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Theory of Pressure Broadening of Microwave Spectral Lines

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A theory of pressure broadening of spectral lines is presented which is applicable to microwave spectra. It is an extension of the Anderson theory to the case of overlapping lines. The interference of neighboring lines is taken into account by the use of a relaxation matrix. The diagonal elements of this matrix correspond to linewidths and are calculated in the same way as in previous theories. The off-diagonal matrix elements are also calculated from the intermolecular interaction. Application is made to the ammonia and oxygen spectra.

INTRODUCTION

The phenomenon of pressure broadening of spectral lines has been extensively discussed in the literature.[1] The Van Vleck-Weisskopf[2] modification of the Lorentz theory has served as the standard line shape used in interpreting atomic and molecular absorption spectra. Foley[3] and Anderson[4] have shown how one may obtain the widths and shifts of spectral lines from a knowledge of the intermolecular potential. At low pressures, where individual spectral lines are isolated from each other, their theories have enjoyed much success. At high pressures, where the lines merge together to form a band, marked disagreement between experimental data and theory has been noted.

More recently, by extending Fano's[5] work on relaxation phenomena, Ben-Reuven[6] derived a general theory of microwave pressure broadening. He was able to account for overlapping lines by introducing a matrix which represented a quantum-mechanical interference term between the various transitions. A first principles calculation of these quantities has not been made, however.

In the present article a theory of pressure broadening of spectral lines is proposed which is meant to be applicable at all pressures. Three crucial approximations are employed: the binary collision assumption, the classical path approximation, and the impact approximation. The theory is compared with previous treatments and is shown to be a generalization of Anderson's[4] formalism. Finally the theoretical predictions are compared with the experimental data for ammonia and oxygen.

THEORY

The quantity relating the macroscopic absorptive properties of a gas to its microscopic properties is the dipole autocorrelation function, $F(\tau)$. It is defined by

$$F(\tau)=\mathrm{Re}\langle\mathrm{Tr}\rho_0\vec{\mu}(t)\cdot\vec{\mu}(t+\tau)\rangle_t\ , \tag{1}$$

where $\vec{\mu}$ is the dipole moment of the system and ρ_0 is the density matrix for the system in the equilibrium state. We shall imagine the gas to be in contact with a thermal bath so ρ_0 will remain a time-independent operator. The line shape can be obtained by taking the Fourier transform:

$$G(\omega)=\int_0^\infty d\tau\cos\omega\tau F(\tau)\ . \tag{2}$$

The absorption coefficient is proportional to $G(\omega)$. By using the ergodic hypothesis the time average may be replaced by an average over all collisions

$$F(\tau)=\mathrm{Re}\langle\mathrm{Tr}\rho_0\vec{\mu}(0)\cdot\vec{\mu}(\tau)\rangle\ . \tag{3}$$

The temporal evolution of the dipole operator is governed by the Heisenberg equation (let $\hbar=1$)

$$\frac{d\vec{\mu}(t)}{dt}=i[H,\vec{\mu}(t)]=i[H_0+V,\vec{\mu}(t)]\ , \tag{4}$$

where H is the total Hamiltonian. We shall make the classical path approximation and assume that the molecular trajectories are prescribed functions of time. Then $V(t)$ will represent a time-dependent interaction between the partners of a collision. It is further assumed that the pressure is sufficiently low so only binary encounters need be considered. It is convenient to transform to the interaction picture

$$\vec{\mu}'(t)=e^{-iH_0t}\vec{\mu}(t)e^{iH_0t}\ , \tag{5}$$

$$\frac{d\vec{\mu}'(t)}{dt}=i[V'(t),\vec{\mu}'(t)]\ , \tag{6}$$

$$V'(t)=e^{-iH_0t}V(t)e^{iH_0t}\ . \tag{7}$$

In the impact approximation it is assumed that the duration of a collision is small compared with the mean time between collisions (or any other characteristic period). Therefore the effect of the impact is described entirely by an S matrix. The post-collision dipole is related to the pre-collision dipole by

$$\vec{\mu}'(\tau^+)=S'^{-1}\vec{\mu}'(\tau^-)S' \tag{8}$$

where the collision has occurred at time τ and

$$S'=T\exp[-i\int_{-\infty}^{\infty}dt\ e^{-iH_0t}V(t-\tau)e^{iH_0t}]\ . \tag{9}$$

Collisions may be classified according to their impact parameter, b, and their relative speed, v. Thus S will depend on these quantities. The probability of having a collision in a time $d\tau$ is given simply by

$$dP=nvf(v)dv2\pi bdbd\tau\ , \tag{10}$$

$f(v)$ being the speed distribution function and n the perturber density. Thus combining Eqs. (8) and (10) gives

$$\vec{\mu}'(\tau+d\tau)-\vec{\mu}'(\tau)=\langle nv\int d\sigma[S'^{-1}\vec{\mu}'(\tau)S'-\vec{\mu}'(\tau)]\rangle d\tau\ . \tag{11}$$

In a basis where H_0 is diagonal,

$$(S')_{bi}=e^{-i\omega_{bi}\tau}S_{bi}\ , \tag{12}$$

$$\text{where}\quad S=T\exp[-i\int_{-\infty}^{\infty}dt\ V'(t)]\ , \tag{13}$$

we obtain the differential equation

$$\frac{d\vec{\mu}_{fi}(\tau)}{d\tau}-i\omega_{fi}\vec{\mu}_{fi}(\tau)+\sum_{ab}\Pi_{fiab}\vec{\mu}_{ab}(\tau)=0\ . \tag{14}$$

A relaxation matrix $\underline{\Pi}$ has been introduced and is defined by

$$\Pi_{fiab}=\langle nv\int d\sigma[\delta_{fa}\delta_{bi}-(S^{-1})_{fa}(S)_{bi}]\rangle\ . \tag{15}$$

A quantity similar to Π has appeared in Anderson's formulation of pressure-broadening theory. The crucial difference is that only the diagonal elements Π_{fifi} were involved in the line shape. As we shall soon see Anderson's treatment is obtained if the lines do not overlap.

Gordon[7] in his semiclassical description of absorption postulates an equation similar in form to (14). The relaxation matrix, as we have defined it, is somewhat different than his. The fact that the relaxation matrix is indexed with four subscripts makes it a rather strange object from the usual quantum-mechanical viewpoint. Ben-Reuven[6] recognized that such matrices do appear in the Liouville space formulation of quantum mechanics. His theory is based on this formulation but we see from Eqs. (14) and (15) that the basic content of the theory follows directly from the Heisenberg equations.

Under some special circumstances the relaxation matrix simplifies considerably. To obtain criteria which will enable us to distinguish various limiting cases assume the pulse $V(t)$ to be characterized by some duration Δ. In the first case let us assume that the frequency is high, i.e.,

$$\omega_{bi}\Delta \gg 1 . \tag{16}$$

Then neglecting time ordering for the present we have

$$\langle b|\int dt\, V'(t)|i\rangle = \int_{-\infty}^{\infty} dt\, V_{bi}(t) e^{-i\omega_{bi}t} . \tag{17}$$

The integrand is the product of a slowly varying function with a rapidly oscillating exponential so the integral will be a small number. Similar conclusions will result if time-ordered products are analyzed also. Therefore we obtain an adiabatic limit

$$S_{bi} \approx 0 . \tag{18}$$

A second case of interest is when ω_{bi} is small, i.e.,

$$\omega_{bi}\Delta \ll 1 . \tag{19}$$

Then

$$\langle b|\int_{-\infty}^{\infty} dt\, V'(t)|i\rangle \approx \int_{-\infty}^{\infty} dt\, V_{bi}(t) . \tag{20}$$

We shall for simplicity neglect time-ordering effects. Arguments for the neglect of such effects have already been given by Anderson[4] and Byron and Foley.[8] Therefore

$$S_{bi} \approx \{\exp[-i\int_{-\infty}^{\infty} dt\, V(t)]\}_{bi} . \tag{21}$$

A formal solution to Eq. (14) can be written down if we employ the Liouville space notation. The combination (a,b) will be indicated by a single index α. Fixing our attention on a particular spherical component of the dipole moment, Eq. (14) can be recast into a matrix equation

$$\left(\frac{d}{d\tau} - i\underline{\omega}_0\right)\underline{\mu}_q(\tau) + \underline{\Pi}\,\underline{\mu}_q(\tau) = 0 . \tag{22}$$

This formally integrates to

$$\underline{\mu}_q(\tau) = \exp[-(\underline{\Pi} - i\underline{\omega}_0)\tau]\,\underline{\mu}_q(0) . \tag{23}$$

Inserting Eq. (23) into (3) and (2) gives

$$G(\omega) = -\tfrac{1}{2}\,\mathrm{Im}\sum\nolimits_q (-)^q\,\mathrm{Tr}\rho_0\mu_{-q}(0)$$
$$\times\left(\frac{1}{\omega_0+\omega+i\Pi} + \frac{1}{\omega_0-\omega+i\Pi}\right)\mu_q(0) . \tag{24}$$

This formula for the line shape is still rather complicated because of degeneracy. We shall deal with this problem shortly.

