

## Pressure Broadening in the Microwave and Infra-Red Regions\*

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In this paper a generalized theory of collision broadening is developed, adequate for predicting line breadths in the microwave and infra-red regions. This theory differs from previous ones in taking into account transitions among quantum states caused by collisions, although it is limited to a classical picture of the relative motion of the colliding molecules as a whole. Formulas are derived for computing approximate line broadening collision cross-sections from known intermolecular interactions, and the results of the theory are successfully compared with experiments on self-broadening in the ammonia inversion spectrum and the vibrational band spectra of HCl and HCN. Some cases of foreign gas broadening in the microwave region are examined, but it is concluded that in general the Van der Waals interaction, commonly assumed to be the force important in causing foreign gas broadening, is not adequate to cause the observed broadenings. The more complicated types of forces which become important at short range would have to be taken into account to give good agreement with experiment in these cases.

### PART I. THEORY

#### A. Introduction

THE theories of pressure broadening presented up to this time can easily be shown to be inapplicable in the microwave and infra-red regions of the spectrum. The primary purpose of this paper is, therefore, to develop a theory which can give accurate results in these regions, and to compare these results with the available experimental data.

The older theories, in particular the Fourier integral treatment developed primarily by Lorentz, Lenz, and Weisskopf,<sup>1-4</sup> have given good results in the optical region.<sup>4,5</sup> However, this theory is essentially in contradiction to the theory of dielectric relaxation developed by Debye and others,<sup>6-8</sup> which treats broadening in the limiting case of a spectral line of zero frequency.<sup>8</sup> Both theories involve computing the spectrum due to a radiating molecule randomly interrupted by collisions with other molecules. However, the mechanism by which the interruption is effected is essentially different in the two theories. Debye's relaxation theory considers interruptions due only to reorientations of the radiating molecule; in a quantum theory, this is equivalent to considering transitions among the various spacially degenerate quantum states. Contrariwise, the Fourier integral theory explicitly assumes that no transitions are caused by collisions. Then the effect of a collision is

computed by means of the adiabatic approximation and is equivalent to a relative phase-shift of the radiation before and after the collision, with no amplitude change.

#### B. Generalization of the Fourier Integral

It is clear that it is necessary, in order to compute pressure broadening in any frequency range, to develop an expression for the spectral shape of a pressure-broadened line which encompasses the two limiting cases of high and low frequencies. In other words, a formula must be obtained which includes the effects both of phase-shifts and of transitions. Before presenting this formula, we should emphasize the physical picture upon which it is based. This picture is equivalent to that employed by Foley<sup>9</sup> in his re-derivation of the standard Fourier integral formula by means of quantum radiation theory. The basic assumption we call the "assumption of a classical path": we assume that for all collisions of interest the colliding molecules can be taken to be point dipoles following definite paths; thus their interaction is a definite function of the time  $H_1(t)$ . The justification for this lies in the fact that one can think of the motion of the molecules in terms of packets of translational wave functions; by the uncertainty principle the allowable spreads  $\Delta p$  and  $\Delta q$  in position and momentum space are  $\Delta p \Delta q \doteq \hbar$ . We seldom or never consider in detail collisions in which the molecules under consideration pass at distances less than the kinetic theory diameter,  $\doteq 5A$ . Then an uncertainty in position of  $1A$  will lead to no great ambiguity in magnitude or type of intermolecular forces. The corresponding uncertainty in velocity is

$$\Delta v/v \doteq 0.3/(\text{molecular weight})^{1/2} \quad (1)$$

which is a small percentage for most molecules. Calculations carried out by Lindholm<sup>10</sup> for many optical problems, not using this assumption, have indicated that the assumption is normally valid, in consideration

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<sup>1</sup> H. A. Lorentz, Proc. Amst. Acad. Sci. **8**, 59 (1906).

<sup>2</sup> W. Lenz, Zeits. f. Physik. **80**, 423 (1933).

<sup>3</sup> V. F. Weisskopf, Phys. Zeits. **34**, 1 (1933).

<sup>4</sup> E. Lindholm, Ark. Mat. Astron. Och Fys. **32**, 17 (1945).

<sup>5</sup> H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

<sup>6</sup> P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929), Chapter V.

<sup>7</sup> W. Kauzmann, Rev. Mod. Phys. **14**, 12 (1942).

<sup>8</sup> J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

<sup>9</sup> H. M. Foley, Phys. Rev. **69**, 616 (1946).

<sup>10</sup> E. Lindholm, Dissertation, Uppsala, 1942.

of the large quantum numbers of the partial waves whose contributions were important.

The problem is reduced, by this assumption, to finding the spectrum radiated by a molecule, whose unperturbed Hamiltonian we designate by  $H_0$ . This molecule undergoes random perturbations due to collisions, representable by a time-dependent interaction Hamiltonian  $H_1(t)$ . The problem can be solved following Foley's method, by the use of general radiation theory; or it is possible to extend the correspondence-principle radiation theory of Klein and Pauli to our problem by analogy. Either method leads directly to the following formula, which we present without proof:\*\*

$$I(\omega) = \text{const.} \times \omega^4 \text{Tr} \left[ \rho_0 \int_{-\infty}^{\infty} dt e^{i\omega t} \mu_z(t) \right. \\ \left. \times \int_{-\infty}^{\infty} dt' e^{-i\omega t'} \mu_z(t') \right]. \quad (2)$$

Here  $\omega$  is the angular frequency for which we desire the spectral intensity  $I(\omega)$ ;  $\rho_0$  is an assumed initial density matrix for molecules in the gas, in fact essentially the density matrix for the time  $t = -\infty$ ;  $\mu_z(t)$  is the Heisenberg time-dependent operator (see reference 12) for the  $z$ -component of the dipole moment (if we consider radiation polarized in the  $z$ -direction); and the "Tr" means that one must take the diagonal sum of the indicated matrix product.  $\mu_z(t)$ , of course, satisfies the Heisenberg time equation

$$i\hbar \dot{\mu} = [H\mu - \mu H], \quad (3)$$

where

$$H = H_0 + H_1(t). \quad (4)$$

Finally, we have omitted all numerical factors other than the frequency-dependent one  $\omega^4$ . These factors can easily be shown to come correctly from the general theory.

The formula (2) gives the intensity for spontaneous emission. The approach through spontaneous emission is chosen in order to avoid the use of a time-dependent density matrix.†† The intensity for absorption must be derived from (2) by use of the Einstein relations.<sup>11</sup> Some confusion as to whether the correct Einstein rela-

\*\* The intensity in classical theory is given by the average over all states of

$$\omega^4 \left| \int_{-\infty}^{\infty} \mu_z(t) e^{i\omega t} dt \right|^2$$

The corresponding quantum-mechanical quantity is obtained by replacing all observables (in this case  $\mu_z(t)$ ) by quantum-mechanical operators, in multiplying by the density matrix, and taking the trace. Thus Eq. (21) is reasonable; a rigorous proof can be given. For this procedure see W. Pauli, *Handbuch der Physik*, 2. Aufl., Band 24, 1. Teil, p. 149.

†† See, for instance, R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).

<sup>11</sup> A. Einstein, *Verh. d. D. Phys. Ges.* **18**, 318 (1916); *Phys. Zeits.* **18**, 121 (1917).

tions come out of the theory actually does appear when the classical path method, or equivalent absorption methods, are used;<sup>8</sup> we have been able to clarify this point to some extent, but our work on this point will not be reported in this paper.

It is interesting to rewrite (2) for the case in which the standard Fourier integral of Foley and his predecessors is valid. This is the case in which the perturbing Hamiltonian  $H_1(t)$  is either diagonal already, or can be made so in a simple manner (following Foley) by replacing transitions to high-energy levels by their second-order effects; that is, we replace the so-called Van der Waals forces, a second-order phenomenon, by a first-order Hamiltonian. This, too, can be shown to be valid from the general equations of motion and the radiation theory. Then Eq. (3) integrates explicitly; a typical matrix element is

$$\mu_{mn}(t) = \mu_{mn}(0) \exp \left\{ \frac{1}{i\hbar} (E_m - E_n)t \right. \\ \left. + \int_0^t [(m|H_1|m) - (n|H_1|n)] dt' \right\} \\ = \mu_{mn}(0) \exp[-i\omega_{nm}t - i\eta_{nm}(t)]. \quad (5)$$

The unperturbed frequency is  $\omega_{nm}$ , given by

$$\hbar\omega_{nm} = E_m - E_n.$$

$E_m$  is the  $m$ th eigenvalue of the unperturbed Hamiltonian  $H_0$ . Equation (5) defines the relative phase-shift  $\eta_{nm}$  for the two levels  $n$  and  $m$ . We can then use the Boltzmann density matrix

$$(n|\rho_B|m) = \delta_{nm} \exp(-E_n/kT) \\ \times [\sum_n \exp(-E_n/kT)]^{-1}, \quad (6)$$

for  $\rho_0$ , and  $I$  in (2) separates into the following contributions  $I_{mn}$  for each of the various spectral lines  $m$  and  $n$ :

$$I_{mn}(\omega) = \omega^4 \exp(-E_m/kT) \\ \times \left| \mu_{mn} \int_{-\infty}^{\infty} dt \exp\{-i[(\omega - \omega_{mn})t + \eta_{mn}(t)]\} \right|^2 \quad (7)$$

This is the form of the Fourier integral used by Weisskopf, etc.††

†† It is interesting to note that the derivation of (7) employed by Foley fails to lead to the correct external frequency factor  $\omega^4$ . If carefully followed, Foley's theory gives a factor here of  $\omega^2\omega_{nm}^2$ , which is by no means correct at low or zero frequencies, where the line-breadths are comparable to  $\omega_{nm}$ . Even if Foley's "adiabatic assumption" ( $H_1$  diagonal) were correct at low frequencies, these factors would be in error. The reason is that the general theory must be retained, at least until the point where a partial integration can be performed analogously to that which one would use in the classical theory to go from the Fourier integral of the vector potential  $A(\sim\dot{\mu})$  to that of  $\mu(t)$  itself.

