4^3S \rightarrow 3^3P$	14.8 ± 0.7	9.62 (10%)	2.7	19.0	12.8	-
3335	$5^3S \rightarrow 3^3P$	25.6 ± 2.1	(32) 26* (50%)	14.8	44.4	31.0	-
2940	$6^3S \rightarrow 3^3P$	52.1 ± 6.0	(63) 50* (50%)	76.9	86.5	63.9	-
3835	$3^3D \rightarrow 3^3P$	11.3 ± 0.8	5.96 (10%)	~4	6.13	-	-
3095	$4^3D \rightarrow 3^3P$	18.4 ± 0.7	(18) 15* (25%)	62.5	15.1	-	-

Note: Karstensen and Schramm⁽³³⁾ 4^1D lifetime = 59 nsec. * Indicates theory of Warner (38) was used to add in other transitions to obtain lifetime estimate. For triplet systems, the multiplet wavelength is listed. Columns (1) and (2) specify the wavelength and transition of interest; column (3) gives the measured results of this work; column (4) gives lifetimes calculated from Wiese *et al.* (5); column (5) gives lifetimes calculated from Corliss and Bozman (34); column (6), lifetimes from Warner (38); column (7), lifetimes from Warner (39); and column (8), lifetimes from Lambert and Warner (16). Values in parentheses in columns (4) and (8) have not been corrected for additional transitions.

Table 2. Lifetimes Measured in Mg Singlets Compared with Lifetimes Calculated from the Work of Others.

Wavelength (Å) (1)	Transition (2)	(nsec) (3)	(nsec) (4)	(nsec) (5)	(nsec) (6)	(nsec) (7)	(nsec) (8)
5711	5 ¹ S→3 ¹ P	163±8	-	-	73.3	83.8	230
4730	6 ¹ S→3 ¹ P	201±4	-	-	156.0	160.0	541
8806	3 ¹ D→3 ¹ P	57.0±3.6	71 (50%)	29.4	27.3	-	48
5528	4 ¹ D→3 ¹ P	54.9±1.4	(71)45*(>50%)	31.3	31.6	-	(69)48*
4703	5 ¹ D→3 ¹ P	44.3±2.4	(63)48*(>50%)	21.7	45.0	-	(41)34*
4352	6 ¹ D→3 ¹ P	50.3±2.2	(48)40*(>50%)	-	18.2	-	(57)53*
4167	7 ¹ D→3 ¹ P	73.1±2.7	-	-	80.4	-	(170)149*
4058	8 ¹ D→3 ¹ P	85.4±10.5	-	-	-	-	158
3987	9 ¹ D→3 ¹ P	99.4±9.4	-	-	-	-	-
3938	10 ¹ D→3 ¹ P	66±15	-	-	-	-	-
3904	11 ¹ D→3 ¹ P	37.1±3.4	-	-	-	-	-
3878	12 ¹ D→3 ¹ P	32.1±2.9	-	-	-	-	-

Note: Karstensen and Schramm⁽³³⁾ 4¹D lifetime = 59 nsec. * indicates theory of Warner (38)^o) was used to add in other transition to obtain lifetime estimate. For triplet systems, the multiplet wavelength is listed. Columns (1) and (2) specify the wavelength and transition of interest; column (3) gives the measured results of this work; column (4) gives lifetimes calculated from Wiese *et al.* ((5);); column (5) gives lifetimes calculated from Corliss and Bozman (34); column (6), lifetimes from Warner (38); column (7), lifetimes from Warner (39); and column (8), lifetimes from Lambert and Warner ((16)). Values in parentheses in columns (4) and (8) have not been corrected for additional transitions.

Table 3. Transition Probabilities Calculated from Lifetime Measurements in Mg Compared with Transition Probabilities of Wiese *et al.* (5)

Wavelength (Å) (1)	Transition (2)	A(x10 ⁸ /sec) (3)	A(x10 ⁸ /sec) (4)
5178	4 ³ S→3 ³ P	0.68	1.04
3335	5 ³ S→3 ³ P	0.31*	0.31
2940	6 ³ S→3 ³ P	0.14*	0.16
3835	3 ³ D→3 ³ P	0.89	1.68
3095	4 ³ D→3 ³ P	0.45*	0.56
5711	5 ¹ S→3 ¹ P	0.061	-
4730	6 ¹ S→3 ¹ P	0.032*	-
8806	3 ¹ D→3 ¹ P	0.18	0.14
5528	4 ¹ D→3 ¹ P	0.12*	0.14
4703	5 ¹ D→3 ¹ P	0.16*	0.16
4352	6 ¹ D→3 ¹ P	0.16*	0.21
4167	7 ¹ D→3 ¹ P	0.12*	-
4058	8 ¹ D→3 ¹ P	0.11 [†]	-
3987	9 ¹ D→3 ¹ P	0.099 [†]	-
3938	10 ¹ D→3 ¹ P	0.15	-
3904	11 ¹ D→3 ¹ P	0.27	-
3878	12 ¹ D→3 ¹ P	0.31	-

Note: Karstensen and Schramm⁽³³⁾ 4¹D lifetime = 59 nsec implies A(x10⁸/sec) = 0.10*. * indicates theory of Warner⁽³⁸⁾ was used to convert to transition probabilities. † indicates work of Lambert and Warner⁽¹⁶⁾ used to convert to transition probabilities. Columns (1) and (2) specify the wavelength and transition, column (3) gives the transition probability computed from measured lifetimes, and column (4) gives transition probabilities from Wiese *et al.* (5)

