ABSORPTION AND COLLISION BROADENING OF THE MERCURY RESONANCE LINE

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Abstract

Radiation emitted by a mercury resonance lamp. It is shown how an approximate expression for the frequency distribution of the radiation from a resonance lamp can be arrived at, and that it can be represented approximately by a Gauss error curve with a half-breadth depending upon the geometry of the lamp and upon the vapor density, and in general greater than that of the absorption line.

Absorption coefficient and ratio of emission to absorption line breadth. Assuming that all five components of the mercury resonance line are alike both in emission and in absorption, and that any one component of the emission and of the absorption line is a Gauss error curve of half-breadth $\Delta\nu_E$ and $\Delta\nu_D$ respectively ($\Delta\nu_D$ = Doppler breadth), the absorption of a slab of thickness l is calculated as a function of $\kappa(\nu_0)l$, where $\kappa(\nu_0)$ is the absorption coefficient for the center of any one of the components. From experimental values of the absorption, $\kappa(\nu_0)$ is found to be consistent with the theoretical value $1.41\times10^{-13}N$ (where N is the number of Hg atoms per cc) provided $\Delta\nu_E/\Delta\nu_D$ is taken to be 1.21 in these experiments, 1.46 in Orthmann's, 1.50 in Hughes and Thomas', 1.15 in Kunze's, and 1.15 in Kopfermann and Tietze's.

Lorentz collision broadening of the absorption line. A theoretical expression is obtained for the absorption coefficient when collision broadening is superimposed upon Doppler broadening, and is evaluated for different values of the frequency and of $\Delta\nu_C/\Delta\nu_D$ where $\Delta\nu_C$ is the Lorentz collision breadth and $\Delta\nu_D$ is the Doppler breadth. With $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_D$ equal to the values found for these experiments, the absorption is calculated as a function of $\Delta\nu_C/\Delta\nu_D$. From experimental values of the absorption of mercury vapor in the presence of H_2, N_2, A, CO, NH_3, He, CH_4, and C_3H_8, $\Delta\nu_C$ is found as a function of the pressure of each gas. The curves of $\Delta\nu_C$ against pressure yield the effective broadening radius of each molecule, which is found to be directly proportional to the square root of the molecular diamagnetic susceptibility. On the basis of the Langevin theory this means that the effective broadening area of a molecule varies at the product of the number of outer electrons and the mean square radius of all the electronic orbits. The same result is obtained from the experiments of Füchtbauer, Joos and Dinkelacker.

Absorption Coefficient and Ratio of Emission to Absorption Line Breadth

THE transmission through mercury vapor of the radiation emitted by a mercury resonance lamp has been measured many times under apparently similar conditions, and yet the results have varied very markedly. The resulting values of absorption coefficient have differed from one another by as much as several hundred percent. In an investigation of the quenching of mercury resonance radiation by foreign gases which has been in progress for

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the last two years it was found necessary to know the absorption coefficient of mercury vapor for mercury resonance radiation very accurately. Consequently, this quantity was studied rather carefully with a view to discover, if possible, the causes for the existing discrepancies. The present paper, it is hoped, will clear up those difficulties which have not already been solved by others, and will give a summary of all the work that has been done since 1925, as well as a new set of measurements of the absorption coefficient.

The Radiation Emitted By a Mercury Resonance Lamp

It has been shown by Wood[1] that the mercury resonance line ($\lambda = 2537$) emitted by a mercury arc consists of five components of approximately equal intensity, and that all of these components are absorbed approximately equally by a column of mercury vapor. This has been substantiated by very careful measurements of the Zeeman effect of the mercury resonance line in a recent paper by Schein.[2] The intensity distribution of the radiation emitted by a mercury resonance lamp, however, is not known accurately as a function of the vapor density, the type of resonance lamp, dimensions, etc. It was assumed by Orthmann,[3] Kunze,[4] and Schein that the radiation emitted by a mercury resonance lamp was similar in intensity distribution to radiation whose half-breadth was equal to that of the absorption line but which had been absorbed slightly by passing through a thin layer of mercury vapor on its way out of the resonance lamp. This assumption was used by Orthmann and Kunze to calculate a correction factor which was applied to all the experimental values of the absorption. Schein, however, recognized that this assumption implies that the radiation emitted by a resonance lamp has a half-breadth slightly larger than that of the absorption line, and, by graphical means, estimated that, in his experiments, the ratio was 1.23.

The original supposition, namely, that the radiation emitted by a mercury resonance lamp is similar to that which results when a line of half-breadth equal to that of the absorption line passes through a thin absorbing layer, is only partly true, for when the vapor density in the resonance lamp approaches zero, the intensity should approach zero, whereas, according to the above assumption, it approaches a constant. A more satisfactory picture of the situation can be made on the basis of the following approximations:

1. The original stimulating radiation from the arc has a breadth that is so wide in comparison to the absorption line breadth of the vapor in the resonance lamp that it can be regarded as a continuous spectrum in the limited range of frequencies under consideration. Call this intensity A.

2. The radiation that is re-emitted in the body of the resonance lamp is a fraction ϵ of that amount of A which is absorbed in a column of average thickness l_1. Call this radiation $A_1(\nu)$.

[1] R. W. Wood, Phil. Mag. **50,** 761 (1925).
[2] M. Schein, Helv. Phys. Act. Vol. II, Sup. I (1929).
[3] W. Orthmann, Ann. d. Physik **78,** 601 (1925).
[4] P. Kunze, Ann. d. Physik **85,** 1013 (1928).

3. The radiation that finally emerges from the resonance lamp is the radiation $A_1(\nu)$ after it has passed through a column of vapor of average thickness l_2. Call this radiation $A_2(\nu)$.

The situation is represented graphically in Fig. 1.

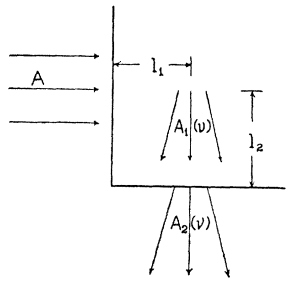

Fig. 1. Schematic representation of a resonance lamp.

