

AN ABSTRACT OF THE THESIS OF

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Title A DIRECT LIFETIME MEASUREMENT FOR
A RESONANCE TRANSITION IN ARGON

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The $4s^3P_1$ state of argon decays radiatively by a resonance transition to the $3p^6^1S_0$ ground state; the wavelength of this radiation is 1067A. By direct observation of the decay of the 1067A radiation from excited argon gas, a value of $0.93 \pm 0.06 \times 10^{-5}$ seconds has been obtained for the natural lifetime of the $4s^3P_1$ state. The failure of this state to appear as a metastable state points up the inadequacy of a description of the argon atom by Russel-Saunders coupling. The calculated value (25) of 1.05×10^{-8} seconds for the natural lifetime of the $4s^3P_1$ state requires a larger degree of mixing of the strict Russel-Saunders terms than does the value measured in this experiment.

The measurement was made using a modified delayed coincidence method (3). Bombardment of argon gas with a pulsed beam of controlled energy electrons was used to produce cyclic excitation and relaxation of the gas. The cyclic regeneration of the argon decay allowed the entire decay curve to be determined by examining

it piecemeal. A small portion of the decay curve is repetetively examined by gating a detector such that it is active only during a small fraction of each cycle. During each cycle the location in time of this sampling interval is set by triggering the gating signal with a delayed pulse which is produced at the termination of the excitation. Different portions of the decay curve are examined by adjusting the delay of the trigger pulse. Because the detector output is a constant which varies only when the location of the sampling interval is shifted along the decay curve, this method avoids the problem of attempting to record a single transient.

The atomic excitation is produced within a nine liter cylindrical volume. A slow molecular type flow of argon is maintained through this excitation chamber. The pressure is essentially uniform within this chamber and is varied over the range of 10^{-3} to 10^{-1} Torr. The electron gun, located at the center of the excitation chamber, consists of the cathode and grid structure of a 6SJ7 electron tube. The spread in energy of electrons from this gun was small enough to allow selective excitation of the 4s multiplet of argon, but selective excitation of levels within this multiplet could not be achieved.

Radiation from the excitation chamber was detected with a Bendix magnetic photomultiplier (20) which was separated from the excitation chamber by a thinly cleaved lithium fluoride window.

This photomultiplier is sensitive only to radiation in the wavelength region between 2A and 1500A. Final identification of the observed radiation as that from the $4s \ ^3P_1 - 3p \ ^6S_0$ transition was made using a vacuum spectrograph.

Since the intensity of radiation from the excitation chamber is directly proportional to the concentration of argon atoms in the $4s \ ^3P_1$ state, it is the decay of these atoms that is determined. This decay will be governed by the radiative decay constant only if collisional transfer of excitation and trapping of resonance radiation can be neglected. Throughout the range of pressure used in this experiment the rate constants associated with both these processes are known to be pressure dependent (21, 22) and the effect of resonance trapping can be observed separately by its dependence upon the enclosure geometry. It is to be expected that the predominant collision process will be the two body collisions which result in the exchange of excitation between the $4s \ ^3P_1$ level and the adjacent metastable levels.

The experimental data consistently yield decay curves which represent the sum of two exponential decays having different decay constants. The larger of these decay constants is independent of gas pressure and the smaller one is approximately directly proportional to pressure. Neither is dependent upon enclosure geometry. Therefore, it is concluded that the effects of resonance trapping

are negligible, and that the de-excitation of argon atoms in the $4s^3P_1$ state is governed predominantly by radiative decay and by two body collisions which result in the transfer of excitation to or from this state. The cross sections for collisional transfer is approximately $4 \times 10^{-15} \text{ cm}^2$ at room temperature.

The fact that resonance radiation from the $4s^1P_1$ state of argon was not observed indicates that this radiation is heavily trapped and that collisional transfer is primarily responsible for the decay of this state. It thus appears that there is a large difference in the natural lifetimes of the two radiative $4s$ levels. This implication is in disagreement with the experimental results obtained by Vaughan & Stacy (35).

A DIRECT LIFETIME MEASUREMENT FOR A
RESONANCE TRANSITION IN ARGON

by

GEORGE FIELDEN DICKERSON

A THESIS

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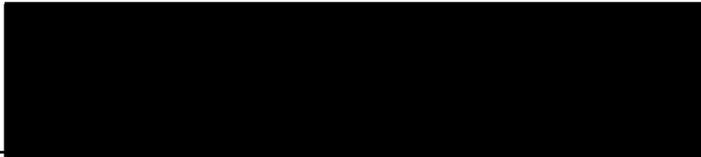
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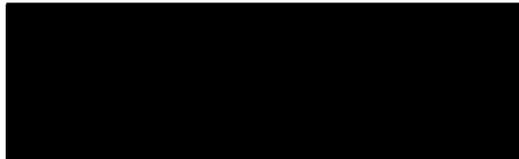
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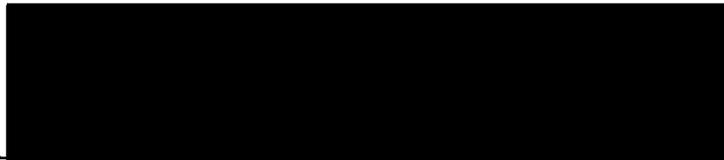


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A DIRECT LIFETIME MEASUREMENT FOR A RESONANCE TRANSITION IN ARGON

INTRODUCTION

Fundamental Concepts

It is of fundamental importance to know the values of basic atomic and molecular physical properties such as charge, mass, and magnetic moment. These data, however, are incomplete for the physical descriptions necessary when dealing with an atomic system. In order to present an adequate characterization of an atomic system, these data must be supplemented with a representation of the possible states of the atomic system. The existence of this representation allows the calculation of energy levels associated with possible electronic configurations and further the calculation of the probability of transitions between levels. Thus the experimental determination of those quantities, which are characteristic of transitions, not only supplies necessary fundamental information about the atomic system, but also supplies the information necessary to evaluate the quality of the representation of the atomic system.

Orientation

This study is concerned with a direct measurement of the transition probability or, equivalently, the radiative lifetime for

a particular transition in argon. It is anticipated that for the argon atom this measurement will serve as a measure of the validity of the approximations used in the calculation of this quantity. That is, the multi-electron problem is far too difficult to be solved exactly, but a solution can be obtained by making certain approximations. As always the ultimate measure of the suitability of these approximations must be evaluated by comparison of calculations with experimental results.

The relatively large energy resonance transitions occurring in argon provide a good test of the approximations which are used in calculating atomic wave functions. Because of this large energy difference between the ground state and any of the excited states, the overlap of the ground state wave function and the excited state wave function which enters into the calculation of a transition probability will be relatively small; additionally, there will be partial cancellation between different parts of the overlap integral. This means that in this situation a comparison between the calculated and the measured value of the transition probability is a particularly good test of the quality of the two wave functions.

The experimental techniques are also taxed because of the large transition energy in argon. For the noble gases and for many other atoms this transition energy is so large that the emitted radiation is in the extreme ultraviolet. Difficulties with optical materials

tend to eliminate high resolution methods and methods requiring polarization measurements. The use of a direct technique in this experiment removes the usual requirement of a high resolution optical system.

In concept a direct measurement of a mean lifetime for a radiative transition is extremely simple. In particular it is simple if the transition is specified, as it is in this experiment, to be that from an excited state to the ground state, i. e., a resonance transition, with no other radiative decay possible. The measurement becomes that of starting with a group of atoms in this excited state at some instant of time and observing the subsequent decay of the intensity of the output radiation which characterizes this transition. This observation determines the temporal behavior of the excited atom density inasmuch as the output intensity is directly proportional to the excited atom concentration.

Past Experiments

Past direct lifetime measurements are few for both intermediate and resonance transitions. For many transitions, it has been easier to determine lifetimes by indirect measurements (29, p. 92-153; 13, p. 1-42); however, most of these methods are not currently feasible for wavelengths in the extreme ultraviolet. The lack of feasibility of the indirect methods in the extreme ultraviolet is

perhaps partly responsible for the lack of past attention to transitions in the extreme ultraviolet.

The experiment described herein is the first unequivocal direct measurement of lifetime for a transition in the extreme ultraviolet, and it is one of the few direct measurements for resonance transitions. The prior direct lifetime measurements for resonance transitions have been in cadmium (26), mercury (12), and zinc (34; 29, p. 146). The experimental difficulties which are peculiar to resonance transitions are discussed in the chapter on Environmental Effects.

Some early direct lifetime measurement work was done on the lowest energy resonance transition in atomic hydrogen by Slack (33). During this same period lifetimes for intermediate transitions in neon were measured directly by Griffiths (16). More recently direct measurements have been made of transition probabilities for intermediate transitions in helium (23, 19) and for various transitions in each of N_2^+ (3), CO^- (4), CH and NH (5).

Description of Argon

Argon is particularly well suited to be the first in a series of elements for which direct lifetime measurements of resonance transitions are to be made. Some of the reasons for the suitability of argon to this type of experiment are its chemical inertness, its existence as a monatomic gas, and its energy level separations; also,

transition probabilities have been calculated for two of the argon resonance transitions (25).

In order later to use the appropriate nomenclature in discussing the argon atom, it is first necessary to consider the description of the argon atom both in its ground state and in an excited state.

In its ground state it has a closed shell electronic configuration, as do all the noble gases, which is represented in the usual spectroscopic notation of $1s^2 2s^2 2p^6 3s^2 3p^6 {}^1S_0$; this notation is abbreviated as $3p^6 {}^1S_0$. Excitation of the argon atom can be achieved by raising one of the electrons from the 3p subshell to a subshell lying higher in energy. This electron will have a spin of $\frac{1}{2}$ and its ℓ -value will be dependent upon the subshell in which it is found. Moreover, the now unfilled 3p subshell has a net spin of $\frac{1}{2}$ plus a net ℓ -value of one. At this point the possible values for the total angular momentum can be written; however, the state cannot be completely described until something is known about the coupling of the angular momenta of the external electron and the partially filled 3p subshell.

The excited state electronic configuration of interest in this study, denoted by $3p^5 4s$, is that for which the electron removed from the 3p subshell is in the 4s subshell. This particular configuration gives rise to the first four excited states of argon. These states are displayed in Fig. 1 in terms of their relative energies (30, p. 212). Note that the usual Russel-Saunders multiplet

12.90 eV ————— $3p^5 4p, J=1$

11.82 eV - - - - - $(^1P_1)$
11.72 eV ————— $(^3P_0)$
11.62 eV - - - - - $(^3P_1)$
11.56 eV ————— $(^3P_2)$

0 eV ————— 1S_0

Figure 1. Partial energy level diagram of argon.

notation appears in parentheses only as a labeling convenience.

Because of the relative size of the spin-orbit term and the residual Coulomb term in the Hamiltonian describing the argon atom, it is thought that LS coupling is not appropriate here and therefore symbols like 3P_1 , etc., have no meaning (9, p. 33). Moreover, the ordering of the $3p^5 4s$ levels in energy tends to substantiate the inappropriateness of LS coupling since these levels do not appear as a clear cut singlet and triplet multiplet; instead they tend to appear as two double levels, which is indicative of being close to the *jj* coupling limit (8, p. 304).

The selection rules on ΔJ allow only two of the $4s$ levels of argon to decay by electric dipole transitions. That is, a transition from the 3P_2 level must be by means of a higher order multipole than electric dipole, and a transition from the 3P_0 level is absolutely forbidden in first order perturbation theory because of the spherical symmetry of both the excited state wavefunction and ground state wave function (32, p. 267). The two allowed transitions are from the $4s^3P_1$ and $4s^1P_1$ states which lie 11.6 and 11.8 electron volts above the ground state. These transition energies correspond to wavelengths of 1067A and 1048A. Only the lifetime for the $4s^3P_1$ state is reported in this study. The experimental situation which allows a measurement of lifetime for the $4s^3P_1$ state but not for the $4s^1P_1$ state is discussed in Experimental Results.

THE DIRECT LIFETIME METHOD

Atomic Transitions

The development of the description of the decay of excited atoms by emission of photons is made by assuming that the decay rate is directly proportional to the number of excited atoms and then constructing the differential equation for the decay. This operational procedure is based upon the acceptance of the situation that the conditions necessary for application of Poisson statistics are satisfied in the case of radiative relaxation of excited atoms (10, p. 751). The solution of the resultant differential equation then gives the excited atom density as a function of time.

The decay is characterized by the transition probability, A_{ji} . This is the probability per unit time that an isolated atom in a state j will spontaneously make a transition to a lower state i with the emission of a photon of frequency ν_{ji} . If there are n_j atoms in the j th energy level and if each atom can make a transition to any level i for which $E_i < E_j$, then the number of atoms leaving the j th energy level per unit time is given by

$$\frac{dn_j}{dt} = \sum_i A_{ji} n_j$$

Integration of this equation gives the number of atoms in a state j at

time t ,

$$n_j(t) = n_j(0)e^{-\sum_i A_{ji} t}$$

However, if decay of this upper j level is possible through only a single transition, then

$$n_j(t) = n_j(0)e^{-A_{ji} t}. \quad (1)$$

Thus, given a group of atoms in the state j for which the only possible transition is radiative de-excitation to state i , an observation of the subsequent emission as a function of time allows a determination of the transition probability for this transition.

The more common quantity used to describe a transition is the mean radiative lifetime. This mean lifetime of an atom in the upper j state can be written as

$$\tau = \frac{\int_0^{\infty} n_j(0) t \, dn_j(t)}{\int_0^{\infty} n_j(0) \, dn_j(t)}$$

Upon making use of expression (1), τ becomes

$$\tau = \frac{n_j(0)}{n_j(0)} \int_0^{\infty} A_{ji} t e^{-A_{ji} t} dt.$$

Integrating by parts and evaluating by orders of infinity gives

$$\tau = \frac{1}{A_{ji}}.$$

Thus it is simply a matter of convenience whether the mean lifetime or the transition probability is used to describe a transition.