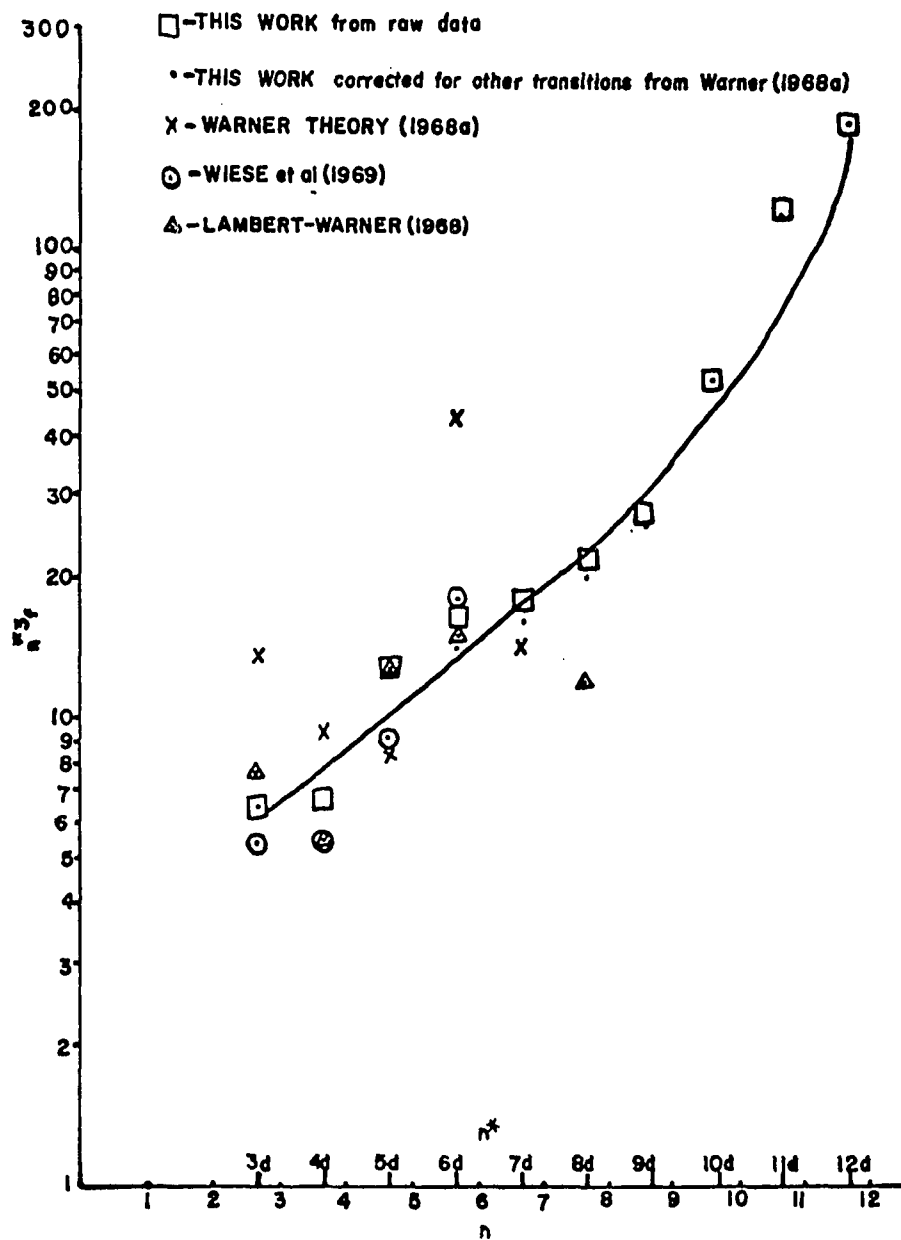


Figure 22. Anomalous Trend in 1D Series of Mg for $(n^*)^3f$ vs. n^* showing Results of Our Work and Others.

Table 4 gives lifetimes of cascade components observed going into given states, along with probable transition assignments. It should be emphasized these are not highly accurate figures, but rather estimates of the cascades made according to standard procedure by fitting a second exponential curve to the data.

Discussion of Results

a) 3S Transitions

The 4^3S transition appears to have a very heavy cascade component due to 3P states. The primary cascade seems to have a lifetime of 80 nsec, which is attributed to $4^3P \rightarrow 4^3S$. The amplitude of the cascade is greater than that of the observed lifetime, making analysis difficult and perhaps somewhat more uncertain than usual. The state appears to be somewhat slower than thought by Wiese *et al.*⁽⁵⁾, is less than that calculated by Warner⁽³⁸⁾, and almost agrees with the subsequent calculation of Warner⁽³⁹⁾. For the upper 5^3S and 6^3S states cascades were less, and agreement is better.

b) 3D Transitions

The 3^3D state was a very good case to measure, as what cascade there was appeared small in amplitude and much slower than the observed transition. It should be mentioned that for all of these triplet measurements no difference was noted in lifetimes of the individual lines of a given multiplet, each of which were resolved and measured in every case but $6^3S \rightarrow 3^3P$. For 3^3D our results are longer than theory gives, but agreement is better for 4^3D .

Table 4. Measured Values and Probable Assignments of Cascade Lifetimes in Mg.

Wavelength Where Observed ($\text{\AA}$)	τ (nsec)	Probable Assignment
5178	80	$4^3P \rightarrow 4^3S$
3835	153	$4^3F \rightarrow 3^3D$
8806	124	$4^1F \rightarrow 3^1D$
5528	200	$5^1F \rightarrow 4^1D$

c) 1S Transitions

These lines are somewhat weaker and slower than others measured. The only available comparisons appear to be the works of Warner^(38,39) and Lambert and Warner⁽¹⁶⁾, and our results appear to lie midway between theirs. Conditions were good for these measurements, so we feel our results are pretty accurate. There does not appear to be any other experimental work on these transitions.

d) 1D Transitions

As pointed out in Condon and Shortley⁽⁹⁾ and discussed by Warner⁽³⁸⁾, there is very significant configuration mixing between $3snd\ ^1D$ and $3p^2\ ^1D$ states in magnesium, and spectroscopists have been uncertain both as to the character of this series, and the exact location of the $3p^2\ ^1D$ autoionizing state, although it seems generally agreed that there is increasing interaction of $3p^2$ with $3snd$ for increasing n . Some years ago Bacher⁽⁴⁰⁾ calculated the energy levels of $3s3d\ ^1D$ and $3s3d\ ^3D$ using Slater wave functions first without mixing, then with mixing through the electrostatic energy component connecting $3s3d\ ^1D$ with $3p^2\ ^1D$. His results are shown in Fig. 23. It is seen that this interaction is more than enough to invert and severely perturb the location of the $3s3d\ ^1D$ state, which is the lowest 1D , as is observed experimentally. This same mixing may account for an anomalous behavior in the trend of transition probabilities for $3snd\ ^1D \rightarrow 3s3p\ ^1P$. Our work agrees reasonably well with the work of Wiese *et al.*⁽⁵⁾ as far as they go, and with the abundance data of Lambert and Warner⁽¹⁶⁾ except for the last two transitions. The calculations