The relaxation matrix has a few simple symmetry properties which follow from the fact that the S matrix is unitary. Thus

$$\Pi^*_{fiab} = \Pi_{ifba} \tag{25}$$

and $$\sum\nolimits_a \Pi_{fiaa} = 0 = \sum\nolimits_f \Pi_{ffab} . \tag{26}$$

COMPARISON WITH PREVIOUS FORMULATIONS

Anderson[4] has developed a theory of pressure broadening which is applicable to the case of nonoverlapping lines. We wish to show that Eq. (24) is consistent with his results. Let us split the $\underline{\Pi}$ matrix into two parts; one diagonal and the other off-diagonal

$$\underline{\Pi} = \underline{\Delta} + \underline{\Omega} . \tag{27}$$

Then

$$\omega_0 - \omega + i\Pi = D^{-1}(1 + i\Omega D^{-1})^{-1}$$
$$= D^{-1} - iD^{-1}\Omega D^{-1} + \cdots , \tag{28}$$

where we have introduced the diagonal matrix $D = \omega_0 - \omega + i\Delta$. If only the leading term is retained we obtain Anderson's line shape. Thus the trace operation in Eq. (24) becomes a sum of terms of the form

$$-\mathrm{Im}\sum\nolimits_q \tfrac{1}{2}[\rho_0\mu_q^+(0)]_\alpha$$
$$\times\left(\frac{1}{D_\alpha(\omega)} + \frac{1}{D_\alpha(-\omega)}\right)[\mu_q(0)]_\alpha .$$

Since

$$\mathrm{Im}\,\frac{1}{D_i} = \frac{\Delta_i}{\Delta_i^2 + (\omega_{0_i} - \omega)^2} , \tag{29}$$

we see that the line shape is essentially just a sum of Van Vleck-Weisskopf line shapes.

When the lines do not overlap it is easy to see that the remaining terms in Eq. (28) do not contribute. This is because the factors D_α^{-1}, $D_\beta^{-1}, \ldots$ are each strongly peaked only in the vicinity of the spectral lines $\alpha, \beta \ldots$. Since $\Omega_{\alpha\beta}$ only connects those terms with $\alpha \neq \beta$ the contribution will be very small.

As was mentioned earlier the Gordon theory[7] has a form which is similar to the one developed here. The essential difference between the two formalisms lies in the structure of the relaxation matrix. Gordon treats the rotational motion of a molecule classically and thus attempts to prescribe the Π matrix *a priori*. Thus in a Hund's case b situation the S matrix is merely replaced by a Wigner rotation matrix, and one has

$$\Pi_{fiab} = \langle nv \int d\sigma [\delta_{fa}\delta_{bi} - D_{fa}^{(s)\dagger}(\alpha) D_{bi}^{(s)}(\alpha)] \rangle \ . \tag{30}$$

The rotation angle $\alpha(b,v)$ is determined by an independent method.

Let us briefly discuss the restrictions imposed on the theory by the assumptions we have made. The main limitation stems from the use of the impact approximation. This assumes the collision's duration to be the smallest characteristic time in the problem. If one should happen to be observing a spectral line in its extreme wings then $|\omega - \omega_0|\Delta$ could become comparable to unity. The impact approximation will then become invalid and the line shape will depend sensitively on the dynamics of the collision process. In practice such a case arises, for example, when one examines the microwave end of the spectra of some systems at high pressures, such as water vapor. At elevated pressures high-frequency lines are broadened into the microwave region and make substantial contributions. Since these frequencies often exceed the inverse collision duration we should expect impact-approximation line-shape theories to be inapplicable.

An additional restriction arises from the use of the classical path approximation. For heavy molecules this is probably not serious because we are then involved with high orbital angular momentum quantum numbers. For very light molecules, however, this is not true and we would probably have to replace the theory with one that took into account the relative motion quantum mechanically.

We must also be careful to fix our attention only on transitions involving energy transfers which are small compared with the kinetic energies. This is because the classical path approximation clearly violates the conservation of energy principle. If the two energies do become comparable one must somehow incorporate the reaction on the perturber into the treatment. These three criteria are not independent, of course.

Before proceeding with applications let us rewrite Eqs. (3), (14), and (15) in a manner in which the rotational degeneracy is removed. This is accomplished through the use of the Wigner-Eckart theorem and orthogonality relations. In terms of reduced quantities we thus obtain

$$f(\tau) = \mathrm{Re}\textstyle\sum_{IF} \rho_I \langle F\|\mu(0)\|I\rangle \langle F\|\mu(\tau)\|I\rangle \ , \tag{3$'$}$$

$$\left(\frac{d}{d\tau} - i\omega_{FI}\right)\langle F\|\mu(\tau)\|I\rangle + \textstyle\sum_{AB} \Pi_{FIAB}\langle A\|\mu(\tau)\|B\rangle = 0 \ , \tag{14$'$}$$

$$\Pi_{FIAB} = -\sum_{l} (-)^{l+J_a-J_f}(2l+1)\begin{Bmatrix} J_i & J_f & 1 \\ J_a & J_b & l \end{Bmatrix} \times \sum_{\substack{m_a m_b \mu \\ m_i m_f}} (-)^{\mu+m_b+m_f} \times \begin{pmatrix} J_a & J_f & l \\ m_a & -m_f & \mu \end{pmatrix}\begin{pmatrix} J_i & J_b & l \\ m_i & -m_b & -\mu \end{pmatrix} \times \langle nv \int d\sigma[\delta_{fa}\delta_{bi} - (S^{-1})_{fa}(S)_{bi}]\rangle \ . \tag{15$'$}$$

In order for the present theory to give results which are different from Anderson's theory three criteria have to be met. First the lines must overlap. Secondly the energy levels which give rise to the two interfering lines must be separated by a relatively low frequency. Finally the S matrix has elements which couple the various levels. In the microwave region these criteria are very often satisfied and hence marked deviations will be expected. The applications to be made will illustrate this.

APPLICATION TO AMMONIA SPECTRUM

The ammonia molecule has been the object of intensive experimental and theoretical study.[9] Anderson's theoretical calculation of linewidths agreed strikingly well with the existing low-pressure data, and the line shapes were found to be consistent with the Van Vleck-Weisskopf formula. At high pressures, however, striking disagreement between theory and experiment was evident. In order to interpret the data it seemed necessary to postulate a large frequency shift for the resonant lines. Ben-Reuven suggested that one should take the interference of the various lines into account. By assigning an empirical relaxation matrix to the entire spectrum he was able to obtain quantitative agreement with the data. We will attempt to generalize his work by making a "first principles" calculation of these matrix elements. Thus a unified theory applicable to the discussion of both the band spectrum and resolved line cases will emerge.

In a collision we shall regard one molecule as the system and the other as a perturber. The former will be treated quantum mechanically while the latter will be described classically. As this procedure does not permit resonance effects to occur we shall have to account for them separately. The dominant interaction is the dipole-dipole potential

$$V = -r^{-3}[3(\vec{d}_1 \cdot \hat{r})(\vec{d}_2 \cdot \hat{r}) - \vec{d}_1 \cdot \vec{d}_2] \ . \tag{31}$$

Since molecule 2 is treated classically this is of the form $\vec{d}_1 \cdot \vec{A}(t)$. This potential pulse induces transitions among the various states of the system and correspondingly affects its absorption properties. As we have seen, the description of this effect can be discussed in terms of the S matrix.
It will be expedient to treat the symmetric and antisymmetric inversion states as forming a spinor in some hypothetical space. The energy operator, H_0, can then be expressed as

$$H_0 = H_{JK} + \tfrac{1}{2}\hbar\omega_{JK}\sigma_z , \tag{32}$$

where σ_z is the usual Pauli spin matrix. The first term is just the energy operator for a symmetric top, and the second term represents a splitting between the states of opposite symmetry.

