

structure separations²⁵:

$$\begin{aligned}\Delta E_{1,2} &= E(J=1) - E(J=2) = 7.15 \text{ kMc/sec}, \\ \Delta E_{1,0} &= E(J=1) - E(J=0) = 5.20 \text{ kMc/sec},\end{aligned}$$

we can calculate all the first-order $g_F^{(1)}$'s and the second-order $E^{(2)}$'s of the $N=1$ rotational level from Eqs. (3.9) and (3.10). The numerical values of $g_F^{(1)}$ and $g_F (= g_F^{(0)} + g_F^{(1)})$ thus calculated are shown in Table I. The signs and the orders of magnitude of $g_F^{(1)}$'s are in agreement with the preliminary experimental values of Lichten and Brooks.^{3,9} However, the absolute values of the calculated $g_F^{(1)}$'s are about a factor of 2 too large in almost all cases. This indicates that the first-order $g_F^{(1)}$'s do account for the discrepancies between $g_F^{(0)}$'s

²⁵ The fine-structure separations used here are the preliminary experimental results of Lichten and Brooks. One can also obtain a set of theoretical energy separations from Ref. 6. They are $\Delta E_{1,2} = 6.54 \text{ kMc/sec}$, $\Delta E_{0,1} = 4.10 \text{ kMc/sec}$. In view of the simple wave function used in Ref. 6, we use the experimental values here to calculate the $g_F^{(1)}$'s.

and the observed g_F 's, but that the hyperfine-structure coupling constants calculated here from a single configuration wave function of the $c^3\pi_u$ are somewhat crude. Since all the operators involved in calculating the coupling constants are one-electron operators, a set of much improved coupling constants can be calculated easily when an accurate electronic wave function for the $c^3\pi_u$ state is available. As mentioned in the last section, these coupling constants can also be determined from the experimental results when they are accurately measured.

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Impact Broadening of Microwave Spectra

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Pressure broadening in resonant and in nonresonant microwave spectra of gases, as well as the transition from resonant to nonresonant shape with increasing pressure, are treated in the impact approximation in a unified manner, based on the theories of Baranger, Kolb and Griem, and Fano. The relaxation rate in nonresonant absorption (Debye relaxation) is expressed in terms of collision cross sections; small deviations from a Debye shape are related to a second moment of the relaxation matrix, with illustrative application to CH_3Cl . A new formula is derived for the shape of resonance lines, as a function of frequency and pressure, which takes into account the special effect of collision-induced transitions between the upper and the lower levels of the line; this formula reproduces the shape of the inversion spectra of NH_3 and of ND_3 .

1. INTRODUCTION

LINES in the microwave spectra of gases may attain pressure widths comparable to their resonance frequencies at rather low pressures (of no more than several atmospheres). Consequently the study of pressure broadening of microwave spectra is distinguished from similar studies in the infrared or higher frequency regions in the following ways:

(a) The shape of the spectrum may be studied at pressures that are sufficiently low to allow certain simplifying assumptions (like the assumption of *binary collisions*, and the commonly used impact approximation), but at the same time high enough to make the *overlapping and merging* of distinct resonance lines the rule,

rather than the exception. It is therefore necessary to use a theory that takes such phenomena into account.

(b) Whenever the width is comparable to the resonance frequency, a significant contribution to the spectrum is attributed to so-called *negative resonance* terms. Such terms can be related to photon absorption in transitions from an upper to a lower energy level of the gas molecule. Since, under conditions of pressure broadening, the absorption of a photon may be attributed to a single molecule only for a limited time (of the order of the inverse line width), such violations of energy conservation are allowed by the uncertainty principle. Though the necessity to include these additional transitions has long been recognized,¹ the proper way to do so has been overlooked, resulting in spectacular disagreements between experiments and

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¹ See, e.g., (a) R. de L. Kronig, *Physica* **5**, 65 (1938); (b) J. H. Van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945); (c) H. Fröhlich, *Nature* **157**, 478 (1946).

existing theories, particularly in the case of the ammonia inversion spectrum.^{2,3}

(c) Absorption of microwave radiation may also result from transitions of zero-resonance frequency, i.e., it may be associated with matrix elements of a multipole operator connecting two degenerate (or even identical) states of the molecule.⁴ By a proper unitary transformation, the multipole operator may be always diagonalized in the subspace of the degenerate states. Pressure broadening may then be ascribed to temporal fluctuations in the expectation values of the multipole (Debye or orientational relaxation).

This article strives to incorporate these various situations into the unifying scheme of pressure broadening theory, under the conditions of the impact approximation. The first consistent treatments of a group of overlapping lines, in the impact approximation, were made by Baranger⁵ and by Kolb and Griem.⁶ Their results were later rederived as a particular case of a more general theory by Fano.⁷ In this theory the shape of the spectrum is simply related to a set of parameters which constitute a relaxation matrix. Its elements describe the shift and width of individual lines, as well as the interference of overlapping lines. In the impact approximation the relaxation matrix is independent of the frequency, and proportional to the gas density. The line shape becomes then a simple function of these two variables.

The various relaxation parameters may be related to elementary scattering processes, following Baranger and Fano. Relevant expressions in terms of the collisional transition (i) matrix are given here, with particular attention to angular-momentum states and the simplifications afforded by rotational invariance.⁸ No attempt is made at any quantitative evaluation of the relaxation parameters. Even under vastly simplifying assumptions, such evaluations encounter formidable difficulties, enhanced by our too scarce knowledge of intermolecular forces.⁹ However, formal expressions in terms of scattering amplitudes suffice to provide some insight on the origin and relative importance of the various relaxation parameters. Following an adaptation of the general theory in Sec. 2, the nonresonant spectra of symmetric-top molecules are discussed as an example of a band of overlapping lines (Sec. 3). An expression is derived for the Debye relaxation rate in terms of cross sections for elastic and inelastic collisions. The problem of "positive" and "negative"

resonance terms and their manner of relaxation, with particular reference to the ammonia inversion spectrum, is dealt with in Sec. 4. The solution to this problem has been outlined in a preliminary publication.¹⁰ A discussion of the potentialities and limitations of the impact-approximation approach closes the article (Sec. 5).

Throughout this article, two types of *transitions* are referred to. Spectral transitions, caused by the interaction with photons, will be distinguished by assigning different letters, or subscripts, to the two levels associated with each transition (e.g., $i \rightarrow f$, or $\alpha_i \rightarrow \alpha_f$). Collisional transitions, caused by the interactions between molecules, will be distinguished by primes (e.g., $i \rightarrow i'$).

2. THE GENERAL THEORY

A. The Impact Approximation

It is the aim of pressure-broadening theories to describe the absorption (or emission) of a photon in a gas sample in terms of a process involving a single molecule (or a small group of molecules, when collision-induced spectra are studied). Such an absorbing molecule (the "system of interest" in Fano's terminology⁷) is not a conservative system. By collisions with other molecules the photon absorbed is eventually dissipated to other degrees of freedom of the gas (the "thermal bath"), with a resulting broadening and shifting of the single molecule's resonance frequencies. Mathematically, this is expressed by adding a non-Hermitian (or complex) perturbation to the resonance frequencies of the system.^{5,7} A perturbed frequency has then an imaginary part, the exponential damping rate.

The perturbation is, in general, a complicated function of the gas density and of the photon frequency. However, the discussion throughout this article is limited to the impact approximation,⁵ in which we assume that (a) collisions are binary, hence the resulting perturbation is proportional to the gas density, and that (b) the duration of the transient effects of collisions is negligibly short, hence the perturbation is independent of frequency over a wide range.

The transient effects exist only during the short period in which the molecular wave function varies with the time (in the interaction picture). This period is inversely proportional to the range of frequencies over which the perturbation varies significantly. Hence the range over which the impact approximation is valid is an intrinsic property of the binary collision system, and does not depend on extrinsic quantities like pressure. In studying a particular "line" in the spectrum it is preferable to make this range much wider than the pressure-dependent width of the line. Only in this indirect sense is the validity of the impact approximation limited by pressure [in so far as the usually less

² B. Bleaney and J. H. N. Loubser, Proc. Roy. Soc. (London) **A63**, 483 (1950).

³ G. Birnbaum and A. A. Maryott, Phys. Rev. **92**, 270 (1953).

⁴ See, e.g., (a) J. H. Van Vleck, Phys. Rev. **71**, 413 (1947); (b) J. E. Walter and W. D. Hersberger, J. Appl. Phys. **17**, 814 (1946); (c) G. Birnbaum, J. Chem. Phys. **27**, 360 (1957).

⁵ M. Baranger, Phys. Rev. **111**, 481 (1958); **111**, 494 (1958); **112**, 855 (1958).

⁶ A. C. Kolb and H. Griem, Phys. Rev. **111**, 514 (1958).

⁷ U. Fano, Phys. Rev. **131**, 259 (1963).

⁸ A. Ben-Reuven, Phys. Rev. **141**, 34 (1966).

⁹ See, e.g., G. Birnbaum (to be published).

¹⁰ A. Ben-Reuven, Phys. Rev. Letters **14**, 349 (1965).

severe requirement (a) of binary collisions is satisfied]. In typical cases, involving simple molecules at room temperature, the impact approximation is valid through a range of several wave numbers, and is therefore generally applicable to microwave spectra in the centimeter region even at pressures where their broadening is comparable to the frequency. One should, however, refrain from using pressure-broadening parameters determined near the peak of the line in analyzing the microwave tail¹ of a far infrared line.

B. The Line-Shape Expression

Pressure broadening of a spectral line is a property of the spectral transition between two energy levels which a molecule undergoes in absorbing (or emitting) a photon. It should not be split up into terms associated with the two levels separately. In other words, it is associated with the time evolution of the multipole operator responsible for the transition, rather than the time evolution of wave functions. Time evolution of operators is governed by the *Liouville operator* \mathbf{L} :

$$dX/dt = i[HX - XH] = i\mathbf{L}X, \quad (1)$$

where H is the Hamiltonian which governs the time evolution of wave vectors.¹¹ The Liouville operator operates on ordinary quantum-mechanical operators; i.e., it is an operator in a Hilbert space whose vectors are ordinary operators.¹² Let $|a\rangle$ and $|b\rangle$ be two eigenvectors of H . Then the operator¹³

$$|a\rangle\langle b| = |ab^+\rangle = \langle\langle ba^+|, \quad (2)$$

to use a notation suggested by Baranger,⁵ is a basis vector in the Hilbert space of operators, also called Liouville space. The Liouville-space vector (2) is an eigenvector of \mathbf{L} with the eigenvalue

$$\omega_{ab} = E_a - E_b. \quad (3)$$

In pressure-broadening proper, where all other broadening effects are neglected, the whole gas sample can be treated in the limit of weak radiation fields as a closed conservative system in thermal equilibrium. The absorption coefficient $\alpha(\omega)$ for electric (magnetic) dipole radiation of angular frequency ω , is given by

$$\alpha(\omega) = (\omega/c)\epsilon''(\omega). \quad (4)$$

Where ϵ'' is the imaginary part of the complex permittivity (permeability) of the gas, $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, given for a conservative system by¹⁴

$$\epsilon(0) - \epsilon(\omega) = \frac{4\pi\omega}{\hbar\mathcal{V}} \sum_{IF} \frac{\rho_F - \rho_I}{\omega_{IF}} |\langle I | \mathfrak{M}_z | F \rangle|^2 R^+(\omega - \omega_{IF}). \quad (5)$$

¹¹ The same units (radians per second) are used here for energies and frequencies.

¹² U. Fano, *Rev. Mod. Phys.* **29**, 74 (1957).