Let us consider only one component of the mercury resonance line, inasmuch as all the components behave the same way. We have

$$A_1(\nu) = \epsilon A(1 - e^{-\kappa(\nu) l_1})$$

$$A_2(\nu) = A_1(\nu) e^{-\kappa(\nu) l_2}$$

where $\kappa(\nu)$ is the absorption coefficient of the vapor in the resonance lamp for the frequency range between ν and $\nu + d\nu$. Let us make the usual assumption:

$$\kappa(\nu) = \kappa(\nu_0) e^{-[2(\nu-\nu_0)/\Delta\nu_A]^2 \log_e 2}$$

where $\kappa(\nu_0)$ is the absorption coefficient for the center of the line of frequency ν_0, and $\Delta\nu_A$ is the half-breadth of the absorption line. Calling $2(\nu-\nu_0)/\Delta\nu_A (\log_e 2)^{\frac{1}{2}} = \omega$, we have then

$$\kappa(\omega) = \kappa(0) e^{-\omega^2}.$$

Let us further assume that the geometry of the resonance lamp has been so arranged that l_1 is very nearly equal to l_2. This is not essential, but it simplifies matters somewhat. Then, after substitution, we have

$$A_2(\omega) = \epsilon A(1 - e^{-xe-\omega^2}) e^{-xe-\omega} \tag{1}$$

where $x = \kappa(\nu_0) l_1 = \kappa(\nu_0) l_2$.

Plotting this expression for different values of x, it is found that it resembles a Gauss error curve fairly well with a half-breadth greater than that for the curve $e^{-\omega^2}$, that is, greater than the half-breadth of the absorption line. Calling this new half-breadth $\Delta\nu_E$, $\Delta\nu_E/\Delta\nu_A$ was found graphically to be 1.16 when $x = 0.25$ and 1.33 when $x = 0.50$. As the vapor density approaches zero, x approaches zero, and Eq. (1) approaches $x\epsilon A e^{-\omega^2}$, which is correct, because the intensity approaches zero, and the half-breadth approaches the absorption line breadth.

Burger and van Cittert[5] considered the broadening of a spectral line by absorption and obtained an expression for the breadth as a function of x. Unfortunately, however, their results can not be applied to the case of a resonance lamp.

If there were some way of estimating x for a particular resonance lamp it might be worth while to use the expression given by Eq. (1) in what is to follow. Since, however, there is no way of knowing how accurately x can be estimated, it is better to replace Eq. (1) by a Gauss error curve of half-breadth $\Delta\nu_E$ where $\Delta\nu_E$ is to be determined by experiment.

Two types of resonance lamp have been used to obtain resonance radiation. In the first one, the resonance radiation is taken off the incident window at about 45° to the incident beam,[6] and in the second, it emerges from a separate window at an angle of 90° to the incident beam.[7] It is obvious that the second type can be designed to correspond to a much smaller value of x than the first. It is therefore to be expected that the experiments conducted with the 90° type will involve a smaller value of $\Delta\nu_E$ than those performed with one of the 45° type.

The Absorption of Radiation

When radiation of frequency between ν and $\nu+d\nu$ and intensity $K(\nu,0)$ passes through an absorbing slab of thickness l with absorption coefficient $\kappa(\nu)$, then the transmitted radiation, $K(\nu, l)$ is given by[8]

$$K(\nu, l) = K(\nu, 0)e^{-\kappa(\nu)l}.$$

Let us suppose, as usual, that the emission and absorption lines are Gauss error curves with half-breadths $\Delta\nu_E$ and $\Delta\nu_A$ respectively. Then

$$K(\nu, 0) = K(\nu_0, 0)e^{-[2(\nu-\nu_0)/\Delta\nu_E]^2\log_e 2}$$
$$\kappa(\nu) = \kappa(\nu_0)e^{-[2(\nu-\nu_0/\Delta\nu_A]^2\log_e 2}$$

and the absorption, A, is

$$A = 1 - \frac{\int_{-\infty}^{\infty} e^{-[\omega^2+\kappa(\nu_0)le^{-(\Delta\nu_E/\Delta\nu_A\omega)^2}]}d\omega}{\int_{-\infty}^{\infty} e^{-\omega^2}d\omega}$$

where

$$\omega = \frac{2(\nu - \nu_0)}{\Delta\nu_E}(\log_e 2)^{1/2}.$$

For values of $\kappa(\nu_0)l \leqq 1.5$, the series expansion of Eq. (2) is satisfactory for numerical computation

[5] H. C. Burger and P. H. van Cittert, Zeits. f. Physik **51,** 638 (1928).
[6] A. L. Hughes and A. R. Thomas, Phys. Rev. **30,** 466 (1927).
[7] P. Kunze, reference 4.
[8] A. v. Malinowski, Ann. d. Physik **44,** 935 (1914).

$$A = \kappa(\nu_0)l \cdot \frac{1}{\left(1+\left(\frac{\Delta\nu_E}{\Delta\nu_A}\right)^2\right)^{1/2}} - \frac{[\kappa(\nu_0)l]^2}{2!} \cdot \frac{1}{\left(1+2\left(\frac{\Delta\nu_E}{\Delta\nu_A}\right)^2\right)^{1/2}} + \cdots$$

$$\cdots + (-1)^n \frac{[\kappa(\nu_0)l]^n}{n!} \cdot \frac{1}{\left(1+n\left(\frac{\Delta\nu_E}{\Delta\nu_A}\right)^2\right)^{1/2}} + \cdots$$

$$A = 1 - \frac{\int_{-\infty}^{+\infty} e^{-[\omega^2+\kappa(\nu_0)le^{-(\Delta\nu_E/\Delta\nu_A\omega)^2}]}\, d\omega}{\int_{-\infty}^{\infty} e^{-\omega^2}\, d\omega}.$$

TABLE I. *Values of A.*

$\kappa(\nu_0)l$ \ $\frac{\Delta\nu_E}{\Delta\nu_A}$	0	.50	1.0	1.27	2.0	3.0
0.25	0.221	0.200	0.160	0.140	0.102	0.0723
.50	.393	.360	.291	.256	.188	.133
1.0	.632	.588	.486	.428	.316	.226
1.5	.777	.736	.619	.550	.400	.287
2.0	.865	.832	.711	.630	.472	.348
3.0	.950	.925	.820	.738	.564	.414
4.0	.982	.967	.878	.805	.622	.461
4.5	.989	.977	.897		.640	.480

For values of $\kappa(\nu_0)l > 1.5$ it was found more convenient to evaluate A graphically. The values of A for different values of $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_A$ are given in Table I, and are plotted in Fig. 2. Curves of A against $\kappa(\nu_0)l$ for various values of $\Delta\nu_E/\Delta\nu_A$ are shown in Fig. 3. DeGroot[9] has given curves of the same character as those of Fig. 2, but in a form that is not very convenient for the purpose at hand.

When $\Delta\nu_E/\Delta\nu_A$ is kown, a curve of A against $\kappa(\nu_0)l$ can be drawn, and from experimental values of A and l, $\kappa(\nu_0)$ can be obtained. Values of $\kappa(\nu_0)$ for mercury vapor at a density corresponding to 20° C obtained by different authors under different conditions are given in Table II.

