Broadening of Microwave Absorption Lines Due to Wall Collisions*

MICHAEL DANOS AND STANLEY GESCHWIND†
Radiation Laboratory, Columbia University, New York, New York
(Received May 8, 1953)

The broadening of microwave absorption lines due to wall collisions is calculated using a method introduced by Johnson and Strandberg. Two types of absorption cell are studied, i.e., infinite plane parallel plates and a circular cylinder, each in a region of uniform microwave field. The usual assumption that the half-power half-width is given by $\Delta\nu=1/2\pi\tau$, where τ is the mean time between collisions is in good agreement with the detailed calculations of the present work which show that the error in the line width as calculated by the above expression is not larger than 30 percent. Experimentally observed line widths agree with the predicted values.

ONE of the effects which limits the resolution obtainable by microwave spectroscopy is broadening of absorption lines due to collisions between absorbing gas molecules and the walls of a containing cell. Several estimates of the magnitude of this type of line broadening have been made.[1–4] Since the most recent and most detailed investigation[4] disagrees with earlier estimates and with some experimental observations, it seems worth while to discuss this question once more. It will be shown below that the earlier rough estimates[3] of line broadening due to molecular collisions with walls are actually not far from correct.

In the earlier investigations[1–3] it was tacitly assumed that this line broadening was Lorentz-shaped with a half-power half-width

$$\Delta\nu=1/2\pi\tau, \tag{1}$$

where τ is the mean time between collisions given by

$$1/\tau=(A/V)(kT/2\pi m)^{\frac{1}{2}}, \tag{2}$$

with A the total area, V the volume of the absorption cell, and m the mass of the molecules.

However, Johnson and Strandberg[4] have shown that in general the line shape will differ from that of a Lorentz line and will depend on the geometry of the absorption cell. They investigated the case of an absorption cell consisting of the space between two infinite parallel planes separated by a distance a. However, their value for the line width is several times too large and is based on an incomplete evaluation of an integral which appears below in Eq. (5).

We summarize their argument up to that point. Assume that the molecules make transitions between states with energies E_i and E_j. In an electric field described by

$$E=0 \text{ for } t<0,$$
$$E=E_0\sin(\omega t) \text{ for } t>0,$$

the increase in the probability of finding a molecule in the upper state j is given[5] by

$$|a_j(t)|^2-|a_j(0)|^2=(\Omega/\kappa)^2(|a_i(0)|^2-|a_j(0)|^2)\times\sin^2(\tfrac{1}{2}\kappa t), \tag{3}$$

where $|a_i(t)|^2$ and $|a_j(t)|^2$ are the probabilities of finding a molecule at the time t in the states i and j, respectively; $\Omega=\mu_{zij}E_0/\hbar$, and μ_{zij} is the matrix element of the Z component of the electric dipole moment between the states i and j; $\hbar\omega_0=E_j-E_i$; $\delta\omega=\omega_0-\omega$; $\kappa^2=(\delta\omega)^2+\Omega^2$. $|a_j(0)|^2$ is given by the Boltzmann distribution by virtue of the assumption that a collision with the wall returns the molecule to thermal equilibrium. Now let $f(t)$ be a distribution function such that, if there are N molecules, then

$$dn=Nf(t)dt$$

is the number which had their last collision between the times t and $t+dt$ in the past. The power attenuation constant is then given by

$$\alpha=\frac{\hbar\omega\rho}{\langle S\rangle}\int_0^\infty dtf(t)\frac{d}{dt}(|a_j(t)|^2-|a_j(0)|^2), \tag{4}$$

where ρ is the density of molecules and $\langle S\rangle$ is the time average of the Poynting vector.

In the case of plane parallel plates separated by the distance a, $f(t)$ is such that Eq. (4) becomes

$$\alpha=(B/\epsilon)\int_0^\infty[1-\exp(-1/\zeta^2)]\sin(\epsilon\zeta)d\zeta, \tag{5}$$

where $\epsilon=\kappa\beta$, $\beta=a(m/2kT)^{\frac{1}{2}}$ and

$$B=16\pi^{5/2}(\nu^2\rho\beta|\mu_{zij}|^2/ckT)(e^{-E_i/kT}/\textstyle\sum_j e^{-E_j/kT}).$$

The integral appearing in (5) can be evaluated approximately in closed form[6] if $1-\exp(-1/\zeta^2)$ is