¹³ This is the operator whose matrix representation has unity at the intersection of the a th row and b th column and zeros everywhere else.

¹⁴ See, e.g., R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954). For the use of resolvents see U. Fano, *Ref. 7*.

The resolvent

$$R^+(\omega - \omega_{IF}) \equiv \lim_{\epsilon \rightarrow 0} [\omega - \omega_{IF} + i\epsilon]^{-1} = P[1/(\omega - \omega_{IF})] - i\pi\delta(\omega - \omega_{IF}) \quad (6)$$

has a real part (the Cauchy principal value denoted by P) and an imaginary part (the Dirac δ function). In (5), \mathfrak{M}_z is the projection of the electric (magnetic) dipole moment of the gas in the direction of the electric (magnetic) field of the photon; \mathcal{V} is the sample's volume; I, F , etc., are its eigenstates, and $\omega_{IF} = E_I - E_F$, etc., are the corresponding energy differences; ρ is the (normalized) density operator of the sample.

In the summation over I and F , only those terms with $\omega_{IF} = \omega$ contribute significantly to (5), particularly to its imaginary part. We may therefore substitute¹⁵

$$\frac{\rho_F - \rho_I}{\omega_{IF}} \approx \frac{e^{\hbar\omega/k_B T} - 1}{\omega} \rho_I, \quad (7)$$

where k_B is the Boltzmann constant, assuming the gas is in thermal equilibrium (weak radiation fields).

As ω_{IF} is an eigenvalue of the Liouville operator for the sample, Eq. (5) can be rewritten, using (7), as

$$\epsilon(0) - \epsilon(\omega) = (4\pi/\hbar\mathcal{V})(e^{\hbar\omega/k_B T} - 1) \times \text{Tr}[\mathfrak{M}_z R^+(\omega - \mathbf{L})(\rho \mathfrak{M}_z)], \quad (5a)$$

where \mathfrak{M}_z and $(\rho \mathfrak{M}_z)$ are vectors, $R^+(\omega - \mathbf{L})$ is a matrix, and the trace is a scalar product, in the Liouville-space formalism.

The reduction of the resolvent in (5a) to an operator in the space of a single elementary "system" (i.e., an absorbing molecule), by summing over all other degrees of freedom, has been formally accomplished by Fano.⁷ Assume that the density operator ρ can be decomposed into the two uncorrelated factors,

$$\rho \approx \rho^{(s)} \times \rho^{(b)}, \quad (8)$$

the first representing the particular system, and the second the rest of the gas (the "bath"). Then (5) becomes

$$\epsilon(0) - \epsilon(\omega) = (4\pi n_1/\hbar)(e^{\hbar\omega/k_B T} - 1) \times \text{Tr}^{(s)} \left\{ \mu_z \frac{1}{\omega - \mathbf{L}^{(s)} - \langle \mathbf{M}_c(\omega) \rangle} \rho^{(s)} \mu_z \right\}, \quad (9)$$

where the trace now is over the degrees of freedom of a single system, with unperturbed Liouville operator $\mathbf{L}^{(s)}$, density matrix $\rho^{(s)}$, and dipole moment $\boldsymbol{\mu}$. n_1 is the number of such (identical) systems in a unit volume of the sample (i.e., the molecular density of the absorbing gas).

The effect of the interaction with the thermal bath is represented by the so-called relaxation matrix⁷ $\langle \mathbf{M}_c(\omega) \rangle$, which adds as a perturbation to the matrix

¹⁵ In our notation, I stands for the upper level and F for the lower.

$\mathbf{L}^{(s)}$ of unperturbed resonance frequencies of the system. In case the impact approximation is valid through all frequencies from zero to the highest frequency at which measurements are carried out, we may substitute

$$\langle \mathbf{M}_c(\omega) \rangle \approx n_2 \langle \mathbf{m}(0) \rangle \equiv \Lambda, \quad (10)$$

where n_2 is the density of the bath molecules (not necessarily identical with n_1 , as in foreign-gas broadening), and $\mathbf{m}(\omega)$ is a binary-collision transition operator in Liouville space, defined by Fano.⁷ Λ is not Hermitian and can be expressed in terms of two Hermitian operators in Liouville space, Δ and Γ :

$$\Lambda = \Delta - i\Gamma. \quad (11)$$

Both Δ and Γ are proportional to the gas density (n_2) and independent of the frequency. The first (Hermitian) term of (11) has real eigenvalues, and therefore represents pressure shifts, while the second (anti-Hermitian) term has imaginary eigenvalues, and therefore represents damping. Where Λ is a diagonal matrix, the trace in (9) is composed of Lorentz terms

$$\rho_i |\langle i | \mu_z | f \rangle|^2 (\omega - \omega_{if} - \delta_{if} + i\gamma_{if})^{-1}, \quad (12)$$

where δ_{if} and γ_{if} are the matrix elements of Δ and Γ , respectively, for the line $i \rightarrow f$. The relaxation matrix is not diagonal, in general, and its off-diagonal elements yield an interference of overlapping lines, which results in deviations from the Lorentz-shaped terms (12).⁵

C. The Relaxation Matrix

The relaxation matrix Λ may be expressed in terms of transition amplitudes for binary molecular collisions, as demonstrated by Baranger and by Fano. Let the Hamiltonian for the pair of system (s) and bath (b) molecules by

$$H = H_s + H_b + V = H_0 + V, \quad (13)$$

where V is their interaction. A transition matrix t in wave-vector space, obeying the Lippmann-Schwinger equation

$$t(E) = V + V \frac{1}{E - H_0 + i\epsilon} t(E), \quad (\epsilon \rightarrow +0), \quad (14)$$

may be used to construct a transition matrix $\mathbf{m}(\omega)$ in Liouville space [Eq. (55) of Ref. 7]. The only terms to be considered in the impact approximation are^{5,7}

$$\begin{aligned} \langle \langle I'F'^+ | \mathbf{m}(\omega) | IF^+ \rangle \rangle &= \delta_{I'I'} \delta_{F'F'} [\langle I | t(E_{F'} + \omega) | I \rangle \\ &- \langle F | t(E_I - \omega) | F \rangle^*] + \pi i [\delta(E_{I'} - \omega - E_F) \\ &\times \langle I' | t(E_{I'}) | I \rangle \langle F' | t(E_{F'}) | F \rangle^* \\ &+ \delta(E_{F'} + \omega - E_I) \langle I' | t(E_I) | I \rangle \langle F' | t(E_{F'}) | F \rangle^*], \quad (15) \end{aligned}$$

where $|I\rangle$, $|F\rangle$, etc., are now eigenvectors of the pair, with E_I , E_F , etc., the respective eigenvalues of H_0 . In the microwave case where the relaxation matrix is in-

dependent of ω , we may write

$$\begin{aligned} \langle \langle I'F'^+ | \mathbf{m}(\omega) | IF^+ \rangle \rangle &\approx \delta_{I'I'} \delta_{F'F'} [\langle I | t(E) | I \rangle \\ &- \langle F | t(E) | F \rangle^*] + 2\pi i \delta(E' - E) \\ &\times \langle I' | t(E) | I \rangle \langle F' | t(E) | F \rangle^*, \quad (15a) \end{aligned}$$

with $t(E)$ evaluated at an energy $E \approx E_I \approx E_F$.

The operator Λ in the system subspace in Liouville space is obtained by an averaging over bath variables [Eq. (17) of Ref. 7],

$$\Lambda = n_2 \text{Tr}^{(b)} [\mathbf{m}(\omega) \rho^{(b)}] = n_2 \langle \langle 1^{(b)} | \mathbf{m}(\omega) | \rho^{(b)} \rangle \rangle. \quad (16)$$

Here $1^{(b)}$ is the unit operator in the bath subspace, i.e.,

$$|1^{(b)}\rangle \equiv \sum_b |b\rangle \langle b|,$$

summed over the complete Hilbert space of the bath molecule (including its translatory motion). So with $|i\rangle$, $|f\rangle$, etc., as eigenvectors of the system molecule,

$$\begin{aligned} \langle \langle i'f'^+ | \Lambda | if^+ \rangle \rangle &= n_2 \sum_b \rho_b \{ [\langle ib | t | ib \rangle - \langle fb | t | fb \rangle^*] \delta_{i'i'} \delta_{f'f'} \\ &+ 2\pi i \sum_{b'} \delta(E' - E) \langle i'b' | t | ib \rangle \langle f'b' | t | fb \rangle^* \}, \quad (17) \end{aligned}$$

with the summation over b' (which is, in part, an integration over quantum numbers with a continuous spectrum, such as describe the translatory motion), restricted by the Dirac δ function.

D. Rotational Invariance

The relaxation matrix Λ is considerably simplified by rotational invariance.⁸ For a given pair of sets of *principal* quantum numbers i , f , there are $(2j_i + 1) \times (2j_f + 1)$ -degenerate vectors in Liouville space,

$$| \alpha_i j_i m_i (\alpha_f j_f m_f)^+ \rangle = | \alpha_i j_i m_i \langle \alpha_f j_f m_f | \rangle, \quad (18)$$

where j_i is the total angular momentum number of the level i , and m_i the magnetic number which describes the projection of the angular momentum along a fixed axis in space; α_i stands for all other quantum numbers of level i . However, by the transformation [Eq. (7) of Ref. 8]

$$\begin{aligned} | \alpha_i j_i (\alpha_f j_f)^+; KQ \rangle &= \sum_{m_i m_f} (-1)^{j_f - m_f} \\ &\times C(j_i j_f K; m_i - m_f Q) | \alpha_i m_i j_i (\alpha_f j_f m_f)^+ \rangle, \quad (19) \end{aligned}$$

where C is a Clebsch-Gordan coefficient,¹⁶ the relaxation matrix is reduced, since it is diagonal in K and Q , and independent of Q .⁸ It may be written as

$$\begin{aligned} \langle \langle i'f'^+; K'Q' | \Lambda | if^+; KQ \rangle \rangle \\ = \langle \langle i'f'^+ | \Lambda^{(K)} | if^+ \rangle \rangle \delta_{KK'} \delta_{QQ'} \quad (20) \end{aligned}$$

The Liouville vectors labeled by K behave like members

¹⁶ Cf. M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

of irreducible tensorial sets of the order $(2K+1)$,¹⁷ just as the components of a 2^K -pole operator. Multipole operators are characterized in addition by their parity ($\Pi = \pm 1$). But Λ is parity-invariant too.⁸ Therefore Λ has no elements connecting Liouville vectors belonging to different multipole transitions. For a given set of principal quantum numbers, and a given kind of multipole transition, it has only one matrix element, repeated $(2K+1)$ times. Magnetic quantum numbers are no longer required.

The trace in Eq. (9) may be rewritten in the reduced scheme by expressing $\mu_z(K=1, Q=0)$ by its reduced elements. Thus

$$\langle j_i m_i | \mu_z | j_f m_f \rangle = (1/\sqrt{3}) (-1)^{j_f - m_f} \times C(j_i j_f 1; m_i - m_f 0) \mu_{if}. \quad (21)$$

Here μ_{if} is the *reduced matrix element* of the dipole moment,¹⁷ which is independent of magnetic numbers, including Q . Equation (9) becomes then

$$\epsilon(0) - \epsilon(\omega) = (4\pi n_1 / 3\hbar) (e^{\hbar\omega/k_B T} - 1) \times \sum_{i_f, i'_f} \mu_{if} \left[\frac{1}{\omega - \mathbf{L}^{(s)} - \Lambda^{(K=1)}} \right]_{i_f, i'_f} \rho_{i'_f} \mu_{i'_f}, \quad (22)$$

where the summation indices do not include magnetic numbers, and where (20) is used for the matrix elements of Λ , with $K=1$ for dipole radiation.