To a good approximation the $\Delta J \neq 0$ transitions can be disregarded. If we assume that $\Delta J = 1, b \sim 10$ Å, and $v \sim 5\times10^4$ cm/sec, then

$$\omega b/v \sim 8\langle J+1\rangle \gg 1 .$$

From Eqs. (16) and (18) this implies that the corresponding S matrix vanishes. On the other hand, for inversion transitions $\omega b/v < 0.25$. Since this is small we shall neglect the inversion splitting entirely. The S matrix may then be expressed as

$$S = \exp(-i\sigma_x \vec{c} \cdot \vec{d}_1) , \tag{33}$$

$$\text{where } \quad \vec{C} = \hbar^{-1}\int_{-\infty}^{\infty} dt\, \vec{A}(t) . \tag{34}$$

By restricting ourselves to transitions which do not couple different J states we are permitted to write

$$\vec{d}_1 = \alpha\vec{J} , \tag{35}$$

where it is easily shown that

$$\alpha = \mu K/J(J+1) , \tag{36}$$

K being the symmetric top quantum number. S thus has the form of a rotation operator which operates in two spaces, i.e.,

$$S = \exp(-i\sigma_x \vec{C} \cdot \vec{J}) , \tag{37}$$

$$\text{where } \quad \vec{C} = \frac{\mu K}{J(J+1)} \int_{-\infty}^{\infty} \frac{dt}{\hbar}\, \frac{\vec{d}_2 - 3(\hat{r}\cdot\vec{d}_2)\hat{r}}{r^3} . \tag{38}$$

The σ_x matrix may be rotated to diagonal form by a matrix R:

$$S = \mathrm{R}e^{i\sigma_z \vec{C}\cdot\vec{J}} R^+ , \tag{39}$$

$$\text{where } \quad R = e^{i\pi\sigma_y/4} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} . \tag{40}$$

The S-matrix elements are therefore

$$\langle JKS'M'|S|JKSM\rangle = \sum_{S''} R_{S'S''} R^+_{S''S} \langle JM'| e^{iS''\vec{C}\cdot\vec{J}} |JM\rangle . \tag{41}$$

The reduced relaxation matrix will be labeled by symmetry indices only, since we have decided to neglect rotational excitation. To perform the degenerate sums implicit in the definition of this reduced matrix it is convenient to expand the S matrix in terms of irreducible tensors. Such expansions were originally discussed by Fano[10] and later applied to the problem of the relaxation of excited atomic states by Omont.[11] We define a set of basis matrices $J_{l\omega}$:

$$J_{l\omega} = N\mathcal{Y}_{l\omega}(\vec{J}) , \tag{42}$$

where the argument of the spherical harmonic is the angular momentum operator. The matrix elements of these objects are normalized so that

$$\langle JM'|J_{l\omega}|JM\rangle = (-)^{J-M'} \begin{pmatrix} J & l & J \\ -M' & \omega & M \end{pmatrix} (2l+1)^{1/2} . \tag{43}$$

By employing the orthogonality relation for spherical harmonics one can show the fact that they are orthogonal:

$$\mathrm{Tr}[J_{l\omega} J^+_{l'\omega'}] = \delta_{ll'}\delta_{\omega'\omega} . \tag{44}$$

They also form a complete set of matrices for the expansion of any $2J+1$ rowed square matrix. Therefore, for example, we may expand

$$\exp(iS''\vec{C}\cdot\vec{J}) = \sum_{l\omega} s_{l\omega}(S'') J_{l\omega} , \tag{45}$$

$$\exp(-iS'\vec{C}\cdot\vec{J}) = \sum_{l\omega} s^*_{l\omega}(S') J^*_{l\omega} . \tag{46}$$

These relations may be inserted into Eq. (41) and that in turn into the definition of the reduced relaxation matrix, Eq. (15′). The sum over the degeneracy index can now be found directly from the orthogonality properties of the three J symbols:

$$\Pi_{FIAB} = \Big\langle nv\int d\sigma \Big[\delta_{FA}\delta_{BI} + \sum_{l\omega}\sum_{S''S'} (-)^l \times \begin{Bmatrix} J & J & 1 \\ J & J & l \end{Bmatrix} R_{FS'} R^+_{S'A} R_{BS''} R^+_{S''I}\, s^*_{l\omega}(S')\, s_{l\omega}(S'') \Big] \Big\rangle . \tag{47}$$

Inserting Eq. (44) into (46) we obtain

$$\mathfrak{s}^*_{l\omega}(S') = \mathrm{Tr} J_{l\omega}\, e^{-iS'\vec{\mathfrak{C}}\cdot\vec{\mathrm{J}}} \; . \tag{48}$$

By a rotation of the axes through some angles θ, ϕ this may be diagonalized

$$e^{-iS'\vec{\mathfrak{C}}\cdot\vec{\mathrm{J}}} = \mathfrak{D}(\phi,\theta,0)\, e^{-iS'CJ_z}\, \mathfrak{D}(0,-\theta,-\phi)\, , \tag{49}$$

so

$$\mathfrak{s}^*_{l\omega}(S') = \sum_{M'M''M} (-)^{J-M} \begin{pmatrix} J & l & J \\ -M & \omega & M'' \end{pmatrix} \times \mathfrak{D}_{M''M'}^{(J)}\, e^{-iS'M'C}\, \mathfrak{D}^{+(J)}_{M'M}(2l+1)^{\frac{1}{2}} . \tag{50}$$

Using elementary properties of the Wigner matrices and letting

$$\xi_l(S') = \sum_{M'} (-)^{M'} e^{-iS'M'C} \begin{pmatrix} J & J & l \\ M' & -M' & 0 \end{pmatrix} \tag{51}$$

we obtain

$$\Pi_{FJAB} = \left\langle nv \int d\delta \left[\delta_{FA}\delta_{BI} + \sum_{S'_l S''} (-)^l (2l+1) \times \begin{Bmatrix} J & J & 1 \\ J & J & l \end{Bmatrix} \xi_l(S')\xi^*_l(S'')R_{FS'}R^+_{S'A}R_{BS''}R^+_{S''I} \right] \right\rangle .$$

The only indices that need be considered are those corresponding to transitions with non-vanishing dipole matrix elements. Since the dipole operator only connects states of different symmetry it follows that $A \neq B$ and $F \neq I$. Therefore the relaxation matrix will be

$$\Pi = \begin{bmatrix} \Pi_{+-+-} & \Pi_{+--+} \\ \Pi_{-++-} & \Pi_{-+-+} \end{bmatrix} . \tag{53}$$

The sums over S' and S'' are readily carried out and we find, after some algebraic manipulation,

$$\Pi = -2\sum_l{}' (-)^l (2l+1) \begin{Bmatrix} J & J & l \\ J & J & 1 \end{Bmatrix} \sum_{M'M''} \begin{pmatrix} J & J & l \\ J & J & 1 \end{pmatrix} \times \begin{pmatrix} J & J & l \\ M'' & -M'' & 0 \end{pmatrix} \left\langle nv \int d\sigma \sin^2 \tfrac{1}{2}(M'-M'')\, C \right\rangle . \tag{54}$$

The sums here extend only over even l terms when the indices are $+-+-$ or $-+-+$ and only over odd terms when they are $-++-$ or $+--+$.

Let us now return to the explicit evaluation of the dynamical vector $\vec{\mathfrak{C}}$ of Eq. (38). It is convenient to replace it with a dimensionless quantity $\vec{\mathfrak{D}}$ by writing

$$\vec{\mathfrak{C}} = \eta\vec{\mathfrak{D}} , \tag{55}$$

where $\eta = (\mu^2/\hbar v b^2) K/J(J+1)$, (56)

and $\vec{\mathfrak{D}} = vb^2 \int_{-\infty}^{\infty} dt[\hat{r}_2 - 3(\hat{r}\cdot\hat{r}_2)\hat{r}]/r^3$. (57)

For very small impact parameters, of course, one has to account for the repulsive core, but we argue that the cross section for such collisions is relatively small. Therefore the spherical components of D may be expressed as (assuming straight-line trajectories)

$$D_\sigma = -4\pi\sqrt{2} \sum_{\alpha\beta} (-)^\sigma \begin{pmatrix} 1 & 1 & 2 \\ -\sigma & \alpha & \beta \end{pmatrix} \int_{-\infty}^{\infty} du \left(\frac{1}{1+u^2}\right)^{\frac{3}{2}} \times \cos\omega_I bu/v\, \mathcal{Y}_{1\alpha}(\hat{r}_2)\mathcal{Y}_{2\beta}(\hat{r}) , \tag{58}$$

where ω_I is the inversion frequency. The axis $\hat{r}_2$ is actually the figure axis of the second molecule, which is a symmetric top. This precesses around the direction of its angular momentum with an angular speed

$$\omega_2 = J/I_1 . \tag{59}$$

Letting R represent the direction of the angular momentum with respect to some standard frame we can write

$$\mathcal{Y}_{1\alpha}(\hat{r}_2) = \sum\nolimits_\lambda \mathcal{Y}_{1\lambda}(\hat{r})\mathfrak{D}_{\lambda\alpha}{}^{(1)}(R) , \tag{60}$$

where $\hat{n} = \sin\theta_2 \cos\omega_2 t\, \hat{i}$

$$+ \sin\theta_2 \sin\omega_2 t\, \hat{j} + \cos\theta_2\, \hat{k} , \tag{61}$$

and $\cos\theta_2 = K_2/J_2$. (62)

