THE

PHYSICAL REVIEW

*A journal of experimental and theoretical physics established by E. L. Nichols in 1893*

SECOND SERIES, VOL. 158, NO. 1 5 JUNE 1967

# Role of Self-Absorption in Hg+Tl Sensitized Fluorescence Experiments

C. F. GALLO
*Xerox Research Laboratories, Rochester, New York*
(Received 13 January 1967)

When a Hg+Tl gas mixture is excited by Hg 2537-Å resonance radiation, microscopic energy-transfer processes occur which are manifested by the appearance of Tl emission lines. At constant thallium gas density, Swanson and McFarland have determined the intensity ratio ($R$) of the Tl 3776-Å line to the Tl 5350-Å line as the mercury density is varied. The functional form of the dependence of $R$ on mercury density has been successfully interpreted in terms of the self-absorption theory of Holstein. Specifically, the Tl 3776-Å line is strongly self-absorbed at low Hg densities. As the Hg density increases, Hg-Tl collisions occur more frequently and the Tl 3776-Å absorption line broadens, thus allowing more 3776-Å radiation to escape. In this region, $R$ varies as the square root of the mercury density. At still higher mercury densities, the Tl 3776-Å radiation readily escapes, and $R$ becomes a weak function of mercury density and finally levels off to a constant value. Similar considerations apply to the intensity ratio of the thallium 2580-Å and 3230-Å lines. These results constitute a semiquantitative verification of Holstein's self-absorption theory for the case where the shape of the absorption line is determined by impact broadening. In particular, this is the first experimental verification of Holstein's theory for the case of *foreign-gas* broadening and one may consider this as a new experimental technique for investigating self-absorption phenomena.

## INTRODUCTION, EXPERIMENTAL DETAILS, AND RESULTS

THE phenomenon of sensitized fluorescence[1] simply refers to the collisional transfer of excitation energy from an excited molecule of one species to an unexcited molecule of another species. For instance, when Hg 2537-Å radiation is directed into a Hg+Tl gas mixture, mercury atoms are excited and microscopic energy-transfer processes occur which are manifested by the appearance of thallium emission lines. At constant thallium atomic density, Swanson and McFarland[2] have directed Hg 2537-Å radiation into a Hg+Tl gas mixture and observed the variation in intensity of various thallium lines as the mercury atomic density was varied. The Hg and Tl vapor pressures were independently controlled with separate ovens as shown in Fig. 1. This vapor system may reach a steady-state condition, but the gas phase will not be in equilibrium since the thallium (which is in the hot oven) will always be diffusing from the hot region to the cooler region as long as any solid thallium remains in the hot region. Thus, the actual vapor pressure of thallium in the hot region will be less than one would predict from the known equilibrium vapor pressure of thallium at the hot oven temperature. However, throughout the system, the mercury vapor pressure will be accurately predicted by the known equilibrium vapor pressure of mercury at the cold oven temperature. These facts about the Hg and Tl vapor pressures will be important for the interpretation to be presented and we shall refer to them again.

In Swanson and MacFarland's experiment,[2] the Hg 2537-Å radiation directed into the Hg+Tl gas mixture excites mercury atoms as shown in Fig. 2. These excited

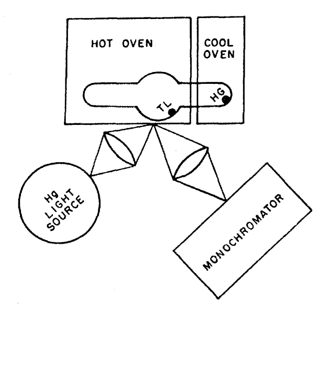


FIG. 1. Schematic diagram of the experimental arrangement employed by Swanson and McFarland (Ref. 2) in the study of Hg+Tl sensitized fluorescence. The mercury and thallium vapor pressures were independently controlled with separate ovens.

[1] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), pp. 56–69.

[2] R. E. Swanson and R. H. McFarland, Phys. Rev. 98, 1063 (1955).

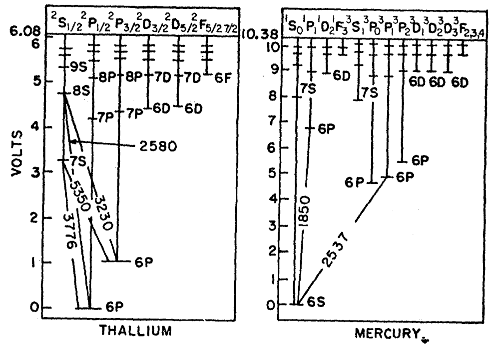


FIG. 2. Simplified term diagrams of mercury and thallium.