Concepts

Any measurement which yields directly the lifetime for an excited atomic state must ultimately be reduced to the determination of the number of atoms in the particular excited state as a function of time. Due to the particular time dependence in Equation(1) only the relative changes in population must be ascertained. As a consequence, those experimental measurements which sample the atomic concentration need only be proportional in some fashion to the excited atom concentration, with the proportionality factor independent of both concentration and time. Henceforth, it is to be understood that the phrase "measurement of the concentration of excited atoms" implies a measurement which is proportional to this concentration.

There are many methods which are appropriate to the measurement of atomic lifetimes. The method used in this study is, for reasons which will become apparent, among a group normally referred to as direct methods. The designation of a particular experimental method as either a direct or an indirect method is made upon the basis of the form of the data which the method yields. If the data appears as representing an exponential decay in time, then the method is said to be direct. A detailed description of the many

methods of lifetime measurements, both direct and indirect, is beyond the scope of this presentation and is presented elsewhere (29, p. 92-153). The particular method of direct measurement used in this experiment is one of determining, as a function of time, the intensity of the light emitted during the decay of the excited atoms. Since the number of photons emitted in the time interval t to $t + dt$ is directly proportional to the number of excited atoms existing at the time t , a determination of the photon flux as a function of time is equivalent to determining the number of excited atoms as a function of time. This method, as was mentioned in the Introduction is probably the most suitable method for many extreme ultraviolet transitions.

Requirements

The mechanics of making a lifetime measurement by this particular direct method are in concept quite simple for an idealized system in which the effects of interatomic interactions and the multiple absorption of emitted photons can be neglected. A concentration of excited atoms must be produced. After the production of excitation ceases, a measurement of the subsequent photon emission as a function of time determines the decay rate. For such a direct lifetime measurement, the requirements are excitation of the atoms to the energy state under study, detection of the emergent

photons, and the existence of a technique which is capable of fixing the time dependence of the photon emission.

Many possible options are available which satisfy the demands for excitation and detection; the ultimate consideration which fixes the choices among these alternatives is that of satisfactorily fabricating a technique of obtaining the emergent photon flux as a function of time.

Production of Excitation

The production of excitation is, of course, simply a matter of supplying energy from an external source to the atoms. However, the experimental method demands that the excitation energy supplied to the atoms be interrupted in a time which is short with respect to an atomic lifetime, and it demands that the input energy be adjustable in such a fashion that only the energy levels of interest be excited. Thus the production of excitation must be considered in the light of these two requirements.

The energy necessary to produce excitation is most easily furnished by electrical discharge, absorption of light, or bombardment with controlled energetic electrons. The electrical discharge method is not satisfactory for the purposes of this experiment because it cannot be used to produce selective excitation. The problem of termination is the drawback of the absorption technique.

Other than mechanical interruption, which is extremely slow, an electrical technique may be used to pulse an incident photon beam (15). However, this technique is unsatisfactory for extreme ultraviolet photons because it intrinsically requires selection of polarization, which is not feasible in the extreme ultraviolet. The third of the above mentioned methods, the use of controlled energetic electrons, gives a means of production of excitation which can be quickly terminated, and it is also readily usable for selective excitation. The production of electrons is a relatively easy task and the upper bound on their energy is readily adjusted within the limits of their thermal distribution by controlling the accelerating potentials. Moreover, an electron beam can be interrupted by means of a control grid surrounding the emitter. The time necessary to stop the production of excitation depends only upon the characteristics of the signal applied to the control grid and the time of transit of the electrons across the enclosure in which the atoms are being excited. It should be possible, utilizing recent electronic developments, to provide shut off times of less than 10^{-8} seconds.

If the condition demanding selective excitation is not satisfied, there exists the possibility of higher lying levels cascading to the ground state with the transition under study being only the final step in the cascade. The 4s levels of argon are particularly well suited for selective excitation because the next higher levels, the 4p levels,

are relatively far removed from the 4s levels.

It is to be noted that selective excitation has an additional advantage. If selective excitation is combined with a detector sensitive only in the extreme ultraviolet, a vacuum spectrometer may not be required.

The demand upon the termination of excitation arises as a consequence of some necessary conditions upon the observation of the decay. It is necessary that the termination of the excitation be well defined in time in order that excitation does not occur during the period of observation. However, the observation period should begin as soon after termination of the excitation as possible in order to minimize the error in the observed decay curve. That is, the larger the intensities being monitored, the better defined is the decay curve. Also, since selective excitation among the 4s levels is not possible, it is important to begin monitoring the decay early in time in order to determine whether or not the decay curve is a composite curve.

Detection of Radiation

Detection of the photon emission associated with the $4s-3p^6$ transitions in argon can be accomplished by any detector which is capable of responding to vacuum ultraviolet photons. Beyond this physical capability of detection, it is of great convenience if this detector is not responsive to visible light. As has been mentioned,

this feature of insensitivity of the detector to visible light coupled with selective excitation of the atoms permits the resonance transition of interest to be monitored without the necessity of using a monochromator. Further, as always, it is desirable that a low noise level exist for the detector. A photomultiplier satisfying these requirements is available and its description will be included in the discussion of the apparatus.

Photon Intensity as a Function of Time

Although the problems of production and detection of excitation have been considered, the ultimate problem is that of measuring, after the termination of production of excited atoms, the decay of the photon emission as a function of time. The difficulties associated with this measurement arise as a consequence of the time scale involved. Consider, for example, a lifetime measurement for a radioactive nuclide with a half-life of the order of minutes or hours. The magnitude of the efflux of particles or γ -rays, resulting from the decay, is determined as a function of time by measuring the total efflux in an interval of time Δt at each of the times t_1, t_2, \dots, t_n , where Δt is the order of tens of seconds and the sampling points t_1, t_2, \dots, t_n are separated by as much as minutes. If this procedure is used to examine the decay of atomic excitation, Δt may be of the order of 10^{-10} seconds and the sampling points

separated by intervals of 10^{-9} seconds. With this situation it would be necessary that the total sequence of measurements must be carried out in a time span of 10^{-8} seconds. A much simpler program is to begin with n identical sources and n sets of experimental apparatus and to measure the activity of source n_1 at t_1 , n_2 at t_2 , etc.. An equivalent process entails working with a single source and reproducing its initial activity after each measurement has been made. That is, if a source has an activity A at $t = 0$ and if a measurement of the photon emission is made during an interval Δt at t_1 , the source can then be reactivated to the initial activity A and, since the time is again $t = 0$, a photon emission measurement can be made during an interval Δt at t_2 . Subsequently, this process is repeated again and again until the final measurement is made at t_n . This process is used as one of the two detection methods in this study. This detection method is a technique which, for each decay cycle, allows a measurement to be made of that part of the decay curve which occurs in a small, fixed interval of time at a predetermined point in the time elapsed after the termination of the production of excitation. Subsequently, the small time interval over which the measurement is made is shifted within the decay period for successive reactivations of the source, thus allowing a determination of the total decay curve. A pulsed detection system makes possible the realization of such a program. For apparent reasons this

detection technique is called a pulsing technique.

The other detection method used in this experiment also utilizes the process of regeneration of the source, but it does not utilize any pulsing of the detector. It is a direct method in that the detector operates continuously and thus records a complete decay curve after each regeneration of the source. Regeneration of the source is necessary because it is impossible to observe the display of a single transient.

Since both of the detection techniques which are utilized in this experiment depend upon the repetitive attainment of a given initial source activity, it is necessary to determine if such a program of source regeneration can be accomplished. For cyclic bombardment of a group of atoms with energetic electrons, the problem is that of determining whether or not it is possible to attain a given excited atom concentration at the conclusion of each bombardment interval. Qualitatively it can be seen that an equilibrium condition must ultimately occur in this instance. The production rate of excited atoms, for constant electron flux f , is proportional, at any time, to the number of ground state atoms. Since the number of ground state atoms is reduced by the excitation, the production rate must be monotonic with its maximum value at the beginning of the bombardment. The decay rate is proportional to the number of excited atoms and it must monotonically increase from zero. Thus, at

some time the decay rate will be equal to the production rate. Because the rate of change of the decay rate is directly proportional to the production rate minus the decay rate, equilibrium must occur at this crossing. As a consequence, the same number density of excited atoms can be repeatedly attained by sustaining the bombardment until equilibrium is reached.

A quantitative treatment of the problem will allow a determination of the duration of the bombardment necessary to produce equilibrium. Consider a group of N_0 atoms all initially in the ground state. Let $m(t)$ and $n(t)$ be the number of atoms in the first excited state and the ground state respectively. The flux of electrons is represented by f , and σ is the cross section for excitation of the atom. The total time rate of change of excited state concentration is equal to the production rate minus the decay rate. That is,

$$\frac{dm(t)}{dt} = n(t)\sigma f - m(t)\frac{1}{\tau}.$$

Conservation of atoms demands that

$$n(t) + m(t) = N_0;$$

therefore,

$$\frac{dm(t)}{dt} + \left(\frac{1}{\tau} + \sigma f\right)m(t) = N_0 \sigma f.$$

The solution for this expression is

$$m(t) = \frac{N_0 \sigma f}{\frac{1}{\tau} + \sigma f} \left\{ 1 - e^{-\left(\frac{1}{\tau} + \sigma f\right)t} \right\}.$$

Equilibrium is approached with desired accuracy by adjusting the relation between t and τ . With the assurance that the excitation is easily reproducible, the detection techniques can be considered in detail.

The method of direct display of the photomultiplier output utilizes the realization that the photomultiplier is simply a current source and further that the output current is equivalent in its time dependence to the photon flux incident upon it. Hence, if the magnitude of the current output is measured as a function of time, the lifetime measurement is made. However, the time dependence of the current cannot be measured directly. In place of measuring a time dependent current, the photomultiplier output is shunted through a resistor and the time dependent voltage across the resistor is measured. With the introduction of the necessity for measuring voltage, the simplicity of the method begins to become lost. Because of stray capacitance there now effectively exists a parallel RC circuit through which all charge leaving the photomultiplier must flow. Thus the time dependence of the potential drop across the resistor does not represent the time dependence of the photomultiplier current output; instead, it represents the response of a parallel RC circuit to a particular input. Nevertheless the method is still workable if the atomic lifetime being measured is sufficiently long. Consider the situation depicted in Fig. 2. The solution for the potential across the resistor is readily obtained as

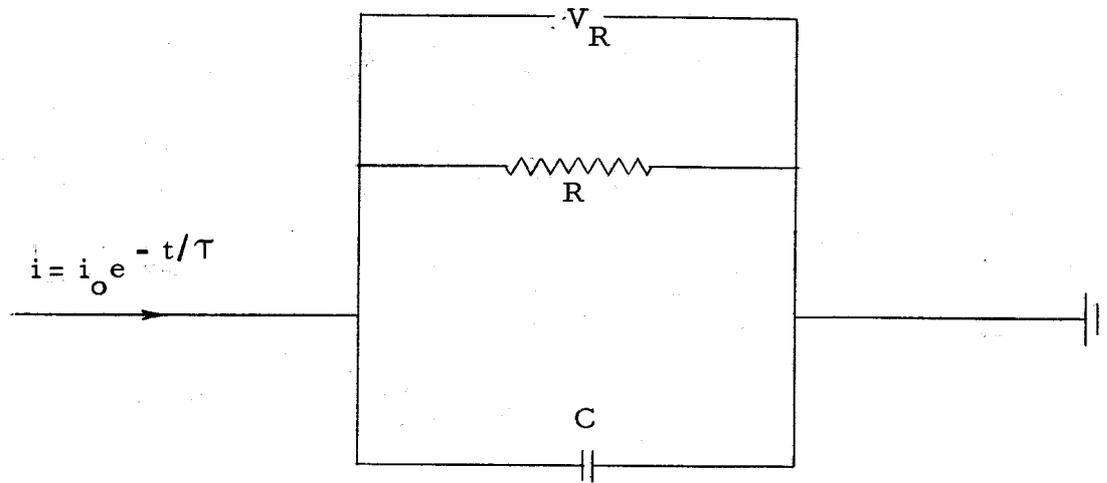


Figure 2. Effective detector circuit for the method of direct display.

$$V_R = \left(\frac{i_0 R}{\tau/RC - 1} \right) \left(\frac{\tau}{RC} e^{-t/\tau} - e^{-t/RC} \right)$$

An essential condition is that R be sufficiently large to produce a measurable potential. However, in order that a measure of V_R as a function of time be a measure of the photomultiplier output as a function of time, it is necessary that R be small enough that the second exponential term can be ignored. Since the magnitudes of both the atomic lifetime and the stray capacitance also enter into the determination of the acceptability of the method, the ultimate measure of the suitability of this technique must be determined experimentally.