We will assume that the angular average is to be performed at this stage. Again, this is necessary to make the problem tractable. This is tantamount to replacing D by its root-mean-square value, thus

$$\overline{D^2} = \frac{32\pi^2}{15} \sum_{\lambda\beta} \left| \int_{-\infty}^{\infty} du \left(\frac{1}{1+u^2}\right)^{\frac{3}{2}} \times \cos\omega_I bu/v)\mathcal{Y}_{1\lambda}(\hat{r})\mathcal{Y}_{2\beta}(\hat{r}) \right|^2 . \tag{63}$$

For most b values, ω_2 will be larger than the duration of the collision and the integral will be small, unless $\lambda = 0$. As before we will neglect ω_I and so

$$\overline{D^2} = \tfrac{8}{5}\pi\cos^2\theta_2 \textstyle\sum_\beta |\mathcal{Y}_{2\beta}(\tfrac{1}{2}\pi, 0)|^2$$
$$\times \left| \int du(1+u^2)^{-\frac{3}{2}} (\cos\theta + i\sin\theta)^\beta \right|^2 . \qquad (64)$$

Evaluation of this integral is quite trivial and finally

$$\Pi_{FIAB} = -\frac{\pi^2}{2}\frac{n\mu^2}{\hbar}\left(\frac{8}{3}\right)^{\frac{1}{2}} \cos\theta_2 \frac{k}{J(J+1)}$$
$$\times \sum_{l'} (2l+1) \begin{Bmatrix} J & J & l \\ J & J & 1 \end{Bmatrix} \sum_{M'M''} (-)^{M'+M''}$$
$$\times \begin{pmatrix} J & J & l \\ M' & -M' & 0 \end{pmatrix} \begin{pmatrix} J & J & l \\ M'' & -M'' & 0 \end{pmatrix} |M' - M''| . \qquad (65)$$

The term $\cos\theta_2$ must, of course, be averaged over the thermal distribution. In terms of the moments of inertia of the symmetric top,

$$\langle \cos\theta_2 \rangle = I_3^{1/2}/(I_1^{1/2} + I_3^{1/2}) . \qquad (66)$$

Referring back to Eq. (65) we see that the following quantity must be known

$$P = \sum_l{}' (2l+1) \begin{Bmatrix} J & J & l \\ J & J & 1 \end{Bmatrix} \sum_{M'M''} (-)^{M'+M''}$$
$$\times |M' - M''| \begin{pmatrix} J & J & l \\ M' & M' & 0 \end{pmatrix} \begin{pmatrix} J & J & l \\ M'' & -M'' & 0 \end{pmatrix} . \qquad (67)$$

A computer program was employed to evaluate it for the two cases where the sum runs over the even and odd l values respectively. The graphs turn out to be just straight lines. Let

$$\alpha = \Pi_{+-+-} = 2\pi c\bar{\alpha} , \qquad \beta = \Pi_{-++-} = 2\pi c\bar{\beta} . \qquad (68)$$

The dipole moment of ammonia is taken to be 1.468 Debye and the rotational constants are $A_1 = 6.309\ \text{cm}^{-1}$ and $A_2 = 9.941\ \text{cm}^{-1}$. The density n is converted to amagat density $\bar{\rho}$ for the sake of comparison to experimental data. Then we find the relaxation matrix elements

$$\begin{Bmatrix} \bar{\alpha} \\ \bar{\beta} \end{Bmatrix} = 1.30\bar{\rho}\frac{K}{J(J+1)} \begin{Bmatrix} -0.5047J + 0.1714 \\ +0.5047J + 0.4953 \end{Bmatrix} \text{cm}^{-1} . \qquad (69)$$

We notice that each J, K state has associated with it a unique relaxation matrix. This is a generalization of the Anderson result which specified only a linewidth for each state. It is also interesting to note that in the high-J limit $\bar{\alpha}$ and $\bar{\beta}$ become equal in magnitude but opposite in sign.

The final task is to evaluate the line shape for an individual inversion transition and then superimpose all possible absorption curves to obtain the band spectrum. Since the matrices are two dimensional, the algebraic operations are quite trivial. The reduced dipole matrix elements are

$$\mu_{+-} = \mu_{-+} = \mu K[(2J+1)/J(J+1)]^{1/2} . \qquad (70)$$

The population of the two states partaking in the inversion transition are roughly the same since they are only separated by a microwave frequency. Therefore the power spectrum function becomes

$$G = (\mu^2/\pi c)[(2J+1)K^2/J(J+1)]\rho_{JK}$$
$$\times \frac{2\bar{\alpha}\bar{f}^2 + (\bar{\beta} - \bar{\alpha})(\bar{f}^2 - f_0^2 + \bar{\beta}^2 - \bar{\alpha}^2)}{(\bar{f}^2 - \bar{f}_0^2 + \bar{\beta}^2 - \bar{\alpha}^2)^2 + 4\bar{\alpha}^2\bar{f}^2} . \qquad (71)$$

Here $\bar{f}$ is the frequency of the incident radiation and $\bar{f}_0$ is the resonant inversion frequency, both expressed in units of cm^{-1}.

The evaluation of the density matrix was discussed, essentially, when the average of $\cos\theta_2$ was evaluated. The frequencies of the lines can be found using an empirical formula given by Simmons and Gordy.[12] The temperature is taken to be 300°K. The superposition of the various line shapes was done on an IBM 360 computer. All levels from $(J,K) = (1,1)$ to $(17,17)$ were included in the calculation.

As mentioned earlier, we have not calculated the resonance contribution. This turns out to be relatively small, being only about 10% of the total effect, so the major effect is the one which we have considered. Since Anderson did, however, calculate the resonance contribution to the linewidth, we will augment $\bar{\alpha}$ by his result. This term is discussed by Townes and Schalow.[13]

A comparison of the theory with the experimental data of Bleany and Loubser is made in Figs. 1 to 6. The prediction of the Van Vleck-Weisskopf theory with Anderson's calculation of the linewidths accompanies each of these figures. Data of the ammonia compressibility were used to convert Amagat density to pressure. We see that at low pressures both theories are in good agreement with the data. This, of course, is what we would expect because the lines overlap relatively slightly at low pressure. It is just there that we showed how our theory reduced to Anderson's. At high pressures the deviation is quite striking, In Fig. 7 the theory is compared with the data of Nethercot *et al.* Again we see that the agreement of our theory with experiment is satisfactory whereas the Van Vleck-Weisskopf line-shape theory is not.

This work can easily be generalized to the case of foreign gas broadening. Experimental data in this realm are lacking, however.

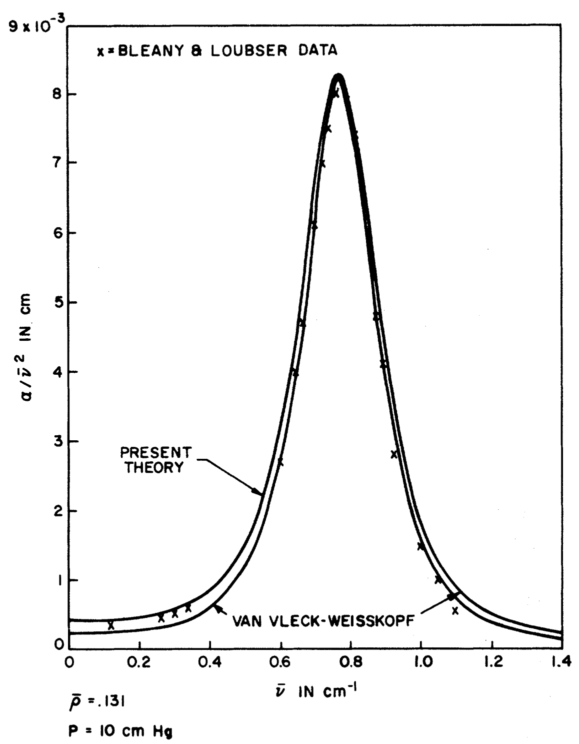

FIG. 1. Absorption coefficient of ammonia as a function of wave number at amagat density 0.131.