With the bath molecule's wave vectors

$$|b\rangle = |\beta l m_l\rangle, \quad (23)$$

where l is the total angular momentum for all degrees of freedom (translatory and internal), we may construct the invariant Liouville vectors ($K_b = Q_b = 0$) for the

bath molecule,

$$|1^{(b)}\rangle = \sum_{\beta l} (2l+1)^{1/2} |\beta l(\beta l)^+; 00\rangle, \quad (24)$$

and

$$|\rho^{(b)}\rangle = \sum_{\beta l} (2l+1)^{1/2} \rho(\beta) |\beta l(\beta l)^+; 00\rangle, \quad (25)$$

required for the calculation of Λ . The irreducible-representation vectors for the product space of the system and bath molecules are in this case ($K_b = 0$) the simple products of the vectors for the separate molecules:

$$|\alpha_i j_i (\alpha_f j_f)^+, K; \beta l(\beta l)^+, 0; KQ\rangle = |\alpha_i j_i (\alpha_f j_f)^+; KQ\rangle \times |\beta l(\beta l)^+; 00\rangle. \quad (26)$$

Rotational invariance can be further exploited by noting that the transition matrix t is invariant under rotations, and therefore diagonal in the total angular momentum

$$\mathbf{J} = \mathbf{j} + \mathbf{l} \quad (27)$$

of the pair. A transformation to a scheme in which j and l are first coupled to J may be accomplished by Racah recoupling methods [Eq. (20) of Ref. 8]:

$$|\alpha_i j_i (\alpha_f j_f)^+, K; \beta l(\beta l)^+, 0; KQ\rangle = \sum_{J_i J_f} (-1)^{j_i + J_f + l + K} \times (2l+1)^{-1/2} [(2J_i+1)(2J_f+1)]^{1/2} \begin{pmatrix} J_i & J_f & K \\ j_f & j_i & l \end{pmatrix} \times |\alpha_i \beta (j_i l) J_i; [\alpha_f \beta (j_f l) J_f]^+; KQ\rangle. \quad (28)$$

Application of (28) to (17), using (20), (24), (25), and the orthogonality relations of the Wigner 6- j symbols,¹⁷

$$\sum_{J_f} (2J_f+1) \begin{pmatrix} J_i & J_f & K \\ j_f & j_i & l \end{pmatrix}^2 = \frac{1}{2j_i+1}, \quad (29)$$

etc., results in

$$\begin{aligned} \langle i' f' | \Lambda^{(K)} | i f \rangle &= n_2 \sum_{\beta l} \rho(\beta) \left\{ \sum_{J_i} ((2J_i+1)/(2j_i+1)) \langle \alpha_i \beta j_i l | t(J_i) | \alpha_i \beta j_i l \rangle - \sum_{J_f} ((2J_f+1)/(2j_f+1)) \right. \\ &\times \langle \alpha_f \beta j_f l | t(J_f) | \alpha_f \beta j_f l \rangle^* \left. \right] \delta_{i' i} \delta_{f' f} + 2\pi i \sum_{\beta' l' J_i J_f} (-1)^{l' - l + j_i - j_i'} (2J_i+1)(2J_f+1) \begin{pmatrix} J_i & J_f & K \\ j_f & j_i & l \end{pmatrix} \begin{pmatrix} J_i & J_f & K \\ j_i' & j_i' & l' \end{pmatrix} \\ &\times \langle \alpha_i' \beta' j_i' l' | t(J_i) | \alpha_i \beta j_i l \rangle \langle \alpha_f' \beta' j_f' l' | t(J_f) | \alpha_f \beta j_f l \rangle^* \delta(E' - E) \left. \right\}, \quad (30) \end{aligned}$$

where i and f are a shorthand for α_i, j_i , and for α_f, j_f , respectively.

In the present work we neglect the effects of the translatory motion of the system molecules (such as Doppler broadening and its narrowing by collisions). The angular momentum of the bath molecule may then be split into

$$\mathbf{l} = \mathbf{j}_b + \mathbf{l}_0, \quad (31)$$

¹⁷ U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

where \mathbf{j}_b is the angular momentum for the rotation of the bath molecule in its center-of-mass coordinates, and \mathbf{l}_0 is the orbital angular momentum of its motion relative to the system. Then,

$$|\beta l m_l\rangle = |\alpha_b k (j_b l_0) l m_l\rangle, \quad (32)$$

where $\hbar k$ is the linear momentum of the bath molecule, relative to the system, and α_b stands for the remaining bath quantum numbers. The following substitutions

should then be made in (30):

$$\sum_{\beta l} = \sum_{\alpha_b j_b l_0} \sum_k \rightarrow \sum_{\alpha_b j_b l_0} \frac{1}{2\pi^2} \int_0^\infty k^2 dk, \quad (33)$$

and

$$\rho(\beta) = \rho(k)\rho(\alpha_b, j_b). \quad (34)$$

Here $\rho(k)$ is the distribution function for the translational motion,

$$\rho(k) = (2\pi\hbar^2/m_r k_B T)^{3/2} \exp(-\hbar^2 k^2/2m_r k_B T), \quad (35)$$

and m_r is the reduced mass of the pair. Equation (33) holds provided the translatory wave functions are normalized to a unit volume; i.e.,

$$\langle \mathbf{R} | kl_0 m_0 \rangle = 4\pi j_{l_0}(kR) Y_{l_0, m_0}(\theta, \varphi). \quad (36)$$

Here $\mathbf{R} = (R, \theta, \varphi)$ is the radius vector from the system to the bath molecule, j is a spherical Bessel function, Y is

a spherical harmonic, and m_0 is the projection of l_0 on a space-fixed axis.

E. The Width of Individual Lines

The diagonal matrix elements of Λ consist of two parts—one is composed of forward scattering amplitudes in the initial and final levels, and the other of cross-products of scattering amplitudes. The first part does not appear in off-diagonal elements. In writing down the diagonal elements of Γ (the anti-Hermitian part of Λ), we may use the optical theorem,¹⁸ which says

$$\text{Im}\langle A | t | A \rangle = -\pi \sum_{A'} |\langle A | t | A' \rangle|^2 \delta(E' - E), \quad (37)$$

where $|A\rangle$ is a two-molecule wave vector. In applying (37) to the first part of Λ , we split the sum into two parts, one with the single term $i', f' = i, f$ and the other with all terms $i', f' \neq i, f$. The single term may be combined with the part of (30) composed of cross products, to give

$$\begin{aligned} \langle \langle i f^+ | \Gamma^{(K)} | i f^+ \rangle \rangle &= -\text{Im} \langle \langle i f^+ | \Lambda^{(K)} | i f^+ \rangle \rangle = n_2 \pi \sum_{\beta \beta' l l'} \rho(\beta) \left\{ \sum_{J_i} \sum_{i' \neq i} \frac{2J_i + 1}{2j_i + 1} |\langle \alpha_i \beta j_i l | t(J_i) | \alpha_i' \beta' j_i' l' \rangle|^2 + \sum_{J_f} \sum_{f' \neq f} \frac{2J_f + 1}{2j_f + 1} \right. \\ &\times |\langle \alpha_f \beta j_f l | t(J_f) | \alpha_f' \beta' j_f' l' \rangle|^2 + \sum_{J_i J_f} (2J_i + 1)(2J_f + 1) \left(\begin{matrix} J_i & J_f & K \\ j_f & j_i & l \end{matrix} \right) \langle \alpha_i \beta' j_i' l' | t(J_i) | \alpha_i \beta j_i l \rangle \\ &\left. - (-1)^{l-l'} \left(\begin{matrix} J_i & J_f & K \\ j_f & j_i & l' \end{matrix} \right) \langle \alpha_f \beta' j_f' l' | t(J_f) | \alpha_f \beta j_f l \rangle \right\} \delta(E' - E). \quad (38) \end{aligned}$$

Equation (38) is the equivalent of Eq. (III, 77c) of Baranger.⁵ The first two terms are one-half the total rates of inelastic transitions from the levels i and f , respectively, and the last term results from the differences in the elastic scattering in the two levels. The right-hand side of (38) is obviously positive, as required for a damping process.

F. The Off-Diagonal Elements

The off-diagonal elements of Δ and Γ , which connect different transitions (lines) in the spectrum, are generally complex. A simple relation binds, however, their real and imaginary parts, provided the transition matrix t is *symmetrical*, i.e.,

$$\langle A | t | A' \rangle = \langle A' | t | A \rangle. \quad (39)$$

A sufficient condition for (39) is the requirement that the interaction V be symmetrical (i.e., real). This requirement does not impose a limitation on the usually encountered types of intermolecular potentials. The transposed of (30), that is, the matrix element $\langle \langle i f^+ | \Lambda | i' f'^+ \rangle \rangle$, is then given by an expression similar to (30) except that $\rho(\beta')$ replaces $\rho(\beta)$. Thanks to the δ function in (30),

$$\rho(\beta)\rho_i = \rho(\beta')\rho_{i'}. \quad (40)$$

Hence

$$\langle \langle i f^+ | \Lambda | i' f'^+ \rangle \rangle \rho_{i'} = \langle \langle i' f'^+ | \Lambda | i f^+ \rangle \rangle \rho_i. \quad (41)$$

Also, Δ and Γ are Hermitian, i.e.,

$$\langle \langle i f^+ | \Delta - i\Gamma | i' f'^+ \rangle \rangle = \langle \langle i' f'^+ | \Delta + i\Gamma | i f^+ \rangle \rangle^*. \quad (42)$$

From (41) and (42) follow

$$\text{Im} \langle \langle i' f'^+ | \Gamma | i f^+ \rangle \rangle = [(\rho_i - \rho_{i'}) / (\rho_i + \rho_{i'})] \times \text{Re} \langle \langle i' f'^+ | \Delta | i f^+ \rangle \rangle \quad (43a)$$

and

$$\text{Im} \langle \langle i' f'^+ | \Delta | i f^+ \rangle \rangle = [(\rho_{i'} - \rho_i) / (\rho_{i'} + \rho_i)] \times \text{Re} \langle \langle i' f'^+ | \Gamma | i f^+ \rangle \rangle. \quad (43b)$$

Obviously Δ and Γ become real, and Λ symmetrical, in the limit

$$|E_i - E_{i'}| \ll k_B T / \hbar. \quad (44)$$

With the exception of few light molecules, condition (44) is quite common in microwave spectra at room temperature. Anyhow, in many cases where (44) is not satisfied the corresponding elements of Λ are expected to be small, since the transitions $i \leftrightarrow i'$ and $f \leftrightarrow f'$ are less probable. For most practical purposes, Γ and Δ may be considered real.

It is appropriate to mention here that the off-

¹⁸ Cf. Eq. (58) of Ref. 7.

diagonal elements depend on the probability of occurrence of both transitions, $i \leftrightarrow i'$ and $f \leftrightarrow f'$, in collisions. It may happen that two lines, i, f , and i', f' , lie close together though their respective initial (and final) levels are widely separated. The corresponding element of Λ is then vanishingly small and the two lines will not interfere with each other.