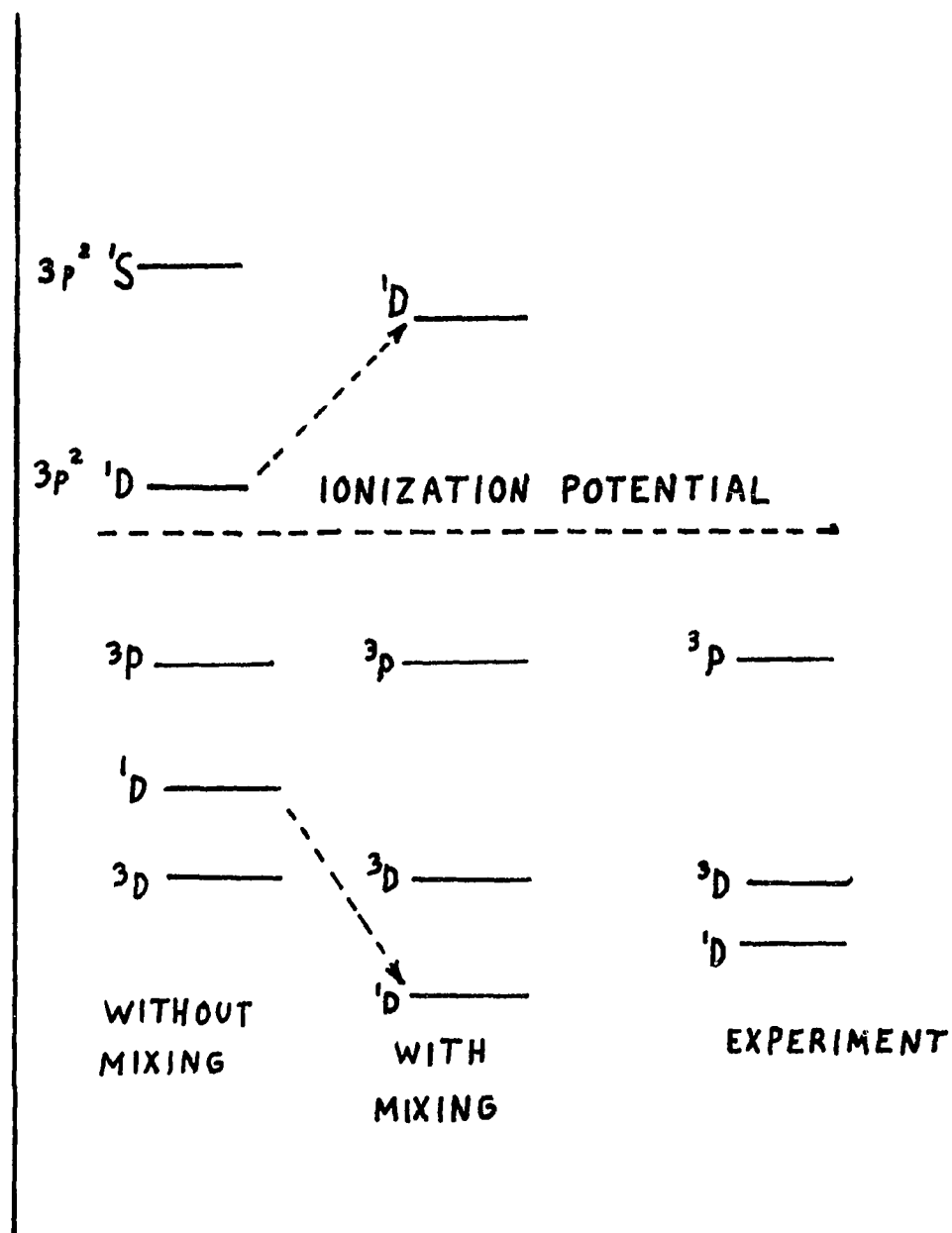


Figure 23. Results of Bacher⁽⁴⁰⁾ Showing Calculated and Experimental Configuration Mixing Perturbation of $3s3d\ ^1D$ and $3p^2\ ^1D$.

by Warner⁽³⁸⁾ were admittedly difficult for this sequence because of the mixing factor, so the disagreement is not too surprising. One possible explanation of the downward trend in lifetimes for the upper n levels in 1D may therefore be the increased configuration mixing with the $3p^2\ ^1D$ state, coupled with the fact that there are more and more possible transitions downward to lower excited P and F states from these near continuum high levels. It is also possible that photoionization of the upper lying states due to infrared photons emitted by the invertron may be responsible for the observed shortened lifetimes of the upper states. Figure 22 displays the anomalous trend of $n^{*3}f$ vs. n^* , where we have used the values of Warner⁽³⁸⁾ to convert our lifetimes to absorption oscillator strengths, and also plotted the results of others. We should note that the upper transition lifetimes have not been corrected for nearly all of the possible transitions, consequently exaggerating the upswing. For normal trends in atoms we expect $(n^*)^3f$ to approach a constant for increasing n^* , the hydrogenic solution.

Measurements of Lifetimes in Mg^+

Several magnesium ion lines were observed and measured. Due to their expected short lifetimes, it was feared that measurements made with the real cable excitation pulser might not be valid. Therefore the measurements were also made with the mercury wetted relay pulser described earlier; which, although only running at 120 Hz, has a cut-off of better than 0.5 nsec. No significant differences in lifetimes were seen when the results of the two methods were compared. We present

the results of our measurements, along with results of Wiese *et al.*⁽⁵⁾, and Warner⁽³⁸⁾ in Table 5. There is some disagreement between our results and the largely theoretical ones presented; however, our measurements appeared to be quite self consistent.

Table 5. Measured Lifetimes in Mg^+ Ion Compared with Lifetimes Calculated from the Work of Others.

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)
2798	$3^2\text{P} \rightarrow 3^2\text{S}$	6.20 ± 0.38	3.75	3.92
2934	$4^2\text{S} \rightarrow 3^2\text{P}$	6.21 ± 0.48	3.09	3.18
4481	$4^2\text{F} \rightarrow 3^2\text{D}$	7.07 ± 0.69	4.44	-

Note: Multiple wavelength given. Columns (1) and (2) identify the transition, column (3) gives measured lifetimes, column (4) gives lifetimes calculated from Wiese *et al.*⁽⁵⁾, and column (5) gives lifetimes calculated from Warner⁽³⁸⁾.

CHAPTER II

CADMIUM

Previous Work

Although there have been some measurements of excited state lifetimes in cadmium, they are not numerous. Most measurements have been made on the resonance transitions and on the forbidden line $5^3P_1 \rightarrow 5^1S_0$ $\lambda 3261$. Due to the lack of excited state measurements, and to the recent interest in Penning lasers, we have used our technique to make lifetime measurements in cadmium.

References to earlier work in cadmium were obtained largely from the National Bureau of Standards bibliography of Miles and Wiese⁽⁶⁾. We shall briefly mention here the works to which we have compared our results. There have been many measurements of the $5^3P_1 \rightarrow 5^1S_0$ 3261 Å forbidden line in cadmium. Among them are those of Koenig and Ellet⁽⁴¹⁾ and Soleillet⁽⁴²⁾ using a spatial beam decay technique, King and Stockbarger⁽⁴³⁾ by absorption, Webb and Messenger⁽⁴⁴⁾ by electron beam excitation, Matland⁽⁴⁵⁾, Geneux and Wanders-Vincenz⁽⁴⁶⁾, and Barrat and Butaux⁽⁴⁷⁾ by optical excitation, Bieniewski⁽⁴⁸⁾ by absorption, Byron *et al.*⁽⁴⁹⁾ by optical excitation, and Moise⁽⁵⁰⁾ by absorption. Garstang⁽⁵¹⁾ has calculated the transition probability for this state.