Hg atoms then collide with and excite thallium atoms by an energy-transfer mechanism whose details are the subject of study.[1–3] For the moment, we shall pay exclusive attention to the data on the ratio ($R$) of the intensity[4] of the Tl 3776-Å line to the Tl 5350-Å line as the Hg density is varied. At constant Tl density, this ratio varies by a factor of $\sim 10$, while the Hg density varies by a factor of $\sim 10^3$. These two lines (see Fig. 2) originate from the same $7\,^2S_{1/2}$ state. A transition to the $6\,^2P_{1/2}$ ground state gives rise to 3776-Å radiation and a transition to the $6\,^2P_{3/2}$ metastable state gives rise to 5350-Å radiation. There are no other radiative transitions from the $7\,^2S_{1/2}$ state. Thus, the intensity[4] ratio ($R$) of these lines is given by

$$R \equiv \frac{I_{3776\,\text{Å}}}{I_{5350\,\text{Å}}} = \frac{G_r N^* E_r A_r}{G_m N^* E_m A_m} = \frac{G_r E_r A_r}{G_m E_m A_m}, \qquad (1)$$

where $I_{3776\,\text{Å}}$ is the power radiated[4] in the Tl 3776-Å line, $I_{5350\,\text{Å}}$ is the power radiated in the Tl 5350-Å line, $G$ is the self-absorption escape factor, $E$ is the photon energy, $A$ is the transition probability, and $N^*$ is the total number of thallium atoms in the $7\,^2S_{1/2}$ state. The subscript $r$ denotes parameters pertinent to the Tl 3776-Å resonance radiation, and the subscript $m$ denotes parameters pertinent to the Tl 5350-Å radiation which terminates on the metastable level. The important point is that $N^*$ is exactly the same for the two thallium lines in question since they originate from the same excited state. Thus, the $N^*$'s cancel in the ratio and we are left with a constant times the ratio of escape factors. In the absence of self-absorption, the escape factors equal unity and it is clear that Eq. (1) yields a ratio which is a constant independent of mercury density. The fact that Swanson and MacFarland have observed a ratio which is strongly dependent on mercury density indicates that thallium self-absorption is an important factor and that the mercury affects the thallium self-absorption in some way. At first glance, this may be surprising, since it is quite generally known[5] that the integral under the absorption curve is directly proportional to the thallium density which is constant in Swanson and MacFarland's experiment:

$$\int \kappa(\nu)d\nu = \left(\frac{\lambda^2 A}{8\pi}\right)\left(\frac{g_u}{g_l}\right)N = \text{const}\times N, \qquad (2)$$

where $\kappa(\nu)$ is the absorption coefficient, $\lambda$ is the wavelength, $A$ is the transition probability, $N$ is the density of absorbing atoms, and the $g$'s are statistical weights for which the subscript $u$ denotes the upper state and the subscript $l$ denotes the ground state. Although the integral under the absorption curve is a constant, an alteration in the line shape changes the effective absorption coefficient. For instance, consider a narrow thallium absorption line in pure thallium vapor. As mercury atoms are slowly introduced, Hg-Tl collisions become more frequent and perturb the energy levels. These collisions broaden the thallium absorption line and the effective absorption coefficient is *decreased* even though the integral under the absorption curve is constant. This enables more radiation to escape and I believe that this is a qualitative description of what occurs to the imprisoned Tl 3776-Å radiation in Swanson and McFarland's experiment. It will be shown that the functional form of experimental data is consistent with the self-absorption theory developed by Holstein[6,7] for this case of impact line broadening.

## THEORETICAL INTERPRETATION

In Eq. (1), the photon energies $E_r$ and $E_m$ are known with great accuracy but the transition probabilities $A_r$ and $A_m$ are less accurately known.[3,8,9] As will be shown later, our interpretation of Swanson and McFarland's data indicates that $E_rA_r/E_mA_m \cong 0.9$ and this is within the range of the other[3,8,9] determinations. Thus, this value will be used here. In any event, this constant will not affect the functional form of our analysis.

Now consider $G_r$—that is, self-absorption of the Tl 3776-Å resonance radiation. Over the range of mercury and thallium densities investigated by Swanson and McFarland, the shape[10] of the Tl 3776-Å line is

[3] R. A. Anderson and R. H. McFarland, Phys. Rev. **119**, 693 (1960).

