

THE COLLISION BROADENING OF SPECTRAL LINES

By R. W. PARSONS,* V. I. METCHNIK,* and R. J. DYNE*

[Manuscript received July 14, 1967]

Summary

The shape of a collision-broadened spectral line depends on the assumptions made about the collision processes involved. If the collision cross section varies inversely as the relative speed of the colliding molecules, the half-width to the half-power points and to the points of steepest slope should be $1/2\pi\bar{\tau}$ and $1/(2\sqrt{3})\pi\bar{\tau}$ respectively, where $\bar{\tau}$ is the mean interval between line-broadening collisions. It is shown that, in a gas of "hard-sphere" molecules, the shape of the line is modified and the above half-widths are reduced by 6.4 and 9.7% respectively. While it is not suggested that gas molecules behave entirely as hard spheres, it is suggested that some deviations from the Van Vleck-Weisskopf-Lorentz shape may occur, and that it may be possible to detect these deviations experimentally.

I. INTRODUCTION

The shape of collision-broadened spectral lines was considered by Lorentz (1915). He assumed that molecules perform internal forced oscillations under the influence of an applied oscillating electromagnetic field, and that these oscillations are interrupted by collisions. If x represents the amplitude of the molecular oscillation, Lorentz assumed that immediately following a collision the mean values of x and \dot{x} , averaged over a sufficiently large number of molecules, are zero; it follows from this that oscillation energy is dissipated and distributed among the various degrees of freedom available, so that energy is absorbed from the applied electromagnetic field. Lorentz then deduced an expression for the power absorption coefficient α in terms of the frequency of the applied field ν and the natural frequency of molecular oscillation ν_0 .

The Lorentz expression was modified by Van Vleck and Weisskopf (1945). They pointed out that if ν_0 approaches zero, the absorption coefficient should approach the expression found by Debye (1925) for non-resonant absorption. The Lorentz expression does not do this, and Van Vleck and Weisskopf showed that the discrepancy could be removed by assuming that the mean values of x and \dot{x} immediately following a collision are not zero but are related to the instantaneous value of the applied field by a Boltzmann factor.

In both formulations, an expression for x at time t is found for those molecules that experienced their last collisions at time $t_0 = t - \theta$; it is then assumed that collisions occur completely at random, so that the probability that the last collision before t occurred in $(t - \theta - \delta\theta, t - \theta)$ is

$$\tau^{-1} \exp(-\theta/\tau) \delta\theta,$$

* Department of Physics, University of Queensland, St. Lucia, Brisbane, Qld. 4067.

where τ is the mean interval between collisions and is assumed to be constant for a given gas at a constant pressure. On integrating with respect to θ , it then follows that the absorption coefficient α at frequency ν is given by

$$\alpha(\nu) = \frac{Ne^2}{mc} \left(\frac{\nu}{\nu_0} \right)^2 f(\nu, \nu_0) \Delta\nu, \quad (1)$$

where

$$f(\nu, \nu_0) = \left(\frac{1}{(\nu - \nu_0)^2 + (\Delta\nu)^2} + \frac{1}{(\nu + \nu_0)^2 + (\Delta\nu)^2} \right) \quad (2)$$

and $\Delta\nu = (1/2\pi\tau)$ is the line-width parameter.

Van Vleck and Weisskopf showed that this result can be generalized to a quantum mechanical form in which the shape factor $f(\nu, \nu_0)$ is preserved. If, as is frequently the case, $\nu_0 \gg \Delta\nu$ the second term in the parentheses in equation (2) may be neglected; for such a spectral line the half-widths to the half-power points and to the points of steepest slope are $\Delta\nu$ and $\Delta\nu/\sqrt{3}$ respectively.

This has formed the basis for much of the interpretation of experimental measurements of the widths of spectral lines in the microwave region; selected references will be found in the paper by Rinehart, Legan, and Lin (1965). Either the width between the half-power points, or, in the case of the work of Rinehart, Legan, and Lin, the width between the points of steepest slope, is measured for various gas pressures and the mean intervals between collisions are calculated from the results; these are then discussed in terms of collision processes. Microwave spectral lines are particularly suitable for this type of investigation since, at the comparatively low frequencies involved, natural or radiation broadening is negligible and, at pressures above a few millitorr, collision broadening is far greater than the only other significant mechanism, namely Doppler broadening (Parsons and Roberts 1965).

