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The Pressure Broadening of Spectral Lines

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The Fourier integral expression for the intensity distribution in a pressure broadened line is derived from the quantum radiation theory with an adiabatic collision approximation. The phase shift approximation to the solution is obtained with the actual distribution of phase shifts taken into account. It is shown that in general there is a shift in line position as well as a line broadening both proportional to the pressure. The ratio of the shift to the broadening depends only on the power of the intermolecular distance with which the interaction decreases. Experimental values of this ratio in foreign gas broadening are on the average consistent with the inverse sixth power. The predicted line widths are slightly larger than those given by Weisskopf. Good agreement with the observed line width is found for most of the alkali metals absorption lines. Calculated line widths and shifts are given for the vibration-rotation lines of linear polar molecules. A method for treating non-adiabatic collisions is given. The conditions for which the Lorentz line form transforms to the Margenau-type line form are indicated. It is shown that the Jablonski wave mechanical treatment of translational motion leads to the same line forms as the Fourier integral method under the proper physical conditions.

INTRODUCTION

THE earliest treatment of the effects on spectral lines due to the interaction of radiating atoms and molecules is that of Lorentz.[1] A classical radiating oscillator is taken as the model for the radiating atom. The atoms or molecules are assumed by Lorentz to have a definite collision radius, and each radiating system periodically suffers a sudden disruption to the radiation mechanism. The collision either stops the radiating process or changes the phase by an arbitrary amount. The Fourier integral analysis of the wave train yields the observed frequency distribution of spectral intensity. The result is the well-known dispersion line form

$$I(\omega)=\frac{c}{\pi}\frac{n\pi a^2\bar{v}}{(n\pi a^2\bar{v})^2+(\omega-\omega_0)^2}$$

with a half-width, in angular frequency units, of $2n\pi a^2\bar{v}$ with n the number of atoms per cc, a the collision radius, and $\bar{v}$ the mean velocity of the atoms.[1]

This result agrees with the experimental data in that the dependence of line width on pressure is found to be linear up to pressures of several atmospheres. In many cases, particularly for self-broadening, a dispersion type of line form is found. The theory furnishes no values of the collision radius nor, consequently, of the spectral line half-widths.[2]

Weisskopf[3] has extended the ideas of Lorentz by taking as the model for the radiating atom a classical oscillator whose frequency varies in time according to the collision perturbations on the system. The intensity distribution is given by

$$I(\omega)=\left|A\int_{t_i}^{\infty}\exp\left[-i\int_{t_i}^{t}\omega'(x)dx+i\omega t\right]dt\right|^2, \quad (1)$$

where

$$\begin{aligned}\omega'(t)&=[E_i(t)-E_f(t)]/h\\&=\omega_0+[P_i(t)-P_f(t)]/h,\end{aligned} \quad (2)$$

with $P_i(t)$ and $P_f(t)$ the collision perturbations of the initial and final radiation states of the atoms and $E_i(t)$ and $E_f(t)$ the corresponding total energies of these states. The time t_i corresponds to the initial time of the radiation process. Under conditions such that the duration of the collision is small compared to the interval between collisions, the main effect of the perturbations is to produce phase shifts in the oscillation. Weisskopf has evaluated the expression for the intensity distribution with the assumption that all phase shifts with magnitudes greater than unity are equivalent to arbitrary phase shifts, and the effects of smaller phase shifts are negligible. A

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[1] H. A. Lorentz, Proc. Amst. Acad. Sci. 8, 591 (1906).

[2] H. Margenau and W. W. Watson, Rev. Mod. Phys. 8, 22 (1936).

[3] V. Weisskopf, Zeits. f. Physik 75, 287 (1932).

Lorentz-type line form is obtained, with the collision radii given directly from the force law. With interaction energies varying as the inverse third and inverse sixth powers of the separation distance, the values of the collision radii are, respectively,

$$a=(2\beta/\bar{v})^{\frac{1}{2}} \quad \text{and} \quad a=(3\pi\beta/8\bar{v})^{1/5}$$

where β is defined by

$$[P_i(t)-P_f(t)]/\hbar=\beta/R^p. \tag{3}$$

The phase shift approximation, as will be shown later, is valid for low densities and high velocities of the gas molecules. This assumption, namely, that the effects of the small phase shifts can be neglected and that the larger phase shifts are equivalent to arbitrary shifts, brings about the result that the shift of line centers, an important feature of the pressure effect, is not contained in the solution.

A very different type of solution has been given by Kuhn and London.[4] Their method consists essentially in taking as the intensity distribution, not the Fourier integral transform of the oscillations of varying frequency, but the frequencies which occur instantaneously in the oscillations. The intensity given to any frequency is proportional to the fraction of time that this frequency occurs in the oscillations. If the particles move with uniform velocity, the intensity for any frequency is proportional to the volume in space in which that time varying frequency is emitted. Thus if the frequency scale ω is measured from the unperturbed line position, we have for the inverse sixth-power law

$$I(\omega)d\omega\approx R_\omega{}^2dR_\omega=\beta d\omega/2\omega^{\frac{3}{2}}. \tag{4}$$

This result of Kuhn and London has the obvious defect of giving a divergent intensity at the line center.

Margenau[2, 5] has improved this result by taking into account the additive effect of all the perturbing atoms that interact simultaneously with the emitting atom. Thus, for N perturbing atoms, the intensity for any frequency is proportional to the volume in the $3N$-dimensional configuration space corresponding to the perturbation energy difference $\hbar\omega$. Margenau's expression for the normalized line form is

$$I(\omega)=\frac{2\pi}{3}\beta^{\frac{1}{2}}\frac{n\exp[-\pi\lambda/\omega]}{\omega^{\frac{3}{2}}}\text{ with }\lambda=4\pi^2\beta n^2/9 \tag{5}$$

and n the density. This formula indicates a line width and shift of peak intensity which are proportional to the square of the density.

The expressions of Kuhn and London and of Margenau represent essentially "static" solutions in which the particles are considered to be held in fixed positions. All effects due to the translational motion are neglected. This formulation is valid for conditions of low velocity and high density. How this line form transforms into the dispersion form of Lorentz at high velocities and low densities will be indicated later.