The pulsing method is similar to that technique of delayed coincidence originally applied to nuclear physics experiments (1). The delayed coincidence method is used in nuclear physics to measure the lifetime of the intermediate state in a two step gamma decay. For a particular delay of the signal arising from the first step of the cascade there is a given probability, which is dependent upon the lifetime of the intermediate state, that this delayed signal will be in coincidence with the signal arising from the second step of the cascade. Typical operation is to do coincidence counting as a function of the delay, thus arriving at a value for the lifetime of the intermediate state. This process is not suitable for determining atomic lifetimes when the initial excitation is produced by

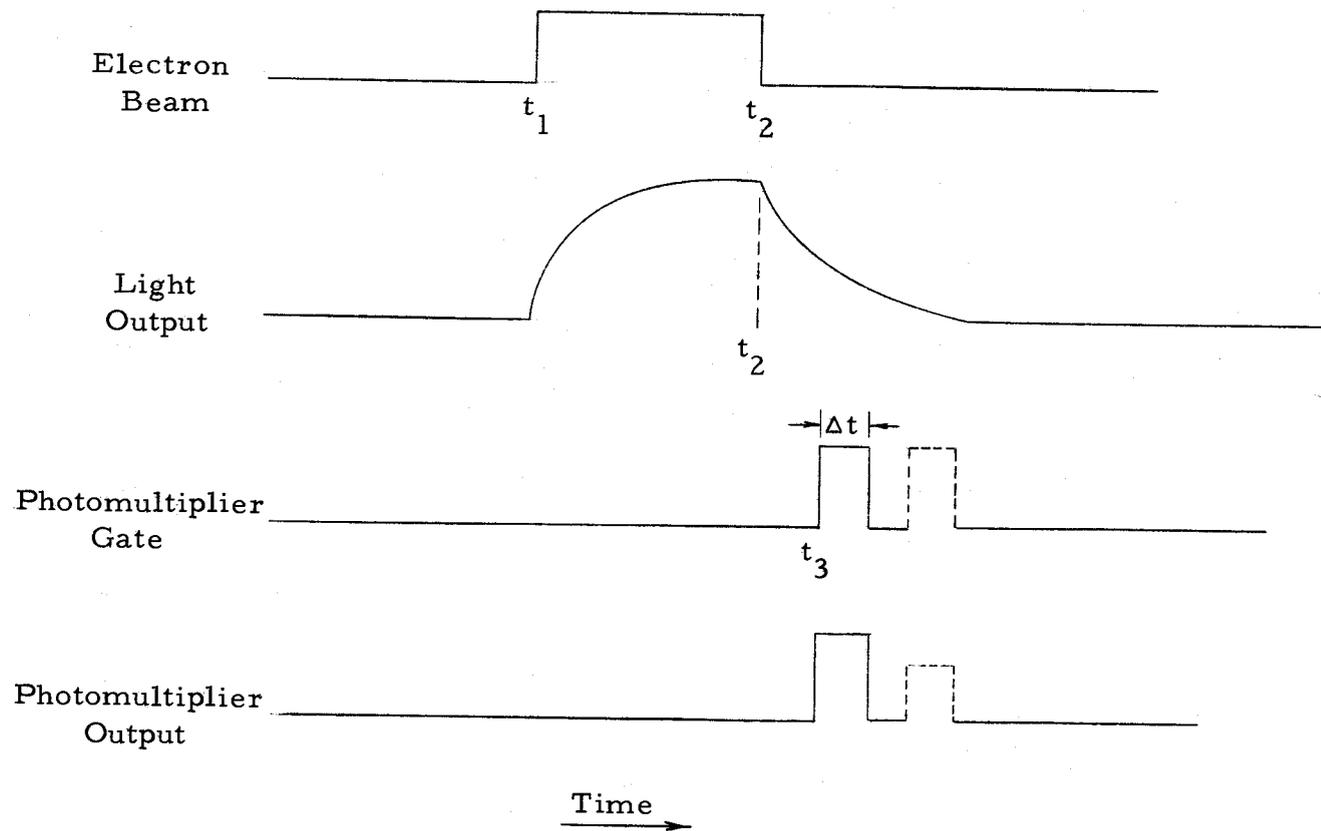


Figure 3. Sequence of events in one excitation - relaxation cycle using a pulsed detection system.

electron bombardment because both the excited levels of the cascade will be populated. This situation gives rise to a poor true to chance ratio with coincidence counting. A program similar to delayed coincidence can be used to measure an atomic lifetime by exciting only a single atomic level with electron bombardment and using the termination of the electron beam in place of that signal from the first step of a cascade (3). That is, if the signal which terminates the excitation is delayed and used to trigger the "gating on" of the photomultiplier, this becomes a type of delayed coincidence experiment. The sequence of events in this pulsing method is perhaps best explained by means of Fig. 3. At time t_1 the electron beam is turned on and atomic excitation begins. At t_2 the electron beam is turned off and the emission begins to decay in its characteristic fashion. After a delay, $t_3 - t_2$, the photomultiplier is gated on for an interval Δt . The repetition of this sequence of events a few thousand times per second gives a photomultiplier output which represents a single point on the decay curve. Thus increasing the delay of the photomultiplier gate in discrete steps ultimately produces a sufficient number of data points to represent the entire decay curve. A distinct advantage of this method is that the quantity being measured is a constant. That is, for a particular delay between the halting of production of excitation and the gating on of the photomultiplier, the cyclic excitation-relaxation process can continue as long as

desired. The quantity being measured is simply the average output current from the photomultiplier.

A conventional delayed coincidence method yields only a single output count when a coincidence occurs. However, with the modified method used here the desired information is the number of incident photons which are in coincidence with the "on time" of the photomultiplier. The gain of the photomultiplier is time dependent with a value of zero everywhere except within an interval of time Δt . Ideally the gain is time independent during the interval Δt . However, it is impossible to turn a photomultiplier on or off in zero time; thus it is necessary to determine how a gain which has finite rise and fall times will affect the photomultiplier output. Consider an exponentially decaying photon flux incident upon the photomultiplier. Let the photomultiplier be turned on at t_1 and turned off at t_2 . The incident intensity at ζ , where ζ is a time measured from t_1 , is given by the equation

$$I(\zeta) = Ae^{-\lambda t_1} e^{-\lambda \zeta}.$$

If $g(\zeta)$ describes the gain of the photomultiplier, the photomultiplier output in the interval ζ to $\zeta + d\zeta$ is

$$dR = \left(Ae^{-\lambda t_1} e^{-\lambda \zeta} \right) g(\zeta) d\zeta.$$

Thus the total photomultiplier output in the interval t_1 to t_2 is given by

$$R = Ae^{-\lambda t_1} \int_0^{t_2 - t_1} e^{-\lambda \zeta} g(\zeta) d\zeta.$$

But the definite integral is simply a number. Therefore the time t_1 may be varied, provided the time interval $t_2 - t_1$ is held constant, and the photomultiplier output will describe the incident photon flux. Additionally, if the background counting rate is small, it will be practical to use values of $t_2 - t_1$ much greater than $1/\lambda$.

DESCRIPTION OF APPARATUS

Orientation

The experimental method described in the previous chapter is directly applicable if the individual atoms in the excited state interact only with the zero point electromagnetic field. Interatomic interactions and multiple absorption and emission of individual photons give rise to mean lives which are different from the natural lifetimes. Although the method must be modified to accommodate these environmental effects, the apparatus modifications are minor; therefore, it is convenient to defer the detailed discussion of both environmental effects and apparatus modifications until a later time.

Figure 4 is a semi-schematic top view of the atomic excitation apparatus and photomultiplier. The electronics will be discussed separately. Atomic excitation is produced throughout a cylindrical volume (denoted by A in Fig.4) ten inches in height with an outer diameter of nine inches. The production of excitation is by impact with electrons from the cylindrically symmetric electron gun. The region between B and the outer wall of the excitation chamber is a field free region at ground potential. The pulsing limitations imposed by the transit time of the electrons across this field free region are discussed later. The argon gas within this

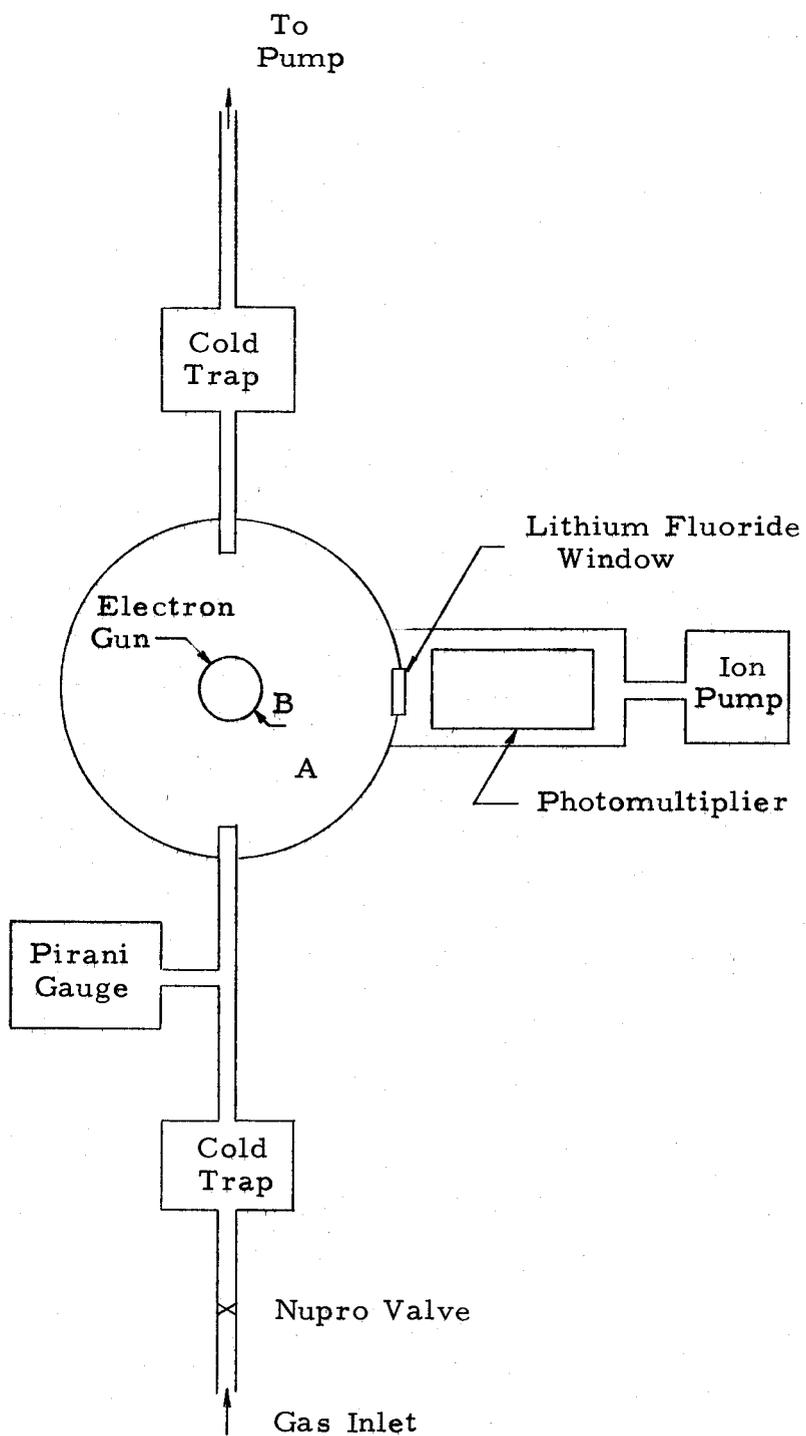


Figure 4. Semi-schematic view of the vacuum system.

excitation chamber is not static; instead, a slow molecular type flow of argon through the excitation chamber serves to reduce impurities arising from both external leaks and the oxide coated cathode. Further purification is obtained with the two liquid nitrogen traps shown.

Radiation from the excitation chamber is viewed by the photomultiplier through a thinly cleaved, one inch diameter lithium fluoride window. The properties of lithium fluoride are discussed in conjunction with the detection apparatus later in this chapter. At the moment it suffices to recognize that special windows are necessary to transmit extreme ultraviolet radiation. Since the particular photomultiplier used in this experiment has no intrinsic encapsulation, its vacuum chamber is built into the system. The vacuum requirements of the photomultiplier are such that it must be separated from the excitation chamber by either a window or by differential pumping. These vacuum requirements are satisfied by suspending the photomultiplier in an appendage vacuum system which is maintained at 10^{-6} Torr by a small sputter pump. The photocathode, which is a plane surface 0.2 inches by 0.4 inches, is centered immediately behind and parallel to the lithium fluoride window.

Gas Handling System

The gas handling system consists of the glass and rubber tubing and valves necessary to move gas from a supply tank through

the excitation chamber. The excitation chamber is protected from contaminants by liquid nitrogen traps. The gas flow throughout the system is slow enough that the excitation chamber is essentially at a uniform pressure. This pressure is measured with a Pirani gauge and is adjusted with a nickel plated Nurpro needle valve. The Pirani gauge has been calibrated with a McLeod gauge. The ultimate vacuum of about 10^{-3} Torr is set by leaks and forepump capability and an upper pressure limit of about 2×10^{-1} Torr is set by electron gun requirements. This pressure range was adequate for this experiment. For any value of pressure in this range, the Nurpro valve can be adjusted finely enough that the drift in pressure over a period of an hour is not of sufficient magnitude to be read with the Pirani gauge.

The excitation chamber is a thick-walled brass pot which has a removable lid. The removable lid is necessary for installation of the electron gun. Electrical connections to the electron gun are made through Stupakoff terminals soldered into the bottom of the chamber. Both the inlet and the outlet of the excitation chamber are of three-quarter inch diameter brass tubing. The volume of the chamber is between nine and ten liters.

The mechanical forepump used in this gas handling system is a Cenco, Hyvac 7. Throughout the pressure range of this experiment its pumping speed is less than one liter per second. This pumping speed together with the large volume of the excitation

chamber insures that the gas flow is slow with a uniform pressure throughout the excitation chamber.

Electron Source

The electron source consists of an indirectly heated cathode and grid assembly taken from a 6SJ7 electron tube. This electron tube is a sharp-cutoff pentode with a maximum rated cathode emission current under standard operating conditions of the order of 10 ma. Interruption and energy definition of the electron emission are readily accomplished with the conventional arrangement of this 6SJ7 grid system. The external grid of the grid system, which is approximately one-half inch in diameter, is held at ground potential together with the metal walls of the excitation chamber; therefore, there is a large field free region between the external grid and the walls. The energy of the electrons arriving in the field free region is defined by the potential difference between the grounded accelerating grid and the negatively biased cathode. The innermost grid is utilized as a control grid to pulse the electron emission. This central grid is biased to a sufficiently negative potential to prevent emission. The emission is pulsed by applying positive pulses of magnitude such that emission will exist during the duration of each applied pulse. The details of this pulsing are discussed in the section on electronics. The recommended heater voltage for this tube

is 6.3 volts; however, this rating is for normal use at a pressure of about 10^{-5} Torr. Because of the higher pressures in this experiment, convection cooling of the cathode is significant to the extent that an appropriate temperature for satisfactory emission cannot be maintained unless the heater voltage is raised to approximately ten volts.

