heavier ion-atom collisions, $P_0$ is expected to decrease with increasing energy and scattering angle.

### z. $Ar^+$ on Ar, Angle Varied

Figure 10(b) shows the data for $P_0$ vs $\theta_{lab}$ at 10 and 25 kev with $Ar^+$ on Ar. The results are similar to those obtained for $Ne^+$ on Ne described above.

### aa. $Kr^+$ on Kr, Angle Varied

Figure 10(c) presents data for $P_0$ vs $\theta_{lab}$ at 25 kev with $Kr^+$ on Kr. The results are similar to those obtained for $Ne^+$ on Ne and $Ar^+$ on Ar.

### bb. $N^+$ on A, Angle Varied

Figure 10(d) presents data for $P_n$ vs $\theta_{lab}$ at 100 kev with $N^+$ on A. The fractions $P_n$ are seen to be nearly independent of $\theta_{lab}$, unlike the results obtained for other heavy ion-atom collisions studied in references 8 and 9.

### 5. ACKNOWLEDGMENTS

We wish to thank Dr. A. Russek for many valuable discussions of the data, Dr. P. R. Jones for helpful advice in the earlier phases of this work, and Mr. Seymour Kessler for his assistance in taking the data.

PHYSICAL REVIEW VOLUME 118, NUMBER 6 JUNE 15, 1960

# Experimental Verification of the "Incoherent Scattering" Theory for the Transport of Resonance Radiation

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(Received January 20, 1960)

The predictions of the incoherent scattering theory of the transport of resonance radiation developed by Holstein and by Biberman are shown to agree with laboratory measurements of the decay constants for the intensity of the mercury 2537 A resonance radiation following a period of optical excitation. Also, the relative importance of the diffusion of resonance atoms and the escape of resonance radiation as mechanisms for the destruction of mercury atoms in the $^3P_1$ or resonance state are determined from measurements of decay constants as a function of mercury density and cell radius. The experimental results show that diffusion of the resonance atoms is negligible and that the predictions of imprisonment theory are confirmed to within 15%. The experiment sets an upper limit to the diffusion coefficient at unit gas density for atoms in the $^3P_1$ state of $5\times10^{17}$ cm$^{-1}$ sec$^{-1}$ at 340°K, which is consistent with a value of $4\times10^{16}$ cm$^{-1}$ sec$^{-1}$ predicted using the frequency of excitation transfer collisions calculated by Holstein. The success of the theories based on completely incoherent scattering of resonance radiation points to the desirability of including this feature in the treatment of those astrophysical problems in which the spectral line shape is determined by Doppler broadening or by collision broadening.

## I. INTRODUCTION

A NUMBER of theories have been developed to describe the transport of resonance radiation through the parent gas. When this process involves a large number of successive absorption and reemission events, the predictions of the theories are found to vary considerably with the assumed relation between the frequency of the absorbed photon and the frequency of the reemitted photon. In most treatments of radiative transfer[1] it is assumed that the frequency of the absorbed and re-emitted photons are identical, i.e., the scattering is "coherent" with regard to frequency (although not necessarily so with regard to phase). These theories have been used to predict the rate of escape of resonance radiation in laboratory experiments,[1] e.g., the decay of intensity of the mercury 2537 A line following a period of optical excitation. The predicted decay constants for radiation at the center of the resonance line are two orders of magnitude too small to explain experimental observations at the higher gas densities. This fact led to the use of an average absorption coefficient or "equivalent opacity" for the resonance radiation[2] in

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[1] S. Chandrasekhar, *Radiative Transfer* (Oxford University Press, New York, 1950). See especially Sec. 90. See also R. v.d. R. Woolley and D. W. N. Stibbs, *The Outer Layers of a Star* (Oxford University Press, New York, 1953), Chap. VIII. For a recent discussion of coherence in scattering at low densities see J. P. Barrat, J. Phys. radium **20**, 541, 633, and 657 (1959).