A rather different but quite rigorous approach to the pressure broadening problem has been given by Jablonski.[6–8] The gas is considered to be analogous to a very large molecule, and the stationary states of intermolecular motion, subject to the Van der Waals interaction, are computed. The interaction force depends on the state of internal motion of the interacting atoms or molecules, with the result that, in general, the translational wave functions for different states of internal motion are not orthogonal. Thus, subject to the assumption that the interaction forces are additive and that the effect of the intermolecular motion on internal states is an adiabatic perturbation, the matrix elements for optical transition contain as a factor the products of the "overlap" integrals of the translational wave functions of all the perturbing atoms or molecules. The probability amplitude for an optical transition from an initial state of the emitting (or absorbing) atom of energy E_i and translation energies of interatomic motion $e(n_1)\cdots e(n_K)\cdots e(n_N)$ to a final state with energy E_f of internal motion and with translational energies $e(n_1')\cdots e(n_K')\cdots e(n_N')$ is

$$A(i\rightarrow f)=S_{if}\prod_{K=1}^{N}\int_0^{R_0}dR_KR_K{}^2L_{eK}{}^{(R_K)}L_{eK'}{}^{(R_K)}, \tag{6}$$

where $L_{eK}{}^{(R_K)}$ is the radial wave function of the K perturber. This transition corresponds to the

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[4] H. Kuhn and F. London, Phil. Mag. 18, 983 (1934).

[5] H. Margenau, Phys. Rev. 48, 755 (1935).

[6] A. Jablonski, Acta Phys. Polonica 6, 371 (1937).

[7] A. Jablonski, Physica 7, 541 (1940).

[8] A. Jablonski, Phys. Rev. 68, 78 (1945).

emission (or absorption) of radiation of frequency

$$\omega=\frac{\Delta E}{\hbar}=\omega_0+\frac{i}{\hbar}\sum_{K=1}^{N}\left[e(n_K)-e(n_K{}')\right].$$

Jablonski has calculated an expression for the line form which is essentially the same as that of Kuhn and London. With *WKB* radial wave functions, each "overlap" integral has the form

$$\frac{1}{R_0}\int_0^{R_0} dR\cos\left\{\frac{1}{\hbar}\int_0^{R}\left[p(R)-p'(R)\right]dR+\eta-\eta'\right\}, \tag{7}$$

with $p(R)$, $p'(R)$ the momenta in initial and final states, and η, η' the phases in these states. In analogy with the Frank-Condon principle for discrete vibrational transitions, Jablonski has evaluated the integral at the points where $p(R)=p'(R)$, as the integral oscillates slowly at these values of R. This assumption is obviously equivalent to that of Kuhn and London, and in fact, Jablonski arrives at their formula on averaging the expressions for a single perturber over all possible transitions. It is clear that in any line broadening theory, a treatment which considers only a single perturbing atom and then averages over all transitions of this system will always yield a line form which diverges at the center, since, for a large vessel, the perturber will spend an infinitesimal fraction of time within the effective range of the forces.

Jablonski considers that the fact that the intensity distribution calculated by this method does not agree with the Lorentz-Weisskopf formula indicates that the Fourier integral method is fundamentally incorrect. However, it will be shown that the wave mechanical treatment does, in fact, yield both of these formulas under the assumption of physical conditions proper for each.

DERIVATION OF THE CLASSICAL FOURIER INTEGRAL

In this section a derivation will be given of the Fourier integral expression for the intensity distribution assumed by Lorentz and Weisskopf. The quantum theory of radiation is employed in calculating the probability of radiation emission by a system of interacting atoms or molecules. The treatment of the intermolecular motion is classical in that classical orbits are assumed. Thus the coordinates of the colliding particles become known functions of the time. In the Hamiltonian of the system, these coordinates appear not as dynamical variables but as time dependent parameters. The molecular interaction becomes a function of the time and may be treated as a time dependent perturbation on the system. The justification of this treatment lies in the fact that when the velocity of a "packet" representing the molecular motion is determined to good accuracy, the positions may be known, for all except the very light molecules, to one or two A. The ranges of the interaction forces which are important in line broadening are many times this packet size.

The Hamiltonian is taken to be of the form

$$H=H_1(p_l,q_l)+H_2(p_l,q_l,Q_i(t))+H_3(p_l,q_l,p_s,q_s)+H_4(p_s,q_s). \tag{8}$$

Here H_1 is the energy function of the variables of the internal motion of the isolated molecules, H_2 is the term representing the interaction of the molecules, and contains the molecular coordinates $Q_i(t)$. H_3 is the interaction with the radiation field, and H_4 is the energy of the charge-free radiation field. The terms H_2 and H_3 are treated as perturbations. The eigenfunction solutions of the unperturbed Hamiltonian consist of products of wave functions of the atomic systems and of the radiation field oscillators. When the complete wave function is expanded in terms of these eigenfunctions and inserted in the wave equation, the usual set of equations for the growth of the states is obtained. The state equations which do not involve optical transitions are of the form

$$\dot{a}_n=-(i/\hbar)V_m{}^n(t)a_m(t)\times\exp\left[-i(E_m-E_n)t/\hbar\right], \tag{9}$$

where $V_m{}^n(t)$ is the matrix element of H_2, that is, of the intermolecular interaction. For adiabatic collision conditions the solution is

$$a_n(t)=\frac{V_m{}^n(t)a_m(t)}{E_m-E_n}\exp\left[-\frac{i}{\hbar}(E_m-E_n)t\right]\quad\text{for } V(0)=0. \tag{10}$$

The equations containing optical transition matrix elements are of the form

$$\dot{a}_f = S_i{}^f a_i \exp\left[-\frac{i}{\hbar}(E_i - E_f - \hbar\omega_s)t\right] - \frac{i}{\hbar}V_n{}^f(t)a_n(t)\exp\left[-\frac{i}{\hbar}(E_n - E_f)t\right],$$

in which $S_i{}^f$ is the ordinary matrix element for the spectral transition. The increase of the coefficient a_f corresponds to the emission (or absorption) of a radiation quantum of frequency ω_s. The insertion of expression (10) into the state equations involving the optical matrix element permits an explicit solution for the probability amplitude for emission of a quantum of frequency ω_s

$$A_{\omega_s}(T) = \exp\left[-\frac{i}{\hbar}\int_0^T P_f dt\right]\int_0^T dt S_f{}^i \times \exp\left[-\gamma_N t - \frac{i}{\hbar}\int_0^t (P_i(t) - P_f(t)dt + i\omega t\right], \quad (11)$$

in which γ_N is the natural line width, and P_i and P_f are the instantaneous interaction energies in the initial and final states, respectively. For foreign gas broadening these terms are the second-order Van der Waals interactions. For self-broadening the collisions may produce a resonance interaction of like molecules as well as the Van der Waals interactions. In this case of first-order resonance splitting of the levels, it may be shown that the expression for the spectral intensity consists of the sum of two terms similar to that of Eq. (11), in which, however, the P_i or P_f values are now the resonance splitting, with the symmetric level in one term and the antisymmetric in the other. With the neglect of natural line width* and the extension of the radiation time interval to infinity, the Eq. (11) is identical with the Fourier integral formula of Lorentz and Weisskopf.[1] From the derivation it is clear that this expression may be described as the Fourier integral of the optical matrix element between the adiabatic, or instantaneous solutions of the time dependent wave equation. For the self-broadening case the instantaneous solution is that which diagonalizes the energy matrix of $H_2(t)$, i.e., the symmetric and antisymmetric combinations of the wave functions of the resonating states.

