Decay of the Triplet P Levels of Neon*

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The current and pressure dependence of the decay of the $^3P_0$ metastable level of neon was measured by using a light absorption method. The decay was found to be nonexponential and current dependent at normal excitation currents. At extremely low excitation current, however, the $^3P_0$ decay becomes exponential and current independent. The mean lives associated with such exponential decays were measured as a function of pressure. The results are in agreement with the usual theoretical relation based on metastable destruction by diffusion to the container walls at low pressure and two-body collisions at high pressures. The pressure dependence of the $^3P_2$ level was also studied. It was found, as previously reported by Grant, that the experimental results for the pressure range from 2 to 20 mm of mercury, where diffusion loss is small, do not agree with the usual theoretical prediction.

INTRODUCTION

THE first excited configuration of neon (Fig. 1) consists of a singlet P level, and two metastable levels ($^3P_0$ and $^3P_2$) separated by a radiating level ($^3P_1$). The energy separations of the triplet levels are of the order of $2kT$ at room temperature, so that possibly collision-induced transitions between these levels play an important role in their decay.

In the afterglow of an electrical discharge, atoms leave the metastable levels by the following processes:

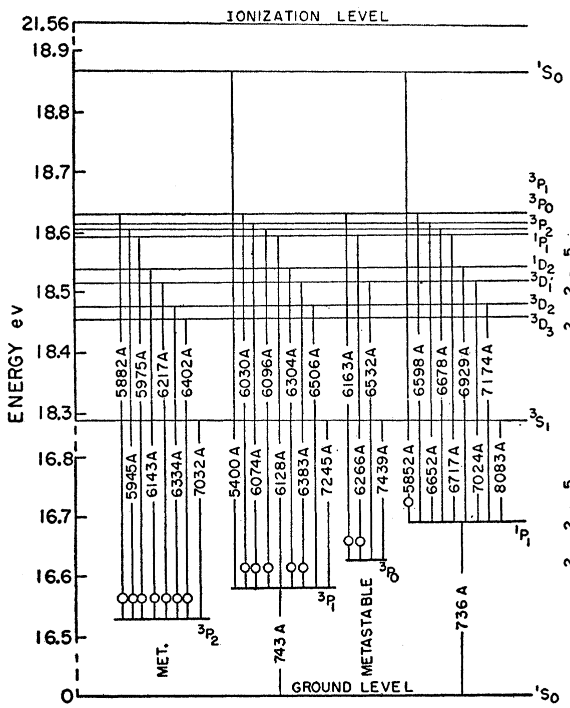

FIG. 1. Energy level diagram, first two excited configurations of neon.

(1) diffusion and complete de-excitation at the walls of the container; (2) the emission of forbidden radiation with a destruction frequency independent of the temperature and pressure; (3) the emission of radiation induced by two-body collisions; (4) transitions to a radiating level by two-body collisions; (5) ionization of impurities with an ionization potential less than the excitation potential of a metastable atom—the Penning effect; (6) the formation of metastable molecules by three-body collisions; (7) collisions of metastable atoms with ions and electrons early in the afterglow; (8) collisions between pairs of metastable atoms, and the ionization of one of them, also in the early afterglow.

Under the conditions of this research, processes (2), (5), (6), and (8) were not observed. Part of the present investigation was concerned with the conditions under which process (7) could be rendered unimportant.

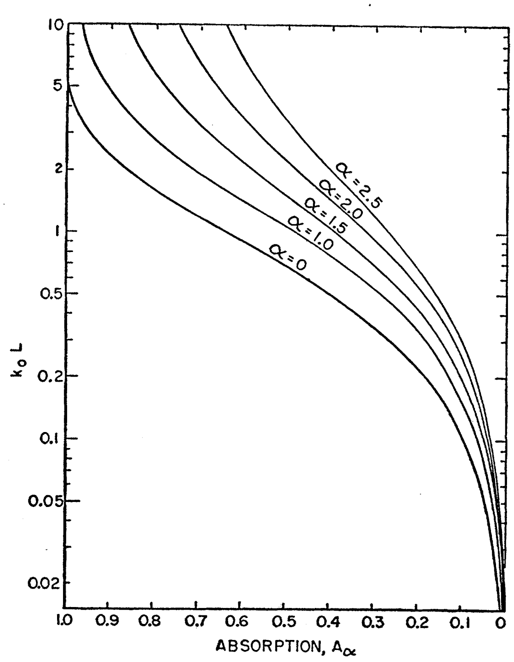

FIG. 2. k_0L *vs* absorption A calculated using Eq. (1), assuming various values of α.