[2] A discussion of early efforts to bring the theory into agreement with experiment are given in reference 3 and A. G. C. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), pp. 230–236. The values of $g$ obtained using Milne's formula for the decay constant of the central portion of the resonance line vary from 0.63 to 0.012 times those in reference 11 as $k_0L$ increases from 2 to 400. The values of $g$ obtained using Sampson's equivalent opacity in Milne's formula for the decay constant for the intensity of resonance radiation vary from 1.1 to 28 times those given in reference 11 as $k_0L$ changes from 2 to 400. Finally, the $g$ values obtained by Zemansky from Kenty's size dependent diffusion coefficients (reference 18) are about 20% below the values given in reference 11 and are in very good agreement with the values obtained by Holstein.[3]

which it was assumed that the spectral distribution of the incident photons is the same as the frequency distribution of the absorption coefficient, i.e., the photon scattering is incoherent. This procedure leads to decay constants which are as much as an order of magnitude larger than the observed values depending upon the procedure used to obtain the average absorption coefficient. The problem was finally solved by Holstein,[3] who showed that the proper theory leads to the conclusion that when the number of absorption and re-emission events is large and when the line shape is determined by Doppler broadening or collision broadening the radiation behaves as if it were scattered incoherently. It has also been shown by both Holstein[3] and by Biberman[4] that one cannot properly solve the transport equation for incoherently scattered resonance radiation using an average absorption coefficient or photon mean free path. Holstein[3] solved the transport equation using variational techniques while Biberman[4] used numerical methods.

A number of predictions of the theory of the imprisonment of resonance radiation developed by Holstein and by Biberman have been shown to agree well with the results of experiments. Thus, Alpert, McCoubrey, and Holstein[5] found good agreement between theoretical and experimental values of the absolute magnitude and variation with vapor density of the decay constants for the intensity 2537 A resonance radiation of mercury. In addition, Holstein, Alpert, and McCoubrey[6] found that the decay constants for isotopic $Hg^{198}$ were approximately five times smaller than the decay constants for natural mercury, in excellent agreement with theory. Biberman and Gurevich[7] showed that the minimum in the transmission of mercury resonance radiation occurred at the mercury density predicted by theory. These and other[8–11] successes of the theory are strong experimental evidence that the solutions of the transport equation for resonance radiation given by Holstein and by Biberman are correct.

An implicit assumption of the theories of the transport of resonance radiation is that the diffusion of the atoms in the resonance state makes a negligible contribution to the escape of the excitation energy. However, Fowler[12] pointed out that one could obtain an equally good fit to the then (1956) available experimental decay times for natural mercury by assuming that the only mechanisms responsible for the escape of resonance energy are the diffusion of the excited atoms to the wall and their destruction in collisions with normal atoms. One obvious difficulty with this hypothesis is that the diffusion coefficient for resonance atoms in nearly pure $Hg^{198}$ would have to be approximately five times that for resonance atoms in natural mercury in order to explain the observations of Holstein, Alpert, and McCoubrey.[6] The argument used by Fowler for neglecting the escape of the resonance photons is that the "diffusion coefficient" for resonance photons calculated using the coherent scattering treatments of radiative transfer[1] is negligible compared to gas kinetic values for atoms.

In this paper we shall present an analysis of measurements of the decay of mercury resonance radiation taken under experimental conditions designed to check Holstein's predicted decay constants over a different range of experimental parameters than used previously and to separate the contributions of atomic diffusion and radiation transport to the escape of the resonance excitation energy.

## II. THEORY

The transport equation governing the density of resonance atoms, $n(\mathbf{r})$, in the absence of production and of destruction in collisions with normal atoms is[3,13]

$$\frac{\partial n(\mathbf{r},t)}{\partial t}=\frac{D}{N}\nabla^2 n(\mathbf{r},t)-An(\mathbf{r},t)+A\int_V n(\mathbf{r}',t)G(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'. \quad (1)$$

Here $D$ is the diffusion coefficient at unit gas density for the resonance atoms, $N$ is the mercury density, $A$ is the Einstein transition probability for the resonance transition, and the integration is to be carried out over the volume of the enclosure. The quantity $G(|\mathbf{r}-\mathbf{r}'|)$ is the probability that resonance radiation emitted at $\mathbf{r}'$ will be absorbed at $\mathbf{r}$ and its calculation is based upon the demonstration by Holstein[3] that for the purposes of the problem under discussion the absorption and re-radiation of the resonance line are completely incoherent and are controlled by Doppler broadening. The first term on the right of Eq. (1) gives the diffusion loss while the sum of the last two terms gives the net rate of change of density as the result of radiation of resonance photons.