PHASE SHIFT SOLUTION OF THE FOURIER INTEGRAL

The Fourier integral amplitude may be written as

$$A(\omega) = N^{\frac{1}{2}}\int_0^\infty dt \exp\left[-i\int_0^t P(x)dx + i\omega t\right],$$

in which $P(t)$ is the difference of $P_i(t)$ and $P_f(t)$ in angular frequency units, and the frequency is measured from the unperturbed line position. N is a normalization factor. The intensity distribution is given by

$$I(\omega) = N\int_0^\infty dt_1 \int_0^\infty dt_2 \times \exp\left[-i\int_{t_2}^{t_1} P(x)dx + i\omega(t_1 - t_2)\right]$$

or, with $t_1 - t_2 = \tau$ and $t_2 = t_0$,

$$\begin{aligned} I(\omega) &= N\int_{-\infty}^{+\infty} d\tau \int_0^\infty dt_0 \exp\left[-i\int_{t_0}^{t_0+\tau} P(x)dx + i\omega\tau\right] \\ &= \mathcal{R}N\int_0^\infty d\tau \int_0^\infty dt_0 \exp\left[-i\int_{t_0}^{t_0+\tau} P(x)dx + i\omega\tau\right], \end{aligned} \quad (12)$$

in which $\mathcal{R}$ signifies that only the real part of the integral is to be taken.

Now the function

$$\bar{y}(\tau) = \int_0^\infty dt_0 \exp\left[-i\int_{t_0}^{t_0+\tau} P(x)dx\right], \quad (13)$$

in which the integral in t_0 is extended over the complete interval of the radiation process, is a measure of the average correlation of the function

$$\exp\left[-i\int_0^\tau P(x)dx\right]$$

over the interval τ. τ is the time interval over

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* As is well known the natural line width is extremely small for optical transitions, about 10^{-4} cm^{-1}, and even smaller still, about 10^{-7} cm^{-1}, for infra-red lines.

which the correlation is to be determined. Thus the radiation intensity may be expressed as the Fourier amplitude of this correlation function.

For time intervals which are large compared to the collision duration, the integral

$$\int_{t_0}^{t_0+\tau} P(x)dx$$

is simply the sum of the phase shifts of the collisions occurring in this interval. The phase shift approximation consists in the assumption that the duration of the collisions is vanishingly small, so that this integral may be expressed as the sum of an integral number of collision phase shifts for all values of τ. It will be shown later that this approximation is valid for low densities and high velocities of the gas molecules. Thus we have

$$\int_{t_0}^{t_0+\tau} P(x)dx=\sum_{i=1}^{n} \alpha_i$$

for n phase shifts in the interval. If the mean time between collisions is τ_0, the expected number of collisions in the interval τ is τ/τ_0, and the probability of n collisions is given by $(\tau/\tau_0)^n(e^{-\tau/\tau_0}/n!)$. The average value of the correlation function for all cases with n collisions becomes

$$\int dt_0 \exp\left[-i\sum_{i=1}^{n}\alpha_i\right]=\prod_{i=1}^{n}\int_{-\infty}^{+\infty} d\alpha p(\alpha) \times(\cos\alpha-i\sin\alpha)=(A-iB)^n, \quad (14)$$

in which $p(\alpha)d\alpha$ is the distribution in phase shifts, and A and B are, respectively, the average values of $\cos\alpha$ and $\sin\alpha$. The forces may be considered to be "cut off" at a collision distance ρ_0, corresponding to τ_0, and the phase shifts cut off at a corresponding value α_0. This cut-off distance is only a device for convenience and is eventually to be extended to infinity to include all phase shifts. The correlation function is thus given by

$$\bar{g}(\tau)=\sum_{n=0}^{\infty}\frac{e^{-\tau/\tau_0}}{n!}\left(\frac{\tau}{\tau_0}\right)^n(A-iB)^n =\exp\left[\frac{A-iB}{\tau_0}\tau-\frac{\tau}{\tau_0}\right]. \quad (15)$$

The intensity formula is

$$I(\omega)=\Re N\int_0^\infty d\tau\exp\left[\frac{A-1}{\tau_0}\tau-i\frac{B-\omega}{\tau_0}\tau\right] =\frac{(1-A)/\pi\tau_0}{[(1-A)/\tau_0]^2+[(B/\tau_0)-\omega]^2}. \quad (16)$$

This expression for the line shape yields a half-width $2(1-A)/\tau_0$ and a shift of the line center B/τ_0, both of which are proportional to n, that is, to the density.

For the evaluation of the constants in this formula we shall assume the interaction energy to be of the form $V=\beta\hbar/R^p$. For the phase shifts, we have

$$\alpha=\int_{-\infty}^{\infty}\frac{V_i-V_f}{\hbar}dt=\int_{-\infty}^{\infty}\frac{\beta_i-\beta_f}{(\rho^2+v^2t^2)^{p/2}}dt=\frac{\gamma}{v\rho^{p-1}},$$

with v the relative velocity. In addition to the distribution in velocities $f(v)dv$, there may be a distribution in force law constants g_k, corresponding to the various excitation states of the colliding molecules. The total number of collisions per second producing phase shifts larger than the minimum cut-off value α_0 is

$$\frac{1}{\tau_0}=n\sum_k\int_0^\infty dvf(v)g_k\pi\rho_{vk}{}^2v,$$

where n is the density of particles. ρ_{vk} is the collision distance corresponding to a phase shift α_0 for a collision between particles of relative velocity v and with a force law β_k/R^{p_k}. The probability for a phase shift for this case is

$$p(\alpha)d\alpha=\frac{D\gamma_k{}^{2/(p_k-1)}g_kf(v)v^{(p_k-3)/(p_k-1)}}{\alpha^{(p_k+1)/(p_k-1)}(p_k-1)},$$

in which D is a normalization factor. On averaging all types of collisions and velocities the expression for the half-width becomes

$$8\pi n\sum_k g_k\frac{\gamma^{2/(p_k-1)}}{p_k-1}\langle v^{(p_k-3)/(p_k-1)}\rangle_{\text{Av}} \times\int_0^\infty\frac{d\alpha\sin^2\alpha}{|\alpha|^{(p_k+1)/(p_k-1)}}, \quad (17)$$

for the case in which all phase shifts have positive sign. For resonance broadening phase shifts with positive and negative signs occur with equal probability and the integration is then extended