Other measurements include $6^1D_2 \rightarrow 5^1P_1$ $\lambda 4663$ by Geneux and Wanders-Vincenz⁽⁴⁶⁾ using electron beam excitation, and the transitions $6^3S_1 \rightarrow 5^3P_{0,1,2}$ $\lambda 4678, 4800, 5086$ by Laniepce⁽⁵²⁾ using Hanle effect. Helliwell⁽⁵³⁾ has done a modified self consistent field calculation for this transition.

The principal works which we have used in tabulating reference lifetimes are those of Verolainen and Osherovich⁽⁵⁴⁾ using electron beam excitation with delayed coincidence analysis, Warner⁽³⁹⁾, a scaled Thomas Fermi calculation, a Coulomb approximation calculation we did using the method of Bates and Damgaard⁽¹⁰⁾ and the matrix elements given in Griem⁽³⁾, the emission study of Corliss and Bozman⁽³⁴⁾, and the earlier emission study measurements of van Hengstum and Smit⁽⁵⁵⁾. Of these the measurements of Verolainen and Osherovich⁽⁵⁴⁾, since they use a modern delayed coincidence technique of measurement, should probably be the more precise. The work of van Hengstum and Smit⁽⁵⁵⁾ suffers the difficulties of arc intensity measurements, besides being only relative measurements, depending on an absolute value assignment to $3261 \text{ \AA}$ of 2.1 microsec for their absolute calibration. The work of Corliss and Bozman⁽³⁴⁾, as noted earlier, is not entirely suitable for lifetime comparisons.

Results

In Tables 6 and 7, we present the results of our lifetime measurements plus or minus standard deviation of the measurements, which we estimate as the approximate accuracy compared with the works of others. In Table 8 we give individual lifetime determinations of

Table 6. Lifetimes of Cd Triplet Excited States.

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)	τ (nsec) (6)	τ (nsec) (7)	τ (nsec) (8)
4678, 4800, 5086	$6^3S \rightarrow 5^3P$	18.5 ± 2.0	17.6	10.6 ± 0.8	9.86	0.57	3.1
3081, 3133, 3253	$7^3S \rightarrow 5^3P$	29.9 ± 4.5	41.5	-	24.1	12*	4.2*
3611	$5^3D \rightarrow 5^3P$	14.7 ± 2.2	8.5	14.5 ± 1.5	-	1.1	1.6
3613, 3466							
3615, 3468, 3404							
2981	$6^3D \rightarrow 5^3P$	18.7 ± 2.4	17.1	-	-	21*	4.0*
2981, 2881							
2982, 2881, 2837							

Note: *Denotes the Coulomb approximation was used to obtain branching ratios for calculation of lifetimes. Columns (1) and (2) identify the transitions, column (3) gives results of our measurements, column (4) is lifetimes from Coulomb approximation, column (5) lifetimes from Verolainen and Osherovich⁽⁵⁴⁾, column (6) lifetimes from Warner,⁽³⁹⁾ column (7) lifetimes calculated from Corliss and Bozman⁽³⁴⁾, and column (8) lifetimes calculated from von Hengstum and Smit⁽⁵⁵⁾.

Table 7. Lifetimes of Cd Singlet Excited States.

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)	τ (nsec) (6)	τ (nsec) (7)	τ (nsec) (8)
5155	$7^1S \rightarrow 5^1P$	115 ± 10	78.7	20.2 ± 0.5	68.5	-	-
4308	$8^1S \rightarrow 5^1P$	230 ± 2	158.	44.0 ± 2.0	136	-	-
3983	$9^1S \rightarrow 5^1P$	327 ± 8	291.	-	-	-	-
6438	$5^1D \rightarrow 5^1P$	27.6 ± 1.4	13.3	19.8 ± 1.8	-	-	3.7
4663	$6^1D \rightarrow 5^1P$	85.2 ± 1.2	36.6	37.5 ± 2.0	-	-	41*
4141	$7^1D \rightarrow 5^1P$	84.2 ± 4.5	78.1	65.5 ± 4.5	-	-	-
3905	$8^1D \rightarrow 5^1P$	94.7 ± 6.8	145.	-	-	-	-
3261	$5^3P \rightarrow 5^1S_0$	2490 ± 130	-	-	-	3300	2100

Note: * denotes the Coulomb approximation was used to obtain branching ratios for calculation of lifetimes. Columns (1) and (2) identify the transitions, column (3) gives results of our measurements, column (4) is lifetimes from Coulomb approximation, column (5) lifetimes from Verolainen and Osherovich⁽⁵⁴⁾, column (6) lifetimes from Warner,⁽³⁹⁾ column (7) lifetimes calculated from Corliss and Bozman⁽³⁴⁾, and column (8) lifetimes calculated from von Hengstum and Smit⁽⁵⁵⁾.

Table 8. Individual Cd Lifetime Results of Others.

$\lambda(\text{\AA})$	Reference	τ nsec
3261	Koenig and Ellett ⁽⁴¹⁾	2500 $\pm$ 250
	Soleillet ⁽⁴²⁾	2450
	King and Stockbarger ⁽⁴³⁾	2100
	Webb and Messenger ⁽⁴⁴⁾	2140 $\pm$ 60
	Matland ⁽⁴⁵⁾	2050 $\pm$ 50
	Geneux and Wanders-Vincenz ⁽⁴⁶⁾	2180 $\pm$ 70
	Barrat and Butaux ⁽⁴⁷⁾	2250
	Bieniewski ⁽⁴⁸⁾	2500
	Byron, McDermott, Novick ⁽⁴⁹⁾	2390 $\pm$ 40
	Moise ⁽⁵⁰⁾	2320
	Garstang ⁽⁵¹⁾	2300
--	--	--
4663	Geneux and Wanders-Vincenz ⁽⁴⁶⁾	210 $\pm$ 20
--	--	--
5086	Helliwell ⁽⁵³⁾	7.4
4800		
4678	Lanierce ⁽⁵²⁾	9.20 $\pm$ 0.03

other authors also for sake of comparison. Table 9 shows lifetime results obtained in Cd^+ ion.

