Decay of Resonance Radiation in a Pulsed Discharge in Krypton

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(Received 24 May 1965)

The decay of resonance radiation λ1236 Å in the afterglow of a pulsed dc discharge in krypton has been measured as a function of time for krypton pressures between 0.2 and 6 Torr. The analysis of the decay curves is interpreted in terms of transitions involving the $1s_4$, $1s_5$ levels and the ground state. The decay time for the escape of resonance radiation has been measured and the radiative lifetime of the $1s_4$ level calculated to be 4.15×10^{-9} sec using the theory of radiation trapping due to Holstein. Previous interpretations of the decay of metastable atoms have been confirmed.

INTRODUCTION

In an experiment performed earlier,[1] hereafter referred to as I, the afterglow of a pulsed dc discharge in krypton was studied using an optical absorption technique. In that experiment the decay of the population of atoms in the $1s_5$ metastable level was investigated. A possible destruction mechanism for the metastable atoms was proposed in terms of two- and three-body collisions between a metastable atom and one or two ground state atoms. It was suggested that the metastable atoms were converted by such collisions to the $1s_4$ resonance level, from which level the atoms passed to the ground state by the emission and escape of resonance radiation λ1236 Å. The rate of decay of the $1s_4$ population under the conditions of the experiment is expected to be determined by the rate of escape of the trapped resonance radiation. Due to limitations in the time resolution of the apparatus used in I, it was impossible to do more than set an upper limit of 40 μsec to the decay time of the $1s_4$ population.

The present paper describes an apparatus and measurements designed to determine the decay time of krypton resonance radiation and thereby to test the destruction processes proposed in I. A value for the radiative lifetime of the $1s_4$ level was also sought.

The apparatus used in the experiment to be described was capable of measuring decay times in the microsecond region. The method of optical absorption used in I was abandoned in favor of the method of direct observation of the resonance radiation at λ1236 Å. This latter technique has the advantage of simplicity and is more suited to experiments where the densities of excited atoms are low. The most sensitive methods of determining optical absorption[2] are capable of measurements of fractional absorption down to 1 in 10^4. With the small densities of absorbing atoms encountered in measurements of excited atom populations, the maximum fractional absorption observed in an experiment may be only 1%, so that the signal is effectively measured to 10^{-4} in 10^{-2}, i.e. 1%. In the case of the direct observation of resonance radiation as described below, measurement of the signal to better than 1% was relatively easy.

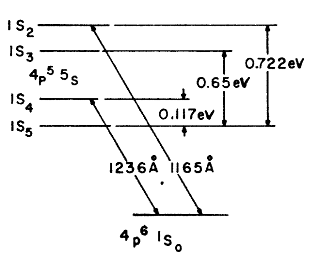

Fig. 1. Diagram showing the first four excited levels of krypton.

Further improvement of the present apparatus over that used in I was achieved by the inclusion of the M. K. S. Baratron pressure gauge, which made possible the determination of gas pressures to an accuracy of 0.001 Torr.

The value of experiments such as those described in the present paper lies mostly in the accumulation of data from which a sound theory can be built to explain the processes of energy transfer between atoms during collisions. The probability of a collision-induced transition should be related to the difference in energy between the initial and final atomic states and to the kinetic energy of the colliding atoms. No satisfactory theory expressing this relation yet exists. Moreover, the interpretation of experimental results is frequently complicated by the variety and complexity of competing processes. In the case of krypton, the situation is simplified by the relatively large energy gap between the two groups of levels comprising the first excited state (Fig. 1). The energy discrepancies are large enough so that the probability of collision-induced transitions between the lower pair of levels $1s_4$, $1s_5$ and the upper pair $1s_2$, $1s_3$ must be regarded as small compared with the probability of transitions within one pair of levels.

APPARATUS

The apparatus used to measure the population of $1s_4$ atoms at various times in the afterglow of a pulsed dc discharge in krypton is shown schematically in Fig. 2.

The discharge tube was excited by an 80-μsec pulse triggered by a "clock" oscillator at a frequency of

[1] D. S. Smith and R. Turner, Can. J. Phys. 41, 1949 (1963).

[2] A. V. Phelps and J. L. Pack, Rev. Sci. Instr. 26, 45 (1955).