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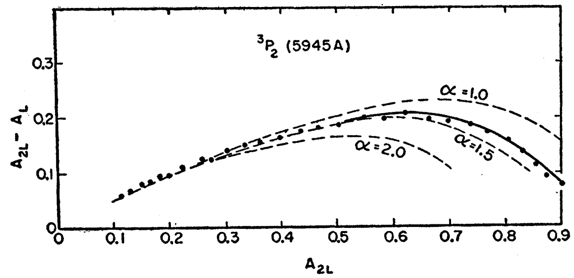

FIG. 3. $A_{2L}-A_L$ *vs* A_{2L}. The effect on the total light absorption of the doubling of the path length. Broken curves—calculated using Eq. (1); plotted points—obtained experimentally. $^3P_2$ metastable level. 5945 A spectral line.

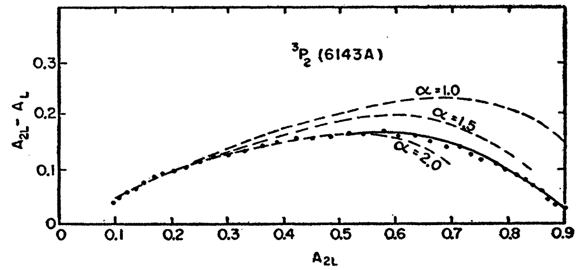

FIG. 4. $A_{2L}-A_L$ *vs* A_{2L}. The effect on the total light absorption of the doubling of the path length. Broken curves—calculated using Eq. (1); plotted points—obtained experimentally. $^3P_2$ metastable level. 6143 A spectral line.

Since resonance radiation is emitted in process (4), the effect of the imprisonment of resonance radiation must be considered. Under certain conditions, the effective mean life of the radiating level may be increased by a factor of several thousand.

OPTICAL ABSORPTION TECHNIQUE

Light from the "emission tube" traverses the "absorption tube" and then a monochromator, which rejects all but one neon spectral line. The light flux is then measured by a photomultiplier tube and the output displayed on a cathode-ray tube as a function of time. The relative absorption of the light beam is a measure of the population of the corresponding excited level in the absorption tube.

Experimental Determination of Effective α

When all except Doppler-type broadening of the emission and absorption spectral lines may be neglected, the relation between the absorption A_α and k_0L is given by the equation[1]:

$$A_\alpha=\frac{(k_0L)}{(1+\alpha^2)^{\frac{1}{2}}}-\frac{(k_0L)^2}{2!(1+2\alpha^2)}+\cdots, \qquad (1)$$

where k_0 is the absorption coefficient at the center of the absorption line, and L the path length. Provided that the population of the upper (final) level involved in the absorption transition is negligible in comparison with that of the lower (initial) level, k_0 is proportional to the density of the absorbing atoms. The quantity α is defined by the equation

$$\alpha=\text{(emission line breadth)}/\text{(absorption line breadth)}.$$

By using Eq. (1), the relation A_α *vs* k_0L has been calculated for various values of α and plotted in Fig. 2.

Although the average gas temperature was practically that of the walls of the container, the observed absorption *vs* k_0L relation was not consistent with a value of α equal to unity. Under most conditions, however, it was possible to describe this relation in terms of an "effective α" of 1.5 to 2.0, depending upon the particular spectral line used. No attempt was made to investigate the mechanisms responsible for the greater emission line breadth.[2]

The "effective α" was determined experimentally by measuring the absorption under otherwise identical conditions, for two path lengths L and $2L$. If the corresponding values of the absorption are denoted by A_L and A_{2L}, then the curve of $A_{2L}-A_L$ *vs* A_{2L} is characteristic of the corresponding value of α. The broken curves of Figs. 3 to 5 represent the relations calculated by using Eq. (1), assuming pure Doppler broadening, and taking values of α equal to 1.0, 1.5, and 2.0.

A doubling of the absorption path length was obtained by exciting the neon first in one half, and then in both halves of a three-electrode absorption tube. To ensure the same metastable atom density for corresponding measurements, the current pulse in the absorption tube was carefully controlled in amplitude and in time. The current pulse was of sufficient duration to enable equilibrium conditions to be achieved. All these measurements were made at equilibrium currents in the neighborhood of 15 milliamperes.

Our results indicated that up to $A_{2L}=0.80$ the lines 5882 A, 5945 A, 6217 A, 6334 A, and 6163 A may be described adequately in terms of a constant effective α. The corresponding values of this parameter were 1.4, 1.35, 1.4, 1.5, and 1.5, respectively. Above $A_{2L}=0.5$, the 6143 A, 6402 A, and 6266 A spectral lines cannot be described in terms of a constant effective α. The results for the 5945 A, 6143 A, and 6266 A spectral lines are plotted in Figs. 3, 4, and 5, respectively.