* Work supported jointly by the Signal Corps and the U. S. Office of Naval Research.
† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.
[1] W. Gordy, Revs. Modern Phys. **20**, 668 (1948).
[2] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **60**, 83 (1948).
[3] C. H. Townes, J. Appl. Phys. **22**, 1365 (1951).
[4] R. H. Johnson and M. W. P. Strandberg, Phys. Rev. **86**, 811 (1952).
[5] I. I. Rabi, Phys. Rev. **51**, 652 (1937).
[6] W. Magnus and F. Oberhettinger, *Formeln und Sätze für die speziellen Funktionen der mathematischen Physik* (J. Springer, Berlin, 1943).

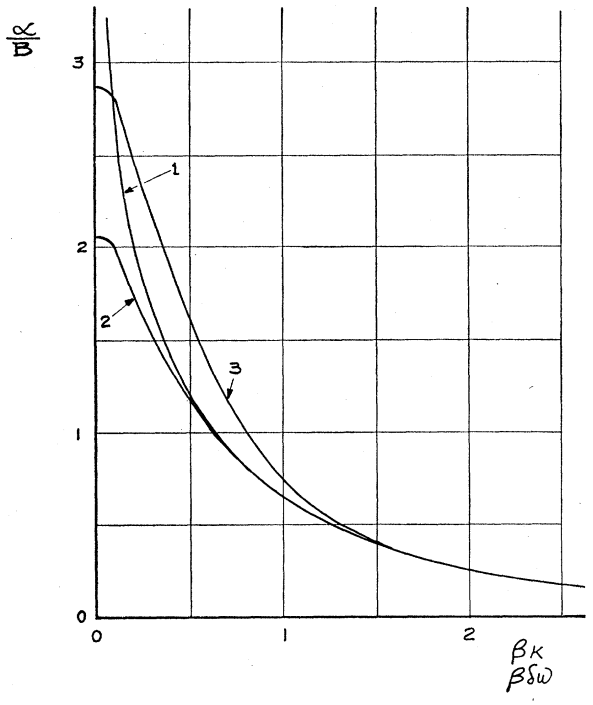

FIG. 1. Line shapes due to wall broadening; infinite parallel planes. Curve 1: α/B as function of $\kappa\beta$; curve 2: α/B as function of $\beta\delta\omega$ at a power level where $\beta\Omega=0.2$; curve 3: Lorentz-line with $2\pi\beta\Delta\nu=0.6$ as function of $\kappa\beta$.

replaced by $1/(1+\zeta^2)$. The result so obtained is exact both for $\epsilon\to 0$ and $\epsilon\to\infty$ and has its maximum error around $\epsilon\approx 0.5$. The maximum error is less than 30 percent. With this approximation the power attenuation constant is

$$\alpha=(B/2\epsilon)[e^{-\epsilon}\,\mathrm{Ei}(\epsilon)-e^{\epsilon}\,\mathrm{Ei}(-\epsilon)], \qquad (6)$$

where $\mathrm{Ei}(\epsilon)$ is the exponential integral.[6]†

α varies as $1/\epsilon^2$ down to $\epsilon\approx 1.5$. [As a matter of fact any nonadiabatic collision process will yield a line shape which varies asymptotically as $1/(\delta\omega)^2$.] For $\epsilon\to 0$, the attenuation constant goes logarithmically to infinity (see curve 1, Fig. 1). This last feature makes the definition of a line width ambiguous for vanishingly small power. However, in the presence of a finite amount of power the singularity is removed because $\epsilon\geq\beta\Omega$. Under this condition the line width is well defined by Eq. (6) (plotted as curve 2 in Fig. 1 for $\beta\Omega=0.2$) and a measure of the contribution of wall collisions to this line width can be obtained in the following manner. We define a quantity η such that

$$2\pi\beta\Delta\nu=(\beta^2\Omega^2+\eta^2)^{\frac{1}{2}},$$

where $\Delta\nu$ is the half-power half-width. We find that for $\beta\Omega\geq 0.2$, η is essentially constant and has the value $\eta\approx 0.6$. This term η appearing in addition to the power term $\beta\Omega$ is properly identified as arising from wall collisions, giving

$$\Delta\nu(\text{wall collisions})=\eta/2\pi\beta\approx 0.1(1/a)(2kT/m)^{\frac{1}{2}}. \qquad (7)$$

A Lorentz line given by $1/(\epsilon^2+\eta^2)$ (curve 3, Fig. 1) with $\eta=0.6$ gives the same line width as Eq. (6) down to a power level $\beta\Omega=0.2$. This, for example, corresponds to a power level of roughly 10^{-7} watt/cm^2 for OCS at room temperature and for a plate separation equal to one cm. With decreasing power level, i.e., $\beta\Omega\to 0$, $\eta\to 0$.