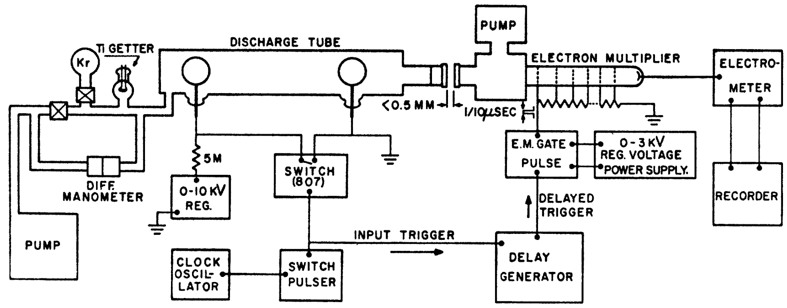

FIG. 2. Block diagram of apparatus.

about 1.8 kc/sec. Light from the discharge passed through lithium fluoride windows and was incident on the first dynode of a CBS 14-stage electron multiplier. (n.b. The short path travelled by the resonance radiation through air causes no significant attenuation of the signal.) The photoelectric current resulting from the ejection of electrons from the dynode material (AgMg) by ultraviolet photons was amplified in the multiplier and measured by the use of a Keithley 610A electrometer followed by a pen recorder. Time resolution was achieved by "gating" the dynodes of the electron multiplier at known times after the termination of the discharge-tube pulse. Depending on the decay times to be measured, the gate pulse on the electron multiplier dynodes was $\frac{1}{10}$ to 2 μsec long and up to 2.5 kV high. The times at which the gate pulses occurred were determined by the setting of the delay generator on the Tektronix 535A oscilloscope, which was triggered by the trailing edge of the electrical pulse used to excite the discharge tube.

The vacuum system to which the discharge tube was connected throughout the experiment was bakable to 450 °C. Ultimate low pressures in the order of 10^{-9} Torr were achieved. A titanium getter was used to keep the residual gas pressure down in the 10^{-9}-Torr range after the system was closed off from the diffusion pump. Gas samples were taken from a krypton isotope separating column. By taking the lighter fraction the xenon present in the original gas was eliminated. No trace of xenon was detected by spectroscopic analysis of the samples used in the experiments.

The discharge tubes were of two geometrical configurations, namely spherical and cylindrical. The tubes were fitted with lithium fluoride windows cemented on with AgCl via silver tubes.[3]

The electron multiplier (CBS type MS305), 14 stage, AgMg dynodes, hereafter called photomultiplier, was mounted in a stainless steel vacuum vessel having a lithium fluoride window. The pressure in the photomultiplier was maintined at approximately 10^{-7} Torr by continuous pumping with a getter-ion pump.

The circuit used to pulse the photomultiplier dynodes was similar to that described by Hendee and Brown.[4] The discharge tube was pulsed by a circuit which was designed to minimize drifts during the course of an experiment. A regulated 0–10-kV dc supply was connected to the discharge tube electrodes through a 5-MΩ resistor. The discharge was pulsed on and off by opening and closing a switch connected in parallel with the discharge tube. An 807 tube was used as a switch, giving a cutoff time of under 1 μsec. With this circuit, drifts of photomultiplier output were less than 0.2% during the course of an experiment. Other parts of the electronic circuitry were highly stabilized and their contributions to the drift of the output signal were negligible.

Measurements were carried out at a room temperature of 295±3°K. Power dissipated by the electrical pulse in the discharge tube was not expected to cause significant variation of the temperature of the discharge tube (see I).

EXPERIMENTAL DETAILS

When making measurements on the resonance radiation at λ1236 Å it is important to exclude other radiations which might activate the detector. The AgMg dynode used as a photosurface is insensitive to the visible end of the spectrum[5] and wavelengths shorter than about 1100 Å cannot pass through the lithium fluoride windows. A check on the emission spectrum of the discharge tube and the transmission of the lithium-fluoride samples used in the experiment was made with the aid of a vacuum spectrometer. It was found that the discharge light, after passing through one lithium fluoride window, was mainly λ1236 Å. No significant intensity of radiation at longer wavelengths was observed until the visible region of the spectrum was reached, while at shorter wavelengths only a small amount of radiation at λ1167 Å was detected. Also, one sample of lithium fluoride was tested and found to give a discrimination of three to one in transmission of λ1236 Å over λ1167 Å. Thus in the experiments described below, a check was made to detect effects

[3] P. C. Wildy, AERE (U.K.) Research Report, R. 3201, 1960 (unpublished).