[3] T. Holstein, Phys. Rev. **72**, 1212 (1947); **83**, 1159 (1951).
[4] L. M. Biberman, J. Exptl. Theoret. Phys. U.S.S.R. **17**, 416 (1947); **19**, 584 (1949).
[5] D. Alpert, A. O. McCoubrey, and T. Holstein, Phys. Rev. **76**, 1257 (1949). It should be noted that the values of $\nu$ reported in this reference are about 20% lower than the corresponding values given in Figs. 2–4. Thus far, efforts to explain this discrepancy have been unsuccessful. Earlier experiments (reference 2) are not compared with theory in this paper because of uncertain dimensions or excessive gas densities.
[6] T. Holstein, D. Alpert, and A. O. McCoubrey, Phys. Rev. **85**, 985 (1952).
[7] L. M. Biberman and I. M. Gurevich, J. Exptl. Theoret. Phys. U.S.S.R. **19**, 507 (1949); **20**, 108 (1950).
[8] S. Heron, R. W. P. McWhirter, and E. H. Rhoderick, Proc. Roy. Soc. (London) **A234**, 565 (1956). Recent measurements by R. G. Bennett and F. W. Dalby, J. Chem. Phys. **31**, 434 (1959) and private communication from Dr. Bennett appear to confirm the 40% discrepancy between theory and experiment found by Heron et al., using their small diameter collision chamber. At least part of this discrepancy is due to the fact that the initial distribution of excited atoms is far from that of the lowest spatial mode.
[9] A. V. Phelps, Phys. Rev. **100**, 1230(A) (1955); **114**, 1011 (1959).
[10] R. Siewert, Ann. Physik **17**, 371 (1956); **18**, 35 and 54 (1956).
[11] A. V. Phelps, Phys. Rev. **110**, 1362 (1958).
[12] R. G. Fowler, *Handbuch der Physik* (Springer—Verlag, Berlin, 1956), Vol. 22, pp. 217–226.
[13] W. Jost, *Diffusion in Solids, Liquids, and Gases* (Academic Press, Inc., New York, 1952), pp. 35–42.

TABLE I. Imprisonment factor for cylindrical geometry.[a]

| $k_0R$ | 5 | 10 | 20 | 50 | 100 | 200 | 400 |
|---|---|---|---|---|---|---|---|
| $g(k_0R)$ | $1.35\times10^{-1}$ | $7.0\times10^{-2}$ | $3.3\times10^{-2}$ | $1.12\times10^{-2}$ | $4.8\times10^{-3}$ | $2.2\times10^{-3}$ | $1.03\times10^{-3}$ |

[a] For a plot of $g(k_0R)$ versus $k_0R$ see Fig. 4 of reference 11. The values of $g(k_0R)$ for $k_0R<20$ (not $k_0R<2$ as stated in reference 11) are scaled from $g(k_0L)$ values calculated using the variational procedure of reference 3 for parallel plane geometry. The values of $g$ given here for $k_0R>20$ are approximately 20% larger than those given by Holstein.[3]

We assume that, as for the case of the simple diffusion equation and for the case of the imprisonment problem in the absence of diffusion, there is a solution of the form

$$n(\mathbf{r},t)=n(\mathbf{r})e^{-\nu t}, \tag{2}$$

where $\nu$ is the decay constant for the intensity of the resonance radiation.

Since we expect the diffusion term to make a very small contribution to the loss of resonance atoms, a solution to Eqs. (1) and (2) could be obtained by regarding the diffusion term as a perturbation on the solution obtained neglecting the diffusion term.[14] For our purposes the diffusion and imprisonment terms can be replaced by the lowest mode solutions to their individual decay equations. The reflection coefficient for resonance atoms and photons at the wall is assumed to be zero. With these assumptions the solution to Eq. (1) is

$$\nu=gA+5.78D/(NR^2), \tag{3}$$

where $R$ is the radius of the cylindrical tube used for the experiments and $g$ is the "escape factor" for the imprisoned resonance radiation for cylindrical geometry. The values of $g$ used in this paper were calculated according to the technique given by Holstein[3] but using the more accurate evaluation of $G(|\mathbf{r}-\mathbf{r}'|)$ given by Biberman.[4] Table I gives values of $g(k_0R)$ as a function of $k_0R$, where $R$ is the radius of the experimental tube and $k_0$ is the absorption coefficient at the center of the Doppler-broadened line. As shown by Holstein,[3] the effect of the hyperfine structure of the 2537 A line of mercury is to reduce the effective value of $k_0$ by a factor of five from that calculated for mercury with a single hyperfine component.