**C. Introduction of the Time-Development Matrix  $T$**

It is well known that it is possible to write the time-dependent operators  $\mu(t)$  in Eq. (2) in the following manner:<sup>12</sup>

$$\mu(t) = U^{-1}(t)\mu_0U(t), \tag{8}$$

where

$$i\hbar(d/dt)U = (H_0 + H_1(t))U. \tag{9}$$

If  $\mu_0$  is the value of  $\mu$  at a time  $t_0$ , then  $U(t_0) = 1$  is the initial condition on Eq. (9). The time-development operator  $U$  is not as useful to us as another operator  $T$ , which is defined in much the same way. However, in deriving  $T$  one uses a Heisenberg representation in relation to the unperturbed energy  $H_0$ . Therefore the equation for  $\mu(t)$  is

$$\mu(t) = T^{-1}(t) \exp(-H_0t/i\hbar)\mu_0 \exp(H_0t/i\hbar)T(t), \tag{8'}$$

and that for  $T$  is

$$i\hbar\dot{T}(t) = H_1'(t)T. \tag{9'}$$

$H_1'$  is the interaction Hamiltonian with the time-dependence due to  $H_0$  inserted:

$$(m|H_1'|n) = (m|H_1(t)|n) \exp[(E_m - E_n)t/i\hbar]. \tag{10}$$

The diagonal elements of  $T$  give the phase-shifts due to the interaction  $H_1$ , while the off-diagonal elements—or their squared absolute values—give the transition probabilities due to this interaction. In terms of eigenstates of  $H_0$ , (8') is

$$(m|\mu(t)|n) = \sum_{k,l} (m|T^{-1}|k) \times \exp(-i\omega_{kl}t)(k|\mu_0|l)(l|T|n). \tag{8''}$$

We may now insert this explicit form for  $\mu(t)$  into the Fourier integral formula (2), and obtain the following complicated expression:

$$\begin{aligned} I(\omega) = \text{const.} \times \omega^4 \sum_{abcde} (a|\rho_0|b) & \\ \times \int_{-\infty}^{\infty} dt e^{i\omega t} (b|T^{-1}(t)|c)(c|\mu_0|d) & \\ \times \exp(i\omega_{cd}t)(d|T(t)|e) & \\ \times \int_{-\infty}^{\infty} dt' e^{-i\omega t'} (e|T^{-1}(t')|f)(f|\mu_0|g) & \\ \times \exp(-i\omega_{fg}t')(g|T(t')|a). \tag{11} & \end{aligned}$$

**D. Re-expression in Correlation-Function Form, and Simplification Using the Assumption of Short Collisions**

Formula (10) can be simplified greatly by the insertion of a new time-development matrix

$$T(t \rightarrow t') = T(t')T^{-1}(t). \tag{12}$$

<sup>12</sup> Born u. Jordan, *Elementare Quantenmechanik* (Verlag J. Springer, Berlin, 1930).

This operator is the solution of (9') with initial condition  $T(t) = 1$ ; it answers the question "what happens in the time-interval  $t \rightarrow t'$ ?" In addition, we use the fact that the density matrix, as a function of time, transforms according to  $T(t)$  but inversely to other matrices. Then (11) becomes:

$$\begin{aligned} I(\omega) = \text{const.} \times \omega^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega(t-t')} & \\ \times \sum_{abcde} (a|\rho(t)|b)(b|\mu_0|c) \exp(-i\omega_{bc}t) & \\ \times (c|T^{-1}(t \rightarrow t')|d)(d|\mu_0|e) & \\ \times \exp(-i\omega_{de}t')(e|T(t \rightarrow t')|a). \tag{13} & \end{aligned}$$

In order to use the considerable simplification made available by the Wiener-Khintchine relations in evaluating our formulas,<sup>13</sup> it is expedient to re-express them in correlation-function form. By means of the simple substitution

$$t' = t + \tau,$$

we obtain

$$I(\omega) = \omega^4 (\text{const.}) \sum_{de} \int_{-\infty}^{\infty} d\tau \exp[i(\omega - \omega_{de})\tau] \varphi_{de}(\tau), \tag{14}$$

where

$$\begin{aligned} \varphi_{de}(\tau) = \int_{-\infty}^{\infty} dt \sum_{abc} \exp[-i(\omega_{bc} + \omega_{de})t] & \\ \times (a|\rho(t)|b)(b|\mu_0|c)(c|T^{-1}(t \rightarrow t + \tau)|d) & \\ \times (d|\mu_0|e)(e|T(t \rightarrow t + \tau)|a). \tag{15} & \end{aligned}$$

We observe that (15) has the form of an average over the time  $t$ . It consists of three essentially different terms:  $\rho(t)$ , which depends on the state of the molecule at  $t$ ; the  $T(t \rightarrow t + \tau)$  factors, which depend on the collisions which occur between  $t$  and  $t + \tau$ ; and the phase-factor. At this point we first limit ourselves to the "impact" type of theory: we assume that the collisions are short compared to the time between them. Under this assumption, it is easy to show that unless  $\omega_{bc} + \omega_{de}$  is less than  $1/\tau$ , the inverse of the time between collisions, (15) will essentially vanish. For this reason, and for other reasons which we shall not consider here, it is considered legitimate to drop from (15) all terms for which  $\omega_{bc} + \omega_{de} \neq 0$ . This is equivalent to assuming that all lines considered are either not resolved at all compared to the line-breadth—in which case we treat them as degenerate—or are well separated.\*\*\*

It is also legitimate, since the phase and  $T$ -factors are independent of the actual state of the molecule, to take the average of  $\rho(t)$  over the history of the molecule

<sup>13</sup> See, for instance, M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).

\*\*\* In Section H we will discuss further the terms which are here dropped.

separately. Clearly, we obtain for  $\rho_{Av}$  the Boltzmann distribution (6). Let us now introduce a degenerate index  $m$ . Each state will be designated by a non-degenerate index ( $a, b, c, d \dots$ ) and a degenerate index ( $m, m' \dots$ ). Then, letting the "initial" state be designated by  $i$ , the final by  $f$ , (14) and (15) are

$$I = \sum_{i,f} \int_{-\infty}^{\infty} d\tau \exp[i(\omega_{if} - \omega)\tau] \langle i | \rho_B | i \rangle \varphi_{if}(\tau), \quad (16)$$

where

$$\begin{aligned} \varphi_{if}(\tau) = & \sum_{m,m',m'',m'''} \int_{-\infty}^{\infty} dt \langle i, m | \mu | f, m' \rangle \\ & \times \langle f, m' | T^{-1}(t \rightarrow t + \tau) | f, m'' \rangle \\ & \times \langle f, m'' | \mu | i, m''' \rangle \langle i, m''' | T(t \rightarrow t + \tau) | i, m \rangle, \end{aligned} \quad (17)$$

or

$$\begin{aligned} \varphi_{if}(\tau) = & Tr \left[ \int_{-\infty}^{\infty} dt \mu^{if} (T^{-1}(t \rightarrow t + \tau))^f \right. \\ & \left. \times \mu^{fi} (T(t \rightarrow t + \tau))^i \right], \end{aligned} \quad (17')$$

where the superscripts designate "Teilmatrices" for the given non-degenerate indices.

### E. Solution for the Correlation Function in the Standard Optical Case

To illustrate our method of finding the correlation function and to furnish some introduction to the line-shapes to be expected, we shall re-derive the impact theory solution of the standard Fourier integral (7). This formula, re-written in correlation-function form by means of (13), and exclusive of numerical factors, is

$$\begin{aligned} I(\omega) &= \int_{-\infty}^{\infty} d\tau \exp[i(\omega_{if} - \omega)\tau] \varphi(\tau), \\ \varphi(\tau) &= \int_{-\infty}^{\infty} dt \exp\{i[\eta_{if}(t + \tau) - \eta_{if}(t)]\}. \end{aligned} \quad (18)$$

The assumption of the impact theory is that the collisions are short compared to the time between them. Then

$$\eta_{if}(t + \tau) - \eta_{if}(t) = \sum_{\substack{\text{collisions from} \\ t \text{ to } t + \tau}} \eta_c, \quad (19)$$

where  $\eta_c$  are the phase-shifts due to the various collisions occurring in the interval  $t \rightarrow t + \tau$ :

$$\eta_c = \int_{\text{collision}} dt [i \langle H_1'(t) | i \rangle - \langle f | H_1'(t) | f \rangle]. \quad (20)$$

We divide the types of collisions into classes according to the paths followed by the molecules; then, corresponding to each "element of cross section"  $d\sigma_k$  we can assume that there is a definite phase-shift  $\eta_k$ . Then the probability that a collision in  $d\sigma_k$  occurs in a given, short time  $dt$  is given by

$$\rho(d\sigma_k) = nvdtd\sigma_k, \quad (21)$$

where  $n$  is the number of molecules per cc, and  $v$  is their velocity (assuming, as is always justifiable for collision-broadening problems, that all molecules have the average velocity  $\bar{v}$ ).