[4] C. F. Hendee and W. B. Brown, Philips Tech. Rev. 19, 50 (1957).

[5] L. Dunkelman, J. Opt. Soc. Am. 45, 134, (1955).

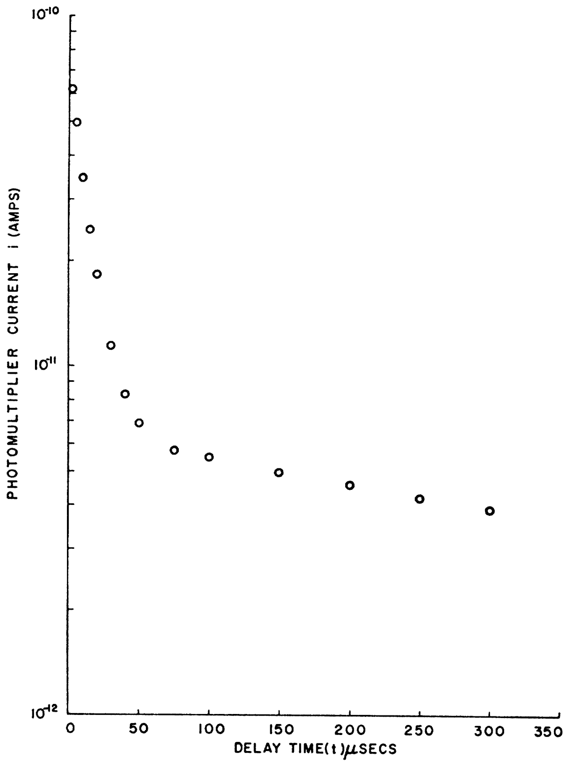

FIG. 3. Decay of resonance radiation. Spherical discharge tube. Krypton pressure 4.886 Torr. Discharge tube current pulse 1 mA peak.

from the only possible unwanted radiation which could produce a signal at the detector (namely that at 1167 Å) by making measurements with and without the tested sample of lithium fluoride between the discharge tube and the detector. Since no changes in the measured decay times were observed when the relative amount of 1167-Å radiation was reduced by a factor of three it was concluded that the signal from this radiation was so small that it could be ignored.

With regard to other unwanted signals at the photomultiplier output, it should be noted that the "dark-current" normally associated with photomultipliers is completely absent with the AgMg photon detector used here. It is therefore possible to measure output currents in the 10^{-13}-A range without interference from dark-current noise.

MEASUREMENTS

The output of the photomultiplier, being proportional to the intensity of the resonance radiation λ1236 Å emitted by the discharge tube, gives a measure of the population of resonance atoms in the discharge tube. The decay time (τ) of the resonance radiation was measured by recording the photomultiplier current (i) for various values of delay time (t). Such measurements were made at a variety of (fixed) pressures and with three discharge tubes, two cylindrical and the other spherical. A typical result is shown in Fig. 3 where log$i$ is plotted versus t. (The data shown in this figure were obtained using the spherical discharge tube, krypton pressure 4.886 Torr, discharge current 1 mA, photomultiplier gate pulse $\frac{1}{10}$ μsec long, 2.2 kV high.) Measurements were made at the values of t indicated by the points on the graph. The temperature and pressure in the discharge tube were kept fixed during the experiment. Measurements were made at a large number of pressures in the range 0.1 to 6 Torr, accurate values of the pressure (to 10^{-3} Torr) being obtained using the capacitance manometer mentioned earlier. From Fig. 3 it is seen that the decay curve shows an initial fast decay followed by a slow decay. A discussion of this effect is given below.

INTERPRETATION OF THE RESULTS

The excited krypton atoms in the afterglow may be destroyed in a variety of ways which will now be discussed. The destruction processes may be enumerated as follows:

(1) Collisions between excited atoms and one or two ground state krypton atoms.