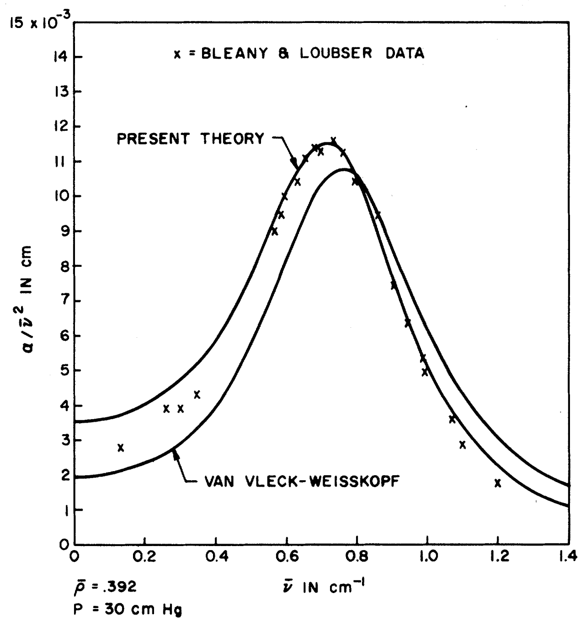

FIG. 2. Absorption coefficient of ammonia as a function of wave number at amagat density 0.392.

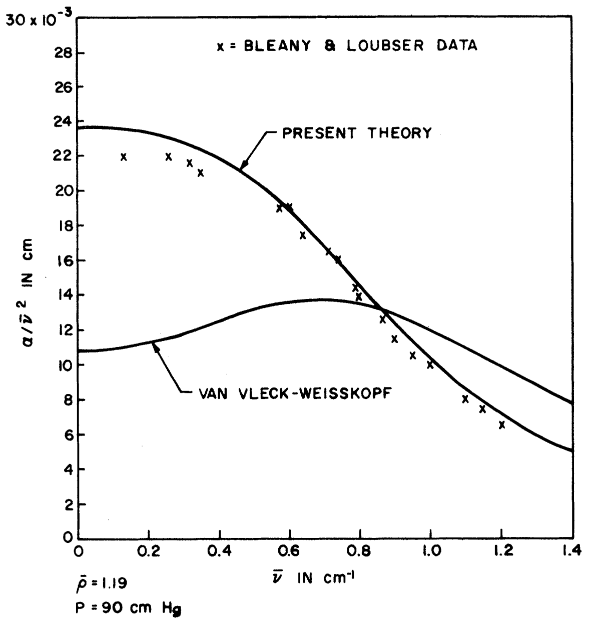

FIG. 3. Absorption coefficient of ammonia as a function of wave number at amagat density 1.19.

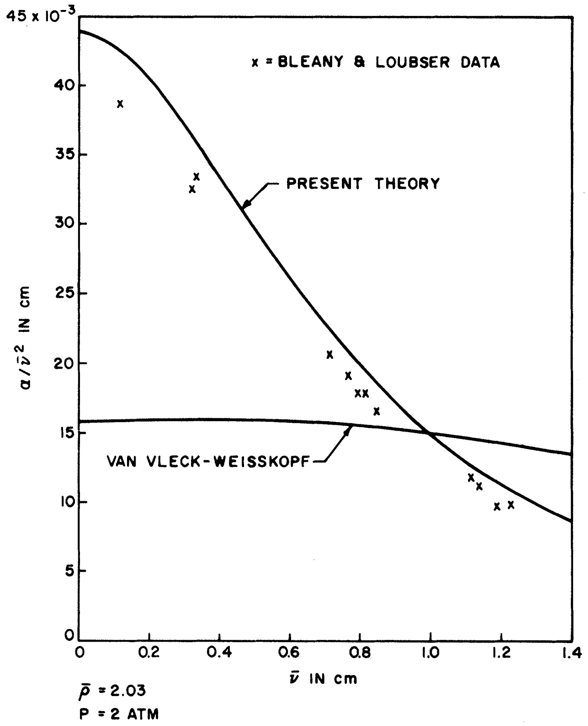

FIG. 4. Absorption coefficient of ammonia as a function of wave number at amagat density 2.03.

APPLICATION TO OXYGEN SPECTRUM

Van Vleck[14] gave the first theoretical discussion of the absorption spectrum of oxygen. He assumed that a superposition of Van Vleck-Weisskopf line shapes ought to provide an adequate description for the problem. Since oxygen can also absorb radiation nonresonantly, he included a term with zero resonant frequency.

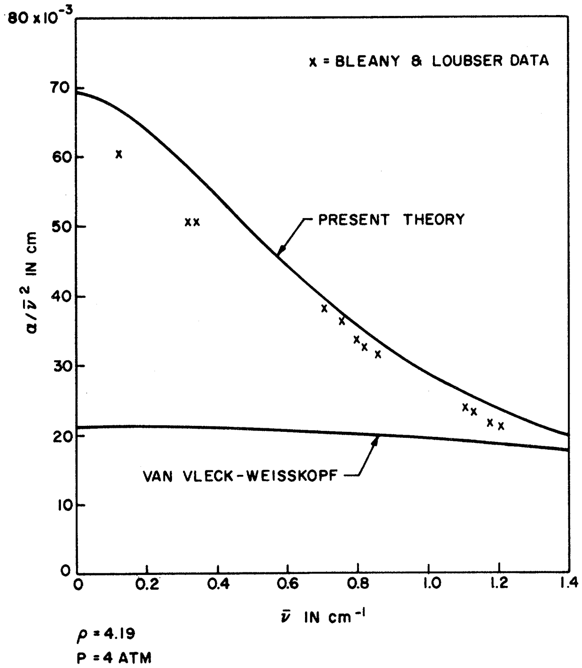

FIG. 5. Absorption coefficient of ammonia as a function of wave number at amagat density 4.19.

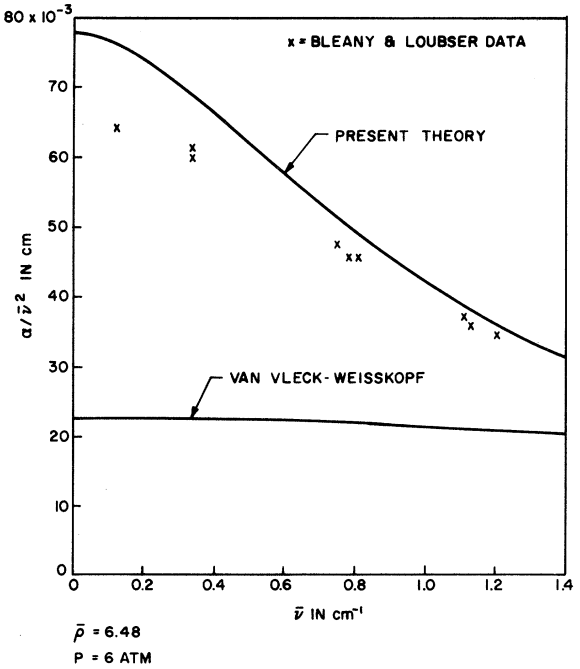

FIG. 6. Absorption coefficient of ammonia as a function of wave number at amagat density 6.48.

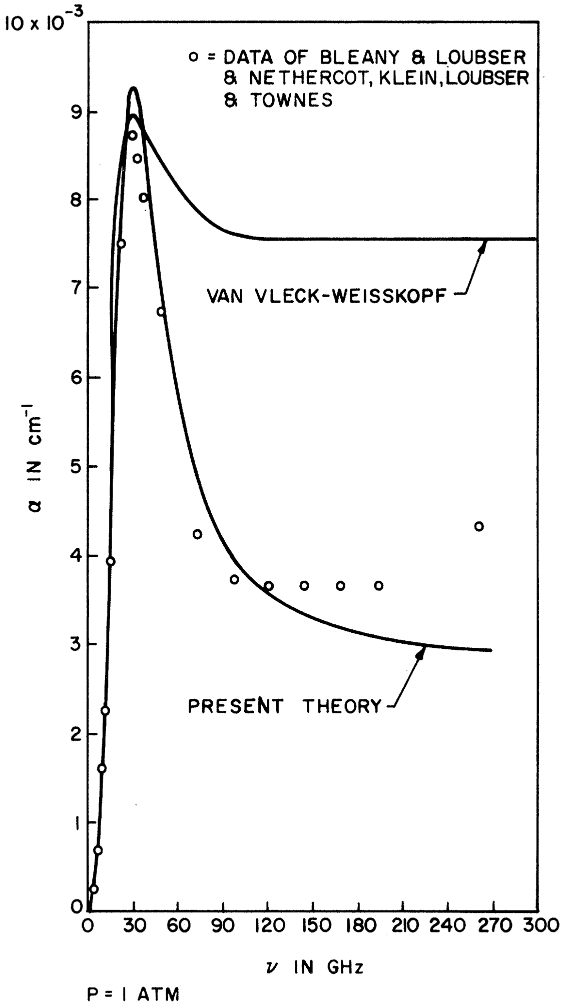

FIG. 7. Absorption coefficient of ammonia as a function of frequency at one atmosphere pressure.