G. A Note on Self-Broadening

In a recent article by Di Giacomo¹⁹ explicit expressions were given for the relaxation of individual transitions $i \rightarrow f$ (i.e., the diagonal elements of Λ). As was noted there, self-broadening is distinguished from foreign-gas broadening as it involves collisions of identical molecules. There the properly symmetrized wave vectors

$$|ab\rangle_s = (1/\sqrt{2})\{|a\rangle|b\rangle \pm |b\rangle|a\rangle\} \quad (45)$$

of the pair should be used, with the upper (lower) sign in (45) to be taken with molecules obeying Bose-Einstein (Fermi-Dirac) statistics. The effect of indistinguishability of the molecules, as observed by Di Giacomo, is to allow following an arbitrary line in the Feynman diagram for a succession of collisions, as representing the system molecule. (In foreign-gas broadening, the line which represents the system is distinguished from all other lines.)

But the same effect may be obtained by introducing exchange terms in the interaction energy, as was briefly noted in Ref. 8. By using

$$V' = V(1 \pm F), \quad (46)$$

instead of the interaction V , where F is the exchange operator defined by

$$F|a\rangle|b\rangle = |b\rangle|a\rangle, \quad (47)$$

we may keep to the unsymmetrized product representation,

$$|a\rangle|b\rangle = |a \times b\rangle. \quad (48)$$

This results from

$${}_s\langle a'b'|V|ab\rangle_s = \langle a' \times b'|V'|a \times b\rangle, \quad (49)$$

as V is invariant under the exchange of the two molecules. The Lippmann-Schwinger equation for t [Eq. (14)] may be expanded as a power series in V , with coefficients depending only on the exchange-invariant H_0 . Therefore t may be defined in the product representation (48), with (46) substituted for V . The density matrix of the pair, in the absence of correlations, is a function of H_0 alone and may be factorized into $\rho^{(a)} \times \rho^{(b)}$. We may thus carry on using the formalism of Fano just by labeling one set of quantum numbers (say, a) the "system," and the other (b) the "bath," even though they no longer identify distinct molecules. All the subsequent discussion remains valid, provided

¹⁹ A. Di Giacomo, Nuovo Cimento 34, 473 (1964).

these exchange effects are taken into account in the calculation of t .

3. BANDS OF OVERLAPPING LINES; NONRESONANT SPECTRA

A. Expansion in Moments of $\mathbf{L}^{(s)} + \Lambda$

Equation (22) describes the profile of a band of overlapping lines in terms of their individual resonance frequencies (the elements of $\mathbf{L}^{(s)}$) and the relaxation matrix elements. However, in some cases we may study a bunch of many closely spaced lines, whose structure is completely washed out at the applied pressures. Such is, for example, the case with the ammonia inversion spectrum at pressures exceeding several cm Hg. In still other cases the resonance frequencies of the spectral transitions are degenerate to begin with. This occurs particularly in nonresonant spectra, which are composed of an infinite number of transitions, all with the resonance frequency $\omega_{if} = 0$. In the study of these absorption spectra it is impossible, and useless, to know individual elements of the relaxation matrix. Fortunately in most of these cases the band profile resembles the profile of a single isolated line, whose intensity is equal to the band's total intensity. We may therefore expand the sum in (22) in a perturbation series around a certain mean value of $\mathbf{L}^{(s)} + \Lambda$. The zero-order term will represent the single-line shape, and the next nonvanishing term will be usually sufficient to describe small deviations from the single-line shape (such as are sometimes described by the Cole and Cole parameter in nonresonant spectra²⁰).

Let us expand the sum in (22) in power series around the matrix of constant eigenvalue²¹ $\bar{\omega}_0 + \bar{\delta} - i\bar{\gamma}$:

$$\begin{aligned} (\omega - \mathbf{L}^{(s)} - \Lambda)^{-1} &= (\omega - \bar{\omega}_0 - \bar{\delta} + i\bar{\gamma})^{-1} \\ &\times \left[1 + \sum_{n=1}^{\infty} (\mathbf{L}^{(s)} + \Lambda - \bar{\omega}_0 - \bar{\delta} + i\bar{\gamma})^n (\omega - \bar{\omega}_0 - \bar{\delta} + i\bar{\gamma})^{-n} \right]. \end{aligned} \quad (50)$$

The first-order perturbation ($n=1$) is made to vanish by defining $\bar{\omega}_0 + \bar{\delta} - i\bar{\gamma}$ as the *mean value* of $\mathbf{L}^{(s)} + \Lambda$, as follows:

$$\begin{aligned} \bar{\omega}_0 + \bar{\delta} - i\bar{\gamma} &= \text{Tr}\{\mu(\mathbf{L}^{(s)} + \Lambda)\rho\mu\} / \text{Tr}\{\rho\mu^2\} \\ &= \sum_{if'f''} \mu_{if'}(\omega_{if}\delta_{i'f''} + \Lambda_{if',if})\rho_{if} / \sum_{if} \rho_{if} \mu_{if}^2, \end{aligned} \quad (51)$$

Then the band profile is given by a single-line expression, with a width parameter $\bar{\gamma}$ and a shift parameter $\bar{\delta}$ for the resonance frequency $\bar{\omega}_0$, plus a correction which, to the first approximation, is proportional to the

²⁰ K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 341 (1941). For the use of the Cole and Cole line shape in dilute gases, see G. Birnbaum, Ref. 4c.

²¹ In dealing with electric (magnetic) dipoles, we mean by Λ the reduced submatrix labeled by $K=1$ and the parity $\Pi = -1(+1)$.

second moment of $\mathbf{L}^{(s)} + \Lambda$ around its mean,

$$\text{Tr}\{\mu(\mathbf{L}^{(s)} + \Lambda - \bar{\omega}_0 - \bar{\delta} + i\bar{\gamma})^2 \rho\mu\} / \text{Tr}\{\rho\mu^2\}. \quad (52)$$

In the calculation of $\bar{\gamma}$ we may apply the optical theorem (37) to the forward scattering amplitudes in the diagonal elements of Λ . Inserting (15a) into the imaginary part of (51) we get

$$\begin{aligned} [\text{Tr}(\rho\mu^2)]\bar{\gamma} = n_2\pi \sum_{\substack{b,i,f \\ b',i',f'}} \rho_b \rho_i \delta(E' - E) \\ \times \{ \mu_{if}^2 [\langle i'b' | t | ib \rangle]^2 + | \langle f'b' | t | fb \rangle |^2 \\ - \mu_{if} \mu_{i'f'} [\langle i'b' | t | ib \rangle \langle f'b' | t | fb \rangle^* + \text{c.c.}] \}. \quad (53) \end{aligned}$$

But, in light of (40) and since the set of numbers b, i, f , is interchangeable with b', i', f' in the summation, (53) may be written as

$$\begin{aligned} [\text{Tr}(\rho\mu^2)]\bar{\gamma} = n_2\pi \sum_{\substack{b,i,f \\ b',i',f'}} \rho_b \rho_i \delta(E' - E) \\ \times | \mu_{if} \langle i'b' | t | ib \rangle - \mu_{i'f'} \langle f'b' | t | fb \rangle |^2 \quad (54) \end{aligned}$$

which is nonnegative.

B. Nonresonant Spectra

A typical case of a band of degenerate transitions in the microwave region is the case of nonresonant spectra, where the dipole moment has matrix elements between states of equal energy, and the corresponding resonance frequencies are zero. Examples of such bands are encountered in the magnetic-dipole spectrum of oxygen,^{4a} or in the electric dipole spectrum of symmetric-top molecules with no detectable inversion splitting (such as the methyl halides).^{4b,c} In this class may be considered, as will be shown in the next section, also bands of lines with finite resonance frequencies whenever these frequencies are negligibly small compared to their relaxation parameters (as the ammonia spectrum at elevated pressures).

In all these cases, the two levels, i and f , of a transition are either identical or degenerate, for all practical purposes, and can be made identical by a unitary transformation. The nonresonant spectrum is then associated with the relaxation of the expectation values of the dipole moment.²²

The association of a photon absorption with the diagonal elements of a multipole operator may sound paradoxical. However, we should remember that the distinction of a single molecule as the absorbing system is only a simplification. In case the molecular interactions are weak enough, we may associate with each particular single-molecule state i a large set of states of the whole gas sample (the I 's of Sec. 2B) whose number is of the order of magnitude of the number of molecules in the sample, and whose degeneracy is

²² The author is indebted to L. Frenkel for the clarification of this point.

partly removed by the molecular interactions. Nonresonant absorption then results from transitions in which both initial and final states belong to the same set, labeled i .

The relaxation matrix may be simplified by its symmetry properties under Liouville conjugation.⁸ Since any operator in ordinary wave vector space and its Hermitian conjugate are both vectors in Liouville space, they are transformed to each other by an (antilinear) operation, called Liouville conjugation:

$$\mathbf{C}_L \sum_{if} d_{if} |i\rangle \langle f| \equiv \sum_{if} d_{if}^* |f\rangle \langle i|, \quad (\mathbf{C}_L^{-1} = \mathbf{C}_L). \quad (55)$$

The Liouville conjugate of a matrix A in Liouville space (to be distinguished from its Hermitian conjugate) is defined by

$$\langle \langle i' f'^+ | \mathbf{C}_L A \mathbf{C}_L | i f^+ \rangle \rangle \equiv \langle \langle f' i'^+ | A | f i^+ \rangle \rangle. \quad (56)$$

According to Sec. 5 of Ref. 8, the relaxation matrix Λ obeys the symmetry relation

$$\mathbf{C}_L \Lambda \mathbf{C}_L = -\Lambda^*, \quad (57)$$

where the asterisk denotes complex conjugation. In our case, either i and f are identical, and $|i f^+\rangle$ is self-conjugate, or i and f are degenerate, and we can form the self-conjugate vectors

$$\begin{aligned} |\alpha\rangle &= (1/\sqrt{2}) [|i f^+\rangle + |f i^+\rangle], \\ |\beta\rangle &= (i/\sqrt{2}) [|i f^+\rangle - |f i^+\rangle], \end{aligned} \quad (58)$$

which are eigenvectors of $L^{(s)}$ too. In either case, (57) turns into

$$\Lambda = -\Lambda^*, \quad (59)$$

i.e., Λ is pure imaginary. Since i and f are degenerate, ρ_i is unaffected by the transformation leading to (58), and the consequences of (43) remain valid. In particular, $\langle \langle i' f'^+ | \Delta | i f^+ \rangle \rangle$ vanishes whenever $|E_{i'} - E_i|$ or $|E_{f'} - E_f|$ is much smaller than $k_B T / \hbar$, according to (44).

In any case, we may split Λ into a real and an imaginary matrix,²³

$$\Lambda = \Lambda' - i\Lambda'' \quad (60)$$

so that $\bar{\delta}$ and $\bar{\gamma}$ are the mean values of Λ' and Λ'' , respectively. Since in nonresonant spectra Λ' vanishes,

$$\bar{\omega}_0 + \bar{\delta} = 0, \quad (61)$$

and we may expand (50) around $-i\bar{\gamma}$ as the mean value of $\mathbf{L}^{(s)} + \Lambda$. Thus, the complex permittivity (permeability) for a nonresonant spectrum is given up to second-order terms in the perturbation expansion (50)

²³ So far we have tacitly restricted the discussion to a representation in which the matrix elements of the dipole operator μ_x are all real. This is not necessary, however. We might have chosen some of them as pure imaginary, but then the corresponding Liouville vectors should be multiplied by the imaginary unit i , to keep μ_x Hermitian, and the vectors (58) would change sign under Liouville conjugation. All the results remain therefore unaltered.

by

$$\epsilon(0) - \epsilon(\omega) = (4\pi n_1/3\hbar)(e^{\hbar\omega/k_B T} - 1) \left(\sum_{if} \rho_{i\mu_{if}^2} \right) \times (\omega + i\tilde{\gamma})^{-1} [1 + \lambda\tilde{\gamma}^2/(\omega + i\tilde{\gamma})^2]. \quad (62)$$

Here

$$\lambda = \text{Tr}\{\mu(\Delta'' - \tilde{\gamma})^2 \rho \mu\} / \tilde{\gamma}^2 \text{Tr}\{\rho \mu^2\} \quad (63)$$

serves as a perturbation-strength parameter. It may be considered as a "fractional mean-square deviation" of the relaxation matrix elements from their average value $\tilde{\gamma}$.