Activation of Electron Source

A problem associated with an indirectly heated cathode is that of activation. When an indirectly heated, oxide coated cathode is exposed to air the free barium and strontium on its surface combine with various components of the atmosphere to produce hydroxides and carbonates. Heating in a vacuum will reduce these compounds to barium and strontium oxides. Further heating and the application of a field gradient will ultimately cause free barium and strontium to exist on the surface of the cathode; it is this situation which gives rise to the copious electron emission of indirectly heated cathodes.

Since no activation schedule was available for the indirectly heated cathodes from the 6SJ7 tubes, it was necessary to work out by trial and error, a method of reactivation. This method consists of starting with the cathode in the excitation chamber, which is evacuated to the limiting fore pump pressure of about 10^{-3} Torr.

The heater voltage is increased in discrete steps until its increase no longer gives a corresponding pressure increase in the vacuum system. This is interpreted as indicative that the breakdown of initial compounds to oxides is complete. At this time an accelerating potential of 25 to 50 volts is applied by biasing the cathode negative with respect to the grounded accelerating grid. The heater voltage is increased until emission begins. Under normal circumstances this final heater voltage is in the range of eight to ten volts for decent emission. When the electron emission is not being pulsed, the cathode normally stabilizes at an emission current of approximately 20 ma after 30 to 45 minutes. However, under pulsed conditions the mean emission current drops lower than expected to about four milliamperes.

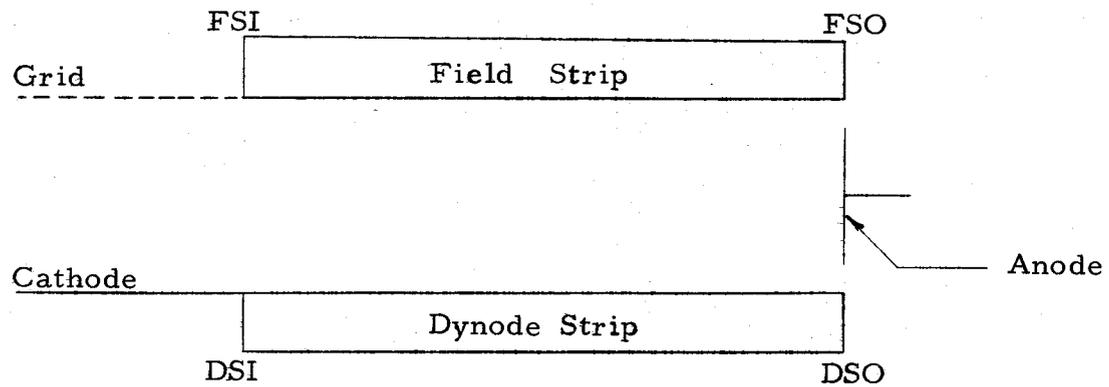
It was found that this same activation schedule could be used almost every time after exposure of the cathode to the atmosphere, thus allowing repeated reactivations of a single cathode. Ultimately either the heater would burn out or the cathode would become so contaminated that it could not be reactivated.

Detector

The photon emission from the excitation chamber, after passing through a thinly cleaved lithium fluoride window, is detected with a Bendix magnetic photomultiplier (20, 2). The physical

arrangement of the photomultiplier is schematically depicted in Fig. 5. Basically this photomultiplier is composed of a tungsten photocathode, a metallic grid which serves to give initial control of the photoelectrons, a high resistance dynode strip, a high resistance field strip, an anode, and a magnet assembly which is not shown. The magnet assembly is a structure of permanent magnets which provides a uniform magnetic field perpendicular to the plane of Fig. 5. Actually the grid is a section of the field strip and the photocathode is a section of the dynode strip. The entire assembly including the permanent magnets weighs only 2.4 ounces and is 2.43 inches long, 1.49 inches high, and 0.93 inches wide.

As in conventional magnetic multipliers, electron multiplication is controlled with crossed electric and magnetic fields; however, in the present device, the conventional series of individual dynodes has been replaced by the continuous surface of the high resistance dynode strip. The resistance of both the dynode strip and the field strip is of the order of 100 megohms. Appropriate adjustment of the strip voltages will cause the electrons to execute cycloidal motion and to gain energy during each cycle. For the maximum multiplier gain of approximately 10^7 , the potential difference across each strip is roughly 1800 volts. The maximum recommended output current of this device is 10^{-7} amperes because output currents greater than this value cause deposits to form on the high resistance



DSI - Dynode Strip Input

Figure 5. Physical arrangement of the Bendix magnetic photomultiplier.

dynode strip.

This photomultiplier is particularly suitable to this experiment because of its spectral response. Since the work function of the photocathode and the dynode structure is about 8.3 electron volts, none of the usual concern with regard to shielding the photomultiplier from visible light is necessary. The range of spectral response is that wavelength region from 1500A to 2A. Because of this range of sensitivity it is not necessary, as it is for a conventional photomultiplier, that a phosphor be used in front of the photocathode in order to view extreme ultraviolet radiation. Additionally, this large work function gives rise to an extremely low dark current.

For a conventional photomultiplier the gain can be controlled either by adjusting the potentials between dynode stages or by varying the number of stages. However, the Bendix photomultiplier has no fixed number of stages. Instead, the effective number of stages is fixed by the combination of the constant magnetic field due to the permanent magnets and the electric field between the high resistance strips (14). The gain per stage is, of course, determined by the potential gradient existing along the high resistance dynode strip.

Thus the change of the total gain of the photomultiplier will have a higher order dependence upon a change in the potential across the dynode strip than would a conventional photomultiplier. A process which makes use of this feature to pulse the photomultiplier gain

is discussed with the description of the electronics.

It has been mentioned that this photomultiplier does not have an envelope. However, in order to prevent gas multiplication, the region between the high resistance strips must be maintained at a pressure less than 10^{-5} Torr. The satisfaction of this requirement demands that the photomultiplier be separated from the excitation region by a window or by differential pumping. This is accomplished by attaching a small brass can six inches long and three inches in diameter to the exterior of the excitation chamber as an appendage vacuum system. The pressure is maintained and measured in this appendage system by a small one liter per second sputter pump. The photomultiplier is supported within the vacuum system by a teflon holder. The electrical connections are Stupakoff terminals which are soldered into the wall of the appendage system. The photomultiplier and its vacuum system are physically separated from the excitation region by a 25 mm diameter lithium fluoride window which is two millimeters thick. Lithium fluoride in crystalline form is the only mechanically stable window which will satisfactorily transmit the extreme ultraviolet radiation of interest here.

The absorption coefficient for lithium fluoride, which is shown in Fig. 6, increases very rapidly for wavelengths of less than approximately 1100A (27; 17, p. 25-27). The absorption characteristics of lithium fluoride are such that the combination of a lithium

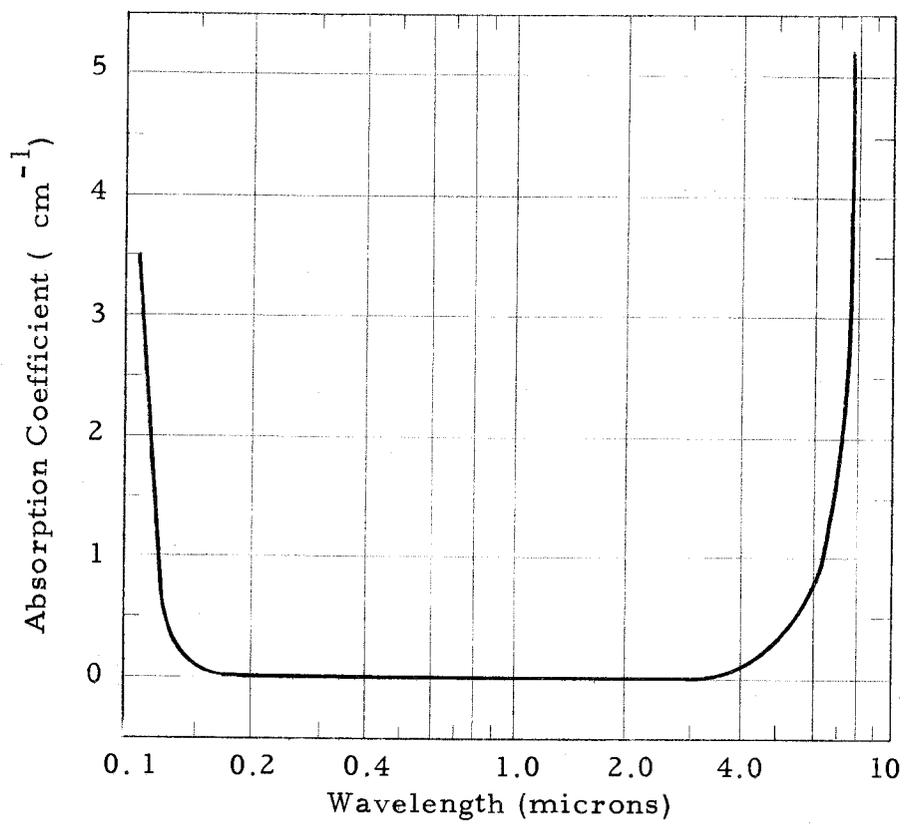


Figure 6. Wavelength dependence of the absorption coefficient of lithium fluoride.

fluoride window and the Bendix photomultiplier form a spectral filter whose passband is approximately 1500-1000A. The intermediate or non-resonance transitions in argon are all of wavelengths greater than 1500A and hence cannot be seen by the detection system because of the limited sensitivity region of the photomultiplier. However, although the photomultiplier is capable of responding to all the resonance transitions, only those lowest in energy, i. e., from the 4s levels, will be transmitted by the lithium fluoride window. Thus even if selective excitation were not used in this experiment, only the 1067A and the 1048A lines would be monitored by the detection system.

Electronics

Initially, when this experiment was begun, a pulsing system for the electron emission was designed such that the relaxation portion of the excitation-relaxation cycle would be only about two percent of the total cycle. Preliminary measurements of the lifetime of the argon resonance transition indicated that the lifetime was too long to allow use of this pulsing system; therefore, the system was replaced by a more conventional pulsing system. Since no quantitative measurements were made using the original pulsing system, it will not be discussed here.

In the discussions of the pulsing method used in this experiment,

the electronic requirements were discussed qualitatively. The quantitative demands upon the circuitry depend upon the magnitude of the lifetime being measured. A system designed to measure lifetimes as short as 100 nanoseconds proved to be adequate for this experiment. In addition to the electronics, the electron transit time across the field free excitation region is also a limitation upon the effective shut off time of the electron emission. In this experiment, the size of the excitation chamber is such that the transit time of ten electron volt electrons is about 5×10^{-8} seconds.

The energy of the electrons emitted from the cathode of the electron gun is fixed by the potential difference between the cathode and the grounded accelerating grid. The cathode emission is controlled by means of a control grid located, as indicated in Fig. 7, between the cathode and the accelerating grid. When the potential of this control grid is sufficiently negative with respect to the cathode, emission ceases. Pulsing of the emission is accomplished by applying to the control grid, in combination with the constant negative bias, a train of square waves so that emission exists within each cycle for the positive half of the square wave. The square waves are supplied by a conventional square wave generator which is capacitively coupled into the control grid. It is typically operated at 3000 cycles per second. The cathode emission is monitored by placing a small resistor in series with the cathode and displaying

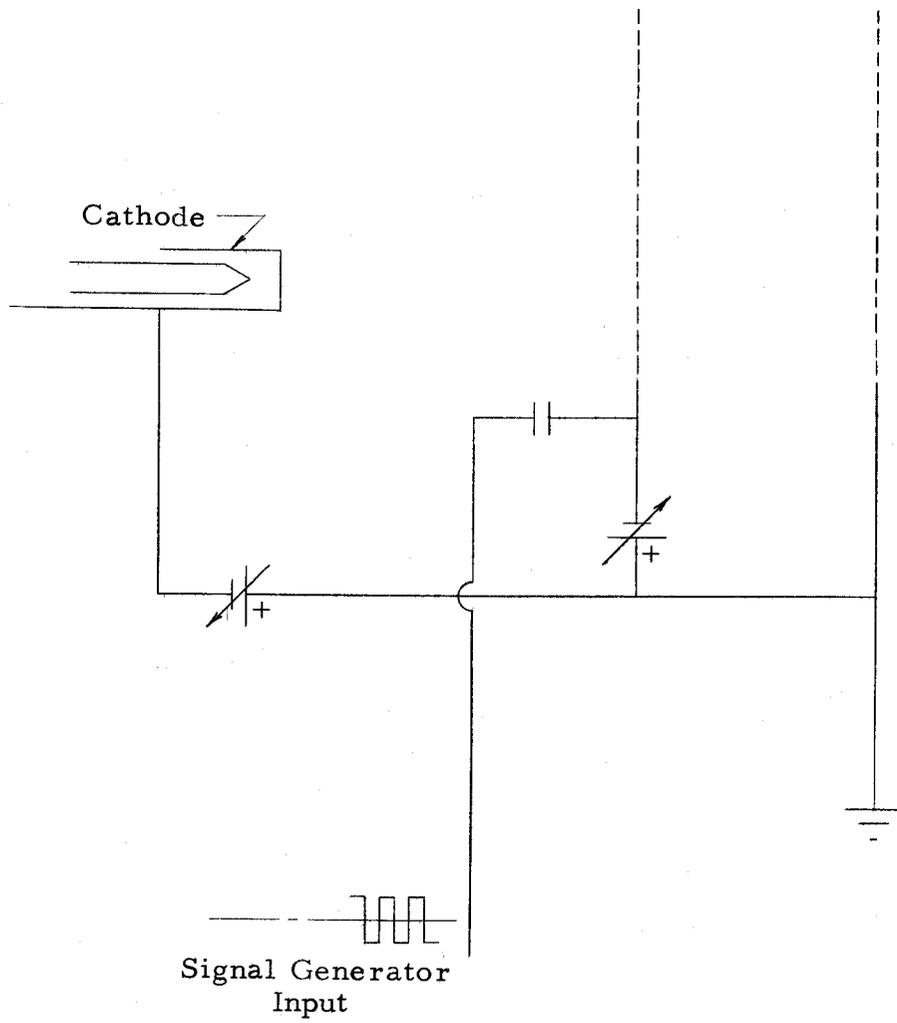


Figure 7. Schematic for pulsed electron emission.

the potential across this resistor on an oscilloscope.