Discussion of Results

a) 5^3P_1 Term

The transition at $3261 \text{ \AA}$ of $5s5p \text{ } ^3\text{P}_1 \rightarrow 5s^2 \text{ } ^1\text{S}_0$ was observed to be a relatively strong transition. There also appeared to be resonance trapping of this line to a large extent, so the following method was utilized to make the measurement. The sample containing crucible was withdrawn below the cathode to a relatively cool area so that the cadmium vapor pressure was quite low ($\sim 10^{-3} \mu\text{Hg}$). At this pressure there are insufficient cadmium atoms present to accomplish electron wave penetration and excitation in the invertron, so a background of hydrogen gas was used. With this gas present the 3261 Cd line was faintly present and could be measured. By using different pressures of hydrogen background and extrapolating to zero pressure hydrogen, the value of $2.49 \pm 0.13 \text{ } \mu\text{sec}$ was obtained for the life of the state. This is lower than the value of Corliss and Bozman⁽³⁴⁾, and greater than that of van Hengstum and Smit⁽⁵⁵⁾, who set their reference value equal to that of King and Stockbarger⁽⁴³⁾ of $2.10 \text{ } \mu\text{sec}$. It is interesting to note the earlier measurements shown in Table 8 tend to agree with ours, the intermediate ones tend to be less, and the later ones approach our value again, although remaining a little less. Our measurement of this state is probably not quite so reliable as those of higher excited states.

Table 9. Lifetimes of Cd⁺ Excited States

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)
4416	5s ² ² D _{5/2} →5p ² P _{3/2}	994±54	-	830±70
4136	7d ² D _{5/2} →6p ² P _{3/2}	11.7±0.5	4.90	-
2749	6s ² S _{1/2} →5p ² P _{3/2}	5.7±0.9	2.89	-
3251	5s ² ² D _{3/2} →5p ² P _{1/2}	310±10	-	465±20
3536	5s ² ² D _{3/2} →5p ² P _{3/2}	290±10	-	465±20

Note: Columns (1) and (2) identify the transition, column (3) gives results of this work, column (4) lifetimes from a Coulomb approximation calculation, and column (5) lifetimes from Geneux and Wanders-Vincenz⁽⁶³⁾.

b) 3S Transitions

Each line of the 6^3S and 7^3S states was measured. Our values for both states do not differ too greatly from the Coulomb approximation calculation. Our 6^3S value appears somewhat longer than other measurements would indicate. As found with the lowest 3S state in magnesium, there appears to be a heavy cascade, probably $6^3P \rightarrow 6^3S$, of about 85 nsec, which makes the analysis of this state admittedly more uncertain than usual. The emission measurements of van Hengstum and Smit⁽⁵⁵⁾ and Corliss and Bozman⁽³⁴⁾ appear to be clearly too short for both 6^3S and 7^3S , and agreement between ourselves and Warner⁽³⁹⁾ is closer for 7^3S .

c) 3D Transitions

In the 5^3D multiplet the three lines 3611-13-15, 3466-68, and 3404 were each measured, and similarly in 6^3D 2981-81-82 and 2881-81 were measured, without noticing appreciable fine structure dependence in the multiplet lifetime. This time agreement is excellent for 5^3D with Verolainen and Osherovich⁽⁵⁴⁾, although except for 6^3D of Corliss and Bozman⁽³⁴⁾, the emission values again appear too short.

d) 1S Transitions

Our values for 1S transitions are markedly longer than those of Verolainen and Osherovich⁽⁵⁴⁾. Analysis conditions for this series were quite good (low background, low cascade). Also the Coulomb approximation and theory of Warner⁽³⁹⁾ predict longer lifetimes, as does our own experience with the Mg 1S series reported in the last chapter. Hence we conclude perhaps the Russian measurements are somewhat in error for this series.

e) 1D Transitions

Our results in the 1D series are in closer agreement with those of Verolainen and Osherovich⁽⁵⁴⁾, except for 6^1D . It would be of interest to measure higher transitions in this series to investigate a possible anomalous behavior similar to that of the 1D series in Mg.

Results - Cd^+ Ion

The lifetimes measured in Cd^+ are presented in Table 9. There appears to be little other data on Cd^+ . Of recent interest is the inverted doublet arising from the two electron transition $4d^95s^2$ $^2D_{5/2,3/2} \rightarrow 4d^{10}5p$ $^2P_{3/2,1/2}$, which has been utilized with helium to form a Penning laser at wavelengths 4416 Å and 3251 Å. We measured lifetimes of all three possible transitions, obtaining 300 nsec for the life of $^2D_{3/2}$ and 994 nsec for the life of $^2D_{5/2}$. Although the values are somewhat different, this same difference in lives of $^2D_{3/2}$ and $^2D_{5/2}$ was observed by Geneux and Wanders-Vincenz.^(46,63) These transitions appeared fairly intense, in accordance with the fact that a fairly high cross section for excitation of the 2D upper level, coupled with better than a 100 to 1 lifetime ratio of this state to the lower 5^2P state can produce the laser phenomena.

CHAPTER III

BARIUM

As noted earlier, several barium and barium ion lines were present when magnesium was introduced into the system, and a very cursory set of measurements was taken on a few of them. It must be emphasized that these results should not be assumed to be of the same validity as the other measurements on magnesium and cadmium. It is hoped that a later effort will be made by someone who will introduce barium into the system and do a more complete analysis. However, due to the scarcity of transition probabilities in barium and wide divergence of results, we list our measurements in Tables 10 and 11.

Most of the references are obtained again from the bibliography of Miles and Wiese⁽⁶⁾. The most extensive other works in barium are those of Friedrich and Trefftz⁽⁵⁶⁾ from a configuration mixing calculation, Warner⁽⁵⁷⁾ from his scaled Thomas Fermi calculations, and Eicke⁽⁵⁸⁾ using emission measurements. There are also measurements by Bucka *et al.*⁽⁵⁹⁾ and Gallagher⁽⁶⁰⁾ of barium ion lifetimes using Hanle effect, and some barium oscillator strength "hook" measurements by Penkin and Shabanova⁽³²⁾. Ostrovskii and Penkin⁽⁶¹⁾ have made some earlier relative hook measurements in barium, which have been normalized to an absolute scale by setting the lifetime of $\lambda 5535 \text{ } 6^1\text{P} \rightarrow 6^1\text{S}$ to 9.78 nsec.

Table 10. Lifetime Measurements in Barium

Wavelength (λ) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)	τ (nsec) (6)	τ (nsec) (7)
3501	5d6p $^1P \rightarrow 6s^2 ^3S$	29 $\pm$ 2	34*	-	23	-
3910	$4^3F_2 \rightarrow 5^3D_1$	35 $\pm$ 3	-	18*	5.8	-
3993	$4^3F_4 \rightarrow 5^3D_3$	31 $\pm$ 3	-	21*	6.0	63
4132	5d6p $^3D \rightarrow 6s^2 ^1S$	11.1 $\pm$ 2.3	-	10*	-	-

Note: Columns (1) and (2) identify the transition, column (3) gives results of this work, column (4) lifetimes calculated from Penkin and Shabanova(32), column (5) results from Ostrovskii and Penkin(61), column (6) results from Friedrich and Trefftz(56), and column (7) from Eicke(58). * denotes values selected in the compilation of Miles and Wiese(62).