Consider the integrand of the expression (18) for  $\varphi(\tau)$ :

$$f(t, \tau) = \exp\{i[\eta_{if}(t + \tau) - \eta_{if}(t)]\}. \quad (22)$$

If in the time  $d\tau$  after  $\tau$  a collision of type  $k$  occurs, we have

$$\begin{aligned} f(t, \tau + d\tau) &= \exp(i\eta_k) f(t, \tau), \\ f(t, \tau + d\tau) - f(t, \tau) &= [\exp(i\eta_k) - 1] f(t, \tau). \end{aligned} \quad (23)$$

Now let us take the integral, which is equivalent to averaging over all times  $t$ :

$$\begin{aligned} \varphi(\tau + d\tau) - \varphi(\tau) &= d\varphi(\tau) \\ &= \langle [\exp(i\eta_k) - 1] f(t, \tau) \rangle_{\text{average over } t}. \end{aligned} \quad (24)$$

This is the point at which the impact theory assumption is vital. We must be able to say that the time  $d\tau$  is short compared to the interval between collisions, and so contains at most one collision; on the other hand,  $d\tau$  must be quite long compared with the duration of a collision, so that there is no correlation between what happens in the interval  $d\tau$  and what happens in the preceding or following times. Then we can take the averages in (24) separately, and have

$$\begin{aligned} d\varphi(\tau) &= \varphi(\tau) \langle \exp(i\eta_k) - 1 \rangle_{\text{average over collisions}} \\ &= \left[ \eta v d\tau \int d\sigma_k (\exp(i\eta_k) - 1) \right] \varphi(\tau), \end{aligned} \quad (25)$$

so that

$$\varphi(\tau) = e^{-\eta v \sigma \tau}, \quad (26)$$

where

$$\sigma = \int d\sigma (1 - e^{i\eta}) = \sigma_r + i\sigma_i.$$

It is easy to see that

$$\varphi(-\tau) = \varphi^*(\tau)$$

as is required for the reality of  $I(\omega)$ ; then we get for the intensity distribution

$$I(\omega) = \text{const.} \times \frac{2(nv\sigma_r)}{(\omega - \omega_{if} - nv\sigma_i)^2 + (nv\sigma_r)^2}. \quad (27)$$

This is a dispersion line-form with half-width

$$2\pi(\Delta\nu)_\frac{1}{2} = nv\sigma_r, \quad \text{shift } 2\pi\Delta\nu_{if} = nv\sigma_i. \quad (28)$$

**F. Solution for the Correlation Function in the Classical Debye Case**

Since the classical Debye problem of the spectrum of a rotating dipole perturbed by collisions has frequently been considered by absorption methods,<sup>6-8</sup> in particular the very general method in the appendix of the paper by Van Vleck and Weisskopf, it is of interest to show how easily this problem is solved by correlation function methods. Here we can see that the spectrum is

$$I(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \varphi(\tau), \tag{29}$$

$$\varphi(\tau) = \int_{-\infty}^{\infty} dt \mu_z(t+\tau) \mu_z(t),$$

where  $\mu_z(t)$  is the  $z$ -component of the rotator's dipole moment at a time  $t$ . Again we consider the function

$$f(t, \tau) = \mu_z(t+\tau) \mu_z(t), \tag{30}$$

$$f(t, \tau+d\tau) - f(t, \tau) = \mu^2 (\cos\psi(t+\tau+d\tau) - \cos\psi(t+\tau)) \cos\psi(t),$$

where  $\mu_z(t) = \mu \cos\psi(t)$ ,  $\psi$  being the angle of the dipole relative to the  $z$ -axis.

Our basic assumptions will be (a) that the probability of a collision taking the rotator from the element of solid angle  $d\omega$  into  $d\omega'$  in a time  $d\tau$  is

$$nvd\sigma_{\omega \rightarrow \omega'} d\tau, \tag{31}$$

and (b) that this probability is obviously independent of the azimuthal angle  $\varphi$  between  $d\omega$  and  $d\omega'$ , and therefore is a function only of the polar angle  $\theta$  between these two directions. We know that

$$\cos\psi(d\omega') = \cos\psi(d\omega) \cos\theta + \sin\psi(d\omega) \sin\theta \cos\varphi. \tag{32}$$

Since, upon averaging the difference of cosines in (30) over all possible collisions, the last term in (32) will vanish because of the factor  $\cos\varphi$ , we can use

$$\cos\psi(t+\tau+d\tau) - \cos\psi(t+\tau) = \cos\psi(t+\tau) (\cos\theta - 1). \tag{33}$$

Then we actually perform the average of (30) over all times, using again our impact theory assumption of short collisions. It is clear that the result is:

$$d\varphi(\tau) = \left[ nvd\tau \int d\sigma_{\omega \rightarrow \omega'} (\cos\theta - 1) \right] \varphi(\tau),$$

$$\varphi(\tau) = e^{-nv\sigma\tau}, \tag{34}$$

$$\sigma = \int d\sigma (1 - \cos\theta) \text{ (real)}.$$

This gives, with the correct external factor  $\omega$ , the Debye line form:

$$I(\omega) = nv\sigma\omega / [\omega^2 + (nv\sigma)^2]. \tag{35}$$

The two terms in  $\sigma$  (34) correspond to the  $\gamma$  and  $\delta$  of the Van Vleck-Weisskopf paper.

**G. The General Quantum-Mechanical Case**

It is possible to do the quantum-mechanical non-resonant, or Debye, case by a generalization of the above arguments similar to that employed in the paper by Van Vleck and Weisskopf. However, the arguments for this and for the general quantum-mechanical case involving spacial degeneracy are quite equivalent. We shall give only the latter, regarding the Debye case as an obvious special application.

We want to find the breadth of the line corresponding to a dipole transition between two states  $i$  and  $f$ , of angular momenta  $j_i$  and  $j_f$ , with  $j_j = j_i \pm 1$  or  $j_i$ .††† Equation (17) for the correlation function applies here, with the spectrum given by (16). Before proceeding farther, we must prove a theorem about the expression (17), or rather about the following part of it:

$$\sum_{m', m''} \langle (m | T^{i-1}(t \rightarrow t+\tau) | m') (m' | \mu_z^{if} | m'') \rangle \times \langle (m'' | T^f(t \rightarrow t+\tau) | m''') \rangle_{\text{average over } t} = (m | \langle T^{i-1}(t \rightarrow t+\tau) \mu_z^{if} T^f(t \rightarrow t+\tau) \rangle_{\text{average over } t} | m''') \tag{36}$$

Suppose we apply a rotation of the coordinate axes to (36) in the sense that we do all of our computations with respect to a new set of axes  $x', y', z' = R(x, y, z)$ . We must use the fact that, since in the course of the time average we consider collisions from all conceivable directions and of all possible types in equal number, the affect of the  $\langle T^{i-1} T^f \rangle$  factor is essentially an isotropic one. (This is equivalent to the step (32)→(33).) Mathematically,

$$R \langle T^{-1} \mu_z T \rangle_{Av} = \langle (RT^{-1})(R\mu_z)(RT) \rangle_{Av} = \langle T^{-1}(R\mu_z)T \rangle_{Av} = \lambda_{z'x} \langle T^{-1} \mu_x T \rangle_{Av} + \lambda_{z'y} \langle T^{-1} \mu_y T \rangle_{Av} + \lambda_{z'z} \langle T^{-1} \mu_z T \rangle_{Av}, \tag{37}$$

where the  $\lambda$ 's are the direction cosines of the new axis system with respect to the old. Thus the quantity (36) has the transformation property of a vector component. But the  $i, f$  matrix elements of any vector component are determined, exclusive of a constant factor, by the transformation property.<sup>14</sup> Thus we can say

$$(m | \langle T^{i-1}(t \rightarrow t+\tau) \mu_z^{if} T^f(t \rightarrow t+\tau) \rangle_{Av \text{ over } t} | m''') = F(\tau) (m | \mu_z^{if} | m'''), \tag{38}$$

where  $F(\tau)$  is a scalar.

We are now in a position to set up the differential

††† The case of higher multipole transitions is easily worked out and, interestingly, leads usually to a different breadth.  
<sup>14</sup> E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), Chapter III.

equation for  $\varphi(\tau)$ , or, equivalently, for  $F(\tau)$ , since

$$\begin{aligned}\varphi(\tau) &= \sum_{m, m'''} |m| \mu_z^{ij} |m'''|^2 F(\tau), \\ d\varphi(\tau) &= \sum_{m, m'''} |m| \mu_z^{ij} |m'''|^2 dF(\tau), \\ &= \text{Tr} \left\{ \int_{-\infty}^{\infty} dt \mu_z^{f'i} [T^{i-1}(t \rightarrow t + \tau + d\tau) \mu_z^{ij} \right. \\ &\quad \times T^j(t \rightarrow t + \tau + d\tau) - T^{i-1}(T \rightarrow t + \tau) \mu_z^{ij} \\ &\quad \left. \times T^j(t \rightarrow t + \tau) \right\}. \quad (39)\end{aligned}$$

We introduce a matrix  $T_d = T(t + \tau \rightarrow t + \tau + d\tau)$  (the notation  $T_d$  indicates that this matrix is not a differential); then

$$T(t \rightarrow t + \tau + d\tau) = T(t \rightarrow t + \tau) T_d. \quad (40)$$

Again we can make use of the reasoning of Section E, (24)→(25): we use the assumption of short collisions to enable us to take independent averages of the happenings in  $t \rightarrow t + \tau$  and  $t + \tau \rightarrow t + \tau + d\tau$ . Then we introduce Eq. (40), Eq. (38) for  $F(\tau)$ , and get for (39):

$$\begin{aligned}\sum_{m, m'} |m| \mu_z(m')|^2 dF(\tau) \\ = F(\tau) \text{Tr} [\langle \mu_z^{f'i} T_d^{i-1} \mu_z^{ij} T_d^j - \mu_z^{ij} \rangle]_{\text{Av. over all } d\tau}. \quad (41)\end{aligned}$$

Now we introduce the probability assumption (21) for types of collisions:

$$p(d\sigma \text{ in } d\tau) = n v d\sigma d\tau.$$

If a collision of type  $d\sigma$  occurs in  $d\tau$ , the  $T$  matrix  $T_d$  will be characteristic of the collision  $d\sigma$ . In fact,  $T$  is obtained by integrating Eq. (9') from  $t = -\infty$  to  $+\infty$ , using for  $H_1'(t)$  the time-dependent interaction Hamiltonian for just one collision of type  $d\sigma$  occurring in the whole range of  $t$ . The initial condition is  $T(-\infty) = 1$ . This integration is legitimate because of our assumption that  $d\tau$  can be chosen long compared to the duration of one collision. We call the resulting  $T$  matrix  $T(d\sigma)$ ; then the average in (41) gives the following equation for  $F$ .

$$[dF(\tau)/d\tau] = -n v \sigma F(\tau), \quad F(\tau) = e^{-n v \sigma \tau}, \quad (42)$$

$$\sigma = \int d\sigma \left[ \frac{\text{Tr}(T^i(d\sigma)^{-1} \mu_z^{ij} T^j(d\sigma) \mu_z^{f'i})}{\text{Tr}(\mu_z^{ij} \mu_z^{f'i})} - 1 \right]. \quad (43)$$

It is obvious that the shift in frequency and the line-breadth follow from the real and imaginary parts of the number  $\sigma$ , precisely according to (28). Thus the problem of the line-shape is solved in principle.