Effective α *vs* Absorption Cross Section

If k_0 is the absorption coefficient of a given spectral line, and M the density of absorbing atoms, then the absorption cross section k_0/M is a measure of the ability

[1] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1934), p. 323.

[2] K. Lang, Acta Phys. Austriaca **5**, 376 (1952) and Sitzber. österr. Akad. Wiss., Physik-math. Kl. **161**, 65 (1952), using a Fabry-Perot interferometer, has measured the half-width of a number of neon spectral lines as a function of pressure. His emission tube had an inside diameter of 1 mm, the same as that used in the present research.

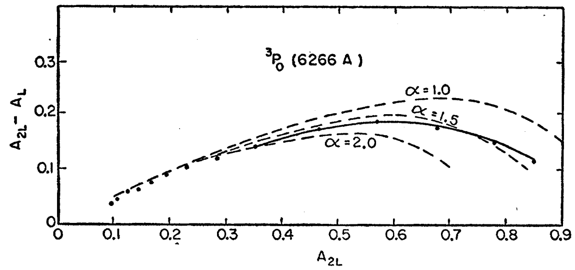

FIG. 5. $A_{2L}-A_L$ *vs* A_{2L}. The effect on the total light absorption of the doubling of the path length. Broken curves—calculated using Eq. (1); plotted points—obtained experimentally. $^3P_0$ metastable level. 6266 A spectral line.

of the atoms to absorb light of that spectral line. The absorption cross sections for the various sampling lines used in the study of the $^3P_2$ level have been calculated from the results of Ladenburg[3] and tabulated in the fifth column of Table I in order of increasing magnitude. A comparison of results of the type illustrated in Figs. 3 to 5 with the absorption cross sections of Table I showed that for absorption less than 0.5, the four lines having the smallest absorption cross sections have α of approximately 1.4, whereas the remaining two lines, having the largest absorption cross sections have α of about 2. Qualitatively, one would expect this result if the emission lines were broadened by self-absorption. A

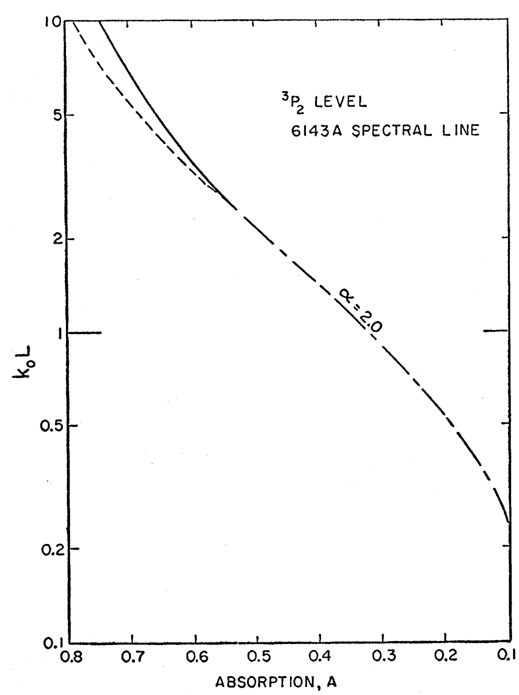

FIG. 6. k_0L *vs* absorption A. $^3P_2$ metastable level, 6143 A spectral line. Solid curve —— calculated using Eq. (1) and Fig. 2, which are based on the pure Doppler assumption. Broken curve – – corrected relation based on the experimental results of Fig. 4. Broken curve — – — coincident curves.

[3] R. Ladenburg, Revs. Modern Phys. 5, 251 (1933).

decrease in the effective α of the 6143 A and 6402 A spectral lines at higher values of k_0L would also be expected as the result of this mechanism.

Upon using the foregoing results, it becomes possible to adjust the absorption *vs* k_0L curve for the 6143 A spectral line to compensate for the variation in effective α. In Fig. 6, the solid curve is the absorption *vs* k_0L relation calculated for $\alpha=2$; the broken curve was calculated by making the appropriate correction for the observed variation in the effective α at higher values of absorption as obtained from Fig. 4. The improved decay curves obtained from the use of the curve of Fig. 6 are shown in Fig. 7. The circles represent the values of k_0L obtained when a constant α equal to 2 was assumed. The crosses represent the values obtained from the use of Fig. 6, which includes the effect of the variation in effective α for the 6143 A spectral line.