(2) Collisions between excited atoms and other excited atoms.

(3) Collisions between excited atoms and electrons or ions.

(4) Collisions between excited atoms and foreign gas atoms (the Penning effect).

(5) The emission of radiation which escapes from the discharge tube.

(6) The diffusion of excited atoms to the walls of the discharge tube.

In the analysis given below, only processes 1, 5, and 6 will be considered "important." Processes 2, 3, and 4 have negligible effect for the following reasons:

Excited atom densities are too low for excited-atom—excited-atom collisions to be probable. Densities of metastable atoms and resonance atoms relative to ground-state atoms are estimated to be of the order 10^{-6} to 10^{-8}.

The cross section for collision between excited atoms and electrons is relatively high.[6] The best way to avoid the complication of such collisions and also of collisions with ions is to ensure that the densities of charged species is low. In the present experiment, measurements were made of the decay times for various values of current in the discharge tube during the exciting pulse. At currents of about 0.8–2 mA (peak pulse current) no current sensitivity of the fast decay was observed and the effect of the current on the slow decay was slight. The influence of discharge tube current was observed at higher currents (up to 10 mA) made by changing the discharge tube ballast resistor (Fig. 2). After final analysis, the results were seen to

[6] A. V. Phelps, Phys. Rev. **114**, 1011 (1958).

be independent of discharge tube current in the range 0.8–2 mA and therefore collisions between excited atoms and ions or electrons can be neglected.

Collisions with impurities were also made improbable by the use of ultrahigh-vacuum and gas purification techniques. As noted above, the krypton was obtained free from xenon by taking samples from an isotope separating column. No xenon could be detected spectroscopically. An attempt to pump any xenon into a detectable concentration was made using cataphoresis[7] but again xenon was not detected. In addition, a titanium getter was used to reduce the amounts of nonrare gases to a low level.

Consider now the more probable destruction processes numbered 1, 5 and 6. Collisions between excited atoms and ground state krypton atoms can induce a variety of transitions, but because of the large energy discrepancies involved, collision-induced transitions between the upper pair of levels, $1s_2$ and $1s_3$, and the lower pair of levels, $1s_4$ and $1s_5$, are ignored (see above and Fig. 1).

Because of the low probability of forbidden radiation, only resonance atoms are important in 5. In the case of diffusion of excited atoms, it has been shown that this effect is negligible for resonance atoms[8] and therefore only metastable atoms are important for 6.

The most probable destruction processes as discussed above are shown schematically in Fig. 4. R and M are the populations of the resonance level $1s_4$ and the metastable level $1s_5$ respectively. β represents the rate of escape of resonance radiation (β is a function of the geometry of the discharge tube) and the rate of loss of resonance atoms due to this cause is therefore βR. The probabilities per excited atom for collision-induced transitions are α_{RM} and α_{MR} for transitions $R\rightarrow M$, $M\rightarrow R$, respectively. Since these collisions involve ground state krypton atoms, α_{RM} and α_{MR} are therefore pressure dependent. The level of excitation is such that the ground state population is effectively constant at fixed pressure. The rate of loss of metastable atoms by diffusion to the walls is represented by α_d (α_d is inversely proportional to pressure).

The differential equations representing the rates of change in the populations R and M are then

$$\delta R/\delta t=-\beta R-\alpha_{RM}R+\alpha_{MR}M\,, \quad (1)$$

$$\delta M/\delta t=-\alpha_d M-\alpha_{MR}M+\alpha_{RM}R\,. \quad (2)$$

The equations can be solved, the general form of the solution being

$$R=Ce^{-t/\tau_1}+De^{-t/\tau_2} \quad (3)$$

with the values of $1/\tau_1$ and $1/\tau_2$ given by

$$1/\tau_1,\ 1/\tau_2=\tfrac{1}{2}[(\alpha+\gamma)\pm(\alpha-\gamma)\times\{1+4\alpha\alpha_{RM}/(\alpha-\gamma)^2\}^{1/2}], \quad (4)$$

[7] A. L. Schmeltekopf, Ph.D. thesis, University of Texas, 1962 (unpublished) and J. Appl. Phys. **35**, 1712 (1964).