The photomultiplier is pulsed in synchronization with the electron gun pulsing by means of the network indicated in block form in Fig. 8. The same square wave generator which pulses the electron emission supplies the trigger pulse to the pulsing apparatus for the photomultiplier. In preparation to operate the photomultiplier under pulsed conditions, the voltages on the high resistance strip terminals, except for the dynode strip input, are fixed at the values appropriate for DC operation. The potential on the dynode strip input is insufficient to give a measurable photomultiplier anode current. The pulsed operation of the photomultiplier is achieved by applying a 500-700 volt gating pulse to the dynode strip input. The excitation-detection cycle is repeated at 3000 cycles per second and the average photomultiplier current, which is of the order of 10^{-10} amperes, is measured with a Hewlett Packard DC microammeter. The delay between the termination of excitation and the gating of the photomultiplier is measured by displaying both pulses on an oscilloscope.

The gating network for the photomultiplier (18) is shown in Fig. 9. The variable delay of the photomultiplier gate is accomplished by means of the variable resistor in the input to the 2D21. The input trigger pulse to the 2D21 must reach a particular voltage value before this tube will fire. Since the input trigger has a finite rise time, there is a delay between the time the leading edge of the

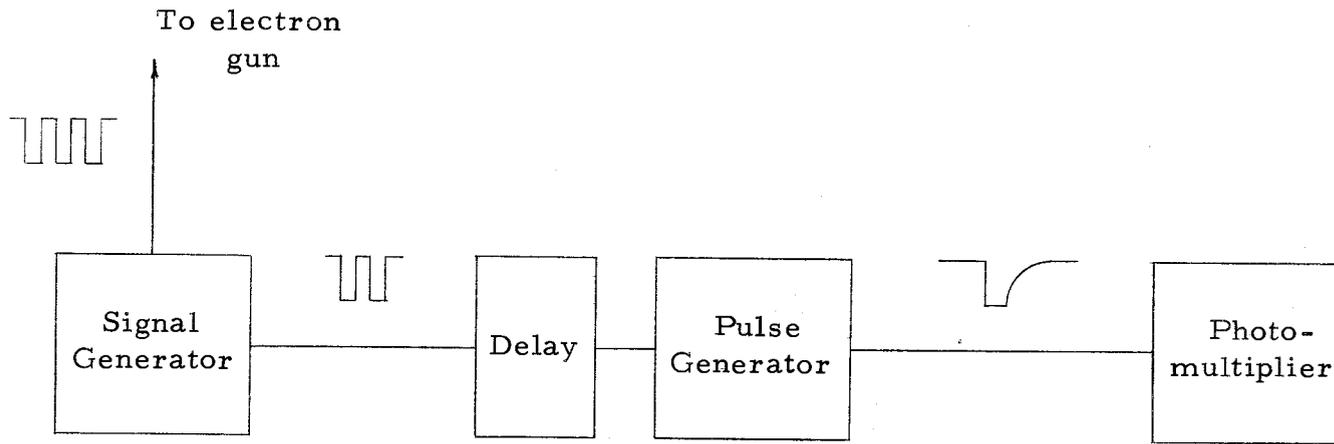


Figure 8. Block diagram representing the pulsing system for the method of modified delayed coincidence.

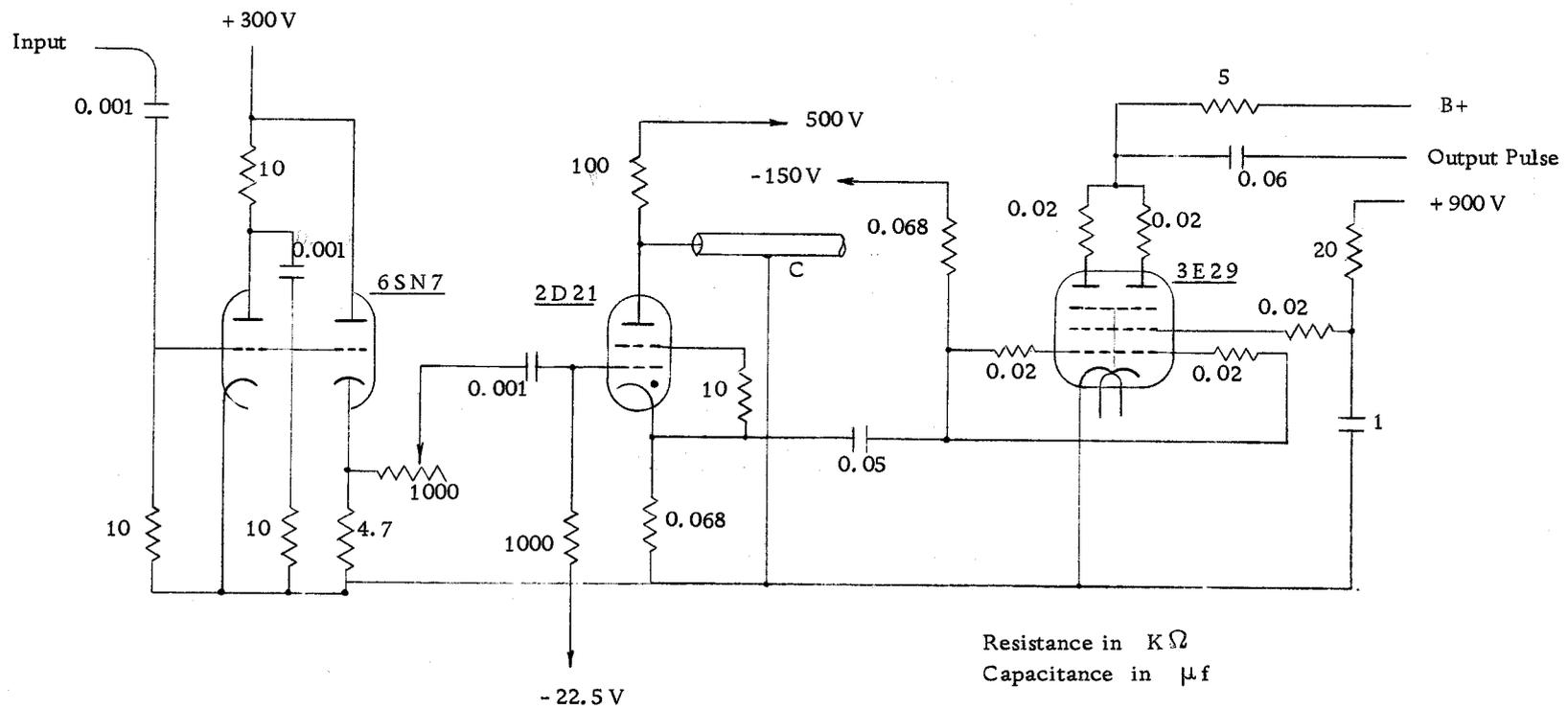


Figure 9. Circuit diagram of the pulsing network for the photomultiplier.

trigger is applied and the time the firing value is reached. By attenuating this trigger pulse, the delay can be varied. The duration of the output pulse is determined by the coaxial cable C. For this experiment the output pulse is maintained at its maximum value for 400 nanoseconds and then it tapers off with an RC curve such that its total duration is approximately one microsecond. As has been discussed, the observed decay is independent of the shape of the gating pulse.

It has been previously mentioned that the decay of the argon excitation is so slow that the decaying photomultiplier current can be displayed directly with a Tektronix 545A oscilloscope. With this direct display the electron emission is pulsed as discussed above and the photomultiplier is operated under DC conditions. The output from the photomultiplier is shunted to ground through a resistance, R, as shown in Fig. 10. The potential across the resistor is amplified with a Tektronix 1121 amplifier and is displayed with a Tektronix 545A oscilloscope. The amplifier and oscilloscope have rise times of 21 nanoseconds and 15 nanoseconds respectively. The sweep of the oscilloscope is triggered by the square wave generator which pulses the electron emission. The resulting data are photographically recorded.

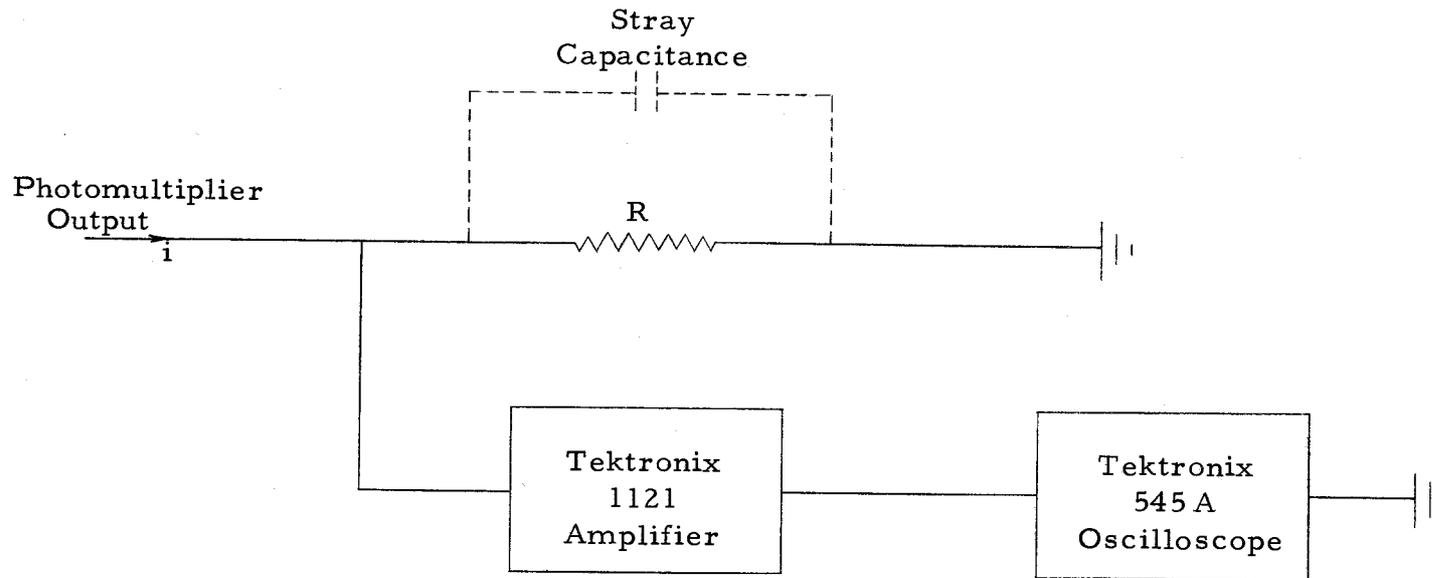


Figure 10. Representation of the circuitry for the direct display of the photomultiplier output.

ENVIRONMENTAL EFFECTS

General

As previously described, the application of the method and the apparatus of this experiment is restricted by the condition that, subsequent to the cessation of excitation by electron impact, radiative decay be the only process responsible for the change in concentration of atoms in the excited state. In practice this condition cannot be satisfied. Through interatomic interactions, excitation may be transferred to and from the state of interest; also, an individual photon may suffer several absorptions before it finally escapes from the excitation region. It will be shown that these two environmental effects do not alter the exponential form of the decay of excited state atoms, but that they do affect the duration of the decay. This circumstance, coupled with the particular dependence of these processes upon gas pressure and enclosure geometry, allows their effects to be individually observed. The natural lifetime for the excitation can be obtained by appropriate extrapolation of the measured lifetimes to zero pressure and to a zero volume excitation region. It is the purpose here to show how these processes, in the event that their effects cause the measured lifetime to differ significantly from the natural lifetime, will manifest themselves in the

experimental data.

Collisional Transfer

Collisional transfer is the process by which an atom in a particular energy level suffers an interaction with another atom and as a result of the interaction finds itself in an energy level different from its initial level. The transfer of excitation energy among the four states of the 4s multiplet in argon is the only type of collisional transfer which affects the lifetime measurement in this experiment. Transfer to kinetic energy, to the walls, and to other levels are of negligible effect. As has been mentioned, all four states of the 4s multiplet are excited by the electron bombardment used in this experiment. Since separations between individual members of this multiplet are approximately three times the average gas kinetic energy at room temperature, the 4s 3P_1 state will be simultaneously populated and depopulated by collisional transfer.

Because collisional transfer involves a collision of an excited atom with a ground state atom, the rate for this process must certainly be pressure dependent. The question which must be answered is whether or not it is possible to measure the radiative lifetime of a state whose population is also being affected by collisional transfer. If the total population density of all those metastable levels which can accept atoms from a particular radiative state through collisional

transfer is denoted by m , then the rate equation for the metastable population is

$$\frac{dm}{dt} = -amN_0 + bnN_0$$

and that for the radiative state is

$$\frac{dn}{dt} = -\lambda n + amN_0 - bnN_0.$$

The constants a and b include cross sections and relative velocities.