The absorption of the 5945 A line is characterized by a constant "effective α." For this reason the corresponding data for this spectral line are included in Fig. 7

TABLE I. $^3P_2$ metastable densities calculated by using data from various sampling lines.

Sampling line (angstrom units)	$M/(k_0L)$ (atoms/cm³) $L=120.5$ cm	$(k_0L)_t$ $t=10$ msec $L=120.5$ cm	M (atoms/cm³) $t=10$ msec	Absorption cross section k_0/M (cm²/atom)
6217	83×10^8	0.170	14×10^8	1.0×10^{-12}
5882	71×10^8	0.215	15×10^8	1.2×10^{-12}
5945	51×10^8	0.375	19×10^8	1.6×10^{-12}
6334	34×10^8	0.675	23×10^8	2.4×10^{-12}
6143	24×10^8	1.05	25×10^8	3.4×10^{-12}
6402	8.3×10^8	3.00	25×10^8	10.0×10^{-12}

to show that the decay of the $^3P_2$ metastable level under the specified conditions is indeed exponential.

Dependence on Spectral Line—$^3P_2$ Level

In Fig. 8 the decay curves of the $^3P_2$ metastable neon level have been plotted from the results obtained from the use of the 6402 A, 6143 A, 6334 A, 5945 A, 5882 A, and 6217 A spectral lines. The results agree within five percent, which is the limit of the experimental error.

Calculation of Metastable Atom Density

The density of the $^3P_2$ metastable neon level was calculated using the absorption cross sections of Table I. The numerical values tabulated in the fourth column of Table I refer to the density ten milliseconds after the cessation of the excitation. The reason for this choice was that the absorption has then fallen into the region where the decay may be described in terms of a constant "effective α."

The calculated value of the metastable atom density appears to depend upon the choice of spectral line, unless it is assumed that the Ladenburg transition probabilities used in the preparation of the fifth column of Table I are in error.

CURRENT DEPENDENCE OF THE DECAY OF THE TRIPLET P LEVELS

To investigate the current dependence of the decay of the triplet levels of neon, currents through the absorption tube were measured and monitored using the method described above. The recorded values of current refer to the amplitude of the absorption tube pulse immediately prior to the interruption of the excitation.

$^3P_0$ Level

By using the previously described method, the relation between the absorption A and k_0L was determined experimentally for the 6266 Å spectral line (Fig. 9). The decay curves were then measured for various values of the excitation current. Some of these curves are plotted in Fig. 10.

For large values of excitation current, the decay is characterized by an early fast decay and a current independent slow decay. The current-dependent component is seen to disappear completely for excitation currents below 0.5 milliampere, and under these conditions the decay is exponential.

The experimental results suggest that the fast component of the decay is due to the effect of the electrons and positive ions left over from the absorption tube excitation pulse. When this current pulse is large, the metastable atom decay is further complicated by the relaxation of the gas temperature in the early afterglow. We have ruled out the collisions of pairs of metastable atoms as the dominant mechanism in the fast decay

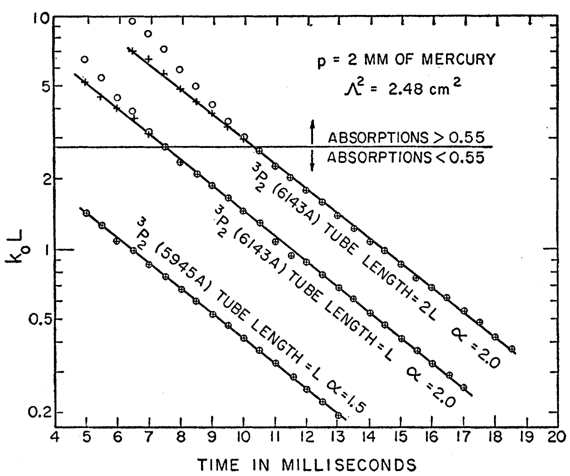

FIG. 7. Experimental data illustrating the breakdown of the "pure Doppler" assumption. Circles—experimental data transformed using the "pure Doppler" relation, Eq. (1) and Fig. 2. Crosses—experimental data transformed by means of the corrected curve of Fig. 6.