TABLE I. Ratio, R, of shift to half-width.

p:	5	6	7
R:	0.500	0.363	0.288

over the complete range of the distribution. Similarly the line center shift is given by

$$2\pi n \sum g_k \frac{\gamma^{2/(p_k-1)}}{p_k-1} \langle v^{(p_k-3)/(p_k-1)} \rangle_{\mathrm{Av}} \times \int_0^\infty \frac{d\alpha \sin\alpha}{|\alpha|^{(p_k+1)/(p_k-1)}}, \quad (18)$$

and the same conditions hold for the range of integration of α as with the half-width. In these expressions the cut-off distance has been allowed to become infinite. The phase shift integrals may be evaluated in terms of gamma-functions. It is to be emphasized that both the shift and broadening expressions are found in the same low density approximation to the solution of the Fourier integral. If the phase shift distribution $p(\alpha)$ is an even function of α, as it is in the resonance broadening case, there will be no shift in the line position. In other cases such as the foreign gas broadening, the phase shifts have predominantly one sign (i.e., either positive or negative) and hence the shift is not zero. For foreign gas broadening in atomic spectra, the phase shifts in most cases have only one sign, which may be either positive or negative. It is of considerable interest that in this case the ratio of the shift to broadening is independent of the pressure, in the phase shift approximation, and, for the case of one sign in the phase shifts, depends only on the form of the interaction law between molecules. For an inverse power law β/R^p this ratio is

$$\mathrm{Ratio} = \tfrac{1}{2} \cot \left\{ \frac{p-3}{2(p-1)} \pi \right\}.$$

The values are given for a few cases in Table I.

The half-width obtained by Weisskopf is

$$2\pi n \langle v^{(p-3)/(p-1)} \rangle_{\mathrm{Av}} \gamma^{2/(p-1)}.$$

Our formula shows the same dependence on the variables of the system, but the half-width is greater than that given by Weisskopf by a factor which, for the important cases of inverse third- and sixth-power laws, has the values 1.57 and 1.21, respectively. For the more slowly decreasing force laws the neglect of small phase shifts is more important, hence the greater discrepancy with the Weisskopf formula for the third-power force law.

NON-ADIABATIC EFFECTS

The Fourier integral expression for the intensity distribution in a spectral line is valid under conditions such that the collisions induce no transitions among states defined by the instantaneous solutions of the Hamiltonian equation

$$H(t)\psi_n(t) = E_n(t)\psi_n(t). \quad (19)$$

An expression for the probability of non-adiabatic transitions which serves as an indication of the validity of the adiabatic assumption in any particular case will be derived here. Resonance transitions which are necessarily also non-adiabatic were discussed previously and are excluded from consideration.

The complete wave function describing the molecular system may be expanded in terms of these instantaneous solutions

$$\Psi(t) = \sum_n a_n(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_n(t) dt \right] \psi_n(t).$$

This function must satisfy the wave equation

$$H(t)\Psi(t) = -(\hbar/i)(\partial\Psi/\partial t),$$

leading to the equation for the rate of growth of the amplitude for any state

$$\dot{a}_k = -\sum_n a_n(t) \left[\psi_k^*, \frac{\partial \psi_n}{\partial t} \right] \times \exp\left[-\frac{i}{\hbar} \int_0^t (E_n - E_k) dt \right],$$

in which the first bracketed expression is

$$\int dq \psi_k^* \cdot (\partial \psi_n / \partial t)$$

integrated over all coordinates of the wave functions. The time-dependent term in the Hamiltonian is contained in the collision interaction and may be treated as a perturbation. The solutions of Eq. (29) may then be given as

$$\psi_n(t) = {}_0\psi_n + \sum_i \frac{H_i^n(t)}{E_i - E_n} {}_0\psi_i.$$

${}_0\psi_i$ is a solution of the time independent zero-order Hamiltonian and H_i^n is the matrix element of the collision interaction. If the system is initially in state m, the probability amplitude for transition to state k during the collision becomes

$$a_k=\frac{-i\omega_{km}}{E_k-E_m}\int_{-\infty}^{\infty}H_m{}^k(t)\exp\left[i\omega_{km}t\right]dt$$

with

$$\omega_{km}=(E_k-E_m)/\hbar.$$

For the usual case of dipole-dipole interaction, we have

$$H_m{}^k(t)=\beta_{km}/(\rho^2+\nu^2t^2)^{\frac{3}{2}}.$$

The probability amplitude for this case is given by

$$a_k=\frac{\beta_{km}\pi K^2}{\rho^3(E_k-E_m)}H_1(iK),\tag{20}$$

in which $K=\rho\omega_{km}/v$ and $H_1(iK)$ is the first-order Hankel function with imaginary argument. In any particular case of line broadening this formula indicates whether non-adiabatic transitions are numerous enough to play an important part in the radiation process. It will be found that for most cases of atomic line spectra, the level separations are so large that the probability of such transitions is negligible. Exceptions are found in cases of "quenching" collisions. In molecular infra-red spectra, cases of non-adiabatic transitions may occur due to a near coincidence of the rotational levels of a foreign molecule with those of the radiating molecule. Generally the level to which such a transition takes place does not radiate in the same spectral region as the original state, so that when such a non-adiabatic "jump" occurs, the radiation process ceases. This fact furnishes an approximate method for including the non-adiabatic effects in the preceding treatment. The termination of the radiation process is equivalent to an arbitrary phase shift and may be treated as such by introducing into the phase shift distribution $p(\alpha)$, a probability for arbitrary phase shifts equal to the total probability for non-adiabatic transitions.