It will be seen from Fig. 3 that, if a curve of A against $\kappa(\nu_0)l$ for $\Delta\nu_E/\Delta\nu_A = a$, where a is any number, be used in a situation which really requires the use of a curve for $\Delta\nu_E/\Delta\nu_A > a$, the resulting values of $\kappa(\nu_0)l$ will be too small. It is to be expected, therefore, that the smallest values of $\kappa(\nu_0)$ will correspond to the largest values of $\Delta\nu_E/\Delta\nu_A$. This is seen to be the case, for it was pointed out in the beginning that the 45° type of resonance lamp yields a broader line than the 90° type.

There is another important error that can result in a final value of $\kappa(\nu_0)$ that is too small, namely, the reception by the photoelectric cell of scattered

[9] W. de Groot, Physica **9**, 263 (1929).

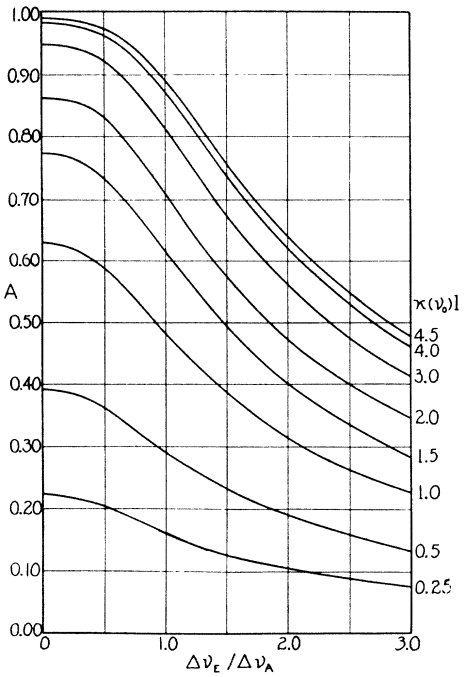

Fig. 2. Values of A for different values of $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_A$.

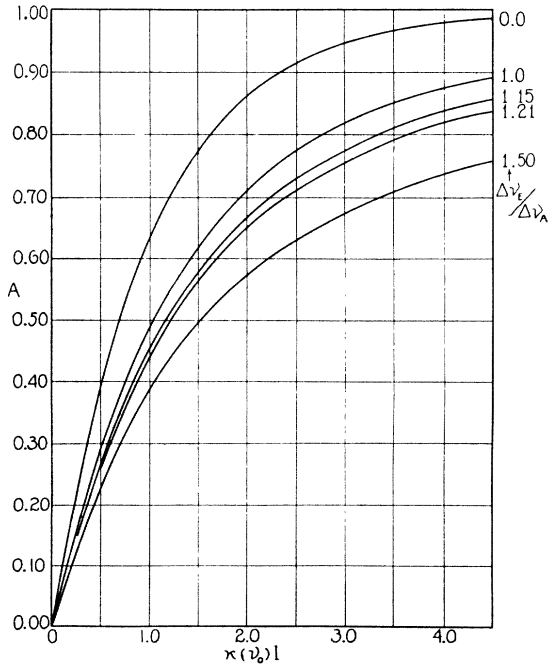

Fig. 3. Curves of A against $\kappa(\nu_0)l$ for various values of $\Delta\nu_E/\Delta\nu_A$

TABLE II.

	Type of Resonance Lamp	Method of computing $\kappa(\nu_0)$ from A	at 20°C
Orthmann[3]	45°	Used curve of A against $\kappa(\nu_0)l$ for $\Delta\nu_E/\Delta\nu_A=1$ and applied a correction factor to A to take into account absorption in the resonance lamp.	3.1
Hughes and Thomas[6]	45°	Used exponential law of absorption which is equivalent to assuming $\Delta\nu_E/\Delta\nu_A=0$	1.24
Schein[2]	90°	Used curve of A against $\kappa(\nu_0)l$ for $\Delta\nu_E/\Delta\nu_A=1.23$ but computed $\Delta\nu_E/\Delta\nu_A$ inaccurately.	3.77
Kunze[4]	90°	Same as Orthmann	5.2
Kopfermann and Tietze[10]	90°	Used formula due to Ladenburg for a situation in which the emitting and absorbing slabs are both infinitesimally thin.	5.2
Author	90°	Used curve of A against $\kappa(\nu_0)l$ for $\Delta\nu_E/\Delta\nu_A$ equal to that value which makes $\kappa(\nu_0)l$ vary linearly with Nl. This value was found to be 1.21.	5.61

radiation along with the transmitted radiation. If the photoelectric cell is placed close to the emerging window, and if the diaphragm which limits the incident beam is in front of the incident window, then a portion of the scattered radiation emitted by the *whole* emerging face is received by the photoelectric cell, resulting in a smaller value of A. It has been found by experiment that no scattered radiation reaches the photoelectric cell if the following conditions are adhered to:

1. The diaphragm limits the incident beam to a diameter of about 1 cm, and is placed over the *emerging* window.
2. The photoelectric cell is no nearer than 7 cm from the diaphragm.

It is believed that, in the experiments of Orthmann and in those of Hughes and Thomas, this was a possible source of error when the mercury vapor density was high enough to give rise to appreciable scattering. In all of the previous experiments, it is believed, an incorrect curve of A against $\kappa(\nu_0)l$ was used to compute the absorption coefficient.

APPARATUS

There is nothing essentially new in the apparatus used in these experiments, so that we shall limit ourselves to a very brief description.

Arc. Quartz mercury arc made by Cooper Hewitt, water-cooled and magnetically deflected.

Resonance lamp. 90° type with crystalline quartz windows cemented on with picein wax. Between it and the mercury diffusion pump there was a trap which was kept surrounded by ice. The drop of liquid mercury in a side tube was also kept in an ice bath. The exciting radiation from the arc illu-

[10] H. Kopfermann and W. Tietze, Zeits. f Physik **56**, 604 (1929).

minated about 5 mm of the incident window and the resonance radiation was taken off an area of the emerging window about 5 mm in diameter.

Absorption cell. A disk of heavy Pyrex glass about 4.5 cm inside diameter, and 0.792 cm in length was cut as shown in Fig. 4. Two crystalline quartz windows were cut in the same way and cemented on with picein wax. This was then cemented to a Pyrex tube about 10 cm long and 2 cm in diameter in which was placed a drop of mercury. There was thus a large opening between the tube containing the drop of mercury and the absorption cell proper, which enabled equilibrium conditions to be obtained rapidly.