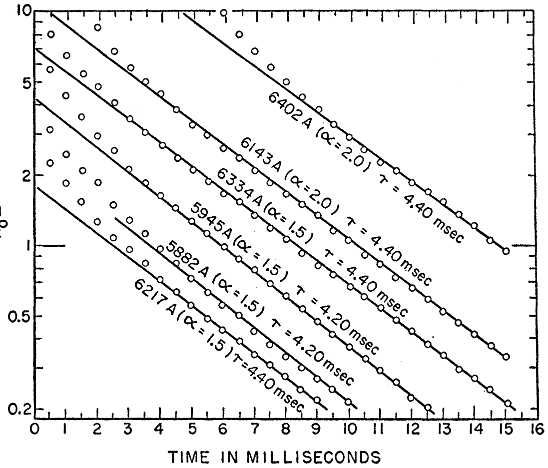

FIG. 8. Decay of the $^3P_2$ metastable level of neon as determined by various sampling lines under identical experimental conditions.

because the 0.5-milliampere curve, which has no fast-decay component, crosses the 30-milliampere curve.

$^3P_1$ Level

Similar results obtained for the $^3P_1$ level are plotted in Fig. 11. As in the case of the $^3P_0$ level, the decay is strongly current dependent.

A final, current-independent, decay was not observed at 2 mm of mercury. Such a final decay component may,

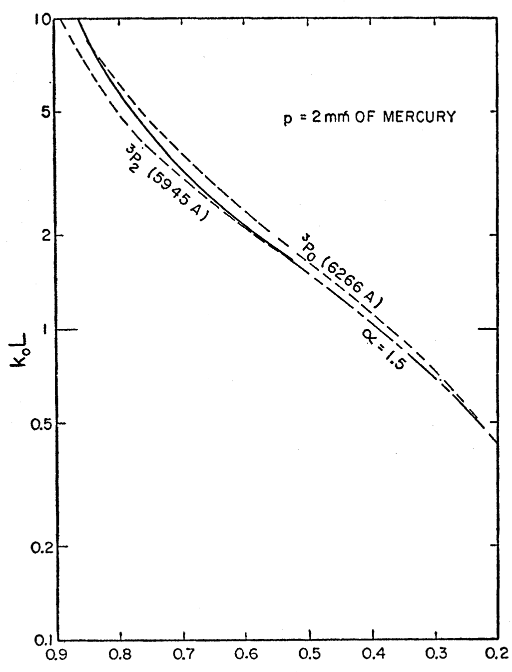

FIG. 9. k_0L vs absorption A. Solid curve —— calculated using Eq. (1) and Fig. 2, which are based on the "pure Doppler" assumption. Broken curves – – – obtained from the experimental data of Figs. 3 and 5.

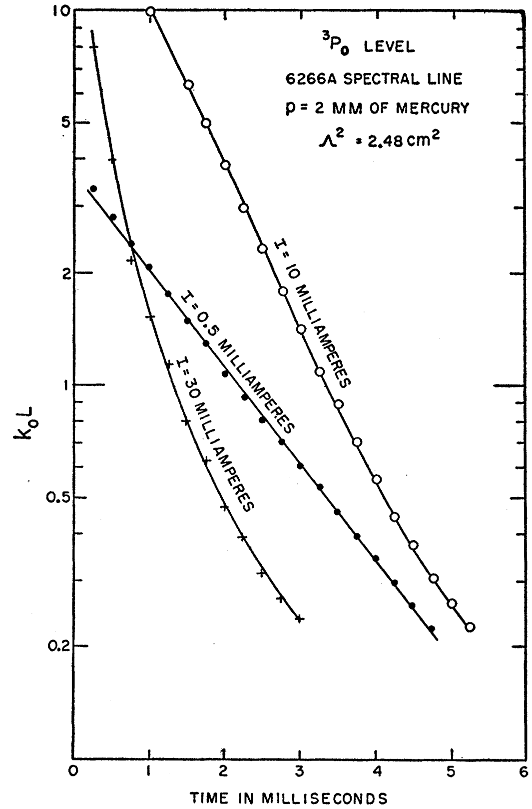

FIG. 10. Curves derived from experimental results illustrating the current dependence of the decay of the $^3P_0$ metastable level of neon for currents of 0.5, 10, and 30 milliamperes.