Since in the microwave region at ordinary temperatures

$$e^{\hbar\omega/k_B T} - 1 \approx \hbar\omega/k_B T, \quad (64)$$

we may write the loss coefficient $\epsilon''(\omega)$ as

$$\epsilon''(\omega) = (4\pi n_1/3k_B T) \left(\sum_{if} \rho_{i\mu_{if}^2} \right) [\tilde{\gamma}\omega/(\omega^2 + \tilde{\gamma}^2)] \times \{1 - \lambda[\tilde{\gamma}^2(3\omega^2 - \tilde{\gamma}^2)/(\omega^2 + \tilde{\gamma}^2)^2]\}. \quad (65)$$

The zero-order term is the familiar Debye shape, and the second-order term describes small deviations from a Debye shape. With λ small enough ($\lambda \lesssim 0.2$), the peak value of $\epsilon''(\omega)$ is smaller by a factor $(1 - \frac{1}{2}\lambda)$ than the corresponding Debye maximum, and its position is shifted from $\omega = \tilde{\gamma}$ to $\omega = \tilde{\gamma}(1 - \frac{1}{2}\lambda)$.

It is interesting to compare Eq. (65) with the Cole and Cole expression commonly used to describe deviations from a Debye shape²⁰:

$$\epsilon'' = -(4\pi n_1/3k_B T) \left(\sum_{if} \rho_{i\mu_{if}^2} \right) \text{Im}\{1 + (i\omega/\gamma_0)^{1-\alpha}\}^{-1}. \quad (66)$$

With small values of the parameter α , Eq. (66) expresses a reduction of the peak intensity by $(1 - \frac{1}{2}\pi\alpha)$, but with no shift of its position. Comparisons of (65) with (66) should be therefore made with

$$\lambda = \pi\alpha, \quad (67)$$

and with

$$\tilde{\gamma} = \gamma_0(1 + \frac{1}{2}\lambda), \quad (68)$$

to the first power of λ .

The comparison of the two line shapes has been carried out in connection with the dielectric-loss measurements of methyl chloride²⁴ (Fig. 1). The dielectric-loss coefficient, measured by Frenkel, Kryder, and Maryott at a frequency of 0.0365 cm⁻¹, is plotted in Fig. 1 as a function of pressure, alongside the theoretical shapes of Debye and of Cole and Cole ($\alpha = 0.05$), and Eq. (65) ($\lambda = 0.05\pi$), with a common intensity factor of 0.80×10^{-4} atm⁻¹ (as compared to a calculated²⁴ value of 0.812×10^{-4} atm⁻¹). The value of $\tilde{\gamma}/p$ used with Eq. (65), 0.11 cm⁻¹ atm⁻¹, is about 8% higher than the value of γ_0/p taken for the Debye and the Cole and Cole plots. It should also be noted that Eq. (65), plotted versus the logarithm of the pressure, is not

²⁴ L. Frenkel, S. J. Kryder, and A. A. Maryott (to be published).

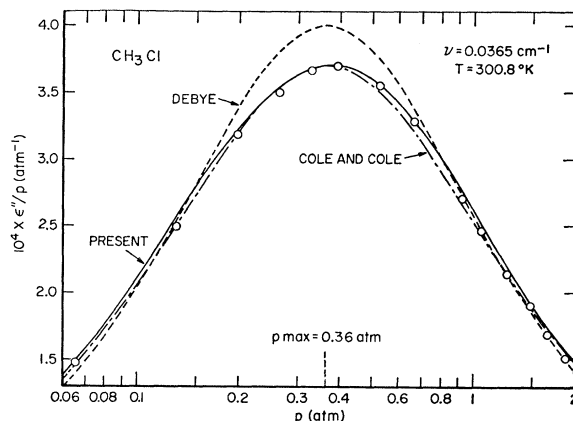


FIG. 1. Dielectric loss in methyl chloride as measured by Frenkel, Kryder, and Maryott (Ref. 24) (circles), compared with the line shapes of Debye and of Cole and Cole ($\alpha = 0.05$), and with Eq. (65), with $\lambda = 0.05\pi$.

symmetrical about its peak, whereas the Debye and the Cole and Cole plots are symmetrical.

Equation (65) properly describes small deviations from a Debye shape under conditions where the impact approximation is valid. Even though the Cole and Cole expression has been successfully applied in a much wider range of conditions (such as the dielectric loss in liquids), it is based on the rather arbitrary assumption of a particular continuous distribution of relaxation rates. Equation (65) relates deviations from the Debye shape to fundamental principles.

C. The Rate of Nonresonant Relaxation

The calculation of the mean relaxation parameter for the band of nonresonant transitions,

$$\tilde{\gamma} = \text{Tr}\{\mu\Delta''(\rho\mu)\} / \text{Tr}\{\rho\mu^2\} \quad (69)$$

implies taking a trace over a subspace of system wave vectors. Any orthonormal set of wave vectors within this subspace can serve as a basis for this operation. But since i and f are degenerate, if not identical, we can choose a basis in which the dipole operator is diagonal. Thus, for example, in the case of the dielectric loss by symmetric-top molecules of the methyl halide group, i and f are identical in all quantum numbers but parity. But if the two parity states are practically degenerate, we may choose as a basis their even and odd combinations in which μ is diagonal.

We have so far referred to i and f as principal quantum numbers, and to μ_{if} as a reduced matrix element. But since we take a trace in (69) we can go back to the representation in which \mathbf{j} and \mathbf{l} are uncoupled, and μ_z is diagonal in the magnetic quantum number m . We may now set $i = f = a$ in (53), where a stands for all quantum numbers of the system (m included). The two t -matrix elements in (53) are now

identical. So

$$\bar{\gamma} = n_2 \pi \sum_{aa'bb'} \rho_a \rho_b \delta(E' - E) |\mu_{a'} - \mu_a|^2 \times |\langle a'b' | t | ab \rangle|^2 / (\sum_a \rho_a \mu_a^2), \quad (70)$$

where μ_a is the expectation value of μ_z in state a , etc.

Equation (70) depends only on absolute squares of scattering amplitudes, which may be translated into cross sections. The average rate of transitions $a \rightarrow a'$ which a system molecule undergoes by collisions is given by

$$n_2 \langle v \sigma_{a \rightarrow a'} \rangle = 2\pi n_2 \sum_{bb'} \rho_b |\langle a'b' | t | ab \rangle|^2 \delta(E' - E), \quad (71)$$

where $v = \hbar k / m_r$ is the relative velocity of the pair, σ is the relevant partial cross section, and $\langle \dots \rangle$ stands for averaging over the bath particle states.

The relaxation rate of a nonresonant band is therefore

$$\bar{\gamma} = n_2 \sum_{aa'} \langle v \sigma_{a \rightarrow a'} \rangle \rho_a (\frac{1}{2} |\mu_{a'} - \mu_a|^2 / \sum_a \rho_a \mu_a^2). \quad (72)$$

Equation (72) is an analytical expression of the concept of Debye relaxation, which associates nonresonant absorption with variations of the projection of the dipole moment along a space-fixed axis. Notice that only collisions that change the expectation value of μ_z contribute to (72). Collisions that leave all the system's quantum numbers (m included) unaltered do not contribute to the Debye relaxation.

In the simple case of a classical rigid dipole we obtain, after averaging over all initial orientations of \mathbf{u} ,

$$\frac{1}{2} |\mu_{a'} - \mu_a|^2 / \sum_a \rho_a \mu_a^2 \rightarrow 1 - \cos \theta, \quad (73)$$

where θ is the angle by which the dipole is rotated in the collision. The classical solution of the Debye problem^{1b, 25} is thus retrieved. Equation (72) extends this solution to the quantum-mechanical case, with inelastic collisions properly included.

It is worth while noting that, whereas most pressure-broadening problems involve scattering *amplitudes* and their relative phases, nonresonant relaxation involves only *cross sections*, and can therefore be more readily connected with other experiments, such as molecular beam scattering, in which cross sections are measured.

The dipole-dependent factor (73) distinguishes Debye relaxation from other collision effects (such as rotational relaxation). It favors large changes in the magnetic quantum number at each collision, in agreement with former observations.^{9, 24}

4. THE RELAXATION OF RESONANCE LINES

A. The Two-Level System

Consider a pair of levels, i and f ($E_i > E_f$), which gives rise to an isolated line in the microwave region, with

²⁵ P. W. Anderson, Phys. Rev. **76**, 647 (1949).

resonance frequency ω_{if} . Suppose that the spectral transitions $i \rightarrow i$ and $f \rightarrow f$ are forbidden (i.e., they belong to a higher multipole species). Thanks to its invariance under rotations and inversion in an isotropic gas,⁸ the relaxation matrix has no elements connecting transitions of different multipole species (such as $|if^+\rangle$ and $|ii^+\rangle$), say, in the present case). In the case of a 2^K -pole transition, with parity Π (e.g., electric dipole transitions have $K=1$, $\Pi=-1$; magnetic dipole transitions have $K=1$, $\Pi=+1$), the relaxation matrix reduces into the space of the two vectors,

$$|if^+; \Pi K Q\rangle \text{ and } |fi^+; \Pi K Q\rangle, \quad (74)$$

only. Q may take any of its $(2K+1)$ allowed values, as Λ is diagonal in Q and independent of it.

In considering the whole gas sample as one absorbing system, as in Sec. 2B, absorption is restricted to states I and F with $E_I - E_F = \omega > 0$. The single-molecule system, however, is not conservative, and absorption (as well as induced emission) may result in either an upward or a downward energy jump, provided the line width is sufficiently large. Both eigenvectors (74) in Liouville space, with the respective eigenvalues $\omega_{if} = \omega_0 > 0$ and $\omega_{fi} = -\omega_0$, participate in the absorption (or induced emission). Of the four elementary processes which are thus associated with a resonance line (Fig. 2), the two "positive resonance" processes involve an energy imbalance of $\omega - \omega_0$, and the two "negative resonance" processes involve an imbalance of $\omega + \omega_0$.

Formally, the absorption line may be considered as composed of one line with a resonance frequency ω_0 , and the tail of another with the negative resonance frequency $-\omega_0$.

If the relaxation matrix had no elements coupling the two vectors (74), the line shape would consist of two Lorentz terms, i.e., (as $\rho_i \approx \rho_f$),

$$\epsilon(0) - \epsilon(\omega) = \frac{4\pi n_1 \omega}{3k_B T} \rho_i \mu_{if}^2 \left[\frac{1}{\omega - \omega_0 + i\gamma} + \frac{1}{\omega + \omega_0 + i\gamma} \right]. \quad (75)$$

This is the familiar Van Vleck and Weisskopf^{1b} line

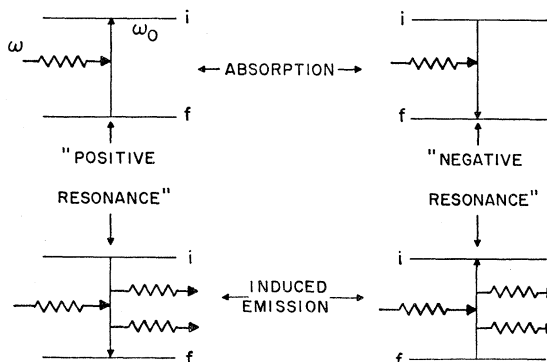


FIG. 2. The four elementary processes that contribute to a microwave absorption line.

shape. There is no reason, however, to assume that the relaxation matrix has no off-diagonal elements connecting the two vectors of opposite eigenvalues.