The error introduced by the approximation used in going from Eq. (5) to Eq. (6) is such that the actual line width is no more than 30 percent larger than the line width given by Eq. (7).

Returning now to Eqs. (1) and (2) and specializing to the present geometry, we have

$$\Delta\nu=\frac{1}{2\pi^{\frac{3}{2}}}\left(\frac{1}{a}\right)\left(\frac{2kT}{m}\right)^{\frac{1}{2}}=0.09\left(\frac{1}{a}\right)\left(\frac{2kT}{m}\right)^{\frac{1}{2}}, \qquad (8)$$

a result only 10 percent smaller than the value given by Eq. (7).

As can be seen from Eq. (3), the absorption of energy by a molecule at resonance and for vanishing power level increases proportionally to the time. This, together with the fact that there are too many molecules with infinitely long times of flight, gives rise to the singularity of α at the origin. As this singularity is only logarithmic, one is led to expect that any reduction in the long times of flight would remove it. Such a reduction can be achieved for example, by the addition of side walls somewhere at a finite distance. We shall therefore investigate the simplest case of this kind, which is that of a circular cylindrical absorption cell located in a region of a wave guide where the electric field is essentially uniform.

For this calculation it is easier to use directly the expression, Eq. (3), which after multiplication with $\hbar\omega$ gives the energy $W(t)$ a molecule has absorbed between two collisions, if one specifies t as the time of flight between collisions.

If N is the number of molecules colliding with the wall per unit length of the cell per second, and $F(t)$ the distribution function of the times of flight from their last collisions of those molecules which at the present time are colliding with the wall, then the power absorbed per unit length of cell is

$$\Delta P=\int_0^\infty NF(t)W(t)dt.$$

The power absorption coefficient α is therefore

$$\alpha=\frac{\hbar\omega N}{\pi R^2\langle S\rangle}\int_0^\infty(|a_j(t)|^2-|a_j(0)|^2)F(t)dt, \qquad (9)$$

where R is the radius of the cell.[7]

† *Note added in proof.*—A similar result has been obtained by G. S. Newell, thesis, Princeton University, 1952 (unpublished).

[7] The connection of $F(t)$ in Eq. (9) with $f(t)$ of Eq. (4) can be established by integrating Eq. (4) by parts.

The function $F(t)$ depends on the geometry of the absorption cell and in our case can be found as follows. Since the length of the cell in the x direction is assumed infinite only components of the velocity of the molecules in the y and z direction contribute to a motion approaching the walls. Let θ be the projection on the y–z plane of the angle between the normal to the wall and the direction of motion of a molecule colliding with the wall. If v is the projection of the velocity on the y–z plane then the probability for such a collision, dw is

$$dw \sim dA \cos\theta v \exp(-mv^2/2kT) d\theta v dv,$$

where dA is the surface element. The time of flight for the considered molecule is given by

$$t = 2R\cos\theta/v.$$

Expressing v in terms of t and inserting (3) in (9) we find that the integral in Eq. (9) is proportional to

$$I = \int_0^\infty dt \int_0^{\pi/2} d\theta \cos^4\theta \sin^2(\kappa t/2) t^{-4} \exp(-\sigma^2 \cos^2\theta/t^2), \tag{10}$$

TABLE I. Comparison of line width parameters Q [see Eq. (14)] of microwave absorption lines broadened by wall collisions.

