# Note on the Equivalent Absorption Coefficient for Diffused Resonance Radiation

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It is shown that the ideas expressed in the preceding theoretical paper by Kenty when applied to the diffusion of resonance radiation in a layer of gas of finite thickness provide a method of calculating an equivalent absorption coefficient of the gas for all the frequencies due to the Doppler effect that are present in the diffusing radiation. This average absorption coefficient is calculated and compared with a similar quantity calculated on the basis of a different point of view by Samson. Both average absorption coefficients are discussed in connection with the author's experiments (1927) on the rapidity of escape of resonance radiation emitted from a slab of mercury vapor after the cut-off of the excitation.

IN THE preceding theoretical paper, Kenty gives a treatment of the emission and absorption of quanta by moving atoms, in which it is pointed out that, owing to the Doppler effect, the group of frequencies comprising a Doppler line can pass from one part of a gas to another much more readily than an infinitesimal frequency band at the center of the line when no Doppler effect is present. According to Kenty, his equations are strictly applicable only to a gas of infinite volume, in which case both the diffusion coefficient and the mean free path of the radiation are found to be infinite. An approximate method is given, however, of treating the case of a finite layer of gas. It is not the purpose of this note to scrutinize Kenty's ideas carefully, but instead to examine the consequences of his method of handling the finite case. It will be seen that this method is essentially a device for obtaining an equivalent absorption coefficient of a gas for the group of frequencies generated by the Doppler effect.

According to Kenty, the diffusion coefficient of Doppler radiation in a gas is given by his Eq. (7).

$$D = (1/3\tau k_0^2)\int_0^\infty Rf_1(R)dR \qquad (1)$$

where $k_0$ is the absorption coefficient of the gas for the center of the line, $\tau$ the lifetime of the excited state to which the atoms are raised by the radiation, and $f_1(R)$ is a distribution function corresponding to a situation in which the atoms are originally excited by a continuous spectrum (in practise by a line much broader than the Doppler line). Of the two distribution functions, $f_1(R)$ and $f_2(R)$, given by Kenty, $f_1(R)$ has been chosen because it is believed that it approximates more closely the actual conditions of an experiment. $f_1(R)$ is given by his Eq. (4), namely

$$f_1(R) = (4/\pi^{1/2}) \int_0^\infty \int_0^y y e^{-y^2} e^{-Re^{-x^2}} dx dy. \tag{2}$$

Substituting Eq. (2) in Eq. (1) and integrating $R$ from 0 to $\infty$, we obtain

$$D = [2(2)^{1/2}/3\pi^{1/2}\tau k_0^2] \int_0^\infty y e^{-y^2} dy \int_0^{2^{1/2}y} e^{x^2} dx. \tag{3}$$

The integration over $y$ is an integration over the velocities of the emitting atoms. If all velocities are taken into account $D$ becomes infinite. Kenty's approximate method of handling a practical situation is to integrate $y$ from 0 to an upper limit $y_1$, where $y_1$ is given by the formula

$$k_0 e^{-y_1^2} = 1/l, \tag{4}$$

$l$ being the thickness of the layer of gas. Eq. (3) then becomes

$$\begin{aligned} D &= [2(2)^{1/2}/3\pi^{1/2}\tau k_0^2] \int_0^{y_1} y e^{-y^2} dy \int_0^{2^{1/2}y} e^{x^2} dx \\ &= [2^{1/2}/3\pi^{1/2}\tau k_0^2] \int_0^{y_1} 2y e^{y^2} F(2^{1/2}y) dy \end{aligned} \tag{5}$$

where

$$F(t) = e^{-t^2} \int_0^t e^{x^2} dx. \tag{6}$$

The integral in Eq. (5) can be expressed in terms of the $F$ function defined by Eq. (6) as follows: Integrating by parts,

$$\int_0^{y_1} 2y e^{y^2} F(2^{1/2}y) dy = [e^{y^2} F(2^{1/2}y)]_0^{y_1} - \int_0^{y_1} e^{y^2} dF(2^{1/2}y)$$

and, in virtue of the relation $(d/dt)F(t) = 1 - 2tF(t)$,

$$\begin{aligned} \int_0^{y_1} 2y e^{y^2} F(2^{1/2}y) dy &= e^{y_1^2} F(2^{1/2}y_1) - 2^{1/2} \int_0^{y_1} e^{y^2} [1 - 2(2)^{1/2} F(2^{1/2}y)] dy \\ &= e^{y_1^2} F(2^{1/2}y_1) - 2^{1/2} e^{y_1^2} F(y_1) + 2 \int_0^{y_1} 2y e^{y^2} F(2^{1/2}y) dy \end{aligned}$$

whence, finally

$$\int_0^{y_1} 2y e^{y^2} F(2^{1/2}y) dy = e^{y_1^2} [2^{1/2} F(y_1) - F(2^{1/2}y_1)]. \tag{7}$$