Before proceeding further with the evaluation of  $\sigma$ , the "collision cross section for line-broadening," it is necessary to generalize formula (43) to a case which we shall frequently treat—that in which the interaction Hamiltonian  $H_1'(t)$  is a matrix involving the quantum-mechanical states of both the perturbing molecule and the radiating molecule. The line of reasoning is prac-

tically identical, except, of course, that the radiation occurs according to the operator

$$\mu_z(1) + \mu_z(2). \quad (44)$$

The two molecules of interest are called (1) and (2). It is clear that it is legitimate to use only the first half of (44), regarding, therefore, molecule (1) as the radiator, (2) as a perturber (the line-shape for molecule (2) will be included in the implicit average over all molecules in the gas). Then, in place of the transformation property "vector component," we use essentially "vector" molecule (1) "scalar" molecule (2). Without going through the reasoning for the case of two molecules, which differs from the preceding only in that the Boltzmann factors for molecule (2) must be included and that  $T$ -matrices involving any transition whatever for molecule 2 are of interest, we present the correct result for  $\sigma$ :

$$\begin{aligned}\sigma = \int d\sigma \left\{ \left[ \sum_{\substack{m_1, m_1' \\ m_1'', m_1''' \\ a_2 b_2}} (m_1 a_2 | T^{i-1}(d\sigma) | m_1' b_2) (\rho_B)_{b_2} \right. \right. \\ \times (m_1' | \mu_z^{ij} | m_1'') (m_1'' b_2 | T^j(d\sigma) | m_1''' a_2) \\ \times (m_1''' | \mu_z^{f'i} | m_1) \left. \right] \\ \times \left[ \sum_{m_1 m_1'} |(m_1 | \mu_z^{ij} | m_1')|^2 \right]^{-1} - 1 \left. \right\}. \quad (45)\end{aligned}$$

$a_2, b_2$  designate the various states of the second molecule. Two possible cases occur in which this expression can be simplified to a usable form. First we have the case in which no transitions occur in molecule (2) quantum numbers, except perhaps for degenerate ones; second, that case in which transitions in molecule (2) quantum numbers can occur only simultaneously with those of molecule (1), so that  $T^i$  and  $T^j$  are still essentially diagonal in molecule (2) because they are so in molecule (1) (this is the interesting case corresponding to resonant interactions). In either case,  $\sigma$  reduces to the following simple form:

$$\begin{aligned}\sigma = \sum_{a_2} \sigma_{a_2}, \\ \sigma_{a_2} = (\rho_B)_{a_2} \\ \times \int d\sigma \left[ \frac{\text{Tr}(T^{i, a_2}(d\sigma)^{-1} \mu_z^{ij} T^{j, a_2}(d\sigma) \mu_z^{f'i})}{\text{Tr}(\mu_z^{ij} \mu_z^{f'i}) (2j_{a_2} + 1)} - 1 \right]. \quad (46)\end{aligned}$$

The trace includes a summation over  $m_2$ , the molecule (2) degenerate index, and  $2j_{a_2} + 1$  is the degeneracy of the  $a_2$  level.

## H. Reduction of $\sigma$ to Computable Form

### 1. Use of Rotational Invariance to Relate Matrix Elements to "Collision Axes"

In the form (43) it is still practically impossible to compute  $\sigma$ , since we must find the  $T$ -matrices not only

for every impact parameter, or distance of closest approach of the two molecules during collision, but for every set of direction angles of the colliding molecules relative to the polarization direction. It is possible to use the fact that the  $\int d\sigma$  implies an average over all conceivable sets of direction angles to remove this latter difficulty. We do not do this rigorously, since it involves some rather long group theory. The following argument, however, indicates the method.

The integrand of (43) is, as it stands, rotation invariant, since it is a trace. Essentially, this means that the component of  $\mu$  we deal with is immaterial. Suppose we can compute the  $T$ -matrices for one specific set of direction angles (for instance, suppose we know them for a system quantized along  $b$ , the impact parameter). Then it is possible to leave these  $T$ -matrices as they stand and to take the direction average by rotating the  $z$ -axis, i.e., the component of  $\mu$  which is used in (43). Since (43) is quadratic in  $\mu_z$ , it is allowable merely to average over the  $x$ ,  $y$ , and  $z$ -directions. Then we get simply

$$\sigma \text{Tr}(\mu_z^{if} \mu_z^{fi}) = \frac{1}{3} \sum_{x, y, z} \int_0^\infty 2\pi b db \times \text{Tr}[T^{i(-1)}(b) \mu_{x, y, z}^{if} T^f(b) \mu_{x, y, z}^{fi} - \mu_{x, y, z}^{if} \mu_{x, y, z}^{fi}], \quad (47)$$

where  $T^i(b)$  designates the  $T$ -matrix in the "collision-axis" coordinate system.

Since a great deal of further manipulation with (47) is necessary, we shall use an alternative form for it, based on the identity between the vector matrix and the Wignerian coefficients.<sup>12</sup>

$$(m | \mu_z^{if} | \mu) = (j_f 1 j_i m | j_f 1 \mu 0) \quad (48)$$

and similarly for  $1/\sqrt{2}(\mu_x \pm i\mu_y)$ , with 0 replaced by  $\pm 1$ . Then it is easy to show that (47) is the same as

$$\sigma = \int_0^\infty 2\pi b db \sum_{\substack{M, m, m' \\ \mu, \mu'}} \frac{(j_f 1 j_i m | j_f 1 \mu M)}{(2j_i + 1)} (j_f 1 j_i m' | j_f 1 \mu' M) \times [\delta_{mm'} \delta_{\mu\mu'} - (m | T^{i-1}(b) | m') (\mu' | T^f(b) | \mu)]. \quad (47')$$

A similar formula can be written in the two molecule case of Eq. (46).

### 2. Introduction of an Approximate Form for $T$ .

For the purpose of computing  $\sigma$  from (47), an expression for the  $T$ -matrices in terms of the interatomic forces must still be found. This cannot be done exactly. However, a device which has been frequently used is the following expansion of  $T$  in successive approxima-

tions with the assumption that  $\int H_1' dt/\hbar$  is small. We use the following procedure:

$$T = T_0 + T_1 + T_2 + \dots, \quad T_0 = 1,$$

$$i\hbar \dot{T}_1 = H_1' T_0; \quad T_1(t) = \int_{-\infty}^t \frac{H_1'(t')}{i\hbar} dt', \quad (49)$$

$$i\hbar \dot{T}_2 = H_1' T_1; \quad T_2(t) = \int_{-\infty}^t \frac{H_1'(t')}{i\hbar} dt' \int_{-\infty}^{t'} \frac{H_1'(t'')}{i\hbar} dt'', \text{ etc.}$$

If we could assume that  $H_1'(t')$  commuted with  $H_1'(t'')$  at all times, the result of this process would be simply the scalar solution of the linear differential Eq. (9'):

$$T(t) = \exp \left[ \int_{-\infty}^t \frac{H_1'(t')}{i\hbar} dt' \right]. \quad (50)$$

On the other hand, it is clear from the definition (10) of  $H_1'$  that it does not commute with itself at all times, but only because  $H_1$  and  $H_0$  do not commute.  $H_1(t)$  is a function of the coordinates only, in general, and will always commute with itself.

An investigation was made into the size and meaning of the "non-commuting" terms by which (50) differs from the accurate solution of (49). Those terms involving high frequency elements of  $H_1'$  ("high" compared to the rate of change of  $H_1$ ) were found to be precisely equivalent to the terms obtained in (50) by including, in  $H_1$  itself, the 2nd-, 3rd-, etc., order forces due to the high frequency elements of  $H_1'$ . On the other hand, such terms are small if they involve low frequency elements of  $H_1'$ .

Therefore it seems permissible to ignore the non-commuting terms and to use (50) for  $T$ , including at least the second-order (Van der Waals') forces in  $H_1$ . These terms have not been computed accurately according to (49), because they appear first in the successive terms  $T_2$  (shift) and  $T_4$  (broadening). The Van der Waals' procedure introduces the second-order forces in the same manner as the first-order ones in  $T_1$  and  $T_2$  where they are much easier to handle. It is an interesting check on our method to note that the second order effects of high levels would derive naturally in the correct form from the general theory.

For simplicity we limit ourselves to the first three terms of (50). These are

$$T(b) \cong T_0 + T_1 + T_2, \quad (51)$$

$$T_0 = 1; \quad T_1 = -iP; \quad T_2 = P^2/2,$$

where

$$P = \frac{1}{\hbar} \int_{-\infty}^\infty H_1'(t) dt. \quad (51')$$

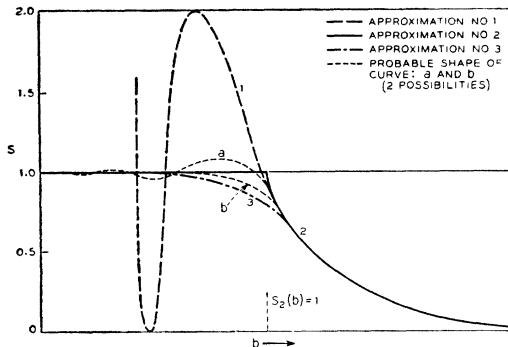


FIG. 1.