TABLE II. Experimental ratios of shift to half-width in foreign gas broadening.

Spectral line	Perturber	Ratio	Reference
Hg 2537	A	0.39	a
	N_2	0.45	a
	O_2	0.47	a
Na 5890	A	0.35	b
	N_2	0.44	
K 7665	N_2	0.47	c
		0.37	d
7699	N_2	0.50	c
		0.44	d
4044	N_2	0.50	c
4047	N_2	0.57	c
Hg 2537	CO_2	0.25	a
2537	H_2O	0.22	a
2537	H_2	0.16	a
Na 5890	H_2	0.23	b
K 7665	A	0.36	d
7699	A	0.42	d
Rb 4216	He	0.33	
4202	He	0.23	
4216	Ne	0.17	
4202	Ne	0.22	e
4216	A	0.56	
4202	A	0.39	
Cs 4555	He	0.30	
4555	Ne	0.23	
4555	A	0.42	f
4555	N_2	0.62	
3876	He	0.62	
3876	Ne	0.37	
3876	A	0.77	
3876	N_2	0.32	

[a] C. Fuchtbauer, G. Joos, and O. Dinkelacher, Ann. d. Physik **71**, 204 (1923).
[b] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).
[c] H. Margenau and W. W. Watson, Phys. Rev. **44**, 748 (1933).
[d] G. F. Hull, Phys. Rev. **50**, 1148 (1936).
[e] T-Z Ny and S-Y Chen, Phys. Rev. **52**, 1158 (1937).
[f] C. Fuchtbauer and F. Gossler, Zeits. f. Physik **87**, 89 (1933).

FOREIGN GAS BROADENING IN ATOMIC SPECTRA

The calculation of the line broadening and line shift produced by a foreign gas requires the determination of the electronic dispersion interaction in both levels involved in the optical transition. For the ground states, fairly accurate values of the interaction can be obtained by the use of the polarizability,[9] but for the excited states only rough estimates can be given. Thus the lack of accurate knowledge of the atomic Van der Waals forces precludes any close experimental verification of the theory of line widths. For the inverse sixth-power interaction law, our analysis, taking the distribution of collision phase shifts into account, yields, as has been shown, a twenty percent greater line width than that of Weisskopf. This author[3] has estimated upper and lower limits to the foreign gas broadening in a number of cases by his method. These estimates are so uncertain, however, that our increase in predicted line width is not very significant. The

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[9] H. Margenau, Rev. Mod. Phys. **8**, 1 (1939).

linear dependence of line breadth and line shift on pressure is observed at low pressures in all cases.

For the ratio of shift to half-width, the situation is somewhat more favorable. It was shown above that this ratio is independent of the strength of the interaction and, in fact, depends only on the power of the separation distance which occurs in the interaction law. The observed ratios of shift to half-widths are given for a number of cases in Table II. These ratios show such a spread in values that it cannot be said that the inverse sixth-power law is confirmed. The experimental uncertainties in the determination of the half-widths are large and the values found by different investigators are not always consistent. The average of the ratios given in Table II is 0.375, which is very close to the value for the theoretical sixth-power law. It is believed that the ratio of shift to broadening is sufficiently sensitive to the form of the force law to permit a determination of the law by careful experiments.

SELF-BROADENING IN ATOMIC SPECTRA

The line widths of the first members of the principal series of the alkali metals have been examined by several investigators.[10–13]

Houston[14] has discussed these cases of resonance broadening with special reference to the question as to whether the component lines of such multiplet transitions are equally broadened. The calculations of this author are based on a method due to Fursow and Wlassow,[15] in which the probability per collision for the transfer of the excitation energy of the emitting atom to the normal state atom is obtained. This transfer of excitation energy is regarded as a damping in the oscillation of the radiating atoms which leads to a spectral distribution following the dispersion law with a half-width equal to the "decay constant" of the oscillation. The results of Houston are given in Table III. The ratio of line widths of the doublet components is unity in all cases, according to these calculations.

TABLE III. Half-widths of alkali resonance lines.

Reference			Observed		Calculated (this paper)		Calculated (Houston)	
		J	$10^7\Delta\nu n$	Ratio	$10^7\Delta\nu n$	Ratio	$10^7\Delta\nu n$	Ratio
11	Na	1/2	0.712	1.55	0.71	1.42	0.49	1.00
		3/2	1.10		1.01		0.49	
10	K	1/2	3.2	1.0	0.91	1.42	0.63	1.00
		3/2	3.2		1.29		0.63	
12	Rb	1/2	0.55	1.75	0.52	1.38	0.65	1.00
		3/2	0.96		0.72		0.65	
13	Cs	1/2	0.84	1.72	0.95	1.52	0.71	1.00
		3/2	1.45		1.44		0.71	

It appears to the writer that the method of averaging the transfer probabilities which take place between the degenerate sub-levels of the initial state and those of the resonant state resulting from the collision over all possible transitions is incorrect. The transfer probabilities from any sub-level of the initial state should be summed over all final states and then averaged over the initial levels. This process, if employed in the calculations of Houston, leads to line width ratios of the doublet components in agreement with those calculated by the phase shift method derived below.

From Eq. (17) the half-width of a resonance broadened line is

$$\Delta\nu_{\frac{1}{2}}=4\pi^3 n\beta_{\mathrm{Av}}, \tag{21}$$

in which β_{Av} is the average absolute value of the coefficient in the resonance interaction β/R^3. These coefficients are given by the roots of the $2(2J+1)(2J'+1)$ secular equations of the interaction of an excited atom with an atom in the ground state. J is the angular momentum quantum number of the ground state and J' that of the excited state. Half of these $2(2J+1)(2J'+1)$ degenerate states are symmetric and half are antisymmetric with respect to exchange of the two atoms. Only the symmetric states may combine optically with the final state of the radiation process in which both atoms are in the ground states. Therefore, in computing the average value of β_i, we shall sum these coefficients over all the symmetric states and divide by the total number of states, since all states have equal probability of occurrence. We shall employ the root mean square value of β_i, as this quantity is readily obtained by summing the diagonal elements of the matrix of the square of the interac-

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[10] P. E. Lloyd and D. S. Hughes, Phys. Rev. **52**, 1215 (1937).

[11] K. Watanabe, Phys. Rev. **59**, 151 (1940).

[12] Shang-Ui Ch'eng, Phys. Rev. **58**, 844 (1940).