There were two groups of experiments which were performed. The first group was concerned with measurements of absorptivity at moderate to high pressures.[15] The linewidth was chosen to be that value of τ_0 which gave the best agreement of the Van Vleck theory with experiment. The other set of experiments was performed at pressures which were low enough to enable the individual lines to be resolved.[16] These, of course, provided a direct measurement of the linewidth. Comparison of the linewidths per unit pressure seemed to indicate considerable discrepancy. The high-pressure results yielded a much smaller value than the corresponding low-pressure values. Birnbaum and Maryott tried to explain this by assuming that a pressure-dependent frequency shift was involved. Mizushima[17] thought that the collisions might be introducing some low-frequency resonance lines into the picture. These explanations were not, unfortunately, theoretically justified.

Gordon[18] suggested that the discrepancy might be due to an inadequacy of the Van Vleck-Weisskopf line shape itself. By constructing a semiclassical theory which permitted the interference of various transitions he was able to demonstrate that high-pressure absorption was not anomalous. Ben-Reuven and Lightman[19] have recently indicated how the oxygen spectrum can be understood within the framework of their theory. Both of these explanations, unfortunately, involved the fitting of one or more empirical values which were not directly related to the molecular interactions. In the following section we will show how one can go about calculating the high-pressure spectrum from first principles.

Zimmerer and Mizushima[16] have shown that the unperturbed Hamiltonian is almost diagonal in the representation $|NSJM\rangle$, where N is the end-over-end rotational angular momentum and S is the electronic spin.

The intermolecular interaction we will employ will only affect the end-over-end part of the motion and will not be coupled to the spin. Therefore the S matrix should be diagonal in the spin index. From the requirements of nuclear symmetry N is restricted to assuming odd values only. The frequencies associated with $\Delta N \neq 0$ transitions are rather high compared with the inverse duration of a collision so the S matrix for such transitions must be small. For example, the transition from the state $N=1$, $J=1$ to $N=3$, $J=2$ has an angular frequency of 2.3×10^{12} rad per second, as compared with the inverse duration which is roughly 2.5×10^{11} rad per second. The former quantity is around an order of magnitude greater than the latter. Therefore we will regard the S matrix as connecting states of different m_N only.

Since we have elected to stay with a given $2N+1$ dimensional basis we are permitted to expand the S matrix in terms of the irreducible matrices:

$$S = \sum_{\Omega\omega} \mathcal{S}^*_{\Omega\omega} J_{\Omega\omega}(\vec{\mathrm{N}}). \tag{72}$$

We must average over all orientations of the collision plane. This is accomplished through the use of the Wigner rotation matrices. We average over all Euler angles

$$\int \frac{d\Gamma}{8\pi^2} \langle f | DS^{-1}D^{-1} | a \rangle \langle b | DSD^{-1} | i \rangle = \sum_{\Omega\Omega'} \sum_{\substack{\omega\omega' \\ \mu\mu'}} \mathcal{S}^*_{l\omega} \mathcal{S}_{l'\omega'} \int \frac{d\Gamma}{8\pi^2} \mathfrak{D}_{\mu\omega}{}^{\Omega}(\Gamma) \mathfrak{D}_{\mu'\omega'}{}^{\Omega'*}(\Gamma) \langle f | J^+_{\Omega'\mu'} | a \rangle \langle b | J_{\Omega\mu} | i \rangle. \tag{73}$$

Employing the Wigner-Eckart theorem and the orthogonality relations we can carry out the degeneracy sums implicit in Eq. (15′) and obtain

$$\Pi_{FIAB} = \left\langle nv \int d\sigma \left[\delta_{FA}\delta_{BI} + \sum_{l\omega} \frac{(-)^{l+J_a+J_b}}{2l+1} \begin{Bmatrix} J_i & J_f & 1 \\ J_a & J_b & l \end{Bmatrix} \langle F \| J_l \| A \rangle \langle B \| J_l \| I \rangle | \mathcal{S}_{l\omega} |^2 \right] \right\rangle. \tag{74}$$

To proceed further it is convenient to switch to a representation where N and S are uncoupled, the relevant relation being

$$\langle NSJ' \| J_l \| NSJ \rangle = (-)^{N+S+J+l} (2J+1)^{\frac{1}{2}} (2J'+1)^{\frac{1}{2}} \begin{Bmatrix} N & J' & S \\ J & N & l \end{Bmatrix} \langle N \| J_l \| N \rangle . \tag{75}$$

Therefore the reduced relaxation matrix becomes

$$\Pi_{FIAB} = \left\langle nv \int d\sigma \left[\delta_{J_F J_A} \delta_{J_B J_I} + [(2J_I+1)(2J_F+1)(2J_A+1)(2J_B+1)]^{1/2} \right.\right.$$
$$\left.\left. \times (-)^{J_B+J_I} \sum_{l\omega} (-)^l | \mathcal{S}_{l\omega} |^2 \begin{Bmatrix} J_I & J_F & 1 \\ J_A & J_B & l \end{Bmatrix} \begin{Bmatrix} N & J_F & S \\ J_A & N & l \end{Bmatrix} \begin{Bmatrix} N & J_B & S \\ J_I & N & l \end{Bmatrix} \right] \right\rangle , \tag{76}$$

where $S=1$ for oxygen.

Artman and Gordon[16] attempted to calculate the oxygen linewidths on the basis of Anderson's theory. They considered four interactions which might contribute to the linewidth: the magnetic dipole potential, the molecular electric quadrupole potential, the London dispersion force, and the exchange interaction.

The first two of these were found to be negligible and only the exchange and dispersion forces contributed significantly. Such a potential can be cast into the form

$$V=f(R)+g(R)\sum_m \mathcal{Y}^*_{2m}(\hat{R})[\mathcal{Y}_{2m}(\hat{r}_1)+\mathcal{Y}_{2m}(\hat{r}_2)]\ , \tag{77}$$

where r_1 represents the orientation of the molecular axis relative to a space-fixed frame, and R is the intermolecular separation. The reason why no $\mathcal{Y}_{1m}$ terms appear is that the molecules are homonuclear.

Since we have decided to regard H_0 as being diagonal in N we can make the approximation

$$e^{-H_0 t}V(t)\,e^{iH_0 t}\approx V(t)\,, \tag{78}$$

so the S matrix will assume the simple form

$$S=e^{-i\Gamma'}\ , \tag{79}$$

where

$$\Gamma'=\int_{-\infty}^{\infty}dt\,f(R)+\sum_m\int_{-\infty}^{\infty}dt\,g(R)\mathcal{Y}^*_{2m}(R)[\mathcal{Y}_{2m}(\hat{r}_1)+\mathcal{Y}_{2m}(\hat{r}_2)]\ . \tag{80}$$

The first term does not couple states of different m_N so it simply multiplies the S matrix by a constant phase factor. The complex conjugate of this quantity factors out of S^{-1} so they just cancel each other. Therefore, effectively,

$$\Gamma=\sum_m\int_{-\infty}^{\infty}dt\,g(R)\mathcal{Y}^*_{2m}(\hat{R})[\mathcal{Y}_{2m}(\hat{r}_1)+\mathcal{Y}_{2m}(\hat{r}_2)]\ . \tag{81}$$

For the sake of simplicity we will again neglect the resonance contribution to the relaxation matrix. This approximation will not result in more than a 10% error. If we wanted to include the resonance effect we would have to expand the S matrix in a perturbation expansion. This, in turn, would require cut-off impact parameters to prevent the divergences which would occur for small impact parameters. Since this procedure is also somewhat approximate we feel that our approximation is not much worse.

We see that the S matrix is only influenced by the noncentral part of the potential. Thus we would expect the study of line shapes to provide valuable information about the ainsotropy of molecular forces.