Rewriting these equations in operator notation gives

$$(D+aN_0)m = bN_0n$$

and

$$(D+\lambda+bN_0)n = aN_0m.$$

Premultiplying the second equation by the operator $(D+aN_0)$

gives

$$(D+aN_0)(D+\lambda+bN_0)n = aN_0(D+aN_0)m = abN_0^2n$$

or

$$\{D^2 + (aN_0 + \lambda + bN_0)D + a\lambda N_0\}n = 0.$$

The solution of this differential equation is the sum of two exponentials. If $\lambda \gg (a+b)N_0$, the solution reduces to

$$n \approx c_1 e^{-(\lambda+bN_0)t} + c_2 e^{-aN_0 t} \quad (2)$$

Thus when the effect of collisional transfer is small, the effective decay constant of the first term is just that representing the natural

lifetime and the decay constant of the second term is a linear function of pressure. By measuring this pressure dependent decay constant at a known gas pressure and temperature, the sum of the cross sections for collisional transfer can be obtained. Further mention of these cross sections will be made later. Additionally, it will be shown that the data in this experiment are adequately described by the approximate solution shown above.

Resonance Trapping

Resonance radiation emitted in an excitation volume escapes from this enclosure by diffusion, i. e., it is successively absorbed and re-emitted until it reaches the wall of the container and escapes. The initial theoretical development of the imprisonment of resonance radiation was begun by Milne (28) and Compton (7) using a type of kinetic theory model where all photons were assigned a common mean free path. In more recent papers, Holstein (21, 22) has shown that the concept of a photon mean free path is falacious because at any time, the resonance radiation has a non-uniform spectral distribution and over this distribution, the absorption coefficient of the gas is also non-uniform. Only the main features of Holstein's treatment will be given here.

The essential feature of the treatment by Holstein is the determination of the probability, $T(\rho, \nu)$, of a photon of frequency ν

traversing a distance ρ in the gas before being absorbed. The older treatments assumed a uniform absorption coefficient or equivalently a mean free path $\bar{\ell}$, so that $T(\rho, \nu)$ was independent of frequency and was given by the relation

$$T(\rho) = e^{-\rho/\bar{\ell}}.$$

Since, however, the absorption coefficient of the gas, $k(\nu)$, is a sensitive function of frequency, the monochromatic transmission factor takes the form

$$T(\rho, \nu) = p(\nu) e^{-k(\nu)\rho},$$

where $p(\nu)$ represents the frequency distribution of the emitted radiation. Thus the total transmission becomes

$$T(\rho) = \int p(\nu) e^{-k(\nu)\rho} d\nu.$$

Once $T(\rho)$ is known, equations can be set up describing the transfer of excitation between different volume elements of the enclosure. This description is achieved by an integro-differential equation whose general development is now considered.

Let $G(r', r)$ be the probability that a quantum emitted at r' is absorbed in a volume element dr around the point r . Denoting the concentration of excited atoms by $n(r, t)$ and utilizing the law of conservation of particles gives

$$dt dr \frac{\partial n(r, t)}{\partial t} = a - b,$$

where a and b are the increase and decrease in the number of excited atoms in a volume element dr in a time dt . For b the description is

$$b = \gamma n(r, t) dr dt,$$

where γ is the natural decay constant, and a is given as

$$a = \gamma dt dr \int n(r', t) G(r', r) dr'.$$

Thus the excited atom density is given as

$$\frac{\partial n(r, t)}{\partial t} = -\gamma n(r, t) + \gamma \int n(r', t) G(r', r) dr'.$$

For this integro-differential equation there exists solutions of the type

$$n(r, t) = n(r) e^{-\beta t}$$

with β and $n(r)$ satisfying the equation

$$\left(1 - \frac{\beta}{\gamma}\right) n(r) = \int G(r', r) n(r') dr'.$$

The quantity β is determined in principle from this expression by establishing a relation between $G(r', r)$ and $T(\rho)$. This relation can be shown to be

$$G(r', r) = -\frac{1}{4\pi\rho^2} \frac{\partial T(\rho)}{\partial \rho}.$$

It is apparent that the functional form of β will depend upon spectral line shape. For a general physical line shape the above integral can only be evaluated numerically. Even if the line shape is determined by a single broadening mechanism, only an approximate

solution can be obtained. Moreover, a solution can be obtained only in the approximation that trapping is fairly strong. The following solutions have been obtained:

$$\beta_{\text{Dop}} \propto \frac{1}{N \left[\ell_n A_p N \gamma \right]^{\frac{1}{2}}}$$

for a Doppler broadened line,

$$\beta_{\text{pres}} \propto \frac{\gamma}{\rho^{\frac{1}{2}}}$$

for a pressure broadened line, and

$$\beta_{\text{nat}} \propto \frac{\gamma}{(\rho N)^{\frac{1}{2}}}$$

for a natural line shape. The symbol N is the concentration of ground state atoms.

An interesting feature which appears is the predicted pressure independence of the effective decay constant when pressure broadening is predominant. This situation means that there is an effective saturation of trapping. Intuitively it can be seen that such a saturation effect should arise. As the pressure of the gas increases the total trapping should increase, however, an increase in pressure also causes a broadening of the emission spectrum. By itself the broadening tends to cause an increase in transmission since the absorption coefficient falls off away from the center of the line. In

the event an experimentally obtained value of the decay constant is pressure independent, this possibility of saturation of trapping can be checked by utilizing the dependence of β upon ρ , since ρ can be varied by moving the electron source within the excitation chamber. In the pressure range of this experiment, however, this saturation effect cannot arise because the natural line width completely overwhelms the pressure broadening. It can be shown (11) that the pressure width and the natural width are related by

$$\gamma_p = \frac{N\lambda_o^3}{(2\pi)^2} \gamma_N \quad (3)$$

With N taken at 10^{-1} Torr as 3.2×10^{15} atoms/cm³, this gives

$$\gamma_p \doteq 0.16\gamma_N$$

Thus in the event of observable trapping effects, within the pressure range of this experiment, the measured decay constant must appear as pressure dependent.

EXPERIMENTAL RESULTS

Origin of Radiation

This experiment was designed, due to the spectral discrimination built into the detection system, so that only resonance transitions from the 4s states, i. e., the singlet transition (1048A) and the intercombination transition (1067A), could give rise to a photomultiplier output. However, since direct spectroscopic identification of the radiation from the excitation region was not possible, it was necessary to perform a series of related measurements in order to identify this radiation.

Throughout the experiment the signal to noise ratio for the photomultiplier current was greater than a factor of 10^3 . The photomultiplier output, when the excitation chamber was filled with argon, was dependent upon the existence of energetic electrons within the excitation chamber, and it was nonzero only when the electron energy exceeded a particular value. The transition from zero photomultiplier output to a large output occurred over about a one volt change in accelerating voltage. This threshold value of the electron energy was determined by a standard Franck-Hertz type experiment utilizing a collecting plate and retarding potentials. A typical threshold curve appears in Fig. 11. The threshold curve is not particularly

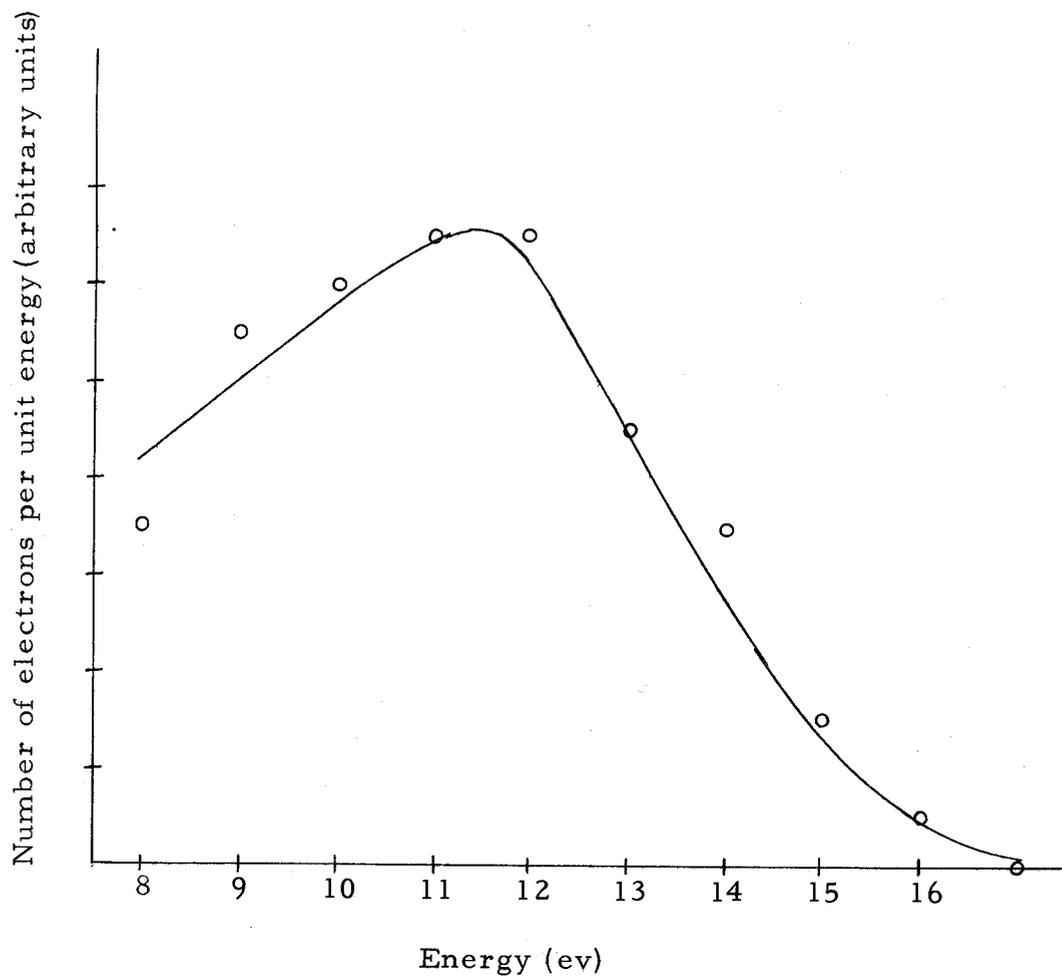


Figure 11. Threshold curve for Argon excitation.

well resolved, however, its maximum value definitely occurs at the appropriate energy for excitation of the 4s states.

Since, as will be discussed, the observed decay in argon could be consistently interpreted only if the observed radiation originated from a single state (instead of two states), it was finally necessary to attempt to make a spectroscopic identification of this radiation. This work was done with the vacuum spectrometer at the University of Washington. The initial efforts using the electron gun as a source of excitation gave no results. The intensity of the emission was simply too small to give photographic results in any reasonable period of time. However, the emission from excited argon was successfully observed spectroscopically by means of the apparatus in Fig. 12. A weak r-f discharge in argon at a pressure of one Torr was established such that a layer of ground state argon atoms $1-1\frac{1}{2}$ inches thick existed between the excitation region and the lithium fluoride window. For the particular circumstances of this observation, the r-f discharge was quite adequate for duplicating the excitation used in this experiment. The photographic records are shown in Fig. 13. The spectroscopic measurements leave no doubt that only the 1067A line is emitted from the excitation tube and that the 1048A line is missing in the emission. Since it is certain that the $4s^1P_1$ state is excited in this discharge, the absence of the 1048A line must be due either to a predominance of collisional deactivation of the $4s^1P_1$

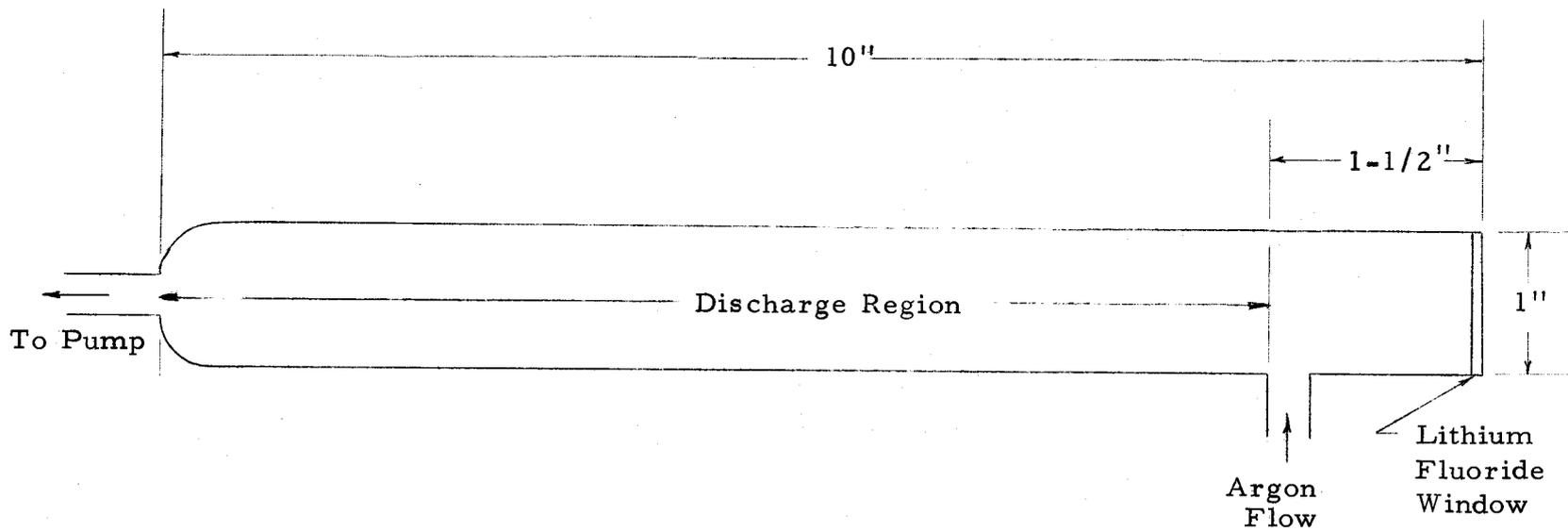


Figure 12. Top view of the discharge tube used for spectroscopic identification of the argon radiation.