The absorption cell was connected to the pumps through a glass spiral about a foot in diameter, which had sufficient flexibility to allow the cell to be moved in and out of the path of the light beam. A diaphragm with an

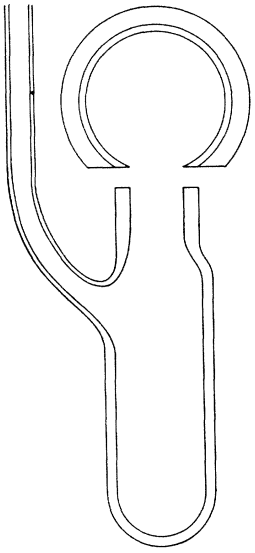

Fig. 4. Absorption cell.

aperture of about 1 cm remained fixed in space on the emerging side of the cell.

The photoelectric cell. The cell was made of fused quartz and had a platinum plate. It was first thoroughly cleaned and baked out, and then about 5 cm of H_2 was admitted. A discharge was passed through the H_2 by a small induction coil and then the H_2 was pumped out. This was repeated a few times until the platinum became slightly discolored. About 4 mm of H_2 was then introduced and the cell was sealed off. It was run on about 200 volts and a sensitive Compton electrometer was used to measure the current. The linearity of the cell at various voltages was tested with calibrated screens.

METHOD

With liquid air on the absorption cell the transmission of the quartz windows was measured and compared with the transmission of a piece of

cellophane which was mounted beside the cell and which came in front of the diaphragm when the cell was moved aside. The cellophane was used to cut down the intensity of the incident light by a known amount when it was measured. The mercury vapor in the absorption cell was maintained at constant density by a suitable substance contained in a Dewar flask which moved with the cell. Melting Benzol was used for the temperature 4.2°C and melting paraxylene for 12.1°C. Water was used for temperatures between 15 and 20°C. The absorption cell proper was always at room temperature which was held as near 20°C as possible. In calculating the number of mer-

TABLE III.

(1)	(2) Thickness l in cm	(3) Temp. °C	(4) Nl $\times 10^{-13}$	(5) Absorption A	(6) $\frac{\Delta\nu E}{\Delta\nu A}$	(7) $\kappa(\nu_0)l$ from Exp. plus Eq. (2)	(8) $\kappa(\nu_0)l$ Theor. Eq. (4)
Orthmann	0.85	2.7	0.706	0.346	1.46	0.82	0.995
		6.1	.970	.419		1.10	1.37
		11.5	1.60	.571		1.91	2.26
		12.0	1.68	.582		2.00	2.37
		15.5	2.28	.700		3.22	3.22
		18.0	2.85	.723		3.52	4.02
		19.3	3.18	.763		4.25	4.49
Hughes and Thomas	1.62	−13	.244	.202	1.50	.43	.344
		−8	.431	.309		.72	.608
		−3	.745	.440		1.23	1.05
		2	1.27	.554		1.83	1.78
		7	2.01	.660		2.79	2.84
		12	3.20	.755		4.32	4.51
Kunze	.301	0	.191	.161	1.15	.27	.269
		10	.494	.356		.72	.696
		15	.776	.489		1.12	1.09
		20	1.20	.620		1.70	1.69
Kopfermann and Tietze	.54	−11	.102	.115	1.15	.19	.144
		0	.343	.291		.55	.483
		10	.886	.539		1.31	1.25
		15	1.39	.661		1.95	1.96
		20	2.15	.741		2.60	3.03
Author	.792	0	.503	.370	1.21	.77	.71
		4.2	.752	.490		1.18	1.06
		12.1	1.58	.681		2.26	2.23
		15.4	2.11	.753		2.94	2.98
		20.0	3.15	.840		4.45	4.44

cury atoms per cc the vapor pressure was obtained from the International Critical Tables and the Knudsen correction was applied. In determining the transmission at a particular temperature, readings were taken through the cell and then through the cellophane at least six times.

Liquid air was put on the resonance lamp and the sensitivity of the photoelectric cell was increased by increasing the voltage. The absorption of the radiation emitted by the resonance lamp was then measured and found to be less than the radiation emitted by the lamp at 0°C. This was due to diffuse reflection in the resonance lamp of the edges of the broad 2537 line

from the arc. Other wave-lengths did not affect the photoelectric plate, for the reason that platinum treated with hydrogen has a long wave-length limit only a little above 2537. It was estimated that about 1 percent of the radiation from the resonance lamp at 0°C consisted of unabsorbable radiation. Every reading was therefore corrected to take account of this.

The results, along with those of others, are shown in Table III, and plotted in Fig. 5.

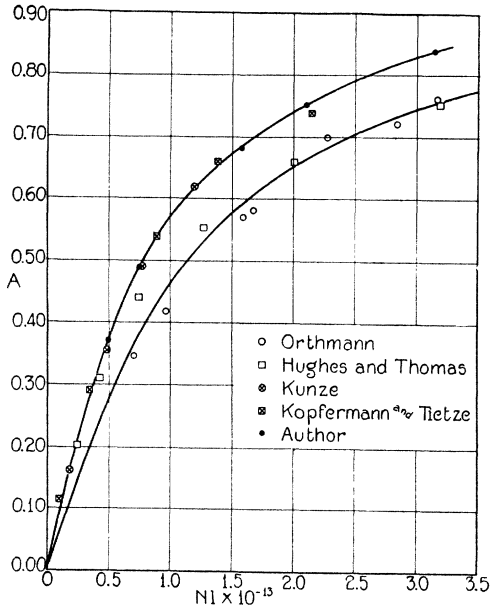

Fig. 5. A as a function of Nl.

It will be seen in Fig. 5 that all the measurements fall into two groups. those taken with the 90° type of resonance lamp, and those taken with the 45° type, the former yielding much larger values of the absorption. Both groups, however must correspond to the same values of $\kappa(\nu_0)l$. Inasmuch as it is impossible to calculate accurately $\Delta\nu_E/\Delta\nu_A$, the particular curve of A against $\kappa(\nu_0)l$ for each group is not immediately at hand. It must be chosen by appeal to theory as follows:

It is a well-known result that:[11]

$$\int_0^\infty (\kappa\nu)d\nu = \frac{h\nu_0 N}{4\pi} B_{1\to 2}$$

where N = no. of absorbing atoms per cc

ν_0 = frequency of center of line

$B_{1\to 2}$ = Einstein coefficient defined in terms of light intensity, and where the integration is to be taken over all the fine structure components of the absorption line. Using the Einstein relations

[11] E. A. Milne, M.N. of R.A.S. **85**, 111 (1924).