Further reduction of Γ can be accomplished by replacing $\mathcal{Y}_{2m}(r)$ by an irreducible matrix. Then

$$\mathcal{Y}_{2m}(\hat{r})=\alpha_N J_{2m}(\vec{\mathrm{N}})\,. \tag{82}$$

The proportionality constant can be found by using the Wigner-Eckart theorem, i.e.,

$$\alpha_N=(-)^N\frac{(2N+1}{(4\pi)^{1/2}}\begin{pmatrix}N & N & 2\\ 0 & 0 & 0\end{pmatrix}=-\left(\frac{N(N+1)(2N+1)}{4\pi(2N-1)(2N+3)}\right)^{\frac{1}{2}}\ . \tag{83}$$

Combining Eqs. (81) and (82) yields

$$\Gamma=A_0J_{20}+A_2(J_{22}+J_{2-2})\,, \tag{84}$$

where we have let

$$A_0=-(5/16\pi)^{1/2}\alpha_N\int dt\,g(R)\,, \tag{85}$$

$$A_2=(15/32\pi)^{1/2}\alpha_N\int dt\,g(R)\cos 2\phi\,. \tag{86}$$

We must next specify the form of the potential $g(R)$. The long-range part of the dispersion force is known to vary as R^{-6} (except at extremely large distances as R^{-7}). The exchange interaction, on the other hand, is short ranged and is usually taken to vary exponentially. For computational ease we will assume a power-law potential, i.e.,

$$g(R)=C/R^q\ . \tag{87}$$

We will also assume that the trajectories are straight lines, as is conventionally done in pressure-broadening theory. These two approximations enable A_0 and A_2 to become a simple function of impact parameter and hence to obtain an analytic answer for the db integration. Thus

$$A_0 = \xi a_0 = \xi \left(\frac{5N(N+1)(2N+1)}{64\pi(2N-1)(2N+3)} \right)^{\frac{1}{2}} \frac{\Gamma(\frac{1}{2}(q-1))}{\Gamma(\frac{1}{2}q)} , \tag{88}$$

$$A_2 = \xi a_2 = -\xi \left(\frac{15N(N+1)(2N+1)}{128\pi(2N-1)(2N+3)} \right)^{\frac{1}{2}} \frac{q-2}{q} \frac{\Gamma(\frac{1}{2}(q-1))}{\Gamma(\frac{1}{2}q)} , \tag{89}$$

where we have let

$$\xi = C/vb^{q-1} . \tag{90}$$

The calculation of the S matrix has thus been reduced to the exponentiation of a $2N+1$ by $2N+1$ matrix. There are two ways of carrying this program out. The first consists of expanding the S matrix in a power series in ξ and considering each term separately. As mentioned before this leads to divergences. Anderson[4] proceeded in this manner in his theory of pressure broadening. Byron and Foley[8] have shown that such an approach can be circumvented. Their procedure involves the diagonalization of Γ directly. If one can find a unitary matrix which does this the exponentiation becomes a rather trivial matter. For their problem they were fortunate enough to find the matrix analytically. In the oxygen problem, however, such a matrix can only be found for the $N=1$ case. For the higher N states one must have recourse to numerical methods to find it. Let R represent this transformation. Then, if we factor ξ from the Γ matrix,

$$\xi \Lambda = \xi R \Gamma \tilde{R} . \tag{91}$$

This expression is then combined with Eqs. (72) and (79) to obtain an explicit value for $\mathcal{S}_{l\omega}$. Let us define the auxiliary quantity

$$\lambda_{m''}^{(l\omega)} = \sum_{mm'} R_{m''m} R_{m''m'} \langle Nm | J_{l\omega} | Nm' \rangle . \tag{92}$$

The reduced relaxation matrix may be expressed, after some tedious algebraic manipulations, as

$$\Pi_{FIAB} = -2[(2J_I+1)(2J_F+1)(2J_A+1)(2J_B+1)]^{1/2} (-)^{J_B+J_I} \sum_{l\omega} (-)^l$$
$$\times \begin{Bmatrix} J_I & J_F & 1 \\ J_A & J_B & l \end{Bmatrix} \begin{Bmatrix} N & J_F & 1 \\ J_A & N & l \end{Bmatrix} \begin{Bmatrix} N & J_B & 1 \\ J_I & N & l \end{Bmatrix} \sum_{a \neq b} \lambda_a \lambda_b \langle nv \int d\sigma \sin^2[\tfrac{1}{2}\xi(\Lambda_a - \Lambda_b)] \rangle . \tag{93}$$

We find

$$\int d\sigma \sin^2[\tfrac{1}{2}\xi(\Lambda_a - \Lambda_b)] = \frac{\pi^2}{2(q-1)} \frac{\csc[\pi/(q-1)]}{\Gamma((q+1)/(q-1))} \left[\frac{C|\Lambda_a - \Lambda_b|}{v} \right]^{2/(q-1)} . \tag{94}$$

The thermal averaging of the relative speeds may also be evaluated analytically. Thus, letting μ be the reduced mass and T the temperature,

$$\langle v(v)^{-2/(q-1)} \rangle = \Gamma((5q-7)/(2q-2))(2kt/\mu)^{\frac{1}{2}} (\mu/2kt)^{1/(q-1)} . \tag{95}$$

Therefore we can write the reduced relaxation matrix as

$$\Pi_{FIAB} = \mathcal{D} M_{FIAB} , \tag{96}$$

where $\mathcal{D}$ represents a "dynamical" factor

$$\mathcal{D} = n(2kt/\mu)^{\frac{1}{2}} (C^2\mu/2kt)^{1/(q-1)} , \tag{97}$$

and M_{FIAB} is a numerical matrix defined by

$$M_{FIAB}=-\frac{\pi^2}{q-1}\,\frac{\Gamma((5q-7)/(2q-2))}{\Gamma((q+1)/(q-1))}\,\frac{1}{\sin[\pi/(q-1)]}\sum_{l=0}^{2N}\sum_{\omega}\sum_{ab}(-)^{l}$$

$$\times[(2J_I+1)(2J_F+1)(2J_A+1)(2J_B+1)]^{1/2}(-)^{J_B+J_I}\lambda_a^{(l\omega)}\lambda_b^{(l\omega)}$$

$$\times\begin{Bmatrix} J_I & J_F & 1\\ J_A & J_B & l\end{Bmatrix}\begin{Bmatrix} N & J_F & 1\\ J_A & N & l\end{Bmatrix}\begin{Bmatrix} N & J_B & 1\\ J_I & N & l\end{Bmatrix}(\Lambda_a-\Lambda_b)^{2/(q-1)}\ . \tag{98}$$

The selection rules permit only the following values of J_F and J_I for a given value of N:

$J_F=N+1,\ N+1,\ N,\ N,\ N-1,\ N-1;$

$J_I=N+1,\ N,\ N+1,\ N,\ N-1,\ N,\ N-1.$

Thus we see that the M matrix will be a seven-dimensional array.

The reduced matrix elements of the magnetic dipole can easily be evaluated. The dipole operator is given by

$$\vec{\mu}=-2\mu_0\vec{S}, \tag{99}$$

where μ_0 is the Bohr magneton and $\vec{S}$ is the electronic spin. The factor 2 arises from the g factor for the electron. Its matrix elements are simply

$$\langle J_F\|\mu\|J_I\rangle=2\mu_0 6^{1/2}(-)^{J_F}[(2J_I+1)(2J_F+1)]^{\frac{1}{2}}\begin{Bmatrix} 1 & J_F & N\\ J_I & 1 & 1\end{Bmatrix}\ . \tag{100}$$

The density matrix for oxygen is also given by a rather simple expression. The nuclei are Bose particles so the nuclear weighting factor is

$$g=0,\quad \text{for } N \text{ even};\quad g=1,\quad \text{for } N \text{ odd}. \tag{101}$$

Each rotational level is split into three fine-structure levels so the partition function may be expressed as

$$Q=\sum_{N\text{ odd}}3(2N+1)e^{-\beta E_N}\ , \tag{102}$$

and the density matrix becomes

$$\rho_N=Q^{-1}e^{-\beta E_N},\quad \text{for } N \text{ odd};\quad \rho_N=0,\quad \text{for } N \text{ even}. \tag{103}$$

In evaluating the energy E_N we neglect the fine-structure splitting and use just the energy for a rigid rotor. The rotational constant is $B_0=43\,102$ MHz and the temperature is taken to be 300°K.

The frequencies for the various fine-structure transitions have been tabulated by Kisliuk and Townes.[20] Thus all the elements necessary for the calculation of the oxygen spectrum have been assembled. The actual computation of the M matrix has been done using an IBM 360 computer. The Λ and R matrices were evaluated using the Jacobi method of diagonalization for the cases $N=1,\ 3,\ 5,\ 7,\ 9,\ 11$, and 13. The values of M for $N=15$ through 25 were obtained by extrapolating the low N results.