[4] By "intensity" we mean the *total integrated line intensity* which is, of course, proportional to the power. The measurements of Swanson and McFarland are proportional to the power, since the equivalent slit width of their monochromator was very large compared with the actual line width (private communication from R. H. McFarland, and Refs. 2 and 3).

[5] A. C. G. Mitchell and M. W. Zemansky, Ref. 1, pp. 92–96.

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

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

[8] C. H. Corliss and W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements* (U. S. Government Printing Office, Washington, D. C., 1962), National Bureau of Standards (U. S.) Monograph No. 53.

[9] A. Gallagher and A. Lurio, Phys. Rev. **136**, A87 (1964).

[10] Throughout this analysis, it shall be assumed that Tl 3776 Å is a simple single line—the hyperfine structure and isotopic components will be ignored. This is justified since these considerations will affect the proportionality constants in our analysis, but they should not seriously affect the functional dependence.

determined by impact broadening. For this case, Holstein gives[7]

$$G_r = 1.150/(\pi\kappa_p L)^{1/2}, \tag{3}$$

where we shall take $L$ as the thickness of the gas layer through which the Tl 3776-Å photons must travel before escaping from the enclosure. Note that $\kappa_p$ is the absorption coefficient at the peak of the absorption line and is given by[7]

$$\kappa_p = \left(\frac{\lambda^2 N_0}{4\pi}\right)\left(\frac{g_2}{g_0}\right)\left(\frac{A_r}{Z_T}\right), \tag{4}$$

where $\lambda$ is the Tl 3776-Å wavelength, $A_r$ is the transition probability associated with the Tl 3776-Å line, $Z_T$ is the total collision frequency of the thallium atoms, $g_2=2$ and $g_0=2$ are the statistical weights of the excited ($7\,^2S_{1/2}$) and termination ($6\,^2P_{1/2}$) states, respectively, and $N_0$ is the atomic density of thallium atoms in the ground state. The total collision frequency is given by

$$Z_T = Z_{\mathrm{Hg}} + Z_{\mathrm{Tl}}, \tag{5}$$

where $Z_{\mathrm{Hg}}$ is the collision frequency of thallium atoms with mercury atoms and $Z_{\mathrm{Tl}}$ is the collision frequency of thallium atoms with other thallium atoms. To evaluate $Z_{\mathrm{Hg}}$, the classical equation of Lorentz[11,12] will be used.

$$Z_{\mathrm{Hg}} = 2\rho^2 D(2\pi \mathcal{R} T)^{1/2}(1/M_1 + 1/M_2)^{1/2}, \tag{6}$$

where $\rho$ is the *optical* collision diameter, $D$ is the number density of Hg atoms, $\mathcal{R}$ is the universal gas constant, and $M_1$ and $M_2$ are the atomic weights of Hg and Tl. An expression for $Z_{\mathrm{Tl}}$ has been given by Furssov and Vlassov[13]:

$$Z_{\mathrm{Tl}} = \tfrac{2}{3}(\lambda e^2/mc) f N_0, \tag{7}$$

where $m$ is the electron mass, $e$ is the electron charge, $c$ is the velocity of light, and $f$ is the "oscillator" strength for the absorption of the resonance line. For the two thallium pressures studied by Swanson and McFarland[2] (Figs. 3 and 4 in their paper), the Hg-Tl collision frequency ($Z_{\mathrm{Hg}}$) and the Tl-Tl collision frequency ($Z_{\mathrm{Tl}}$) can be numerically evaluated. Most of the information is readily available. The Tl 3776-Å "oscillator" strength ($f$) is probably most accurately given by Gallagher and Lurio.[9] Information on the mercury ($D$) and thallium ($N_0$) atomic densities can be obtained from the oven temperatures given by Swanson and McFarland[2] and the vapor pressures tabulated by Nesmeyanov.[14] Data on the *optical* collision diameter ($\rho$) for the Hg+Tl system do not seem to be available, so we shall use a reasonable estimate of 17-Å from the compilation and review by Chen and Takeo.[11] With this information, we find $Z_{\mathrm{Hg}} > Z_{\mathrm{Tl}}$ over most of the mercury density range studied by Swanson and McFarland. In fact, the thallium atomic density will be lower than our estimates from the equilibrium vapor pressure as previously discussed, and thus the Tl-Tl collision frequency ($Z_{\mathrm{Tl}}$) will be even lower [Eq. (7)] than our above numerical estimates. Thus, it shall be assumed that $Z_{\mathrm{Hg}} \gg Z_{\mathrm{Tl}}$ and $Z_T \cong Z_{\mathrm{Hg}}$. It will be seen that the experimental data confirm these numerical calculations. Combining Eqs. (3)–(7), one obtains

$$G_r = 2.3/\lambda[N_0(g_2/g_0)A_r]^{1/2}(Z_T/L)^{1/2} \tag{8}$$

and

$$G_r \cong 2.3/\lambda[N_0(g_2/g_0)A_r]^{1/2}(Z_{\mathrm{Hg}}/L)^{1/2}, \tag{9}$$

where $Z_{\mathrm{Hg}}$ is given by Eq. (6).