3. Use of the Approximation for  $T$  in Computing  $\sigma$  and Line-Broadening

Let us repeat the formula (47) here, in a slightly different form:

$$\sigma = \int_0^\infty 2\pi b db S(b), \tag{52}$$

$$S(b) = \sum_{\substack{m, m', M \\ \mu, \mu'}} \frac{(j_f 1 j, m | j_f 1 \mu M)(j_f 1 j, M | j_f 1 \mu' M)}{2j_i + 1} \times (\delta_{\mu\mu'} \delta_{mm'} - (m | T^{i-1}(b) | m')( \mu' | T^f(b) | \mu).$$

We are going to expand  $S(b)$  in powers of the  $P$ -matrix of Eq. (51'):

$$S = S_0 + S_1 + S_2 + \dots \tag{53}$$

In order to get terms of the zero'th order in  $P$ , we must pick  $T^i = T_0^i, T^f = T_0^f$ , and we get

$$S_0 = 0. \tag{54a}$$

The first-order terms are obtained by including either  $T^i = T_0, T^f = T_1$  or *vice versa*. The result is

$$S_1 = - \sum_{\substack{M, m, m' \\ \mu, \mu'}} \frac{(j_f 1 j, m | j_f 1 \mu M)}{2j_i + 1} (j_f 1 j, m' | j_f 1 \mu' M) \times [(m | T_1^{i-1} | m) \delta_{\mu\mu'} + (\mu' | T_1^f | \mu) \delta_{mm'}].$$

This is greatly simplified by the fact that the Wignerian coefficient  $(j_f 1 j, m | j_f 1 \mu M)$  vanishes unless  $m = \mu + M$ ; thus if  $\mu = \mu', m = m'$ , or *vice versa*, and  $S_1$  is simply

$$S_1 = - \sum_M \sum_{m \text{ or } \mu} |(j_f 1 j, m | j_f 1 \mu M)|^2 \times [(m | T_1^{i-1} | m) + (\mu | T_1^f | \mu)].$$

The sums over  $M$  are easily performed, one by the unitarity of the Wignerian coefficients, and one by this and the "permutation of indices" property of these coefficients which appears most easily from Racah's

paper.<sup>15</sup> Also using the fact that  $T_1^{-1} = -T_1$ , we get

$$S_1 = i \left[ \sum_{m=-j_i}^{j_i} \frac{(m | P^i | m)}{2j_i + i} - \sum_{\mu=-j_f}^{j_f} \frac{(\mu | P^f | \mu)}{2j_f + 1} \right]. \tag{54b}$$

Referring to the definition (51) of  $P$ , it appears that this, the first "shift" term in  $\sigma$ , is just the first term in the simple phase-shift approach, averaged over all directions.

There are two possibilities for obtaining second-order terms in the  $S$  sum. We have the choice of taking  $T_0^i \times T_2^f$  or *vice versa*, or of taking the terms involving  $T_1^i \times T_1^f$ . The former pair of terms follow precisely as did the  $S_1$  terms; we call these  $(S_2)_{\text{outer}}$ .

$$(S_2)_{\text{outer}} = - \left[ \sum_m \frac{(m | T_2^{i(-1)} | m)}{2j_i + 1} + \sum_\mu \frac{(\mu | T_2^f | \mu)}{2j_f + 1} \right] = \frac{1}{2} \left[ \sum_m \frac{(i, m | P^2 | i, m)}{2j_i + 1} + \sum_\mu \frac{(f, \mu | P^2 | f, \mu)}{2j_f + 1} \right]. \tag{54c'}$$

The second type of term, however, must be left in its original form; we call the sum of these  $(S_2)_{\text{middle}}$ :

$$(S_2)_{\text{middle}} = - \frac{1}{2j_i + 1} \sum_{\substack{M, m, m' \\ \mu, \mu'}} (j_f 1 j, m | j_f 1 \mu M) \times (j_f 1 j, m' | j_f 1 \mu' M) (im | P | im') (f\mu' | P | f\mu). \tag{54c''}$$

Further terms are prohibitively difficult; in any case, the "non-commuting" part of  $T$  can no longer be neglected in  $T_3$ .<sup>†††</sup>

4. The Interpolation Process

Since the expansion (53) of  $S(b)$  is valid only for small  $P$ , and  $P$  increases very strongly with decreasing  $b$  ( $\tau^{-3}$  for first-order,  $\tau^{-6}$  for second-order forces), obviously the first two non-vanishing terms of  $S$ , derived above, are of no help for collisions for which  $b$  is small. For this range of  $b$  we must use physical reasoning, based on the fact that "strong" collisions such as these must have an effect equivalent to complete interruption of the radiation. The  $T$ -matrix for complete interruption

<sup>15</sup> G. Racah, Phys. Rev. 62, 438 (1942).

††† It is clear that in (54c) the degenerate and non-degenerate levels play essentially different parts. One can interpret these terms by saying that transitions to non-degenerate levels act like complete interruptions of the radiation, while transitions among degenerate levels take on the character of phase-shifts to a greater or lesser extent, whence the terms (54c''). This phenomenon, and the question of when a level is or is not "degenerate," are allied to the general problem of coherence of radiation of different frequencies which crops up in many fields.

In this case, the problem is fairly simple. It is easy to see that the different behavior of degenerate and non-degenerate levels follows from the step of dropping the terms of finite frequency in Section D, Eqs. (13) and (14). We noted there that this step was allowable if the frequency difference of the levels was much greater than  $1/\tau$ . In addition, (54c'') can be shown to vanish for first-order dipole-dipole interactions in any case, so that observable effects of this cause seldom appear.



can have two forms: For the pure phase-shift case, that of an arbitrary phase-factor, averaging to zero; for the transition case, that of complete off-diagonality, meaning that the molecule has certainly changed its state. In either case  $S(b)$  contains only the  $\delta_{mm'}\delta_{\mu\mu'}$  factors, and a simple summation shows that

$$S(b \text{ small}) = 1 \text{ or averages to } 1. \quad (55)$$

The problem of interpolating between the region of large  $b$ , where  $S(b)$  is small and satisfies (54), and that of small  $b$ , or (55), is insoluble in principle. However, several simple models and some general reasoning have led us to conclude that a definite upper limit for the real part of  $\sigma$ , and a probable lower limit, can be assigned on the basis of two rather arbitrary choices of  $S(b)$ , while a third choice gives a good working approximation.

Figure 1 illustrates the various possibilities. Our three approximate "ideas" for curves are labeled "approximation # 1, 2, 3." # 1 is essentially the  $S(b)$  curve used in the phase-shift theory.

$$S\#_1(b) = 1 - \cos(2S_2(b))^{\frac{1}{2}}. \quad (56)$$

It is easy to show that because of the factor  $b$  in (52a) this is an upper limit for all conceivable shapes. One can look upon the true curve as an average of several curves like # 1, with different asymptotic strengths; then it might well resemble curve (a) or (b). # 2 is the approximation obtained by using  $S_2(b)$  from (54c) to the point at which  $S = 1$ ; then we use exactly (55). # 3 is a rather arbitrarily set lower limit

$$S\#_3(b) = 1 - \exp[-2S_2(b)]. \quad (56')$$

We will find that the three approximations are never more than 20 percent from each other, which is usually less than experimental error. Where the experiments are more accurate, # 2 does indeed seem to be the best choice.

### 5. Some Remarks on the Matrix "P"

Before concluding the theoretical part of this work it is well to make some remarks about the magnitude of the  $a, b$  elements of  $P$  as a function of the separation in energy of the levels  $a, b$ . An element of  $P$  is given by

$$(a|P|b) = \int_{-\infty}^{\infty} dt \exp(i\omega_{ab}t) (a|H_1(t)|b). \quad (57)$$

$H_1(t)$  will always be either a first- or second-order dipole-dipole interaction; therefore it will have a form like

$$H_1(t) = Kr^{-3} \text{ or } Kr^{-6}. \quad (58)$$

We can always assume that the paths followed by the colliding molecules are straight lines, since one can show that if the molecules collide with sufficient strength to have curved paths it is quite certain that the radia-

tion will be completely interrupted. Then

$$r^2 = b^2 + v^2 t^2, \quad (59)$$

and

$$(a|P|b) = K \int_{-\infty}^{\infty} dt \exp(i\omega_{ab}t) (b^2 + v^2 t^2)^{-\frac{3}{2}} \text{ or }^{-3}. \quad (60)$$

Now we define

$$x = vt/b, \quad k = b\omega_{ab}/v, \quad (61)$$

following Foley;<sup>9</sup> then (60) becomes

$$(a|P|b) = \frac{k}{b^2v \text{ or } b^5v} \int_{-\infty}^{\infty} dx \frac{e^{ikx}}{(1+x^2)^{\frac{3}{2}} \text{ or } \frac{3}{2}}. \quad (60')$$

These integrals can easily be done by contour integration; however, the main features of the two solutions are the same. Both integrals have nearly the same value as at  $k=0$  ("fast" collisions or degenerate levels) for a fairly large region of the parameter  $k$  (relating speed of collision to frequency) approaching  $k=1$ . Then there is quite a rapid falling off until at  $k=4$  or 5 (60') essentially vanishes.

We may interpret this according to the uncertainty principle. As long as the collisions are sufficiently fast ( $k < 1$ ), the energy-difference corresponding to  $\omega_{ab}$  acts as though it were negligible:  $\Delta E \Delta t > h$  implies that there is a region of "vagueness in energy" of the width  $h/\Delta t$ , with  $\Delta t$  the time in which a collision occurs. Since the  $P$ -matrix element gives, by (51), the probability of occurrence of transitions between the states  $a$  and  $b$ , these transitions will occur as though these states were resonant throughout the region  $k < 1$ . This is a point which is frequently ignored in the theory; qualitatively, it was previously made by Foley. We shall find opportunity to use the "region of resonance" idea repeatedly in the applications of our theory. On the other hand, for large  $k$ —slow collisions—no non-adiabatic transitions will occur, since the motion is adiabatic.

### SUMMARY OF THE THEORY

At this point it will clarify the exposition to present a summary of the theory up to this point. We have, essentially, found the line shape of a pressure-broadened spectral line under the following assumptions:

(a) that the relative motion of the molecules is classical; this enables us to write down the generalized Fourier integral (2).

(b) that the time between collisions is long compared to the duration of the collisions; this enables us to separate the Fourier integral into component parts referring to the separate spectral lines ((16) and (17)), to find a general expression for the correlation function (42), and to write down the broadening cross-section  $\sigma$  occurring in this expression in terms of collision operators  $T$  (43).

(c) that the collision operators are smooth functions of the collision parameter  $b$  between large  $b$  (where we have the expansion (51)) and small  $b$ , where complete interruption occurs. Then we are able to apply the interpolation process, and obtain for  $\sigma$  the expression (52),  $S(b)$  given by the formulas (56) fitted to the large  $-b$  expansion (54).

TABLE I. Comparison of theory and experiment.

Approx. #1 $\Delta\nu_1 =$	Theory			Experiment 0.74 cm <sup>-1</sup> /atmos.
	#2	#3		
0.86	0.77	0.68 cm <sup>-1</sup> /atmos.		

TABLE II. Comparison of theory with experiment—relative breadths in the ammonia spectrum.