[8] A. V. Phelps and A. O. McCoubrey, Phys. Rev. **118**, 1561 (1960).

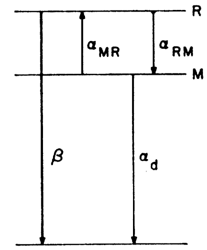

FIG. 4. Transitions between ground state, resonance level R and metastable level M during afterglow.

where

$$\alpha=\alpha_d+\alpha_{MR}\,, \quad (5)$$

$$\gamma=\alpha_{RM}+\beta\,. \quad (6)$$

Assuming that (see later)

$$4\alpha\alpha_{RM}/(\alpha-\gamma)^2\ll 1\,, \quad (7)$$

the solution becomes

$$R=Ce^{-\alpha t}+De^{-\gamma t}\,,$$

or

$$R=Ce^{-\alpha t}+De^{-(\alpha_{RM}+\beta)t}\,. \quad (8)$$

Considering the first term on the r.h.s. (right-hand side) of Eq. (8), we observe from Eq. (5) that α represents the loss processes for metastable atoms which have already been measured in I. Values of α obtained from the present experiment can therefore be compared with those obtained in I (from I, $\alpha\approx 10^2$).

In the second term on the rhs of Eq. (8), α_{RM} is pressure dependent. The variation of β with pressure can be calculated from theory. Using the work of Biberman and Gurevich[9] and Holstein,[10,11] it is estimated that in the region of pressures 10^{16} atoms/cc and above, the lifetime of trapped resonance radiation in krypton is determined by pressure broadening of the resonance line. Under such conditions the decay constant $\beta(r)$ for a cylindrical tube, radius r, is independent of pressure and is given by[6]

$$\beta(r)=(1/\tau_N)[0.205(\lambda/r)^{1/2}]\,, \quad (9)$$

where τ_N is the natural lifetime of the $1s_4$ state, and λ is the wavelength of the resonance radiation λ1236 Å. Using $\tau_N=10^{-8}$ sec in Eq. (9), $r=1$ cm gives an estimate of $\beta(r=1)\sim 10^5$.

The slow and fast decays in Fig. 3 are therefore explained in terms of Eq. (8) with the decay constants α and $\alpha_{RM}+\beta$ respectively, where $\beta=\beta(r)$ is the decay constant appropriate to the geometry of the discharge tube.

A. Slow Decay

A comparison may be made between the values of α obtained from the slow part of the decay (Fig. 3) in

[9] L. M. Biberman and I. M. Gurevich, Zh. Eksperim. i Teor. Fiz. **20**, 108 (1950) [English transl.: SLA RT-1635].

[10] T. Holstein, Phys. Rev. **72**, 1212 (1947).

[11] T. Holstein, Phys. Rev. **83**, 1159 (1951).

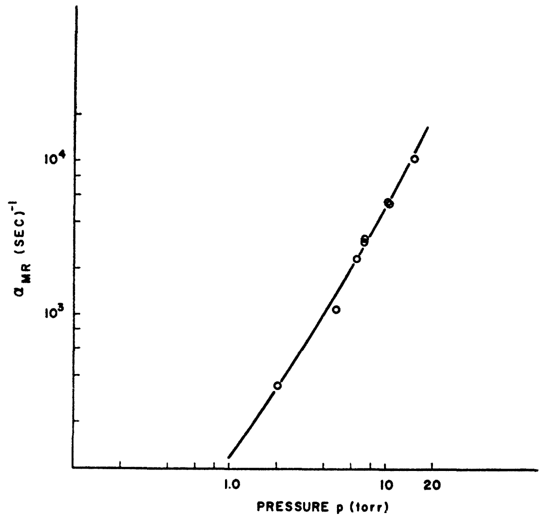

FIG. 5. Slow decay. Comparison of results from 1 (line) and present experiment (circles).

the present experiment and the expression $\alpha=30/p+75p+44p^2$ obtained from I.