A similar situation is encountered in the equations of motion of a classical damped harmonic oscillator in phase space. Instead of the displacement q and momentum p of the oscillator, one often chooses

$$\begin{aligned} x &= -p - im\omega_0 q, \\ y &= p - im\omega_0 q, \end{aligned} \quad (76)$$

(where m is the oscillator mass, and ω_0 its resonance frequency) as the canonical variables. In the case of undamped oscillations, x and y obey the first-order differential equations

$$\dot{x} = i\omega_0 x, \quad \dot{y} = -i\omega_0 y, \quad (77)$$

similar to those obeyed by $|if^+\rangle$ and $|fi^+\rangle$, respectively, in the Liouville space of the free system molecule. In the quantization of the equations of motion of the harmonic oscillator,²⁶ x and y assume the position of excitation and de-excitation operators, similar to that held by $|if^+\rangle$ and $|fi^+\rangle$. The analogy between radiation processes and harmonic oscillators is thus best carried out in the framework of the Liouville representation. Vectors in Liouville space correspond to the phase-space coordinates of a classical system.²⁷

Damping is sometimes introduced in the classical picture as a velocity-dependent friction force, i.e.,

$$\dot{p} = -m\omega_0^2 q - 2\gamma p. \quad (78)$$

The resulting equations of motion in phase space

$$\begin{aligned} \dot{x} &= i\omega_0 x - \gamma x + \gamma y, \\ \dot{y} &= -i\omega_0 y - \gamma y + \gamma x, \end{aligned} \quad (79)$$

may be rewritten in a vector notation,

$$\dot{\mathbf{x}} = i(\mathbf{L}^{(s)} + \Lambda_{e1})\mathbf{x}, \quad (79a)$$

where

$$\mathbf{x} = \begin{pmatrix} x \\ y \end{pmatrix}, \quad (80)$$

$$\mathbf{L}^{(s)} = \begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix}, \quad (81)$$

and

$$\Lambda_{e1}^\dagger = i \begin{pmatrix} \gamma & -\gamma \\ -\gamma & \gamma \end{pmatrix}. \quad (82)$$

Λ_{e1} is apparently the equivalent of the quantum-mechanical Λ . We use here the Hermitian conjugate Λ^\dagger instead of Λ itself, since we deal with the evolution in time of observables, whereas Fano's formalism, by which Λ is defined, deals with the evolution of density

²⁶ Cf. P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, London, 1958), 4th ed., Sec. 34.

²⁷ See, e.g., R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106.

matrices. This distinction is illustrated by the identity

$$\text{Tr}\{\mu(e^{-i\mathcal{L}t}\rho\mu)\} = \text{Tr}\{(e^{i\mathcal{L}^\dagger t}\mu)\rho\mu\}, \quad (83)$$

where $\mathcal{L} = \mathbf{L}^{(s)} + \Lambda$.

In Eq. (82), Λ has off-diagonal elements which are equal in magnitude to the diagonal elements, but with opposite sign. In the general quantum-mechanical case this is not so. Consider the relaxation matrix in the two-dimensional vector space (74). With

$$i' = f, \quad f' = i, \quad (84)$$

and ω_{if} a microwave frequency, condition (44) is satisfied, and Δ and Γ are real. Furthermore, as results from (57),

$$\langle\langle if^+ | \Delta | fi^+ \rangle\rangle = \langle\langle fi^+ | \Delta | if^+ \rangle\rangle = 0, \quad (85)$$

$$\langle\langle fi^+ | \Delta | fi^+ \rangle\rangle = -\langle\langle if^+ | \Delta | if^+ \rangle\rangle, \quad (86)$$

and

$$\langle\langle fi^+ | \Gamma | fi^+ \rangle\rangle = \langle\langle if^+ | \Gamma | if^+ \rangle\rangle, \quad (87)$$

since

$$C_L |if^+; \Pi K 0\rangle = |fi^+; \Pi K 0\rangle. \quad (88)$$

Λ may therefore be written in the form

$$\Lambda = \begin{pmatrix} \delta - i\gamma & i\zeta \\ i\zeta & -\delta - i\gamma \end{pmatrix}, \quad (89)$$

where δ , γ , and ζ are real. Equation (89) is similar to the simple classical analog (82) is $\delta=0$ and $\zeta=\gamma$. In general, however, ζ is different from γ . Whereas ζ may still be associated with the velocity-dependent friction, the excess damping ($\gamma-\zeta$) should be attributed in the classical picture to such effects as radiation-interrupting collisions.

B. The Coupling Element ζ

An expression of ζ in terms of scattering amplitudes is obtained by inserting (84) into (30):

$$\begin{aligned} \zeta &= 2\pi n_2 \sum_{\beta l} \rho(\beta) \sum_{\beta' l' J J'} (-1)^{l-l'+j_i-j_f} \delta(E'-E) \\ &\times (2J+1)(2J'+1) \begin{pmatrix} J & J' & K \\ j_f & j_i & l \end{pmatrix} \begin{pmatrix} J & J' & K \\ j_i & j_f & l' \end{pmatrix} \\ &\times \langle \alpha_f \beta' j_f l' | t(J) | \alpha_i \beta j_i l \rangle \langle \alpha_i \beta' j_i l' | t(J') | \alpha_f \beta j_f l \rangle^*. \end{aligned} \quad (90)$$

Equation (90) is composed solely of products of transition amplitudes combining i with f . However, the two matrix elements of t stand for two opposite transitions. $i \rightarrow f$ and $f \rightarrow i$, respectively. Since $E_i \neq E_f$, energy cannot be strictly conserved in both transitions simultaneously. In the impact approximation we can replace $\delta(E'-E)$ in (90) by $\delta(E_{\beta'} - E_\beta)$. It is interesting, though to examine the restrictions on energy variations imposed by the δ functions in the more exact Eq. (15).

Whereas the expression for γ implies the relations $\pm(E_f - E_i) + E_{\beta'} - E_{\beta} = \pm\omega$, only transitions obeying $E_{\beta'} - E_{\beta} = \pm\omega$ are allowed in ζ . One may say that in γ the imbalance between the energy absorbed or emitted by the system and that of the photon is compensated by a change in the bath molecule's energy. In ζ , however, the whole of the photon's energy is compensated by a change in the bath molecule's energy.

The expression (90) for ζ may be considerably simplified under the three conditions usually encountered in the so-called *classical-path* assumption:

(a) The scattering is very nearly energy conserving (i.e., ω_{if} should be small).

(b) The t matrix remains practically unaffected by transposition of the bath variables alone (i.e., they are treated as parameters defining the classical collision trajectory as practically independent of the system's state).

(c) The total angular momentum J is much larger than internal angular momenta, and t hardly varies with it, as long as the triangular conditions [Eq. (27)] are observed. Under this condition, the orbital angular momentum l_0 may be considered sufficient to describe the rotational part of the relative motion (the impact-parameter approach).

We further assume that

$$j_i = j_f = j \quad (91)$$

as in many microwave spectra (the ammonia inversion spectrum, for one). A summation over J and J' , with t considered independent of J , letting J vary from $J' - K$ to $J' + K$, and J' vary from $l - j$ to $l + j$, yields then

$$\zeta \approx 2\pi n_2 \sum_{\beta\beta'l'l'} \rho(\beta)(2l+1) |\langle \alpha_f \beta' j l' | t | \alpha_i \beta j l \rangle|^2 \delta(E' - E). \quad (92)$$

This is the rate of inelastic transitions from i to f , or vice versa. Under the same "classical path" conditions, the part of the diagonal element of Γ [Eq. (38)] due to inelastic collisions is

$$\gamma(\text{inel.}) \approx 2\pi n_2 \sum \rho(\beta)(2l+1) \delta(E' - E) \times \frac{1}{2} \{ |\langle \alpha_f \beta' j l' | t | \alpha_f \beta j l \rangle|^2 + |\langle \alpha_i \beta' j l' | t | \alpha_i \beta j l \rangle|^2 \}, \quad (93)$$

i.e., ζ is that part of γ which corresponds to the inelastic transitions $i \rightarrow f$ and $f \rightarrow i$. Obviously, in this limit

$$\gamma \geq \zeta \geq 0. \quad (94)$$

The classical-path approximation may serve as a working approximation particularly in cases of foreign-gas broadening when the internal degrees of freedom of the bath molecule may be ignored. The applicability of the above assumptions, particularly (b), to other cases, such as self-broadening, may be somewhat doubtful.

C. The Line Shape

The 2×2 matrix $\omega - \mathbf{L}^{(s)} - \Lambda$, with $\mathbf{L}^{(s)}$ given by (81), and Λ by (89), is readily inverted to give

$$[\omega - \mathbf{L}^{(s)} - \Lambda]^{-1} = \frac{\begin{pmatrix} \omega + \omega_0 + \delta + i\gamma & i\zeta \\ i\zeta & \omega - \omega_0 - \delta + i\gamma \end{pmatrix}}{(\omega + i\gamma)^2 - (\omega_0 + \delta)^2 + \zeta^2}. \quad (95)$$

Inserting (95) and (64) into (22), with $\rho_i \approx \rho_f$ and $\mu_{if} = \mu_{fi}$, we get

$$\epsilon(0) - \epsilon(\omega) = (4\pi n_1 \omega / 3ck_B T) \rho_i \mu_{if}^2 F(\omega), \quad (96)$$

and

$$\alpha(\omega) = (4\pi n_1 \omega^2 / 3ck_B T) \rho_i \mu_{if}^2 F''(\omega), \quad (97)$$

with a complex "shape factor"

$$F(\omega) = F'(\omega) - iF''(\omega), \quad (98)$$

where

$$F'(\omega) = \frac{2\omega[\omega^2 - (\omega_0 + \delta)^2 + (\gamma + \zeta)^2]}{[\omega^2 - (\omega_0 + \delta)^2 - \gamma^2 + \zeta^2]^2 + 4\omega^2\gamma^2} \quad (99)$$

and

$$F''(\omega) = \frac{2(\gamma - \zeta)\omega^2 + 2(\gamma + \zeta)[(\omega_0 + \delta)^2 + \gamma^2 - \zeta^2]}{[\omega^2 - (\omega_0 + \delta)^2 - \gamma^2 + \zeta^2]^2 + 4\omega^2\gamma^2}. \quad (100)$$

Alternatively, $F(\omega)$ may be derived by diagonalizing the perturbed Liouville matrix $\mathcal{L} = \mathbf{L}^{(s)} + \Lambda$ for the two-level system. We distinguish then between the two cases:

(a) The "low pressure" case, where

$$\omega_0 + \delta > \zeta, \quad (101a)$$

in which \mathcal{L} has two complex eigenvalues with opposite real parts,

$$\pm [(\omega_0 + \delta)^2 - \zeta^2]^{1/2} - i\gamma, \quad (102a)$$

representing a damped harmonic oscillation.

(b) The "high-pressure" case, where

$$\omega_0 + \delta < \zeta, \quad (101b)$$

in which \mathcal{L} has pure-imaginary eigenvalues,

$$-i\{\gamma \pm [\zeta^2 - (\omega_0 + \delta)^2]^{1/2}\}, \quad (102b)$$

representing critical damping.