$J =$ (a)	$K =$ (b)	Theoretical breadths: this thesis (c)	Experimental data: Bleaney (d)	Quasi-empirical formula: Bleaney (e)
2	1	2.6	2.6	2.7
3	1	2.3	2.4	2.2
3	2	3.3	3.2	3.4
3	3	4.5	4.5	4.5
4	4	4.6	4.5	4.6
5	1	1.8	1.8	1.6
5	2	2.5	2.6	2.5
5	3	3.3	3.3	3.3
5	5	4.8	4.7	4.65
6	3	2.8	3.1	3.1
6	4	3.5	3.6	3.6
6	6	4.8	4.7	4.7
7	5	3.7	4.1	3.8
7	6	4.3	3.9	4.3
8	7	4.3	4.1	4.35
10	9	4.5	4.2	4.5
11	9	4.1	2.9	4.2

Data are half-widths in cm<sup>-1</sup> × 10<sup>-4</sup> at 0.5 mm Hg pressure.

The procedure to be followed in computing line shapes is this: given an assumed type of intermolecular forces, one computes the matrix  $P$  (51') in the collision-parameter coordinate system. The interaction energy  $H_1'$  is given by (10). The elements of this matrix involving the initial and final states are then averaged over directions according to (54b) and (54c' and c''). The  $S_2$  averages (54c) are employed in the approximations (56) and the  $\sigma$ -integral (52) to obtain a broadening cross-section, which gives the line-breadth from (28); a shift, if present, can be computed similarly from  $S_1$  (54b), (52), and (28).

## PART II. APPLICATIONS OF THE THEORY TO SPECTRA

### A. Cases Involving Permanent Dipole Interactions

#### 1. Ammonia Self-Broadening

We shall begin with various problems involving permanent dipole interactions, since there is much experimental work on them and since, in general, the "difficult" term  $(S_2)_{\text{middle}}$  vanishes in these problems. Self-broadening in the inversion spectrum of ammonia has been studied most extensively.

The states of the ammonia molecule, exclusive of vibrational and electronic quantum numbers, are specified by four quantum numbers:  $J$  (total angular momentum),  $M$  (equatorial),  $K$  (symmetric top quantum number), and  $\pm$ , denoting the symmetry of the wave-

function with respect to inversion.

$$\sqrt{2}\psi_+ = \psi_{+K} + \psi_{-K}, \quad \sqrt{2}\psi_- = \psi_{+K} - \psi_{-K}. \quad (1)$$

Here  $+K$  and  $-K$  denote the "single-ended" states, whose degeneracy is raised by the well-known inversion or "tunnel effect."

First we consider the interaction between two ammonia molecules (first-order only). The Hamiltonian of this interaction is

$$H = \left[ \mathbf{u}_1 \cdot \mathbf{u}_2 - 3 \frac{(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})}{r^2} \right] r^{-3}, \quad (2)$$

where  $\mathbf{u}_1$  and  $\mathbf{u}_2$  are the dipole moment matrices of the two molecules considered, and  $\mathbf{r}$  is the distance between the molecules. Equation (2) can easily be expanded in terms of direction-angles in a system of reference in which the impact parameter  $b$  is the polar axis of spherical coordinates for each molecule. Then  $\theta_1$ ,  $\varphi_1$  and  $\theta_2$ ,  $\varphi_2$  are the polar angles of  $\mu_1$  and  $\mu_2$  referred to  $b$ , while  $\psi = \tan^{-1}[(v)/(b)]$  is the angle which  $\mathbf{r}$  makes with  $b$ . The result for  $H$  is

$$H = \mu^2/r^3 [\cos\theta_1 \cos\theta_2 (1 - 3 \cos^2\psi) + \sin\theta_1 \sin\theta_2 \times (\cos(\varphi_1 - \varphi_2) - \sin^2\psi \cos\varphi_1 \cos\varphi_2) + \text{terms in } \cos\psi \sin\psi]. \quad (3)$$

We must obtain the matrix elements of the combinations of functions of  $\theta$  and  $\varphi$  which occur here. One theorem simplifies this problem greatly. All matrix elements vanish between states which are both  $+$  or both  $-$ , while the  $(+|\mathbf{u}| -)$  elements are precisely those of the ordinary symmetrical top for states of the correct  $J$ ,  $K$  and  $M$ . The proof is obvious upon observing that

$$(K|\mathbf{u}|K) = -(-K|\mathbf{u}|-K); \quad (K|\mathbf{u}|-K) \cong 0. \quad (4)$$

The latter holds true within the order of the tunnel frequency compared to a vibrational frequency, or  $10^{-3}$ . Then (1) leads directly to our theorem.

We present here a tabulation of the required matrix elements:<sup>16</sup>

$$\begin{aligned} (J K M | \cos\theta | J K M) &= KM/J(J+1) \\ (J K M | \sin\theta e^{\pm i\varphi} | J K M \pm 1) &= \mp K/J(J+1)((J \pm M + 1)(J \mp M))^{\frac{1}{2}}, \\ (J K M | \cos\theta | J+1 K M) &= \frac{\{[(J+1)^2 - K^2][(J+1)^2 - M^2]\}^{\frac{1}{2}}}{(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}}, \\ (J K M | \cos\theta | J-1 K M) &= -\frac{[(J^2 - K^2)(J^2 - M^2)]^{\frac{1}{2}}}{J[(2J+1)(2J-1)]^{\frac{1}{2}}}, \end{aligned}$$

<sup>16</sup> R. de L. Kronig, and I. Rabi, Phys. Rev. **29**, 262 (1927).

$$\begin{aligned} & (J K M | \sin\theta e^{\pm i\varphi} | J-1 K M \pm 1) \\ &= \frac{[(J^2 - K^2)(J \mp M - 1)(J \mp M)]^{\frac{1}{2}}}{J[(2J-1)(2J+1)]^{\frac{1}{2}}}, \\ & (J K M | \sin\theta e^{\pm i\varphi} | J+1 K M \pm 1) \\ &= \frac{\{[(J+1)^2 - K^2](J+1 \pm M)(J+2 \pm M)\}^{\frac{1}{2}}}{(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}}. \end{aligned}$$

Of course, these elements are to be understood, according to our theorem above, as always off-diagonal in the index  $\pm$ , which is not explicitly written in.

There are two kinds of matrix elements of the "interaction matrix"  $P$  which do not vanish, for all practical purposes: (a) those corresponding to a simple "first-order Stark effect" interaction involving the  $J \rightarrow J$  elements of (5), and (b) those corresponding to rotational resonance and involving  $J \rightarrow J \pm 1$  elements of (5). All others are negligible because of the large energy-changes (order of  $10 \text{ cm}^{-1}$ ) involved; we neglect the second order effects and vibrational resonances, the latter because few vibrationally excited molecules are present.

However, it is necessary to observe that there is no resonance effect as far as the inversion frequency is concerned. The parameter  $k$  of Section H-5, Part I, is small for the inversion frequency, and therefore collisions of + molecules with + molecules or of - with -, in which each type must undergo a  $+\rightarrow-$  transition (total energy change about  $1.6 \text{ cm}^{-1}$ ) are as effective in broadening as the truly resonant  $\left\{ \begin{matrix} + \rightarrow - \\ - \rightarrow + \end{matrix} \right\}$  collisions. This applies as far as both effects (a) and (b) are concerned. The parameter  $k$  is actually

$$k = \frac{b\omega}{v} \doteq \frac{b(A) \times 10^{-8} \times 3 \times 1.6 \times 10^{18} \times 2\pi}{8 \times 10^4} \doteq b(A) \times 0.035. \quad (5)$$

We shall never consider impact parameters  $b$  greater than  $15A$ . A  $k$  of 0.5 may lead to an error of a few percent.

These considerations lead us to the following procedure: we shall calculate the  $P$ -matrix (Part I, Eq. (51)) ignoring the exponential time factors entirely, and then substitute the resulting  $P$ -matrix into the sum  $S_2$  (I, Eq. (54c)). Since we are ignoring the time-factor, it is permissible to perform the time-integral of (3) previously to taking the matrix elements. We use the formulas:

$$r^2 = b^2 + v^2 t^2 \quad \cos\psi = b/r \quad \sin\psi = vt/r, \quad (6)$$

and the result is

$$\int_{-\infty}^{\infty} \frac{H_1 dt}{h} = \frac{2\mu^2}{b^2 v h} [-\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \sin\varphi_1 \sin\varphi_2]. \quad (7)$$

At this point it is very easy to calculate the correct  $S_2$  sums. We present merely the result, which includes the identical sums for initial and final states. For the simple Stark effect we get the following  $S_2$  sum, applicable to collisions of the radiating molecule, quantum numbers  $J_1$  and  $K_1$ , with molecules of any  $J_2$  and  $K_2$  ( $n_2$  in the general formula (46) of Part I for the two-molecule case being here  $J_2, K_2$ ).

$$S_2(J_2, K_2) = \frac{8 \mu^4}{9 b^4 v^2 h^2} \frac{K_1^2 K_2^2}{J_1(J_1+1)J_2(J_2+1)} \quad (\text{Stark effect}). \quad (8)$$

For the two rotational resonance  $S_2$ 's, in case the radiating molecule  $J_1, K_1$  collides with a molecule with  $J_2 = J_1 \pm 1$ , we get

$$S_2(J_1-1, K_2) = \frac{8 \mu^4}{9 b^4 v^2 h^2} \times \frac{(J_1^2 - K_1^2)(J_1^2 - K_2^2)}{J_1^2(2J_1+1)(2J_1-1)} \quad (\text{rot. res.}) \quad (9a)$$

$$S_2(J_1+1, K_2) = \frac{8 \mu^2}{9 b^4 v^2 h^2} \times \frac{[(J_1+1)^2 - K_1^2][(J_1+1)^2 - K_2^2]}{(J_1+1)^2(2J_1+1)(2J_1+3)}. \quad (9b)$$

For collisions with molecules of  $J_2 = J_1 \pm 1$ , one must add (9a) or (9b) and (8) together to get the total  $S_2$  sum. These are ( $S_2$ )<sub>outer</sub> sums; no ( $S_2$ )<sub>inner</sub> sums enter in this problem because the elements of  $\mathbf{u}$  are all off-diagonal in the non-degenerate index  $\pm$ .