	L	Q Elementary theory	Q Present work
Parallel planes	a	0.09	0.10
Circular cylinder	$2R$	0.18	0.20

where $\sigma^2 = (2R)^2 m/2kT$. By substituting

$$\xi = t/(\sigma\cos\theta), \quad \lambda = \kappa\sigma,$$

we obtain

$$I = \frac{1}{2\sigma^3} \int_0^\infty d\xi \exp(-1/\xi^2)\xi^{-4} \int_0^{\pi/2} d\theta [1 - \cos(\xi\lambda\cos\theta)]$$

$$= (\pi/4\sigma^3) \int_0^\infty d\xi \exp(-1/\xi^2)\xi^{-4} H_1(\xi\lambda), \tag{11}$$

where $H_1(x)$ is the Struve-function of the first order.[6] Using the expansion,

$$H_1(x) = \frac{2}{\pi}\left[\frac{x^2}{3} - \frac{x^4}{45} + \cdots\right],$$

one finds for the peak absorption

$$\alpha(0) = (64/3)\pi^{5/2}(\nu^2 \rho\sigma |\mu_{zij}|^2/ckT) \times (e^{-E_i/kT}/\textstyle\sum_j e^{-E_j/kT}). \tag{12}$$

The shape of the line has been found by numerical integration (plotted as curve 1 in Fig. 2), yielding a

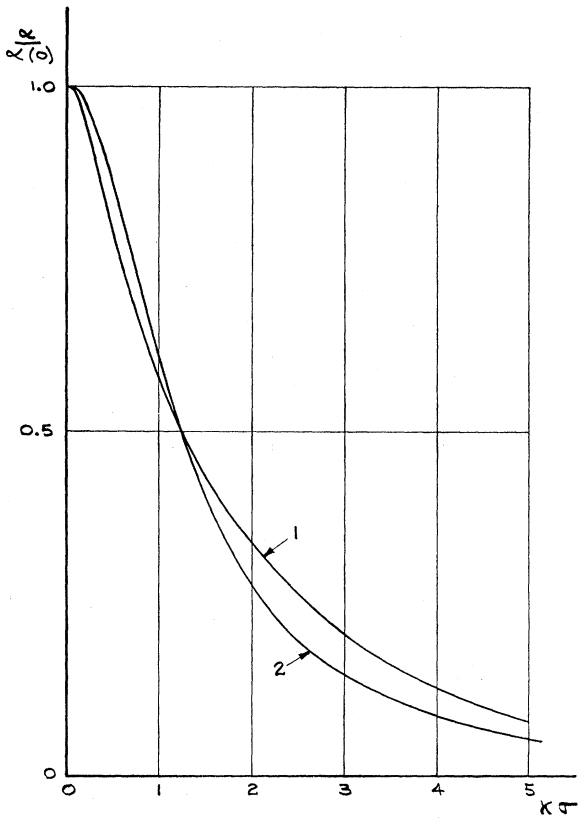

FIG. 2. Line shapes due to wall broadening in a circular absorption cell; curve 1: $\alpha/\alpha(0)$ as a function of $\kappa\sigma$; curve 2: Lorentz line with the same peak absorption and half-width as a function of $\kappa\sigma$.

half-power half-width due to wall collisions, of

$$\Delta\nu = \frac{1.25}{2\pi}\frac{1}{2R}\left(\frac{2kT}{m}\right)^{\frac{1}{2}}. \tag{13}$$

For purposes of comparison, a Lorentz line having the same peak absorption and the same half-width is plotted as curve 2 in Fig. 2.

The results may be summarized in the following way. Let us express the half-width of the line broadening due to wall collisions by

$$\Delta\nu = \frac{Q}{L}\left(\frac{2kT}{m}\right)^{\frac{1}{2}}, \tag{14}$$

where Q is a numerical factor and L is a length characteristic of the absorption cell. Specifying L, then Q as calculated both by the elementary theory [Eqs. (1) and (2)] and by the present work, are listed in Table I.

As seen from the table, the agreement between the elementary and the more exact calculation is sufficiently good to justify the use of the elementary theory is calculating line width due to wall collisions. The values of the line widths calculated this way can be expected to have an error of at most 30 percent.