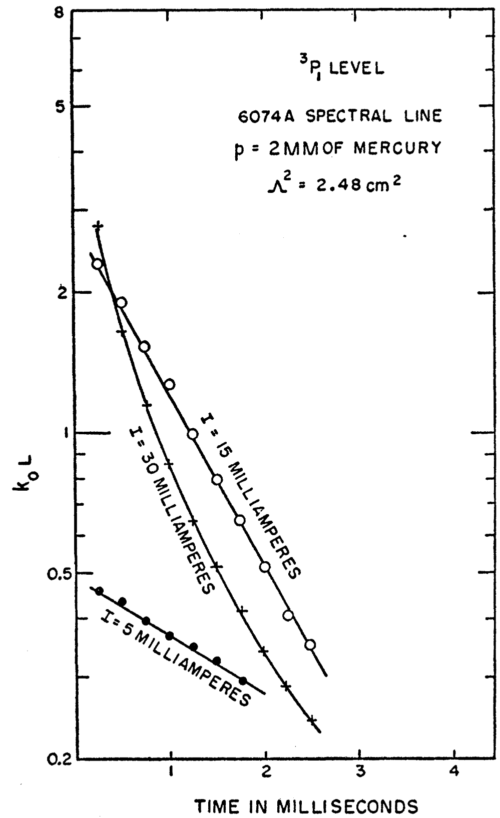

FIG. 11. Curves illustrating the current dependence of the decay of the $^3P_1$ level of neon for excitation currents of 5, 15, and 30 milliamperes.

however, exist in the range of small absorption which is beyond the limit of the equipment used in this research. The difficulties in obtaining decay data at low excitation currents are evident in Fig. 12. (The lengths of the inverted spikes are proportional to the flux of the light pulses from the emission tube incident on the photomultiplier tube. The seven shortest spikes indicate the higher $^3P_1$ atom population in the absorption tube during the excitation pulse, the remainder correspond to the afterglow.)

$^3P_2$ Level

The initial decay of the $^3P_2$ level appears to be current dependent to a much smaller degree than that of the other triplet levels. As in the case of the $^3P_0$ level, the decay becomes exponential at sufficiently small excitation currents (Fig. 13).

MEAN LIFE OF THE TRIPLET P LEVELS OF NEON AT 300°K

The mean lives of the triplet P levels of neon were measured as a function of the gas pressure. All measurements at a given pressure were made under identical conditions of excitation, as determined by the current in the absorption tube. Results were not obtained for pressures higher than 17 mm of mercury because the voltages required for excitation were beyond the limit

TABLE II. Diffusion and two-body collision cross sections of metastable neon atoms.

	Diffusion coefficient at 1 mm of Hg D cm² sec⁻¹	Diffusion cross section Q_d cm²	Frequency of two-body quenching collisions at 1 mm of Hg A sec⁻¹	Density of normal atoms at 1 mm of Hg n cm⁻¹	Mean relative velocity $\bar{v}$ cm sec⁻¹	Effective cross section for quenching by two-body collisions Q_{eff} cm²	Q_d/Q_{eff}
Ne*($^3P_0$) in Ne	170±10	42.7×10^{-16}	265±15	3.22×10^{16}	7.94×10^4	10.4×10^{-20}	41 000
Ne*($^3P_2$) in Ne	170±10	42.7×10^{-16}					
Ne*($^3P_2$) in He and Ne	310±20	40.5×10^{-16}	270±15	3.22×10^{16}	13.75×10^4	6.1×10^{-20}	66 500
Ne*($^3P_0$) in He and Ne	310±20	40.5×10^{-16}					

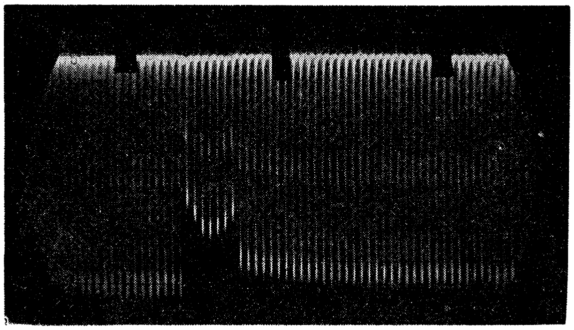

FIG. 12. Oscilloscope pattern illustrating absorption *vs* time. Excitation current 0.5 milliampere, $^3P_1$ level, 6074 A spectral line, pressure 2 mm of mercury.

of the apparatus used. For pressures less than 9 mm of mercury the $^3P_1$ absorption was too low to be measured accurately.

The results for the $^3P_1$ and $^3P_2$ levels are plotted in Fig. 14. In the pressure range 9 to 17 mm of mercury these levels decay with a time constant which is identical within the limits of the experimental error. The long solid curve represents an attempt to fit a curve of the form of Eq. (2) to the experimental data. The short solid curve passing through the experimental points shows the improvement resulting from the use of Phelps's theoretical relation,[4] which takes into account the effect of imprisonment of resonance radiation and transitions between these levels induced by collision.