$$\frac{A_{2\to1}}{B_{1\to2}} = \frac{2h\nu^3}{c^2}\cdot\frac{q_1}{q_2}$$

and $A_{2\to1} = 1/\tau$, we have

$$\int_0^\infty \kappa(\nu)d\nu = \frac{\lambda_0^2}{8\pi\tau}\cdot\frac{q_2}{q_1}\cdot N$$

and substituting $\lambda_0 = 2.537 \times 10^{-5}$ cm, $\tau = 10^{-7}$ sec.[12] and $q_2/q_1 = 3$, we get

$$\int_0^\infty \kappa(\nu)d\nu = 7.68 \times 10^{-4}N.$$

Since each component of the absorption line obeys

$$\kappa(\nu) = \kappa(\nu_0)e^{-[2(\nu-\nu_0)/\Delta\nu_A]^2\log_e 2}$$

and since there are five components,

$$\int_0^\infty \kappa(\nu)d\nu = 5\left(\frac{\pi}{4\log_e 2}\right)^{1/2}\kappa(\nu_0)\Delta\nu_A$$
$$= 5 \times 1.07\kappa(\nu_0)\Delta\nu_A$$

whence finally

$$\kappa(\nu_0)l = \frac{1.44 \times 10^{-4}}{\Delta\nu_A}\cdot Nl. \tag{3}$$

In none of the experiments did the mercury vapor pressure ever become high enough to involve Lorentz collision broadening or Holtzmark coupling broadening of the absorption line. $\Delta\nu_A$ therefore, is the Doppler breadth $\Delta\nu_D$, and since the temperature of the absorption cell proper was always at 20°C, $\Delta\nu_D$ is constant. The Doppler breadth of a line is known to be $7.16 \times 10^{-7}\,\nu_0(T/M)^{1/2}$ sec^{-1} where T is the absolute temperature and M is the molecular weight. For mercury at 20°C, $\Delta\nu_D = 1.02 \times 10^9$ sec^{-1}, and consequently Eq. (3) becomes

$$\kappa(\nu_0)l = 1.41 \times 10^{-13}Nl. \tag{4}$$

In Fig. 6, Eq. (4) is shown as a heavy line. The individual points were obtained as follows:

A curve between $\kappa(\nu_0)l$ and A was sought which, in conjunction with the author's values of A, would give values of $\kappa(\nu_0)l$ that varied linearly with Nl. It was found that the curve corresponding to $\Delta\nu_E/\Delta\nu_A$ equal to 1.21 achieved this, and at the same time, agreed well with Eq. (4). Curves of $\kappa(\nu_0)l$ and A were then sought which, in conjunction with the other experimental values of A, would give values of $\kappa(\nu_0)l$ that agreed best with Eq. (4). In this way the curves corresponding to the values of $\Delta\nu_E/\Delta\nu_A$ given in Table III,

[12] R. Ladenburg, Naturwiss. **14,** 1208 (1926), H. W. Webb and H. A. Messenger, Phys. Rev. **33,** 319 (1929). For other references see M. W. Zemansky, Phys. Rev. **29,** 519 (1927).

column (6) were obtained, and the values of $\kappa(\nu_0)l$ in column (7) were obtained from these curves and experimental values of A. The values of $\kappa(\nu_0)l$ in column (8) were computed from Eq. (4). The agreement with theory is shown in Fig. 6.

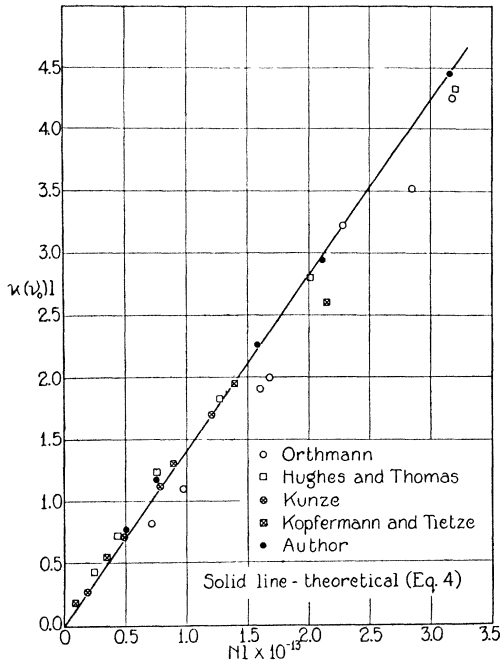

Fig. 6. $\kappa(\nu_0)l$ as a function of Nl.

Lorentz Collision Broadening

When an absorption line is broadened by Doppler broadening only, the absorption coefficient is given by

$$\kappa(\nu) = \kappa(\nu_0)e^{-[2(\nu-\nu_0)/\Delta\nu_D]^2 \log_e 2}$$

where $\Delta\nu_D$ = Doppler breadth. Under the influence of collision broadening, the absorption coefficient varies with the frequency according to a curve of the type

$$\frac{1}{1+\left[\dfrac{2(\nu-\nu_0)}{\Delta\nu_C}\right]^2}$$

where $\Delta\nu_C$ = collision breadth = no. of impacts per sec./π. With collision broadening superimposed on Doppler broadening

$$\kappa(\nu) = \frac{2\kappa(\nu_0)}{\pi\Delta\nu_C}\int_{-\infty}^{\infty}\frac{e^{-(2\delta/\Delta\nu_D)^2\log_e 2}}{1+\left[\dfrac{2}{\Delta\nu_C}(\nu-\nu_0-\delta)\right]^2}d\delta$$

$$= \frac{2\kappa(\nu_0)}{\pi\Delta\nu_C}\int_{-\infty}^{\infty}\frac{e^{-[2/\Delta\nu_D(\nu-\nu_0-\delta)]^2\log_e 2}}{1+\left(\frac{2}{\Delta\nu_C}\delta\right)^2}d\delta$$

where $\kappa(\nu_0)$ =abs. coeff. of center of line when Doppler broadening only is effective, i.e., for zero pressure of foreign gas. Call

$$\frac{2(\nu-\nu_0)}{\Delta\nu_D}(\log_e 2)^{1/2} = q \quad \text{and} \quad \frac{\Delta\nu_C}{\Delta\nu_D}(\log_e 2)^{1/2} = p$$

and let

$$x = \frac{2\delta}{\Delta\nu_D}(\log_e 2)^{1/2}.$$

Then

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \frac{p}{\pi}\int_{-\infty}^{\infty}\frac{e^{-(q-x)^2}}{p^2+x^2}dx$$

$$= \frac{2p}{\pi}e^{-q^2}\int_0^{\infty}\frac{e^{-x^2}\cos 2iqx}{p^2+x^2}dx.$$

Now

$$\frac{1}{p^2+x^2} = \int_0^{\infty}e^{-(p^2+x^2)u}du$$

whence

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \frac{2p}{\pi}e^{-q^2}\int_0^{\infty}e^{-p^2u}du\int_0^{\infty}e^{-(1+u)x^2}\cos 2iqxdx$$

$$= \frac{2p}{\pi}e^{-q^2}\int_0^{\infty}e^{-p^2u}du\,\frac{1}{2}\left(\frac{\pi}{1+u}\right)^{1/2}e^{q^2/1+u}.$$