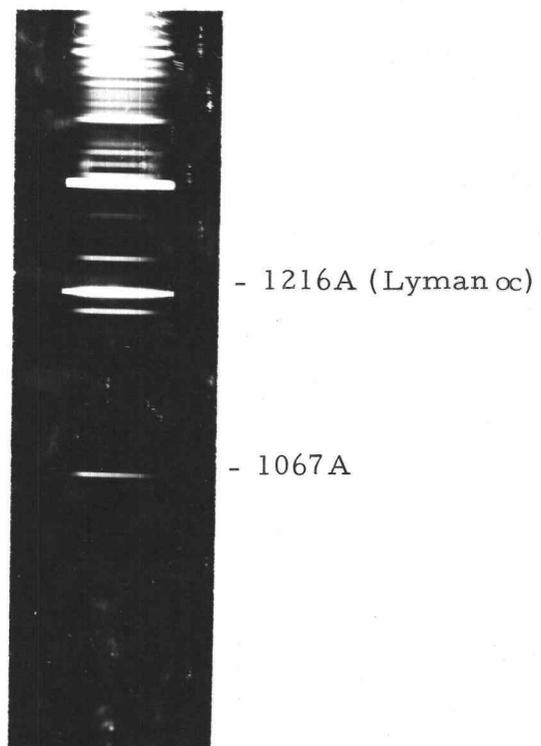


Figure 13. Spectrogram of argon emission.

state or to attenuation by the lithium fluoride window. The latter situation would require that the transmission coefficient of the window at 1048A be smaller by several orders of magnitude than its value at 1067A; such a situation is highly unlikely. Thus it is presumed that this radiation is trapped to the extent that a net depletion of the $4s^1P_1$ level concentration occurs only by collisional transfer. Since the degree of trapping obviously increases with decreasing natural lifetime, it is also speculated that the lifetime of the $4s^1P_1$ state is much smaller than that of the $4s^3P_1$ state.

Results from Direct Display

As has been mentioned, the initial data obtained using the modified delayed coincidence method indicated a lifetime which was so long that the decay could be displayed directly with an oscilloscope. Since data could be obtained easily and rapidly with direct display, this technique was used first. This technique is the less accurate of the two; therefore, the measurements were later repeated using the modified delayed coincidence technique.

With the direct display, the photomultiplier output appeared as shown in Fig. 14. Excitation occurred during the time interval t_A to t_B and relaxation occurred during the interval from t_B to t_C . In the discussion of this direct display method it was pointed out that the photomultiplier output could be displayed only by determining

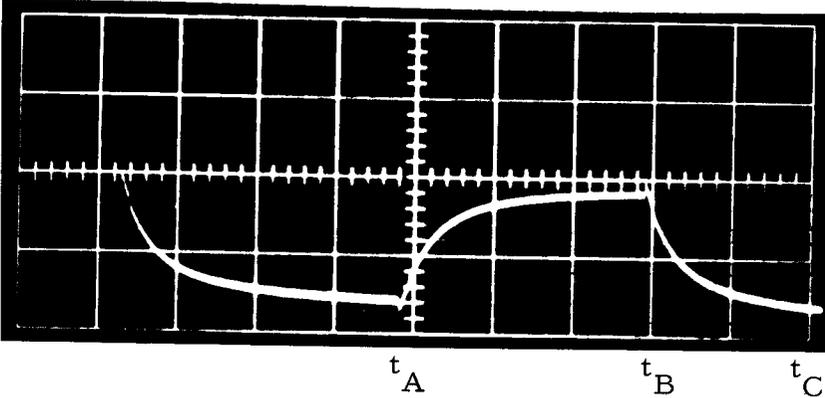


Figure 14. Oscilloscope trace of the argon decay.

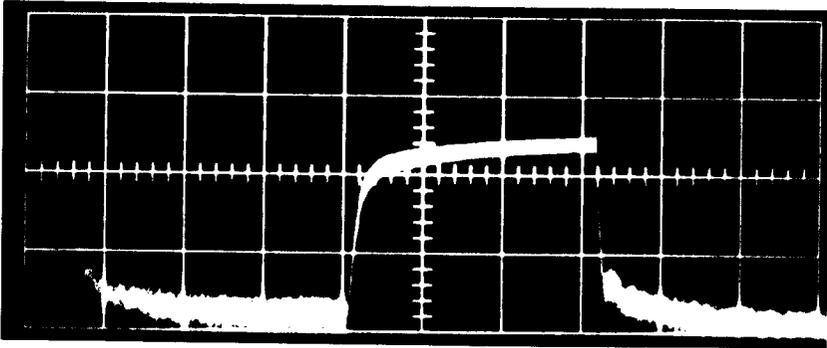


Figure 15. Oscilloscope trace of residual gas decay.

the response of a circuit to the output. This response has a finite RC time built into it. Because of this circumstance the possibility arose that the response time of the circuit was obliterating the time dependence of the photomultiplier output. This possibility was checked by introducing a gas other than argon in order to ascertain if a decay curve could be obtained which was fast with respect to that obtained in argon. Such a curve is shown in Fig. 15. Upon the basis of this result it was concluded that the display by the oscilloscope was representative of the decay of excitation in argon.

The pressure dependence of the relaxation time was initially investigated by means of this method of direct display. Due to amplifier noise only the first 15 microseconds of the direct display curves was quantitatively usable. The usable portion of these curves shows an exponential decay in all cases. The lack of pressure dependence is shown in Fig. 16.

Additionally the direct display method was used to investigate the possibility of resonance trapping occurring. This was done by varying the effective transmission distance through argon by both moving the electron source within the excitation chamber and introducing a collimating system in front of the detector. The observed lifetime of the decay failed to vary from its initial value.

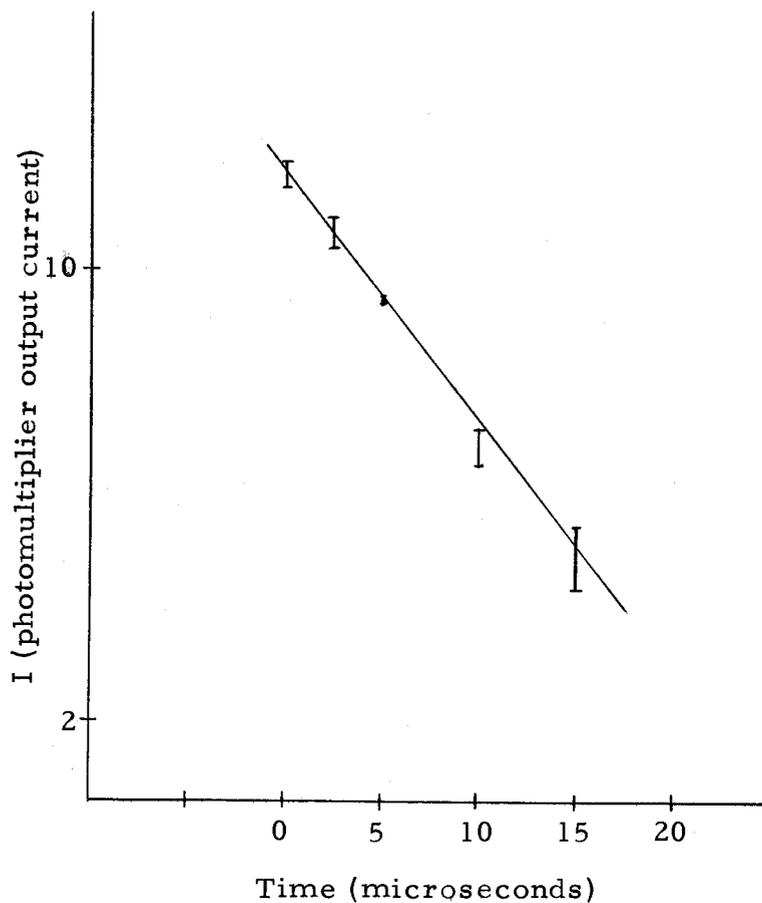


Figure 16. Semilogarithmic plot of the $4s\ ^3P_1$ decay. Direct display method. (Each data point has been determined at five different gas pressures over the pressure range from 30×10^{-3} Torr to 200×10^{-3} Torr. The error bars represent the scatter in these values at each data point)

Results With Modified Delayed Coincidence

The final measurements of the lifetime of the excitation were made using the modified delayed coincidence technique. These measurements were also made over a range of pressures. The superiority of the modified delayed coincidence technique allows the observation of the decay curve to extend over 40 to 45 microseconds. Over the extended observation period the decay was a composite of two exponential decays. The decomposition was effected graphically. The smaller of these lifetimes, i. e., the one which primarily affects the early portion of the decay was not dependent upon pressure and its value of 0.93×10^{-5} seconds is in rough agreement with that obtained by the direct display method. The longer lifetime was nearly inversely proportional to pressure and its value ranged from 1.4×10^{-4} seconds to 3.4×10^{-5} seconds over a pressure range from 3×10^{-2} Torr to 1×10^{-1} Torr. Figures 17, 18, and 19 display on semilogarithmic plots the raw data for three different gas pressures. Each plot shows a decay and the two components into which it can be separated.

Evaluation of Data

There arise from this experiment certain irrefutable results and there is a single consistent interpretation of these results. It was determined that the observed decay curves are characteristic

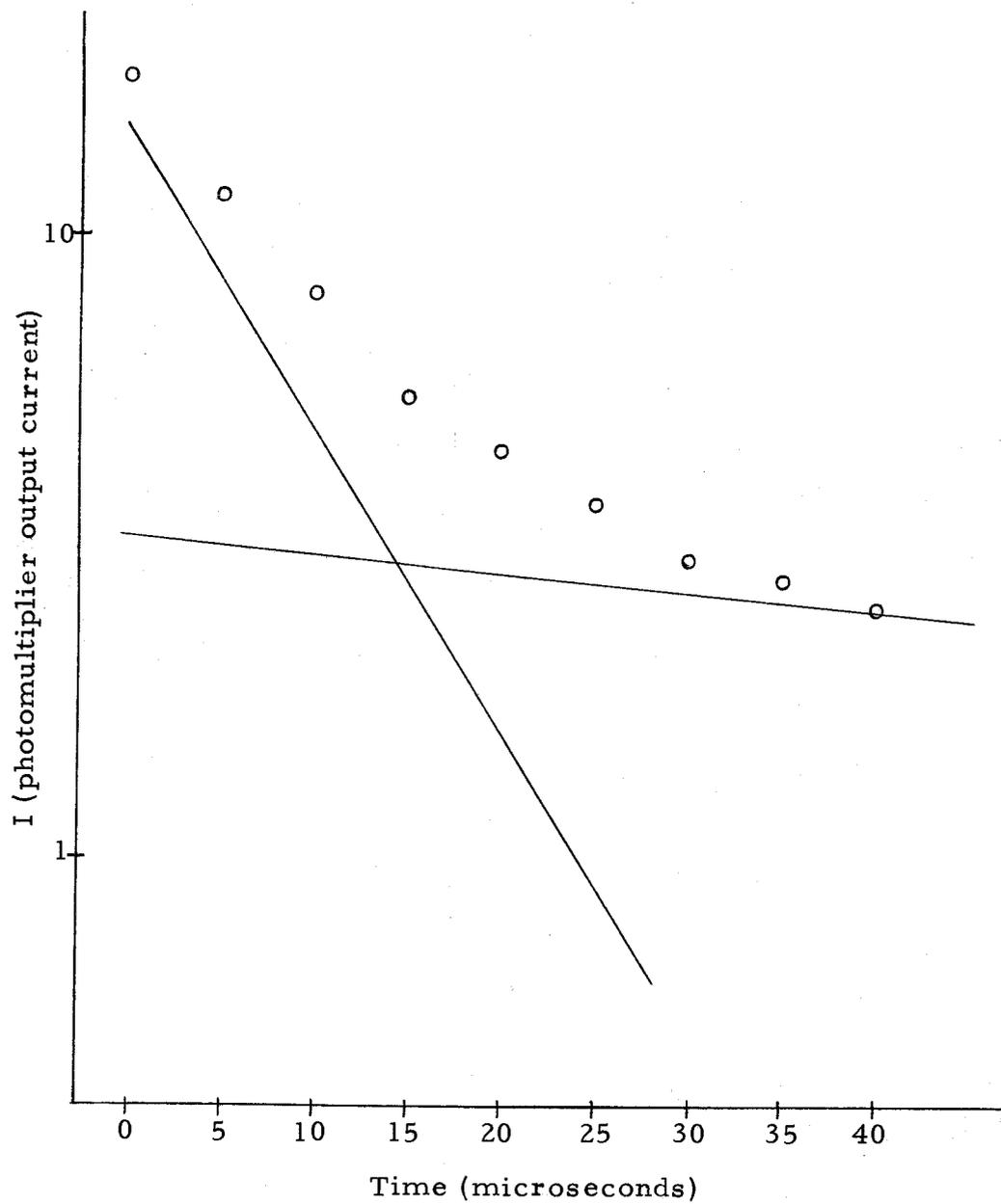


Figure 17. Semilogarithmic plot of the $4s^3P_1$ decay at 30×10^{-3} Torr. Pulsing method.