[13] C. Gregory, Phys. Rev. **61**, 465 (1942).

[14] W. V. Houston, Phys. Rev. **54**, 884 (1938).

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tion energy. This sum is

$$\textstyle\sum_i \sum_j V_j^i V_i^j = \sum_i \sum_j (V_j^i)^2 \qquad (22)$$

for symmetrical matrices. The matrix elements are of the form

$$V_j^i = \frac{e^2}{R^3}[X_1(m_i', m_i)X_2(m_j, m_j') + Y_1(m_i', m_i)Y_2(m_j, m_j') - 2Z_1(m_i', m_i)Z_2(m_j, m_j')], \qquad (23)$$

in which the X, Y, Z are the coordinates of the optical electrons in the two atoms denoted by the subscripts 1 and 2, respectively. This matrix element connects the state of the system in which the first atom is excited and has a magnetic quantum number m_i' and the second atom is in the ground state with a magnetic quantum number m_j, with the state in which the first atom is in the ground state and the second atom is excited and the quantum numbers are m_i and m_j', respectively. After the computation of expression (22) and division by the number of states, the value of the line half-width is obtained. The half-width is given by

$$\Delta\nu_{\frac{1}{2}} = 2\sqrt{3}\pi^3 n \frac{\hbar e^2}{m\Delta E_{JJ'}}\left(\frac{2J+1}{2J'+1}\right)^{\frac{1}{2}} f_{JJ'}, \qquad (24)$$

in which $f_{JJ'}$ is defined in the usual manner

$$f_{JJ'} = \frac{2m}{3\hbar^2}\frac{\Delta E_{JJ'}}{2J+1}\textstyle\sum_{m'} |X(Jm, J'm')|^2.$$

For the alkali doublets the ratio of the half-widths of the $\frac{3}{2}$ and $\frac{1}{2}$ components is approximately $\sqrt{2}$. In Table III the experimental half-widths are compared with those calculated from Eq. (24) and with those calculated from Houston's formula. Except in the case of potassium, the agreement we obtain appears to be quite satisfactory. The experimental value for potassium differs from those of the other elements by such a large factor, although essentially the same interaction is present, that it surely seems to be in error.

LINEAR MOLECULES

In order that an interaction be effective in line broadening, it is necessary, in the adiabatic approximation, that there be a difference in the perturbations on the two levels of the optical transition. It may be shown that in the calculation of the second-order "electronic dispersion" forces, the summation over the matrix elements for any vibration-rotation state in a particular electronic level leads to the same result. The denominators of these terms contain the energy differences between the state being perturbed and states of different electronic quantum numbers. Thus all the levels in the same electronic state will have very nearly the same "dispersion" interaction energies. The effect of the dispersion forces in vibration or rotation spectra is therefore negligible.

For polar molecules the interaction between the permanent dipoles is a first- or second-order effect depending on the presence of resonance in the collision. A molecule of angular momentum quantum number l will show resonance interaction with another molecule in state $l \pm 1$, regardless of whether the two molecules are in the same vibrational state.* The mean value of the resonance interaction is zero. We shall approximate the mean absolute value by the root mean square value which has been shown by Margenau[5] to be

$$\langle V^2\rangle_{\mathrm{Av}}^{\frac{1}{2}} = \left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{l+1}{[(2l+1)(2l+3)]^{\frac{1}{2}}}\cdot\frac{\mu^2}{R^3}, \qquad (25)$$

in which μ is the dipole moment and l is the smaller of the angular momentum quantum numbers of the interacting molecules. Either the initial or the final level of the optical transition may undergo resonance. For a vibration band spectrum, both the symmetric and antisymmetric states of the resonance splitting will combine optically with the final state of the transition and the expression (25) may be used directly as the average β_i in Eq. (21).

For non-resonating collisions of polar molecules the second-order perturbation solutions of Eq. (10) are identical with those given by London.[16]

$$V_{\mathrm{Av}} = \frac{2\mu^4 I}{3\hbar^2 R^6} \times \frac{l_1(l_1+1)+l_2(l_2+1)}{(l_1+l_2)(l_1+l_2+2)(l_1-l_2-1)(l_1-l_2+1)}, \qquad (26)$$

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* This assumes that the convergence of the rotation levels in the excited vibration state is negligible.

[16] F. London, Zeits. f. Physik **63**, 245 (1930).

TABLE IV. Calculated half-width in cm^{-1} for one atmosphere pressure at 25°C.

	HCl		HCN			
			Half-widths cm^{-1}			
l	Half-width cm^{-1}	l	Sec. order	Resonance	Total	Shift cm^{-1}
0	0.39	0	0.32	0.54	0.86	+0.12
1	0.60	1	0.39	0.92	1.31	+0.14
2	0.72	2	0.44	1.33	1.87	+0.14
3	0.70	3	0.48	1.69	2.17	+0.14
4	0.58	4	0.50	1.98	2.48	+0.13
5	0.42	5	0.53	2.20	2.73	+0.12
6	0.27	6	0.54	2.35	2.89	+0.10
7	0.158	7	0.54	2.41	2.95	+0.065
8	0.080	8	0.55	2.41	2.96	+0.040
9	0.038	9	0.56	2.34	2.90	+0.010
10	0.016	10	0.55	2.24	2.79	−0.018
		11	0.54	2.06	2.60	−0.043
		12	0.53	1.87	2.40	−0.067
		13	0.51	1.67	2.17	−0.082
		14	0.50	1.46	1.96	−0.10
		15	0.48	1.25	1.73	−0.11
		16	0.44	1.05	1.49	−0.11
		17	0.42	0.87	1.29	−0.12
		18	0.38	0.71	1.09	−0.11
		19	0.36	0.56	0.92	−0.11
		20	0.32	0.44	0.76	−0.10
		21	0.30	0.34	0.64	−0.10
		22	0.26	0.26	0.52	−0.088

where V_{Av} is the mean interaction energy between molecules in states denoted by l_1 and l_2. It is the difference in the interaction between the two levels involved in the transition which produces the phase shifts in pressure broadening. In contrast to the "dispersion interaction" in foreign gas broadening in atomic spectra, this difference in perturbations may be either positive or negative depending on the quantum numbers of the colliding particles. Hence, as will be shown for certain of the fine structure lines of a band, the shift in position may be positive while in others it is negative.