Table 11. Lifetime Measurements in Ba⁺

Wavelength (Å) (1)	Transition (2)	τ (nsec) (3)	τ (nsec) (4)	τ (nsec) (5)	τ (nsec) (6)	τ (nsec) (7)
4554	$6^2P_{3/2} \rightarrow 6^2S_{1/2}$	11.5 ± 0.6	6.27 ± 0.25	6.29	-	7.0 0.6
4934	$6^2P_{1/2} \rightarrow 6^2S_{1/2}$	13.7 ± 0.6	$7.74^* \pm 0.4$	7.78	-	-
4899	$7^2S_{1/2} \rightarrow 6^2P_{3/2}$	9.4 ± 1.4	-	6.15*	3.8	-

Note: Columns (1) and (2) identify the transition, column (3) gives result of this work, column (4) gives results of Gallagher⁽⁶⁰⁾, column (5) gives lifetimes calculated from results of Warner⁽⁵⁷⁾, column (6) result from Eicke⁽⁵⁸⁾, and column (7) result from Bucka *et al.*⁽⁵⁹⁾. * denotes values selected in the compilation of Miles and Wiese⁽⁶²⁾.

These works are the ones with which we compare in Tables 10 and 11. Miles and Wiese⁽⁶²⁾ have compiled and evaluated transition probabilities for Ba I and Ba II in a similar manner as their other works on the first twenty elements^(4,5). They have studied the results of the above mentioned authors extensively, and attempted to pick the most reliable result for each transition. The situation for barium, as they note, needs quite a lot of improvement with respect to good measurements of transition probabilities. In Tables 10 and 11 we have placed an asterisk beside the values selected by Miles and Wiese for each transition. The results have been converted to lifetimes for comparison as before.

A few comments are in order on the results. $\lambda 3501$ $5d6p$ $1p \rightarrow 6s^2$ $1S$, an anomalous term, appears in pretty good agreement, although Penkin and Ostrovski⁽⁶¹⁾ show a transition probability of $1 \times 10^8/\text{sec}$ for $5d6p$ $1p \rightarrow 6s5d$ $1D$, which would indicate a shorter life than we observed. The $3F$ state measurements $\lambda 3910$ and $\lambda 3993$ seem to agree fairly well with the experimental "hook" measurement. The one result of Eicke⁽⁵⁸⁾ appears long, and the theoretical calculations of Friedrich and Trefftz⁽⁵⁶⁾ are probably much shorter than one would expect of $3F$ transitions. The line $5d6p$ $3D \rightarrow 6s^2$ $1S$ $\lambda 4132$ one would expect to have quite a small transition probability, and indeed Ostrovskii and Penkin⁽⁶¹⁾ indicate this in their hook measurement; however, they claim $5d6p$ $3D \rightarrow 6s5d$ $3D$ to cause the state to have a 10 nsec lifetime, which is in agreement with our result.

For barium ion the $6^2P_{3/2}$ and $6^2P_{1/2}$ states were both measured by Gallagher using Hanle effect⁽⁶⁰⁾. We think perhaps our cutoff was not fast enough for these measurements, since we were not particularly trying

for fast cutoff at the time. For $7^2S_{1/2}$ Warner's calculation indicates a lifetime a little shorter than that which we obtained. After surveying the inconsistencies of the literature we are certainly of the opinion that much more work needs to be done in barium to obtain reliable transition probabilities.

CHAPTER IV

CONCLUSION

We hope this work will satisfy two goals; that of providing some valuable, accurate, and heretofore unobtainable lifetime data for the excited states of magnesium and cadmium, and also that of providing a sound basis of understanding of some of the problems and ideas involved in obtaining transition probabilities, particularly by our lifetime method. We should emphasize that the invertron, by virtue of its cylindrical design and high current capability, is able to yield much higher intensities of light than other comparable sources, yet due to its low inductance design can still have a fast enough cutoff to study many atomic and molecular lifetimes. The extra intensity enables us to use narrow slits on our monochromators and thereby obtain high resolution.

In the future we would like to see developed, or perhaps someday have opportunity to develop, a system which would use an invertron with metals of low vapor pressure such as iron. We believe it would be possible to design such a system using a well collimated atomic beam passing through the hollow invertron and being terminated on a cold trap. This would eliminate electrode shorting and pressure problems, and allow almost any material to be studied in the invertron.

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APPENDIX A

In this appendix we have presented a short, simple program which can be used with the matrix elements presented in Griem⁽³⁾ to calculate transition probabilities according to the Coulomb approximation method. Of course more sophisticated versions are available, but this was written to do simple rapid calculations. It does not include the case of equivalent electrons. The variables first called for are: L, the total lower orbital angular momentum quantum number; S, the total spin number; LP, the total upper orbital number; L1, the parent configuration orbital number; S1, the parent configuration spin number; LL the lesser of the jumping electron's before and after transition orbital angular quantum number; LLG, the greater of these for the transition electron; WM, the appropriate multiplet Racah Coefficient; TL, the term ionization limit of the atom.

The program then asks if a new line is considered. Yes inputs a new value of J, JP, and WL. No accepts these from the last iteration, except on the first time through. J is the total angular momentum of the atom for the lower state, JP the total for the upper state, and WL the line Racah Coefficient.

TNG and TNL are the energy levels of the term of LLG and LL, respectively, in inverse centimeters. The program then prints "DIFF=" numerical value of $n_{\ell-1}^* - n_{\ell}^*$, the difference in effective principal quantum numbers for the transition, and "NG=" the value of n_{ℓ}^* , the way in which the matrix elements ϕ are tabulated. Next the program calls for ϕ , which is looked up in the appropriate table, and ALAM, the multiplet wavelength. It prints "A=" the numerical transition probability, and returns to ask if a new line is desired. When finished the program is manually interrupted.