From Eq. (24) we obtain an expression for the absorptive part of the dielectric coefficient

$$\epsilon''=-(2\pi\omega n/3kt)\,\mathrm{Im}\,\mathrm{Tr}\{\rho\mu[(\omega_0+\omega+i\pi)^{-1}+(\omega_0-\omega+i\pi)^{-1}]\}\ , \tag{104}$$

where n is the number of molecules per unit volume. We can formally expand the denominators to obtain

$$\mathrm{Im}\,\frac{1}{\omega_0\pm\omega+i\pi}=\mathrm{Im}\,\frac{1}{\omega_0\pm\omega}\,\frac{1}{1+i\pi(\omega_0\pm\omega)^{-1}}=\frac{1}{\omega_0\pm\omega}\,\mathrm{Im}\sum_{n=0}^{\infty}(-)^n(i)^n\left(\pi\frac{1}{\omega_0\pm\omega}\right)^n. \tag{105}$$

The imaginary part of this expression can now easily be extracted. Let

$$Q_{\pm} = [\Pi \cdot I/(\omega_0 \pm \omega)]^2 \quad . \tag{106}$$

Then we may rewrite the sum as a single fraction

$$\epsilon'' = \frac{2\pi\omega n}{3kt} \operatorname{Tr}\left[\rho\mu\left(\frac{1}{\omega_0+\omega}\,\Pi\frac{1}{\omega_0+\omega}\,\frac{1}{1+Q_+} + \frac{1}{\omega_0-\omega}\,\Pi\frac{1}{\omega_0-\omega}\,\frac{1}{1+Q}\right)\mu\right] \; . \tag{107}$$

All the quantities appearing in this expression are now real numbers.

The actual matrix inversion was accomplished numerically using the Gauss-Jordon reduction procedure. The band spectrum was assembled from the rotational fine-structure components for $N=1$ through $N=25$.

We have assumed that $q=6$, in other words, that the dispersion forces are chiefly responsible for line broadening. We still have no idea what the size of the coefficient C appearing in Eq. (87) is. We can adjust C to obtain the best fit of the experimental data, however. The widths measured by various researchers are, unfortunately, not in full agreement with one another. The experimental situation has been summarized by Kaufman.[15] Anderson, Smith, and Gordy[16] found a width of 1.71 MHz per mm Hg for the 3^+ transition. We shall use this value to evaluate the factor $\mathfrak{D}$. At low pressures we have seen that the diagonal elements of Π are to be identified with the linewidths. Therefore, from Eq. (131) we obtain

$$\Delta\omega/P = 2\pi(\Delta\nu/P) = (\mathfrak{D}/P)M_{\mathrm{diag}} \, . \tag{108}$$

For the transition 3^+ we find $M = 0.604$, so

$$\mathfrak{D}/P = 17.77 \text{ MHz/mm Hg} \, . \tag{109}$$

Kaufman has investigated the variation of ϵ'' with amagat density at a frequency of 9260 MHz. Pressures can be converted to amagat units using the tables of Hilsenrath *et al.*[21] In Fig. 8 we compare Kaufman's data with the prediction of the present theory. We notice that the agreement is quite good at low pressures but becomes worse at higher pressures. The Van Vleck-Weisskopf theory, however, has difficulty explaining even the low-pressure data. It also predicts a peak in the absorption curve which is simply not observed.

Comparison has also been made with the data of Birnbaum and Maryott[15] in Figs. 9–11. Although the theoretical curves seem to follow the same trends as the experimental points, the numerical agreement is not too good here. This probably reflects the omission of the resonance contributions to the line shape.

In order to obtain an accurate theory for oxygen one would have to relax some of the assumptions made here. Firstly, a more realistic potential should be employed which takes into account the short-ranged overlap and exchange effects. This would require one more degree of numerical complication, however, because the computation would then involve an integration over impact parameters. Secondly, we should attempt to use more realistic trajectories. Finally, we could include the resonance effects. Again these refinements would entail quite a bit of additional labor.

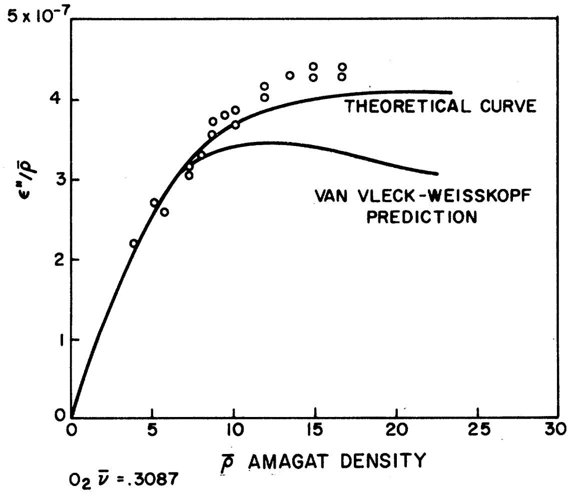

FIG. 8. Absorptive part of dielectric constant of oxygen as a function of amagat density at 0.3087 wave numbers.

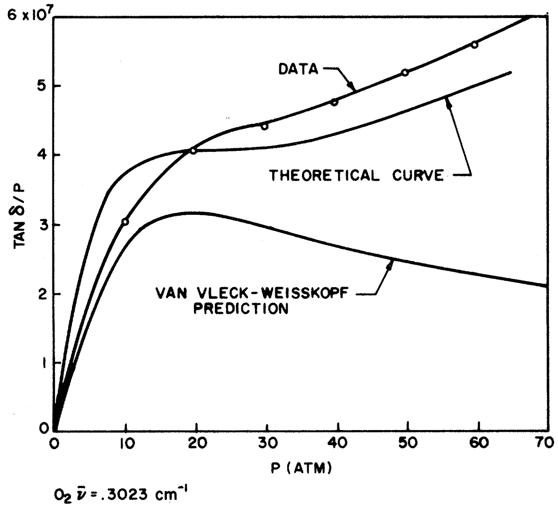

FIG. 9. Absorptive part of dielectric constant of oxygen as a function of pressure at 0.3023 wave numbers.

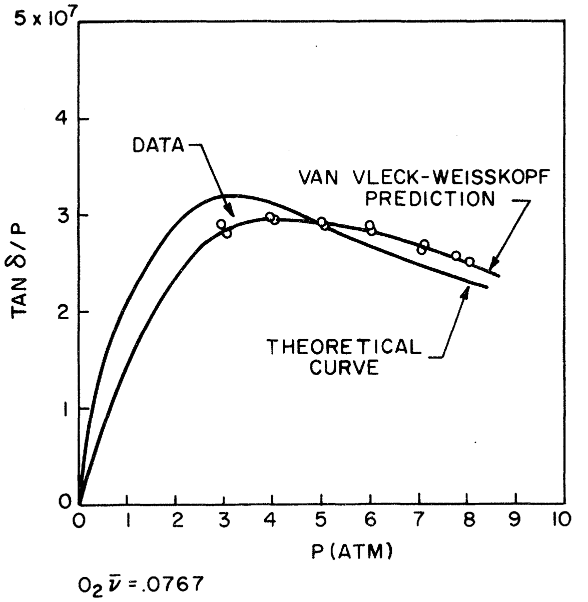

FIG. 10. Absorptive part of dielectric constant of oxygen as a function of pressure at 0.0767 wave numbers.

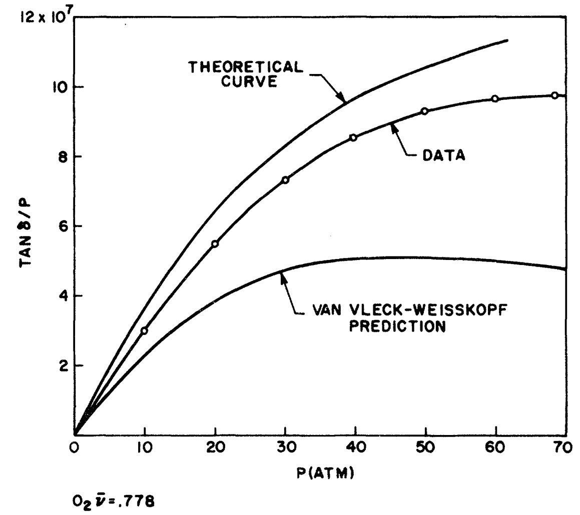

FIG. 11. Absorptive part of dielectric constant of oxygen as a function of pressure at 0.778 wave numbers.

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[†] Present address: Office of Naval Research, London, England.

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