We must now obtain the quantity  $\sigma$  (or rather the separate  $\sigma(J_2, K_2)$  to average over  $J_2$  and  $K_2$  by Part I, Eq. (46)). Without bothering to do the integrals,<sup>17</sup> we present here the three possible  $\sigma$ 's for our three approximations of Part I, Section H-4. We use the notation

$$S_2(J_2, K_2) = A^2/b^4. \quad (10)$$

Then the three approximations give

$$\begin{aligned} \# 1. \quad \sigma_1(J_2, K_2) &= \rho_B(J_2, K_2) 2\pi(1.11A), \\ \# 2. \quad \sigma_2(J_2, K_2) &= \rho_B(J_2, K_2) 2\pi A, \\ \# 3. \quad \sigma_3(J_2, K_2) &= \rho_B(J_2, K_2) 2\pi(0.885A), \end{aligned} \quad (11)$$

or

$$\sigma(J_2, K_2) = 2\pi A \rho_B(J_2, K_2) \times C,$$

where  $C$  has the values

$$\begin{aligned} C = 1.11 & \quad \# 1, \\ C = 1.00 & \quad \# 2, \\ C = 0.885 & \quad \# 3. \end{aligned} \quad (11')$$

<sup>17</sup> H. Jensen, Zeits. f. Physik. **80**, 448 (1933).

Then we have Eq. (46) of Part I

$$\sigma = \sum_{J_2, K_2} \sigma(J_2, K_2),$$

and

$$(\Delta\nu) \text{ cm}^{-1} = (nv/2\pi c)\sigma \quad (12)$$

which determine the line-breadth from Eqs. (8)–(11).

Two types of experimental information are available. The most extensively measured single line in the ammonia inversion spectrum is the  $J_1=3, K_1=3$  line.<sup>18,19</sup> For this line we can neglect, with one or two percent error, the effect of the rotational resonance sums (9a) and (9b). Then we can compare our theoretical values from (8)–(12) with the experimental results. § The result shown in Table I (all breadths are half-widths in  $\text{cm}^{-1}/\text{atmos.}$  at  $0^\circ\text{C}$ ). This shows the agreement of our theory with experiment as far as absolute values of the broadening are concerned. Certainly the experimental value lies within our computational error, and it is interesting that the working approximation #2 is fairly close.

The second type of experimental data available is that on the relative breadths for all the lines in the ammonia spectrum, taken by Bleaney and Penrose.<sup>20</sup> In Table II we present our theoretical results on relative values. In order to avoid the ambiguity due to the interpolation procedure, we have normalized the theoretical value for the 33 line to fit the experimental value precisely. Columns (a) and (b) give the  $J$  and  $K$  values for the various lines; column (c) gives our values using the Stark effect, from Eq. (8), plus an approximately

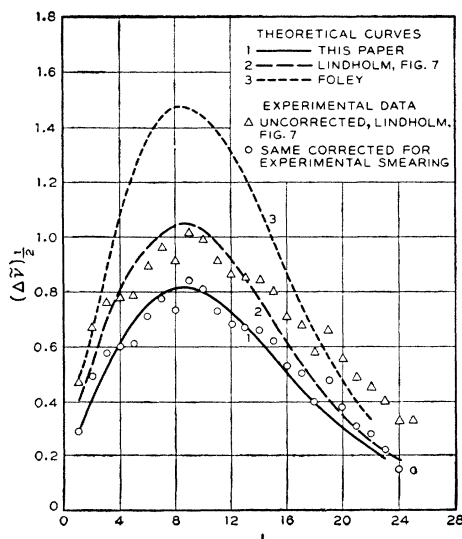


FIG. 2. Comparison of theoretical and experimental results.

<sup>18</sup> B. Bleaney and R. P. Penrose, Proc. Roy. Soc. A189, 358 (1947).

<sup>19</sup> C. H. Townes, Phys. Rev. 70, 166 (1946).

§ Bleaney's experimental value seems the soundest.

<sup>20</sup> B. Bleaney and R. R. Penrose, Proc. Phys. Soc. London 59, 424 (1947); 60, 540 (1948).

computed correction for the rotational resonance effect, from Eq. (9). These values are normalized as explained above. Column (d) gives Bleaney and Penrose's experimental data, and column (e) gives predictions from a theoretical formula of Bleaney based on the arbitrary assumption that the broadening effect of a collision depends on the *maximum* interaction energy of the two molecules. This formula is

$$(\Delta\nu)_i \sim (K^2/(J(J+1)))^{1/2}.$$

It does not seem very well based since it takes no account of rotational resonance. All breadths are in  $10^{-4} \text{ cm}^{-1}$  at 0.5 mm pressure.

The computational error in our approximate method for the rotational resonance is about  $0.1 \text{ cm}^{-1} \times 10^{-4}$ . Bleaney states that his experimental error is of the order of  $0.2 \text{ cm}^{-1} \times 10^{-4}$ . Within these errors, our agreement is excellent, except for the last four lines, which seem to allow no reasonable explanation. The fortuitous agreement of Bleaney's formula (e) with experiment is interesting, but not, apparently, significant.

## B. Other Cases: HCN and HCl Vibrational Band Spectra

Lindholm<sup>21,16</sup> has taken a great deal of experimental data on line-breadths in the vibrational bands of HCl and HCN. He has also made theoretical calculations of the line-breadths for these spectra, as has Foley.<sup>9</sup> Before giving our own theory, it will make our procedure somewhat clearer to indicate how these older theories worked.##

For cases in which resonances occur, as in the molecules under consideration, the standard practice has been to find a mean square direction-averaged energy perturbation due to resonance, for instance<sup>22</sup>

$$\langle (V^2)_{av} \rangle^{1/2} (J \rightarrow J-1) = \left(\frac{2}{3}\right)^{1/2} \left[ \frac{J^2}{(2J-1)(2J+3)} \right]^{1/2} \frac{\mu^2}{R^3} \quad (13)$$

in the case of rotational resonance of dumbbell molecules. Then this energy change is inserted as the diagonal  $H(t)$  in the simple phase-shift theory. This is for precise resonance; if imprecise resonance occurs, the "quasi-resonance" type of calculation such as the following is used. If two levels are separated by a small difference in energy  $\Delta$ , and an interaction  $V_{ik}$  is assumed between them, the energy  $E$  of the perturbed levels is computed from the secular equation

$$\begin{vmatrix} (\Delta/2) - E & V_{ik} \\ V_{ik} & (-\Delta/2) - E \end{vmatrix} = 0. \quad (14)$$

<sup>21</sup> E. Lindholm, Zeits. f. Physik 109, 223 (1938).

## Lindholm in reference 10 himself stated that he found this type of theory very bad in atomic resonance problems and that he used it only because his own rigorous theory was too difficult in these cases.

<sup>22</sup> H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

Then

$$E = \pm((\Delta/2)^2 + (V_{ik})^2)^{1/2}.$$

In the application of the method used by these authors, a mean square perturbation such as (13) is introduced as  $V_{ik}$ , and that solution of (14) chosen which reduces to the correct level at  $V_{ik}=0$ . Then this  $E$  is used in the phase-shift method.

Two objections can be made to this idea, considered simply as an interpolation method between the first order, resonance region and the second-order,  $r^{-6}$  force region for  $V$ . In the first place, the criterion for the point at which the change in type of forces occurs is whether  $V \doteq \Delta$ , apparently independent of the speed of collisions, which enters into the criterion for our own theory. This can be shown to be not a serious discrepancy, using the fact that on both theories a collision must be both long and strong enough to cause a certain  $P$ -matrix element before it has an appreciable effect. However, the two criteria are not identical; the quantitative results of the two theories differ considerably.

The second objection is more fundamental. A particular choice of the solution of (14) is made; thus in general it appears that a center-frequency shift should be expected, larger the closer to resonance the levels come. However, experimentally and theoretically it can be shown that there is no shift due to precisely resonant collisions: both signs in (14) occur when  $\Delta=0$ . This contradiction is a true defect in the quasi-resonance theory.

We are not able to present a good theory of the interpolation region between first order ( $r^{-3}$ ) forces and  $r^{-6}$  forces, or even, in the particular case of the rotator, of the second-order,  $r^{-6}$ , region. Therefore, since the answers for HCl depend strongly on how these regions are treated, we do not present detailed work on this molecule. We are able to attain fair (30 percent) agreement with Lindholm's observed widths for this spectrum, but no better agreement than that of his quasi-resonance theory. However, his theory predicts much greater breadths for the  $P$  than the  $R$  branch, which are not observed; our method of treating near-resonance could never lead to such a great difference, and thus agrees better with experiment.

We have been able to make fairly quantitative calculations for the HCN molecule. This molecule is a dumbbell rotator with a large dipole moment  $2.65 \times 10^{-18}$  esu. The observed spectra are the  $P$ -branches of the two bands at  $11500 \text{ cm}^{-1}$  ( $v_1=1, v_3=3$ ) and  $12500 \text{ cm}^{-1}$  ( $v_3=4$ ). There are several types of interactions to be considered.

(1) Vibrational resonance; this is neglected because the dipole moment for this interaction is quite small.

(2) Rotational resonance of the ground state ( $J=J_1$ ) with unexcited colliding molecules, having  $J=J_1 \pm 1$ .

(3) Rotational resonance of the excited state ( $J=J_1-1$ ) with unexcited colliding molecules having  $J=J_1, J_1=2$ .

(4) Second-order Keesom alignment forces, operative primarily when the colliding molecule is not in resonance with either state of the radiator.