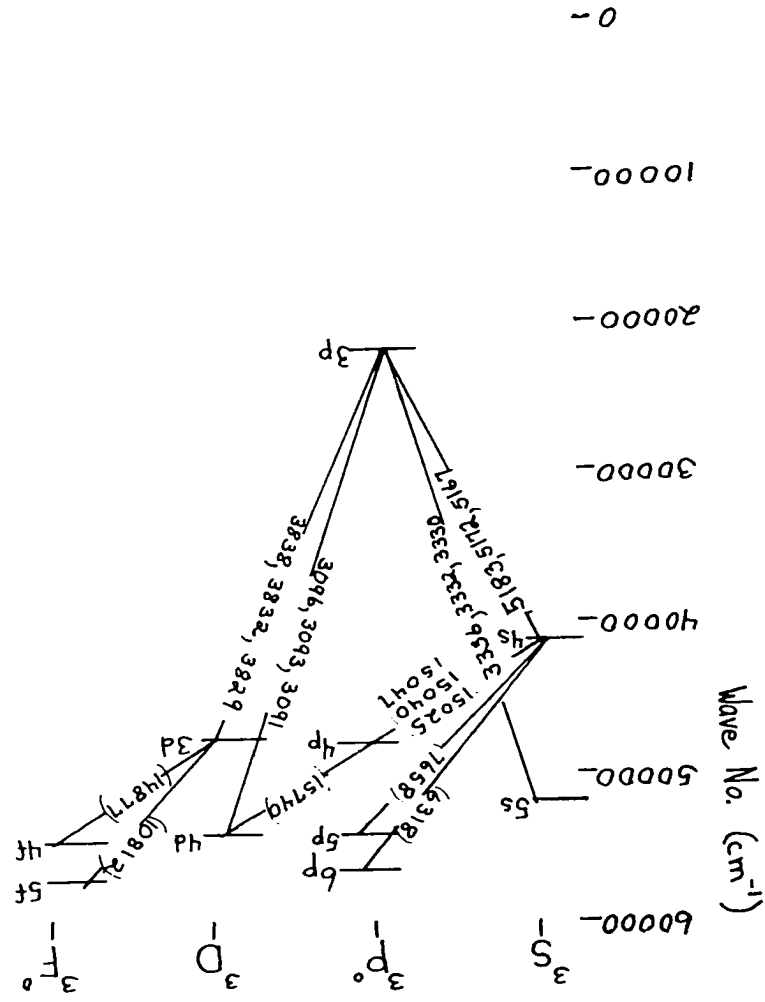
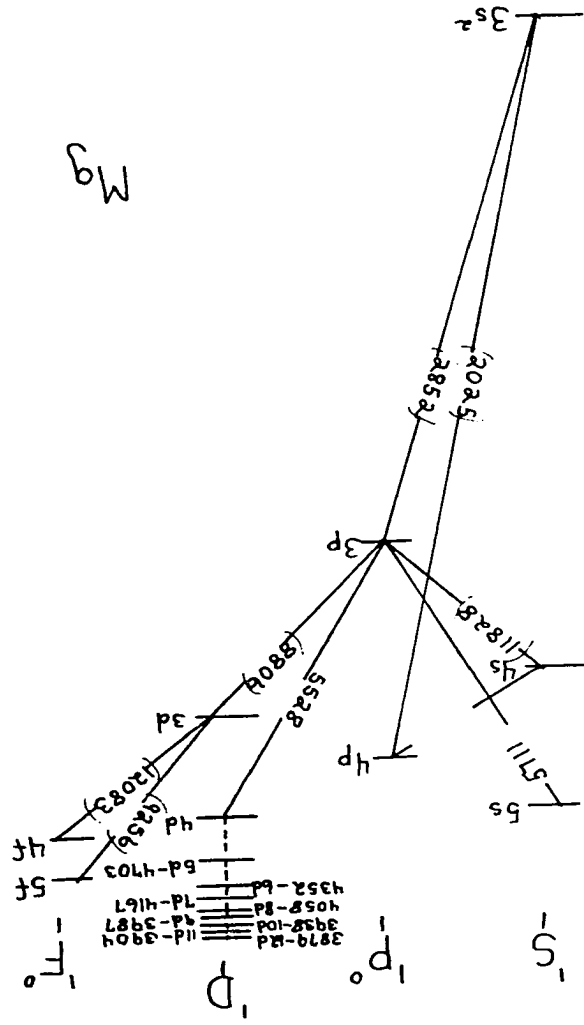
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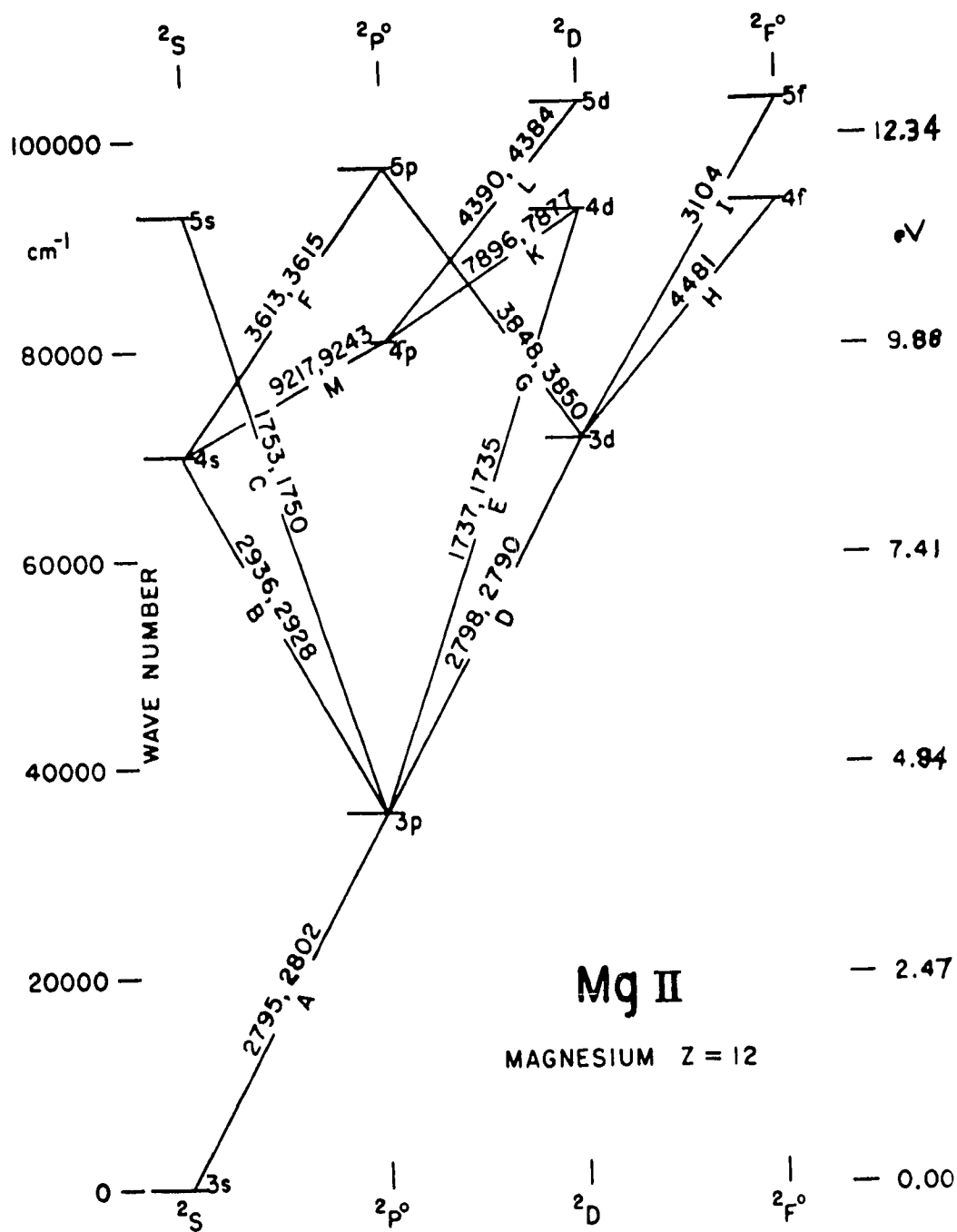
$NDM
  DIMENSION AL(1),S(1),ALP(1),AL1(1),S1(1),AJ(1),AJP(1),ALL(1),
&ALG(1),WL(1),WM(1),TL(1),TNG(1),TNL(1),APHI(1),K(1),ALAM(1)
  PRINT,'L,S,LP,L1,S1,LL,LLG,WM,TL?'
  INPUT,AL,S,ALP,SL1,S1,ALL,ALG,WM,TL
  SM=0.0
  SM=((2.0*S)+1.0)*((2.0*AL)+1.0)*((2.0*ALP)+1.0)
&*ALG*((4.0*ALG*ALG)-1.0)*WM*WM
15 CONTINUE
  PRINT,'NEW LINE? YES=1'
  INPUT,K
  IF(K-1)20,10,10
10 SL=0.0
  PRINT,'J,JP,WL?'
  INPUT,AJ,AJP,WL
  SL=((2.0*AJ)+1.0)*((2.0*AJP)+1.0)/((2.0*S)+1.0)*WL*WL
20 SIG=0.0
  ANG=0.0
  ANL=0.0
  ADIF=0.0
  PRINT,'TNG,TNL?'
  INPUT,TNG,TNL
  ANG=SQRT(109737.31/(TL-TNG))
  ANL=SQRT(109737.31/(TL-TNL))
  ADIF=ANL-ANG
  PRINT 100,ADIF
  PRINT,'NG=',ANG
100 FORMAT(1H,'DIFF=',F6.3)
  PRINT,'PHI,ALAM?'
  INPUT,APHI,ALAM
  SIG=(SQRT((ANG*ANG)-(ALG*ALG))/((4.0*ALG*ALG)-1.0))*(3.0
&*ANG/2.0)*APHI
  STR=0.0
  STR=SIG*SIG*SL*SM
  A=0.0
  A=(STR*2.026E+18)/(((2.0*AJP)+1.0)*ALAM*ALAM*ALAM)
  PRINT,'A=',A
  GO TO 15
END