Since \mathcal{L} is non-Hermitian, the transformation which diagonalizes it is not unitary, and $F(\omega)$ will not be formed of two Lorentz-shaped terms. We thus get for the imaginary part of the shape factor in case (a)

$$F''(\omega) = \frac{\gamma + \zeta(1 - \omega/\eta)}{(\eta - \omega)^2 + \gamma^2} + \frac{\gamma + \zeta(1 + \omega/\eta)}{(\eta + \omega)^2 + \gamma^2}, \quad (100a)$$

and in case (b)

$$F''(\omega) = \left(\frac{\zeta}{\eta} + 1\right) \frac{\gamma - \eta}{\omega^2 + (\gamma - \eta)^2} - \left(\frac{\zeta}{\eta} - 1\right) \frac{\gamma - \eta}{\omega^2 + (\gamma + \eta)^2}, \quad (100b)$$

where in both cases

$$\eta = |(\omega_0 + \delta)^2 - \zeta^2|^{1/2}. \quad (103)$$

The sum of the two terms, which in both cases is identical to (100), varies smoothly with pressure, though the separate terms diverge on approaching the critical pressure where $\zeta = \omega_0 + \delta$.

Consider now the two extreme cases.

(c) The limiting case

$$\zeta \ll \omega_0 + \delta. \quad (104)$$

$F(\omega)$ turns then into the familiar Van Vleck and Weisskopf expression

$$F_{VVW}(\omega) = \frac{1}{\omega - \omega_0 - \delta + i\gamma} + \frac{1}{\omega + \omega_0 + \delta + i\gamma}, \quad (105)$$

with a width parameter γ .

(d) The limiting case

$$\zeta \gg \omega_0 + \delta \quad (106)$$

$F(\omega)$ turns then into the familiar Debye shape

$$F_D(\omega) = \frac{2}{\omega + i(\gamma - \zeta)}, \quad (107)$$

with a *different* width parameter $\gamma - \zeta$. The factor 2 in (107) reflects the fact that we have taken the sum $\rho_i + \rho_f \approx 2\rho_i$ in the calculation of $F(\omega)$.

D. The Transition to the Nonresonant Limit

At sufficiently high pressures, where ω_0 is negligibly small, compared to the relaxation matrix, a resonance line attains the nonresonant Debye shape. Obviously the Debye-limit parameter $\gamma - \zeta$ must be positive in order to maintain damping. A negative $\gamma - \zeta$ would mean stimulated emission.²⁸

That $\gamma - \zeta$ is positive may be seen by noting that it is the mean value of Λ'' , in the sense of (69), in the particular case (89) of the two-level system. $\gamma - \zeta$ corresponds to that part of (54) with $i' = i$ or f and $f' = f$ or i , which is obviously positive.

In reality, we hardly even encounter a system with a single pair of levels, but with a group of such pairs (as with the ammonia inversion spectrum). Then we can still define a mean value of Λ'' , $\bar{\gamma} - \bar{\zeta}$, given by (54), with i and f spanning the same subspace in the Hilbert space of the system. Furthermore, since $\rho_i \approx \rho_f$ we can transform to a representation in which the dipole

²⁸ Note that the second part of (100b) is also negative, but the sum of the two parts is positive.

moment is diagonal in the relevant subspace, leaving ρ unaffected. The relaxation parameter $\bar{\gamma} - \bar{\zeta}$ may then be interpreted²⁹ in the same manner as the parameter $\bar{\gamma}$ for nonresonant relaxation [Eq. (72)], though a and a' are no longer *energy* eigenstates.

E. The Classical Analog and ζ

It is interesting to establish what ζ means in terms of the analogy to a single-mode classical oscillator discussed in Sec. 4A. ζ represents collision-induced transitions from the vector $|if^+\rangle$ to $|fi^+\rangle$ in Liouville space, and vice versa. Corresponding transitions between the phase-space coordinates x and y of the classical oscillator imply a reversing of the momentum p without affecting the position q . In plotting $q(t)$ as a function of the time t , the occurrence of such a transition will show up as a cusp [Fig. 3(a)]. It is equivalent to a change of phase from $\phi(t)$ to $2\pi - \phi(t)$, where $\phi(t)$ is the phase of the oscillator just before the collision. Case (c) of Sec. 4C ($\zeta \ll \omega_0$) means a small frequency of such collisions, compared to ω_0 . A new collision is about equally likely to occur at any moment along a time interval covering many oscillation periods. Therefore its effect, on the average, is equivalent to that of randomly distributed phase shifts. Such collisions will therefore contribute to the damping of the oscillation (whose total rate is γ).

In the other extreme case ($\zeta \gg \omega_0$) many momentum-inverting collisions will occur during a single oscillation period. But since they reverse the direction of motion, they will tend to keep q constant [Fig. 3(b)];

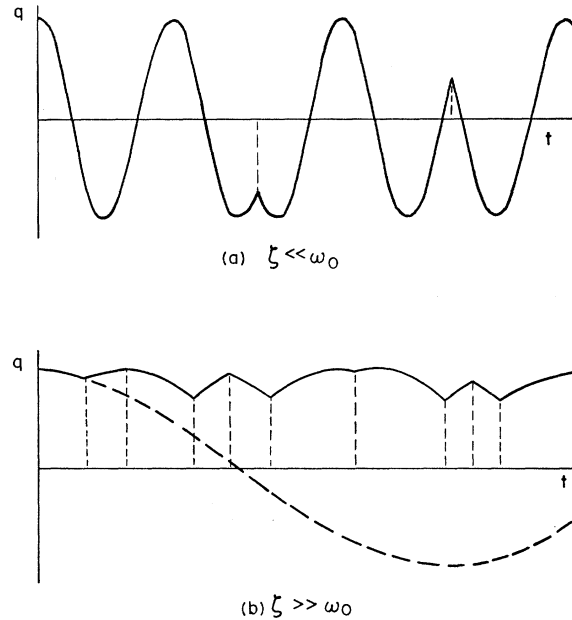


FIG. 3. The displacement of an harmonic oscillator undergoing momentum-reflecting collisions whose average rate is (a) much smaller, or (b) much larger, than the oscillation frequency.

²⁹ As proposed by G. Birnbaum and A. A. Maryott, *J. Chem. Phys.* **29**, 1422 (1958).

i.e., to keep it from oscillating (hence the shift to zero-resonance frequency) without contributing to its damping (hence the reduction to $\gamma-\zeta$).

Equation (89), with $\zeta \neq \gamma$, may be inserted into the classical equations (79a), which in turn may be transformed back by (76) to the q, p representation resulting in

$$\ddot{q} = -[(\omega_0 + \delta)^2 + \gamma^2 - \zeta^2]q - 2\gamma\dot{q}, \quad (108)$$

and an identical equation for p . A similar differential equation has been derived by Korst and Nikitin,³⁰ in a recent article which proposes a model for the relaxation of the two-level system. Our line shape could be obtained from its solution by Fourier transforms,³¹ provided appropriate initial conditions were used.

F. The Ammonia Inversion Spectrum

In the ammonia molecule (NH_3) the rotational energy levels, labeled by the symmetric-top quantum numbers j and κ , are split into the inversion doublets with the parity $\pi = \pm 1$ ³² of the vibrational wave function for the stretching mode (ν_2). Since the electric dipole moment has an odd parity, the transitions

$$\alpha j \kappa \pi_i \leftrightarrow \alpha j \kappa \pi_f \quad (109)$$

with

$$\Pi = \pi_i \times \pi_f = -1 \quad (110)$$

give rise to the inversion spectrum of ammonia, with resonance frequencies lying in the vicinity of 0.8 cm^{-1} . Since all quantum numbers, except π , are common to the levels i and f in (109), Π is also the parity of the corresponding Liouville vectors $|\alpha j \kappa \pi_i (\alpha j \kappa \pi_f)^+; \Pi K Q\rangle$ and $|\alpha j \kappa \pi_f (\alpha j \kappa \pi_i)^+; \Pi K Q\rangle$. The relaxation matrix is invariant under inversion,⁸ and therefore will not couple Liouville vectors with opposite values of Π . We may therefore exclude those vectors with $\pi_i \times \pi_f = +1$.

The various rotational levels j, κ , of NH_3 are quite widely separated, and we may approximately neglect elements of the relaxation matrix connecting the inversion doublets of different rotational levels. Λ thus reduces to 2×2 matrices (with given K and Q) for the various inversion doublets, as in the two-level system of Sec. 4A. Alternatively, we may write down $\mathbf{L}^{(s)} + \Lambda$ as a 2×2 super matrix

$$\mathbf{L}^{(s)} + \Lambda = \begin{pmatrix} \omega_0 + \delta + i\gamma & i\gamma \\ i\zeta & -\omega_0 - \delta - i\gamma \end{pmatrix}, \quad (111)$$

where ω_0, δ, γ , and ζ are all diagonal matrices, whose eigenvalues are the corresponding parameters of the individual lines. The eigenvalues of ω_0 and γ for many of the lines are known, together with their corresponding

³⁰ N. N. Korst and E. E. Nikitin, *Teor. i Experim. Khimii* (U.S.S.R.) **1**, 11 (1965).

³¹ E. E. Nikitin (private communication).

³² Cf. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955). The hyperfine splitting is too small to be considered here.

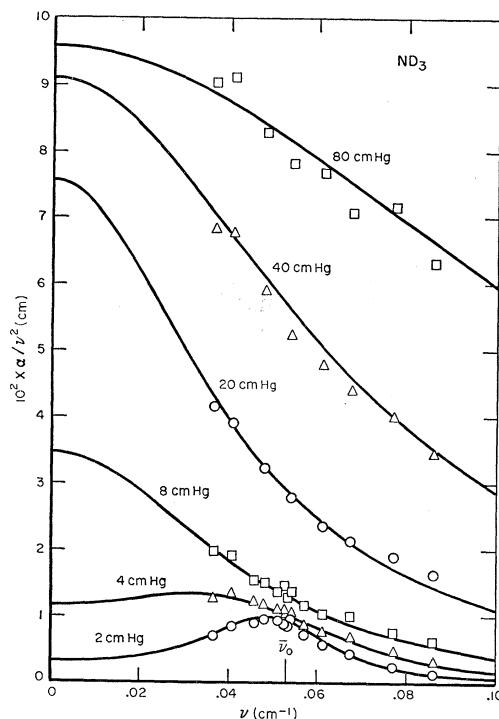


FIG. 4. The inversion spectrum of ND_3 . Comparison of the theoretical line shape, Eq. (100) (solid lines) with the measurements of Birnbaum and Maryott (Ref. 35) at several pressures. $\nu = \omega/2\pi c$.

intensities, from high-resolution measurements.³³ The mean value and second moment of the matrices ω_0 and γ calculated from these data are³⁴

$$\bar{\omega}_0 = 0.78 \text{ cm}^{-1}, \quad \bar{\gamma}/p = 0.62 \text{ cm}^{-1}/\text{atm},$$

$$\Delta^2 \omega_0 = (\langle \omega_0^2 \rangle_{\text{av}} - \bar{\omega}_0^2)^{1/2} = 0.07 \text{ cm}^{-1},$$

$$\Delta^2 \gamma/p = (\langle \gamma^2 \rangle_{\text{av}} - \bar{\gamma}^2)^{1/2}/p = 0.10 \text{ cm}^{-1}/\text{atm}.$$

At pressures where $\bar{\gamma} \gg \Delta^2 \omega_0$ (i.e., when the line structure of the band is completely washed out), the spectrum may be approximated by a single resonance-line shape with $\bar{\omega}_0$ as the resonance frequency, and $\bar{\delta}, \bar{\gamma}$, and $\bar{\zeta}$ as the shape parameters. Provided $\bar{\delta}$ is small, the relative error introduced by this approximation at frequencies around $\bar{\omega}_0$ is

$$[(\Delta^2 \gamma)^2 + (\Delta^2 \omega_0)^2] \bar{\gamma}^{-2} = 0.026 + 0.013 p^{-2},$$

where p is the pressure in atmospheres. At pressures of 30 cm Hg or below, the error exceeds 10%, mainly owing to the spread of resonance frequencies, and the spectrum will look broader than the single-line curve. At frequencies far removed from the band, the second moment of ω_0 will not contribute to the error, but there an additional error may result from the second moment of ζ , of which we know nothing.