The $^3P_0$ level was studied in the pressure range in which the time constants were sufficiently great to permit their accurate measurement with our apparatus. The results are plotted in Fig. 15. The solid curve shows an attempt to represent the experimental data by an equation of the type

$$1/\tau = (D_1/\Lambda^2 p) + Ap, \qquad (2)$$

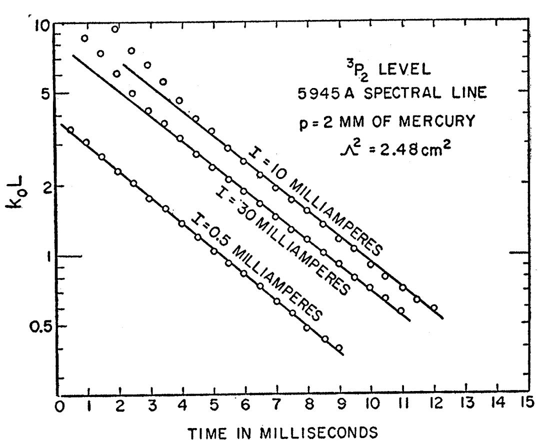

FIG. 13. Curves illustrating the current dependence of the decay of the $^3P_2$ metastable level of neon for excitation currents of 0.5, 10, and 30 milliamperes.

[4] A. V. Phelps, Phys. Rev. 99, 1657(A) (1955).

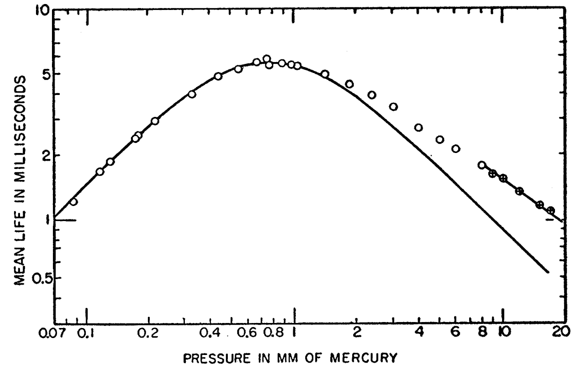

FIG. 14. The pressure dependence of the mean life of the $^3P_1$ and $^3P_2$ neon levels. The solid curve was obtained by using Eq. (2) with $D_1 = 170$ cm^2 mm sec^{-1}, and $A = 113$ mm^{-1} sec^{-1}, $\Lambda^2 = 2.48$ cm^2. The short straight line at higher pressures was calculated by using Phelps's theoretical relation. The crosses correspond to the $^3P_1$ level.

where τ is the mean life in milliseconds, and D_1 the diffusion coefficient of $^3P_0$ metastable atoms in the parent gas at a total gas pressure of 1 mm of mercury. The term Ap, where p is the total pressure in millimeters of mercury, represents the frequency of two-body quenching collisions. Λ is the diffusion length of the container, which for a cylindrical tube of radius a and length L is given by the equation[5]:

$$\frac{1}{\Lambda^2} = \left(\frac{5.81}{a^2} + \frac{\pi^2}{L^2}\right). \qquad (3)$$

The absorption tube used throughout this research was 240 cm long and had an inside diameter of 7.6 cm, so that $\Lambda^2 = 2.48$ cm^2.

The values of D_1 and A determined from Fig. 15 are tabulated in Table II. It is of interest that the $^3P_0$ and

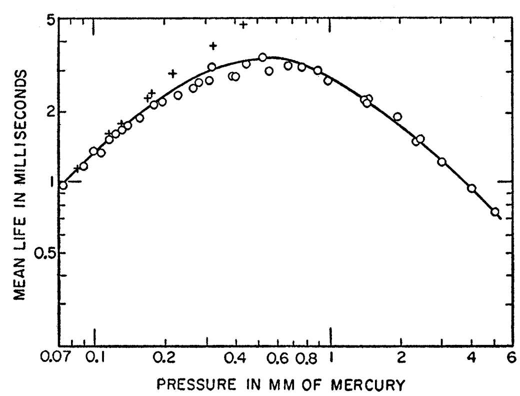

FIG. 15. The pressure dependence of the mean life of the $^3P_0$ metastable neon level in pure neon. Sampling line 6266 A. Circles—experimental results for the $^3P_0$ level. Crosses—experimental results for the $^3P_2$ level. The solid curve was obtained by using Eq. (2) with $D_1 = 170$ cm^2 mm sec^{-1}, $A = 265$ mm^{-1} sec^{-1}, and $\Lambda^2 = 2.48$ cm^2.

[5] M. W. Zemansky, Phys. Rev. 34, 213 (1929).