The infra-red band spectra of linear molecules are a favorable case for the comparison of line broadening theory with experiments, as they are among the few cases in which the interaction forces may be evaluated with any accuracy. With expressions (25) and (26) we obtain the phase shift probability distribution for both resonance and non-resonance cases. Since the effects of these types of interactions, when they occur in different collisions, enter linearly in the total phase shift distribution, we may calculate the half-widths produced by each type of collision and simply add these contributions to obtain the total half-widths. All possible collision interactions must be taken into account, with probabilities assigned according to the thermal distribution in states. Molecules in states near the maximum of the Maxwell-Boltzmann distribution encounter molecules in states differing by one unit of angular momentum very often, and these lines will show the greatest broadening. The shifts in line positions, due to the second-order interaction, show a rather interesting behavior. The lines near the edge of the band are moved toward the band center, and those near the center, closer than the most intense lines, move away from the band center. The molecules in states corresponding to the most intense region of the band encounter other molecules with lower quantum numbers about as often as those in higher states. For these molecules the phase shift distribution is nearly symmetrical and there will be no shift in line position. Actually these second-order interactions, proportional to the fourth power of the dipole moment, are negligible in almost all cases. Only in the case of HCN, which has a very strong polarity, are the shifts within the range of experimental detection. The calculated half-widths in cm^{-1} for one atmosphere pressure at 25°C are given in Table IV for HCl and HCN. For HCN the second-order effects are negligible, and only the resonance broadening values are given in the table. Actually the effects of quadrupole and exchange forces determine a lower limit on the collision radius of 3–5A, and a consequent lower limit on the broadening per atmosphere of 0.04–0.10 cm^{-1}. Therefore the widths given for the lines at the edge of the HCl band are not very significant. For HCN the resonance, second-order, and total half-widths are given. The calculated shift per atmosphere is also shown.

PROPERTIES OF THE GENERAL SOLUTION OF THE FOURIER INTEGRAL FOR FOREIGN GAS BROADENING

The statistical problem in the determination of the Fourier integral intensity distribution may be reduced to the calculation of the correlation function (13). For very small values of τ, this expression may be written approximately as

$$\int dt_0 \exp\left[-iP(t_0)\tau\right]. \tag{27}$$

The integral in t_0 is to be interpreted as the average over all interactions occuring in the radiation process. Thus, for small values of τ, this expression becomes

$$\int dPD(P)e^{-iP\tau}, \tag{28}$$

in which $D(P)$ is the distribution in the function $P(t)$. For large values of τ the expression (15) becomes the correct approximation for the correlation function. If the correlation function (28) is inserted in the intensity expression (12) and the integration over τ is extended to infinity, the exponential factor takes on the properties of a so-called delta-function, $\delta(P, \omega)$, and the resulting intensity distribution is $I(\omega)=D(P)$ which is identical with that of Margenau. Thus the use of the correlation approximation (15) over the complete interval yields the phase shift line form, and the use of expression (28) leads to the "static" distribution. The exact correlation function transforms from (15) to (28) at values of τ of the magnitude of the duration of a collision producing unit phase shift.

In Table V are given the values of the half-width and the shift of peak intensity for these two cases. χ is the ratio of the volume enclosed by the collision radius for unit phase shift to the volume corresponding to the average distance between molecules. This quantity serves as a criterion as to which approximation is the more accurate for any condition of density, temperature, and strength of interaction. As conditions change such that χ increases through the value of unity, the dependence of line width on density goes from the first power to the second power. The two formulas give the same width and shift for values for χ of 1.51 and 1.48, respectively. Preliminary calculations, employing higher approximations to the correlation function, indicate fairly good agreement of the half-width and line shifts with the phase shift values, for χ less than unity, and with the "static" values for χ greater than unity.

THE WAVE MECHANICAL TREATMENT OF INTERMOLECULAR MOTION

In the formulation of Jablonski, the probability amplitude for any particular combination of translation transitions (6) is to be squared, summed over all transitions from these initial states, and averaged over the distribution in initial translational states, subject to the conditions on the total energy change of the system

$$\Delta E=\omega\hbar=E_i-E_f+\sum_{i=1}^{N}(e_i-e_i'), \tag{29}$$

in which the summation is extended over all the perturbing particles. With the WKB approximation to the radial wave functions, each "overlap" integral may be written in the form

$$\int_{\rho}^{R_0} dR\frac{c^2}{p(R)}\cos\left\{\int_{\rho}^{R}\frac{m}{\hbar}\frac{\Delta e-\Delta U(R)}{p(R)}dR\right\} \tag{30}$$

in which $p(R)$ is the classical radial component of momentum, Δe is the translation energy difference for the perturber in the initial and final states, and $\Delta U(R)$ is the difference in potential energy in initial and final states. The effects due to the extension of the wave functions into the "non-classical" region $R<\rho$ are neglected. At the edge of the container, the boundary conditions are of the form

$$\frac{p(R_0)\cdot R_0}{\hbar}-\frac{l\pi}{2}+\eta_{el}=\tfrac{1}{2}(2n+1)\pi$$

for both initial and final states. The argument of the cosine in the integrand of (30) satisfies the asymptotic condition

$$[p(R_0)-p'(R_0)](R_0/\hbar)+\eta_{el}-\eta_{e'l}'=m\pi, \tag{31}$$

in which primed quantities refer to the final state of the transition. We now introduce the variable

$$dt=\frac{mdR}{p(R)}=\frac{mdR}{(2m)^{\frac{1}{2}}[e-U(R)-(l^2\hbar^2/2mR^2)]^{\frac{1}{2}}}$$

and employ the classical approximation for the angular momenta $l^2\hbar^2=m^2v^2\rho^2$. The boundary Eq.

TABLE V. Half-widths and shift of peak intensity.

Approximation	Half-width	Shift
Phase shift		
$\chi\ll 1$	$8.53\omega_0/\chi$	$3.10\omega_0/\chi$
Static		
$\chi\gg 1$	$5.63\omega_0$	$2.10\omega_0$

$$\omega_0=4\pi^2\beta n^2/9 \qquad \chi=\frac{4}{3}\pi n\left(\frac{3}{8}\pi\frac{\beta}{v}\right)^{3/5}$$

(31) at $R_0 = T/v$ becomes

$$\omega_i T_i - \int_0^{T_i} \frac{\Delta U_i}{\hbar} dt = m\pi \tag{32}$$

with $\omega_i = \Delta e_i/\hbar$ for each perturber. The overlap integral expressed in the new variable is

$$c^2 \int_0^{T_i} dt_i \cos\left[\omega_i t_i - \int_0^{t_i} \frac{\Delta U_i(t)}{\hbar} dt\right]. \tag{33}$$

The phase at the boundary in the integrand,

$$\alpha_i' = \int_0^{T_i} \frac{\Delta U_i(t)}{\hbar} dt,$$

is exactly half the phase shift for such a collision which would appear in the Fourier integral expression for the intensity.