³³ Tables 12-3 and 13-3 of Ref. 32.

³⁴ Widths of lines for which data are not available in Ref. 32 were estimated by using the empirical formula of B. Bleaney and R. P. Penrose, *Proc. Phys. Soc. (London)* **60**, 83 (1948).

The fitting of the line-shape expression [Eqs. (97) and (100)] to the NH_3 data of Bleaney and Loubser² has been already published in a preliminary note.¹⁰ A similar fitting has been done to the data of Birnbaum and Maryott³⁵ on deuterated ammonia (ND_3), whose inversion spectrum lies around $\bar{\omega}_0 = 0.053 \text{ cm}^{-1}$. The latter results are shown in Fig. 4. The values of $\bar{\gamma}$ and $\bar{\zeta}$, used in the two cases as empirical parameters, were

$$\begin{aligned}\bar{\gamma}_{\text{NH}_3}/p &= 0.58 \text{ cm}^{-1}/\text{atm}, & \bar{\gamma}_{\text{ND}_3}/p &= 0.64 \text{ cm}^{-1}/\text{atm}, \\ \bar{\zeta}_{\text{NH}_3}/p &= 0.38 \text{ cm}^{-1}/\text{atm}, & \bar{\zeta}_{\text{ND}_3}/p &= 0.52 \text{ cm}^{-1}/\text{atm}.\end{aligned}$$

These values were obtained by trial and error, and it is desirable to repeat the measurements with better accuracy before an attempt is made to obtain better values of the parameters.

The intensity factors, defined by

$$I_0 p = (4\pi p / 3c(k_B T)^2) \sum_{ij} \rho_i \mu_{ij}^2, \quad (E_i > E_j), \quad (112)$$

were also adjusted to the data, giving

$$\begin{aligned}I_0 &= 6.8_5 \times 10^{-3} \text{ atm}^{-1} \quad \text{for } \text{NH}_3 \\ &= 5.8_5 \times 10^{-3} \text{ atm}^{-1} \quad \text{for } \text{ND}_3.\end{aligned}$$

The calculated values are³⁶

$$\begin{aligned}I_0 &= 7.1_6 \times 10^{-3} \text{ atm}^{-1} \quad \text{for } \text{NH}_3 \text{ (at } 288^\circ\text{K)} \\ &= 6.8_0 \times 10^{-3} \text{ atm}^{-1} \quad \text{for } \text{ND}_3 \text{ (at } 298^\circ\text{K)}.\end{aligned}$$

The discrepancy of about 14% in the case of ND_3 could not be accounted for by anything like the finite spread of relaxation rates (which in NH_3 causes a reduction of 3% to 5% in $\alpha(\omega)$ at pressures from 60 cm Hg up in frequencies around $\bar{\omega}_0$, where most of the available data are). However, recent measurements³⁷ with a high-purity ND_3 sample produced data about 10% to 12% higher than the previous ones, suggesting that the discrepancy may have resulted from the presence of impurities in the gas.³⁸

The shift parameter $\bar{\delta}$ is too small to be reliably derived from the existing data. A negative value of magnitude $0.015 \text{ cm}^{-1} \text{ atm}^{-1}$ was used in the NH_3 calculations. With ND_3 , no shift parameter was taken into account.

ND_3 has a larger value of $\bar{\zeta}$, and a smaller value of $\bar{\gamma} - \bar{\zeta}$, than NH_3 has. This may be qualitatively explained in terms of their isotopic mass differences. The heavier ND_3 has smaller inversion splittings, and therefore inelastic transitions between the two levels of an inversion doublet are more likely to occur; hence the larger $\bar{\zeta}$. On the other hand, changes of orientation, which are a major factor in $\bar{\gamma} - \bar{\zeta}$, are less likely to occur in ND_3 with its larger moment of inertia.

³⁵ Reference 3 and unpublished data.

³⁶ Based on calculations of G. Birnbaum and A. A. Maryott, Ref. 3.

³⁷ A. A. Maryott and S. J. Kryder (to be published).

³⁸ Notice that 4 molar % ^1H suffices to reduce the intensity by 12% by producing ND_2H , which has negligible absorption at the frequencies studied.

The discrepancy between the observed and calculated values of $\bar{\gamma}$ with NH_3 , to the extent it is significantly above error limits, may be attributed to the neglected elements of Γ connecting different inversion lines.

5. DISCUSSION

The Liouville-space formalism, which turns the attention from wave vectors and energy eigenvalues to multipole transition operators and resonance frequencies, has been helpful in many ways in understanding pressure effects in microwave spectra. Even though the theoretical tool devised by Fano may be used to study higher pressure effects, or non-Markoffian (frequency-dependent) effects of the collisions, its success in the impact approximation is particularly striking thanks to the relative simplicity of the results.

Thus we saw how the notion of a "distribution of relaxation rates," vaguely used in the past in connection with nonresonant absorption, may be accurately defined and traced to the microscopic equations of motion of the molecular systems. The effect of inelastic collisions, without which the average relaxation rate could not be explained, is properly taken into account by means of the off-diagonal elements of the relaxation matrix.

It has not been possible to account for the shape of resonance lines adequately until it was associated with a pair of vectors in Liouville space (i.e., a pair of canonical variables in phase space, in the classical analog), and with the corresponding 2×2 relaxation matrix. The single additional pressure-proportional parameter (ζ) introduced by this matrix suffices to account quantitatively for both the "shift" to zero-resonance frequency and the reduction in the width-per-unit-pressure, observed in the resonance microwave spectra of NH_3 and ND_3 . It furthermore accounts for the discrepancy between the Van Vleck and Weisskopf line shape and measurements in the low-frequency wing,³⁹ and for most of the discrepancy in the high-frequency wing,⁴⁰ in the ammonia spectrum even at rather low pressures. The Van Vleck and Weisskopf line shape becomes proportional to $\bar{\gamma}$ in both wings, as $p \rightarrow 0$, whereas Eq. (100) becomes proportional to $(\bar{\gamma} - \bar{\zeta})$ when $\omega \gg \bar{\omega}_0$, and to $(\bar{\gamma} + \bar{\zeta})$ when $\omega \ll \bar{\omega}_0$.

The approximations used here have the following main limitations:

(a) Correlations between molecules are neglected, by treating each molecule as a separate absorbing system. We thus exclude such effects as collision-induced spectra⁴¹ which are related to groups of molecules as the absorbing system, or local field effects.

³⁹ G. Birnbaum and A. A. Maryott, J. Chem. Phys. **21**, 1774 (1953).

⁴⁰ A. H. Nethercot, J. A. Klein, J. H. N. Loubser, and C. H. Townes, Nuovo Cimento **9**, Suppl. **3**, 358 (1952).

⁴¹ A. A. Maryott and G. Birnbaum, J. Chem. Phys. **36**, 2026 (1962).

(b) The low-pressure assumption of binary collisions is made to keep the relaxation matrix proportional to the density of the perturbing gas.

(c) The transient effects of collisions (non-Markoffian effects) are neglected. By this we limit ourselves to a finite (temperature-dependent) range of frequencies.

(d) It is required that the radiation field be weak enough to avoid saturation effects.

(e) The translatory motion of the system molecules (Doppler broadening) is neglected, thus precluding the application of the theory at too low pressures.

(f) We should finally remark that pressure and density have been interchangeably used throughout the present work. This is obviously not allowed at elevated pressures, where deviations from the ideal gas laws are not negligible. There "density" is meant whenever "pressure" is said.

The ammonia inversion spectrum is the most striking example of the adequacy of the impact approximation. But its characteristics, particularly the transition to the nonresonant shape, should be shared by practically any line, or group of lines, at low enough frequencies, provided collisions do not couple it to other parts of the spectrum. Every line, under such conditions, should eventually shift to a nonresonant shape.

Measurements of ζ furnish additional information on molecular collisions by sorting out the transitions $i \leftrightarrow f$ from all other collision-induced transitions. Selection rules for these transitions limit the choice of the types of intermolecular forces that should be considered. Therefore measurements of ζ may furnish more direct information on intermolecular forces. The knowledge of ζ is particularly relevant to saturation phenomena since only the transitions $i \leftrightarrow f$ are responsible for counterbalancing the saturation by the radiation field.³²

The most obvious extension of the ammonia self-broadening studies would be foreign-gas broadening. Recent measurements of the ND₃ spectrum in mixture with one of several foreign gases³⁷ resulted in values of $\bar{\zeta}$ and $\bar{\gamma}$ varying in accordance with the expected effectiveness of the foreign gas in coupling the two inversion levels, or reorienting the absorbing molecule.

Other possible evidence on the transition to nonresonant shape is provided by the spectrum of O₂. Oxygen has a finite-frequency spectrum in the region around 2 cm⁻¹, in addition to a nonresonant spectrum, all arising from magnetic-dipole transitions.^{4a} The resonant spectrum behaves like the ammonia spectrum

at pressures above 10 atm.⁴² However, the presence of the nonresonant spectrum, and possible deviations from the impact approximation at such wide ranges of frequency and pressure, complicate its analysis.

Information from microwave studies may be tied up with pressure broadening in other spectral regions. Consider, for example, ammonia. Collisional transitions between the two levels of an inversion doublet may also occur at excited vibrational levels, and the relaxation matrix will have an element connecting the two lines of an inversion doublet in the infrared, making them merge as the pressure is increased. Though this element differs from $i\zeta$ (it may be complex, whereas ζ is real) it furnishes complementary information on the inelastic transitions between the inversion levels. An attempt at such a study has been made in the past.⁴³ A value of the ratio of the off diagonal element to the width probably lower than the microwave ratio $\bar{\zeta}/\bar{\gamma}$, and a poorer resolution in the measurements, might have combined to make the doublet dissolve before the "shift" (i.e., the variation with pressure of the real part of the eigenvalues of $\mathbf{L}^{(s)} + \langle \mathbf{M}_e \rangle$) becomes conspicuous. Nevertheless, a considerable reduction in the width-per-unit-pressure has been observed.^{44,45}

The implications of the coupling of positive and negative resonance terms are relevant to the low-frequency studies of other relaxation phenomena (such as in nuclear magnetic resonance). The details may vary, though, particularly whenever rotational invariance is lacking.

ACKNOWLEDGMENTS

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⁴² A. A. Maryott and G. Birnbaum, *J. Chem. Phys.* **32**, 686 (1960).

⁴³ A. H. Nethercot and C. W. Peters, *Phys. Rev.* **79**, 225(A) (1950).

⁴⁴ A. H. Nethercot (private communication).

⁴⁵ Note added in proof. W. S. Benedict kindly tells me that in his studies with E. K. Plyler of the ammonia infrared spectrum, which were mostly done with well-resolved lines, no deviations from the Lorentz shape have been observed. It may still be desirable to study inversion doublets at higher pressures, where the doublets dissolve.