Values of the slow decay constant were obtained from the graphs like Fig. 3 at large t where the effect of the fast decay is negligible. In order to include on the same graph measurements made with different discharge tubes, the part α_d has been calculated and subtracted from the measured α's. Thus in Fig. 5 the circles represent values of α_{MR} as obtained from the present experiment. These are compared with the line $\alpha_{MR}=75p+44p^2$ as obtained from I. The fit is seen to be good, lending support to the analysis advanced above.

B. Fast Decay

Having obtained the slow decay from the measurements at large t, the fast decay can be separated by subtraction of the slow decay from the measured points at small t. The graphs of the fast decay so obtained, plotted as $\log i$ versus t, were found to be linear over a wide range (see Fig. 6) showing that the observed decay curves like Fig. 3 can be represented by an expression which is the sum of two exponentials.

The values of $\alpha_{RM}+\beta$ obtained from the graphs of the fast decays at various currents and pressures have been plotted against pressure in Fig. 7 for three configurations of discharge tube, a sphere and two cylinders. The points marked by X were measured using Kr^{86} isotope (99% enriched). Other points were obtained using natural krypton. The reason for using krypton isotope will appear later. In Fig. 7, the three lines parallel to the pressure axis have been drawn to compare experiment with theory [Eq. (9)]. The discharge tubes used in the experiments were (i) a cylinder of radius 0.625 cm; (ii) a cylinder of radius 1.65 cm; and (iii) a sphere of radius 9.5 cm. Using an equivalent cylinder of radius $(1/\sqrt{2})\times 9.5$ for the sphere,[6] the ratio of the β's of Eq. 9 for the three discharge tubes is $1/2.02:1:1.62$.

The three lines are therefore separated by intervals of $1/2.02$ and 1.62. A good fit between the lines and the experimental points for the three discharge tubes is possible.

Since the coefficient α_{RM} represents the probability of collision-induced transitions, α_{RM} increases with pressure. Also, α_{RM} is independent of the geometry of the discharge tube. The absence of any indication of the measured decay constants with pressure (except in the case of the sphere) shows that α_{RM} is small compared with β at the pressures used in the experiments. Evidence of the effect of α_{RM} was observed at pressures over 3 Torr with the spherical discharge tube and further work is in progress to investigate the variation of α_{RM} with pressure and temperature.

The theory of resonance radiation trapping is complicated by considerations of isotopic and magnetic hyperfine structure. A decrease in β at lower pressures due to this effect has been calculated[6] to produce a minimum in the graph of β versus pressure in the case of neon. It was to eliminate the difficulties associated with hyperfine structure effects that the measurements with krypton isotope (mass 86) were made.

From Fig. 7 it is seen that the values of β obtained with natural and isotopic krypton are in good agree-

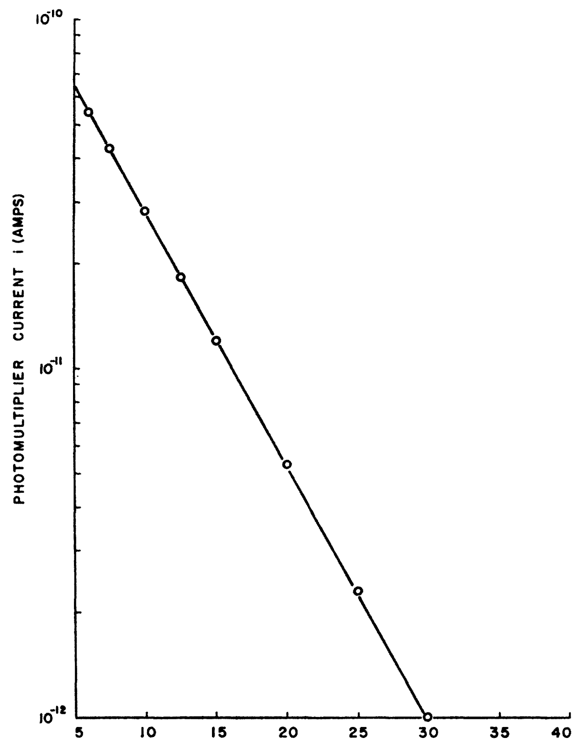

FIG. 6. Fast decay. Spherical discharge tube. Kr pressure 4.886 Torr.