At low enough gas densities such that the escape of the resonance radiation is controlled by the Doppler-broadened portion of the spectral line the decay constant, $gA$, is a function only of the "optical thickness," $k_0R$, of the experimental arrangement.[3] Therefore, if imprisonment theory governs the decay of the resonance radiation, i.e., $gA\gg5.78D/NR^2$, we expect the measured values of $\nu$ to be a unique function of $k_0R$, or of $NR$ at a fixed temperature. If diffusion theory governs the decay, we expect $\nu$ to be inversely proportional to $NR^2$. The experiment, therefore, consists of measurements of $\nu$ as a function of mercury density, $N$, using experimental tubes with various radii, $R$.

[14] P. J. Walsh, Phys. Rev. **107**, 338 (1957). A perturbation procedure is used to solve a steady state problem in which the perturbation is the de-excitation of resonance atoms in collisions with electrons.

## III. EXPERIMENT

The experimental arrangement used for these measurements[15] is identical with that used by McCoubrey[16] to study the band fluorescence of mercury. Briefly, the arrangement is as follows: Radiation from a mercury discharge lamp is used to excite the mercury vapor contained in a cylindrical quartz tube. This incident radiation is interrupted periodically with a rotating shutter. The decay of the intensity of the resonance radiation is observed through an interference filter centered at 2537 A with an ultraviolet sensitive photomultiplier using a "time sampling" technique.[16] With this technique the photomultiplier is made sensitive to the resonance radiation for a short period of time by the application of a high voltage pulse to the photomultiplier dynodes. By measuring the photomultiplier output as a function of the time of application of the voltage pulse relative to the time of closing of the rotating shutter one

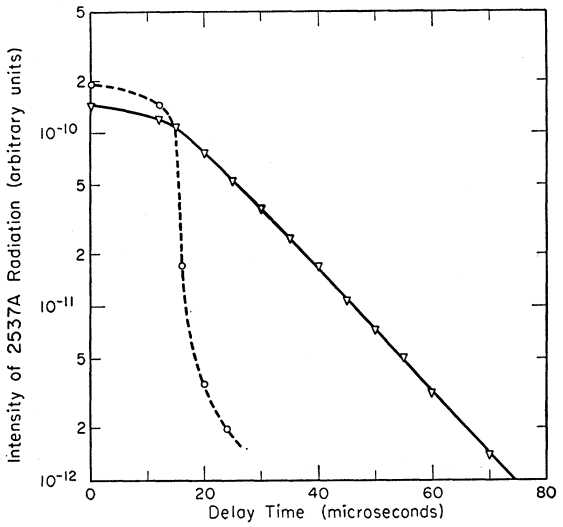


FIG. 1. Intensity of 2537 A radiation as a function of the time of the application of a 2.5 microsecond pulse of voltage to the photomultiplier dynode. The solid curve is drawn through points obtained with a reservoir temperature of 62.5°C and an observation region temperature of 63.5°C using a tube of 0.65-in. radius. The dashed curve is drawn through points obtained with the tube at 26°C. The reduction in 2537 A intensity during the excitation period, e.g., at $t=0$, as the mercury density is increased is due to the combined effects of the back scattering of the radiation from the source by the mercury vapor and the re-radiation of resonance photons. The units of the ordinate give the photomultiplier output current in amperes.

[15] A. V. Phelps and A. O. McCoubrey, Bull. Am. Phys. Soc. **3**, 83 (1958).

[16] A. O. McCoubrey, Phys. Rev. **93**, 1249 (1954).