Now $L$ is the thickness of the gas layer through which the Tl 3776-Å photons must travel before escaping from the enclosure. This thickness is essentially determined by the penetration depth of the Hg 2537-Å excitation radiation—that is to say, the distance which the Hg 2537-Å photons travel into the Hg+Tl cell before all their energy is dissipated by absorption and subsequent transformation to other forms by various energy transfer and radiationless de-excitation processes. Although Holstein's theory is not strictly applicable[15] to this case, the penetration depth can be estimated by combining the appropriate modifications of Eqs. (3), (4), (5), and (7) to obtain the following expression[16] for the case where the shape of the Hg 2537-Å absorption line is determined by Hg-Hg collisions:

$$G_{\mathrm{Hg}} = (0.211)(\lambda/L)^{1/2}, \tag{10}$$

where $G_{\mathrm{Hg}}$ is the self-absorption factor for Hg 2537-Å radiation. By using the appropriate modifications of Eqs. (6) and (7), it can be shown that Hg-Hg collisions determine the Hg 2537-Å absorption line shape for most of the mercury pressures that Swanson and McFarland have examined. Notice in Eq. (10) that $G_{\mathrm{Hg}}$ is *independent of the mercury density as long as Hg-Hg collisions* are dominant. This startling equation results from the fact that both the absorption integral and the line broadening are directly proportional to the mercury density and thus cancel exactly. This has been confirmed experimentally by several investigators.[16–18] Now $G_{\mathrm{Hg}}$ is essentially the reciprocal of the number of absorptions and re-emissions of a Hg 2537-Å photon as it travels a distance $L$. Thus, taking $G_{\mathrm{Hg}} \cong \frac{1}{10}$, the penetration depth $L$ is estimated as $10^{-4}$ cm, which is consistent

[11] S. Chen and M. Takeo, Rev. Mod. Phys. **29**, 20 (1957).

[12] A. C. G. Mitchell and M. W. Zemansky, Ref. 1, p. 170.

[13] W. Furssov and A. Vlassov, Physik Z. Sowjetunion **10**, 378 (1936). This reference was taken from Ref. 6, Eq. (5.17).

[14] A. N. Nesmeyanov, *Vapor Pressure of the Elements* (Academic Press Inc., New York, 1963), Tables 119, 120, 129, and 167.

[15] At first glance, one may question the applicability of Holstein's theory since the 2537-Å emission line shape from the excitation lamp may be quite different from the Hg 2537-Å absorption line shape in the fluorescence chamber. However, after the first absorption of a Hg 2537-Å photon, the line shape requirements of Holstein's theory are met as the photon is successively absorbed and re-emitted within the fluorescence chamber.

[16] A. V. Phelps, Phys. Rev. **114**, 1011 (1958), Eq. 10.

[17] D. Alpert, A. O. McCoubrey, and T. Holstein, Phys. Rev. **76**, 1257 (1949).

[18] P. J. Walsh, Phys. Rev. **116**, 511 (1959).

with the experimental observations.[2,19]

$$L=4.46\times10^{-2}\lambda/G_{\mathrm{Hg}}^2\approx10^{-4}\ \mathrm{cm}. \tag{11}$$

The important thing that Holstein's theory indicates is that $L$ is a constant independent of mercury density, and we have simply shown that a value of $10^{-4}$ cm is reasonable. From another point of view, the magnitude of $L$ is simply a curve-fitting constant. Information on another experiment is also presented in Swanson's thesis[20] which experimentally confirms the fact that $L$ is essentially independent of mercury atomic density in the range of interest. In this other experiment, Swanson[20] has measured the relative penetration of the Hg 2537-Å line through an absorption cell in which the mercury vapor pressure was varied as shown in Fig. 3. At low Hg pressures, the penetration is large but rapidly decreases as the mercury concentration increases. In this range, the Hg 2537-Å absorption line shape is determined by natural and Doppler broadening. However, as the Hg concentration increases, Hg-Hg collisions become more frequent and eventually determine the absorption line shape. In this range, Swanson has observed that the Hg 2537-Å absorption is essentially independent of the Hg density. This is additional confirmation that the Hg 2537-Å penetration depth ($L$) is independent of Hg density as shown in Eq. (11). In fact, Swanson's experiment (Fig. 3) is additional confirmation of Holstein's self-absorption theory for the case where the absorption line is determined by impact self-broadening. Many previous investigators[16,17] have used other techniques to investigate this aspect of Holstein's self-absorption theory.