The mean intervals between collisions are usually interpreted in terms of equivalent "hard-sphere" collision diameters, and these are significantly greater than the corresponding diameters deduced from transport phenomena. As an example, the collision diameter of methyl chloride deduced from viscosity data is 5 Å, while that deduced from the self broadening of the $J = 0 \rightarrow 1$ line in the rotational spectrum is 15.9 Å (Roberts and Parsons 1966). This is presumably because in transport phenomena the energy of interaction on collision must be of the order of kT , while for the interruption of radiation it is of the order of $h\nu$, and in the microwave region for gases at room temperature $h\nu \ll kT$.

The purpose of this paper is to point out that the expression (2) for the shape factor is valid only if τ is constant for all the molecules in a gas at a given pressure. This will be so if the collision cross section is inversely proportional to the relative speed of the colliding molecules and, under the assumption of weak collisions such that the interacting molecules pass along straight line paths with constant velocities, this will be true (Anderson 1949; Tsao and Curnutte 1960). It will not be so for hard-sphere molecules, since those moving with high speeds will on the average experience more collisions per second than the slower ones, and the following analysis shows

that under these circumstances the line shape is modified so that the half-width between the half-power points is 5.4% less than $\overline{\Delta\nu}$, while between the points of steepest slope it is 9.7% less than $\overline{\Delta\nu}/\sqrt{3}$, where $\overline{\Delta\nu}$ is the mean value of $\Delta\nu$ averaged over all the molecules. Since half-widths may be determined experimentally to an accuracy of 2%, the effect may be significant; and if the shape of a complete spectral line can be measured to an accuracy of this order, it may be necessary to interpret the results in terms of collisions between molecules that behave as hard-sphere cores (possibly with diameters of the order of those deduced from transport phenomena) surrounded by "soft-sphere" regions for which the collision probability is inversely proportional to the relative speed of the colliding molecules.

II. CALCULATION OF LINE SHAPE

(a) *Hard-sphere Molecules*

The calculation of the mean interval between collisions $\bar{\tau}$ averaged over all the molecules may begin from the expression

$$\bar{v}_r \bar{\tau} \sigma N = 1, \quad (3)$$

where \bar{v}_r is the mean relative speed of the molecules, σ the cross section, and N the number of molecules per unit volume (Present 1958); for a Maxwellian distribution of particles of mass m at a temperature T

$$\bar{v}_r = 4(kT/\pi m)^{\frac{1}{2}}. \quad (4)$$

Now, however, consider those molecules whose speeds, relative to the laboratory frame of reference, lie in the range $(v, v + \delta v)$. It is shown in the Appendix that the mean speed of these molecules relative to the remainder is

$$v_r = 4(kT/\pi m)^{\frac{1}{2}} F(\beta),$$

where

$$F(\beta) = \frac{1}{\sqrt{2}} \left(\frac{1}{2} \exp(-\beta^2) + (\beta + 1/2\beta) \int_0^\beta \exp(-y^2) dy \right)$$

and

$$\beta = v(m/2kT)^{\frac{1}{2}}.$$

It follows from (3) that, if τ_v is the mean interval between collisions involving at least one molecule whose speed lies in the range $(v, v + \delta v)$, then

$$\tau_v / \bar{\tau} = \bar{v}_r / v_r, \quad (5)$$

and hence the corresponding line-width parameter is

$$\begin{aligned} \Delta\nu_v &= \overline{\Delta\nu} (v_r / \bar{v}_r) \\ &= \overline{\Delta\nu} F(\beta), \quad \text{where} \quad \overline{\Delta\nu} = 1/2\pi\bar{\tau}. \end{aligned}$$