From Eqs. (4), (5) and (7) the diffusion coefficient is found to be

$$D = [(2)^{1/2} l/3\pi^{1/2}\tau k_0][2^{1/2} F(\ln k_0 l)^{1/2} - F(2 \ln k_0 l)^{1/2}]. \tag{8}$$

On the basis of the Einstein theory of radiation, without appeal to the analogy with molecular diffusion, and neglecting Doppler effect, Milne showed that radiation of infinitesimal spectral width diffused through a gas with a diffusion coefficient equal to

$$D' = 1/4\alpha^2\tau \tag{9}$$

where $\alpha$ stands for the absorption coefficient of the gas for the radiation in question. In the case of the diffusion of a band of frequencies comprising a line we may define an *equivalent absorption coefficient* as a quantity, $\bar{k}$ which, when substituted for $\alpha$ in Eq. (9), will give the correct diffusion coefficient to be used when the diffusing radiation is not of infinitesimal spectral width.

Kenty's expression for the diffusion coefficient, Eq. (8), enables us to compute $\bar{k}$ when the Doppler effect is present. For, by definition of $\bar{k}$,

$$1/4\bar{k}^2\tau = [2^{1/2}l/3\pi^{1/2}\tau k_0][2^{1/2}F(\ln k_0l)^{1/2} - F(2 \ln k_0l)^{1/2}]$$

and

$$\bar{k}l = \left[\frac{3}{4}\left(\frac{\pi}{2}\right)^{1/2}\right]^{1/2}\left[\frac{k_0l}{2^{1/2}F(\ln k_0l)^{1/2} - F(2\ln k_0l)^{1/2}}\right]^{1/2}. \tag{10}$$

From the splendid table of values of the $F$ function given by Miller and Gordon,[1] $\bar{k}l$ was evaluated for various values of $k_0l$ and the result is shown in Table I and curve $A$ of Fig. 1. It is seen from the curve that Kenty's method breaks down for small values of $k_0l$, which is to be expected in view of the approximations made.

TABLE I. *Kenty's equivalent absorption coefficient.*

| $k_0l$ | $\bar{k}l$ | $k_0l$ | $\bar{k}l$ |
|---|---|---|---|
| 1.5 | 3.05 | 100 | 21.2 |
| 2 | 2.76 | 200 | 31.4 |
| 3 | 2.97 | 500 | 54.2 |
| 4 | 3.31 | 1000 | 77.8 |
| 5 | 3.70 | 2000 | 114 |
| 10 | 5.39 | 3000 | 142 |
| 15 | 6.85 | 4000 | 166 |
| 20 | 8.10 | 5000 | 186 |
| 30 | 10.4 | 6000 | 205 |
| 40 | 12.3 | 7000 | 223 |
| 50 | 14.1 | 8000 | 240 |

The problem of calculating an equivalent absorption coefficient for Doppler radiation to be used in conjunction with Milne's radiation diffusion equation was attacked in a different way by Samson[2] without considering the motions of individual atoms or the free paths of individual groups of quanta. Samson defined an equivalent absorption coefficient $\bar{k}$ as the absorption coefficient that a gas would have for that infinitesimal frequency band which would show the same percentage transmission that is shown by a Doppler line.

The transmission of an infinitesimal frequency band by a gas whose absorption coefficient is $\bar{k}$ is $e^{-\bar{k}l}$, whereas the transmission of a line of the form

[1] W. L. Miller and A. R. Gordon, Phys. Chem. **35**, 2878 (1931).
[2] E. W. Samson, Phys. Rev. **40**, 940 (1932).