Using appropriate modifications of Eqs. (3)–(7), it is possible to numerically demonstrate that self-absorption of the Tl 5350-Å line is negligible since it terminates on the $6\,^2P_{3/2}$ state, whose atomic density is many orders of magnitude less than the ground state at these low temperatures. Thus, $G_m$ equals unity and Eqs. (1), (6), (9), and (11) can be combined to show that

$$R\propto D^{1/2}. \tag{12}$$

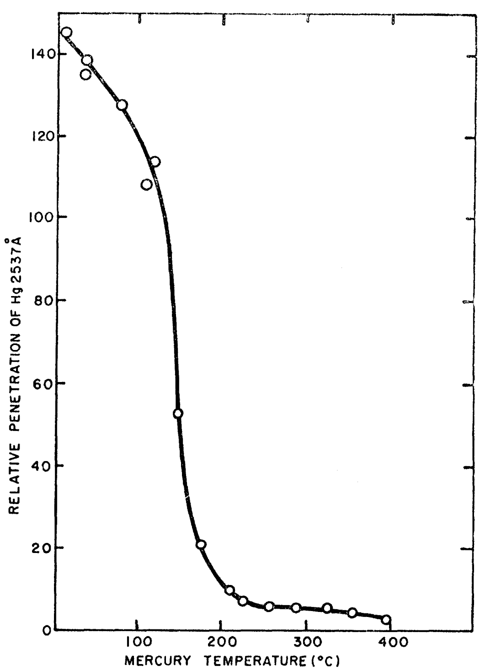


FIG. 3. Relative penetration of Hg 2537-Å radiation through a mercury vapor absorption cell in which the mercury vapor pressure was controlled by an oven. (This curve is from Ref. 20.) We are particularly interested in the vapor-pressure range corresponding to mercury oven temperatures ranging between ~200 and 400°C where the penetration of Hg 2537-Å radiation is essentially independent of mercury atomic density. This startling phenomenon occurs in the region where Hg-Hg collisions determine the Hg 2537-Å absorption line shape. The theory describing this phenomenon has been developed by Holstein (Refs. 6 and 7) and Phelps (Ref. 16) and is shown in Eq. (10).

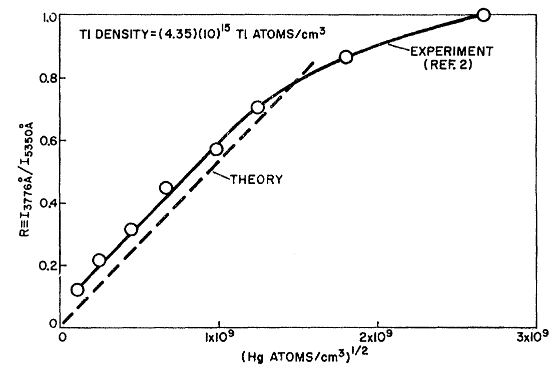


FIG. 4. The (Tl 3776-Å)/(Tl 5350-Å) intensity ratio ($R$) versus the square root of the mercury density. Over a considerable range of mercury density, the data (Ref. 2) exhibit the expected square-root dependence. At higher mercury densities, $R$ levels off, since the Tl 3776-Å absorption line becomes sufficiently broadened that the Tl 3776-Å radiation readily escapes.

This equation simply demonstrates that we expect the intensity ratio ($R$) of the Tl 3776-Å to Tl 5350-Å line to be simply proportional to the square root of the mercury density under the conditions investigated by Swanson and McFarland.[2] As previously discussed, sufficient data are available in the literature to evaluate the constants, and a comparison of theory and experiment is shown in Figs. 4 and 5, where the line ratio $R$ is plotted against the square root of the mercury density. Over two or three orders of magnitude, Swanson and McFarland's data exhibit the expected square-root dependence. At high Hg densities, the experimental curves level off. This is due to the fact that the Tl 3776-Å absorption line becomes sufficiently broadened by collisions with mercury that the radiation begins to escape readily and Holstein's theory is no longer applicable. In this case, we expect the self-absorption escape factor to asymptotically approach

[19] R. H. McFarland (private communication).