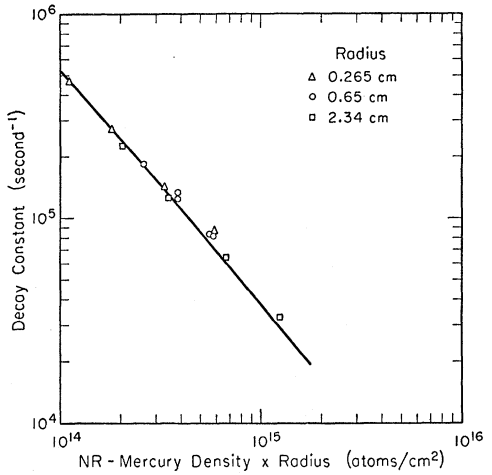


FIG. 2. Decay constant for mercury (2537 A) resonance radiation as a function of the product of mercury density and tube radius. The portion of the tube used for these measurements was maintained at 340±10°K. The solid line is that predicted by theory using the values of $g(k_0R)$ in Table I and a natural lifetime for the resonance state of $1.08\times10^{-7}$ second.

obtains the time variation of the intensity of the resonance radiation.

These experimental techniques differ from those of Alpert, McCoubrey, and Holstein[5] in that the time sampling technique is used to reduce the statistical fluctuations in the signal, an interference filter is used to separate the resonance radiation from the band fluorescence, and a better temperature controller is used to regulate the mercury vapor pressure and temperature.[17]

## IV. RESULTS AND DISCUSSION

An example of the time variation of the intensity of resonance radiation observed in these experiments is shown by the solid curve of Fig. 1. These data show that the intensity of the resonance radiation decreases exponentially with time over more than an order of magnitude. The dashed curve shows the time variation of the radiation reaching the detector by the reflection from the tube walls when the mercury vapor pressure is low enough ($\sim7\times10^{13}$ atom/cc) so that imprisonment effects are negligible. This curve shows that the intensity of radiation admitted to the resonance cell through the entrance slit is negligible during the important portion of the decay.

The decay frequencies obtained from the slopes of curves such as that of Fig. 1 at various mercury densities and for resonance cells of different radii are summarized in Figs. 2 and 3. Figure 2 shows the measured decay frequencies as a function of the quantity $NR$, while Fig. 3 is a plot of the same data as a function of $NR^2$. Thus we see that the variation of $\nu$ with the radius of the resonance cell is in good agreement with that predicted by imprisonment theory. In order to fit the results to the diffusion theory one would need a diffusion coefficient which varies with the size of the container. This is in accordance with the predictions of the work of Kenty[18] who showed that attempts to solve the problem of the transport of resonance radiation using conventional diffusion theory lead to diffusion coefficients which depend upon the dimensions of the container.

In order to set an upper limit to the diffusion coefficient consistent with these measurements we rewrite Eq. (3) in the form:

$$\frac{\nu}{gA}=1+\left(\frac{5.78}{gANR^2}\right)D. \tag{4}$$

This shows that if we plot $\nu/gA$ as a function of $5.78(gANR^2)^{-1}$ we should obtain a straight line whose slope is $D$. Figure 4 shows such a plot and indicates that the diffusion coefficient at unit gas density for the resonance atoms is less than $5\times10^{17}$ cm$^{-1}$ sec$^{-1}$ at 340°K. A theoretical value for the diffusion coefficient for resonance atoms in mercury can be obtained by noting that collisions of resonance atoms with ground-state atoms at large impact parameters which lead to the transfer of excitation are equivalent to elastic collisions which result in 180° scattering. The product of cross section and the speed of collision for excitation transfer has been computed by Holstein[3] using the theory of Furssov and Vlassov[19] and is $3.4\times10^{-9}$ cm$^3$/sec. Since the excitation transfer leads to 180° scattering, the frequency of momentum transfer collisions at unit density is twice this value or $6.8\times10^{-9}$ cm$^3$/sec. When this value is substituted into the standard expressions for the diffusion

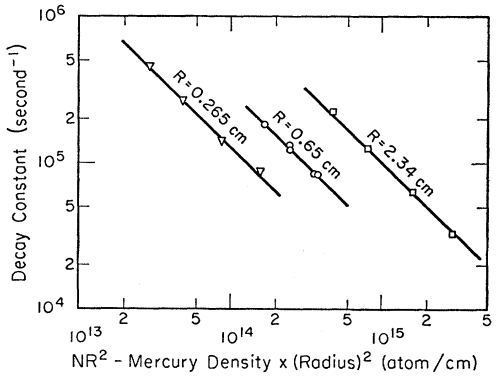


FIG. 3. Decay constant for mercury (2537 A) resonance radiation as a function of the product of the mercury density and the square of the radius of the tube at 340°K. The solid lines are drawn through the experimental points with a slope of −1 as expected if the decay of excited atoms were controlled by conventional diffusion. The fact that the diffusion coefficient required to fit the experimental data varies with the radius of the cell shows that conventional diffusion theory is not applicable to this problem.