If conditions are such that the effective range of forces is large compared to the average distance between molecules, that is, if the overlap integrals for perturbing molecules with ρ comparable with the particle separation show phase values larger than unity, then the procedure employed by Jablonski in calculating the integral (30) is correct, and the static type of solution is obtained. Jablonski has obtained the Kuhn-London line form by considering only a single perturber, but it is clear that the averaging over all possible simultaneous transitions, subject to condition (29), is completely equivalent to the calculation of Margenau and leads to the line form given by that author.

Under conditions such that the effective range of the forces is small compared to the molecular separation, the effect of the interaction forces is simply the introduction of the phase into the integrand (33), and the integrand is a harmonically oscillating function over the range of integration. The result of this calculation will yield the same formula for the intensity distribution as would be obtained in the phase shift approximation to the Fourier integral.

As an example of this calculation, we shall show that the wave mechanical treatment leads to the Lorentz line form for the same conditions that were assumed in that calculation. We assign a definite cut-off radius to the interaction forces, but we assume that the forces inside this radius are sufficiently great that the phases of expression (33) are arbitrarily large. Then this integral becomes simply

$$\int_0^{T_i} dt_i \cos(\omega_i t_i - \alpha_i) = \frac{\sin \alpha_i}{\omega_i} = \frac{\sin \omega_i T_i}{\omega_i} \tag{34}$$

with the use of the boundary condition (32). Of the total number of molecules in the container, N, only a fraction of them, N', will have angular momenta, or collision distances, sufficiently small to enable them to come within the range of the forces. For the other molecules the translational wave functions in the upper and lower states of the radiation process form identical sets of orthogonal functions, and no change in energy is permitted in the transition. Therefore we need only concern ourselves with the N' molecules which may actually collide with the radiating molecule. Leaving off numerical factors, the expression (34) becomes

$$A(\omega) = \prod_{i=1}^{N'} \frac{\sin \omega_i T_i}{\omega_i}, \tag{35}$$

with

$$\omega = \sum_{i=1}^{N'} \omega_i. \tag{36}$$

The intensity distribution is obtained by averaging $|A(\omega)|^2$ over all combinations of simultaneous transitions. The distribution in the parameter $T_i = R_0/v$ is taken to be $e^{-T_i/T_0}/T_0$ in which $T_0 = R_0/\bar{v}$ and $\bar{v}$ is the average velocity. To obtain the intensity distribution, the expression

$$\prod_{i=1}^{N'} \int_0^{\infty} dT_i \frac{\sin^2 \omega_i T_i}{\omega_i^2} \frac{e^{-T_i/T_0}}{T_0} = \prod_{i=1}^{N'} \frac{T_0^2}{1+4\omega_i^2 T_0^2}$$

must be averaged over all values of the ω_i. The assumption of arbitrarily large phases allows each perturber to make any energy transition. The intensity is given by

$$I(\omega) \approx \prod_{i=1}^{N'} \int_{-\infty}^{\infty} \frac{d\omega_i}{1+4\omega_i^2 T_0^2}$$

with the condition (36). This N'-fold integration may be performed in successive steps, and leads to

$$I(\omega) \approx [1+(2\omega T_0/N')^2]^{-1}.$$

The number of molecules in the container which may collide with the radiating atom is

$N'=2\pi nR_0a^2$ with n the density. Thus the line form is given by

$$I(\omega)=A/[(n\pi a^2\bar{v})^2+\omega^2] \qquad (37)$$

which is the Lorentz formula, with frequencies measured from the line center.

Under the two extreme physical conditions the wave mechanical and classical treatments lead to the same expressions for the line form.

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Self-Broadening in the 14μ Band of HCN

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The intensity distribution in the positive branch of the 14μ HCN band has been measured at pressures of 2.5 cm, 16 cm, 40 cm, and 58 cm. Because of the large permanent dipole moment of this molecule, there is considerable line broadening at these pressures. The overlapping of lines, slit width effects, and finite thickness of the absorbing layer of gas are taken into account in relating the theoretical line widths to the intensity distribution. The two constants giving the effective slit width and the absolute vibration intensity are determined from the low pressure lines, and these constants with the theoretical line widths determine the intensity distribution throughout the band. Reasonably good agreement is found at all pressures, and no systematic disparity of theory and experiment is indicated. The predicted shifts in the lines, which are just within the limits of detection, are in qualitative agreement with the observed values. The absolute value of the dipole strength of this vibration transition is determined.

IN a preceding paper,[1] formulas were developed for the width and shifts of the lines of the infra-red vibration bands of polar molecules. Table IV of reference 1 gives the widths and half-widths per atmosphere of the rotational lines for bands of HCl and HCN.

Inasmuch as the polar molecules are among the few cases in which the interactions important in line broadening may be calculated accurately, it has appeared worth while to determine experimentally the intensity distribution at various pressures in a band of such a molecule. Hydrogen cyanide gas was chosen for several reasons. Since it is a linear molecule, the spectrum is especially simple. It has a very large dipole moment (2.65×10^{-18} c.g.s. e.s.u.), which indicates that considerable broadening will occur at moderate pressures. The spectrum is not complicated by the lines due to an isotope, as is the case with HCl. The positive branch of the 14μ band was chosen for measurement, as there are no interfering bands of atmospheric H_2O or CO_2 in this region. The line positions in the band have been measured previously by Barker and Choi.[2]

The infra-red spectrometer employed was that described by Hardy.[3] The writer was very kindly permitted the use of the instrument by Professor E. F. Barker. The grating used was of the echelette type, ruled with 700 lines to the inch. This spectrometer is equipped with a KBr fore prism to remove the higher order spectra of short wave-lengths.

Measurements of the absorption of the gas were made at pressures of 2.5 cm, 16 cm, 40 cm, and 58 cm of mercury, with absorption cell lengths of 12 cm, 2.5 cm, 1 cm, and 1 cm, respectively. The total amount of gas through which the radiation passed was thus roughly constant. 58 cm was the highest pressure that could be maintained at

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