The contribution $\delta\alpha$ to the absorption coefficient is then found from (1) on replacing N by

$$\delta N_v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \delta v; \quad (6)$$

and hence, on integrating over all values of v and making the assumption $\nu_0 \gg \overline{\Delta\nu}$ so that the second term in equation (2) may be neglected, it follows that

$$\alpha(\nu) = A \left(\frac{\nu}{\nu_0} \right)^2 \frac{1}{\overline{\Delta\nu}} \int_0^\infty \frac{\beta^2 F(\beta) \exp(-\beta^2)}{(\nu - \nu_0)^2 + \{\overline{\Delta\nu} F(\beta)\}^2} d\beta, \quad (7)$$

where $A = 4Ne^2/mc\pi^{\frac{1}{2}}$. The quantum mechanical expression for A may be found from equation (2) of Van Vleck and Weisskopf (1945), but the dependence of α on ν is still described by the above equation (7). In this equation, it is convenient to introduce the dimensionless parameter $u = (\nu - \nu_0)/\overline{\Delta\nu}$; it then becomes

$$\alpha(u) = (A/\overline{\Delta\nu})(\nu/\nu_0)^2 G(u).$$

where the shape function $G(u)$ is given by

$$G(u) = \int_0^\infty \frac{\beta^2 F(\beta) \exp(-\beta^2)}{u^2 + \{F(\beta)\}^2} d\beta. \quad (8)$$

This was evaluated numerically for a series of values of u with the aid of a GE225 computer, and the results are plotted in Figure 1. It has a maximum when $u = 0$, and falls to half the maximum value when $u = \pm 0.946$.

The points of steepest slope, which are of particular interest since their frequency separation may be measured directly, are given by the solutions of

$$d^2G/du^2 = 0.$$

This equation was solved numerically and the result was $u = \pm 0.521$. The term $(\nu/\nu_0)^2$ in the expression for α may be equated to unity without significant error provided $\nu_0 \gg \overline{\Delta\nu}$; thus if a spectral line of frequency $\nu_0 = 30$ GHz and width $\overline{\Delta\nu} = 500$ kHz is to be studied in the frequency range $\nu_0 \pm 3\overline{\Delta\nu}$, for example, $(\nu/\nu_0)^2$ will not differ from unity by more than 1 part in 10^4 .

(b) "Soft" Molecules

If the result of Anderson (1949) that $\sigma \propto v_r^{-1}$ is assumed to be valid for all collisions, irrespective of the distance of closest approach of the molecules, it follows from equation (3) that $\tau_v = \bar{\tau}$ and hence that τ_v is independent of v . The absorption coefficient is then given directly by equation (1), and may be expressed in the form

$$\alpha(u) = \frac{A}{\overline{\Delta\nu}} \left(\frac{\nu}{\nu_0} \right)^2 \frac{1}{4} \pi^{\frac{1}{2}} \left(\frac{1}{u^2 + 1} \right). \quad (9)$$

In order to facilitate comparison with equation (8), the shape function

$$H(u) = \frac{1}{4}\pi^{\frac{1}{2}} \left(\frac{1}{u^2 + 1} \right)$$

is also plotted as a function of u in Figure 1. It has a maximum when $u = 0$ but falls to half the maximum value when $u = \pm 1$; this implies a half-width of $\overline{\Delta\nu}$, as has been already stated. The points of steepest slope are given by the solutions of

$$d^2H/du^2 = 0,$$

which are $u = 0.577\overline{\Delta\nu}$.