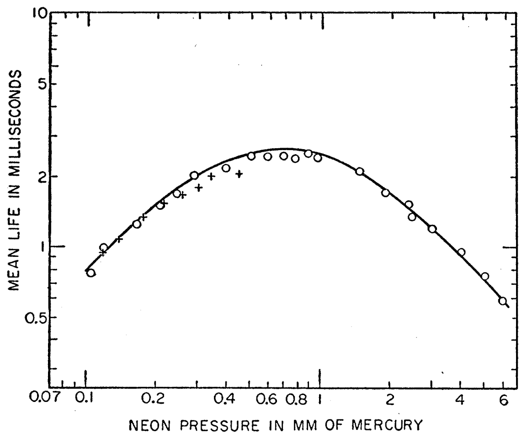

FIG. 16. The pressure dependence of the mean life of the $^3P_0$ metastable neon level in a 2:1 helium:neon mixture. Sampling line 6266 A. $\Lambda^2=2.48$ cm^2. Circles—experimental results for the $^3P_0$ level. Crosses—experimental results for the $^3P_2$ level. Solid curve calculated using Eq. (2) with $D_1=310$ cm^2 mm sec^{-1}, $A=270$ mm^{-1} sec^{-1}, and $\Lambda^2=2.48$ cm^2.

$^3P_2$ curves coincide at low pressures; hence the two types of atom have the same diffusion coefficient.

MEAN LIFE OF $^3P_0$ LEVEL OF NEON IN HELIUM AND NEON MIXTURE

The mean life of the $^3P_0$ level of neon was measured at 300°K in a 2:1 mixture of helium and neon. The results are plotted in Fig. 16. As in pure neon, it was possible to represent the experimental data by an equation of the type

$$1/\tau=(\bar{D}_1/\Lambda^2p)+\bar{A}p, \tag{4}$$

where $\bar{D}_1$ and $\bar{A}$ refer to diffusion and two-body collisions of metastable neon atoms in mixtures of helium and neon. The values of $\bar{D}_1$ and $\bar{A}$ determined from Fig. 16 are tabulated in Table II. Also plotted in Fig. 16 are measurements made of the mean life of the $^3P_2$ level at lower pressures, where diffusion is dominant. Once again the two levels have the same diffusion coefficient.

DIFFUSION COEFFICIENTS AND CROSS SECTIONS

From the data of Figs. 14, 15, and 16, the diffusion cross sections and atomic radii have been calculated by using the formulas[6]:

$$\bar{Q}_d=\frac{3\pi}{32}\left(\frac{\bar{v}}{n_2D}\right), \tag{5}$$

$$\bar{v}=\left[\frac{8\kappa T(M_1+M_2)}{\pi M_1M_2}\right]^{\frac{1}{2}}, \tag{6}$$

and are tabulated in Table II. Since the $^3P_0$ and $^3P_2$ levels have identical diffusion cross sections within the limits of experimental error, it seems unlikely that exchange interaction between a metastable atom and a normal atom plays an important role in the diffusion process.

TWO-BODY QUENCHING COLLISION CROSS SECTIONS

The two-body quenching collision cross sections, given in Table II, have been calculated using the relation

$$\nu=n\bar{v}Q_{\mathrm{eff}}, \tag{7}$$

where ν equals the frequency of two-body quenching collisions, n is the density of normal atoms per cc, $\bar{v}$ is the mean relative velocity in cm per sec, and Q_{eff} is the effective cross section for the process in cm^2.

CONCLUSION

By reducing the amplitude of the current of the absorption tube excitation pulse, the decay of the triplet P atoms in the afterglow has been made current-independent. The identity of the mean lives of the $^3P_1$ and $^3P_2$ levels in the pressure range 9 to 17 mm of mercury is in agreement with the relation derived by Phelps and postulating the imprisonment of resonance radiation.

[6] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 367.

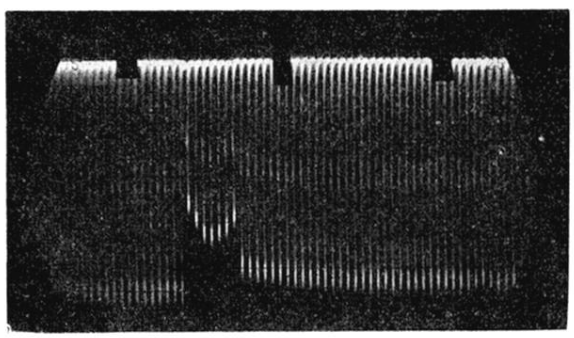

FIG. 12. Oscilloscope pattern illustrating absorption *vs* time. Excitation current 0.5 milliampere, $^3P_1$ level, 6074 A spectral line, pressure 2 mm of mercury.