Let $1+u = t^2/p^2$, and we have, finally

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \frac{2}{(\pi)^{1/2}}e^{p^2-q^2}\int_p^{\infty}e^{-t^2+(p^2q^2/t^2)}dt. \tag{5}$$

When there is no collision broadening, $p=0$, and

$$\kappa(\nu) = \kappa(\nu_0)e^{-q^2}\frac{2}{(\pi)^{1/2}}\int_0^{\infty}e^{-t^2}dt = \kappa(\nu_0)e^{-q^2}.$$

At extremely high foreign gas pressures p is very large, and the original expression for $\kappa(\nu)/\kappa(\nu_0)$ can be shown to reduce to $1/(\pi)^{1/2}\cdot p/p^2+q^2$. It can readily be verified that, for all values of p,

$$\int_0^{\infty}\kappa(\nu)d\nu = \left(\frac{\pi}{4\log_e 2}\right)^{1/2}\kappa(\nu_0)\Delta\nu_D$$

which is required by the constancy of the Einstein B coefficient.

In order to evaluate the integral in Eq. (5), we proceed as follows:[13]

Expanding $e^{p^2q^2/t^2}$ we have

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \sum_{n=0}^{\infty} I_n(p)\frac{e^{-q^2}q^{2n}}{n!}$$

where

$$I_n(p) = \frac{2}{(\pi)^{1/2}} e^{p^2} p^{2n} \int_p^{\infty} e^{-t^2} \frac{dt}{t^{2n}} .$$

Integrating by parts (starting with (dt/t^{2n})) we obtain a convenient means for computing successively all the $I_n(p)$,

$$I_n(p) = \frac{p}{2n-1}\left(\frac{2}{\pi^{1/2}} - 2pI_{n-1}(p)\right)$$

and

$$I_0(p) = e^{p^2}\frac{2}{(\pi)^{1/2}}\int_p^{\infty} e^{-t^2}dt$$

which can be obtained from tables.

$\kappa(\nu)/\kappa(\nu_0)$ was evaluated for different values of p and q and the results are given in Table IV.

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \frac{2}{\pi^{1/2}} e^{p^2-q^2}\int_p^{\infty} e^{-t^2+(p^2q^2/t^2)}dt$$

$$p = (\log_e 2)^{1/2}\frac{\Delta\nu_C}{\Delta\nu_D}, \qquad q = (\log_e 2)^{1/2}\frac{2(\nu-\nu_0)}{\Delta\nu_D}$$

TABLE IV. *Values of* $\kappa(\nu)/\kappa(\nu_0)$.

q \ p	0	0.5	1.0	1.5
0	1.0000	0.6157	0.4276	0.3216
0.2	.9608	.6015	.4215	.3186
.4	.8521	.5613	.4038	.3097
.6	.6977	.5011	.3766	.2958
.8	.5273	.4294	.3425	.2779
1.0	.3679	.3549	.3047	.2571
1.2	.2369	.2846	.2662	.2349
1.4	.1409	.2233	.2292	.2123
1.6	.0773	.1728	.1954	.1902
1.8	.0392	.1333	.1657	.1695
2.0	.0183	.1034	.1402	.1504

The absorption is given, as before, by

$$A = 1 - \frac{K(\nu_0, 0)\int_0^{\infty} e^{-[2(\nu-\nu_0)/\Delta\nu_E]^2\log_e 2}\cdot e^{-\kappa(\nu)l}d\nu}{K(\nu_0, 0)\int_0^{\infty} e^{-[2(\nu-\nu_0)/\Delta\nu_E]^2\log_e 2}d\nu}$$

[13] I am indebted to Dr. T. H. Gronwall for the method of evaluating Eq. (5), and to Professor H. P. Robertson for valuable help throughout the calculation.

which becomes

$$A = 1 - \frac{\int_{-\infty}^{\infty} e^{-[(q/\Delta\nu_E/\Delta\nu_D)^2+\kappa(\nu)/\kappa(\nu_0)\cdot\kappa(\nu_0)l]}dq}{\int_{-\infty}^{\infty} e^{-(q/\Delta\nu_E/\Delta\nu_D)}\,dq}$$

and which can be evaluated graphically for any situation in which $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_D$/are known. This was done for these experiments at 20 °C for which $\kappa(\nu_0)l = 4.44$ and $\Delta\nu_E/\Delta\nu_D = 1.21$, and for Orthmann's experiments at 15.5°C for which $\kappa(\nu_0)l = 3.22$ and $\Delta\nu_E/\Delta\nu_D = 1.46$. The results are given in Table V and Fig. 7.

$$A = 1 - \frac{\int_{-\infty}^{\infty} e^{-[(q/\Delta\nu_E/\Delta\nu_D)^2+\kappa(\nu)/\kappa(\nu_0)\cdot\kappa(\nu_0)l]}dq}{\int_{-\infty}^{\infty} e^{-(q\Delta\nu_E/\Delta\nu_D)^2}dq}$$

$$\frac{\kappa(\nu)}{\kappa(\nu_0)} = \frac{2}{\pi^{1/2}}e^{p^2-q^2}\int_p^{\infty} e^{-t^2+(p^2q^2/t^2)}dt.$$

TABLE V.

$\kappa(\nu_0)l$	$\frac{\Delta\nu_E}{\Delta\nu_D}$	p	$\frac{\Delta\nu_C}{\Delta\nu_D}$	A
4.44	1.21	0	0	0.840
		0.5	0.6	.833
		1.0	1.2	.775
		1.5	1.8	.707
3.22	1.46	0	0	.700
		.5	.6	.687
		1.0	1.2	.630
		1.5	1.8	.562

From the curves in Fig. 7 it is possible to obtain the collision breadth of the mercury absorption line merely by measuring the absorption. The advantage of this is that low enough foreign gas pressures may be used so that the five fine structure components of the mercury resonance line will not merge into one another, as was the case in the experiments of Füchtbauer Joos and Dinkelacker[14] who broadened the line by foreign gases at pressures up to fifty atmospheres. There is one disadvantage, however, in that the asymmetry in the line broadening predicted by theory and observed by Minkowski[15] in the case of sodium cannot be taken into account. It will be seen later how this affects the final results. Nevertheless it is believed that this method of measuring the magnitude of the collision breadth

[14] C. Füchtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 204 (1923).