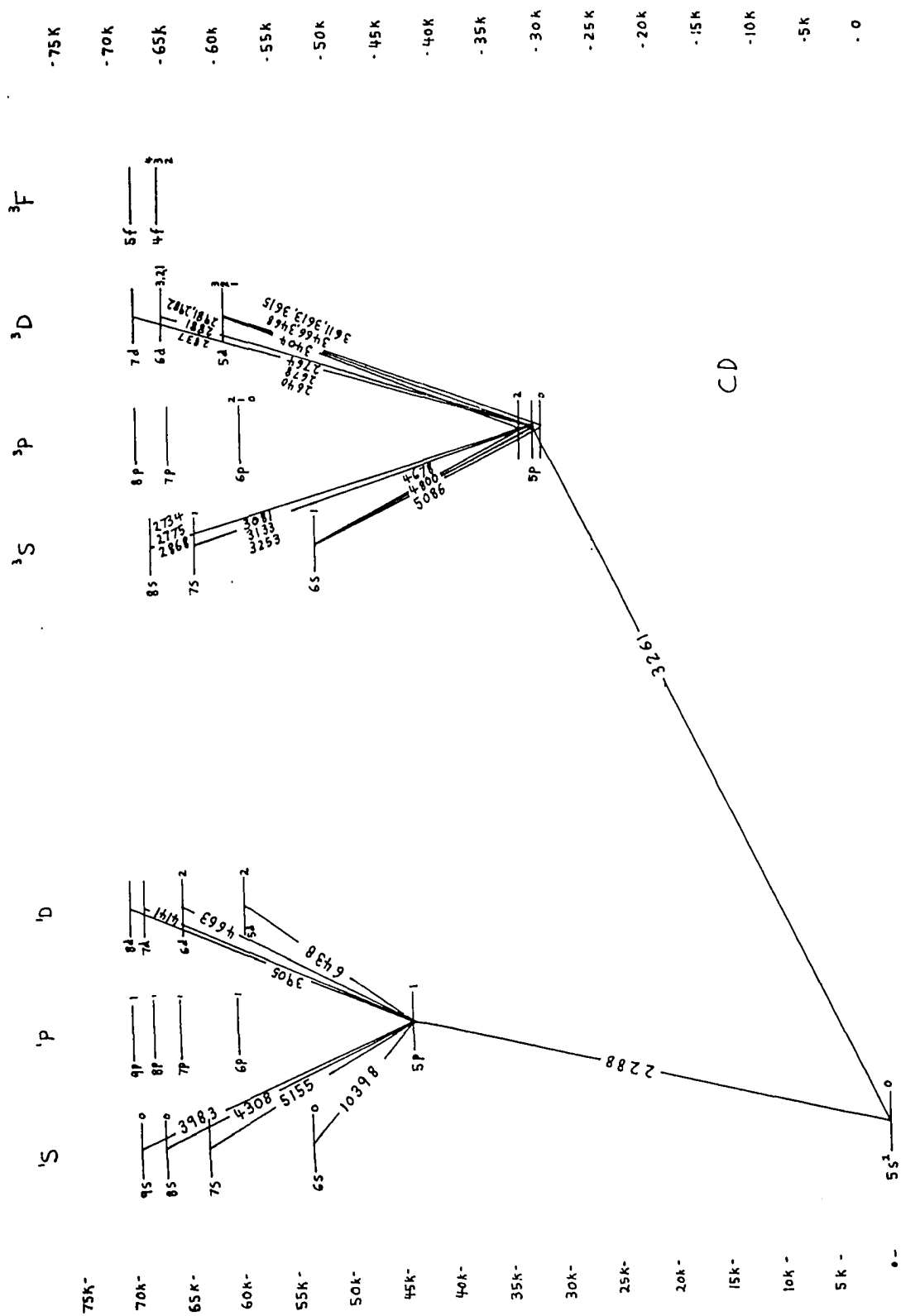
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APPENDIX B

Energy Level Diagrams for
Mg, Mg^+ , Cd, Cd^+ , Ba, and Ba^+









BA^+