Effect (1) is ignored. Effect (2) we can compute on much the same basis we have already used for ammonia: in fact, we can take over the  $S_2$  sums (9) bodily from the ammonia problem, if we specialize to  $K=0$  and realize we must take only half of the sum there used, since only one state of the two involved in the radiation is undergoing the first-order perturbation.

$$S_2(J_2=J_1+1) = \frac{4 \mu^4}{9 b^4 v^2 \hbar^2} \frac{(J_1+1)^2}{(2J_1+1)(2J_1+3)},$$

$$S_2(J_2=J_1-1) = \frac{4 \mu^4}{9 b^4 v^2 \hbar^2} \frac{J_1^2}{(2J_1-1)(2J_1+1)}.$$
(15)

The effect (3) is not a precise resonance, because the moment of inertia of the HCN molecule depends on vibrational quantum number. If we express the rotational energy approximately as

$$E_R(J) = B_v J(J+1).$$
(16)

Then<sup>23</sup>

$$B_v = 1.4878 - 0.0093(v_1 + \frac{1}{2}) + 0.0007(v_2 + 1) - 0.0108(v_3 + \frac{1}{2}).$$

$B$  is therefore about  $0.04 \text{ cm}^{-1}$  different in excited and normal states. Since the quantum exchanged in the rotational resonance is about  $2BJ$  wave numbers, the total amount by which the excited and ground states fail to be in resonance is approximately

$$\Delta\omega(\text{off resonance}) = 0.08J \text{ cm}^{-1}.$$
(16)

Then our parameter  $k$  is

$$k = b\Delta\omega/v = 2.9 \times 10^{-3} b(A)J.$$
(17')

The maximum collision parameters for this problem are about 30A; then

$$k \leq 0.09J$$
(17'')

and it is only for values of  $J \sim 10$  that an appreciable correction for failure to resonate should appear. We shall ignore this correction entirely, both because it should not be large for the interesting lines and because it is extremely difficult to compute. Then for the effect (3) we also use Eqs. (15), except that  $J_1$  must be replaced by  $J_1+1$ .

Lindholm finds a large correction for quasi-resonance in this case, not depending much on  $J$ . We do not agree with this result. In addition, this is the point in which his HCl treatment differs greatly from ours: we find that if (as is necessary for most lines) a correction is to be applied for this effect, it should be fairly symmetric between the  $P$  and  $R$  branches of the band.

<sup>23</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand, New York, 1945), p. 393.

Effect (4) we have not been able to treat rigorously by our own methods, since the sums required become quite difficult for the second-order alignment forces. It seems likely that the results for these forces obtained by the simple direction-averaged phase-shift theory should not be very far wrong; in order to include this important effect, we have simply borrowed the result of Lindholm and Foley for these forces (they agree) and added their line-breadths for these forces to our own for resonant forces. This simple addition is legitimate, since the important contributions these forces make come from different collisions from those contributing to the resonant line breadth.

We use the "working approximation" number (2). Then the cross section is given by (11) with  $C=1$ , and  $A$  defined by (10). We use  $S_2$  from (15). The line breadth can then be computed from (12) and Eq. (46) of Part I, for all resonant collisions (effects (2) and (3): sum over  $J_2=J_1-2, J_1-1, J_1, J_1+1$ ) with a contribution computed from Lindholm's figure (7) added in for the alignment forces.

Before comparing our results with Lindholm's experiments in Fig. 2, we should like to make some comments about his experimental data. These were taken in the photographic infra-red, by means of densitometer analysis of plates. His best data are those on the  $11.5 \times 10^3 \text{ cm}^{-1}$  band at pressures of 25 cm and 58 cm Hg; he also has data on the  $12.5 \times 10^3 \text{ cm}^{-1}$  band at three pressures, 25, 40, and 58 cm Hg. The most obvious fact about his original breadth data is that they are not proportional to the pressure, as one would expect on any theory at these pressures, but that instead they are given by

$$\&\nu = \text{const.} + (\text{const.}) \times \text{pressure}, \quad (18)$$

within the experimental fluctuations. One can interpret the constant in this expression as an experimental broadening due to slit width, finite resolving power, etc.; this would be the case if these effects were summarized by a dispersion form of curve, to be smeared with the true line breadth. This constant is about  $0.13 \text{ cm}^{-1}$  in half-width, a very reasonable value for experimental effects. To get the true width one should subtract this constant from all data.\*\*\*\*

In Fig. 2 we present both sets of experimental data: the actual observations at 58 cm extrapolated to 1 atm. pressure using simple proportionality to pressure, and the same with the constant term in (18) subtracted, which we expect to be the true impact theory line breadth. The legend explains that the lower (o) values

\*\*\*\* In a private communication, Lindholm suggests that while there must be some error of the type suggested here, he cannot agree that it could be quite so large. One may consider that the correction for experimental error is uncertain by perhaps half its total value, and thus that the data is uncertain by  $0.06 \text{ cm}^{-1}/\text{atmos}$ . Gordy has recently reported microwave measurements on the HCN rotational spectrum (Rev. Mod. Phys. **20**, 668 (1948)) and it is to be hoped that the observation of one or two of these lines will definitely settle the question.

TABLE III. Comparison of measured and computed diameters.

Molecules Radiator Perturber		Line-breadth		(c) Kinetic theory diameter(A)
		(a) Computed collision diameter A	(b) Measured diameter A	
NH <sub>3</sub>	He	1.5	2.4	3.2
NH <sub>3</sub>	H <sub>2</sub>	1.9	3.5	3.4
NH <sub>3</sub>	N <sub>2</sub>	2.6	6.4	3.4
NH <sub>3</sub>	O <sub>2</sub>	2.5	4.8	3.5
NH <sub>3</sub>	A	2.6	4.6	3.7
H <sub>2</sub> O	Air	3.3	5.6	3.5

are the corrected data. In addition, we present three theoretical curves for comparison: (1) is our own theory for resonance, borrowing the Lindholm-Foley values for the small contribution of alignment forces; (2) is Lindholm's curve for this spectrum; and (3) is Foley's published values for the HCN spectrum. Lindholm's curve is appreciably lower than Foley's for two reasons. He has a correction for quasi-resonance, which is, in our opinion, unfounded. Foley need not use this correction in any case, since his theory applied to the  $14\mu$  fundamental band. In addition, it seems that even taking into account this correction Foley's values are some 20 percent higher than Lindholm's; perhaps this is a numerical error in Foley's work, since we get agreement with Lindholm's values upon re-computing by their common method.

Two forms of agreement can be claimed for our curve: (a) excellent agreement with the experimental variation with  $J$ , a factor which is unchanged by any method of correcting for experimental error; and (b) good agreement quantitatively with the corrected data.

### C. Foreign Gas Broadening: Van der Waals Interactions

Broadening of microwave lines by pressures of foreign gases has been the subject of some experimental investigations.<sup>20,24</sup> The theoretical approach to the problem of foreign gas broadening has generally been that of computing the Van der Waals interactions between the molecules concerned and using these to obtain broadening cross sections. We have followed this procedure with our more accurate theory. In general, it can be shown that the  $r^{-6}$  term in the interaction between two molecules is, for the Debye induction type of forces:

$$H_{\text{ind.}} = (\alpha_2 \mu_1^2 / 2r^6)(1 + 3 \cos^2 \theta), \quad (19a)$$

where  $\alpha_2$  is the polarizability for the non-polar molecule, assumed isotropic,  $\mu_1$  the dipole moment of the polar molecule, and  $\theta$  the angle which  $\mathbf{u}_1$  makes with the intermolecular distance  $\mathbf{r}$ . Very similarly, the London dispersion forces for two interacting non-polar molecules, one assumed isotropic, are approximately given

<sup>24</sup> G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).

by

$$H_{\text{disp.}} = \frac{I_1 I_2}{I_1 + I_2} \frac{3\alpha_2}{4r^6} (3\alpha' + \alpha'' + (\alpha'' - \alpha') \cos^2 \theta), \quad (19b)$$

where  $\alpha_2$  is still the polarizability of the isotropic molecule,  $I_1$  and  $I_2$  are the fundamental frequencies from one-term dispersion formulas, or the ionization potentials, for the two molecules, and  $\alpha'$  and  $\alpha''$  are the polarizabilities along the two different axes of the polarizability ellipsoid of the non-isotropic molecule, assumed to be an ellipsoid of rotation. (A somewhat similar formula holds in case the anisotropic molecule has three different polarizabilities.)  $\theta$  is the angle between the axis of the polarizability ellipsoid and the intermolecular distance  $r$ .

For states separated by microwave frequency differences, the isotropic parts of (19) make no contribution to broadening, and one need consider only an interaction of the form

$$H = \text{const.} \times (\cos^2 \theta / r^6). \quad (20)$$

$S_2$  sums can be computed using this interaction, and inserting appropriate constants for various cases. These sums are quite difficult, both because the  $\cos^2 \theta$  term introduces essentially a second-order Legendre polynomial symmetry into the matrix  $P$ , and because the difficult term  $(S_2)_{\text{inner}}$  does not vanish. They are evaluated easily only by using the group-theoretical methods of Racah;<sup>15</sup> however, using these methods they can be done in general, even for forces of more complicated symmetry.

We do not present this evaluation because the results, in general, do not have any relation to experimental results. It is found that the collision broadening

cross sections  $\sigma$  calculated by means of the known Van der Waals forces come out usually to be considerably smaller than the kinetic theory cross sections computed from viscosity, etc. This means that the forces which cause broadening must be the higher order and exchange forces which come into prominence at the diameter corresponding to the kinetic theory cross-section. As would be expected, the measured broadening cross sections are at least as great as the kinetic theory ones in most cases.

Table III summarizes the situation very well. Column (b) is from Bleaney and Penrose's paper,<sup>22</sup> except the H<sub>2</sub>O line, which comes from Becker and Autler.<sup>24</sup> Column (c) is from Stuart's book.<sup>25</sup>

One more problem was computed. The microwave spectrum of oxygen has been measured<sup>26</sup> in some detail. This case is even more complicated than the preceding, because transitions among states having different total angular momenta ( $J$ ) but the same  $K$ , or molecular quantum number, must be considered.  $\mathbf{J} = \mathbf{K} + \mathbf{S}$ , where  $\mathbf{S}$  is the spin angular momentum of O<sub>2</sub>,  $|S| = 1$ . The splitting of the states  $J = K \pm 1$ ,  $K$  is very small, since this is the line observed at microwave frequencies, and thus this type of transition occurs easily upon collision. Another theorem of Racah was used to simplify this computation. Here the agreement with experiment was somewhat better than would be expected from the kinetic theory diameters and Table II, but this is not significant since the experimental data are only on the entire unresolved set of lines near 2 cm<sup>-1</sup>.

I should like to express my gratitude for the wise direction, help, and encouragement given me in my work on this problem by Professor J. H. Van Vleck.

<sup>25</sup> H. A. Stuart, *Molekülstruktur* (Verlag J. Springer, Berlin, 1934), Table II.

<sup>26</sup> J. H. Van Vleck, *Phys. Rev.* **71**, 413 (1947).