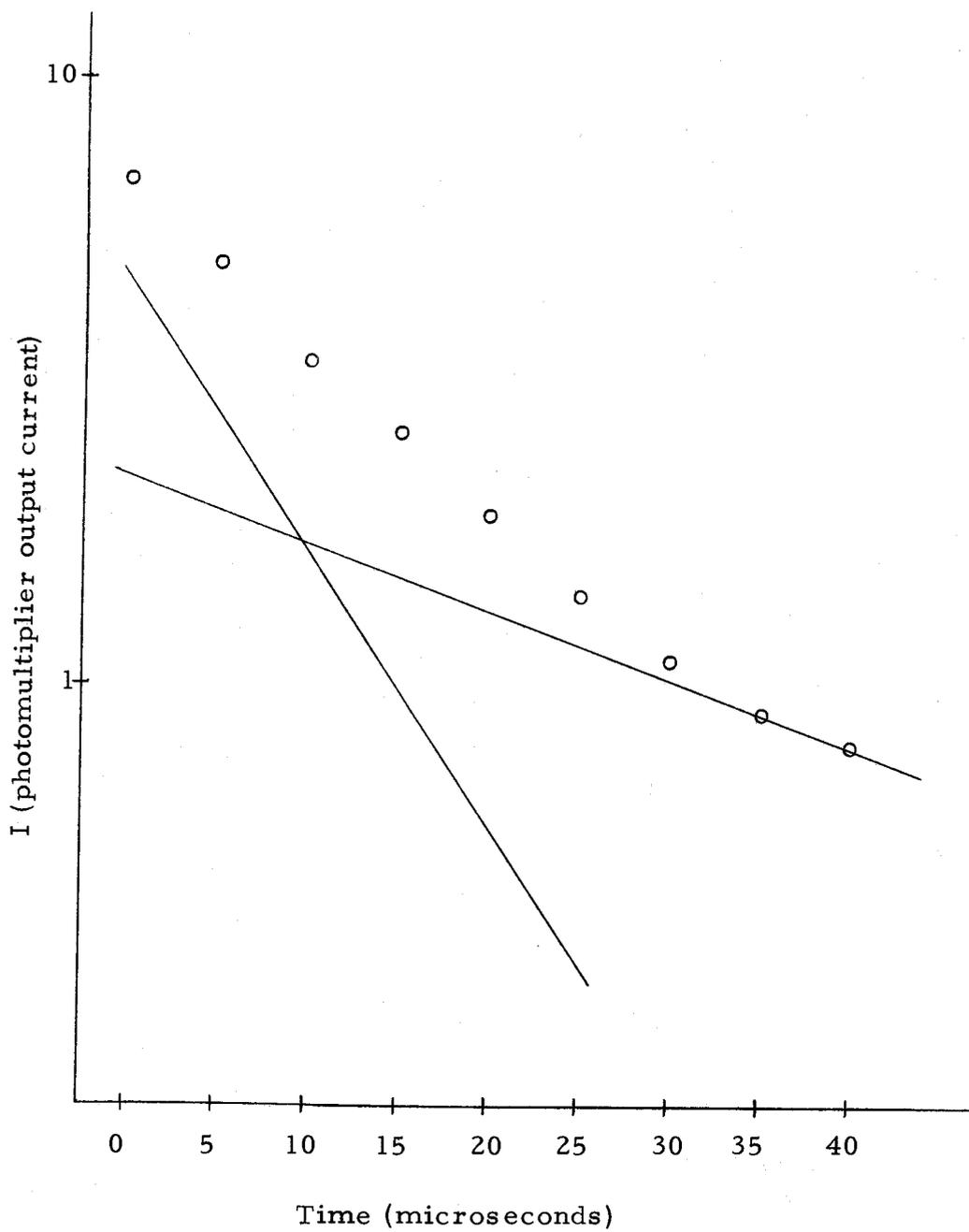


Figure 18. Semilogarithmic plot of the $4s^3P_1$ decay at 60×10^{-3} Torr. Pulsing method.

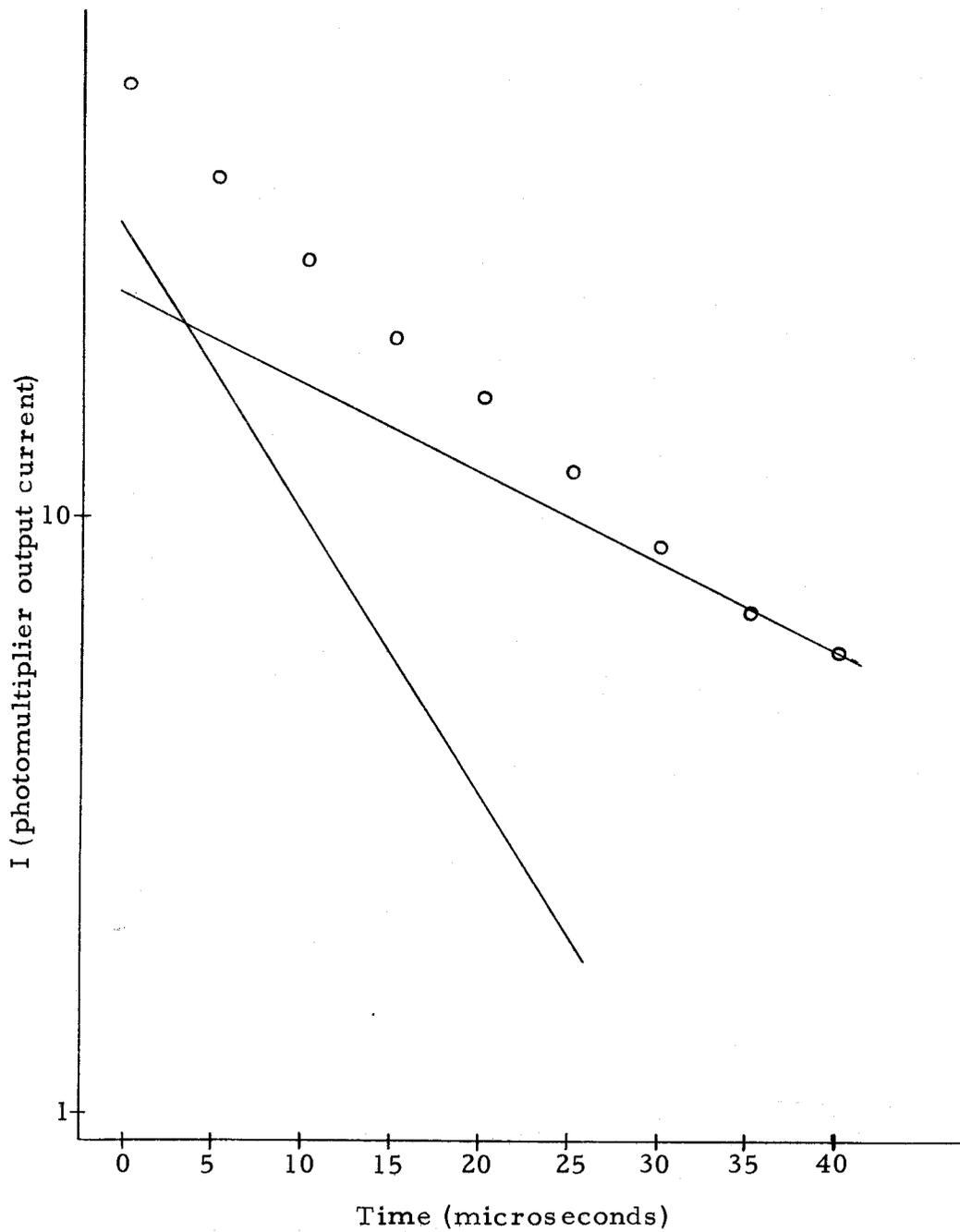


Figure 19. Semilogarithmic plot of the $4s\ ^3P_1$ decay at 100×10^{-3} Torr. Pulsing method.

of argon, and in particular, the observed radiation which gives rise to these decay curves arises from the $4s^3P_1-3p^6^1S_0$ transition. The next important feature is that the environmental effects which might cause a spurious lifetime to appear must in this experiment be pressure dependent. It is because of this feature that the appearance of a reproducible, pressure independent decay is extremely significant. This pressure independent decay represents the natural lifetime of the $4s^3P_1-3p^6^1S_0$ transition. This lifetime has a value of $(0.93 \pm 0.06) \times 10^5$ seconds. The assigned error of this value is the probable error obtained from a series of six determinations.

The pressure dependent component of the decay is assumed to result from collisional processes. These processes appear to be two body collisions giving rise to a collisional transfer of electronic energy between the 3P_1 state and nearby metastable states. From Equation (2), it appears that this pressure dependent decay constant will yield a transfer cross section. A measured decay constant of 1.4×10^{-4} seconds at a pressure of 3×10^{-2} Torr gives a cross section which is approximately 4×10^{-15} cm². The significance of this value has been of secondary importance in this work and has not been carefully studied.

DISCUSSION

Comparison With Theory

The transition probability for the $4s^3P_1-3p^61S_0$ transition of argon has been calculated by Knox (25). The value of the predicted lifetime is

$$\tau = 1.05 \times 10^{-8} \text{ seconds}$$

with an estimated error of 10 to 20%. The relatively strong dependence of such a calculation upon variations in radial wave functions has been discussed in the Introduction chapter. An additional complication arises with argon because the coupling of the angular momenta falls into neither of the two classes which are readily treated. For these two classes the terms which are regarded as perturbations in the calculation are quite different in magnitude. For light atoms the usual situation is that of the residual Coulomb term being large with respect to the spin-orbit interaction, and for this case the perturbation calculation yields LS wave functions. In the case where the spin-orbit term is large with respect to the residual Coulomb term, jj wave functions are obtained. The separation of energy levels within the 4s multiplet of argon indicates that here the residual Coulomb interaction and the spin-orbit term are of the same order of magnitude. Knox chooses to describe the final wave

function for each state as a mixture of LS wave functions. That is, the complete set of LS wave functions provide a basis set; thus any state vector can be written as a linear combination of LS wave functions. The 3P_1 state of argon is described by Knox as a sum of 4s triplet and singlet terms, i. e., configuration mixing is ignored. It is noted that the calculated lifetime of this state should be extremely sensitive to the amount of singlet term entering into its description.

The result of the present experiment disagrees by nearly three orders of magnitude with Knox's prediction. Using the predicted lifetimes, Knox has calculated a combined oscillator strength for the two allowed transitions from the $3p^5 4s$ configuration. The oscillator strength is related to the lifetime by

$$f = \frac{mc}{8\pi} \frac{g_u}{e^2 g_l} \lambda^2 \frac{1}{\tau}$$

where g_u and g_l are the statistical weights of the upper and lower states respectively. This calculated oscillator strength was compared to a combined oscillator strength determined upon the basis of a particular interpretation of dispersion experiments in argon (36). It was found that the predicted sum was ten times larger than the experimental value. Since this dispersion experiment yielded only oscillator strength sums, these results cannot be compared to the present experiment.

Relation to Other Experiments

The only published experimental results which can be compared directly with the results presented here are those of Vaughan and Stacey (35). Their experiment was designed to measure oscillator strength ratios. The method was one of determining pressure broadening of lines resulting from intermediate transitions which terminated on the 4s states. Using the relation between natural width and pressure width (Equation(3)) these results predict a lifetime for the $4s\ ^3P_1 - 3p\ ^6S_0$ transition of $(1.46 \pm 0.15) \times 10^{-8}$ seconds. The short letter in which this result was published did not contain enough information about the experimental method to permit its criticism.

An experiment by Kenty (24) supports indirectly the existence of a long lived resonance transition in both argon and neon. This experiment was a study of the diffusion of discharge products through their parent gases. It was concluded that radiation from at least one of the resonance transitions in both argon and neon was suffering almost no resonance trapping. Since a spectroscopic identification of this radiation was not made, Kenty could only speculate that in each case it originated from the first excited 3P_1 state. This information is sufficient to conclude that these states have lifetimes which are much longer than 10^{-8} seconds.

The result of the present experiment compares very well with

data obtained by Phelps and Molnar (31) in an investigation of the decay, by collisional transfer, of the metastable states of argon and neon. Metastable atoms were produced in a weak discharge and after cessation of the discharge, their decay was observed by measuring the absorption of line emission from a low pressure discharge. Although Phelps and Molnar discuss only the decay of the truly metastable $4s^3P_0$ and $4s^3P_2$ states in argon, they do present a decay curve for the $4s^3P_1$ state for a gas pressure of one Torr. This decay has a lifetime of about 4×10^{-4} seconds. Taking pressure and geometry into account this value is consistent with the predicted resonance trapping of radiation which has a natural lifetime of about 10^{-5} seconds.

Summary

For convenience the results of the studies reflecting upon the lifetime of the considered argon transition are listed in Table 1.

A calculation of transition probabilities for argon is beyond the scope of this work. It is assumed here that it is possible for approximate calculations to be in gross error either because the approximations are poor or because of a calculational error.

TABLE 1. Summary of lifetime values.

Author	Lifetime
Present Study	$(0.93 \pm 0.06) \times 10^{-5}$ seconds
Knox (25)	1.05×10^{-8} seconds
Vaughan and Stacey (35)	$(1.46 \pm 0.15) \times 10^{-8}$ seconds
Phelps and Molnar (31)	consistent with 10^{-5} seconds
Kenty (24)	indicated to be much greater than 10^{-8} seconds

Future Plans

The immediate plans are to extend these direct lifetime measurements to other noble gases. Those experiments which tend to support the long lifetime measured in this study of argon also indicate that a long lifetime exists for the comparable transition in neon. The present technique should work as well with other noble gases as it does with argon. In neon, krypton, and xenon the P^5 configuration of the first excited state gives rise to a multiplet in which there exists triplet terms and a singlet term. A determination of the lifetime of the allowed triplet transition for each of the noble gases is in effect a measure of the variation in coupling of angular momenta with increasing atomic number. Since it appears that the technique is also applicable to examination of collisional transfer cross sections, such measurements are also being anticipated.

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