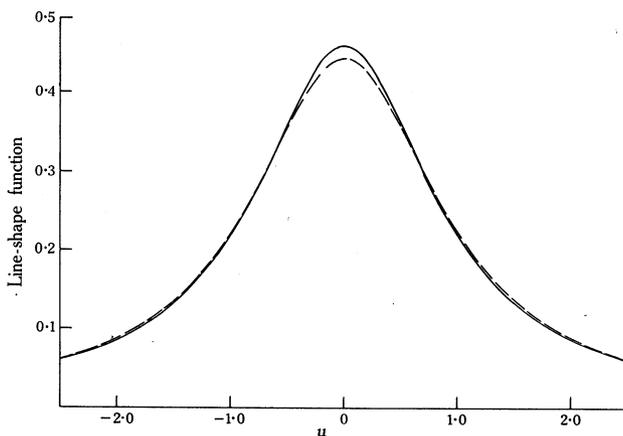


Fig. 1.—The line-shape function $G(u)$ for hard-sphere interactions (full curve) is compared with the Lorentz shape $H(u)$ (dashed curve). The abscissa u represents the dimensionless parameter $(\nu - \nu_0)/\overline{\Delta\nu}$.

III. CONCLUSIONS

It has been shown that the predicted shape of a collision-broadened spectral line depends on the assumptions made about the nature of the collision processes involved. If the cross section for line-broadening collisions varies inversely as the relative speed of the colliding molecules, the line shape is described by the Van Vleck-Weisskopf modification of the Lorentz theory; if not, departures from the Van Vleck-Weisskopf shape may be expected, and in the limiting case of hard-sphere collisions, these departures are of the order of several per cent. While it is not for a moment suggested that molecules do, in fact, behave entirely as hard spheres, it is suggested that some deviations from the Van Vleck-Weisskopf shape may occur, and hence it would be of interest if the shape of a collision-broadened line could be measured to an accuracy of, for example, 1%. A line in the microwave region of the spectrum appears most suitable for such an investigation, since at pressures above a few millitorr collisions provide the only line-broadening mechanism of significance. A line broadened by non-polar foreign gas collisions would be more

appropriate for study than a self-broadened line, since in the former case the collision diameters for line broadening are not greatly in excess of those deduced from transport phenomena (Burton *et al.* 1965; Roberts and Parsons 1966), and hence the effect of a "hard-sphere core" may be more apparent. This may not now be beyond the range of possibility, since existing microwave line-width spectrometers are capable of an accuracy of better than 2%. However, such instruments merely measure one parameter of a spectral line (the half-width); the development of an instrument for measuring the complete line shape presents difficult experimental problems but these appear worthy of investigation.

IV. ACKNOWLEDGMENT

This investigation was performed as part of the microwave research programme of the University of Queensland, which receives support from the Australian Research Grants Committee.

V. REFERENCES

- ANDERSON, P. W. (1949).—*Phys. Rev.* **76**, 647.
 BURTON, C. H., NOON, J. H., LASICH, W. B., and PARSONS, R. W. (1965).—*Aust. J. Phys.* **19**, 283.
 DEBYE, P. (1925).—"Polar Molecules." Ch. 5. (Dover: New York.)
 LORENTZ, H. A. (1915).—"The Theory of Electrons." Note 57. (Dover: New York.)
 PARSONS, R. W., and ROBERTS, J. A. (1965).—*J. molec. Spectrosc.* **18**, 412.
 PRESENT, R. D. (1958).—"Kinetic Theory of Gases." (McGraw Hill: New York.)
 RINEHART, E. A., LEGAN, R. L., and LIN, C. C. (1965).—*Rev. mod. Phys.* **36**, 511.
 ROBERTS, J. A., and PARSONS, R. W. (1966).—*J. molec. Spectrosc.* **20**, 195.
 TSAO, C. J., and CURNUTTE, B. (1960).—Line widths of pressure broadened spectral lines. Geophysical Research Papers No. 69, A. F. Cambridge Research Laboratories, U.S. Air Force, Bedford, Mass.
 VAN VLECK, J. H., and WEISSKOPF, V. (1945).—*Rev. mod. Phys.* **17**, 227.