Line widths regularly observed on a high resolution

microwave spectrometer at the Columbia Radiation Laboratory have been in general agreement with the above calculations. As an example, we cite the recent experimental work of Gunther-Mohr and White on an additional fine structure in the ammonia quadrupole spectrum,[8] where the measured total width at half-maximum for NH_3 at dry ice temperature in X-band Stark guide was found to be 68 ± 5 kc/sec. The calculated Doppler broadening and collision broadening for NH_3 under these conditions are, respectively, $2\Delta\nu_{\text{Doppler}}=60$ kc/sec and $2\Delta\nu_{\text{coll}}=25$ kc/sec. Born has tabulated the resultant shape for a Lorentz line broadened by Doppler effect.[9] His tabulated results show that the total line width is given to a good approximation by

$$\Delta\nu\simeq[(\Delta\nu_{\text{Doppler}})^2+(\Delta\nu_{\text{coll}})^2]^{\frac{1}{2}}. \quad (15)$$

Extrapolating from the results of the present paper, one is led to expect that in practice, quite generally (and at least for a rectangular wave guide) the line shape of broadening due to collisions with the wall will be sufficiently close to that of a Lorentz line so that expression (15) can be used. Thus the combined theoretical line width is $2\Delta\nu=(60^2+25^2)^{\frac{1}{2}}=65$ kc/sec in agreement with the observed value.

We wish to thank Professor Townes for his active aid. We also wish to thank Professor Strandberg for an interesting discussion. The help of Mr. George Dousmanis who performed the numerical calculations is gratefully acknowledged.

[8] G. R. Gunther-Mohr and R. White (to be published).
[9] M. Born, *Optik* (J. Springer, Berlin, 1933), Table 38, p. 486, and p. 431 and the following.

PHYSICAL REVIEW VOLUME 91, NUMBER 5 SEPTEMBER 1, 1953

Polarizability of the Deuteron*

N. F. RAMSEY, B. J. MALENKA, AND U. E. KRUSE
Harvard University, Cambridge, Massachusetts

(Received May 25, 1953)

The theory of the polarizability of the deuteron in a uniform electric field is developed. Using the properties of the deuteron Green's function, we obtain an expression for polarizability of the deuteron which exhibits its dependence upon the spin orientation of the deuteron. This dependence arises from the inclusion of a tensor force in the neutron-proton interaction. In terms of the magnetic quantum number m, with respect to the direction of the electric field, the polarizability α is $\alpha_{SS}+(3m^2-2)\alpha_{SD}+(3m^2-2)^2\alpha_{DD}$. When Hulthén wave functions are used for the deuteron, α_{SS} is found to be approximately 0.56×10^{-39} cm^3 and α_{SD} 0.027×10^{-39} cm^3. The applicability of the theory to intramolecular interaction measurements and deuteron scattering experiments is discussed.

I. INTRODUCTION

THE particles which constitute the deuteron do not all have the same ratio of charge to mass so that, because of reorientation and stretching, the deuteron will exhibit a polarizability with respect to an external electric field.

It has been pointed out earlier by Ramsey[1] that this polarizability of the deuteron should give rise to a measurable departure from Rutherford scattering in certain cases where deuterons are scattered by heavy nuclei. In addition, the dependence of the deuteron polarizability upon its spin orientation should also give rise to a small change in the deuteron quadrupole interaction in D_2 and HD as a result of the difference is amplitude of zero-point vibration in the two molecules and consequently of the oscillating electric field at the deuteron.

In this paper, we calculate the polarizability of the deuteron in an adiabatically applied uniform external electric field. The electric scattering of the deuteron will be examined in a subsequent paper.

The polarizability of a nucleus is related to its polarization energy W_p, in an adiabatically applied, uniform electric field $\mathcal{E}$, by the equation[2]

$$\alpha=-2W_p/\mathcal{E}^2. \quad (1)$$

The W_p is the energy of the second-order Stark effect arising from the perturbation

$$V=-\tfrac{1}{2}ez\mathcal{E}, \quad (2)$$

where z is the component along the direction of the electric field $\mathcal{E}$ of the relative distance $\mathbf{r}=\mathbf{r}_p-\mathbf{r}_n$ of the proton from the neutron. The factor $\frac{1}{2}$ enters because we are concerned with the displacement of the proton with respect to the center of mass of the deuteron. The polarization energy is then

$$W_p=-\tfrac{1}{4}e^2\mathcal{E}^2\sum_{n\neq0}{}'(0|z|n)(n|z|0)/(E_n-E_0), \quad (3)$$

where $\sum'_{n\neq0}$ represents the sum over all the discrete and continuum intermediate states except the ground

* This work was partially supported by the joint program of the U. S. Office of Naval Research and the U. S. Atomic Energy Commission.
[1] N. F. Ramsey, Phys. Rev. **83**, 659 (1951).
[2] D. Bohm, *Quantum Theory* (Prentice Hall, Inc., New York, 1951) p. 461.