[15] R. Minkowski, Zeits. f. Physik **55**, 16 (1929).

of a line is superior to the photographic method, because it enables one to separate the collision breadth from the Doppler breadth easily. A spectrogram of an absorption line which has been broadened only slightly by a foreign gas could be used to obtain the collision breadth provided one plotted

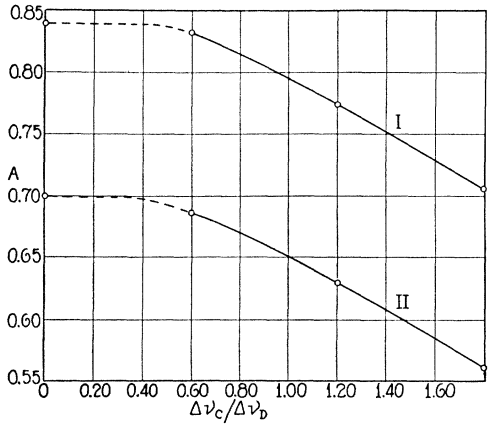

Fig. 7. A as a function of $\Delta\nu_E/\Delta\nu_D$. Curve I, $\kappa(\nu_0)l=4.44$, $\Delta\nu_E/\Delta\nu_D=1.21$. Curve II, $\kappa(\nu_0)l=3.22$, $\Delta\nu_E/\Delta\nu_D=1.46$.

measured values of $\kappa(\nu)/\kappa(\nu_0)$ against frequency, and compared these curves with those obtained from Eq. (5). A correction would have to be made, of course, for the frequency shift due to asymmetrical broadening. It is doubtful whether existing experimental data on absorption lines are sufficiently ac-

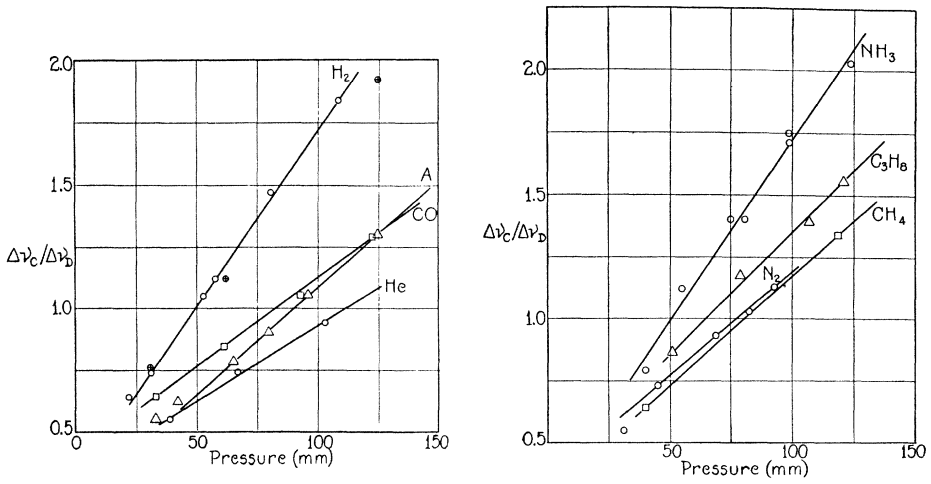

Fig. 8a and b. $\Delta\nu_C/\Delta\nu_D$ as a function of pressure.

curate for this purpose. The spectrograms of the 2537 absorption line obtained by Füchtbauer, Joos and Dinkelacker at very high foreign gas pressures yield values of the collision breadth that are somewhat in doubt be-

cause of the fact that the fine structure of the line has been completely wiped out. Nevertheless the values obtained by them are very interesting and will be referred to later.

TABLE VI.

Gas	Pressure in mm p'	Absorption A	$\frac{\Delta\nu_C}{\Delta\nu_D}$ from Fig. 7
H_2	0	0.840	0
	22	.830	.64
	31	.821	.74
	53	.790	1.05
	58	.783	1.12
	81	.746	1.47
	109	.702	1.84
H_2 (Orthmann)	0	.700	0
	31	.674	.76
	62	.638	1.12
	125	.548	1.92
N_2	0	.840	0
	31	.836	.55
	45	.822	.73
	69	.802	.93
	83	.792	1.03
	93	.782	1.13
A	0	.840	0
	33	.836	.55
	42	.831	.62
	65	.817	.78
	80	.806	.90
	96	.790	1.05
	125	.764	1.30
CO	0	0.840	0
	33	.830	.64
	61	.812	.84
	93	.790	1.05
	123	.766	1.29
He	0	.840	0
	39	.836	.55
	67	.821	.74
	103	.802	.94
NH_3	0	.840	0
	40	.817	.79
	55	.783	1.12
	75	.754	1.40
	81	.754	1.40
	99	.717	1.71
	99	.712	1.75
	124	.680	2.03
CH_4	0	.840	0
	40	.830	.64
	119	.760	1.34
C_3H_8	0	.840	0
	51	.810	.86
	79	.777	1.17
	107	.755	1.39
	121	.736	1.55

A number of foreign gases were used to broaden the line, and the results are given in Table VI and in Fig. 8. It is seen in Fig. 8 that the collision breadth plotted against the pressure of the foreign gas does not yield a straight line passing through the origin, as it should according to the relation:

$$\Delta\nu_C = \frac{\text{no. of impacts per sec.}}{\pi}$$

It is believed that this is due to the failure to take into account the asymmetry in line broadening, but that the error will not be large if the linear portions of the curves are considered. The three points for H_2 shown in Fig. 8 obtained by Orthmann five years ago under entirely different conditions as to mercury vapor density, thickness of cell, type of resonance lamp, etc., agree well enough to constitute an excellent check on the method as a whole.

Calling Z the number of impacts per mercury atom per sec, we have from kinetic theory

$$Z = 2\sigma^2_E \frac{9.71 \times 10^{18} p'}{T}\left(2\pi kT\left(\frac{1}{m}+\frac{1}{M}\right)\right)^{1/2}$$

where T is the absolute temperature, p' the pressure in mm, k Boltzmann's constant, m the mass of a mercury atom, M the mass of a foreign gas molecule, and σ_E the effective distance between centers.
Since $\Delta\nu_C = Z/\pi$,

$$\frac{Z}{p'} = \pi\Delta\nu_D \frac{\Delta\nu_C/\Delta\nu_D}{p'} = \pi \times 1.02 \times 10^9 \times \text{slope of line in Fig. 8} \quad (6)$$

and

$$\frac{Z}{\sigma_E^2 p'} = \frac{2 \times 9.71 \times 10^{18}}{T}\left(2\pi kT\left(\frac{1}{m}+\frac{1}{M}\right)\right)^{1/2} \quad (7)$$

from which σ_E^2 can be calculated.[16] The values of Z/p', $Z\sigma^2_E p'$, and σ^2_E obtained from these experiments along with those from the work of Füchtbauer, Joos, and Dinkelacker are given in Table VII.

TABLE VII.