[17] P. R. Malmberg and C. G. Matland, Rev. Sci. Instr. **27**, 136 (1956). In the present experiments the relays of this instrument were replaced with saturable reactors. With this arrangement the oven temperatures are maintained constant to within 0.01°C.

[18] C. Kenty, Phys. Rev. **42**, 823 (1932). See also M. W. Zemansky, Phys. Rev. **42**, 843 (1932).

[19] V. Furssov and A. Vlassov, Physik. Z. Sowjetunion **10**, 378 (1936).

coefficients[20] one finds $D=4\times10^{16}$ cm$^{-1}$ sec$^{-1}$ at unit mercury density. The solid line of Fig. 4 is plotted using this diffusion coefficient.

If the loss of excitation by the transport of resonance radiation were negligible compared to theoretical estimates then the experimental data of Fig. 4 would lie on a straight line through the origin. The dashed line of Fig. 4 shows a fit of such a straight line to the data obtained in a tube of 0.65-cm diameter. Although the apparent diffusion coefficient from this curve is only about 3 times that for atomic mercury metastables,[16] we note that it is about 100 times that expected for mercury atoms in the resonance state.

## V. SUMMARY

The agreement of the experimentally measured decay constants for mercury 2537 A resonance radiation with the predictions of the theory of imprisoned resonance radiation provides an experimental justification of the solution of the transport equation for resonance radiation given by Holstein and by Biberman. We, therefore, expect that the techniques used by Holstein and by Biberman will give satisfactory results when applied to problems such as the calculation of the role of resonance radiation in the positive column of an electrical discharge[14] or in the electrical breakdown of gases.[21] In addition, since the Holstein-Biberman solutions for the transport of resonance radiation are based upon the assumption of completely incoherent scattering, the results of the present investigation show that more reliance should be placed on this assumption in those astrophysical calculations[1] in which the shape of the important portions of the spectral line are determined by Doppler broadening or by collision broadening.

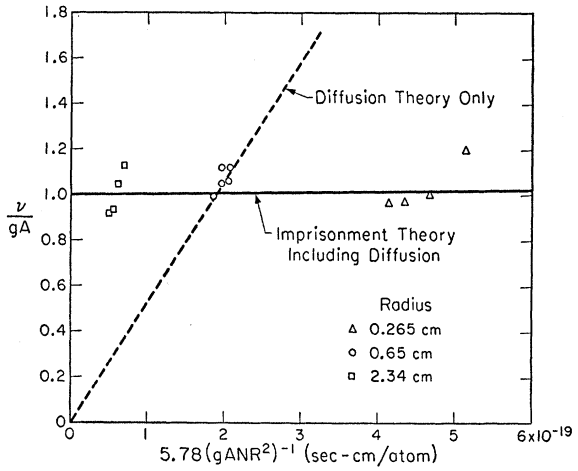


FIG. 4. Ratio of measured decay constant to theoretical imprisonment decay constant as a function of 5.78 $(gANR^2)^{-1}$. The solid line shows the predictions of our combined imprisonment and diffusion theory. The dashed line should pass through all of the points if conventional diffusion theory describes the loss of excited atoms. About half of the spread in the data points for a given value of $R$ would be removed if the effects of collisional broadening of the spectral line were included in the calculation of the values of $gA$.

## VI. ACKNOWLEDGMENTS

The authors wish to express their appreciation to their associates in the atomic physics group for valuable discussions and assistance during the course of this work. They are especially indebted to T. Holstein, the late C. G. Matland, and P. R. Malmberg.

[20] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), Chap. VII. It appears that the expression for $P_{12}$ in this reference is too large by a factor of two.

[21] A. V. Phelps, Phys. Rev. **117**, 619 (1960).