APPENDIX

Consider first a problem in geometry. Suppose that a sphere of radius a has a large number of points uniformly distributed over its surface and that one of these points is P . Suppose further that a second sphere, concentric with the first but of radius a_1 , has points, one of which is Q_i , uniformly distributed over its surface, there being a large number n of points per unit surface area. It is required to find the mean distance PQ_i averaged over all the points Q_i . Using the nomenclature of Figure 2, this mean distance \bar{s} will be defined as

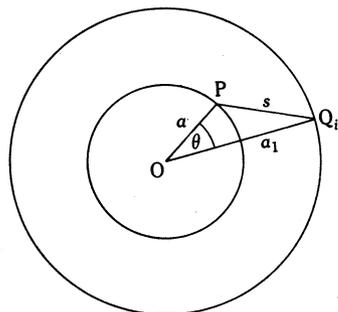


Fig. 2

$$\begin{aligned}\bar{s} &= \lim_{n \rightarrow \infty} (4\pi a_1^2 n)^{-1} \sum PQ_i \\ &= (4\pi a_1^2)^{-1} \int_0^\pi 2\pi a_1^2 s \sin \theta \, d\theta.\end{aligned}$$

On writing $s^2 = a^2 + a_1^2 - 2aa_1 \cos \theta$, this becomes

$$\bar{s} = (2aa_1)^{-1} \int_{s_1}^{s_2} s^2 ds,$$

where the limits of integration are

$$s_1 = a_1 - a \quad \text{and} \quad s_2 = a_1 + a \quad \text{if } a < a_1,$$

or

$$s_1 = a - a_1 \quad \text{and} \quad s_2 = a + a_1 \quad \text{if } a > a_1.$$

Hence

$$\bar{s} = a_1 + a^2/3a_1 \quad \text{if } a < a_1$$

and

$$\bar{s} = a + a_1^2/3a \quad \text{if } a > a_1.$$

Now consider a large number of molecules whose speeds are distributed according to the Maxwellian function, equation (6). It follows from the above analysis that the mean speed of all those molecules whose speeds are v in the laboratory frame relative to those whose speeds are v_1 in the same frame will be $v_1 + v^2/3v_1$ if $v < v_1$ and $v + v_1^2/3v$ if $v > v_1$. On averaging over all values of v_1 , the result is

$$v_r = \frac{1}{N} \left(\int_0^v (v + v_1^2/3v) dN_{v_1} + \int_v^\infty (v_1 + v^2/3v_1) dN_{v_1} \right),$$

where

$$dN_{v_1}/dv_1 = 4\pi N(m/2\pi kT)^{3/2} \exp(-mv_1^2/2kT).$$

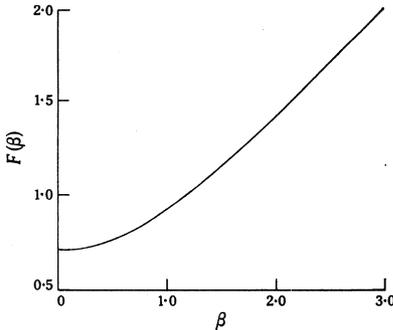


Fig. 3.—Relative speed distribution function $F(\beta)$ plotted as a function of the dimensionless parameter $\beta = v(m/2kT)^{1/2}$.

Successive integration by parts then gives the expression for v_r used in the text, namely

$$\begin{aligned} v_r &= 2 \left(\frac{2kT}{\pi m} \right)^{1/2} \left(\frac{1}{2} \exp(-\beta^2) + (\beta + 1/2\beta) \int_0^\beta \exp(-y^2) dy \right) \\ &= 4(kT/\pi m)^{1/2} F(\beta), \end{aligned} \tag{A1}$$

where $\beta = v(m/2kT)^{1/2}$.

In Figure 3, $F(\beta)$ is plotted as a function of β . When $v = 0$, $v_r = 2(2kT/\pi m)^{\frac{1}{2}}$, and this is the mean speed relative to the laboratory frame of reference; for very large values of v , $v_r \rightarrow v$ and this also is as expected. As a further check of the validity of equation (A1), the quantity

$$\int_0^{\infty} \beta^2 F(\beta) \exp(-\beta^2) d\beta$$

was evaluated numerically, and gave a result equal to $\frac{1}{4}\pi^{\frac{1}{2}}$; this then yields the value $4(kT/\pi m)^{\frac{1}{2}}$ for the mean relative speed averaged over the whole distribution, in agreement with equation (4).