$I_0e^{-\omega^2}$ by a gas whose absorption coefficient has the form $k_0e^{-\omega^2}$ is

$$\frac{\int_{-\infty}^{\infty}\exp(-\omega^2)\exp(k_0le^{-\omega^2})d\omega,}{\int_{-\infty}^{\infty}\exp(-\omega^2)d\omega}.$$

whence Samson's $\bar{k}l$ is given by the relation

$$\exp(-\bar{k}l) = \frac{\int_{-\infty}^{\infty}\exp(-\omega^2)\exp(-k_0le^{-\omega^2})d\omega}{\int_{-\infty}^{\infty}\exp(-\omega^2)d\omega}. \qquad (11)$$

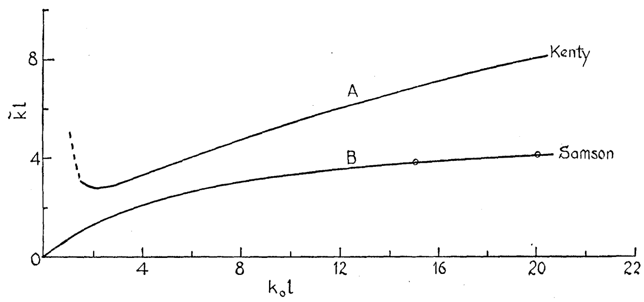


Fig. 1.

Samson's equivalent absorption coefficient is given for a number of values of $k_0l$ in Table II, and is shown as curve $B$ in Fig. 1. The curve shows that

TABLE II. *Samson's equivalent absorption coefficient.*

| $k_0l$ | $\bar{k}l$ | $k_0l$ | $\bar{k}l$ |
|---|---|---|---|
| 0 | 0 | 4 | 2.104 |
| 1 | 0.665 | 9.7 | 3.29 |
| 2 | 1.241 | 14.4 | 3.76 |
| 3 | 1.715 | 19.9 | 4.15 |

for small values of $k_0l$, $\bar{k}l$ behaves as it should, becoming zero when $k_0l$ is zero. For large values of $k_0l$ however, judging from the very slow rate at which the curve is rising, it appears that $\bar{k}l$ is too small. One might hazard the guess that Samson's method is valid at low opacities (small values of $k_0l$) and Kenty's method at high opacities.

In Kenty's experimental paper, the author's experiments on the escape of resonance radiation[3] from mercury vapor after the cut-off of the excitation, are interpreted as being due entirely to radiation diffusion rather than to metastable atoms. A complete discussion of the relative merits of these two interpretations is beyond the scope of this note. It should be pointed out,

[3] M. W. Zemansky, Phys. Rev. **29**, 513 (1927).

however, that, since the two theories are not mutually exclusive, it is quite possible that the correct explanation involves both radiation diffusion and metastable atoms, in a manner similar to Samson's treatment of the afterglow of mercury resonance radiation from a mixture of mercury vapor and nitrogen.

With the assumption that radiation diffusion takes place in these experiments it is instructive to calculate the equivalent absorption coefficient by both Kenty's and Samson's method, and with the aid of Milne's equation for the exponential constant of decay of the escaping radiation, calculate the exponential constant to be expected. This is done as follows:
With the equation[4]

$$5\left(\frac{\pi}{4 \ln 2}\right)^{1/2} k_0 \Delta\nu_D = \frac{\lambda_0^2}{8\pi\tau} \frac{g_2}{g_1} N, \tag{12}$$

it is possible to compute $k_0 l$ at a given vapor pressure (which determines $N$), a given temperature (which determines $\Delta\nu_D$), and with the most reliable value of $\tau$[5]($1.08\times10^{-7}$ sec.). Knowing $k_0 l$, $\bar{k}l$ is obtained either by Kenty's or by Samson's method. Then making use of Milnes equation for the decay constant neglecting impacts,

$$\beta = (1/\tau)/[1 + (\bar{k}l/\lambda_1)^2] \tag{13}$$

where $\lambda_1$ is approximately $\pi/2$, $\beta$ is calculated and compared with the experimental values of $\beta$ at low vapor pressures before impacts begin to play an important role.

With Kenty's method of calculating $\bar{k}l$, the results are shown in Table III, where it is seen that there is agreement in order of magnitude. With

TABLE III.

| $T°K$ | $l=1.95$ cm | | $l=1.30$ cm | |
|---|---|---|---|---|
| | Exp. $\beta$ | $\beta$ from Eq. (13) | Exp. $\beta$ | $\beta$ from Eq. (13) |
| 333 | 26600 | 29500 | | |
| 343 | 14200 | 15000 | 28100 | 24500 |
| 353 | 8810 | 7940 | 19300 | 12000 |
| 363 | 7070 | 4380 | 12100 | 6750 |

Samson's equivalent absorption coefficient, the results show a disagreement by a factor of at least 10. This is in line with the statement made previously, namely, that Samson's equivalent absorption coefficient is too small at large values of $k_0 l$.

[4] M. W. Zemansky, Phys. Rev. **36,** 219 (1930).
[5] P. H. Garrett, Phys. Rev. **40,** 779 (1932).