[20] R. E. Swanson, Ph.D. thesis, Kansas State College, 1953 (unpublished).

unity and $R$ to eventually become independent of mercury density as observed experimentally.

To this point, we have analyzed the behavior of the intensity ratio of the Tl 3776-Å line to the Tl 5350-Å line. However, in Swanson's thesis,[20] data are also presented on the Tl 2580-Å and Tl 3230-Å lines which both originate from the same $8\,^2S_{1/2}$ state (see Fig. 2). The Tl 2580-Å line terminates on the $6\,^2P_{1/2}$ ground state and the Tl 3230-Å line terminates on the $6\,^2P_{3/2}$ metastable level. This is exactly analogous to the Tl 3776-Å and Tl 5350-Å intensity ratio which we have just analyzed, and similar considerations also apply to the interpretation[21] of this (Tl 2580-Å)/(Tl 3230-Å) intensity ratio. In Fig. 5, this (Tl 2580-Å)/(Tl 3230-Å) ratio is plotted versus the square root of the mercury density, and again a linear dependence is observed as suggested by Eq. (12).

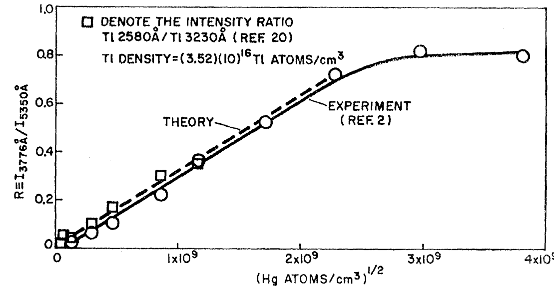


FIG. 5. The (Tl 3776-Å)/(Tl 5350-Å) intensity ratio ($R$) versus the square root of the mercury density. Over a considerable range of mercury density, the data [Ref. 2] exhibit the expected square-root dependence. At higher mercury densities, $R$ levels off, since the Tl 3776-Å absorption line becomes sufficiently broadened that the Tl 3776-Å radiation readily escapes. Data [Ref. 20] are also presented (squares) on the (Tl 2580-Å)/(Tl 3230-Å) intensity ratio and again a square-root dependence is observed.

## SUMMARY AND CONCLUSIONS

In sensitized fluorescence experiments at constant thallium gas density, Swanson and McFarland[2] have determined the intensity ratio ($R$) of the Tl 3776-Å line to the Tl 5350-Å line as the mercury density is varied. The functional form of the dependence of $R$ on mercury density has been successfully interpreted in terms of the self-absorption theory of Holstein.[6,7] Specifically, it has been shown that: (1) The shape of the Hg 2537-Å absorption line is determined by Hg-Hg collisions and the penetration depth of the Hg 2537-Å excitation radiation is independent of mercury density. This has been confirmed by an interpretation of experimental data available in Swanson's thesis.[20] (2) The Tl 5350-Å line is not self-absorbed. (3) The shape of the Tl 3776-Å absorption line is determined by Hg-Tl collisions and the self-absorption escape factor varies as the square root of the mercury density. (4) Thus, the intensity ratio should vary as the square root of the mercury density, and this is in agreement with the experimental data.

In other words, we are led to the following picture: The Tl 3776-Å line is strongly self-absorbed at low Hg densities. As the Hg density increases, Hg-Tl collisions occur more frequently and the Tl 3776-Å absorption line broadens, thus allowing more 3776-Å radiation to escape. In this region, $R$ varies as the square root of the mercury density. At still higher mercury densities, the Tl 3776-Å absorption line becomes sufficiently broadened that the radiation readily escapes and $R$ becomes a weak function of mercury density and finally levels off to a constant value. Similar considerations apply to the intensity ratio of the Tl 2580-Å and Tl 3230-Å lines. These results constitute a semiquantitative verification of Holstein's self-absorption theory for the case where the shape of the absorption line is determined by impact broadening. In particular, this is the first experimental verification of Holstein's theory for the case of *foreign-gas* broadening, and one may consider this as a new experimental technique for investigating self-absorption phenomena.

[21] Swanson has also presented data on the intensity ratios of the Tl 2768-Å and Tl 3529-Å lines which originate from the same excited state. However, the Tl 3529-Å line was not resolved from the Tl 3519-Å line, and so no analysis of this data has been made.