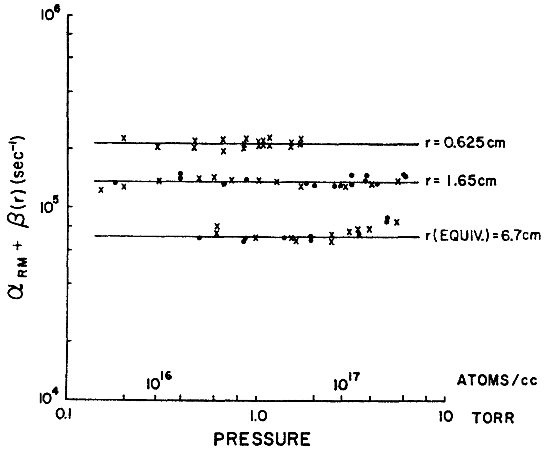

FIG. 7. Fast decay time as a function of pressure. Two cylindrical discharge tubes $r=0.625$ cm and $r=1.65$ cm and one spherical discharge tube r (equivalent) $=6.7$ cm.

ment and therefore the effects of hyperfine structure are negligible at the pressures used in the experiments.

JUSTIFICATION OF THE APPROXIMATION, (7)

Inequality (7) may be justified experimentally as follows. At a pressure of 1 Torr, we have that

α is of the order 1.5×10^2 (from I),

β is of the order 10^5 (Fig. 7),

and

$\alpha_{RM}<\beta$ (Fig. 7),

$$\therefore\quad \gamma\sim\beta\gg\alpha;$$

the left-hand side of (7) becomes

$$4\alpha\alpha_{RM}/(\alpha-\gamma)^2=4\times(\alpha/\beta^2)\times\alpha_{RM}$$
$$=(6.10^2/10^5)\times(\alpha_{RM}/\beta)=6.10^{-3}(\alpha_{RM}/\beta).$$

Since $\alpha_{RM}/\beta<1$, $6\times10^{-3}\alpha_{RM}/\beta\ll1$.

$$\therefore\quad 4\alpha\alpha_{RM}/(\alpha-\gamma)^2\ll1.$$

RADIATIVE LIFETIME OF THE $1s_4$ LEVEL

The relation between the radiative lifetime τ_N and the decay constant β of the resonance radiation is given (see above) by

$$\beta(r)r^{1/2}=(0.205/\tau_N)\lambda^{1/2}, \tag{9}$$

where r, λ are in cm and τ_N is in sec. The value of $\beta(r)r^{1/2}$ obtained from the results shown in Fig. 7, which represents an average of all the data taken in the experiment, is

$$\beta(r)r^{1/2}=1.73\times10^5 \text{ cm sec}^{-1}.$$

Substituting in Eq. (9) and with $\lambda=1.236\times10^{-5}$ cm, the value of τ_N obtained is

$$\tau_N=4.15\times10^{-9} \text{ sec}. \tag{10}$$

The radiative lifetime τ_N is related to the f value by the equation[12]

$$f\tau_N=(mc/8\pi e^2)\times(g_2/g_1)\times\lambda^2=1.499(g_2/g_1)\lambda^2, \tag{11}$$

where g_2 and g_1 are the statistical weights of the upper and lower levels respectively and λ is in centimeters.

For $\lambda=1.236\times10^{-5}$, $\tau_N=4.15\times10^{-9}$ sec, $g_2=3$, $g_1=1$, Eq. (11) yields $f=0.166$.

The sum of f values for the transitions between the $1s_4$ and $1s_2$ levels and the ground state has been measured by Geiger using electron scattering techniques.[13]

$$f(1s_4)+f(1s_2)=0.346\pm0.06$$

Thus by subtraction $f(1s_2)=0.180$.

CONCLUSION

The decay of resonance radiation in a pulsed discharge in krypton has been measured. Experimental results fit a simple theory which involves an interchange of atoms between the $1s_4$ and $1s_5$ levels caused by collisions of the excited populations with ground state krypton atoms. Trapping of resonance radiation occurs under conditions of pressure broadening of the resonance line. The theory of this effect and the experimental results are in agreement. The f value and radiative lifetime of the $1s_4$ level have been obtained.

[12] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1961).

[13] J. Geiger, Z. Physik **177**, 138 (1964).