	Gas	$\frac{Z}{p'}\times10^{-7}$ from Eq. (6)	$\frac{Z}{\sigma_E^2 p'}\times10^{-22}$ from Eq. (7)	$\sigma_E^2\times10^{16}$	$\sigma_E\times10^8$	$(\sigma_E\times1.80)\times10^8$	$-\chi_M\times10^6$	$(-\chi_M)^{1/2}\times10^3$
Author	He	1.94	1.29	15.0	3.88	2.08	1.87	1.37
	H_2	4.48	1.83	24.5	4.95	3.15	3.94	1.99
	CO	2.32	.521	44.5	6.68	4.88	10.6	3.26
	N_2	2.66	.521	51.0	7.15	5.35	11.8	3.44
	A	2.76	.448	61.5	7.85	6.05	18.0	4.24
	NH_3	4.65	.653	71.2	8.45	6.65	19.0	4.36
	CH_4	2.84	.671	42.3	6.51	4.71	12.2	3.50
	C_3H_8	3.17	.431	73.5	8.58	6.78	40.5	6.37
F. J. and D.	H_2	5.09	1.83	27.8	5.27	3.47	3.94	1.99
	N_2	3.38	.521	64.8	8.05	6.25	11.8	3.44
	A	3.98	.448	88.9	9.44	7.64	18.0	4.24
	CO_2	5.40	.431	125	11.2	9.40	18.7	4.32
	H_2O	4.37	.638	68.5	8.28	6.48	13.0	3.61
	O_2	3.20	.491	65.1	8.07	6.27	para.	

DISCUSSION

It is seen from Table VII that all the values of σ^2_E are larger than the normal ones, which vary from about 9 to 12×10^{-16} cm, in agreement with the ideas of Kallmann and London.[17] The most striking result, however, is obtained if we adopt the point of view that, in the collision process, the mercury atom has a constant radius equal to the gas-kinetic radius (1.80×10^{-8} cm) and that each broadening gas has its own effective radius. The effective radius of each gas is then obtained by substracting 1.80×10^{-8} from σ_E. Values of $\sigma_E - 1.80 \times 10^{-8}$ are given in Table VII along with values of

[16] The values of σ^2_E obtained from these experiments are to be regarded as lower limits because of the error in neglecting asymmetry. Relative values, however, are probably quite reliable.

[17] Kallmann and London, Zeits. f. Phys. Chem. Abt. **B**, 2 (1929).

the molecular diamagnetic susceptibility, χ_M. All the values of χ_M are experimental ones[18] except that for CO which was obtained by adding the susceptibilities of C and O. The justification for this is that it yields a result almost equal to that of N_2 which is known to be similar to CO in most of its properties.

In Fig. 9 the effective radius is plotted against the square root of the susceptibility, and very good straight lines are obtained for both Füchtbauer's and these results. The agreement between the two lines is no less remarkable than the lines themselves, inasmuch as the two methods are so radically different. It is possible that the correct line lies between the two

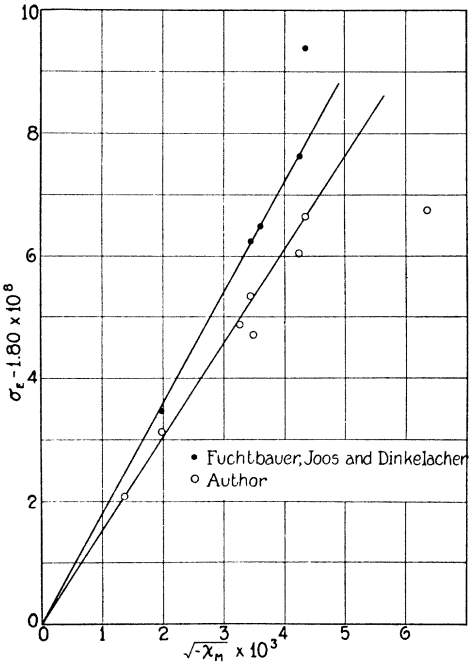

Fig. 9. σ_E as a function of $(-X_M)^{1/2}$.

because of the error that is peculiar to each method. The Langevin theory of diamagnetism allows us to give a meaning to this linear relation. According to the simple theory of diamagnetism for an atom, the atomic susceptibility is given by $-(e^2/6mc^2)\, n\overline{r^2}$ where n is the number of outer electrons of the atom, and $\overline{r^2}$ is the mean square radius of all the electronic orbits. Applying this relation to all the molecules in question, we get the result that the effective cross-section of a molecule for collision broadening is proportional to the number of outer electrons and to the mean square radius of the electronic orbits, a result that is quite interesting.

[18] A. P. Wills and G. Hector, Phys. Rev. **23,** 209 (1924), G. Hector, Phys. Rev. **24,** 418 (1924), F. Bitter, Phys. Rev. **33,** 389 (1929), Stoner "Magnetism and Atomic Structure."

According to this result, oxygen, although it is strongly paramagnetic, and cannot be plotted in Fig. 9, ought to behave like N_2 or CO, because O_2 has 16 electrons and a gas-kinetic radius of 1.47×10^{-8} cm, whereas N_2 and CO have each 14 electrons and radii equal to 1.58×10^{-8} cm and 1.60×10^{-8} cm respectively. The effective broadening radius of O_2, according to Füchtbauer's results is 6.27×10^{-8} cm in good agreement with Füchtbaur's value for N_2, 6.25×10^{-8} cm. The author did not use O_2 as a broadening agent for fear that at such high O_2 pressures, the inside walls of the absorption cell would become covered with HgO, which would lower their transmission and completely obscure any slight change in the absorption of the mercury vapor.

The only points that lie seriously off their respective straight lines in Fig. 9 are Füchtbauer's point for CO_2 and the author's for C_3H_8. There is a possibility that the value for the diamagnetic susceptibility of CO_2, -18.7×10^{-6} is too small. It was measured by Soné, whose value for N_2 is considerably smaller than the accepted value. It is not likely, however, that the value for the susceptibility of C_3H_8, measured by Bitter, is too large, because it was based on Hector and Wills' values for N_2 and H_2, and also because it fits in well with the higher hydrocarbons. Its departure from the line in Fig. 9 is much too great to be accounted for on the basis of experimental error. There is a possibility that, in the time that elapsed between its preparation and its use, it became contaminated. Unfortunately there was not sufficient time at the author's disposal to settle the question definitely. It would be very interesting to measure the effective broadening radius of all the gaseous hydrocarbons, as well as other organic gases, and it is quite likely that this will be done next year.

In conclusion, the author would like to express his indebtedness to Mr. L. J. Buttolph of the General Electric Vapor Lamp Co. for the loan of a mercury arc, and to Dr. J. R. Bates for his kindness in supplying methane and propane. It is a pleasure also to acknowledge my debt to the National Research Council for the opportunity of engaging in this research and to Professor K. T. Compton for the privilege of working in Palmer Physical Laboratory.